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Vibronically coherent ultrafast triplet-pair formation and subsequent thermally activated dissociation control efficient endothermic singlet fission.

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Abstract

Singlet exciton fission (SF), the conversion of one spin-singlet exciton (S_1) into two spin-triplet excitons (T_1), could provide a means to overcome the Shockley-Queisser limit in photovoltaics. SF as measured by the decay of S_1 has been shown to occur efficiently and independently of temperature even when the energy of S_1 is as much as 200 meV less than $2T_1$. Here, we study films of TIPS-tetracene using transient optical spectroscopy and show that the triplet pair state (TT), which has been proposed to mediate singlet fission, forms on ultrafast timescales (in 300 fs) and that its formation is mediated by the strong coupling of electronic and vibrational degrees of freedom. This is followed by a slower loss of singlet character as the excitation evolves to become only TT. We observe the TT to be thermally dissociated on 10-100 ns timescales to form free triplets. This provides a model for 'temperature independent', efficient TT formation and thermally activated TT separation.

Singlet exciton fission (SF) is a quantum mechanical phenomenon unique to organic chromophores that could provide a route to breaking the Shockley-Queisser limit on the efficiency of single junction photovoltaics (PVs)[1,2,3]. In this process, a photogenerated spin-0 singlet exciton (S_1) is converted to two spin-1 triplet excitons (T_1). It has been proposed that this conversion is mediated by a triplet pair intermediate state (TT), which forms an overall spin-0 state[4]. This means that SF does not require a spin flip and can proceed on <100 fs timescales when SF is exothermic, i.e $E(S_1)>2E(T_1)$, allowing for near unity efficiency (200% triplet yield) in materials such as pentacene[5].

But intriguingly, SF also proceeds very efficiently in endothermic systems, where $E(S_1)<2E(T_1)$, overcoming energy barriers ($E_b = 2E(T_1) - E(S_1)$) of up to 200 meV[6]. Such systems are of particular technological importance, as most of the materials with $E(T_1)$ comparable to the bandgap of silicon (1.1eV) fall into this category, including perylenediimides[7] and acenes such as tetracene ($E_b \cong 180$ meV), which is the most well studied endothermic SF system[6,8,9]. Extensive work by Bardeen and others has unambiguously shown that free triplets are produced in a high yield in polycrystalline tetracene, yet S_1 decays independently of temperature on a 70-90 ps timescale [6,10,11,12]. The rate of decay is three orders of magnitude slower than in pentacene, despite similar electronic couplings between the relevant electronic states[13]. So, what controls the decay rate of S_1 and how can this state efficiently overcome an endothermic barrier to generate free triplets?

To investigate the mechanism of endothermic SF we study solid-state TIPS-tetracene[14], which has the same molecular core as tetracene but is made solution processable via the addition of triisopropylsilyl (TIPS) ethynyl side groups, see Figure 1b. As we discuss below, TIPS-tetracene possesses sharp signatures for S_1 and T_1 states. We use ultrafast spectroscopy to show that the photoexcitated population acquires TT character on sub-300 fs timescales and evolves to lose S_1 character on a morphology-dependent 6-20 ps timescale. The TT state is long-lived and thermally dissociates into separated T_1 on 10 ns timescales in disordered films at room temperature, but surprisingly, remains bound for tens of μs in polycrystalline films due to a low triplet-hopping rate.

Results and Discussion

Ultrafast TT formation

Figure 1a shows the energetics of TIPS-tetracene, where the energies of S_1 (2.3 eV) (from UV-Vis absorption) and T_1 (1.20-1.30 eV) (from phosphorescence)[15], indicate that fission is similarly endothermic to tetracene. In this study we investigate two film types, 'disordered' and 'polycrystalline' that differ in morphology (see SI for structural characterization). The UV-Vis and photoluminescence spectra of TIPS-tetracene dilute solution, disordered and polycrystalline films are shown in Figure 1c. The TIPS-tetracene chemical and crystal structure is shown in Figure 1b.

To investigate the dynamics of SF we use ultrafast broadband transient absorption (TA) spectroscopy with 16 fs time resolution. Figures 2a and b show the room-temperature TA spectra from 50 fs to 2 ps of the two film types, optically excited close to the absorption edge. The spectral shapes observed in both films are consistent with the S_1 and TT species previously identified in concentrated solutions of TIPS-tetracene[15]. The initial positive signal at 570 nm (Figures 2a and b) is consistent with photoluminescence maximum of the 0-1 band of the S_1 emission and is assigned to S_1 stimulated emission (SE), as seen for dilute solution (Figure 2c). The broad negative signal from 600-1300 nm corresponds manily to S_1 photo-induced absorption (PIA) and is similar to the solution.

