Identification of a triplet pair intermediate in singlet exciton fission in solution

Hannah L. Stern[a], Andrew J. Musser[a], Simon Gelinas[a], Patrick Parkinson[b], Laura M. Herz[b], Matthew J. Bruzek[c], John Anthony[c], Richard H. Friend[a,1], and Brian J. Walker[a]

[a]Cavendish Laboratory, University of Cambridge, Cambridge, CB30HE, United Kingdom; [b]Clarendon Laboratory, University of Oxford, Oxford, OX13PU, United Kingdom; and [c]Department of Chemistry, University of Kentucky, Lexington, KY 40506

Edited by Harry B. Gray, California Institute of Technology, Pasadena, CA, and approved May 19, 2015 (received for review February 18, 2015)

Singlet exciton fission is the spin-conserving transformation of one spin-singlet exciton into two spin-triplet excitons. This exciton multiplication mechanism offers an attractive route to solar cells that circumvent the single-junction Shockley–Queisser limit. Most theoretical descriptions of singlet fission invoke an intermediate state of a pair of spin-triplet excitons coupled into an overall spin-singlet configuration, but such a state has never been optically observed. In solution, we show that the dynamics of fission are diffusion limited and enable the isolation of an intermediate species. In concentrated solutions of bis(triisopropylsilylethynyl)[TIPS]—tetracene we find rapid (<100 ps) formation of excimers and a slower (∼10 ns) break up of the excimer to two triplet exciton-bearing free molecules. These excimers are spectroscopically distinct from singlet and triplet excitons, yet possess both singlet and triplet characteristics, enabling identification as a triplet pair state. We find that this triplet pair state is significantly stabilized relative to free triplet excitons, and that it plays a critical role in the efficient endothermic singlet fission process.

singlet fission | photochemistry | TIPS–tetracene | triplet | excimer

The fission of photogenerated spin-singlet excitons into pairs of spin-triplet excitons is an effective way to generate triplet excitons in organic materials (1, 2). Because the triplets produced are coupled into an overall singlet state, spin is conserved and triplet formation can proceed on sub-100-fs timescales (1, 3–5) with yields of up to 200% (1, 6, 7). Current interest in singlet fission is driven by its potential to improve the efficiency of solar cells by circumventing the Shockley–Queisser limit for single-junction devices (8–10). Incorporating singlet fission material within a low-band-gap solar cell should make it possible to capture the energy normally lost to thermalization following the absorption of high-energy photons (11, 12). An external quantum efficiency of 129% (13) and an internal quantum efficiency of >180% (14) have been reported using pentacene as the singlet fission material and fullerene (C_{60}) as electron acceptor. Despite such significant advances, many questions remain about the underlying mechanism of triplet formation, such as the role of intermediate electronic states and the ability of systems to undergo endothermic fission.

The basis of most kinetic descriptions of singlet fission is the triplet pair state ^{1}(TT), which is entangled into an overall singlet and is an essential intermediate for the formation of two free triplet excitons (1, 15). Whether this intermediate state is present only transiently, as expected in exothermic systems such as pentacene, or whether it can be sufficiently long lived to also play a central role in the fission process in slower systems is unclear. Transient absorption measurements of the canonical systems pentacene and tetracene in the solid state allow clear identification of only the singlet and triplet states (3, 6, 16, 17), meaning the character of any intermediate has not been observed directly. Other factors affect fission in the solid state that can complicate analysis, such as exciton diffusion, delocalization of excitations, and the heterogeneity of materials.

Singlet fission in solution offers an alternative approach to investigate the intermolecular interactions that mediate fission. The conformational freedom of molecules and diffusional timescales enable access to fission in systems where the essential photophysics, such as the progression of excited states and relative zero-point energies, are not expected to differ largely from the solid state. Some of the authors have recently demonstrated that quantitative singlet exciton fission can be achieved in bis(triisopropylsilylethynyl)[TIPS]—pentacene when a molecule with a singlet exciton collides with a molecule in its ground state through diffusion, with triplet yields reaching 200% at high concentrations (18). Although the triplet yields are comparable to the solid state, fission proceeds orders of magnitude more slowly in solution, offering a clearer picture of the evolution of the states involved. These results pointed to excimer formation as the driving force enabling singlet fission, but this state was too short lived for a clear identification.

To resolve the role of such intermediates in solution-based singlet fission, we draw on the well-established study of pentacene and tetracene in the solid state. Whereas singlet fission in pentacene is exothermic by ∼100 meV (1), in tetracene it is found to be endothermic by ∼180 meV (1, 19–21). Accordingly, triplet formation is significantly faster in pentacene films (∼80 fs) (5) than in tetracene (∼90 ps) (22), although curiously in the latter material the process remains highly efficient and fully independent of temperature (22, 23). In this study, we look at solutions of TIPS–tetracene, a tetracene derivative also capable of singlet fission (24). Analogous to tetracene films, TIPS–tetracene is determined to

Significance

We use transient spectroscopy to investigate the mechanism of singlet exciton fission, a quantum mechanical phenomenon in some organic molecules in which a spin-singlet excited state can split into two spin-triplet states. This process may be harnessed to boost solar cell efficiencies, but the underlying mechanism remains poorly understood. Central to most models is a triplet pair state, consisting of two triplets entangled into an overall spin-singlet configuration, but it has never before been optically detected. In a solution-based system, we detect a state with simultaneous singlet and triplet exciton character that dissociates to form triplet excitons in 120% yield. We consider that this intermediate constitutes a triplet pair state, and its observation allows important insight into the nature of triplet exciton coupling.

