Magnetic Field Effects on Singlet Fission and Fluorescence Decay Dynamics in Amorphous Rubrene

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Supporting Information

ABSTRACT: Picosecond time-resolved fluorescence experiments are used to study the dynamics of singlet fission in highly disordered films of rubrene. The fluorescence spectral lineshapes are not temperature-dependent, indicating that intermolecular excitonic effects are absent in these films. The temperature-dependent fluorescence decays in the amorphous films are nonexponential, containing both prompt and delayed components. The kinetics are qualitatively consistent with the presence of singlet fission, but to confirm its presence, we examine the effects of magnetic fields on the fluorescence decay. A quantum-kinetic model is developed to describe how magnetic fields perturb the number of triplet pair product states with singlet character and how this in turn affects the singlet state kinetics. Simulations show that the magnetic field effect is very sensitive to mutual chromophore alignment, and the direction of the effect is consistent with a local ordering for rubrene molecules that participate in fission. From our analysis, the dominant fission rate is 0.5 ns⁻¹, about 10 times slower than that observed in polycrystalline tetracene films, but we still estimate that ~90% of the initially excited singlets undergo fission. Kinetic modeling of our fluorescence decay data and magnetic field dependence reveals that at the low laser intensities used in this experiment geminate triplet pairs do not interact with each other, and that spin–lattice relaxation between triplet sublevels is not complete on the 100 ns time scale. When both exciton fission and fusion are occurring, dynamic measurements in the presence of a magnetic field can elucidate molecular-level details of both processes.

INTRODUCTION

Solar energy has the potential to supply the world’s energy requirements, but the high cost of photovoltaic devices has prevented them from becoming a significant part of the world’s energy supply. Organic semiconductors provide a possible avenue for making cheaper photovoltaics, but their efficiencies lag those of their inorganic counterparts. In the effort to raise efficiencies, novel photophysical phenomena are being investigated. One example is multiple exciton generation (MEG), where a single high-energy photon generates two or more lower energy excitons, allowing one to harvest the excess energy of photons above the semiconductor bandgap. The analogous process in organic semiconductors is singlet fission (SF), where a photogenerated singlet exciton spontaneously splits into a pair of triplet excitons. This spin-allowed process converts the energy of a single photon into a pair of triplets, which can then be ionized to produce two electron–hole pairs. In conjunction with a second, low-bandgap material, this process can raise the efficiency of a single junction solar cell by up to 40%. First observed in crystalline anthracene and tetracene, SF has now been shown to occur in a wide variety of organic materials with triplet yields approaching 200% and reaction times on the order of 100 fs. Despite considerable theoretical work, the detailed mechanism of this reaction remains unclear. In particular, how solid-state features like molecular packing and orientations affect the SF reaction rate is a subject of active theoretical investigation. Whereas most observations of SF have occurred in crystalline or polycrystalline samples, there have also been claims of SF in biological assemblies, amorphous molecular films and polymers. Because the processing of amorphous materials tends to be less costly, the observation of efficient SF in such materials could bring it closer to practical applications.

Recently, our group and others have studied exciton dynamics in crystalline tetracene, where SF occurs on a 50–200 ps time scale to generate triplet pair superposition states with overall singlet character. Tetracone readily crystallizes under almost any preparation conditions at room temperature. It is possible to prepare amorphous films on substrates held at low temperatures, but these films tend to show strong excimer-like emission, suggesting that rapid intramolecular charge transfer between pi-stacked molecules competes effectively with SF in such films. When phenyl groups are added to tetracene, for example, rubrene, it is less prone to crystallization, and amorphous films can be formed by vacuum evaporation and solvent casting. The singlet and triplet energies of rubrene are very similar to those of tetracene, and SF has been documented in both single crystals and in amorphous...
Figure 1. (a) Normalized absorption spectra of rubrene in polystyrene, rubrene in toluene, and the excitation spectrum of amorphous rubrene. (b) Normalized fluorescence spectra of rubrene in polystyrene, rubrene in toluene, and amorphous rubrene at an excitation wavelength of 470 nm.

33 Solid rubrene thus represents a system where the influence of intermolecular packing and disorder on SF can be investigated. In this article, we present a study of the photophysics of highly disordered rubrene. We find that it is very difficult to eliminate all signs of excitation coupling in evaporated thin films, finally turning to rapid spin coating to generate ultrathin films that are free of the spectral signatures of delocalization. By studying the temperature-dependent steady-state absorption and fluorescence spectral linewidths, we confirm that these films do not exhibit the intermolecular excitonic effects seen in more crystalline materials like tetracene. The temperature-dependent fluorescence decays of the next films are consistent with the dominant relaxation channel being a thermally activated SF process. To confirm the role of SF, we extend previous theories of magnetic field effects on SF and triplet fusion (TF) to simulate the room-temperature fluorescence decays in orientationally disordered systems. We get good qualitative agreement between theory and experiment when we assume that the fusion event occurs at ordered pairs within the next film. Furthermore, our results suggest that the geminate triplets remain correlated with each other for >100 ns, necessitating the use of a different model than that assumed by previous workers in the field. From a practical perspective, it is encouraging that SF can proceed efficiently in amorphous rubrene without the benefit of single delocalization or strong intermolecular coupling, albeit with a rate significantly slower than in crystalline tetracene.

EXPERIMENTAL SECTION

All rubrene used was purchased from Aldrich at 99% purity and was used as received. Amorphous rubrene films were prepared by spin-coating a filtered chloroform solution containing 7 mM rubrene (saturated solution) onto a glass microscope cover slip for 30 s at 3000 rpm. The resulting films were found to be <10 nm thick, as estimated from their optical absorption. The film was characterized as amorphous due to the lack of any peaks in powder X-ray diffraction measurements and the absence of any crystalline domains observable by polarization and fluorescence microscopy. Polystyrene films were produced by drop-casting a toluene solution containing ~1% by weight polystyrene and ~0.7 mM rubrene.

