The entangled triplet pair state in acene and heteroacene materials

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Entanglement of states is one of the most surprising and counter-intuitive consequences of quantum mechanics, with potent applications in cryptography and computing. In organic materials, one particularly significant manifestation is the spin-entangled triplet-pair state, which mediates the spin-conserving fission of one spin-0 singlet exciton into two spin-1 triplet excitons. Despite long theoretical and experimental exploration, the nature of the triplet-pair state and inter-triplet interactions have proved elusive. Here we use a range of organic semiconductors that undergo singlet exciton fission to reveal the photophysical properties of entangled triplet-pair states. We find that the triplet pair is bound with respect to free triplets with an energy that is largely material independent (~30 meV). During its lifetime, the component triplets behave cooperatively as a singlet and emit light through a Herzberg-Teller-type mechanism, resulting in vibronically structured photoluminescence. In photovoltaic blends, charge transfer can occur from the bound triplet pairs with >100% photon-to-charge conversion efficiency.

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The entangled pair of triplet excitons $^1$TT is thought to be essential to the rapid, spin-allowed formation of two triplets from a single absorbed photon$^{1-3}$. Its overall singlet character may allow for surprisingly fast, long-distance triplet exciton transport following singlet fission$^4$. The very same state also mediates the reverse of singlet fission: triplet–triplet annihilation (TTA), where two triplets fuse to form an emissive singlet, a process exploited for biomedical imaging$^{5,6}$, high-density secure data storage$^7$, incoherent energy up-conversion$^8$ and high-efficiency blue organic light-emitting diodes$^9$. Beyond applications of singlet fission and TTA, a clearer understanding of the $^1$TT state will shed light on the nature of the interaction between triplet excitons and may open the way to new physics involving entangled bosons$^{10,11}$. Despite significant theoretical effort$^{10-20}$, few experiments have succeeded in directly probing the $^1$TT state in any system$^{21-25}$, particularly in solid films relevant to eventual singlet fission devices. We are aware of a recent study of the $^1$TT state in solid films of 6,13-Bis(triisopropylsilyl)ethynyl) (TIPS)-tetracene, which crystallizes into a structure unique among singlet fission materials$^{26}$. The nature of this state and its role in singlet fission in the wider range of acene and heteroacene singlet-fission materials are not clear, nor its importance in the physics of singlet fission-based solar cells. During the review process, several other reports have emerged describing properties of triplet-pair states, including dynamic equilibrium with S$_1$ (ref. 27), the formation of quintet-coupled triplet pairs$^{28,29}$, ultrafast formation in a strongly exothermic system$^{30}$ and theoretical re-evaluations of triplet-pair interactions$^{31-33}$. These works highlight the ongoing debate about the nature of $^1$TT. Of those that discuss energetics, all consider $^1$TT to be higher in energy than $T_1 + T_1$. Here we demonstrate this is incorrect and show that $^1$TT is bound with respect to free triplets.

Here we probe the $^1$TT state experimentally and theoretically in a range of acene and heteroacene materials (Fig. 1a). We demonstrate the generality of the presence of a bound $^1$TT state as the immediate product of singlet fission. The processes of formation and decay of $^1$TT are shown in Fig. 1b, a schematic inspired by Tayebjee et al.$^{34}$ and references therein$^{35,36}$. Formation of $^1$TT is temperature-independent in polycrystalline films and is thought to occur via a combination of intra- and intermolecular motion from the photoexcited singlet$^{12-14,21,34,36,37}$. Once formed, $^1$TT can undergo one of three detectable decay processes as follows: (i) form free (unbound) triplets, a process aided by disorder at low temperatures and thermally activated above 50 K; (ii) emit (red arrows) by way of symmetry-breaking distortions enabling intensity borrowing from nearby bright states; and (iii) with sufficient energy, ‘back transfer’ to S$_1$ leading to delayed fluorescence. We also infer that a significant proportion of $^1$TT states undergo non-radiative decay, presumably directly to the ground state. In photovoltaic blends, we find that charge transfer from this bound, entangled triplet pair is as efficient as the ground state. In photovoltaic blends, we find that charge transfer from this bound, entangled triplet pair is as efficient as the ground state.

