

Optomagneto control of singlet fission charge multiplication dynamics in single organic semiconductor crystals

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Abstract: Over a 0-7 T range, transient absorption microscopy on anthradithiophene organic crystals shows that singlet to triplet pair state conversion is anticorrelated with fluorescence yield. This shows how the dominant singlet fission charge multiplication pathway can be switched-off with increasing B-field or by changing the molecular packing motifs. © 2022 The Author(s)

Singlet fission is a charge multiplication process that converts one singlet Frenkel exciton state to two triplets, thus having the potential to increase the photoconversion efficiency of emerging organic photovoltaic technology[1]. Singlet fission is a spin-conserved process that occurs by forming an intermediate correlated triplet pair (TT) before dissociating to free triplets as $S_1 + S_0 \rightarrow TT \rightarrow T_1 + T_1$. We isolate the B-field-dependent dynamics of TT-state formation using transient absorption (TA) microscopy on single organic crystals of anthradithiophene (ADT) for four different molecular packing motifs. Figure 1b (*inset*) shows a four-electron system consisting of a singlet exciton S_1 and ground S_0 state that can exchange electrons via either a concerted electronic super-exchange or a charge-transfer intermediate. In endothermic systems ($E(S_1) \leq 2 E(T_1)$, where $E(S_1)$ and $E(T_1)$ are energies of the singlet and triplet states, respectively), the resulting TT-states are remarkably stable with long lifetimes (>100 ps), and exist in three different spin configuration states as singlets ($S=0$), triplets ($S=1$) or quintets ($S=2$) wavefunctions [1]. A basic model for the TT state energy Hamiltonian can be summarized as,

$$H_{TT} = H_{Zeeman} + H_{(zero-field)} = g\mu_B B \cdot S + D \left(S_z^2 - \frac{1}{3} S \cdot S \right) + E(S_x^2 + S_y^2) \quad [1]$$

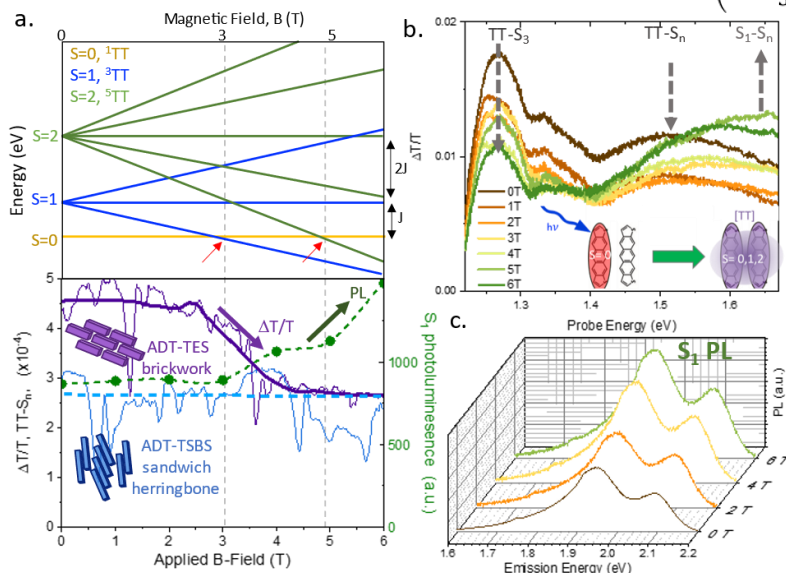


Figure 1: (a) (*top*) Illustration of expected Zeeman splitting of singlet, triplet and quintet TT-pair state showing anti-crossings at ~3 and ~5 T. (*bottom*) TA amplitude of TT state peak at 1.28 eV vs. B-field shows the TT-state decreases while S_1 PL increases (*green dots*) in for ADT-TES crystals with the brickwork packing structure (*purple line*). (b) B-field dependent TA spectra show TT peak decreasing with field while the S_1 singlet peak increases. (c) ADT-TES B-field dependent PL emission spectrum grows with applied B-field, suggesting increased singlet to triplet state population near anti-crossing resonances.

where the first term accounts for the linear Zeeman state splitting and the remaining terms are the zero-field interaction of the two correlated triplet states[1]. Figure 1a illustrates the resulting B-field-induced Zeeman splitting pattern associated with the singlet, triplet, and quintet TT-pair states. Interestingly, avoided anti-crossing regions occur at the lowest energy singlet-triplet and singlet-quintet state crossing (see red arrows in Fig. 1a) [2]. Figs. 1a and 1c show that near these state anti-crossings at B=3 T and 5 T the measured singlet S_1 photoluminescence yield increases (*green dots*) while the corresponding TT-pair population is depleted (*purple line*). The anti-correlated singlet and triplet-pair population is also seen in the TA microscopy spectral peaks in Fig. 1b. Specifically, The TT-S_n excited state absorption peaks decrease while the S_1 -S_n peaks increase.

