

# The Dynamics of Singlet Fission in Crystalline Tetracene and Covalent Analogs

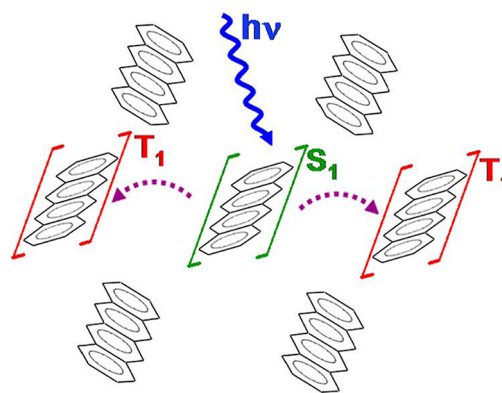
JONATHAN J. BURDETT AND CHRISTOPHER J. BARDEEN\*

*Department of Chemistry, University of California, Riverside,  
501 Big Springs Road, Riverside, California 92521, United States*

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## CONSPECTUS

Singlet fission (SF) is a spin-allowed process in which an excited singlet state spontaneously splits into a pair of triplet excitons. This relaxation pathway is of interest as a mechanism for increasing the efficiency of photovoltaic solar cells, since ionization of the triplets could produce two charge carriers per absorbed photon. In this Account, we summarize our recent work on trying to understand how SF occurs using both covalent and noncovalent assemblies of tetracene. We first give a brief overview of the SF process and discuss why tetracene, where the singlet and triplet pair energies are nearly degenerate, is a particularly useful molecule for studying this process. Then we describe our experiments, beginning with the study of phenylene-linked tetracene dimers as covalent analogs for the crystal form, where SF is known to be very efficient. We found that only 2–3% of the initially excited singlets underwent SF in these dimers. These results motivated us to study crystalline tetracene in more detail. Transient absorption and photoluminescence experiments on polycrystalline thin films provided evidence for a delocalized singlet exciton that decays with a complicated temperature-dependence, but we were unable to unambiguously identify the signature of the triplet pair formed by SF. Then, using ultrathin single crystals, we observed quantum beats in the delayed fluorescence arising from recombination of spin-coherent triplet pairs. Analyzing these quantum beats revealed that SF proceeds through a direct one-step process occurring within 200 ps at room temperature. The product of this reaction is a pair of unperturbed triplets that have negligible interaction with each other.

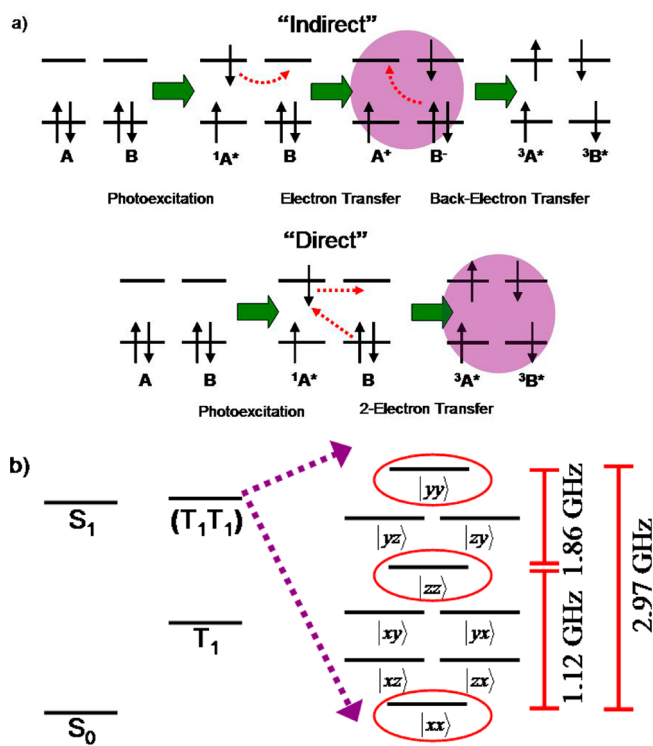


Looking at the overall SF process in tetracene, remaining issues that need to be clarified include the role of exciton diffusion, the temperature dependence of the SF rate, and how to use insights gained from the solid-state studies to generate design principles for high-efficiency covalent systems. Our experiments provide a good illustration of why the polyacenes, and tetracene in particular, play an important role as systems for the study of SF.

