

## ARTICLES

## Spectroscopy and Transport of the Triplet Exciton in a Terthiophene End-Capped Poly(phenylene ethynylene)

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Triplet states of poly(phenylene ethynylene), <sup>3</sup>PPE\*, not easily formed by direct photoexcitation, were produced by pulse radiolysis in toluene, along with triplet states of T<sub>3</sub>PPE having terthiophene end-caps. Intense triplet–triplet absorption maxima,  $\epsilon_{680}({}^3\text{PPE}^*) = 9.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{780}({}^3\text{T}_3\text{PPE}^*) = 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  enable identification of these two species, which have triplet energies of 2.12 and 1.77 eV determined in bimolecular energy transfer equilibria. Bleaching of ground-state absorption measures <sup>3</sup>PPE\* to be the delocalized over a 1.8-nm length. Triplet states formed in the PPE chains were transported to and trapped by the end caps in a time  $\ll 5$  ns.

## Introduction

Over the past decade it has become clear that conjugated polymers are an important class of materials with a large commercial potential. They have found application as the active layer in light-emitting diodes (LEDs) due to the efficient radiative decay of their excited states generated by charge recombination within the polymer.<sup>1</sup> They are also currently being investigated as the active layer in photovoltaic cells, as antennae for light harvesting and energy transport as well as for their ability to dissociate excitons and transport positive and negative charges.<sup>2</sup> For these applications rapid and efficient energy and charge transport are required. While it has been established that organic  $\pi$ -conjugated polymers rapidly transport charges and singlet excited states,<sup>3–6</sup> less is known about their ability to transport triplet excitons. Furthermore, the reaction of triplet excitons with oxygen has been postulated to be a major degradation route for polymers incorporated into an LED.<sup>7</sup> It is clear that to optimize polymers for the above applications, the role of the triplet state must be fully understood.

Theoretical and experimental investigations find triplet states of conjugated polymers to be much more localized than either the singlet excited states or excess charges,<sup>8–10</sup> which might be expected to result in slower energy transport for triplets. Recent photochemical investigations of poly(phenylene ethynylene)s incorporating platinum atoms into the polymer backbone confirmed this slower rate.<sup>11,12</sup> The incorporation of platinum promotes intersystem crossing, leading to a yield of 100% triplet states.<sup>11</sup> Orbital delocalization is known to extend through the metal orbitals.<sup>12–15</sup> The delocalization length of the triplet state in these materials was found to be small,  $\sim 1$  repeat

unit (one phenyl ring); however, it has also been predicted theoretically that the addition of a metal atom into the polymer backbone increases the confinement of charges and excitons.<sup>13</sup> Few experimental studies have addressed this issue; however, the singlet exciton for platinum-based polymers is estimated to be delocalized over  $\leq 6$   $-\text{Pt}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-$  units,<sup>10</sup> whereas in the corresponding all-organic polymer the exciton is delocalized over  $\geq 10$   $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-$  repeat units.<sup>16</sup> Conjugation length was found to increase with a decrease in mole fraction of platinum incorporated into poly(phenylene ethynylene) backbone.<sup>10</sup> These results taken together provide evidence for poorer orbital overlap through a Pt atom compared to the orbital overlap in organic polymers for these conjugated poly(phenylene ethynylene)s and that the Pt atom influences the electronic structure and therefore charge and exciton transport along the polymer chain.

Intersystem crossing within poly(phenylene vinylene)s, poly(phenylene ethynylene)s (PPE) and polyfluorenes to form the triplet state is inefficient, occurring with a quantum yield  $\phi \leq 0.10$ .<sup>10,17,18</sup> As a result, the triplet state is difficult to investigate using standard photochemical techniques. Another convenient method for generating triplet states in solution is via pulse radiolysis.<sup>19</sup> In this case a short electron pulse produces solvent triplet states, which may be transferred to the polymer in solution directly or via a sensitizer. This technique has recently been exploited to investigate the triplet states of primarily poly(phenylene vinylene) as well as a few other conjugated polymers.<sup>20,21</sup>

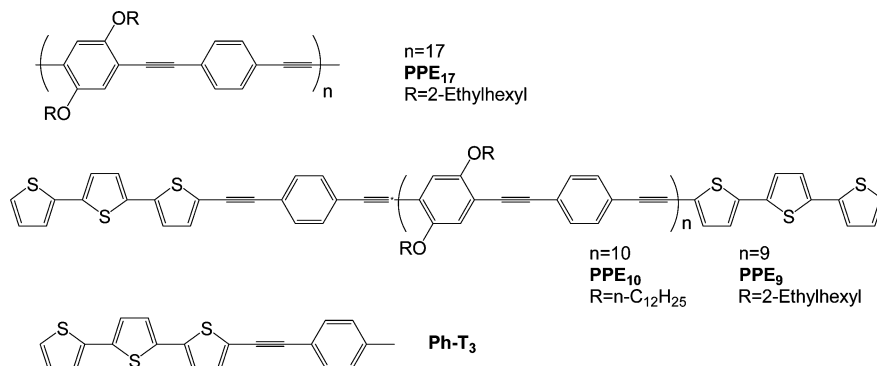
We recently initiated a program to investigate the charge and energy transport properties of conjugated polymers making use of terthiophene (T<sub>3</sub>) end-capped poly(arylene ethynylene)s. The radical ions of the polymer were formed in solution by pulse radiolysis, and a lower limit for the hole transfer from the polymer to the terthiophene end cap was determined as  $k \geq 10^8 \text{ s}^{-1}$ . The current work extends that study to include the

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**Figure 1.** Structures of the polymers and terthiophene endcapped polymers investigated along with their average degree of polymerization,  $\bar{X}_n$ , as calculated from corrected (see text) GPC-derived  $M_n$  values and the molecular weight of the polymer repeat units. For end-capped polymers,  $\bar{X}_n$  represents the number of arylene ethynylene repeats, and does *not* include end groups.

properties of the triplet state of the terthiophene end-capped poly(arylene ethynylene)s. The polymers investigated are shown in Figure 1. From the reported triplet energy of terthiophene, 1.92 eV,<sup>22</sup> it was anticipated that the triplets initially transferred to the polymer backbone would become trapped at the terthiophene end-cap. We report here the absorption spectrum and energetics of the polymer triplet along with a lower limit for the rate of triplet transfer to the terthiophene end-caps.

