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Delayed Fluorescence (DF) and Photoluminescence (PL)-Detected Magnetic Resonance (PLDMR) Studies of Triplet-Triplet (*T-T*) Annihilation and Other Long-Lived Processes in π-Conjugated Polymers

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Recent studies of frequency resolved DF due to *T-T* annihilation to singlet excitons ($^1S^*$) in π-conjugated polymers are reviewed, and the significance of this process is compared to that of other long-lived processses affecting the PL, in particular the nonradiative quenching of $^1S^*$ by polarons or triplet excitons. While the DF studies suggest that *T-T* annihilation typically accounts for up to ~3% of the total PL, PLDMR and other studies suggest that singlet quenching by polarons and triplets may be a very significant process in the films and organic light emitting devices (OLEDs), especially at high excitation densities.

Keywords: photoluminescence; delayed fluorescence; PLDMR; singlet excitons; triplet excitons; polarons

INTRODUCTION

Very extensive studies of the PL and electroluminescence (EL) of π-conjugated molecules and polymer films have been reported during the

past decade.[1,2] Yet basic issues such as the role of long-lived (> 1 μs) processes involving triplet excitons and polarons remain unsettled. This paper reviews some of them:

(i) DF due to *T-T* annihilation to singlet excitons:

$$^3T + {}^3T \rightarrow {}^1S^* \tag{1}$$

In small π-conjugated molecules such DF was described in detail a long time ago[3-7]. Yet to the best of our knowledge, the frequency-resolved PL studies reported recently[8,9] provided the first evidence for DF in π-conjugated polymers.

(ii) Processes involving polarons. The low-field DC EL of OLEDs is due to carrier injection followed by their relaxation to positive and negative polarons, some of which recombine to singlet excitons:

$$p^+ + p^- \rightarrow {}^1S^*. \tag{2}$$

Since the higher-energy singlet states relax to the lowest 1^1B_u, the EL spectrum is generally identical to the PL spectrum. Simple spin statistics predict a maximum EL yield of 25%, since 75% of the polarons should recombine to the nonluminescent triplets [10]:

$$p^+ + p^- \rightarrow {}^3T \tag{3}$$

However, it has recently been suggested that the strong difference between the $^1S^*$ and ^3T states influences their formation cross section from polarons[11]. It is also believed that the lowest polaron pair energy level is slightly (~0.1 eV) below that of the1^1B_u[12,13] and hence decidedly higher than that of the lowest 1^3B_u triplet [14]. Hence these pairs can decay to triplets but not to singlets.

The positive (PL-enhancing) spin ½ polaron resonance and full- and half-field triplet powder pattern PLDMR demonstrate the unmistakable effect of interchain polaron pairs and intrachain triplet excitons on the PL of π-conjugated polymers.[15-23] Since the low-energy geminate polaron pairs which yield the spin ½ resonance are not sufficiently energetic to recombine to intrachain singlet excitons as given by Eq. (2), other mechanisms have been proposed to account for this resonance:

(i) If off-resonance the population of geminate triplet pairs is lower than that of singlet pairs, the enhanced formation of triplet pairs by a resonant p^+ or p^- spin flip would increase the formation rate of ^3T (Eq.

(3)), which would increase the rate of *T-T* annihilation to intrachain singlet excitons (Eq. (1)), resulting in enhanced PL.[23] Yet recent photoinduced absorption-detected magnetic resonance measurements have shown that in ladder-type poly(*p*-phenylene) the spin ½ resonance conditions decrease the ^3T population [24]. Hence we rule out this mechanism.

(ii) Enhanced nonradiative recombination of polarons reduces their population and hence the rate at which $^1S^*$, which are highly diffusive, are quenched by polarons:[20-22]

$$^1S^* + p^{+/-} \rightarrow {}^1S_0 + \textit{phonons} \qquad (4)$$

This paper reviews results that suggest that while DF due to *T-T* annihilation is observable in π-conjugated polymers, it is a marginal process. In contrast, the quenching process (Eq. (4)) is suggested to be significant, possibly accounting for the low efficiency of OLEDs.

