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**Comment on “Magnetic Field Effects on Singlet
Fission and Fluorescence Decay Dynamics in
Amorphous Rubrene”**

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Introduction

In a recent paper, Piland, Burdett, Kurunthu and Bardeen¹ (PBKB) present data from time-resolved fluorescence measurements on amorphous rubrene films and explain the observed prompt and delayed fluorescence intensities in terms of competing singlet-fission and triplet-fusion processes. The dynamics of such processes are of interest due to their relevance to strategies for boosting efficiencies of photovoltaic devices.² The rate of crossing between the singlet and triplet manifolds depends on the overlap of the pure singlet and the triplet-pair state wavefunctions, which itself can be affected by the molecular orientation and any applied magnetic field. To explain their experimental results, a hybrid quantum-kinetic model is used to simulate fluorescence decays from systems of ordered or disordered rubrene molecular pairs. A spin Hamiltonian is constructed to describe the interactions of the triplet excitons residing on the molecular pair and was used to compute the singlet character of each of the nine triplet-pair states. This quantum-mechanical model of the interactions of triplet excitons and the influence of an applied magnetic field closely follows the theory pioneered by Merrifield in the late 1960s.³⁻⁶ The singlet character of the triplet-pair states is then used in a system of kinetic equations to simulate the crossings between the singlet and triplet exciton states, with the fluorescence intensity taken to be proportional to the exciton population in the pure singlet state at any point in time.

The simulations predict markedly different behavior for the magnetic-field dependence of the fluorescence intensity for ordered and disordered systems at zero and high (8.1 kG = 0.81 T) fields: for a model ordered system, the prompt fluorescence increases with field strength at the expense of the delayed fluorescence due to a reduction in the number of triplet-pair states with singlet character, whereas for a model disordered system, the opposite trend is predicted. As only the behavior of the ordered system matches the experimental data for the same magnetic fields, it is concluded that singlet exciton migration to ordered regions of the film must occur prior to singlet fission. These results suggest that measurements of magnetic-field effects on fluorescence decay dynamics can provide a sensitive probe of

molecular-level morphology in systems that undergo singlet fission.

Although we do not dispute the validity of this interesting method of combining magnetic fields and spectroscopy to probe molecular order, we have identified some errors in the quantum-mechanical model presented by PBKB, most crucially in the representation of the pure singlet state in the basis of triplet pair states. The incorrect calculation of the singlet character of the triplet-pair states propagates through to the kinetic model and causes significant qualitative and quantitative discrepancies between their results and those obtained when the pure singlet is correctly represented. In particular, for physically reasonable molecular parameters, the corrected model predicts magnetic-field effects on the fluorescence intensity decays for both ordered and disordered systems that are consistent with the experimental data. Thus, it cannot be concluded from the data that singlet exciton migration occurs to ordered regions of the film prior to singlet fission. Nevertheless, the variation of the spin states with magnetic field does differ for ordered and disordered systems, and we identify a regime of magnetic field strengths much lower ($\ll 0.81$ T) than those studied in the experiments in which the fluorescence decay dynamics relative to zero field should be qualitatively different for amorphous and ordered regions of a rubrene film.

Model

It should be noted that the underlying theory presented by PBKB is sound and therefore will not be reiterated here in detail. We refer readers interested in the quantum mechanical theory of interactions of triplet excitons and magnetic fields to the text in question¹ and to previous literature.³⁻⁸ Here we simply present the elements of the theory needed to explain the inconsistencies in the approach used. The construction of the spin Hamiltonian for an interacting pair of triplets and its matrix representation in terms of triplet pair states, as well as other minor differences between our model and that of PBKB, are described in detail in the Supporting Information.

The general form of the spin Hamiltonian is

$$\hat{H}_{\text{total}} = \hat{H}_{\text{magnetic}} + \hat{H}_{\text{zero-field}} + \hat{H}_{\text{AB}} \quad (1)$$

where $\hat{H}_{\text{magnetic}}$ describes the Zeeman effect of the magnetic field on the triplet pair, $\hat{H}_{\text{zero-field}}$ is the intramolecular electron spin-spin interaction and \hat{H}_{AB} is the intermolecular coupling between the triplets on molecules A and B. The zero-field term can in turn be decomposed into the individual spin-spin contributions from the two unpaired electrons on each of the two molecules, A and B:

$$\hat{H}_{\text{zero-field}} = \hat{H}_{\text{SS}_A} + \hat{H}_{\text{SS}_B} \quad (2)$$

The zero-field term for a molecule such as tetracene (which has the same polyaromatic backbone as rubrene) in the (x, y, z) coordinate system defined by the molecular symmetry axes is^{6,9,10}

$$\hat{H}_{\text{SS}} = D \left(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E \left(\hat{S}_x^2 - \hat{S}_y^2 \right) \quad (3)$$

where D and E are the molecular zero-field splitting parameters.