## I. Introduction

The widespread use of photovoltaic cells for solar energy conversion is hampered by their high cost and limited efficiencies. Because efficiency is a critical parameter, much research is being directed toward investigating physical phenomena that can enable single-junction solar cells to surpass the Shockley–Queisser efficiency limit of 32%. In a standard solar cell, if an incident photon has an energy above the semiconductor bandgap, that excess energy is usually wasted as heat when the exciton relaxes to the lowest excited state. But if a photon with an energy equal to or greater than twice the bandgap energy could be converted into two low-energy excitons instead of one “hot”

exciton, the theoretical efficiency could increase substantially, with an upper limit of 44%.<sup>1</sup> In organic materials, optical excitation usually generates a neutral Frenkel exciton, analogous to a molecular excited state, with singlet character. Singlet fission (SF) is a spin-allowed process whereby this exciton spontaneously splits into a pair of triplet excitons. First observed in crystalline anthracene in 1965,<sup>2</sup> this phenomenon was the subject of considerable research interest 30–40 years ago. Today, the potential of organic photovoltaics for low-cost solar energy conversion has led to a renewal of interest in photophysical processes occurring in organic solid-state materials, including SF. A recent review by Smith and Michl provides much historical



**FIGURE 1.** (a) Schematic illustration of electron configurations involved in the two-step "indirect" and one-step "direct" mechanisms of SF. (b) Diagram of states involved in the singlet  $\rightarrow$  triplet pair transition, showing the zero-field triplet pair states  $|xx\rangle$ ,  $|yy\rangle$ , and  $|zz\rangle$  and their splittings.

and theoretical background on SF.<sup>3</sup> In this Account, we will focus on a specific molecular system, tetracene, and review our recent work on trying to understand how SF occurs in both covalent and noncovalent assemblies of this molecule.

## II. Brief Overview of Singlet Fission

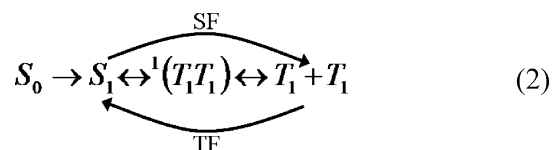
The conversion of singlets into triplets has long been a subject of interest for physical chemists. In a two-electron system, the generation of a triplet from a singlet through intersystem crossing can only occur if one electron flips its spin, that is, changes state from  $\alpha$  to  $\beta$  or vice versa. But the situation changes dramatically if two molecules, with a total of four electrons, are considered. Figure 1a gives a schematic outline of how an initially excited singlet configuration, localized on molecule A, can undergo two electron transfer events to generate two triplets on molecules A and B with an overall singlet spin state. Note that the generation of this state, which we will henceforth refer to as a "triplet pair", in a four-electron system does not require a spin flip, unlike intersystem crossing. Energy must be conserved, and the singlet and triplet energy levels of the molecule must fulfill the condition  $2E(T_1) \leq E(S_1)$ . Fortunately, recent theoretical<sup>4,5</sup>

and experimental work<sup>6–10</sup> has identified several classes of conjugated organic molecules that fulfill this requirement and undergo SF. Although the cartoons in Figure 1a should be viewed with caution, they can be used to motivate the question of whether the electron transfers occur simultaneously in a one-step "direct" mechanism or whether they occur sequentially in a two-step "indirect" mechanism with a charge-transfer intermediate.<sup>3</sup>

The cartoon model in Figure 1a can be made more rigorous if we examine the triplet state in detail, as outlined in Figure 1b. In the absence of a magnetic field, the three triplet states  $|x\rangle$ ,  $|y\rangle$ , and  $|z\rangle$  are the eigenstates for the zero-field Hamiltonian.<sup>11,12</sup> Note that this Hamiltonian takes into account dipolar spin–spin coupling between the two electrons, and its eigenstates are not eigenstates of the total spin  $\hat{S}^2$  operator. For a two-molecule, four-electron system, the nine possible triplet pair states are just the product states  $|xx\rangle$ ,  $|xy\rangle$ , etc. When the  $\hat{S}^2$  operator is diagonalized in the triplet pair basis, we find that the four-electron system has the well-known solutions of one singlet, three triplet, and five quintet states. The overall singlet state is given by the superposition

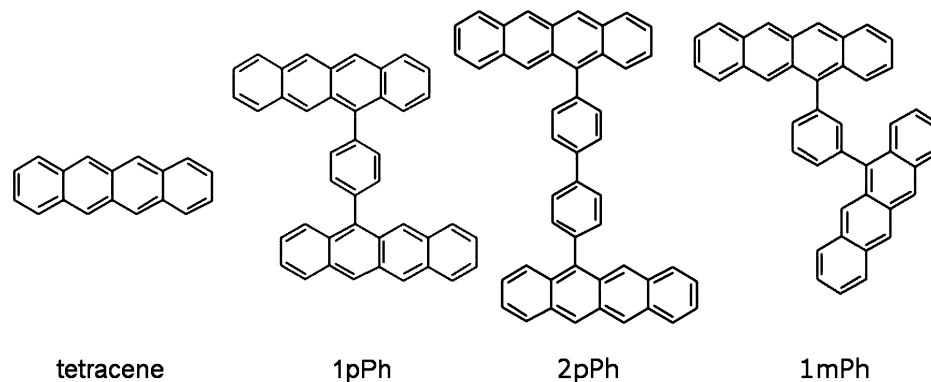
$$|\text{singlet}\rangle = \frac{1}{\sqrt{3}} (|xx\rangle + |yy\rangle + |zz\rangle) \quad (1)$$