Steady-state absorption measurements were taken on a Cary 50 UV–vis spectrometer. Steady-state excitation and emission spectra were obtained on a Horiba Jobin Yvon Spex Fluorolog-3 fluorimeter using right-angle detection with an excitation wavelength of 470 nm.

Time-resolved fluorescence data were obtained using front face detection with a Hamamatsu C4334 streakscope picosecond streak camera with an excitation wavelength of 500 nm. The 500 nm excitation was provided by generating a continuum by focusing the 800 nm output of a 4 kHz Spectra-Physics Spitfire Ti:sapphire regenerative amplifier into a sapphire crystal and using a 500 nm interference filter (10 nm bandwidth) to isolate the 500 nm beam. The pulse length was <300 fs, and the excitation fluence at the laser focus was typically on the order of 0.2 microjoules/cm². A 515 nm cutoff filter was used to remove scattered laser light before the detector. The streak camera data captures the decay dynamics of the entire fluorescence spectrum with 2 nm wavelength resolution and 15 ps temporal resolution. All film measurements were done inside of an evacuated cryostat at pressures below 1 × 10⁻³ Torr. The cryostat could be evacuated to prevent oxygen exposure of the sample, and cooled to liquid-nitrogen temperatures. Magnetic field effects were tested through the use of a pair of cylindrical magnets (K&J Magnetics, part number DY080-NS) that were positioned on both sides of a custom-built, brass cryostat. A Gauss-meter was used to measure an 8.1 KG magnetic field strength at the sample position when the magnets were placed around it with a spacing of 1.5 cm.

RESULTS AND DISCUSSION

1. Steady-State Spectroscopy. We found that the preparation of truly amorphous rubrene films to be somewhat more challenging than what is usually presented in the literature. Although films made by both drop-casting and vacuum evaporation gave no discernible peaks in a powder X-ray diffraction measurement, inspection of these films under a polarizing microscope revealed the existence of multiple crystalline spherulites in the films. The variable degree of crystallization made it difficult to prepare samples that gave consistent results. To make samples that could provide reproducible results, we made concentrated (>1 mM) solutions in a volatile solvent (CHCl₃), filtered them, and used rapid spin coating (3000 rpm) to generate stable, ultrathin films. We hoped that the rapid solvent evaporation would prevent crystal assembly under these highly nonequilibrium growth conditions. Indeed, under a polarizing microscope, no crystal domains could be observed, although this optical measurement would
not be able to resolve nanocrystalline domains if they exist. These samples were stable for at least 1 week and were used for the spectroscopic measurements reported in this article. In the remainder of this article, we will refer to these samples prepared in this way as “amorphous” films.

For the purposes of this article, the most important question was whether there exist intermolecular interactions that give rise to delocalized singlet excitonic states. The presence of such states can complicate the interpretation of the spectroscopy. In an amorphous solid where randomly oriented molecules interact only weakly, the spectra of the rubrene molecules should resemble those of molecules in solution. In Figure 1a, we compare the absorption spectra of dilute rubrene in toluene and polystyrene solutions to the fluorescence excitation spectrum of the amorphous film. Polystyrene and toluene were chosen as solvents because their high density of aromatic groups should most closely mimic that of an amorphous rubrene film. The three spectra are very similar, although the spectrum of the amorphous film is slightly red-shifted and broadened. These spectra are also similar to recent spectra derived for single crystals of rubrene, where intermolecular interactions are known to be relatively weak. The combination of higher polarizability and static disorder (inhomogeneous broadening) in the amorphous sample would be expected to lead to a spectral red shift and broadening. The steady-state fluorescence spectra are also very similar and are shown in Figure 1b. Again, the red shift and broadening of the amorphous film spectrum are consistent with our expectations for this sample. For the neat rubrene samples, care was taken to minimize air exposure, and we saw no sign of the red-shifted emission attributed to an oxygen−rubrene complex. The much weaker broadening of the emission spectrum is consistent with the fluorescence line-narrowing effect due to energy transfer within the rubrene film. The overall shapes of the three fluorescence spectra are very similar. In particular, there is no sign of a change in the ratio of the 0−0 vibronic peak to the 0−1 peak, as seen in crystalline tetracene versus monomeric tetracene, for example.

A final test of whether our amorphous films support significant intermolecular excitonic interactions is to measure the temperature-dependent line shape. As Spano has shown theoretically, the temperature-dependent change in the vibronic progression due to intramolecular vibrational modes can be a sensitive indicator of exciton delocalization. This can be understood in terms of the exciton coherence length, which basically measures the extent of the wave function. As the temperature decreases, the coherence length increases the extent of the exciton wave function. When this happens, the coupling of the intermolecular exciton to intramolecular vibrational modes within a single molecule decreases, analogous to what is seen in conjugated polymers. In polycenes, the main intramolecular vibrational modes consist of carbon−carbon stretching modes in the 1200−1400 cm−1 region, and thus changes in exciton structure are expected to lead to changes in these vibronic peaks. Specifically, in J-type aggregates like crystalline tetracene, the 0−0 peak becomes enhanced, whereas in H-type aggregates like oligo- and polythiophenes, the 0−0 peak loses intensity relative to the other peaks. If there is no excitonic coupling or delocalization, then lowering the temperature should result in a sharpening of the spectrum and possibly a shift due to changes in the refractive index but no redistribution of vibronic intensities. In Figure 2a, we see that this is indeed the case for monomeric rubrene in polystyrene, as expected. The slight red shift at 77 K is most likely due to an increase in the polymer dielectric constant as its density increases, whereas the slight narrowing is consistent with a longer electronic dephasing time due to a decreased phonon population at lower temperatures. In Figure 2b, we see that the fluorescence of the amorphous film changes in the same way as it does for an isolated molecule embedded in polystyrene. This is in contrast with the fluorescence spectrum of crystalline rubrene, where the region around 580 nm (corresponding to the 0−0 peak) becomes more pronounced at low temperatures. These changes in the fluorescence line shape may indicate the presence of an intermolecular exciton in crystalline rubrene, or they may stem from experimental artifacts like self-absorption. It is beyond the scope of this article to speculate about the nature of excitons in crystalline rubrene. Here we simply emphasize that the temperature-dependent fluorescence provides no evidence of a delocalized singlet exciton in our amorphous rubrene films.

