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ABSTRACT

The intermediate state of a correlated triplet pair [^{1}(TT)] is pivotal for understanding the mechanism of the singlet fission process in molecule systems. Recently, a spatially separated state of a triplet pair [^{1}(T···T)] has been proposed to drive the dissociation of exchange-coupled ^{1}(TT) into free triplets. Here, we study the correlated triplet pairs by monitoring quantum beats in delayed fluorescence from tetracene crystals upon applying magnetic fields of different amplitudes and alignments. We argue that the triplet pairs probed by the quantum beat spectrum are weakly coupled, i.e., the spatially separated ^{1}(T···T) state. The experimental data suggest the existence of a direct channel of $S_1 \rightarrow {}^1$(T···T) in addition to the widely accepted channel of $S_1 \rightarrow {}^1$(TT) $\rightarrow {}^1$(T···T) for singlet fission. Our work suggests that the quantum beat spectrum is a useful tool to directly probe the ^{1}(T···T) state which is valuable for elucidating the intrinsic mechanism of singlet fission.

I. INTRODUCTION

Singlet fission converts a photo-excited singlet excited state (S_1) into two triplet excited states ($T_1 + T_1$) in molecular systems.[1–5] Such a process of multiple exciton generation avoids one key assumption adopted in deriving the Shockley-Queisser efficiency limit in singlet junction solar cells,[6] which holds the potential to boost the device efficiency for solar energy harvesting.[7,8] In the past decade, tremendous efforts have been made in developing singlet fission-based devices,[9–14] synthesizing new singlet fission materials,[15–39] and elucidating the intrinsic physical mechanism.[40–55]

In early works, singlet fission has been regarded as a two-step process[1–3,56] with a key intermediate state, i.e., $S_1 \rightarrow {}^1$(TT) $\rightarrow T_1 + T_1$. The intermediate ^{1}(TT) state refers to a pair of triplets with spin coherences to ensure the spin conservation for the initial step of singlet fission. The nature of the ^{1}(TT) state has been intensively studied to illustrate the dynamics of different excited states in singlet fission materials. The generation of ^{1}(TT) states triggers the process of single fission through a direct coupling scenario or indirect mediation by a charge-transfer state.[24,27,34,45,46,52,57–59] Very recently, the necessity of a spatially separated triplet pair state ^{1}(T···T) has been highlighted.[5,60–64] The ^{1}(T···T) state was originally proposed to be resulted from ^{1}(TT) separation by triplet energy transfer,[60,62] which has been recently connected to the electronic decoherence of the two triplet excited states.[5] In this scheme, the final products of two free triplet excitons ($T_1 + T_1$) are generated as a consequence of the loss of spin coherence at the ^{1}(T···T) state [(1–3), Fig. 1] following the kinetic scheme,[5,60,63]

$$S_0 + S_1 \xrightarrow{(1)} {}^1(\mathrm{TT}) \xrightarrow{(2)} {}^1(\mathrm{T\cdots T}) \xrightarrow{(3)} T_1 + T_1. \quad (1)$$

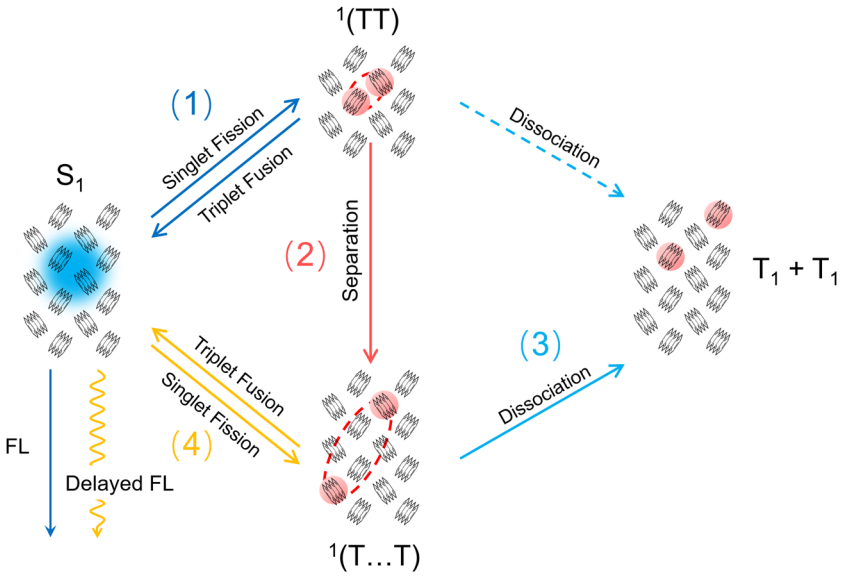

FIG. 1. Schematic diagram of the singlet fission process in tetracene crystals.

