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Singlet Fission in a *para*-Azaquinodimethane-Based Quinoidal Conjugated Polymer

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ABSTRACT: The exploitation of singlet fission (SF) in photovoltaic devices is restricted by the limited number of SF materials available and the conflicting requirement of intermolecular interactions to satisfy both efficient SF and subsequent triplet extraction. Intramolecular SF (iSF) represents an emerging alternative, and may prove simpler to implement in devices. On account of the excellent chemical structure tunability and solution processability, conjugated polymers have emerged as promising candidates for iSF materials despite being largely underexplored. It remains a significant challenge to develop SF-capable conjugated polymers and achieve efficient dissociation of the formed triplet pairs simultaneously. In this contribution, we present a new iSF material in a *para*-azaquinodimethane-based quinoidal conjugated polymer. Using transient optical techniques, we show that an ultrafast iSF process dominates the deactivation of excited state in such polymer, featuring ultrafast population (< 1 ps) and stepwise dissociation of triplet pairs. Notably, these multiexciton states could further diffuse apart to produce long-lived free triplets (tens of μ s) in strongly coupled aggregates in solid thin film. Such findings not only introduce a new iSF-active conjugated polymer to the rare SF material family, but also shed unique insight into interchain interaction-promoted triplet pair dissociation in aggregates of conjugated polymers, thus open new avenues for developing next-generation SF-based photovoltaic materials.

Singlet fission (SF) is a spin-allowed down-conversion process in which absorption of one photon in organic molecules forms two triplets from an excited singlet exciton.¹⁻³ It has attracted extensive attention in the last decade on account of the great potential to offset thermalization losses and increase the maximum efficiency of solar cells.⁴⁻⁷ Although the range of SF-capable materials continues to grow, a highly efficient system integration into real photovoltaic applications remains to be discovered. Besides the limited choice of practical SF materials, the major hurdle is rooted in the need for subtle control over the intermolecular interactions required to drive an efficient SF process, which

necessitates careful control of molecular orientation/inter-chromophore coupling and crystallinity/morphology in aggregates or thin films.^{1-3, 7}

Intramolecular SF (iSF) holds particular appeal for functional device applications because iSF is an intrinsic molecular property that undermines the influence of intermolecular interactions.⁸ This feature motivates the use of conjugated polymers as SF sensitizers given the ease of tailoring chemical structures for desired electronic and physical properties, together with solution processability for good phase separation and film morphology. However, in contrast to the more extensively studied small-molecule-based iSF

systems (such as acene dimers),⁹⁻¹⁸ iSF materials based on conjugated polymers remain largely unexplored.¹⁹⁻²³ Busby et al. pioneered the first efficient iSF donor-acceptor conjugated polymer with an ultrafast SF rate of ~ 7 ps and a high SF yield of $\sim 170\%$ in solution.²⁰ A subsequent study on such iSF system by Pace et al. revealed that interchain interactions in polymer film could promote the separation of iSF-formed triplet pairs, but with only a low triplet yield of $\sim 25\%$.²² Hu et al. reported another efficient iSF-active isoindigo-based conjugated polymer with a 160–200% SF yield in solution.²³ However, it was discovered that aggregation in films significantly lowers the singlet energy, suppressing the SF process because the energy conservation criterion is no longer met.²³ It is therefore a significant challenge to develop new iSF-active conjugated polymers and achieve efficient triplet pair dissociation simultaneously. In this contribution, we present a new iSF material based on a *para*-azaquinodimethane (AQM)-containing quinoidal conjugated polymer (PAQ, Figure 1a), in which triplet pairs are formed at an ultrafast rate from the optically populated singlet state in dilute solution, and these multiexcitons could further diffuse apart to produce long-lived free triplets in solid state thin films.

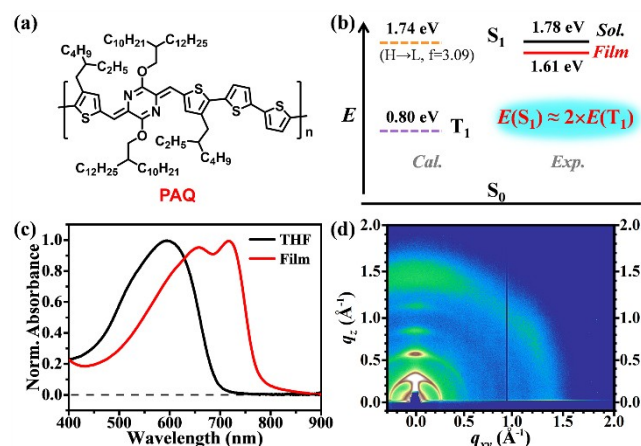


Figure 1. (a) Chemical structure of polymer PAQ. (b) Energy diagrams from experimental data and DFT theoretical calculations. (c) Normalized absorption spectra in dilute solution and thin film. (d) The GIWAXS pattern of the polymer thin film.

