

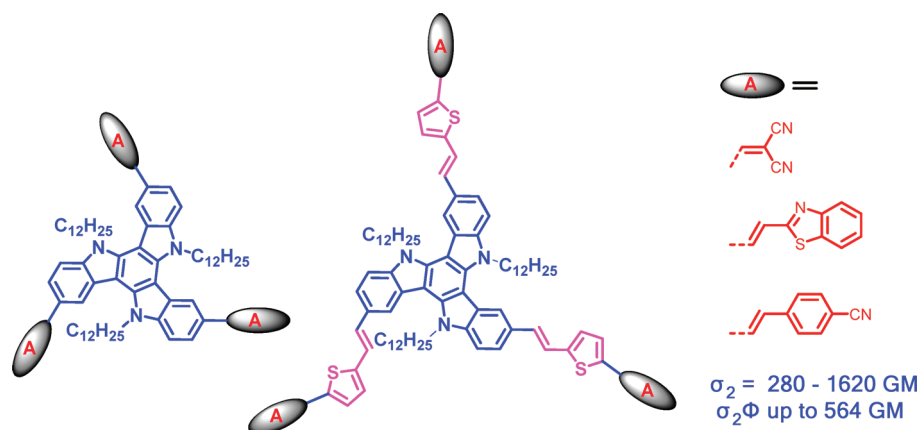
## Synthesis and Characterizations of Star-Shaped Octupolar Triazatruxenes-Based Two-Photon Absorption Chromophores

Junjun Shao, Zhenping Guan, Yongli Yan, Chongjun Jiao, Qing-Hua Xu,\* and Chunyan Chi\*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543

chmxqh@nus.edu.sg; chmcc@nus.edu.sg

Received September 15, 2010



A series of star-shaped octupolar triazatruxenes (TATs, **1–6**) with intramolecular “push–pull” structure were synthesized and their photophysical properties have been systematically investigated. These chromophores showed obvious solvatochromic effect, i.e., significant bathochromic shift of the emission spectra and larger Stokes shifts were observed in more polar solvents mainly due to photoinduced intramolecular charge transfer (ICT). The two-photon absorption (2PA) cross-section values were determined by two-photon excited fluorescence (2PEF) measurements in toluene and THF. These chromophores exhibited large two-photon absorption cross-sections ranging from 280 to 1620 GM in the near-infrared (NIR) region. Compound **6** showed the largest 2PA action cross-section ( $\sigma_2\Phi$ ) of 564 GM and could be a potential two-photon fluorescent (2PF) probe. In addition, compounds **1–6** all displayed good thermal stability and photostability.

### Introduction

In recent years, two-photon absorption (2PA) has attracted growing interest due to its potential applications in materials science and biological imaging,<sup>1</sup> including three-dimensional optical data storage,<sup>2</sup> lithographic microfabrication,<sup>3</sup> optical power limiting,<sup>4</sup> two-photon fluorescence imaging,<sup>5</sup> and

photodynamic therapy.<sup>6</sup> These applications strongly depend on the high 2PA cross-section of the specifically engineered

(1) For a recent review, see: (a) He, G. S.; Tan, L.-S.; Zheng, Q.; Prasad, P. N. *Chem. Rev.* **2008**, *108*, 1245. (b) Kim, H. M.; Cho, B. R. *Chem. Commun.* **2009**, 153. (c) Kim, H. M.; Cho, B. R. *Acc. Chem. Res.* **2009**, *42*, 863. (d) Terenziani, F.; Katan, C.; Badaeva, E.; Tretiak, S.; Blanchard-Desce, M. *Adv. Mater.* **2008**, *20*, 4641. (e) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3244.

(2) (a) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843. (b) Strickler, J. H.; Webb, W. W. *Opt. Lett.* **1991**, *16*, 1780. (c) Belfield, K. D.; Schafer, K. J. *Chem. Mater.* **2002**, *14*, 3656. (d) Corredor, C. C.; Huang, Z.-L.; Belfield, K. D.; Morales, A. R.; Bondar, M. V. *Chem. Mater.* **2007**, *19*, 5165.

(3) (a) Zhou, W.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106. (b) Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, K. *Nature* **2001**, *412*, 697. (c) Maruo, S.; Nakamura, O.; Kawata, S. *Opt. Lett.* **1997**, *22*, 132. (d) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D.; Qin, J.; Rockel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51. (e) Joshi, M. P.; Pudavar, H. E.; Swiatkiewicz, J.; Prasad, P. N.; Reinhardt, B. A. *Appl. Phys. Lett.* **1999**, *74*, 170. (f) Dvornikov, A. S.; Bouas-Laurent, H.; Desvergne, J.-P.; Rentzepis, P. M. *J. Mater. Chem.* **1999**, *9*, 1081. (g) Sun, H.-B.; Kawakami, T.; Xu, Y.; Ye, J.-Y.; Matuso, S.; Misawa, H.; Miwa, M.; Kaneko, R. *Opt. Lett.* **2000**, *25*, 1110. (h) Wang, I.; Bourriau, M.; Baldeck, P. L.; Martineau, C.; Andraud, C. *Opt. Lett.* **2002**, *27*, 1348. (i) Lu, Y.; Hasegawa, F.; Goto, T.; Ohkuma, S.; Fukuhara, S.; Kawazu, Y.; Totani, K.; Yamashita, T.; Watanabe, T. *J. Mater. Chem.* **2004**, *14*, 75. (j) Nguyen, L. H.; Straub, M.; Gu, M. *Adv. Funct. Mater.* **2005**, *15*, 209. (k) Jhaveri, S. J.; McMullen, J. D.; Sijbesma, R.; Tan, L.-S.; Zipfel, W.; Ober, C. K. *Chem. Mater.* **2009**, *21*, 2003.

organic molecules. This has led to a great number of works on building  $\pi$ -conjugated dipolar,<sup>6</sup> quadrupolar,<sup>7</sup> and octupolar<sup>8</sup> molecules with  $\pi$ -centers and functional groups of electron-donating and/or electron-withdrawing groups at the terminal sites.

