# One-Dimensional Singlet Exciton Diffusion in Poly(3-hexylthiophene) Crystalline Domains

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ABSTRACT: Singlet exciton dynamics in crystalline domains of regioregular poly(3hexylthiophene) (P3HT) films was studied by transient absorption spectroscopy. Upon the selective excitation of crystalline P3HT at the absorption edge, no red-shift of the singlet exciton band was observed with elapse of time, suggesting singlet exciton dynamics in relatively homogeneous P3HT crystalline domains without downhill relaxation in the energetic disorder. Even under such selective excitation conditions, the annihilation rate coefficient  $\gamma(t)$  was still dependent on time:  $\gamma(t) \propto t^{-1/2}$ , which is attributed to anisotropic exciton diffusion in P3HT crystalline domains. From the annihilation rate coefficient, the singlet exciton diffusion coefficient D and exciton diffusion length  $L_{\rm D}$  in the crystalline domains were evaluated to be 7.9  $\times$  10<sup>-3</sup> cm<sup>2</sup> s<sup>-1</sup> and 20 nm, respectively. The origin of the time-dependent exciton dynamics is discussed in of dimensionality. terms

**TOC GRAPHICS** 



**KEYWORDS:** polythiophene, annihilation, transient absorption, organic photovoltaics, *H*-aggregate

Singlet excitons are one of the most primary photoexcitations formed in organic materials after photon absorption. Excitons are Coulombically bound electron-hole pairs, and hence cannot generate the photocurrent in themselves but can diffuse as electron-hole pairs before deactivating to the ground state. In donor/acceptor blend films, some excitons can reach a donor/acceptor interface by the exciton diffusion, at which they can be dissociated into free charge carriers because of the LUMO energy offset between donor and acceptor materials enough to break the Coulomb attraction, and therefore can contribute to the photocurrent generation.<sup>1–7</sup> Thus, the exciton diffusion is one of the most important photophysical properties for organic solar cells, but is not fully understood particularly for crystalline conjugated polymers such as regioregular poly(3-hexylthiophene) (P3HT). For example, there is not much difference in the diffusion length of singlet exciton reported for poly(p-phenylene vinylene) (PPV) amorphous films, which is typically as short as 5–7 nm.<sup>8–13</sup> In contrast, there is a significant difference in the diffusion length of singlet exciton reported for P3HT crystalline films (2.6–27 nm): it has been reported to be typically <10 nm on the basis of exciton quenching in donor/acceptor bilayered films  $^{14-18}$  and >10 nm on the basis of singlet-singlet annihilation (SSA).<sup>19</sup> Furthermore, dimension of singlet exciton diffusion in P3HT crystalline films is also still controversial: both isotropic and anisotropic exciton diffusions have been reported.<sup>17,19,20</sup> These discrepancies are probably due to lack of morphological discussion on the exciton diffusion.

In crystalline polymer films like P3HT, there should be crystalline and disordered amorphous domains at the same time. Indeed, both crystalline and disordered amorphous domains are observed for P3HT films by scanning probe microscope (SPM) and transmission electron microscope (TEM) measurements. In crystalline domains, P3HT self-organizes into two-

dimensional  $\pi$ -stacked lamellar structures to form crystalline fibrils, which are typically 10–20 nm in width and tens of nm to  $\mu$ m in length.<sup>21–24</sup> In amorphous domains, on the other hand, conjugated chains are entangled each other, which connect neighboring crystalline domains. This is in sharp contrast to molecular single crystals, in which no disordered amorphous domains are involved.

Herein, we study the diffusion dynamics of singlet excitons in P3HT crystalline domains by transient absorption spectroscopy. To focus on the exciton diffusion dynamics in crystalline domains alone, we carefully select the excitation wavelength so as to excite crystalline domains selectively. More specifically, P3HT crystalline domains can be selectively excited by the laser excitation at the absorption band-edge of P3HT. The diffusion dynamics of singlet excitons can be discussed by analyzing a diffusion-limited exciton quenching in the SSA.<sup>17,19,25–32</sup> In order to discuss time dependence of the exciton diffusion dynamics in details, we measure the SSA over the wide temporal range from pico- to nanoseconds. On the basis of these careful analyses, we evaluate the diffusion coefficient and diffusion length of singlet excitons in P3HT crystalline domains, and further discuss the dimensionality of the exciton diffusion.