### Experimental Section

**Materials.** The poly(arylene ethynylene) parent polymer PPE<sub>17</sub> and its end-capped derivatives T<sub>3</sub>PPE<sub>10</sub>, and another preparation, T<sub>3</sub>PPE<sub>9</sub>, were synthesized as previously described.<sup>3</sup> Anhydrous toluene (Aldrich, 99.8%), 2,2':5',2''-terthiophene (T<sub>3</sub>) (Aldrich, 99%), pyrene (Aldrich, sublimed, 99%), and triphenylethylene (Alfa Cesar, 98+%) were used as received. Naphthalene (Matheson, Coleman and Bell) was zone refined, and acridine (Aldrich, 97%) was sublimed. Each of the polymer samples was analyzed by gel permeation chromatography (GPC) and by proton NMR spectroscopy. GPC for T<sub>3</sub>PPE<sub>10</sub> gave  $M_n = 6970$  and  $M_w = 18,700$  based on polystyrene standards. These data, and the known tendency of GPC based on polystyrene standards to over-estimate molecular weights by approximately 40% for linear rigid-rod polymers,<sup>23</sup> lead to an estimate of 10 polymer repeat units (PRUs) for the number-averaged chain length. We refer to this material as T<sub>3</sub>PPE or T<sub>3</sub>PPE<sub>10</sub> when the size needs to be noted. A preparation described previously<sup>3</sup> was used in some reference experiments. In the same way that its  $M_n = 6450$  and  $M_w = 13,600$  give an estimated average length of 9 PRUs, this material is referred to as T<sub>3</sub>PPE<sub>9</sub>.

**Radiation Techniques.** The slower kinetic measurements were carried out with 2 MeV electrons from the Brookhaven National Laboratory van de Graaf accelerator with pulse widths in the range 40–500 ns. The electron pulses and light from a 200-W xenon arc lamp were passed through a 2-cm cell, wavelengths were selected using an IDADH-10 monochromator with 8-nm band-pass. All experiments were performed with temperature stabilization at  $25 \pm 1$  °C in Ar-purged solutions. Dosimetry was performed with N<sub>2</sub>O-saturated 10 mM KSCN aqueous solution using  $G\epsilon = 4.87 \times 10^4$  ions (100 eV)<sup>-1</sup> M<sup>-1</sup> cm<sup>-1</sup> for the (SCN)<sub>2</sub><sup>-</sup> radical at 472 nm.

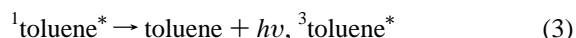
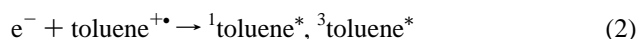
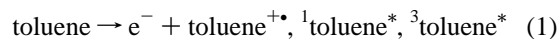
Nanosecond measurements were carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF).<sup>24</sup> The electron pulse ( $\leq 50$  ps duration) was focused into quartz cells having optical path lengths of 1, 10, or 20 mm containing the solutions of interest. For the polymer solutions, the concentration of repeat units used was typically 0.2–4 mM.

The monitoring light source was a 75-W xenon arc lamp pulsed to a few hundred times its normal intensity. Wavelengths were selected using either 40- or 10-nm band-pass interference filters. Transient absorption signals were detected with an FND-100Q silicon diode and digitized with a Tektronix TDS-680B oscilloscope. The transmission/time data were analyzed with Igor Pro software (Wavemetrics). Bimolecular rate constants were determined using the linearity of the observed pseudo-first-order growth of the product with respect to the solute concentration. Where not stated, uncertainties are 15%.

The total dose per pulse was determined before each series of experiments by measuring the absorption of the electron in water. The dose received was calculated using  $\epsilon$  (700 nm, e<sup>-</sup><sub>aq</sub>) = 18,500 M<sup>-1</sup> cm<sup>-1</sup> and  $G(e^-_{aq}) = 2.97$  at 10 ns following the electron pulse and was corrected for the differences in electron densities of the organic solvents used compared to that of water. Radiolytic doses of 5–20 Gy per pulse were employed. Dissolved oxygen was removed by purging with argon gas for at least 10 min, the cells were then sealed with septa and Parafilm. Samples were prepared immediately prior to use. During irradiation, samples were exposed to as little UV light as possible to avoid photodecomposition, although no evidence of this occurring was found within the time frames monitored. For measurements carried out at temperatures below 20 °C, a temperature-controlled sample block cooled by the blow-off from liquid nitrogen was used while a thermostated water bath was used to control the cell at temperatures above ambient. Activation energies were measured over the temperature range 20–80 °C.

### Results

**Triplet Formation.** A pulse of high-energy electrons traversing a solution results in the ionization and excitation of solvent molecules. In polar solvents substantial yields of ions are formed, but in less-polar solvents, such as benzene and toluene, the vast majority of the initially formed electron–hole pairs recombine geminately to form excited states within 20 ps<sup>25</sup> (equations 1–3).



