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Spin-dependent delayed luminescence from nongeminate pairs of polarons in π-conjugated polymers

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We measured cw photoinduced absorption (PA) and spin-$\frac{1}{2}$ PA- and photoluminescence detected magnetic resonance (PADMR and PLDMR, respectively) in films of two representative π-conjugated polymers; poly(phenylene-vinylene) and polythiophene. From the dependences of the polaron PA and PLDMR on the laser excitation intensity we conclude that the PLDMR is due to spin-dependent delayed luminescence from nongeminate pairs of polarons. Our findings imply that spin-dependent exciton formation in polymer light-emitting diodes leads to enhanced emission efficiency.

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The maximum internal quantum efficiency η_{max} of fluorescence-based organic light emitting diodes (OLED's) is determined by the fraction of injected electrons and holes that recombine to form emissive spin-singlet excitons, rather than nonemissive triplet excitons.[1] From simple spin-degeneracy statistics we have $\eta_{max}=1/4$.[1] However values for η_{max} between 22% to 83% have been reported.[2–8] We have recently developed[5,7] a spectroscopic/magnetic resonance technique that allows direct measurement of the ratio, $r=\sigma_S/\sigma_T$ of the formation cross section, σ of singlet (S) and triplet (T) excitons from oppositely charged polarons in films of π-conjugated materials. We showed that $r>1$ and since it is expected that $\eta_{max}=r/(r+3)$,[5,9] then $\eta_{max}>1/4$ should be possible. The direct experimental demonstration of the enhanced formation of singlet excitons and therefore increased η_{max} as a consequence of $r>1$ has however remained outstanding.

Here we report on spin $\frac{1}{2}$ optically detected magnetic resonance (ODMR) experiments at 10 K in films of two representative π-conjugated polymers, namely poly-para-phenylene-vinylene [PPV, see Fig. 1(a) inset] and regio-random poly-3-hexyl-thiophene [RRa-P3HT, Fig. 2(b) inset]. In spin-$\frac{1}{2}$ ODMR we measure the effect of changing the spin state of recombining pairs of polarons on the photoinduced absorption (PA) and/or photoluminescence (PL). We show that the spin-$\frac{1}{2}$ PLDMR signal in these materials is due to spin-dependent delayed luminescence from nongeminate pairs of polarons. Our findings imply that spin-dependent exciton formation in OLEDs indeed leads to enhanced emission efficiency. We note that the spin-$\frac{1}{2}$ PLDMR origin in π-conjugated polymers has remained controversial,[10–12] and we expect that our work is a crucial contribution to answering this question.

The PA spectroscopy has been widely used in π-conjugated materials for studying long-lived photoexcitations.[13–15] An Ar$^+$ laser beam modulated with a chopper was used as the pump beam. An incandescent tungsten-halogen lamp and a variety of diffraction gratings and solid-state detectors were used to span the probe transmission T in the spectral range $\hbar\omega$ between 0.3 and 3 eV. The PA spectrum $\Delta\alpha(\omega)$ was obtained by dividing $\Delta T/T$, where the modulated transmission ΔT was measured by a phase-sensitive technique, and $\Delta\alpha=-d^{-1}\Delta T/T=n\Sigma$, where d is the film thickness, n is the photoexcitation density associated with the PA band, and Σ is its optical absorption cross section. In PADMR (Refs. 5,7 and 15) we measure the transmission changes δT that are induced in ΔT by μ-wave absorption in magnetic field $\mathbf{H}$ in resonance with the Zeeman split spin-$\frac{1}{2}$ sublevels of polarons. δT is proportional to δn that is induced in n due to changes in the spin-dependent