Spin-entanglement of $^1$TT observed by quantum beating. Interestingly, following femtosecond excitation at 300 K we observed temporal oscillations of the PL, as shown in Fig. 3a. Similar to tetracene$^{47,48}$ (right panel), the amplitude reduces gradually within an 8 ns window and follows the extracted delayed emitter kinetics. The Fourier transform reveals the existence of three beat frequencies (Fig. 3b) at 1.1, 2.0 and 2.9 ± 0.1 GHz that are strikingly similar to those in tetracene (1.0, 1.9 and 3.1 ± 0.1 GHz, respectively), as discussed in Supplementary Note 1. These quantum beats have never been reported in other materials than tetracene, and are a manifestation of the spin properties of triplet pairs following singlet fission$^{47,48}$. Briefly, in the simplest two-electron two-hole picture of singlet fission, there are 16 possible combinations of 4 spins: 2 singlets, 9 triplets and 5 quintets. Singlet fission entails spin-allowed conversion between the two singlet states, one of which is a superposition of triplet-pair states of the form $|S\rangle = \frac{1}{\sqrt{3}}(|XX\rangle + |YY\rangle + |ZZ\rangle)$ in the zero-field basis (see...
Supplementary Notes 1 and 2 for details including magnetic resonance characterization (Supplementary Fig. 6) and details relating to quantum beating (Supplementary Fig. 7). [S] is not an energy eigenstate of the system and [XX], [YY] and [ZZ] acquire relative phases, evolving in time with frequencies governed by their energy spacing. As the state periodically approaches its initial composition (that is, 1(TT)), there is significant enhancement of the rate to re-form the original, fluorescent singlet through TTA if this is energetically allowed. The observed PL quantum beats thus reveal modulation of the radiative TTA probability due to spin conservation. The oscillation amplitude follows the extracted delayed PL kinetics in F2-TES ADT and tetracene, clearly linking the delayed emission to the 1(TT) state generated by singlet fission. The beats’ persistence over the 1(TT) lifetime indicates that spin coherence is maintained over at least that timescale, and that 1(TT) is thus an entangled triplet-pair state.

1(TT) emission through Herzberg–Teller symmetry breaking. It is unexpected for this doubly excited state 1(TT) to emit, especially with the well-defined vibronic progression seen in

Figure 1 | Singlet exciton fission in polyacenes. (a) Molecules investigated in this study. (b) Schematic potential energy surface denoting key photophysical processes (dashed arrows) in singlet fission materials. Photoexcitation (Exc.) is followed by singlet (black) relaxation along inter- and intramolecular coordinates, resulting in the observed Stokes shift (PLS1). Further relaxation into the bound, spin-coherent triplet pair state 1(TT) (red) constitutes singlet exciton fission (SEF). Three detectable decay processes are possible from 1(TT). (i) Thermally activated dissociation into free triplets (purple), which is aided by disorder/grain boundaries and exhibits a typical activation energy of 20–40 meV. (ii) Direct ‘delayed’ emission from 1(TT) (PLTT) through Herzberg-Teller intensity borrowing. As a consequence of this mechanism, the 0-0 transition is suppressed. (iii) Thermally activated back-transfer into the singlet manifold. This process results in delayed fluorescence (PLS3), and is suppressed in tetracene and F2-TES ADT at ≤ 200 K, indicating the presence of a slight energy barrier. (c) Temperature-dependent absorption and PL spectra of F2-TES ADT films.
As discussed above, tetracene demonstrates very similar temperature-dependent PL to F2-TES ADT (Fig. 2d, Supplementary Note 3, Supplementary Figs 8 and 9, and refs 34,41–43), with a red-shifted delayed component34,42 that decays with the same lifetime as the quantum beating (Fig. 3a). Even on much longer timescales, structured 1(TT) emission may be preferentially regenerated by annihilation from ‘trapped’ triplets due to its lower electronic energy34,50. Rubrene (Supplementary Fig. 10) likewise shows evidence of a temperature-dependent long-lived PL feature, somewhat obscured by the similarity of the S1 and 1(TT) energies; even pentacene has been shown to demonstrate similarly shaped emission in films51 and crystals52. Under Herzberg–Teller coupling the 0–0 peak is suppressed53, thus, we assign the most prominent feature in the 1(TT) spectrum to the 0–1 peak, akin to emission from the ‘triplet-pair’-like54 S1 state in polyenes55. Following this model, we determine the energy of the 1(TT) 0–0 peak from the spacing between observed 0–1 and 0–2 peaks (Supplementary Fig. 1). We find that the energy extracted from PL scales with the expected 2 × T1 energy from independent measurements of the triplet energy, with an offset which could account for the binding energy of the triplets in 1(TT). This is shown in Fig. 4.

This model has critical implications for singlet fission energetics in ‘slow’ tetracene-like materials. In F2-TES ADT and similar materials, 1(TT) and S1 are roughly isoenergetic. Indeed, the delayed spectra in Fig. 2c reveal temperature-dependent broadening consistent with delayed singlet re-formation, which is turned off <200 K. The implicit small barrier to singlet re-formation can only be reconciled with the observed 1(TT) PL spectrum through the Herzberg–Teller model. The ability of 1(TT) to emit and the spin-conservation considerations above suggest that quantum beating could likewise be anticipated in the direct 1(TT) emission, suggesting a need for spectrally resolved quantum beating studies.

