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Perspective

Singlet Fission in Crystalline Organic Materials: Recent Insights and Future Directions

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ABSTRACT: Singlet fission (SF) involves the conversion of one excited singlet state into two lower excited triplet states and has received considerable renewed attention over the past decade. This Perspective highlights recent developments and emerging concepts of SF in solid-state crystalline materials. Recent experiments showed the crucial role of vibrational modes in speeding up SF, and theoretical modeling has started to define an optimal energetic landscape and intermolecular orientation of chromophores for highly efficient singlet fission. A critical analysis of these developments leads to directions for future research to eventually find singlet fission chromophores with excellent optoelectronic properties.

Singlet exciton fission (SF) is a photophysical process by which a singlet excited state is converted into two triplet excited states, each with about half of the energy of the initial singlet. SF was initially described in the 1960s and 1970s as an explanation for the observed delayed fluorescence in acene crystals.[1,2] In the early 2000s the interest in singlet fission was renewed as it was realized that it could be exploited as a route to increase the photon-to-electricity efficiency of organic photovoltaic devices (OPV). Incorporation of singlet fission into OPV devices can boost the maximum attainable photon-to-electricity efficiency from 33 to 47% by minimizing the thermal relaxation losses included in the Shockley−Queisser limit.[3] Such increases will be hard to reach in practice, but simulations have indicated that combining a SF layer with a state-of-the-art silicon solar cell can increase the efficiency by up to 4.2% absolute.[4]

In order to capitalize on the promise of singlet fission for improving the efficiency of organic solar cells, both the yield of SF itself and the separation of the generated triplets into charge carriers are essential requirements. Currently, efficient extraction of charges after singlet fission has been demonstrated in only a few systems, with low efficiency or limited to very specific excitation wavelengths.[5−7] Most work on such devices and other more fundamental SF research is done on molecules that belong to the acene family. However, these acenes do not possess all the characteristics that are optimal when considering SF-based OPV devices.[8] A specific problem related to acenes is that they are particularly prone to photodegradation.[9] Therefore, fundamental knowledge on the mechanism and dynamics of SF in solid-state systems is essential in establishing guidelines for the design of chromophores that do possess optimal SF characteristics. These characteristics include being minimally exoergic, ultrafast, and highly efficient but displaying good charge transport properties.[10] Important electronic and structural conditions that play a role in attaining optimal SF characteristics include (1) fulfilment of adiabatic energy conditions $E(T_2) - E(S_0) >$

$E(S_1)$ and $E(S_1) - E(S_0) \geq 2[E(T_1) - E(S_0)]$, (2) a suitable molecular packing that optimizes the intermolecular electronic coupling for SF but at the same time minimizes competitive singlet deactivation pathways, and (3) efficient separation of triplet excited states into free charges.

> Fundamental knowledge of the mechanism and dynamics of SF in solid-state systems is essential in establishing guidelines for the design of chromophores that possess optimal SF characteristics.

These electronic and structural conditions for SF have been explored in a multitude of theoretical studies. First, electronic structure calculations by time-dependent density functional theory or configuration interaction-based methods from which accurate S_1, S_2, T_1, and T_2 energies are obtained allowed the identification of SF candidates based on the adiabatic energy conditions.[11,12] Second, calculations of the electronic coupling for singlet fission have been mostly calculated in dimer systems, revealing that the molecular packing strongly affects the fission rate and yield. In order to study the dynamics of fission and explore the importance of different pathways, density matrix propagation methods have been used. The latter have also emphasized the role of vibronic coupling in the singlet fission process.[13] These theoretical studies on SF in dimers have resulted in many new insights; however, the subsequent processes, such as the dissociation of the correlated

triplet pair into free triplets, the diffusion of triplets, and their separation into free charges, have remained largely unexplored. The latter processes are of pivotal importance when SF compounds are to be applied in the solid state in actual devices.