**Crystalline Selective Excitation.** As shown in Figure 1, P3HT films exhibit a characteristic absorption shoulder at around 600 nm, which is attributable to the absorption band of crystalline P3HT. The characteristic vibronic band structures can be well simulated by weakly interacting H-aggregate model.<sup>33–35</sup> The gray lines in the figure represent the absorption spectra of crystalline P3HT simulated with each vibronic band. The difference between the measured and simulated spectra is attributed to the absorption of amorphous P3HT in the film. From the ratio of the crystalline and amorphous absorption bands, the crystallinity of the P3HT film was evaluated to be 64% (details are described in the Supporting Information).<sup>35</sup>



**Figure 1.** Absorption spectrum of the P3HT film. The black line represents the absorption spectrum measured. The gray lines represent the absorption spectra of crystalline P3HT simulated by the weakly interacting *H*-aggregate model.

Figure 2 shows transient absorption spectra of P3HT films measured from 0 ps to 1 ns after the laser excitation at 620 nm (absorption of P3HT crystalline domains) and at 400 nm (absorption of P3HT disordered domains). Experimental details are described in the Supporting Information and previous our reports in more details.<sup>36-38</sup> Upon the photoexcitation of P3HT films at 620 nm, as shown in the panel (a), a broad absorption band was observed at around 1300 nm immediately after the laser excitation. This band is ascribed to singlet excitons as reported previously (detailed assignments are described in the Supporting Information).<sup>6,37–39</sup> Negligible polaron absorption was observed at around 1000 nm after the excitation at 620 nm. Upon the photoexcitation of P3HT films at 400 nm, as shown in the panel (b), a broad absorption band was observed at around 1200 nm immediately after the laser excitation and then red-shifted to 1300 nm on a time scale of picoseconds (the spectral shift can be clearly seen in the enlarged absorption spectra shown in the Supporting Information). Such spectral shift is indicative of the fast downhill energy relaxation towards lower energy sites in the density of states (DOS). This is

because singlet excitons at higher energy sites in the DOS are selectively generated by the excitation at 400 nm and hence can easily hop to more ordered sites. After the downhill relaxation, singlet excitons can hop among neighboring sites by thermal activation. In other words, the exciton diffusion dynamics induced by the 400-nm excitation does not only reflect singlet excitons in crystalline domains to be addressed in this study. In contrast, as shown in the panel (a), no spectral shift was observed over the whole time range measured after the band-edge excitation at 620 nm. This is because singlet excitons at around the bottom in the DOS are selectively generated by the excitation at 620 nm and hence are not involved in the downhill relaxation. In other words, the band-edge excitation at 620 nm is of particular importance for studying singlet exciton dynamics in P3HT crystalline domains. We therefore focus on the decay dynamics by the excitation at 620 nm in order to discuss the exciton diffusion in crystalline domains.



**Figure 2.** Transient absorption spectra of a P3HT film measured at 0, 1, 10, 100, and 1000 ps after the laser excitation from top to bottom. The excitation wavelength (fluence) was (a) 620 nm ( $2.7 \mu J \text{ cm}^{-2}$ ) and (b) 400 nm ( $5.7 \mu J \text{ cm}^{-2}$ ).

One-Dimensional Exciton Diffusion. The exciton density decayed faster at an early time stage up to ~100 ps under higher excitation intensities as shown in the Supporting Information, suggesting bimolecular decay due to SSA based on the exciton diffusion. The annihilation rate coefficient can be directly extracted from experimental decay curve (Figure 3) as reported previously (details are described in the Supporting Information.).<sup>30,40</sup> Note that charge photogeneration is negligible in this study because of the band-edge excitation, although a charge photogeneration yield of <10% has been reported for P3HT films excited above the absorption edge.<sup>41-43</sup> Therefore, such small population of polarons does not affect the singlet exciton dynamics at all (details are described in the Supporting Information). As shown in Figure 4a, the extracted annihilation rate coefficient is not constant over the time range measured but exhibits almost  $t^{-1/2}$  dependence for P3HT films. On the other hand, the annihilation rate coefficient in P3HT films has been reported to be both time-dependent<sup>19,20</sup> and time-independent.<sup>17</sup> In Ref. 17, the exciton dynamics is analyzed by using time-independent formula, and is reproduced only for the later time stage from 300 to 800 ps. As shown in Figure 3, the majority of singlet excitons have been already deactivated before 300 ps, and hence the monomolecular decay is dominant rather than the bimolecular decay at the later time stage. Therefore, it would be difficult to discuss the time dependence of the annihilation rate coefficient from the exciton decay at a later time stage. Thus, we emphasize that it is of particular importance to measure the annihilation

