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Achieving Long-Lived Triplet States in Intramolecular SF Films through Molecular Engineering



Establishing molecular control of singlet fission dynamics in the condensed phase is vital to the development of novel multiple-exciton energy-harvesting schemes. Xia and co-workers demonstrate a molecular engineering approach to independently tune the triplet generation and decay in intramolecular singlet fission films by using three pentacene tetramers. They observed mobile-free and long-lived triplets with a lifetime of up to several microseconds in the solutionprocessed films.



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HIGHLIGHTS

Three terphenyl-bridged pentacene tetramers were designed and synthesized

Singlet and triplet decay were independently tuned in the solid states

Long-lived and mobile-free triplets were generated in high yields by SF in the films

Huang et al., Chem 5, 2405–2417 September 12, 2019 © 2019 Elsevier Inc. https://doi.org/10.1016/j.chempr.2019.06.007

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Achieving Long-Lived Triplet States in Intramolecular SF Films through Molecular Engineering

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SUMMARY

Tuning singlet fission (SF) dynamics in the solid states in a controllable way is vitally important yet still a challenge due to the electronic coupling, which is highly sensitive to molecular packing. Here, we demonstrate a molecular engineering approach to independently optimize the triplet generation and decay process in intramolecular SF films by using terphenyl-bridged TIPS-pentacene tetramers. By controlling the degree of steric hindrance within individual tetramers, we can systematically tune the degree of intermolecular SF processes allows us to maintain a rapid triplet pair generation process, even in the case of weak intermolecular coupling. This approach allows us to maintain a picosecond triplet generation process while simultaneously varying the rate constants for triplet-triplet annihilation over three orders of magnitude.

INTRODUCTION

Singlet fission (SF) is a multiple-exciton generation process which coverts one singlet exciton into two triplet excitons and has received considerable attention because of its potential to overcome the Shockley-Queisser limit on the power conversion efficiency (PCE) of solar cells.¹⁻³ Despite the strict electronic conditions required for SF,⁴ ultrafast generation of free triplet excitons in nearly quantitative yields has been widely observed in highly ordered molecular crystals⁵⁻⁸ and nanoparticles of SF molecules^{9,10} (intermolecular SF [xSF]) and within isolated molecules bearing covalently linked SF chromophores¹¹⁻¹⁴ or within single polymer chains¹⁵⁻¹⁸ (intramolecular SF [iSF]). In particular, the recent discovery and subsequent proliferation of iSF materials demonstrated the power of using the versatile toolbox of organic synthesis to control the SF properties of materials.¹⁹⁻²⁴ Among many recent successes is the discovery that molecular engineering approach can be employed to control the triplet generation and decay rates and tune them over several orders of magnitude in iSF solution.^{12,21,25,26} Still, the triplet generation and decay processes are highly correlated, such that strong electronic coupling leads to fast SF and fast triplet decay, and conversely, weak electronic coupling yields slow SF and slow triplet decay (Scheme 1A).

This same level of electronic tunability is difficult to achieve in the solid states given that wave-function overlap is highly sensitive to slight changes in chromophore alignment.^{27,28} Although it has been clearly shown that small chemical modifications can have drastic consequences for the triplet-pair generation rate of iSF,⁷ less emphasis has been placed on the factors that dictate the overall triplet lifetime and diffusivity

The Bigger Picture

Singlet exciton fission (SF) is highly promising for developing photovoltaic cells capable of overcoming the Shockley-Queisser limit. While the growing field of intramolecular SF has established important structurefunction relationships that can be used to optimize exciton dynamics for isolated molecules in solution, it has not been shown that these characteristics can be consistently maintained in films. This is a major outstanding issue for the field because it is essential to tune the SF dynamics in the solid state because of the inherent necessity of the condensed phase for devices. Here, using an approach in which small chemical modifications induce large changes in the equilibrium geometry of pentacene tetramers, we demonstrate a molecular design strategy that can be used to achieve independent control of the singlet and triplet decay in the condensed phase. Our results shed light on the optimization of SF materials for future device applications.