Author contributions: H.L.S., A.J.M., R.H.F., and B.J.W. designed research; H.L.S. performed research; H.L.S., A.J.M., S.G., and R.H.F. analyzed data; P.P., L.M.H., M.J.B., and J.A. contributed new reagents/analytic tools; H.L.S. and A.J.M. wrote the paper; and R.H.F. provided supervision: feedback on results, discussions, and help with interpretation.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Data deposition: Data from transient absorption and photoluminescence spectroscopy have been uploaded to the University of Cambridge data repository, DSpace, www.repository.cam.ac.uk/handle/1810/248239.

[1]To whom correspondence should be addressed. Email: rhf10@cam.ac.uk.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1503471112/-/DCSupplemental.

be an endothermic singlet fission system; however, here the combination of the energetics, dynamics in solution, and sharply resolved spectral features allow the intermediate state to be isolated.

The absorption and emission energies in solutions of TIPS–tetracene give a singlet exciton energy of 2.3 eV (Fig. 1). No phosphorescence could be detected in solution, but in films of dilute TIPS–tetracene in a polystyrene matrix we detect weak phosphorescence centered at ~1.25 eV at room temperature (Fig. 1*B*, *Inset*). This is consistent with what has been measured for tetracene (1.35 eV), using the same method (25). The endothermicity of fission in TIPS–tetracene is thus on the order of 100–300 meV, comparable to that observed in tetracene films, and films of TIPS–tetracene at room temperature display a similarly slow (tens of picoseconds) rate of fission as tetracene with no distinct intermediate species (*SI Appendix*, Fig. S5).

In solution, however, using transient absorption (TA) and time-resolved photoluminescence (PL) spectroscopy, we directly monitor the conversion of photogenerated singlet excitons into an excimer in <100 ps. The excimer subsequently dissociates into free triplets over tens of nanoseconds, with a final triplet yield of 120%. We observe that the excimer carries absorption signatures of both a singlet and triplet character state as soon as it is formed. The rapid formation of this intermediate with spin-triplet absorption signature and emissive singlet character indicates that it is a bound state of two spin-triplet excitons. We consider that one triplet is localized on each molecule and that they are coupled into an overall spin-zero state, such that these results constitute a direct optical observation of a ^{1}(TT) state. In this solution system, the nonendothermic formation of this stabilized, multiexciton excimer intermediate reduces radiative decay from the singlet and enables thermal dissociation into two free triplet excitons, with an overall energy higher than that of the original singlet exciton, in high yield.

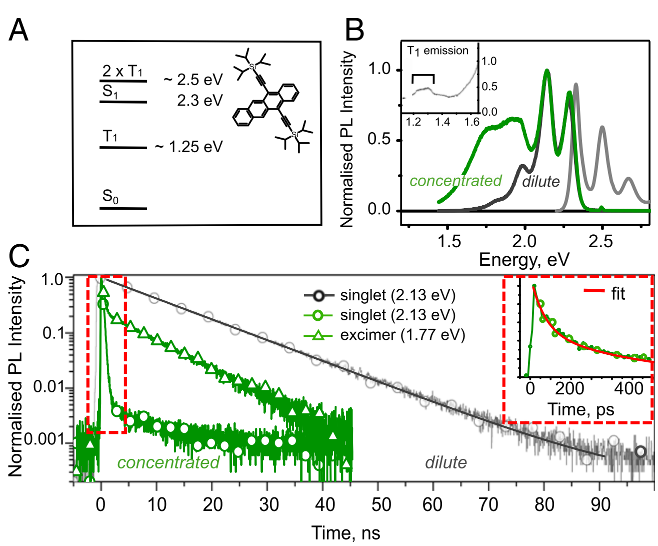

Fig. 1. The absorption and emission spectra of TIPS–tetracene show excimer formation in concentrated solutions. (*A*) The excited state energy diagram and chemical structure of TIPS–tetracene. The triplet energy was obtained from the phosphorescence observed in a film of dilute TIPS–tetracene and polystyrene (*B, Inset*). (*B*) UV-Vis absorption (light gray) of 0.3 mg/mL TIPS–tetracene in $CHCl_3$. UV-Vis spectra were recorded for solutions from 0.03 to 300 mg/mL and no change was observed in the absorption peak positions (*SI Appendix*, Fig. S3). The normalized steady-state photoluminescence spectra of 300 mg/mL (dark green) and 3 mg/mL (dark gray) show that excimeric emission, centered at 1.75 eV, in the concentrated solution is absent in the dilute solution. The phosphorescence observed in a film in the *Inset* (25). Interference at 1.2 eV, from the excitation source, has been removed for clarity. (*C*) The normalized time-resolved photoluminescence decay of the dilute solution at the excitonic (2.13 eV) region and the excitonic and excimer (1.77 eV) regions for the concentrated solution. In the dilute case (gray) the time constant of the excitonic decay is 11.6 ns and this is shortened to 140 ps in 300 mg/mL, shown in the *Inset*. The <600 ps decay at 2.13 eV was measured using PL up-conversion with a time resolution of 200 fs. The excimeric emission of 300 mg/mL decays with two time constants; < 300 ps and 8.7 ns.

