

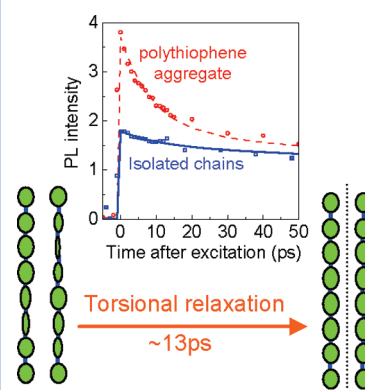
Role of Ultrafast Torsional Relaxation in the Emission from Polythiophene Aggregates

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ABSTRACT An understanding of aggregation effects in semiconducting polymers is essential for their use in optoelectronic devices; however, the dynamic evolution of such interchain states is not well understood. Here, we have investigated a blend of semiconducting poly(3-hexylthiophene) (P3HT) with an electronically inert ultrahigh-molecular-weight polyethylene (UHMW-PE) matrix that is shown to allow precise control over the extent to which the P3HT chains aggregate. We determined the singlet exciton population within isolated and aggregated P3HT regions using femtosecond time-resolved photoluminescence measurements and found a strong ultrafast decay pathway in the aggregated case only. Comparison of the emission from the two lowest vibronic bands demonstrates a changeover from an initial vibrationally “hot” photoexcited state to a geometrically relaxed aggregate state within ~ 13 ps, corresponding to time scales for torsional relaxation in these materials. We conclude that formation of an aggregate excited state in conjugated polymers is mediated by vibrational relaxation from a low-symmetry to a high-symmetry ordered state for the ensemble.

SECTION Kinetics, Spectroscopy



Organic semiconductors have many fundamental, technological, and practical advantages over traditional inorganic semiconductors, particularly in the field of opto- and nanoelectronics.^{1,2} It has been widely observed that several aspects of material handling and device preparation can lead to large changes in the optoelectronic properties of the resultant device.^{3,4} In particular, aggregation of the macromolecular chains is known to be a critical factor, capable of changing the emission spectrum, absorption spectrum, and charge transport in these polymeric semiconducting systems.^{5–7} The physics underlying the effect of aggregation upon the optoelectronic properties has been hypothesized by several groups to be related to the high symmetry of aggregate phases.^{8,9} However, the evolution of an excited state from an initial vibrationally “hot” state to a geometrically relaxed aggregate state is still not understood; in particular, the dissipation of excess exciton energy and the relationship with the polymer backbone requires further investigation. Polythiophenes and specifically poly(3-hexylthiophene) (P3HT), as investigated here, are model material systems for both fundamental studies and use in optoelectronic devices, with blends of P3HT and an electron acceptor currently exhibiting one of the highest certified photovoltaic efficiencies for all-organic materials.¹⁰ We chose to investigate tensile-drawn guest/host blends of P3HT and UHMW-PE because similar semiconducting/insulating binary systems have been shown to permit precise

control over the level of guest aggregation through variation of both blend composition and draw ratio (cf. refs 11 and 12). Indeed, tensile deformation can disrupt the crystalline domains creating molecular dispersions also in blends of higher P3HT content, especially at higher draw ratios.¹¹

The steady-state absorption and photoluminescence spectra for UHMW-PE containing a range of P3HT concentrations are shown in Figure 1. The linear absorption and emission of polythiophene has been well modeled by Clark et al.^{13,14} In this Letter, we use the model described in ref 13; however, we concentrate on the photoluminescence spectrum to avoid complications associated with absorption and scattering from the UHMW-PE matrix. The emission has been effectively modeled using an equation of the form

$$I(\omega) \propto (\hbar\omega)^3 n(\omega) \times \left[\alpha \Gamma(E_0, L) + \sum_{m=1}^{\infty} \frac{S^m}{m!} \Gamma(E_0 - mE_{\text{ph}}, \sigma) \right] \quad (1)$$

where $n(\omega)$ is the refractive index at the given optical frequency (ω), m represents the Franck–Condon vibronic index, S is the Huang–Rhys factor, E_0 is the 0–0 emission energy,

