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Electronic structure and energy band gap of poly (9,9-dioctylfluorene) investigated by photoelectron spectroscopy

L. S. Liao
Center Of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, SAR, China and Surface Physics Laboratory, Fudan University, Shanghai 200433, China

M. K. Fung, C. S. Lee, and S. T. Lee[a]
COSDAF and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, SAR, China

M. Inbasekaran, E. P. Woo, and W. W. Wu
Central and New Businesses R & D, The Dow Chemical Company, Midland, Michigan 48674

The electronic structure of poly (9,9-dioctylfluorene) (PFO) film on a Au-coated Si substrate was investigated by ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). From the UPS measurement, we obtained the ionization potential (Ip) of the PFO film, $Ip = 5.60 \pm 0.05$ eV. From the XPS shake-up peaks of the C$1s$ core level, we estimated the electron energy band gap (E_g) of the film, $E_g = 3.10 \pm 0.10$ eV. By comparing the E_g with the optical absorption gap, we found that the value of E_g is closer to the optical absorption maximum than to the optical absorption edge. Therefore, we suggest that the optical absorption maximum may be a better approximation than the optical absorption edge in estimating E_g. © 2000 American Institute of Physics. [S0003-6951(00)00924-4]

Conjugated polymer light-emitting devices (PLEDs) are in a stage that is ready for commercial applications.[1] Poly (9,9-dioctylfluorene) (PFO), an efficient and stable blue light-emitting material, is now attracting much interest due to its low turn-on voltage, high brightness, and high efficiency.[2,3] In order to optimize the device performance with PFO as a light-emitting layer, the design of device structure is crucial since PFO has a large optical gap that may result in a large barrier or unbalanced injection for carriers. Therefore, information on the electronic structure of PFO is greatly needed.

Usually, ultraviolet photoelectron spectroscopy (UPS) is the single most applicable method to give much information needed to reveal electronic structures of materials.[4] Ionization potential (Ip) and the energy level of the highest occupied molecular orbital (HOMO) can be measured with UPS. However, information on the lowest unoccupied molecular orbital (LUMO) is usually not readily available from photoelectron spectroscopy techniques. Fortunately, since conjugated polymers have their delocalized electronic π and π^* states along their backbones, their $\pi \rightarrow \pi^*$ transition may be detected from the shake-up peaks on the high binding energy (BE) side of the main core level peaks in the spectra obtained by x-ray photoelectron spectroscopy (XPS).[5,6] Therefore, for some conjugated polymers, both the Ip and the electron energy band gap (E_g) could be measured by photoelectron spectroscopy in an identical experimental setting.

Janietz *et al.* reported that the Ip and the electron affinity (E_{affin}) of PFO in an electrolyte solution were 5.80 and 2.12 eV, respectively, using cyclic voltammetry.[7] However, it is

obviously more desirable for PLED application to have these data measured directly from the solid film of PFO. In this letter, we report the determination of the Ip and E_g of PFO film using UPS and XPS, and discuss the relation between electron energy band gap and optical energy band gap using photoluminescence excitation spectra as a reference.

The chemical structure of PFO is shown in the inset of Fig. 1. PFO was spin coated from a toluene solution (1.5 wt. %) to form ~100-nm-thick films on quartz substrates, and ~15-nm-thick films on Au coated Si substrates. PFO on

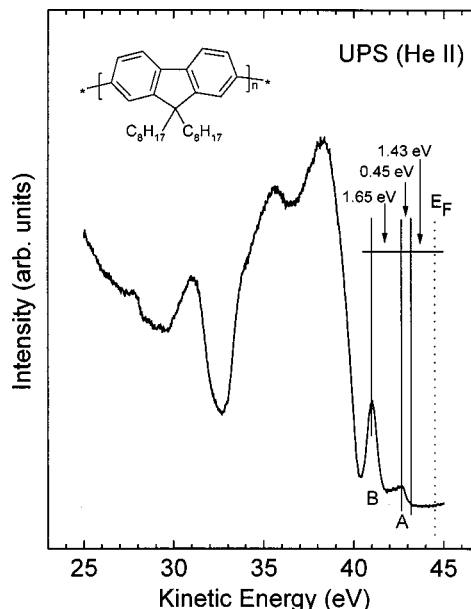FIG. 1. UPS spectrum of a PFO film obtained with He II excitation. The inset is the chemical structure of PFO.