Crystalline organic materials offer an ideal platform for experimental studies on SF dynamics as the intermolecular packing in the solid can be controlled by altering the chemical structure of the individual molecules. Moreover, they naturally consist of extended arrays of molecules where the coherent triplet pair state can separate into uncoupled triplets.[14] Furthermore, the solid-state structure allows the study of the relation between the nature of the excited state and exciton transport and charge separation.[15] It should be noted that efficient SF has also been reported for polycrystalline and amorphous materials with high efficiency, showing that sufficiently strong electronic interactions exist in such systems.[16,17] The drawback of such systems is that they are less well-defined, and hence, it is more difficult to derive detailed structure–property relations.

In this Perspective we discuss some of the fundamental issues in the field of singlet fission and theoretical and experimental approaches that may answer the key questions about the singlet fission mechanisms and dynamics, in particular for crystalline materials. We discuss observations that suggest the existence of a mixed charge transfer (CT) intermediate or quintet state in the singlet fission mechanism,[18] assess the role of phonon–electron coupling rate in the fission dynamics,[19] and investigate how decoherence studies may unravel triplet pair state dissociation and how the exciton diffusion is influenced by this. Finally, some direction is given to address the current challenges in the field of SF.

A first-order picture of the states involved in transforming a singlet into a combination of two triplets is given in Figure 1
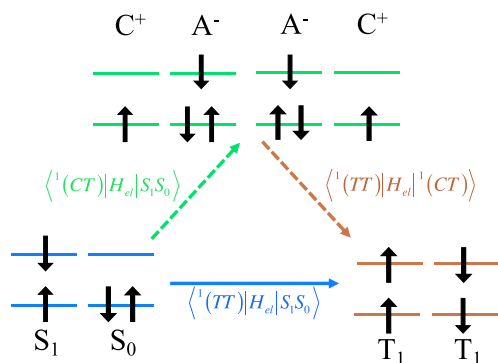

Figure 1. Schematic representation of the direct (blue lines) and indirect, CT-state-mediated (green and orange) singlet fission mechanism. The matrix elements are shown in bra-ket notation that represents the electronic coupling involved in the mechanism steps.

where the SF process starts from the S_1 state. This S_1 excited state is, in first approximation, considered to be localized on a single molecule but can also be a delocalized exciton state. After the initial excitation, the multiexciton triplet state or correlated triplet pair state $^1(TT)$ can be formed via the direct pathway (blue arrow). Alternatively, SF may proceed through virtual intermediate states that have CT character, provided that these states are not too high in energy (green and orange arrow).[8] These different energy states of the system involving two molecules A and B can be expressed in a "basis" of diabatic

states in the singlet ground state $S_0^A S_0^B$, localized excited singlets $S_1^A S_0^B$ and $S_0^A S_1^B$, a lowest-energy triplet pair or correlated triplet pair $^1(T_1^A T_1^B)$, and the charge transfer states $^1(C^{+A} A^{-B})$ and $^1(A^{-A} C^{+B})$. In this description, C^+ represents the ground state of a radical cation while A^- represents the ground state of the respective radical anion. In the following discussion we will omit the superscripts A and B that denote the SF dimer components for clarity. Using these diabatic basis states we can write the rate of the singlet fission process in terms of the electronic Hamiltonian operator H_{el}.

The simplest quantum mechanical description of the SF rate, $w(SF)$, via the direct pathway is governed by the electronic coupling between $S_1 S_0$ and $^1(TT)$, $\langle ^1(TT)|H_{el}|S_1 S_0\rangle$, and in a first-order perturbation theory approximation is given by

$$w(SF) = \left(\frac{2\pi}{\hbar}\right)|\langle ^1(TT)|H_{el}|S_0 S_1\rangle|^2 \rho[E] \tag{1}$$