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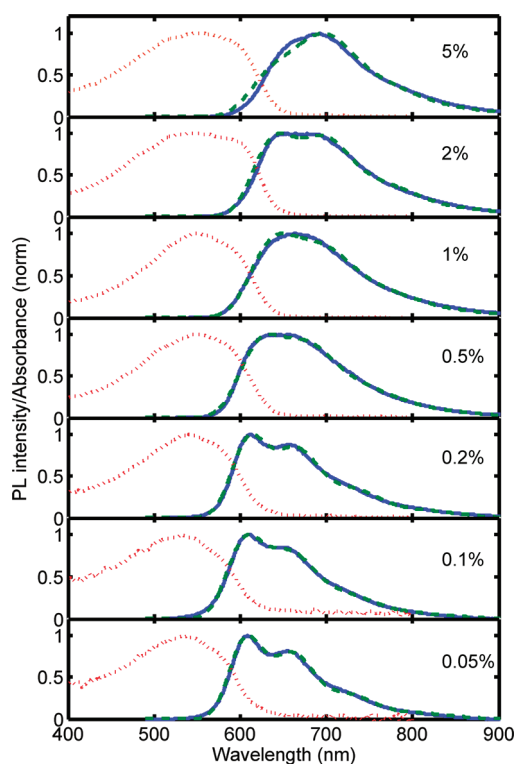


Figure 1. Steady-state, normalized absorbance (red dashed line) and photoluminescence spectra (blue solid line) of P3HT embedded in a PE matrix. The concentration of P3HT is varied, $c = 0.05, 0.1, 0.2, 0.5, 1, 2,$ and 5 wt % (from bottom to top). Fits using the Spano model are overlaid (green dashed line).

E_{ph} is the phonon energy of the C–C stretch mode, and Γ represents the line shape function (assumed to be Gaussian with a width σ). As all samples have a minority P3HT concentration, we assume that the refractive index is constant across the frequency range explored here. The dimensionless factor α is determined by the relative amount of emission from the zero-phonon (0–0) transition. In the case of $\alpha = 1$, eq 1 reduces to the standard Franck–Condon progression.¹⁵ However, in an aggregate, the electronic coupling between chains leads to emission via the 0–0 transition becoming symmetry-forbidden. In this case, the 0–0 emission peak is quenched, leading to a decoupling of the amplitude of this peak from the rest of the Franck–Condon progression ($\alpha < 1$).

The level of aggregation of the P3HT chains (or chain segments) was determined by comparing the steady-state photoluminescence spectrum to this model. The formation of clusters of P3HT macromolecules into geometrical arrangements known as H-aggregates is responsible for quenching the absorption and emission arising from the 0–0 transition. The theoretical background to this quenching is given in a model developed by Spano et al., based on the symmetry of emitting dipoles in the H-aggregate arrangement.^{9,16,17} The application of time-resolved measurements to this model allow the electronic evolution from hot exciton to conformationally relaxed (or self-trapped) exciton to be understood.

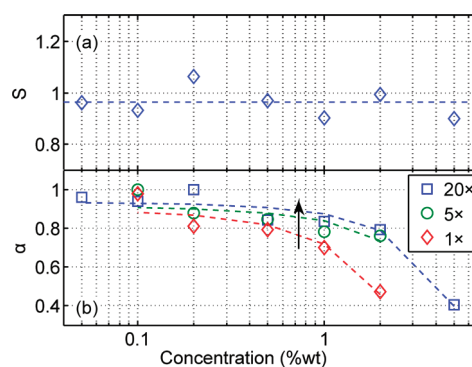


Figure 2. Parameters extracted from the Spano model are shown as a function of concentration. (a) The Huang–Rhys factor and (b) the relative strength of the 0–0 transition (α) are shown. The latter can be interpreted as the level of optoelectronic isolation in the material ($\alpha = 1$ for full isolation). The dashed lines are a guide to the eye. The green circles and red diamonds represent the values extracted from samples with other stretch ratios; the arrow indicates the trend in isolation with increasing stretch ratio.