At longer time delays we observe a sharply peaked absorption spectrum (90ps time slice in fig 2a and b) that is assigned to the TT state. This assignment is based on the results from the previous solution study revealing that the T_1 absorption in TIPS-tetracene shows sharp peaks across the visible and NIR(, regularly spaced by a vibrational frequency of ~1300 cm^{-1}.). The TT state was shown to display the same sharp T_1 absorption peaks, but shifted by up to 5 meV[15]. The assignments of S_1 and TT to the spectral species are based on the similarity of the spectral features we observe to those of individual S_1 and T_1 excitons in solution, but does not preclude mixing of CT states, which our spectroscopic measurements can not give information on, into these states[13].

In Figure 2c we present the TT absorption spectrum at 100 ps obtained from a TA measurement of the polycrystalline film. Notably, the sharp TT absorption bands at 670, 850 nm and 960 nm enable us to track the conversion of S_1 to TT.

Figure 2d and 2e show the loss of S_1 SE and growth of the TT absorption for the two film types over the first 2 ps. To single out the TT growth we use kinetics at 860 nm and 835 nm, at the maximum and to the side of the sharp TT absorption band (see TT absorption in Figure 2c) and normalise to the peak initial signal when only S_1 is present. The difference between the two kinetics provides a background-free kinetic and captures TT population evolution. Both films show a rise time of 250 fs for the TT absorption that is matched by the rate of loss of SE intensity at 570-580 nm. We confirm this time for the ultrafast interconversion of S_1 and TT using a spectral deconvolution method that takes into account all spectral changes across the visible-NIR region (see Supplementary Information section 5). At longer times, there is a further ~10 ps rise in the TT state, matching the decay of S_1.

Vibrationaly coherent TT formation

The ultrafast pump pulse impulsively excites the system as has been discussed previously[16]. This vibrational coherence results in strong oscillations in the TA spectra and kinetics, as seen in Figure 2d-e. We globally fit the population decay for the TA measurements and Fourier transform the residuals that contain the modulation on top of the electronic response (Supplementary Fig. 14). In Figure 3a we compare these Fourier spectra obtained from integration across the whole optical spectrum of both film types (560 –1300 nm) with dilute solution (grey trace) and the ground state resonance Raman spectrum (black trace).

The presence of additional modes in the films in comparison with solution results from additional excited states present in the films that are absent in dilute solutions. To explore this, we compare the 315 cm^{-1} mode which is associated with the S_1 state as seen in the dilute solution, with the 760 cm^{-1} mode that is only present in the films. We plot the strength of these modes as a function of wavelength in Figure 3b, for polycrystalline films that afford the best signal to noise. These plots show which parts of the spectrum the modes are associated with and hence which excited states they are coupled with. As can be seen in Figure 3b, the distribution of the 315 cm^{-1} mode reveals nodes at the positions of maximum absorption intensity of the polycrystalline film at early time delays when the system is dominated by S_1, as expected in the case where the 315 cm^{-1} mode is related to the lateral shifting of the S_1 absorption spectrum (Supplementary Fig. 17)[17]. The 315 cm^{-1} mode also shows intensity at lower energies (~ 1300 nm) where there is a strong S_1 PIA. In contrast, the intensity of the 760 cm^{-1} mode is strongest in the 600 nm- 900 nm region, with a node at 860 nm, where there is a sharp TT PIA, and is very weak at wavelengths > 1000 nm, where the TT state does not absorb strongly. This mode is absent in the vibrational spectra of dilute solutions where SF does not occur and no TT state is formed.

In Figure 3c we present sliding-window Fourier transform plots of the 315 cm^{-1} and 760 cm^{-1} modes. This analysis uses a 1 ps-wide sliding window, represented on the x axis by the earliest time point in the window. The 315 cm^{-1} mode is plotted for 570 nm and the 760 cm^{-1} mode is plotted for 850 nm, the regions associated with SE and strong TT absorption in the polycrystalline films respectively. We find the 315 cm^{-1} mode shows a decrease over time, as expected for a mode where vibrational coherence is generated upon photoexcitation and subsequently damped, either by movement away from the S_1 PES or by scattering on the phonon bath. Scattering is unlikely, as damping times for this phenomenon are expected to be on the picosecond timescale. In contrast, the 760 cm^{-1} mode shows an initial increase, as the window slides from 0-1 ps to 0.4-1.4 ps. The time period of the 760 cm^{-1} mode, 43 fs, is much shorter than the TT rise time (250 fs), which means that vibrational coherence cannot be created impulsively via the SF process populating TT. Rather, the 760 cm^{-1} mode is likely to be a product mode of the reaction, formed as the nuclear wavepacket moves from the S_1 to the TT PES. Hence, the increase in strength seen in Figure 3c as the underlying TT state grows in (Figure 2e) indicates the formation of the TT state occurs via a vibrationally coherent process. This is similar to vibrationally coherent SF observed in exothermic SF systems, which has been explored both theoretically[18,19], and experimentally[20,21,22], and also vibrationally coherent ultrafast internal conversion in polyenes[23] and energy transfer in biological light harvesting systems[24].