The introduction of ^{1}(T···T) well explains the difference in the spectral feature of free triplet and intermediate states due to excitonic coupling in the proximately coupled dimer systems.[48,61–63] It has been shown that the ^{1}(T···T) state promotes the dissociation process[60] and drives the initial stage of singlet fission.[61]

Transient absorption (TA) spectroscopy is the most widely applied tool to study the dynamics of different excited states involved in singlet fission processes. However, it is difficult to extract an unambiguous spectral feature of the ^{1}(T···T) state because of its entanglement and similarity to those of ^{1}(TT) and $T_1 + T_1$ states.[63] Time-resolved electron spin resonance (ESR) measurements have also been used to probe spin decoherence of these intermediate states.[52,65–69] However, the dynamics of ^{1}(T···T) and ^{1}(TT) states cannot be well distinguished due to the limited temporal resolution. The different strength of intertriplet interaction is a key feature for the ^{1}(T···T) and ^{1}(TT) states. Recently, optically detected magnetic resonance measurements have estimated the interaction strength of 0.3–3 meV for the exchange-coupled triplet pairs.[70] Apparently, very weak strength of intertriplet interaction has been characterized for the geminate triplet pairs.[71,72] These marked differences are possibly related to the correlated triplet pairs with different separation distances.

Quantum beating in the delayed fluorescence (FL) may also provide valuable information about the triplet pair states. The beating signal is intrinsically caused by the interference between the sublevels of triplet pair states, which has been regarded as an unambiguous evidence of singlet fission.[73] In 1980s, the quantum beating behavior has already been reported by Chabr and co-workers.[74] Nonetheless, quantum beats in the delayed FL have been observed in very few material systems of tetracene,[40,72,75] rubrene,[76] and a tetracene derivative.[77] Nonetheless, it remains unexplored whether the ^{1}(TT) or ^{1}(T···T) state make substantial contribution to the quantum beats in the delayed FL.

In this work, we revisit the quantum beats in the delayed FL from tetracene crystals by systematically studying the dependences of quantum beats on the strength and alignment of magnetic field, excitation density, and sample temperature. By combining experimental data with theoretical modeling, we argue that the quantum beating behavior is induced by the weakly coupled spatially separated ^{1}(T···T) state. The results imply the possible existence of a direct channel of $S_1 \rightarrow {}^1$(T···T) for singlet fission [(4) in Fig. 1] in addition to the channel involving exchange-coupled ^{1}(TT) state [i.e., $S_1 \rightarrow {}^1$(TT) $\rightarrow {}^1$(T···T)], which may shed light on some enduring controversies in singlet fission dynamics of tetracene crystals.

II. METHODOLOGY

A. Experimental methods

Tetracene single crystals with the thickness of ~400 nm and size up to ~5 × 5 mm^2 were prepared by the method of physical vapor deposition. The b-axis of the crystal was determined by the polarization-dependent absorption spectra.

A pulsed laser (LDH-D-C-405M, Picoquant) at 405 nm with a repetition rate of 5 MHz was employed to excite the FL emission. The emission light was collected and routed to a spectrograph. The time-resolved FL (TRFL) spectra at ~535 nm was recorded with the technique of time-correlated single-photon counting by an avalanche photodiode having a temporal resolution of ~50 ps. To extract the signal of quantum beats, the multiexponential decay components were subtracted from TRFL traces. For magnetic-field-dependent experiments, we used a precalibrated magnetic coil driven by a direct current power supply. The magnetic field is aligned by rotating the coil and adjusting the sample position. For temperature-dependent experiments, the samples

were mounted on a heater with a thermocouple mounted near the sample.