Results and Discussion

Formation of Excimers. In Fig. 1*B* we present the absorption spectrum of TIPS–tetracene in 0.3 mg/mL solution and the normalized steady-state photoluminescence spectra of both 3 mg/mL (dilute) and 300 mg/mL (concentrated) solutions in chloroform. We measured the UV-Vis absorption of solutions over several orders of magnitude in concentration and although the highest optical densities caused saturation of the detector, we observed no change in the absorption edge, line shape, or any other signs of ground-state aggregation (*SI Appendix*, Fig. S3). In an additional measurement, we used diffusion-ordered nuclear magnetic spectroscopy to determine the diffusion constant of the TIPS–tetracene molecules in the same solutions. Although the highest concentrations result in a clear increase in viscosity, this effect is of comparable magnitude for the $CHCl_3$ molecules and TIPS–tetracene (*SI Appendix*, Fig. S1). These measurements provide strong evidence that over the entire concentration range the solutions contain only free, unaggregated TIPS–tetracene molecules in the ground state. In this situation, TIPS–tetracene follows the same molecular motion picture established for the solution-mediated fission in TIPS–pentacene (18). We note, however, that the principal finding in the present paper (of the formation of a triplet pair intermediate state, discussed below) can be obtained also in the presence of some molecular preorganization. The concentration-dependent photoluminescence spectra reveal excimer character in the excited state: we observe a broad, low-energy emissive band at high concentrations, similar to the excimer identified in TIPS–pentacene solutions.

Time-resolved photoluminescence decay of the dilute and concentrated solutions is shown in Fig. 1*C*. In the dilute regime, the decay of the photoluminescence is monoexponential across the emissive bandwidth and has a time constant of 11.6 ns. The emission at the 0–1 emissive peak in the concentrated solution is also monoexponential, but is heavily quenched to 140 ps (Fig. 1*C*, *Inset*). In accordance with this quenching, the photoluminescence quantum yield drops from 75% in the dilute solution to 2% in the concentrated. The singlet is not quenched into a completely dark state, but forms a new weakly emissive species with a featureless, red-shifted emission spectrum. Seen only in concentrated solutions, this species decays with a lifetime of 8.7 ns and is assigned to an excimer. From these photoluminescence results of the concentrated solution we can confirm the presence of two distinct emissive species that possess significantly different radiative lifetimes.

To gain a better understanding of the long-time decay kinetics, we recorded the time- and spectrally resolved photoluminescence of the concentrated solution with an intensified CCD camera (Fig. 2 *A* and *B*). In this more sensitive measurement we detect a weak long-lived component to the singlet emission decay with the same time constant as the excimeric emission (8.7 ns; Fig. 2*C*). This observation indicates that the singlet can be repopulated by a state that is close in energy and that also gives rise to weak excimeric emission, as depicted in Fig. 2*D*. These decay kinetics also enable us to determine the photoluminescence quantum efficiency (PLQE) of the individual components. Using spectral deconvolution methods (described below and in the *SI Appendix*) we can separate the PL into contributions from the prompt singlet, excimer, and delayed singlet species. The delayed singlet corresponds to singlet emission after 6 ns, when we observe the onset of delayed emission kinetics (Fig. 2*C*). Integration of the PL associated with each component gives us their contribution to the PLQE of the solution. The photogenerated singlet emission exhibits a

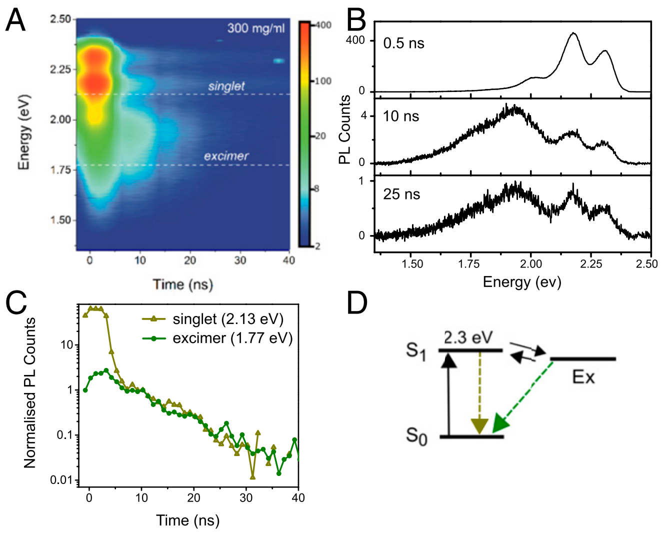

Fig. 2. The time-resolved photoluminescence of the concentrated sample indicates the singlet and excimer states are close in energy. (*A*) The time-resolved and spectrally resolved photoluminescence of 300 mg/mL TIPS–tetracene measured with an intensified CCD camera. (*B*) Time slices at three time points in measurement *A*: At 0.5 ns we observe strong singlet emission. At 10 and 25 ns this has decayed to show weak excimeric and singlet emission. (*C*) The normalized kinetics of the excimeric and singlet decay. The kinetics are normalized at 6 ns, by which time the photogenerated singlet population has fully decayed and only trace singlet emission is detected. The decay of the excimeric emission and trace singlet emission are well matched, indicating they are populated by the same excited state species. (*D*) Schematic showing the relationship of the singlet and excimer states. Solid arrows represent absorption of light and population transfer between the two states and dashed lines indicate weak radiative decay.

yield of 1.3%, and the reformed singlet and excimer emission have efficiencies of 0.3% and 0.4%, respectively. Given the low likelihood of a singlet exciton emitting before forming an excimer, we determine that 98% of the reformed singlets return to the excimer manifold, meaning singlet reformation and emission are both minor decay pathways from the excimer state. The most important insight we take from this measurement is that the singlet and excimer states are close in energy.