A yield,  $G < 0.126$  molecules/100 eV (where  $G$  is the radiation chemical yield), of electron–hole pairs that escape the Coulombic attraction to become longer-lived negative and

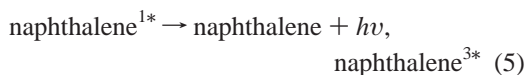
**TABLE 1: Rates Constants for the Formation and Decay of the Polymer Triplet States, ( $M^{-1} s^{-1}$ )**

	$k_4, {}^3\text{toluene}^*{}^a$		$k_7, {}^3\text{naphthalene}^*{}^b$		$k_{\text{decay}} (M^{-1} s^{-1}){}^c$	
	monomer	polymer <sup>d</sup>	monomer	polymer <sup>d</sup>	monomer	polymer <sup>d</sup>
PPE <sub>17</sub> *	$(1.5 \pm 0.1) \times 10^{10}$	$(2.6 \pm 0.2) \times 10^{11}$	$(3.6 \pm 0.2) \times 10^9$	$(6.1 \pm 0.5) \times 10^{10}$	$(7 \pm 1) \times 10^7$	$(1.2 \pm 0.2) \times 10^9$
T <sub>3</sub> PPE <sub>10</sub> *	$(1.6 \pm 0.1) \times 10^{10}$	$(1.9 \pm 0.2) \times 10^{11}$	$(3.4 \pm 0.2) \times 10^9$	$(4.8 \pm 0.2) \times 10^{10}$	$(1.2 \pm 0.3) \times 10^7$	$(8.8 \pm 0.2) \times 10^9$

<sup>a</sup> Reaction of <sup>3</sup>toluene\* with polymers. <sup>b</sup> Reaction of <sup>3</sup>naphthalene\* with polymers. <sup>c</sup> Bimolecular triplet decay from slopes of growth and decay rates vs polymer concentration (see text) at 800 nm for <sup>3</sup>PPE\* and 650 nm for <sup>3</sup>T<sub>3</sub>PPE\*. <sup>d</sup> Polymer concentrations were calculated using 17 and 12 monomer/polymer (counting T<sub>3</sub> as 1 unit) for PPE and T<sub>3</sub>PPE<sub>10</sub> respectively.

positive free ions.<sup>27</sup> The two main pathways for formation of the toluene triplet are via (1) direct electron–hole recombination and (2) intersystem crossing from the singlet excited state with a yield  $\phi^T = 0.45$ .<sup>28</sup> In these experiments the lifetime of the toluene singlet determined by observation of the singlet absorption ( $\lambda_{\text{max}} = 550$  nm) was  $\tau = 33$  ns, in good agreement with reported values.<sup>27</sup> For benzene the reported radiation chemical yields of the triplet range from 1.85 to 4.2.<sup>27,29</sup> There have been few (but varied) reports of the radiation chemical yield of the toluene triplet;<sup>27,28</sup> its short lifetime has been estimated as  $\sim 20$  ns.<sup>27,28</sup> There was no evidence for the presence of radical anions and cations of PPE in the transient absorption data at room temperature. The known spectra of the PPE radical ions differ significantly from the spectrum of the triplet. The ions have large molar absorption coefficients<sup>3</sup> that would have enabled their detection if present at concentrations  $\sim 4\%$  of the triplets. If triplet yields in toluene are similar to those in benzene, they are expected to be  $\sim 20$ – $40$  times larger than yields of ions at room temperature. The spectrum at low temperature contains a small feature near 680 nm that may be due to PPE<sup>+</sup>• (Figure 3).

In these experiments the polymer triplet states were formed either via direct energy transfer from the toluene triplet (eq 4) or through naphthalene as an intermediate having a longer triplet lifetime (eqs 5–7). While the singlet state of the polymer is also formed via reaction with the toluene singlet or the naphthalene singlet (the quantum yield for intersystem crossing of the naphthalene singlet to the triplet is  $\phi \approx 0.8$ <sup>30</sup>), its lifetime is  $\tau \approx 0.5$  ns.<sup>3</sup> Therefore, within a few tens of nanoseconds, the major excited species in toluene solutions of PPEs is the polymer triplet. A short-lived absorption attributed to the polymer singlet state is observed in T<sub>3</sub>PPE<sub>10</sub> and PPE<sub>17</sub> solutions at wavelengths around 900 nm.



The rates of triplet transfer reactions to form the polymer triplet (eqs 4 and 7) are given in Table 1.<sup>5,31,32</sup> It has been demonstrated that the time-dependent term of Smoluchowski's classic equation,<sup>33</sup> eq 8, for the diffusion-controlled reaction of two spherical particles becomes larger and persists to longer times for long polymers with a few hundred or more repeat units,<sup>4,5</sup> using a theory derived by Traytak.<sup>32</sup> In this model the reaction radius is defined in terms of the number of repeat units,

$n$ , the reaction radius of the repeat unit,  $R_m$  and the distance between the repeat units,  $a$ , as shown in eq 9.

$$k(t) = 4\pi R_{\text{eff}} D N_a \left( 1 + \frac{R_{\text{eff}}}{(\pi D t)^{1/2}} \right) \quad (8)$$

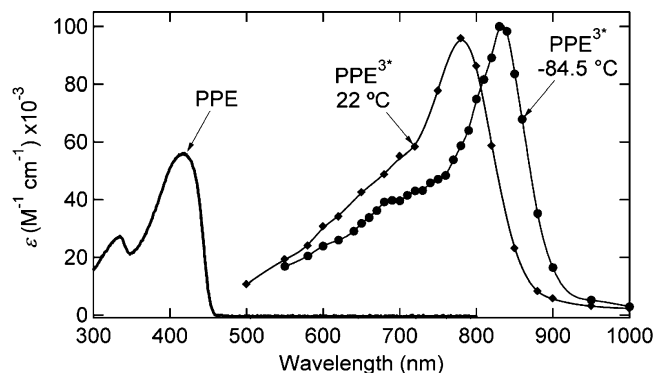
$$R_{\text{eff}} = \frac{n R_m}{1 + \frac{2 R_m}{a} \ln(n)} \quad (9)$$

In the polymers investigated here, comprising 20 or 34 phenyl–ethynyl repeat units, eqs 8–9 predict the contribution of the transient term to be less than 15% after 10 ns. Therefore, for these experiments, the transient term is expected to have a small effect. The growth of the polymer triplets was observed to follow reasonable pseudo-first-order kinetics, being linear with concentration in the range  $(8 \times 10^{-6})$ – $(1.2 \times 10^{-3})$  M (polymer units).