in thin films.²⁹ In part, this stems from the difficulty in independently tuning the generation and decay rates in crystalline materials given that both processes depend strongly on the intermolecular coupling strength (Scheme 1B).^{4,30} Still, thin films overcome the primary drawback of the solution phase of iSF materials in which triplets excitons remain localized, i.e., there is no viable transport channel for the triplet excitons even though ultralong lifetimes (>1 μ s) can be achieved. Clearly, the next frontier for SF materials concerns their integration into new device architectures that allow full utilization of the charge amplification process. Surprisingly, very little work has been reported that demonstrate the dynamics of iSF materials in condensed phases or their efficacy as triplet generating and transporting materials.³¹

Here, we show that by combining intra- and intermolecular SF in thin films, we could combine the molecular control inherent in iSF systems with the favorable transport properties of xSF systems (Scheme 1C). Using this approach, we systematically tuned the triplet exciton lifetime and diffusivity while maintaining a nearly constant, picosecond generation rate. We demonstrated this concept in thin films fabricated from a series of terphenyl-bridged TIPS-pentacene (TPc) tetramers. Within these materials, we systematically tuned the degree of electronic coupling between neighboring molecules by adjusting the steric hindrance, which in turn modulated the ability of the molecules to π stack. The ability of these molecules to undergo fast iSF in their isolated form guaranteed rapid formation of triplet excitons, even when interactions between nearest neighbor molecules became weak. Although we observed bimolecular recombination indicative of mobile-free triplets in all films, a large decrease in triplet diffusivity in weakly coupled compounds led to a factor of ~10³ increase in lifetime.

RESULTS AND DISCUSSION

We designed three distinct terphenyl-bridged TPc tetramers: TPTP-1, TPTP-2, and TPTP-3 (Figure 1; the synthesis is detailed in the Supplemental Information). The tetramer design offers a distinct advantage relative to simpler (e.g., dimer) motifs because it offers additional degrees of freedom to tune sterics within the structure and dictate the degree of intermolecular coupling in the solid state. This steric effect is controlled by changing the bonding position of the TPc chromophores along the outer terphenyl ring. Although twisting of TPc in intramolecular SF materials has been shown to have a minimal effect on the triplet generation process,²⁵ we expected the relative planarity to have dramatic effects on the degree of intermolecular π -stacking in thin films of our TPTP materials. We conducted X-ray diffraction (XRD) measurements on the thin films and bulk samples of mBP1, BP1, and tetramers (Figures 1B and S1-S4). The XRD pattern of BP1 in the film showed three main diffraction peaks at 20 values of 5.4°, 12.6°, and 16.3°, and the mBP1 film displayed a strong diffraction peak at 20 values of 6.1°, indicating that a stronger intermolecular packing was formed in the BP1 film. Also, more BP1 domains with long-range crystalline order were observed in the powder XRD measurements of mBP1 and BP1. In the powder XRD diffraction, only two small diffraction peaks were found at 20 values of 5.6° and 6.9° for TPTP-1; no obvious peak was detected for TPTP-2 and TPTP-3, indicating that the intermolecular interaction in the solid state decreases in the order of TPTP-1 > TPTP-2 > TPTP-3. However, the thin-film XRD diffraction results showed that the tetramers were all amorphous, suggesting that the intermolecular packing was suppressed by the tetramer motif in the film.

We verified this molecular engineering strategy by calculating the dihedral angles of the TPTP compounds in their relaxed ground-state geometry by using density functional theory (DFT) (Figures 2 and S5). When all the TPc molecules were bonded in ¹State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Center of Smart Materials and Devices, Wuhan University of Technology, Wuhan 430070, China

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A Solution: intramolecular (i)

	i i		
Strong coupling:	Weak coupling:		
- rapid SF	- slow SF		
- rapid <i>T₁</i> decay	- slow <i>T</i> , decay		

^B Monomer and dimer films: *intermolecular (x)*



c TPTPn films: intra- (i) + intermolecular (x)

- Fast SF (Strong coupling)
- Tunable T, decay (Weak Strong coupling)
- x depends on degree of steric hindrance



Scheme 1. Summary of Structure-Function Relations and the Design Strategy Based on TPTPn Compounds in This Work

Solid blue lines correspond to through-bond interactions, and dashed orange lines denote through-space interactions.

- (A) Typical solution-phase intramolecular SF dynamics.
- (B) Film dynamics for monomer and dimer materials.