Figure 1 shows the best fit parameters to the photoluminescence data using eq 1. The free parameters are the Huang–Rhys factor S , the Gaussian width σ , α , and the 0–0 emission peak energy E_0 , while the phonon energy was set at 0.17 eV.^{15,18} Figure 2 shows that the extracted values for α vary from 1 to 0.4, indicating that the material is fully isolated below 0.1 wt % and increasingly aggregated with increasing concentration. Concomitantly, E_0 undergoes small red shifts of ~ 70 meV as the concentration is increased, and the Huang–Rhys factor is constant with $S \approx 1$, as expected. To explore the impact of tensile deformation on phase separation and interactions between conjugated chain segments in our blend systems, a comparison of α as a function of concentration for three different draw ratios was measured. Figure 2 shows that as the draw ratio is increased, the level of chain aggregation at a given concentration is decreased. This confirms that such guest/host systems are ideal for investigating aggregation effects as they permit control over the optoelectronic interaction of the guest P3HT chains within the insulating UHMW-PE host matrix.

We now use the knowledge of the degree of coupling between conjugated chain segments provided by the steady-state photoluminescence measurements to interpret time-resolved photoluminescence measurements. The early time 0–0 emission dynamics are shown in Figure 3 for a range of blend compositions encompassing samples of both predominantly isolated ($c \leq 0.2$ wt %) and aggregated ($c = 2$ wt %) P3HT. A nonexponential component can be seen during the first 20 ps, increasing in size for higher P3HT content. The later time ($\tau > 100$ ps) decays are qualitatively identical regardless of the polymer concentration; these exhibit a monoexponential decay for times between 100 and 1000 ps.

Figure 4 shows the photoluminescence lifetime for two blend systems composed of P3HT of largely aggregated (2 wt %) and isolated (0.2 wt %) chains at two emission wavelengths, 610 and 660 nm, corresponding to emission from the 0–0 and 0–1 transitions, respectively. It is notable that while the emission lifetime from the isolated P3HT

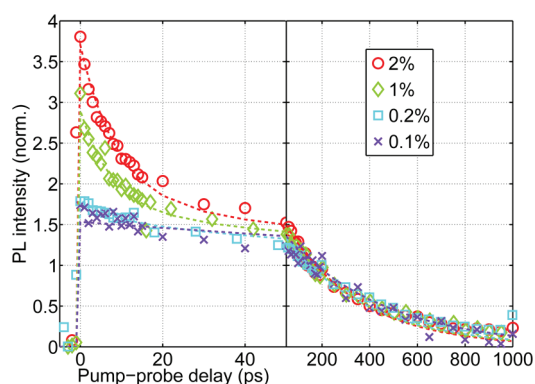


Figure 3. Time-resolved photoluminescence from a selection of samples (concentrations as indicated; stretch ratio, $\lambda = 20$ throughout). The lines are fits using the model described in the text. All measurements are normalized at 150 ps after excitation and are measured at 610 nm (the 0–0 emission).

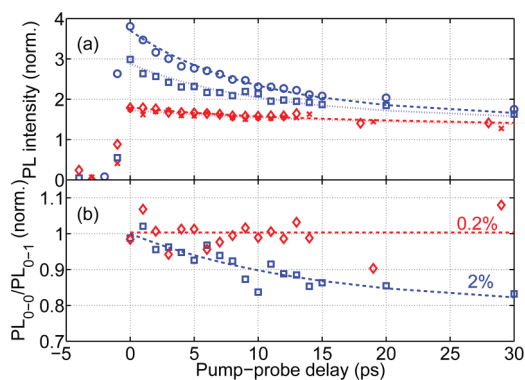


Figure 4. (a) Time-resolved photoluminescence shown for two emission wavelengths (610 nm, circles, and 660 nm, squares, corresponding to the 0–0 and 0–1 transitions, respectively) for nominally aggregated (2 wt %, blue symbols and lines) and isolated (0.2 wt %, red symbols and lines) samples (stretch ratio $\lambda = 20$). The lines are fits using the model described in the text. All data are normalized at 150 ps, after which all decays follow a similar trend as that shown in Figure 3. (b) The normalized ratio of the emission from the 0–0 peak to the 0–1 peak is shown, which is proportional to α . The dashed lines show monoexponential fits to the data.

macromolecules appears to be independent of wavelength, that from the sample composed of P3HT chain aggregates shows a clear difference between the emission dynamics at the two wavelengths, with the emission from the 0–0 peak decaying faster than that from the 0–1 peak. The lower pane of Figure 4 shows the ratio of 0–0 emission to 0–1 emission as a function of time; by studying eq 1, it can be seen that this is proportional to α . This ratio is constant for isolated P3HT chains, which show a time-independent photoluminescence spectrum. However, a clear dynamic change in the emission spectrum is seen when P3HT chain aggregation occurs. In this case, a monoexponential fit reveals a decay in the symmetry-forbidden 0–0 emission relative to the 0–1 emission with a time constant of 13 ± 1 ps.

