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Exciton Dynamics of P3HT:PCBM Blend Films with Different Polymer Regioregularities Using Transient Absorption Spectroscopy

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The poly(3-hexylthiophene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) blending is one of the most intensively studied active material systems for bulk-heterojunction (BHJ) organic photovoltaic devices. For the active layer with BHJ structure, the charge tranfer (CT) and exciton dissociation processes between P3HT and PCBM are the important initial steps to form free charge carriers in the active layer. To compare the CT related species from the transient absorption dynamics in P3HT:PCBM blend systems with different orderings of the polymer, we investigated the charge carrier dynamics in P3HT:PCBM blend films with regiorandom and regioregular polymer structures using femtosecond transient absorption spectroscopy.

Keywords Exciton dynamics; organic photovoltaics; P3HT:PCBM; transient absorption spectroscopy

Introduction

For organic photovoltaics with P3HT:PCBM BHJ active layer, the regioregularity (RR) of the P3HT polymer acts as an important factor for the successful performance of the device because RR determines the morphology or crystallinity of the polymer and PCBM domains during the preparation of the film. The structural change with RR affects the CT states and mobilities of the charge carriers in device [1, 2]. The electron transfer from P3HT to PCBM at their interface occurs in a very short time scale and decay kinetics obtained from CT states can give the information about the recombination and dissociation of initially generated electron and hole pairs. Many researchers have, therefore, investigated the ultrafast transient absorption (TA) spectroscopic studies to understand the initial excitonic dynamics formed in the BHJ system [3∼9]. However, most of the previous reports have been focused on the films with regioregular polymers and their device characteristics. Of course, previous some papers have been reported with the significant results of the polymer system of different RR

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using TA spectroscopy in millisecond [10] and picosecond time scales [11]. In this work, in order to monitor more carefully the effect of RR in the viewpoint of the generations of excitons and CT related transitions, we investigated the TA decay kinetics of P3HT:PCBM films with regiorandom and regioregular polymers prepared with optimized conditions for the precise comparison of the TA signal intensities using femtosecond transient absorption measurements.

Experimental

The films used in this study were prepared as in the following procedure. The glass were cleaned and treated with O_2 plasma for about 15 min. A 2 wt% chlorobenzene solution of P3HT (Rieke):PCBM (Nano-C) with a 1:0.7 weight ratio was stirred under nitrogen atmosphere at 60°C overnight. Finally, the prepared rraP3HT:PCBM (50% RR) and rrP3HT:PCBM (98% RR) solutions were spin-coated on glass, giving film thicknesses of ∼100 nm at spin-coating speeds of 1,000 rpm. Each sample was encapsulated with an engraved cover-glass under N_2 atmosphere, followed by annealing at 150°C (rraP3HT) and 160°C (rrP3HT) for 5 min. The femtosecond TA measurement was performed utilizing a Ti:sapphire regenerative amplifier laser system (Libra, Coherent, pulse width of 100 fs, repetition rate of 1 kHz) and a pump-probe spectrometer (Helios, Ultrafast Systems LLC). The pump beam (490 nm) was generated using an OPA (TOPAS, Coherent) system and white light continuum for probe beam from sapphire crystals. The TA kinetics was measured from 1 ps to 1 ns time scales and the probing wavelength was covered from 450 to 1600 nm.

