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A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor–acceptor organic materials

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The ability to advance our understanding of multiple exciton generation (MEG) in organic materials has been restricted by the limited number of materials capable of singlet fission. A particular challenge is the development of materials that undergo efficient intramolecular fission, such that local order and strong nearest-neighbour coupling is no longer a design constraint. Here we address these challenges by demonstrating that strong intrachain donor–acceptor interactions are a key design feature for organic materials capable of intramolecular singlet fission. By conjugating strong-acceptor and strong-donor building blocks, small molecules and polymers with charge-transfer states that mediate population transfer between singlet excitons and triplet excitons are synthesized. Using transient optical techniques, we show that triplet populations can be generated with yields up to 170%. These guidelines are widely applicable to similar families of polymers and small molecules, and can lead to the development of new fission-capable materials with tunable electronic structure, as well as a deeper fundamental understanding of MEG.

The vast efforts towards developing efficient solar cells based on organic materials[1,2] have led to advancements in processing and characterizing semiconducting molecules and polymers[3–5], as well as engineering organic photovoltaic (OPV) device architectures that have yielded significant increases in efficiency[6–9]. To raise the theoretical limit of power conversion efficiency above the Shockley–Queisser limit[10,11], organic materials capable of generating multiple excitons from a single photon have been explored in devices[12,13], with reported external quantum efficiencies exceeding 100% (ref. 14). In these systems, the primary multiexciton generation mechanism is intermolecular singlet fission (xSF) within molecular aggregates or crystals[15], wherein the absorption of one photon leads to the formation of two triplet excitons on adjacent molecules[16]. Because of the intermolecular nature of this process, strong electronic coupling between nearest neighbours is required and, as such, the efficiency of this process is highly sensitive to the crystallinity of the film[17] and the presence of functional groups that expand the unit cell[18]. A more widely applicable route to functional devices would preferably be based on intramolecular processes, where the fission efficiency is an intrinsic property of the designed material—that is, it is not dependent on molecular orientation, intermolecular coupling, or long-range order, among other constraints. Furthermore, this enhances the possibility of using polymers as fission materials that have tunable chemical structure to control solution processability, film morphology, and various other physical and electronic properties. However, intramolecular singlet fission (iSF) has not been observed with high yield and, as a result, the mechanism is poorly understood. iSF has been observed in a few systems (including several vinylene-containing polymers)[19–21], but fission in these systems is typically an activated process requiring a photon with energy in excess of the bandgap. Only the oligoenes (such as carotenoids) have demonstrated non-activated intramolecular singlet fission, although yields have not exceeded 30% (refs 22,23). The present understanding of iSF provides little insight into how multiple exciton generation can be modularly designed as a feature in molecular materials[24].

Here we address a core challenge in developing materials capable of efficient intramolecular singlet fission by coupling a modular prima facie chemical design strategy with mechanistic studies of the fission process in isolated organic molecules and polymers. We show that singlet-fission systems can be designed on the basis of strong intramolecular donor–acceptor interactions in a copolymer architecture, and we demonstrate this with a new family of singlet-fission materials. Although many strong-acceptor moieties will probably be compatible, we use thiophene-1,1-dioxide (TDO), notable for its high electron affinity[25,26] and relatively low triplet energy (see below). The modularity of the donor–acceptor scheme allows us to choose an arbitrary donor unit (benzodithiophene, B) to tune the absorption relative to the triplet energy. With this model system, we found iSF with triplet quantum yields up to 170% in an isolated polymer chain. Furthermore, we show that significant fission can be achieved in small molecules that contain the minimum necessary functionality of two acceptor subunits with low-energy triplet states. These studies allow us to deduce that iSF can be imparted to a variety of systems, although some configurations may introduce competing relaxation channels. In general, this approach could open avenues for exploration by developing entire families of singlet-fission-capable materials for next-generation SF-OPV and hybrid PV applications.

Although iSF is not yet well understood, some general guidelines for efficient SF have been suggested from studies of intermolecular

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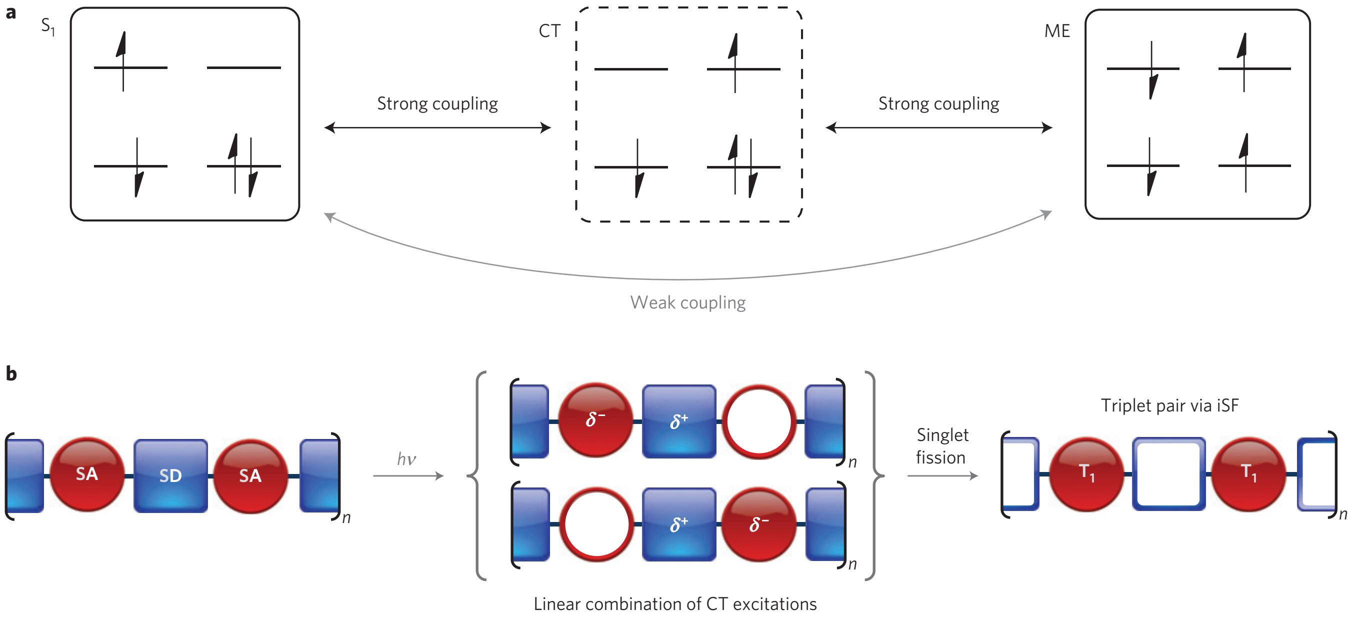

