Effect of an External Magnetic Field on the Up-Conversion Photoluminescence of Organic Films: The Role of Disorder in Triplet-Triplet Annihilation

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We have investigated the influence of the magnetic field on the triplet-triplet annihilation process in organic films using a model multicomponent system for blue delayed up-conversion photoluminescence. In such a way, we have derived simple analytical expressions to estimate the overall annihilation probability, outlining the peculiar role played by the disorder and demonstrating that the triplet-triplet fusion in solid films is a diffusion limited process.

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There is widespread interest in the phenomenon of triplet-triplet annihilation in organic molecular solids. This process plays a crucial role in up-conversion photoluminescence, and it is presently considered one of the most promising ways of improving the efficiency of solar cells [1,2]. On the other hand, the triplet-triplet fusion, being a quenching mechanism, is responsible for reduction of electroluminescence quantum efficiencies in phosphorescent organic light emitting devices operating at high current densities [3–5]. For these reasons, understanding the triplet-triplet annihilation process in organic films is of essential importance.

The theory of magnetic field effects developed by Merrifield and Suna allowed the mechanism of interaction between the triplet states in single crystals of polyacenes to be established [6–9]. Some preliminary results concerning the liquid solutions have also been reported [10], but the role of molecular order in mutual annihilation of triplet states is still an open question. The kinetics of triplet excitons at high excitation densities in thin films of organic materials has been studied extensively during the last decade, providing detailed information about the overall bimolecular annihilation rate constants in different compounds [3,11,12]. Magnetic field modulation of electroluminescence in organic light emitting devices has been reported and is currently under intense debate [13–15]. The mechanism of interaction between the triplet excitons in disordered films of molecular materials, however, remains not understood to date. In particular, it has never been clarified how the positional disorder of the molecules affects the fusion of triplets, and whether the interaction rate in films is limited by the diffusive motion of excitons or by the probability of annihilation after their collision.

In this Letter we describe the magnetic field effects in thin films of a model multicomponent system for blue delayed up-conversion photoluminescence. The observed modulation of the up-converted emission is attributed to the magnetic field effect on the triplet-triplet annihilation, and it is discussed within the framework of the Merrifield's model. By generalizing his approach to the case of randomly oriented molecules, we obtain simple analytical expressions allowing the estimation of the overall annihilation probability.

The experiments were performed on 100 nm thick films of DPA (9,10-diphenylanthracene) doped with 2% PtOEP [platinum (II) octaethylporphyrin], which were cast in a glove box onto silica substrates from 10 mg/ml deoxygenated chloroform solutions. The samples were placed between the poles of an electromagnet at an angle of 50° to the magnetic field direction and excited at 532 and 355 nm, with light flux density ranging between 10^{18} and 10^{20} $\mathrm{ph/cm^2\,s}$, at which the intensity of luminescence is proportional to the square of the exciting power. The emission spectra were collected by an optical fiber coupled to a spectrograph and a liquid nitrogen-cooled CCD detector. All the measurements were performed at room temperature, under argon atmosphere.

The delayed fluorescence (DF) emitted from the samples under studies is quite strong due to sensitization of the DPA triplet states by the phosphorescent PtOEP complex [16], allowing for high sensitivity measurements of magnetic field effects. The inset of Fig. 1 shows the photoluminescence spectrum of 2% PtOEP:DPA films excited within the Q absorption band of PtOEP at 532 nm. The main peak at 430 nm is blueshifted by about 100 nm with respect to the excitation wavelength. The spectrum of this up-converted emission is similar to the prompt fluorescence spectrum observed upon direct excitation into the DPA absorption band at 355 nm. The up-conversion mechanism in this model system is well understood [16,17]. Under excitation at 532 nm, the PtOEP triplet states are rapidly populated due to the strong spin-orbit coupling in this compound. Afterwards, the triplet levels of DPA are excited via energy transfer from PtOEP. The subsequent mutual annihilation of these states leads to the formation of DPA excited singlets ($T_1 + T_1 \rightarrow S_1 + S_0$) and highly efficient DF ($S_1 \rightarrow S_0 + h\nu_{\mathrm{DF}}$), the rate of this process being described by the second order annihilation rate constant γ_S.