Design of a star-shaped multipolar molecular structure is one of the strategies<sup>7a,9</sup> to obtain a large 2PA cross-section. The coherent coupling between the branches will significantly increase the 2PA cross-section. In addition, it was also found that a planar, extended  $\pi$ -conjugated core usually afforded better performance than the three-dimensionally twisted, nonconjugated cores. Star-shaped octupolar triphenyl amines and dendrimers based on planar truxene molecules<sup>10</sup> have proved to be good 2PA chromophores. To further exploit good 2PA active materials, we expect that the  $C_3$ -symmetry molecule, triazatruxene (TAT), could be another good candidate (Figure 1). This idea is based on the following considerations: (1) TAT can be considered as an extended delocalized  $\pi$ -system in which three carbazole units share one aromatic ring; (2) in comparison with its analogue truxene, triazatruxene contains three nitrogen atoms which can serve as good electron-donating groups like those in triphenyl amines; and (3) selective chemical functionalizations around the TAT core allow us to introduce electron-withdrawing groups to form star-shaped octupolar chromophores such as 1–6 (Figure 1). So this design combines the advantages of the electron-donating properties of aryl amines and the branched feature of truxene. The additional thienylene vinylene units in 4–6 can further improve the  $\pi$ -conjugation in each arm and tune the 2PA properties. Although some research has been done for the TAT-based materials,<sup>11</sup> this interesting

building block has not been used to develop 2PA chromophores. In this article, for the first time, we report the synthesis of a series of TAT-based octupolar chromophores which show large 2PA cross-section in the near-infrared (NIR) range.

## Results and Discussion

**Synthesis.** The synthesis of the octupolar TAT molecules 1–6 is shown in Scheme 1. Three different electron-withdrawing

(4) (a) He, G. S.; Xu, G. C.; Prasad, P. N.; Reinhardt, B. A.; Bhatt, J. C.; Dillard, A. G. *Opt. Lett.* **1995**, *20*, 435. (b) Ehrlich, J. E.; Wu, X. L.; Lee, I.-Y. S.; Hu, Z.-Y.; Röckel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843. (c) Bouit, P.-A.; Wetzel, G.; Berginc, G.; Loiseaux, B.; Toupet, L.; Fenevrou, P.; Bretonniere, Y.; Kamada, K.; Maury, O.; Andraud, C. *Chem. Mater.* **2007**, *19*, 5325.

(5) (a) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73. (b) Larson, D. R.; Zipfel, W. R.; Williams, R. M.; Clark, S. W.; Bruchez, M. P.; Wise, F. W.; Webb, W. W. *Science* **2003**, *300*, 1434. (c) Picot, A.; D'Aléo, A.; Baldeck, P. L.; Grichine, A.; Duperray, A.; Andraud, C.; Maury, O. *J. Am. Chem. Soc.* **2008**, *130*, 1532. (d) Gao, Y.; Wu, J.; Li, Y.; Sun, P.; Zhou, H.; Yang, J.; Zhang, S.; Jin, B.; Tian, Y. *J. Am. Chem. Soc.* **2009**, *131*, 5208. (e) Kim, H. J.; Han, J. H.; Kim, M. K.; Lim, C. S.; Kim, H. M.; Cho, B. R. *Angew. Chem., Int. Ed.* DOI: 10.1002/anie.201002907. Published Online: Aug 16, 2010. (f) Kim, H. M.; Seo, M. S.; An, M. J.; Hong, J. H.; Tian, Y. S.; Choi, J. H.; Kwon, O.; Lee, K. J.; Cho, B. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5167. (g) Kim, M. K.; Lim, C. S.; Hong, J. T.; Han, J. H.; Jang, H.-Y.; Kim, H. M.; Cho, B. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 364. (h) Tian, Y. S.; Lee, H. Y.; Lim, C. S.; Park, J.; Kim, H. M.; Shin, Y. N.; Kim, E. S.; Jeon, H. J.; Park, S. B.; Cho, B. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 8027. (i) Kim, H. M.; Jung, C.; Kim, B. R.; Jung, S. Y.; Hong, J. H.; Ko, Y. G.; Lee, K. J.; Cho, B. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 3460. (j) Kim, H. M.; An, M. J.; Hong, J. H.; Jeong, B. H.; Kwon, O.; Hyon, J. Y.; Hong, S. C.; Lee, K. J.; Cho, B. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 2231. (k) Kim, H. M.; Kim, B. R.; Hong, J. H.; Park, J. S.; Lee, K. J.; Cho, B. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 7445. (l) Lee, J. H.; Lim, C. S.; Tian, Y. S.; Han, J. H.; Cho, B. R. *J. Am. Chem. Soc.* **2010**, *132*, 1216. (m) Morales, A. R.; Schafer-Hales, K. J.; Marcus, A. I.; Belfield, K. D. *Bioconjugate Chem.* **2008**, *19*, 2559. (n) Morales, A. R.; Yanez, C. O.; Schafer-Hales, K. J.; Marcus, A. I.; Belfield, K. D. *Bioconjugate Chem.* **2009**, *20*, 1992. (o) Mohan, P. S.; Lim, C. S.; Tian, Y. S.; Roh, W. Y.; Lee, J. H.; Cho, B. R. *Chem. Commun* **2009**, 5365. (p) Wang, X.; Nguyen, D. M.; Yanez, C. O.; Rodriguez, L.; Ahn, H.-Y.; Bondar, M. V.; Belfield, K. D. *J. Am. Chem. Soc.* **2010**, *132*, 12237.

