

Energy level alignment of poly(3-hexylthiophene): [6,6]-phenyl C₆₁ butyric acid methyl ester bulk heterojunction

Zheng Xu,¹ Li-Min Chen,¹ Mei-Hsin Chen,² Gang Li,³ and Yang Yang^{1,a)}

¹Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095, USA

²Graduate Institute of Photonic and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan

³Solarmer Energy, Inc., 3445 Fletcher Ave., El Monte, California 91731, USA

(Received 19 March 2009; accepted 30 May 2009; published online 6 July 2009)

Photoelectron spectroscopy was used to investigate poly(3-hexylthiophene) (P3HT), [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM), and their blends on various conductive substrates. The study shows a P3HT-rich layer at the top of the P3HT:PCBM blend films. The energy level alignment of the top P3HT changes with the work function of the substrate and the PCBM concentration at the bottom surface of the blend film. The results can be explained using the integer charge transfer model. © 2009 American Institute of Physics. [DOI: 10.1063/1.3163056]

Polymer solar cells have attracted considerable attention recently owing to their advantages of low-cost fabrication. The state-of-the-art device structure is the bulk heterojunction (BHJ),^{1,2} in which two organic materials with energy level offsets are intimately blended. The blend system consisting of regioregular poly(3-hexylthiophene) (RR-P3HT) and fullerene derivative [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) has shown power conversion efficiencies of about 4%–5%.^{3–7} Additionally, fundamental researches on the energy level alignment at organic-organic and organic-inorganic interfaces have drawn immense interest because of their crucial roles in charge separation and collection.^{8–12} Recently, the integer charge transfer (ICT) model, which assumes weak interaction and electronic coupling via tunneling at the interface has been proposed and has been applied to various organic-metal interfaces and organic donor-acceptor heterojunctions.^{13–18} However, flat bilayer interfaces do not exist in blend systems and works revealing the electronic structures in the BHJs are scarce. In this paper, ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) were used to investigate the energy level alignment of the P3HT:PCBM BHJs and it was shown that the ICT model can be employed to explain the results.

In the experiments, following substrates with different work functions (Φ_{SUB}) were used: Al with a native oxide layer ($\Phi_{\text{SUB}}=3.3$ eV), Au exposed to air ($\Phi_{\text{SUB}}=4.1$ eV), Pt exposed to air ($\Phi_{\text{SUB}}=4.25$ eV), indium tin oxide (ITO) ($\Phi_{\text{SUB}}=4.35$ eV), Ag exposed to air ($\Phi_{\text{SUB}}=4.6$ eV), ozone-treated Pt ($\Phi_{\text{SUB}}=5.2$ eV), ozone-treated Au ($\Phi_{\text{SUB}}=5.3$ eV), ITO coated with Cs₂CO₃ ($\Phi_{\text{SUB}}=3.5$ eV), and ITO coated with Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) ($\Phi_{\text{SUB}}=5.0$ eV). Cs₂CO₃ layers were spin-coated on ITO from 5 mg/ml 2-ethoxyethanol solution at 3000 rpm for 60 s, and annealed at 170 °C for 20 min inside the glove box. PEDOT:PSS layers were formed by spin coating the aqueous solution at 4000 rpm for 60 s, and baked at 150 °C for 30 min. P3HT, PCBM, and P3HT:PCBM blend films were prepared from 1, 2-dichlorobenzene solutions, and spin-coated at 3000 rpm for 60 s. The concentrations of the PCBM and P3HT solu-

tions were 20 and 5 mg/ml, respectively. In the blend solutions, the P3HT concentration was kept at 5 mg/ml, while the PCBM concentration was varied from 1 to 25 mg/ml for different blend ratios. XPS and UPS measurements were performed in an Omicron XPS/UPS system with Al K α (1486.6 eV) and He I (21.2 eV) excitations, respectively.