where $\rho[E]$ is the Franck–Condon weighed density of states at $E = E(S_0 S_1) = E^1(TT)$. The matrix element for this direct pathway, $\langle ^1(TT)|H_{el}|S_0 S_1\rangle$, is usually very small, even though energetically this is the most favorable process, and the expression for $w(SF)$ improves by incorporating terms from additional electronic states. Incorporating pathways due to additional electronic states such as charge transfer states can significantly increase the SF rate from that of the simple direct pathway in eq 1, depending on the energy of these states. Important virtual states that play a role are low-energy CT states and result in additional matrix terms $\langle ^1CA|H_{el}|S_1 S_0\rangle$, $\langle ^1AC|H_{el}|S_1 S_0\rangle$, and $\langle ^1TT|H_{el}|^1AC\rangle$, $\langle ^1TT|H_{el}|^1CA\rangle$ from interaction with the $S_0 S_1$ and TT states. A simplified Hamiltonian matrix for a dimer system in terms of the singlet CT and triplet pair states is given in eq 2, with the excited-state energies on the diagonal and the electronic coupling between the different states on the off-diagonals. The blue elements are involved in the direct pathway, while the green and orange matrix elements are involved in the virtual intermediate pathway.

$$H_{el} = \begin{pmatrix} E(S_0 S_1) & 0 & t_{LL} & -t_{HH} & t_{2e} \\ 0 & E(S_1 S_0) & -t_{HH} & t_{LL} & t_{2e} \\ t_{LL} & -t_{HH} & E(CT) & 0 & \sqrt{\frac{3}{2}}t_{LH} \\ -t_{HH} & t_{LL} & 0 & E(CT) & \sqrt{\frac{3}{2}}t_{HL} \\ t_{2e} & t_{2e} & \sqrt{\frac{3}{2}}t_{LH} & \sqrt{\frac{3}{2}}t_{HL} & E(T_1 T_1) \end{pmatrix} \tag{2}$$

The matrix elements that make up the Hamiltonian in eq 2 are strongly dependent on the mutual orientation and distance of neighboring molecules, which is intricately linked to the nodal structure of the frontier molecular orbitals. A typical example orbital schematic is shown in Figure 2 for the charge transfer coupling matrix element, t_{HL}, which involves coupling between the HOMO (h) and LUMO (l) orbitals on molecules A and B. In this case, in a perfect face-to-face stacking arrangement the coupling is exactly zero, while a slip-stacked geometry leads to a maximum in the coupling. A similar picture exists for the electronic coupling of the direct process, t_{2e}; however, the maximum coupling will occur at a different displacement.
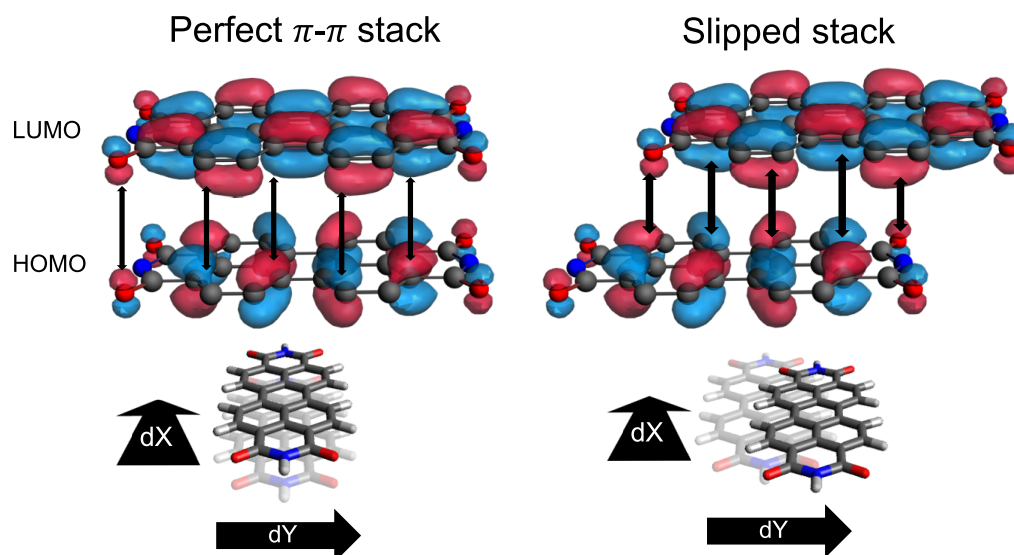
Perfect π-π stack　　　　　　Slipped stack

Figure 2. Schematic representation of frontier molecular orbitals (HOMO and LUMO) and their overlaps for a perfect stacking and slipped stack configuration of two PDI molecules. The slipping directions along the long axis (x) and short axis (y) are indicated as used in Figure 3.

