Organic Letters
Letter
pubs.acs.org/OrgLett

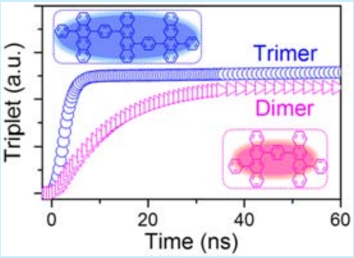
A Covalently Linked Tetracene Trimer: Synthesis and Singlet Exciton Fission Property

Heyuan Liu,[†,∥] Rui Wang,[‡,∥] Li Shen,[†] Yanqing Xu,[‡] Min Xiao,[‡,§] Chunfeng Zhang,*[,‡,§] and Xiyou Li*[,†]

[†]College of Science, China University of Petroleum (East China), Qingdao, Shandong 266580, China
[‡]National Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing 210093, China
[§]Synergetic Innovation Center in Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

Supporting Information

ABSTRACT: A linear tetracene trimer linked by phenyl groups has been prepared for the first time. The triplet quantum yield formed via intramolecular singlet fission can reach up to 96% in this trimer, which is enhanced significantly compared with that in the dimer. This can be attributed to the stronger electronic coupling between tetracene subunits and more delocalized excitons in the trimer.

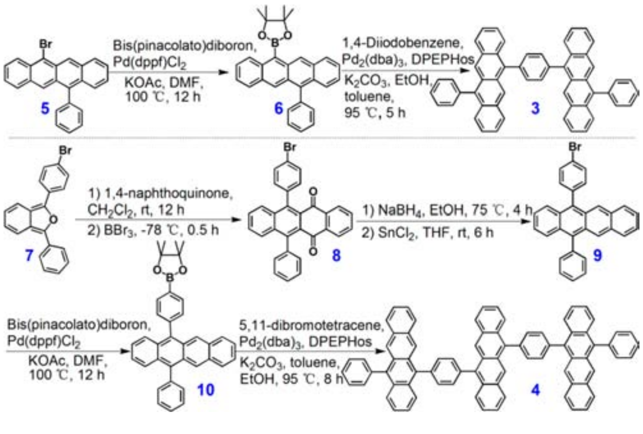


Singlet fission (SF),[1] which splits a singlet state into a pair of triplet states, is regarded as a promising approach to overcome the Shockley–Queisser limit on the efficiency of single-junction solar cells.[2−4] SF is highly efficient in crystalline polyacenes, especially tetracene and pentacene,[5−7] and concentrated solutions of polyacene derivatives.[8,9] These intermolecular SF (xSF) processes involve multiple molecules, where two free triplet excitons are located on separate molecules. Intramolecular SF (iSF), where SF occurs in a single molecule, has recently attracted considerable interest from scientists working in a variety of different fields. iSF sensitizers, which typically consist of covalently linked dimers of conjugated molecules, represent ideal platforms for exploring the mechanisms of SF processes based on well-defined structure–property relationships.[1,10] Molecules with the iSF property, in principle, are easily processed from solution and retain their SF properties regardless of crystal packing or dispersion within another material.[11]

It has been reported that iSF is quick and efficient in pentacene dimers.[12−16] However, efficient iSF is extremely difficult to achieve in tetracene dimers, probably because iSF in tetracene is slightly endothermic.[10,17,18] Recently, the effects of exciton delocalization on SF in polyacenes have been highlighted theoretically.[19,20] These effects have been further experimentally supported, in part, by the weak magnetic interactions observed between SF-induced triplet states in tetracene crystals and the delocalization-enhanced SF rate observed in acene nanoparticles and polypentacene.[21−23] On the basis of these results, we speculated that the iSF efficiency may be enhanced by increasing the number of subunits in a tetracene oligomer. In addition, this kind of larger oligomer could provide extra space for the delocalization of the triplet states, which could stabilize the triplet states and should be favorable for the application of iSF in organic solar cells.