rate coefficient over a wide temporal range at an early time domain of 1 to 100 ps in order to discuss the time dependence in details as is the case with this study. On the other hand, the timedependent annihilation rate coefficient has been reported in Ref. 19. However, the  $t^{-1}$  dependence reported in Ref. 19 is different from the  $t^{-1/2}$  dependence we observed in this study. As is discussed in the literature, the  $t^{-1}$  dependence is due to downhill relaxation in the energetic disorders in P3HT films. In contrast, the  $t^{-1/2}$  dependence we observed is not ascribed to the downhill relaxation in the energetic disorders because no spectral shift is observed by the laser excitation at the absorption edge of crystalline P3HT. Rather, we ascribe the  $t^{-1/2}$  dependence to anisotropic exciton diffusion. In other words, the inherent exciton dynamics in crystalline domains would be masked by the downhill relaxation when both amorphous and crystalline domains are excited at the same time. Thus, we conclude that ultrafast transient spectroscopy by the selective excitation is of particular importance to study the inherent exciton dynamics in crystalline domains of crystalline polymer films.



**Figure 3.** Singlet exciton decay of a P3HT film measured at 1400 nm. The excitation wavelength (fluence) was 620 nm (2.7  $\mu$ J cm<sup>-2</sup>). The broken line represents the fitting curve with the 1D exciton diffusion model.



**Figure 4.** (a) The extracted annihilation rate coefficient for a P3HT film excited at 620 nm extracted from Eq. S13 in the Supporting Information. The solid line represents the fitting curve using the 1D model. The broken lines represent the annihilation rate coefficient calculated by the 3D (gray) and 2D (black) models. (b) Transient anisotropy decay of a P3HT film measured at 1400 nm. The anisotropy is calculated by  $r(t) = (\Delta OD_{/}(t) - \Delta OD_{\perp}(t))/(\Delta OD_{/}(t) + 2\Delta OD_{\perp}(t))$ . The excitation wavelength (fluence) was 620 nm (2.7 µJ cm<sup>-2</sup>, solid line) and 400 nm (5.7 µJ cm<sup>-2</sup>, broken line).

The diffusion-limited bimolecular reaction rates significantly depend on the dimensionality of the system. Thus, we can discuss the dimensionality of the exciton diffusion dynamics on the basis of the time dependence of the annihilation rate coefficient. Details are described in the Supporting Information, but here we simply summarize the time-dependence of models we used. The bimolecular rate coefficient becomes time-independent for the three-dimensional (3D) system and  $t^{-\alpha}$  ( $\alpha < 1/2$ ) dependent for the 2D system at larger t, and is consistently  $t^{-1/2}$ dependent for the 1D system over the all time domain. Note that one-step annihilation model based on Förster resonance energy transfer would also exhibit  $t^{-1/2}$  dependent annihilation rate coefficient as reported for other materials.<sup>26,44</sup> However, this is not the case because of negligible spectral overlap between the S<sub>1</sub>-S<sub>n</sub> absorption and photoluminescence spectra, and very low photoluminescence quantum efficiency of the P3HT film. As shown in Figure 4a, the time dependence of the extracted annihilation rate coefficient is best fitted with the 1D exciton diffusion model over the wide temporal range. In contrast, there is a considerable discrepancy both in the 2D and 3D exciton diffusion models: they deviate from the  $t^{-1/2}$  dependence at a longer time region. The 1D exciton diffusion is strongly supported by the anisotropy decay measurements as shown in Figure 4b. The solid line represents the time evolution of the anisotropy r calculated by the following equation:  $r(t) = (\Delta OD_{1/2}(t) - \Delta OD_{1/2}(t))/(\Delta OD_{1/2}(t) + t)$  $2\Delta OD_{\perp}(t)$ ). Upon the excitation at 620 nm, as shown by the solid line in Figure 4b, the anisotropy r was nearly 0.4 at 1 ps, and still as large as 0.2 even at 100 ps, which is in sharp contrast with the anisotropy decay after the excitation at 400 nm. Note that a slight decrease at a later time stage is probably due to the SSA under the parallel probe light, where the apparent exciton density is higher than under the perpendicular probe light. Upon the excitation at 400 nm, the anisotropy r was as small as  $\sim 0.1$  even at 0 ps, similar to our previous report on the