Figure 1 | Design template for singlet-fission-capable molecular and polymeric materials. a, The mechanism for singlet fission: a singlet exciton (S_1) is strongly coupled to a charge-transfer (CT) state, which is in turn strongly coupled to the multiexcitonic triplet state (ME). This charge-transfer mediated process strongly couples the S_1 and ME states, whereas the direct S_1-to-ME coupling is very weak[28,29]. **b**, Fundamental design for charge-transfer-mediated intramolecular singlet fission using strong-donor (SD) and strong-acceptor (SA) units. Singlet excited states can be viewed as a linear combination of intramolecular CT states (denoted as singlet excitons with partial positive (δ^+) and negative (δ^-) charges on the donor and acceptor, respectively), which mediate the population of localized triplet states (T_1) within the SA units through singlet fission.

processes. In xSF, it has been found that the energy of the singlet state should be greater than or equal to twice the energy of the triplet state. Furthermore, both experiments and calculations have suggested that direct coupling between the singlet state and the multiexcitonic (triplet pair) states is weak, but coupling mediated by an intermediate charge-transfer (CT) state can be strong (Fig. 1a)[27–31]. This insight provides design criteria for the selection of building blocks for new iSF-capable materials that satisfy two key requirements for efficient SF: a reduced singlet–triplet pair gap, such that the triplet energy is close to half the singlet energy[16,32]; and a lowest-lying optical excitation with significant CT character that can mediate the SF process[30,33].

The connectivity and conceptual design template for iSF materials based on a framework to meet the above criteria is shown in Fig. 1b. A material composed of alternating electron-rich (strong donor) moieties and electron-deficient (strong acceptor) units will contain significant charge-transfer character in the lowest-energy optical excitation[34]. The resulting charge-transfer state can be directly photoexcited with a large cross-section and can more strongly couple to multiexciton triplet states than singlet Frenkel excitons[28,29,33]. A general understanding of the design can be gained by looking at the fundamental units that can support singlet fission, which in this example consists of two acceptor moieties coupled to an appropriate donor (Fig. 1b). Because two triplets are formed during the fission process, at least two strong-acceptor (SA) units with a low-energy triplet state are required. These properties can be introduced into push–pull polymers in one of two ways: incorporating strong electron-withdrawing substituents into an aromatic system to stabilize the quinoidal resonance structure[35–37], or incorporating oligoene-like moieties[21]. We also note that the acceptor units must be coupled to an appropriate donor(s), such that a minimum CT character is obtained. As well as providing an excited electronic state with significant charge-transfer character (denoted as partial positive, δ^+, and partial negative, δ^-, charges, Fig. 1b), the modular nature of the donor–acceptor motif allows us to choose units which satisfy the energy requirement: that fission is favoured when the energy of the singlet state is at least twice the energy of the triplet state (that is, $E[S_1] \geq 2E[T_1]$).

Table 1 | Material properties.

Material	Bandgap, optical (eV)	HOMO (eV)	LUMO (eV)	Triplet quantum yield	Triplet pair lifetime (ps)
BTD01	1.85	−5.7	−3.8	0.4 ± 0.2	75 ± 15
BTD02	1.65	−5.8	−4.1	0.56 ± 0.1	13 ± 8
PBTD01	1.79	−5.7	−3.9	1.7 ± 0.1	80 ± 20
PBTD02	1.53	−5.6	−4.1	0.6 ± 0.1	23 ± 3

The photophysical and electronic material properties are listed for the TDO-containing materials studied here. The optical bandgap for each material was determined from the linear absorption spectra (Fig. 2c). The highest occupied molecular orbital (HOMO) was determined by means of cyclic voltammetry (Supplementary Fig. 1). The lowest unoccupied molecular orbital (LUMO) is approximated using the HOMO energy level and optical bandgap. The triplet pair lifetimes were determined by exponential fitting of TA bleach recovery kinetics. The triplet yields were determined by fitting of TA bleach recovery kinetics and using the triplet absorption cross-section. The values shown are the average of the yields from the two techniques (Fig. 3, details in Supplementary Information).