With this in mind, we designed and synthesized tetracene trimer **4**. For the purpose of comparison, tetracene dimer **3** and the monomers 5,11-diphenyltetracene (**1**) and 5,12-diphenyltetracene (**2**) were also prepared. Dimer **3** and trimer **4** are new compounds that were synthesized by Suzuki coupling between the tetracene boronic ester and the corresponding halide (Scheme 1).[10] Detailed synthetic procedures and corresponding structural characterizations are shown in the Supporting Information (SI). All of these new compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis.

Scheme 1. Synthesis of Dimer 3 and Trimer 4



Received: December 15, 2016
Published: January 26, 2017

DOI: 10.1021/acs.orglett.6b03739
Org. Lett. 2017, 19, 580−583

The absorption and fluorescence spectra of monomers **1** and **2** were almost identical except for a slight difference in their molar extinction coefficients (Figure 1a), implying that the connection positions of the phenyl groups did not affect the optical properties significantly. The absorption spectra of dimer **3** and trimer **4** were similar to those of the monomers except for slight red shifts in the absorption and emission bands, indicating the presence of weak ground-state interactions between the tetracene subunits.[10] The optimized molecular structures of dimer **3** and trimer **4** were calculated at the B3LYP/6-31G** level.[24] These structures revealed that the neighboring tetracene subunits in these compounds adopted an orthogonal configuration (Figure S1), which prevented strong ground-state interactions between the tetracene subunits within these molecules. Notably, the maximum absorption peak of trimer **4** is further red-shifted by about 2 nm compared with that of dimer **3**, suggesting the presence of stronger ground-state interactions between the subunits in trimer **4**. On the basis of the concentration-dependent spectra and Beer's law plots of trimer **4** and dimer **3** (Figures S2−S5), we can conclude that no molecular aggregates were formed under our experimental conditions. This ensures that the photophysical measurements probed molecules that were fully dissolved and that intermolecular coupling effects can be excluded in the spectroscopic studies of trimer **4** and dimer **3**.

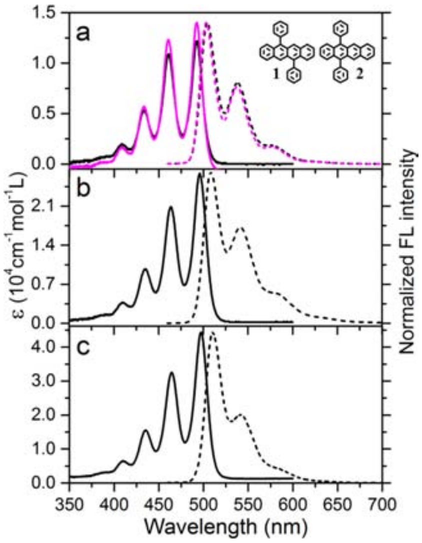


Figure 1. Absorption and fluorescence spectra of (a) monomers **1** (black) and **2** (magenta), (b) dimer **3**, and (c) trimer **4** in toluene (10^{-5} M). The inset shows the molecular structures of monomers **1** and **2**.

Notably, the fluorescence quantum yield of trimer **4** was much smaller than that of dimer **3** (Table S1). A fast component with a lifetime of around 1.9 ns was observed in the fluorescence decay profile of trimer **4** (Figure S6), indicating the presence of a fast nonradiative decay channel of the excited states of trimer **4** in comparison with that in dimer **3**. According to the previous report,[25−28] a strong magnetic field can decrease the number of triplet pair states coupled to the singlet states, which allows more singlet excitons to emit. As shown in Figures 2 and S7, a clear enhancement can be seen in the fluorescence spectrum of trimer **4** in the presence of a magnetic field. This magnetic field effect is also observed in the fluorescence decay dynamics (Figure S6). Similar results have also been observed in crystalline tetracene,[28] crystalline diphenylhexatriene,[26] an amorphous rubrene film,[25] and concentrated diphenyltetracene solution,[27] in which SF is efficient. This result suggested that iSF might be involved in the decay of the singlet excitons in trimer **4**. In contrast, the magnetic field effect was not observed for the fluorescence of monomers **1** and **2** and dimer **3**, probably because the SF channel is not available or extremely weak.