anisotropy decay in regiorandom P3HT.<sup>37</sup> The small anisotropy at 0 ps suggests that the polarization memory of singlet excitons rapidly disappears within the laser excitation (~100 fs), which is indicative of exciton self-trapping by structural relaxation as reported previously.<sup>37,45-48</sup> The relatively large anisotropy observed after the 620-nm excitation indicates that singlet excitons generated in crystalline domains retain the orientation of their transition moments during diffusion. In other words, singlet excitons generated in P3HT crystalline domains do not diffuse randomly in all the directions but rather diffuse along a particular direction. We therefore conclude that singlet excitons formed in P3HT crystalline domains mainly diffuse in the 1D motion.

Exciton Diffusion Length. Finally, we evaluated the diffusion coefficient *D* and the diffusion length  $(D\tau)^{1/2}$  of P3HT crystalline film. From the annihilation rate coefficient as shown in Figure 4a, the diffusion coefficient *D* and the diffusion length  $(D\tau)^{1/2}$  are evaluated to be  $7.9 \times 10^{-3}$  cm<sup>2</sup> s<sup>-1</sup> and 20 nm, respectively (details are described in the Supporting Information).<sup>49</sup> Note that the diffusion coefficient estimated depends on the effective interaction radius of singlet excitons, which is estimated to be 3.4 nm in this study (see the Supporting Information). Compared with previous literatures reported for P3HT films, the diffusion length we evaluated (20 nm) is much longer than those evaluated by the exciton quenching in donor/acceptor bilayered films.<sup>14-18</sup> This is probably because disordered domains in the P3HT crystalline donor layer are not negligible for the exciton diffusion to the acceptor layer. On the other hand, the diffusion length we evaluated (20 nm) is rather comparable to those evaluated by the SSA,<sup>19</sup> which is the same as our analysis. As mentioned before, this is because the SSA in crystalline domains can be selectively observed by the selective excitation of the absorption band due to the crystal phase. We therefore emphasize again that the SSA analysis with crystalline band-edge excitation is

more suitable for evaluating the exciton diffusion length in crystalline polymer films rather than the exciton quenching analysis for donor/acceptor bilayered films.

In conclusion, we have studied the diffusion dynamics of singlet excitons in P3HT crystalline domains by femtosecond transient absorption spectroscopy. By selective excitation of crystalline P3HT at the absorption edge, only singlet excitons in crystalline domains were observed exclusively. Immediately after the laser excitation, the exciton band was observed at around 1300 nm and was not shifted with time. This finding is indicative of no downhill relaxation in the energetic disorder. With increasing excitation intensity singlet excitons decayed faster, suggesting SSA. The annihilation rate coefficient of singlet excitons exhibited  $t^{-1/2}$  dependence over the wide temporal range from 1 to 100 ps. We conclude that the  $t^{-1/2}$  dependence is due to 1D anisotropic exciton diffusion in P3HT crystalline domains rather than the downhill relaxation. From the detailed analysis of the annihilation, the exciton diffusion coefficient *D* and the diffusion length  $L_D = (D\tau)^{1/2}$  are evaluated to be  $7.9 \times 10^{-3}$  cm<sup>2</sup> s<sup>-1</sup> and 20 nm, respectively. These findings provide in-depth understanding of singlet exciton diffusion in crystalline conjugated polymers.

### ASSOCIATED CONTENT

**Supporting Information**. Experimental methods, analytical details of crystalline absorption simulation, fluorescence spectrum and decay, AFM phase image, enlarged transient absorption spectra, assignments of transient absorption spectra, estimation of exciton density, estimation of effective interaction radius of singlet exciton, excitation intensity dependence of singlet exciton decay, excitation wavelength dependence of charge photogeneration, details of analytical

methods, fitting results for the P3HT film using other diffusion models. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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