The pure singlet state $|S\rangle$ that can be formed by the pair of interacting triplets is defined as the eigenstate of the total four-electron $\hat{S}^2 = (\hat{\mathbf{S}}_{A1} + \hat{\mathbf{S}}_{A2} + \hat{\mathbf{S}}_{B1} + \hat{\mathbf{S}}_{B2})^2$ and $\hat{S}_z = (\hat{S}_{z,A1} + \hat{S}_{z,A2} + \hat{S}_{z,B1} + \hat{S}_{z,B2})$ operators with eigenvalue zero in both cases. Here, ‘‘A’’ and ‘‘B’’ label the two molecules and ‘‘1’’ and ‘‘2’’ label the two unpaired electrons on each molecule. Using standard identities for spin operators,¹¹ the singlet state is readily shown to be

$$|S\rangle = 3^{-1/2} (|xx\rangle + |yy\rangle + |zz\rangle) \quad (4)$$

$$\equiv 3^{-1/2} (|x\rangle_A |x\rangle_B + |y\rangle_A |y\rangle_B + |z\rangle_A |z\rangle_B) \quad (5)$$

where $|xx\rangle \equiv |x\rangle_A |x\rangle_B$ and so on and $|x\rangle_j$, $|y\rangle_j$, and $|z\rangle_j$ are two-electron spin states on

molecule $j = A$ or B ,

$$|x\rangle_j = 2^{-1/2} \left(|\beta_1\beta_2\rangle_j - |\alpha_1\alpha_2\rangle_j \right) \quad (6)$$

$$|y\rangle_j = i2^{-1/2} \left(|\beta_1\beta_2\rangle_j + |\alpha_1\alpha_2\rangle_j \right) \quad (7)$$

$$|z\rangle_j = 2^{-1/2} \left(|\alpha_1\beta_2\rangle_j + |\beta_1\alpha_2\rangle_j \right) \quad (8)$$

and α and β have their usual meaning as individual up and down electron spins, respectively, quantized along the z axis.

The choice of Cartesian axes x , y , and z used to define the singlet state $|S\rangle$ is arbitrary, but it is clear from eqs 4–8 that the axes must be the *same* for *both* molecules A and B . A convenient choice (which we have made) is to take the coordinate system in which the zero-field term for molecule A , $\hat{H}_{SS_A} = \hat{H}_{SS}$, is diagonal in the basis $\{|x\rangle_A, |y\rangle_A, |z\rangle_A\}$, which corresponds to x , y , and z being aligned with the molecular symmetry axes of the rubrene backbone. This coordinate system is indicated in Figure 1.

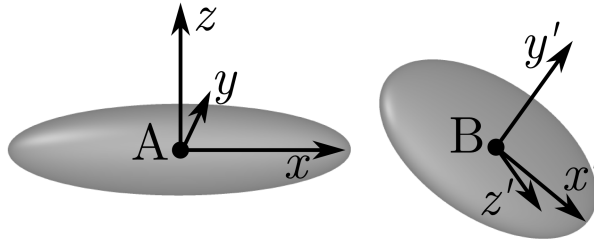


Figure 1: Schematic defining the molecular axes of the rubrene pair. The x , y and z axes correspond, respectively, to the long, short and perpendicular axes of the tetracene backbone of molecule A , while the primed x' , y' and z' axes refer to the corresponding axes of molecule B , which could be rotated with respect to those of molecule A .

In their paper,¹ PBKB appear to use the definition of the singlet state $|S\rangle$ given in eqs 4 and 5, but in actuality define the singlet state as $|S\rangle \equiv 3^{-1/2} (|x\rangle_A |x'\rangle_B + |y\rangle_A |y'\rangle_B + |z\rangle_A |z'\rangle_B)$ in which the two-electron spin states $|x'\rangle_B$, $|y'\rangle_B$, and $|z'\rangle_B$ of molecule B are defined with respect to the molecular symmetry axes x' , y' , and z' of molecule B . As illustrated in Figure 1, the coordinate systems (x, y, z) and (x', y', z') do not coincide in general, and thus

the equation above does *not* in general represent the pure singlet state produced by the interacting triplet pair (it is *not* an eigenstate of the total S^2 and S_z operators); it is only the singlet state if the two molecules are perfectly aligned. This error in the representation of the singlet state leads to an incorrect calculation of the projection C_S^l of each eigenstate ψ_l of the spin Hamiltonian (eq 1) on to the singlet state,

$$C_S^l \equiv \langle S | \psi_l \rangle = 3^{-1/2} (\langle xx | + \langle yy | + \langle zz |) | \psi_l \rangle \quad (9)$$