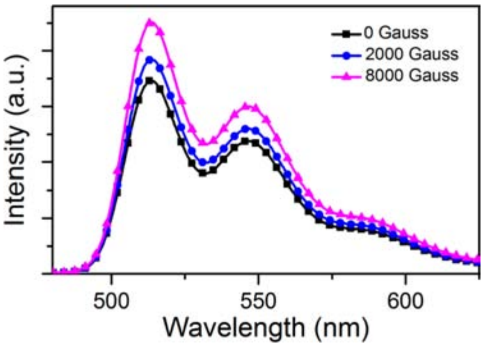


Figure 2. Magnetic-field-dependent fluorescence spectra of trimer **4** in degassed toluene (10^{-5} M).

In order to further prove the presence of iSF in trimer **4**, we employed transient absorption (TA) spectroscopy to study the excited-state dynamics in the dilute solution of trimer **4** (Figures 3 and S8). During the early stage, we observed photoinduced bleaching (PIB) signals at 504 and 540 nm. These features, close to the absorption and fluorescence peaks, can be naturally assigned to the ground-state bleaching (GSB) and/or stimulated emission (SE) relevant to singlet transitions. The photoinduced absorption (PIA) band centered at 650 nm can be assigned to the excited-state absorption (ESA) of singlet excitons according to the previous report.[7] Another PIA band was red-shifted from 482 to 486 nm along with the delay time

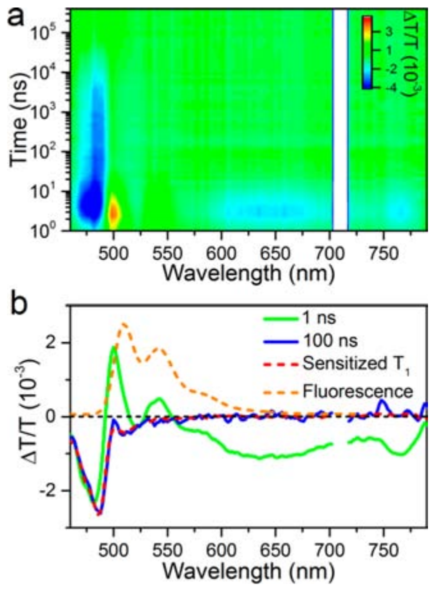


Figure 3. (a) Nanosecond TA spectra of trimer **4** (5×10^{-5} M). (b) TA spectra of trimer **4** recorded at 1 and 100 ns. The dashed lines show the fluorescence spectrum (orange) and triplet absorption spectrum (magenta) from the sensitized experiments (in degassed toluene).

and persisted to a long time after the singlet excitons had decayed completely (Figure 3). This long-lived PIA band at 486 nm can be assigned to the ESA of triplet excitons of tetracene (Figure 3b).[7] This assignment was also supported by the TA spectrum of trimer **4** in the presence of platinum octaethylporphyrin, a triplet sensitizer (for details of triplet sensitization, see the SI). The triplet absorption spectrum derived from the sensitization was almost identical to that of the long-lived species (Figure 3b), which confirmed that the long-lived species of trimer **4** were derived from triplet excitons.