This coupling also modulates the energy levels of the states involved in the SF process, which is likely to help drive TT formation, as has been previously suggested in a computational study of tetracene derivatives[25]. The shifting of the PIA features in the ultrafast TA spectra reveal that the transition energies over all excited states present are modulated by more than 100 meV (Supplementary Fig. 14), indicating that energies calculated with the ground state geometries do not provide a good guide to understanding what happens on the excited state PES.

Our observations show that vibrational modes are involved in the rapid formation of TT in TIPS-tetracene. This is different from a model based on strong-electronic coupling between S_1 and TT, which has previously been invoked to explain the dynamics of tetracene by Zhu *et al.*[26]. Instead of the direct formation of a superposition of S_1 and TT upon photoexcitation, our data suggest that following photoexciation vibrational modes drive the wavepacket from the initially populated Frank-Condon region, modulating both the energies and couplings between S_1 and TT and leading to the evolution of the state from one dominated by S_1 character to one dominated by TT character. While such a process is known for exothermic fission, where $2xT_1$ is lower in energy than S_1, these results show how even in endothermic systems the TT state can be accessed on ultrafast timescales, enabling endothermic fission to be equally efficient at generating triplet excitons.

As seen in Figure 2d and 2e, following the early time ultrafast conversion of S_1 to TT, there is delayed rise in TT with a concomitant decay of S_1. This slower S_1 decay is reminiscent of the S_1 decay observed in tetracene[6,10] – it decays independently of temperature over tens of picoseconds (see Supplementary Fig. 23-24) and shows a morphology-dependent lifetime (6-10 ps for disordered and 15-19 ps for polycrystalline), matching the delayed rise of TT. Correspondingly, a 11 ± 1 ps and 12 ± 1 ps photoluminescence lifetime was measured for the disordered and polycrystalline film types respectively (Supplementary Fig. 10). The variation in lifetime for the S_1 decay we observe between the TA and PL, and within the TA measurements, we consider to arise due to the inhomogeneity across the polycrystalline film. Importantly, in the absence of higher time resolution and sharp TT spectral signatures this S_1 decay time would appear to be the SF rate for TIPS-tetracene. However, as we have shown, this S_1 decay rate gives a misleadingly slow indication of the rate of initial TT formation.

We consider that the ultrafast formation of TT represents SF that occurs at photoexcited sites in the film where intermolecular arrangement is optimal for SF. The picosecond morphology-dependent loss of S_1 and rise of TT may to be related to the time needed for the excitation to diffuse to optimal fission geometries, as has been suggested in tetracene[10,27]. Multiple timescales for TT formation have also been observed in hexacene[22], where fission is exothermic, and most recently in rubrene[28], where in both cases the two timescales of TT formation have been attributed to both coherent and incoherent fission processes. In the later study, it was suggested that coherent TT formation was related to excitation of low-frequency symmetry breaking intermolecular modes, which was followed by a separate incoherent TT formation pathway[28]. However, in TIPS-tetracene we cannot rule out an alternate explanation for the slow loss of S_1 that is also consistent with our data, whereby vibronic coupling sets up an equilibrium between S_1 and TT and the 6-19 ps timescale is related to the time needed to fully shift the S_1-TT equilibrium to only TT. Such a process could be mediated by slow damping of certain low-energy phonon modes that are associated with the photoexcited state and not present within the crystal in the ground state, and thus cannot be easily damped. This could allow for a vibronic equilibrium between S_1 and TT to be setup, which would last as long as the modes are undamped. Damping of vibrational modes over 10s of ps has been previously observed at low temperature in pentacene crystals in naphthalene[29]. This hypothesis would be supported by our observation that the broad PIA (600 nm-1300 nm) in the two films does not show the prompt loss of oscillator strength as seen the SE feature, but shows many sharp features associated with TT from sub-200fs timescales and decays over the picosecond timescale (Figure 2a and b). We predict that the ultrafast TT formation is associated with rapid movement away from the Franck Condon region resulting in loss of SE and that the broad PIA features are due to absorption of the resulting S_1-TT state to higher-lying excited states.

Thermally activated TT dissociation

The fast formation dynamics indicate that the initial TT yield could be very high, as it outcompetes radiative and non-radiative decay channels. However, it is the yield of T_1 + T_1 at longer timescales that is more relevant for photovoltaic device applications.