(6) (a) Bhawalkar, J. D.; Kumar, N. D.; Zhao, C. F.; Prasad, P. N. *J. Clin. Laser Med. Surg.* **1997**, *15*, 201. (b) Kim, S.; Ohulchansky, T. Y.; Pudavar, H. E.; Pandey, R. K.; Prasad, P. N. *J. Am. Chem. Soc.* **2007**, *129*, 2669. (c) Ogawa, K.; Kobuke, Y. *Org. Biomol. Chem.* **2009**, *7*, 2241. (d) Nielsen, C. B.; Arnbjerg, J.; Johnsen, M.; Jørgensen, M.; Ogilby, P. R. *J. Org. Chem.* **2009**, *74*, 9094. (e) Belfield, K. D.; Hagan, D. J.; Stryland, E. W. V.; Schafer, K. J.; Negres, R. A. *Org. Lett.* **1999**, *1*, 1575.

(7) (a) Albota, M.; Beljonne, D.; Brédas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653. (b) Ventelon, L.; Charier, S.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2098. (c) Frederiksen, P. K.; Jørgensen, M.; Ogilby, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 1215. (d) Mongin, O.; Porrés, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2002**, *4*, 719. (e) Abboto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Org. Lett.* **2002**, *4*, 1495. (f) Yang, W. J.; Kim, D. Y.; Jeong, M.-Y.; Kim, H. M.; Jeon, S.-J.; Cho, B. R. *Chem. Commun* **2003**, 2618. (g) Cho, B. R.; Son, K. H.; Lee, S. H.; Song, Y. S.; Lee, Y. K.; Jeon, S. J.; Choi, J. H.; Lee, H.; Cho, M. *J. Am. Chem. Soc.* **2001**, *123*, 10039. (h) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z. Y.; McCord-Maughon, D.; Parker, T. C.; Rockel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9500. (i) Pond, S. J.; Rumi, K. M.; Levin, M. D.; Parker, C. T.; Beljonne, D.; Day, M. W.; Brédas, J.-L.; Marder, S. R.; Perry, J. W. *J. Phys. Chem. A* **2002**, *106*, 11470. (j) Huang, P. H.; Shen, J. Y.; Pu, S. C.; Wen, Y. S.; Lin, J. T.; Chou, P. T. M.; Yeh, C. P. *J. Mater. Chem.* **2006**, *16*, 850. (k) Chung, S.; Rumi, J. M.; Alain, V.; Barlow, S.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 10844. (l) Mongin, O.; Porres, L.; Charlot, M.; Katan, C.; Blanchard-Desce, M. *Chem.—Eur. J.* **2007**, *13*, 1481. (m) Ventelon, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Chem. Commun.* **1999**, 2055. (n) Ventelon, L.; Charier, S.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2098. (o) Werts, M. H.; Gmouh, S.; Mongin, O.; Pons, T.; Blanchard-Desce, M. *J. Am. Chem. Soc.* **2004**, *126*, 16294. (p) Yang, W. J.; Kim, D. Y.; Jeong, M. Y.; Kim, H. M.; Lee, Y. K.; Fang, X.; Jeon, S. J.; Cho, B. R. *Chem.—Eur. J.* **2005**, *11*, 4191. (q) Kim, H. M.; Yang, W. J.; Kim, C. H.; Park, W. H.; Jeon, S. J.; Cho, B. R. *Chem.—Eur. J.* **2005**, *11*, 6386. (r) Zheng, S. J.; Beverina, L.; Barlow, S.; Zojer, E.; Fu, J.; Padilha, L. A.; Fink, C.; Kwon, O.; Yi, Y. P.; Shuai, Z. G.; Stryland, E. W. V.; Hagan, D. J.; Brédas, J.-L.; Marder, S. R. *Chem. Commun.* **2007**, 1372. (s) Zheng, S. J.; Leclercq, A.; Fu, J.; Beverina, L.; Padilha, L. A.; Zojer, E.; Schmidt, K.; Barlow, S.; Luo, J. D.; Jiang, S. H.; Jen, A. K. Y.; Yi, Y. P.; Shuai, Z. G.; Stryland, E. W. V.; Hagan, D. J.; Brédas, J.-L.; Marder, S. R. *Chem. Mater.* **2007**, *19*, 432. (t) Chung, S. J.; Zheng, S. J.; Odani, T.; Beverina, L.; Fu, J.; Padilha, L. A.; Biesso, A.; Hales, J. M.; Zhan, X. W.; Schmidt, K.; Ye, A. J.; Zojer, E.; Barlow, S.; Hagan, D. J.; Stryland, E. W. V.; Yi, Y. P.; Shuai, Z. G.; Pagani, G. A.; Brédas, J.-L.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 14444. (u) Lee, S. K.; Yang, W. J.; Choi, J. J.; Kim, C. H.; Jeon, S.-J.; Cho, B. R. *Org. Lett.* **2005**, *7*, 323. (v) Belfield, K. D.; Bondar, M. V.; Yanez, C. O.; Hernandez, F. E.; Przhonska, O. V. *J. Mater. Chem.* **2009**, *19*, 7498. (w) Yao, S.; Ahn, H.-Y.; Wang, X.; Fu, J.; Stryland, E. W. V.; Hagan, D. J.; Belfield, K. D. *J. Org. Chem.* **2010**, *75*, 3965. (x) Andrade, C. D.; Yanez, C. O.; Rodriguez, L.; Belfield, K. D. *J. Org. Chem.* **2010**, *75*, 3975.

