

## Review

## Magnetic field effects on singlet fission dynamics

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**Singlet fission can double the photon-to-electron conversion efficiency by splitting a singlet exciton into two triplets via an intermediate state of a triplet pair. The spin mixing of triplet pair manifolds with different spin characters is a determining factor for the efficiency of final triplet generation. In this review, we summarize recent studies of magnetic field effects (MFEs) on singlet fission dynamics, from theoretical models to recent experimental results. The analyses of MFEs support a three-step model with dynamic equilibrium between strongly and weakly coupled triplet pairs, suggesting an intermediate regime of intertriplet coupling to be favorable for singlet-quintet mixing toward efficient triplet generation for practical applications.**

## Triplet pair states

Singlet fission is a spin-allowed process that converts two triplets from a photo-excited singlet state in molecular systems [1,2]. Research interest in singlet fission has grown rapidly over the past decade, being motivated by the potential use of such singlet fission in solar cells to exceed the **Shockley–Queisser limit** (see [Glossary](#)) [3–7]. Intensive efforts have been made to study intermolecular and intramolecular singlet fission systems. In a commonly used view of singlet fission, a photo-excited singlet state ( $S_1$ ) on one molecule interacts with the neighboring one in the ground state  $S_0$  to form a triplet pair state  $^1(TT)$  distributed over two molecules [8–12]. This intermediate  $^1(TT)$  state is subsequently dissociated into two individual triplets, that is,  $S_0 + S_1 \leftrightarrow ^1(TT) \leftrightarrow T_1 + T_1$  [9,13–15]. Elucidating the generation and dissociation dynamics of triplet pair states is pivotal for understanding the mechanism of singlet fission [9,10,16–28], which may guide expanding chromophore pools of singlet fission materials for potential applications [29–36].

The effect of magnetic fields (i.e., MFE) has been widely applied in the study of triplet pair states since the inception of singlet fission. As early as 1960s, the MFE on **delayed fluorescence** was observed as experimental evidence for the involvement of triplet pair states in the photophysics of crystalline acenes [37–41]. Utilizing state-of-the-art techniques, including the optically detected sublevel resonance approached by applying a microwave and/or magnetic field [42–47], quantum beat spectroscopy [48–52], and **time-resolved electronic spin resonance** (tr-ESR) [53–60], has deepened our understanding of triplet pair states in recent years [46,61]. MFEs on delayed fluorescence in the weak field regime (<1 Tesla) is relevant for the population redistribution of the manifolds of the triplet pairs with weak exchange coupling. For triplet pairs with strong exchange coupling, the eigenstates at zero magnetic field comprise the pair states with singlet ( $S = 0$ ), triplet ( $S = 1$ ), and quintet ( $S = 2$ ) spin characters. Spin mixings between triplet pairs with different spin characters, as probed by MFE studies, are essential for understanding the dissociation processes of triplet pairs.

## Models of MFEs on triplet pair dynamics

The theoretical understanding of MFEs starts from a model proposed by Johnson and Merrifield that describes triplet–triplet annihilation with triplet pair states [39]. Assuming the spin operators

## Highlights

Singlet fission holds great potential to boost the efficiencies of solar cells by converting one photo-excited singlet exciton into two triplets via an intermediate state of triplet pairs with different exchange couplings.

Magnetic field effects (MFEs) are induced by spin mixing between the triplet pair manifolds with different spin characteristics. The strongly and weakly coupled triplet pairs exhibit MFEs with magnetic field strength in different regimes.

The quintet channel is the major pathway for highly efficient generation of free triplets. Singlet-quintet mixing is enabled by dynamic equilibrium between strongly and weakly couple triplet pairs through spatial separation and/or structure fluctuation.

Intermediate intertriplet coupling is suggested for the efficient generation and dissociation of triplet pairs for highly efficient singlet fission for practical applications.

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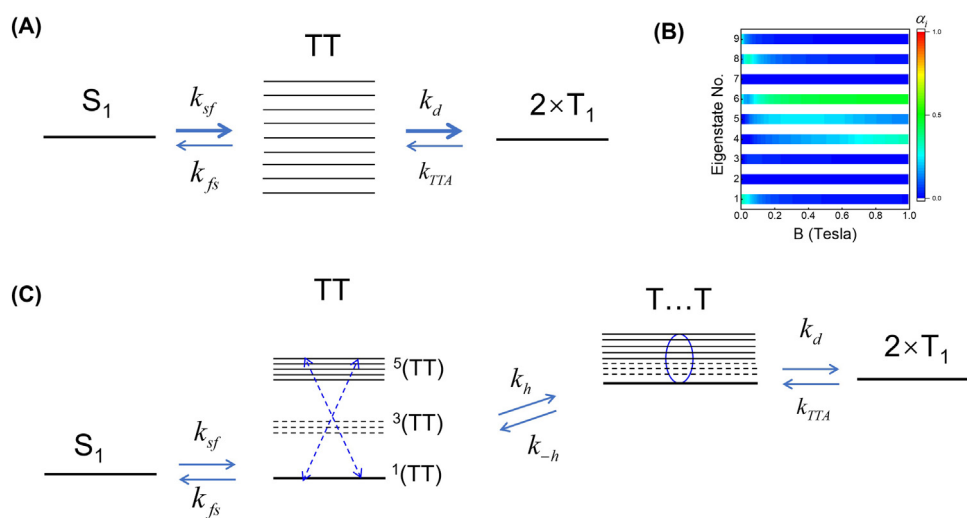