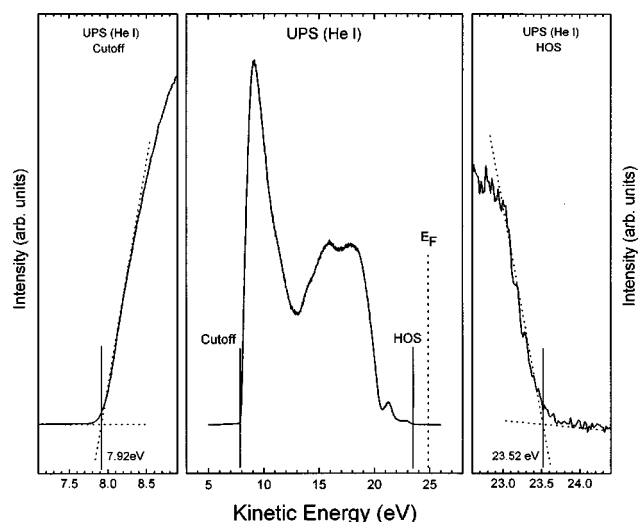[a]Electronic mail: apannale@cityu.edu.hk

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FIG. 2. UPS spectrum of a PFO film obtained with He I excitation.

FIG. 3. XPS C 1*s* core level spectrum of a PFO film.

quartz substrates was used for the measurements of photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra using a Perkin-Elmer LS 50B luminescence spectrometer. PFO on Au coated Si substrates was used for the UPS and XPS measurements with a VG ESCALAB 220*i*-XL photoelectron spectroscopy system. A freshly prepared PFO film sample was immediately loaded in a fast entry air lock, which connects to the photoelectron spectroscopy system. The base pressure in the analysis chamber of the system was 8.0×10^{-11} mbar. We used both a He I excitation line (21.2 eV) and a He II excitation line (40.8 eV) from a He discharge lamp for the UPS measurements and a monochromatic Al $K\alpha$ excitation line (1486.6 eV) for the XPS measurements. The UPS spectra were recorded with a sample bias of −4.00 V to allow observation of the inelastic electron cutoff. A clean Au film on a Si substrate was used for the Fermi level (E_F) and the binding energy calibrations.

Shown in Fig. 1 is a UPS (He II) spectrum of the PFO film. Several peaks are well resolved in the spectrum. Although the valence band structure is a combined contribution from both the phenylene backbone and the alkyl side chains, the first two peaks (peaks A and B, respectively) are attributed to the delocalized π states of the backbone, since they are similar to that of poly (*p*-phenylene).[8] We notice that the energy difference between peak A and peak B is about 1.65 eV, and the interval between the maximum of peak A and its onset is about 0.45 eV.

Figure 2 shows a He I UPS spectrum of the PFO film. Its inelastic electron cutoff and its highest occupied states (HOS) of the HOMO are enlarged as well. According to the values of the cutoff and the HOS, Ip could be obtained as $Ip = 21.22$ eV$-(23.52-7.92$ eV$)=5.62$ eV. In the UPS measurements, we set the energy resolution of the system at 0.036 eV and used an energy-scanning step of 0.02 eV. From more than five measurements for each the seven samples prepared, we obtained Ip with a value of 5.60 ± 0.05 eV for the PFO film.