This is the spin wave function for the triplet pair state with overall singlet character and is the quantum mechanical explanation for how a singlet state can be projected directly onto the triplet pair manifold. Note that when this occurs, the superposition state is not an eigenstate of the zero-field triplet Hamiltonian and will evolve in time. It is this nonstationary aspect of the newly spawned triplet pair that gives rise to the quantum beats described later in this paper. Eventually, the superposition state will collapse into one of its  $|xx\rangle$ ,  $|yy\rangle$ , or  $|zz\rangle$  constituent states as the two triplet excitons diffuse apart. Note that the reverse process, triplet fusion (TF), whereby two triplets can recombine into a singlet state, is also spin allowed. The overall sequence of events is summarized in the reaction scheme<sup>12</sup>



## III. Tetracene as a Model System for SF

In solution, the polyacene series (anthracene, tetracene, pentacene) have singlet energies,  $E(S_1)$ , of 26 600, 21 200,



**FIGURE 2.** Structures of tetracene and bis(tetracene) molecules studied in ref 29. The bis(tetracene) molecules are abbreviated as follows: 1pPh is 1,4-bis(tetracen-5-yl) benzene, 2pPh is 4,4'-bis(tetracen-5-yl) biphenylene, and 1mPh is 1,3-bis(tetracen-5-yl) benzene.

and  $17\,100\text{ cm}^{-1}$ , respectively, and triplet energies  $E(T_1)$  of  $14\,900$ ,  $10\,300$ , and  $6300\text{ cm}^{-1}$ .<sup>13</sup> SF occurs in all three in the solid state, but in anthracene,  $E(2T_1) > E(S_1)$ , and SF can only occur from unrelaxed high-lying states in  $S_1$ , making it a relatively inefficient process.<sup>2</sup> In pentacene, on the other hand,  $E(2T_1) < E(S_1)$  and SF occurs very rapidly ( $\sim 100\text{ fs}$ ) and irreversibly, leading to a population of dark triplet excitons.<sup>14,15</sup> Tetracene, with  $E(2T_1) \approx E(S_1)$ , represents a good compromise where SF is still the dominant relaxation mechanism for the  $S_1$  state, while regeneration of  $S_1$  via triplet fusion allows us to monitor the  $T_1$  dynamics using fluorescence as well. Swenberg and Stacy were the first to propose that the SF relaxation mechanism could provide an explanation for the low fluorescence quantum yield of crystalline tetracene.<sup>16</sup> Measurements of the fluorescence decay in single crystals of tetracene at room temperature yielded lifetimes ranging from 100 to 300 ps and thus a SF rate of  $\sim 5 \times 10^9\text{ s}^{-1}$ .<sup>17–20</sup>

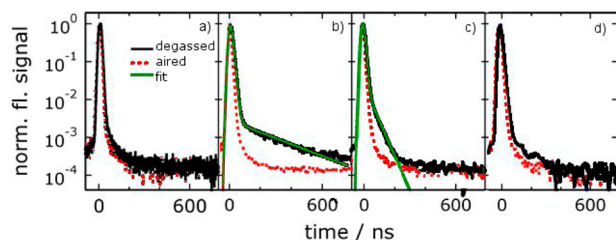
The model for SF in crystalline tetracene was placed on firmer footing with the discovery of magnetic field effects on the fluorescence yield.<sup>21,22</sup> The application of a magnetic field mixes the wave functions of the triplet excitons but leaves the singlets unaffected. Merrifield<sup>23</sup> and Suna<sup>24</sup> developed the theory of how the rates of singlet  $\leftrightarrow$  triplet pair processes (both SF and TF) are perturbed by magnetic fields. In order to distinguish between SF and TF processes, early workers designed experiments to probe “prompt” fluorescence, where the  $S_1$  population is primarily determined by the SF relaxation channel, and “delayed” fluorescence where the  $S_1$  population is created through TF. Although the designations “prompt” and “delayed” suggest that their temporal behavior was measured, in reality “prompt” fluorescence referred to the total luminescence after direct excitation of the  $S_0 \rightarrow S_1$  transition, while “delayed” fluorescence was