$\hat{S}_i = (\hat{S}_{i,x}, \hat{S}_{i,y}, \hat{S}_{i,z})$  ( $i = 1, 2$ ) are the spin operators of the two triplets, the spin part of the **Hamiltonian** for a triplet pair can be expressed using Equation 1 [42,44,61,62]:

$$\begin{aligned} \hat{H}_{spin} &= \sum_{i=1,2} \hat{H}_{i,zfs} + \hat{H}_{ex} + \sum_{i=1,2} \hat{H}_{i,zeeman} \\ \hat{H}_{i,zfs} &= D \left( \hat{S}_{i,z}^2 - \frac{1}{3} \hat{S}_i^2 \right) \\ \hat{H}_{ex} &= J \hat{S}_1 \cdot \hat{S}_2 \\ \hat{H}_{i,zeeman} &= g \mu_B \vec{B} \cdot \hat{S}_i \end{aligned} \quad [1]$$

Here,  $\hat{H}_{i,zfs}$  is the **zero-field splitting interaction** with parameter  $D$ ,  $\hat{H}_{ex}$  is the exchange interaction with the coupling strength  $J$ , and  $\hat{H}_{i,zeeman}$  is the **Zeeman interaction** from the applied external magnetic field.

In term of exchange coupling strength due to orbital overlap, the triplet pairs can be catalogued into weakly ( $J \leq D$ ) and strongly ( $J \gg D$ ) interacting regimes. Weakly and strongly coupled triplet pairs may coexist in the same material, which can be described by a three-step model, that is,  $S_0 + S_1 \leftrightarrow {}^1(TT) \leftrightarrow {}^1(T...T) \leftrightarrow T_1 + T_1$  [13,61,63,64]. This model was first proposed by Scholes and coworkers to describe the spatial separation of triplet pairs in the crystalline pentacene film [63,65]. In aggregates or crystalline solids, the  ${}^1(TT)$  and  ${}^1(T...T)$  states may be distinguished by the intertriplet distance, being strongly and weakly interacting triplet pairs. In dimeric molecules, despite the limitation of spatial separation, exchange coupling is proposed to fluctuate significantly due to intermolecular vibrations [66,67]. The dynamic equilibrium between strongly and weakly interacting triplet pairs in dimers may be also rationalized within the three-step model. From this consideration, we refer to  $(TT)$  and  $(T...T)$  for the triplet pairs with strong and weak exchange interactions, respectively, in the following.



**Figure 1.** Theoretical models describing the magnetic field effects (MFEs) of singlet fission dynamics. (A) The original Merrifield scheme, which involves nine manifolds of correlated triplet pairs [68]. (B) MFEs of singlet projections of the nine states of weakly exchange-coupled triplet pairs in a weak field regime (<1 Tesla). The data are calculated using the parameters of tetracene molecules with  $J = 1 \mu\text{eV}$ . (C) The modified scheme including strongly and weakly coupled triplet pairs [20,61,62].

## Glossary

**Delayed fluorescence:** triplets created by singlet fission fuse back to singlet states, which recombine to the ground state and emit fluorescence. Delayed fluorescence is induced by the regenerated singlets, which has a later arrival in the time domain than the fluorescence emission from direct optical excitation.

**Dexter mechanism:** transfer of excited electrons from one molecule to another via a nonradiative path, which requires a wavefunction overlap between the two molecules.

**Eigenstates:** states of a quantized system in which one of the variables (i.e., energy or angular momentum) defining the state has a fixed value (eigenvalue).

**Hamiltonian:** operator corresponding to the total energy of a system.

**Herzberg–Teller coupling:** on symmetry grounds, certain ‘forbidden’ vibronic transitions are activated due to ‘intensity borrowing’ via a nontotally symmetric mode of appropriate symmetry, known as Herzberg–Teller mixing.

**Level crossing resonances:** energies of two levels are tuned by an external field to near-degeneracy.

**Optically detected magnetic resonance:** in a static magnetic field, the spin degeneracy is lifted with multi-sublevels separated due to Zeeman interactions. An external microwave field may mix the sublevels with resonance energy difference, leading to a change in fluorescence emission. By detecting the emission intensity as a function of magnetic field amplitude, we can observe the resonance phenomenon and calculate the magnitude of the interaction.

**Quantum beats:** time-domain oscillation behaviors of populations of excited states in a superposition, which may be probed by time-resolved spectroscopy.

**Shockley–Queisser limit:** in a single junction organic solar cell, the detailed balanced limit of power conversion efficiency was predicted to be ~30% in a seminal paper by Shockley and Queisser [5].

**Time-resolved electronic spin resonance:** temporal resolution technique used to directly detect changes in microwave intensity due to transitions between levels of different spin characters.

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The original Merrifield model has described the triplet pair manifolds with a nine-spin state representation without considering orbital overlaps [68]. This approach can well describe the MFE of the ( $T\dots T$ ) states with weak exchange coupling. As sketched in Figure 1A, singlet state  $S_1$  undergoes fission to one of the **eigenstates** ( $|P_i\rangle$ ) of triplet pair at a rate  $\Gamma_{sf}\alpha_i$ , where  $\alpha_i$  is the overlap between the spin wave functions of the singlet and triplet pair states, that is,  $\alpha_i = |\langle S|P_i\rangle|^2$  [48,51]. The triplet pair can dissociate into free triplets at rate  $k_d$  or fuse back to reform the singlet exciton at a rate  $k_{fs}\alpha_i$ . The MFE is mainly caused by the Zeeman interaction-induced change of  $\alpha_i$  (Figure 1B). For the weakly coupled ( $T\dots T$ ) states, the zero-field splitting mixes the singlet and quintet states. Magnetic fields with a relatively weak magnitude may strongly alter  $\alpha_i$ , resulting in a marked MFE. Such a model well explains the MFE on the steady-state photoluminescence (PL) emission in crystalline SF materials. Assuming that PL emission is solely from the singlet state, the steady-state PL can be roughly described using Equation 2 [42]:

$$I = I_0 \left[ \sum_i \alpha_i \left( 1 + \frac{k_{sf}}{k_d} \alpha_i \right)^{-1} \right]^{-1} \quad [2]$$

The emission intensity depends nonlinearly on  $\alpha_i$  which varies when the Zeeman interaction changes. Moreover, the coherence between the manifolds of triplet pair states may lead to the **quantum beats** manifesting with oscillations in the time-domain PL traces. The beating frequencies (i.e., the energy differences between the triplet pair eigenstates) are susceptible to the magnetic field, resulting in the MFE of quantum beatings in the delayed fluorescence [48,50].