Diffusional Singlet Exciton Fission. Because the bulk of the excitations generated do not emit from either the singlet or emissive excimer states, we turn to transient absorption spectroscopy to track the evolution of these states. This pump-probe technique is widely used to study the photophysics of organic materials and is well suited to studies of singlet fission due to its ability to provide detailed signatures of emissive and dark excited state species. In brief, transient absorption measures the time evolution of the absorption of a material following photoexcitation. A pump pulse excites the sample, and a broad-band probe pulse then arrives at a series of time delays. The transmission of the probe is measured with and without the pump, and this differential signal is normalized by the total transmission ($\Delta T/T$). The result is a 2D matrix of transmission intensity as a function of time and probe energy, in which the absorption of photoexcited states is negative and photoemission stimulated by the probe is positive.

Fig. 3*A* shows the transient absorption spectra of dilute TIPS–tetracene in chloroform, recorded over a pump-probe range of 1 ps to 3 μs. The positive feature above 2.1 eV matches the position of the 0–1 photoluminescence peak and is therefore assigned to stimulated emission from singlet excitons. The spectrum in the probe range below 2.1 eV reflects the singlet excited state absorption. All features in this system decay uniformly with a time constant of 11 ns, in good agreement with the monoexponential photoluminescence decay discussed above for the same solution. No other excited state signatures are present within the resolution of the experiment. Taking into account the triplet absorption cross-section and the noise level of the measurement, we set an upper limit of 6% as the yield of triplet excitons through intersystem crossing in this solution. We therefore conclude that in the dilute regime only singlet excitons are present.

We observe similar signatures immediately following photoexcitation of the concentrated solution (Fig. 3*B*). The stimulated emission above 2.1 eV and shape of the photoinduced absorption band in the first 300 ps (blue lines) indicate that the initial photoexcited species is the same at both concentrations. The subsequent spectral evolution shows pronounced differences; however, as the initial singlet features evolve over several hundred picoseconds to form a new absorption profile (solid red trace) that was not observed in the dilute solution. This absorption profile displays a broad absorption feature in the visible probe region and sharper peaks in the near IR. We attribute this intermediate transient absorption signal to the excimer formed from singlet excitons. It decays on the same timescale as the excimeric emission and is only present in concentrated solution. We observe that an increase in viscosity by the addition of polystyrene slows the

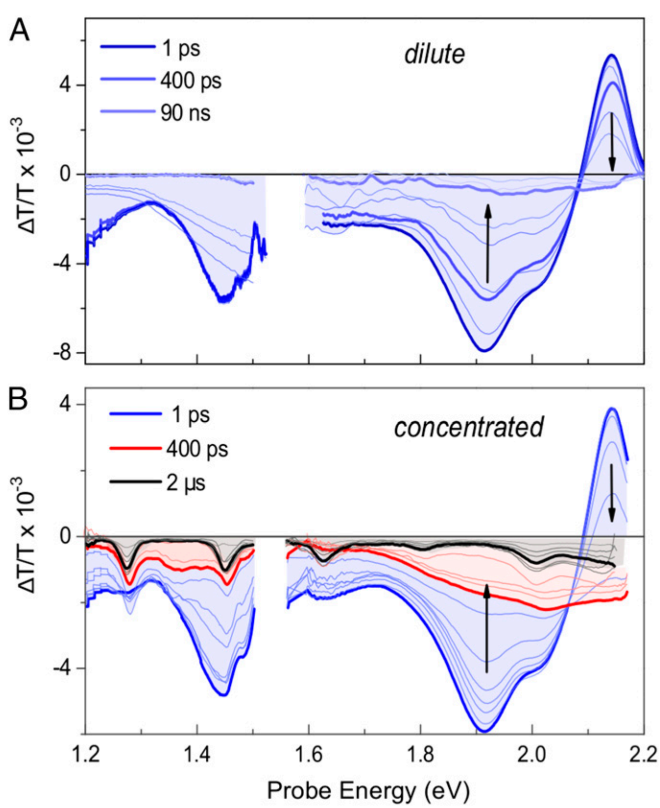

Fig. 3. Transient absorption spectra of dilute and concentrated solutions show excimer and triplet species in the concentrated solution. (*A*) Transient absorption spectra of 3 mg/mL TIPS–tetracene recorded at pump-probe time delays of 1 ps–3 μs. The positive feature at 2.17 eV is assigned to stimulated emission of singlet excitons and decays with the same time constant as the negative photo-induced absorption feature centered at 1.9 eV (*SI Appendix*, Fig. S15). (*B*) Transient absorption spectra of 300 mg/mL TIPS–tetracene recorded over a similar pump-probe delay range (1 ps–3 μs). In this measurement we observe the quenching of the initial species (blue trace) to form an intermediate by 400 ps (red trace), which decays to form triplet excitons (black trace). The triplet exciton absorption spectrum was confirmed from a separate sensitization experiment (*SI Appendix*, Fig. S18). All spectra have been normalized for fluence between the NIR and visible regions. Time slices from the nanosecond measurement are magnified to show the triplet features.

formation of this species, indicating that it is formed via diffusional collisions (*SI Appendix*, Fig. S16). Analysis of the time constant of excimer formation and concentration reveals that the process follows second-order reaction kinetics (Fig. 4*B* and *SI Appendix*, Fig. S11).

