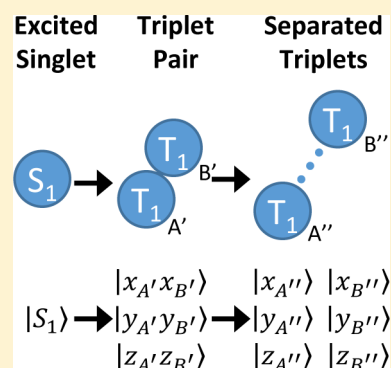


Singlet Fission: From Coherences to Kinetics

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ABSTRACT: Singlet fission, in which an initially excited singlet state spontaneously splits into a pair of triplet excitons, is a process that can potentially boost the efficiency of solar energy conversion. The separate electronic bands in organic semiconductors make them especially useful for dividing a high-energy singlet exciton into a pair of lower-energy triplet excitons. Recent experiments illustrate the role of spin coherence in fission, while kinetic models are used to describe how triplet and singlet states interact on longer time scales. Despite insights gained from recent experiments, the detailed structure and dynamics of the electronic states involved in the initial step of singlet fission remain active areas of investigation. On longer time scales, finding ways to efficiently harvest the triplet excitons will be an important challenge for making devices based on this phenomenon. A full understanding of singlet fission requires consideration of a sequence of photophysical events (decoherence, relaxation, and diffusion) occurring on different time scales.



Concern about global warming due to CO₂ emissions has spurred research into physical processes that can improve solar energy conversion. An important goal is to find materials that convert solar photon energy into electrical potential energy with high efficiency. Shockley and Queisser calculated the maximum energy conversion efficiency of a single-junction photovoltaic cell to be ~33%.¹ One reason that this efficiency is not 100% is the inability of such a cell to fully convert the high-energy photons into electrical energy. When a photon has an energy greater than the band gap, it is absorbed but relaxes to the bottom of the band. The excess energy of the photon is dissipated as heat and cannot contribute to useful energy production. The Shockley–Queisser limit assumes that a single photon creates a single electron–hole pair (1 → 1 conversion). If a 1 → 2 conversion process could be realized for high-energy photons, substantial efficiency gains could be achieved by making more efficient use of the solar spectrum.² The 1 → 2 conversion process, which is the subject of this paper, utilizes the excess photon energy to generate an extra electron–hole pair, boosting the overall solar efficiency by as much as 30%. This conversion can be carried out using photons exclusively, through the use of downconversion or “quantum cutting” that occurs in rare earth glasses, for example. A different approach is to wait until after the photon is absorbed and then rely on the excited-state wave function or exciton to undergo the 1 → 2 conversion. When this process involves a singlet exciton that splits into a pair of triplets, it is termed singlet fission (SF).^{3,4} This process is related to multiple exciton generation (MEG) in inorganic semiconductors but has advantages that derive from the different electronic band structure of organic semiconductors.

In this Perspective, we begin with a brief overview of the electronic states in organic semiconductors, emphasizing the properties that make them useful for the 1 → 2 fission process. The requirements for SF in terms of energy and spin angular

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momentum conservation will be reviewed. The role of spin coherence and the use of kinetic models for understanding how triplet and singlet states interact and evolve will also be discussed, with illustrations from recent experiments. Some open questions in the field concern the electronic structure and dynamics of states involved in the initial step in SF. On longer time scales, the questions concern how triplet excitons diffuse and their ultimate fate in a real device. A key point of this Perspective is that SF is a multistep phenomenon, with different photophysical processes (relaxation, decoherence, exciton diffusion) occurring on multiple time scales. It is this combination of basic photophysics and the potential for practical applications that makes SF an attractive area of study for physical chemists.

Overview of the Electronic Structure of Organic Semiconductors. Figure 1 shows a simplified comparison of the band structures of inorganic and organic semiconductors. The optical properties of inorganic semiconductors are dominated by large-radius Wannier excitons and electron–hole pairs in the conduction band.⁵ If a photon with excess energy excites a state high in the band, it can, in principle, generate additional electron–hole pairs, for example, via impact ionization. However, this MEG

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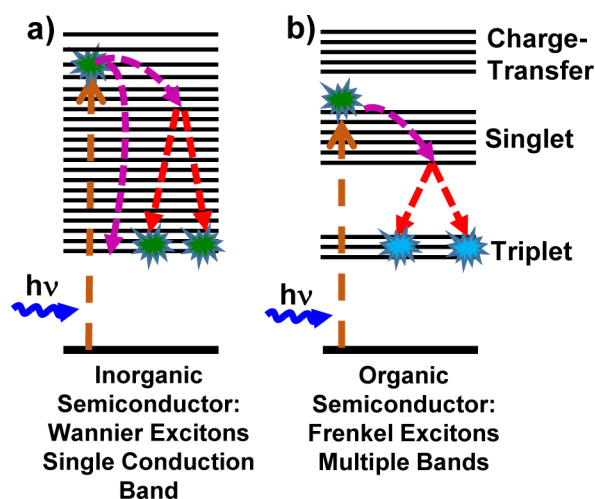


Figure 1. Diagrams of the band structures for (a) inorganic semiconductors and (b) organic semiconductors. In inorganic semiconductors, MEG must compete with subnanosecond intraband relaxation to the bottom of the conduction band. In an organic semiconductor, the initially excited singlet can rapidly relax to the bottom of the singlet band, where its lifetime is on the order of nanoseconds. SF does not have to compete with intraband relaxation, allowing even relatively slow SF reactions to produce high triplet yields.

process must directly compete with intraband relaxation via phonon emission. Nozik proposed that phonon relaxation could be curtailed in nanostructures,⁶ and much work has been done that shows that MEG is enhanced in semiconductor nanoparticles, although the exact mechanism is still a subject of active investigation.^{7,8} Once the multiple excitons are created within a single nanoparticle, their high mobility along with their spatial confinement can lead to rapid annihilation, and indeed, this process is often used as a diagnostic of MEG. However, it also poses a challenge for the efficient harvesting of the multiple excitons because ionization must compete with annihilation.