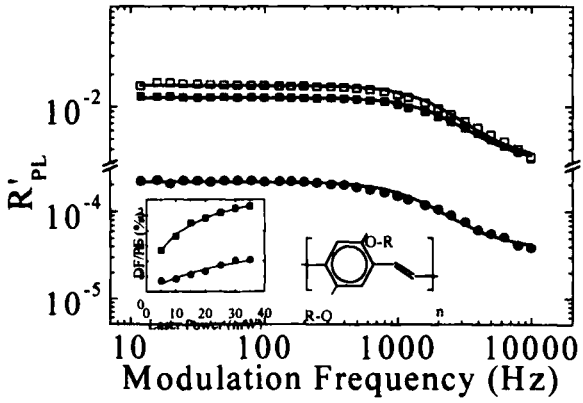

FIGURE 1. The DF R'_{PL} of DHO-PPV powder (open squares), DOO-PPV film (closed squares) and < 0.025 mg/ml frozen DOO-PPV/toluene solution (circles) at 20 K *vs* the laser modulation frequency $\nu = \omega/2\pi$. The observed behavior is fit to a Lorentzian $A/[1 + \omega^2\tau^2] + C$ yielding lifetimes $\tau = 70$ μs in the powder and film and $\tau = 110$ μs in the frozen solution. Inset: The ratio of the cw DF to the PF *vs* laser power. The lines are the behavior predicted by the analysis given in refs. 8 and 9.

RESULTS AND DISCUSSION

DF

The DF was determined by monitoring the response R'_{PL} of the PL at 2ω to the exciting laser, whose power was modulated at ω. Details on the experimental procedure and analysis were given elsewhere[8,9].

Figure 1 shows R'_{PL} vs ω for powder of 2,5-dihexoxy poly(*p*-phenylene vinylene) (DHO-PPV), film of 2,5-dioctoxy PPV (DOO-PPV), and frozen solution of DOO-PPV, at 20 K. The behavior is in excellent agreement with the analysis given in refs. 8 and 9, which yields triplet lifetimes of 70 and 110 μs in the solids and solution,

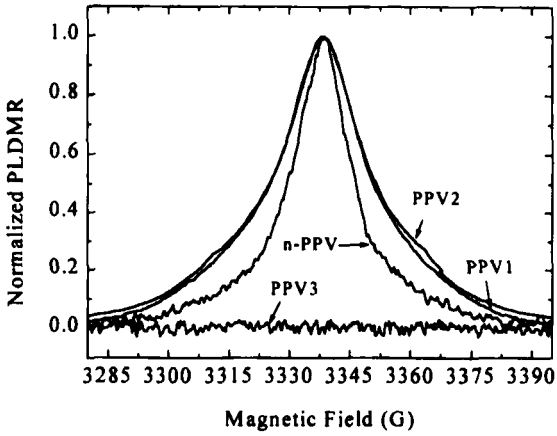

FIGURE 2. X-band polaron PLDMR of various PPV films and PPV chains isolated in a nanostructured host ("n-PPV"; see text).

respectively. The inset shows that the DF contributes up to ~3% of the total emission of these materials. The behavior of R'_{PL} in other polymers and small molecules is qualitatively similar, [8,9]but in general requires two or more lifetimes, typically in the 20 μs – 10 ms range, possibly due to domains with distinct triplet dynamics.

PLDMR

Figure 2 shows the normalized X-band spin ½ polaron PLDMR of different PPV films ("bulk PPV") obtained by thermal conversion of a precursor polymer, and that of isolated PPV chains in a nanostructured

lyotropic liquid crystal host matrix ("n-PPV")[25]. We note that the PL yield of PPV1, PPV2, PPV3, and n-PPV was 5, 17, 20, and 30%, respectively. Analysis of the results, which also showed that in bulk PPV the PL intensity was proportional to the excitation power P but in n-PPV it was sublinear in P, provide strong evidence for the singlet quenching model (Eq. (4)) and suggest that it may considerably impact the PL and EL efficiency [25].

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