Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV)/poly(3-hexylthiophene-2,5-diyl) (P3HT) heterolayer film on gold: two-photon photoemission spectroscopy

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Abstract
The interfacial electronic structure and photoexcitation kinetics of MEH-PPV/P3HT heterolayer film on gold were studied using two-photon photoemission spectroscopy. We observed that the photoelectron kinetic energy distribution and the photoexcitation kinetics exhibit the characteristics of the MEH-PPV layer, and the absolute two-photon photoemission yield is determined by the P3HT layer. On the basis of the photoexcitation kinetics and the photoelectron kinetic energy distribution, we conclude that a charge transfer occurs efficiently from P3HT to MEH-PPV before photoemission.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic conjugated polymers have been extensively studied and applied owing to their low cost manufacturing process, light weight, flexibility and unique optoelectronic properties [1–3]. For the industrial application of conjugated polymers, one of the main challenging projects is to achieve efficiency of inorganic-based devices for mass production. For improving the efficiency, heterolayer conjugated polymer junctions (or mixed conjugated polymers) have been employed [4–6]. For a single-layer device, because the hole mobility is higher than the electron mobility, an emissive exciton is created in the vicinity of the cathode. In this case, the exciton is quenched by the metal cathode [7]. For a heterolayer photovoltaic device, one part acts as a hole acceptor and the other acts as an electron acceptor; then a photogenerated exciton separates more efficiently at the interface to increase the photovoltaic efficiency [8, 9]. Sirringhaus *et al* demonstrated a MEH-PPV light emitting device driven by a P3HT-based FET without direct contact of two different conjugated polymers [10].

Motivated by this, we have studied conjugated polymers on metal substrates using two-photon photoemission (2PPE) spectroscopy [11–16]. In the 2PPE technique (figure 1) [17], the first photon ($\hbar\omega$) creates an electron in an unoccupied intermediate state, and then the second photon ($\hbar\omega$) ejects the electron out of the vacuum level. The photoemitted electron is also directly emitted from the occupied state by a direct two-photon photoemission process as shown in figure 1. The intermediate state energy level and the photoexcitation kinetics are derived from the photoelectron kinetic energy and the photoemission yield versus incident photon energy.

In this paper, we selected two different conjugated polymers with entirely different application properties. One is poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV), showing a high luminescence efficiency [18], and the other is poly(3-hexylthiophene-2,5-diyl) (P3HT), exhibiting a high charge carrier mobility [19]. For our study, we spin-coated MEH-PPV on top of P3HT.

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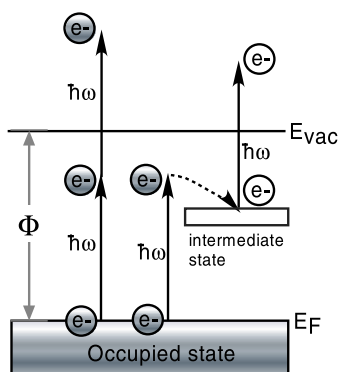
Figure 1. Two different two-photon photoemission processes. A photoemitted electron is directly emitted from an occupied state by a direct two-step excitation, or the electron is ejected from an intermediate state. The intermediate state electron is generated by pumping from an occupied state, followed by a relaxation into the state.

2. Experimental details

The 2PPE experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of about 1×10^{-9} Torr. For the 2PPE of MEH-PPV/P3HT heterolayer film on gold, we first spin-coated >98.5% regio-regular P3HT (Sigma-Aldrich) from a chloroform solution onto a flame annealed gold film substrate, and this was followed by thermal annealing at 150 °C in the UHV chamber. After we took the 2PPE spectra of the P3HT film, we removed the P3HT sample from the chamber, and spin-coated MEH-PPV from a THF solution onto the sample. The heterolayer MEH-PPV/P3HT film on gold was then introduced into the chamber. We took 2PPE spectra for the heterolayer sample before and after thermal annealing (100 and 150 °C).

We used a Lambda-Physik excimer pumped dye laser (~20 ns pulse width) operated at a pulse repetition rate of 20 Hz. The pump–probe laser was incident at 75° from the surface normal, with an estimated spot size of $\sim 3 \times 10^{-3}$ cm². A concentric hemispherical analyser (VG 100AX) was used to record the photoelectron kinetic energy. A sample bias of −10.0 V was applied while measuring the electron kinetic energy and the total photoemitted charge. The total emitted charge was measured using an Oxford TC174 charge amplifier. The thickness of the sample was measured using x-ray photoelectron spectroscopy (XPS) or atomic force microscopy (AFM). The thickness of the P3HT film is estimated to be about 30 nm, and the thickness of the top-layer MEH-PPV is about 3–4 nm.

