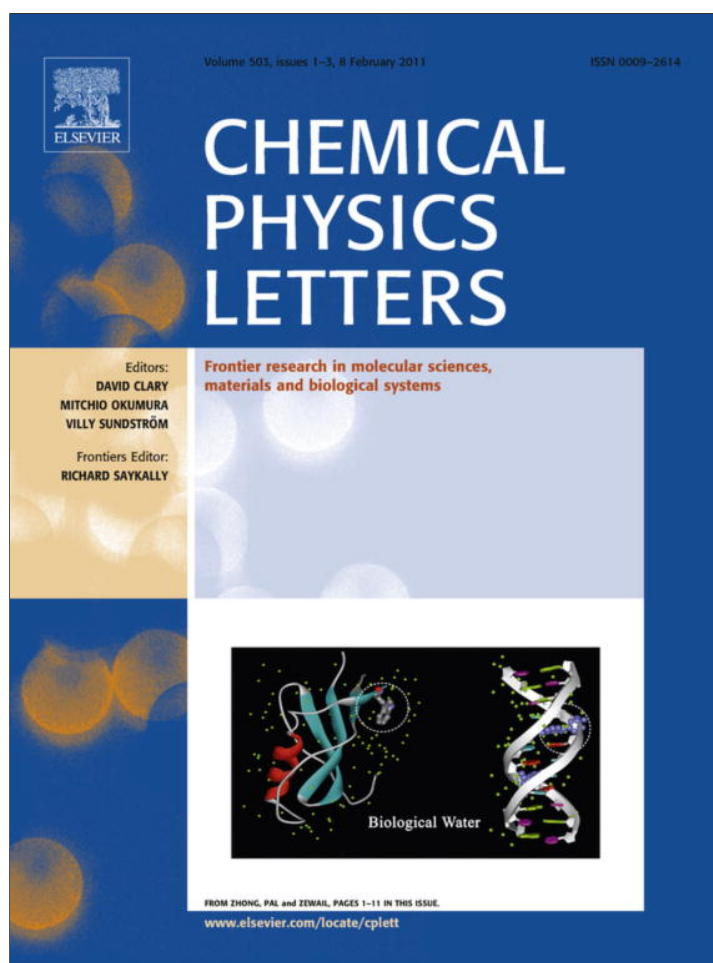


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Energy level alignments at poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] on metal and polymer interfaces

Jung Hwa Seo^a, Shinuk Cho^{b,*}, Mario Leclerc^c, Alan J. Heeger^a^a Center for Polymer and Organic Solids, University of California at Santa Barbara, Santa Barbara, CA 93106, USA^b Department of Physics, University of Ulsan, Ulsan 680-749, South Korea^c Département de Chimie, Université Laval, Quebec City, QC G1K 7P4, Canada

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ABSTRACT

Energy level alignments of poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**PCDTBT**) cast on top of Au and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) were investigated using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) as a function of the concentration of PCDTBT solutions. Although UPS data show similar work functions for Au and PEDOT:PSS, the hole transport barrier (ϕ_h) at the **PCDTBT**/PEDOT:PSS interface is clearly smaller than that at the **PCDTBT**/Au interface. The XPS spectra show that energy level relaxation occurs at the interface between **PCDTBT** and electrodes.

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1. Introduction

Poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**PCDTBT**, see Figure 1a for the molecular structure) has attracted considerable attention as a semiconducting polymer for use in organic thin film transistors (OTFTs) and organic solar cells (OSCs) [1–3]. **PCDTBT** is a thermally stable semiconducting polymer, retaining its electronic properties after annealed up to 150 °C in air and up to 350 °C in N₂ atmosphere. The hole mobility ($\approx 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) obtained from a transistor geometry remained unchanged after annealing at high temperature [3]. Bulk heterojunction (BHJ) solar cells comprising **PCDTBT** and [6,6]-phenyl C₇₀ butyric acid methyl ester (PC₇₁BM) were demonstrated with internal quantum efficiency approaching 100% and optimized power conversion efficiency in excess of 6% under simulated AM 1.5G solar illumination [1].