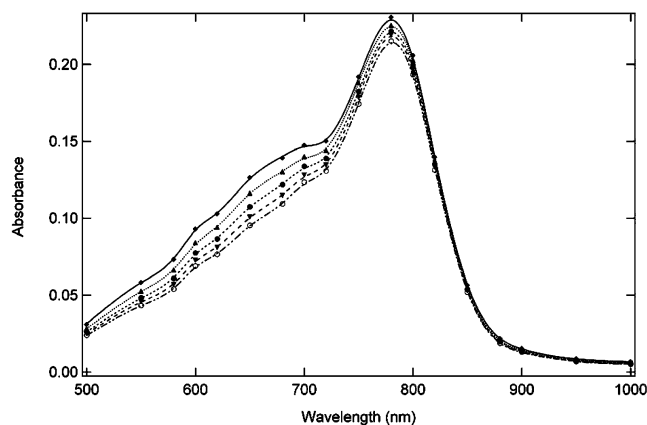
Equations 8 and 9 predict that rate constants for diffusion-controlled reactions with PPE<sub>17</sub> to be a factor of 1.29 faster than those with the shorter T<sub>3</sub>PPE<sub>10</sub>. The rate constants for reaction with toluene and naphthalene triplets in Table 1 are in accord with this prediction. This is unexpected for the slower reactions of PPE<sub>17</sub> and T<sub>3</sub>PPE<sub>10</sub> with <sup>3</sup>naphthalene\*. Those reactions are clearly slower than diffusion-controlled ones; thus, the rate constants might be expected to be linearly proportional to length, but the T<sub>3</sub> end caps may react at a somewhat higher rate.

From the concentration dependence of rates of formation of <sup>3</sup>PPE<sub>17</sub>\* and <sup>3</sup>T<sub>3</sub>PPE<sub>10</sub>\*, the lifetime of the toluene triplet is  $\tau = 23 \pm 3$  ns, in good agreement with previously reported values.<sup>27,28</sup> At the midpoint of the concentration range approximately half the solvent triplets were captured by the polymer prior to their natural decay. The longer lifetime of the naphthalene triplet, 4.8  $\mu$ s under these conditions, resulted in the transfer of  $>95\%$  of the initially formed triplets to the polymer at all concentrations used here. It is worth noting that the triplet spectra of poly(biphenylene ethynylene), PBpE<sup>17,34</sup> (Figure S-1 in Supporting Information), and terthiophene ( $\lambda_{\text{max}} = 470$  nm)<sup>35</sup> determined by triplet transfer from the toluene triplet are identical to those determined previously using laser techniques.

**Triplet Spectra.** The spectrum of the poly(phenylene ethynylene) triplet, <sup>3</sup>PPE<sub>17</sub>\* (Figure 2), has a large absorption in the visible–near-IR with  $\lambda_{\text{max}} = 780$  nm. The spectrum changes slightly with time over 600 ns, resulting in a decrease in absorbance at 650 nm and a relative increase in the absorption at 780 nm, and then decays uniformly over the wavelength range investigated (Figure 3). This change is unimolecular and occurs with  $k = (6 \pm 2) \times 10^5 s^{-1}$ , suggesting a slow conformational relaxation of the triplet excitation within the polymer. Such a slow conformational change is unexpected, and thus this explanation is tentative. The rate of this spectral relaxation is temperature-dependent with an activation energy  $E_a = (6.9 \pm$



**Figure 2.** Absorption spectra of poly(phenylene ethynylene) (PPE<sub>17</sub>) (---) and its triplet excited state (PPE<sup>3\*</sup>) at 20 °C (◆) with [PPE<sub>17</sub>] = 1.5 × 10<sup>-4</sup> M, and at -84.5 °C (●) with [PPE<sub>17</sub>] = 8.6 × 10<sup>-5</sup> M.

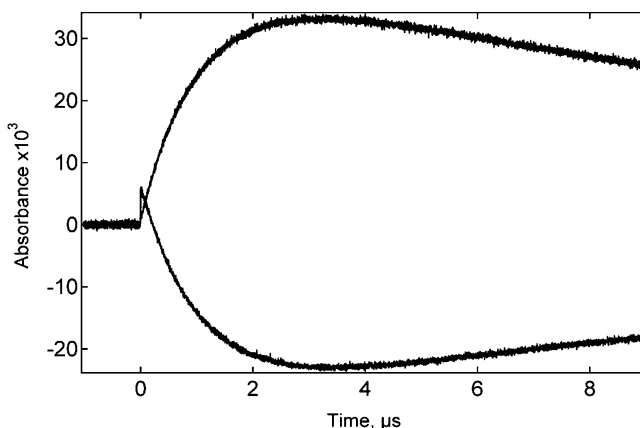


**Figure 3.** Absorption of the PPE triplet at 50 ns (◆), 200 ns (▲), 400 ns (●), 600 ns (▼) and 800 ns (○) following the electron pulse. Polymer concentration = 1.5 × 10<sup>-4</sup> M.