The excimer spectrum decays over nanoseconds to yield a third, sharply peaked absorption profile (Fig. 3*B*, black trace). This final spectral signature has a 1.2-μs lifetime and is assigned to triplet excitons, which we confirmed using a separate triplet sensitization experiment. Briefly, in a degassed solution of *N*-methylfulleropyrrolidine and TIPS–tetracene we selectively excite the fullerene, which rapidly undergoes intersystem crossing to generate a large population of triplets. These are transferred to TIPS–tetracene through diffusional collisions (*SI Appendix*, Figs. S18–S21), resulting in a long-lived signature that closely matches the features observed under direct excitation (Fig. 4*C*, *Bottom*) (26, 27). The remarkably sharp triplet absorption features we observe for the triplet exciton have been observed in a small set of other systems (18, 28), where the rigidity of the molecule gives narrow absorption bandwidths, and are a distinct advantage of solution studies of acenes compared with the solid state. In this case, the sharp features allow us to distinguish the absorption signatures of the three species, and in particular track the evolution of the excimer to the triplet excitons. The sensitization measurement also enabled a determination of the triplet absorption cross-section of 5,400 $\mathrm{L\,mol^{-1}\,cm^{-3}}$ at 1.63 eV, based on the degree of quenching of the triplet excitons on the sensitizer by TIPS–tetracene (27). This value was used to obtain a triplet exciton yield of 120% ± 20% of the singlet exciton concentration. It is not surprising that the triplet exciton yield in this system is lower than in TIPS–pentacene solutions, considering the unfavorable energetics of singlet fission in TIPS–tetracene. This distinction notwithstanding, the high yield and observed concentration dependence of triplet exciton formation, analogous to TIPS–pentacene (18), confirm that the triplet excitons are produced in this system via diffusional singlet exciton fission.

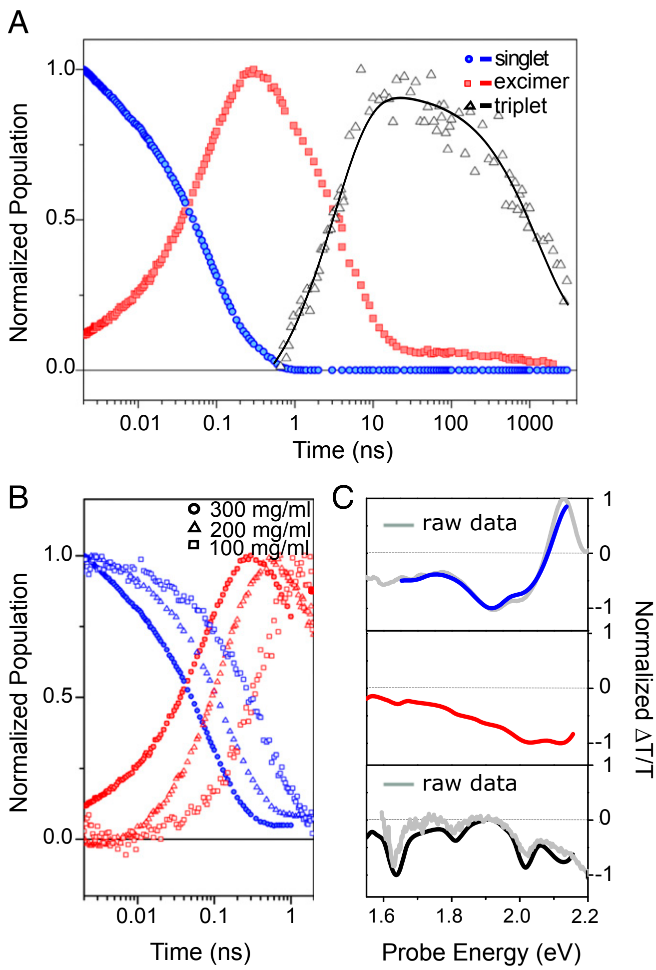

Fig. 4. The evolution of three spectral species in concentrated solution, identified by the genetic algorithm. (*A*) The normalized excited state population from the genetic algorithm in concentrated TIPS–tetracene solution from 100 fs (the peak of the instrument response) to 3 μs after excitation, obtained from transient absorption measurements. The decay and rise of the singlet (blue), excimer (red) populations, and the rise of the triplet (black) were obtained from subpicosecond transient absorption, and the decay of the excimer and the decay of the triplet population were measured with nanosecond transient absorption. A guide to the eye is fitted to the triplet kinetic to show the dynamics with more clarity. (*B*) The corresponding singlet (blue) and excimer (red) kinetics for a range of concentrations (100–300 mg/mL). (*C*) Spectra of the singlet (*Top*), excimer (*Middle*), and triplet (*Bottom*) obtained from genetic algorithm analysis, alongside raw TA spectra (gray) from independent reference measurements (dilute solution and sensitization).

Isolation of a Triplet Character Intermediate. Following the identification of three separate species in concentrated TIPS–tetracene solution, we determine the time evolution of each using singular value decomposition and a spectral deconvolution code (29). This code, based on a genetic algorithm, generates spectra that best reproduce the original transient absorption data and satisfy physical constraints such as spectral shape and population dynamics. The normalized population kinetics of singlet excitons, excimer, and triplet excitons in the 300 mg/mL solution are presented in Fig. 4*A*. The singlet exciton population is shown from 100 fs, the peak of the instrument response, and decays with a 70-ps lifetime, in reasonable agreement with the fast PL decay observed with PL up-conversion (Fig. 1*C*, *Inset*). We observe excimer formation concomitant with the decay of the singlet exciton spectral features. The excimer population then decays with a time constant of 7.9 ns, consistent with the photoluminescence lifetime of 8.7 ns. The triplet exciton population rises with a 5-ns time constant and reaches a maximum between 10 and 50 ns. Considering the short singlet lifetime and the extended lifetime of the excimer, we propose that triplet excitons arise directly from the excimer decay. We thus find that the excimer is in fact an intermediate in the endothermic formation of free triplet excitons. It is interesting to note that when we run the same analysis on the measurements of a TIPS–tetracene film at room temperature, we observe no distinct intermediate state: triplets appear to form directly from the initial state.