The strongly coupled  $^1(TT)$  triplet pair state is particularly important at the initial stage of singlet fission [26,61,64,69,70], which has not been included in the original Merrifield model. In the strong exchange coupling regime ( $J \gg D$ ), the eigenstates have well-defined spin multiplicity. In the nine-spin state representation, the triplet pair manifolds comprises one singlet [ $^1(TT)_0$ ], three triplet [ $^3(TT)_1, ^3(TT)_0, ^3(TT)_{-1}$ ], and five quintet levels [ $^5(TT)_2, ^5(TT)_1, ^5(TT)_0, ^5(TT)_{-1}, ^5(TT)_{-2}$ ]. The MFE is insignificant in the weak-field regime. With a strong magnetic field, Zeeman interaction can detune the energy gaps between the triplet pair manifolds to the regime in which the zero-field splitting can mix the singlet–quintet, singlet–triplet, and triplet–quintet pair states. To explain the MFE in this regime, it is necessary to revise the Merrifield model to include the strongly coupled triplet pairs (Figure 1C) [20,61,62].

### Quantum beats

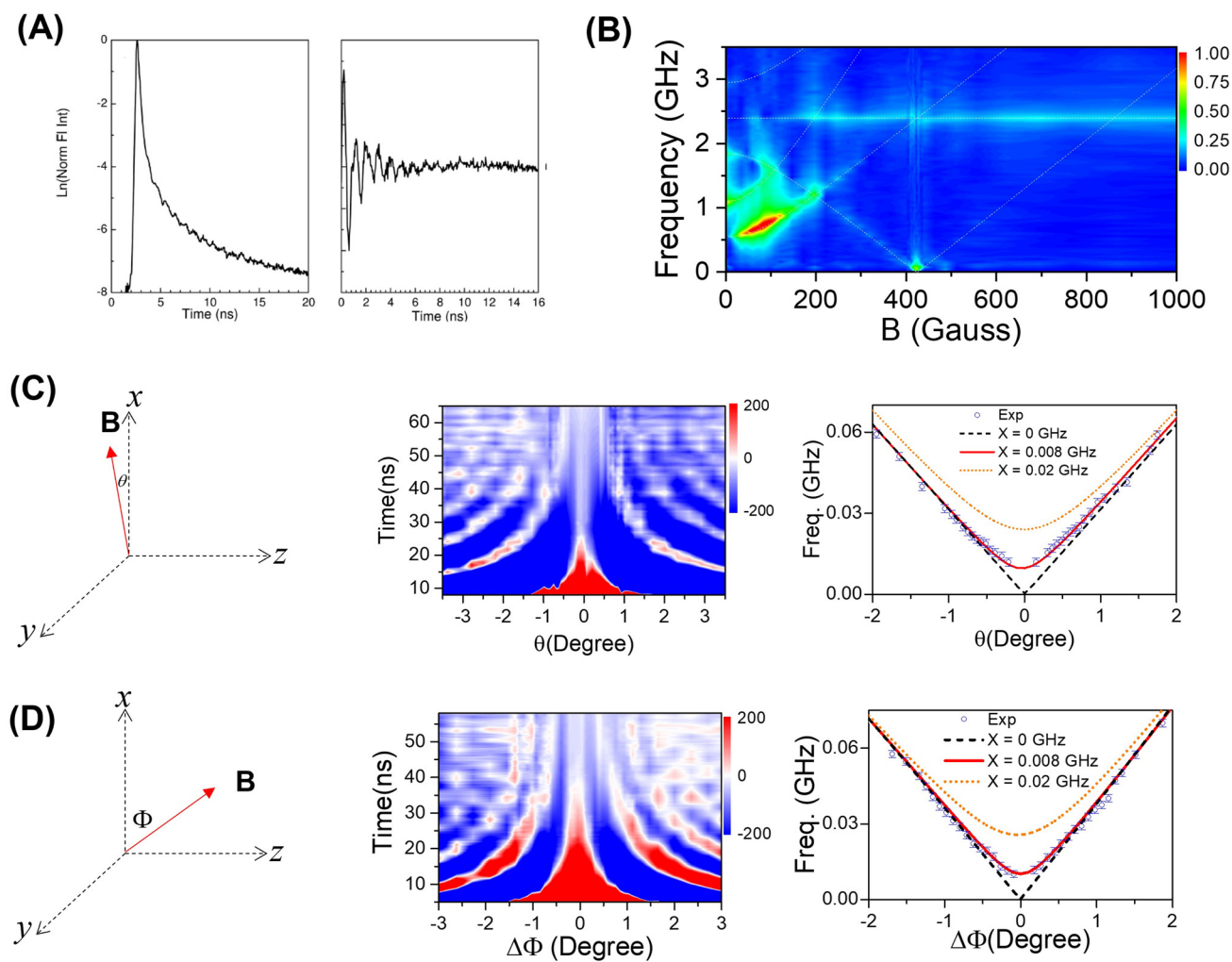
PL emission directly probes the singlet population. The MFE on PL emission suggests the involvement of triplet excitons during the deactivation process of photo-excited singlet states. In the weak field regime, the MFE of PL emission from intermolecular singlet fission systems can be well described with the Merrifield model for the weakly-coupled  $^1(T\dots T)$  states [71,72].