Results and Discussion

Figure 1 shows the femtosecond TA spectra of P3HT and P3HT:PCBM films with different regioregularities of P3HT collected from 1 ps to 1 ns time scales after excitation with 490 nm (3 μJ/cm^2). First, for the rraP3HT film shown in Fig. 1(a), the negative signals around 500 nm and 600 nm are attributed to the superposition of ground-state bleaching and stimulated emission [8, 12]. And the positive signal in near-infrared wavelengths is excited-state absorption from singlet excitons in which the relaxation of the excitonic transition in near-infrared is observed. Most of those features in the TA spectra for rraP3HT decay in 1 ns. On the other hand, for the blend film with PCBM, the TA spectra show the spectral and kinetic changes in the mid-wavelength range as shown in Fig. 1(b). A new long-lived broad absorption is observed between 600 nm and 1000 nm, which was assigned to the CT related states due to the existence of PCBM as an electron acceptor [12∼14]. The CT related states in this discussion include free charge carriers following the CT states. With the transition from excitons to CT species, the decay lifetime of the excitonic absorption after blending rraP3HT with PCBM decreases from ∼70 ps to ∼2 ps as in Fig. 2(a), which is a considerable change in comparison with that (from 30 ps to 8 ps) of the rrP3HT system. This indicates that the regiorandom polymer with PCBM is more effective for the electron transfer from P3HT to PCBM than the rrP3HT:PCBM system. Fig. 1(c) shows TA spectra for a rrP3HT film and the bleaching absorption around 500 nm and 600 nm has more distinctive structures due to the crystallinity of the polymer. Besides, a strong CT related absorption of the polymer is observed around 650 nm, which is related to the interchain absorption from the crystalline polymer. All the TA features shown in the rrP3HT film also recombine to the ground states in 1 ns excluding a very small amount of

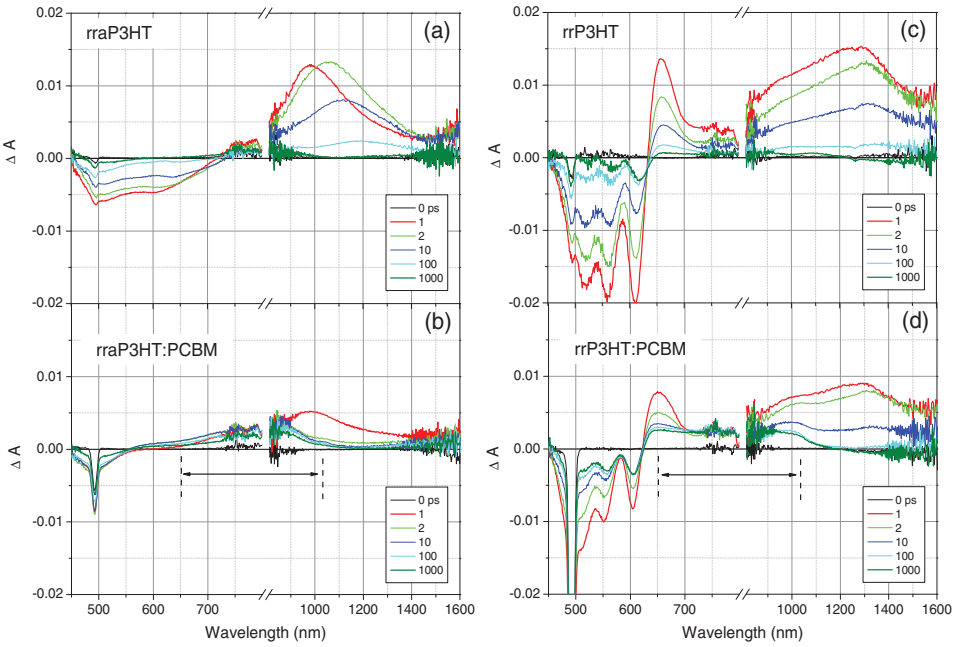

Figure 1. Femtosecond TA spectra measured at 0, 1, 2, 10, 100, 1000 ps for (a) rraP3HT, (b) rraP3HT:PCBM, (c) rrP3HT, (d) rrP3HT:PCBM films excited at 490 nm with 3 μJ/cm^2.

the bleaching absorption. For the kinetic changes in excitonic absorption, the rrP3HT at 1300 nm is decayed two times faster than that of rraP3HT at 1200 nm as in Fig. 2(b) and this shortened decay for rrP3HT can be due to the formation of the strong transition at 650 nm. Fig. 1(d) shows the TA spectral changes with time for a rrP3HT:PCBM film. Similar to the rraP3HT:PCBM, a broad long-lived CT related band is observed in the same wavelength region. Comparing the decay kinetics of the CT related transitions between rraP3HT:PCBM and rrP3HT:PCBM, we found that the TA decays at 700 nm and 900 nm have different kinetic behaviors with RRs. For the decay at 900 nm in Fig. 3(b), it is apparent that the