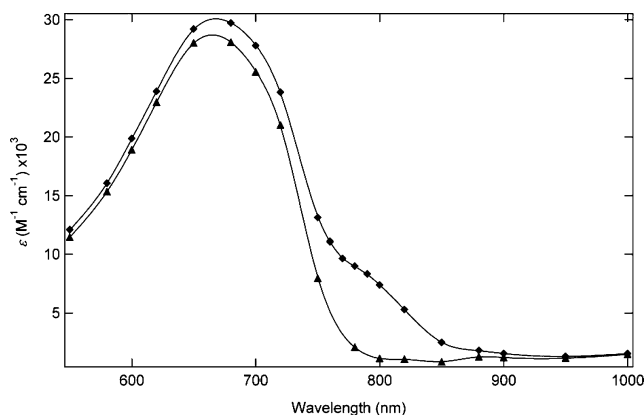
0.7) kJ mol<sup>-1</sup>, somewhat higher than the energy barrier for rotation of adjacent ground-state phenyl-ethynyl groups (2–4 kJ mol<sup>-1</sup>).<sup>36</sup>

The rate of the long time-scale decay is concentration dependent. The concentration dependence could be explained by a diffusion-controlled reaction with impurities present at 10% of the polymer concentration, but this extent of impurity is unlikely, given the characterization of the polymer material. Another explanation is quenching by ground-state polymers; a self-quenching mechanism has also been reported for poly(phenylene vinylene) triplets.<sup>21</sup> At the low concentration limit (1 μM) the polymer triplet lifetime was  $\tau \approx 300 \mu\text{s}$  and is likely limited by quenching by trace amounts of O<sub>2</sub>. The activation energy for this decay is  $E_a = (10.7 \pm 0.8) \text{ kJ mol}^{-1}$ .

Figure 4 compares the bleach of the ground-state absorption band at 420 nm, for which  $\epsilon = 56,000 \text{ M}^{-1} \text{ cm}^{-1}$  per monomer unit, with the growth of the triplet signal at 780 nm in the presence of naphthalene. By using a procedure similar to that of Seki,<sup>37</sup> the ratio of absorbance changes due to triplet growth and ground-state bleach, and we conclude that the formation of one triplet removes ground-state absorption from 1.3 PPE repeat units (2.6 phenyl ethynyl units). The calculation, described in Supporting Information, utilizes the extinction coefficients of the neutral and triplet and corrects for the natural decay of the naphthalene and PPE triplet species. The molar absorption coefficient of <sup>3</sup>PPE<sub>17</sub>\* was determined with reference to that for the naphthalene triplet in benzene,<sup>19,38</sup> using this and the dosimetry,  $G(\text{naphthalene triplet}) = 2.76 \text{ molecules}/100 \text{ eV}$  in toluene. This approach assumes <sup>3</sup>PPE<sub>17</sub>\* has insignificant absorption at 420 nm; if this assumption does not hold, then the delocalization length given serves as a lower limit.



**Figure 4.** Triplet transfer from naphthalene<sup>3\*</sup> to PPE<sup>3\*</sup> in a solution containing 0.1 M naphthalene and 7.8 × 10<sup>-6</sup> M PPE in a 1 mm path length cell. (Upper trace) Growth of PPE<sup>3\*</sup> at 780 nm. (Lower trace) Absorption and decay of naphthalene and bleach of ground-state PPE observed at 420 nm.



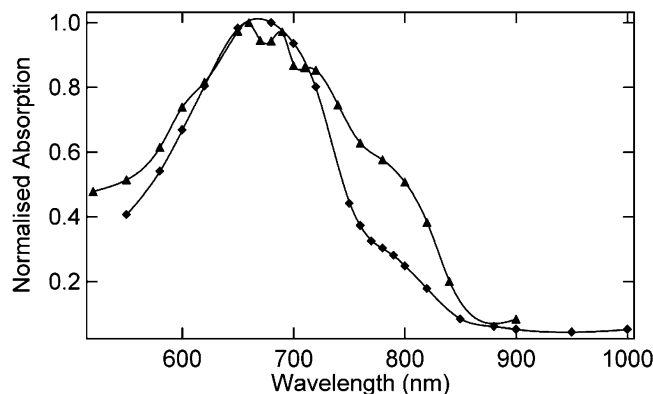
**Figure 5.** Absorption spectra of <sup>3</sup>T<sub>3</sub>PPE<sub>10</sub>\* ( $c(\text{T}_3\text{PPE}_{10}) = 1.4 \times 10^{-4} \text{ M}$ ). Spectrum after 50 ns (◆); same after subtraction of the 50-ns spectrum PPE<sup>3\*</sup> scaled by 0.15 (▲).

Appending terthiophene traps to the end of the polymer changes the triplet absorption spectrum markedly. The spectrum of the end-capped polymer triplet, <sup>3</sup>T<sub>3</sub>PPE<sub>10</sub>\* (Figure 5), has an absorption maximum wavelength ~100-nm shorter than that of <sup>3</sup>PPE<sub>17</sub>\*. A shoulder at 780 nm is identical in position and shape to the absorption band of <sup>3</sup>PPE<sub>17</sub>\*, but its height is only (15 ± 3)% of that in PPE solutions. Decay rates of both the 680-nm <sup>3</sup>T<sub>3</sub>PPE<sub>10</sub>\* absorption band and the 780-nm shoulder depend on T<sub>3</sub>PPE concentration, but the shoulder decays ~40 times faster. The decay rate of the shoulder is linear over a two-decade range in T<sub>3</sub>PPE<sub>10</sub> concentration; the slope yields a bimolecular rate constant of  $(6.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (polymer concentration). The difference between the triplet spectra of the parent and end-capped PPE shows that the triplet excitation is trapped on the terthiophene end-group in <sup>3</sup>T<sub>3</sub>PPE<sub>10</sub>\*. In support of this conclusion, the model compound Ph-T<sub>3</sub> has a triplet-triplet absorption band maximum at 620 nm (Figure S-2 in Supporting Information).

The relative contributions of the two triplet species outlined above are temperature dependent. As shown in Figure 6 a gradual increase of the absorption due to the <sup>3</sup>PPE\* species with decreasing temperature is observed.