Quantum beats arising from superposition of triplet pair manifolds have been detected in delayed fluorescence [49–51,73]. Crystalline tetracene samples are the most widely studied among the few systems showing quantum beats (Figure 2A) [51]. The beating frequencies coincide well with the energy spacings between the eigenstates of triple pairs as direct evidence for the triplet pair states. Nevertheless, the signature of intertriplet interactions was not captured by the ESR measurement at the early stage.

Quantum beats also show MFEs in crystalline tetracene (Figure 2B) [50], which can be well described by the Merrifield model. In tetracene crystals, MFEs on fluorescence decay are observable at the stage when the triplet pair fusion becomes significant. By properly aligning the

**Zeeman interaction:** in a magnetic field, the spin degenerate states are split into several components, first discovered by Pieter Zeeman.

**Zero-field-splitting interaction:** contains various types of interaction that split degenerate states even in the absence of a magnetic field.



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**Figure 2.** Magnetic field effects (MFEs) of quantum beats in delayed fluorescence. (A) Time-resolved photoluminescence (TRPL) trace of a solution-grown single crystal of tetracene and the oscillation components obtained by subtracting the exponential decay components [51]. (B) The beating amplitude is plotted as functions of the frequency and magnetic field amplitude. The field is applied aligning the x-axis with a small angle tilted relative to the x-axis. The dependences of quantum beat amplitude on the field tilt angles near level crossing resonances (C,D) are monitored to evaluate the intertriplet interacting strength for a tetracene single crystal [50]. (C) The field of 420 Gauss is applied in the xy plane with a tilt angle ( $\theta$ ) with respect to the x-axis [50]. (D) The field of 3000 Gauss is applied in the xz plane with a tilt angle ( $\Delta\phi$ ) with respect to the resonance alignment ( $\phi = 69^\circ$ ) [50]. Adapted, with permission, from [50,51].

magnetic field, the energy levels of triplet pairs may be tuned to near degeneracy (Figure 2C). The degeneracy condition can also be approached by field alignment in the strong field limit (Figure 2D). Under these degenerate circumstances, the weak intertriplet interaction becomes detectable in the low beating frequency regime (Figure 2B). In principle, the gap values are linearly proportional to the field tilting angle if the intertriplet is not included. As shown in Figure 2C,D, the dependences of beating frequencies on the field direction are different from the interaction-free case. The strength of intertriplet interaction can be evaluated from the experimental data to be  $\sim 30$  neV at room temperature [50], which is comparable to the value of the intertriplet interaction for geminate triplets at cryogenic temperatures measured by **optically detected magnetic resonance** [43]. The value is much smaller than expected for intertriplet exchange coupling at the adjacent molecules. Assuming

a triplet–triplet dipolar interaction, the two triplets in a pair are separated over an average distance of multiple molecules, implying that the intermediate states are the weakly coupled  $^1(T\dots T)$  state.

While quantum beats and the low-field MFE on PL emission are signatures of triplet pair formation, these effects are not commonly observed in singlet fission materials. For exothermic systems, such as pentacene and its derivatives, PL emissions are weak at room temperature and the MFEs are hardly detected. Recently, the MFE on PL emission from triplet pair states was observed through **Herzberg–Teller coupling** in pentacene at low temperature [20]. For the  $^1(TT)$  state produced in singlet fission dimers, the MFE is insignificant in this field regime because the Zeeman interaction is much weaker than the exchange interaction. In principle, the quantum beats in the time domain can only be detected from the states with the electronic coherence retained. The hopping from the  $^1(TT)$  to  $^1(T\dots T)$  states may cause loss of electronic coherence between the  $^1(TT)$  and  $S_1$  states established at the initial stage of singlet fission. The quantum beats imply a possible coherent formation channel of  $^1(T\dots T)$  states in addition to the incoherent hopping from the  $^1(TT)$  states. In crystalline tetracene, a portion of weakly exchanged triplet pairs is possibly generated through a coherent pathway from the delocalized singlet excitons [74–76].