The strong connection between the stacking geometry in the crystal and magnitude and sign of the coupling matrix elements

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directly points to ways to optimize the initial step in singlet fission. If the mutual orientation, or the degree of "slipping" in a slip-stacked structure can be controlled, it is possible to systematically study the relation between structure and SF efficiency. An example of a class of materials where this is possible are perylene diimides, where the crystal structure can

be tuned to a large extent by varying the substituents on the imid position.[20] Using the geometry-dependent electronic coupling matrix elements, we have shown recently that strong differences are to be expected for different PDI derivatives.[21] Using the Hamiltonian matrix in eq 2 in a Redfield density matrix propagation study, insight was obtained in the dynamics of the initial fission process for different geometries.[13,21] A map of the resulting rates for different geometries, shown in Figure 3a, shows a strong dependence of the SF rate on geometry. In addition, in such a model-Hamiltonian study it is possible to look at the contributions of the individual pathways, i.e., direct versus CT-mediated. In this particular example the geometry dependence of these two pathways is markedly different as shown in Figure 3a, but it is also clear that the overall process is dominated by the CT-mediated contribution.[13,21] Experimentally, the strong effect of the molecular packing on SF dynamics was confirmed by femtosecond transient absorption experiments,[22−24] although the described rates are of a different order of magnitude, as shown in Figure 3c. The
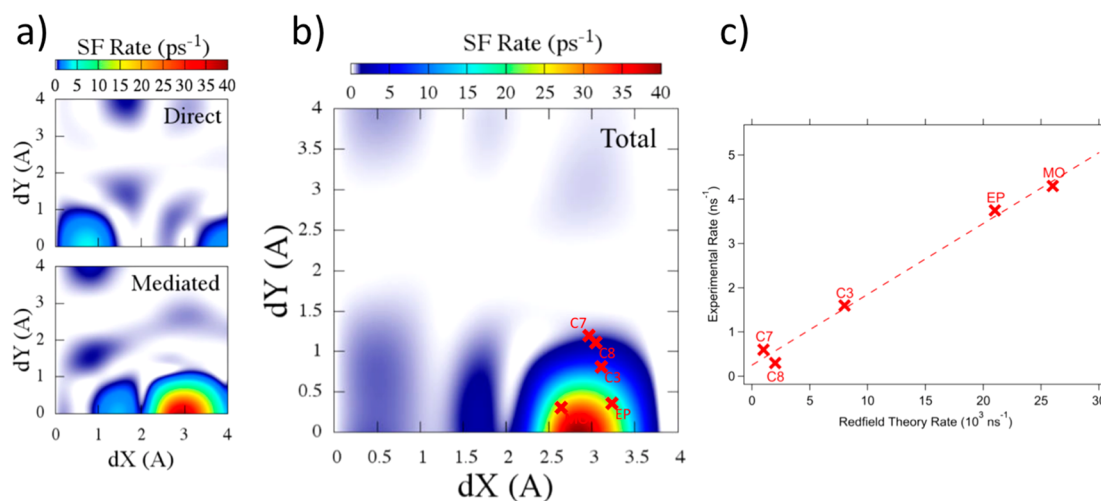