Figure 4e tracks the evolution of both films at 850 nm from 10 ps to 2 ms. In the disordered film, the raw TA kinetic shows the presence of two decay regimes that we can spectrally resolve, using a spectral deconvolution code based on a genetic algorithm[30], into the decay of bound TT state (τ= 10 ns (295 K)) and the decay of separated T_1 (τ= 10 μs (295 K)) (Figure 4b). The near-IR spectra of the concentrated solution, disordered film and polycrystalline film are shown in Figure 4(a,c,e). For the concentrated solution and disordered film we observe a shifting of the TT absorption peaks and loss of absorption between the two peaks over 1 ns - 1 μs, to give the absorption confirmed via sensitisation to be T_1 at microsecond delays[15]. A shift in the TT absorption peaks have also been observed in pentacene derivatives and associated with the changing excitonic interactions of the bound state as it separates[31]. However, in the disordered film of TIPS-tetracene the TT dissociation rate and the yield of $T_1 + T_1$ are both temperature-dependent (Figure 4b). As the temperature is lowered we observe slower TT decay and relatively weaker $T_1 + T_1$ absorption, consistent with a thermally activated TT separation. At the lowest temperatures measured (10 K), we resolve only the TT state. We note that the room temperature TT lifetime measured here is comparable to the TT lifetime in concentrated solution (8.7 ns)[15], indicating that a similar barrier is overcome in both systems. We make two estimates for the yield of the reaction TT to $T_1 + T_1$. From the quenching of the TT PL at room temperature (see below), we obtain a value of 180 ± 10 %, and from the evolution of the TA, using T_1 cross-sections obtained from sensitization measurements a value of 130 ± 20 % (see Supplementary Information section 7).

The TT absorption, including the weaker TT feature at 900 nm, decays more slowly and is present over the full decay in the polycrystalline film, Figure 4e. Furthermore, the spectrum cannot be de-convoluted into multiple species. The decay of the spectrum does not show an evident temperature dependence, nor is its decay accelerated under increased fluence (from 80-400 μJcm^{-1}). Taken together, these observations suggest that in polycrystalline films the TT state does not dissociate to $T_1 + T_1$ even at room temperature.

To understand why the crystalline morphology gives rise to a long-lived TT state, we calculate the triplet-hopping rates in two distinct intermolecular situations that represent the extreme case for structure difference between the polycrystalline and disordered films - two molecules from the crystal structure and two pi-pi stacked dimers, respectively (see Supplementary Information section 2 for details). We find that the two intermolecular geometries present very different hopping integrals: 15 and 0.2 meV for the pi-stacked dimer and the crystal structure respectively. Using a reorganization energy of 0.33 eV and the Marcus model[32] these hopping integrals correspond to a T_1 hopping time of 2.5 ps and 52 ns, respectively. As we cannot know how large or dense the pi-stacked domains are in the disordered film, this value represents an upper limit. Importantly, these calculations highlight the unusually poor triplet-triplet coupling in the TIPS-tetracene crystal structure and suggest that in polycrystalline films, triplet hopping is very slow and significantly slow the dissociation of the bound TT state.

Photoluminescence from the TT state

Photoluminescence measurements also reveal information on the energetics and evolution of the TT state. The photoluminescence quantum efficiency in both film types is moderately low: 3% and 1% for the disordered and polycrystalline films respectively, at room temperature. However, as we report below, the PL yield for the disordered film increases rapidly with reducing temperature, by a factor of 20 at 10 K, implying a PL yield of around 60%. Fig. 5c and 5f show the temperature-dependent steady-state PL of the two films. The disordered film shows a broad PL centered at ~650 nm, with two vibronic peaks clearly visible at low temperature. The polycrystalline film shows three different peaks, and the overall temperature-dependent behavior is similar to tetracene[5,6], with the second peak at 580 nm dominating at higher temperatures and the high-energy feature at 540 nm, associated with the 0-0 transition of S_1 dominating at low temperature.

The time-resolved PL at 10 K reveals that in both film types there are two emissive species, a prompt high-energy component, and a red-shifted emissive state (time slices at 0.5 ns and 50 ns in Figure 5a and 5d). The high-energy state has the same spectrum as the dilute solution and decays with a temperature-independent lifetime (Figure 5b and 5e); we assign this to emission from S_1 in both disordered and polycrystalline films. For the crystalline film, the S_1 feature has a delayed component, similar to the well-studied delayed PL in tetracene[6,33]. For the disordered film, no delayed component of S_1 is detected, indicating that any regeneration of the S_1 from TT is too weak to detect.

In both films the red-shifted emission region shows a thermal-dependence. From the kinetic traces at 650 nm of the disordered film we obtain an activation energy, out of the red-shifted emissive state, of ~90 meV (Supplementary Fig. 8). This temperature-dependent emission tracks the temperature dependence for the TT state we observe in TA (Figure 4b). We note that the high PL yield from the red-shifted emission in the disordered film at 10 K allows direct comparison of the PL decay with the time evolution of the TA spectra. As shown in Figure 4d the PL decay occurs on a 50 ns timescale and matches the TT state decay measured via TA, as seen in solution (Figure 4b). We thus consider that the red-shifted emission in the disordered film also derives from the TT state. We note that 50 ns lifetime with 60% PL yield at 10K suggests a radiative lifetime for the TT state in the disordered film of 80 ns. From the PL yield in the disordered film, we can estimate the yield of the reaction TT to T_1 + T_1 to be ~180%.