2. Time-Resolved Fluorescence. We next turn to the dynamics of the fluorescence decays. For both isolated molecules and films, the fluorescence spectrum did not change over time (see Figure S1 in the Supporting Information), indicating that in both systems the emission originates from a single species, namely, the excited singlet state. Isolated rubrene molecules have a high fluorescence quantum yield (0.98) and a very low yield for intersystem crossing to the triplet state (<1%). The lack of activated nonradiative decay channels means that for rubrene molecules embedded in a polymer, one expects to see a temperature-independent decay whose lifetime is close to the radiative lifetime of the molecule. Indeed, this is what we observe. The fluorescence decays, integrated over the whole spectral range, at 298 and 77 K for rubrene in polystyrene are shown in Figure 3a. The single exponential decays allow us to extract a fluorescence lifetime at both temperatures of 16.3 ± 0.2 ns, which is close to the radiative lifetime of 16.5 ns for rubrene solution. The fluorescence decays observed in our amorphous rubrene films are qualitatively different from those of the dilute samples, as shown in Figure 3b. At both 298 and 77 K, they are highly nonexponential, but there is considerable slowing of the decay at 77 K. When the room temperature decay in a 20 ns detection window is fit using a biexponential decay function, we obtain
\[ H_{\text{magnetic}} = g \left[ \hbar S_x^A S_x^A + \hbar S_y^A S_y^A + \hbar S_z^A S_z^A \right] \\
+ g \left[ \hbar S_x^B S_x^B + \hbar S_y^B S_y^B + \hbar S_z^B S_z^B \right] \]  
\[ H_{\text{zero field}} = D (S_x^A)^2 + \frac{1}{3} (S_y^A)^2 + \frac{1}{3} (S_z^A)^2 + E [ (S_x^B)^2 + (S_y^B)^2 + (S_z^B)^2 ] \]  
\[ H_{AB} = S_x^A S_x^B \]  

\[ H_{\text{magnetic}} \] describes the interaction of an external magnetic field with the electron spin system, where \( S_x, S_y, \) and \( S_z \) are the \( x, y, \) and \( z \) components of the two-electron spin operators for molecule \( A \), \( g \) is the gyromagnetic ratio, and \( \hbar \) is the magnetic field coupling constant. The projections of the magnetic field vector onto the molecular axes are given by:

\[ h_x = \sin(\theta) \cos(\phi) \]
\[ h_y = \sin(\theta) \sin(\phi) \]
\[ h_z = \cos(\theta) \]  

\( H_{\text{zero-field}} \) describes the effects of interactions between electrons on a single molecule, which breaks the degeneracy of the three triplet states even in the absence of a magnetic field. These interactions lead to the zero-field splitting, as parametrized by molecular constants \( D \) and \( E \). Lastly, the interaction between electrons on different molecules \( A \) and \( B \) is given by \( H_{AB} \), where the \( X \) term gives the strength of the spin–spin coupling. The total Hamiltonian can be solved using either the zero-field basis for triplets on a single molecule

\[ |x\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |\rangle) \]
\[ |y\rangle = \frac{1}{\sqrt{2}} (|+\rangle - |\rangle) \]
\[ |z\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |\rangle) \]  

or the "high field" basis

\[ |0\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |\rangle) = |z\rangle \]
\[ |x\rangle = \frac{1}{\sqrt{2}} (|+\rangle - i|\rangle) = |y\rangle \]
\[ |y\rangle = \frac{1}{\sqrt{2}} (|+\rangle + i|\rangle) = |\rangle \]  

where \( |x\rangle, |y\rangle, \) and \( |z\rangle \) are the single-electron spin functions. For a four-electron triplet pair system, the basis is just the product of two single triplet wave functions on sites A and B, and there are nine possible product states, that is, \( |xx\rangle, |xy\rangle, |yx\rangle, |yy\rangle, |yx\rangle, \) \( |y y\rangle, \) and so on. Further details can be found in the Supporting Information. In the absence of a magnetic field or intermolecular interactions, the zero-field states (eq 6) are the eigenstates of the system. Because we are interested in how the states evolve as the magnetic field strength increases from zero to hundreds of Gauss, we use the zero-field basis for the calculations in this article. As shown in the Supporting Information, the overall singlet (spin = 0) state for this four-electron system can be written in either the zero-field basis

\[ |S\rangle = \frac{1}{\sqrt{3}} (|xx\rangle + |yy\rangle + |zz\rangle) \]  

or the high-field basis

\[ |S\rangle = \frac{1}{\sqrt{3}} (|00\rangle + |+\rangle + |+\rangle) \]  

Of course, neither of these simple product basis sets is an eigenfunction of the full Hamiltonian in eq 1. We diagonalize it in the zero-field basis to obtain the eigenvectors for the real system. These solutions, \( |1\rangle \) with \( l = 0-9 \), are linear combinations of the simple product basis functions. We can then project these new wave functions onto the singlet wave function to obtain their singlet character \( C_S \) given by

\[ C_S = \frac{1}{\sqrt{3}} (|xx\rangle + |yy\rangle + |zz\rangle) \]  

In zero-field, only three triplet pair states have \( C_S \neq 0 \), that is, the \( |xx\rangle, |yy\rangle, \) and \( |zz\rangle \) states as deduced from eq 8.