Figure 3. Singlet fission rates as obtained via the direct and CT-mediated pathways (a) and the overall SF rate as a function of translation along the short (y) and long axis as indicated in Figure 2 (b). (c) Comparison of the calculated and experimental SF rates.
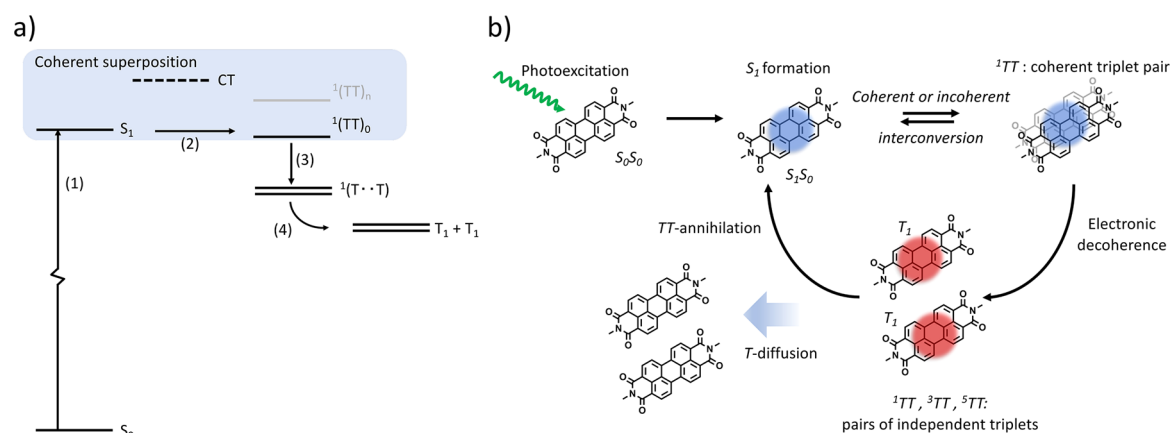
Figure 4. (a) Schematic energy diagram illustrating the different electronic processes and states involved in SF: Photoexcitation from the ground state (1) creates a superposition state of S_1, CT, and $^1(TT)_0$ involving interstate conversion between S_1 and $^1(TT)_0$ (2). Subsequently, $^1(TT)_0$ loses electronic coupling during physical triplet state separation and phonon bath interaction and forms $^1(T\cdot\cdot T)$ (3). The final step is the spin decoherence resulting in the formation of free triplets (4). (b) Schematic representation of triplet exciton formation from singlet fission. The photoexcited superposition state is composed of S_1S_0, CT, and ^1TT states whose formation rate depends on the state mixing. The $^1(TT)$ state can lose coherence, both electronically and relating to spin, to form individual separate triplet excitons that can diffuse.

latter can be due to assumptions made on the energy of the different states involved. A similar correlation between structure and SF dynamic has been described for the acene family where slip stacking is also shown to benefit SF in tetracene and pentacene, making it faster and more efficient when compared to less ordered derivative structures.[22,25−27]

All examples mentioned here primarily relate to the initial fission process in a dimer picture and in a simplified basis with very few states involved. In reality, the relevant states are not so rigorously disconnected and mixed states exist. This is for instance evident from configuration interaction calculations where it is shown that the coherent triplet pair state often has a complex composition, including also CT determinants and mixing of singlet and quintet character.[28−30] This has also been shown experimentally.[31]

In the large majority of theoretical studies, the most focus is on the initial triplet pair state in a dimer. However, if the energy of the two triplets is to be harvested efficiently, the subsequent process where this pair state is split up into two individual triplets that can freely diffuse is essential. This requires extended systems with a detailed description of decoherence, which is a challenge for theoretical work in this field.

Apart from the electronic coupling there is substantial evidence from experiments and theory that the interaction of the exciton with inter- and intramolecular vibrational modes significantly affects singlet fission.[32] This can be due to energy provided to bring the singlet and triplet state in resonance or due to fluctuations in the electronic coupling matrix elements.[33] This electron−phonon (vibronic) coupling can be referred to as Peierls and Holstein for defining exciton coupling with intermolecular and intramolecular vibrational modes, respectively.