(8) (a) Joshi, M. P.; Swiakiewicz, J.; Xu, F.; Prasad, P. N.; Reinhardt, B. A.; Kannan, R. *Opt. Lett.* **1998**, *23*, 1742. (b) Mongin, O.; Brunel, J.; Porres, L.; Blanchard-Desce, M. *Tetrahedron Lett.* **2003**, *44*, 2813. (c) Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z. G.; Vogel, H.; Pond, S. J. K.; Perry, J. W.; Marder, S. R.; Brédas, J.-L. *Adv. Funct. Mater.* **2002**, *12*, 631. (d) Bordeau, G.; Lartia, R.; Metge, G.; Fiorini-Debuisschert, C.; Charra, F.; Teulade-Fichou, M.-P. *J. Am. Chem. Soc.* **2008**, *130*, 16836. (e) Droumaguet, C. L.; Mongin, O.; Werts, M. H. V.; Blanchard-Desce, M. *Chem. Commun.* **2005**, 2802. (f) Fang, Z.; Zhang, X.; Lai, Y. H.; Liu, B. *Chem. Commun.* **2009**, 920. (g) Chung, S. J.; Kim, K. S.; Lin, T. C.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741. (h) Yoo, J.; Yang, S. K.; Jeong, M. Y.; Ahn, H. C.; Jeon, S. J.; Cho, B. R. *Org. Lett.* **2003**, *5*, 645. (i) Wu, J.; Zhao, Y. X.; Li, X.; Shi, M. Q.; Wu, F. P.; Kang, X. Y. *New J. Chem.* **2006**, *30*, 1098. (j) Yang, W. J.; Kim, D. Y.; Kim, C. H.; Jeong, M. Y.; Lee, S. K.; Jeon, S. J.; Cho, B. R. *Org. Lett.* **2004**, *6*, 1389. (k) Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T. J.; Blanchard-Desce, M. *Org. Lett.* **2004**, *6*, 47. (l) Bhaskar, A.; Ramakrishna, G.; Lu, Z. K.; Twieg, R. J.; Hales, M.; Hagan, D. J.; Stryland, E. W. V.; Goodson, T. *J. Am. Chem. Soc.* **2006**, *128*, 11840. (m) Cui, Y. Z.; Fang, Q.; Xue, G.; Xu, G. B.; Yin, L.; Yu, W. T. *Chem. Lett.* **2005**, *34*, 644. (n) Lin, T.-C.; Hsu, C.-S.; Hu, C.-L.; Chen, Y.-F.; Huang, W.-J. *Tetrahedron Lett.* **2009**, *50*, 182. (o) Lin, T.-C.; Huang, Y.-J.; Chen, Y.-F.; Hu, C.-L. *Tetrahedron* **2010**, *66*, 1375. (p) Jiang, Y.; Wang, Y.; Hua, J.; Tang, J.; Li, B.; Qian, S.; Tian, H. *Chem. Commun* **2010**, 46, 4689.

(9) (a) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Organometallics* **1999**, *18*, 5195. (b) Spangler, C. W. *J. Mater. Chem.* **1999**, *9*, 2013.

(10) Zheng, Q. D.; He, G. S.; Prasad, P. N. *Chem. Mater.* **2005**, *17*, 6004.

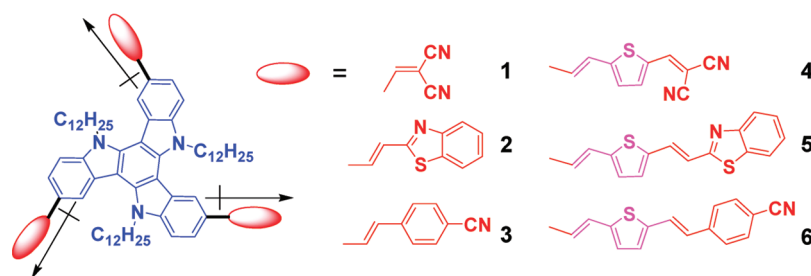


FIGURE 1. Molecular structures of star-shaped octupolar triazatruxenes 1–6.

groups are introduced onto the TAT core at the periphery sites to form a  $C_3$ -symmetric structure and this results in three dipoles at three directions with a net zero permanent dipole moment. The synthesis started from alkylation of the known hexabromotriazatruxene **7**<sup>11a</sup> with 1-bromododecane in the presence of KOH to give compound **8** in a 90% yield. Three dodecyl groups were introduced onto the TAT core to increase the solubility and to facilitate the subsequent synthesis and purification.<sup>11b</sup> The reductive debromination of **8** was performed in refluxing THF in the presence of 10% Pd/C, providing **9** in a 95% yield. The key step is the selective introduction of three  $-CHO$  groups onto the para-positions of the nitrogen atoms in **9**. The Vilsmeier–Haack condition<sup>12</sup> ( $POCl_3/DMF$ ) was first tested, but it failed to give the triformylated compound **10** even by increasing the reaction temperature or prolonging the reaction time. Therefore a more reactive condition, the  $CHCl_2OCH_3/SnCl_4$  system,<sup>13</sup> was performed and compound **10** was obtained in a 55% yield. Compound **1** was then prepared as a red powder in an 83% yield by a 3-fold condensation reaction between the  $-CHO$  groups and excessive malononitrile (**11**) in the presence of  $TiCl_4$  and pyridine in dichloromethane (DCM).<sup>14</sup> The Horner–Wadsworth–Emmons reaction<sup>15</sup> between **10** and compounds

**12**,<sup>14c</sup> **13**,<sup>16</sup> and **14**<sup>17</sup> in dry THF afforded compounds **2**, **3**, and **15** in 84%, 72%, and 85% yield, respectively.