(C) The design strategy based on **TPTPn** compounds in this work.

the outer *meta*-position, steric hindrance was minimized and the **TPc** molecules adopted a conformation similar to that of the *meta*-connected bipentacene compounds.²⁵ However, when the **TPc** chromophores were in the *para*- or inner *meta*-







position, a significant amount of twisting between the TPc and terphenyl bridge was observed. In TPTP-1, the TPc chromophores were relatively unhindered and had nearly uniform dihedral angles that were very similar to the calculated values for bipentacene (\sim 35°). In TPTP-2 and TPTP-3, connections to the TPc chromophores were made at bonding positions closer to the center of terphenyl backbone, resulting in additional steric hindrance that increased the dihedral angles. In TPTP-2, the set of dihedral angles was uniformly increased to \sim 55°. In TPTP-3, we observed two distinct subsets of angles corresponding to unhindered (\sim 35°–38°) and hindered (\sim 50°–55°) TPc chromophores. All of the dihedral angles within the compounds are summarized in Table 1.

The degree of π -stacking in the thin films of our TPTP materials was determined by the relative planarity of the TPc chromophores and systematically varied across the





TPTP series. The intermolecular coupling in the thin films was greatly affected by the molecular geometry, and we could estimate it by comparing the attenuation spectra of the molecules in toluene solution to spin-cast thin films (Figure 3).^{32,33} The variations in the equilibrium geometries for the different tetramers had a minimal effect on the experimental solution-phase absorption spectra (Figure 3A), which were highly similar to each other as well as the phenyl-bridged TPc dimer (BP1 and mBP1 for *para*- and *meta*-connected dimers, respectively).

However, larger differences were exhibited in the attenuation spectra of the thin films, suggesting that increasing the amount of steric hindrance in these compounds

Plane A	P1	P2	P3	P4	B1	B2
Plane B	B1	B1	B3	B3	B2	В3
TPTP-1	36.94°	37.08°	37.31°	37.39°	38.11°	37.11°
TPTP-2	54.44°	54.95°	54.51°	54.97°	54.90°	54.89°
TPTP-3	35.56°	40.77°	50.19°	35.61°	54.35°	50.38°

Table 1. Summary of Dihedral Angles in Optimized Structures of TPTP-1, TPTP-2, and TPTP-3

directly inhibits intermolecular electronic coupling in the condensed phase. We focused primarily on the absorption peak near 650 nm, which primarily resulted from an intramonomer HOMO-to-LUMO excitation polarized along the short axis of TPc.³⁴ To estimate the effect of interchromophore interactions on the extent of delocalization in the singlet excited state, we evaluated the change in energy of the primary absorption peaks as well as the change in the relative amplitudes of the 0-0 and 0-1 vibronic bands.³⁵ The most dramatic change occurred in the mBP1 and BP1 dimers (Figures S6 and S7), in which the 0-0 absorption red shifted and broadened such that considerable attenuation was observed beyond 750 nm. The increase in near-infrared absorption was accompanied by a marked increase in the strength of the 0-1 transition. By comparison, the tetramer films exhibited only a slight red shift and decrease in the 0-0/0-1 ratio in going from solution to film, implying a less delocalized excited state. TPTP-1 exhibited the largest intermolecular coupling most likely because of its guasi-planar backbone, whereas the larger steric hindrances in TPTP-2 and TPTP-3 disrupted crystallization via long-range π -stacking. The peak position of TPTP-1 shifted by ~14 meV, and the 0-0/0-1 ratio decreased by ~0.09, slightly more than in TPTP-2 (~3 meV/0.04) and TPTP-3 (~9 meV/0.03). From these results, it is clear that the strength of the intermolecular coupling decreases with the increasing molecular distortion, giving the trend that para-BP1, mBP1 > TPTP-1 > TPTP-2 > TPTP-3.