In addition to the evolution of the species over time, the distinct spectra of the singlet, excimer, and triplet species were extracted in each spectral region. We are able to achieve such effective spectral and temporal resolution of these states due to the combination of diffusion-limited dynamics, the narrow absorption bands of triplet excitons in solution, and the endothermicity of free triplet formation. As shown in Fig. 4*C*, the extracted spectra for the singlet and triplet excitons closely match reference measurements. The remaining spectrum, which cannot be formed as a linear combination of the other two, is that of the excimer intermediate and reveals crucial information about the nature of that state.

We observe five sharp absorption features in the triplet exciton spectrum across the visible and NIR spectral regions (Fig. 3). The same absorption bands are present in the excimer spectrum and appear from 80 ps, when the process is still diffusion limited. These absorption bands of the excimer are sharp at low energies (1.28 and 1.46 eV) and appear on top of an underlying excited state absorption from 1.6 to 2.2 eV. Notably, we observe that the triplet-like absorption bands of the excimer are shifted and broadened in energy from those of free triplet excitons by 5–10 meV for each band (Fig. 5). The five absorption bands simultaneously red shift over the 1–5 ns timescale as the excimer population is replaced by free triplet excitons. The presence of triplet exciton absorption bands in the excimer indicates that it develops triplet character upon its formation, on a timescale too fast to be explained by intersystem crossing, which is clearly inefficient in the dilute solution. We propose that the shift observed in the triplet pair state absorption reflects the subtle difference in the excited state manifolds of this state and free triplet excitons on isolated molecules.

This result reveals a state that is electronically similar, yet not identical, to free triplet excitons that can be formed in <100 ps from singlet excitons. This state retains enough singlet character to reform singlet excitons and can itself luminesce. These observations—dual singlet-triplet character, showing the absorption of free molecular triplets at the same time as broader singlet-like bands—allow identification as a bound triplet pair state ^{1}(TT). We consider that the formation of this state already constitutes the critical step of singlet exciton fission, although it is the subsequent dissociation into free triplet excitons that determines the final triplet yield. The subtle electronic structural differences that we uncover between the triplet pair intermediate and free triplet excitons could give insight into the nature of triplet pair states. In particular, the nature of coupling between two triplet excitons, which appears to give a substantial stabilization, as we explain below, remains to be well understood.

Endothermic Singlet Fission via a Triplet Pair State. From these results we can put together the energetic picture of singlet fission in this endothermic system. It follows from the photoluminescence results above that the energy of the triplet pair excimer state is equal to or slightly below that of the singlet exciton (2.3 eV). From analysis of the radiative and nonradiative decay rates for the singlet and excimer, and the concentration dependence, we determine that excimers are formed upon the collision of singlet excitons with a ground-state molecule. In addition, the equilibrium between the singlet and excimer manifolds strongly favors excimer formation, and loss via singlet emission represents a minor decay pathway for the excimer.

Our estimate of the endothermic barrier in this system is based on a triplet energy of 1.25 eV, the middle of the broad phosphorescence peak observed in thin films. We consider that an energy barrier of about 200 meV is consistent with activation over a thermal barrier. If we consider a Boltzmann distribution and the 5-ns time constant for free triplet formation, this system would require an attempt frequency on the order of 10^{11}–10^{13} Hz to overcome this energy barrier into independent triplet excitons. We conjecture that the reason such a slow thermal dissociation of the stabilized excimer intermediate into free triplets is able to proceed with such high efficiency is because competing decay channels are slower. Radiative decay via the singlet is substantially reduced in the concentrated solution as a result of forming excimers. The intrinsic radiative lifetime of 2 μs for the excimer is consistent with the microsecond radiative lifetimes reported for excimers of pyrene and anthracene (30, 31), and gives sufficient time for competing nonradiative processes such as thermally activated triplet formation. These nonradiative decay processes shorten the excited state lifetime of the excimer to give the fluorescence lifetime of 8 ns that we measure in transient absorption and PL.

From the data available, it is difficult to ascertain the degree to which the two-step mechanism of fission in solution relates to the solid state. Although we observe no distinct intermediate in films of TIPS–tetracene, it is possible, for instance, that the conformational constraints of the film prevent any significant stabilization of the intermediate state that would measurably distort its absorption spectrum relative to free triplets. Without a clear identification of such effects, though, the mechanism of this endothermic singlet fission will remain in question. We note, however, that it would be surprising for the same material to be capable of singlet fission via two completely distinct mechanisms and propose that a strongly stabilized TT intermediate still plays an important role.

We can compare the results here with studies from films of tetracene, where the first step of highly efficient endothermic singlet fission is temperature independent (22, 23) and has been proposed to involve barrier-free formation of an intermediate state (32, 33) or tunnelling into a bound triplet pair (22). We find that our model is in qualitative agreement with these other studies; our endothermic system reveals rapid formation of a bound intermediate with triplet character that goes on to produce two free triplet excitons over a longer timescale. We speculate that the stabilization we observe in the triplet pair excimer, relative to free triplet excitons, may occur to a lesser degree in the solid state as well and enable the fast formation of bound triplets.

