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REVIEWS

Review

Understanding the Bound Triplet-Pair State in Singlet Fission

Samuel N. Sanders,[1,4] Andrew B. Pun,[1,4] Kaia R. Parenti,[1] Elango Kumarasamy,[1] Lauren M. Yablon,[1] Matthew Y. Sfeir,[2,3] and Luis M. Campos[1,*]

Singlet fission is a photophysical process in which two triplet excitons are produced from one singlet exciton. Understanding the details of this process, especially the properties of intermediates between singlet excitons and free triplet excitons, is particularly important to its optimization and application. Herein, we explore the bound triplet pair, $^{m}(T_1T_1)$, an important intermediate state in singlet fission. We highlight a growing number of studies indicating there is an energetic stabilization of triplet-pair states relative to free triplets. This stabilization enables endothermic singlet fission processes and often results in long lifetimes of the bound triplet-pair state. However, triplets in close proximity demonstrate heightened recombination and reduced excited-state lifetimes. The ubiquity of bound triplet-pair states in recent reports indicates the importance of this state, the need to discern it from free triplets, and the usefulness of having carefully tuned interactions between triplets produced by singlet fission.

The Bigger Picture

While single-junction solar cells continue to be made more efficient, there is a thermodynamic limit to how well they can perform. Materials that are capable of undergoing singlet fission have the capability to dramatically increase the thermodynamic limit of a single-junction solar cell. In spite of the recent advances in the field, the mechanism of singlet fission remains poorly understood, in particular, the role that intermediate states play in the route from one singlet exciton to two free triplet excitons. This review describes recent efforts to study a key intermediate state in singlet fission, the bound triplet pair. We discuss the compounds and spectroscopic techniques that allow this state to be accurately studied and also expound on how this state can be manipulated in order for singlet fission to be applied in photovoltaic devices.

Singlet Fission (SF) is a photophysical process in which a lone singlet exciton decays into two triplet excitons.[1,2] Recently, there has been a surge of interest in this photophysical process—a form of multiple-exciton generation (MEG)—because of its potential in optoelectronics.[3] For example, SF and other MEG strategies can be used to harness energy that is typically lost to thermalization in a photovoltaic (PV) device.[4–6] Thus, by taking advantage of MEG, the overall incident photon-to-current efficiency of an SF-sensitized PV cell could be increased by up to ~10 %.[7–9] As the study of SF continues to mature, one of the areas of great interest is the mechanism of triplet generation. However, SF is not as simple as a transition from the S_1 state to two free triplet states, $2xT_1$, and requires a multiexciton (ME) or coupled triplet-pair intermediate state to permit the conservation of spin angular momentum. Understanding this complex two-step process, including the chemical and electronic factors that promote the fast generation and dephasing of coupled triplet pairs, has been the subject of intense study and will be the primary focus of this perspective. Nonetheless, this is not the only critical issue within the field. There is much that is still unknown about the appropriate description of the photoexcited singlet state that promotes fast and efficient SF, including the role of electronic correlations. Historically, two mechanisms have been debated in the SF literature: (1) the "direct" process and (2) the "charge-transfer (CT)-mediated" process.[10,11] These two mechanisms have been the topic of many studies, and we refer the reader to additional reading on this topic.[12]

The concept of the bound triplet pair is essential to satisfy the energy and momentum conservation requirements that permit a fast energy conversion process.

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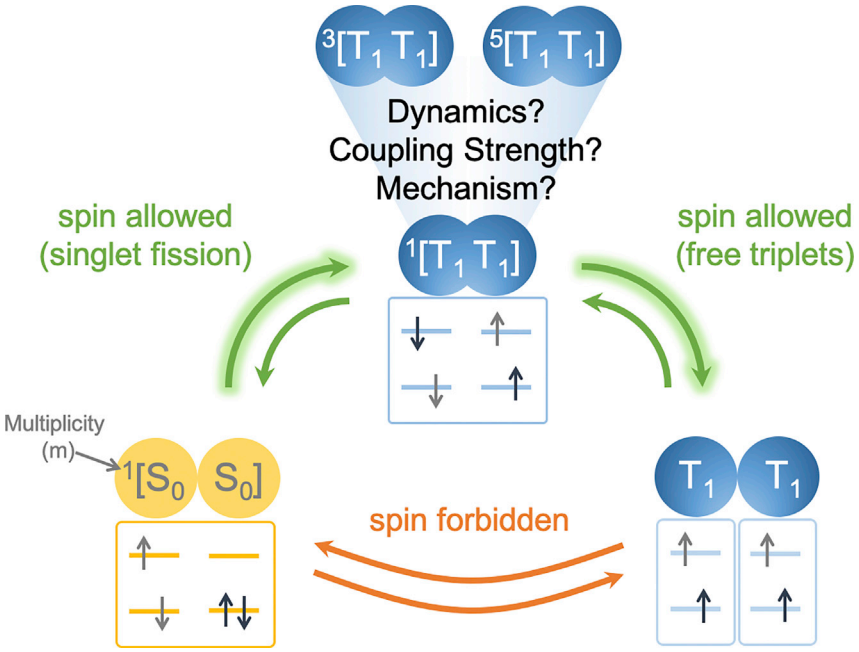

Figure 1. Schematic of Singlet Fission with an Intermediate Bound Triplet-Pair State

Singlet fission from a singlet state ($1[S_0S_0]$) to a spin-correlated triplet pair, which can return to the singlet state or lose spin correlation to form individual triplet excitons (right). Inter-triplet binding energy in the triplet-pair state differentiates it from individual triplets and results in a different lifetime and spectrum for this intermediate state, whose prevalence and importance are just now coming into focus.

Energy conservation dictates that the singlet exciton energy be greater than or equal to twice the triplet exciton energy, but entropic or biexciton effects in the coupled triplet-pair intermediate state appear to relax these criteria. Furthermore, spin conservation mandates that only a triplet pair in a net singlet configuration can be readily accessed. As such, there is an important coupled triplet-pair state with net singlet character (multiplicity, m = 1), $^1(T_1T_1)$, which is generated as part of the allowed process (Figure 1). However, there are nine possible pair excitation states that are the spin eigenfunctions of the Hamiltonian (neglecting small perturbations such as the hyperfine interaction). It has been found from electron paramagnetic resonance (EPR) experiments that $^1(T_1T_1)$ population relaxes into, for example, the quintet $^5(T_1T_1)$ state on a timescale of nanoseconds. Such experiments show how population equilibrates among the $^m(T_1T_1)$ states as a result of the hyperfine interactions.[13,14] Thus, there remains a challenge to fully understand the fundamental properties and dynamics of these intriguing bound triplet-pair states, $^m(T_1T_1)$. Unveiling fundamental pieces of information about the $^m(T_1T_1)$ state could lead to transformative technologies that exploit ME generation, spin processes, and optics. This perspective will highlight recent studies that aim to unmask characteristic spectroscopic signatures of the $^m(T_1T_1)$ state, as well as providing an outlook on what the presence of this intermediate state means for the prospects of SF in PV applications.