Because of the spectral overlap at the early stage, it is not accurate to use single-wavelength dynamics to characterize the kinetics of the singlet state or the triplet state. Therefore, a global analysis method was adopted to disentangle the spectrotemporal features of the singlet and triplet states.[14,16,29] The deconvoluted spectra resulting from global analysis are shown in Figure S12, and the resulting species concentration profiles as functions of time are shown in Figure 4a,b. The decay of singlet excitons corresponds well with the rise of triplet excitons. The time constant for the triplet rise of trimer **4** was around 1.8 ns, which is close to the fast decay of the fluorescence mentioned above. More importantly, this process was much faster than the intersystem crossing (ISC) in the monomers ($1/k_{ISC} = 89$ ns).[7,27] This, taken together with the observation of delayed fluorescence in fluorescence decay experiments, confirmed that trimer **4** underwent iSF. If the triplet state originated from ISC, no delayed fluorescence would be detected in the dilute solution. Notably, the generated rate of the triplet state for trimer **4** (1.8 ns) is much faster than that for dimer **3** (12.3 ns), suggesting that iSF is more efficient in trimer **4** than in dimer **3**. In addition, we have also gotten the dynamics of the triplet states of trimer **4** and dimer **3** by simply subtracting a scaled signal probed at 650 nm (assigned to singlet excitons) from the trace probed at 480 nm (for details, see the SI).[30] The result agreed very well with that obtained from the global analysis (Figure S13), which further confirmed the reliability of our result.

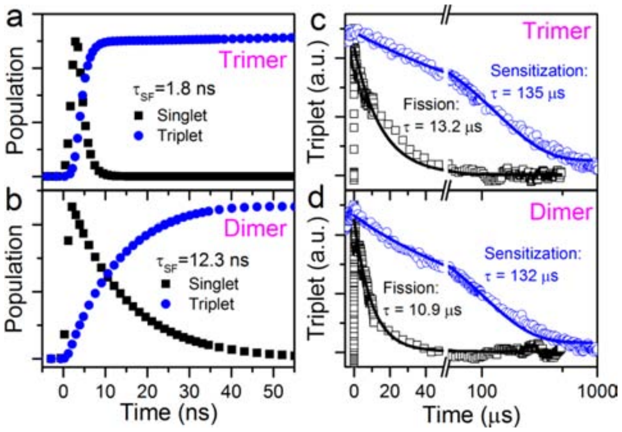


Figure 4. (a, b) Kinetics evolution of the populations of the singlet and triplet states of trimer **4** and dimer **3** obtained from global analysis. (c, d) Comparison of lifetimes of triplets obtained from singlet fission and photosensitization for trimer **4** and dimer **3** (in degassed toluene).

The presence of iSF in trimer **4** is also supported by the decay dynamics of the triplet states. The lifetime of triplet states of trimer **4** was found to be independent of the excitation fluence in the range we studied (Figure S14) as well as over 1 order of magnitude shorter than that observed for the sensitized triplets (Figure 4c,d). These results suggested that geminate triplet−triplet annihilation was the primary pathway of triplet decay in trimer **4** and strongly supported the idea that the triplet states in trimer **4** were generated via an iSF process. If the triplet states were formed via ISC, the triplet lifetime should be similar to that formed in the triplet photosensitization experiments. Furthermore, the triplet lifetime is independent of the concentration of trimer **4**, indicating that the decay of the triplet is an intramolecular process (Figure S15). In addition, the lifetime of triplet states of trimer **4** is only slightly larger than that of dimer **3** (Figure 4c,d), which suggests that the recombination of the triplet states is not significantly affected by the number of repeat units.[23]

The yields of the triplet states of trimer **4** and dimer **3** were calculated on the basis of the TA experiments, following the previous report (for details of the calculation, see the SI).[12] The yield of the triplet state of trimer **4** is 96%, which is much larger than that calculated for dimer **3** (21%). These results suggest that the iSF in trimer **4** is indeed much more efficient than that in dimer **3**.