generated by excitation of the  $S_0 \rightarrow T_1$  transition in the near-infrared.<sup>25,26</sup> The assumption that simply varying the excitation wavelength allows one to exclusively monitor SF or TF was a limiting factor in the quantitative analysis of many early experiments. Nevertheless, Pope and others demonstrated that theory correctly predicted the magnetic field enhancement of the prompt fluorescence as well as its dependence on the orientation of the crystal with respect to the magnetic field.<sup>21,22,27</sup> The direct measurement of the rapid fluorescence decay in tetracene, combined with the magnetic field effects, firmly established SF as the dominant mechanism for singlet decay in crystalline tetracene.

#### IV. Singlet Fission in Bis(tetracene) Derivatives

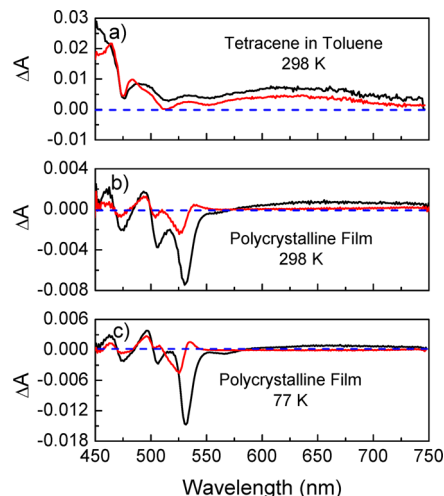
Our interest in tetracene began during a Department of Energy funded project that involved the design of dendrimer molecules to aid solar energy conversion. Aware of the previous work on SF in crystalline tetracene, we decided to mimic the smallest element within the crystal by making a covalent dimer of tetracene.<sup>28,29</sup> The synthesis of the family of dimers shown in Figure 2 was accomplished in the laboratory of Klaus Müllen. The steady-state absorption and fluorescence spectra of these compounds were all very similar to that of unsubstituted tetracene. The lack of electronic communication between the tetracene chromophores was attributed to conformational disorder and the rotation of the linker phenyl groups out of the plane of the tetracene moieties. From a spectroscopic point of view, the covalently linked dimers appeared to behave like two uncoupled tetracenes held in close proximity by their phenylene leashes.

When the time-resolved fluorescence decays of the molecules in Figure 2 were compared, however, the behavior of the bis(tetracenes) clearly deviated from that of monomeric



**FIGURE 3.** Time-resolved fluorescence decays of (a) tetracene, (b) 1pPh, (c) 2pPh, and (d) 1mPh in degassed (solid black lines) and oxygenated (red dashed lines) toluene at room temperature.<sup>29</sup> Also shown are fits to the data (green lines) in degassed toluene with a function that contains the measured instrument response convolved with a biexponential decay that reflects both the prompt  $S_1$  decay and the recombination of the long-lived triplets. The long time window is chosen to illustrate the difference in the delayed fluorescence behavior, while the prompt fluorescence decays, which look like symmetric peaks at time=0 in this time window, are described in the text.

tetracene. The microsecond time scale dynamics are shown in Figure 3, both with and without the presence of oxygen, which quenches the triplet component. Note that on this time scale, the initial fluorescence decays are not resolved and appear as instrument-limited symmetric peaks. Monomeric tetracene showed a single exponential decay with a lifetime of 3.9 ns, while the *para*-phenylene and *para*-biphenylene-linked dimers exhibited clear two-component decays. The fast decay component had lifetimes of 6.1 ns, 5.4 ns, and 6.1 ns for molecules 1pPh, 2pPh, and 1mPh, respectively, but the slower decays lasted much longer than tetracene's  $\sim 25$  ns radiative lifetime. Spectral analysis of the fluorescence at early and late times confirmed that both components originated from the  $S_1$  state, and thus the long-lived component had to be delayed fluorescence. Note that the delayed fluorescence could only arise from recombination of two triplets on the same bis(tetracene) molecule, since the low concentrations used in our experiments precluded intermolecular encounters on the experimental time scale. The delayed fluorescence disappeared at lower temperatures, consistent with SF being an activated process in these molecules. The clear separation of time scales in the fluorescence data allowed us to unambiguously extract kinetic parameters for both SF and TF. SF rates on the order of  $2 \times 10^6 \text{ s}^{-1}$  were deduced from kinetic fits and the amplitude of the delayed fluorescence relative to the prompt fluorescence. The different delayed fluorescence decay rates seen in Figure 3 for 1pPh and 2pPh were attributed to different TF rates due to small energy shifts induced by the different linkers. Although this work provided the first demonstration of SF in a designed covalent molecular assembly, the SF yields were quite low: only 2–3% of the initially