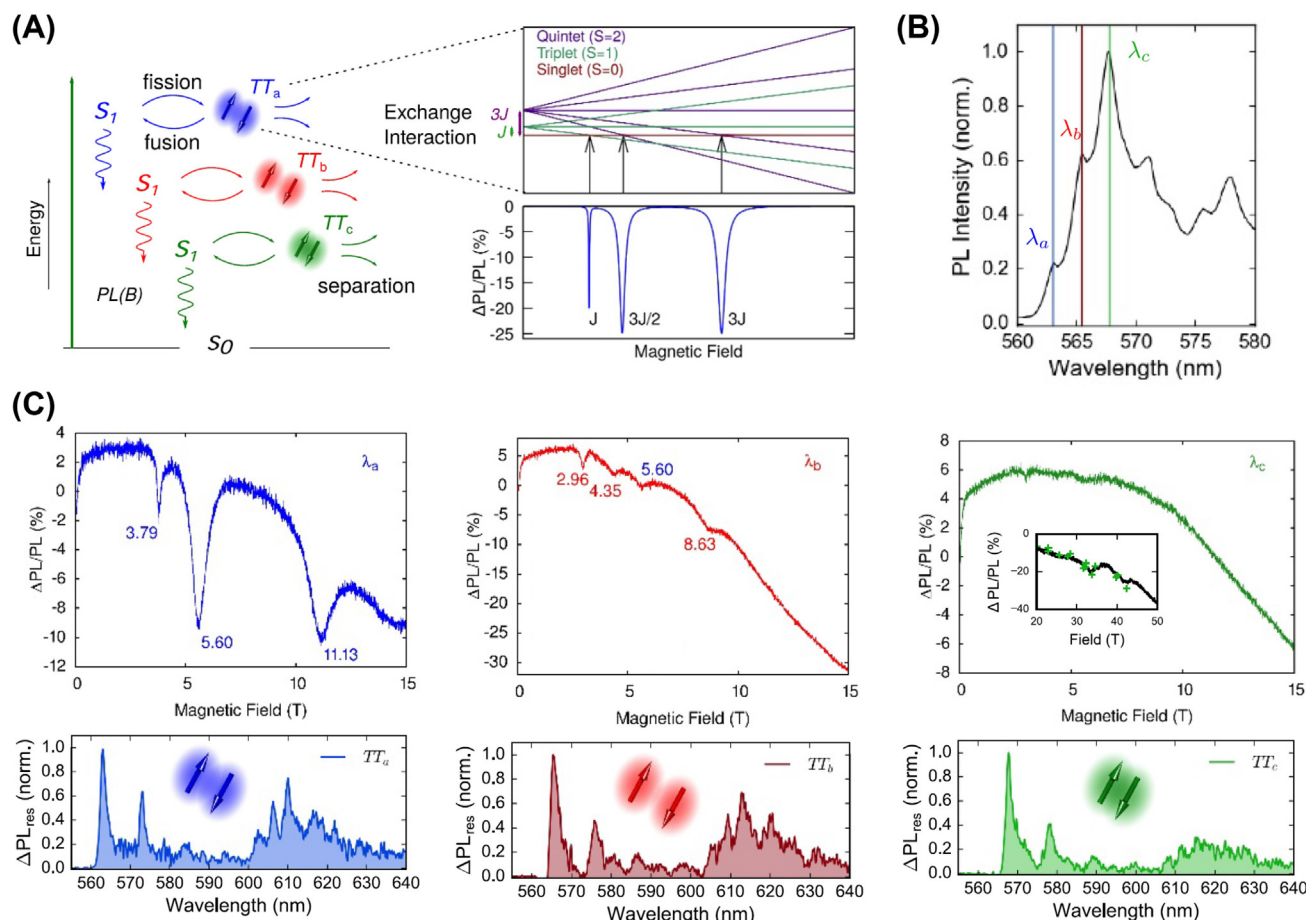
### Level anticrossing resonances

For strongly coupled triplet pairs, spin and energy eigenstates coincide at zero magnetic field. The singlet–quintet and singlet–triplet gaps are  $\sim 3J$  and  $J$ , respectively [42]. For strong magnetic fields with Zeeman interaction comparable to  $J$ , the exchange interaction may be compensated, leading to the singlet–quintet state mixing due to the zero-field splitting interaction [44,61]. Singlet–quintet mixing strongly changes the singlet projections, resulting in a marked change in the PL emission (Figure 3A). The magnitudes of magnetic field on resonances of the quintet states ( $S_z = 1, 2$ ) correspond to  $B = 3J/\mu g$  and  $B = 3J/2\mu g$ , respectively. The singlet–triplet level crossings occur at  $B = J/\mu g$ . Nevertheless, the pair spin eigenstates are symmetric for singlets and antisymmetric for triplets under particle exchange. In principle, the zero-field interaction cannot mix the states with different symmetries when the triplets are equivalent. Nevertheless, this mixing becomes possible when the two triplets are inequivalent with random orientations, which breaks the particle-exchange symmetry. The singlet–triplet mixing results in the MFE of PL emission with magnitude typically less than that for singlet–quintet mixing.

The strong MFEs at the **level crossing resonances** are valuable for quantitatively evaluating the strength of intertriplet exchange interaction [44]. By increasing the magnetic field, three magnetic resonances for each configuration of triplet pairs may be detected by emission dips (Figure 3B,C). Bayliss and colleagues have shown that, in TIPS-tetracene crystallites, three distinct triplet pair sites show triple relative resonance dips at  $< 2$  K. Correspondingly, the strength of exchange interaction is in the range of 0.3–5 meV, implying multiple spatial separations for triplet pairs [44]. These results are consistent with the scenario that the triplet excitons may hope to separate the  $^1(TT)$  states to form the weakly coupled triplet pairs [62,63,77].

### Triplet pair dissociation

Triplet pair dissociation is essential for the final products of free triplets, which has also been intensively studied by transient optical spectroscopy. In crystalline samples, the separation process from the adjacent triplet pair  $^1(TT)$  to  $^1(T\dots T)$  states can be viewed as a triplet energy-transfer process [21,64,65,77]. The triplet pair separation is an entropy-producing process, which may compensate slight endothermicity in crystalline systems. In intramolecular dimer systems, the spatial separation is unavailable; thus, the two triplets stay spatially adjacent. Nevertheless, the subsequent process of spin decoherence may not be captured by transient optical spectroscopy, which is not a spin-sensitive approach.