**Bimolecular Reactions and Triplet Energetics.** The energetics of the triplet states in the polymers were determined via bimolecular triplet transfer to organic triplet acceptors. These experiments were designed to measure the position of the equilibrium of eq 10; the use of acceptors with known triplet





**Figure 6.** Normalized absorption of  ${}^3\text{T}_3\text{PPE}_{10}^*$  at 22 °C ( $\blacklozenge$ ),  $[\text{T}_3\text{PPE}_{10}] = 1.4 \times 10^{-4}$  M and at -24 °C ( $\blacktriangle$ ),  $[\text{T}_3\text{PPE}_{10}] = 4.6 \times 10^{-5}$  M.

**TABLE 2: Energies of the Polymer Triplet States**

	$E_T$ (eV)
${}^3\text{T}_3^*$	1.92 <sup>22</sup>
${}^3\text{PPE}_{17}^*$	$2.12 \pm 0.05^a$
${}^3\text{T}_3\text{PPE}_{10}^*$	$1.77 \pm 0.03^b$

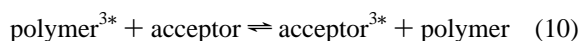
<sup>a</sup> Obtained by bracketing (see text). <sup>b</sup> From the observed equilibrium with  $\text{T}_3$ .

**TABLE 3: Rate Constants for Energy Transfer from  ${}^3\text{PPE}_{17}^*$  or  ${}^3\text{T}_3\text{PPE}_{10}^*$  to Acceptors**

	$k_8$ ( $\text{M}^{-1} \text{s}^{-1}$ )		
	$\text{O}_2$	$\text{T}_3$	acridine
$\text{PPE}_{17}$	$(3 \pm 1) \times 10^9$	$(7 \pm 2) \times 10^9^a$	$(6.7 \pm 2) \times 10^9$
$\text{T}_3\text{PPE}_{10}$	$(2 \pm 1) \times 10^9$	$(7 \pm 1) \times 10^9^b$	

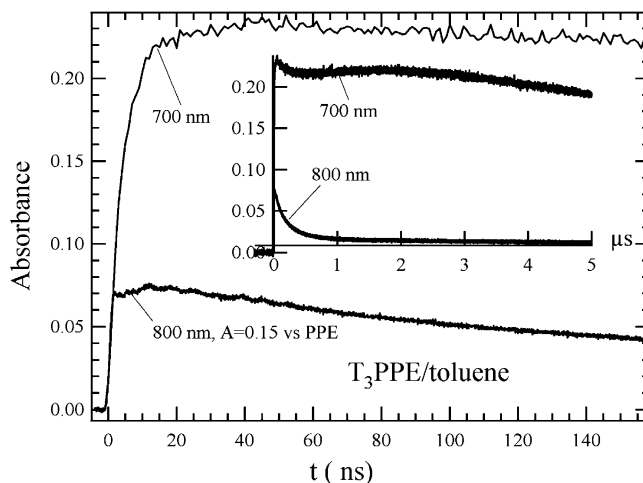
<sup>a</sup> Energy transfer from  ${}^3\text{PPE}_{17}^*$  to  $\text{T}_3$ . <sup>b</sup> Energy transfer from  ${}^3\text{T}_3^*$  to  ${}^3\text{T}_3\text{PPE}_{10}^*$ .

energy allows the energy level of the polymer triplet to be determined.



For  $\text{PPE}_{17}$  reaction 10 goes to completion with the acceptors acridine,  $\text{O}_2$ , or  $\text{T}_3$  with rate constants (Table 3) that are close to diffusion-controlled. Triplet transfer from  ${}^3\text{pyrene}^*$  to  $\text{PPE}_{17}$  and from  ${}^3\text{PPE}_{17}^*$  to triphenylethylene allowed the energy level of  ${}^3\text{PPE}_{17}^*$  to be bracketed between the energy level of these two acceptors.  ${}^3\text{T}_3^*$  transfers energy to  $\text{T}_3\text{PPE}_{10}$ , proceeding to an equilibrium. The free energy change observed for this reaction along with the reported triplet energy of  ${}^3\text{T}_3^*$  gives the triplet energy  $E({}^3\text{T}_3\text{PPE}_{10}^*)$  reported in Table 2. These data show the triplet state of  $\text{T}_3\text{PPE}_{10}$  is stabilized relative to that of  $\text{T}_3$  by 150 meV. This stabilization most likely arises from conjugation with the PPE chain. In the end-capped polymer, the driving force for triplet transfer from the polymer chain to the terthiophene end cap is 350 meV.

**Dynamics of Intrachain Triplet Transfer.** When solvent triplets attach to  $\text{T}_3\text{PPE}_{10}$ , the 780-nm absorption band of  ${}^3\text{PPE}^*$  is almost absent; instead a band at 680 nm is formed (Figures 5 and 6). At the maximum soluble concentration of  $\text{T}_3\text{PPE}_{10}$ ,  $7.7 \times 10^{-4}$  M (polymer units),  ${}^3\text{T}_3\text{PPE}_{10}^*$  triplet absorption grows at 700 nm, near the maximum of this band, with  $\tau = 5$  ns (Figure 7) as triplets are captured from the solvent. At short times a 780-nm band is seen, as noted above, having an intensity only 15% of that seen in solutions of  $\text{PPE}_{17}$ . The bimolecular decay of that small remaining  ${}^3\text{PPE}_{17}^*$  band observed at 800 nm is clear in Figure 7, however the formation of  ${}^3\text{T}_3\text{PPE}_{10}^*$  at 700 nm is less obvious. Because  $\epsilon$  ( ${}^3\text{PPE}_{17}^*$ ) is larger than  $\epsilon$



**Figure 7.** Transient absorbance at 700 and 800 nm in solutions of  $\text{T}_3\text{PPE}_{10}$  in toluene ( $T = 22$  °C) showing a  ${}^3\text{PPE}_{17}^*$  band at 800 nm having only 15% of that in PPE, which decays slowly ( $t = 217$  ns) in a bimolecular process.