**FIGURE 4.** Broadband transient absorption spectra reported as  $\Delta A$ , the differential absorbance change, for (a) a 7 mM solution of tetracene in toluene at 100 fs (black) and 1.75 ns (red) delays,<sup>31</sup> (b) a polycrystalline film at 298 K at the same delays,<sup>31</sup> and (c) a polycrystalline film at 77 K at the same delays.<sup>32</sup> The 400 nm pump pulse fluence was  $1.5 \times 10^{-3} \text{ J/cm}^2$  for the toluene solution, while the excitation density was  $6 \times 10^{18} \text{ cm}^{-3}$  for the polycrystalline films, which is above the threshold of exciton–exciton annihilation in the polycrystalline film.

excited singlets decayed via the SF channel. The SF rates in the covalent dimers are approximately 3 orders of magnitude smaller than those deduced for crystalline tetracene, suggesting that simple proximity is not sufficient to ensure efficient SF and that geometric factors may play an important role.

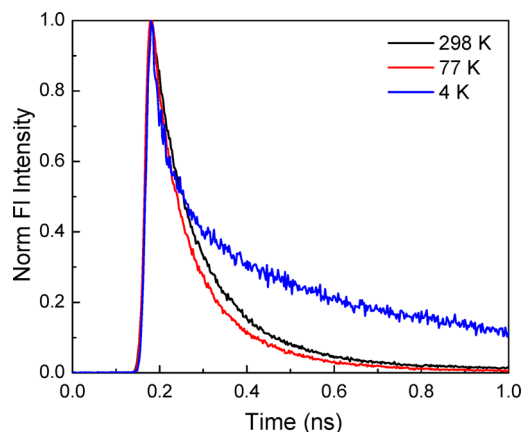
## V. Singlet Fission in Polycrystalline Tetracene Thin Films

The low SF rates in our bis(tetracene) derivatives motivated us to re-examine SF in crystalline tetracene, with the goal of elucidating its detailed mechanism and then applying those insights to the design of new dimer architectures. In order to detect triplets, we planned to use transient absorption (TA) spectroscopy, since previous nanosecond flash photolysis experiments had identified signature  $T_1 \rightarrow T_N$  absorption features of this species.<sup>30</sup> Surprisingly, we could find no previous reports on the femtosecond–picosecond TA dynamics of tetracene in solution, and we decided to characterize the dynamics of the isolated molecule before attempting to understand the more complicated solid-state system. We found that the  $S_1$  state exhibited a number of excited state absorption features, shown in Figure 4a, that completely obscured the ground state bleach and stimulated emission signals that we expected to see.<sup>31</sup> After 20 ns, we could easily detect the strong, long-lived  $T_1 \rightarrow T_N$  absorption feature located at 480 nm that had been characterized by

earlier flash photolysis experiments.<sup>30</sup> These earlier experiments also identified other  $T_1 \rightarrow T_N$  absorption features extending into the infrared but with absorption coefficients much lower than the 480 nm feature. The 480 nm feature should act as a marker for the triplet excitons formed via SF and provide a convenient way to measure SF kinetics. Since the prompt singlet decay in the solid occurs within 80 ps, we expected this absorption to appear within the first nanosecond of data.

Our preliminary TA experiments on polycrystalline thin films of tetracene brought to light several complications, however. First, the lower sensitivity of the TA measurement required the use of higher pulse fluences, and this can be a problem for solid state systems where singlet excitons can diffuse rapidly and encounter each other, leading to a reaction where one of the excitons is quenched by the other. Our first experiments were done using high laser intensities where such exciton–exciton annihilation resulted in rapid singlet decays, causing us to erroneously conclude that the bulk of the SF was occurring on the order of 10 ps.<sup>31</sup> Later, we returned to this system with improved signal-to-noise and characterized the TA over a wide range of pump pulse energies.<sup>32</sup> From our measurements, the singlet exciton–exciton annihilation rate was  $1 \times 10^{-8} \text{ s}^{-1} \text{ cm}^3$ , in reasonable agreement with earlier workers.<sup>19</sup> To extract accurate kinetic information, we had to use low pump fluences and single wavelength detection methods that afforded sensitivity to absorbance changes on the order of  $10^{-5}$ .<sup>32</sup> Even after these effects were taken into account, interpretation of the solid-state TA data still presented difficulties. For example, the induced absorption features seen in the isolated molecules were now dwarfed by the bleach and stimulated emission signals (Figure 4b). The decay of the stimulated emission signal matched that of the fluorescence, but there was no significant growth of absorption in the region around 480 nm where we expected to see the free triplets formed by SF. Finally, there was no significant change in the dynamics when the temperature of the sample was lowered to 77 K (Figure 4c), where SF had been previously assumed to become inoperative.