When considering the ideal criteria for TT state formation in organic crystals and thin-film photovoltaics, the molecular packing motif plays a critical role by modulating intermolecular electronic

coupling strength (J) [3,4]. Using single-crystal ultrafast microscopy methods, we isolate the packing configuration that best promotes TT formation and singlet fission [4]. Singlet fission dynamics are indicated in Fig. 2a by the matching singlet (blue) and matching ~ 70 ps rising TT-state formation dynamics (orange) that are revealed only when the probe-beam is polarized along the crystal charge-transfer axis. Difluorinated anthradithiophene (diF ADT) single crystals are grown with different molecular packings including *brickwork*, *sandwich herringbone*, and *twisted columnar* packing morphologies. In each ADT molecular packing morphology, both the dynamic and spectral signatures of TT-state formation are measured over broad temperature ranges (1.5 to 295 K) and applied magnetic fields (0 to 7 T). As shown in Fig. 1a (blue line), some ADT packing derivatives such as the sandwich-herringbone (ADT-TSBS) packing morphology show no spectral or dynamic signatures of TT formation due to a preferential exciton self-trapping pathway.[4]

The dynamics associated with TT-state formation are observed to change markedly near the ‘singlet-triplet’ and ‘singlet-quintet’ B-field anti-resonances shown in the Zeeman splitting diagram of Fig. 1a. Strikingly for B-fields > 4 T, Fig. 2b shows the slowly rising kinetics associated with the triplet-pair formation become effectively ‘turned-off.’ and only the residual single-state relaxation remains. At $B = 5-6$ T, the single-crystal TA kinetics of brickwork-packed ADT-TES crystal become indistinguishable from that of a dilute solution at 0 T (open circles in Fig. 2b); suggesting a $J \rightarrow 0$ coupling limit and no singlet fission.

The impact of high B-fields is most clearly seen in Fig. 2b (lower) when the pump beam is polarized orthogonal to the crystal stacking axis. In this pump polarization configuration, coherent vibrationally-mediated TT formation processes are mitigated such that primarily thermally-activated triplet pair formation processes dominate. Suddenly for $B > \sim 4$ T, the rising kinetics associated with TT formation are abruptly absent and only the residual long pure singlet kinetic relaxation component remains. This apparent ‘singlet-fission turn-off’ suggests that the four-electron superexchange needed for singlet fission is suppressed from resonant mixing of the singlet ($S=0$), triplet ($S=1$) and quintet ($S=2$) intermolecular exciton states for $B > \sim 4$ T. In summary, for three different molecular packings of diF-ADT crystals, the singlet PL emission is observed to be anti-correlated with the population of triplet pair (TT) states; clearly showing how both B-fields and packing morphology[4] rigidly controls the $S=1$ and $S=2$ triplet pairs formation pathways that are required for singlet fission.

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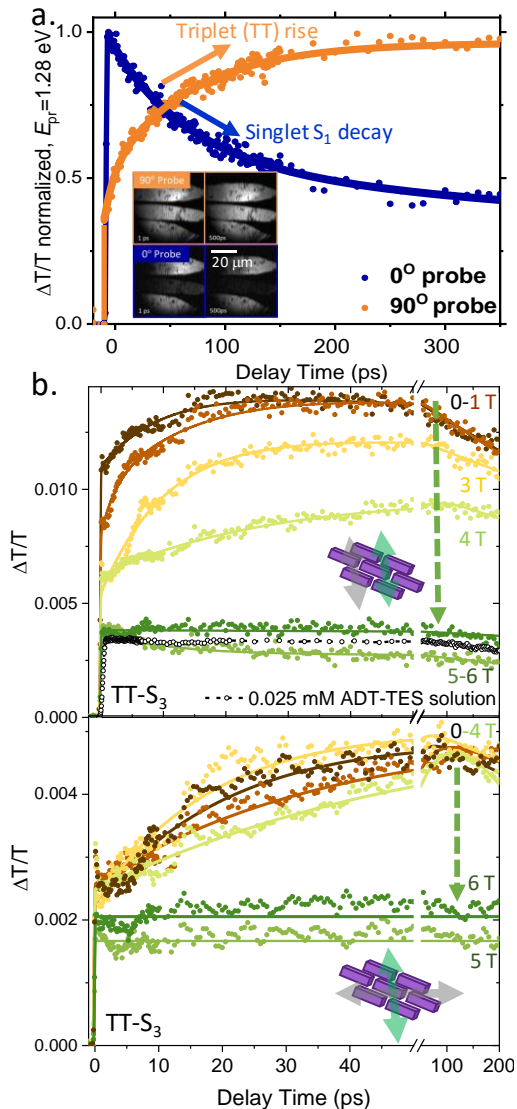


Figure 2: (a) By changing probe polarization, singlet fission is indicated by the matching singlet fall (S_1 - S_n) vs. TT rise (TT- S_n). (inset) Single crystal TA microscopy maps of TT state formation. (b) The rising TA dynamics shown are suppressed differently by B-fields for the parallel (top) vs. orthogonal (bottom) pump and probe polarizations (see insets). The rising kinetics of TT formation are ‘switched off’ for $B > \sim 4$ T, leaving only residual singlet relaxation kinetics.