Considerations for the Structure and Dynamics of $^m(T_1T_1)$

The initial photoexcited state of an organic chromophore is, at first approximation, a two-spin state accessible via the dipole operator. The four

[1]Department of Chemistry, Columbia University, New York, NY 10027, USA

[2]Photonics Initiative, Advanced Science Research Center, City University of New York, New York, NY 10031, USA

[3]Department of Physics, Graduate Center, City University of New York, New York, NY 10016, USA

[4]These authors contributed equally

*Correspondence: lcampos@columbia.edu

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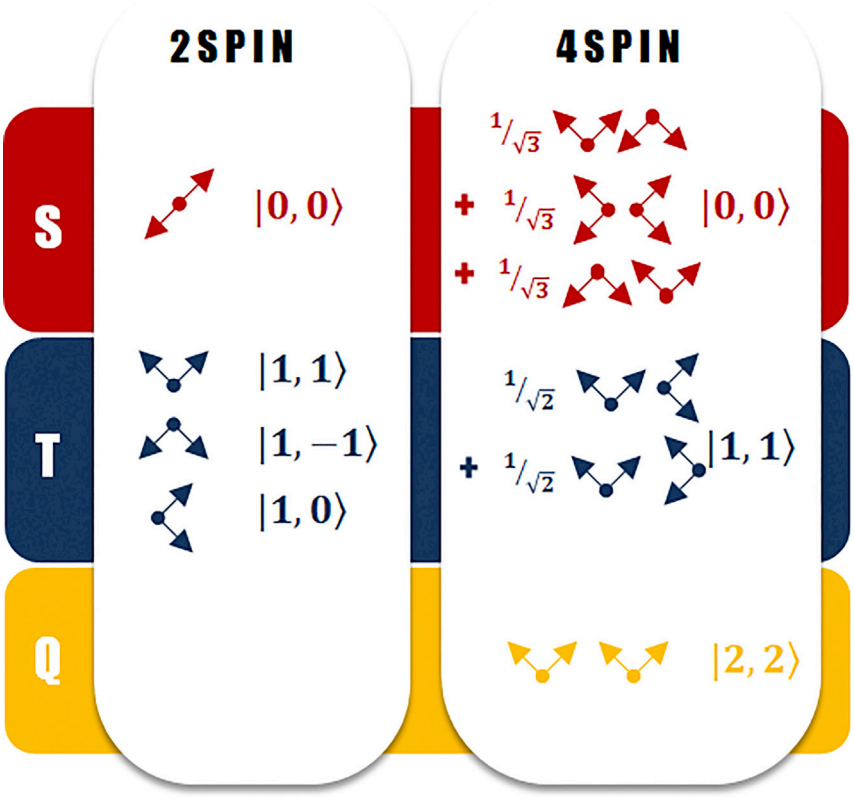

Figure 2. Spin Configurations for Two- and Four-Spin Systems
Example two- and four-spin configurations with net singlet (S), triplet (T), and quintet (Q) multiplicities.

possible two-spin states for a localized excitation are shown in Figure 2 and are labeled by $|s,m_s>$, which represents the total spin angular momentum (s) and projection along the z axis (m_s). These four states include the singlet state |0,0> and three triplet states with a total spin angular momentum of 1. The types of organic molecules under consideration for optical and optoelectronic applications typically have closed-shell ground states, which means that the absorption of a photon yields a net singlet state because no change in angular momentum is provided by the photon. While the triplet states are lower in energy than the singlet state because of the exchange interaction, intersystem crossing to any of the three possible two-spin triplet states is slow because of the angular momentum conservation requirement; i.e, intersystem crossing requires a spin flip.

However, we can satisfy the conservation of angular momentum if a singlet state decays to a final state that is a four-spin ME. This can be clearly seen if one constructs the possible triplet-pair ME configurations using only angular-momentum-coupling considerations. There are nine distinct four-spin states that can be constructed from two particles with a total spin angular momentum of 1. These nine states are nominally degenerate without considering any other interactions and can be readily constructed using Clebsch-Gordon coefficients. The resulting solutions are given in terms of the two-spin basis:

$$|s, m_s> = \begin{bmatrix} |1,1>|1,1> \\ \frac{1}{\sqrt{2}}|1,1>|1,0> + \frac{1}{\sqrt{2}}|1,0>|1,1> \\ \frac{1}{\sqrt{6}}|1,1>|1,-1> + \frac{2}{\sqrt{6}}|1,0>|1,0> + \frac{1}{\sqrt{6}}|1,-1>|1,1> \\ \frac{1}{\sqrt{2}}|1,0>|1,-1> + \frac{1}{\sqrt{2}}|1,-1>|1,0> \\ |1,-1>|1,-1> \\ \frac{1}{\sqrt{2}}|1,1>|1,0> - \frac{1}{\sqrt{2}}|1,0>|1,1> \\ \frac{1}{\sqrt{2}}|1,1>|1,-1> - \frac{1}{\sqrt{2}}|1,-1>|1,1> \\ \frac{1}{\sqrt{2}}|1,0>|1,-1> - \frac{1}{\sqrt{2}}|1,-1>|1,0> \\ \frac{1}{\sqrt{3}}|1,1>|1,-1> - \frac{1}{\sqrt{3}}|1,0>|1,0> + \frac{1}{\sqrt{3}}|1,-1>|1,1> \end{bmatrix} = \begin{bmatrix} |2,2> \\ |2,1> \\ |2,0> \\ |2,-1> \\ |2,-2> \\ |1,1> \\ |1,0> \\ |1,-1> \\ |0,0> \end{bmatrix} \rightarrow \begin{bmatrix} Q_{+2} \\ Q_{+1} \\ Q_0 \\ Q_{-1} \\ Q_{-2} \\ T_{+1} \\ T_0 \\ T_{-1} \\ S \end{bmatrix}.$$

Of these nine solutions, five of the triplet-pair states are $^5(T_1T_1)$ with a total spin of 2 and multiplicity of 5, three are $3(T_1T_1)$ triplet-pair states with a total spin of 1 and multiplicity of 3, and one is a net singlet $^1(T_1T_1)$ triplet pair with a total spin of 0 and multiplicity of 1. While other ME states are theoretically possible,[15,16] only the nine triplet-pair states will meet the energy conservation criterion for SF. For example, angular momentum addition that couples a spin-0 singlet and a spin-1 triplet yield three additional four-spin states with net triplet multiplicity, but the total energy of this configuration will exceed that of the optically pumped singlet state.