Adding or withdrawing charges to organic materials induces substantial electronic and geometric relaxation effects, leading to self-localized polaronic states, which exist in the band gap of the neutral molecule/polymer. Here, the positive charge transfer state, which is the fully relaxed state formed by taking away one electron from the molecule/polymer, is marked by P⁺ and the negative charge transfer state is marked by CT⁻.¹⁷ According to the ICT model, the energy level alignment of an organic/conductive substrate system with weak interfacial interaction can be determined by the substrate work function (Φ_{SUB}) and the charge transfer states. When Φ_{SUB} lies between the energies of P⁺ (E_{P^+}) and CT⁻ (E_{CT^-}) states [Fig. 1(a)], no spontaneous charge transfer occurs. Therefore, vacuum level alignment holds and the work function of the substrate coated with organic layer $\Phi_{\text{ORG/SUB}}$ equals Φ_{SUB} . If Φ_{SUB} is larger than E_{P^+} [Fig. 1(b)], electrons spontaneously flow from the organic layer to the substrate, creating an interfacial dipole that downshifts the vacuum level. This process continues until the interface dipole equals $E_{\text{P}^+}-\Phi_{\text{SUB}}$ and the Fermi level is pinned to P⁺.

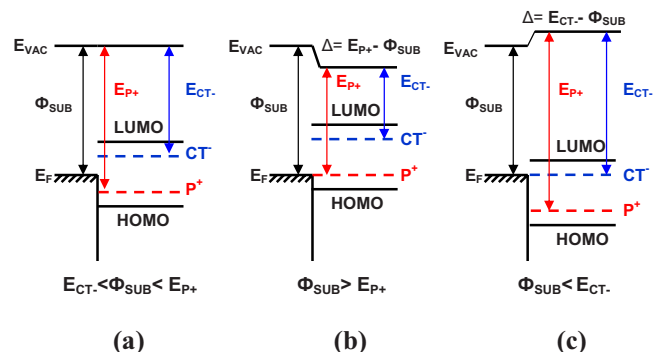


FIG. 1. (Color online) Schematic illustration of the energy level alignment at the organic/conductive substrate system with weak interfacial interaction when (a) $E_{\text{CT}^-} < \Phi_{\text{SUB}} < E_{\text{P}^+}$, (b) $\Phi_{\text{SUB}} > E_{\text{P}^+}$, and (c) $\Phi_{\text{SUB}} < E_{\text{CT}^-}$.

^{a)}Electronic mail: yangy@ucla.edu.

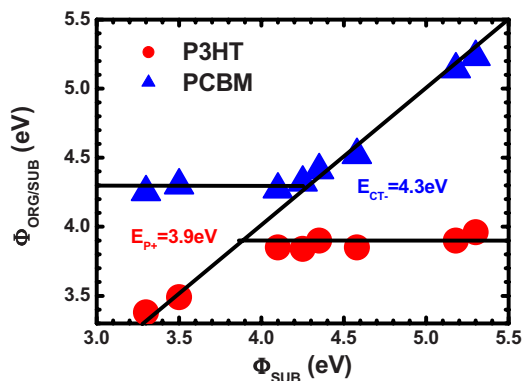


FIG. 2. (Color online) Dependence of the work function of the substrate coated with organic semiconductor, $\Phi_{\text{ORG/SUB}}$, on the work function of bare substrate, Φ_{SUB} , for P3HT and PCBM.

Consequently, in this condition, $\Phi_{\text{ORG/SUB}}$ remains invariant while the interface dipole changes with Φ_{SUB} . When Φ_{SUB} is smaller than $E_{\text{CT-}}$ [Fig. 1(c)], an interface dipole equivalent to $E_{\text{CT-}} - \Phi_{\text{SUB}}$ is formed and the Fermi level is pinned to CT^- . The $\Phi_{\text{ORG/SUB}}$ in this condition is also independent of Φ_{SUB} .

Figure 2 shows the dependence of $\Phi_{\text{ORG/SUB}}$ on Φ_{SUB} for P3HT and PCBM. Abrupt transitions between the vacuum level alignment ($\Phi_{\text{ORG/SUB}} = \Phi_{\text{SUB}}$) and Fermi-level pinning (constant $\Phi_{\text{ORG/SUB}}$) regimes are observed. The $E_{\text{P+}}$ of P3HT and the $E_{\text{CT-}}$ of PCBM are thus estimated as 3.9 and 4.3 eV, respectively.