B. Theoretical model

To uncover the intrinsic mechanism underlying the quantum beats in the delayed FL, we conduct theoretical calculation considering the spin-dependent Hamiltonian of two correlated triplets. The Hamiltonian includes the zero-field splitting of two isolated triplets (e.g., A and B), the Zeeman interaction induced by applied external magnetic field ($\hat{H}_{zeeman}$), and the mutual interaction of two triplets ($\hat{H}_{AB}$), i.e.,

$$\hat{H} = \hat{H}_A^{zfs} + \hat{H}_B^{zfs} + H_{Zeeman} + \hat{H}_{AB}. \tag{2}$$

Here, we adopt the effective Hamiltonian of triplet excitons in tetracene crystals used to interpret the ESR experiments in the form of[78]

$$\hat{H}_{AorB}^{zfs} = D^*(\hat{S}_z^2 - \hat{S}^2) + E^*(\hat{S}_x^2 - \hat{S}_y^2). \tag{3}$$

The two terms give the zero-field Hamiltonian with parameters of D^* and E^* determined by ESR experiments ($D^* = -0.0062$ cm^{-1}, $E^* = 0.0248$ cm^{-1}). It is worthy to note that the two triplets may be configured with multiple orientations. The Hamiltonian provides an excellent approximation by averaging out the orientation effect as established in the literature.[40,75,78] $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ are the x*, y*, and z* components of the spin operator $\hat{S}$, respectively. The orthogonal system of magnetic axes (x*, y*, and z*) is transformable with the system of (a′, b, and c′) by the following matrix equation:[78]

$$\begin{pmatrix} a' \\ b \\ c' \end{pmatrix} = \begin{pmatrix} 0.9634 & 0.2634 & -0.0372 \\ -0.0269 & 0.2463 & 0.9714 \\ 0.2663 & -0.9330 & 0.2390 \end{pmatrix} \begin{pmatrix} x^* \\ y^* \\ z^* \end{pmatrix}. \tag{4}$$

The Zeeman interaction induced by an applied external magnetic field is given by

$$\begin{aligned} H_{zeeman} = {} & g\mu_B\left(B_x \cdot \hat{S}_x^A + B_y \cdot \hat{S}_y^A + B_z \cdot \hat{S}_z^A\right) \\ & + g\mu_B\left(B_x \cdot \hat{S}_x^B + B_y \cdot \hat{S}_y^B + B_z \cdot \hat{S}_z^B\right), \end{aligned} \tag{5}$$

where μ_B and g are the Bohr magneton and the Lande g-factor, respectively. B_x, B_y, and B_z are the x*, y*, and z* components of the external magnetic field **B**, respectively. The intertriplet interactions generally include the magnetic dipolar interaction and the exchange interaction. The strength of magnetic dipolar interaction is very weak which is ~1% of zero-field splitting in tetracene crystals.[72] Recent measurement suggests that the interaction strength for the exchange-coupled triplet pair is at a higher level of 0.3–3 meV.[66,70,79] We neglect the effect of the magnetic dipolar interaction during the calculation, i.e.,[79]

$$\hat{H}_{AB} = J\hat{S}_A \cdot \hat{S}_B, \tag{6}$$

where J is the strength of exchange interaction. The calculation of the energy of each sublevel is conducted following the method as described in the literature.[40,75,80,81] In brief, the energy and the eigenfunction of each sublevels ($|\phi_{TP^l}\rangle$) are calculated using the zero-field basis set ($|x_Ax_B\rangle$, $|x_Ay_B\rangle$, $|x_Az_B\rangle$, $|y_Ax_B\rangle$, $|y_Ay_B\rangle$, $|y_Az_B\rangle$, $|z_Ax_B\rangle$, $|z_Ay_B\rangle$, $|z_Az_B\rangle$), where $|x_i\rangle$, $|y_i\rangle$, and $|z_i\rangle$ are two-electron spin states of individual triplet i (i = A or B), i.e.,[40]

$$\begin{cases} |x_i\rangle = \frac{1}{\sqrt{2}}(|\downarrow\downarrow\rangle - |\downarrow\downarrow\rangle) \\ |y_i\rangle = \frac{1}{\sqrt{2}}(|\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle), \\ |z_i\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{cases} \tag{7}$$

$|\uparrow\rangle$ and $|\downarrow\rangle$ are individual up and down electron spins, respectively, quantized along the magnetic z^* axis.

The transition rates between the singlet and each sublevels of triplet pair state are assumed to be proportional to the singlet projection ($|C_S^l|^2$) as

$$\left|C_S^l\right|^2 = \left|\left\langle \frac{1}{\sqrt{3}}(|x_Ax_B\rangle + |y_Ay_B\rangle + |z_Az_B\rangle)|\phi_{TP^l}\right\rangle\right|. \tag{8}$$

The sublevels of triplet pair state with nonzero singlet projections are involved in the singlet fission process. Quantum beating is detectable with two levels having nonzero singlet projection. For weakly coupled triplet pair state, multiple sublevels make substantial contributions to the quantum beats.[40] For strongly exchange-coupled triplet pair, there is only one sublevel with near unit singlet projection so that the quantum beating is not detectable.[70,79]