We now examine the qualitative reasoning as to how magnetic fields affect the rates of SF and TF.

We note that the exact form of \( H_{AB} \), the intermolecular interaction term in eq 4, is not important as long as it is small and present in some form. This term was usually assumed to exist by previous workers, but not considered explicitly.\(^{36,60}\) One first has to recognize that although the zero-field states with singlet character are nondegenerate, in the high-field case the \( 100, | + + \rangle \), and \( | - - \rangle \) states are degenerate only if the magnetic field part of the Hamiltonian is considered. If the zero-field term is added, then the \( 100 \) state shifts to a different energy, but the \( | + + \rangle \) and \( | - - \rangle \) states are still degenerate. The \( H_{AB} \) term serves to break this degeneracy and generate two new combination states

\[ |T\rangle = \frac{1}{\sqrt{2}} (|+\rangle - |\rangle) \]  

In this new basis

\[ |S\rangle = \frac{1}{\sqrt{3}} (|00\rangle + \sqrt{2} |T\rangle) \]
and thus only two high-field states have a singlet projection, whereas in the zero-field case there are three. It is this change in the number of accessible triplet states that leads to a different partitioning of population between the singlet and triplet manifolds. The application of a magnetic field changes the total amount of prompt and delayed fluorescence because it changes both the number and degree of singlet character of the dark triplet pair states that the population can reside in.

The change in the number of eigenstates with singlet character can be quantitatively illustrated for two simple examples. We set \( X = 0.0001 \text{ cm}^{-1} \) and \( g = 10^6 \text{ cm}^{-1}/\text{Gauss} \) and use the zero-field parameters for crystalline tetracene.\(^{46} \) \( D = -0.0062 \text{ cm}^{-1} \) and \( E = 0.0248 \text{ cm}^{-1} \), which are the same as those of rubrene to within the experimental error.\(^{67} \) It turns out that the actual values for \( D \) and \( E \) have no effect on the kinetics of SF and TF in the treatment that follows, as long as they are small relative to the energy shifts induced by the magnetic field (i.e., in the high-field limit). For example, we obtained identical results using the \( D \) and \( E \) parameters for molecular tetracene.\(^{60} \) Using the crystalline tetracene values, the high-field limit, where the triplet pair wave functions stop evolving with magnetic field strength, was achieved by \(~200 \text{ G}. \) First, we consider the case of two parallel molecules with their magnetic axes aligned parallel to the magnetic field (\( A_{1} = A_{2} = 0 \)). This situation, which is most relevant for the case of a polyacene crystal whose \( ab \) crystal plane is aligned between the poles of a magnet, is the one most commonly assumed when magnetic field effects are considered. The evolution of the singlet character for two parallel chromophores is shown in Figure 5a. As described in the previous paragraph, the three states with equal singlet character at zero-field evolve into two states with a 2:1 ratio of \( |\chi_{S}\rangle \) at high field. At small field strengths, additional states temporarily gain singlet character before the two states \( 00 \) and \( 11 \) become dominant. It is this transient opening of new states that leads to the enhancement of the SF rate at intermediate field strengths seen in the theoretical plots of the overall SF rate versus magnetic field strength by previous workers,\(^{40} \) but it should be emphasized that if the two molecules are not parallel, then the presence of the magnetic field can change singlet character over more than three triplet pair eigenstates, as shown in Figure 5b for \( A = 0^\circ, A = 90^\circ \) and \( A = 45^\circ \). Swenberg and Geacintov\(^{60} \) recognized the possibility that a collection of randomly oriented molecules could give rise to an enhancement of the SF/TF rates due to the presence of intermolecular arrangements like that in Figure 5b. Our numerical simulations confirm that a singlet–triplet processes should become more facile in a random system under application of a magnetic field. To model a randomly oriented amorphous sample, we obtain the singlet projection given by every possible orientation of the magnetic field with respect to both molecule A and molecule B, which in turn are randomly oriented with respect to each other. The sum of the singlet projections is then divided by the number of angles that were sampled to give the singlet projection averaged over all possible angles. As shown in Figure 5c, the number of states with nonzero singlet character steadily increases from 3 to 9 as the magnetic field increases.

The next question concerns how to describe the kinetics of the SF/TF process in terms of the singlet character \( |\chi_{S}\rangle \). Following previous workers,\(^{45,46} \) we assume that the transition matrix element (and thus the rate) coupling the singlet to a specific triplet pair state \( |\chi_{T}\rangle \) is proportional to \( |\langle \chi_{S}|\chi_{T}\rangle|^{2} \). This assumption is analogous to the Franck–Condon approximation used in molecular spectroscopy, where the transition probability is proportional to the square of the wave function overlap.\(^{68} \) The operator that couples the initial and final states is assumed to be independent of magnetic field and contributes a constant factor, which is incorporated into \( k_{i,j} \) and \( k_{j,i} \) for fission and fusion, respectively. The application of a magnetic field changes the triplet pair wave function and thus the overlap \( |\chi_{S}|\chi_{T}\rangle \) leading to changes in the transition probability and thus the transfer rate. We first consider the early period of the fluorescence decay, commonly referred to as prompt fluorescence. During this period, the population exchanges between the singlet and triplet pair manifolds, but the correlated pairs do not interact with other triplets. We have previously shown that such correlated pairs can survive for at least 10 ns in room-temperature tetracene crystals.\(^{25} \) The evolution of the early time fluorescence signal will be governed by the kinematics of the populations of the singlet state \( N_{S1} \) and of the nine possible triplet pair states \( N_{T_{ij}} \) as shown in Figure 6 and described by the following equations:

\[
\frac{dN_{S1}}{dt} = \left( k_{\text{rad}} + k_{\text{f}} \right) N_{S1} - \sum_{i=1}^{9} k_{i} |\langle \chi_{S}|\chi_{T_{i}}\rangle|^{2} N_{T_{i}} \tag{13a}
\]

\[
\frac{dN_{T_{ij}}}{dt} = k_{j} |\langle \chi_{S}|\chi_{T_{j}}\rangle|^{2} - \sum_{i=1}^{9} k_{i} |\langle \chi_{S}|\chi_{T_{i}}\rangle|^{2} N_{T_{i}} + k_{\text{f}} N_{T_{ij}} + k_{\text{relax}} N_{T_{ij}} \tag{13b}
\]