3. Results and discussion

Figure 2 shows the 2PPE spectra for 150 °C-annealed P3HT/Au, unannealed, 100 °C-annealed, 150 °C-annealed MEH-PPV/P3HT/Au. For the 150 °C-annealed P3HT/Au, the low energy cut-off is located at 3.8 eV above the Fermi level, referenced to the work function ($\Phi = 5.1$ eV) of a bare Au film substrate. We attribute the work function lowering of 1.3 eV
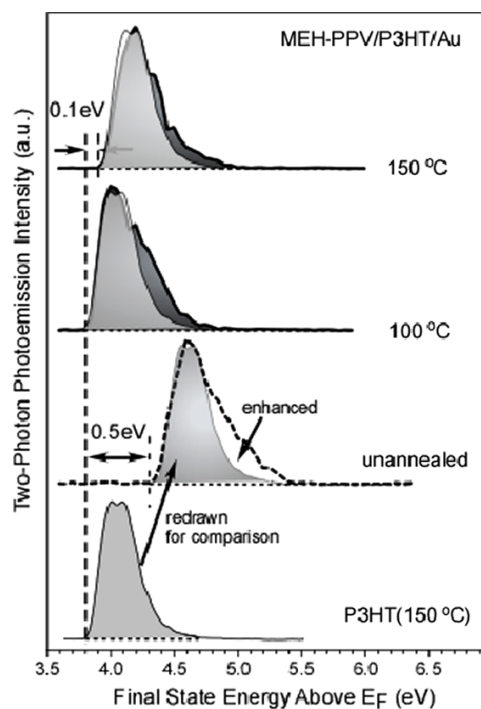

Figure 2. 2PPE spectra for a 150 °C-annealed P3HT/Au, and unannealed, 100 °C-annealed and 150 °C-annealed heterolayer MEH-PPV/P3HT/Au.

to interface dipole effects [20]. Upon spin coating of MEH-PPV on top of the P3HT film, the work function increases by +0.5 eV. We attribute this increase to residual oxygen (or water and solvent) impurities acting as p-type dopants [13]. Upon removing the impurities by annealing to 100 °C, the work function returns to 3.8 eV. This indicates that no interface dipole is created between the MEH-PPV and the P3HT layers. It is well known that the interface dipole at most of organic–organic interfaces is negligibly small [21]. Upon annealing to 150 °C, the work function increases by +0.1 eV. We also observed a similar work function change for a single MEH-PPV film upon annealing to 150 °C. This was not observed for a single P3HT film [13]. For MEH-PPV/Au, we attribute the work function increase to a degradation effect.

Because the 2PPE spectra for conjugated polymers are broad, it is difficult to extract information on the unoccupied energy levels. We carefully compared the 2PPE spectrum of the P3HT/Au with that of the MEH-PPV/P3HT/Au. We clearly found that for the heterolayer film the photoemission intensity at ~0.65 eV above the low energy cut-off was enhanced. The emission signal at ~0.65 eV for the unannealed film is more enhanced than that for the 100 °C-annealed film. Actually, these are the characteristics of photoemission from a single MEH-PPV film [15]. It appears that the enhanced emission is due to photoemission from an unoccupied energy level of MEH-PPV [15]. On the basis of this observation, we tentatively conclude that a charge transfer occurs from P3HT to MEH-PPV. This is further discussed below.