One of the most important factors affecting device performance is charge carrier injection into (for OTFTs) or extraction from (for BHJ solar cells) the semiconducting polymer [4,5]. For hole injection, Au is often used in OTFTs, and for hole extraction from BHJ solar cells, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is often used. It is therefore important to investigate the work functions (WF) of Au and PEDOT:PSS, and to determine the energy level alignments with respect to the highest occupied molecular orbital (HOMO) energy of **PCDTBT**. We herein report

hole injection barriers (ϕ_h) with respect to **PCDTBT** determined by UPS and demonstrate different mechanisms leading to energy level alignments for Au and PEDOT:PSS using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS).

2. Experimental

For XPS and UPS experiments, 80 nm-thick Au films were deposited on pre-cleaned Si wafers with a thin native oxide; 40 nm-thick PEDOT:PSS (Baytron PH) was spin cast from aqueous solution and dried for 10 min at 140 °C. **PCDTBT** layers were then spin cast from chlorobenzene onto the Au and PEDOT:PSS layers. Control of film thickness was achieved by varying the spin-casting speed and the solution concentration [6]. The total spin casting time was kept at 60 s for all samples. Film fabrication was done in a N₂ atmosphere. To minimize possible influence by exposure to air, the films were then transferred from the N₂-atmosphere dry box to the analysis chamber inside an air-free sample holder. Subsequently, all samples were kept inside a high-vacuum chamber overnight to remove any residual solvent.

The XPS and UPS analysis chamber was equipped with a hemispherical electron energy analyzer (Kratos Ultra Spectrometer) and was maintained at 1×10^{-9} Torr. The XPS was measured using monochromatized Al K α ($h\nu = 1486.6 \text{ eV}$) excitation, while UPS measurements were measured using a He I ($h\nu = 21.2 \text{ eV}$) source. The electron energy analyzer was operated at constant pass energy of 40 eV (for XPS) and at 10 eV (for UPS). During UPS measurements, a sample bias of -9 V was used in order to separate the sample and the secondary edge for the analyzer.

* Corresponding author. Fax: +82 52 259 1693.

E-mail address: sucho@ulsan.ac.kr (S. Cho).

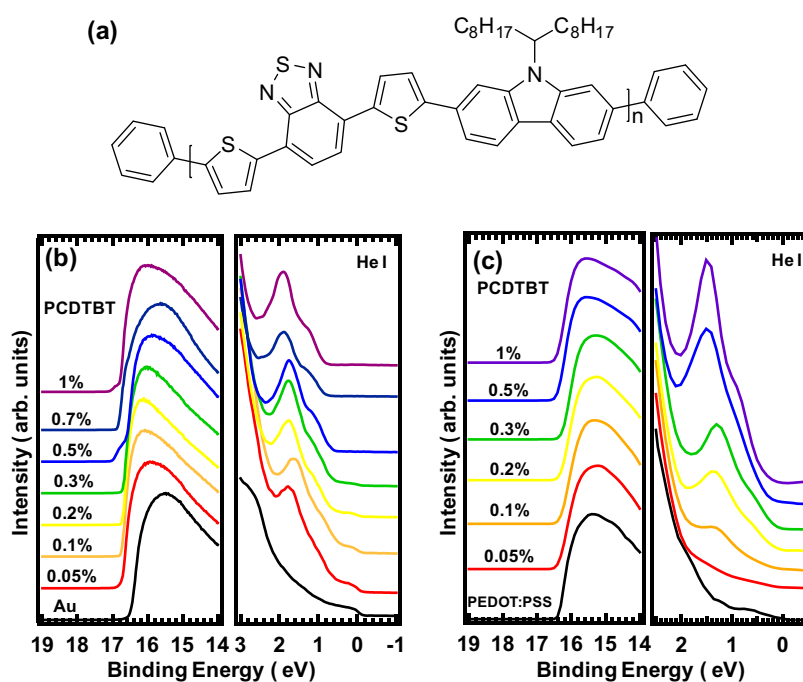


Figure 1. (a) A molecular structure of **PCDTBT**. UPS spectra of **PCDTBT** on Au (b) and on PEDOT:PSS (c) with increasing the concentration of **PCDTBT** solutions.