By inspection, we can clearly see that within this approximation, the photoexcited two-spin singlet S_1 can directly couple to the $^1(T_1T_1)$ triplet-pair state in a way that conserves both energy and angular momentum. Interestingly, this state is a linear combination of electron configurations that can be intuitively seen to have net zero spin angular momentum, for example, two triplets with antiparallel alignment of their spin projections. The formation of the other triplet-pair states is possible, and the $^5(T_1T_1)$ has been observed experimentally in several systems. The kinetic pathways to these states are more complex and necessitate consideration of the full spin Hamiltonian, as described in these recent reviews.[16,17] While these kinetic pathways have not yet been fully established experimentally, viable mechanisms, including direct formation of $^5(T_1T_1)$ via dipolar mixing with $^1(T_1T_1)$ and dephasing of $^m(T_1T_1)$ followed by rephrasing, have been suggested.[18]

Stabilization and Importance of $^m(T_1T_1)$

The role of $^m(T_1T_1)$ in SF has yet to be fully understood. Many of the very first kinetic models for SF included evolution from singlet to triplet pair followed by a subsequent population of individual triplets. However, in later reports, this intermediate triplet-pair state $^m(T_1T_1)$ was largely overlooked or presumed to be similar to separated triplets.[2] Recent theoretical work suggested the rationale for the stabilization of the $^m(T_1T_1)$ energy relative to two free triplets. Through stabilization of this intermediate state, its role in SF can be significant. Krylov and coworkers suggested that the energetic proximity of $^m(T_1T_1)$ to S_1 and CT states enables mixing with these states that lowers the $^m(T_1T_1)$ energy.[19] In this work, we will focus on the manifestations of this stabilization in experimental work, rather than the origins of this stabilization, although the discussion of the electronic structure of $^m(T_1T_1)$ also constitutes an interesting topic.[20]

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The ability to design and engineer molecules that can lead to persistent excited states in organic molecules is a major fundamental challenge.[21] For example, the ability to generate exceptionally long-lived polarons—which are key species orchestrating function in optoelectronic devices—has been accomplished using a combination of highly ordered discrete assemblies of a conjugated polymer that acts as an electron donor and a fullerene as an acceptor.[22] Similar guidelines to control the lifetime of the excitons in SF chromophores, especially to generate long-lived $^{m}(T_1T_1)$ or separated T_1 states are only beginning to emerge. Therefore, it is imperative to understand the nature of the bound triplet-pair state in order to appropriately design (macro)molecules capable of generating persistent triplets by SF. Electronic and spin interactions in $^{m}(T_1T_1)$ may make this state persistent and have a significant effect on the photophysics of SF materials. However, until recently, this state received relatively little attention, mainly because it can be short lived or because it may not be well distinguished from free triplets in transient absorption spectroscopy (TAS), one of the most common techniques for probing SF.

Three key factors have led to the recent surge in papers identifying long-lived and/or strongly bound $^{m}(T_1T_1)$ states. These three factors serve as the outline for our perspective here: first, structure-property relationships have been uncovered because of the advent of molecular SF systems that can be altered with a high degree of synthetic control, modulating the formation and decay of $^{m}(T_1T_1)$.[23] Second, there has been an increase in the number of reports of endothermic SF systems, where a strongly bound $^{m}(T_1T_1)$ state can explain the fast, efficient SF in these systems. And third, different groups leveraging advanced spectroscopies have revealed the presence of $^{m}(T_1T_1)$ states.

For the sake of consistency, we will refer to the bound triplet-pair state as $^{m}(T_1T_1)$ for the cases where it has been observed but the multiplicity was not assigned. In the cases where studies report the spin state through the appropriate characterization strategies, the multiplicity will be stated.

$^{m}(T_1T_1)$ in Molecular Materials

For much of the history of SF, crystalline tetracene was the prototypical molecule where a $^{m}(T_1T_1)$ state was invoked, with this state also having been explored in materials such as diphenylisobenzofuran.[24,25] However, the discovery of SF in non-crystalline systems has led to a huge increase in the number of systems with a resolvable and long-lived $^{m}(T_1T_1)$ state.[13,26–32] In the case of dimers (two covalently bound chromophores), the triplets generated are constrained to be adjacent to one another, and their proximity and orientation can be fine-tuned through chemical modifications. This control can lead to the understanding of the properties of the $^{m}(T_1T_1)$ state and assist in its identification and characterization.[33–35] For example, in directly connected pentacene dimers, the photoinduced absorption signature for the $^{m}(T_1T_1)$ state is clearly distinguished from that of individual triplets populated in triplet sensitization experiments (Figure 3A).[26] The spectral discrepancy is corroborated by a reduced lifetime for the $^{m}(T_1T_1)$ state relative to the individual triplet. We can resolve this by spatially separating the triplets through the inclusion of a biphenyl bridge between the pentacene chromophores. This bridge results in nearly indistinguishable spectra for the $^{m}(T_1T_1)$ state generated from SF and the individual triplet state generated from sensitization. However, a reduced lifetime for $^{m}(T_1T_1)$ and clear signatures of strongly exchange coupled $^{m}(T_1T_1)$ states in subsequent electron spin resonance studies on this biphenyl bridged pentacene dimer confirm the presence of a persistent $^{m}(T_1T_1)$ state.[13] These results indicate that the absence of clear photoinduced absorption signatures is not enough to exclude the presence

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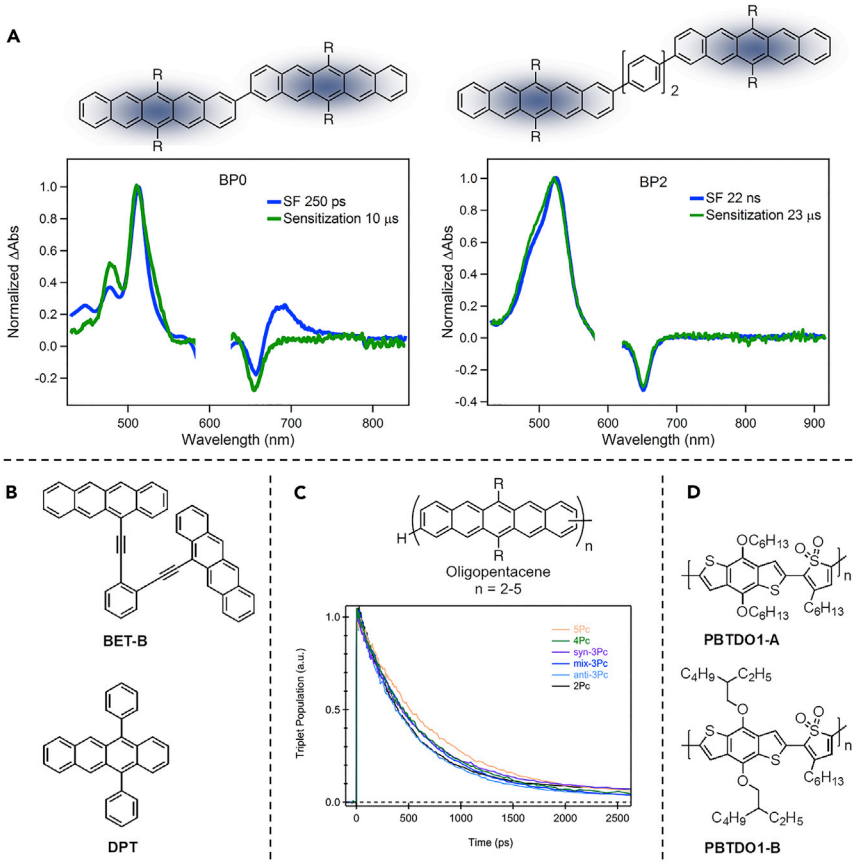

Figure 3. The Bound Triplet-Pair State within Intramolecular Singlet Fission

(A) Comparison of triplet pair $^{m}(T_1T_1)$ spectrum obtained from iSF and individual triplet spectrum obtained from sensitization of directly linked pentacene dimer (**BP0**) and biphenylene spaced pentacene dimer (**BP2**).

(B) Structures of tetracene dimer (**BET-B**) and diphenyl tetracene (**DPT**).