From the $E_{\text{P+}}$ and $E_{\text{CT-}}$ values, the energy level alignment between the P3HT (or PCBM) layer and inert substrates can be predicted using the ICT model. For PEDOT:PSS-coated ITO, the work function determined by UPS is 5.0 eV, which is larger than the $E_{\text{P+}}$ of P3HT and between the $E_{\text{P+}}$ and $E_{\text{CT-}}$ of PCBM. Hence, Fermi-level pinning and vacuum level alignment are expected at the P3HT/PEDOT:PSS and PCBM/PEDOT:PSS interfaces, respectively. As a result, the $\Phi_{\text{ORG/SUB}}$ is anticipated to be 3.9 eV for P3HT/PEDOT:PSS [Fig. 3(a)] and 5.0 eV for PCBM/PEDOT:PSS [Fig. 3(b)]. These values are consistent with the results obtained from the secondary electron cutoffs shown in Fig. 3(d).

Since only weak van der Waals interactions exist at most organic/organic interfaces, the ICT model can also be used to predict the behavior of organic/organic heterojunctions such as C_{60} /P3HT.^{16–18} Consider the P3HT/PCBM heterojunction on PEDOT:PSS as an example. Because the $E_{\text{P+}}$ of P3HT is smaller than the $E_{\text{CT-}}$ of PCBM, electrons will flow from P3HT to PCBM until the P^+ of P3HT aligns with the CT^- of PCBM. Therefore, an interface dipole of -0.4 eV forms and downshifts the vacuum level of the P3HT layer to 4.6 eV above the Fermi-level ($\Phi_{\text{ORG/SUB}} = 4.6$ eV) [Fig. 3(c)]. For BHJs, Fig. 3(d) shows the UPS spectra of P3HT:PCBM blends of various ratios on PEDOT:PSS. From the highest occupied molecular orbital (HOMO) structure (right), it can be found that the UPS signals are dominated by the P3HT component. This is consistent with previous reports, which indicate that P3HT tends to accumulate at the top surface due to its lower surface energy.^{19,20} Moreover, the ionization potentials (IPs) calculated from the UPS spectra are around 4.6 eV, in agreement with the IP value of P3HT reported by Osikowicz *et al.*¹⁷ Thus, the energy level alignment of P3HT

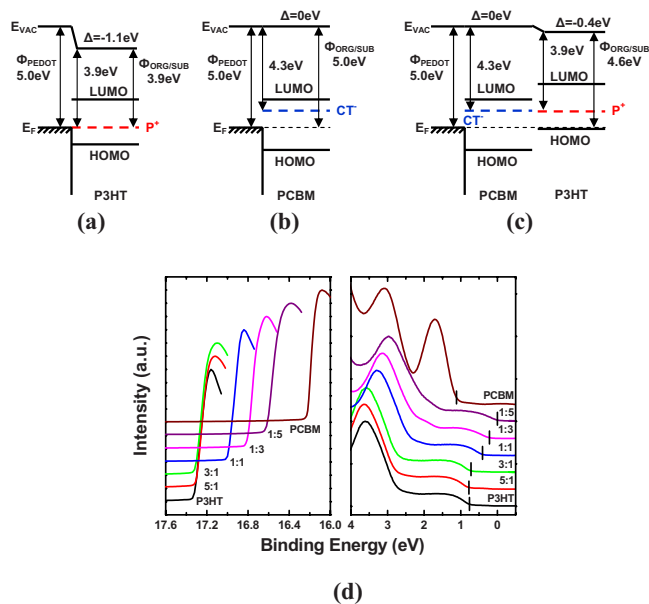


FIG. 3. (Color online) Schematic energy level alignment diagrams of (a) P3HT/PEDOT:PSS, (b) PCBM/PEDOT:PSS, (c) P3HT/PCBM/PEDOT:PSS as predicted by the ICT model, and (d) UPS spectra of P3HT, P3HT:PCBM, and PCBM films spin-coated on PEDOT:PSS. The PCBM concentration increases from bottom to top.

