Investigation of Polaron Pair Dynamics in Poly(3-hexylthiophene) Film by Time Resolved Spectroscopy

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Abstract—Polaron pair dynamics in regioregular Poly (3-hexylthiophene) (RR-P3HT) film was studied by applying both femtosecond transient absorption and fluorescence up-conversion techniques. The comparison of the dynamics of the pure fluorescence, the ground state bleaching recovery and the polaron pair absorption reveals that the polaron pairs decay back to the ground state of certain morphological places with distinct absorption features, instead of the singlet excited state.

Index Terms—Fluorescence up-conversion, morphology, polaron pair, transient absorption.

I. INTRODUCTION

POLYMER solar cells are promising candidates for future power generation because of the advantages they offer, such as easy processing, low cost and flexibility. In particular, regioregular Poly (3-hexylthiophene) (RR-P3HT) has attracted wide attention as one of the most efficient organic photovoltaic materials [1-12]. This is because thin films can organize themselves into two-dimensional π-stacked lamellar structures [13, 14] resulting in high mobility of the order of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, a property closely related to the exciton and carrier behavior. Therefore, a clear understanding of the generation and decay dynamics of the excitations is essential to explore the underlying physics of photoexcitations and to further improve device operations. Time-resolved spectroscopy is a powerful tool to investigate the key photophysical processes in materials [13, 15-22]. Transient absorption studies, carried out earlier to study P3HT, reveal that exciton, polaron and polaron pairs in RR-P3HT thin film are the main photoexcitations [23-33]. The transient absorption measurement can give spectra signatures of different excitations, but the large spectra overlap of the ground state bleaching (GSB), its stimulated emission and excited state absorption make it hard to find a pure spectral signature for each excitation. So, the generation

and relaxation mechanism of polaron and polaron pairs are still far from fully understood. In this work, a combination of applying both transient absorption and fluorescence up-conversion techniques is proposed to be applied to investigate polaron pair dynamics in P3HT film. Direct measurement of photoluminescence (PL) by time-resolved emission can facilitate a clean probe of the exciton dynamics without interference from other species. Knowing one pure species helps one to extract relatively pure dynamics of the other species from the transient absorption signal.

A polaron pair is a coulomb bound pair of a negative and a positive polaron, situated on different molecules. At the intermediate state of an exciton and a pair of free polarons (mutually too far to be attracted by the other), it is important to investigate their dynamics to further understand the charge generations in polymers. Although it is well acknowledged that polaron pairs are generated in RR-P3HT film after photoexcitation and decay with a lifetime of about 0.7 ps [34, 35], little work was done to investigate their detailed dynamics. For example, it is believed that polaron pairs are easily generated where polymer chain has defects like kinks, torsions or bends [24, 25], but until now there has been no spectroscopic signature to verify whether polaron pairs can be generated from anywhere in the film or just from some specific domains like defects. Furthermore, it is still unclear which state they decay to: Do they directly recombine to the ground state? Or, do they just come closer to form excitons? It is previously reported that polaron pair decays to the singlet excited state [36]. They reached the conclusion based on the mismatching dynamics of the GSB of 510 nm and the excited state absorption of 660 nm, thus excluded the possibility of the polaron pairs recombining to the ground state. However, in the present experiments, by comparing the PL dynamics with the GSB recovery dynamics, it is found that the polaron pairs actually decay to the ground state. Furthermore, the wavelength dependent GSB recovery dynamics reveal that the polaron pairs decay to a certain morphological domain with a distinct absorption feature.

II. EXPERIMENTAL STUDIES

A. Materials, Steady-State Properties

Regioregular P3HT (Luminescence Technology Corp) with MW = 60 k and regioregularity greater than 95% were

Fig. 1.   Steady state absorption (red square) and emission (blue down triangle) spectra of RR-P3HT film.

Fig. 2.   Transient absorption spectra recorded at 0.5, 5, 20, 100, and 1200 ps respectively at excitation power of (a) 40 nJ/pulse and (b) 5 nJ/pulse. The excitation wavelength is 610 nm.

used as purchased without further purification. Solution of P3HT in dichlorobenzene, with a concentration of 30 mg/ml, was heated at approximately 50 °C until all the samples were dissolved. The solution was then ultrasonic oscillated for four minutes. The solution was spin-coated onto a pre-cleaned quartz substrate and sealed between two quartz slides. The peak absorbance of the film was about 0.5. To avoid degradation by oxygen, the spin-coating and sealing process were carried out under nitrogen environment in a glove box with oxygen concentration less than 0.1 ppm.