3. Results and discussions

Figure 1b shows UPS spectra of **PCDTBT** films on Au. The Fermi energy (E_F) was determined from the Au surface and all other spectra are plotted with respect to this value. In other words, the abscissa is the binding energy relative to the E_F of Au. The normalized secondary edges of **PCDTBT** are shown in left side of Figure 1b. The vacuum levels (VLs) of the samples were determined by linear extrapolation of secondary electron cutoffs on the high binding energy side of the UPS spectra (14–19 eV) [7,8]. As the concentration of **PCDTBT** solution becomes increase, the secondary edges shift toward higher binding energies. The total VL shift at the saturated coverage (where the **PCDTBT** layer was deposited from 1% chlorobenzene solution.) is 0.31 eV. The VL shift indicates the magnitude of the interfacial dipole, which is equal to subtracting the work function of the Au from the difference between the vacuum level of the organic layer and the E_F of Au [5,7,8]. The right side of Figure 1b also shows the evolution of the HOMO onsets for **PCDTBT**. The Au peak is completely suppressed by the **PCDTBT** emission when the film was deposited from 0.5% solution, indicating a continuous film. Comparing the shift in the HOMO onset at the sufficient thick film (0.86 eV) to the E_F of Au provides the relative position of the HOMO level.

UPS spectra of **PCDTBT** layers and a PEDOT:PSS layer are shown in Figure 1c. In contrast to **PCDTBT**/Au, the total shifts of the VL and HOMO level are estimated to be 0.04 and 0.41 eV, respectively, with negligible changes up to complete coverage, indicating the absence of a dipole shift. Because the surface-dipole contribution from a metal originates from the polarization of electron density into at the metal surface, the surface-dipole is not significant for PEDOT:PSS, since the PEDOT:PSS has fewer free electrons than Au [9–11]. Thus, there is no significant VL shift at the **PCDTBT**/PEDOT:PSS interface.

For interfaces with thick organic layers, the effect of energy level relaxation should be considered. XPS can probe the energies of the core levels, and these energies can probe the band bending [6,12]. Figure 2a–c show the C 1s, N 1s and S 2p emission lines from the **PCDTBT** layers on Au as a function of the concentration of **PCDTBT** solutions. The bottom line of Figure 2a shows a weak C 1s peak at

284.2 eV from the Au surface, indicating a small amount of unavoidable hydrocarbon contamination [13]. As the concentration of **PCDTBT** solution increases up to 1%, the C 1s, S 2p and N 1s emissions increase in intensity, while the Au 4f emissions become attenuated due to the thicker **PCDTBT** layers (not shown here). No evidence of a chemical reaction is detected from the Au 4f emission lines. Therefore, we suggest that the Au surface remains chemically intact and gives rise to no energy level relaxation in the metal. With the first deposited **PCDTBT** layer (red curve), the C 1s, N 1s, and S 2p core levels are 284.2, 399.3, and 163.5 eV, respectively. A shift in the C 1s peak of 0.15 eV toward higher binding energies for **PCDTBT** is observed from the thickest layer. Furthermore, because the general shape of the peak does not change, we see no evidence of a chemical reaction at the **PCDTBT**/Au interface. Band bending thus leads to a 0.15 eV shift in the C 1s, N 1s and S 2p peaks.