These results provide an important and surprising insight into the nature of the triplet pair state, which has long played a central role in theories of singlet fission but never been directly observed. The bound state can be significantly stabilized relative to two free triplet excitons, here by 100–300 meV, indicating a substantial interaction between the triplets. A similar effect is observed in some polyene-type systems, in which the doubly excited $2A_g$ state can be identified as a bound triplet pair (34). In poly(3-dodecylthienylenevinylene), for instance, the $2A_g$ state is substantially lower in energy than the threshold for singlet exciton fission, and indeed offers a rapid decay channel for triplet pairs (35). Multiexciton states with A_g symmetry have also been invoked to explain fission in calculations of crystalline pentacene, although in that system there is no evidence of any significant energetic

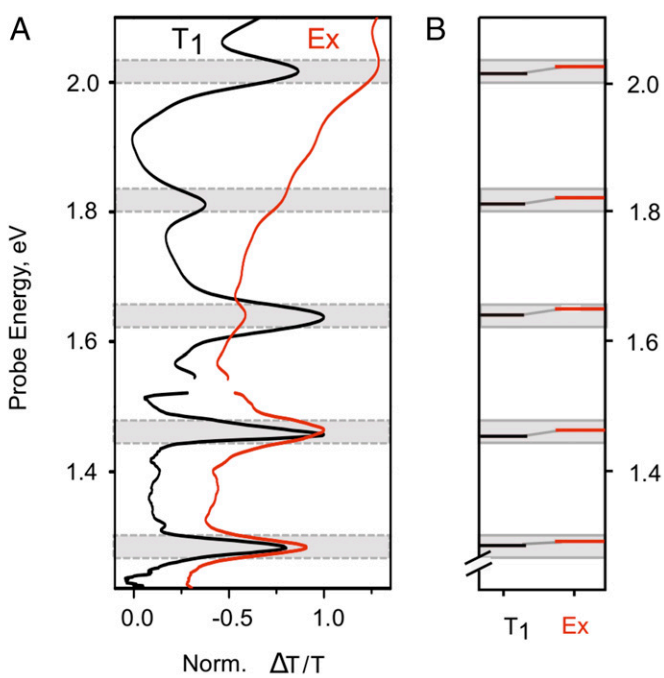

Fig. 5. The transient absorption spectra reveal the shift in absorption peak energies between the excimer intermediate and free triplet excitons. (*A*) The normalized excimer and triplet absorption spectra with the common absorption bands highlighted. (*B*) An energy level diagram of the higher-lying excited states of the excimer and free triplet excitons, obtained from the transient absorption bands in *A*. We observe that the triplet absorption is red-shifted by 5–10 meV for each band, relative to the excimer triplet pair state.

stabilization in this state (36). It is possible that stabilized triplet pair states akin to the one presented here play an important role in fission across different molecular systems, especially nominally endothermic materials such as tetracene, but more exploration of this phenomenon is needed. In this TIPS–tetracene system, the stabilization we observe and the accompanying effects of this coupling on the transient absorption spectra should provide fertile ground for advanced theoretical investigations of the interactions between adjacent triplet excitons. Explorations of the nature and electronic structure of this triplet pair intermediate via multipulse techniques will enable a more complete understanding of the mechanism of singlet fission and may establish the importance of such stabilized states for mediating triplet formation in endothermic systems.

Materials and Methods

TIPS–tetracene was synthesized according to the procedure in ref. 37.

For most of the photophysical characterization (see *SI Appendix* for details) TIPS–tetracene was measured in solutions of chloroform (3–300 mg/mL) in sealed 1-mm pathlength cuvettes. Steady-state UV-Vis absorption spectra were taken at room temperature using a Cary 400 UV-Visible Spectrometer. For these measurements 200- and 5-μm pathlength cells were used. Steady-state and time-resolved fluorescence spectra were acquired with a PicoQuant LDH400 pulsed laser and SpectroPro2500i spectrograph. Photoluminescence up-conversion was measured using a Jobin Yvon:Triax90 spectrometer and Jobin Yvon:Symphony CCD.

Femtosecond and nanosecond transient absorption measurements were carried out with an amplified Ti:Sapphire (Spectra Physics Solstice) laser system and imaged using an Andor Shamrock SR 303i spectrometer. See *SI Appendix* for more details regarding the TA setup and data analysis techniques.

ACKNOWLEDGMENTS. We thank A. Bakulin and A. Rao for general discussion, the Centre for Advanced Photonics and Electronics for UV-Vis absorption cells, and D. Howe for assistance with diffusion-ordered NMR spectroscopy. The laboratory and H.L.S. were supported by the Winton Programme for the Physics of Sustainability. A.J.M. received funding from the Engineering and Physical Sciences Research Council.