The kinetics of the population at the singlet and the sublevels can be expressed as[40,72]

$$\begin{aligned} \frac{dN_{S_1}}{dt} &= -k_{fis}N_{S_1} + \sum_{l=1}^{9}\left|C_S^l\right|^2 k_{fus}N_{TP^l} - k_{rad}N_{S_1}, \\ \frac{dN_{TP^l}}{dt} &= k_{fis}\left|C_S^l\right|^2 N_{S_1} - k_{fus}\left|C_S^l\right|^2 N_{TP^l} - k_{diss}N_{TP^l} (l = 1,2\ldots 9), \\ \frac{dN_{T_1}}{dt} &= 2k_{diss}\sum_{i=1}^{9} N_{TP^l} - k_T N_{T_1}, \end{aligned} \tag{9}$$

where N_{S_1}, N_{TP^l}, and N_{T_1} represent population of the singlet state and the lth sublevel of triplet pair state and the free triplet state, respectively. The parameters k_{rad}, k_{fis}, k_{fus}, k_{diss}, and k_T are the rates of the radiative decay, fission, fusion, dissociation of the triplet pair state, and recombination of the free triplet state, respectively. During our calculation, the sublevels of the triplet pair state with over 1% projections to singlet state are considered to make significant contribution to the quantum beats.

III. RESULTS AND DISCUSSION

A. Strong field limit

Figure 2 shows the magnetic-field dependence of quantum beating in the delayed FL. The oscillations are obtained by subtracting the multi-exponential decay components in TRFL traces [Fig. 2(a)], which are further converted to the beat spectra [Fig. 2(b)] by performing Fourier transformation. The beating exhibits multiple peaks with frequencies susceptible to the field magnitude in the weak field regime (<0.05 T). Nonetheless, the single peak dominates the beating behavior with the frequency nearly unchanged with further increasing the field (>0.05 T), which has been assigned as the strong field limit where the Zeeman interaction dominates the Hamiltonian.[75]

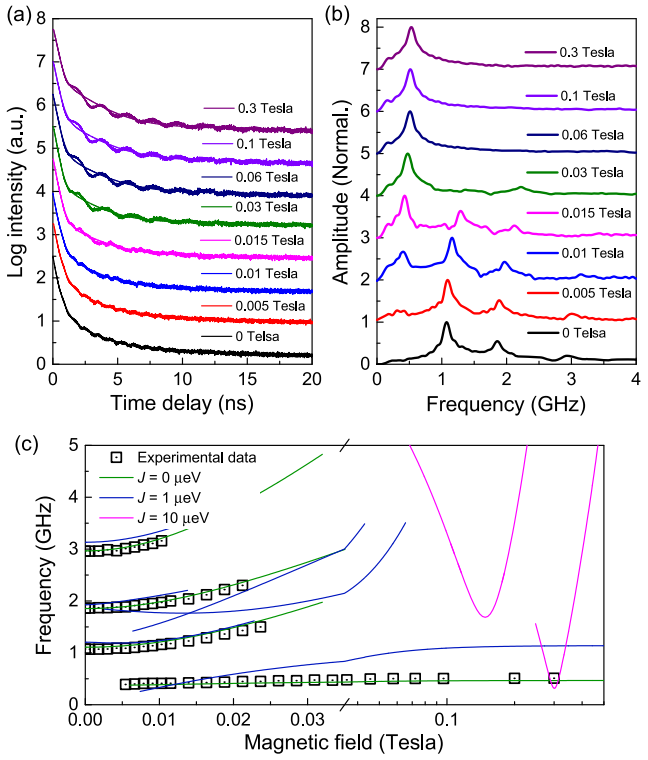

FIG. 2. Magnetic-field-dependent quantum beats. (a) TRFL traces recorded from a tetracene crystal under magnetic field of different strengths. (b) The normalized quantum beat spectra recorded under magnetic field of different strengths. The beating spectra are obtained by Fourier transformation of the oscillatory components in the TRFL traces. The curves in (a) and (b) are vertically shifted for clarity. The magnetic field is applied in parallel with the b axis of the tetracene crystal. (c) The magnetic field-dependent beating frequencies are compared with theoretical calculations considering different exchange interaction (J).