( ${}^3\text{T}_3\text{PPE}_{10}^*$ ) at all wavelengths, even at the 680-nm maximum for  ${}^3\text{T}_3\text{PPE}_{10}^*$ , the absorption there still decays slightly as the loss of  ${}^3\text{PPE}_{17}^*$  produces  ${}^3\text{T}_3\text{PPE}_{10}^*$ . The present experiments show that transport of triplets is rapid in this  $\pi$ -conjugated polymer.

## Discussion

**Spectral Relaxation.** The  $(6 \pm 2) \times 10^5 \text{ s}^{-1}$  rate of the spectral changes tentatively attributed to conformational relaxation (Figure 3) are unexpectedly slow. It is likely that faster components exist but were not observed in these experiments. The presence of a dynamic conformational equilibrium is supported by low-temperature data ( $-84.5$  °C, see Figure 2) in which the  ${}^3\text{PPE}_{17}^*$  absorption is shifted to lower energy and the transition sharpened. These results support to the notion<sup>39</sup> that planar conformations have lower energies in both the singlet ground state ( $S_0$ ) and the lowest triplet state of PPE, while at room-temperature entropy favors the presence of nonplanar rotamers in the ground-state singlet. In this picture, at reduced temperature, such as  $-84.5$  °C, PPE has a somewhat greater degree of planarity in its ground state and is predominantly planar in the triplet excited state. Aggregation, found especially in the presence of methanol,<sup>40</sup> might provide an alternative, but apparently less satisfactory explanation. In this connection temporal evolution of the spectrum at  $-84.5$  °C is important. The spectrum seen in Figure 2 grows in smoothly without shift and with no hint of other species, except for the small band near 680 nm attributed to ions. (See figure S-3 in Supporting Information.) If the substantial spectral shift at the reduced temperature were due to aggregation, the presence of more than one aggregate would be likely, leading to changes of the spectrum with time. For the data at room temperature we offer a less clear, but plausible interpretation: PPE in its ground state exists as an equilibrium mixture of planar and more numerous nonplanar conformations. Upon triplet formation the initial, mainly nonplanar, conformations relax toward more planar ones. For triplets having initial, nonplanar conformations, barriers are substantially larger than  $kT$ . Therefore the relaxations of the triplet (Figure 3) are slow and proceed to an equilibrium in which the planar conformations are more numerous than for equilibrated ground state, but are not dominant.

**Delocalization Length,  $\text{T}_3\text{PPE}$  Spectra and Energetics.** Formation of a PPE triplet removed ground-state absorption

from an average of  $1.3 \pm 0.2$  repeat units. From the length of the repeat unit, 1.36 nm, this measurement indicates that a triplet state in PPE is fairly large, with a length of  $1.8 \pm 0.3$  nm, although much smaller than either excited singlets, electrons or holes.<sup>41</sup> If a delocalization length near 1.8 nm were typical, the partial delocalization of  ${}^3\text{T}_3\text{PPE}_{10}^*$  end-cap triplets into the chain might be expected.

The triplet state of  $\text{T}_3\text{PPE}$  is found here to have an energy 150 meV lower than that of  $\text{T}_3$  and 350 meV lower than that of PPE. Its triplet-triplet absorption spectrum with  $\lambda_{\text{max}} = 680$  nm and  $\epsilon_{\text{max}} = 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  is quite unlike that of  $\text{T}_3$  ( $\lambda_{\text{max}} = 470$  nm,  $\epsilon_{\text{max}} = 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). While  ${}^3\text{T}_3\text{PPE}_{10}^*$  is clearly localized at the end-cap, these observations indicate that it is not fully confined within the  $\text{T}_3$  group but is substantially stabilized by delocalization into the PPE chain, just as delocalization makes the triplet energy of tetrathiophene lower than that of terthiophene.<sup>22</sup> The 1.8-nm length of the PPE triplet, which is 50% longer than the 1.2-nm length of a  $\text{T}_3$ , also implies the possibility of delocalization, but suggests that  ${}^3\text{T}_3\text{PPE}_{10}^*$  might be fully or almost-fully confined in the 1.7-nm length of the model compound  $\text{Ph}-\text{T}_3$ . The 620-nm triplet-triplet absorption band of  $\text{Ph}-\text{T}_3$ , is closer, but still not identical to the 680 nm maximum of  ${}^3\text{T}_3\text{PPE}_{10}^*$ . If the upper ( $T_n$ ) state of  ${}^3\text{T}_3\text{PPE}_{10}^*$  were more delocalized than the  $T_1$  state found for poly(phenylene vinylene) and poly(thiophene),<sup>8</sup> and therefore of lower energy than that of  $\text{Ph}-\text{T}_3$ , the lower (680 nm) transition would be accounted for. The triplet of  $\text{PPE}_{17}$ , delocalized over 2.6  $\text{Ph}-\text{C}\equiv\text{C}$  units vs shorter lengths reported for metal-containing polymers,<sup>12-15</sup> provides further evidence that the introduction of metal atoms (for example Pt) within the repeat unit of the polymer backbone results in the confinement of the triplet. This may reflect weaker conjugation of the Pt-acetylide  $d\pi/p\pi$  overlap compared to the organic  $p\pi/p\pi$  overlap. Expanding the number of aromatic units between the platinum atoms is known to increase the delocalization length of the triplet.<sup>10,15</sup>