To demonstrate that materials with strong charge-transfer character and low triplet energies undergo efficient iSF, we synthesized polymers (PBTDOn) and small molecules (BTDOn) based on building blocks comprising benzodithiophene (B) as the electron-rich unit and mono- or bi-thiophene-1,1-dioxide (TDO1, and TDO2, respectively) as the strong electron acceptor with low triplet energy (Fig. 2a). Control systems with unoxidized thiophenes are shown in Fig. 2b. Steady-state extinction spectra of all materials (Fig. 2c) show that a large redshift is observed in the optical gap relative to the unoxidized thiophene analogues. As such, we assign the lowest-energy optical excitation to a singlet exciton with significant charge-transfer character. The reduction in bandgap on oxidation ranges from 300 to 760 meV, and is more prominent in systems with more TDO units (see Table 1 and Supplementary Fig. 1)[25]. The small molecules show a broad visible absorption

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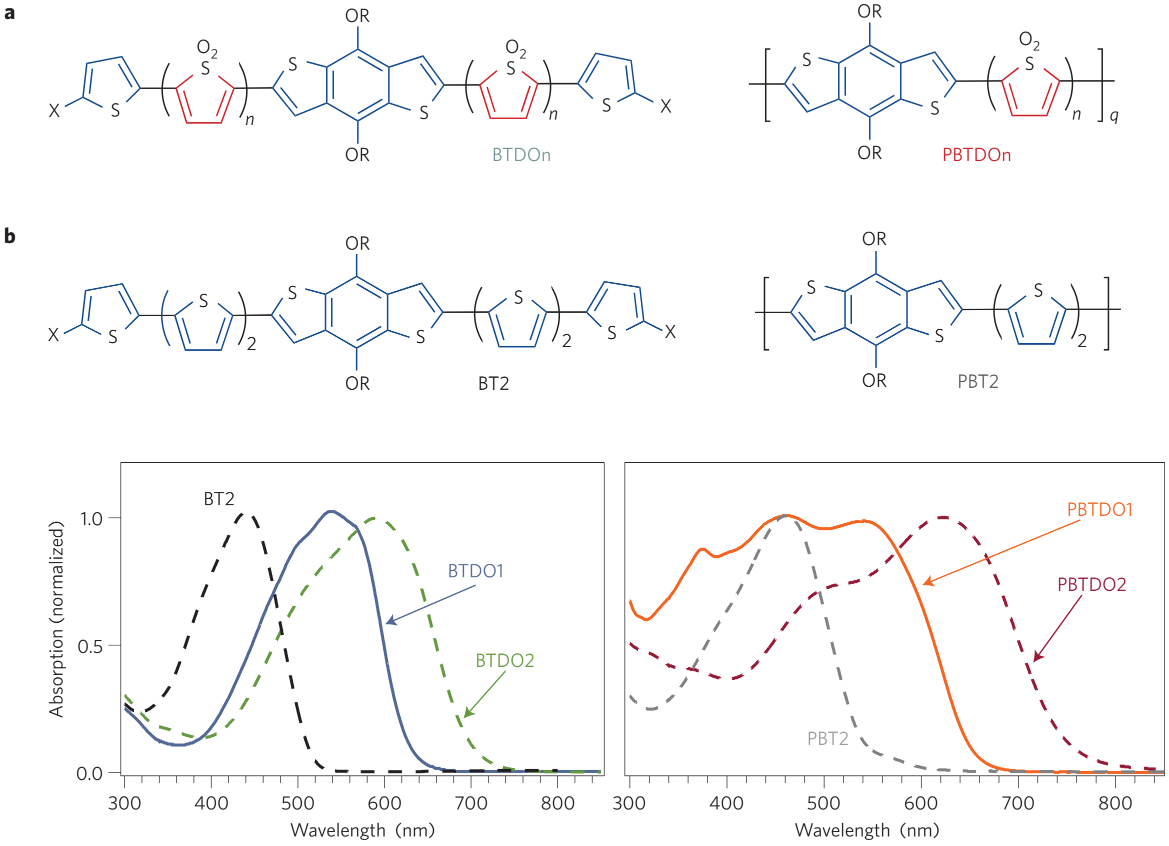

Figure 2 | Structures and absorption spectra of singlet-fission-exhibiting and control materials. a, Singlet fission small molecules and polymers ($n=1,2$). The strong electron acceptor units based on TDO are shown in red and the donor units are shown in blue. **b**, Control small molecule and polymer without SA units. **c**, Absorption spectra of the molecules and polymers. Unoxidized materials are shown for reference. See the Supplementary Information for detailed structures with solubilizing groups, which are here omitted for clarity.

feature with a single peak and no prominent structure. The PBTDOn polymers, however, show additional excitonic structure, which is typical to other donor–acceptor polymers[38].

To confirm that singlet fission is occurring, three parameters are verified: triplet formation occurs on an ultrafast timescale, the transient spectrum of the SF-generated triplets matches that of triplets generated through other means (for example, pulse radiolysis), and the triplet pairs generated through SF decay faster than the native triplet owing to the reverse of the singlet-fission process in the former. We stress that the measurements were carried out on dilute solutions (in chloroform) of these materials to eliminate bimolecular interactions. The associated optical spectra and dynamics were verified to be insensitive to the concentration of the molecules in solution (Supplementary Fig. 3). Combined, these criteria unambiguously establish the fact that the triplets are being formed by iSF rather than intersystem crossing (ISC) or intermolecular SF.

