Delayed Fluorescence and Triplet-Triplet Annihilation in π-Conjugated Polymers

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The delayed fluorescence of poly(p-phenylene vinylene) (PPV) and poly(p-phenylene ethynylene) (PPE) derivative solids and frozen solutions at 20 K is described. It provides strong evidence for triplet-triplet annihilation to singlets excitons, accounting for up to ~3% of the total emission in PPV films and ~1.5% in PPE powder. It also yields triplet lifetimes of 70 and 110 μs in PPV films and frozen solutions, and ~200 and ~500 μs in PPE powder and frozen solutions, respectively. [S0031-9007(99)09010-9]

Very extensive studies of the photoluminescence (PL) of π-conjugated polymer films and the electroluminescence (EL) of polymer light-emitting devices (LEDs) have been reported during the past fifteen years [1]. However, several basic issues have remained unanswered. In particular, no quantitative observations of long-lived (microseconds to milliseconds) emission due to delayed fluorescence (DF) have been reported. In contrast, in small π-conjugated molecules such DF due to triplet-triplet (T-T) exciton annihilation to singlet excitons,

$$^{3}T + {}^{3}T \rightarrow {}^{1}S^{*}, \tag{1}$$
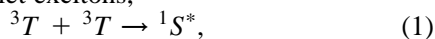
which relax to the lowest (luminescent) $1^{1}B_{u}$ state was identified unambiguously and studied in detail [2,3]. On a broader level, understanding triplet dynamics is important for small organic molecular and polymer LEDs, as they may be the most prolific of states generated by fusion of the positive and negative polaronic carriers [4]. Indeed, the 25% theoretical upper limit of the EL yield of such LEDs is derived from spin statistics, which should yield nonluminescent triplets in 75% of these fusion events [4]. This argument is obviously simplistic, and an established picture of the nature of the coupling between the singlet excitons, triplet excitons, and the intermolecular or interchain polaron pairs may lead to significant modifications of the simple spin-statistical result.

The lowest energy level of the interchain polaron pairs is widely believed to be slightly (~0.1 eV) lower than that of the $1^{1}B_{u}$ [5] and consequently decidedly higher than that of the lowest intrachain $1^{3}B_{u}$ triplet [6]. Some studies have suggested that under steady-state photoexcitation the population of the triplet (parallel spin) polaron pairs is greater than that of the singlet (antiparallel spin) pairs, which is depleted by nonradiative recombination to the ground state [7]. Other studies, however, have suggested that the triplet pair population, which may recombine to intrachain triplet excitons, is lower than that of the singlet pair population [8]. These latter studies also predicted that, in addition to direct nonradiative decay to the ground

state, the intrachain triplets decay by T-T annihilation to singlets [Eq. (1)], resulting in DF.

The unmistakable presence of intrachain triplet excitons in π-conjugated polymers has been observed by optically detected magnetic resonance (ODMR) [8–14] and their dynamics were studied by this technique and photoinduced absorption (PA) [6,11]. Indeed, the numerous cw and time-resolved PA studies showed that the polarons and triplet excitons are the only significant long-lived photoexcitations in such polymers [15]. Hence T-T annihilation would be the only plausible source of any DF, yet no direct evidence for such DF has been reported. This Letter provides such evidence by describing the PL response to the modulated excitation of 2,5-dihexoxy poly(p-phenylene vinylene) (DHO-PPV) powder, 2,5-dioctoxy PPV (DDO-PPV) film and frozen toluene solution, and 2,5-dibutoxy poly(p-phenylene ethynylene (DBO-PPE) powder and frozen toluene solution. The results show that bimolecular recombination, due ostensibly to T-T annihilation to singlets, is the source of DF which contributes up to ~3% of the total emission in DOO-PPV film, ~1.5% in DBO-PPE powder, and ~2% in frozen dilute DBO-PPE/toluene solution at 20 K at an absorption rate of ~10^{22} photons/cm^3 s. The measurements also yield triplet lifetimes of 70 and 110 μs in the PPV solids and frozen solutions, and ~200 and ~500 μs in PPE powder and frozen solutions, respectively.

Both PPVs and PPEs are strongly luminescent materials [12,13,16]. The latters' gap is ~2.6 eV [12,13,16], and they have been used as the emitting layer in polymer LEDs [13,17–20]. Powder and free-standing films of the PPV and PPE derivatives were vacuum sealed in quartz tubes. Solution samples were frozen, degassed, and then vacuum sealed. The PL system, which is part of an ODMR spectrometer, was described previously [9,10,14]. In this work, however, the 488 nm Ar$^+$ laser excitation power $5 \leq P \leq 35$ mW was modulated at frequencies 10 Hz $\leq \nu = \omega/2\pi \leq 10$ kHz by the Pockels cell of a Cambridge

Instruments Model LS100 laser stabilizer, so the photon absorption rate $G(t) = \alpha P(t)$ was given by

$$G(t) = G_0(1 + a\sin\omega t). \quad (2)$$

The PL was detected by a fast Hamamatsu photomultiplier tube, and the in-phase x and quadrature y Fourier components of the incident laser signal and the PL at $\nu = \omega/2\pi$ and 2ν were monitored by an EG&G 5210 lock-in amplifier.