(C) Triplet pair decay kinetics of oligopentacenes.

(D) Thiophene dioxide copolymers investigated for triplet pair dynamics. (Reprinted with permission from Sanders et al., Korovina et al., Sanders et al., and Pace et al.[26,28,34,38])

of a long-lived $^{m}(T_1T_1)$ state. Photoinduced absorption from $^{m}(T_1T_1)$ is highly sensitive to inter-triplet proximity, and less proximate $^{m}(T_1T_1)$ states can remain undetected in many cases.

Thompson, Bradforth, and coworkers noted similarly distinct spectral features and decay dynamics for $^{m}(T_1T_1)$ states in a covalently linked cofacial tetracene dimer (BET-B).[28] Photoexcitation of BET-B (Figure 3B) leads to efficient intramolecular singlet fission (iSF) to an intermediate $^{m}(T_1T_1)$ state, but this $^{m}(T_1T_1)$ state is then trapped on the molecule and recombines rapidly. The authors were able to separate this $^{m}(T_1T_1)$ state by doping BET-B within a diphenyl tetracene (DPT) host that resulted in the successful transfer of one triplet on to DPT, leading to one triplet on both DPT and BET-B.

Early studies on SF dimers showed that electronically coupled chromophores exhibited rapid triplet-pair recombination.[10,26] To expand from dimers to extended systems, our group synthesized discrete oligomers and a conjugated polymer of pentacene.[36] However, while the SF rate steadily increased with oligomer length,

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triplet-pair lifetimes saturated (Figure 3C).[34,36] Irrespective of the number of pentacene units in the chain, the triplet-pair recombination dynamics remained the same after the trimer, suggesting $^{m}(T_1T_1)$ remains bound without sufficient driving force for separation, especially in the absence of π stacking to allow for triplet hopping. This lack of driving force in extracting triplet suggests significant effort must be invested in designing systems that are conducive for triplet migration and extraction. This difficulty in extracting triplet pairs is exemplified in studies on bipentacenes connected to iron oxo clusters discussed in further detail below.[29]

In the solid state, π stacking facilitates Dexter transfer of triplets and can help separate bound $^{m}(T_1T_1)$ states.[37,38] By altering the conjugation length and microstructure of iSF materials, Johnson, Rumbles, and coworkers found a favorable balance between the rate of SF and the separation of triplet pairs could be attained. Through careful control of the microstructure of thin films, they tuned the side chain of thiophene dioxide derivatives (Figure 3D) and studied its influence on the triplet separation efficiency.[38] While the majority of $^{m}(T_1T_1)$ states in this system decay geminately, similar to the solution photophysics of these molecules, a small population diffuses to form long-lived individual triplets in films whose lifetimes exceed 5 ns. Interestingly, for the conjugated polymer poly(benzothiophene dioxide) derivative PBTDO1-A with a linear alkyl side chain, the free triplet yield was significantly higher (~24%) than PBTDO1-B with a branched alkyl side chain (~12%). The authors suggest that the high-chain density in thin films enables better interchain interactions and provides a lower-energy barrier for triplet migration that also inhibits singlet-singlet annihilation. The ability to control the solid-state microstructure is paramount to the separation and harvesting of triplets from iSF.

Our group designed soluble polymers of tetracene derivatives (PolyTc's) that undergo intramolecular SF in solution, analogous to polypentacene in Figure 3C. Thin-film studies revealed a combination of intermolecular and intramolecular SF, where spectral features of the $^{m}(T_1T_1)$ state were evident.[37] TAS experiments revealed the formation of correlated triplet pairs, as evidenced by the slight blue shift of the $T_1 \rightarrow T_n$ photoinduced absorption signal around 500 nm and the rise of a new absorption profile in the infrared region (650–750 nm) that was absent in individual triplets generated by sensitization.

Further, the lifetime of these correlated triplet pairs in solution was ~8 ns compared to an individual triplet (μs timescale) obtained from sensitization experiments. Since iSF proceeds under roughly isoergic conditions in PolyTcs, the correlated triplet pair can also repopulate the singlet excited state, leading to long-lived delayed fluorescence with a similar lifetime to the triplet-pair lifetime from TAS. This observation confirms that the $^{m}(T_1T_1)$ state remains coupled for several nanoseconds, similar to other studies where delayed PL could be observed for tens of ns. However, the photophysics are different in thin films. There, SF and triplet-pair recombination are both accelerated, likely a consequence of enhanced planarity of individual acenes in the film, leading to interchain interactions. As a result, a significant population of triplet pairs produces free triplets with considerably longer lifetimes. These results are consistent with the study on PBTDO1 and show the potential to dissociate $^{m}(T_1T_1)$ states from iSF polymers in thin films. In the future, further experiments such as annealing, side chain engineering, or selection of polymers with longer $^{m}(T_1T_1)$ lifetimes may enhance free triplet generation in the solid state.

The ability to tune the SF properties of iSF materials via synthetic modifications is one of their primary benefits. In particular, various studies have shown that it is

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possible to increase the lifetime of the $^{m}(T_1T_1)$ state generated from iSF, which in turn may enhance free triplet generation. In general, decreasing the coupling between covalently linked chromophores leads to a longer-lived $^{m}(T_1T_1)$ state.[10] This has primarily been observed by increasing the distance between SF chromophores.[13,26,39] Recently, it has been shown that coupling can be dramatically reduced by introducing a non-conjugated bridge between SF chromophores.[40,41] In these cases, the SF chromophores can still be spatially near one another but electronically very decoupled, leading to $^{m}(T_1T_1)$ states that can live up to microseconds. It should be noted that in all cases reporting that the $^{m}(T_1T_1)$ lifetime can be systematically enhanced, a slowdown in the rate of iSF has also been observed. The synthesis of iSF-capable molecules that can generate long-lived $^{m}(T_1T_1)$ states in a sub-ps timescale has not yet been accomplished.

$^{m}(T_1T_1)$ Necessary in Endothermic SF

The energetic requirement for SF chromophores is that the energy of the singlet state is more than twice the energy of its triplet state. However, exceptions to this rule have been reported. Tetracene and its derivatives are prototypical chromophores that have been observed to undergo endothermic SF, where the energy of the singlet state is less than twice the energy of the triplet state. Endothermic SF materials are able to overcome energy barriers of up to 200 meV.[42] These materials show promise for PV applications, as they typically have triplet energies that are high enough to donate into known high-performance semiconductors such as Si. The mechanism underlying endothermic SF is widely debated, although it is generally accepted that some type of intermediate state is needed to explain the unfavorable energetics. An intermediate like the $^{m}(T_1T_1)$ state that is lower in energy than the singlet state likely explains the existence of endothermic SF.