Figure 3 shows the 2PPE yields for a 150 °C-annealed P3HT/Au, unannealed, 100 °C-annealed, 150 °C-annealed MEH-PPV/P3HT/Au, and a 100 °C-annealed MEH-PPV/Au,
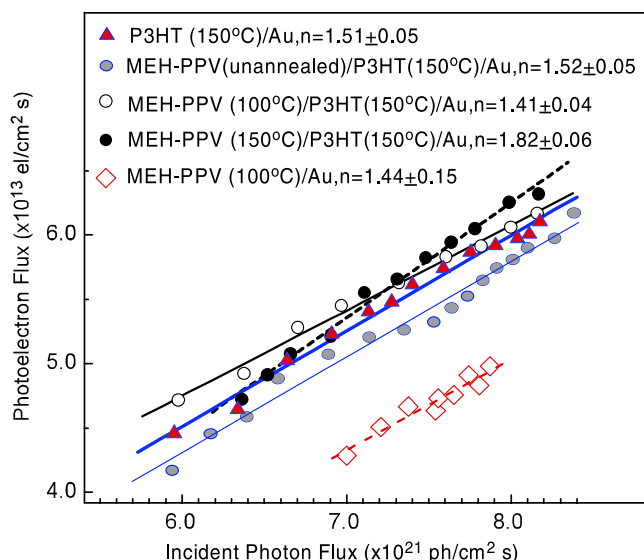
Figure 3. Natural log of photoemitted electron flux
(electrons cm^{-2} s^{-1}) versus incident photon flux (photons cm^{-2} s^{-1})
for P3HT/Au, MEH-PPV/Au, and unannealed, 100 °C-annealed and
150 °C-annealed heterolayer MEH/P3HT/Au.

as a function of incident photon flux. For the single-layer
films, the 2PPE yield of P3HT/Au is much higher than
that of MEH-PPV/Au [13]. Upon MEH-PPV coating on
top of the P3HT film, the yield is decreased, as shown
in figure 3. We attribute this decrease to impurities that
quench the photoexcitations [13]. As we mentioned earlier,
the work function is also lowered by impurity effects for
the unannealed film. Upon annealing the heterolayer film to
100 °C (or removing the impurities), the yield increases, and
the yield is slightly higher than that of the P3HT/Au. Upon

further annealing the heterolayer film to 150 °C, the yield
does not change much, but the slope dramatically changes
from 1.4 to 1.8. For others, the slopes (1.5 ± 0.1 eV) are
very similar. We attribute the slope of 1.5 to a bimolecular
recombination kinetics, which is commonly observed for
conjugated polymers [22]. The 2PPE yield of a conjugated
polymer is proportional to $I^n \times I^1 = I^{n+1}$, where I is the
incident photon flux, and $0 < n < 1$ is determined by the
photoexcitation kinetics [23]. For the slope of 1.8, we attribute
this to a degradation effect. Actually, we also observed a
slope of 1.8 for a single 150 °C-annealed MEH-PPV film [13].
This strongly indicates that the photoexcitation kinetics of the
MEH-PPV/P3HT film follows that of the MEH-PPV film. In
other words, a charge transfer occurs from P3HT to MEH-PPV
before photoemission.

Briefly, for the degradation effect (including a change
in polymer conformation), we assume that the polymer
degradation mainly eliminates interfacial contact (or a
wavefunction mixing) between two MEH-PPV polymer chains
without forming a significant photoexcitation quenching
site [15]. Then, the first-order kinetics could be dominant
because of a reduced wavefunction mixing between two
polymer chains, without impacting the 2PPE yield.