Identification of 1(TT) in TA spectroscopy. For further insight into the formation and decay of 1(TT) we used TA spectroscopy. Figure 5a shows the TA spectra of F2-TES ADT films collected at 300 K and we can immediately distinguish two primary species:
the initially formed singlet exciton and a subsequent long-lived photo-induced absorption (PIA) band centred at 970 nm. To aid assignment of this feature, we examine F2-TES ADT solutions at several concentrations\(^{21,36}\) (Fig. 5b,c). For simplicity, we focus on the probe range 800–1,100 nm, where all states of interest have distinct PIA features (full characterization in Supplementary Figs 5, 11–13). In dilute solutions (Fig. 5b,c top), we observe \(\sim 12\) ns singlet decay consistent with measured PL (Fig. 2a). Concentrated solutions (32 mM, Fig. 5b,c middle) exhibit faster singlet decay and spectral evolution over 100s of nanoseconds to yield long-lived triplets (\(T_1 + T_1\); sensitization\(^{36}\) in Supplementary Fig. 11). Between singlet and triplet, we observe an intermediate, which decays with the same kinetics (red trace) as the delayed \(1(TT)\) emission (pink dashed trace), enabling assignment to \(1(TT)\). The last panels in Fig. 5b,c reveal a similar progression in thin films at 50 K (Supplementary Fig. 13 for other temperatures), demonstrating that \(1(TT)\) acts as a distinct singlet fission intermediate even in the solid state. We expect the \(1(TT)\) PIA absorption cross-section to be similar to that of two free triplets. Therefore, the reduction in signal from 3–100 ns in the raw TA kinetic (pink trace in Fig. 5c) suggests significant decay without forming free triplets. The total PL quantum yield of 10% at 50 K indicates that this decay is largely non-radiative.

We observe the same progression in rubrene, \(1(TT)\), pentacene (Fig. 6), confirming the presence of the \(1(TT)\) intermediate in all three (see also Supplementary Figs 14–18). In rubrene, these features match the red-shifted delayed PL kinetics (Supplementary Fig. 10). No PL was detected in TIPS-pentacene and pentacene films. We performed similar measurements on polycrystalline tetracene films (Supplementary Fig. 19) but, as discussed in Supplementary Note 3, find that these are difficult due to small triplet absorption cross-sections\(^{43,57–59}\), coupled with the need for low excitation density to avoid exciton–exciton annihilation\(^{60}\) in the other materials (Supplementary Fig. 20), \(1(TT)\) decay was completely independent of intensity, indicating that any recombination is geminate. By contrast, free triplets exhibit fluence-dependent recombination. Interestingly, our results show that \(S_1\) decay and \(1(TT)\) growth are largely temperature-independent (Fig. 5 and Supplementary Figs 13 and 14), even in rubrene\(^{39}\).

### Table 1 | Diabatic mixing in \(1(TT)\).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Bright (S_1)</th>
<th>Dark (S_1)</th>
<th>CT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS-Pn (T (T_{equilibrium}))</td>
<td>0.00</td>
<td>0.28</td>
<td>1.34</td>
</tr>
<tr>
<td>TIPS-Pn (T (G_{equilibrium}))</td>
<td>0.22</td>
<td>0.10</td>
<td>1.22</td>
</tr>
<tr>
<td>F2-TES ADT (T (T_{equilibrium}))</td>
<td>0.00</td>
<td>0.24</td>
<td>0.96</td>
</tr>
<tr>
<td>F2-TES ADT (T (G_{equilibrium}))</td>
<td>0.46</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Mixing ratios (%) of other diabatic states into \(1(TT)\) in two geometries. \(1(TT)\) is optically dark at equilibrium (T \(T_{equilibrium}\)). Distortion of one molecule (T \(G_{equilibrium}\)) activates mixing with the bright singlet and thus \(1(TT)\) emission, exemplifying Herzberg-Teller coupling. Details in the Methods section.

Figure 4 | \(1(TT)\) energies. \(1(TT)\) and \(2 \times T_1\) energies for materials studied here: \(1(TT)\) energy extracted from PL spectra, see Supplementary Fig. 1, \(T_1\) from phosphorescence measurements (F2-TES ADT, rubrene Supplementary Figs 2, 3) and literature\(^{61,73}\). Error bars reflect uncertainty in fitting the \(1(TT)\) vibronic progression.

Stabilization of \(1(TT)\) versus \(S_1\) and \(2 \times T_1\). A temperature dependence does, however, appear in the subsequent process, in which the bound triplet pair separates into free triplet excitons (Fig. 5 and Supplementary Fig. 13). It is noteworthy that this is even observed in TIPS-pentacene and pentacene (Supplementary Note 4 and Supplementary Figs 16 and 18), where the overall process of singlet fission is exothermic (Supplementary Fig. 21 and ref. 61). In Fig. 7a we plot \(1(TT)\) and free triplet population dynamics for F2-TES ADT films from 4–250 K. Data for other molecules can be found in Supplementary Fig. 20 (F2 ADT single crystal), Supplementary Fig. 13 (rubrene), Supplementary Fig. 15 (TIPS-pentacene) and Supplementary Fig. 17 (pentacene). From an Arrhenius fit to the corresponding rates of free triplet formation at elevated temperature, we obtain a general phenomenological activation barrier \(\sim 20–40\) meV (Fig. 7b), although the underlying rates vary by nearly two orders of magnitude. These results demonstrate that \(1(TT)\) is stabilized with respect not only to the initial singlet but also to two free triplet excitons, confirming its bound nature\(^{21}\). We consider that this behaviour is general to the acenes and is likely to be a common property of all singlet fission materials, recalling the well-known stabilization of the triplet-pair 2\(A_g\) state in polyenes relative to two free triplets\(^{54,56,62}\).