The XPS C 1*s* core level with its shake-up feature is shown in Fig. 3. There are three peaks in the spectrum. The main peak (peak π) has a full width at half maximum of 0.91 eV, and it is positioned at a BE of 285.0 eV. The two
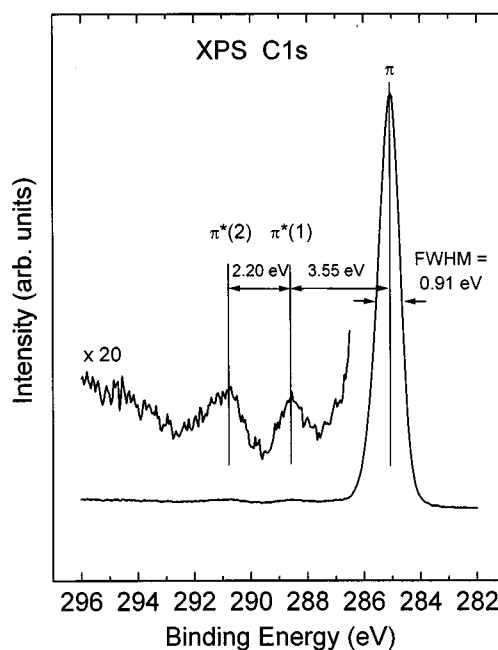
shake-up peaks [peak $\pi^*(1)$ and peak $\pi^*(2)$, respectively] are well discernible after being enlarged 20 times. These peaks correspond to a shake-up process of both core-electron excitation and $\pi \rightarrow \pi^*$ transition. The energy differences of $\pi \rightarrow \pi^*(1)$ and $\pi \rightarrow \pi^*(2)$ are estimated as 3.55 ± 0.10 and 5.75 ± 0.10 eV, respectively.

Figure 4 shows the PL (curve a) and PLE (curve b) spectra of the PFO film. The PL spectrum has a maximum at 2.83 eV, a subpeak at 2.66 eV, and a shoulder at 2.91 eV. The PLE spectrum, similar to the absorption spectrum, has a maximum at 3.13 eV (peak 1), a small peak at 4.24 eV (peak 2), and a shoulder at about 5.36 eV (peak 3). The onset of peak 1 is at 2.85 eV. The present spectra are similar to corresponding spectra in Ref. 2, except that the maximum absorption peak (peak 1) is 0.1 eV less in the present case. These slight differences may be due to the use of different solvents in the preparation of the PFO solutions.[9]

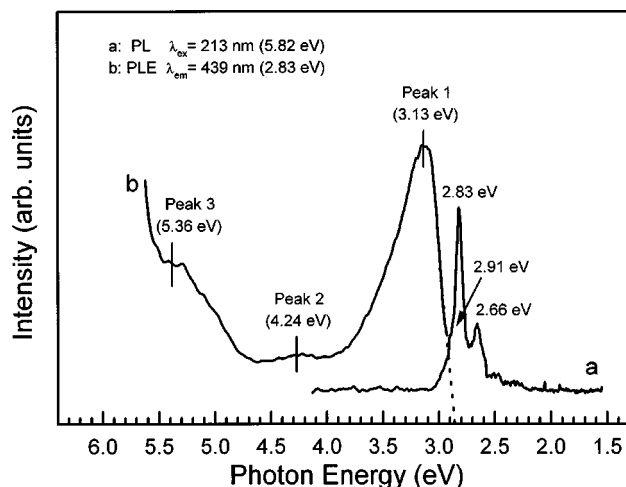In order to illustrate the electron energy gap of the PFO

FIG. 4. PL spectrum (curve a) and PLE spectrum of a PFO film on a quartz substrate.
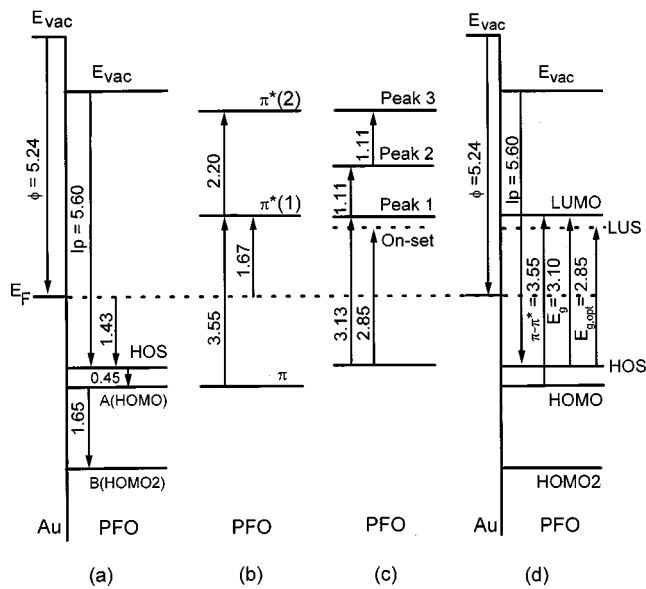
FIG. 5. Diagrams for energy level alignment as derived from information in (a) the UPS spectra in Figs. 1 and 2, (b) the XPS spectrum in Fig. 3, and (c) the PLE spectrum in Fig. 4. (d) A summary overlap of (a)–(c). E_{vac} is the vacuum energy level and ϕ is a work function.