The electronic band structure of an organic semiconductor is qualitatively different from that of an inorganic material.⁴ Weaker electronic interactions between molecules and a lower dielectric constant lead to a situation in which states with large electron–hole separations are high in energy. The low-lying excited states are generally Frenkel excitons composed of linear combinations of neutral molecular excited-state wave functions. The absence of strong charge-transfer (CT) character means that other interactions become important, in particular, the exchange interaction that lowers the triplet spin state relative to the single spin state in organic molecules. If this energy is greater than the exciton bandwidth, then the solid will have two separated electronic bands, rather than a single broad conduction band. If electron transfer between neighboring sites is now considered, we obtain a third exciton band composed of linear combinations of radical cation/anion states, also known as charge resonance or CT states.⁹ This band is typically higher in energy than the Frenkel bands. For CT excitons, the exchange interaction is typically much smaller because the unpaired electrons reside on different molecules, leaving the singlet and triplet energies almost indistinguishable.¹⁰ It is only for Frenkel excitons that the electron spin effects are strong enough to produce energetically distinct singlet and triplet bands.

The energetically distinct bands of organic semiconductors, illustrated in Figure 1, make these materials especially useful for manipulating energy and repackaging it into new discrete units. Excitation into the singlet band is followed by rapid relaxation to the bottom of that band, but the exciton is prevented from further relaxation into the triplet band by spin selection rules in a two-electron system (e.g., a single molecule), even though such relaxation would be downhill energetically. Conversion between the singlet and triplet states is spin-forbidden, and thus, the singlet state can have a long (>10 ns) lifetime despite the fact that it is not technically the lowest-energy excited state. Furthermore, once the triplets are created, the same spin selection rules mean that the triplet states cannot easily relax to the singlet ground state. Triplet-state lifetimes on the order of μ s to ms are not uncommon, resulting in long diffusion lengths^{11,12} and ample opportunity for the exciton to be ionized or otherwise harvested.

If we can find a mechanism to split the singlet into a pair of triplets, then the $1 \rightarrow 2$ conversion can take place from the relaxed singlet state and does not have to compete with intraband relaxation. Of course, in order for one singlet state to create two triplets, we still must fulfill energy conservation. In practice, this means $E(S_1) \geq 2E(T_1)$, which implies that a large exchange interaction is required. It turns out that there exist molecular design principles that enable many classes of organic molecules make it possible to fulfill this condition.^{13,14} In cases where $E(S_1) < 2E(T_1)$, the SF reaction may require excess photon energy, but there is also evidence (discussed below) that this reaction can proceed “uphill” as a thermally activated process facilitated by a gain in entropy.

The key to understanding SF is to realize that singlet \rightarrow triplet conversion can be spin-allowed when a four-electron system is considered.

How SF Connects Singlet and Triplet States. As discussed above, the $1 \rightarrow 1$ conversion of a singlet into a triplet (intersystem crossing) is spin-forbidden and typically slow, on the order of nanoseconds. The key to understanding SF is to realize that singlet \rightarrow triplet conversion can be spin-allowed when a four-electron system is considered. To understand how this occurs, we consider two molecules, A and B, each with two electrons. There are 16 possible spin states that can exist in a 4-particle spin $1/2$ system. If we use the usual α/β spin basis, we find that there are two $S = 0$ (singlet), nine $S = 1$ (triplet), and five $S = 2$ (quintet) eigenfunctions of the total spin angular momentum operator \hat{S}^2 . We are concerned with the two singlet solutions. One can be factored as the product of two-electron singlet states

$$|S_1^{(4)}\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle_A - |\beta\alpha\rangle_A) \frac{1}{\sqrt{2}}(|\alpha\beta\rangle_B - |\beta\alpha\rangle_B) \quad (1)$$

where the superscript refers to the total number of electrons in the wave function. This solution represents a system of two molecules, each in a singlet state, forming an overall singlet state. An example would consist of molecule A in its excited singlet state and B in its singlet ground state, that is, the $|S_1\rangle_A|S_0\rangle_B$ product wave function. The second solution is

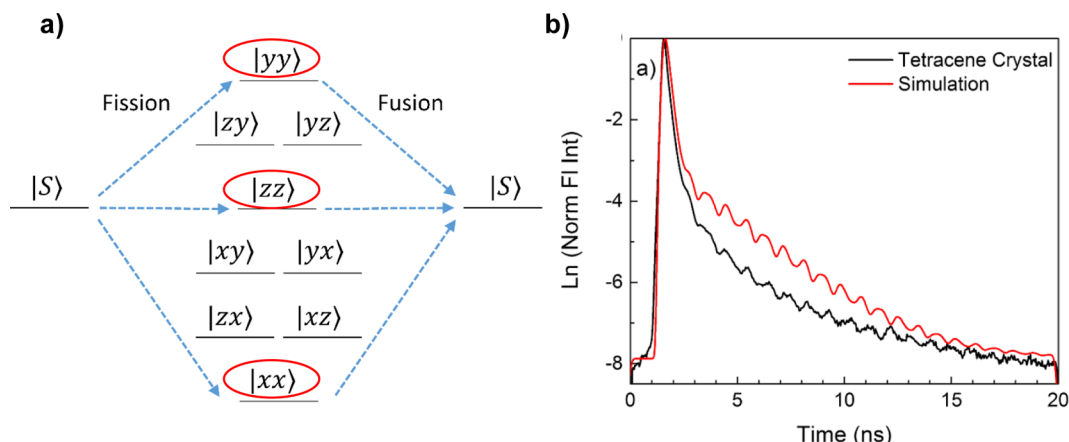


Figure 2. (a) Diagram illustrating the fission from the singlet state to the triplet manifold where the singlet projects onto a superposition of the triplet pair states $|xx\rangle$, $|yy\rangle$, and $|zz\rangle$. After a period of evolution as a superposition state, the triplet pair can fuse back into the singlet state. Interference between the $|xx\rangle$, $|yy\rangle$, and $|zz\rangle$ terms leads to time-dependent oscillations in the projection. (b) Time-resolved photoluminescence of a tetracene single crystal displaying quantum beats in the delayed fluorescence, overlaid with a simulated signal calculated using a density matrix approach; from ref 19.