To better understand this binding and thermally activated decay, we have analysed conversion from \(1(TT)\) into free triplets based on Marcus–Levich–Jortner rate theory parameterized against \(ab\) initio calculations (Table 2 and Fig. 7c, full details in the Methods section). We considered the \(\pi\)-stacked crystal geometries of F2-TES ADT, TIPS-pentacene and rubrene, in which separation is one dimensional. The enthalpy change \(\Delta H\) for separation was determined using trimer models in which molecules adopted either the fully relaxed triplet geometry (\(T\)) or the ground-state geometry (\(G\)). Bound and separated triplet pairs then correspond to TTG and TGT configurations, respectively. The free energy stabilization going from TGT to TTG completely dominates the activation energy \(\Delta E\). The stabilization energies are overestimated by these calculations, probably due to the presence of polymorphism and the assumed single crystal geometry. For instance, we calculate that increasing the \(\pi\)-stack distance in TIPS-pentacene by 0.1 Å decreases the \(\Delta H\) by \(\sim 30\%\). Nonetheless, the predicted trends in the \(\Delta E\) values match well with measurements.

Moreover, the magnitudes of \(\Delta H\) (50–100 meV) correlate well with the admixture of singlet and charge-transfer configurations (Table 1), indicating that this mixing is a primary driver of \(1(TT)\) stabilization, although orbital delocalization also contributes. The
electronic coupling for intermolecular triplet transfer $V_{T-T}$ was estimated using $\pi$-stacked dimer models and agrees well with previous studies\textsuperscript{38}.

As shown in Fig. 7d, the resulting rate equation yields a strong temperature dependence for $^1$(TT) separation, in good agreement with experimental results given the simple model. Importantly, we reproduce the large rate difference between TIPS-pentacene and F$_2$-TES ADT, and the smaller difference between F$_2$-TES ADT and rubrene. These differences cannot be attributed to $\Delta H$ (comparable for all three) and instead follow $V_{T-T}$. Thus, the underlying rate for $^1$(TT) separation is governed by the intrinsic triplet mobility. At the same time, we note that the overall activation energy is dominated by $\Delta H$ rather than the inter- or intramolecular reorganization energies. We can thus conclude that the measured high-temperature activation energies reflect the energy stabilization of bound versus free triplet pairs, and that triplet-pair separation can be described in terms of triplet hopping from the bound state. The most significant discrepancy between theory and experiment is at low temperature: the model predicts vanishingly small $^1$(TT) separation, whereas we measure very little change in the rate from ~50 K to lower temperatures. We propose that structural and/or energetic disorder, for instance as would be found at grain boundaries, accounts for the persistence of low-barrier free triplet formation.

To verify this, we have performed similar detailed TA and PL measurements on single crystals of difluorinated anthradithiophene (F$_2$-ADT, Fig. 7d,e and Supplementary Fig. 20). We observed similar singlet and $^1$(TT) emission,
with clear temperature dependence of the $^1\text{TT}$ lifetime above 200 K but little temperature dependence below. In TA, we found free triplet formation at $\geq 200$ K but observed no free triplets at lower temperature. These results support our model for the role of disorder: in the absence of structural or energetic disorder, the $^1\text{TT}$ state must be separated through thermal energy alone, leading to complete suppression of the process at low temperature.

Concerted two-electron transfer from $^1\text{TT}$ in solar cells. The low rate for $^1\text{TT}$ separation in F$_2$-TES ADT, tetracene$^{47}$ and rubrene suggests that this state may play a significant role in fission-sensitized solar cells, unlike in pentacene-based devices where the extrapolated room-temperature $^1\text{TT}$ lifetime is only $\sim 200$ fs (ref. 22). To elucidate the behaviour of $^1\text{TT}$ in photovoltaic blend films and devices, we have studied bulk-heterojunction films of F$_2$-TES ADT and [6,6]-phenyl C71 butyric acid methyl ester (PC$_{71}$BM) in 4:1 molar ratio, in which we expect significant demixing. The device structure is shown schematically in Fig. 8a with electrical characteristics in Fig. 8b,c. We focus here on two representative temperatures: 300 and 50 K, where the primary long-lived species in F$_2$-TES ADT should either be free or bound spin-entangled triplets, respectively (for other temperatures, see Supplementary Fig. 22). As noted above, the yield of free triplets relative to $^1\text{TT}$ drops as the temperature is lowered (Fig. 8f).