Following the Redfield density matrix study on SF dynamics in PDI molecules, the inclusion of Peierls vibrational coupling in the simulation was shown to result in accelerated triplet pair state formation from a picosecond to subpicosecond time scale.[13] The rate acceleration was shown to be unaffected by the CT-state level energy from which the authors deduced that the CT-state acts as a virtual intermediate in a superexchange singlet fission mechanism. Similar findings were reported for

acenes, where Holstein vibronic coupling increased the singlet and triplet pair state coupling in tetracene.[34] Secondly, in pentacene the incorporation of coherent vibrational mixing was found to accelerate SF.[35,36]

These vibronic effects cannot be measured directly in linear transient absorption measurements, but such techniques do allow the detection of coherent phonons from the presence of strong oscillations at early times (1 ps) in photoinduced absorption or emission measurements.[18,37−40] The frequency of such oscillations can be compared to FT Raman spectra of the same material to confirm that these coherent phonon signatures are indeed related to specific vibrational modes that influence different excited-state processes. Relating these vibronic coupling effects to different excitonic states can be achieved with complex two-dimensional spectroscopic techniques such as the four-wave mixing. Two-dimensional spectroscopy allows monitoring both the electronic and electron−phonon coupling between electronic states and the excitation pathway by which they are created.[41] Normally the triplet pair state cannot be directly observed because of its low oscillator strength and needs to be obtained from a SF global or target analysis model,[31,42,43] although very recently ultrafast mid-IR spectroscopy did allow the direct observation of triplet pair states.[44,45]

One example of a four-wave mixing technique that is used for studying singlet fission is two-dimensional electronic photon-echo spectroscopy (2DES).[18,46] A 2DES study on thin films of pentacene and derivatives revealed the presence of an otherwise dark triplet pair state. This observation was possible because of the increased sensitivity of the 2DES technique, in comparison to regular pump−probe absorption spectroscopy.[18] Furthermore, quantum beating signatures were observed in the kinetic traces of singlet and triplet pair states that corresponded to vibronic modes observed in Raman spectra. These vibronic modes were found to be present in the spectral region of both the singlet exciton and the triplet pair state, indicating their influence in mixing the two states.

The relevance of vibrational mode coupling and CT-state intermediate mixing in accelerating intermolecular singlet fission is generally accepted.[32] However, the extent to which both factors are involved depends on the singlet fission

mechanism that one follows. A schematic representation for the singlet fission process is shown in Figure 4a where the singlet excited state S_1 can form an electronically coupled (electronically coherent) triplet pair state or an electronically decoupled (electronically decoherent) triplet pair state.[47] The formation of the electronically coherent triplet pair state can be described by a coherent quantum mechanism as described above or by an incoherent mechanism that allows a classical kinetic treatment. In the incoherent mechanism, a photoexcited singlet state (1) evolves into a triplet pair state $^1(TT)$ as the electronic coupling between S_1 and $^1(TT)$ is weaker than their coupling to the phonon bath and is therefore a thermally assisted process. On the other hand, in the coherent mechanism the photoexcitation creates an excited state that is a superposition of singlet, CT, and $^1(TT)$. Recent experiments[37−39] show that both mechanisms occur concurrently during the singlet fission process at different time scales. The observation of such a dual mechanism can be expected as photoexcitation generates a superposition of a singlet excited state, triplet pair states, and CT intermediate states. Such superposition states, created by coherent excitations, can explain ultrafast femtosecond time scale SF rates. The extent to which these different species are formed within the superposition depends on the excited-state energetics which in turn is dictated by the singlet fission chromophore and its molecular packing.[32] Furthermore, quantum calculations show that such coherent excitations are possible only when a conical intersection exists between a singlet and triplet pair state[38] as described earlier.[40] The slower SF component, on the order of hundreds of femtoseconds, may then come from the incoherent mechanism for forming $^1(TT)$. The loss in electronic coherence of ^1TT to form two spin entangled but electronically decoupled triplets $^1(T··T)$ can occur by coupling to the phonon bath, i.e., vibronic coupling and by physical separation occurring via triplet energy transfer that is driven by enthalpic and entropic driving forces. Finally, the loss in spin coherence or spin coupling between triplets can occur slowly on a nanosecond to microsecond time scale.