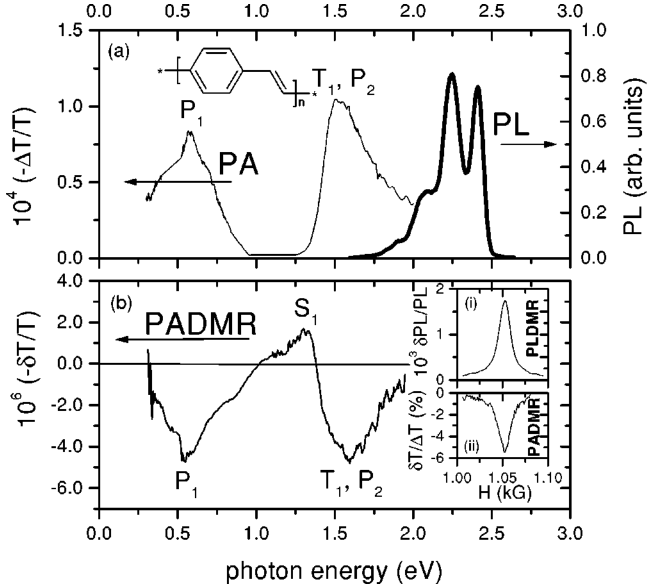

FIG. 1. (a) The photoinduced absorption (PA) and photoluminescence (PL) spectra of PPV (see inset); (b) the PA-detected magnetic-resonance (PADMR) spectrum at magnetic field $H=1.05$ kG that corresponds to $S=\frac{1}{2}$ resonance. Inset (i) shows the spin-$\frac{1}{2}$ PLDMR resonance, whereas inset (ii) shows spin-$\frac{1}{2}$ PADMR resonance. Both spectra, (a) and (b), show two main bands [P_1 and (T_1, P_2) (see text)]. P_1 and P_2 are due to polarons, T_1 is due to triplet absorption. The positive PADMR band S_1 is assigned to singlet absorption in agreement with the positive H-PLDMR response [see inset (i) in (b)]. The PA and PL (PADMR and PLDMR) were measured at 80 K (10 K), excitation was 457 nm Ar$^+$ laser line (300 mW), modulated at 1 kHz.

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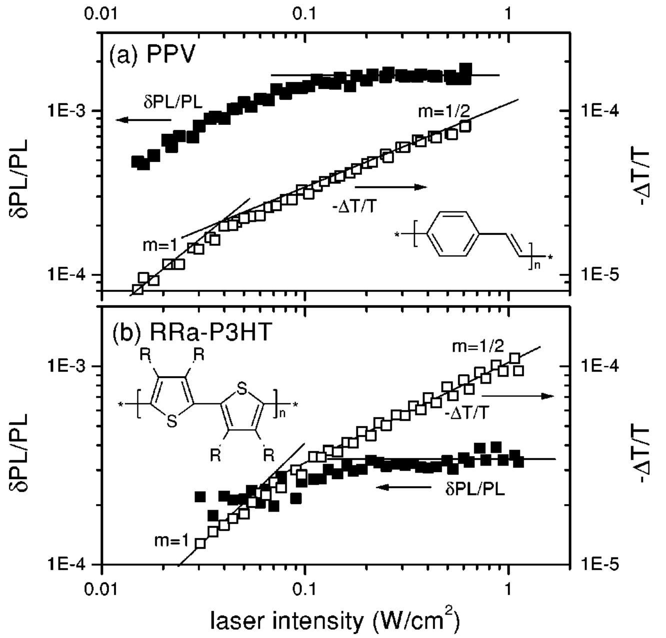

FIG. 2. The laser intensity dependences of the PLDMR signal ($\delta PL/PL$, solid squares) and the polaron PA band P_1 ($-\Delta T/T$, open square) measured at 10 K and modulated at 1 kHz in a PPV film (a) and RRa-P3HT (b). Inset to (a) shows the PPV repeat unit, inset to (b) shows RRa-P3HT. Excitation was at 457 nm for (a) and at 488 nm for (b). Solid lines show a power-law plot with exponent m as assigned.

polaron recombination rates. Two types of PADMR spectra are possible: the H-PADMR spectrum where δT is measured at a fixed probe wavelength λ as the magnetic field H is scanned; and the λ-PADMR spectrum where δT is measured at a resonant H, while λ is scanned. PLDMR (Refs. 10–12,15,16) is closely related to PADMR, except that it measures changes, δPL induced in PL upon magnetic resonance. We note that PA, PADMR, and PLDMR can all be measured using the same experimental setup and under identical conditions, allowing accurate comparison between data obtained using the three methods.