Figure 2d–f show the C 1s, N 1s and S 2p emission lines from the **PCDTBT** layers on PEDOT:PSS become more intense as the concentration of **PCDTBT** solutions. A N 1s peak from the PEDOT:PSS surface in Figure 2e indicates unavoidable air contamination, since the layer was formed in air. The C 1s, N 1s, S 2p peaks from the first **PCDTBT** layer exhibit fairly distinct maxima at 284.6, 399.5, 163.8 eV, indicating chemical environment that is different than for **PCDTBT** on Au. For **PCDTBT**/PEDOT:PSS, a shift in the C 1s peak of 0.2 eV toward higher binding energies is observed for **PCDTBT** after a sufficient coverage, as is the case for other core levels (N 1s, and S 2p). Thus, the magnitude of the energy level relaxation at the **PCDTBT**/PEDOT:PSS interface is 0.2 eV.

As shown in Figure 3, an energy diagram for **PCDTBT** can therefore generated by combining the UPS and XPS data presented above. The energy of the lowest unoccupied molecular orbital (LUMO) level was estimated by using the optical band-gap (E_g) [14,15]. The I_P and E_A of **PCDTBT** are, approximately, 5.2 and 3.3 eV for Au and PEDOT:PSS substrates. Although optical E_g is smaller than the true E_g because it does not take into account the exciton binding energy, it can be generally used to estimate HOMO–LUMO energy difference [5,15]. ϕ_h can be estimated by the energy difference between the E_F and HOMO level. The ϕ_h of **PCDTBT**/PEDOT:PSS is smaller than that of Au, as a result of the