One such derivative, 5,12-bis(triisopropylsilylethynyl)tetracene (TIPS-tetracene), has recently been used to study endothermic SF. TIPS-tetracene exhibits sharp singlet and triplet absorption features, which facilitates the tracking of these states as they evolve over time. Stern et al. proposes a mechanism for endothermic SF in TIPS-tetracene films where $^{m}(T_1T_1)$ formation is independent of temperature and free triplet formation is thermally activated.[43] Vibrational coherence aids the equilibrium between the singlet and $^{m}(T_1T_1)$ state; as vibrations are dampened, the population moves toward the lower-energy-bound triplet-pair state. The $^{m}(T_1T_1)$ state is long lived but can be thermally dissociated to form higher-energy free triplets (Figure 3). The formation of free triplets depends not only on thermal activation but also on crystal morphology. The authors observe that the crystalline TIPS-tetracene film has longer-lived $^{m}(T_1T_1)$ states than the disordered TIPS-tetracene film because of more favorable orientations for triplet hopping. These differences in lifetime based on film morphology strongly suggest the need for film characterization data when reporting new work, as discussed further below. Overall, this work sets an important foundation for describing a holistic picture of endothermic SF.

Friend and coworkers have also probed the character of this intermediate state in solutions of TIPS-tetracene (Figure 4). They observe the rapid formation of an intermediate in concentrated solutions, which dissociates into free triplets over a longer timescale.[44] This intermediate has both singlet and triplet character and is labeled as an excimeric state. No such intermediate is observed in films of TIPS-tetracene, which is justified by a lesser degree of stabilization from the excimer in the solid state.

In contrast to these results, Schmidt and coworkers argued that endothermic SF involves an excimer state that acts as a trap rather than an intermediate.[45] The authors

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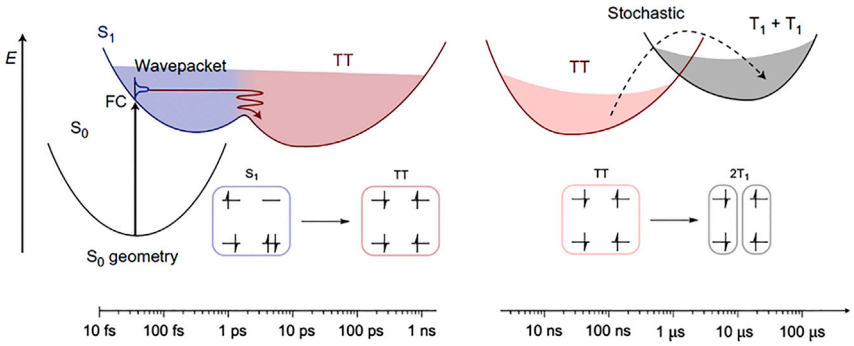

Figure 4. Mechanism of Endothermic Singlet Fission via a Bound Triplet-Pair State

Comprehensive mechanism of endothermic SF from literature where vibrations facilitate the equilibrium between the singlet state and the lower energy bound triplet-pair state.[78] Upon thermal activation, the bound triplet pair stochastically dissociates into free triplets (reprinted with permission from Stern et al.[43]).

claim that if the excimer is observed as an intermediate in SF, then it should also be observed as an intermediate in the reverse process, triplet-triplet annihilation. Discrepancies between the emission spectra of sensitized triplet-triplet annihilation on TIPS-tetracene and concentrated solutions of TIPS-tetracene prompted the authors to employ various kinetic models to discern the states involved. The best fit to both the time-resolved and steady-state data observed is with a model necessitating the excimer as a trap in SF. By this model, eight times as many triplets are generated from the S_1 state as from the excimer. Removing excimer formation from the model could drastically increase the triplet yield. Whether the $^m(T_1T_1)$ state can be termed an excimer or what role an excimer has, if any, in endothermic SF is still under discussion. Continued research is necessary to elucidate the nature of the $^m(T_1T_1)$ state and better understand the excited-state dynamics of endothermic SF systems.

Endothermic SF also occurs in intramolecular SF systems of tetracene derivatives. In pentacene-tetracene dimers, sensitization experiments conclude that the triplets generated from iSF are similar, but not identical, to photosensitized free triplets.[33,46] This is used to support the formation of a bound triplet pair. iSF in these systems generates bound triplet pairs that do not significantly dissociate into free triplets—the $^m(T_1T_1)$ state is presumed to be lower in energy than the free triplet state to justify the existence of endothermic SF.

Outside of acenes and their derivatives, endothermic SF has been reported in films of perylenediimides (PDIs) and zethrenes, among others. In films of PDI, Le et. al. did not observe more than one type of triplet state and thus did not distinguish between the bound triplet-pair state and the free triplet state.[47] They instead examined how CT states mediate endothermic SF. In these systems, CT states introduce a lower-energy state, which must be escaped to undergo SF. Structural differences between their PDI derivatives change the solid-state packing and therefore the amount of CT interactions and the rate of SF.

Lukman et al. reported a family of zethrene diradicaloids, some of which undergo endothermic SF.[48] They observed temperature-independent $^m(T_1T_1)$ formation in their endothermic SF materials and no subsequent dissociation into free triplets. They suggested that the inter-triplet binding energy brings the energy of the $^m(T_1T_1)$ state below the singlet energy, and they found that thermal fluctuations at room temperature are insufficient in most zethrene films to separate the bound triplets.

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$^{m}(T_1T_1)$ Revealed by a Variety of Spectroscopic Techniques

Applying innovative spectroscopic techniques has led to the observation of the $^{m}(T_1T_1)$ state in greater detail and across a larger range of samples. For example, recent work has demonstrated the presence of a $^{m}(T_1T_1)$ state from SF in well-studied materials such as pentacene, tetracene, TIPS-pentacene, and TIPS-tetracene, where this state was previously overlooked.[14,43,44,49–52]

Pentacene is possibly the most prototypical SF material and has been studied extensively by photoluminescence and TAS measurements for decades.[2,53] A particularly recent and detailed study by Friend and coworkers used TAS with corrections for thermal heating and other considerations to assign the SF and triplet lifetimes in the material. Using these lifetimes, they constructed the model shown below (Figure 5A).[54,55] Notably, there is no $^{m}(T_1T_1)$ state in this model. However, work by Zhu and coworkers on the same material, but employing time-resolved two-photon photoemission spectroscopy, resolved the presence of an intermediate $^{m}(T_1T_1)$ state (Figure 5B).[56] They interchangeably referred to $^{m}(T_1T_1)$ as the ME state and found that this state falls between the singlet exciton and dissociated triplets. The advantage of two-photon photoemission spectroscopy is that by measuring the kinetic energy of emitted photons this technique resolves state energies. In contrast, TAS only probes transitions between states. This technique is therefore able to more sensitively resolve differences in the energy of triplets in the ME state relative to free triplets.