As a consequence, the rate of crossing between the triplet-pair states and the pure singlet state, which in the kinetic model depends on the singlet character $|C_S^l|^2$ of each pair state $|\psi_l\rangle$, and the resulting fluorescence decay dynamics are not correctly computed.

The parameters in eq 3 are defined such that x , y , and z axes correspond to the molecular symmetry axes: for the tetracene parameters used here, x is the long axis, y is the short axis, and z is perpendicular to the molecular plane. As we have defined the coordinate system for the interacting molecular pair in terms of the symmetry axes of molecule A, in eq 1 for the total spin Hamiltonian, the zero-field component for molecule A is $\hat{H}_{SS_A} = \hat{H}_{SS}$, but a rotation operation must be applied to \hat{H}_{SS} to give \hat{H}_{SS_B} , the zero-field component for molecule B, in this coordinate system, i.e.

$$\hat{H}_{SS_B} = R^T \hat{H}_{SS} R. \quad (10)$$

where the rotation matrix R uses the three Euler angles that define the sequence of rotations needed to rotate the axes of molecule A on to the axes of molecule B (see Supporting Information). PBKB do not apply any such rotation operation to determine \hat{H}_{SS_B} , because they effectively compute the contributions of molecule A and molecule B to the total spin Hamiltonian in different coordinate systems.

For the magnetic-field-dependent term in the spin Hamiltonian,

$$\hat{H}_{\text{magnetic}} = g\beta\mathbf{H} \cdot (\hat{\mathbf{S}}_{\text{A}} + \hat{\mathbf{S}}_{\text{B}}) \quad (11)$$

where \mathbf{H} is the applied magnetic field and the coefficient $g\beta$ determines the magnitude of the influence of the magnetic field. For our choice of basis, the two-electron spin operators $\hat{\mathbf{S}}_{\text{A}} = \hat{\mathbf{S}}_{\text{A1}} + \hat{\mathbf{S}}_{\text{A2}}$ and $\hat{\mathbf{S}}_{\text{B}} = \hat{\mathbf{S}}_{\text{B1}} + \hat{\mathbf{S}}_{\text{B2}}$ for both molecules, which do not depend explicitly on molecular orientation and can therefore be represented in any coordinate system, are most conveniently represented in the (x, y, z) coordinate system defined by the molecule A axes.

The intermolecular spin–spin interactions are typically much smaller than intramolecular zero-field interactions, and have a small influence on the triplet pair wavefunction and hence on the magnetic field dependence of the triplet-fusion or singlet fission rate.^{2,5} Nevertheless, these interactions must be present for these processes to occur and to split otherwise degenerate eigenstates, for example at high field.^{2,5} There is evidence to suggest that the intermolecular interaction between molecular triplets in crystalline or solution-phase polyaromatic hydrocarbons such as anthracene and tetracene is predominantly a dipole–dipole interaction⁶

$$\hat{H}_{\text{AB}} = -X \left[3 \left(\hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{r}} \right) \left(\hat{\mathbf{S}}_{\text{B}} \cdot \hat{\mathbf{r}} \right) - \hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \right] \quad (12)$$

where $\hat{\mathbf{r}}$ is the unit vector joining the two triplets and the coefficient X describes the magnitude of the interaction (in which the $1/r^3$ dependence on the inter-triplet distance r is implicit). Thus, we have assumed an intermolecular interaction of this form. Because the intermolecular interactions are dominated by the intramolecular and magnetic field interactions, the specific form used for the intermolecular interaction is not important. PBKB assumed an exchange-type interaction,

$$\hat{H}_{\text{AB}} = X\hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \quad (13)$$

which depends on the orientation, but not on the spatial arrangement of the triplets. Nevertheless, both forms of interaction give similar results for the spin eigenstates and time-resolved fluorescence. In this work, we have set $\hat{\mathbf{r}}$ to a unit vector in the z direction and used $X = D/100$. This simulates molecule B being aligned along the z -axis of molecule A and assumes the intermolecular spin interactions are approximately two orders of magnitude smaller than the intramolecular interactions at typical molecular separations present in the rubrene film.¹²