Under typical experimental conditions where the modulation frequency is ≈ 1 kHz, n of polarons was estimated to be $\approx 10^{17}$ cm^{-3}. Spin-$\frac{1}{2}$ PADMR probes the polaron recombination or charge-transfer (CT) reactions, which lead to the formation of strongly bound excitons, either spin singlet or triplet. The PADMR experiments have been successfully interpreted[5,7,15] in a model where the polarons form distant pairs in which they are correlated with either a spin-parallel or spin-antiparallel recombination partner, respectively. We found that the spin-relaxation time exceeds the modulation period of the experiments at low temperatures,[17] and therefore the following rate equations describe the polaron pair dynamics at steady state[15]:

$$\frac{dN_{(A)P}}{dt}=0=\frac{\eta}{2}\Phi-R_{(A)P}N_{(A)P}\,, \qquad (1)$$

where η is the photogeneration quantum efficiency for polarons, Φ is the absorbed laser photon flux, and N_P and N_{AP} are the polaron densities correlated in parallel or antiparallel pairs, respectively. The CT reaction rate R_P of N_P pairs ($\uparrow\uparrow,\downarrow\downarrow$) is proportional to $2\sigma_T$, whereas R_{AP} of N_{AP} pairs ($\uparrow\downarrow,\downarrow\uparrow$) is proportional to $(\sigma_S+\sigma_T)$.[5] Since $\sigma_S>\sigma_T$ in π-conjugated compounds,[5,7] then $R_{AP}>R_P$, and the spin polarization of the recombining polaron pairs is built up over time, such that $N_P>N_{AP}$ at steady-state conditions. During the half-period of modulation where the μ-wave field is turned on, saturated magnetic resonance, however, enforces $\tilde{N}_{AP}=\tilde{N}_P$ and the new steady-state polaron density $\tilde{N}$ can be obtained from the rate equation

$$\frac{d\tilde{N}}{dt}=0=\eta\Phi-\frac{R_P+R_{AP}}{2}\tilde{N}. \qquad (2)$$

It follows from Eqs. (1) and (2) that PADMR detects a reduction $\delta N=\tilde{N}-N$ (measured as δT) in the polaron density N (measured as ΔT). This happens since slowly recombining parallel pairs are converted to the more efficiently recombining antiparallel pairs. From Eqs. (1) and (2) we obtain

$$\frac{\delta N}{N}=\frac{\delta T}{\Delta T}=-\left(\frac{R_{AP}-R_P}{R_{AP}+R_P}\right)^2=-\left(\frac{r-1}{r+3}\right)^2. \qquad (3)$$

Since parallel pairs are converted to antiparallel pairs, it follows that upon magnetic resonance the number of triplet excitons decreases, whereas the singlet exciton population and thus the PL should increase. *This is a direct consequence of* $\sigma_S>\sigma_T$.

The PA and PADMR spectroscopies are presented for PPV in Figs. 1(a) and 1(b), respectively; the PL spectrum is also shown for completeness. Similar spectra were obtained for RRa-P3HT (not shown here). The assignment of the PA bands in PPV is well established from previous studies:[18] P_1 is the low-energy polaron absorption band and the higher-energy band contains contributions from T_1 due to triplet exciton absorption and P_2, the high-energy polaron absorption band. The PADMR spectrum clearly shows the negative magnetic-resonance response at the polaron bands. We measure $r\approx 2.2$ (determined from $\delta T/\Delta T$ at P_1 [see Fig. 1(b) inset (ii)] and Eq. (3)) in both PPV and RRa-P3HT films (for r values of other materials see Ref. 7). The negative response at T_1 is also assigned, but just as in the PA spectrum the T_1 and P_2 bands cannot be resolved individually. We assign the positive PADMR band S_1 to the expected increased singlet exciton density.[7] This assignment is also based on similarities between the S_1 band and the picosecond transient absorption band due to singlet excitons.[17] *It is the focus of this paper to show that* $r>1$ *results in enhanced singlet population and therefore enhanced PL emission* δPL.

We can calculate the expected resonant increase, δS in singlet population, S (and thus the increase δPL in PL) from rate equations for the singlet exciton densities S and $\tilde{S}$ during the half-periods where the saturated magnetic-resonance conditions are turned off or on, respectively,

$$\frac{dS}{dt}=0=\eta_S\Phi+\frac{1}{2}\frac{\sigma_S}{\sigma_S+\sigma_T}R_{AP}N_{AP}-\frac{S}{\tau_S}, \qquad (4)$$

$$\frac{d\tilde{S}}{dt}=0=\eta_S\Phi+\frac{1}{2}\frac{\sigma_S}{\sigma_S+3\sigma_T}\frac{R_P+R_{AP}}{2}\tilde{N}-\frac{\tilde{S}}{\tau_S}. \qquad (5)$$