The high time resolution and ability to resolve state energies has also revealed unusual kinetics for the rise of $^{m}(T_1T_1)$, which Zhu and coworkers further explored in later work on hexacene.[57] They concluded that vibronic coherence produces a coherent channel for SF that coexists with a slower, incoherent pathway. This conclusion agrees well with measurements of pentacene and its derivatives using 2D electronic spectroscopy, another emerging spectroscopic technique that provides insight into the coupling of the singlet and $^{m}(T_1T_1)$ state by vibrational modes.[58] Zhu and coworkers also investigated harvesting of $^{m}(T_1T_1)$ from variable height layers of pentacene on C_{60} fullerene and found more efficient harvesting from $^{m}(T_1T_1)$ than from individual triplets (T).[56] This interesting result is consistent with other recent results suggesting significant differences in the harvesting from $^{m}(T_1T_1)$ state compared to T.[29]

New spectroscopic strategies have proven effective to interrogate $^{m}(T_1T_1)$. For example, probing in the near or even mid infrared region has been effectively leveraged to study $^{m}(T_1T_1)$.[29,52,59,60] This region is typically free of ground-state bleaching because it is well beyond the absorbance onset of most SF chromophores, simplifying interpretation. Furthermore, these regions have been found to feature signatures unique to the $^{m}(T_1T_1)$ state. Indeed, these features were assigned to a $^{m}(T_1T_1)$-to-singlet transition,[29] indicating strong electronic coupling between the two. A similar result was found in theoretical work by Mazumdar and coworkers who assigned a photoinduced transition near 1400 nm in pentacene dimers to from $^{1}(T_1T_1) \rightarrow S_2$.[61,62] Such transitions between one and two exciton manifolds have been reported previously in work by the Knoester group.[63]

Additional information can be gleamed from TAS by probing even further into the infrared; Grieco et al. have identified transitions between $^{1}(T_1T_1)$ and S_1 that lie near 0.3 eV.[64] Using this spectroscopic handle, they can follow the dissociation of $^{m}(T_1T_1)$ to (T…T) and eventually to free triplets. These studies highlight the utility of longer-wavelength probes to interrogate the formation and dissociation of $^{m}(T_1T_1)$.

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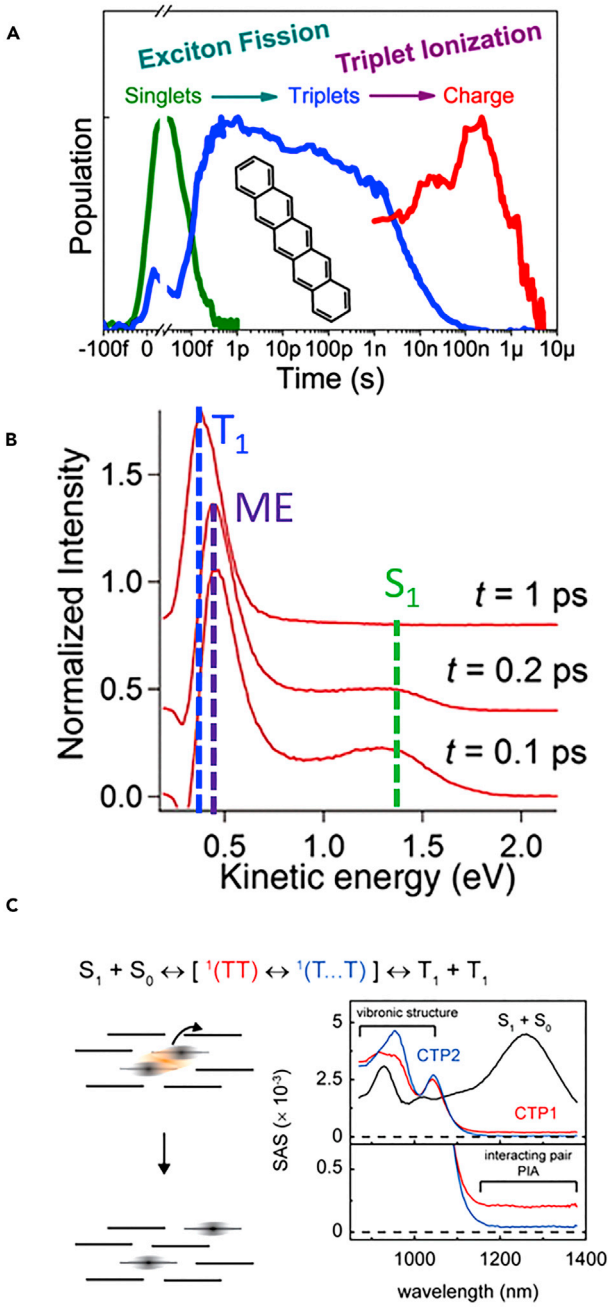

Figure 5. Time-Resolved Spectroscopy on the Bound Triplet-Pair State in Pentacene

(A) TAS study that does not resolve $^{m}(T_1T_1)$ in solid pentacene.

(B) Time-resolved two photon photoemission study on solid pentacene that does resolve a $^{m}(T_1T_1)$ state.

(C) TAS study of pentacene-based aggregates where probing in the near infrared resolves several stages of triplet-pair separation. Reprinted with permission from Wilson et al., Chan et al. and Pensack et al.[15,55,61]

It is common for different spectroscopic signals in TAS to overlap. An innovative approach to reduce overlapped signals was reported in two independent studies on crystals of rubrene,[65] and hexacene.[57] In both cases, highly polarized singlet absorption was used to provide a reduction in signal overlap and provided a key

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insight: the coherent pathway for $^{m}(T_1T_1)$ promotion. The presence of a nearly instantaneous signal at time zero is most clearly observed because of the suppression of singlet signals based on the selective probing along a specific facet. A similar conclusion was found by Miyata et al. using temperature as a variable, where they saw that the coherent $^{m}(T_1T_1)$ population was temperature independent, while the incoherent process was strongly affected by temperature.[66]

Another emerging technique for probing the role of $^{m}(T_1T_1)$ in SF is time-resolved electron spin resonance (tr-ESR).[40,67,68] This technique has recently been used to directly interrogate $^{m}(T_1T_1)$ in films of TIPS-tetracene or solutions of bipentacene.[13,14] In this experiment, an optical pulse populates excited states that evolve in time, and transiently populated paramagnetic species are probed by a continuous wave microwave source. The experiment is repeated at different magnetic fields to compile a dataset of microwave absorption and emission as a function of magnetic field and time. This approach can find magnetic resonances for transitions between magnetic sublevels of T or $^{m}(T_1T_1)$. However, it is only sensitive to relatively long-lived paramagnetic species (>50 ns) with a net spin polarization. As such, $^{1}(T_1T_1)$ cannot be observed, and $^{3}(T_1T_1)$ has not been observed directly. Still, the ability to directly measure spin states is extremely powerful. For example, in films of tetracene, the Behrends group found that at low temperatures, $^{5}(T_1T_1)$ states are populated and feature ~3 microsecond lifetimes and nearly 1 microsecond coherence times.[14] This result, as well as the ESR line shape observed, suggests strong exchange coupling between triplets produced by SF and the need for thermal activation to separate these states.

In the case described above, intermolecular interactions contributed to the long lifetimes of the excited state. However, the ability to engineer covalent intramolecular interactions in pentacene dimers has allowed us to correlate population and magnetization dynamics in the same system. For example, these studies have led to the first observation of an excited quintet state in individual closed-shell molecules. Recently, our group studied SF in pentacene dimers using tr-ESR (Figure 6A).[13,40] In these dimers, it is impossible for triplets to diffuse apart because they are constrained to isolated molecules. Therefore, pure $^{5}(T_1T_1)$ states were observed at all temperatures studied, indicating strong exchange coupling (Figure 6B). Similar to the studies above, the spin multiplicity was determined through nutation experiments, where coherent manipulation of the spin state compared to a triplet state yields the expected nutation frequency for quintets. The unambiguous observation of $^{5}(T_1T_1)$ in these publications suggests the strength of the tr-ESR technique for yielding new insights into systems that have already been well investigated by standard techniques. It should be noted that it is dangerous to simply assume spin states in the absence of magnetic resonance data. Spin states cannot always be inferred from optical spectroscopy alone, and such assumptions can lead to confusion in the literature.[69,70]

Photoluminescence measurements can also be used to provide powerful insights into the nature of $^{m}(T_1T_1)$. For example, photoluminescence spectroscopy can yield information about $^{m}(T_1T_1)$ in cases where singlet and $^{m}(T_1T_1)$ exist in equilibrium. In one such work, our group used the discrepancy between the triplet lifetime observed in TAS and the lifetime of delayed fluorescence in pentacene-tetracene heterodimers to establish the $^{m}(T_1T_1)$ lifetime.[33] The presence of triplet signal in TAS after the decay of the delayed fluorescence suggests a change in exciton correlation from the $^{m}(T_1T_1)$ state to a dark state, likely a single pentacene triplet.