$$|S_2^{(4)}\rangle = \frac{-1}{\sqrt{3}}(|\alpha\alpha\rangle_A |\beta\beta\rangle_B + |\beta\beta\rangle_A |\alpha\alpha\rangle_B) + \frac{1}{2\sqrt{3}}(|\alpha\beta\rangle_A + |\beta\alpha\rangle_A)(|\alpha\beta\rangle_B + |\beta\alpha\rangle_B) \quad (2)$$

This wave function cannot be reduced to a product of singlets, but it can be written as a superposition of product pairs of two-electron triplet states. In the absence of a magnetic field, the three triplet wave functions are determined by the zero-field Hamiltonian. This Hamiltonian describes the effective dipole–dipole interaction between two electrons and is parametrized by the zero-field parameters D and E , which depend on the molecule and its environment.^{15–17} The eigenstates of this Hamiltonian do not depend on D and E , however, and are given by

$$|x\rangle = \frac{1}{\sqrt{2}}(|\beta\beta\rangle - |\alpha\alpha\rangle) \quad (3a)$$

$$|y\rangle = \frac{i}{\sqrt{2}}(|\beta\beta\rangle + |\alpha\alpha\rangle) \quad (3b)$$

$$|z\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \quad (3c)$$

Note that these wave functions are not eigenstates of \hat{S}^2 . We find

$$|S_2^{(4)}\rangle = \frac{1}{\sqrt{3}}(|x\rangle_A |x\rangle_B + |y\rangle_A |y\rangle_B + |z\rangle_A |z\rangle_B) \quad (4)$$

A transition from $|S_1^{(4)}\rangle$ to $|S_2^{(4)}\rangle$ conserves the total spin angular momentum, unlike intersystem crossing in a two-electron system, as long as the triplets are produced in a superposition state with overall singlet character.

Direct evidence for the creation of this triplet superposition state by SF was first obtained by Chabr et al.¹⁸ and later in more detail by our group¹⁹ through the observation of quantum beats in the delayed fluorescence of crystalline tetracene. The basic idea is outlined in Figure 2, where SF projects the initially excited singlet population onto the $|xx\rangle$, $|yy\rangle$, and $|zz\rangle$ triplet pair states. The resulting superposition evolves for a period of time and then couples back to the luminescent singlet state through triplet fusion. While the wave function is in the triplet

pair coherent superposition state, it acquires a phase, and this phase leads to constructive and destructive interference in the triplet fusion pathways, which in turn leads to observable quantum beats in the singlet fluorescence. We analyzed our results using a density matrix model that assumed the existence of four states, one singlet plus three triplet pair states, wherein long-lived coherences between the triplet pair states were allowed.¹⁹ This model permitted us to quantitatively simulate our fluorescence data (the simulation is overlaid with the data in Figure 2). On the basis of this analysis, our data were consistent with the direct formation of the triplet pair, where the triplets were effectively noninteracting on the nanosecond time scale.

Evolution of the Triplet Pair States and Magnetic Field Effects. Obviously the $S_2^{(4)}$ spin superposition state is not an equilibrium state of the system, and the next question is how to describe the evolution of the nascent triplet pair. In the absence of a magnetic field, the initial state formed by SF, denoted $^1(\text{TT})$, can be identified as

$$^1(\text{TT}) \cong |T\rangle_A |T\rangle_B (|x\rangle_A |x\rangle_B + |y\rangle_A |y\rangle_B + |z\rangle_A |z\rangle_B) \quad (5)$$

where $|T\rangle_A$ is the electronic part of the triplet wave function on site A. We generally assume that the sites A and B are nearest neighbors, although if the parent singlet state is delocalized, then this assumption is questionable. After the $^1(\text{TT})$ state is formed, the triplets can simultaneously diffuse and undergo spin relaxation. In terms of spin relaxation, the $^1(\text{TT})$ state will first decohere into one of its three constituent states ($|xx\rangle$, $|yy\rangle$, and $|zz\rangle$ in zero-field), followed by spin–lattice relaxation that distributes population across all nine possible triplet pair states ($|xx\rangle$, $|xy\rangle$, $|xz\rangle$, $|yx\rangle$, $|yy\rangle$, $|yz\rangle$, $|zx\rangle$, $|zy\rangle$, and $|zz\rangle$ in zero-field). Note that the triplets may diffuse to different sites during this period. It should also be emphasized that the product spin states are eigenstates of the zero-field Hamiltonian but not \hat{S}^2 and can be thought of as mixtures of singlet, triplet, and quintet states.

In principle, a full density matrix treatment is required to describe this phase of the SF process,²⁰ but in our work, we have relied on simpler kinetic models. These models cannot take the triplet coherences into account; therefore, we apply them only to systems where there is evidence that the

coherences are very short lived. Examples of such a system include polycrystalline tetracene thin films, where the pronounced quantum beats seen in single-crystal data tend to be much less pronounced or absent altogether,¹⁹ and amorphous rubrene.¹⁷ Neglecting the quantum coherences allows us to describe the dynamics in terms of population exchange between the different spin states. The standard Merrifield model^{16,21} explicitly takes into account nine “associated” intermediate triplet pair states that act as intermediates between the singlet and the so-called “free” triplets. The kinetic equations associated with this model are given below

$$\frac{dN_{S_1}}{dt} = -k_{-2} \sum_{l=1}^9 |C_S^l|^2 N_{S_1} + \sum_{l=1}^9 k_2 |C_S^l|^2 N_{(TT)_l} \quad (6a)$$