Figure 8d,e shows that at 300 K free triplets are formed, revealing that a significant proportion of F$_2$-TES ADT molecules must be far from the fullerene interface. Spectral decomposition (Fig. 8d) reveals a third species, identified as a hole polaron (radical cation) in F$_2$-TES ADT from comparison with charge-modulation spectroscopy (dashed line in Fig. 8d and Supplementary Fig. 23). Charge-modulation spectroscopy is used to determine the optical spectra and absorption cross-section of hole polarons in the solid-state (see Supplementary Note 5 for details). From the strength of the hole polaron contribution to the TA signal we can then directly extract the charge population formed (see Supplementary Note 5 and Supplementary Table 1), resulting in a photon-to-charge quantum yield of $\sim 120\%$. Equivalent device characterization in Fig. 8b,c shows that, although the power conversion efficiency of the device is low (1.7%), the peak internal quantum efficiency approached 120% in the spectral range of F$_2$-TES ADT (Fig. 8c) in excellent agreement with the TA results.

The 300 K extracted kinetics shown in Fig. 8e reveal that these charges form at the expense of both bound and free triplet excitons, resulting in a reduction of both the $^1\text{TT}$ PL and free triplet TA lifetimes. There is thus a competition between two modes of $^1\text{TT}$ decay: diffusion to a PC$_{71}$BM interface with direct charge generation, and thermally activated separation into free triplets, which in turn diffuse to the interface to form charges.

At 50 K, the contribution of $^1\text{TT}$ to charge formation can be isolated, as free triplet formation is strongly suppressed. Indeed, we find that the relative yield of free triplets is $> 50\%$ lower at 50 K than at 300 K (Fig. 8f). In the TA dynamics, following formation of both 1(TT) separation to free triplets and charge separation from $^1\text{TT}$: exciton diffusion to the interface. In blend films this is to a PC$_{71}$BM-rich phase; in neat films diffusion is to grain boundaries or other defect sites (see above). To determine qualitatively the contribution of $^1\text{TT}$ and free triplets to the charge yield, we focus on Fig. 8f. Although the yield of free triplets varies significantly from 50 to 300 K, the charge yield remains constant. If charges were only generated from free triplets, their yield should track the free triplet yield. As this is not
the case, we find that multi-electron transfer from \( ^1(TT) \) should be the dominant pathway at low temperature.

**Discussion**

We have demonstrated the general presence of the bound, entangled triplet-pair state \( ^1(TT) \). An interesting property of \( ^1(TT) \) is that it emits as a singlet but can transfer charge from each of its constituent triplets. We find that non-radiative decay of \( ^1(TT) \) is a dominant loss mechanism limiting further exploitation. Similarly fast non-radiative \( ^1(TT) \) decay has been observed in covalent acene dimers\(^{24,63}\), carotenoid aggregates\(^{62,64}\) and polymers\(^{56,65,66}\), and understanding the mechanism of this process and minimizing it could allow for efficient solar cells with direct charge transfer from \( ^1(TT) \). Our work also has critical implications for TTA upconversion efficiency models\(^{67}\), where the implicit assumption is that the singlet-character TTA encounter complex (that is, \( ^1(TT) \)) converts to \( S_1 \) with unity efficiency. Instead we find that \( ^1(TT) \rightarrow S_1 \) conversion efficiency is determined by the competition between singlet formation, triplet-pair separation and non-radiative decay.

More broadly, we consider that the generality of our findings across singlet fission materials affords a powerful platform to study the interactions between triplet excitons and the properties of bound multiexciton states and could lead to a new material set for solid-state quantum computing applications.

**Methods**

**Materials.** \( F_2 \)-TES ADT was synthesized as described previously\(^{68}\). \( PC_71 \)BM, tetracene, rubrene, TIPS-pentacene and pentacene were purchased from Sigma.

**Table 2 | Parameters for triplet hopping model from ab initio calculations.**

<table>
<thead>
<tr>
<th>Material</th>
<th>( V_T ) (meV)</th>
<th>( \Delta H ) (meV)</th>
<th>( \Delta E ) (meV) at ( \lambda_{\text{intra}} = 50 \text{ meV} )</th>
<th>( \lambda_{\text{intra}} ) (meV)</th>
</tr>
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<tr>
<td>TIPS-Pentacene</td>
<td>22</td>
<td>87</td>
<td>94</td>
<td>177</td>
</tr>
<tr>
<td>( F_2 )-TES ADT</td>
<td>33</td>
<td>67</td>
<td>68</td>
<td>195</td>
</tr>
<tr>
<td>Rubrene</td>
<td>18</td>
<td>47</td>
<td>47</td>
<td>242</td>
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</table>

Electronic coupling for triplet transfer \( V_T \), enthalpy of \( ^1(TT) \) separation \( \Delta H \), activation energy \( \Delta E \) and intramolecular reorganization energy for triplet diffusion \( \lambda_{\text{intra}} \) in units of meV. Details in the Methods section.
Aldrich. F2-TES ADT and TIPS-pentacene thin film samples were spin-cast (15 mg ml\(^{-1}\), toluene) on polyimide precoated fused-silica substrates (the polyimide aids wetting of the organic semiconductor). For F2-TES ADT:PC\(_{71}\)BM thin film samples, 4:1 F2-TES ADT:PC\(_{71}\)BM blend solutions (15 mg ml\(^{-1}\) total material, mesitylene) were spin-cast on polyimide precoated fused-silica substrates. Samples were dried on a hot-plate at 50 °C for 10 min. Tetracene, rubrene and pentacene thin-film samples were prepared via thermal evaporation at a base pressure of \(< 6 \times 10^{-6} \text{ mbar}\).

