

Packing Morphology-Dependent Singlet Fission in Single Crystal Anthradithiophene Derivatives

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Abstract: Single crystal excited state dynamics in functionalized anthradithiophene (ADT) derivatives were compared across four distinct packing morphologies. Using polarization-dependent transient absorption microscopy, morphology-dependent singlet fission was observed in only three of the four ADT derivatives. © 2020 The Author(s)

Singlet fission in organic materials has the advantage of multiplying the number of electron-hole pairs generated per incident photon. While the ultrafast dynamics of singlet fission in solution-phase is well-characterized, there is still considerable controversy over the criteria for singlet fission in solid-state thin-film organic photovoltaics (OPVs.) In particular, how do particular packing motifs modulate intermolecular electronic coupling to enhance or suppress the efficiency of singlet fission? To respond and investigate which packing morphologies are most conducive to singlet fission, we compare the transient absorption (TA) microscopy response of four single crystal morphologies of functionalized derivatives of fluorinated anthradithiophene: R-ADT (R = TES, TSBS, TDMS, TBDMS.)

Consistent with the signature matching ‘singlet fall’, ‘triplet rise’ dynamics in established singlet fission systems like pentacene and tetracene, previous ultrafast studies have shown that ADT is also an emerging singlet fission organic semiconductor [1,2]. However, these ADT studies were confined to solution-based samples and thin-film measurement that lack the diffraction-limited spatial resolution needed to isolate ultrafast dynamics within a single crystal. Using ultrafast TA microscopy on single TES-ADT crystals, we observe characteristic singlet fall times (*blue circles*) of ~1.1 ps in Fig. 1b and ~85 ps in Fig. 1c that match the corresponding rise (*red circles*) in excited state absorption (ESA) response. We associate these clear matching rising and falling dynamics with triplet formation via coherent or incoherent singlet fission mechanisms previously reported in ADT [1].

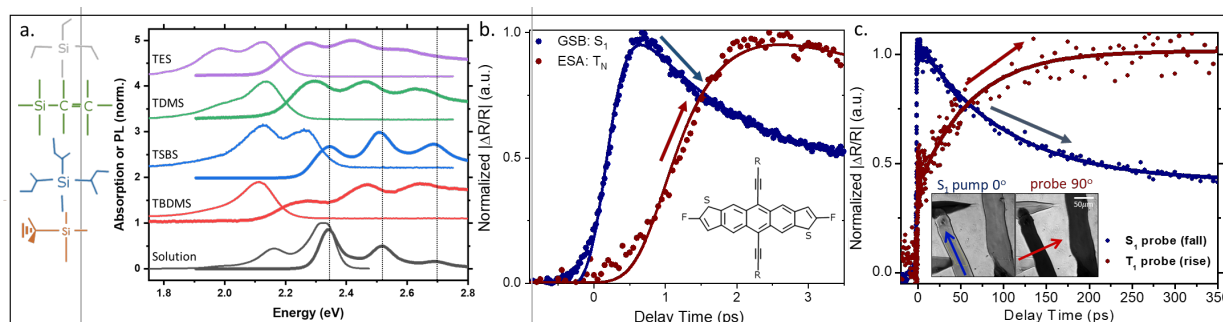


Figure 1: Matching dynamics isolate singlet fission processes in single crystals of ADT. (a) Absorption (polarized along the long crystal axis) and photoluminescence spectra of R-ADT derivatives of differing morphology. Molecular structures of the side groups R are also shown. (b-c) Single crystal TA microscopy of TES-ADT shows matching rise/fall dynamics on the ~1.1 ps timescale associated with fast singlet fission and a longer ~85 ps timescale associated with a slower singlet fission conversion between singlet and triplet states. (inset) Single crystal dipole orientations of TES-ADT shown are identified by polarization-dependent hyperspectral absorption microscopy.

R-ADT derivatives all share the same conjugated ring structure that forms the backbone of the molecule with different side groups R, shown in Fig. 1a, that attach off the core of the molecule, shown in Fig. 1b (inset.) Changing the different side groups alters the molecular packing properties of each derivative, which changes the crystal electronic structure and optical properties. For instance, when ADT is functionalized with the TES side-group, it packs in a two-dimensional (2D) brickwork configuration. These variations in molecular packing cause shifts in the steady-state absorption and PL spectra of the different ADT derivatives relative to their spectra in solution, shown in Fig. 1a. TES-ADT and TDMS-ADT both exhibit 2D brickwork packing structures, TSBS-ADT exhibits a 1D sandwich-herringbone packing structure, and TBDMS-ADT exhibits a 1D twisted-columnar packing structure.