$$\frac{dN_{(TT)_l}}{dt} = k_{-2} |C_S^l|^2 N_{S_1} - (k_2 |C_S^l|^2 + k_{-1}) N_{(TT)_l} + k_1 N_{T_1}^2 \quad (6b)$$

$$\frac{dN_{T_1}}{dt} = 2k_{-1} \sum_{l=1}^9 N_{(TT)_l} - k_1 N_{T_1}^2 \quad (6c)$$

where $|\phi_l\rangle$ are the nine triplet pair states and $C_S^l = \langle S_2^4 | \phi_l \rangle$ is called the “singlet character” of state $|\phi_l\rangle$. In the absence of a magnetic field, these nine states are just the zero-field product states $|xx\rangle$, $|xy\rangle$, and so forth. If we assume steady-state conditions ($dN_{(TT)_l}/dt \cong 0$), one can solve for the time dependence of the S_1 and T_1 populations, finding

$$\frac{dN_{S_1}}{dt} = -\gamma_S N_{S_1} + \gamma_T N_{T_1}^2 \quad (7a)$$

$$\frac{dN_{T_1}}{dt} = 2\gamma_S N_{S_1} - \gamma_T N_{T_1}^2 \quad (7b)$$

where

$$\gamma_S = \sum_{l=1}^9 \frac{k_{-2} |C_S^l|^2}{1 + \varepsilon |C_S^l|^2} \quad (8a)$$

$$\gamma_T = \frac{1}{9} k_1 \sum_{l=1}^9 \frac{\varepsilon |C_S^l|^2}{1 + \varepsilon |C_S^l|^2} \quad (8b)$$

and $\varepsilon = k_2/k_{-1}$. These are the “classical” Merrifield results for SF, but it should be emphasized that they are derived under somewhat restrictive conditions and cannot describe the full time evolution of the populations.

We have found that the standard Merrifield model is not sufficient to describe the magnetic field effects in our time-resolved fluorescence experiments. We have developed an expanded version of the Merrifield model, outlined in Figure 3, to describe our time-resolved fluorescence experiments on rubrene and tetracene films.²² The overall scheme is similar to one proposed by Bouchriha and co-workers.²³ The kinetic equations are given by

$$\frac{dN_{S_1}}{dt} = -(k_{\text{rad}} + k_{-2}) N_{S_1} + k_2 \sum_{l=1}^9 |C_S^l|^2 N_{(TT)_l} \quad (9a)$$

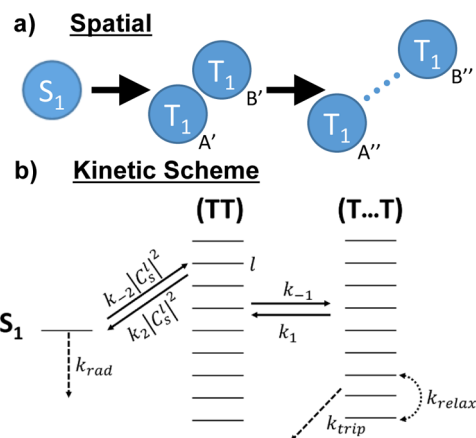


Figure 3. (a) Illustration of the different stages of SF. The singlet transitions to an associated triplet pair state (note that these are individual product states that bypass the coherent superposition defined in eq 5). The triplet excitons can then separate spatially as they diffuse. (b) Schematic representation of the kinetic model. $(TT)_l$ refers to a associated triplet pair state, while $(T\cdots T)_l$ refers to a spatially separated triplet pair state. This diagram only shows transfer rates to the l th triplet, but transfer can occur between the singlet state and all triplet pair states. k_{rad} represents the radiative decay from the singlet state, k_{trip} represents triplet relaxation, and k_{relax} describes spin–lattice relaxation between the separated triplet pair spin states.

$$\begin{aligned} \frac{dN_{(TT)_l}}{dt} = & k_{-2} |C_S^l|^2 N_{S_1} - (k_2 |C_S^l|^2 + k_{-1}) N_{(TT)_l} \\ & + k_1 N_{(T\cdots T)_l} \end{aligned} \quad (9b)$$

$$\begin{aligned} \frac{dN_{(T\cdots T)_l}}{dt} = & k_{-1} N_{(TT)_l} - (k_1 + k_{\text{relax}}) N_{(T\cdots T)_l} \\ & + \sum_{j \neq l} \frac{1}{8} k_{\text{relax}} N_{(T\cdots T)_j} \end{aligned} \quad (9c)$$

There are two main differences between our kinetic model and that of Merrifield. (1) Our model explicitly takes spin–lattice relaxation into account via k_{relax} . (2) We consider two types of triplet pairs, associated (TT) and separated $(T\cdots T)$, that are both geminate pairs. We do not consider “free” triplets that would give rise to a kinetic term proportional to $N_{T_1}^2$. These equations are valid under low laser intensity conditions, where our experiments are typically performed.

In both models, the key quantity that determines the magnitude of the magnetic field effect is C_S^l , the singlet character of the triplet pair states. The C_S^l coefficients are used as inputs to scale the transition rates between the singlet and triplet pair states, while the rate constants remain fixed. In the presence of a magnetic field, the new Hamiltonian generates a new set of $\{|\phi_l\rangle\}$ triplet pair states, each with a new C_S^l value. In Figure 4, we show an example of how C_S^l changes for each of the nine triplet pair states as the magnetic field strength increases for a tetracene pair oriented in a magnetic field. For tetracene, the distribution of singlet character changes from being evenly distributed over three states at zero-field ($|xx\rangle$, $|yy\rangle$, and $|zz\rangle$) to being distributed across nine states at low field, before condensing into two states at high field. The exact details of this change in singlet character are sensitive to the orientation of the molecules with respect to each other and with respect to the magnetic field,²² but the general features shown in Figure 4 will be seen for most molecules that are