Imperative to our goal of independently optimizing both the rates of triplet formation and decay in films is the fact that all of these molecules are capable of SF in dilute solution (i.e., without any intermolecular coupling) via iSF. This allows us to maintain rapid SF even in the limit of weak intermolecular coupling. The solution-phase SF dynamics of BP1 and mBP1 have been previously reported, ^{12,22,23} and we observed similar characteristics here (Figure S14). Our tetramers compounds have not been previously reported, and we found that the SF dynamics were derived primarily from the TPc-pair interactions along the short axis of the triphenylene bridge, which were much stronger than those along the long axis.^{12,23,36} As such, the tetramers in solution can be thought of as a set of weakly interacting dimers, and the SF dynamics highly resemble the dimer building blocks. In other words, the SF dynamics of the meta-connected TPTP-1 and TPTP-2 compounds resemble those of mBP1, and the para-connected TPTP-3 compound resembles BP1. We briefly summarize the SF dynamics here, and we note that we employed wellestablished and widely employed protocols for identifying triplet pairs generated by iSF.12,21,36

We used broadband transient absorption spectroscopy to study the excited-state dynamics of these molecules in dilute toluene solution. We photoexcited a dilute solution (~50 μ M) of TPTP molecules in toluene with 100 fs pump pulses tuned to the 0–1 vibronic feature at ~600 nm (fluence of ~50 μ J/cm²). The excited-state dynamics showed rapid generation of triplets after photoexcitation, suggestive of a SF mechanism (Figures 4A, 4B, and S15). The singlets were identified by their characteristic broad excited-state absorption bands of TPc (425–580 nm) resulting from the S₁-S_n



Figure 3. UV-Visible Spectra of mBP1, TPTP-1, TPTP-2, and TPTP-3 in Diluted Toluene Solution and in Neat Film Casted from Chlorobenzene

Normalized steady-state absorption spectra of **TPTP-n** molecules and **mBP1** in (A) diluted toluene solution and (B) neat film.

transition and by coincidence of the decay time constant to time-resolved photoluminescence measurements (Figure S16). The decay of the singlet absorption bands was correlated to the rise in the characteristic triplet T_1 - T_n excited-state absorption, which peaked near 520 nm.⁷ The triplet assignment was confirmed by triplet photosensitization measurements (Figures S17 and S18; Tables S2 and S3). Similar to other **TPc**-based iSF materials, no other competing product was observed and the overall triplet yield in solution was nearly quantitative such that only small losses occurred because of kinetic competition between fluorescence from the singlet ($k \sim 1/13$ ns) and iSF.¹² A detailed determination of the triplet yield in solution from both kinetic and sensitization measurements is provided in the Supplemetal Information. In order to get an accurate time scale for SF, we performed global analysis with a sequential kinetic decay model ($S_1 \rightarrow 2 \times T_1 \rightarrow S_0$).³⁷ The deconvoluted spectra generated from this global analysis are shown in Table 2.

Although qualitatively similar transient spectra were observed for these three TPTP molecules in toluene solution, quantitative differences in the rates of SF and triplet decay were observed. We found that the primary factor determining the iSF rate constant was the connectivity along the short phenylene bridge. Similar to dimers, connection at the meta-position resulted in iSF time constants that were ${\sim}20\, m x$ slower than para-substitution. As such, SF in TPTP-1 was nearly identical to that in mBP1 (~400 ps), and SF in TPTP-3 was nearly identical to that in BP1 (~20 ps). Although SF in TPTP-2 was \sim 3× slower than expected on the basis of the parent dimer, these differences can be understood from the significant deviation from planarity of the TPc chromophores. A similar phenomenon has been observed and modeled in dimers.²⁵ The decay of the T₁-T_n transition on the nanosecond-tomicrosecond time scale provides a direct measure of the time-dependent loss of the triplet population. Our TPc tetramers exhibited the typical biexponetial decay commonly seen in iSF materials, reflecting the different recombination dynamics for two triplet populations (fast decay, ~100 ns) and one triplet population (slow decay, \sim 30 µs) within the individual molecules.³⁸ Again, the relative amplitudes of the two decay components are largely determined by the intermolecular coupling. Triplet-pair decay in all meta-substituted compounds (mBP1, TPTP-1, and TPTP-2) is dominated by an Auger-type recombination process that reduces the overall triplet population by 50% for the long time-constant component.³⁹ The para-substituted compounds have an asymptote that is considerably lower than that of the corresponding meta-compounds (~15% in TPTP-3 and <5% in BP1). This is typical of

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Figure 4. Transient Absorption Spectroscopy of TPTP-1 and TPTP-3 in Solution and Neat Films Spin-Coated from Chlorobenzene

Transient absorption spectroscopy of (A) TPTP-1 in solution, (B) TPTP-3 in solution, (C) TPTP-1 in neat film, and (D) TPTP-3 in neat film. The pump wavelength is 600 nm.