Absorption spectra were measured with Shimadzu UV-1700 spectrophotometer at 1 nm resolution, and Emission spectra recorded with AvaSpec-2048 fiber optic spectrometer at 0.6 nm resolution.

B. Femtosecond Transient Absorption Measurements

The femtosecond transient absorption spectroscopy was performed as follows [37]. The output of a Ti:Sapphire laser (Tsunami, Spectra Physics), pumped by Nd:YVO$_4$ laser (Millennia, Spectra Physics), was amplified in a regenerative amplifier (RGA, Spitfire, Spectra Physics). The amplifier provides 800 nm fundamental pulses at a repetition rate of 250 Hz with an energy of 1.5 mJ and a pulse width of 100 fs, which was split into two parts. One part of the RGA output (800 nm) was then used to generate a white light continuum as probe beam by focusing the beam into a 2-mm water cell. The other part was used either to pump OPA to generate excitation pulse at 610 nm, or sent to a 1 mm thick BBO to get double the frequency of 400 nm excitation pulse, which was in turn sent to a delay line and modulated by a synchronized optical chopper (Newport Model 75160) with a frequency of 125 Hz as the pump beam to excite the sample. Time-resolved transient absorption spectra were recorded with a highly sensitive spectrometer (Avantes AvaSpec-2048×14). Traces of the dynamics were obtained by controlling the relative delay between the pump and the probe pulses with a stepper-motor-driven optical delay line (Newport M-ILS250CC). The group velocity dispersion of the whole experimental system was compensated by a chirp program. The intensities of the pump pulses were measured with a laser power meter (Sanwa LP1). The excitation spot was about
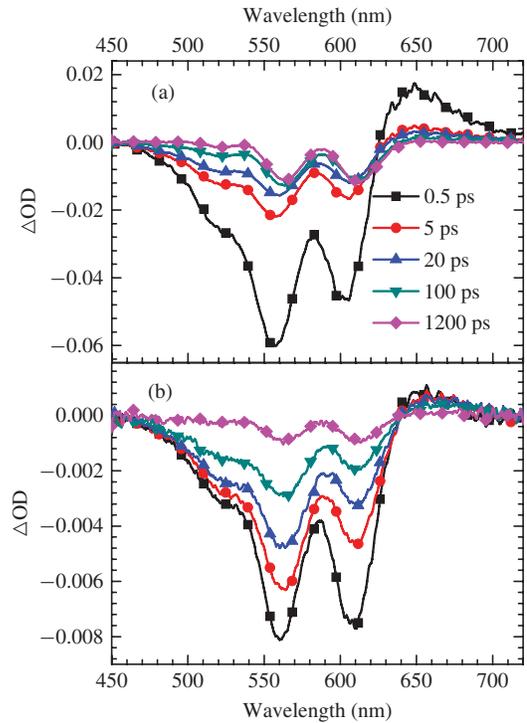
300 μm in diameter. All the measurements were performed at room temperature.

C. Time-Correlated Single-Photon Counting

Nanosecond fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20 MHz) was used to excite the samples. The fluorescence was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). Time constant of the instrument response function (IRF) was about 220 ps.