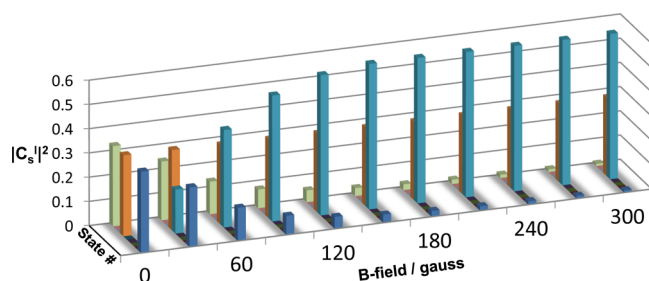


Figure 4. Histogram of singlet character (vertical axis) for each of the nine triplet pair states as a function of the magnetic field strength (long horizontal axis) for molecules with parallel z-axes. The magnetic field is also oriented along the z-axis. The triplet pair states are ordered from lowest to highest energy.

parallel or close to parallel. The number of triplet states with singlet character controls the equilibration of excited-state population between the bright singlet and dark triplet pairs and thus the total fluorescence signal. When more triplet pair states communicate with the singlet, the amount of prompt fluorescence decreases, and when fewer states interact with the singlet, more prompt fluorescence is observed. It should be kept in mind that within this framework, the magnetic field only affects the singlet population if there is facile exchange of population back and forth between the singlet and triplet manifolds ($k_2 \neq 0$). This means that one should expect a magnetic field effect for systems where $E(S_1) \approx 2E(T_1)$, for example, tetracene, rubrene, and diphenylhexatriene. It is less likely that such effects will be observed in systems where there is a larger energetic mismatch, $E(S_1) > 2E(T_1)$, like pentacene. This is not to say that such systems will be immune to the effects of a magnetic field because the triplet pairs can be involved in other interactions (ionization, charge quenching) where spin statistics can also be important. However, for “downhill” systems, there is a straightforward explanation if the singlet population dynamics are unaffected by a magnetic field.

In Figure 5, we illustrate the application of our expanded theory to describe the fluorescence decay of a polycrystalline tetracene film. The theory accurately describes the magnetic-field-induced enhancement in the prompt fluorescence at early times (1 ns) as well as the suppression of the delayed fluorescence at later times (>20 ns). These results can both be understood in terms of the 3 state \rightarrow 2 state transition seen in Figure 4. Fewer triplet pair states with $C_s^i \neq 0$ means that additional excited-state population is partitioned into the singlet state, where it can contribute to the fluorescence. At later times, after spin–lattice relaxation has randomized the population across all nine triplet pair states, the 3 \rightarrow 2 change means that there are fewer gateway states from the triplet manifold back to the singlet and thus less delayed fluorescence. The steady-state fluorescence signal is dominated by the higher-amplitude prompt fluorescence component, and this is the origin of the magnetic-field-enhanced steady-state fluorescence signal measured by early workers in the field.^{24,25} The calculated fluorescence signal qualitatively describes the long time (>10 ns) decay but underestimates the magnetic field effect in this time regime, possibly because our kinetic model is still too simplistic to describe the full evolution of the triplet pair.

Open Questions in SF. From the discussion above, it is clear that SF must be considered a multistep process, rather than a single event. Michl has emphasized this idea, arguing that only after two fully independent triplets have been produced can it

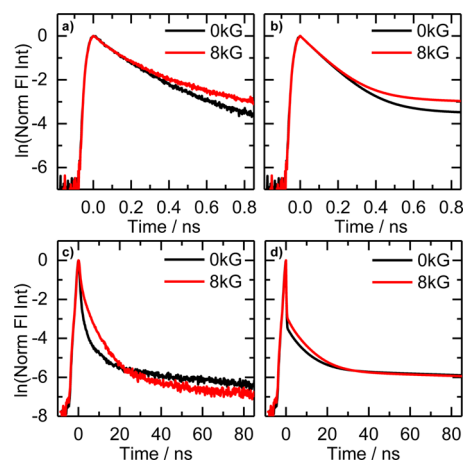


Figure 5. Magnetic field effects on fluorescence decay of polycrystalline tetracene. (a) Experimental fluorescence decay in the 1 ns window without a magnetic field (black) and with an 8 kG magnetic field (red). (b) Simulated fluorescence decay displaying the magnetic field effect using the model given in Figure 4 with $k_{\text{relax}} = 0.3 \text{ ns}^{-1}$. (c) Experimental fluorescence decay in the 100 ns window without a magnetic field (black) and with an 8 kG magnetic field (red). (d) Simulated fluorescence decay displaying the magnetic field effect using the model given Figure 4. $k_{\text{rad}} = 0.18 \text{ ns}^{-1}$, $k_1 = 0.1 \text{ ns}^{-1}$, $k_{-1} = 0.2 \text{ ns}^{-1}$, $k_2 = 1 \text{ ns}^{-1}$, $k_{-2} = 9.3 \text{ ns}^{-1}$, $D = -0.0063 \text{ cm}^{-1}$, and $E = 0.0248 \text{ cm}^{-1}$, where D and E are the zero-field splitting parameters. Reprinted with permission from ref 22, Copyright 2013 Elsevier B.V.

be said that fission has occurred.²⁶ Most other workers define SF as the initial event, where the optically allowed singlet state transitions to an electronically distinct (and usually optically dark) state. It turns out that dividing the overall process into a series of steps is helpful for clarifying some of the remaining questions in the field.

The first question concerns the factors that determine k_{-2} . The involvement of the CT states, as either real or intermediate states, has been explored by several theoretical groups.^{27–31} We do not want to delve into this question in detail, other than to point out that this approach (1) highlights how the three different exciton bands in Figure 1 can interact with each other and (2) provides a way to rationalize how k_{-2} can depend on the geometry of the molecular packing. There is certainly ample experimental evidence that SF is sensitive to molecular orientation and spacing. First, although SF has been observed to occur in amorphous films of rubrene^{17,32} and diphenyltetracene,³³ in both systems, there is strong evidence from the magnetic field dependence and kinetic modeling that SF is dominated by events at specific oriented pairs and does not occur with equal probability for any disordered site. Second, investigation of different crystal polymorphs has revealed different SF rates for the same molecule in different packing arrangements. We recently studied the dynamics of SF in the monoclinic versus orthorhombic forms of diphenylhexatriene. We found that a small change in the intermolecular overlap and distance results in a relatively large ($\sim 50\%$) change in the k_{-2} rate.³⁴ These results are summarized in Figure 6. Studies on crystalline materials can provide benchmarks for theoretical estimations of SF rates because in these cases, the molecular geometry is well-defined, as opposed to more disordered and amorphous solid systems.