For both films, the red-shifted species shows pronounced vibronic structure, as observed in a recent study of singlet fission in heteroacenes undergoing fission[34]. These are sharper in the polycrystalline material and broadened in the disordered, where the emission has the same spectrum as the TT emission in concentrated solution (Fig. S14). We therefore predict that the weak, red-shifted emission in the polycrystalline film is also due to the TT state and that the transition dipole moment of the TT state in the polycrystalline film is significantly reduced compared to the disordered material. This is likely to be due to the ability of the molecules in the disordered film to rearrange into an excimer-like TT state geometry that can more easily radiatively couple to the ground state.

The activation energy we extract for TT dissociation from the PL measurements (50-90 meV), is comparable to the activation energies measured for tetracene using PL and TA (40-70 meV)[35,36]. Taking into account the entropic gain following the dissociation of TT to free triplets, which has been discussed by others[26,36], we expect the activation energy to be one half of the value of E_b which we estimate to be 200 meV.

Conclusions

In summary, we have tracked the photophysical behavior of TIPS-Tetracene over ten orders of magnitude (Figure 6) and our results show that ultrafast, activation-less formation of stabilized, long-lived TT states, that quench radiative losses via S_1 and protect the excitation from competing decay channels, is key to efficient endothermic formation of $T_1 + T_1$. These states can be formed on sub 300 fs timescales, the ultrafast conversion mediated by vibronic coupling. These results unify the observation in tetracene of the simultaneous ultrafast rise of S_1 and multiexciton features by Zhu *et al.* by photoelectron spectroscopy[26] with the slower S_1 dynamics observed in optical measurements[6,10,12]. At later times, the long-lived TT states can be thermally dissociated to free T_1, if the crystal morphology supports efficient triplet hopping. If not, TT can remain bound on µs timescales without being dissociated to free T_1.These results pave the way for further studies of how the optimisation of the chemical structure of endothermic fission materials can alter vibronic coupling and the ultrafast fission process.

Methods

Sample preparation. TIPS-tetracene was synthesized according to the procedure in reference[37]. For all of the optical measurements TIPS-tetracene was either spin coated or drop cast onto 13 mm diameter fused silica substrates in an oxygen free environment. Samples were measured under vacuum or, for low temperature measurements, in a helium dynamic flow cryostat.

Spectroscopic measurements. UV-Vis absorption spectra were measured on a Cary 400 UV-Visible Spectrometer over the photon energy range 1.55 eV-3.54 eV. Steady-state photoluminescence spectra were collected using a pulsed laser at 2.64 eV (PicoQuant LDH400 40 MHz) and collected on a 500 mm focal length spectrograph (Princeton Instruments, SpectraPro2500i) with a cooled CCD camera. Time-resolved photoluminescence decay was measured using time-correlated single photon counting (TCSPC), an intensified CCD camera (ICCD) and a transient grating set-up (TGPL). For all measurements the sample was measured in either a side-on or backward reflection geometry, to mitigate self-absorption. The TCSPC set-up uses the same excitation source and camera as the steady-state PL and has a temporal resolution of 300 ps. Transient grating measurements were measured by a home-built transient-grating photoluminescence spectroscopy, setup described elsewhere[38]. The photoluminescence quantum efficiencies of the films were measured using an integrating sphere and a 2.33 eV excitation source. Picosecond and nanosecond transient absorption spectra were recorded on a setup that has been previously reported[39]. The ultra-fast (20 fs) transient absorption experiments were performed using a Nd :YAG based amplified system (PHAROS, Light Conversion) providing 14.5W at 1025 nm and 38 kHz repetition rate. See the supplementary information section 1b for more details on the transient absorption setups.

Structural measurements. Grazing incidence wide angle X-ray scattering measurements were performed at beamline I07, Diamond Light Source, UK, using a Pilatus 1M detector and beam energy of 12.5 keV. X-ray diffraction measurements were performed using a Bruker D8 setup and a wavelength of 1.5406 angstrom

Data availability. The data sets generated during and/or analysed during the current study are available in the University of Cambridge data repository at https://doi.org/xxxx.

References

(1) Smith, M. B.; Michl, J. Singlet fission. *Chem. Rev.* **110**, 6891–6936 (2010)

(2) Pope, M.; Swenberg, C. Electronic Processes in Organic Crystals and Polymers; Oxford University Press (1999)

(3) Hanna, M. C.; Nozik, a. J. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers, *J. App. Phys.* **100**, 074510 (2006)

(4) Merrifield RE. Magnetic Effects on Triplet Exciton Interactions. *Pure App. Chem.* **27**, 481–498 (1971)

(5) Wilson, M.W.B.; Rao A.; Clark. J.; Kumar R. S. S.; Brida D.; Cerullo G.; Friend R.H. Ultrafast dynamics of exciton fission in polycrystalline pentacene. *JACS* **133**, 11830-11833 (2011)