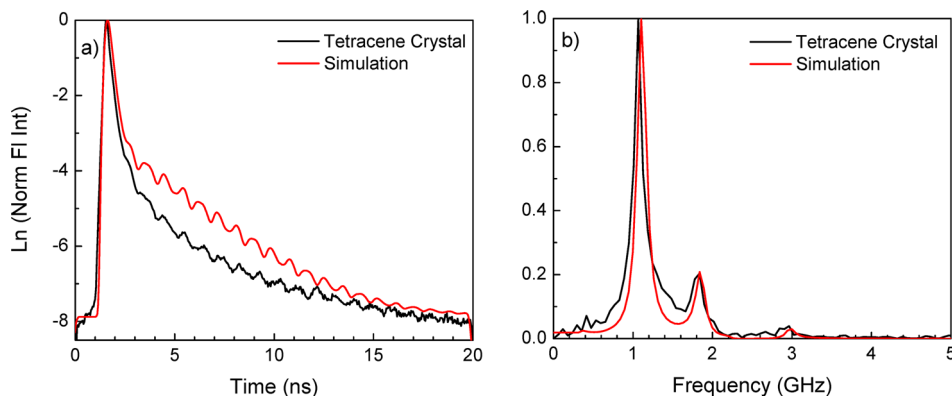
At room temperature, the two main spectroscopic differences between tetracene in the solid-state and in solution could be rationalized in terms of the different characteristics of these samples. First, the dominance of the bleach/stimulated emission signals in the solid-state TA arose from the enhanced  $S_0 \rightarrow S_1$  transition strength due to the same cooperative effects that lead to an enhanced radiative rate (superradiance) in the solid state, as characterized by our



**FIGURE 5.** Time-resolved fluorescence of a polycrystalline tetracene film at 298 (black), 77 (red) and 4 K (blue), exhibiting a fast initial singlet decay at all temperatures.

group and others.<sup>33–35</sup> Second, the difficulty in observing the expected  $T_1 \rightarrow T_N$  absorption, which appears to be a general feature of polyacene crystals beginning with naphthalene,<sup>36</sup> could be due to several complicating factors. As pointed out for pentacene,<sup>37</sup> the strong  $T_1 \rightarrow T_N$  transition is polarized along the long molecular axis and thus cannot efficiently interact with the polarization of light propagating through the sample. But it is unclear whether this is the sole effect acting to diminish the 480 nm feature in tetracene. The parallel orientations of the  $T_1 \rightarrow T_N$  transition dipole moments in the crystal might also lead to new aggregate-induced features in the excited state absorption.<sup>38</sup>

The lack of an obvious temperature dependence in the TA signal motivated us to perform additional picosecond time-resolved fluorescence experiments. The advantage of this type of measurement is its higher sensitivity, which allows the use of excitation densities well below the threshold for exciton–exciton annihilation, and its greater time range. SF in tetracene is expected to be an activated process, with an activation energy estimated to lie in the range  $1000\text{--}2000 \text{ cm}^{-1}$ .<sup>12,20,21,25,26</sup> For the polycrystalline films, measurements of the prompt fluorescence decay at 298, 77, and 5 K showed little difference in their initial decay rates, as seen in Figure 5. Moreover, the decay of the prompt fluorescence at both 298 and 77 K showed no dependence on the excitation wavelength, as would have been expected if the SF process required excess energy in the  $S_1$  state. The main change in the fluorescence dynamics at low temperatures was the early appearance of new emitting species that were red-shifted from the prompt fluorescence and also shorter lived than the delayed fluorescence at room temperature. The effect of these new emitting states can be seen



**FIGURE 6.** (a) Time-resolved fluorescence of a solution-grown single crystal of tetracene (black) along with simulated data convolved with an instrument response (red). The parameters used in the simulation are summarized in ref 42, and the initial singlet decay is given by the sum of the three singlet  $\rightarrow$  triplet pair rates of  $1.65 \text{ ns}^{-1}$ . (b) Normalized Fourier transforms of the extracted frequencies from the single crystal of tetracene (black) along with simulated data convolved with an instrument response (red) with the same parameters as those for panel a.

in the 4 K data in Figure 5, where they give rise to a second decay component even in the 1 ns time window. This slower component is not delayed fluorescence since its spectrum is different from that of the 100 ps component. It is likely that these emitting species were responsible for the enhanced “prompt” fluorescence at low temperatures reported by earlier workers.<sup>21</sup> The fact that the initial decay is rapid at all temperatures suggested that SF is not thermally activated in the solid, but it should be kept in mind that solid tetracene undergoes at least one phase transition at around 150 K,<sup>39</sup> and possible changes in packing and disorder complicate the interpretation of temperature-dependent dynamics.

