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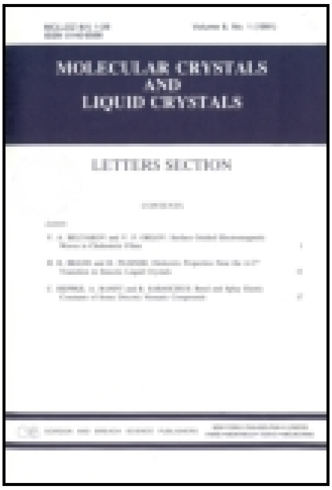

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Characterization of P3HT:PCBM Thin Film Interfaces by Doubly Resonant Sum-Frequency Generation Spectroscopy

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The surface structures and the electronic states of poly(3-hexylthiophene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) blend films are studied by using doubly resonant infrared-visible sum frequency generation (DR-SFG) spectroscopy. The SFG spectra of P3HT indicate the co-existence of the ordered and disordered P3HT at the interface. In the P3HT:PCBM blend film, the peak located at 1460 cm^{-1}, which is originated from the charge transfer state of PCBM, is observed.

Keywords Sum frequency generation; organic photovoltaic device; poly(3-hexylthiophene)

1. Introduction

Polymer-based organic photovoltaic (OPV) devices are promising alternatives to their inorganic counterparts due to their low-cost, easy fabrication, and compatibility with large-area and flexible substrates [1]. The blend of poly(3-hexylthiophene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) has been most intensively studied as the OPV materials in recent years. In organic devices, the electronic structures of the molecules at the interface are important factors, because the charge carriers have to be passing through the organic/electrode interfaces. However, the optical and electronic properties of the molecules used in OPV at an interface remain unexplored due to the lack of a suitable probing technique. In this study, we apply doubly resonant sum-frequency generation (DR-SFG) spectroscopy to investigate the surface vibrational and electronic structure of the P3HT:PCBM thin films.

2. Experimental Section

Regioregular poly(3-hexylthiophene) (RR-P3HT) and PCBM were purchased from Merck and Solenne B.V., respectively, and they were used as received. The composite films of RR-P3HT and PCBM (blending ratio of 10:7 by weight) were spin-coated from chlorobenzene solution at 1200 rpm onto Si(100) or fused quartz substrates inside a glovebox with nitrogen atmosphere.

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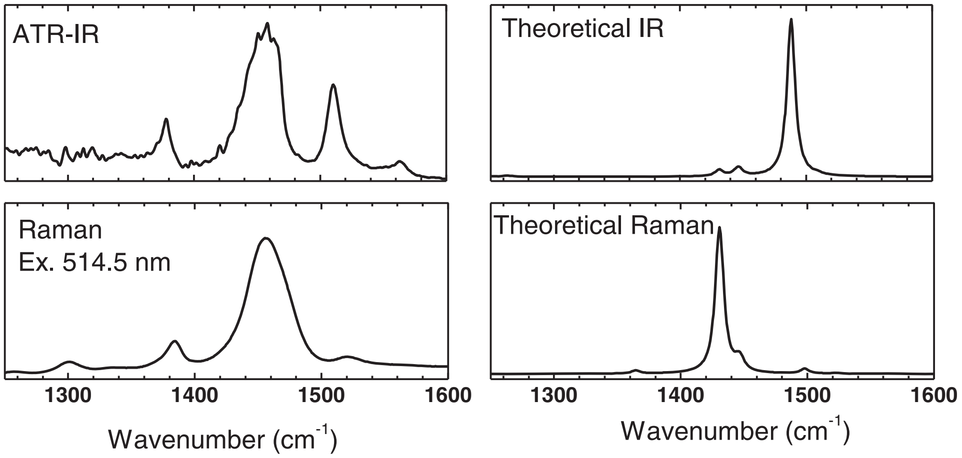

Figure 1. Experimental IR and Raman spectra of P3HT (left panels) and theoretical ones of oligothiophene 8T (right panels).

The basic SFG system employed in this experiment has been described in detail in the previous publication [2].

The density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level using GAUSSIAN 09 package [3]. Note that the calculated Raman spectra are under non-resonant condition.

3. Results and Discussions

Figure 1 shows the experimentally observed IR and Raman spectra of RR-P3HT as cast films and compares them with the calculated spectra of oligothiophene, 8T. In the theoretical spectra, vibration frequencies were scaled by a standard scaling factor of 0.9614 for B3LYP/6-31G(d). The observed and simulated Raman spectra agree well with those in a literature [4]. The main peak at around 1445 cm^{-1} is attributed to the symmetric C=C stretch mode and the peak at 1381 cm^{-1} is derived from the intra-ring C-C stretch mode. In the IR spectrum, the peak at 1510 cm^{-1} is assigned to the asymmetric C=C stretching of thiophene ring of P3HT.