Single crystals of F2-ADT were grown through a physical vapour growth technique. Unless otherwise noted, pump intensities were kept below 5 mJ cm\(^{-2}\) to avoid bimolecular singlet–singlet annihilation effects and the pump and probe polarization were set to magic angle (54.7°) to avoid reorientation effects. For ns-TA measurements, pump pulses were generated using a frequency-doubled Q-switched \(~500 \text{ ps}\) Nd:YVO\(_4\) laser (532 nm). Delay times from 1 ns to 1 ms were achieved using an electronic delay generator. For time-resolved PL measurements to generate spectral maps, the samples were excited by 40 ps pulses (excitation wavelength: 470 nm) operating at a repetition rate of 2.5 MHz. PL decay dynamics were resolved using electronic gating through time-correlated single-photon counting with a temporal resolution of 180 ps and detection based on a cooled silicon single-photon avalanche diode, yielding a temporal resolution of around 40 ps. For all solid-state time-resolved optical measurements, samples were kept at a fixed temperature in a cryostat with dynamic helium gas flow. For solution measurements, a fused silica 1 mm path length cuvette was used.

**Triple sensitization.** Blends of N-methylfulleropyrrolidine (NMFP) and F2-TES ADT in a molar ratio of 4:1 were prepared at a concentration of 1 mg ml\(^{-1}\) in chloroform. The NMFP was excited by the 355 nm frequency tripled output of a Q-switched sub-nm Nd:YVO\(_4\) laser. Following intersystem crossing on NMFP, stage.

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**Figure 8 | 1(TT) in photovoltaic blends.** (a) Schematic photovoltaic (PV) device structure. (b) Typical IV curve for F2-TES ADT:PC\(_{71}\)BM blend PV with corresponding power conversion efficiency (PCE), fill-factor (FF), open-circuit voltage (\(V_{oc}\)) and short-circuit current (\(J_{sc}\)) as indicated. (c) Despite the low PCE of 1.7%, a plot of external and internal quantum efficiency (external quantum efficiency [EQE] and internal quantum efficiency [IQE] respectively) shows \(>100%\) IQE in the region where F2-TES ADT absorbs. (d) TA spectra of bulk-heterojunction films of F2-TES ADT and PC\(_{71}\)BM in 4:1 molar ratio, at 300 K (top) and 50 K (bottom) and averaged over the indicated delay ranges (thin lines). Thick lines: species extracted from spectral decomposition. The F2-TES ADT hole polaron (radical cation or ‘charge’) spectra extracted through spectral decomposition closely match those obtained with charge-modulation spectroscopy (CMS, dashed). (e) Triplet and charge population kinetics extracted from data in (d) and Fig. 6. (neat films, dash-dotted) and equivalent transient PL maps. Shortening of both the \(1(TT)\) PL lifetime and the free triplet lifetime at 300 K suggest both species contribute to charge formation. At lower temperatures, no free triplets are detected prior to charge transfer at the interface. The kinetics of interfacial charge transfer closely match those of triplet-pair separation in neat films (dash-dotted). (f) Top panel: photon-to-charge conversion yield determined from TA measurements (errors from uncertainty in amplitude of TA signal and charge cross-section) of blend films reveals negligible temperature dependence. In contrast, the yield of free triplets in neat films (bottom panel, error bars reflect noise in raw TA signal), plotted as a ratio of \(T_1+T_1\) to \(1(TT)\) from TA measurements and normalized to the 300 K value, varies with temperature.
triplet transfer to $F_2$-TES ADT occurs and is monitored by TA spectroscopy. Results are shown in Supplementary Fig. 11.

**Phosphorescence.** To obtain samples that gave phosphorescence, the molecule of interest was spin-coated into films doped with platinum octaethylporphyrin (purchased from Sigma Aldrich). The weight ratio of target molecules to platinum octaethylporphyrin in solution was varied from 95:5 to 98:2, to give the clearest phosphorescence signal. Mixtures were spin-coated on Spectrosil at 800–1,200 r.p.m. for 1–2 min in a nitrogen-filled glove box and the films were then annealed in a nitrogen box at 30 °C for 10 min. The final samples were encapsulated to prevent sample degradation and triplet quenching by oxygen. Phosphorescence was detected using a calibrated infrared InGaAs photodiode array (ANDOR iDus 490A) coupled to a spectograph (ANDOR Shamrock), with CW excitation at 332 nm (~0.5 mW).