To figure out why the iSF in trimer **4** is more efficient than that in dimer **3**, we performed DFT calculations of the energies of the singlet excited states and triplet states of trimer **4** and dimer **3**. The calculated results (Table S2) indicated that the energy differences between the singlet and triplet pair states are similar in dimer **3** and trimer **4**, which suggested that the difference between the iSF in trimer **4** and dimer **3** should not be caused by a thermodynamic effect. Krylov[19,20,31] theoretically examined the potential effects of molecular size on the SF processes in polyacenes and proposed that the broad distribution of the singlet exciton would be beneficial for SF. This suggestion was confirmed recently by an experimental result on the iSF in pentacene oligomers.[23] In the optimized molecular structure shown in Figure S1, the dihedral angle between the adjacent tetracene units in trimer **4** is smaller than that in dimer **3**, which indicates that the adjacent tetracene subunits in trimer **4** are more planar than those in dimer **3**, which allows stronger ground-state electronic coupling between tetracene subunits and more delocalized excitons in trimer **4**. This corresponds well with the 2 nm red shift in the absorption maximum of trimer **4** in comparison with that of dimer **3**. This may be the reason for the more efficient iSF in trimer **4** than in dimer **3**.

In summary, we have successfully synthesized a tetracene trimer for the first time. The iSF efficiency in this tetracene trimer is significantly larger than that in the corresponding tetracene dimer. The yield of triplet states formed via iSF is as high as 96% in this trimer, which is the largest yield achieved to date in solution for tetracene compounds. These results suggest that tetracene oligomers are promising candidates for iSF research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03739.

Experimental section, concentration dependence study, fluorescence properties, MFE of the fluorescence, transient absorption spectra, computational details, and synthetic details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: xiyouli@upc.edu.cn.
*E-mail: cfzhang@nju.edu.cn.

ORCID

Xiyou Li: 0000-0003-2548-2053

Author Contributions

‖H.L. and R.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

X.L. thanks the National Natural Science Foundation of China (Grants 21173136 and 91233108). C.Z. acknowledges the financial support from the National Natural Science Foundation of China (11574140 and 11227406) and Jiangsu Provincial Funds for Distinguished Young Scientists (BK20160019). H.L. thanks the China Postdoctoral Science Foundation (2016M602215), the Fundamental Research Funds for the Central Universities (15CX05067A), and the Qingdao Postdoctoral Fellowship Program (2015245).