The rate constants are defined as follows: \( k_{\text{rad}} \) is the radiative lifetime of the singlet state, \( k_{\text{up}} \) is the intrinsic lifetime of the triplet state, \( k_{\text{relax}} \) is the rate of population transfer between triplet pair states (also known as the spin–lattice relaxation rate), \( k_{j} \) is the rate of triplet pair fusion back to the singlet, and \( k_{\text{i},j} \) is the rate of SF. Although we have assumed that \( S_{1} \) decays
“prompt” fluorescence observed by previous workers? This is due to the interplay of SF and TF rates at slightly later times and can be best illustrated if we assume that the S1 and T1 manifolds rapidly reach a quasi-equilibrium state, before triplet relaxation and radiative decay begin to play a significant role. We first define a simplified model, where there are M triplet pair states, each with equal singlet character |C[S]i|^2 = 1/M and kM = kMR = krelax = 0. Note that changing the magnetic field will change M. We can now simplify eqs 13a and 13b in terms of the total triplet pair population N_{TT} = \sum_{i=1}^{M} N_{(TT)i}.

\[
\frac{dN_{S1}}{dt} = -k_{rad}N_{S1} + k_{2}N_{S1} + k_{3} \frac{1}{M} N_{TT}\]

\[
\frac{dN_{TT}}{dt} = k_{2}N_{S1} - k_{2} \frac{1}{M} N_{TT}^{\text{tot}}
\]

After the initial depopulation of the singlet state that occurs within the first nanosecond or so, we assume the system reaches a quasi-equilibrium with (dN_{S1}/dt) \approx 0, which leads to an effective equilibrium constant for the reaction

\[
\frac{N_{S1}}{N_{TT}^{\text{tot}}} = \frac{1}{M k_{2}}
\]

Thus, the amount of singlet population available to generate fluorescence during this period is inversely proportional to the number of dark triplet pair states where the population can “hide”. This is the origin of the enhanced “prompt” fluorescence signal for oriented molecules in high magnetic fields. The magnetic field decreases M, the number of triplet pair states, and more population in the S1 state leads to more fluorescence. If the molecules are randomly oriented, then the increased number of available triplet pair states will decrease the amount of fluorescence in this time regime. It should be emphasized that this treatment assumes that at early times the (TT) triplet pair produced by the SF event can be considered in isolation and the geminate triplets do not diffuse and interact with other triplets.

At longer times, the relaxation of the triplet (k_{trip}) and singlet states (k_{rad}) cannot be neglected, and we must consider the full time evolution of eqs 13a and 13b. In Figure 7, we show a series of calculated curves for different values of M. The kinetic parameters used in Figure 7a are k_{rad} = 0.06 ns^{-1}, k_{relax} = 0.0 ns^{-1}, k_{2} = 1 ns^{-1}, and k_{3} = 1 ns^{-1}. As predicted in the previous paragraph, as M decreases, the amount of prompt fluorescence is enhanced due to the increased partitioning of the population into the singlet state, but at longer times the “delayed” fluorescence for lower M values actually decays more rapidly. This can again be understood in terms of the increased partitioning of the population into S1. More population in S1 leads to greater signal at the beginning, but the total excited-state population decays more rapidly due to the fact that the radiative decay from S1 acts as a loss channel. Note that this will always be the case if the singlet decay is more rapid than the triplet decay. If the reverse were true, then the decay of the “delayed” fluorescence would get slower as M increases. In most cases, however, the triplet state is longer lived than the singlet state and Figure 7a should provide a better qualitative guide.

Only via k_{rad}, the inclusion of nonradiative decay pathways is trivial and would not affect our conclusions. Before making a detailed analysis, we first explore how eqs 13a and 13b behave in some simple limits that illustrate how changes in the quantum structure induced by a magnetic field can affect the kinetic behavior of the fluorescence.

The first important aspect of eqs 13a and 13b is that they predict that the initial decay of the S1 state should be independent of the magnetic field strength. This is because the sum of singlet projections will always be unity, that is, \sum |C[S]i|^2 = 1, and thus changing individual C[S] terms by changing the magnetic field only affects terms where the sum also runs over the l states, for example, the second term in eq 13a. From an experimental standpoint, this means that at very short times, before there is appreciable population in the (TT) states, the fluorescence decay should be dominated by first-order kinetics of the form

\[
\frac{dN_{S1}}{dt} = (k_{rad} + k_{2} \sum |C[S]i|^2)N_{S1} = (k_{2} + k_{2})N_{S1}
\]

In other words, the effect of the magnetic field on the “prompt” fluorescence signal really comes after the triplet and singlet levels begin to equilibrate due to the competition between fission and fusion processes. At very early times, the decay should not depend on magnetic field at all. If only fission is occurring, with negligible fusion, then the transfer between the singlet and triplet levels is one-way and the k2 fusion rate is negligible. In this case, no magnetic field effect on the singlet decay is expected on any time scale. This situation may hold in systems that undergo very rapid SF, for example, pentacene or the carotenoids, and where the triplets are not energetic enough to fuse back into the singlet.

However, if the magnetic field cannot affect the initial singlet decay, then what is the physical origin of the enhanced
longer times, smaller $M$ values lead to a higher apparent delayed fluorescence signal. Furthermore, because $K$ is small, the loss of triplet population due to fusion and subsequent radiative decay due to $K_{rad}$ is smaller and the delayed fluorescence decay is much slower, appearing flat in the 200 ns time window.