Due to the high reactivity of the  $\alpha$ -position of the periphery thiophene molecule, the key intermediate compound **16** was easily obtained in a 93% yield by treating **15** with the Vilsmeier–Haack condition ( $POCl_3/DMF$ ).<sup>12</sup> Afterward, the chromophore **4** was prepared through a 3-fold condensation reaction between **16** and malononitrile (**11**) with  $TiCl_4$ /pyridine in dichloroethane (DCE) instead of DCM because a higher temperature was necessary to complete the conversion. Chromophores **5** and **6** were synthesized via the Horner–Wadsworth–Emmons reaction<sup>17</sup> between **16** and compounds **12**<sup>14c</sup> and **13**<sup>16</sup> by using *t*-BuOK as the base in 82% and 85% yield, respectively. It is worth noting that chromophores **1**, **2**, and **3** were prepared via only four steps with an overall yield of 39%, 40%, and 34%, respectively, and chromophores **4**, **5**, and **6** were synthesized via six steps with a good overall yield of 28%, 30%, and 32%, respectively. In addition, all the double bonds formed under the Horner–Wadsworth–Emmons reaction condition in the chromophores **2**, **3**, **15**, **16**, **4**, **5**, and **6** were *E*-configured which could be confirmed from the  $^1H$ – $^1H$  coupling constants of the protons of the vinylic  $\pi$ -bridges ( $J = \sim 16$  Hz) in their  $^1H$  NMR spectra.<sup>18</sup>  $^1H$  NMR,  $^{13}C$  NMR spectroscopy, mass spectrometry (MS), and elemental analysis were used to identify the chemical structure and purity of all of these chromophores (see the Experimental Section and the Supporting Information (SI)).

**One-Photon Spectral Properties.** The one-photon UV–vis absorption and fluorescence spectra of chromophores **1**–**6** were recorded in different solvents and the data are shown in Figure 2, Figure S1 (in the SI), and Table 1. Compounds **1**–**3** in THF displayed broad intense absorptions with maxima at 428, 400, and 388 nm, and the emission peaks appeared at 575, 503, and 499 nm, respectively (Figure 2a), while chromophores **4**–**6** showed absorption maxima at 512, 454, and 441 nm and emission maxima at 671, 570, and 554 nm, respectively (Figure 2b). Interestingly, the absorption maxima of **5** and **6** are 54 and 53 nm red-shifted from those of **2** and **3**, respectively, while that for **4** is 84 nm red-shifted from **1**, which is probably because of attachment of very strong electron-withdrawing dicyanomethylene groups.

Although the solvent polarity has only little effect on the absorption spectra (Figure 3a and in the SI Figure S1), significant bathochromic shift of the emission band was observed for each chromophore with increasing solvent polarity. Taking compound **1** as an example, the fluorescence spectra

(11) (a) Robertson, N.; Parsons, S.; MacLean, E. J.; Coxall, R. A.; Mount, A. R. *J. Mater. Chem.* **2000**, *10*, 2043. (b) Gomez-Lor, B.; Alonso, B.; Omenat, A.; Serrano, J. L. *Chem. Commun.* **2006**, 5012. (c) Gomez-Lor, B.; Echavarran, A. M. *Org. Lett.* **2004**, *6*, 2993. (d) Gomez-Lor, B.; Gunther, H.; Beatriz, A.; Angeles, M.; Enrique, G.-P.; Antonio, M. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 4491. (e) Lai, W.-Y.; Chen, Q.-Q.; He, Q.-Y.; Fan, Q.-L.; Huang, W. *Chem. Commun.* **2006**, 1959. (f) Lai, W.-Y.; Zhu, R.; Fan, Q.-L.; Hou, L.-T.; Cao, Y.; Huang, W. *Macromolecules* **2006**, *39*, 3707. (g) Talarico, M.; Termine, R.; Garcia-Frutos, E. M.; Omenat, A.; Serrano, J. L.; Gomez-Lor, B.; Golemme, A. *Chem. Mater.* **2008**, *20*, 6589. (h) Lai, W.-Y.; He, Q.-Y.; Zhu, R.; Chen, Q.-Q.; Huang, W. *Adv. Funct. Mater.* **2008**, *18*, 265. (i) Garcia-Frutos, E. M.; Gómez-Lor, B. *J. Am. Chem. Soc.* **2008**, *130*, 9173. (j) Luo, J.; Zhao, B. M.; Shao, J.; Lim, K. A.; Chan, H. S. O.; Chi, C. *J. Mater. Chem.* **2009**, *19*, 8327. (k) Zhao, B.; Liu, B.; Png, R. Q.; Zhang, K.; Lim, K. A.; Luo, J.; Shao, J.; Ho, K. H.; Chi, C.; Wu, J. *Chem. Mater.* **2010**, *22*, 435.

(12) (a) Vilsmeier, A.; Haack, A. *Ber* **1927**, *60*, 119. (b) Meth-Cohn, O.; Stanforth, S. P. *Comp. Org. Syn.* **1991**, *2*, 777. (c) He, F.; Tian, L.; Tian, X.; Xu, H.; Wang, Y. H.; Xie, W.; Hanif, M.; Xia, J.; Shen, F.; Yang, B.; Li, F.; Ma, Y.; Yang, Y.; Shen, J. *Adv. Funct. Mater.* **2007**, *17*, 1551.