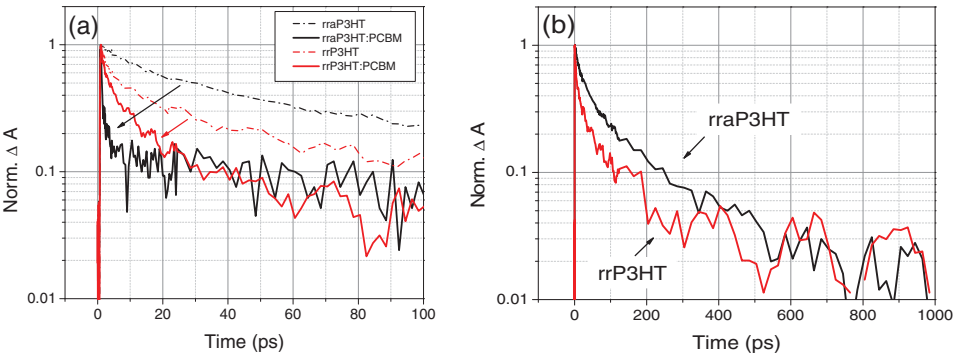

Figure 2. TA decay kinetics of the excitonic transitions for (a) rraP3HT & rraP3HT:PCBM (black) monitored at 1200 nm, rrP3HT & rrP3HT:PCBM films (red) at 1300 nm, (b) rraP3HT (black) at 1200 nm, rrP3HT (red) films at 1300 nm.

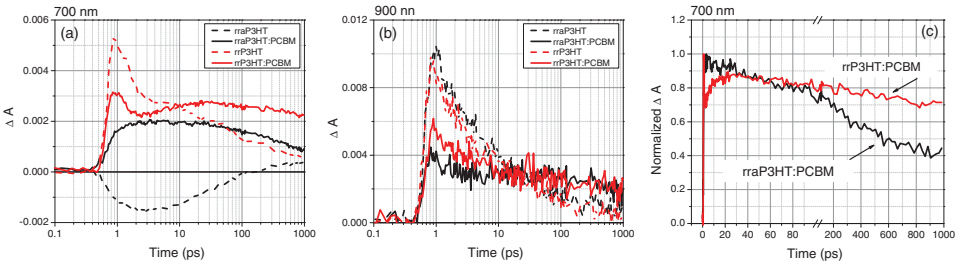

Figure 3. (a) TA decay kinetics monitored at 700 nm for rraP3HT, rraP3HT:PCBM (black) and rrP3HT, rrP3HT:PCBM (red), (b) at 900 nm, (c) rraP3HT:PCBM (black) and rrP3HT:PCBM (red) films at 700 nm.

decay with different RRs shows almost identical kinetics suggesting that the origin of this state is from the common structures existing in both RRs like single chains or amorphous domains. However, for the decay kinetics at 700 nm, the decay kinetics shows quite different shapes with RRs as shown in Fig. 3(a). First, most of the population for rrP3HT:PCBM still remains after 1 ns while that for rraP3HT:PCBM is reduced to 40% in the same time scale. Consequently, for rraP3HT:PCBM, although the blend system initially induces lots of electron transfers as shown in Fig. 2(a), its CT states quickly decay to the ground states rather than being in long-lived CT related states. The fast term at ∼1 ps for rrP3HT system is considered to be influenced by the intensity of the pump beam and, thus, this topic will be discussed in the next study. Above many points observed from the decay kinetics of the CT related states, one of the noticeable features found in the comparison at 700 nm is the delayed decay within ∼20 ps for the blend film with regioregular P3HT while the blend film with regiorandom P3HT has a prompt decay as in Fig. 3(c). From this comparison, it can be suggested that the delayed kinetics is assoicated with the excitonic diffusion in a well-ordered structure of the polymer. Although there still exists an ambiguity of the fact that the emission around 700 nm could influence the shape in the initial decay, the relatively weak emission yield for rrP3HT:PCBM could be negligible. This issue will be discussed in the further study since the stimulated emission can be dependent on the intensity of the pump beam as well.

Acknowledgments

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