Figure 1 shows the relative change of the intensity of this sensitized DF as a function of the magnetic field $\delta = (I_B - I_0)/I_0$, where I_0 and I_B are the DF intensity at the zero magnetic field and at the applied field B, respectively. The

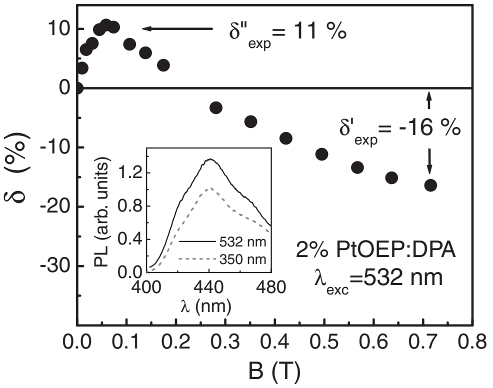

FIG. 1. Magnetic field modulation of the up-converted photoluminescence in a 2% PtOEP: 98% DPA film, excited at 532 nm. The dependence was obtained by integrating the emission spectra in the spectral region 410–470 nm. The spectra of the prompt fluorescence excited within the DPA absorption band at 355 nm (dashed line) and the sensitized delayed fluorescence observed upon excitation at 532 nm (solid line) for a 2% PtOEP: 98% DPA film are compared in the inset. PL is photoluminescence.

dependence is nonmonotonic with an initial increase below 50 mT, and the roll-off for higher fields. Over 200 mT δ becomes negative and it tends to saturation at the highest fields above 600 mT. The largest DF intensity reduction ($\delta'_{\rm exp}$) exceeds 16%.

In general the observed modulation may originate from the following main effects: (i) magnetic field-induced modification of the monomolecular decay rates of singlet and triplet excited states in both DPA and PtOEP; (ii) modification of the energy transfer rate between the PtOEP and DPA triplet states; (iii) influence of the magnetic field on the triplet-triplet annihilation in DPA. The first two mechanisms can, however, be easily excluded, because the DPA prompt fluorescence directly excited at 355 nm and the weak PtOEP emission at 650 nm are magnetic field independent within the experimental accuracy (0.5%). The observed modulation of the sensitized DF must be, in this regard, attributed to the magnetic field effect on the mutual annihilation of the DPA triplet excitons. Since the emission intensity resulting from this bimolecular fusion is proportional to $\gamma_S[T]^2$,

$$\delta = \frac{\gamma_s(B)[T]^2 - \gamma_s(0)[T]^2}{\gamma_s(0)[T]^2} \cong \frac{\gamma_s(B) - \gamma_s(0)}{\gamma_s(0)}. \tag{1}$$

As proved by the quadratic dependence of the luminescence output on the excitation flux density, the measurements were performed at low exciton concentrations ($[T]$), where the triplet lifetime was limited by its monomolecular decay only [11,12,17]. In these conditions, $[T]$ is not affected significantly by a possible variation of the annihilation rate. Therefore, the dependence from Fig. 2 can be attributed solely to the magnetic field-induced modification of γ_S, and rationalized employing the Merrifield's phenomenological annihilation-dissociation scheme.

The triplet excitons diffuse and collide to form the intermediate complex state $(T \cdots T)$:

$$T + T \underset{k_{\rm dis}}{\overset{k_{\rm coll}}{\rightleftarrows}} (T\cdots T) \begin{cases} \xrightarrow{k_{\rm annih}\,|C_S^i|^2} S + S_0 \\ \xrightarrow{k_{\rm annih}\,|C_T^i|^2} T + S_0 \end{cases}, \tag{2}$$

where $k_{\rm coll}$ is the rate constant for the encounter of two triplets. The triplet pairs can either annihilate or scatter without reaction, the latter process being described by the dissociation rate constant $k_{\rm dis}$. Therefore, in general, the overall reaction rate is determined by both the diffusive motion of triplet excitons, and the competition between the annihilation and dissociation decay pathways of the $(T \cdots T)$ pairs. Upon interaction, nine collision pair states can be formed, whose wave functions are [18]

$$\Psi_i = \varphi_S C_S^i |S\rangle + \varphi_T C_T^i |T\rangle + \varphi_Q C_Q^i |Q\rangle, \tag{3}$$

where φ_S, φ_T, and φ_Q are the orbital parts of the wave functions. $|S\rangle$, $|T\rangle$, and $|Q\rangle$ are the singlet, triplet, and quintet spin parts with contributions given by the fractional