(6) Burdett, J. J.; Gosztola, D.; Bardeen, C. J. The dependence of singlet exciton relaxation on excitation density and temperature in polycrystalline tetracene thin films: kinetic evidence for a dark intermediate state and implications for singlet fission. *J. Chem. Phys.* **135**, 214508 (2011)

(7) Eaton, S.W.; Shoer, L. E.; Karlen, S. D.; Dyar, S. M.; Margulies, E. A.; Veldkamp, B. S.; Ramanan, C.; Hartzler, D. A.; Savikhin, S.; Marks, T. J.; Wasielewski, M. R.; Singlet exciton fission in polycrystalline thin films of a slip-stacked perylenediimide. *JACS* 135, 14701-14712 (2013)

(8) Swenberg, C. E.; Stacy, W. T. Bimolecular radiationless transitions in crystalline tetracene. *Chem. Phys. Lett.* **2**, 327 (1968)

(9) Merrifield, R. E. Theory of magnetic field effects on the mutual annihilation of triplet excitons. *J. Chem. Phys.* **48**, 4318 (1968)

(10) Piland, G. B.; Bardeen, C. J. How morphology Affects Singlet Fission in Crystalline Tetracene. *J. Phys. Chem. Lett.* **6**, 1841–1846 (2015)

(11) Burdett, J.J.; Muller, A.M.; Gosztola, D.; Bardeen, C.J.; Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission. *J. Chem. Phys.* **133**, 144506 (2010)

(12) Wilson, M. W. B.; Rao, A.; Johnson, K.; Gelinas, S.; di Pietro, R.; Clark, J.; Friend, R. H. Temperature-independent singlet exciton fission in tetracene. *JACS* **135**, 16680–8 (2013)

(13) Yost, S.R.; Lee, J.; Wilson, M.W.B.; Wu T.; McMahon, D.P.; Parkhurst, R.R.' Thompson, N.J.; Congreve, D.N.; Rao, A.; Johnson, K.; Sfier, M.Y.; Bawendi, M.G.; Swager, T.M.; Friend, R.H.; Baldo, M.A.; Van Voorhis, T.; A transferable model for singlet-fission kinetics. *Nat. Chem.* **6**, 492-497 (2014)

(14) Odom, S. A.; Parkin, S. R.; Anthony, J. E. Tetracene derivatives as potential red emitters for organic LEDs. *Org. lett.* **5**, 4245–8 (2003)

(15) Stern, H. L.; Musser, A. J.; Gelinas, S.; Parkinson, P.; Herz, L. M.; Bruzek, M. J.; Anthony, J.; Friend, R. H.; Walker, B. J. Identification of a triplet pair intermediate in singlet exciton fission in solution. *PNAS* **112**, 7656-7661 (2015)

(16) Liebel, M.; Kukura, P.; Broad-band impulsive vibrational spectroscopy of excited electronic states in the time domain. *J. Phys. Chem. Letts.* **4**(8) 1358-1364 (2013)

(17) Rafiq, S. ; Scholes, G.D. ; Slow Intramolecular Vibrational Relaxation Leads to Long-Lived Excited-State Wavepackets. *J. Phys. Chem. A.* 120, 120, 6792−6799 (2016).

(18) Berkelbach, T.C.; Hybertson, .S.; Reichman, .R.; Microscopic theory of singlet exciton fission. I. General formulation. *J. Chem. Phys.* **138**, 114102 (2013)

(19) Fuemmeler, E.G.; Sanders, S. N.; Pun, A.P.; Kumarasamy, E.; Zeng, T.; Miyata, K.; Steigerwald, M.L.; Zhu, X.Y,; Sfier, M.Y.; Campos, L.M.; Ananth, N.; A direct mechanism of ultrafast intramolecular singlet fission in pentacene dimers. *ACS Central Science*, **2**, 316-324 (2016)

(20) Bakulin, A. A.; Morgan, S. E.; Kehoe, T. B.; Wilson, M. B.; Chin, A.; Zigmantas, D.; Egorova, D.; Rao, A, Real-time observation of multiexcitonic states in ultrafast singlet fission using coherent 2D electronic spectroscopy. *Nat. Chem.* 8, 16-23 (2016)

(21) Musser, A. J.; Liebel, M. Schnedermann, C.; Wende, T.; Kehoe, T.B.; Rao, A.; Kukura, P.; Evidence for conical intersection dynamics mediating ultrafast singlet exciton fission. *Nat. Phys.* 11, 352-357 (2014)

(22) Monahan, N. R.; Sun, D.; Tamura, H.; Williams, K. W.; Xu, B.; Zhong, Y.; Kumar, B.; Nuckolls, C.; Harutyunyun, A. R.; Chen, G.; Dai, H-L.; Beljonne, D.; Rao, Y.; Zhu, X-Y. Dynamics of the triplet-pair state reveals the likely coexistence of coherent and incoherent singlet fission in crystalline hexacene. *Nature Chem*, doi:10.1038/nchem.2665 (2016)