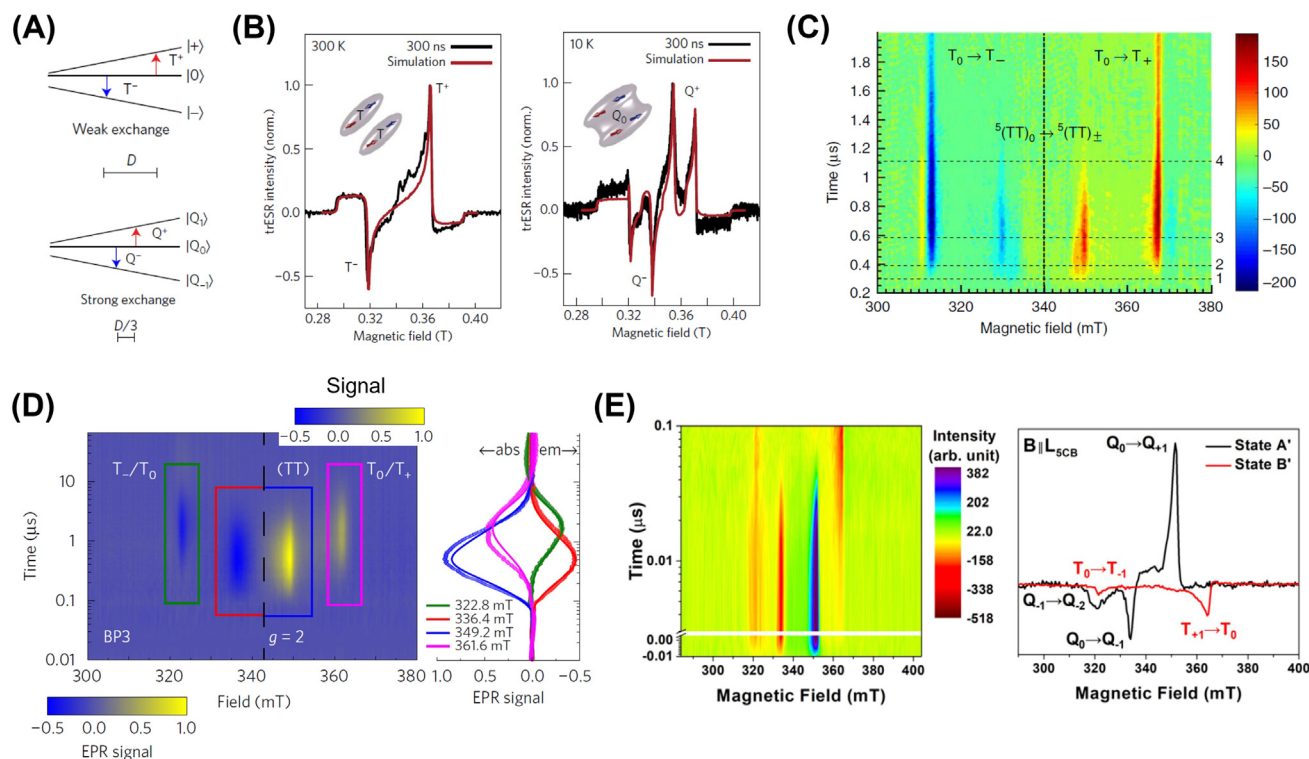


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**Figure 3.** Magnetic field effects (MFEs) arising from singlet–quintet and singlet–triplet mixing of triplet pair states. (A) Schematic of spin-pair generation with different exchange interactions. The Zeeman interaction drives the mixing of triplet pair states with different spin characters, inducing the magnetic field resonances of fluorescence changes. (B) Photoluminescence (PL) spectrum of a crystal of TIPS-tetracene recorded at 1.4 K showing three peaks at  $\lambda_a$ ,  $\lambda_b$ , and  $\lambda_c$  corresponding to three different sites of triplet pairs. (C) MFE of fluorescence emission showing the field resonances measured at three peaks and the triplet pair-associated emission spectra. Adapted, with permission, from [44].

Tr-ESR measurements penetrate deeper into the dynamics of spin characters of triplet pairs (Figure 4A), providing direct evidence of  $^5(TT)$  states during the conversion from  $^1(TT)$  to free triplet pairs. In a study of crystalline TIPS-tetracene, Weiss and colleagues reported different ESR features of transient species at a delay of 300 ns at 300 K and 10 K (Figure 4B) [56]. By simulating the experimental results, these features are attributed to the ESR transitions for the weakly coupled triplet pairs [ $^1(T\dots T)$ ] and strongly coupled triplet pairs [ $^5(TT)$ ], respectively. The significant difference in ESR response at room and cryogenic temperatures raised the question whether different pathways are involved in the formation of independent triplets. In the semidiluted pentacene sample,  $^5(TT)$  is also observed at room temperature when diffusion is suppressed (Figure 4C) [54]. These results suggest that efficient thermally driven diffusion results in short-lived  $^5(TT)$  at room temperature that cannot be resolved by time-resolved ESR in crystalline samples.

Quintet states have also been observed in intramolecular dimer systems. In pentacene dimers with p-phenylene bridges, Tayebjee and colleagues observed the features of quintet and triplet species in sequence (Figure 4D) [55]. The data support that singlet–quintet mixing is also viable