(13) Kedrowski, B. L.; Hoppe, R. W. *J. Org. Chem.* **2008**, *73*, 5177. (14) (a) Kochurani, J.; Becker, J. Y.; Ellern, A.; Khodorkovsky, V. *Tetrahedron Lett.* **1999**, *40*, 8625. (b) Sanguinet, L.; Williams, J. C.; Yang, Z.; Twieg, R. J.; Mao, G.; Singer, K. D.; Wiggers, G.; Petschek, R. G. *Chem. Mater.* **2006**, *18*, 4259. (c) Lartia, R.; Allain, C.; Bordeau, G.; Schmidt, F.; Fiorini-Debuisschert, C.; Charra, F.; Teulade-Fichou, M. P. *J. Org. Chem.* **2008**, *73*, 1732.

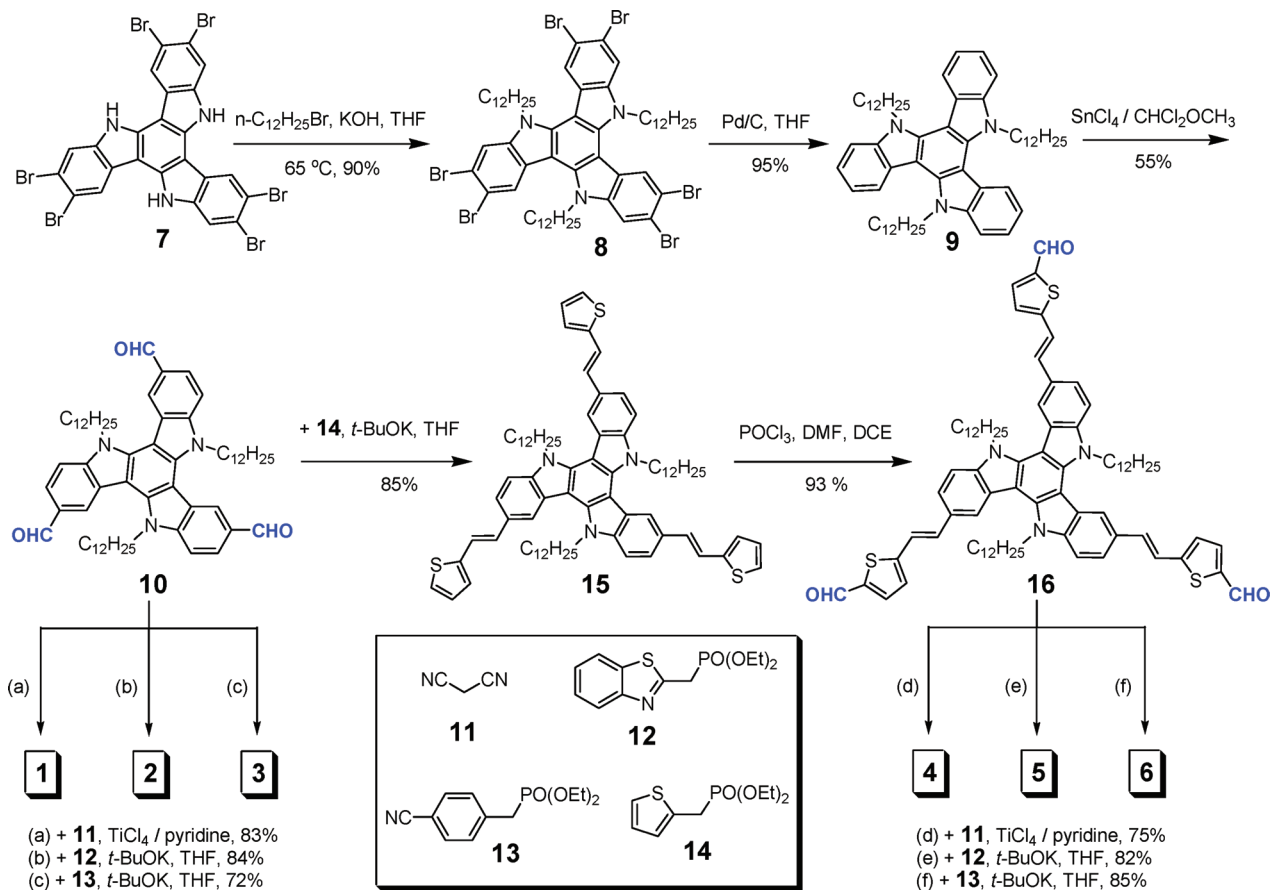
(15) Guldi, D. M.; Swartz, A.; Luo, C.; Gomez, R.; Segura, J. L.; Martin, N. *J. Am. Chem. Soc.* **2002**, *124*, 10875.

(16) Messmore, B. W.; Hulvat, J. F.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2004**, *126*, 14452.

(17) (a) Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2005**, *70*, 6004. (b) Zheng, S.; Barlow, S.; Parker, T. C.; Marder, S. R. *Tetrahedron Lett.* **2003**, *44*, 7989. (c) Jen, A. K. Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90.

(18) Pretsch, E.; Bühlmann, P.; Affolter, C. *Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, Germany, 2000.

## SCHEME 1. Synthetic Route of Chromophores 1, 2, 3, 4, 5, and 6



show pronounced bathochromic shift with the increasing solvent polarity, i.e., from less polar toluene to highly polar DCM, the emission maximum red-shifted from 528 to 591 nm (Figure 3b). Such a positive solvatochromism was commonly observed for many 2PA chromophores due to the photo-induced intramolecular charge transfer (ICT)<sup>1b</sup> from the center to the periphery. This could be explained by that the symmetry of our octupolar molecules was broken in the excited state by forming a relaxed, dipolar excited state localized on one of the donor–acceptor pairs.<sup>8k</sup> It could also be ascribed to the large steady state octupole moments in polar solvents.