1. Smith M-B, Michl J (2010) Singlet fission. *Chem Rev* 110(11):6891–6936.
2. Pope M, Swenberg C (1999) *Electronic Processes in Organic Crystals and Polymers* (Oxford Univ Press, New York).
3. Wilson MWB, et al. (2011) Ultrafast dynamics of exciton fission in polycrystalline pentacene. *J Am Chem Soc* 133(31):11830–11833.
4. Wilson MWB, Rao A, Ehrler B, Friend RH (2013) Singlet exciton fission in polycrystalline pentacene: From photophysics toward devices. *Acc Chem Res* 46(6):1330–1338.
5. Yost SR, et al. (2014) A transferable model for singlet-fission kinetics. *Nat Chem* 6(6): 492–497.
6. Burdett JJ, Müller AM, Gosztola D, Bardeen CJ (2010) Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission. *J Chem Phys* 133(14):144506.
7. Johnson JC, Nozik AJ, Michl J (2010) High triplet yield from singlet fission in a thin film of 1,3-diphenylisobenzofuran. *J Am Chem Soc* 132(46):16302–16303.
8. Hanna MC, Nozik AJ (2006) Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *J Appl Phys* 100(7):074510.
9. Lee J, Jadhav P, Baldo MA (2009) High efficiency organic multilayer photodetectors based on singlet exciton fission. *Appl Phys Lett* 95(3):033301.
10. Rao A, et al. (2010) Exciton fission and charge generation via triplet excitons in pentacene/C60 bilayers. *J Am Chem Soc* 132(36):12698–12703.
11. Ehrler B, Wilson MWB, Rao A, Friend RH, Greenham NC (2012) Singlet exciton fission-sensitized infrared quantum dot solar cells. *Nano Lett* 12(2):1053–1057.
12. Ehrler B, et al. (2012) In situ measurement of exciton energy in hybrid singlet-fission solar cells. *Nat Commun* 3:1019.
13. Congreve DN, et al. (2013) External quantum efficiency above 100% in a singlet-exciton-fission-based organic photovoltaic cell. *Science* 340(6130):334–337.
14. Tabachnyk M, Ehrler B, Bayliss S, Friend RH, Greenham NC (2013) Triplet diffusion in singlet exciton fission sensitized pentacene solar cells. *Appl Phys Lett* 103(15):153302.
15. Merrifield RE (1971) Magnetic effects on triplet exciton interactions. *Pure Appl Chem* 27:481–498.
16. Burdett JJ, Bardeen CJ (2012) Quantum beats in crystalline tetracene delayed fluorescence due to triplet pair coherences produced by direct singlet fission. *J Am Chem Soc* 134(20):8597–8607.
17. Thorsmølle VK, et al. (2009) Morphology effectively controls singlet-triplet exciton relaxation and charge transport in organic semiconductors. *Phys Rev Lett* 102(1):017401.
18. Walker BJ, Musser AJ, Beljonne D, Friend RH (2013) Singlet exciton fission in solution. *Nat Chem* 5(12):1019–1024.
19. Swenberg C, Stacy W (1968) Bimolecular radiationless transitions in crystalline tetracene. *Chem Phys Lett* 2(5):327–328.
20. Tomkiewicz Y, Groff RP, Avakian P (1971) Spectroscopic approach to energetics of exciton fission and fusion in tetracene crystals. *J Chem Phys* 54(10):4504–4507.
21. Merrifield R, Avakian P, Groff R (1969) Fission of singlet excitons into pairs of triplet excitons in tetracene crystals. *Chem Phys Lett* 3(3):155–157.
22. Wilson MWB, et al. (2013) Temperature-independent singlet exciton fission in tetracene. *J Am Chem Soc* 135(44):16680–16688.
23. Burdett JJ, Gosztola D, Bardeen CJ (2011) 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(21):214508.
24. Bayliss SL, et al. (2014) Geminate and nongeminate recombination of triplet excitons formed by singlet fission. *Phys Rev Lett* 112(23):238701.
25. Reineke S, Baldo MA (2014) Room temperature triplet state spectroscopy of organic semiconductors. *Sci Rep* 4:3797.
26. Apperloo J, Martineau C, van Hal PA, Roncali J, Janssen RAJ (2002) Intra- and intermolecular photoinduced energy and electron transfer between oligothienylene-vinylenes and N-methylfulleropyrrolidine. *J Phys Chem* 106:21–31.
27. Busby E, et al. (2015) A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor-acceptor organic materials. *Nat Mater* 14(4):426–433.
28. Kraabel B, Hulin D, Aslangul C, Lapersonne-meyer C, Schott M (1998) Triplet exciton generation, transport and relaxation in isolated polydiacetylene chains subpicosecond pump-probe experiments. *Chem Phys* 227:83–98.
29. Gelinas S, et al. (2011) The binding energy of charge-transfer excitons localized at polymeric semiconductor heterojunctions. *J Phys Chem* 115:7114–7119.
30. McVey JK, Shold D, Yang N (1976) Direct observation and characterization of anthracene excimer in solution. *J Chem Phys* 65(8):3375–3376.
31. Birks JB, Dyson DJ, Munro IH (1963) 'Excimer' fluorescence. II. Lifetime studies of pyrene solutions. *Proc Royal Soc, Math Phys Eng Sci* 275:575–588.
32. Piland GB, Burdett JJ, Dillon RJ, Bardeen CJ (2014) Singlet fission: From coherences to kinetics. *J Phys Chem Lett* 5:2312–2319.
33. Tayebjee MJY, Clady RGCR, Schmidt TW (2013) The exciton dynamics in tetracene thin films. *Phys Chem Chem Phys* 15(35):14797–14805.
34. Tavan P, Schulten K (1987) Electronic excitations in finite and infinite polyenes. *Phys Rev B Condens Matter* 36(8):4337–4358.
35. Musser AJ, et al. (2013) Activated singlet exciton fission in a semiconducting polymer. *J Am Chem Soc* 135(34):12747–12754.
36. Zimmerman PM, Zhang Z, Musgrave CB (2010) Singlet fission in pentacene through multi-exciton quantum states. *Nat Chem* 2(8):648–652.
37. Odom SA, Parkin SR, Anthony JE (2003) Tetracene derivatives as potential red emitters for organic LEDs. *Org Lett* 5(23):4245–4248.

CHEMISTRY