more strongly coupled iSF systems and indicates that concerted triplet-triplet annihilation processes are significant.¹²

Although the tetramer structure resulted in minor changes to the solution phase (iSF) triplet dynamics compared with those of the corresponding dimer, much greater deviations were found in the films (Figures S23-S25) as a result of the engineered molecular distortions that affected the strength of intermolecular coupling. In all materials, much faster SF occurred in films than in solution. In compounds with significant intermolecular coupling, including mBP-1, TPTP-1, and TPTP-2, this occurred because of an additional xSF triplet-generation channel.⁴⁰ For these compounds, iSF was too slow to account for the triplet formation rates in films. For example, the SF time constant in TPTP-2 was reduced from \sim 1.5 ns to \sim 7 ps (Table 3). Similar magnitude changes were observed in mBP1 (~400 ps to an instrumentresponse-function limited value of \sim 200 fs) and TPTP-1 (\sim 500 ps to \sim 2 ps). In TPTP-3, the relatively fast solution phase iSF time constant (~20 ps) was maintained in the film (\sim 4 ps). The solution and film time constants and relatively weak intermolecular interactions suggest that triplet formation occurred via a combination of iSF and xSF in TPTP-3. The net result was that SF remained fast and efficient over a wide range of intermolecular coupling strengths.

The similarity of the triplet-generation rate constants in films of the different compounds implies that SF is a local effect. On the other hand, the triplet-recombination rate constants show orders-of-magnitude differences, consistent with disruption of exciton transport due to poor long-range intermolecular coupling. By inspection, it is immediately obvious that the effective lifetimes (in which

Table 2.	Summary of	Kinetic Param	eters for 1	Triplet Gener	ation and De	ecay in Dilute (~50 μM)
Toluene	Solution						

	$ au_{SF}$	$ au_{ ext{TT}}$	$ au_{T}$
BP1 ^a	20 ps	16.5 ns	25.4 μs
mBP1	396 ps	165 ns	21.3 µs
TPTP-1	498 ps	131 ns	34.5 μs
TPTP-2	1.49 ns	269 ns	34.0 µs
TPTP-3	21 ps	21 ns, 580 ns	36.4 µs

^aValues are taken from Sanders et al.¹²

the 1/e value was used for easy comparison) changed by over 3 orders of magnitude within the series of films. For example, for the fluences used in our experiment, the effective triplet lifetime (1/e) of mBP1 was shortened from ~20 μ s in solution to ~14 ns in films for an overall change of 10³ (Figures 5A and 5B). However, for a similar exciton density in the tetramers, the overall effective lifetime of triplets was ~50× larger than the dimer. Importantly, this means that even under high-power pulsed laser conditions, the effective lifetime of triplets in the films remains in the μ s range, comparable to their solution values.

Even though the long lifetimes imply highly localized triplets with low diffusivities, power-dependent measurements confirm that mobile free triplets exist in all tetramer films. We could distinguish mobile triplets from localized triplets in these films by their concentration-dependent bimolecular decay dynamics (Figure 5C for TPTP-1 and Figures S26 and S27). In other words, the effective triplet lifetime systematically shortened at higher fluence, an effect that was notably absent in the solution phase (Figures S28-S30). To analyze the overall population dynamics, we used a standard second-order kinetic analysis in which the slope of the normalized ΔA^{-1} versus time is the bimolecular rate constant for triplet-triplet annihilation (k_{TTA}) multiplied by the initial exciton concentration. Details of the fitting can be found in Figure S31. Again, the effects of intermolecular coupling were most pronounced in the mBP1 film, in which we found a bimolecular rate constant of $\sim 1 \times 10^{-1}$ 10⁻¹⁰ s⁻¹ cm³. In fact, our results here (that extremely rapid triplet decay occurred in thin films of dimers) are typical of many amorphous thin films of xSF materials (with triplet lifetimes on the order of 10 ns). We note that the largest bimolecular rate constant for our iSF materials was slightly higher than those reported from thin films of monomeric TPc, which range from 10^{-12} to 10^{-11} cm³ s⁻¹ depending on the processing conditions.²⁹ In contrast to the dimer, the tetramer geometry considerably slowed down the net triplet diffusion. Although the SF rate constant changeed by only a factor of 10 (and still occurred on picosecond time scales), the bimolecular rate constants were reduced by two orders of magnitude in TPTP-1 and three orders of magnitude in TPTP-2 and TPTP-3. These results indicate that although local chromophore interactions remain strong, the overall triplet exciton mobility is reduced because of the tetramer motif.