film, we align the energy levels shown in Fig. 5 according to the data in the above figures. The electron energy level alignment of Fig. 5(a) is obtained from the measurement by UPS (from Figs. 1 and 2). We did not consider possible band bending at the interface of PFO/Au in this comparison. Figure 5(b) is derived from Fig. 3. The π-state level (the base line) could be aligned with the HOS or peak A (HOMO) in Fig. 5(a). However, since those transitions are from a maximum to a maximum in Fig. 3, the base line should be aligned with A (HOMO). After we settled this alignment, $\pi*(1)$ is obviously the LUMO of the PFO film. There are then two choices for the assignment of E_g: E_g could be the energy differences either between π and $\pi*(1)$ (3.55 eV) or between the HOS and $\pi*(1)$ (3.10 eV). If E_g were the gap between the π state and LUMO, there would be two problems: The first problem is that the Fermi level (E_F) would be at a level higher than the midgap. It then means PFO is an n-type-doped semiconductor material. In general, polymers are usually p type doped unintentionally,[10] and their E_F is just below the midgap. That is also why the hole transport mobility can be measured but the electron transport mobility could not be obtained.[11] The second problem is that the threshold energy (1.88 eV) to inject holes into PFO from Au would be higher than the reported value (1.50 ± 0.05 eV).[12] Alvarado *et al.* measured the single particle energy gap ($E_{g,s}$) of PFO film with a scanning tunneling microscope.[12] According to them, $E_{g,s}$ is 3.20 ± 0.10 eV and the threshold energy for hole injection is 1.50 ± 0.05 eV whereas the threshold energy for electron injection is 1.70 ± 0.05 eV (referenced to the E_F of the Au substrate). To be in line with these values, we found that E_g could be more appropriately assigned as the energy difference between the HOS and the LUMO in our experiment. In this way, our E_g(3.10 ± 0.10 eV), the threshold for hole injection (1.43 ± 0.10 eV), and the threshold for electron injection (1.67 ± 0.10 eV) are more consistent with the results of Alvarado

et al.[12] Thus, we have obtained the Ip and the E_g by the UPS and the XPS measurements. The corresponding energy level assignments are shown in Fig. 5(d).

As is known, using $E_{g,\text{opt}}$ as E_g is a common practice in determining E_{affin}. But E_g is usually 0.3–0.4 eV larger than $E_{g,\text{opt}}$.[12] Here, we tentatively illustrate the relation between the E_g and $E_{g,\text{opt}}$ of the PFO film. The energy level diagram in Fig. 5(c) is derived from the PLE spectrum in Fig. 4. Before we derived the diagram, we have examined the possible absorption from HOMO2 and from other valence peaks. But we did not find any corresponding peak in the PLE spectrum. For the same reason mentioned above, we align the base line with the HOS. Obviously, if we use the optical absorption peak to determine $E_{g,\text{opt}}$ (instead of the optical absorption edge), the E_g and $E_{g,\text{opt}}$ will be the same or closer in value. The optical absorption edge could then be treated as the lowest unoccupied states (LUS) of the LUMO. Therefore, combining the information from Figs. 5(a)–5(c), we can get the energy level alignments including the LUS in Fig. 5(d).

The present result of $E_{\text{affin}} = Ip - E_g = 2.50$ eV seems reasonable in view of the bulk-limited electron transport in PLED with PFO as the emitting layer.[3] If E_{affin} were as low as 2.12 eV,[7] only low work-function materials such as K, Na, Cs, and Rb would be compatible as metal electrodes to achieve bulk-limited operation.

In summary, the electronic structure and the electron energy gap of PFO film have been obtained by using photoelectron spectroscopies. From the UPS measurements, we obtained $Ip = 5.60 \pm 0.05$ eV, and from the XPS measurements, we estimated $E_g = 3.10 \pm 0.10$ eV. By comparing E_g with $E_{g,\text{opt}}$, we found that the optical absorption maximum is closer to the value of E_g than the optical absorption edge. Therefore we suggest that the optical absorption maximum may be a better approximation of E_g.

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