The total spin Hamiltonian (eq 1) was diagonalized in the $\{|xx\rangle, |xy\rangle, |xz\rangle, |yx\rangle, |yy\rangle, |yz\rangle, |zx\rangle, |zy\rangle, |zz\rangle\}$ basis of pair states to determine the eigenstates $\{\psi_l\}$, from which the singlet character $|C_S^l|^2$ of each eigenstate is readily determined from eq 9, since $\langle\gamma\delta|\epsilon\zeta\rangle = \delta_{\gamma\epsilon}\delta_{\delta\zeta}$. (PBKB instead diagonalize the Hamiltonian in the $\{|xx'\rangle, |xy'\rangle, |xz'\rangle, |yx'\rangle, |yy'\rangle, |yz'\rangle, |zx'\rangle, |zy'\rangle, |zz'\rangle\}$ basis, in which the singlet character of the eigenstates can only be determined by first applying a rotation operation to the primed pair states on molecule B.) It should be pointed out that the spin operators $\hat{\mathbf{S}}_A$ and $\hat{\mathbf{S}}_B$ in eqs 11 and 12 do not depend explicitly on molecular orientation, and thus any dependence of the matrix representations of $\hat{H}_{\text{magnetic}}$ and \hat{H}_{AB} on molecular orientation comes from the choice of basis. So in the basis of pair states that we have used, the matrix representations of $\hat{H}_{\text{magnetic}}$ and \hat{H}_{AB} (given in the Supporting Information) do not depend on the orientation of molecule B, since the basis states are defined with respect to the symmetry axes of molecule A. The orientation of molecule B with respect to molecule A (and thus also with respect to the magnetic field) is defined in the total spin Hamiltonian only by the zero-field term \hat{H}_{SSB} . Nevertheless, the spin eigenstates and eigenvalues that result from diagonalizing the total Hamiltonian, and thus the magnetic field and intermolecular contributions to the energy, do depend on the orientation of molecule B with respect to molecule A and the magnetic field.

The singlet character of each eigenstate was then used in a system of ten differential

equations,

$$\frac{dN_{S1}}{dt} = - \left(k_{\text{rad}} + k_{-2} \sum_{l=1}^9 |C_S^l|^2 \right) N_{S1} + \sum_{l=1}^9 k_2 |C_S^l|^2 N_{(TT)l} \quad (14a)$$

$$\frac{dN_{(TT)l}}{dt} = k_{-2} |C_S^l|^2 N_{S1} - k_2 |C_S^l|^2 N_{(TT)l} \quad (14b)$$

which represent the rate of crossing between the triplet-pair states and the pure singlet state, where k_2 is the rate constant for the crossing into the singlet state from the triplet manifold, k_{-2} is the rate constant for the reverse process, and k_{rad} is the radiative rate from the singlet state. Equations 14a and 14b are equivalent to the kinetic equations used by PBKB¹ in which mixing of and decay from the triplet states is considered to be negligible. For the purposes of comparison, we have also used the same values for the rate constants:¹ $k_{\text{rad}} = 0.06 \text{ ns}^{-1}$, $k_2 = 0.5 \text{ ns}^{-1}$, and $k_{-2} = 0.5 \text{ ns}^{-1}$.

To simulate the time-resolved fluorescence, the system of equations was solved numerically to find the populations in the singlet N_{S1} and triplet-pair $N_{(TT)}$ states, with the initial condition that all population began in the singlet state. The fluorescence intensity was then assumed to be proportional to the population in the pure singlet state at any instant in time. When an ensemble of orientations of the molecular pairs was simulated, such as in the model of a fully disordered rubrene film, a uniform distribution of molecular or magnetic field orientations were selected from the unit sphere. For each unique orientation of the magnetic field or molecular pair, the singlet character and fluorescence decay kinetics were computed. The final time-resolved fluorescence data was then determined as the mean of the individual fluorescence contributions from each molecular pair.