at the top surface of the blend films can be acquired by UPS. The UPS spectra of blend films with low PCBM concentration (5:1, 3:1) are almost identical with pristine P3HT. Therefore, the energy level alignment of P3HT at the top surface of the blend films is the same as P3HT on PEDOT:PSS. The ICT model also suggests similar results for the P3HT layer on top of a multilayer stack of alternating P3HT and PCBM layers with P3HT layer adjacent to PEDOT:PSS (P3HT/PCBM/.../P3HT/PEDOT:PSS). As the PCBM concentration increases, the UPS spectrum shifts to a lower binding energy, indicating a higher work function and a shallower HOMO level. Interestingly, the energy levels obtained from the UPS spectrum of the 1:5 weight ratio blend film are the same as those of the P3HT layer shown in Fig. 3(c). Using the ICT model, similar results can be predicted for the P3HT layer on top of a multilayer structure of alternating P3HT and PCBM layers, where PCBM layer is close to PEDOT:PSS (P3HT/PCBM/.../PCBM/PEDOT:PSS). These resemblances suggest that P3HT covers most of the bottom surface (blends/PEDOT:PSS interface) of the 5:1 blend film and PCBM dominates the same region in the 1:5 blend film. In our previous research, water was used to separate the blend films from the PEDOT:PSS-coated substrate and the composition at the buried interfaces were investigated via XPS.¹⁹ The P3HT:PCBM weight ratio at the bottom surface of the 5:1 film is estimated to be 4:1 and the corresponding ratio of the 1:1 film is estimated to be 1:1.8. The results indicate a much higher PCBM concentration at the bottom surface of the 1:1 film. Campoy-Quiles *et al.*²⁰ have recently used variable angle spectroscopic ellipsometry to model the vertical composition profile of the P3HT:PCBM thin films. Accordingly, the PCBM concentration at the PEDOT:PSS interface of the 1:1 film is 65% in volume. Based on these data, a full coverage of PCBM at the PEDOT:PSS side is expected in the 1:5 blend film.

The blend films prepared on Cs_2CO_3 -coated ITO further confirm this observation. The work function of Cs_2CO_3 /ITO

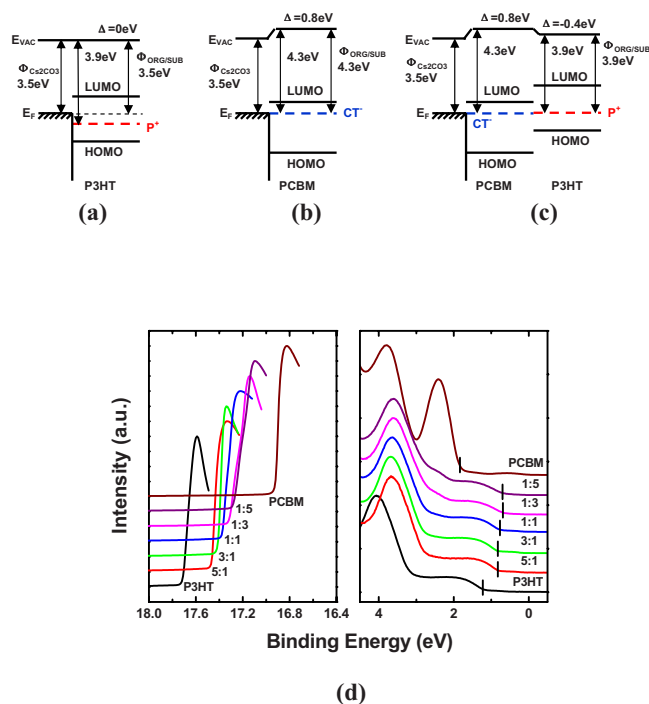


FIG. 4. (Color online) Schematic energy level alignment diagrams of (a) P3HT/Cs₂CO₃, (b) PCBM/Cs₂CO₃, and (c) P3HT/PCBM/Cs₂CO₃ as predicted by the ICT model and (d) UPS spectra of P3HT, P3HT:PCBM, and PCBM films spin-coated on Cs₂CO₃. The PCBM concentration increases from bottom to top.

