Triplet state photophysics in an aryleneethynylene π-conjugated polymer

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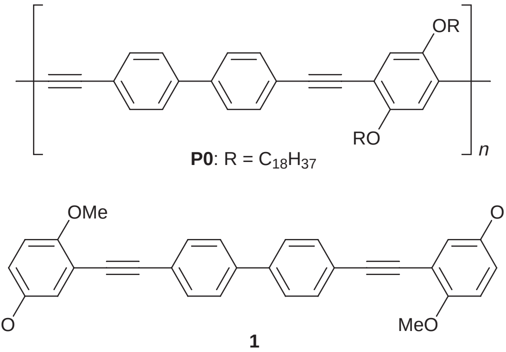
The triplet state photophysics of a polyaryleneethynylene π-conjugated polymer and a related model compound are investigated with various techniques, including laser flash photolysis and time-resolved thermal lensing (TRTL).

The photophysical and photochemical properties of π-conjugated polymers have been of significant recent interest.[1] Although most work on the photophysics of π-conjugated polymers has focused on the $^1\pi,\pi^*$ manifold, considerable evidence suggests that $^3\pi,\pi^*$ excitons are also involved in their rich photochemistry.[2–5] Unfortunately, owing to the absence of phosphorescence in most π-conjugated polymers[2] little is known about the absolute energies and yields of the triplets produced by direct excitation.

We recently initiated a photophysical study of aryleneethynylene-based π-conjugated polymers that contain a photoactive transition metal chromophore in the π-conjugated backbone.[6,7] A primary objective of this work is to understand the interaction between backbone-based $^1\pi,\pi^*$ and $^3\pi,\pi^*$ excited states and metal complex-based $d \rightarrow \pi^*$ charge transfer excitations. However, in order to pursue this line of investigation in the metal–organic polymers, it is necessary to have a firm understanding of the properties of the $^1\pi,\pi^*$ and $^3\pi,\pi^*$ excited states of the all-organic polymers. Here, we report the results of a detailed photophysical study which compares the photophysical properties of the singlet and triplet manifolds of aryleneethynylene polymer **P0** and model compound **1** in dilute THF solution (Scheme 1).[‡]



Scheme 1

Pulsed laser excitation (355 nm, 10 ns FWHM, 4 mJ pulse^{-1}) of **1** and **P0** affords a long lived transient [τ(**1**) = 142 μs, τ(**P0**) = 169 μs[§]], which is assigned to a $^3\pi,\pi^*$ state. The triplet state difference absorption spectra of **1** and **P0** (Fig. 1) are characterized by bleaching of the ground state π,π* absorption band [λ_{max}(**1**) = 360 nm, λ_{max}(**P0**) = 410 nm] and a broad (triplet–triplet) absorption band that extends to longer wavelengths. Interestingly, the difference spectra of **1** and **P0** are remarkably similar, except that the bleach and absorption bands are red-shifted in the polymer. The qualitative similarity in the triplet–triplet absorption spectra implies that the electronic structure of the triplet state is similar in the model and polymer.

In order to determine the triplet energies of **1** and **P0** (E_T), Stern–Volmer quenching studies were carried out with a series of triplet acceptors of varying energy.[8,9][¶] Triplet quenching rate constants (k_q) were obtained from Stern–Volmer analysis of the observed triplet decay lifetimes in vacuum degassed THF solutions as a function of quencher concentration. The triplet energies were then estimated by fitting the experimental Sandros plots (Fig. 2)[10] with a Marcus equation that is appropriate for bimolecular reactions which occur at or near diffusion control,[11,12]

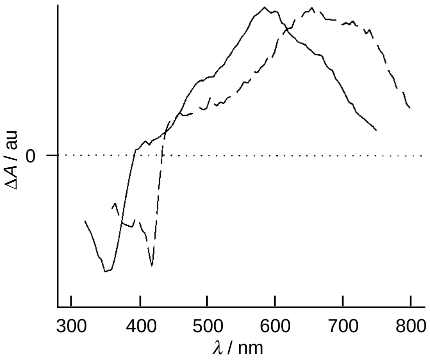


Fig. 1 Triplet state difference absorption spectra of (solid line) **1** and (dashed line) **P0** in degassed THF solution

$$k_q = \frac{k_d}{1+\exp(\Delta G/RT) + (k_{-d}/k_{en}^0)\exp(\Delta G^\ddagger)} \qquad (1a)$$

$$\Delta G^\ddagger = \Delta G + \frac{\lambda}{\ln 2}\ln\{1+\exp[-(\Delta G \ln 2)/\lambda]\} \qquad (1b)$$

where k_d and k_{-d} are the rate constants for forward and reverse diffusion in solution, k_{en}^0 is a pre-exponential factor, λ is the reorganizational energy and $\Delta G = (E^{00}_{Acceptor} - E_T)$. By using parameters derived from a previous study[13] (k_d = 1.0 × 10^{10}

