



Excited-states spectroscopies and its magnetic field effect of π -conjugated polymer-fullerene blends with below-gap excitation



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ABSTRACT

We used continuous wave photoinduced absorption (PIA) spectroscopy to investigate long-lived polarons in blend of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and regio-regular poly (3-hexylthiophene) (RR-P3HT) with below-gap excitation. Compared to above-gap excitation, the polarons exhibited thermally activated and multi-trap limited bimolecular recombination too, but with narrower distribution profile in polaron states in millisecond time regime. However, magnetophoto-induced absorption (MPA) of polarons presented much weaker magnetic field effect in below-gap excitation (~ 0.5 mT) than in above-gap excitation (order of ~ 10 mT), although the underline mechanism is same as spin mixing of polaron pairs by the hyperfine interaction at small field region.

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1. Introduction

Organic photovoltaic (OPV) cells utilizing π -conjugated polymer (PCP) is a rapidly developing research field because of its increasing power conversion efficiency (PCE) recently [1–3]. To achieve efficient exciton diffusion to the charge separation interface, donor/acceptor blend films, or “bulk heterojunctions” were introduced [4,5]. How the free charges are photogenerated and recombined in blends is one of the fundamental questions [6,7]. To achieve such knowledge, the photoexcitations in PCPs as well as their blends with fullerene derivatives have been extensively studied using transient and continuous wave photoinduced absorption (PIA) spectroscopies [8–16]. The PIA spectrum is a difference in the optical absorption (Δa) spectrum of the polymer when it contains nonequilibrium photoexcitations in the excited states and that in the equilibrium ground state. Therefore, the optical transitions of the various photoexcitations are of importance. For the blend of disordered PCP such as poly[2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylene-vinylene] and fullerene, a single charge carrier added onto the polymer chain forms a polaron, which is characterized by two allowed optical transitions below the optical gap in the spectral range of mid IR (0.45 eV) and near IR

(1.4 eV), respectively [17]. For highly ordered PCP such as regio-regular poly (3-hexylthiophene) (RR-P3HT) film, self-organization of the polymer chains results in the formation of lamellae structure perpendicular to the film substrate. So there are four optical transition bands characterizing charge carriers in RR-P3HT/PCBM blends, two PIA bands (at 0.09 eV and at 1.8 eV) are due to 2D delocalized polarons (DPs) in the RR-P3HT lamellae structure; whereas the other two PIA bands (at 0.35 eV and at 1.25 eV) are due to localized intrachain polarons (LPs) [10,18–23].

Although there are still many unanswered questions [24–29], a series of work have shown that the charge photogeneration process in the blends involves intermediate steps, such as a charge transfer complex (CTC) state that is formed by charges in the polymer and fullerene phase, separately. Furthermore, using so called below gap excitation [17,30], CTC state as well as polarons can be photogenerated without involving intrachain excitons in the polymer phase. It is well accepted that the polarons generated using BG excitation were trapped [12]; however, to the best of our knowledge, the recombination mechanism is not studied in the millisecond time regime yet.

In this work, we used continuous wave photoinduced absorption (cw-PIA) measurements with below gap excitation to study the dynamics of long-lived polarons at various excitation intensities and temperatures in films of RR-P3HT/PCBM blends. Our measurements show that the recombination mechanism for polarons photogenerated using BG excitation is trap limited

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bimolecular recombination too, which is same to the polarons from AG excitation, but BG polarons presents narrower distribution of life time. Furthermore, the recombination processes of DP and LP with BG excitation are thermally activated process with similar activation energies.

2. Experimental

RR-P3HT and PCBM were purchased from Lumtec and used as received. The mixing ratio of the RR-P3HT/PCBM blend was 1.2:1 by weight [31,32]. The films were drop casting onto a cleaned glass substrate from a dilute chlorobenzene solution. A standard cw setup was used to obtain the PIA spectrum [10,33]. We used a diode laser at $\hbar\omega_L = 1.53$ eV ($\lambda = 808$ nm) for below-gap (BG) excitation and $\hbar\omega_L = 2.77$ eV ($\lambda = 447$ nm) for above-gap (AG) excitation, respectively; and an incandescent tungsten/halogen lamp as the probe. The pump and probe beams were overlapped on the samples in a cryostat in which the sample temperature can vary from 77 K to 300 K, the transmitted probe beam was detected by a silicon detector after through a monochromator. The samples were annealed at 425 K for 30 min and then measured in dynamic vacuum. The change of the transmitted probe beam (ΔT), which was caused by the modulated pump beam, was detected by the phase sensitive technique. Although the photoluminescence (PL) in polymer/PCBM blend is weak, its contribution to the PIA spectra was eliminated. For the modulation-frequency dependence measurement at a fixed probe wavelength, the pump beam was modulated from 5 Hz to 30k Hz; the data were corrected by normalizing to the system response. An additional band pass filter (700 ± 5 nm) for DP band or a long pass filter (>900 nm) for LP bands was put before the sample to minimize additional influences from probe beam absorption, especially for low modulation frequencies [8,34]. For P3HT/PCBM blends, the DP band of 0.1 eV dominates PIA spectrum, LP band at 0.35 eV is almost invisible [10,13,18]. Moreover, the DP band at 0.1 eV shows the anti-interference resonance with phonons [10], which may complicate the analysis in intensity and temperature dependence measurements. In addition, the other long lived photoexcitations such as triplet exciton or anion in PCBM have been proved much less important in RR-P3HT/PCBM blends.