The observed large Stokes shifts (5970, 5119, 5733, 4628, 4482, and 4625 cm<sup>-1</sup> for **1–6** in THF, respectively) indicate that significant charge redistribution occurs upon excitation, prior to emission, and that the emission originates from a strongly dipolar emissive state.<sup>8k</sup> Potentially large 2PA cross-sections can be obtained for these chromophores. All compounds except **1** and **4** have moderate fluorescence quantum yields ( $\Phi$ , Table 1), which also depend on the solvent polarity. The significant decrease in quantum yields for compounds **1** and **4** could be due to the strong intramolecular charge transfer. This would promote the solute–solvent interactions, by which the excited state of the chromophore would be readily quenched and the quantum yield decreases.<sup>8i,19</sup> The fluorescence lifetime was measured by using a time-correlated single

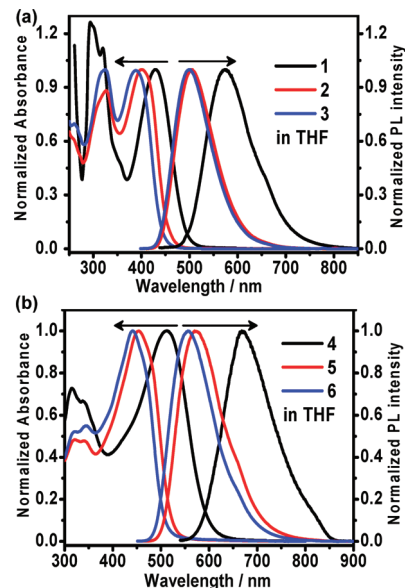


FIGURE 2. Normalized steady state absorption and fluorescence spectra of chromophores (a) **1–3** and (b) **4–6** in THF.

photon counting (TCSPC) technique. The frequency-doubled output of a mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) at 400 nm was used for excitation of the sample. The output pulses from Ti:sapphire centered at 800 nm had a pulse duration of 50 fs with a repetition rate of 80 MHz.

(19) Ko, C.-W.; Tao, Y.-T.; Danel, A.; Krzeminska, L.; Tomasiak, P. *Chem. Mater.* **2001**, *13*, 2441.

TABLE 1. Photophysical Data of Chromophores 1–6

compd	solvent	$\lambda_{\text{abs}}$ (nm) <sup>a</sup>	$\epsilon$ (cm <sup>-1</sup> ·M <sup>-1</sup> ) <sup>b</sup>	$\lambda_{\text{em}}$ (nm) <sup>c</sup>	Stokes shift (cm <sup>-1</sup> ) <sup>d</sup>	$\Phi^e$ (%)	$\sigma_2$ (GM) <sup>f</sup>	$\sigma_2\Phi$ (GM) <sup>g</sup>
1	toluene	436	67200	528	3996	3	730 [820 nm]	22
	THF	428	65700	575	5970	4	840 [820 nm]	34
2	toluene	401	80700	480	4104	19	770 [800 nm]	146
	THF	400	86000	503	5119	22	1110 [800 nm]	244
3	toluene	388	83200	462	4128	15	1050 [800 nm]	158
	THF	388	89800	499	5733	16	1580 [800 nm]	253
4	toluene	514	48700	606	2950	8	540 [770 nm]	43
	THF	512	59300	671	4628	2	280 [770 nm]	6
5	toluene	455	137500	524	2894	21	1620 [740 nm]	340
	THF	454	142700	570	4482	22	1600 [740 nm]	352
6	toluene	444	122900	508	2837	34	1050 [740 nm]	357
	THF	441	133000	554	4625	40	1410 [740 nm]	564

<sup>a</sup>One-photon absorption maximum, the experimental uncertainty is  $\pm 1$  nm. <sup>b</sup>Molar extinction coefficient at the absorption maximum. <sup>c</sup>One-photon emission maximum, the experimental uncertainty is  $\pm 1$  nm. <sup>d</sup>Stokes shift =  $(1/\lambda_{\text{abs}} - 1/\lambda_{\text{em}})$ . <sup>e</sup>Fluorescence quantum yields by using fluorescein (pH  $\sim 11$ , NaOH aqueous solution) as a standard; the experimental uncertainty is  $\pm 5$ –10%. <sup>f</sup>2PA cross-section maximum in the measurable range; 1 GM =  $10^{-50}$  cm<sup>4</sup>·s·photon<sup>-1</sup>; the corresponding excitation wavelengths are shown in the square brackets; the experimental uncertainty on  $\sigma_2$  is of the order of ( $\pm$ )12–15% of the corresponding values for 2, 3, 5, and 6 and ( $\pm$ )25% of the corresponding values for 1 due to its low quantum yield. <sup>g</sup>2P action cross-section.

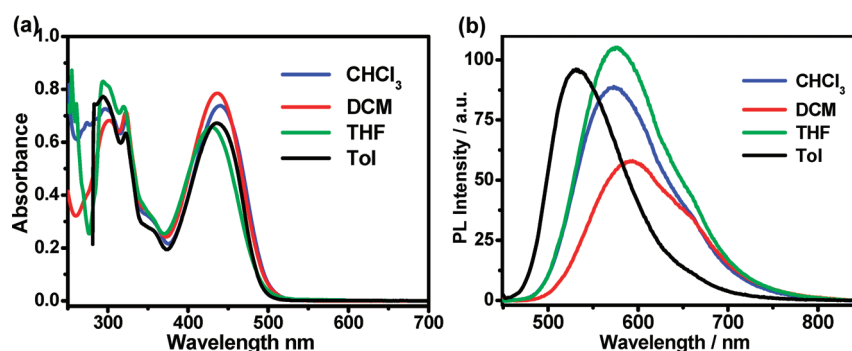


FIGURE 3. (a) Absorption spectra of chromophore 1 in different solvents with the same concentration of  $1.0 \times 10^{-5}$  M; (b) fluorescence spectra of compound 1 in different solvents with the same concentration of  $1.0 \times 10^{-6}$  M under excitation at 440 nm.