In Eq. (4) singlet excitons are generated directly upon laser photon absorption with quantum efficiency η_S, but also as a result of delayed polaron recombination[19,20] [second term on the right-hand side(rhs)]. The delayed singlet exciton formation rate is proportional to the polaron recombination term $R_{AP}N_{AP}$, since only spin-antiparallel pairs can form singlets. However, antiparallel pairs can also form one of the spin triplet states, therefore we add a weight $\sigma_S/(\sigma_S+\sigma_T)$ to the delayed singlet formation. The third term on the rhs is the singlet exciton recombination with lifetime τ_S. Since singlets are the primary photoexcitations in π-conjugated polymers, η_S is close to unity and will be discarded below. Similarly, Eq. (5) is the rate equation for singlet excitons under saturated magnetic-resonance conditions, where the distinction between antiparallel and parallel pairs is lost. Solving Eqs. (4) and (5) we obtain the following result for $\delta S/S$, and therefore also for the emission enhancement ($\delta PL/PL$) upon saturated magnetic-resonance:

$$\frac{\delta PL}{PL}=\frac{\delta S}{S}=\frac{S_{delayed}}{S_{total}}\frac{(r-1)}{(r+3)}=\frac{\eta}{4}\frac{r}{(r+1)}\frac{(r-1)}{(r+3)}, \qquad (6)$$

where $\eta \ll 1$ is the polaron photogeneration efficiency. $S_{delayed}/S_{total}$ in Eq. (6) is the fraction of singlet excitons that are produced by delayed polaron recombination. Figure 1(b) inset (i) shows the measured spin-$\frac{1}{2}$ H-PLDMR of PPV. We report here only the magnetic-resonance effects on the spectrally integrated PL; spectrally resolved PLDMR data was reported previously.[11,12] Equation (6) elucidates the reason why $\delta PL/PL$ is positive ($r>1$) and a rather small effect [Fig. 1(b) inset (i)]: only the delayed PL due to polaron recombination is spin dependent, rather than the much stronger prompt PL. From Eq. (6) and the measured r we obtain the polaron photogeneration efficiency η. We obtain $\eta=6\%$ for PPV and $\eta=1\%$ for RRa-P3HT, in good agreement with recent measurements.[21,22] From Eq. (6) we also obtain $S_{delayed}/S_{total}=PL_{delayed}/PL_{total}=8\times10^{-3}(1.5\times10^{-3})$ for PPV (RRa-P3HT). These estimates are supported by the ratio $PL_{delayed}/PL_{total}\approx10^{-2}$ that was determined in PPV using cw PL measurements.[23] The effect on the electroluminescence (EL), however, can be strong since *all* EL is due to nongeminately recombining injected polarons. Indeed, since $\eta_{max}=r/(r+3)$ the efficiency roughly doubles for $r=4.5$, as observed in polymers with long conjugation length,[7] compared to that based on $r=1$. It would therefore be desirable to study the magnetic-resonance effect directly on the EL. The interpretation of magnetic-resonance directly in OLEDs, however, is very involved as was clearly shown by Greenham *et al.*[24] Magnetic-resonance effects on the transport, luminescence, and interface states all contribute to the observed signal, making a quantitative interpretation very difficult.

At the core of our model lies the notion that the PLDMR signal is due to a spin-dependent delayed PL arising from nongeminately recombining pairs of polarons. We therefore anticipate that an intimate relation exists between the polaron density and kinetics to the PLDMR kinetics. We first study the polaron kinetics. Figure 2 shows that the polaron PA scales as $\Phi^{1/2}$ at large Φ, in both PPV and RRa-P3HT. This shows that polarons under the present conditions recombine bimolecularly, i.e., the recombination term is proportional to N^2:$dN/dt=\eta\Phi-\beta N^2$, where β is the bimolecular recombination constant. Such a rate equation yields the $\Phi^{1/2}$ law at large Φ, which corresponds to steady-state condition. However at low intensity (far from steady state condition, since the effective lifetime τ becomes longer at small Φ) the exponent of Φ deviates from $\frac{1}{2}$ even for pure bimolecular kinetics; this was also observed in our measurements. The crossover between the two regimes occurs at $\omega\tau\approx1$, where $\omega=2\pi f$ [f is the modulation frequency and τ is the (effective) lifetime], where $\tau\propto\Phi^{-1/2}$ for bimolecular recombination close to steady-state conditions. Indeed, we observe a shift in the measured frequency dependences when changing Φ in agreement with an effective lifetime that decreases with increasing Φ.[25]