**Optically detected magnetic resonance.** Optically detected magnetic resonance (ODMR) experiments were performed to investigate the presence of free triplets in $F_2$-TES ADT. In these measurements, the change in PL is monitored under magnetic resonance. ODMR gives a direct way of identifying triplet excitons, as the dipole–dipole interaction between electron and hole spins within the triplet exciton magnetic resonance. ODMR gives a direct way of identifying triplet excitons, as the dipole–dipole interaction between electron and hole spins within the triplet exciton magnetic resonance. ODMR gives a direct way of identifying triplet excitons, as the dipole–dipole interaction between electron and hole spins within the triplet exciton magnetic resonance. ODMR gives a direct way of identifying triplet excitons, as the dipole–dipole interaction between electron and hole spins within the triplet exciton magnetic resonance.

**Structural characterization.** Spectral X-ray diffraction was performed with a PANalytical Empyrean system in Bragg–Brentano geometry using a sealed copper tube (1 = 1.5418 Å, 40 kV, 40 mA) and an X'Celerator detector operating in a one-dimensional mode. A variable slit optics choosing an interleaved length of 10 mm was used in combination with 0.025° Soller slits at the primary as well as at the secondary side. Low temperatures down to 85 K were reached with the low temperature attachment TTK600 from Anton Paar Ltd using vacuum (2 × 10⁻⁵ bar) conditions. Starting from room temperature the samples were cooled down in steps of 25 K with a cooling rate of 5 K min⁻¹. After reaching a temperature of 85 K, the sample was rapidly heated up to room temperature and cooled down again in steps to a temperature of 230 K, to confirm the measurements were reproducible after thermal cycling. Careful alignment of the sample height and sample tilt were made to obtain reliable results. Peak parameters were determined by a fit of a Gaussian curve to the experimentally observed Bragg peaks.

**Photovoltaic device fabrication and characterization.** Solar cells were fabricated on 10 mm × 15 mm indium tin oxide-coated glass substrates that served as the anode. The substrates were ultrasonically cleaned in detergent, deionized water, acetate and isopropanol. A layer of 30 nm PEDOT:PSS (poly([3,4-ethylenedioxythiophene]/poly(styrene sulphonate) (Clevios PH 1000) was spin-coated onto the indium tin oxide substrate and dried in air at 120 °C for 10 min. Fifteen milligrams of 4:1 $F_2$-TES ADT/PC71BM blend was dissolved in 1 ml of mesitylene and spin-coated on top of the PEDOT layer at 1,500 r.p.m. and annealed for 10 min at 80 °C. Finally, the LiF/Al cathode (50 nm) was vacuum-evaporated onto the annealed photovoltaic active layer. All devices were encapsulated before testing. A 100 W tungsten halogen lamp (500–1,500 nm) and a 120 W Xenon lamp (350–500 nm) dispersed through a monochromator (Oriel Cornerstone 260) were used for external quantum efficiency measurements. For wavelengths between 375 and 900 nm, a set of silicon diodes (ThorLabs SM50PD1A) were used. A Keithley 2635 source measure unit was used to measure the short-circuit current as a function of wavelength. The intensity incident light was 0.1 mW/cm² using a set of lenses to illuminate individual pixels of size 0.08 cm². The current–voltage (I–V) characteristics of the devices were measured under standard AM 1.5G conditions using an Abet Sun 2000 solar simulator, at an intensity equivalent to 100 mW/cm². The spectral mismatch correction was determined for excitation wavelengths. The model and characteristic I–V characteristics were measured using the Keithley 2635 source measure unit.

**Internal quantum efficiency plots were calculated from external quantum efficiency (η/η(A))/η(A), where η is the absorbance of the photovoltaic layer, which was computed with a transfer matrix approach, and A was modelled according to published literature.**

Ab initio calculations. PL from the triplet pair state: to clarify the origin of $\{1(TT) PL\}, we analyse the bright exciton component in the $\{1(TT)\} state based on ab initio excited-state calculations. The $\{1(TT)\} states of π-stacked dimers are calculated using the complete active space self-consistent field (CASSCF) method, where the active orbitals consist of the highest-occupied molecular-orbital and lowest-unoccupied molecular-orbital of two monomers, that is CASSCF(4,4). The doubly excited $\{1(TT)\}$ diabatic state is optically dark and thus the $\{1(TT)\}$ PL necessitates mixing with singly excited bright exciton states. Yet, as found for the acene crystals16, the bright exciton component to the adiabatic $\{1(TT)\}$ states completely vanishes due to the relative phase factor of the wavefunctions in H-aggregates. In this case, the symmetric $\{1(TT)\}$ mixes only with the dark exciton and charge transfer states, while the antisymmetric $\{1(TT)\}$ mixes only with the bright exciton states and the ground-state geometry ($\{1(TT)\}$ via symmetry-breaking effects due to intra-molecular vibronic coupling. We model this in the simplest way possible by displacing the geometry of one of the monomers from the triplet minimum to the ground state minimum, (see Fig. 5f in the main text for results and discussion). Such a scenario is consistent with intensity borrowing induced by coupling to vibrational modes, that is, the Herzberg–Teller mechanism.