The single crystal absorption and photoluminescence (PL) spectra are shown in Fig. 1a. The peak amplitudes suggest each ADT derivative has distinct electronic coupling signatures. The PL measurements show the lowest singlet state of ADT crystals is centered between 2.1–2.3 eV. The first excited triplet state energy, T_1 has been reported to be around 1.08 eV, which is consistent with prior DFT predictions [1]. These energies suggest that when singlet fission occurs in ADT crystals, it may need to overcome a slight energy barrier. Similar to other organic crystals, the structure of ADT crystals leads to anisotropic electronic and optical properties. Optical transitions are highly anisotropic for both the $S_0 \rightarrow S_1$ transition and excited state absorption to higher S_N and T_N states [3]. Fig. 1c (*inset*) shows a microscopy image of TES-ADT for resonant excitation at 2.3 eV. The strong axial absorption at 0° vs. 90° polarized light demonstrates the anisotropy of the 0-0 line of the $S_0 \rightarrow S_1$ transition of the single crystal.

Excited-state ultrafast dynamics were measured using TA microscopy to reveal signatures of singlet fission from individual crystals of ADT. Ultrafast laser pulses were generated using a Ti:Sapphire laser with an optical parametric oscillator with second-harmonic generation (SHG) or whitelight supercontinuum generation outputs. The TA data presented in Fig. 1 uses a tunable above-resonance pump centered near 2.8 eV and a spectrally-resolved supercontinuum probe. The TA microscopy data presented in Fig. 2c-d instead uses a SHG pump near the resonance of each ADT derivative, followed by a probe with half the energy of the pump to be resonant with the triplet excited state absorption (from 1.19 eV to 1.32 eV) peak shown in Fig. 2b. Since each transition has a different transition dipole orientation, specific dipole transitions were selected using TA microscopy by varying the probe beam polarization, as shown in Fig. 2c. Pump and probe beams are further raster-scanned through a 50XIR objective to optimally align individual domains of ADT with the dipole-matched polarization along the single crystal axis. The spot size is diffraction-limited, and the transient reflection signal is retrieved by lock-in detection at 200 kHz. The contribution from different transitions is determined by the polarization-dependent coupling strength between the electric field of the probe and the available transition dipole moments [4]. Singlet fission dynamics in pentacene and tetracene have previously been studied using polarization-dependent transient absorption, where the anisotropy of exciton dynamics was utilized to identify the contributions from singlet and triplet excitons [5][6]. All ADT samples were measured under a high-vacuum environment inside of a cryostat to prevent sample oxidation.