substrate is determined to be 3.5 eV, which is between the E_{P+} and E_{CT-} of P3HT and smaller than the E_{CT-} of PCBM. Therefore, vacuum level alignment was perceived at the P3HT/Cs₂CO₃ interface ($\Phi_{ORG/SUB}=3.5$ eV) [Fig. 4(a)] and Fermi-level pinning was found at the PCBM/Cs₂CO₃ interface ($\Phi_{ORG/SUB}=4.3$ eV) [Fig. 4(b)]. The UPS spectra of different P3HT:PCBM blend films also imply a P3HT-rich region near the top surface. However, unlike on PEDOT:PSS-coated substrates, even the blend film with the lowest PCBM concentration (5:1) shows obviously different energy levels from pristine P3HT on Cs₂CO₃. As the PCBM concentration increases, the energy level alignment of the top P3HT approaches that of P3HT on PCBM/Cs₂CO₃, as predicted by the ICT model [Fig. 4(c)]. The results are consistent with previous findings where PCBM tends to accumulate at the Cs₂CO₃ surface.¹⁹ Similar to PEDOT:PSS, the blend films coated on Cs₂CO₃ can also be lifted off in water to examine the P3HT:PCBM ratio at the bottom surface. The P3HT:PCBM weight ratio at the bottom surface of the 5:1 film is about 1:2. This value is close to 1:2.2, which is the corresponding ratio of the 1:1 film.

In summary, the ICT model can be used to predict the energy level alignment of P3HT or PCBM on various inert

conductive substrates. UPS study also indicates that P3HT tends to accumulate at the top of the P3HT:PCBM blend films. The energy level alignment of the top P3HT changes with the work function of the substrate and the PCBM concentration at the bottom surface of the blend film. These results provide us better insights into the energy level alignment in the BHJs and are beneficial to understand the performance of polymer solar cells.

The authors appreciate financial supports from the Office of Naval Research (ONR) (Grant No. N00014-1-04-10434) and Program Manager Dr. Paul Armistead. L.-M. Chen would like to acknowledge NSF IGERT: Materials Creation Training Program (MCTP) (DGE-0114443) and the California Nano-Systems Institute. M. H. Chen would also like to acknowledge the National Science Council of Taiwan, Project NSC-0962917-I-002-113.

- ¹G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).
- ²J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Nature (London)* **376**, 498 (1995).
- ³W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).
- ⁴M. D. Irwin, D. B. Buchholz, A. W. Hains, R. P. H. Chang, and T. J. Marks, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 2783 (2008).
- ⁵Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, and M. Ree, *Nature Mater.* **5**, 197 (2006).
- ⁶G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nature Mater.* **4**, 864 (2005).
- ⁷H.-H. Liao, L.-M. Chen, Z. Xu, G. Li, and Yang Yang, *Appl. Phys. Lett.* **92**, 173303 (2008).
- ⁸W. Zhao, E. Salomon, Q. Zhang, S. Barlow, S. R. Marder, and A. Kahn, *Phys. Rev. B* **77**, 165336 (2008).
- ⁹H. Vázquez, F. Flores, and A. Kahn, *Org. Electron.* **8**, 241 (2007).
- ¹⁰J. X. Tang, K. M. Lau, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.* **88**, 232103 (2006).
- ¹¹J. X. Tang, C. S. Lee, and S. T. Lee, *J. Appl. Phys.* **101**, 064504 (2007).
- ¹²B. H. Hamadani, H. Ding, Y. Gao, and D. Natelson, *Phys. Rev. B* **72**, 235302 (2005).
- ¹³C. Tengstedt, W. Osikowicz, W. R. Salaneck, I. D. Parker Che-H. Hsu, and M. Fahlman, *Appl. Phys. Lett.* **88**, 053502 (2006).
- ¹⁴S. Braun, W. Osikowicz, Y. Wang, and W. R. Salaneck, *Org. Electron.* **8**, 14 (2007).
- ¹⁵A. Crispin, X. Crispin, M. Fahlman, M. Berggren, and W. R. Salaneck, *Appl. Phys. Lett.* **89**, 213503 (2006).
- ¹⁶S. Braun, M. P. de Jong, W. Osikowicz, and W. R. Salaneck, *Appl. Phys. Lett.* **91**, 202108 (2007).
- ¹⁷W. Osikowicz, M. P. de Jong, and W. R. Salaneck, *Adv. Mater.* **19**, 4213 (2007).
- ¹⁸S. Braun, W. R. Salaneck, and M. Fahlman, *Adv. Mater.* **21**, 1450 (2009).
- ¹⁹Z. Xu, L.-M. Chen, G. Yang, C.-H. Huang, J. Hou, Y. Wu, G. Li, C.-S. Hsu, and Y. Yang, *Adv. Funct. Mater.* **19**, 1227 (2009).
- ²⁰M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. C. Bradley, and J. Nelson, *Nature Mater.* **7**, 158 (2008).