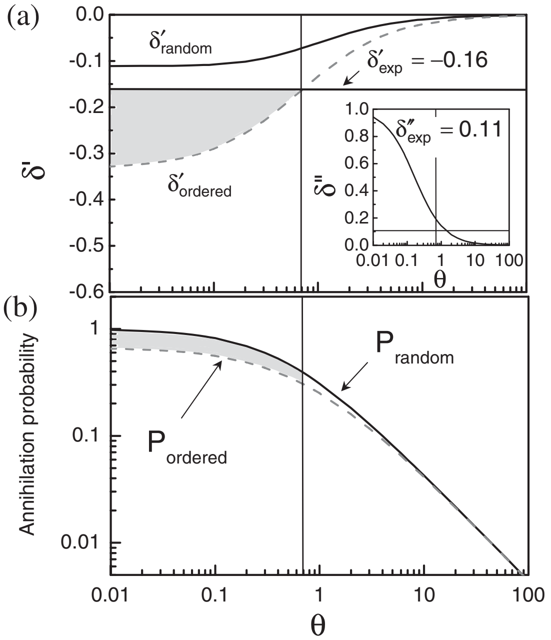

FIG. 2. (a) The maximum reduction of the delayed fluorescence intensity in high magnetic fields (δ') as a function of the branching ratio for the dissociation to the triplet exciton pair annihilation rate constants $\Theta = k_{\rm dis}/k_{\rm annih}$. The corresponding dependence of the overall annihilation probability after the collision of two triplet excitons ($P = P_S + P_T$) is shown in panel (b). The solid and dashed lines represent the limiting cases calculated for entirely disordered and ordered films, respectively. The inset shows the Θ dependence of the largest enhancement of the delayed fluorescence at intermediate magnetic fields for ordered systems.

spin characters $|C_S^i|^2 = |\langle\Psi_i|S\rangle|^2$, $|C_T^i|^2 = \sum_{m=1}^{3}|\langle\Psi_i|T_m\rangle|^2$, and $|C_Q^i|^2 = \sum_{m=1}^{5}|\langle\Psi_i|Q_m\rangle|^2$, which satisfy the closure relationships $\sum_{i=1}^{9}|C_S^i|^2 = 1$, $\sum_{i=1}^{9}|C_T^i|^2 = 3$, and $\sum_{i=1}^{9}|C_Q^i|^2 = 5$. The quintet states require simultaneous excitation of two electrons and are usually unattainable energetically. Thus, the intermediate collision complex can decay either to a singlet or a triplet exciton with rates proportional to these amplitudes: $k_{\text{annih}}|C_S^i|^2$ and $k_{\text{annih}}|C_T^i|^2$. The constant k_{annih} has approximately the same value for both the annihilation channels [18].

The spin Hamiltonian of the intermediate pair state is approximately given by the sum of two single exciton Hamiltonians $\hat{H}_S = \hat{H}_S(a) + \hat{H}_S(b)$, where $\hat{H}_S(a,b) = (g\beta\vec{H}\vec{S}_{a,b} + \vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b})$, $\vec{H}$ is the external magnetic field, $\vec{S}_{a,b}$ represent the spin operators, $\hat{D}_{a,b}$ are the zero field splitting tensors, and the indices a and b denote the two excitons in the pair state. The terms $g\beta\vec{H}\vec{S}_{a,b}$ and $\vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b}$ describe the Zeeman and the spin-spin interactions, respectively. Because of the interplay between these terms, the spin amplitudes in the pair state wave functions [Eq. (3)] are effectively modified by an external magnetic field. The second order annihilation rate constants for both the fusion channels depend on the collision rate k_{coll} and on the average probabilities of singlet (P_S) or triplet (P_T) exciton formation from the ($T\cdots T$) pair; that is, $\gamma_S = k_{\text{coll}}P_S$ and $\gamma_T = k_{\text{coll}}P_T$. These probabilities are given by the spin amplitudes and are greater with a larger number of pair states with $C_S^i \neq 0$ and $C_T^i \neq 0$:

$$P_{S(T)} = \frac{1}{9}\sum_{i=1}^{9}\frac{k_{\text{annih}}|C_{S(T)}^i|^2}{k_{\text{dis}} + k_{\text{annih}}|C_S^i|^2 + k_{\text{annih}}|C_T^i|^2} = \frac{1}{9}\sum_{i=1}^{9}\frac{|C_{S(T)}^i|^2}{\Theta + |C_S^i|^2 + |C_T^i|^2}, \tag{4}$$

where $\Theta = k_{\text{dis}}/k_{\text{annih}}$ is the branching ratio for the dissociation to the pair state annihilation rate constants. As follows from Eq. (4), the annihilation probabilities, and thus the magnetic field dependence of the DF, are largely determined by the branching ratio Θ and the degree of mixing of different multiplicities in the pair state wave function. This mixing, in turn, depends on the symmetry of the spin Hamiltonian, and thus on the relative orientations of the molecules which form the pair state.

Since typically the relative orientation of the molecules in thin films of organic materials is not known exactly, here we consider two limiting cases: (i) the ordered system where all molecules have the same orientation and (ii) an entirely isotropic system with random orientation of the molecules. In the following, we describe the characteristic features of the magnetic field dependence of DF predicted for these two cases, and we derive two equations allowing the calculation of the branching ratio Θ and the estimation of the probability of annihilation after the collision of the triplet excitons.

In the case of ordered systems, $\hat{H}_S$ is invariant under interchange of the two excitons and the pair states can be classified into even states, which are singlet-quintet mixtures, and odd states, which are pure triplets. Merrifield has shown that at zero magnetic field there are 3 pair states with nonzero singlet amplitudes $|C_S^1|^2 = |C_S^2|^2 = |C_S^3|^2 = 1/3$. In the intermediate field range, where $\vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b} \approx g\beta\vec{H}\vec{S}_{a,b}$, six pair states can have some singlet character, which leads to the initial increase of the photoluminescence intensity. At high magnetic fields there are, however, only two states with nonzero singlet contribution; that is, $|C_S^1|^2 = 1/3$ and $|C_S^2|^2 = 2/3$. As a result, the magnetic field dependence of γ_S is *nonmonotonic* with an initial increase at low magnetic fields and the saturation when $g\beta\vec{H}\vec{S}_{a,b} \gg \vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b}$. The largest reduction of the DF (δ'_{ordered}) is determined by the ratio Θ and can be obtained from Eq. (4). Because of the interchange symmetry, the singlet and triplet channels of the fusion are independent in this case. Thus, taking $|C_T^i|^2 = 0$, one obtains

$$\delta'_{\text{ordered}} = -\tfrac{1}{3}(\tfrac{3}{2}\Theta + 1)^{-1}. \tag{5}$$

In order to understand what is the effect of disorder on magnetic field DF dependence in the films under studies, we generalize this approach to the case of randomly oriented molecules. Here, the principal axes of the zero field splitting tensors of the interacting molecules have different orientations and the interchange symmetry of the spin Hamiltonian is broken. Thus, at low magnetic fields ($\vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b} \gg g\beta\vec{H}\vec{S}_{a,b}$) each pair state is expected to be a singlet-triplet-quintet mixture; i.e., $C_S^i \neq 0$ and $C_T^i \neq 0$ for all nine pair states. In the high field limit, however, the spins are quantized along the direction of the external field, and independently of the relative orientation of the molecules in the intermediate pair, there are always only two Zeeman states with nonzero singlet contributions $|C_S^1| = 1/3$ and $|C_S^2| = 2/3$. This is because the anisotropic spin-spin interaction becomes irrelevant for $g\beta\vec{H}\vec{S}_{a,b} \gg \vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b}$. Thus, γ_S and consequently the DF intensity are expected to *monotonically* decrease with increasing magnetic field and finally saturate at sufficiently high fields. If we consider the case of complete mixing, where all the 9 pair states in zero field have equal distributions of different spin characters, i.e., $|C_S^{1-9}|^2 = 1/9$ and $|C_T^{1-9}|^2 = 3/9$, the largest DF reduction becomes

$$\delta'_{\text{random}} = -\tfrac{1}{9}(\Theta + \tfrac{2}{9})(\Theta + \tfrac{1}{3})^{-1}(\Theta + \tfrac{2}{3})^{-1}. \tag{6}$$

As will become apparent, this is the limiting case, in which the smallest magnetic field effects are expected.