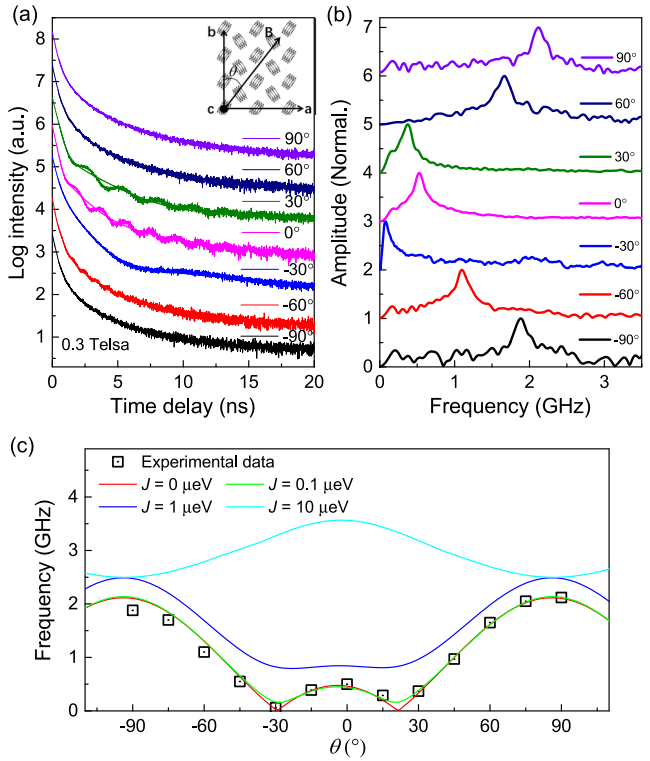

FIG. 3. Field alignment-dependent quantum beats. (a) TRFL traces recorded under a magnetic field of 0.3 T aligned with an angle θ against the b-axis of the crystal (inset). (b) The normalized beating spectra recorded at different angles (θ). (c) The θ-dependent beating frequencies are compared with theoretical calculations considering different strength of exchange interaction J.

The anomalous field dependences of the beating behaviors are informative for the interaction between the correlated triplet pair. The spin Hamiltonian of the triplet pair [Eq. (2)] suggests that the magnitude of magnetic field effect is determined by the interplay between Zeeman interaction and the intertriplet interaction. The field-induced modification of the energy levels is negligible if $J \gg g\mu_B B$. The Zeeman interaction for a magnetic field of 0.05 T is less than 10 μeV. The strong field dependence of the beating behavior in the weak field regime, as well as the strong field limit approached at a relatively weak field, suggests that the interaction between the triplet pair is very weak.

To further support the assessment, we compare the experimental data with the calculated results of field-dependent beating frequencies with different interaction strengths. As shown in Fig. 2(c), the field-dependent frequencies obtained from numerical calculations well reproduce the experimental results when the interaction is neglected (J = 0). Theoretical results show significant disparity from the experimental data when J increases to the order of microelectron volt, which is orders of magnitude weaker than the strength of J (0.3–3 meV) for the exchange-coupled triplets in 5,12-Bis((triisopropylsilyl)ethynyl)-tetracene-tetracene.[70]

The weak interaction between the triplet pair is also confirmed by the effect of magnetic field alignment. The field is aligned in the ab plane with the angle θ against the b axis [inset, Fig. 3(a)]. Figure 3 shows the θ-dependent quantum beats recorded in the strong field limit with an applied field of 0.3 T. The experimental data agree well with the theoretical calculation with negligible interaction [Fig. 3(c)]. The disparity between theoretical calculations and experimental results becomes significant when $J > 1$ μeV.

The experimental results have explicitly shown that the interaction is weak between the correlated triplet pair responsible for the quantum beats in the delayed FL. In fact, theoretical results suggest that only one sublevel has significant projection to singlet for exchange-coupled triplets (J = 0.3–3 meV), which should not contribute to the quantum beats.[79] Since the exchange interaction is strongly susceptible to the wavefunction overlap, the weakly coupled triplet pairs probed by quantum beats can be assigned to the spatially separated triplet pairs, i.e., the ^{1}(T···T) states.