The intrachain triplet exciton population n_T is governed by the rate equation [3,8]

$$\frac{dn_T}{dt} = G(t)\beta_T - k_T n_T - \gamma n_T^2, \quad (3)$$

where β_T is the yield of intrachain triplet excitons, k_T is their monomolecular decay rate, and γn_T^2 is the rate of triplet-triplet annihilation. At low excitation intensity γn_T^2 can be neglected and, assuming a solution of the form

$$n_T(t) = A[1 + B\sin(\omega t + \varphi)] \quad (4)$$

and substitution of this expression and Eq. (2) into Eq. (3), yields

$$n_T(t) = G_0\beta_T\tau_T\left[1 + \frac{a}{\sqrt{1 + \omega^2\tau_T^2}}\sin(\omega t + \varphi)\right], \quad (5)$$

where $\tau_T = 1/k_T$ is the monomolecular triplet decay (life)time and the phase shift $\varphi = \arctan(-\omega\tau_T)$. The intensity per unit volume of the DF I_{DF} is given by [3,8]

$$I_{DF} = \beta_S\frac{\gamma}{9}n_T^2, \quad (6)$$

where β_S is the prompt fluorescence (PF) yield and the spin-statistical factor of $1/9$ is the fraction of pairs of triplets which are in the singlet configuration. Substitution of Eq. (5) into Eq. (6) yields a component $I_{DF,2\omega}$ of the DF which oscillates at 2ω:

$$I_{DF,2\omega} = \frac{\gamma}{9}G_0^2\tau_T^2 a^2\beta_T^2\beta_S$$

$$\times\frac{1}{1 + \omega^2\tau_T^2}\sin\left(2\omega t + 2\varphi - \frac{\pi}{2}\right). \quad (7)$$

Since the component $I_{PF,\omega}$ of the PF at ω is given by

$$I_{PF,\omega} = G_0\beta_S a\sin(\omega t), \quad (8)$$

the ratio of the amplitude of $I_{DF,2\omega}$ to the amplitude of $I_{PF,\omega}$ is

$$R_{PL} = \frac{1}{9}\frac{\gamma G_0 a\beta_T^2\tau_T^2}{1 + \omega^2\tau_T^2}. \quad (9)$$

Hence, a measurement of R_{PL} vs ω yields τ_T. In addition, the fraction I_{DF}/I_{PF} of the total emission due to DF, resulting from T-T annihilation under cw conditions, is then equal to the value of R_{PL}/a at low ω, where $\omega\tau_T \ll 1$.

To correct for the system response and any Fourier component of the modulated laser beam at 2ω, the ratios

of the amplitudes of the x and y components of the laser beam signal at 2ω to the modulus at ω ($R_{las,x}$ and $R_{las,y}$, respectively) were subtracted from the similarly defined $R_{PL,x}$ and $R_{PL,y}$, respectively. The value of R_{PL}, corrected for the system response, is then

$$R'_{PL} = \sqrt{(R_{PL,x} - R_{las,x})^2 + (R_{PL,y} - R_{las,y})^2}. \quad (10)$$

Figure 1 shows R'_{PL} vs $\nu = \omega/2\pi$ of (i) aged DHO-PPV powder [21], (ii) fresh DOO-PPV film [22], and (iii) <0.025 mg/ml toluene solution of that DOO-PPV at 20 K. The phases of the laser and PL signals at 2ω confirmed that the PL signal at 2ω is positive [see Eq. (7)] and, indeed, results from DF due to a bimolecular process. We also note that the 3ω component of the PL was negligible. The excellent agreement between the results shown in Fig. 1 and a Lorentzian $A/[1 + \omega^2\tau^2] + C$ (allowing for an additive constant C) yields lifetimes $\tau = 70$ μs in the DHO-PPV powder and DOO-PPV film and $\tau = 110$ μs in the frozen DOO-PPV/toluene solutions.