The question of how molecular packing affects k_{-2} is intimately related to the exact nature of the states involved. For example, in many cases, it is unclear if the initially excited

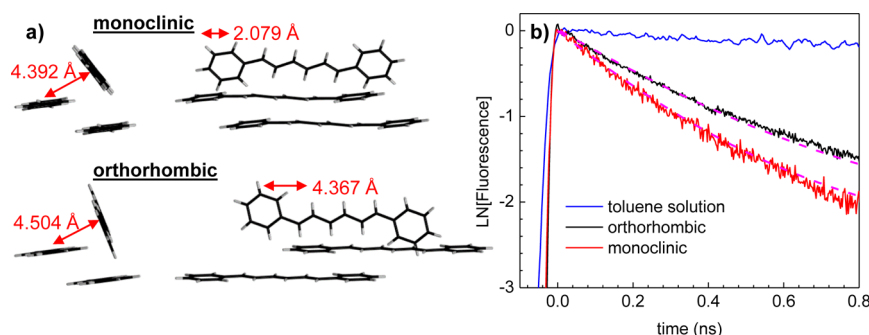


Figure 6. (a) Unit cell of the monoclinic and orthorhombic forms of diphenylhexatriene illustrating the different intermolecular spacings of the two polymorphs. (b) Time-resolved fluorescence decays of diphenylhexatriene in solution, an orthorhombic crystal, and a monoclinic crystal. The monoclinic crystals undergo more rapid SF, with $k_{-2} = 3.4 \text{ ns}^{-1}$ as opposed to $k_{-2} = 2.3 \text{ ns}^{-1}$ for the orthorhombic form. From ref 34.

singlet state is localized or delocalized over several molecules.³⁵ While two independent triplet excitons are eventually produced by the SF reaction, the exact nature of the $^1(\text{TT})$ intermediate in Figure 3a is still a matter of debate. In tetracene, our data are consistent with the idea that the $^1(\text{TT})$ state is a spin-entangled triplet pair formed directly from the singlet state. However, it is also possible that there exist additional short-lived “multi-exciton” intermediate states, perhaps with CT character, on the path to a state that is recognizable as a triplet pair. Thus, the step that we have parametrized with a single k_{-2} rate may consist of multiple steps passing through other types of dark states on the way to the triplet pair. It should be noted that such intermediates are usually spectroscopically dark, and their existence is usually inferred indirectly via kinetic analysis. The direct observation and characterization of such dark states will probably require new modes of time-resolved spectroscopy.

The presence of a dark intermediate state formed early in the SF process might aid in understanding a puzzling aspect of this reaction. SF appears to proceed rapidly even in cases where $2E(\text{T}_1) > E(\text{S}_1)$. Recent experiments on several different molecules suggest that SF can go uphill. The best characterized example is tetracene, where $2E(\text{T}_1) - E(\text{S}_1) \cong 1500 \text{ cm}^{-1}$.³⁶ Early workers assumed that the SF reaction was thermally activated based on a temperature-dependent increase in the steady-state luminescence yield of single crystals.²⁴ Our group and others have found that the initial decay of the S_1 state in polycrystalline films takes place in less than 100 ps even down to 4 K.^{36–39} Although interpretation of the temperature dependence is complicated by possible crystal-phase transitions,³⁶ all of the experimental groups have suggested that the first step in SF in tetracene involves barrierless relaxation to a dark intermediate state.^{36–39} This state would be electronically distinct from both the singlet and the triplet pair. It would then undergo an activated dissociation reaction into a pair of triplets, possibly aided by entropic factors as first proposed by Frankevich.⁴⁰ Recently, a kinetic scheme based on this idea has been developed that is broadly consistent with measurements in tetracene and other polyacenes.⁴¹ However, the exact nature of this intermediate state remains a subject for future experiments.

If we shift our attention to the later stages of the SF process, after the triplets have been formed and are able to diffuse independently, we face a different set of questions. It is possible that spatial diffusion of the $|\text{T}\rangle$ wave functions can occur while they remain in an entangled spin state. The spin relaxation of the triplet states, and how it depends on magnetic field, has important implications for both recombination and for

quantitatively understanding the magnetic field effects. Another question is how the triplets move. It is not clear that we currently have a predictive understanding of what molecular characteristics lead to rapid triplet diffusion, unlike the case of singlet energy transfer (e.g., Forster theory).⁴² Once the triplets arrive at their destination, another challenge is to transform them into electron–hole pairs.⁴³ Direct ionization by an electron acceptor (fullerenes or inorganic nanocrystals) has been demonstrated by several groups.^{44,45} The possibility of turning the two triplets back into photons also exists, if a way could be found to transfer their energy to molecules with appreciable oscillator strength. Finally, it may be possible to couple the triplet exciton energy directly into an inorganic semiconductor to generate a pair of Wannier excitons.⁴⁶ The use of an organic system to absorb a photon, generate an exciton pair, and then sensitize two excitons in a well-established photovoltaic material, for example, silicon, would comprise a hybrid system that takes advantage of the strengths of both classes of materials.⁴⁷ In many respects, understanding and controlling triplet exciton dynamics holds the key to making SF a viable technology.