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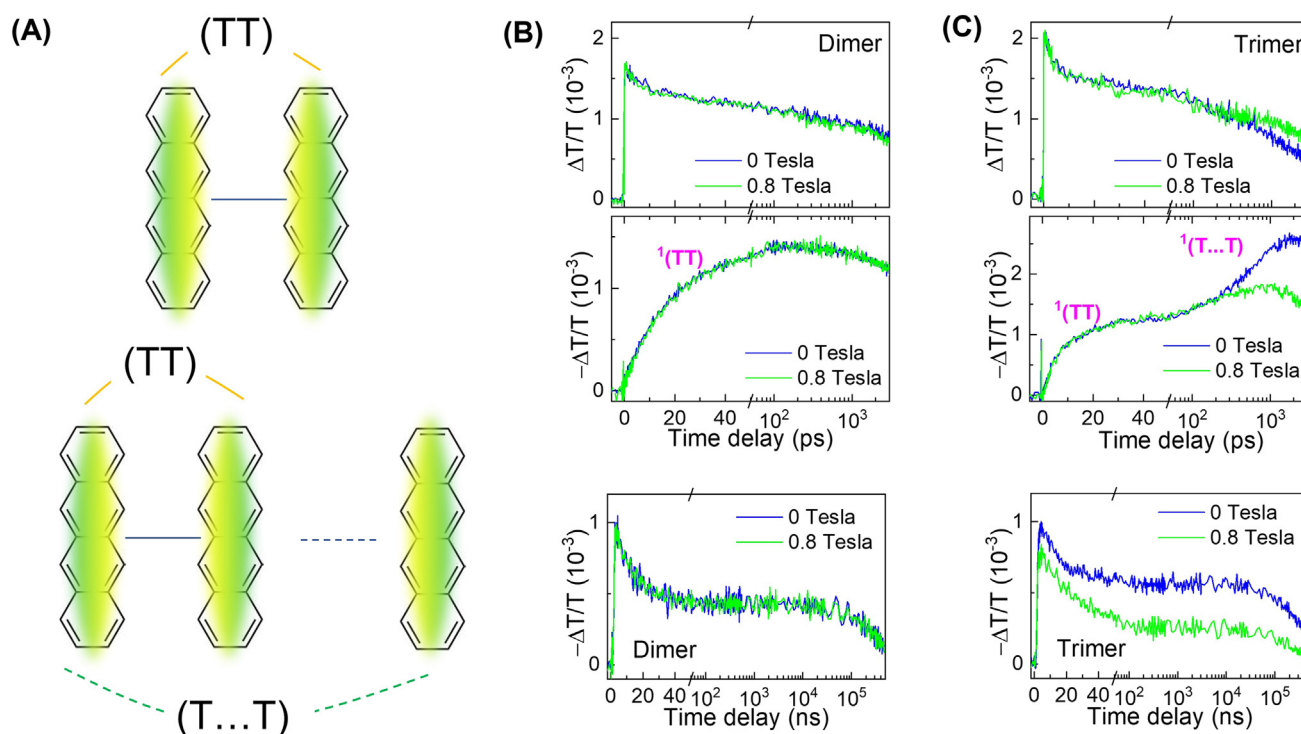
**Figure 4.** Time-resolved electronic spin resonance (tr-ESR) characterization of triplet pair dissociation. (A) ESR transitions for weakly and strongly exchange-coupled triplet pairs showing the transitions related to triplet and quintet sublevels [56]. (B) Tr-ESR spectra recorded from a film of TIPS-tetracene at room temperature and 10 K showing the features of weakly and strongly exchange-coupled triplet pairs with triplet and quintet spin characters [56]. (C) Tr-ESR spectrum recorded from a film of 10% pentacene in *p*-terphenyl showing the triplet pairs with quintet characters at room temperature [54]. (D) Tr-ESR spectra of an intramolecular singlet fission system of 3 *p*-phenylene-linked pentacene dimer (BP<sub>3</sub>) at 40 K and the transients taken at the four peak features [55]. (E) Tr-ESR spectra of a dimer of TD<sub>12</sub> aligned in a nematic liquid crystal. The mixing of triplet pair states with triplet and quintet characters is probably responsible for the unusual signal of triplet state [57]. Adapted, with permission, from [54–57].

for the generation of free triplets in intramolecular SF materials. The interchromophore coupling strength in the intermediate regime is suggested for efficient triplet generation. The coupling needs to be strong enough to allow triplet generation but not too strong to suppress the triplet pair dissociation. Given that the spatial separation of triplet pair is prohibited in dimers, the dissociation pathways may not be the same as those in the crystalline systems. The temperature-dependent measurements suggest the presence of a nonthermal channel in addition to the thermally activated channel that may drive the dissociation of triplet pairs with quintet characters.

In addition to the quintet pair states, triplet pair states with triplet spin characters [ ${}^3(TT)$ ] have also been identified in intramolecular SF materials. In a terrylenediimide dimer, Wasielewski and colleagues observed an unusual spin polarization of the triplet state likely due to enhanced mixing between the quintet–triplet mixing (Figure 4E) [57], which is susceptible to the alignment of molecular axis. The mixing leads to a strong MFE for the final products at the field of resonant magnitudes. Nevertheless, the  ${}^3(TT)$  channel of triplet pair dissociation will lead to the net loss of one triplet due to the triplet channel of triple pair annihilation forming a hot triplet exciton [53]. Such a loss channel, together with the singlet channel of triplet annihilation, is a competing pathway for independent triplet formation. From the available data, it is most likely that formation of a pure quintet state is essential to achieve a high yield of independent triplets because it affords protection from both singlet- and triplet-channel annihilation loss pathways.

Although the formation of quintet state is pivotal for the overall output of independent triplets from triplet pairs, it remains elusive how the quintet state is converted from the singlet state. In crystal-line materials, triplet hopping allows the spatial separation of the triplet pair, which reduces the exchange–split energy gaps, enabling the singlet–quintet mixing of  $^1(T\dots T)$  and  $^5(T\dots T)$  states. Triplet pair separation may also drive the formation of the quintet state in the intramolecular systems. When the hopping channel is activated in oligomers with three or more repeating units, the generation efficiencies of free triplets are significantly enhanced in multiple systems [53,62,78]. In the dimer systems without spatial separation, Collins and coworkers proposed a model with fluctuating exchange interactions [67]. Due to nuclear reorganization of the dimer bridge in the ground and excited states, the time-varying exchange interaction in dimeric SF drives interconversion between the singlet and quintet pair manifolds. This scenario well explains the strong linker dependence of independent triplet generation in dimers [79].