Capitalizing on the unique quinoidal characters of the AQM building block, PAQs have recently debuted as low band gap conjugated polymers that feature unusual optoelectronic behavior, excellent electronic performance (charge carrier mobility over $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), facile synthetic accessibility and high chemical stability.²⁴⁻²⁶ We envision PAQ to be a good SF candidate given that the energetic requirement for SF is met based on theoretical calculations of an oligomer model (Figure 1b). At the optimized ground state geometry, energy of the lowest singlet (S_1) and triplet (T_1) state is 1.74 and 0.80 eV above the

ground state, respectively. These results suggest that this system features an exothermic SF energetics [$E(S_1) > 2E(T_1)$], which is primarily ascribed to the distinctive biradical character of the heterocyclic quinoidal AQM core.^{1, 27-28}

The model polymer PAQ ($M_n = 24.5 \text{ kDa}$, $D = 1.8$) was synthesized by Stille copolymerization.²⁴⁻²⁵ UV-vis-NIR absorption spectra of PAQ were recorded both in dilute solution and spin-coated solid thin film (Figure 1c). In THF solution, it exhibits a broad featureless absorption peak with the band edge at 696 nm (1.78 eV), which matches well with the calculated S_1 energy. In the thin film, the spectrum displays an obvious redshift towards longer wavelength with the edge around 772 nm (1.61 eV), indicating strong interchain interactions in the solid state. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement further confirms ordered chain packing within the polymer film (Figure 1d). The appearance of higher order out-of-plane ($n00$) (n up to 4) peaks indicate the formation of lamellar structures with preferential edge-on orientation of the polymer chains on the substrate. Despite the aggregation induced band edge shift, the energetic requirement for SF process could still be met in the solid state, which is different from the known isoindigo-based conjugated polymer,²³ and is conducive to the subsequent dissociation of triplet pairs. The polymer exhibits very low photoluminescence efficiency ($\Phi_F < 0.01$) in both solution and thin film, corroborating with the presence of nonradiative pathways for excited state deactivation.¹⁸

Femtosecond transient absorption (fs-TA) experiments were carried out to verify the SF process associated with the polymer. Polymer PAQ was found to efficiently produce triplet pairs via an ultrafast iSF process in THF solution, as revealed by the combination of TA spectroscopy and triplet sensitization experiments, a general protocol that has been widely applied to identify iSF in small molecules and polymers.^{10-13, 15-21, 23} Upon photoexcitation at 550 nm, the resulting fs-TA spectrum (Figure 2a) exhibited a clear ground state bleaching (GSB) band at 630 nm and a broad excited-state absorption (ESA) band around 850 nm assigned to the initial populated S_1 state. This ESA from S_1 rose within the instrument response function and started to decay rapidly in < 1 ps. Concurrent with the decay of this feature, a new absorption band appeared around ~ 710 nm, which subsequently blue-shifted further to ~ 680 nm and eventually recovered to the baseline along with GSB signals (Figure 2a and 2b). There was no long-lived signal observed in solution.

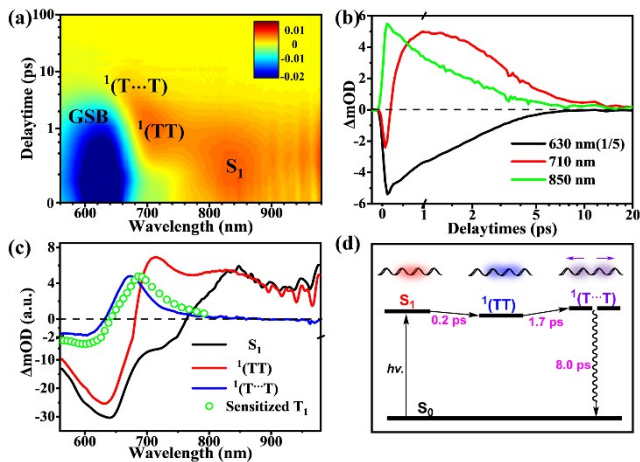


Figure 2. (a) fs-TA spectrum and (b) selected kinetic traces in PAQ THF solution (excited at 550 nm). (c) Evolution-associated spectra from global analysis of fs-TA data based on (d) a sequential three-state model. A sensitized triplet curve is provided in **c** to help assign the triplet-like species.