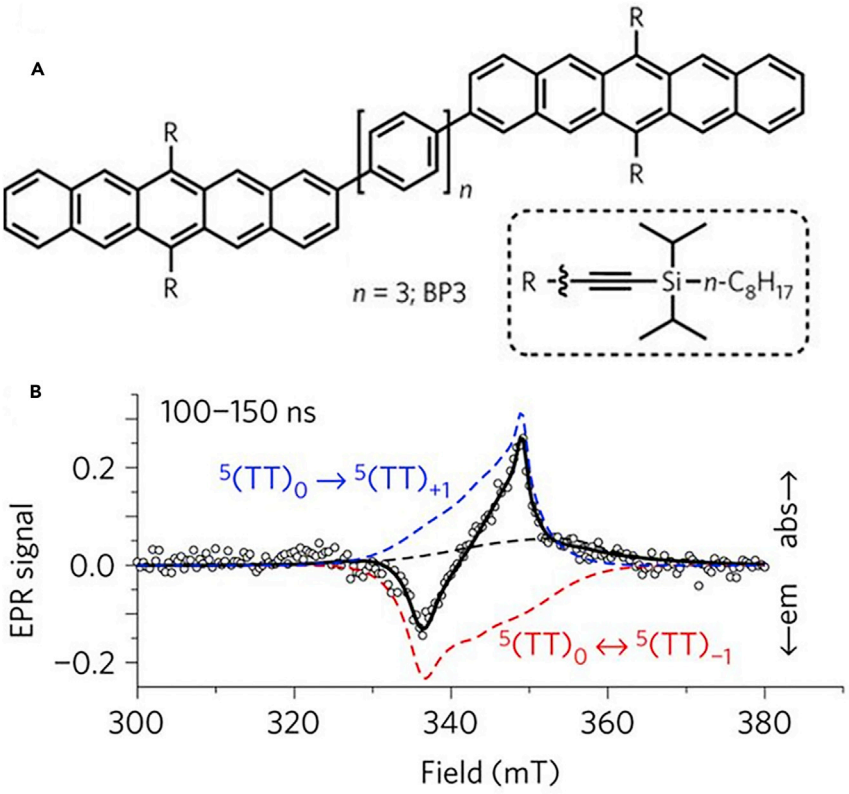

Figure 6. Time-Resolved Electron Spin Resonance of BP3

(A) Structure of pentacene dimer BP3 studied by the McCamey group.

(B) Time-resolved two-electron spin resonance (tr-ESR) showing the presence of quintets in this molecular system. Reprinted with permission from Tayebjee et al.[13]

Bardeen and coworkers took this approach one step further by using quantum beating in the delayed photoluminescence to make inferences about the spin states involved in SF.[18] In solid tetracene, even in the absence of a magnetic field, zero field splitting lifts the degeneracy of triplet states. SF is faster in solid tetracene than the oscillation between different $^{m}(T_1T_1)$ states. Over time, the system oscillates between the different states based on their energy differences and acquires a phase, affecting the rate of triplet fusion and therefore manifesting in intensity oscillations in delayed fluorescence. The authors also studied the effects of a magnetic field on the quantum beating of delayed photoluminescence. These measurements represent an indirect but rapid and inexpensive way to interrogate $^{m}(T_1T_1)$.

Transient absorption microscopy can also be employed to gain insights into $^{m}(T_1T_1)$, specifically the mechanism of how this state relates to the transport of singlet and triplet excitons in a film. An example of this approach was shown by Huang and coworkers with tetracene as the substrate.[59,60] In this experiment, the researchers were able to observe the spatial evolution of an exciton as a function of time. Interestingly, the authors found a faster exciton mobility for the triplets at early times and slower movement at later times (Figure 7A). The authors attributed this difference to the equilibrium between the triplet-pair state and the singlet exciton (Figure 7B). As long as the triplet pair remains bound and in equilibrium with the singlet, it can move by Forster transport or Dexter transfer, while individual triplet excitons may move only by Dexter transfer. Therefore, the $^{m}(T_1T_1)$ state is much more mobile than

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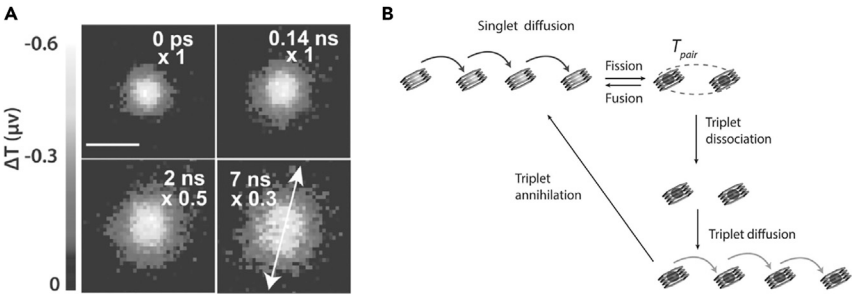

Figure 7. Exciton Diffusion of the Bound Triplet-Pair State via Ultrafast Microscopy
(A) Intensity map of triplet absorption as a function of distance from the excitation. The exciton diffuses biexponentially, which can be explained by (B) inclusion of a $^{m}(T_1T_1)$ state in the kinetic model in equilibrium with the singlet at early times. Reprinted with permission from Zhu et al.[60]

individual triplets. It should be noted that the early work of Huang and coworkers did not posit the $^{m}(T_1T_1)$ state in their model of SF. They have since expounded on this model to include $^{m}(T_1T_1)$ and observed that the $^{m}(T_1T_1)$ state has transport properties similar to the bright singlet exciton from which it originates because of equilibrium between these states.[71] Similar observations were also reported for rubrene, while TIPS-pentacene displayed a shorter-lived $^{m}(T_1T_1)$ state and less singlet-mediated transport.[60] Ginsberg and coworkers recently employed transient absorption microscopy with polarization dependence as an additional tool to study TIPS-pentacene.[50] Their results suggested a ~300 picosecond lifetime for $^{m}(T_1T_1)$. While this value is longer than the value reported by Huang and coworkers, studies by Christopher et al. have shown a dependence of sample morphology on $^{m}(T_1T_1)$ separation rates in TIPS-pentacene, and it is plausible that these measurements are all self-consistent, but on slightly differently prepared TIPS-pentacene substrates.[72] Thus, it is imperative to keep in mind that thin-film-based measurements should be accompanied by proper structural characterization, in the vein of the major strides made in second-generation PVs.[73,74] For example, at a minimum, X-ray scattering and thin-film absorption spectra should be reported for any thin-film SF studies.