Because the charge transfer process is much faster than
the 20 ns laser probe pulse the primary photoexcitations—
mainly created in the Au substrate and the thick P3HT—
could transfer to MEH-PPV, and they reside in the MEH-
PPV film until the second probe photon arrives. Without a
charge transfer process, the photoexcited electrons propagate
for emission only with the characteristics of P3HT. Then,
the photoexcitations kinetics and the photoemission spectral
profiles of the heterolayer film will not resemble those of the
single MEH-PPV film. Thus, we could conclude that the
charge transfer is efficient without a quenching at the polymer
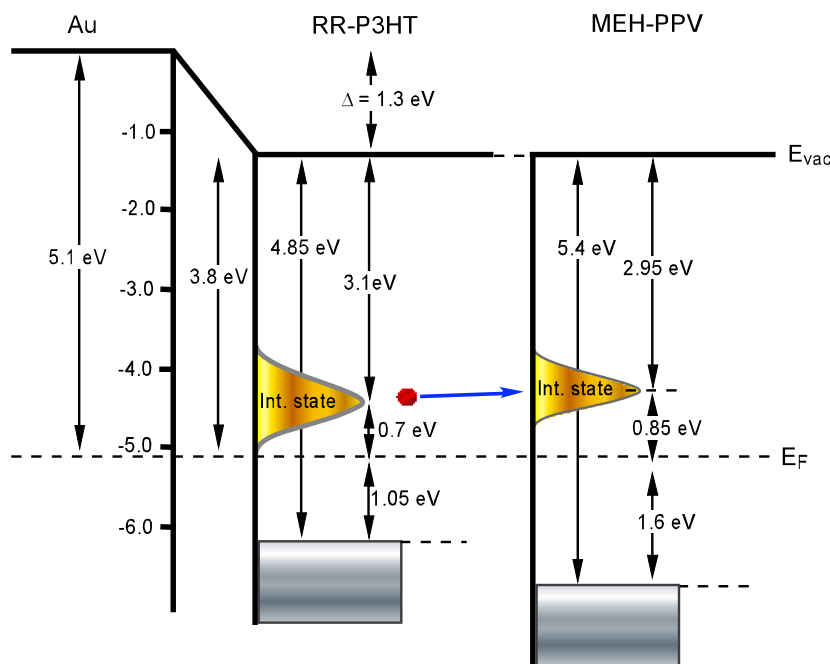
Figure 4. Interfacial energy diagram for MEH-PPV/P3HT/Au.
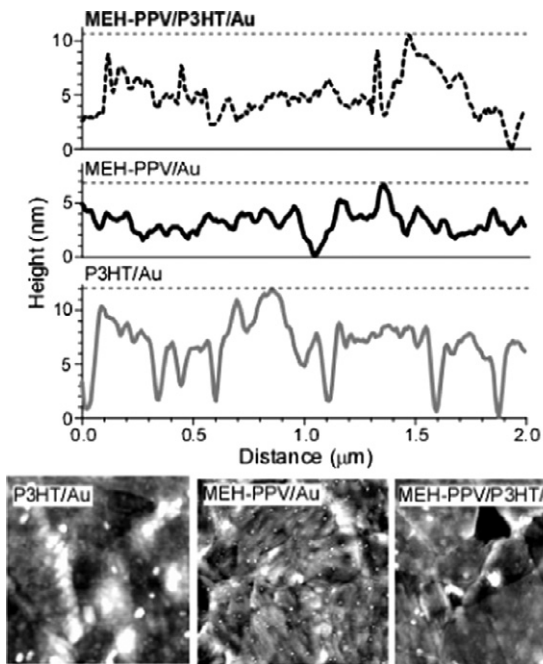
Figure 5. AFM images (2 μm $\times$ 2 μm) and the corresponding line profiles for 150 °C-annealed P3HT/Au, 100 °C-annealed MEH-PPV/Au, and 150 °C-annealed heterolayer MEH-PPV/P3HT/Au.

interface because the yield of the heterolayer film is not smaller than that for the single P3HT film. Our studied system is thinner MEH-PPV (3–4 nm) film coated on top of thicker P3HT ($\sim$30 nm) film directly in contact with a Au substrate.

Figure 4 displays the interfacial energy level for the 100 °C-annealed heterolayer MEH-PPV/P3HT/Au based on the interfacial energy levels of P3HT/Au and MEH-PPV/Au [14, 16]. The work function is measured to be 3.8 eV. In the diagram, although the intermediate state of the P3HT is 0.15 eV lower than that of the MEH-PPV, the wavefunction mixing could efficiently occur because the intermediate states are broad.

For a good wavefunction coupling, a good interfacial contact is essential. Figure 5 shows the AFM images (2 μm $\times$ 2 μm) and the corresponding line profiles for 150 °C-annealed P3HT ($\sim$30 nm), 100 °C-annealed MEH-PPV ($\sim$20 nm) and 150 °C-annealed heterolayer MEH-PPV/P3HT films. As seen in the height profiles, the single MEH-PPV film is smoother than the single P3HT film. After MEH-PPV coating on the P3HT film, the surface becomes smoother, and the holes seen in the single P3HT film disappears. This indicates that the MEH-PPV is highly compatible with the P3HT, without showing any segregation. The good compatibility could increase the chance of wavefunction mixing of the two conjugated polymers.

4. Conclusion

We have first employed 2PPE technique for studying photoexcitation kinetics, interfacial energy levels and charge transfer process of heterolayer conjugated polymer films. The photoexcitation kinetics and the photoemission profiles of the heterolayer MEH-PPV/P3HT film on Au resemble those of the single MEH-PPV film. The 2PPE yield of the heterolayer film is larger than that of the single P3HT film. The surface of the heterolayer film is smoother than that of the single P3HT film. On the basis of the results we conclude that the wavefunction mixing of the intermediate states of P3HT and MEH-PPV is efficient, and a charge transfer process efficiently occurs from P3HT to MEH-PPV.

Acknowledgment

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