**Triplet pair separation rate:** we analysed the transfer rate from the bound $\{1(TT)\}$ to free triplets based on the Marcus–Levich–Jortner rate parameterized against $\{ab initio\}$ calculations. The electronic coupling for the intramolecular triplet transfer, $V_{TT}$, $\gamma$, (see Fig. S5 in the main text) was estimated using time-dependent density functional theory as applied to π-stacked dimer models. The intramolecular reorganization energy, $\delta_{reorg}$ for the triplet diffusion was computed on the monomers at the DFT level. The enthalpy change, $\DeltaH$, for the $\{1(TT)\}$ separation was obtained from CASSCF(4,4)/CASPT2 calculations on π-stacked trimer model where the monomer geometry is the symmetric $\{1(TT)\}$ and the ground-state geometry (Y). Thus, in this notation, the bound and separated triplet pairs correspond to TTG and TGT configurations, respectively.
The \( \Gamma(TT) \) separation rate, \( K_{\Gamma(TT)} \), is evaluated by the Marcus–Levich–Jortner theory:

\[
K_{\Gamma(TT)} = \frac{2\pi}{\hbar} \sqrt{\frac{V_{\text{TT}}^2}{4\Gamma_{\text{TT}}}} \left| \langle 0 | 0 \rangle \right|_{\text{true}} \exp \left( -\frac{\Delta H + \lambda_{\text{TT}}^2}{4\Gamma_{\text{TT}}} - \frac{\Delta S}{k} \right)
\]

where \( k \) and \( S \) are the Boltzmann constant, temperature and entropy change, respectively. The Franck–Condon factor for the intramolecular effective mode, \( \langle 0 | 0 \rangle_{\text{true}} \), is evaluated from the reorganization energy, \( \lambda_{\text{TT}} \), and the frequency of 0.18 eV corresponding to the usual breathing/stretching mode in aromatic/conjugated molecules. The low-frequency intermolecular reorganization energy, \( \lambda_{\text{TT}} \), is calculated for covalent excitations such as triplets and its calculation is cumbersome. Here we take a conservative value of 0.05 eV, modifying it in a reasonable range (up to a factor of 3) hardly affects the conclusions below.

The free-energy contribution for a reasonable range (up to a factor of 3) hardly affects the conclusions below. The \( \delta \) value computed in that case reflects only the energy stabilization associated with direct wavefunction overlap between neighbouring triplets. The relatively large \( \Gamma(TT) \) separation rate of TIPS-pentacene compared with F$_2$-TES ADT and rubrene can be regarded as a one-dimensional chain; in this case, the spatial \( \Delta S \) from the bound \( \Gamma(TT) \) to nearest-neighbour \( \Gamma \) is unity. Considering the dissipation of spin correlation, the number of spin configurations of the separated \( T \rightarrow T \) (5 \times 3) is three times as many as the total-singlet \( \Gamma(TT) \), that is, \( \exp(\Delta S/k) = 3 \).

The calculated \( \Delta S \) indicates that the \( \Gamma(TT) \) separation is endergonic for the three molecular materials investigated (see Fig. 5d in the main text). The bound \( \Gamma(TT) \) is stabilized by orbital delocalization as well as the admixture of singlet excited electronic configurations into the nearest-neighbour TT pairs (TTG), both contributing vanishing in the case of separated triplets (TGT). The free-energy stabilization going from TGT to TTG configuration results in a vacuum energy change \( \Delta E \). Although these are overestimated by the calculations, the predicted trends in the \( \Delta E \) values (namely larger in TIPS-pentacene compared to rubrene) match reasonably well with the measurements. It is interesting to point out that for rubrene in its equilibrium crystal structure at 0 K, the singlet-triplet mixing is strictly molecular because \( \Delta S = 0 \); thus, the finite (yet smaller) \( \Delta E \) value computed in that case reflects only the energy stabilization associated with direct wavefunction overlap between neighbouring triplets. The relatively large \( \Gamma(TT) \) separation rate of TIPS-pentacene compared with F$_2$-TES ADT and rubrene is rationalized by the difference in electronic coupling for triplet diffusion. Thus, based on these theoretical results, we believe the measured activation energies reported in Fig. 5 essentially reflect the energy stabilization of bound vs free triplet pairs, rather than the reorganization energy for the migration of free triplets. This is borne out by the fact that measurements in anthracene single crystals have borne out by the fact that measurements in anthracene single crystals have

Data availability. The data that support the findings shown in both the main figures and Supplementary Figures in this study are available with the identifier https://doi.org/10.17863/CAM.9032.


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Author contributions
C.K.Y. measured most of the data presented in the manuscript. C.K.Y., A.J.M. and J.C. prepared the manuscript and analyzed the data. H.S. and J.C. conceived the project and, together with A.J.M., supervised its execution. S.L.B. measured the ODMR data, performed the related calculations and helped prepare the manuscript. S.L. performed the phosphorescence measurements, O.B. prepared and measured the OPV devices, and J.E.A. supervised the measurements. H.T. and D.B. performed the calculations and helped prepare the manuscript.

Additional information
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