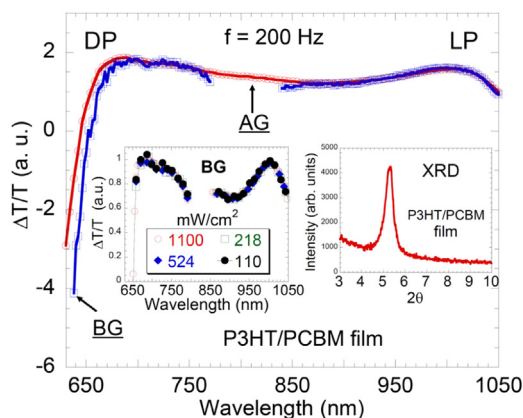


Fig. 1. (Color online) PIA spectra of RR-P3HT/PCBM film measured at 77 K for a modulation frequency of $f = 200$ Hz using above gap (AG, circle with line) and below gap (BG, square with line) excitation, respectively. The bands DP (delocalized polaron) and LP (localized polaron) are assigned. Left inset shows identical PIA spectra after normalization with BG excitation at various excitation intensities. Right inset is x-ray diffraction (XRD) pattern of the film.

3. Results and discussions

Fig. 1 shows quasi-steady-state PIA spectra for P3HT/PCBM blend film while the pump beam was modulated at 200 Hz, with both AG (~ 100 mW/cm²) and BG (~ 1100 mW/cm²) excitations respectively. Left inset of Fig. 1 shows almost identical PIA spectra with BG excitation at various excitation intensities after normalization. Right inset of Fig. 1 shows x-ray diffraction (XRD) pattern of the film, using the Cu K α line ($\lambda = 0.154$ nm). The (100) diffraction band proves the existence of lamella in the P3HT film. Using the Scherrer's relation ($L \sim 0.9\lambda / (\Delta\theta \cos\theta)$), where $\Delta\theta$ is the full width at half maximum (FWHM) of the peak, we estimate that the P3HT domain size is about 17 nm, which is close to the domain size in pure P3HT film [35,36]. Both PIA spectra are very similar, consisting of two strong bands, DP at 700 nm and LP at 1000 nm. The LP band is associated with intrachain localized polaron confined in a polymer chain, whereas the DP band is associated with delocalized polaron in lamellar structure [10,18–23]. In addition, with 447 nm excitation, the PIA spectra which is same with the results in Ref. [10] is observed in pristine RR-P3HT film; on the other hand, with 808 nm excitation, there is no PIA signal observed in both pristine RR-P3HT and PCBM films. According to the Drori's work [12], this can be taken as an evidence for the existence of charge transfer states. However, the polarons generated from BG excitation was thought to be different with AG, for they could not contribute to the photocurrent directly [12,17]. We also should point out that PIA spectra in mid-IR spectra range (~ 0.1 eV) with both BG and AG excitation are roughly same (not shown).

To illustrate properties of polarons from BG excitation, we show the dependence of PIA signal on modulation frequency (f) as well as pump beam's intensity (I), from both AG and BG excitations in Fig. 2. The diminishing PIA signal with increasing modulation frequency was observed in insets of Fig. 2 (a) and Fig. 2 (b) for DP and LP with BG excitation, respectively. To classify the mechanism of recombination, the average lifetime at various pump intensities were analyzed by fitting the total PIA signal, $R = (\text{in-phase}^2 + \text{out-of-phase}^2)^{0.5}$, with dispersive recombination equation [37],

$$\frac{\Delta T}{T} = \frac{(\frac{\Delta T}{T})_0}{1 + (\omega\tau)^\gamma} \quad (1)$$

where $(\Delta T/T)_0$ is steady state response at 0 Hz relating to the pump intensity, ω is the modulation frequency of the pump, τ is the average lifetime, and the γ is the dispersive parameter which stands for the degree of dispersity of the lifetimes. Values of γ should be no larger than one, with smaller values of γ correspond to a situation of broader distribution of lifetimes which can be readily explained by multi-traps limited dispersive recombination processes [22,23,33,34].

In Fig. 2, we found that the average lifetimes of both DP and LP are inverse proportional to the square root of intensity: $\sim I^{-0.5}$ in the millisecond time regime with BG excitation. According to the Yang's analysis [33], we ascribe the decay dynamics of both DP and LP to bimolecular recombination here [22,38], no matter the CTC states are photogenerated directly or from the dissociation of exciton indirectly [17]. For the life time is the function of pump intensity, simply comparing the lifetime of polarons may not be enough to judge the difference between BG and AG excitation processes. In Fig. 2 insets, we found that the value of γ is the function of pump intensity. For BG excitation, the γ increases from 0.86 (0.9) to 0.96 (0.99) for DP band (LP band) while the pump intensity decreases 15 times (1200 mW/cm² to 74 mW/cm²) (insets of Fig. 2(a) and (b)); on the other hand, for AG excitation, the γ increases from 0.81 (0.85) to 1 (1) for DP band (LP band) while the

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