■ REFERENCES

(1) Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891.
(2) Chan, W. L.; Tritsch, J. R.; Zhu, X. Y. *J. Am. Chem. Soc.* **2012**, *134*, 18295.
(3) Tabachnyk, M.; Ehrler, B.; Gélinas, S.; Böhm, M. L.; Walker, B. J.; Musselman, K. P.; Greenham, N. C.; Friend, R. H.; Rao, A. *Nat. Mater.* **2014**, *13*, 1033.
(4) Congreve, D. N.; Lee, J.; Thompson, N. J.; Hontz, E.; Yost, S. R.; Reusswig, P. D.; Bahlke, M. E.; Reineke, S.; Van Voorhis, T.; Baldo, M. A. *Science* **2013**, *340*, 334.
(5) Burdett, J. J.; Muller, A. M.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2010**, *133*, 144506.
(6) Wilson, M. W.; Rao, A.; Clark, J.; Kumar, R. S.; Brida, D.; Cerullo, G.; Friend, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 11830.
(7) Roberts, S. T.; McAnally, R. E.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 6388.
(8) Stern, H. L.; Musser, A. J.; Gelinas, S.; Parkinson, P.; Herz, L. M.; Bruzek, M. J.; Anthony, J.; Friend, R. H.; Walker, B. J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 7656.
(9) Walker, B. J.; Musser, A. J.; Beljonne, D.; Friend, R. H. *Nat. Chem.* **2013**, *5*, 1019.
(10) Müller, A. M.; Avlasevich, Y. S.; Schoeller, W. W.; Müllen, K.; Bardeen, C. J. *J. Am. Chem. Soc.* **2007**, *129*, 14240.
(11) Low, J. Z.; Sanders, S. N.; Campos, L. M. *Chem. Mater.* **2015**, *27*, 5453.
(12) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Trinh, M. T.; Choi, B.; Xia, J.; Taffet, E. J.; Low, J. Z.; Miller, J. R.; Roy, X.; Zhu, X. Y.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M. *J. Am. Chem. Soc.* **2015**, *137*, 8965.
(13) Zirzlmeier, J.; Lehnherr, D.; Coto, P. B.; Chernick, E. T.; Casillas, R.; Basel, B. S.; Thoss, M.; Tykwinski, R. R.; Guldi, D. M. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5325.
(14) Lukman, S.; Musser, A. J.; Chen, K.; Athanasopoulos, S.; Yong, C. K.; Zeng, Z.; Ye, Q.; Chi, C.; Hodgkiss, J. M.; Wu, J.; Friend, R. H.; Greenham, N. C. *Adv. Funct. Mater.* **2015**, *25*, 5452.
(15) Fuemmeler, E. G.; Sanders, S. N.; Pun, A. B.; Kumarasamy, E.; Zeng, T.; Miyata, K.; Steigerwald, M. L.; Zhu, X. Y.; Sfeir, M. Y.; Campos, L. M.; Ananth, N. *ACS Cent. Sci.* **2016**, *2*, 316.
(16) Zirzlmeier, J.; Casillas, R.; Reddy, S. R.; Coto, P. B.; Lehnherr, D.; Chernick, E. T.; Papadopoulos, I.; Thoss, M.; Tykwinski, R. R.; Guldi, D. M. *Nanoscale* **2016**, *8*, 10113.
(17) Korovina, N. V.; Das, S.; Nett, Z.; Feng, X.; Joy, J.; Haiges, R.; Krylov, A. I.; Bradforth, S. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2016**, *138*, 617.
(18) Cook, J. D.; Carey, T. J.; Damrauer, N. H. *J. Phys. Chem. A* **2016**, *120*, 4473.
(19) Feng, X.; Kolomeisky, A. B.; Krylov, A. I. *J. Phys. Chem. C* **2014**, *118*, 19608.
(20) Aryanpour, K.; Shukla, A.; Mazumdar, S. *J. Phys. Chem. C* **2015**, *119*, 6966.
(21) Pensack, R. D.; Tilley, A. J.; Parkin, S. R.; Lee, T. S.; Payne, M. M.; Gao, D.; Jahnke, A. A.; Oblinsky, D. G.; Li, P.-F.; Anthony, J. E.; Seferos, D. S.; Scholes, G. D. *J. Am. Chem. Soc.* **2015**, *137*, 6790.
(22) Wang, R.; Zhang, C.; Zhang, B.; Liu, Y.; Wang, X.; Xiao, M. *Nat. Commun.* **2015**, *6*, 8602.
(23) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M. *Chem.* **2016**, *1*, 505.
(24) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
(25) Piland, G. B.; Burdett, J. J.; Kurunthu, D.; Bardeen, C. J. *J. Phys. Chem. C* **2013**, *117*, 1224.
(26) Dillon, R. J.; Piland, G. B.; Bardeen, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 17278.
(27) Thompson, N. J.; Hontz, E.; Chang, W.; Van Voorhis, T.; Baldo, M. *Philos. Trans. R. Soc., A* **2015**, *373*, 20140323.
(28) Burdett, J. J.; Piland, G. B.; Bardeen, C. J. *Chem. Phys. Lett.* **2013**, *585*, 1.
(29) Snellenburg, J. J.; Laptenok, S. P.; Seger, R.; Mullen, K. M.; van Stokkum, I. H. M. *J. Stat. Software* **2012**, *49*, 1.
(30) Wilson, M. W.; Rao, A.; Johnson, K.; Gelinas, S.; di Pietro, R.; Clark, J.; Friend, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 16680.
(31) Zang, H.; Ke, Y.; Zhao, Y.; Liang, W. *J. Phys. Chem. C* **2016**, *120*, 13351.

DOI: 10.1021/acs.orglett.6b03739