The material with the longest excited state lifetime and highest SF yield is PBTDO1. Broadband transient absorption (TA) spectroscopy of PBTDO1 is used to follow the time evolution of three spectrally distinct states following optical excitation (Fig. 3a). We assign the initially formed state as a singlet exciton with significant charge-transfer character, as is commonly observed in donor–acceptor polymer systems[38]. This state and its associated near-infrared-induced (nIR-induced) absorption band (dark red region >750 nm in Fig. 3a and black kinetic trace in Fig. 3b) have a ~7 ps decay, which is correlated with the rise of a second spectral feature (red region ~675 nm in Fig. 3a and red kinetic trace in Fig. 3b). We assign this population as a triplet exciton formed as the product of singlet fission (this assignment is confirmed below). Our data indicates that all photogenerated singlets are converted to triplets because the amplitude of the ground state bleach (blue region ~600 nm in Fig. 3a), which tracks the overall excited state population, remains constant during the interconversion process. The triplet population decays with a time constant of ~70 ps. A small sub-population (~15%) is generated instantaneously, has a broad induced absorption spanning most of the visible spectral range, and persists well after the triplet population decays back to the ground state (>1 ns). Its dynamics are uncorrelated with either the singlet or triplet populations, suggesting an assignment to a charge-separated state formed by auto-ionization of hot excitons, as has been seen in other neat polymer systems[39]. Similar features are observed for the other TDO-containing materials. Global target analysis (details in the Methods) can be used to separate overlapping spectral signatures of the individual species (Fig. 3c) and model the population evolution versus time (Fig. 3d)[40,41]. Taken together, we quantitatively determine that 85% of the initial excitations go on to form triplets with a formation rate of 7 ps and a decay rate of 70 ps. This gives a triplet quantum yield of 170%, defined by twice the fraction of singlets that initially undergo fission (2 × 85%), and represents the maximum triplet population immediately after fission. The yields of other TDO-containing iSF materials are determined similarly.

Because iSF occurs on isolated molecules, we can use triplet sensitization techniques to confirm the above assignment of the triplet ($T_1 \rightarrow T_n$)-induced absorption feature and to measure triplet absorption cross-sections, which can be used as an independent verification of the triplet quantum yields deduced using rate equations. Specifically, we use pulse radiolysis triplet transfer (PRTT) methods (details in Methods) in which an electron

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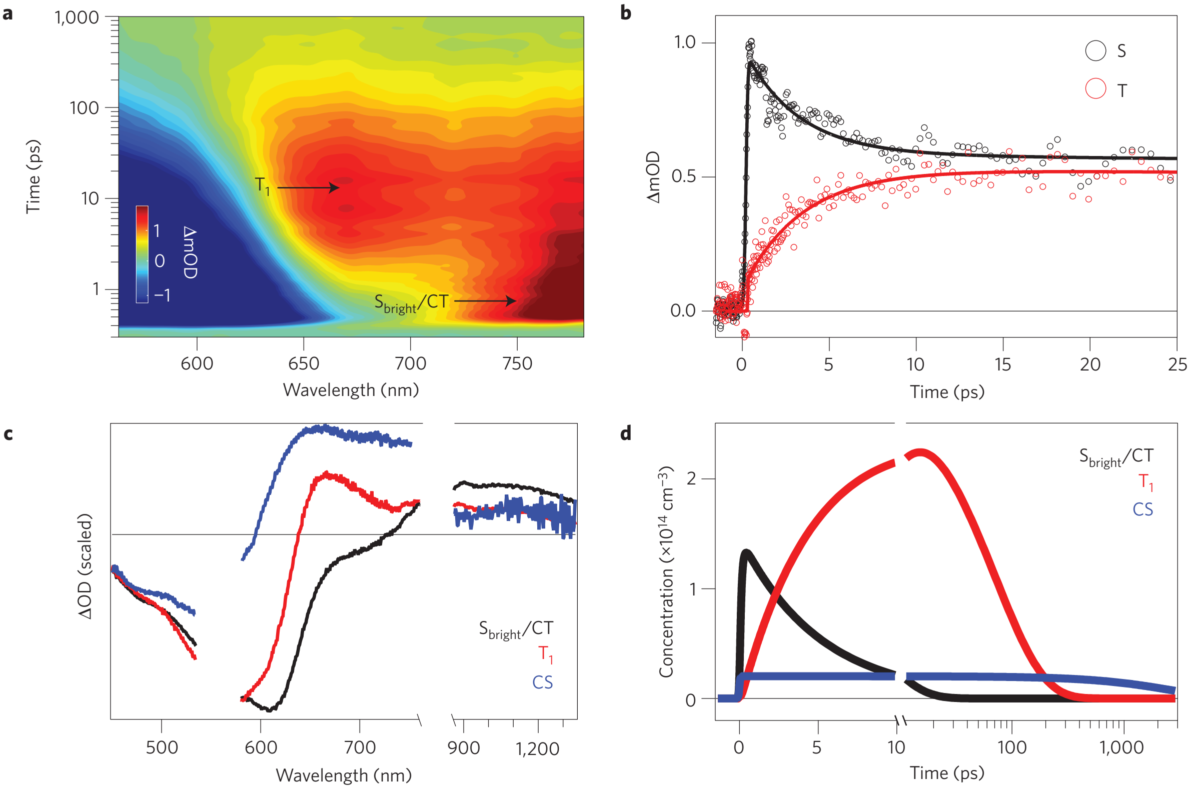