4. Analysis of Rubrene Fluorescence Decay. We confirmed that the presence of the magnetic field had no measurable effect on the fluorescence decay of the rubrene/polystyrene sample, as expected. In Figure 8, we show the experimental rubrene fluorescence decay in three time windows: 1, 20, and 200 ns both with and without an applied magnetic field. Application of a 8.1 kGa magnetic field to the neat film resulted in several noticeable changes in the fluorescence decay. The initial decay (<1 ns) was largely unaffected by the magnetic field, as shown in Figure 8a, as expected based on eq 14. At slightly later times (1–20 ns), there is a clear increase in the fluorescence signal due to increased population in the $S_3$ state, as predicted based on eq 16 if $M$ decreases in the high magnetic field. At much longer times, the delayed fluorescence decay in the magnetic field is more rapid than the zero-field case and the curves cross at ~100 ns, again as expected if $M$ decreases in a magnetic field. Thus our overall signal shape is qualitatively consistent with what is expected based on the “oriented” picture of SF, in contrast with our expectations for a random system. The total fluorescence decay in zero-field on all time scales can be parametrized using a triexponential decay with amplitudes and time constants summarized in Table 2. In the following analysis, we will not attempt to analyze the small, rapid component with $\tau_1 = 0.23$ ns, but assume that $\tau_2 = 2.2$ ns reflects the SF time for the majority of the singlet excitons. Note that the delayed fluorescence extends beyond the 200 ns time window, which was the longest used in our experiments. This provides a lower bound for the triplet lifetime in our samples, but the actual lifetime is expected to be longer because it has been measured to be 20 s in single crystals of rubrene.41

Before trying to simulate the data in Figure 8, we first note that calculations based on the simplified kinetic model in eqs 15a and 15b capture the main features of the fluorescence signal with consideration of only geminate pair triplets. Most
previous workers have used a three-state model of the following form to analyze magnetic field effects on the fluorescence\textsuperscript{5,5,6,60}

\[
S_1 \rightarrow \left( T_1 T_1 \right) \rightarrow \left( T_1 + T_1 \right)
\] (17)

In this model, the \(T_1 + T_1\) state implies that the triplets are uniformly distributed in space. In this limit, the probability that a triplet will recombine with its twin is equal to the probability that it will recombine with a triplet exciton captured by a completely separate photon absorption event. If this is the case, then the signal shape will change as the excitation density is increased: the amount of prompt fluorescence should increase linearly, whereas the delayed fluorescence, dominated by encounters between triplet excitons created by separate photons, should increase approximately quadratically, as observed previously in tetracene thin films,\textsuperscript{23} but at very low excitation densities, only geminate (formed from the same singlet) triplets are expected to contribute to the signal. To test whether nongeminate triplets play a significant role in our amorphous samples, in Figure 9, we show the total fluorescence decay in a 100 ns window for excitation densities ranging from \(1.8 \times 10^3\) to \(1.9 \times 10^4\) m\(^{-3}\). These excitation densities were calculated as done previously for tetracene,\textsuperscript{24} and they result in an average distance between excitation of 89 and 34 nm, respectively. The similarity of the decay curves in this fluence range suggests that recombination of nongeminate triplets makes a negligible contribution to the signal on the 100 ns time scale. Further evidence that we are not in the uniform triplet density regime is provided by a log–log plot of the fluorescent decay. As shown in Figure S2 in the Supporting Information, the delayed fluorescence decay in this time regime yields an asymptotic slope close to 1.3, much less than the value of 2.0, which would be expected if bimolecular \(T_1 + T_1\) reactions played an important role at these early times. Of course, on microsecond time scales, the triplets become uniformly distributed and one expects to see the bimolecular reaction kinetics seen in rubrene crystals.\textsuperscript{51}

Because nongeminate triplets do not appear to play an important role in the dynamics in amorphous rubrene, we concentrate on the kinetic scheme given in Figure 6. To quantitatively model our fluorescence signal, we undertake a more complete analysis using eqs 13a and 13b. The rate constants are defined as previously, and we assume all of the population starts in the singlet state with the experimentally measured excitation density. We then numerically solve eqs 13a and 13b and assume the fluorescence signal is proportional to \(N_{T_1}\). Our simulations of the data are designed to address two issues. The first concerns the relative orientation of the two chromophores that participate in SF. As shown in Figure 7, our data are qualitatively consistent with the magnetic field decreasing the number of triplet pair states with singlet character. In Figure 10a, we show the experimental data in the 20 ns time window, which can be compared with two different simulations. In Figure 10b, we show a simulation that gives a reasonable match to the data. In this simulation, we have assumed that the two molecules participating in the SF event lie parallel to each other but are still randomly oriented with respect to the magnetic field. The kinetic parameters are given in Table 3. In Figure 10c, we show the simulated data using the same rate parameters but now assuming perfectly random orientation of the chromophores with respect to each other and the magnetic field. As expected, the two different scenarios show opposite magnetic field effects, with the parallel case agreeing with the data. The agreement is not quantitative, however, because the simulated data overestimates the prompt fluorescence decay rate and does not do a good job of reproducing the nonexponential curvature in the 1–20 ns time regime.

Previously, in our analysis of tetracene data on this time scale, we found that tuning \(k_{\text{up}}\) could introduce nonexponential character into the zero-field decay simulations and bring them closer to experiment.\textsuperscript{55} Adjusting \(k_{\text{up}}\) probably reflects the time scale of this diffusion-controlled loss of fusion, rather than the true lifetime of the triplet excitons. This strategy can also be employed for rubrene but at the expense of changing the

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Figure 9. Fluorescence decay of amorphous rubrene at different excitation densities. The decay shape does not depend on laser power, which indicates that only geminate pair triplets play a role in the dynamics on this time scale.