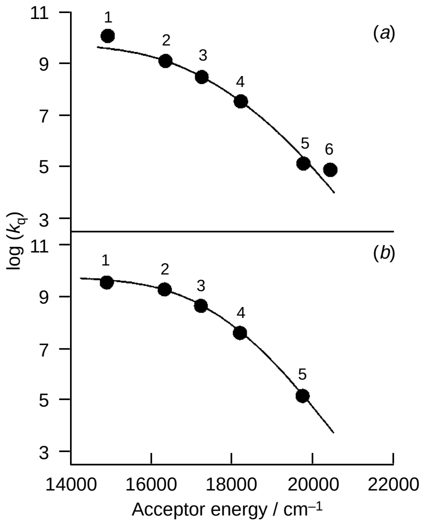


Fig. 2 Sandros plots for (*a*) **P0** and (*b*) **1**. Points are experimentally determined rate constants with various triplet energy acceptors,[¶] and fitted lines are calculated as explained in the text.

Table 1 Photophysical properties of model compound **1** and polymer **P0**[a]

Compound	τ_{fl}/ns	Φ_{fl}[b]	E_S/cm^{-1} (kcal mol^{-1})	λ^c/cm^{-1}	$E_T{}^c$/cm^{-1} (kcal mol^{-1})	Φ_T	$10^{-8}\,k_r$/s^{-1}	$10^{-8}\,k_{nr}$/s^{-1}	$10^{-8}\,k_{isc}$/s^{-1}
1	1.15	0.90	24 200 (69.2)	1000	17 700 (50.6)	$\leqslant$0.10[d,e]	7.8	$\leqslant$0.87	$\leqslant$0.87
P0	0.53	0.60[f]	23 100 (66.0)	1200	17 500 (51.2)	0.12[e]	11	5.7	2.3

[a] THF solutions at 298 K. [b] Fluorescence quantum yields determined using 9,10-dicyanoanthracene (DCA) and perylene as actinometers ($\Phi_{DCA}{}^{EtOH} = 0.89$, $\Phi_{Perylene}{}^{EtOH} = 0.89$). [c] Values based on a Marcus fit to quenching data as described in text. [d] Upper limit. [e] See footnote §. [f] See foonote **.

$\text{M}^{-1}\,\text{s}^{-1}$, $k'_{-d} = 2.0 \times 10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$, $k_{en}{}^0 = 5 \times 10^{10}\,\text{s}^{-1}$), best fits of the Sandros plots for **1** and **P0** were attained by varying λ and E_T in eqn. (1). These values are listed in Table 1, and plots of the fitted quenching data are shown in Fig. 2. Surprisingly, E_T for the model compound and the polymer is the same within experimental error (±5%).

A second objective of the present study was to determine the triplet yields (Φ_T) for **1** and **P0**. However, in order to determine this parameter it is necessary to know the fluorescence quantum yields (Φ_{fl}). Therefore, fluorescence spectra of **1** and **P0** were obtained [$\lambda_{max}(\mathbf{1}) = 413$ nm, $\lambda_{max}(\mathbf{P0}) = 433$ nm], and Φ_{fl} values were determined from the integrated fluorescence spectra (Table 1).[14]‖ Fluorescence lifetimes (τ_{fl}) for **1** and **P0** are also listed in Table 1. Next, the triplet yield (Φ_T) for **P0** was determined by time-resolved thermal lensing (TRTL).[15,16] In this method, Φ_T is derived from the ratio of the 'slow' and 'total' heat deposition signals (U_{slow} and U_{total}, respectively) after correcting for the energy of the pump laser ($E_{h\nu}$) and the fluorescence quantum yield,

$$U_{slow}/U_{total} = E_T\Phi_T/(E_{h\nu} - E_S\Phi_{fl}) \qquad (2)$$

where E_S is the energy of the singlet state (Table 1). The U_{slow}/U_{total} ratio of a vacuum degassed THF solution of **P0** was determined to be 0.15, and the triplet yield calculated with eqn. (2) is listed in Table 1.** Unfortunately, Φ_T for **1** could not be measured with TRTL owing to strong triplet–triplet absorption at the thermal lensing probe wavelength (633 nm). However, the experimentally derived Φ_{fl} for **1** (0.90) provides an upper limit for Φ_T ($\leqslant 0.1$).**