The radiative recombination of singlet state is typically on the timescale of  $\sim 10$  ns for molecules. For efficient triplet generation, the spin dynamics of triplet pairs on the timescale is particularly important. While the spin characters of triplet pairs are available with Tr-ESR measurements, the temporal resolution has been limited on the timescale of  $\sim 100$  ns or longer. The dynamics of singlet–quintet mixing on the earlier stage cannot be fully extracted even though the MFE may also be significant. In recent work on tetracene oligomers, Wang *et al.* showed a marked MFE of triplet generation dynamics on a sub-ns timescale in tetracene oligomers with three or more repeating units (Figure 5) [62]. The MFE with a relatively weak field ( $< 1$  Tesla) can be connected to the formation of a spatially separated ( $T\dots T$ ) state in the trimer or tetramer



**Figure 5. Magnetic field effect (MFE) of singlet fission dynamics on the sub ns timescale.** (A) Schematics of spatially adjacent ( $TT$ ) and separated ( $T\dots T$ ) states. Kinetic curves representing singlet and triplet dynamics in a tetracene dimer (B) and trimer (C) recorded with and without the application of an external field of 0.8 Tesla. Adapted, with permission, from [62].

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(Figure 5A). The efficiency of free triplet generation has been significantly promoted in the trimer and tetramer (Figure 5B,C), which suggests that the singlet-quintet mixing occurs on a timescale faster than the radiative recombination.

### MFEs in singlet fission-based devices

Singlet fission can be integrated in host solar devices through energy transfer or charge transfer processes to boost the overall solar conversion efficiency [3,80–83]. Triplet energy transfer is generally governed by the **Dexter mechanism** relying on the short-range exchange interaction [84], making interface and surface treatments challenging in combining singlet fission with photovoltaic devices. Recently, highly efficient sensitization of silicon by singlet fission was successfully demonstrated by Baldo and coworkers by integrating an ultrathin protective  $\text{HfO}_x\text{N}_y$  layer [82]. In the silicon- $\text{HfO}_x\text{N}_y$ -tetracene structure, the overall yield of photon-to-exciton conversion reached 133%, establishing the potential of breaking the Shockley–Queisser efficiency limit. Efficient energy transfer from singlet fission materials to semiconductor nanocrystals was demonstrated with efficiency near 100% in the pentacene/PbSe [85] and tetracene/PbS [86] hybrid systems. The hybrid design improves the performance of nanocrystal solar cells [87], which could be applied as photon multipliers [4]. Charge transfer has also been demonstrated in the organic blends with singlet fission materials to improve the efficiencies of the photodetectors and photovoltaic devices. Based on the pentacene/C60 systems, external quantum efficiency of 130% at the featured spectral range has been realized in the organic solar cells [3]. To break the Shockley–Queisser limit, we need to overcome the challenges of finding proper hybrid systems with optimized band alignments and reducing the loss of open circuit voltage [4].

MFEs have been widely characterized in these singlet fission-based devices. Typically, the photocurrent and/or light emission from the active hybrid layers show MFEs in the weak field regime ( $<0.5$  Tesla), suggesting that the  $^1(T\dots T)$  triplet pairs are critical intermediates in these working devices. The results are consistent with current solid-state devices using intermolecular singlet fission systems. The intramolecular singlet fission materials may act as light harvesters for dye-sensitized solar cells. Moreover, the strongly coupled  $^1(TT)$  triplet pairs with orbital overlaps in dimers may serve as a molecular platform for potential quantum information applications [88–90].

### Concluding remarks

In summary, MFEs on singlet fission dynamics mainly arise from the mixing of triplet pair states with different spin characters by zero-field splitting [42]. For strongly coupled triplet pairs, the energy spacings between the triplet pair manifolds, as determined by the exchange coupling strength, are large at zero field [14,91]. MFEs become detectable only when the Zeeman interaction can compensate the energy gaps. For weakly coupled triplet pairs, the singlet and quintet levels are mixed at zero field so that MFEs are observable with a weak magnetic field. The studies of MFEs suggest that the quintet state of triplet pairs is the key intermediate determining the efficiency of free triplet production [55–57]. Nevertheless, the generation dynamics of the quintet triplet pairs are not fully characterized due to the instrumental limitations. The three-step model, that is,  $S_0 + S_1 \leftrightarrow ^1(TT) \leftrightarrow ^1(T\dots T) \leftrightarrow T_1 + T_1$ , is current the most widely accepted scheme in the literature [13]. It remains unclear whether the  $^1(T\dots T)$  triplet pair is a sequential intermediate step or has a distinct role in singlet fission (see [Outstanding questions](#)). Understanding the orbital overlaps of the triplet pairs also provides a fascinating model for the investigations of many-body interactions in molecule systems [65,91–94]. The magnitude of MFE is much larger than the value predicted by Merrifield model [62], implying that the spin decoherence effect is also critical [46,61]. Interpreting the spin decoherence (i.e., how the correlated spins interact with the dephasing environment [95]) may facilitate the applications of singlet fission materials in the spintronics [96] and quantum information science [88,90]. Implementing these new perspectives in designing intramolecular singlet fission

### Outstanding questions

Can the dynamics of spin mixing between triplet pair states with singlet and quintet characteristics be probed on a timescale of nanoseconds or shorter?

Is the  $^1(T\dots T)$  triplet pair only a sequential intermediate step or generated directly from the singlet state? Can the coherence retain as the triplets separate?

How can the quintet pathway of triplet pair deactivation be promoted to avoid the losses of singlet and triplet channels?

Is it possible to synthesize materials with highly efficient singlet fission and bandgaps suitable for excitation transfer to semiconductors in state-of-the-art solar cells?

Could high-yield triplets be harvested for photodynamic therapy or the triplet pair coherence be implanted for quantum information applications?

materials [11,12,23,31–33,35,53,62,70,78,79,97–99] may stimulate research exploring new conceptual optoelectronic devices with unprecedented performances [3,82,100].

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### Declaration of interests

None declared by authors.

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