Results and Discussion

To demonstrate the qualitatively and quantitatively different predictions of the two spin-Hamiltonian implementations, we have first reconstructed the results of PBKB in ref 1 for

reference. Figures 2a–c show three scenarios for molecular and magnetic-field orientations, in which the singlet character of the nine triplet-pair states is shown to evolve with the strength of an applied magnetic field. Here we have used the method and parameters described in

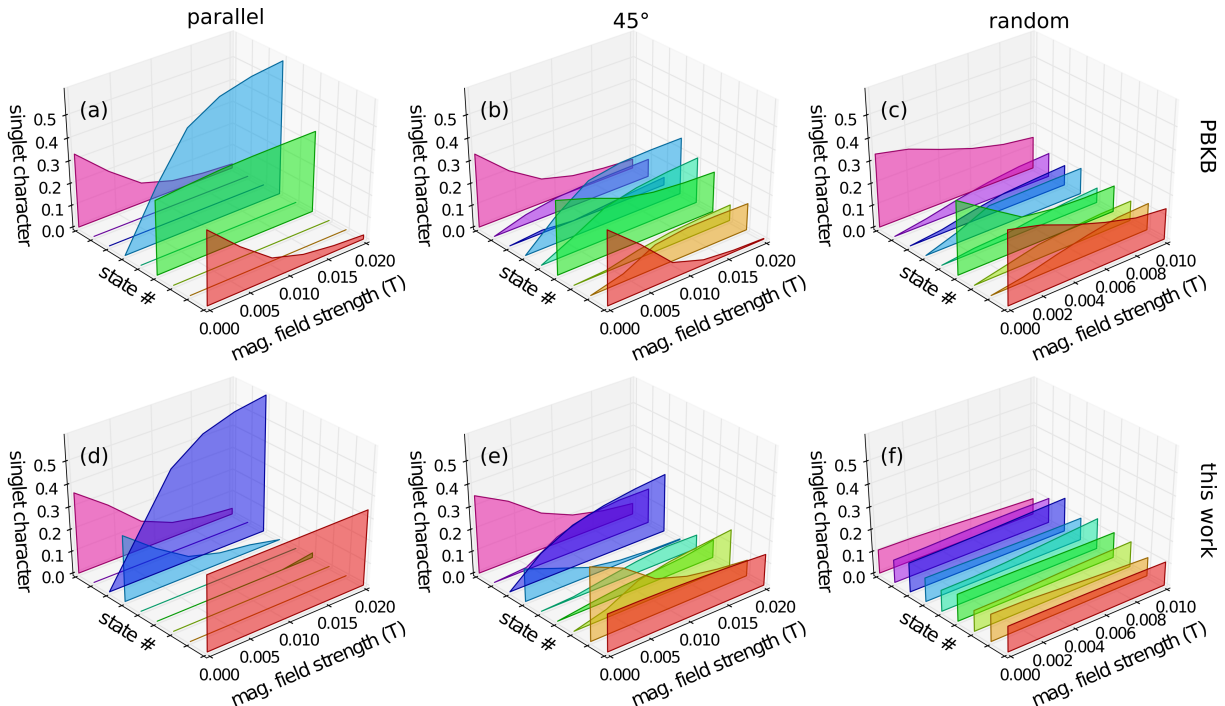


Figure 2: (a–c) Reproduction of the singlet-projection plots in Figure 5 of in ref 1 showing the evolution of the singlet character of each of the nine possible triplet-pair states with magnetic field strength for (a) parallel molecules and magnetic field perpendicular to the molecular planes, (b) second molecule now orientated at 45° to the first, which has its plane perpendicular to the magnetic field, and (c) a random orientation of molecules and magnetic field direction. (d–f) Analogous plots using the model and parameters described in this work.

ref 1. Note that the line plots showing the evolution of the singlet character of the pair states with magnetic field are equivalent to the bar charts presented in Figure 5 of ref 1, and the results reproduced here are identical. The three orientation scenarios are the parallel alignment of the molecules, with the magnetic field oriented perpendicular to the molecular planes (Figure 2a); non-parallel molecules, with molecule B oriented at 45° to molecule A and the magnetic field oriented perpendicular to the plane of molecule A (Figure 2b); and a model of a randomly oriented system constructed from the average of 10^4 combined molecular and magnetic field orientations (Figure 2c).

In the first case of the ordered system, the parallel molecular pair naturally share their symmetry axes (x , y , and z coincide with x' , y' , and z' , respectively) and there is no difference between the definitions of the basis vectors or singlet state of PBKB and those presented in this work. There is also no need to apply the rotation operation (eq 10). Consequently, the results in this case are a textbook example of the expected behavior of the system, in which the number of pair states with singlet character evolve from three at zero-field to two towards the high-field limit.^{5-7,13} The second scenario with the molecules aligned at 45° introduces asymmetry into the system. In this situation it is expected that even at zero magnetic field there should be some mixing of the spin states and consequently more than three of the triplet-pair states should show singlet character. This is in accord with the fact that the singlet character of pair states $|\gamma\delta'\rangle$ of unaligned molecules, where γ and δ span the x , y , and z molecular axes, is $\frac{1}{3} \cos^2 \theta_{\gamma\delta'}$, where $\theta_{\gamma\delta'}$ is the angle between the axes.¹⁴ This behavior is not observed in Figure 2b, with the zero-field result identical to that for parallel molecules. The fully disordered system shown in Figure 2c was constructed from the average singlet character of many molecular orientations and thus should be expected to show a high degree of spin mixing at zero field.¹⁵ Again the results at zero field are identical to that for the parallel molecules, highlighting that the incorrect definition of the overall singlet state by PBKB and consequent lack of the rotation operation on the zero-field term effectively locks the molecular pair in an identical orientation when evaluating the spin eigenstates.