Figure 3 | Transient absorption data and global analysis for PBTDO1. a, Transient absorption of PBTDO1 is shown in a pseudo-colour plot with singlet/charge-transfer exciton (S_{bright}/CT) and triplet exciton (T_1) features denoted. **b**, The dynamics are shown with kinetic traces (open circles) and fits (solid lines) taken through the singlet (>750 nm) and triplet (700–725 nm) absorption features in spectral regions with minimal overlap with other spectral features. **c**,**d**, Global analysis was used to model singlet charge-transfer exciton, triplet and charge-separated (CS) populations to extract time independent spectral signatures (**c**) and population concentration versus time (**d**). **a**–**c** are plotted in the unit-less quantity ΔOD or ΔmOD, the change in optical density or parts-per-thousand change in optical density, respectively. Details of the global analysis and concentration calculation are given in the Methods and Supplementary Information. In **c**, data has been excised in the regions obscured by excitation and fundamental scatter, around 550 nm and 800 nm, respectively. Raw transient absorption data are plotted in Supplementary Fig. 9.

pulse generates triplets that are transferred by a sensitizer to the molecule of interest[42]. These single triplets (as opposed to the triplet pairs produced in iSF) are optically probed to yield the triplet-induced absorption spectrum (Fig. 4a,b, black circles), native triplet lifetime (>1 μs for all TDO-based materials) and extinction coefficient (8,700 and 16,300 M^{-1} cm^{-1} for TDO1-containing and TDO2-containing materials, respectively). The spectral agreement of the PRTT T_1 spectra and proposed T_1-induced absorption from TA confirms that triplets are being formed on an ultrafast timescale following optical excitation in all the TDO-containing materials studied here. Note that all materials with the same number of sequential TDO subunits have similar T_1 spectra, although overlapping ground state bleach contributions may lead to net differences in transient experiments (Fig. 4a,b). Whereas triplet spectra are equivalent, irrespective of the triplet generation mechanism, we find that triplet pairs generated by iSF have recombination kinetics distinct from individual triplets generated by sensitization, as confinement of a triplet exciton pair within a molecule leads to faster biexcitonic recombination rates. Using the single triplet absorption cross-section, it is straightforward to independently determine that the fission yield for PBTDO1 is 173 ± 10% (details in Supplementary Information). This value unambiguously establishes that iSF is occurring and agrees well with our kinetic determination of the triplet yield (170%).

The triplet recombination dynamics also strongly support SF as the mechanism of triplet generation. Whereas the spectra for triplets formed through sensitization and through fission are very similar, their recombination kinetics are highly distinct because triplet pairs can proceed through spin-allowed triplet–triplet annihilation (to repopulate the singlet exciton state or return to the singlet ground state) rather than the much slower spin-forbidden recombination of lone triplet excitons. In our data (Fig. 4c,d), triplets formed by direct photoexcitation recombine more than four orders of magnitude faster than triplets produced through sensitization. We note that the triplet pair lifetime observed here should be regarded as a lower bound, given that the measurements are conducted in a dilute solution where triplets are confined to one dimension along the polymer chain. If triplets are able to diffuse more freely in multiple dimensions, as would happen in the solid state, triplet pair lifetimes can potentially be much longer.

Moreover, the fast formation of triplets (<10 ps) supports singlet fission as the dominant mechanism because observation of ISC on such timescales is generally limited to systems containing heavy atoms that facilitate spin–orbit coupling as a means of circumventing angular momentum conservation selection rules. These assignments are further supported by ultrafast photoluminescence (UFPL) data (Supplementary Fig. 2), which demonstrate that the singlet exciton emission is quenched by iSF in ~7 ps. Furthermore, UFPL data shows that a fraction of the resultant triplet exciton pairs decays radiatively through the reverse of the iSF process, which further confirms the generation of triplet pairs rather than individual triplets. Under weak excitation conditions, only triplets generated in pairs will undergo photoluminescence on ultrafast timescales. Finally, owing to the low excitation fluence used in all transient absorption measurements (fluence-independent dynamics are demonstrated in