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This Perspective has concentrated mainly on applications of the $1 \rightarrow 2$ excitonic process in solar energy conversion. It is an open question as to whether such processes may be useful in other areas of chemistry or even biology.⁴⁸ For example, there may be opportunities for organic materials that can down-convert energy in photochemistry, fluorescence imaging, and lighting. Some of these applications rely on the ability to design stand-alone multichromophore molecules that can undergo fission efficiently in solution or an inert solid matrix.^{49,50} The design of such molecules, in turn, relies on a better understanding of the physical chemistry problems outlined in this Perspective. Once this understanding is achieved, we are optimistic that it will become possible to design qualitatively new molecular photonic materials.

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Notes

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REFERENCES

- (1) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510–519.
- (2) Hanna, M. C.; Nozik, A. J. Solar Conversion Efficiency of Photovoltaic and Photoelectrolysis Cells with Carrier Multiplication Absorbers. *J. Appl. Phys.* **2006**, *100*, 074510/1–074510/8.
- (3) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891–6936.
- (4) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York, 1999.
- (5) Scholes, G. D.; Rumbles, G. Excitons in Nanoscale Systems. *Nat. Mater.* **2006**, *5*, 683–696.
- (6) Nozik, A. J. Quantum Dot Solar Cells. *Physica E* **2002**, *14*, 115–120.
- (7) Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **2010**, *110*, 6873–6890.
- (8) Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Gai, W. K.; Koh, W. K.; Pietryga, J. M.; Klimov, V. I. Carrier Multiplication in Semiconductor Nanocrystals: Influence of Size, Shape and Composition. *Acc. Chem. Res.* **2013**, *46*, 1261–1269.
- (9) Bardeen, C. J. The Structure and Dynamics of Molecular Excitons. *Annu. Rev. Phys. Chem.* **2014**, *65*, 127–148.
- (10) Merrifield, R. E. Ionized States in a One-Dimensional Molecular Crystal. *J. Chem. Phys.* **1961**, *34*, 1835–1839.
- (11) Najafov, H.; Lee, B.; Zhou, Q.; Feldman, L. C.; Podzorov, V. Observation of Long-Range Exciton Diffusion in Highly Ordered Organic Semiconductors. *Nat. Mater.* **2010**, *9*, 938–943.
- (12) Akselrod, G. M.; Deotare, P. B.; Thompson, N. J.; Lee, J.; Tisdale, W. A.; Baldo, M. A.; Menon, V. M.; Bulovic, V. Visualization of Exciton Transport in Ordered and Disordered Molecular Solids. *Nat. Commun.* **2014**, *5*, 3646/1–3646/8.
- (13) Paci, I.; Johnson, J. C.; Chen, X.; Rana, G.; Popovic, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J. Singlet Fission for Dye-Sensitized Solar Cells: Can a Suitable Sensitizer Be Found? *J. Am. Chem. Soc.* **2006**, *128*, 16546–16553.
- (14) Minami, T.; Nakano, M. Diradical Character View of Singlet Fission. *J. Phys. Chem. Lett.* **2012**, *3*, 145–150.
- (15) McGlynn, S. P. *Molecular Spectroscopy of the Triplet State*. Prentice-Hall: Englewood Cliffs, NJ, 1969.
- (16) Swenberg, C. E.; Geacintov, N. E. Excitonic Interactions in Organic Solids. In *Organic Molecular Photophysics*, Birks, J. B., Ed.; Wiley & Sons: Bristol, U.K., 1973; Vol. 1, pp 489–564.
- (17) Piland, G. B.; Burdett, J. J.; Kurunthu, D.; Bardeen, C. J. Magnetic Field Effects on Singlet Fission and Fluorescence Decay Dynamics in Amorphous Rubrene. *J. Phys. Chem. C* **2013**, *117*, 1224–1236.
- (18) Chabr, M.; Wild, U. P.; Funfschilling, J.; Zschokke-Granacher, I. Quantum Beats of Prompt Fluorescence in Tetracene Crystals. *Chem. Phys.* **1981**, *57*, 425–430.
- (19) Burdett, J. J.; Bardeen, C. J. Quantum Beats in Crystalline Tetracene Delayed Fluorescence Due to Triplet Pair Coherences Produced by Direct Singlet Fission. *J. Am. Chem. Soc.* **2012**, *134*, 8597–8607.
- (20) Suna, A. Kinematics of Exciton–Exciton Annihilation in Molecular Crystals. *Phys. Rev. B* **1970**, *1*, 1716–1739.
- (21) Merrifield, R. E. Theory of Magnetic Field Effects on the Mutual Annihilation of Triplet Excitons. *J. Chem. Phys.* **1968**, *48*, 4318–4319.
- (22) Burdett, J. J.; Piland, G. B.; Bardeen, C. J. Magnetic Field Effects and the Role of Spin States in Singlet Fission. *Chem. Phys. Lett.* **2013**, *585*, 1–10.
- (23) Barhoumi, T.; Monge, J. L.; Mejatty, M.; Bouchriha, H. Short and Long Consecutive Pairs Model in the Interpretation of MFE and F-ODMR Experiments in Molecular Crystals. *Eur. Phys. J. B* **2007**, *59*, 167–172.
- (24) Geacintov, N.; Pope, M.; Vogel, F. Effect of Magnetic Field on the Fluorescence of Tetracene Crystals: Exciton Fission. *Phys. Rev. Lett.* **1969**, *22*, 593–596.
- (25) Merrifield, R. E.; Avakian, P.; Groff, R. P. Fission of Singlet Excitons into Pairs of Triplet Excitons in Tetracene Crystals. *Chem. Phys. Lett.* **1969**, *3*, 155–157.
- (26) Smith, M. B.; Michl, J. Recent Advances in Singlet Fission. *Annu. Rev. Phys. Chem.* **2013**, *64*, 361–386.
- (27) Beljonne, D.; Yamagata, H.; Bredas, J. L.; Spano, F. C.; Olivier, Y. Charge-Transfer Excitations Steer the Davydov Splitting and Mediate Singlet Exciton Fission in Pentacene. *Phys. Rev. Lett.* **2013**, *110*, 226402/1–226402/5.
- (28) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. Microscopic Theory of Singlet Exciton Fission. I. General Formulation. *J. Chem. Phys.* **2013**, *138*, 114102/1–114102/16.
- (29) Zimmerman, P. M.; Musgrave, C. B.; Head-Gordon, M. A Correlated Electron View of Singlet Fission. *Acc. Chem. Res.* **2013**, *46*, 1339–1347.
- (30) Johnson, J. C.; Nozik, A. J.; Michl, J. The Role of Chromophore Coupling in Singlet Fission. *Acc. Chem. Res.* **2013**, *46*, 1290–1299.
- (31) Feng, X.; Luzanov, A. V.; Krylov, A. I. Fission of Entangled Spins: an Electronic Structure Perspective. *J. Phys. Chem. Lett.* **2013**, *4*, 3845–3852.
- (32) Jankus, V.; Snedden, E. W.; Bright, D. W.; Arac, E.; Cai, D.; Monkman, A. P. Competition Between Polariton Pair Formation and Singlet Fission Observed in Amorphous Rubrene Film. *Phys. Rev. B* **2013**, *87*, 224202/1–224202/7.
- (33) Roberts, S. T.; McAnally, E. R.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. Efficient Singlet Fission Discovered in a Disordered Acene Film. *J. Am. Chem. Soc.* **2012**, *134*, 6388–6400.