B. Excitation density dependence

The dissociation process from the ^{1}(T···T) state to free triplets ($T_1 + T_1$) is essential for the overall efficiency of singlet fission. In the

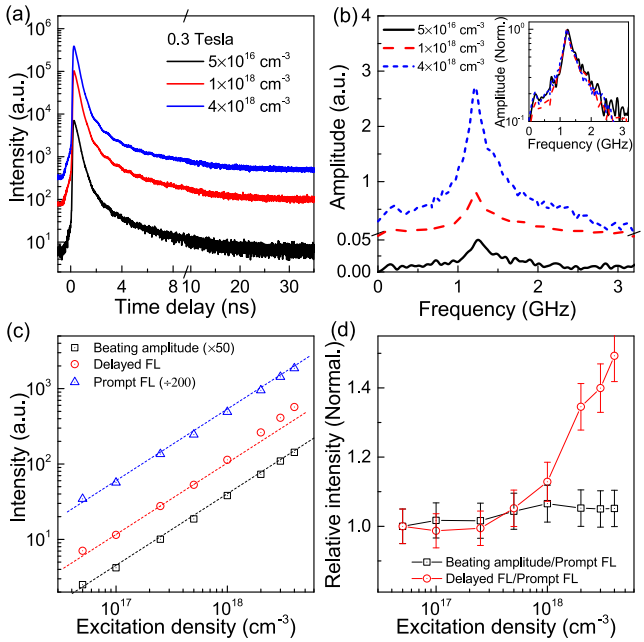

FIG. 4. Excitation density dependence of quantum beats. (a) TRFL traces recorded at different excitation densities. The traces are recorded with a magnetic field of 0.3 T aligned at θ of 55°. (c) The beating spectra recorded at different excitation densities. The inset shows the normalized spectra in a logarithm scale. (c) The beating amplitudes, the intensities of prompt FL at the zero time delay, and delayed FL at the delay of 20 ns are plotted vs excitation density. The dashed lines are linear dependence curves for references. (d) The intensity ratios between quantum beating/delayed FL and promote FL are plotted vs the excitation density.

TA spectral studies, the spectral feature of the ^{1}(T···T) states has been found to be similar to the free triplets ($T_1 + T_1$).[63] For more insights, we investigate the effect of excitation density on the quantum beats. To avoid the interference from multiple frequency beats at zero field, we set the magnetic field in the strong limit with $\theta = 55°$. We monitor the excitation-density dependences of quantum beats together with the prompt FL at the zero time delay and delayed FL at 20 ns. By detuning the excitation density of about two order from 10^{16} to 10^{18} cm^{-3} [Fig. 4(a)], the beating frequency and the linewidth of the beating spectrum are nearly unchanged [Fig. 4(b)]. The amplitudes of prompt FL and quantum beats are linearly dependent on the excitation density, while the delayed FL shows superlinear dependence [Fig. 4(c)]. These differences are better distinguished in the amplitude ratios [Fig. 4(d)]. The superlinear dependence of the delayed FL suggests the involvement of nongeminate triplet-triplet annihilation (TTA) in the regime of excitation density (>10^{18} cm^{-3}). In this same density regime, the amplitude of quantum beating is linearly dependent on the density of singlet excitons, confirming the origin of quantum beating from the germinate recombination of exciton fusion.

The singlet nature of the ^{1}(T···T) state is also manifested in the beating spectra. The profile remains unchanged when TTA becomes important, implying that the spin decoherence process is not sensitive to the triplet exciton interactions. In general, the signal of quantum beating can be captured only when the coherence retains.

It is likely that the ^{1}(T···T) state involved in the quantum beating is generated directly from singlet states. On the other words, two possible pathways exist in the singlet fission process in tetracene crystals: the initial step of singlet fission in a dimerlike configuration resulting in exchange-coupled triplet pairs [i.e., $S_1 \rightarrow {}^1$(TT)] or through a more delocalized scheme resulting in weakly coupled triplet pairs [i.e., $S_1 \rightarrow {}^1$(T···T)]. These scenarios may possibly explain the divergences in the previous experimental and theoretical results.[82] Previous works suggest that the weakly coupled triplet pair states ^{1}(T···T) are generated by spatial separation of ^{1}(TT) together with electronic decoherence,[63] which, however, cannot account for the ^{1}(T···T) state