## VI. Quantum Beat Analysis of SF in Tetracene Single Crystals

Up to this point, our studies of polycrystalline films of tetracene had not resolved important questions like the possible role of intermediate states and the relative importance of the direct versus indirect pathways. The key to answering these questions lay in the characterization of the triplet states produced by the prompt  $S_1$  decay. In the early 1980s, however, it was realized that the nonstationary character of the triplet pair produced via SF should lead to quantum beats in the delayed fluorescence signal due to interference between pathways proceeding through the different  $|xx\rangle$ ,  $|yy\rangle$ , and  $|zz\rangle$  states. The existence of such quantum beats was demonstrated in single crystals under high magnetic fields, but the results were not analyzed in detail due to the lack of a suitable theoretical model.<sup>40,41</sup> We decided to return to the time-resolved fluorescence measurements with the hope of being able to recover more information about the triplet photoproducts by careful

analysis of the delayed fluorescence, shown in Figure 6a.<sup>42</sup> High signal-to-noise measurements showed that both polycrystalline evaporated films and solution-grown ultrathin single crystals exhibited reproducible oscillations in the long-lived fluorescence. These oscillations were much more pronounced in the single crystals, suggesting that the structural disorder in the polycrystalline films destroys the spin coherence for at least some fraction of the triplet pairs produced by SF. The oscillations persisted for more than 10 ns, and after Fourier transformation (Figure 6b), it was found that they exhibited the frequencies predicted from the zero-field splitting parameters determined by Yarnus et al. for triplet excitons in the tetracene crystal.<sup>43</sup> The three possible beat frequencies are highlighted in Figure 1b. The Fourier transforms of the delayed fluorescence can thus be regarded as a crude electron spin resonance experiment, performed in the optical regime, on the newly created triplet pair.

A detailed analysis of the oscillations provided valuable information about the SF process and its product states. We analyzed our results using a density matrix model that assumed the existence of four states: one singlet plus three triplet pair states, where long-lived coherences between the triplet pair states were allowed.<sup>42</sup> We assumed that the singlet  $\rightarrow$  triplet pair reaction was an incoherent process mediated by a weak coupling between the two manifolds and estimated this coupling to be on the order of  $5 \text{ cm}^{-1}$ . The weak coupling could explain why the interaction between the singlet and triplet pair manifolds does not lead to large changes in the shape of the crystalline absorption spectrum. This model permitted us to quantitatively simulate our fluorescence data (the simulation is overlaid with the data

in Figure 6a). Despite the good agreement between our simulations and the data, it should be noted that electronic coherence between the singlet and triplet pair states could affect the dynamics on shorter time scales than those probed in our fluorescence experiments (i.e., <10 ps). Recent time-resolved photoemission experiments have provided evidence for a 7.2 ps decay in thin tetracene films on C<sub>60</sub> that may reflect the loss of coherence between these two electronic manifolds.<sup>44</sup>

Our modeling allowed us to address several questions about the SF process. The first was whether the initially excited singlet decays directly to the triplet pair or whether an indirect pathway takes the singlet through an intermediate state. One can think of the reaction as being similar to a laser pulse that creates a coherent superposition of triplet sublevels if its bandwidth is greater than the level spacing. The triplet pair formation time is analogous to the pulse duration. A slow overall SF rate cannot impulsively excite any quantum beats, while a very rapid SF rate will excite all three of them equally. By analyzing the amplitudes of the different Fourier components, we can estimate the formation time of the triplet pair. Both the magnitude and the relative amplitudes of the oscillations were well-reproduced for the case where the formation time of the triplet pairs mirrored the decay time of the singlet (Figure 6b). This was the expected result for the one-step “direct” mechanism for SF. Our results do not necessarily rule out the “indirect” two-step mechanism for SF, but they do suggest that the lifetime of any intermediate state is so short at room temperature that it is indistinguishable from the single-step mechanism.

The second question involved the structure of the triplet pair. If two triplets, each with a magnetic dipole, were trapped next to each other, the dipole–dipole interaction would be expected to shift the triplet energies and change the beat frequencies by a noticeable amount.<sup>45</sup> To within the experimental error, we did not observe such a shift. We hypothesized that either (1) if the triplets are stationary, they must be spaced apart farther than the nearest neighbor distance in the crystal, or 2) the triplets are moving so rapidly that the dipole–dipole interaction averages to zero. It may seem surprising that spin coherence can be maintained while the excitons diffuse, but other experiments have suggested that spin coherence in organics can be surprisingly robust.<sup>46</sup> The spin coherence can be regarded as a fortunate side product of the SF reaction that allows us to probe the properties of the triplet products without having to detect them directly.