In Fig. 2, we show the SFG vibrational spectra of the RR-P3HT, PCBM, and P3HT:PCBM blend film surfaces with three different visible wavelengths in SSP polarization combination (S-, S-, and P-polarized for SFG, visible, and IR, respectively). In the SFG spectra of the P3HT film, the intensity and the spectral shape at around 1450 cm^{-1} shows excitation-energy dependence. This is due to the fact that the RR-P3HT has some electronic absorption from 400 to 600 nm. In the SFG spectra of RR-P3HT, the broad peak around 1450 cm^{-1} consists with two components. By the global fitting of the SFG spectra of the P3HT, we found two peaks in the C=C mode of the P3HT; the low-frequency feature centered at 1440 cm^{-1} (peak width ~8 cm^{-1}), and high-frequency feature centered at 1450 cm^{-1} (peak width ~12 cm^{-1}), respectively. It has been reported in the resonant Raman study of non-annealed RR-P3HT films that the peak position of the C=C stretch of P3HT is sensitive to the degree of molecular order of P3HT [4]. According to Ref. 4, there are at least two components around 1450 cm^{-1} in the resonant Raman of P3HT. The low-frequency feature is derived from the more ordered P3HT phase, and high-frequency

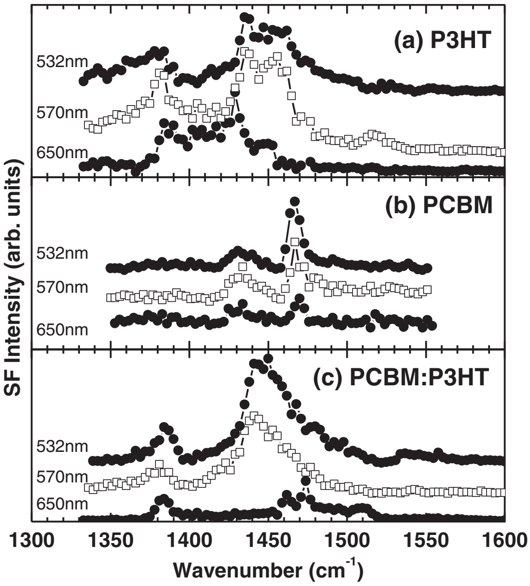

Figure 2. SFG spectra of (a) RR-P3HT, (b) PCBM, and (c) P3HT:PCBM film surfaces with three different visible wavelengths.

feature originates from the disordered component. The intensity of the peak at 1450 cm^{-1} is significantly reduced when the visible probe wavelength was changed from 532 to 650 mm, while a decrease in the intensity of the 1440 cm^{-1} peak is rather small. It is well known that the optical absorption edge of the P3HT is red-shifted by forming the ordered phase as compared with the amorphous phase [4]. Since the intensity variation of the doubly resonant SFG reflects the changes of the electronic transition states of the molecules, the SFG intensity behavior of the 1440 and 1450 cm^{-1} peaks indicates that the 1440 and 1450 cm^{-1} peaks are derived from the ordered and amorphous P3HT, respectively. Thus, we conclude that the surface of the P3HT blend film is co-existence of the ordered and disordered P3HT molecules at the surface.

Next, we will move on to the SFG spectra of the P3HT:PCBM blend films (Fig. 2(c)). We found that the SFG peak position and the feature of the P3HT C=C mode of the P3HT:PCBM film is the same as in that of the pristine RR-P3HT film. Under 650 nm excitation, the C=C mode of P3HT is almost vanished, and instead, the peaks at 1460 and 1470 cm^{-1} are clearly detected. From the SFG spectra of the pristine PCBM films, the peak at 1470 cm^{-1} originates from the vibrational mode of the C_{60} chromophore of PCBM [5]. We attribute the peak at 1460 cm^{-1} is derived from the charge transfer state of the PCBM. In the IR and SFG study of the K-doped C_{60}, A_g pinch mode of C_{60} redshifts by the charge transfer. From Ref. 6, it can be assumed that the transfer of one electron induces a shift of 6.5 cm^{-1} in frequency. Actually, charge transfer from P3HT to C_{60} was observed under illumination at wavelength 700 nm light by electron spin resonance and related measurements [7]. Because the intensity of the 1460 cm^{-1} peak is very small and might be the buried under the large C=C mode of the P3HT above 650 nm visible excitation, this peak could be only detected by the excitation of the long wavelength of the visible light. The charges transferred from P3HT might smear the doubly resonant condition of the SFG. Further experiments with longer wavelength excitation will reveal the character of the excitation of the profiles at the charge transfer at the P3HT:PCBM surfaces.

In conclusion, we have investigated the surface structure of the P3HT:PCBM film by doubly resonant SFG. The SFG spectra of RR-P3HT indicate the co-existence of the ordered and disordered P3HT at the interface. In the P3HT:PCBM blend film, the new peak, located at 1460 cm^{-1} is observed. We attributed this peak to the charge transfer state of PCBM.

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