Figures 2d-f show the identical three scenarios for molecular and magnetic field orientations as in Figures 2a-c, but the results were this time calculated using the model and parameters presented in this work. In the case of the ordered system with parallel molecules (Figure 2d), three states show singlet character at zero field, tending to two at high magnetic field strengths as expected. In the case of molecules at 45° (Figure 2e), four states show singlet character at zero field, indicating the model successfully exhibits the effect of the introduced asymmetry of the molecular orientations. With the application of a magnetic field the spin states are mixed further, resulting in eight states with singlet character. For

the completely disordered system (Figure 2f), on average all nine of the triplet-pair states show singlet character for all magnetic field strengths shown. This behavior is also seen in the disordered system from PBKB (Figure 2c) when a magnetic field is applied.

Note that these disordered scenarios were modeled by averaging the singlet projections over many molecular and magnetic field orientations and that one individual choice of orientation will not cause all nine states to show singlet character simultaneously. Rather, the different orientations will cause the singlet character to be displayed in various subsets of the pair states and it is the averaging process, coupled with the arbitrary eigenstate ordering that is output from the matrix diagonalization algorithms used, which acts to give the appearance of a uniform distribution of the singlet character as shown. In terms of physical observables such as the time-resolved fluorescence, it is not the average singlet character that is important, but the singlet character of the pair states of each molecular pair that contributes to the fluorescence. The further implications of this averaging process on the simulated time-resolved fluorescence data are discussed below.

In the scenarios shown in Figure 2, the magnetic fields are in the mT range, where the number of pair states with singlet character can exceed the number at zero field, depending on the relative orientation of the molecules and the field. So the systems are not yet in the high-field regime in which the magnetic term of the Hamiltonian dominates the zero-field term, where only two pair states should have singlet character.^{3,6,7} To further illustrate that the model of PBKB does not behave qualitatively correctly, while ours does, in Figure 3 we have compared the evolution of the singlet character of the triplet-pair states with magnetic field strength up to very high (100 T) fields. At sufficiently large fields, the orientation of the molecules should become irrelevant as the alignment of the spins is determined solely by the magnetic field orientation. In this example, the two molecules were oriented at 90° so that the corresponding triplet eigenstates of the two molecules would be orthogonal at zero-field. An arbitrary magnetic field orientation was selected at random. Figure 3b shows that our model gives the expected two pair states with singlet character at high field,^{3,6,7}

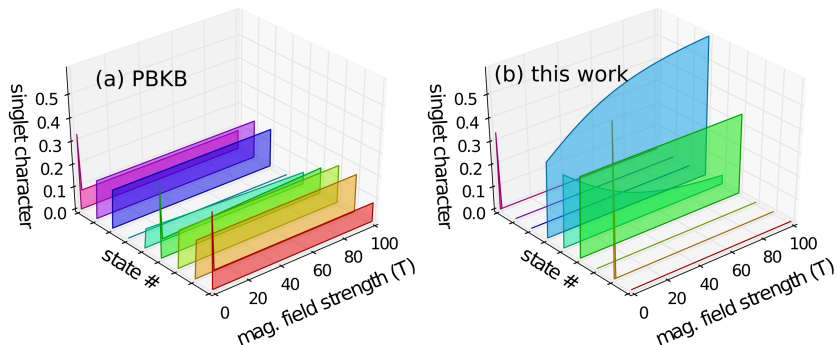


Figure 3: Illustration of the behavior of (a) the model of PBKB¹ and (b) our model in the approach to the high-field limit, where only two pair states are expected to show singlet character.^{3,6,7} Molecules are oriented at $\beta = 90^\circ$ with an arbitrarily oriented magnetic field ($\phi_B = 291^\circ$, $\theta_B = 15^\circ$). (See Supporting Information for definition of angles.)

while the model of PBKB incorrectly gives eight pair states with singlet character and no visible evolution of the states beyond intermediate field strengths.