(23) Liebel, M.; Schnedermann, C.; Kukura,P.; Vibrationally coherent crossing and coupling of electronic states during internal conversion in β-carotene. *Phys. Rev. Letts*. **112**, 198302 (2014)

(24) Tiwari, V.; Peters, W. K.; Jonas, D. M.; Electronic resonance with anticorrelated pigment vibrations drives photosynthetic energy transfer outside the adiabatic framework. *PNAS*, **110**, 1203-1208 (2013)

(25) Casanova, D.; Electronic structure study of singlet fission in tetracene derivatives. *J. Chem. Theory Comput.* **10**, 324-334 (2014)

(26) Chan, WL.; Ligges, M.; Zhu XY.; The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain. *Nat. Chem.* **4**, 840-5 (2012)

(27) Arias, D.H.; Ryerson, J.L.; Cook, J.D.; Damauer, NH.; Johnson, J.C. Polymorphism influences singlet fission rates in tetracene thin films. *Chemical Science*, **7**, 1185 (2016)

(28) Miyata, K.; Kurashige, Y.; Watanabe, K.; Sugimoto, T.; Takashi, S.; Tanaka, S.; Takeya, J.; Yanai, T.; Matsumoto Y.; *Nat. Chem.* doi:10.1038/nchem.2784 (2017)

(29) Chang, T-C.; Dlott, D.D.; Picosecond vibrational cooling in mixed molecular crystals studied with a new coherent raman scattering technique. *Chem. Phys. Lett.* **147**, 18-24 (1988)

(30) Gelinas, S.; Par, O.; Brosseau, C. N.; Albert-Seifried, S.; Mcneill, C. R.; Kirov, K. R.; Howard, I. A.; Leonelli, R.; Friend, R. H.; Silva, C.; Centreville, S. Binding energy of charge-transfer excitons localized at polymeric semiconductor heterojunctions. *J. Phys. Chem.* **115**, 7114–7119 (2011)

(31) Pensack, R, D.; Ostroumov, E. E.; Tilley, A. J.; Mazza, S.; Grieco, C.; Thorley, K. J.; Asbury, J. B.; Seferos, D. S.; Anthony, J. E.; Scholes, G. D. Observation of two triplet-pair intermediates in singlet exciton fission. J. Phys. Chem. Lett. **7**, 2370-2375 (2016)

(32) Yost, S.R.; Hontz, E.; Yeganeh, S.; Van Voorhis, T.; Observation of Two Triplet-Pair Intermediates in Singlet Exciton Fission. *J. Phys. Chem. C*, **116**, 17369-17377 (2012)

(33) Burdett, J.J.; Bardeen, C. J.; Quantum beats in crystalline tetracene delayed fluorescence due to triplet pair coherences produced by direct singlet fission. *JACS* **134**, 8597-607 (2012)

(34) Keong Yong, C.; Musser, A.J.; Bayliss, S.L.; Lukman, S.; Tamura, H.; Bubnova, O.; Hallani, R.K.; Meneau, A.; Resel, R.; Maruyama, M.; Hotta, S.; Herz, L.M.; Beljonne, D.; Anthony, J. E.; Clark, J.; Sirringhaus, H.; The entangled triplet pair state in acene and heteroacene materials. *Nat. Comms,* **8**, DOI: 10.1038/ncomms15953 (2017)

(35) Thorsmølle, V.; Averitt, R.; Demsar, J.; Smith, D.; Tretiak, S.; Martin, R.; Chi, X.; Crone, B.; Ramirez, a.; Taylor, a. Morphology Effectively Controls Singlet-Triplet Exciton Relaxation and Charge Transport in Organic Semiconductors. *Phys. Rev. Lett.* **102**, 017401 (2009)

(36) Kolomeisky, A.B.; Feng, X.; Krylov, A. I.; A simple kinetic model for singlet fission: A role of electronic and entropic contributions to macroscopic rates. *J. Phys. Chem.* **118**, 5188-5195 (2014)

(37) Odom, S.; Parkin, S. R.; Anthony, J. E. *Organic letters,* 2003 , 5 , 4245-8.

(38) Chen K, Gallaher JK, Barker AJ, Hodgkiss JM, *J. Phys. Chem. Lett*, 2014, 5(10), 1732-1737.

(39) Rao, A.; Wilson, M.; Hodgkiss, J. M.; Sei, Basser, H.; Friend, R.H.; *Journal of the American Chemical Society* 2010, 132, 12698-12703.

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Author Contributions

H.L.S and A.C carried out the experiments, interpreted the data and wrote the manuscript. SRY and MHG ran calculations, interpreted the data and wrote the manuscript. NCG and SB interpreted the data. KB, AC, KC and JH performed experiments. KT and JA designed and synthesized the materials. AR, AJM and RHF interpreted the data and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Figure captions:

Figure 1: TIPS-tetracene energies and structure (a) Energy level diagram of TIPS-tetracene. The S_1 energy is determined from the UV-vis spectra (c) whilst the T_1 energy is estimated from phosphorescence measurements[15]. (b) TIPS-tetracene chemical structure and one unit cell of the TIPS-tetracene crystal structure. (c) Normalized UV-vis absorption and steady-state emission of the disordered film (purple) and dilute solution (3 mg/ml in chloroform) (grey) and the excitation and emission spectra of the polycrystalline film (green).