Figure 10. (a) Experimental fluorescence decays of amorphous rubrene in the 20 ns time window. (b) Simulated fluorescence decays, using the parameters in Table 3, showing the enhancement in the prompt fluorescence when the molecules are assumed to be parallel. This simulation agrees qualitatively with the data. (c) Simulated fluorescence decay showing suppressed prompt fluorescence when randomly oriented molecules are assumed.
behavior of the magnetic field dependence at long times. Rather than present a detailed analysis of how varying \( k_{\text{para}} \) affects the decay shapes and magnetic field dependence, we simply state that we were unable to significantly improve the overall agreement between our simulations and the data by tweaking this rate.

An alternative approach to improve the agreement between our simulated signal and the data involves varying \( k_{\text{relax}} \), the rate of relaxation between the triplet pair states within the given pair state manifold. In Figure 11a, the experimental data in the 200 ns time window can be compared with simulations, where \( k_{\text{relax}} = 0 \) (Figure 11b) and where \( k_{\text{relax}} = 0.1 \text{ ns}^{-1} \) (Figure 11c). Clearly, a nonzero \( k_{\text{relax}} \) can add some curvature to the early time decay while maintaining the magnetic field enhancement of the prompt fluorescence. The problem is that at longer times this simulation fails to predict the curve crossing due to the increased total population in the high magnetic field case. Instead, the two curves (high and zero-field) simply merge together. In fact, it is a general result that a nonzero \( k_{\text{relax}} \) eventually erases any effect of the magnetic field on the fluorescence dynamics. This can be understood in terms of the simple M-state model described above. Recall that the magnetic field effect is due to changing the number of triplet pair states with singlet character. If we again assume \( |f|^2 = 1/M \) for \( M \leq 9 \) and furthermore that \( k_{\text{relax}} \) is rapid relative to the other relaxation rates, then the triplet population is equally distributed across all levels, \( N_{(TT)} = 1/9 N_{(TT)} \), and it is straightforward to show that the M dependence cancels out in eqs 15a and 15b, which become

\[
\begin{align*}
\frac{dN_{(S)}}{dt} &= k_2 N_{(S)} + k_2 \frac{1}{M} N_{(TT)}^i \\
&= k_2 N_{(S)} + k_2 \frac{1}{M} N_{(TT)}^i \\
&= k_2 N_{(S)} + k_2 \frac{N_{(TT)}^i}{9} \\
&= k_2 N_{(S)} + k_2 \frac{N_{(TT)}^i}{9} \tag{18a}
\end{align*}
\]

\[
\begin{align*}
\frac{dN_{(TT)}}{dt} &= k_2 N_{(S)} + k_{\text{para}} N_{(TT)}^i \\
&= k_2 N_{(S)} + k_{\text{para}} N_{(TT)}^i \\
&= k_2 N_{(S)} + k_{\text{para}} \frac{N_{(TT)}^i}{9} \tag{18b}
\end{align*}
\]

In the limit of rapid spin relaxation, the dependence on \( M \) disappears and there is no magnetic field effect. If there is a separation of time scales, then the general argument still holds and the difference between high and zero-field data will disappear on a time scale comparable to the inverse of \( k_{\text{relax}} \). Experimentally, we see a measurable difference between the two decays out to 200 ns, where our signal-to-noise becomes limited by the low signal levels. The fact that we see a clearly resolved crossing of the high and zero-field curves at \( \approx 100 \text{ ns} \) indicates that population relaxation between the spin sublevels is not complete on this time scale. Thus we cannot use a rapid \( k_{\text{relax}} \) to improve our agreement with the data in the 20 ns window because it leads to the disappearance of the magnetic field effect in the 200 ns time window.

5. Discussion. The qualitative agreement between our simulations and the experimental data provides support for the idea that SF is occurring in amorphous rubrene films. Although SF has been reported previously in amorphous rubrene, that work mainly focused on the magnetic field effects on triplet spin relaxation and did not even report a fission rate.\textsuperscript{33} It is interesting that a purely amorphous system that shows no sign of excitonic coupling can still exhibit reasonably efficient SF, although as noted in the Introduction, previous work has provided considerable evidence for SF in other disordered systems. Our results suggest that SF events occur mainly within certain ordered locations within the film rather than between totally randomized chromophores. This conclusion is consistent with the recent work on disordered diphenylethacene films, where the transient absorption kinetics were interpreted in terms of exciton migration to preferred sites where rapid SF can occur.\textsuperscript{10} The initial rapid decay (0.2 ns) of the fluorescence may be due to SF by excitons created at or near such preferred sites, whereas the later decay (2.1 ns) may represent a convolution of exciton diffusion, followed by SF. Rapid singlet exciton migration is certainly occurring in our rubrene films. We attempted to measure its rate using polarization anisotropy decay but found that the anisotropy decreased to zero within our instrument response, indicating an exciton transfer time of 15 ps or less, but if the singlet excitons rapidly diffuse through the film until they arrive at a location where two rubrenes are optimally aligned to undergo SF, then this would explain why the magnetic field effect is consistent with an oriented SF chromophore pair, despite the disordered character of the film.
In reality, the kinetics of the SF/TF processes are more complicated than the simple model presented in eqs 13a and 13b. A more sophisticated model would take into account exciton diffusion (both triplet and singlet) as well as the possibility that SF can occur with a distribution of rates due to a distribution of pair distances and orientations. Rather than attempt a detailed modeling of singlet diffusion and variable SF rates in amorphous rubrene, we have approximated these complex processes by simple rate constants. If we assume that the only other singlet decay process is radiative decay, occurring with the monomeric rate $k_{\text{rad}} = 0.06$ ns$^{-1}$, then given $k_{\text{SF}} = k_3 = 0.5$ ns$^{-1}$, we can estimate that more than 90% of the initially excited singlets undergo SF.