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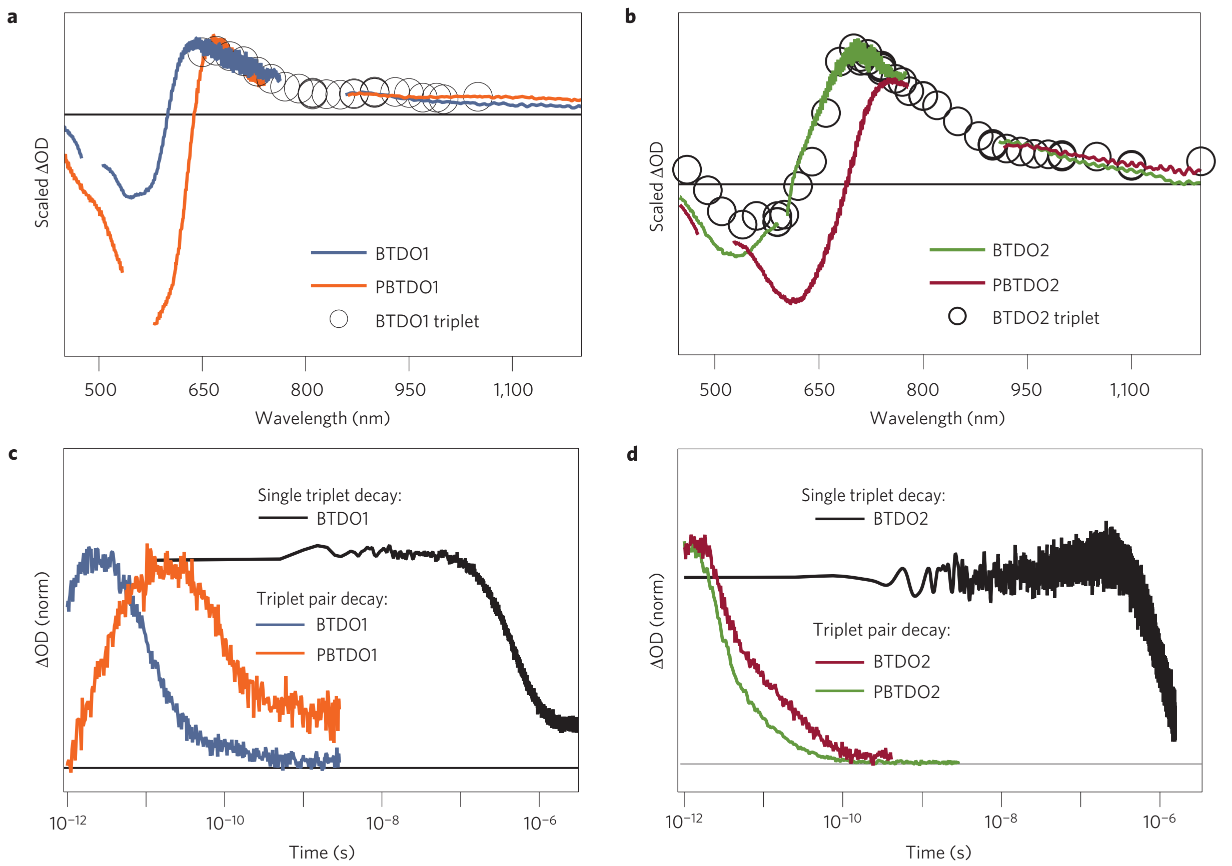

Figure 4 | TA and PRTT for all TDO-containing materials. a,**b**, The triplet spectra are compared in TDO1- (**a**) and TDO2-containing (**b**) molecules and polymers. The spectra of triplets generated from singlet fission (solid lines) are compared against triplets generated through pulse radiolysis (circles). SF-generated spectral traces are from TA data sets; global target analysis[40,41] was used to extract the triplet spectrum when the triplet had significant temporal overlap with other populations (details in the Methods). Note that, because the triplet is localized on the TDO moieties, the triplet spectrum is equivalent for all materials containing the same number of sequential TDO monomers (aside from the contribution of the overlapping bleach band). **c**,**d**, Recombination of triplet pairs generated from singlet fission is compared against recombination of lone triplets generated through pulse radiolysis (black traces) in TDO1- (**c**) and TDO2-containing (**d**) molecules and polymers. The time axes of the pulse radiolysis traces have been offset to exclude the population growth and emphasize the triplet decay. Note that the logarithmic axis highlights several orders of magnitude difference in the triplet and triplet pair recombination lifetimes. In panels **a** and **b**, transient absorption data has been excised from regions obscured by laser scatter. Raw transient absorption data are plotted in Supplementary Fig. 9.

Supplementary Fig. 4), we can further exclude other exotic nonlinear mechanisms that result in the generation of triplets.

Together with photophysical measurements, density functional theory can be used to confirm the design principles that yield efficient iSF in both molecules and polymers. To better understand how the building blocks within the small molecule influence iSF, we focus on BTDO2. The above results and the calculated excited state charge distribution (Supplementary Scheme 1A,B) support our hypothesis that the singlet-fission process in SD–SA copolymers is initiated by direct optical excitation to a charge-transfer state, similar to what has been suggested in select xSF systems[27,30]. However, we note that care must be taken with a simplified picture that depicts the hole carrier density as localized on the 'donor' monomer(s) and the electron density predominately on the 'acceptor' monomer(s)[33]. The charge-transfer character of the S_{bright} state is confirmed by attachment/detachment density analysis[43], which shows the electron density is localized on TDO subunits whereas the hole density is rather delocalized (Supplementary Scheme 1A,B).

The critical role of charge-transfer states in mediating singlet fission has been extensively addressed in xSF (refs 18,27,29). Here, we experimentally explore the concept that there is a minimum amount of CT character needed to drive the iSF process. To test the hypothesis that charge-transfer character facilitates iSF, we synthesized a polymer in which BDT was replaced with a weaker fluorene donor unit (PFTDO1), while keeping the TDO acceptor unit. Transient absorption spectroscopy reveals that iSF does not occur in PFTDO1 with any measurable yield (Supplementary Fig. 5). This demonstrates that, even though the energetic driving force for iSF is stronger in PFTDO1 than in PBTDO1, iSF is not observed because the decrease in charge-transfer character significantly reduces the coupling between the singlet and triplet pair states. PFTDO1 confirms that satisfying the energetic requirement for fission and having a strong acceptor are not sufficient, but that both a strong donor and a strong acceptor are needed to efficiently mediate the iSF process.