Figure 2. Ultrafast TT formation. (a) and (b) Ultrafast transient absorption measurements of disordered and polycrystalline TIPS-tetracene films from 50 fs – 90 ps. We note the polycrystalline film measurement is affected by pump scatter in the SE spectral region. (c) Transient absorption spectra of S_1, from a measurement of solution, and TT, from a measurement of a polycrystalline film at a time delay of 100 ps. (c) and (d) Normalised kinetics (normalised at 2 ps) obtained from the measurements in (a) and (b) respectively. (c) For the disordered film, the kinetic representing the decay of the SE is taken at 570 nm. For the rise of the TT state we plot the difference between the change in absorption at 860 nm (a TT absorption peak) and 835 nm. The two kinetics are normalised at 0 fs and subtracted. At the beginning of the measurement both regions contain S_1 absorption and the difference in the kinetics represents the growth of TT. (d) For the polycrystalline film the loss of SE intensity is represented at 580 nm where there is slightly decreased pump scatter.

The TT kinetic is the difference in absorption intensity between 860 nm and 835 nm, as in the disordered film.

Figure 3: Vibrationally coherent TT formation. (a) Vibrational frequencies of TIPS-tetracene obtained from the ultrafast transient absorption measurements, from 0-2 ps, of solution (grey), disordered film (purple) and the polycrystalline film (green) and the ground state resonance Raman spectrum (black). The highlighted regions indicate a prominent S_1 frequency at 315 cm^{-1} (blue shading) and new modes that exist in the films and not in either solution or ground state (GS) Raman at 760 cm^{-1}, 870 cm^{-1} and 1090 cm^{-1} (red shading). (b) The spectral slices of the 315 cm^{-1} and 760 cm^{-1} modes and timeslices from the transient absorption measurements of the polycrystalline film, taken at 50 fs and 90 ps. (c) Sliding-window Fourier transform plots of the 315 cm^{-1} and 760 cm^{-1} modes in the polycrystalline film, obtained at 570 nm for the 315 cm^{-1} mode and 850 nm for the 760 cm^{-1} mode. The sliding window Fourier transform was performed by sliding a 1 ps time window from 0 fs to 2 ps. The x axis represents the starting time for the sliding window.

Figure 4. Thermally-activated TT separation. (a,c,e) Transient absorption spectra from 1 ns to 3 μs of the (a) concentrated solution, (c) disordered film and (e) polycrystalline film in the near-IR spectral region. For the concentrated solution and disordered film we observe two decay regimes that can be spectrally deconvoluted using a code based on a genetic algorithm (see SI for details) into two distinct spectra corresponding to TT and $T_1 + T_1$. The TT spectrum contains additional absorption intensity between the two peaks at 850 nm and 960 nm and the peaks are blue-shifted by 5 meV. (b,d) The extracted room temperature kinetics for the TT and T_1 decay in

the (b) concentrated solution and (d) the disordered film. The photoluminescence decay of the TT state at room temperature in the concentrated solution and at 10 K in the disordered film are shown plotted against the TA decay (purple trace). (f) Raw kinetics from the transient absorption measurement of the disordered and polycrystalline films at 850 nm highlighting the different decay behaviour.

Figure 5: Thermally-activated TT emission. (a,d) Time-resolved emission scans reveal two emissive states in both the (a) disordered film and (d) polycrystalline films at 10 K. PL Count represents the photoluminescence intensity. The emission from 30-100 ns is shown magnified for the crystalline film (inset (d)). Timeslices at 0.5 ns and 50 ns are shown above the colour plots. (b,e) Temperature-dependent kinetics taken at 540 nm and 600 nm for the (b) disordered and (e) polycrystalline films. We obtained an activation energy in the red-shifted region of ~90 meV and ~50 meV respectively. (c,f) Temperature-dependent steady-state emission for the (c) disordered and (f) polycrystalline films. The spectra are normalised to the peak of the emission at 10 K. At higher temperatures the spectra are plotted to show their intensity relative to the 10 K emission.

Figure 6: The role of the TT state in endothermic singlet exciton fission.

(Top) A schematic diagram of endothermic singlet exciton fission. The wavepacket generated at the Franck Condon (FC) position of the S_1 potential energy surface is passed to the TT state during ultrafast formation of TT. Thermally-activated TT separation occurs over tens of nanoseconds. (Bottom) The kinetics of the S_1, TT and $T_1 + T_1$ species in the disordered film from 10 fs to 100 μs, obtained from the TA measurements using a genetic algorithm for spectral deconvolution.