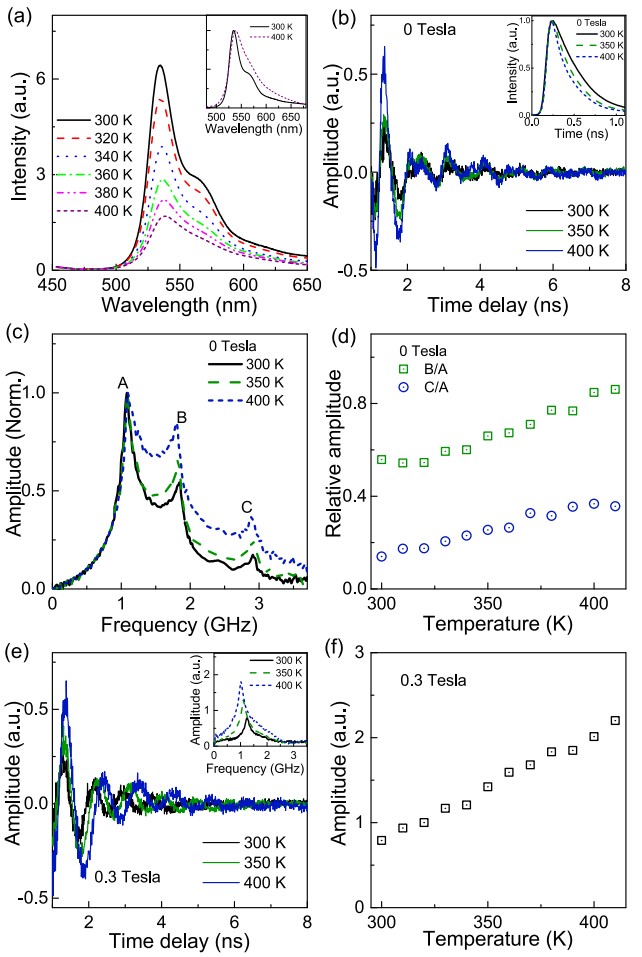

FIG. 5. (a) FL spectra are recorded at different temperatures. The inset shows the normalized FL spectra at 300 and 400 K. (b) Oscillatory components in TRFL traces are recorded at different temperatures. The inset shows the normalized TRPL traces at the early stage. (c) Normalized spectra of quantum beats recorded at different temperatures without applying magnetic field. (d) The amplitude ratios of two higher frequency modes (B and C) and the low frequency mode (A) are plotted vs temperature. (e) Oscillatory components in TRFL traces are recorded at different temperatures with a magnetic field of 0.3 T applied at θ of 55°. The inset shows the spectra of quantum beats obtained from the Fourier transformation of oscillatory components. (f) The beating amplitude in the normalized TRPL trace is plotted vs temperature.

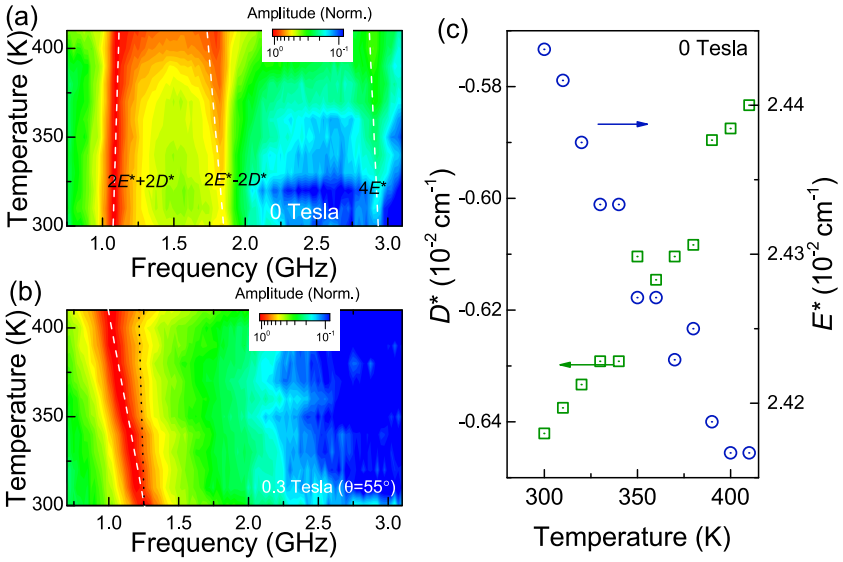

FIG. 6. The beating amplitude is plotted as a function of the beating frequency and temperature for the experiments performed (a) without applying magnetic field and (b) with applying magnetic field of 0.3 T at $\theta = 55°$. The dashed lines are the projection of the peak frequency with the parameters of D^* and E^* derived from z-field data and the transformation matrix [Eq. (4)]. (c) The zero-field parameters D^* and E^* are plotted vs temperature.

probed by the quantum beats since the beat signal can be generated only by the excited states with coherence.