D. Fluorescence Up-Conversion Measurements

Subpicosecond time-resolved emissions were measured by the femtosecond fluorescence up-conversion method [38]. The same laser system was used as above and the output of the amplifier was split into two parts. One was used to pump OPA to generate excitation pulse at 610 nm or sent to a 1 mm thick BBO to get double the frequency of 400 nm excitation pulse. The resulting fluorescence was collected and focused onto a 1 mm thick BBO crystal at a cutting angle of 35 degrees. The other part of the RGA output was sent into an optical delay line where it served as the optical gate for up-conversion of fluorescence. The sum frequency light generated was then collimated and focused into the entrance slit of a 300 mm monochromator. A UV-sensitive photomultiplier tube 1P28 (Hamamatsu) was used to detect the signal. The electrical
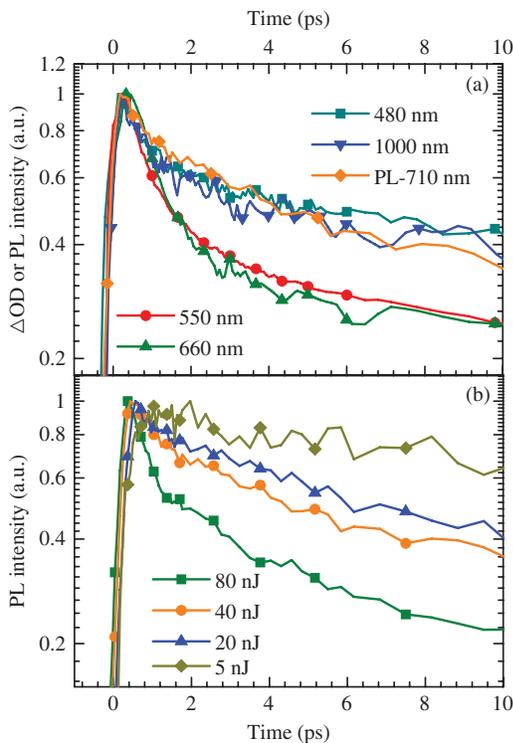
Fig. 3. (a) Normalized dynamics of the ground state bleaching (GSB) recovery of 480 nm and 550 nm and polaron pair (PP) absorption at 660 nm, polaron (P) absorption at 1000 nm and PL dynamics of 710 nm under excitation intensity of 40 nJ/pulse. (b) Fluorescence dynamics of 710 nm under various excitation intensities.

signal from the photomultiplier tube was summed by a digital oscilloscope. The relative polarization of the excitation and the gating beams was set to the magic angle for PL measurements. The FWHM of instrument response function was about 450 fs. The excitation spot was about 300 μm in diameter. All the measurements were performed at room temperature.

The multi-exponential dynamics fits convoluted with the system response function and the global fitting were performed using the fitting program of ASUFIT (available at http://www.public.asu.edu/~laserweb/asufit/asufit.html).

III. RESULTS AND DISCUSSION

A. Steady State and Time-Resolved Measurements

To minimize the effect of exciton migration from subunits of higher energy to those of lower energy [39], the experiments were conducted with red edge (610 nm) excitation. The excitation spot, as measured by a photographic paper, was about 300 μm. Both the transient absorption and fluorescence up-conversion measurements were made under the same excitation powers, namely 80, 40, 20 and at 5 nJ/pulse. The lowest excitation power of 5 nJ/pulse corresponds to the excitation density of about 1×10^{18} cm^{-3}.

Fig. 1 depicts the steady state absorption and emission spectra of RR-P3HT film. The absorption shoulder around 600 nm (0-0 vibronic) is a characteristic feature indicative of formation of crystalline form of P3HT. Fig. 2 depicts the transient absorption spectra of RR-P3HT film at excitation power of 40 and 5 nJ/pulse. The spectra can be assigned as
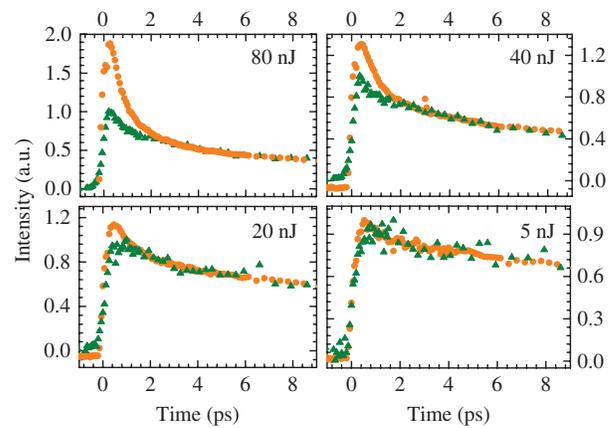

Fig. 4. Comparison of the bleahing dynamics of 550 nm (orange circle) and fluorescence dynamics of 710 nm (green up-triangle) under various excitation intensities. The GSB signal has had an offset of the value of several nanoseconds subtracted from the data.