The quantum efficiency of photoluminescence ϕ from P3HT is low, with typical values of 0.10–0.27 and 0.01–0.08 for emission from isolated chains and aggregates, respectively.^{19–22}

Table 1. Parameter Values Extracted by Fitting the Solutions of Equations 2 and 3 to the Data

parameter	value
τ_{non}	410 ± 15 ps
τ_{relax}	13 ± 5 ps
τ_{r1}	1500 ± 50 ps ^a
τ_{r2}	5100 ± 150 ps ^a

^a The parameters are dependent on the values of quantum efficiency and τ_{non} only and are not independently fit. The errors show the maximum variance in the values for different combinations of fitted data.

Together with the similarity in the long-term decay from isolated and aggregated chain segments shown in Figure 3, this indicates that the emission dynamics in both cases are dominated by nonradiative effects. In studying the emission from regioregular and regiorandom P3HT films, Korovyanko et al. showed that the nonradiative decay rate is unlikely to change upon increased polymer ordering.²³ For this reason, we model the emission dynamics using coupled rate equations. Here, species 1 has the 0–0 peak present ($\alpha = 1$) and a larger quantum efficiency in emission and thus represents either isolated chains or (as shown below) a vibrationally hot aggregate state. In contrast, species 2 shows no 0–0 band ($\alpha = 0$) and a low quantum efficiency in emission and therefore corresponds to a relaxed aggregate state whose zero-phonon transition is symmetry-forbidden

$$\frac{dN_1}{dt} = G_1 N_0 - \frac{N_1}{\tau_{r1}} - \frac{N_1}{\tau_{\text{non}}} - \frac{N_1}{\tau_{\text{relax}}} \quad (2)$$

$$\frac{dN_2}{dt} = G_2 N_0 - \frac{N_2}{\tau_{r2}} - \frac{N_2}{\tau_{\text{non}}} + \frac{N_1}{\tau_{\text{relax}}} \quad (3)$$

In these equations, N_1 and N_2 are the singlet exciton populations for species 1 and 2, $G_1 N_0$ and $G_2 N_0$ are the initial populations (after any femtosecond relaxation processes), τ_{r1} and τ_{r2} are the natural radiative lifetimes from the two states, τ_{non} is the shared nonradiative lifetime, and τ_{relax} is the species 1 to species 2 relaxation time constant. Fitting these coupled equations to the emission decay data for 0.1, 0.2, 1, and 2 wt % samples and using literature values of $\phi_1 = 0.27$ and $\phi_2 = 0.08$ for “isolated” chains and aggregates, respectively, gives a good fit (as shown in Figures 3 and 4) with the parameters listed in Table 1. It is worth noting that our value of 410 ps for τ_{non} is similar to the 470 ps observed by Theander et al.²² Additionally, our value of 1.5 ns for the isolated chain radiative emission lifetime compares closely to those reported by others (1–2 ns).^{21,22}

There are two significant effects of interest shown in Figures 3 and 4, the appearance of a picosecond decay component for the emission from aggregated states and the dynamic value of α observed for the aggregated sample. We propose that these effects are linked and related to molecular relaxation from an initial vibrationally hot to a geometrically relaxed aggregate state over a picosecond time scale, mediated by torsional relaxation. As previously stated, the symmetry of well-ordered H-aggregated polythiophene forbids emission involving the zero-phonon states. However, an initially generated nonequilibrium excitation may populate higher-lying levels of the aggregate state for which such