TA data was best fit to a sequential three-state kinetic model with three distinct time constants of 0.2, 1.7, and 8.0 ps, respectively, which described the dynamic evolution of different excited state species of the polymer (Figure 2c, 2d and S4). Species-associated spectra were shown in Figure 2c and compared with a sensitized triplet curve (for details see Section 3.4 in Supplementary Information, SI). While the spectra of initial and final species were highly distinct, that of intermediate species resembled a combination of the two. The final species-associated spectrum was nearly identical to the line shape of sensitized triplet, suggesting that it was a transient species with distinct triplet character. Therefore, we assigned the intermediate and final species to intramolecular singlet coupled and decoupled pair of local triplets, i.e. $^1(TT)$ and $^1(T\cdots T)$, respectively. Such assignment is consistent with the general understanding and calculated excited state absorption of different multiexciton states, that is, the strongly coupled $^1(TT)$ state displays spectroscopic signatures of both singlet and triplet states, while the loosely coupled $^1(T\cdots T)$ shows almost identical characteristics to the free triplet state.^{3, 29-34} We excluded the formation of polaron species or charge transfer state, given the broad characteristic absorption peak of these transient species extending to 700~1000 nm, and solvent independent dynamics (for details see Section 3.5 in SI).²⁶ Intersystem crossing (ISC) pathway to free triplets was also discounted considering the ultrafast triplet population rate and the short lifetime of the triplet-like species. Returning to the ground state via geminate recombination along the one-dimensional chain was deemed responsible for the short lifetime of 8.0 ps, which was 6 orders of magnitude lower than the lifetime of the free triplet (Figure S5).^{3, 31-33} These results clearly confirm that an ultrafast and quantitative iSF process dominates the

excited state deactivation in the solution of PAQ after photo-excitation.

In contrast with the solution iSF behavior, long-lived triplet signals persisting to microsecond timescale in the thin film were clearly observed, albeit with an obvious redshift. Figure 3 illustrates the fs-TA spectrum and corresponding global analysis results of PAQ polymer films. There were two major notable features distinctive from the solution spectra: (i) the GSB band was red-shifted and overlapped significantly with ESA band; (ii) the ESA band had a long lifetime and extended to well beyond the fs-TA detection window along with the GSB signal. Despite serious overlap, the spectral evolution at the initial stage was found to be similar to that in dilute solution, where the initial ESA band ~ 800 nm was gradually attenuated, while a new species arose at ~ 700 nm, consistent with the GSB band recovery and the concurrent small blueshift of the ESA band (Figure 3a, and S12, for details see Section 4.7 in SI).

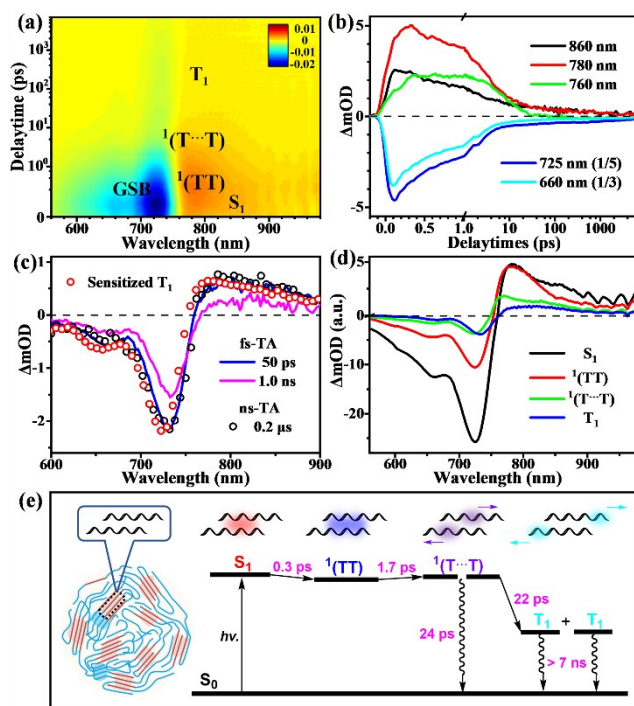


Figure 3. (a) fs-TA spectra and (b) selected kinetic traces (excited at 550 nm). (c) The assignment of end long-lived triplet species at long time delay by matching fs-TA lineshapes with ns-TA curve and sensitized triplet signature in thin film. (d) Evolution-associated spectra from global analysis of fs-TA data based on (e) a branched 4-state model.