By calculating the energy of the relaxed singlet (after reorganization, $S_{\mathrm{bright}} = 1.52$ eV) and uncoupled triplet pair energy (in the optimized double-triplet nuclear geometry, $2T_1 = 1.43$ eV) we determine the following: two relaxed, uncoupled triplets can exist when two TDO units are present and it is energetically downhill to go from the initial to the final states (Supplementary Scheme 1C). The final relaxed triplet pair is analogous to 'free' triplet pairs generated in intermolecular-fission materials. However, their one-dimensional confinement prevents them from diffusing away from each other and leads to a faster bimolecular recombination process under low-fluence conditions. Interestingly, calculations of the spin density distribution suggest that a triplet state generated in the singlet geometry (as would be expected when fission is sufficiently fast) is

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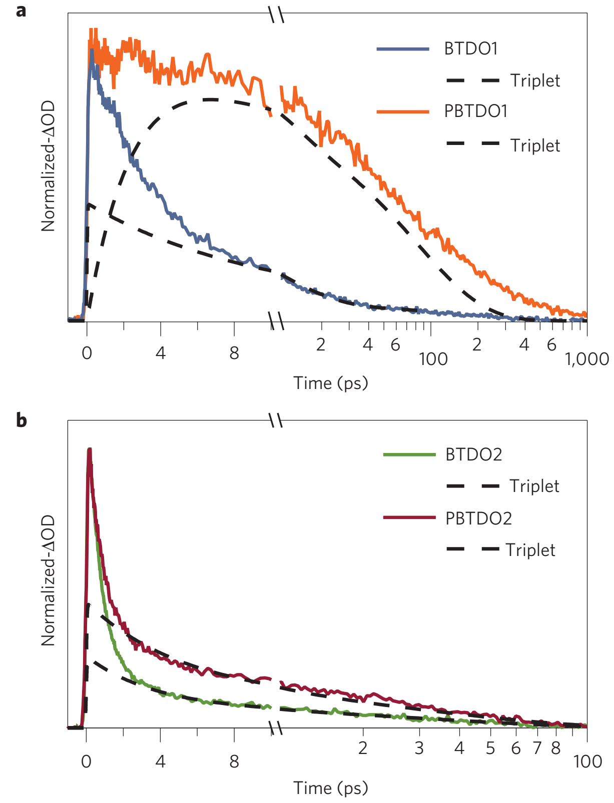

Figure 5 | Bleach recovery in transient absorption measurements. a,**b**, The ground state recovery kinetics are also compared for TDO1- (**a**) and TDO2-containing (**b**) materials. The approximate triplet population dynamics, as extracted using global analysis, is compared against the ground state recovery for each material (black dashes).

partially delocalized across multiple TDO units. This result strongly suggests that multiexciton transition states in intramolecular-fission materials have unique electronic properties, and may involve triplet pairs that are transiently coupled before nuclear relaxation to the final geometry, a process analogous to the multiexciton-to-triplet pair relaxation observed in pentacene aggregates[31]. However, a full mechanistic description based on our calculations, which includes energy level alignment and relaxation dynamics, is beyond the scope of this manuscript. Detailed theoretical studies will follow.

We note that despite their structural similarity, the photophysics of the PBTDO1 system, which exhibits a longer singlet state lifetime and much higher fission yield, is markedly different from PBTDO2 or the small molecule analogues. Table 1 summarizes the singlet fission yields and triplet lifetimes of the TDO-containing small molecules and polymers. The unoxidized control systems did not exhibit SF (Supplementary Fig. 6). The differences among the molecules can be attributed to the introduction of a fast competing singlet deactivation process in the lower-performing materials due to the emergence of a low-energy dark state. The effect of this dark state on the dynamics can be seen in Fig. 5, where fast (∼100 fs) deactivation of the bright singlet state inhibits triplet formation (modelled population density shown with dotted lines). Although the initial $S_{\mathrm{bright}} \rightarrow S_{\mathrm{dark}}$ internal conversion process is not directly observed, it is clear that it is in competition with the SF process (Supplementary Scheme 1C and Fig. 8). Furthermore, the lack of a rise in the triplet population after 100 fs confirms that SF originating from the dark state is not occurring. Details of the relaxation dynamics of BTDO1, BTDO2 and PBTDO2 are given in the Supplementary Information (Supplementary Fig. 7).

We can understand the emergence of the dark state and the resulting marked differences in the overall fission yield by considering the electronic structure of TDO itself. The oxidation of a thiophene monomer results in a transition from a $6\pi \rightarrow 4\pi$ electron system that is an electronic analogue of *cis*-butadiene (or cyclopentadiene). Without appropriate flanking groups, this electronic modification can result in an oligoene-like excited state character, where excitation into a bright singlet excited state (S_{bright} or S_2, B_u symmetry) quickly (∼100 fs) converts internally to a lower-lying dark state (S_{dark} or S_1, A_g symmetry), and finally to the ground state (S_0, A_g)[44]. As evidenced by the ∼7 ps singlet lifetime and the associated transient photoluminescence (Supplementary Fig. 2), this dark state internal conversion process is notably absent in PBTDO1, but apparent both in the lack of photoluminescence and the transient absorption data from the other three materials, where we observe a broad visible–nIR ($S_{\mathrm{dark}} \rightarrow S_n$)-induced absorption feature that decays concomitantly with a significant portion of the bleach (Supplementary Fig. 7). Although the polyene-like behaviour is parasitic to efficient fission, this behaviour is not ubiquitous among all TDO-containing materials. This provides important evidence that this detrimental internal conversion pathway can be controlled with appropriate materials design. The possibility of mitigating the effects of internal conversion is a unique strength of the tunability inherent to donor–acceptor SF copolymer systems.

In summary, the fundamental understanding of intermolecular singlet-fission processes was applied to the design of molecules that can undergo efficient intramolecular singlet fission. The key requirements are: formation of a charge-transfer state immediately following excitation and the presence of a subunit with a low triplet energy such that $E_S \geq 2E_T$. The observation of intramolecular singlet-fission yields up to 170% in this new family of materials provides insight into designed singlet-fission materials using strong intrachain donor–acceptor interactions, which allows us to establish a new design framework for fission-capable materials. This provides a generalized platform for the development of tunable materials to address the challenges of third-generation photovoltaic devices based on multiple exciton-generation processes.