We now turn to the simulation of the time-resolved fluorescence for the rubrene films. Again, we have first reconstructed the simulated results of PBKB¹ for reference. To model the disordered system with randomly oriented molecules, the average of many molecular and magnetic field orientations were used as described above. A parallel molecular pair was used to model an ordered rubrene film system, with the average of many magnetic field orientations used to simulate the random alignment of the molecular pairs relative to the plane of the film. For each system, a single magnetic field strength of 0.81 T was simulated and compared with the zero-field case, matching the experimental conditions.¹ The predicted singlet character of the pair states was used in the kinetic equation system (eq 14a and b) to produce the simulated fluorescence decays shown in Figure 4a. For the disordered randomly oriented system, PBKB predicted that the application of the magnetic field acts to decrease the intensity of the prompt fluorescence compared with zero-field. The ordered, parallel system shows the opposite behavior, with an enhancement of the prompt fluorescence in the presence of the magnetic field. Note that without the magnetic field the behavior for both the ordered and disordered systems are identical due to the lack of rotation in the zero-field term of the Hamiltonian, meaning the same singlet projections C_S^l are input

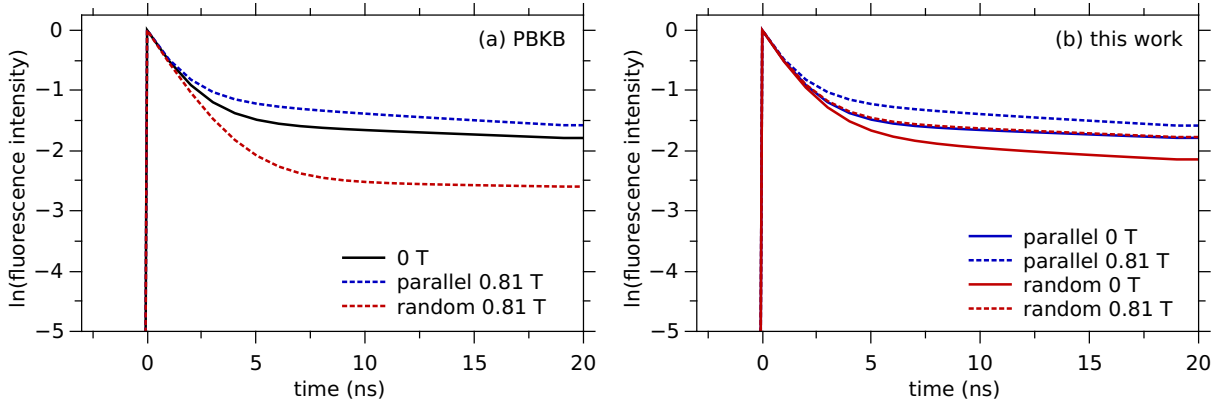


Figure 4: Simulated normalized fluorescence intensity decay for parallel or randomly oriented molecular pairs at zero or 0.81 T magnetic field strength for (a) the model of PBKB¹ and (b) our model.

to the kinetic equations in each case. The different fluorescence decays are explained by noting that for the randomly oriented case, PBKB predict that three triplet pair-states show singlet character at zero-field, increasing to nine with the application of the magnetic field (Figure 2c). With a larger number of dark triplet states in which the excited population can “hide”, the population of the radiative singlet state is reduced at early time scales. In the ordered case, the number of pair states with singlet character evolves from three to two with the magnetic field (Figure 2a). Fewer triplet-pair states at high magnetic field leads to more of the excited state population being in the radiative singlet state. As only the behavior of the ordered, parallel system matched their experimental data, PBKB excluded the possibility of singlet fission occurring from disordered sections of the rubrene film and concluded that singlet exciton migration to localized regions of order must occur prior to singlet fission.

Figure 4b shows the simulated fluorescence decays for the same ordered and disordered systems described above, but using the model described in this work to compute the singlet character of the triplet-pair states prior to use in the kinetic equations. In the absence of the magnetic field, the ordered system of parallel molecules and the disordered, randomly oriented molecules show different behavior, in contrast with the data shown in Figure 4a.