Dependences given by Eqs. (5) and (6) are shown in Fig. 2(a). The magnitude of the magnetic field effect δ' is the largest for small values of Θ, i.e., when the annihilation rate is much higher than the dissociation rate of the intermediate pair. For high values of Θ, the distribution of different spin characters in the pair state becomes irrelevant and no magnetic field effect is expected. Furthermore, since in amorphous films the singlet annihilation channel quantum yield at zero field is reduced due to the competition with the triplet annihilation channel, stronger modulation is expected for ordered layers.

The nonmonotonic behavior of δ vs B (Fig. 1) and its large saturation value at high magnetic field imply that the samples under investigation are partially ordered or polycrystalline. Therefore, the $\delta'(\Theta)$ dependence for these films is expected to lie between the discussed limiting cases. The branching ratio Θ is determined by the intercept of $\delta'(\Theta)$ functions with the abscissa at $\delta' = \delta'_{\mathrm{exp}} \geq -0.16$, falling in the range corresponding to the shaded part of the plot in Fig. 2(a): $\Theta < 0.7$. Thus $k_{\mathrm{annih}} > k_{\mathrm{dis}}$, which implies that the triplet-triplet fusion in the films is controlled by the migration of excitons rather than by the probability of annihilation.

A further confirmation of this result, and an indication about the degree of order in the studied films, follows from the analysis of the initial increase of $\delta(B)$ at intermediate magnetic fields. Assuming that in the ordered system of DPA molecules, the DF maximum is observed when all 6 singlet-quintet mixed pair states have comparable singlet character $|C_S^{1-6}|^2 = 1/6$, the largest DF enhancement can be approximated by $\delta''_{\mathrm{ordered}} = (6\Theta + 1)^{-1}$. This dependence is shown in the inset of Fig. 2(a). The experimental value of $\delta''_{\mathrm{exp}} = 0.11$ (see Fig. 1) is 2 times smaller than that predicted for an entirely ordered system ($\delta''_{\mathrm{ordered}} = 0.2$ for $\Theta = 0.7$), suggesting that about 50% of the annihilation events occur between orientationally nonequivalent DPA molecules. As follows from the comparison between the $\delta'_{\mathrm{ordered}}(\Theta)$ and $\delta'_{\mathrm{random}} = (\Theta)$ plots, Θ decreases with increasing disorder. Therefore the branching ratio in films is most probably significantly smaller than the limiting value of 0.7. Since the pair state wave functions rapidly vary when $\vec{S}_{a,b}\hat{D}_{a,b}\vec{S}_{a,b} \approx g\beta\vec{H}\vec{S}_{a,b}$, it cannot be definitively excluded that the number of states simultaneously having large C_S^i is smaller than 6. However, also in such cases, the estimated values of Θ are always smaller than 0.7, in agreement with the predictions of Eqs. (5) and (6).

Using Eqs. (4)–(6) we calculate the overall annihilation probabilities after the collision in zero magnetic field, $P = P_S + P_T$, for ordered and random systems. Their dependences on Θ are shown in Fig. 2(b). It is apparent that within the experimental range of $\Theta < 0.7$ these probabilities are close to unity. Thus, it can be concluded that the triplet-triplet annihilation rate in the films is controlled by the diffusive motion of triplet excitons.

For comparison, the value of $\Theta = 2.5$ has been found for single crystals of anthracene, indicating a reduced annihilation quantum yield in this material [7,8]. This is most probably due to different values of the triplet pair dissociation rate constants in crystals and disordered films. The value of k_{dis} should be inversely proportional to the triplet exciton hopping time. Since the disorder effects are known to reduce the hopping rate, smaller values of k_{dis} are expected for films.

In conclusion, the magnetic field modulation of up-conversion photoluminescence in PtOEP-doped DPA films can be attributed to the interplay between the Zeeman and fine structure terms in the spin Hamiltonian of the pair of the interacting triplet excitons. The magnitude of the effect is found to be determined by the positional disorder of the molecules and to depend critically on the branching ratio of singlet and triplet fusion channel rates to the triplet pair dissociation rate. We have derived simple expressions allowing the calculation of this ratio and the estimation of the probabilities of annihilation after the collision of triplet excitons. We have shown that the triplet-triplet annihilation in solid films is a diffusion limited process and that the probability of reaction after the collision of excitons approaches unity.

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