follows: The GSB signal, which was in the range of 450 nm to 620 nm, had three peaks that corresponded to 0-0, 0-1 and 0-2 transition, respectively; the positive signals at 620 nm to 700 nm are due to the polaron pairs [34-36] and excited state absorptions; the GSB spectra exhibit gradually red-shift, and significant shape changes as time increases. In previous reports, it is suggested that the spectral red-shift is caused by migration of exciton to lower energy sub-units [40-43]. It shows that, even under red edge excitation, exciton migration also exists. The GSB recovery dynamics show interesting wavelength dependence. As shown in Fig. 3a, during the first few picoseconds, 510 nm recovers more slowly than does 550 nm. In fact, the wavelengths under 510 nm show slower initial GSB recovery than the wavelengths from 520 nm to 620 nm do. These dynamics with PL will be compared with polaron pair absorption dynamics to illustrate the reason for wavelength-dependent GSB recovery.

The dynamics of the PL peak wavelength of 710 nm under varies intensities are shown in fig. 3b. The excitation power dependent dynamics show that E-E annihilation occurs in the film. For low excitations of 5 nJ/pulse, a small rise component can be observed during the early stage of the PL transient, which is caused by the exciton migration to lower energy subunits [39]. Actually, for high intensity, rising component also exists, but because of the competing E-E annihilation, more excitons experience annihilation before migration. The rising component is, therefore, not as obvious as it is at low intensity.

B. Comparison of PL and GSB Recovery Dynamics

The PL dynamics of 710 nm were compared with the GSB recovery dynamics of 550 nm under different excitation powers (Fig. 4). Because the GSB signal contains a very long lifetime of several ns due to the polaron that is absent in PL dynamics, this offset was subtracted from the GSB recovery dynamics. It is found that GSB recovery has an additional fast decay of about 0.7 ps (table 1) compared to the PL decay; the remaining parts of the kinetics perfectly match. As excitation intensity decreases, the amplitude of the additional

TABLE I

FITTING PARAMETERS OF THE PL DYNAMICS AT 710 nm AND TA DYNAMICS AT 550 nm AND 660 nm.
THE NUMBER IN THE BRACKET GIVES THE RELATIVE WEIGHT OF EACH LIFETIME

*P	Probe (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	τ_5 (ps)
80 nJ	PL-710		0.3(59)	2.7(25)	52 (16)	
	TA-550	0.7(46)	0.3(28)	2.7(12)	52(4)	5000(9)
	TA-660	0.7(53)	0.3(28)	3.1(11)	69(8)	
40nJ	PL-710		1.4(50)	19(38)	250(12)	
	TA-550	0.63(45)	1.4(28)	19(15)	250(3)	5000(8)
	TA-660	0.7(73)	3.3(10)	37(11)	877(6)	
20nJ	PL-710		3(49)	32(32)	224(19)	
	TA-550	0.74(39)	3(25)	32(20)	224(9)	5000(7)
	TA-660	0.67(65)	6.3(11)	57(14)	764(10)	
5nJ	PL-710		3.2(31)	43(23)	381(46)	
	TA-550		3.2(25)	43(33)	381(31)	5000(11)
	TA-660	0.7(36)		110(31)	842(32)	

* P denotes "excitation power"

fast component decreases. When the excitation was lowered to 5 nJ/pulse, the two dynamics were almost the same. As the excitons are known to decay to the ground state, the PL decay should correspond to a certain GSB recovery. When a faster GSB recovery than the PL decay is observed, it implies that there must be other species going back to the ground state that contribute to the additional fast recovery. Besides excitons, there are two more excitations in P3HT, one by polaron and the other by polaron pairs. It is previously reported that the excited state absorption band of 1000 nm can be assigned to the polaron [35, 44], although it partly overlaps with the exciton band, which peaks at around 1200 nm [36, 44]. Fig. 3a shows that during the early stages, the decay of 1000 nm was similar to that of PL decay. Although the dynamics of 1000 nm reflect a combination of polaron and exciton dynamics, it is at least known that the initial polaron decay cannot be faster than the exciton decay; otherwise, the combined dynamics should be faster than the PL decay. This indicates that the additional fast GSB recovery was not caused by the polaron, leaving the only possibility of the polaron pairs.