- (34) Dillon, R. J.; Piland, G. B.; Bardeen, C. J. Different Rates of Singlet Fission in Monoclinic Versus Orthorhombic Crystal Forms of Diphenylhexatriene. *J. Am. Chem. Soc.* **2013**, *135*, 17278–17281.
- (35) Lim, S. H.; Bjorklund, T. G.; Spano, F. C.; Bardeen, C. J. Exciton Delocalization and Superradiance in Tetracene Thin Films and Nanoaggregates. *Phys. Rev. Lett.* **2004**, *92*, 107402/1–107402/4.
- (36) Burdett, J. J.; Gosztola, D.; Bardeen, C. J. The Dependence of Singlet Exciton Relaxation on Excitation Density and Temperature in Polycrystalline Tetracene Thin Films: Kinetic Evidence for a Dark Intermediate State and Implications for Singlet Fission. *J. Chem. Phys.* **2011**, *135*, 214508/1–214508/10.
- (37) Chan, W. L.; Ligges, M.; Zhu, X. Y. The Energy Barrier in Singlet Fission Can Be Overcome through Coherent Coupling and Entropic Gain. *Nat. Chem.* **2012**, *4*, 840–845.
- (38) Tayebjee, M. J. Y.; Clady, R. G. C. R.; Schmidt, T. W. The Exciton Dynamics in Tetracene Thin Films. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14797–14805.
- (39) Wilson, M. W. B.; Rao, A.; Johnson, K.; Gelinas, S.; di Pietro, R.; Clark, J.; Friend, R. H. Temperature-Independent Singlet Exciton Fission in Tetracene. *J. Am. Chem. Soc.* **2013**, *135*, 16680–16688.
- (40) Frankevich, E. L.; Lesin, V. I.; Pristupa, A. I. Rate Constants of Singlet Exciton Fission in a Tetracene Crystal Determined from the RYDMR Spectral Linewidth. *Chem. Phys. Lett.* **1978**, *58*, 127–131.
- (41) Kolomeisky, A. B.; Feng, X.; Krylov, A. I. A Simple Kinetic Model for Singlet Fission: a Role of Electronic and Entropic Contributions to Macroscopic Rates. *J. Phys. Chem. C* **2014**, *118*, 5188–5195.
- (42) You, Z.-Q.; Hsu, C.-P.; Fleming, G. R. Triplet–Triplet Energy-Transfer Coupling: Theory and Calculation. *J. Chem. Phys.* **2006**, *124*, 044506/1–044506/10.
- (43) Aryanpour, K.; Munoz, J. A.; Mazumdar, S. Does Singlet Fission Enhance the Performance of Organic Solar Cells. *J. Phys. Chem. C* **2013**, *117*, 4971–4979.
- (44) Ehrler, B.; Wilson, M. W. B.; Rao, A.; Friend, R. H.; Greenham, N. H. Singlet Exciton Fission-Sensitized Infrared Quantum Dot Solar Cells. *Nano Lett.* **2012**, *12*, 1053–1057.
- (45) Congreve, D. N.; et al. External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission-Based Organic Photovoltaic Cell. *Science* **2013**, *340*, 334–337.
- (46) Dexter, D. L. Two Ideas on Energy Transfer Phenomena: Ion Pair Effects Involving the OH Stretching Mode, and Sensitization of Photovoltaic Cells. *J. Luminesc.* **1979**, *18/19*, 779–784.
- (47) Piland, G. B.; Burdett, J. J.; Hung, T. Y.; Chen, P. H.; Lin, C. F.; Chiu, T. L.; Lee, J. H.; Bardeen, C. J. Dynamics of Molecular Excitons near a Semiconductor Surface Studied by Fluorescence Quenching of Polycrystalline Tetracene on Silicon. *Chem. Phys. Lett.* **2014**, *601*, 33–38.
- (48) Wang, C.; Schlamadinger, D. E.; Desai, V.; Tauber, M. J. Triplet Excitons of Carotenoids Formed by Singlet Fission in a Membrane. *ChemPhysChem* **2011**, *12*, 2891–2894.
- (49) Muller, A. M.; Avlasevich, Y. S.; Schoeller, W. W.; Mullen, K.; Bardeen, C. J. Exciton Fission and Fusion in Bis(tetracene) Molecules with Different Covalent Linker Structures. *J. Am. Chem. Soc.* **2007**, *129*, 14240–14250.
- (50) Johnson, J. C.; et al. Toward Designed Singlet Fission: Solution Photophysics of Two Indirectly Coupled Covalent Dimers of 1,3-Diphenylisobenzofuran. *J. Phys. Chem. B* **2013**, *117*, 4680–4695.