With a magnetic field applied, both the ordered and disordered systems exhibit an enhancement in the prompt fluorescence intensity. This result can again be explained in terms of the number of triplet-pair states displaying singlet character. With the ordered system of parallel molecules, the result is the same as shown in Figure 4a, as the definition of the overall singlet state is the same and no rotation of the zero-field terms in the spin Hamiltonian is required. For the disordered system of randomly orientated molecules, however, the number of pair states with singlet character evolves from ≈ 5 at zero field to ≈ 3 with the application of the 0.81 T magnetic field. As both the ordered and disordered systems show a reduced number of pair states with singlet character when the magnetic field is applied, so too do they both show an increase in the prompt fluorescence intensity. Critically, this indicates that the parallel and randomly oriented systems replicate the trend seen in the experimental data, and so it is plausible that singlet exciton fission does occur throughout the disordered regions in the film, eliminating the requirement of exciton migration to sites of localized order prior to fission events put forward by PBKB in their work.¹

Nevertheless, our model does predict a regime of magnetic field strengths substantially lower than that studied experimentally by PBKB in which the time-resolved fluorescence from ordered versus disordered rubrene films may be expected to be qualitatively different. Figure 5 shows the simulated fluorescence intensity relative to the zero-field intensity at short times for several magnetic field strengths for the same systems of parallel or disordered molecules studied in Figure 4. So a positive value indicates that the prompt fluorescence intensity is enhanced compared with the zero-field case, while a negative value indicates that it is diminished. (The simulated curves over longer time scales are given in the Supporting Information.) As already shown in Figure 4b, the prompt fluorescence is enhanced compared with zero field for both the ordered parallel and disordered random systems at a magnetic field strength of 0.81 T. On the other hand, at a low field strength of 0.02 T, the prompt fluorescence is diminished compared with zero field for both systems as the field spreads the singlet character over a larger number of “dark” triplet pair states. But the rate at which

the pair states are mixed by the field differs for the ordered and random systems and so at an intermediate field strength of 0.1 T, the two systems display opposite behavior, with the prompt fluorescence enhanced relative to zero field for the random system, but diminished for the ordered, parallel system. Thus, we suggest that repeating the experiments at 0.1 T instead of 0.81 T may reveal whether singlet fission indeed occurs from the ordered rather than disordered regions of a rubrene film.

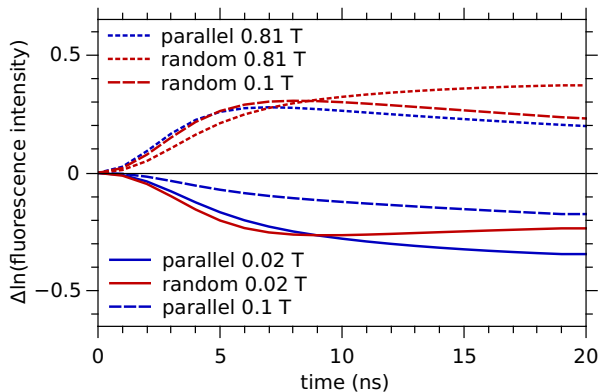


Figure 5: Simulated normalized time-resolved fluorescence intensity with application of a magnetic field relative to zero field for parallel or randomly oriented molecular pairs at several field strengths.

Finally, we note that for the simulated scenarios shown in Figures 4b and 5 we computed the singlet character of the triplet-pair states for each combination of molecular and magnetic field orientation, which were then used separately as input to the kinetic equations. The simulated fluorescence was thus determined as the average of the fluorescence over each individual molecular pair in the system, which physically describes how the emission from each molecular pair contributes to the total measured fluorescence. This method contrasts with that described by PBKB,¹ who calculated the average of the singlet projections for the entire ensemble and used this average singlet character in the kinetic equations. We have shown in Figure 2f that averaging the singlet character over the many orientations overestimates the number of pair states showing singlet character. A figure demonstrating the effect of the two different averaging methods on the simulated fluorescence data is shown in the Supporting Information.

Conclusions

In summary, we have identified errors in the quantum-mechanical model used by PBKB to simulate time-resolved fluorescence decays from amorphous rubrene films. In particular, the incorrect representation of the overall singlet state and thus the singlet character of the triplet-pair states leads to significant qualitative and quantitative errors in the simulated effect of an applied magnetic field on the evolution of the singlet character and fluorescence. PBKB's simulation results led to the conclusion, which we have demonstrated is not substantiated by a more accurate model, that singlet exciton migration must occur in disordered rubrene films to regions of localized order prior to singlet fission. Nevertheless, we show that time-resolved fluorescence experiments at lower magnetic fields than those studied by PBKB may be able to distinguish between singlet fission from ordered or disordered regions of a rubrene film, supporting their suggestion that measurements of magnetic-field effects on fluorescence decay dynamics can provide a sensitive probe of molecular-level morphology in systems that undergo singlet fission.

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Supporting Information Available

Full description of the quantum-mechanical model and additional simulation results. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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