At longer time delays (> 10 ps), following the decay of short-lived states, new spectral species appeared and significantly overlapped with GSB signal around 700 ~ 800 nm. This species turned out to be long-lived and persisted beyond the 7-ns detection time window of our fs-TA apparatus. Then ns-TA and triplet sensitization experiments³⁵⁻³⁷ were carried out on PAQ thin films in order to

track the evolution of and identify this long-lived species (see Section 4.3 and 4.4 in SI for details). The spectral lineshapes of both sensitized triplet and ns-TA spectra overlapped well with the end spectral signatures of fs-TA spectra at 50 ps and 1 ns (Figure 3c), confirming that the end signals in TA data were long-lived free triplets, which persisted in the timescale of tens of microseconds. The triplet spectrum of the PAQ thin film differed from that of the solution because of the apparent GSB redshift over the region of triplet ESA bands in solution.^{18, 35-37} We excluded the formation of polaron species or charge transfer state in thin film, given the broad characteristic absorption peak of these transient species extending to 700~1000 nm (for details see Section 3.5 and 4.7 in SI). The possibility of triplet formation via ISC process mediated by charge recombination or excimer state, or structural twist has also been ruled out due to ultrafast population rate and relatively shorter lifetime of the formed triplet. Another potential pathway of triplet population in polymer film is an intermolecular SF process. Ultrafast intramolecular singlet-to-triplet pair conversion as confirmed in solution, the similar spectral evolution observed in solution, doped PMMA films (for details see Section 4.8 in SI), and thin film, as well as preferential edge-on orientation of polymer chains (Figure 1d), both marginalizes an efficient intermolecular SF process in the thin film.^{1, 3, 8} Therefore, we suppose that these iSF-formed triplet pairs could further diffuse to the suited site and then separate into long-lived free triplets in strongly coupled thin films.

Figure 3d and 3e depicts the energy diagram and the corresponding rate constants for global analysis results of thin film TA data based on a branched four-state kinetic model. The population rates of ¹(TT) and ¹(T··T) states (0.3 and 1.7 ps, respectively) from thin films are comparable to those from solution, but the longer lifetime of ¹(T··T) state suggests that it either dissociates into free triplets (22 ps) or recovers to ground state (24 ps). This result indicates that almost half of the iSF-generated triplet pairs deactivate via geminate recombination before interchain diffusion and dissociation into free triplets, providing a ~52% triplet separation yield. This triplet separation efficiency corroborates with an overall triplet yield of 108% that was obtained using the energy transfer method (see Section 4.6 in SI for details), a widely applied protocol for triplet yield determination in small molecules and polymers.^{20, 35-36} These results reveal that polymer chain aggregation in thin films facilitates triplet pair dissociation via interchain interactions.

An efficient iSF process was discovered in a quinoidal conjugated polymer. Detailed TA spectroscopic studies reveal that triplet pairs are formed at ultrafast rate from the optically populated singlet state. Unlike the short triplet lifetimes observed in other conjugated polymers,

the multiexcitons generated from iSF could further diffuse and separate into long-lived free triplets in strongly coupled polymer thin films. The emergence of such an iSF-active quinoidal polymer with good solution processability, excellent charge carrier mobility, and efficient SF and triplet dissociation properties in the solid state not only broadens the limited scope of iSF materials, but also opens new avenues for developing next-generation SF-based organic solar cells and hybrid photovoltaic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>.

Materials, synthetic details, TA measurements and global fitting analyses, triplet state sensitization, and triplet yield determination (PDF).

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Notes

The authors declare no competing financial interest.

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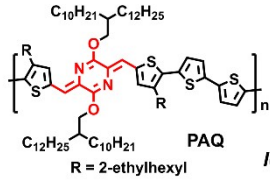
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Solution



ultrafast SF \rightarrow \rightarrow rapid recombination



Aggregates



long-lived free triplets