**Triplet Transfer along PPE Chains.** When triplets are attached to  $\text{T}_3\text{PPE}_{10}$ , 85% became  ${}^3\text{T}_3\text{PPE}_{10}^*$  end-cap triplets absorbing at 680 nm. By contrast most triplets would be expected to attach to the longer PPE chains which consist, on average, of 20  $\text{Ph}-\text{C}\equiv\text{C}$  units with a length of 13.6 nm (for  $n = 10$ ), while the length of two  $\text{T}_3$  end caps is 2.3 nm. If upon triplet capture the partitioning were proportional to length, 86% would be formed as  ${}^3\text{PPE}^*$  chain triplets, and only 14% would be initially captured by the end caps. In contrast to this  $\sim 14\%$  expectation, 85% are observed to be  ${}^3\text{T}_3\text{PPE}^*$  end-cap triplets at  $t = 5$  ns, demonstrating that for the overwhelming majority of triplets intramolecular triplet transport from the PPE chain of  $\text{T}_3\text{PPE}_{10}$  to a  $\text{T}_3$  end cap occurs in a time much shorter than 5 ns, while 15% may not have end caps (see below).

More than 14% of the solvent triplets might initially be captured by the end caps. If chain and end-cap triplets both have lengths of  $\sim 1.8$  nm, then a triplet centered 2.4 nm from the end of the chain might be immediately captured, leading to an estimate that  $\sim 30\%$  of captured triplets would initially become end-cap triplets. Still  $\geq 70\%$  are expected to be formed as PPE chain triplets, which is much larger than the 15% observed. If following the  $\sim 5$ -ns capture of  ${}^3\text{toluene}^*$  these chain triplets transferred to make  ${}^3\text{T}_3\text{PPE}_{10}^*$  in 5 ns, a  $\sim 5$ -ns transient at 780 nm having an amplitude  $\sim 30\%$  of the 780-nm band in the absorption of  ${}^3\text{PPE}^*$  would be expected. That no such transient is observed shows that chain triplets are transported to the  $\text{T}_3$  end caps in a time shorter than 5 ns. This 5-ns limit is conservative: the data appear to indicate that transport is much

faster, but small contributions from short-lived transients such as singlet states complicate the analysis needed to reach that conclusion in a quantitative way. Such transients are observed at other wavelengths.

This finding of fast triplet transport provides an interesting confrontation with the plausible interpretation above that relaxation of  ${}^3\text{PPE}^*$  chain triplets toward more planar conformations occurs slowly (hundreds of nanoseconds) as reflected in Figure 3. If this very tentative interpretation is correct, then fast ( $< 5$  ns) triplet transport of  ${}^3\text{PPE}^*$  must occur without complete relaxation of the triplet at each location in the PPE chain. This picture is consistent with the idea, advanced above, that  ${}^3\text{PPE}^*$  triplet energies depend weakly on conformation.

Remaining to be understood are the 15% of triplets captured by  $\text{T}_3\text{PPE}_{10}$  that appear as  $\text{PPE}^*$  chain triplets. The free energies determined here for formation of chain and end-cap triplets make it plain that once triplets reach the end cap very few ( $< 0.001\%$ ) will return to the chains at equilibrium. While these experiments indicate that most triplets transport to the  $\text{T}_3$  end caps within 5 ns, 15% remain for several microseconds, 1000 times longer. Two possibilities are evident. One is that capture is rapid whenever a  $\text{T}_3$  end cap is present, but 15% of the  $\text{T}_3\text{PPE}_{10}$  molecules do not have even one end cap. Similar incomplete capping has been investigated in detail for polythiophenes.<sup>42</sup> NMR integrations indicated the presence of  $(71 \pm 10)\%$  of the expected two  $\text{T}_3$  end caps per  $\text{T}_3\text{PPE}$  molecule. If end-capping were statistical, then 50% of the  $\text{T}_3\text{PPE}$  molecules would have two  $\text{T}_3$  end caps, 41% would have one  $\text{T}_3$ , and  $(8.4 \pm 5)\%$  would have none. With the assumption that all triplets are transported to end caps if even one is present, the NMR results predict only half of the observed 15% PPE chain triplets, although the results can be regarded as consistent within uncertainties in both measurements. It is also possible that the remaining  $\sim 7\%$  of chain triplets might somehow be trapped in the PPE chains. Such trapping in Pt-containing PPE chains has been recently reported by two of us.<sup>12</sup> Such trapping might involve a large conformation change or possibly chemical imperfections ("kinks") that block transport. Uncertainties in NMR estimates of capping are difficult to evaluate; thus, it is also conceivable that the entire 15% is due to uncapped molecules.

In either case the observed rate constant,  $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , for bimolecular decay of the chain triplets in  $\text{T}_3\text{PPE}_{10}$  is due to transfer of chain  ${}^3\text{PPE}^*$  to the end caps on other  $\text{T}_3\text{PPE}_{10}$  molecules. If only 85% have caps, this rate constant for bimolecular triplet transfer would be adjusted to  $(5.2 \times 10^8)/0.85 = 6.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

## Conclusions

Conjugative interactions between PPE and  $\text{T}_3$  end caps give the end-cap triplet,  ${}^3\text{T}_3\text{PPE}^*$ , a triplet energy 350 meV lower than the  ${}^3\text{PPE}^*$  chain triplet and 150 meV lower than that of  ${}^3\text{T}_3^*$ ; the  ${}^3\text{T}_3\text{PPE}^*$  triplet state is well trapped at the end cap. The 1.8-nm delocalization length of triplet excited states in PPE is significantly larger than that found in metal-containing PPE polymers, supporting the idea that the incorporation of the metal into the polymer backbone leads to the confinement of the triplet exciton. Transport of triplets from  ${}^3\text{PPE}^*$  chain triplets to traps is rapid and occurs in  $< 5$  ns.

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**Supporting Information Available:** Spectra of (1) poly-(biphenylene ethynylene) triplet, (2) Ph-T<sub>3</sub>, (3) PPE triplet evolution at -84 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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