The photophysical characterization of the singlet and triplet states of **1** and **P0** allows us to assess the effect that the extended π-conjugation in the polymer has on its triplet state properties. It is surprising that E_T is the same for the polymer and model compound. However, the more important parameter is the singlet–triplet splitting energy (E_{ST}), which is defined as $E_S - E_T$. Interestingly, E_{ST} is lower by almost 1000 cm^{-1} in **P0** compared to **1** (5600 *vs.* 6500 cm^{-1}). The lower E_{ST} indicates that the electron exchange energy is smaller in the polymer,[17] which presumably is due to the fact that the delocalization of the LUMO (and/or the HOMO) for the $\pi \longrightarrow \pi^*$ transition is greater in **P0** than in **1**. Moreover, it is of interest that the experimentally determined E_{ST} for **P0** is comparable to values calculated using semi-empirical MO theory.[18,19]

The rates of radiative decay, non-radiative decay and intersystem crossing (k_r, k_{nr} and k_{isc}, respectively) for the $^1\pi,\pi^*$ state of **1** and **P0** have been determined by using the experimental Φ_{fl}, τ_{fl} and Φ_T values (Table 1). First, note that k_r is comparable in **1** and **P0**. This is not surprising given that the orbital basis and transition dipole for radiative transitions are similar in the model and the polymer. By contrast, k_{nr} and k_{isc} are significantly larger in **P0** than in **1**. The larger non-radiative decay rate in the polymer may arise from 'defect sites' (*e.g.* unreacted end groups and/or defects in the polymer backbone) that quench the $^1\pi,\pi^*$ exciton. The larger (effective) intersystem crossing rate in **P0** may arise from the smaller E_{ST} value.

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Notes and References

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‡ **P0** was synthesized *via* a Pd-mediated cross-coupling reaction of the polymer subunits (see ref. 7 for complete synthetic details). *Selected characterization*: **P0**: GPC (CHCl$_3$, polystyrene standards) $M_n = 65.2$ kD, $M_w = 209.2$ kD (PDI = 3.2). ^{1}H NMR (CDCl$_3$) δ 0.87 (bt, t), 1.24 (br, s), 1.56 (br, m), 1.84 (br, m), 4.04 (br, t), 6.92 (br, s), 7.0 (br, s), 7.62 (br, s). ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 26.1, 29.4, 29.7, 32.0, 69.7, 87.0, 94.8, 114.0, 116.9, 122.8, 126.8, 132.1, 140.0, 153.7. **1**: ^{1}H NMR (CDCl$_3$) δ 3.79 (s, 6 H, OCH$_3$), 3.89 (s, 6 H, OCH$_3$), 6.86 (m, 4 H, phenyl), 7.08 (d, 2 H, phenyl), 7.63 (d, 8 H, biphenyl). ^{13}C NMR (CDCl$_3$) δ 55.8, 56.5, 86.7, 93.2, 112.2, 112.9, 115.8, 118.0, 122.7, 126.7, 132.1, 139.9, 153.2, 154.5.

§ In ref. 6 we reported the triplet lifetime for a sample of **P0** in Ar-purged THF ($\tau_T = 4$ μs). In that study the lifetime was suppressed due to quenching by residual oxygen. The triplet lifetimes reported herein are for samples that were freeze–pump–thaw degassed five times and sealed at 10^{-5} Torr. It is conceivable that even under these conditions the triplet lifetime is suppressed by oxygen quenching.

¶ Triplet acceptors (see Fig. 2): 1, anthracene; 2, [4,4′-bis(carboethoxy)-2,2′-bipyridyl]Re(CO)$_3$Cl; 3, *trans*-stilbene: 4, (2,2′-bipyridyl)Re(CO)$_3$Cl; 5, biacetyl; 6, *p*-terphenyl.

‖ In ref. 6 we reported the fluorescence quantum yield for **P0** in Ar-purged THF ($\Phi_{fl} = 0.28$). The sample of **P0** used in that study was structurally equivalent to that used in the present study, but it had a substantially lower molecular weight ($M_n = 13.5$ kD, $M_w = 37.4$ kD). The higher molecular weight of the sample of **P0** used in the present study accounts for the larger fluorescence yield reported herein.

** The Φ_T values for **P0** and **1** were confirmed using photoacoustic calorimetry [Φ_T (**P0**) = 0.12, Φ_T (**1**) = 0.05].

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