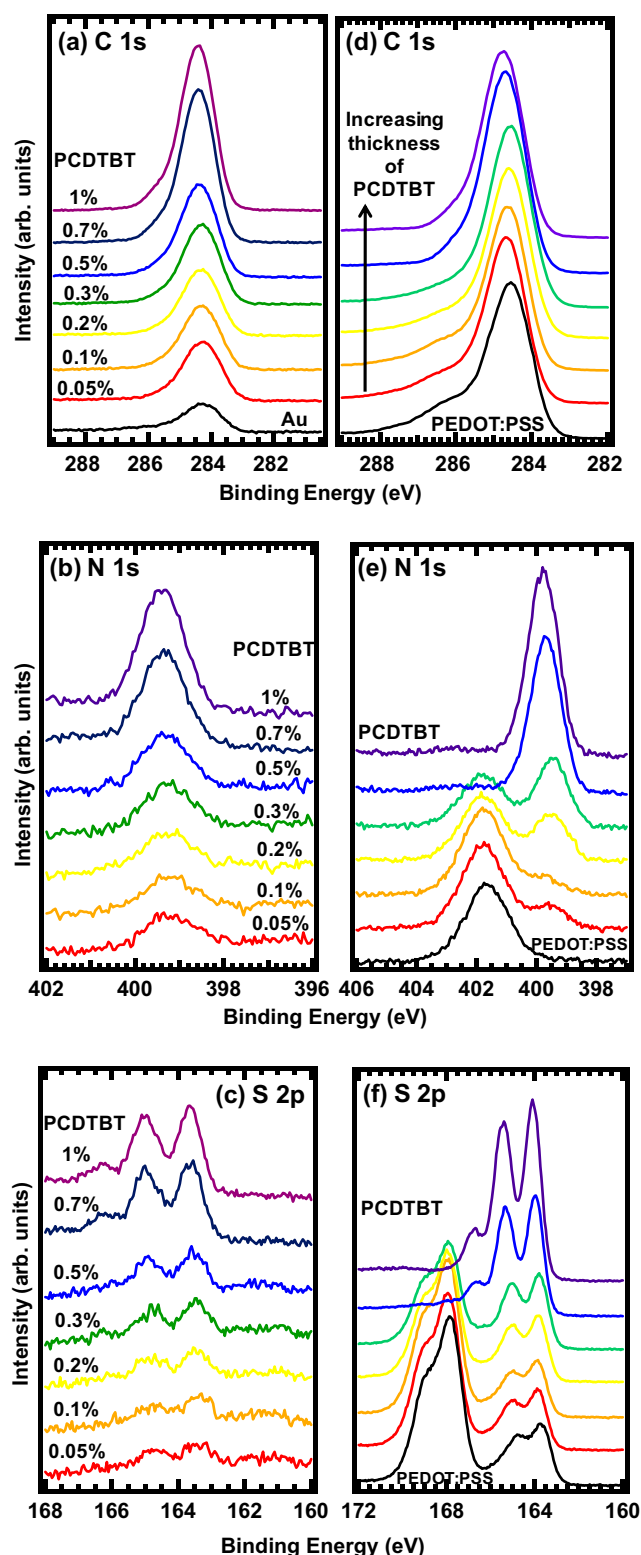


Figure 2. The evolution of XPS (a) C 1s, (b) N 2p, and (c) S 1s core levels of **PCDTBT** on Au with increasing the concentration of **PCDTBT** solutions. XPS spectra of (d) C 1s, (e) S 2p, and (f) N 1s core levels of **PCDTBT** on PEDOT:PSS with the concentration of **PCDTBT** solutions.

absence of the interfacial dipole. Overall values are summarized in Figure 3. When an organic solid contacts a metal, the organic layer may be affected by the potential of the surface dipole. The VL shifts can yield the magnitude and direction of the interfacial dipole (Δ).

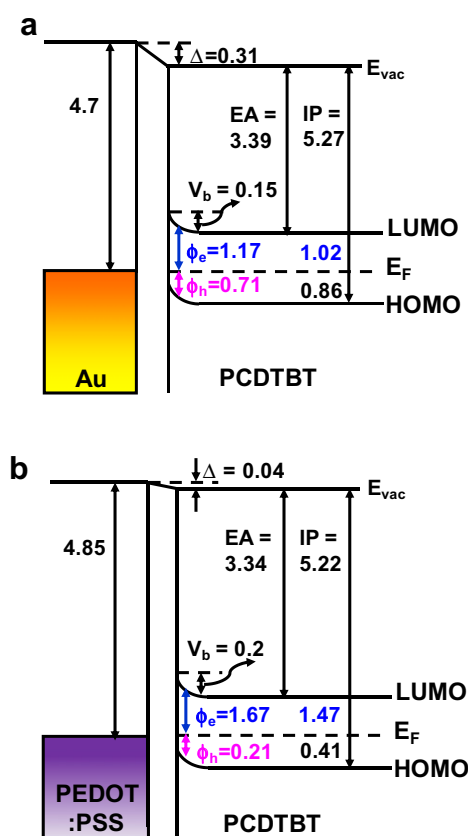


Figure 3. Schematic energy level diagrams of the (a) **PCDTBT**/Au, and (b) **PCDTBT**/PEDOT:PSS. The energy unit is eV. (E_F : Fermi energy level, E_{vac} : Vacuum level, Δ : Interfacial dipole, EA: Electron affinity, IP: Ionization potential, V_b : energy level relaxation, ϕ_e : electron injection barrier, ϕ_h : hole injection barrier).

Generally, a downward shift of VL gives rise to a larger ϕ_h , while an upward shift provides a smaller ϕ_h . Therefore, one can form a contact with PEDOT:PSS with smaller ϕ_h compared to the contact with Au.

4. Conclusions

We have examined energy level alignments at the **PCDTBT**/Au and **PCDTBT**/PEDOT:PSS interfaces by using UPS and XPS measurement. The ϕ_h of **PCDTBT**/PEDOT:PSS is clearly smaller than on Au, although the work functions are similar. Upon depositing **PCDTBT** on Au, the VL shift leads to a large ϕ_h , while the smaller surface electronic polarization contribution on PEDOT:PSS leads to the more favorable energy level alignment for hole injection or extraction. These results are important for understanding how to control molecular level alignment at interfaces with different electrodes.

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