symmetry constraints are lifted. As a result, the emission spectra immediately following excitation may bear some resemblance to those from isolated chains (high α), and the absorption spectra (see Figure 1) display weaker aggregation effects than the time-averaged emission spectra, as observed previously.¹³ Evidence for such effects is also provided by changes in the emission spectra showing an evolution from more to less aggregated signatures (increasing α) as the temperature is raised.^{8,17} These higher-lying allowed transitions may originate from higher-lying states of alternate symmetry⁸ and also disorder, giving rise to an exciton energy distribution.¹⁷ The initial excess energy of the hot exciton creates a non-Boltzmann distribution of energy within the native torsional modes of the P3HT backbone. The population of higher-lying vibrational modes on members of the aggregate introduces disorder in the ensemble of participating chains or chain segments, thereby lowering the symmetry and leading to partially allowed emission. Subsequent cooling thus leads to a relaxation into the fully symmetric aggregate state on the time scale of phonon emission and relaxation. Other possibilities such as bimolecular annihilation or saturable aggregate traps can be eliminated; the photon fluences required for singlet–singlet annihilation are typically over an order of magnitude larger than those used here,²⁴ and aggregate trapping would not cause a dynamic α and has been eliminated in similar experiments.²⁰ In addition, exciton migration from short to longer conjugated segments, which has been shown to lead to ultrafast emission dynamics,²⁵ can be ruled out as a cause of the dynamics displayed in Figure 4. Since shorter segments are associated with a higher Huang–Rhys factor,²⁶ such migration would lead to an increase of the 0–0 to 0–1 emission peak ratio (e.g., as seen for PPV²⁷), which is the opposite of what we observe for P3HT aggregates. An alternative explanation for the measured dynamics could be that excitons simply migrate from “less aggregated” to “more aggregated” regions, which would lead to the observed increase in α . However, as the P3HT concentration in the matrix is increased and the number of chains participating in the aggregates increases, the dynamics of the migration process should then change. In contrast, we observe an initial fast decay constant of 13 ps and subsequent longer decay dynamics that are independent of concentration, suggesting that the enclosed P3HT domains are homogeneous and that the initial fast relaxation reflects an intrinsic process such as vibrational relaxation.

The time scales associated with vibrational relaxation are a function of the energy (and hence frequency) of the vibrational mode. The C–C stretching mode has a relaxation time scale on the order of 25 fs.²⁸ Torsional relaxation typically has a longer (1–100 ps) relaxation time scale and has been observed to have a significant effect on exciton dynamics in conjugated systems.^{29–31} Using computational modeling, Tretiak et al. showed that only small changes in the backbone torsional angle lead to large changes in exciton delocalization and transfer probabilities.³² The ~ 13 ps time scale of relaxation and decay in the value of α is very similar to the observed time scale (15 ps) of torsional relaxation and subsequent exciton delocalization observed by Westenhoff and co-workers for a polythiophenes derivative.³³

In summary, we have presented steady-state and time-resolved photoluminescence measurements on P3HT/UHMW-PE guest/host systems of a range of compositions and draw ratios. Using the model developed by Spano et al., the level of aggregation within the blend has been calculated, allowing samples of predominantly isolated and aggregated chains or chain segments to be identified. This allowed the nanosecond time-resolved photoluminescence of the embedded P3HT to be interpreted as a nonradiatively dominated process with a time constant of 410 ps. A nonmono-exponential picosecond dynamic has been identified; normally symmetry-forbidden 0–0 emission is observed at early times, which decays as the excitons cool with a time scale corresponding to torsional relaxation of the polymer backbone. These measurements demonstrate that formation of an “aggregate” state in conjugated polymers is a dynamic evolution that occurs on the time scale of vibrational relaxation into an ordered, symmetric ensemble state.

EXPERIMENTAL METHODS

Blends were prepared according to previously reported procedures.^{11,12,34,35} Briefly, dilute solutions of P3HT (weight-average molecular weight, $M_w \approx 60$ kDa) and UHMW-PE ($M_w \approx 6$ MDa) were prepared in decahydronaphthalene (decalin) at 140 °C (total solid content of 1 wt % in solutions), which were then cast at ambient to form gel films. Subsequently, tensile deformation was carried out on a Kofler bench at 110–120 °C. Time-resolved photoluminescence was measured using a femtosecond up-conversion technique, which we have previously described (along with the steady-state measurement technique) in detail in ref 30.

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