C. Comparison of the Polaron Pair Absorption and the GSB Recovery Dynamics

If the additional GSB recovery was truly caused by the polaron pairs, the dynamics of the polaron pair absorption should have the same initial decay dynamics as did the GSB recovery. From a comparison of the dynamics of the polaron pair absorption of 660nm directly with that of GSB recovery of 550 nm, it was found that their initial fast decays matched very well (Fig. 3a) under 40 nJ/pulse excitation power, as also under other excitation powers (Fig. 5). They all showed a short lifetime of about 0.7 ps (Table 1) with the amplitude changing with excitation intensities. This lifetime matched well with the polaron pair lifetime reported earlier [35, 36], thus confirming that the fast additional recovery was from the polaron pairs.

Under the low excitation power of 5 nJ/pulse in Fig. 4, the PL dynamics was very much like the GSB recovery at 550 nm, which implies that the polaron pairs cannot be efficiently generated at low excitation power. This is consistent with the previous report that polaron pairs are generated from a higher vibrational state or from a higher singlet exciton state produced by the singlet exciton-exciton annihilation [36]. For the band edge excitation of 610 nm, the polaron pairs could form only by exciton-exciton annihilation. Therefore, at low excitation power, when there is almost no annihilation, polaron pairs cannot be efficiently generated. Without polaron pairs, there is no fast initial GSB recovery of 550 nm. All these observations are consistent with the conclusion that polaron pairs decay back to the ground state. The generation and decay dynamics can be illustrated as in Fig. 6.

D. Morphology-Dependent Polaron Pairs Generation

During the data analysis, it is found that the selection of GSB wavelength is very important for its comparison with the polaron pair absorption decay of 660 nm and PL decay of 710 nm, because the GSB recovery dynamics are wavelength-dependent as described above. Generally, the GSB recovery of wavelength under 510 nm is initially slower than that of the wavelengths range 520 nm to 620 nm. As shown in Fig. 3a, much different from 550 nm, the recovery of 510 nm is almost the same as the PL decay under the same excitation power and is much different from that of the polaron pair absorption of 660 nm, lacking the lifetime component of 0.7 ps. So, if one chooses 510 nm to compare, it looks like that the polaron pair decay is not companioned by a GSB recovery, which indicate that only the excitons and not the polaron pairs decay back to the ground state. It will lead to the improper conclusion that the polaron pairs decay back to the excited state instead of the ground state [36]. This wavelength-dependent GSB recovery also indicates that different ground states may exist
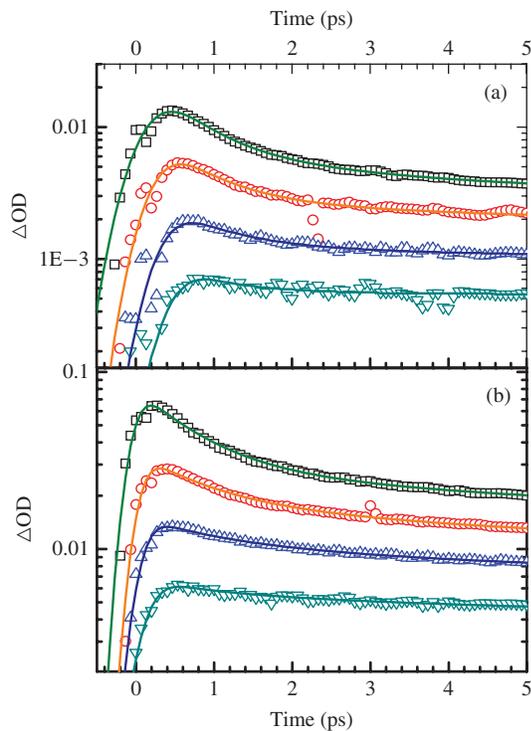
Fig. 5. Transient absorption dynamics at (a) 660 nm and (b) 550 nm under excitation intensity of 80 (green squre), 40 (orange circle), 20 (blue uptriangle), and 5 (dark green down triangle) nJ/pulse.
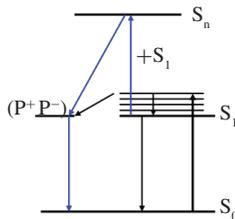

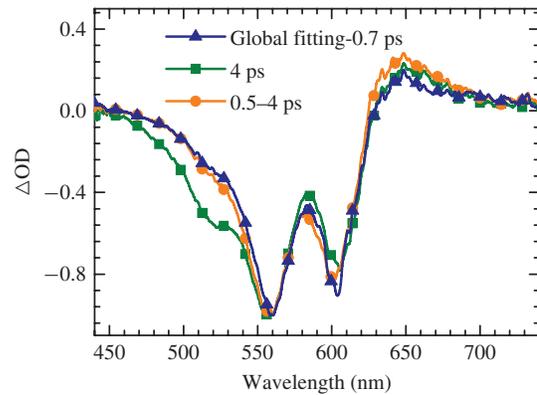Fig. 6. Energy diagram for polaron pair decay in RR-P3HT films.