Methods

Synthesis. All commercially available chemicals were purchased from Sigma-Aldrich and used as received. Acceptor units based on thiophene-1,1-dioxide (TDO) (3 and 6 in the Supplementary information) were prepared using HOF chemistry, according to published procedures[45]. All materials were synthesized using the palladium-catalysed Stille coupling reaction. Detailed procedures are presented in the Supplementary Information. Gel permeation chromatography (GPC) was carried out on a Waters separation module, equipped with a Waters 2414 refractive index detector and a Waters 2998 photodiode array detector, using THF as the eluent. Molecular weights and dispersity are reported relative to polystyrene standards in the Supplementary Information.

Steady-state characterization. Absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer. Electrochemical measurements were performed using a Princeton Applied Research Parastat 2273-SYS (for molecular CV) and a CHI instrument model 660C (for polymer CV) in a standard three-electrode configuration. Small-molecule CV was conducted in dichloromethane with glassy carbon, platinum wire and Fc/Fc+ as the working electrode, counter electrode and reference electrode, respectively. Polymer CV was conducted on polymer films in acetonitrile with Pt disk, Pt wire and Ag/AgCl electrode as the working electrode, counter electrode and reference electrode, respectively. All CV measurements were conducted in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution. Small-molecule CV was conducted in square-wave mode. Further experimental details are included in the Supplementary Information.

Ultrafast spectroscopy. Transient absorption spectroscopy was conducted using a commercial Ti:Sapphire laser system (SpectraPhysics |800 nm|100 fs|3.5 mJ|1 kHz). Excitation light was generated using a commercial optical parametric amplifier (LightConversion). Supercontinuum probe light was generated by focusing the 800 nm fundamental into a sapphire disc. The probe light was split into signal and reference beams, both of which are detected on a shot-by-shot basis with fibre-coupled silicon (visible) or InGaAs (infrared) diode arrays. The pump–probe delay was controlled by means of a mechanical delay stage (Newport). All data shown in this manuscript are from dilute solutions

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using chloroform as a solvent. We have verified that similar behaviour is observed in other organic solvents. The transient photoluminescence was conducted in a photoluminescence up-conversion apparatus under identical sample conditions using the same excitation source. Up-converted signals were detected using a monochromator and a photomultiplier tube.

Global analysis. Global target analysis (GTA) is a differential equations approach to multidimensional data set modelling and deconvolution. This technique is detailed elsewhere[40,41] but described briefly here. GTA begins with a user-defined number of populations and a set of rate constants describing the connectivity between the populations. These parameters are used to solve a system of first-order differential equations to generate time-dependent population evolution. Using these population trajectories as a basis set, the complete experimental transient absorption data set is fitted. This process is iteratively optimized by varying the rate constant matrix. Once complete, this results in the generation of kinetic fits, evolution of populations, and extraction of spectral signatures for each population. This approach was used to separate the triplet difference spectra from the overlapping charge-separated state absorption (Fig. 3c) and to generate the triplet population trajectories (Figs 3d and 5, black dashes). Within this manuscript two models are used. First, for PBTDO1, two populations (assigned as a singlet exciton and a charge-separated state) are generated within the ~100-fs instrument response. The singlet then decays to form an third population (assigned as triplet). The triplet and charge-separated populations then decay independently to re-form the ground electronic state. Second, within the model used for the other three materials (PBTDO2, BTDO1 and BTDO2), two populations are generated within the instrument response (assigned as triplet and S_{dark}). These states then decay independently to re-form the ground electronic state.

Pulse radiolysis. Samples were prepared in p-xylene solution containing 100 mM of biphenyl under Ar and ionized with <50 ps electron pulses from the 10 MeV LEAF accelerator[42], as described previously[46]. Pulse radiolysis ionizes p-xylene to yield electrons and radical cations, most of which recombine rapidly to produce triplet excited states, which then transfer to the TDO-containing materials. The yield of triplets is enhanced by the high concentration of biphenyl, which has a high quantum yield for intersystem crossing and a long triplet lifetime, so low material concentrations can be used. The accelerator pulse produced ~1 μM of triplets. The amount was calibrated using the known molar absorption coefficient[47] for triplet biphenyl. Sensitization measurements were performed on all materials and show that the triplet spectrum is sensitive to the number of sequential TDO units (for example, TDO1 versus TDO2), but not the total number of repeat units (that is, molecule versus polymer). This allows us to use identical absorption coefficients for the respective molecular and polymer materials. The triplet population formed through the sensitization experiment exhibits a slow (>1 ns) rise because of the collisional nature of the triplet transfer process. For visualization purposes, the data in Fig. 4c,d are offset to shift this rise to negative times (not shown). The recombination kinetics are unaffected by this shift.

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Author contributions

E.B., J.X., L.M.C. and M.Y.S. conceived the experiments. L.M.C. and M.Y.S. supervised the project. J.X., J.Z.L. and R.S. synthesized and characterized the materials. E.B. performed transient absorption data acquisition and analysis. Q.W. provided theoretical support. J.R.M. and E.B. performed pulse radiolysis experiments. E.B., L.M.C. and M.Y.S. wrote the manuscript with input from all authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to L.M.C. or M.Y.S.

Competing financial interests

The authors declare no competing financial interests.

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