As mentioned above, one requirement for application of SF chromophores in photovoltaics is to have a sufficiently high triplet diffusion coefficient. In this context one can perceive triplet diffusion as the diffusion of individual triplet states that may interconvert to singlet states via the triplet−triplet annihilation pathway as represented in Figure 4b.[48] Alternatively, triplet diffusion can be understood as correlated triplet pair diffusion where the triplets have mixed singlet−triplet character.[15,49]

A variety of experimental techniques allow the study of triplet diffusion in solid-state materials such as transient absorption spectroscopy, photoluminescence, and microwave conductivity.[50] These studies are necessary as molecular packing and macroscale crystalline domain size are important factors that determine diffusion properties and cannot (easily) be modeled theoretically or studied in solution.[51] However, these techniques are either limited to measuring the ensemble sample morphology (as is the case in transient absorption) or are limited by the spectral features necessary to determine specific exciton species. A recently developed optical measurement technique that tackles both issues is transient absorption microscopy. This measurement technique allows ultrafast (200 fs time resolution) and spatial optical probing of excitons on a micro- and macroscale with a 50 nm spatial resolution.[15] As such, the investigators were able to study triplet exciton

diffusion in a variety of singlet fission chromophores and found that singlet-mediated triplet transport, i.e., an exciton with mixed singlet−triplet character, increases the triplet diffusion coefficient by more than an order of magnitude. In a follow-up study the same group found a correlation between the SF endothermicity and the triplet diffusion length of several acene molecules that was attributed to an increasing singlet-mediated SF pathway.[49] What remains unknown from this study is which triplet pair state is responsible for the singlet-mediated diffusion. The identification of specific triplet pair states formed during singlet fission was performed recently in photoluminescence measurements at high magnetic field.[52] The investigators use the magnetic field to tune the otherwise dark triplet pair state into resonance with the optically bright singlet state thereby decreasing the photoluminescence. As a result, dips in the photoluminescence emerge at specific magnetic field strengths that correspond to specific triplet pair exchange-coupling strengths. The investigators argue that this resonance excitation technique may supplement transient microscopy absorption measurement in identifying triplet pair state specific diffusion.

> Studies on how the coherent triplet pair dissociates into separately diffusing triplets have only recently appeared for some systems; however, these processes are instrumental in actual applications, and therefore, a detailed understand is of prime importance.

This overview demonstrates singlet fission research has significantly evolved over the past decade. The research started from basic characterizations of yield and kinetics of SF by time-resolved fluorescence and ultrafast transient absorption spectroscopy. Combined with theoretical studies, this has given a considerable amount of insight into the efficiency of the initial step in SF, i.e., transforming a singlet state into a coherent combination of two triplets. This has also given some insight into the mechanism by which this occurs, although in most cases this relies on comparisons of experiments and theory and no general picture including vibronic effects is currently available. Studies on how the coherent triplet pair dissociates into separately diffusing triplets have only recently appeared for some systems; however, these processes are instrumental in actual applications, and therefore, a detailed understanding is of prime importance. In all these processes, including triplet diffusion and charge injection, the relevant electronic coupling matrix elements play a key role. This is why more insight into the effect of solid-state morphology and polycrystallinity in particular is important and why SF chromophores of which the crystal packing can be tuned are of particular interest. Systematic variation of the electronic coupling, as is possible for instance in perylene diimides, can be used to unravel the effect of the different coupling values in the different processes. In addition, systematic variations of the energetics of the different states involved can give insight into the nature of the triplet-pair states involved (singlet, triplet, and quintet). The latter is possible by performing optical

spectroscopy in high magnetic fields, and such experiments should prove very valuable in gaining more insight in the SF dynamics and subsequent processes. In addition, the initial formation of a coherent triplet pair and its subsequent decoherence into individual triplet is an important aspect, which can be explicitly studied by two-dimensional coherent spectroscopy. In all these experiments, materials where the crystal structure can be systematically tuned are appropriate, especially in relation with theory because high-level quantum chemical calculations invariably require information on the structure. From the theory side it is important to continue to move beyond the initial step of forming a triplet pair in a dimer, but to study the dynamics in larger aggregates with an explicit description of decoherence and triplet diffusion. The application of methods such as high magnetic field measurements and 2D spectroscopy on samples with well-defined interchromophore geometry will ultimately lead to a more detailed general understanding and design rules for SF chromophores that go beyond simple energy arguments.

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Notes

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