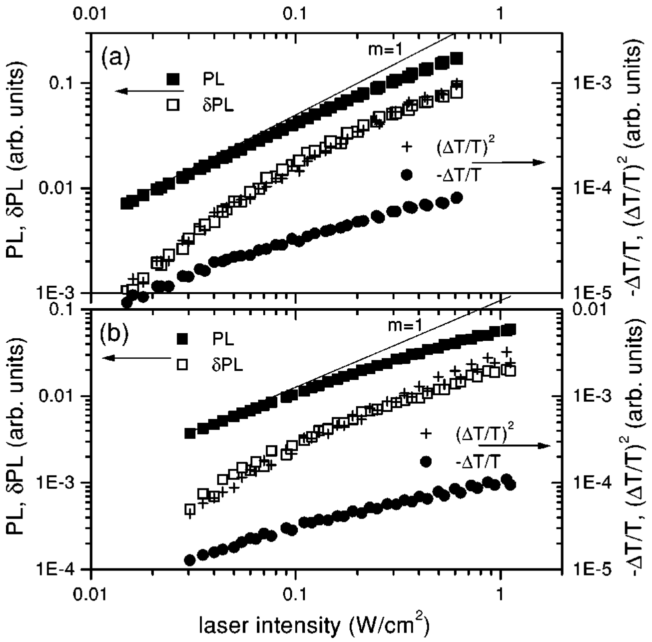

FIG. 3. The laser intensity dependences of the photoluminescence (PL, solid squares), the magnetic-resonance effect on the photoluminescence (δPL, open squares), the polaron PA band P_1 ($-\Delta T/T$, solid circle) and its square (cross, rescaled) measured at 10 K and modulated at 1 kHz in a PPV film (a) and RRa-P3HT (b). Excitation was at 457 nm for (a) and at 488 nm for (b). Solid line is a linear plot (exponent $m=1$).

Figure 3 shows the dependences of PL and δPL on the laser intensity. First we note that the PL becomes somewhat sublinear for larger intensities due to an as yet unexplained quenching mechanism. Second we found a relation between N and δPL. In Fig. 3 we plot $N^2=(\Delta T/T)^2$ vs Φ and find that it coincides with high accuracy with $\delta PL(\Phi)$, i.e., $\delta PL\propto N^2$. This directly shows that δPL is the result of a magnetic-resonance effect on the *nongeminate polaron recombination*, since the delayed PL is proportional to the recombination term in the polaron rate equation. For nongeminate (or bimolecular) kinetics the recombination term is by definition proportional to N^2.

We note that $\delta PL>0$ was observed previously in a number of published studies.[11,12] However the relation between r and δPL was not recognized; as a matter of fact $\delta PL>0$ was explained by exciton quenching by polarons.[11] It was shown[11] that at polaron densities similar to ours the PLDMR signal in a polymer with high polaron mobility/diffusivity, namely, methyl-substituted ladder-type poly(para-phenylene), mLPPP, is accurately described by the "exciton quenching by polarons" model. Both List *et al.*[11] and Bässler *et al.*[26] concluded that the characteristic property of a "quenching model" is that $\delta PL/PL \propto N$ ($\propto \Phi^{1/2}$ in the present case). We note that this scaling is very different from the prediction of Eq. (6), where $\delta PL/PL$ is independent of Φ. Figure 2 shows that the measured $\delta PL/PL$ in our samples does not depend on Φ in the steady-state limit, in agreement with Eq. (6), but in contradiction with a quenching model. We therefore conclude that the quenching model cannot explain the PLDMR signal observed in the PPV and RRa-P3HT films, which are known to have a much smaller polaron mobility than that in mLPPP.[27,28] Bässler *et al.*[26] have shown that singlet exciton quenching by geminate pairs of polarons is important in mLPPP, but their experiments are conducted at considerably higher photoexcitation density than ours.

In summary we have studied the PLDMR signal in two representative π-conjugated polymers with low polaron mobility. We showed that the spin-$\frac{1}{2}$ PLDMR is due to spin-dependent delayed PL from nongeminate polarons. Our results directly show that spin-dependent exciton formation leads to enhanced efficiencies in both PL and OLED's.

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