The higher SF efficiency in the amorphous films most likely arises from the ability of the single excitons to explore their environment and find ordered pairs suitable for rapid SF. The behavior of the amorphous films can be contrasted with that of other acene systems. In covalent tetracene dimers, computational results suggested that a low barrier to rotation around the linker also leads to conformational disorder in solution, yet in those molecules only 2% to 3% of the singlets underwent SF. The disorder in a truly amorphous molecular film may provide a much greater variety of molecular pair geometries, some of which may be optimal for undergoing SF. The possible arrangements of the tetracenes in our covalently linked dimers were much more limited due to the constraints of the covalent linker that enforced large spatial separations. When compared with crystalline and polycrystalline tetracene, where fission occurs with time scales of 200 and 80 ps, the overall rate in our amorphous films is slower. An even more appropriate comparison is with recently reported results in rubrene single crystals, where SF apparently occurs on two different time scales, 5 and 50 ps. In both types of crystalline samples, more rapid SF would be expected if the crystal packing arranges the molecules in an orientation favorable for SF because the excitons no longer have to undergo diffusion to an ordered site.

Our analysis of magnetic field effects has provided some insights into their origin and implications. Changes in both the early and late time fluorescence signals can be most easily understood in terms of changes in partitioning between the singlet and triplet manifolds due to a change in the number of triplet pair states with singlet character. For parallel chromophores, application of a magnetic field decreases the number of triplet states that can couple to the singlet. As this number decreases, less population is able to "hide" in the triplet manifold, which increases the fluorescence signal in the short term but decreases it in the long term as long as $k_{\text{SF}} < k_{\text{rad}}$. At very early times, before any back transfer from the triplet pair can occur, the magnetic field should not affect the fluorescence decay at all, as we observe experimentally. If back transfer cannot occur at all, for example, because the triplet pair energy is much lower than the singlet energy, then we also predict no magnetic field effect. Lastly, rapid population relaxation between triplet pair states (large values of $k_{\text{SF}}$) is also expected to wash out magnetic field effects on the singlet decay, but it is important to emphasize that whereas the quantum-kinetic model we have developed gives a good qualitative description of the data it fails to provide quantitative agreement. As discussed above, adding spin–lattice relaxation is not sufficient. The clearest deficiency of our model is its neglect of the spatial diffusion of the excitons. In reality, the recombination rate parametrized by $k_3$ is most likely time-dependent due to the gradual spatial separation of the geminate triplets as they diffuse in the film. Such a time-dependent $k_3$ rate would effectively smoothen out the sharp biexponential features of the calculated curves in Figures 10 and 11. We are currently working to add diffusion to the kinetic model to improve agreement with experiment.

The last area of interest is the evolution of the newly created triplet excitons. In this article, we only studied relatively low excitation densities due to the limited power of our laser pulse. Given the large spatial separation (≈50 nm) of the triplet pairs produced under these conditions, it is not surprising that triplets from different pairs never encounter each other. Even if the triplets are separating spatially, the lack of intensity dependence in the fluorescence signal means that nongeminate triplets play no role in the dynamics even on a 200 ns time scale. Of course, at higher laser intensities, we would expect that triplets produced by nearby SF events to interact and lead to bimolecular dynamics, including a power-law decay. Another factor that may limit the role of nongeminate triplets is the disordered nature of the film. Disorder limits the triplet diffusion and may allow the pairs to remain associated for much longer times. In a crystal, with more rapid diffusion, triplets created by separate SF events would be more capable of fusing with each other, and nongeminate triplets might become important on shorter time scales. Another important point is that the measurable magnetic field effect at long times means spin population relaxation in this system is slow, longer than 200 ns at room temperature. This lack of population relaxation is consistent with the observation of long spin diffusion lengths in this material. However, it has been found that the spin–lattice relaxation rate ($k_{\text{SL}}$) for triplets in molecular crystals decreases as the magnetic field increases, and this can affect the delayed fluorescence dynamics. Thus the negligible $k_{\text{SL}}$ deduced from the high magnetic field data may not apply to the zero-field dynamics of the triplet. Finally, we cannot say how long the geminate pairs studied in this work maintain spin coherence. Our previous work on tetracene showed that SF produces coherent triplet pairs that can lead to quantum beats in the delayed fluorescence. The SF rate in amorphous rubrene does not appear to be sufficiently rapid to generate beating, and we could not discern any periodic modulation in the delayed fluorescence signal. Whether the triplet sublevel coherences can be maintained on the same time scale as the association of the geminate pair (i.e., >100 ns) remains an open question.

**CONCLUSIONS**

In this work, we have shown that SF can occur in highly disordered films of rubrene that give no indication of intermolecular excitonic effects. Compared with crystalline tetracene films, the dominant SF rate is about 10 times slower, but we still estimate that ~90% of the singlet excitons undergo SF at room temperature. The hybrid quantum-kinetic model pioneered by Merrifield has been extended to model how the dynamics of the geminate triplet pairs are manifested in the fluorescence decay dynamics and their magnetic field dependence. Our simulations show that the magnetic field effect is very sensitive to mutual chromophore alignment, and our data are consistent with a local ordering for rubrenes that participate in the SF event. Overall, our data indicate that SF is indeed possible in a relatively simple amorphous system and demonstrate the utility of making dynamic measurements in the presence of a magnetic field. Varying the film preparation conditions could allow us to probe the dependence of SF on the molecular-level morphology, whereas the effect of the
exciton diffusion rates on the SF dynamics should manifest itself in the temperature dependence of the fluorescence decay. These experiments are currently underway.

**ASSOCIATED CONTENT**

**Supporting Information**

Fluorescence spectra of early and late times, simulation of magnetic field effect and kinetics, and power law analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation under grant CHE-1152677.

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