C. Temperature-dependent quantum beats

Singlet fission in tetracene crystals is a slight endothermic process. Nonetheless, it remains highly controversial whether thermal activation is important for singlet fission in the literature.[51,63,83–85] To gain more insights for the process of $S_1 \rightarrow {}^1(T\cdots T)$, we investigate the temperature-dependent quantum beating behaviors in the range of 300–400 K with the excitation density of 1.0×10^{17} cm^{-3} (Fig. 5). Figures 5(a)–5(d) show the results recorded at different temperatures without applying external magnetic field. When temperature increases, the intensity of FL emission from the tetracene crystal gradually decreases [Fig. 5(a)], while the initial decay becomes faster [inset, Fig. 5(b)]. The faster initial FL decay can be regarded as a signature of faster singlet fission and/or increased nonradiative recombination.[83] As suggested by Bardeen and co-workers,[40] the rate of singlet fission is also reflected in the quantum beat spectrum. When temperature increases, the spectral profile shows remarkable dependence on the excitation density [Figs. 5(b) and 5(c)]. The higher frequency modes become pronounced with increasing temperature [Fig. 5(d)], which is consistent with the scenario of the increased singlet fission rate with increasing temperature.

Such a temperature-dependent singlet fission process is also observed in the results measured in the strong field limit [Figs. 5(e) and 5(f)]. In the normalized TRFL curves, the beating amplitude gradually increases, indicating that more triplet pairs are generated when temperature increases. These results suggest that increasing temperature is favorable for the direct conversion process of $S_1 \rightarrow {}^1(T\cdots T)$. In previous works, both temperature-dependent and independent behaviors have been reported. Bardeen and co-workers suggested the temperature-dependent rate of singlet fission in tetracene crystals by analyzing the beating in the TRFL traces,[40] while Friend and co-workers reported the temperature-independent SF using TA spectroscopy.[85] The disparity may be explained here with the two channels of singlet fission (Fig. 1). The faster fission process of $S_1 \rightarrow {}^1(TT)$ mediated by virtual charge-transfer states is possibly insensitive to the temperature,[43,50,51,86,87] which may be responsible for the major signal probed in TA spectra. Nonetheless, the quantum beat spectroscopy cannot probe the exchange-coupled ${}^1(TT)$ states but the weakly coupled spatially separated ${}^1(T\cdots T)$ states. The temperature variation may compensate the energy difference between S_1 and ${}^1(T\cdots T)$ states, leading to the increased singlet fission rate when temperature increases.

The temperature effect is also manifested in the beating frequency in particularly in the data recorded in the strong field limit [Figs. 5(c) and 5(e)]. We plot the temperature-dependent beating spectra in Fig. 6 where the temperature-dependent shifts of beating frequencies are observed. In theory, the zero-field values of three beating frequencies can be calculated as $2E^* + 2D^*$, $2E^* - 2D^*$, and $4E^*$, respectively, for the ${}^1(T\cdots T)$ states.[40] In this model, the temperature-dependent values of D^* and E^* are shown in Fig. 6(c). The effective values of D^* and E^* are sensitive to the alignment of the two molecules in the unit cells and the relative orientation between the two triplets. The temperature dependence suggests a slight change in the structure parameters in the tetracene crystals. In addition, the temperature-dependence of beating frequency at the strong field limit is more significant which cannot be directly reproduced with the values of D^* and E^* evaluated at zero field [Fig. 6(b)]. This difference is probably caused by the variation of transformation matrix [Eq. (5)] when temperature increases. These temperature-induced structure modification is consistent with the early survey on the structure of tetracene crystals,[88] which is possibly another reason of the increased singlet fission rate at higher temperature.

IV. CONCLUSION

In summary, we study the dynamics of intermediate state of triplet pairs by monitoring the quantum beating in the delay FL

emission from tetracene crystals. While the exchange interaction has not been included in previous studies on quantum beats in the delayed fluorescence from crystalline tetracene,[40,72,75] the experimental data have been well interpreted by modeling with negligible magnetic dipole-dipole interaction, which is conflicting with the recent observation of correlated triplets with marked exchange interaction.[70] Such an issue can be understood if singlet fission in tetracene undergoes two different channels resulting in either exchange-coupled ^{1}(TT) or spatially separated ^{1}(T···T) states. The dependences of beating spectra on the strength and alignment of the magnetic field strongly support that the triplet pair probed by the quantum beat spectrum is weakly coupled, i.e., the spatially separated ^{1}(T···T) state, implying the existence of a direct channel of $S_1 \rightarrow {}^1$(T···T) in addition to the $S_1 \rightarrow {}^1$(TT) $\rightarrow {}^1$(T···T) for singlet fission, which can also explain the previous debates on the temperature dependence of the fission rate. Our work suggests that the quantum beat spectrum is a useful tool to directly probe the spatially separated triplet pair states ^{1}(T···T) and provides new insights about the singlet fission mechanism.

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