Moving forward, it is clear that key information about the $^{m}(T_1T_1)$ state is emerging, thanks to recent advances in spectroscopic techniques. It is important not only to continue developing new and more powerful spectroscopic methods but also to recognize the shortcomings of methods that we may employ. For example, TAS is not always able to spectrally distinguish $^{m}(T_1T_1)$, especially when only employed in the visible. However, if a triplet signal from photoexcitation has a shorter lifetime than the triplet signal from sensitization experiments, one should consider the likelihood of $^{m}(T_1T_1)$ geminate recombination contributing to the shorter lifetime. Moving forward, we must use several different techniques to paint complete pictures of the samples we study, and we must keep in mind the wealth of information reported by others on $^{m}(T_1T_1)$ and factor it into our own analysis.

Outlook—Is $^{m}(T_1T_1)$ a "Problem"?

Despite the growing amount of information on the presence and dynamics of the $^{m}(T_1T_1)$ state, it remains to be seen how this state affects the prospects of SF materials in PV devices. External quantum efficiencies greater than 100% have been demonstrated in solar cells using crystalline pentacene,[8] but the triplet pairs generated in this material are known to rapidly dissociate, generating free triplet excitons. A solution-cast TIPS-pentacene layer was shown to exhibit an internal quantum efficiency (IQE) over 100% in a bilayer architecture with PbSe nanocrystals,[75] which is

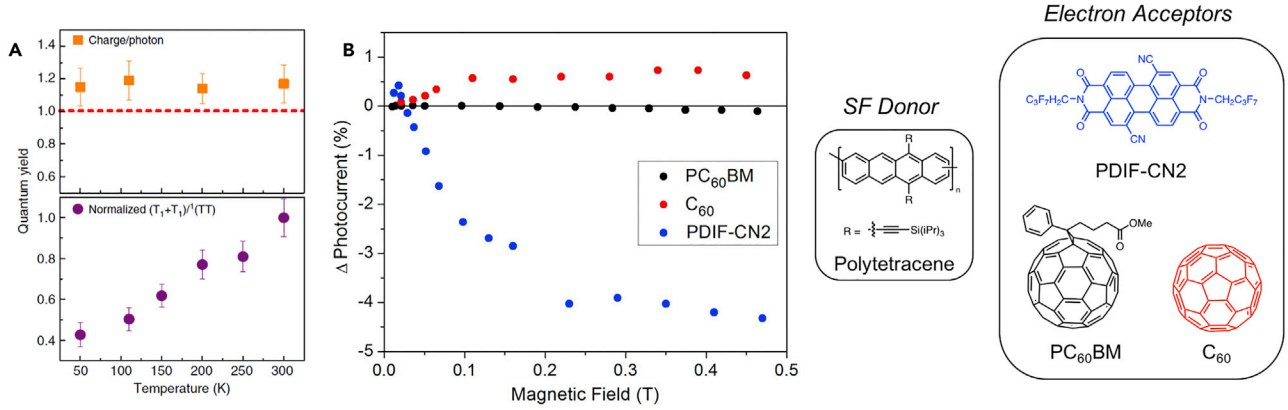

Figure 8. Extracting the Bound Triplet-Pair State in an Optoelectronic Device

(A) Internal quantum efficiency of an F2-TES ADT-PC71BM blend device is independent of temperature (reprinted with permission from Pun et al.[77]).
(B) Magnetic-field effect (MFE) on photocurrent of polytetracene bilayer devices with various acceptors (reprinted with permission from Yong et al.[37]).

known to generate a short-lived $^m(T_1T_1)$ state.[50] These two efficient examples beg the question of whether the decay of $^m(T_1T_1)$ to two individual triplet excitons is a necessity for charge extraction in a device.

Meanwhile, other studies have suggested the $^m(T_1T_1)$ state may be beneficial, in some ways, for charge extraction. It was shown recently by Huang and coworkers that if the energy of the $^m(T_1T_1)$ state was close to that of the singlet, these two states could readily interconvert, leading to long-range diffusion of the $^m(T_1T_1)$ state in a crystal.[59] This long exciton diffusion length is beneficial for charge extraction in PVs. Furthermore, it has been shown several times that it is possible to extract charge directly from the $^m(T_1T_1)$ state. Zhu and coworkers have shown that triplet pairs generated by either pentacene[56] or tetracene[76] can be extracted by C_{60} in a bilayer architecture. Sirringhaus and coworkers demonstrated that by modulating temperature, the population of $^m(T_1T_1)$ relative to free triplets could be tuned.[77] However, in spite of the change in $^m(T_1T_1)$ versus free triplet, the IQE of the anthradithiophene-$PC_{71}BM$ device remained the same across all temperatures (Figure 8A). The constant IQE demonstrates that charge separation is possible for either the $^m(T_1T_1)$ state or free triplets generated from SF. And by observing a photocurrent dependence on applied magnetic field, Campos and coworkers have demonstrated that $^m(T_1T_1)$ states generated from iSF in a tetracene polymer can be extracted, provided the charge acceptor used has a sufficient electron affinity (Figure 8B).[37] In contrast, there have been several publications that have shown that the $^m(T_1T_1)$ state is a tightly bound state that can prevent charge separation.[29,47] Work from our group has shown that in the case of iSF, the $^m(T_1T_1)$ state generated in a directly linked pentacene dimer is too tightly confined and short lived to allow CT to an iron cluster.[29]

In designing materials and devices using SF materials, the important parameters to optimize are as follows: first, SF must occur fast enough to outcompete other singlet decay processes. Second, the $^m(T_1T_1)$ state decay to the ground state must be outcompeted by direct extraction or separation to individual triplets. Considering the contrasting results described above, the role of $^m(T_1T_1)$ must be evaluated on a case-by-case basis. Generally, the coupling of triplet in the $^m(T_1T_1)$ state itself is not a barrier to efficient charge separation and transfer. Instead, the main factor that determines whether or not excitons generated from SF can be extracted properly is whether they have a sufficiently long lifetime, either as $^m(T_1T_1)$ or T+T,

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permitting exciton harvesting before ground-state recombination. These parameters must be satisfied either by molecular engineering of the material itself or by engineering the bulk morphology of the material - the mesoscale. Together, these design rules ensure the two triplets generated by SF can be extracted, either as a $^{m}(T_1T_1)$ state or two individual triplets.

Conclusions

In conclusion, the $^{m}(T_1T_1)$ state continues to be a topic of growing importance within the field of SF. As an intermediate state between the initial photoexcited singlet and free triplets, it is important to understand the nature of this state. The advent of iSF materials and new spectroscopies has allowed us to more accurately probe this state, but questions remain about the exact role this state plays in SF, especially in endothermic SF. And finally, while much attention has been given to understanding how $^{m}(T_1T_1)$ can be separated into individual triplets, recent work has supported the notion that this may not be necessary for eventual device applications. Instead, the focus should be on rapidly generating a high yield of $^{m}(T_1T_1)$ states, which are mobile and persistent, either within the SF material itself or at an interface with an acceptor.

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