The inset of Fig. 1 shows I_{DF}/I_{PF} vs the laser power P. The solid lines are the behavior predicted by the relation

$$\frac{I_{DF}}{I_{PF}} = c_1\frac{(\sqrt{1 + c_2 P} - 1)^2}{P}, \quad (11)$$

where $c_1 = k_T^2/36\gamma$ and $c_2 P = 4\gamma G_0 a\beta_T/\alpha k_T^2$ [see Eq. (12) in Ref. [8]]. The observed saturation of I_{DF}/I_{PF} at $P \geq 10$ mW is due to the significant contribution of the γn_T^2 term in Eq. (3) in lowering the triplet population at these excitation intensities. It can be shown that in the DHO-PPV powder and DOO-PPV film at $P = 10$ mW
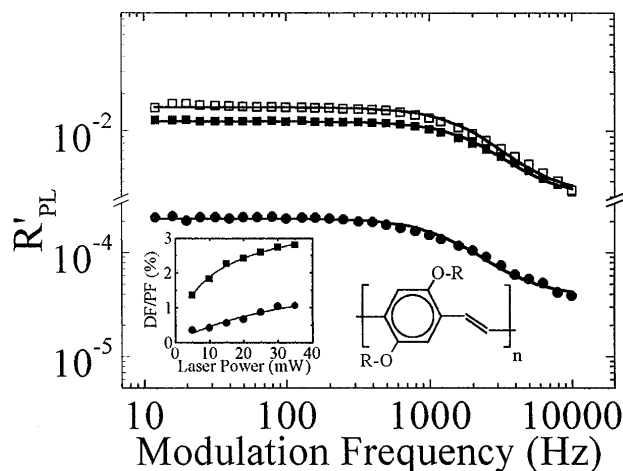

FIG. 1. The delayed fluorescence (DF) R'_{PL} [see Eqs. (9) and (10)] of DHO-PPV powder (open squares), DOO-PPV film (closed squares), and <0.025 mg/ml frozen DOO-PPV/toluene solution (circles at 20 K vs the laser modulation frequency ν. The observed behavior is fit to a Lorentzian $A/[1 + \omega^2\tau^2] + C$ (allowing for an additive constant C) yielding lifetimes $\tau = 70$ μs in the powder and film and $\tau = 110$ μs in the frozen solution. Inset: The ratio of the cw DF to the prompt fluorescence (PF) vs laser power. The solid lines are the behavior predicted by Eq. (11).

the contribution of the γn_T^2 term shortens the overall lifetime of the triplets by $\sim 20\%$ [23]. Hence, in that case, the true monomolecular lifetime is ~ 90 μs rather than 70 μs.

Note that at $P = 35$ mW the DF contributes $\sim 3\%$ and $\sim 1\%$ of the total emission in the DOO-PPV film and frozen solution, respectively. The excellent agreement between the results and Eq. (11) also rules out a significant contribution by a bimolecular singlet quenching process, for which $I_{DF}/I_{PF} \propto n_S n_T / n_S = n_T \propto \sqrt{1 + c_2 P} - 1$. Finally, we note that the assignment of the DF in the PPVs to T-T annihilation is also in agreement with recent measurements of the frequency dependence of the triplet PA and ODMR [24].

Figure 2 shows R'_{PL} vs ν in DBO-PPE powder and <0.025 mg/ml frozen toluene solution at 20 K. While the behavior of the powder is in rough agreement with the simple Lorentzian with $\tau = 210$ μs, the behavior of the frozen solution does not follow the best-fit Lorentzian obtained with $\tau = 520$ μs. The poor agreement may be due to, among others, monomolecular triplet decay that is governed by two or more lifetimes τ_{Ti}. Indeed, very recent measurements indicate that irreversible processes occurring during photoexcitation of some PPV films at room temperature result in the evolution of the DF from the behavior shown in Fig. 1 to the behavior such as shown in Fig. 2.

The inset of Fig. 2 shows similar dependence of I_{DF}/I_{PF} on P in DBO-PPE powder as seen in the inset of Fig. 1 for DOO-PPV film. It also shows that, in this case, I_{DF}/I_{PF} of t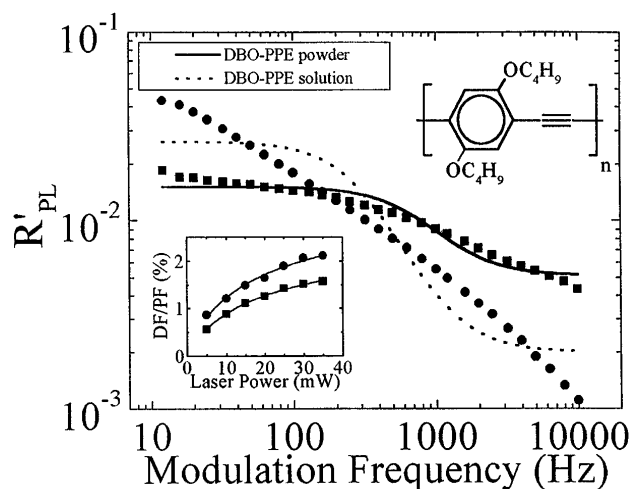he frozen solution is greater than that of the powder, in contrast to the weaker DF of the frozen DOO-PPV solution as compared to the film. This raises the possibility that some triplet formation may be related to specific sites or defects, consistent with their formation by the back-transfer of triplet interchain polaron pairs [8] and the effects of room-temperature photodegradation of some PPVs mentioned above.