Fig. 7. Comparison of the global fitting spectra of 0.7 ps lifetime (blue up-triangle), differential spectra of 0.5 and 4 ps (orange circle) and the spectra at 4 ps (green square), the excitation power is 40 nJ/pulse.

from different morphological places and that the polaron pairs only go back to a certain ground state, which has a relatively smaller absorption below 510 nm. Because, if there is only one kind of morphological place and all excitations are excited from that place, then all the wavelengths of the GSB should recover at the same rate as the excitations decay. But, if there are different morphological places with different absorption features, then the whole GSB is a mixture of the absorption spectra of all the places that are excited. If the excitation dynamics are different for each morphological place, then wavelength-dependent GSB recovery will be observed. To get the specific absorption spectra of the place where the polaron pairs decay, global fitting of the transient absorption measurements were carried out and the spectra for different lifetimes were obtained. The spectra of 0.7 ps lifetime (Fig. 7) is attributed to the spectra of polaron pair because of the consistence of the lifetime. It needs to be noted that "polaron pair spectra" is used to refer to the ground state bleaching spectra of the morphological place where polaron pairs decays. For comparison, the authors tried another way to get the

spectra of polaron pair. Since the lifetimes of the excitons and the polarons are much longer, so that the decay in the first few seconds will mainly reflect the polaron pair decay. If the spectra of 4 ps (where the polaron pairs almost decay to 0) is subtracted from the spectra of 0.5 ps (where the spectra grow to the maximum), then the differential spectra can roughly reflect the spectral shape that disappeared because of the decay of polaron pair. Fig. 7 shows that the spectra of 0.7 ps lifetime from the global fitting is in very good agreement with the differential spectra of 0.5 ps and 4 ps, thus validating spectral assignment to the polaron pair. The spectra at 4 ps could be regarded, more or less, as having resulted from the exciton. Fig. 7 shows a comparison of the three spectra, normalized at 0-1 peak (around 560 nm). It may be noted that the polaron pair spectra have different shapes with the spectra at 4 ps (mainly from excitons) and show much smaller absorption under 510 nm, indicating that the places where the polaron pairs reside are different from that of the exciton, showing distinct absorption spectra. It is previously reported that polaron pairs are easily generated at certain places, possibly where the polymer chain has kinks, torsions or bends [24, 25], whose absorption spectra are different from the spectra of other places. It is still not clear whether or not the polaron pair will move after generation. If it does not move, and if its place of generation is also the place where it decays to, then the polaron pair spectra found here should reflect the absorption spectra of the place that can generate polaron pair. If not, it can at least be shown that the polaron pairs decay back to the ground state of certain morphological places that have distinct absorption features.

IV. CONCLUSION

The authors conducted femtosecond transient absorption and fluorescence up-conversion measurements of RR-P3HT film with red edge excitation of 610 nm under different excitation powers. Comparison of the PL dynamic of 710 nm with the GSB recovery of 550 nm shows that there is an additional fast GSB recovery of 0.7 ps more than the PL decay. This additional recovery indicates that, besides excitons, there must be other species, which decay back to the ground state.

Direct comparison of the polaron pair absorption band of 660 nm with the GSB recovery of 550 nm shows that they match very well under all excitation intensities, showing the same fast initial decay. This leads to the conclusion that the polaron pairs recombine to the ground state, instead of the singlet excited state. Furthermore, the wavelength-dependent GSB recovery dynamics show that polaron pairs decay back to certain morphological places with distinct absorption features, which also indicates the coexistence of multi-morphology in RR-P3HT film. This study provides a clear picture of decay dynamics of polaron pairs, besides showing that the combination of transient absorption and fluorescence up-conversion techniques is a powerful tool to investigate the dynamics of excitations in polymer.

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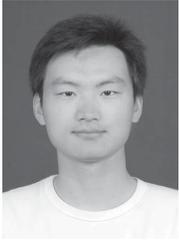
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