## VII. Future Work and Open Questions

At room temperature, our experiments were completely consistent with the direct production of triplet pairs by SF in crystalline tetracene. But there are still open questions regarding the dynamical and structural aspects of SF. The first question concerns the overall kinetics of SF, as outlined in eq 2. The decay of the delayed fluorescence signal is intertwined with both the fission/fusion reaction rates and exciton diffusion dynamics. We did not explicitly consider triplet exciton diffusion in our analysis of the fluorescence decay, but instead approximated it by adding a triplet lifetime component of 2.5 ns. A more detailed understanding of how the triplets evolve after their creation as spin-entangled pairs will be necessary in order to determine whether they can be efficiently harvested and turned into charge carriers. The temperature dependence of the SF reaction is a second issue that needs to be addressed. As discussed above, the energetics of the S<sub>0</sub>–T<sub>1</sub> and S<sub>0</sub>–S<sub>1</sub> transitions indicate that SF should be an activated process in tetracene, but data from our group and others<sup>44</sup> show that the rapid singlet decay in tetracene persists to very low temperatures. Possible explanations might be that (1) the relative S<sub>0</sub>–T<sub>1</sub> and S<sub>0</sub>–S<sub>1</sub> energies need to be reconsidered, (2) the entropic gain due to the production of triplets compensates for the energy mismatch,<sup>44</sup> or (3) crystalline tetracene changes its packing as the temperature is lowered, opening up new channels for the S<sub>1</sub> decay. A final question concerns how the SF rate depends on the details of molecular packing and interactions. The importance of charge-transfer interactions in triplet–triplet processes was recognized early on,<sup>47,48</sup> and recently a theoretical framework based on the role of charge-transfer states has predicted large effects on the SF rates by changing the chromophore–chromophore interaction geometry.<sup>3,49,50</sup> *Ab initio* calculations have shown that the energy surface crossings of singlet and triplet pair states depends sensitively on the molecular orientations within polyacene crystals.<sup>51,52</sup> Some experimental evidence for the existence of preferred conformations for SF is provided by recent results on disordered films of diphenyl tetracene,<sup>53</sup> and it may also be possible to enhance SF through selective excitation of intermolecular vibrational modes.<sup>54</sup> Our results on tetracene also provide some indication that the detailed nature of the sample preparation affects the SF rate as deduced from the prompt fluorescence decay, since this decay in a polycrystalline film is faster than that in a single crystal. One goal of research in the field is to better define the connection

between chromophore packing and SF rate, so that covalent multichromophoric SF sensitizers can be designed.

## VIII. Conclusions

In this Account, we have maintained a focus on tetracene as a model system for the study of the basic mechanisms of SF in both covalent dimers and neat solids. In many ways, tetracene is the prototypical system for studying and understanding the SF reaction, and organic photovoltaic structures based on tetracene have achieved reasonable efficiencies.<sup>55,56</sup> Our efforts to build a covalent SF sensitizer led naturally back to the study of crystalline tetracene in an effort to clarify the nature of the SF reaction and its products. We have confirmed the direct production of a spin coherent triplet pair at room temperature and illustrate some of the complications that arise in the study of SF in crystalline tetracene. Further research should reveal what intermolecular interactions in the crystal make it function as a SF material and provide guidance for the design of covalent systems. Although much of the recent work on SF is driven by its potential utility in solar cells, this phenomenon is also of fundamental interest as a novel excited state relaxation pathway, with implications for energy dissipation in biological systems.<sup>57,58</sup> The spin coherence in the triplet pair states may have applications in areas far from solar energy conversion, such as quantum computing or spintronics. It is likely that the polyacenes, and tetracene in particular, will play an important role in the study of SF.

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## BIOGRAPHICAL INFORMATION

**Jonathan J. Burdett** was born in Riverside, CA, in 1985. He is currently a graduate student at the University of California, Riverside, where his research focuses on the photophysics of singlet fission in organic semiconductors for solar energy conversion.

**Christopher J. Bardeen** received his Ph.D. degree in chemistry from the University of California, Berkeley, in 1995. He was a postdoctoral fellow at the University of California, San Diego, from 1995 to 1998, after which he moved to the Department of Chemistry at the University of Illinois, Urbana–Champaign, as an assistant professor. In 2005, he moved to the University of California, Riverside.

## FOOTNOTES

\*Corresponding author. E-mail: christopher.bardeen@ucr.edu. The authors declare no competing financial interest.

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