Figure 3 compares the DF and PF spectra of powder and solutions. It is interesting to note that, while the DF spectra of the solutions are identical or only slightly redshifted from the PF, they are clearly redshifted in the powders and film. This $\Delta\lambda \sim 10$ nm redshift, which corresponds to an energy shift $\Delta E \sim 30$ meV at $\lambda \sim 600$ nm, is more consistent with the stronger dependence of the $1^1 B_u$ energy $E(1^1 B_u)$ on the conjugation length than that of the triplet $E(1^3 B_u)$: This greater dependence of $E(1^1 B_u)$ is due to its relatively extended size, as compared to the localized triplet [9,10,14,25,26]. Hence, in the longer π-conjugated segments of the solution $E(1^1 B_u) < 2E(1^3 B_u)$, but in the shortest segments resulting from strains and defects in the powder $E(1^1 B_u) > 2E(1^3 B_u)$.

Besides providing strong evidence for the presence and nature of the DF in π-conjugated polymers, the present results also impact our assessment of other processes in these materials. Thus, some ODMR and other studies [7,14,27–29] have suggested that nonradiative quenching of singlet excitons by polarons may be a significant channel competing with the PF. Yet the present results suggest that, at the excitation intensities of this work, bimolecular singlet quenching processes in the PPVs, studied in this work, where agreement with the triplet-triplet annihilation model is excellent, are relatively inefficient.

In summary, we have described frequency-resolved photoluminescence measurements of derivatives of poly(p-phenylene vinylene) and poly(p-phenylene ethynylene) which provide strong evidence for delayed

FIG. 2. The delayed fluorescence (DF) R'_{PL} of DBO-PPE powder (squares) and <0.025 mg/ml frozen DBO-PPE/toluene solution (circles) at 20 K vs the laser modulation frequency ν [see Eqs. (9) and (10)]. The lines are the least-squares Lorentzian $A/[1 + \omega^2 \tau^2] + C$ fits with $\tau = 210$ μs for the powder and $\tau = 520$ μs for the frozen solution. Inset: The ratio of the cw DF to the prompt fluorescence (PF) vs laser power. The solid lines are the behavior predicted by Eq. (11).
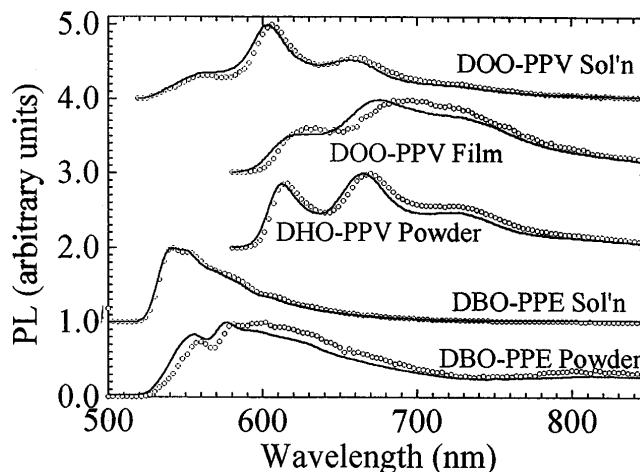
FIG. 3. The uncorrected PF (solid lines) and DF (open circles) spectra of the PPV and PPE samples. Note the redshift of the DF relative to the PF in the film and powders.

fluorescence due to a bimolecular process, ostensibly triplet-triplet exciton annihilation to singlets. At 20 K the lifetimes of this process are 70 μs in PPV derivative powders, 110 μs in dilute toluene solutions of those PPVs, $\sim$200 μs in PPE derivative powders, and $\sim$500 μs in dilute toluene solutions of those PPEs. In PPV derivative films it contributes $\sim$3% of the total emission at an excitation power of 35 mW.

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$$\tau_{T\text{eff}} = k_T(\sqrt{1 + 4G_0\beta_T\gamma/k_T^2} - 1)/(2G_0\beta_T\gamma)$$
$$\approx 1/[k_T + \sqrt{G_0\beta_T\gamma}\,],$$

where the parameter $A = 4G_0\beta_T\gamma/k_T^2$ governs the dependence of the DF on the excitation laser power, and it can be determined from that dependence. If n is the slope of the log-log plot of I_{DF}/I_{PF} vs P, then

$$n = A/\{[\sqrt{1 + A} - 1]\sqrt{1 + A}\} - 1.$$

The upper curve in the inset of Fig. 1 yields $n \approx 0.75$ and $A \approx 0.8$ for $P = 15$ mW.

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