Table 3. Summary of Kinetic Parameters for Triplet Generation and Decay in the Films

	k _{SF} (s ⁻¹)	k_{TTA} (s ⁻¹ cm ³)	Mobile Triplet Yield
mBP1	5.0 × 10 ¹²	$\sim 1 \times 10^{-10}$	1
TPTP-1	5.7 × 10 ¹¹	$\sim 1 \times 10^{-12}$	0.75
TPTP-2	1.4 × 10 ¹¹	$\sim 2 \times 10^{-13}$	0.71
TPTP-3	2.7 × 10 ¹¹	$\sim 2 \times 10^{-13}$	0.40

See also Figure S31 and Table S4.



Figure 5. Triplet Population Evolution in Solution and Film for the Different SF Compounds All films exhibited fluence-dependent triplet recombination dynamics indicative of mobile excitons; **TPTP-1** is shown here as a representative example.

(A) Triplet population evolution of $\ensuremath{\mathsf{TPTP-n}}$ molecules and $\ensuremath{\mathsf{mBP1}}$ in solution.

(B) Triplet population evolution of **TPTP-n** molecules and **mBP1** in film.

(C) Fluence-dependent triplet recombination dynamics indicative of mobile excitons of TPTP-1.

Although bimolecular analysis satisfactorily reproduced the full triplet decay dynamics in mBP1, the tetramer materials exhibited an additional concentration-independent component at early times, which we assign to geminate recombination of localized triplets. We determined the overall yield of mobile triplets versus localized triplets (Tables 3 and S4) by using the procedure described in Figure S31.¹² We note that there was some variability between the tetramer films and that the overall mobile triplet yield was independent of the bimolecular rate constants. For example, TPTP-1 and TPTP-2 exhibited nearly identical yields even though the recombination rate constant varied by a factor of 10. Similarly, the mobile triplet yield in TPTP-1 and TPTP-3 varied by nearly a factor of 2 even though the bimolecular rate constants were identical. This result suggests the co-existence of multiple packing geometries with different effective triplet transfer rates. Detailing how to further direct and control local molecular packing to optimize triplet dynamics is an important topic for future exploration.

Conclusions

In summary, we designed and synthesized three tetramers and realized both fast SF and slow recombination in these molecules by tuning the intermolecular interactions. Long-lived and mobile-free triplets were generated in high yields by SF in the films. In leading proposed SF device architectures, it is desirable to obtain rapid singlet-to-triplet conversion (to prevent singlet energy transfer) and long triplet lifetimes to enable efficient exciton transfer to a phosphor. Some unknown tradeoff between diffusivity and lifetime is necessary for these schemes to be successful. We note that for different triplet-harvesting schemes, it might be important to optimize for either high mobility (e.g., in direct photovoltaic schemes) or long lifetimes (e.g., in sensitizer or photon downconversion schemes).² In either case, maintaining a rapid triplet formation rate to preclude singlet deactivation is a priority. Combining iSF and xSF in a controllable fashion provides the toolbox for achieving such optimization.

EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the Supplemental Information.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.06.007.

ACKNOWLEDGMENTS

J.X. acknowledges financial support from the National Natural Science Foundation of China (51773160, 21801201, and 21502147) and generous start-up funds from Wuhan University of Technology (40122004). This research used resources of the Center for Functional Nanomaterials, which is a US Department of Energy Office of Science facility, and the Scientific Data and Computing Center, a component of the Computational Science Initiative at Brookhaven National Laboratory (contract DE-SC0012704).

AUTHOR CONTRIBUTIONS

J.X. and M.Y.S. conceived and designed this project. H.H. and D.W. synthesized all the compounds studied. G.H. measured most of the data presented in the manuscript. K.X. ran the fluence-dependent TA experiment in solution. Q.W. performed the calculations. H.H., G.H., M.Y.S., and J.X. analyzed the data and co-wrote the manuscript. H.H. and G.H. contributed equally to this work.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: March 6, 2019 Revised: May 19, 2019 Accepted: June 13, 2019 Published: July 3, 2019

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