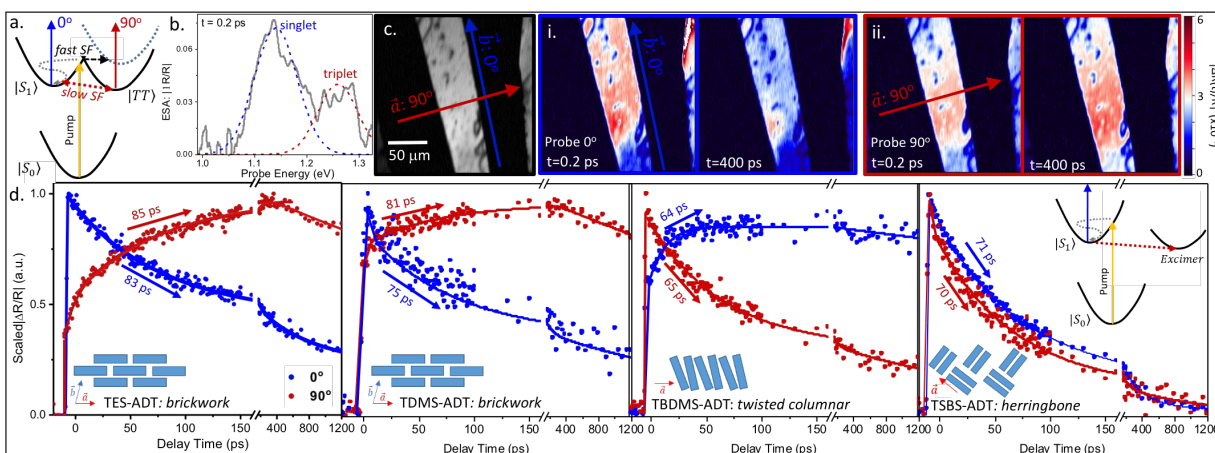


Figure 2: ADT packing morphology-dependent SF. (a) Energy-level diagram shows resonant S_1 pump, followed by a probe polarized to select either a singlet (0°) or triplet (90°) ESA response. (b) TA microscopy ESA spectrum for a 2.65 eV pump. Beyond the ~ 0.2 ps delay shown, the triplet-associated ESA peak at ~ 1.25 eV rises while the singlet ESA peak falls. (c) Spectrally resolved absorption microscopy image of a TES-ADT single crystal enables alignment of pump and probe polarizations with the crystal axes. i.- ii. Corresponding ultrafast TA microscopy spatial maps at $t=0.2$ ps vs. 400 ps show a spatially uniform falling (0° pol.) vs. rising (90° pol.) singlet fission (SF) dynamics. (d) SF-associated TA relaxation dynamics of four differing ADT single crystals with the packing structure of each derivative shown. Each plot compares ESA dynamics at 1.25 eV energy for 0° (blue) vs. 90° (red) probe polarizations. All ADT derivatives except TSBS-ADT exhibit matching rise/fall dynamics in the second exponential fitted lifetime (arrows). (*inset*) Modified energy level diagram for TSBS-ADT illustrating that this derivative may favor stable excimer formation instead of the slow SF observed in ADT derivatives with the other three packing motifs.

Figs. 2c-d show TA pump-probe dynamics taken for probe beams polarized parallel (0°) and perpendicular (90°) to the long axis of the crystal (which corresponds to the a -axis in TBDMS-ADT and TSBS-ADT and the b -axis in TES-ADT and TDMS-ADT.) The ultrafast dynamics in all of the ADT derivatives were largely independent of pump polarization but strongly dependent on probe polarization. Fig. 2d shows a prominent ESA response that rises exponentially when the probe beam was polarized perpendicularly to the long axis of either TES-ADT or

TDMS-ADT single crystals. We associate this $\sim 12 \text{ ns}^{-1}$ growth rate with triplet exciton formation. Conversely, when the probe beam polarization was aligned parallel to the long crystal axis, a matching fast decay associated with singlet exciton state depletion is seen in Fig. 2d (*blue circles*.) The opposite behavior was observed in TBDMS-ADT, where the triplet rise was most prominent when the probe beam was instead polarized perpendicularly to the long axis of the crystal. The polarization-dependent ultrafast dynamics suggest that the excited-state singlet transition dipole orientation is parallel to the long axis of the TES-ADT and TDMS-ADT crystals and the short axis of the TBDMS-ADT crystal. Conversely, the excited state triplet transition dipole is oriented perpendicular to the long axis of the TES-ADT and TDMS-ADT crystals, and the short axis of the TBDMS-ADT crystal.

Using a least-squares deconvolution algorithm that accounts for instrument response, three exponential time components are needed to fit TA relaxation dynamics. Each component can be assigned to three competing processes in the ADT crystals after $S_0 \rightarrow S_1$ excitation. As shown in Fig. 1b-c, for the case of TES-ADT, these include a fast ($\sim 1.1 \text{ ps}$) and a slower ($\sim 85 \text{ ps}$) rise component (negative amplitude) or a slow ($\sim 85 \text{ ps}$) decay (positive amplitude) decay component, depending on the probe polarization. These two shorter time components are associated with fast and slow triplet conversion via singlet fission (SF.) Specifically, the fastest rise components can be assigned to a SF process where the TT state is formed quickly after the excitation to the S_1 state. The second rise component can be assigned to a slower SF process, where the singlet exciton may hop over to the TT state, likely by a slower vibrationally mediated process. The third time component, with the slowest decay rates extracted in fits shown in Fig. 2d, correspond to the relaxation of the optically probed excited state. Depending on packing morphology, this longest component varies from $\sim 1.1 \text{ ns}$ for TSBS-ADT to 5.3 ns for TES-ADT.

Fig. 2d further shows that the matching rise and fall dynamics (which we associate with SF) are observed only for certain molecular packing motifs of ADT crystals, in particular those that support exciton delocalization [7]. In the case of TES-ADT and TDMS-ADT, this is facilitated by a large number (six) of nearest neighbor molecules, whereas in TBDMS-ADT it is facilitated by the large π - π overlap between adjacent molecules which suppresses the formation of localized states such as excimers. Conversely, TSBS-ADT has only two nearest neighbors with a large slip distance between adjacent molecules in the “sandwich” part of the “sandwich-herringbone” packing. As a result, in contrast to other ADT derivatives under study, the exciton delocalization in TSBS-ADT is suppressed, and the formation of highly localized Frenkel exciton and stable room-temperature excimer (inset of Fig. 2d) are favored instead [7]. These relaxation channels outcompete the TT state formation in TSBS-ADT.

In summary, singlet and triplet exciton dynamics in single crystals of ADT were isolated using polarization-dependent TA microscopy. ADT derivatives with brickwork and twisted-columnar packing morphologies that are supportive of exciton delocalization all show matching rising and falling dynamics on a ~ 75 - 85 ps timescale, suggesting singlet fission. By contrast, when ADT molecules form the sandwich-herringbone motif, other relaxation channels are more efficient and this dynamic signature of singlet fission is completely suppressed.

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