The fluorescence intensity was collected by an optical fiber that is directed to an avalanche photodiode (APD). The signals were processed by a PicoHarp 300 module (PicoQuant) with a temporal resolution of  $\sim 150$  ps. Monoexponential decays were observed for all compounds (Figure 4) and the fluorescence lifetimes in toluene were 1.78, 1.35, 2.24, 1.20, 1.44, and 1.29 ns for 1–6, respectively. We noted that the fluorescence lifetimes do not correlate well with their fluorescence quantum yields for different chromophores in the same solvent, although the fluorescence lifetimes of the same chromophore in different solvents were found to correlate well with their quantum yields. The lack of correlation between fluorescence lifetimes and quantum yields for different chromophores might be due to different radiative decay rates of these chromophores because of their different electronic structures.

**Electrochemical Properties.** The electrochemical properties of compounds 1–6 were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in DCM. One or two quasi-reversible oxidation waves were observed for each chromophore (Figure 5). Their HOMO, LUMO energy levels and energy gaps are shown in Table 2. The HOMO energy levels derived from the onset of oxidation potential are  $-5.12$ ,  $-5.15$ ,  $-5.15$ ,  $-5.11$ ,  $-4.97$ , and  $-5.00$  eV for 1–6, respectively.<sup>20</sup> Accordingly, the respective LUMO

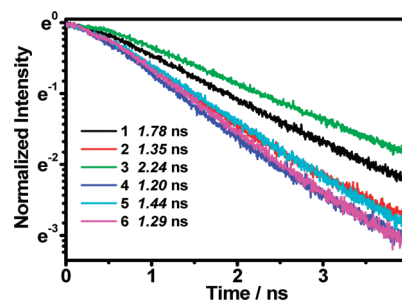
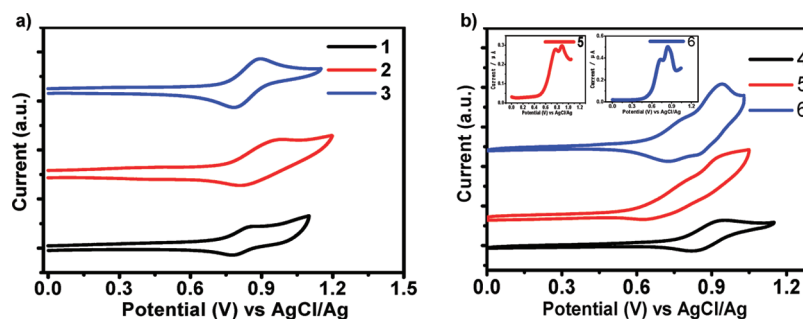


FIGURE 4. Fluorescence decay curves of chromophores 1–6 in toluene.

energy levels are deducted as  $-2.61$ ,  $-2.45$ ,  $-2.36$ ,  $-3.06$ ,  $-2.60$ , and  $-2.57$  eV based on the equation  $\text{LUMO} = \text{HOMO} + E_g$ , where  $E_g$  is the optical energy gap.<sup>20</sup> One can see that compounds 1–3 have similar HOMO energy levels probably because they have a common electron-rich TAT core, but their LUMO energy levels are different due to the attachment of different electron-withdrawing groups. The stronger electron-withdrawing group such as dicyanomethylene pulls down the LUMO energy level and as a result, a smaller energy gap was observed for 1. For compounds 4–6, the additional thienylene vinylene units further increase the  $\pi$ -conjugation and lead to a lower lying HOMO energy level and a convergence of the HOMO–LUMO

(20) (a) Chi, C.; Wegner, G. *Macromol. Rapid Commun.* **2005**, *26*, 1532. (b) Chi, C.; Im, C.; Enkelmann, V.; Ziegler, A.; Lieser, G.; Wegner, G. *Chem.—Eur. J.* **2005**, *11*, 6833.



**FIGURE 5.** Cyclic voltammograms of chromophores **1–6** in DCM with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, AgCl/Ag as reference electrode, Au as working electrode, Pt wire as counter electrode, and a scan rate at 50 mV/s. Inset: The differential pulse voltammograms of chromophores **5** and **6** showing two distinguishable redox waves.

**TABLE 2. Electrochemical Properties of the Chromophores 1–6**

compd	$E_{\text{ox}}^{\text{onset} a}/\text{V}$	HOMO <sup>b</sup> /eV	LUMO <sup>c</sup> /eV	$E_g^d$ /eV
<b>1</b>	0.32	−5.12	−2.61	2.51
<b>2</b>	0.35	−5.15	−2.45	2.70
<b>3</b>	0.35	−5.15	−2.36	2.79
<b>4</b>	0.31	−5.11	−3.06	2.05
<b>5</b>	0.17	−4.97	−2.60	2.37
<b>6</b>	0.20	−5.00	−2.57	2.43

<sup>a</sup> $E_{\text{ox}}^{\text{onset}}$  is the onset potential of the first oxidation wave relative to  $E_{\text{Fc}^+/\text{Fc}}$ . Fc<sup>+</sup>/Fc was used as internal reference for these measurements,  $E_{1/2} = 0.40$  V for Fc<sup>+</sup>/Fc vs AgCl/Ag. <sup>b</sup>HOMO =  $-(4.8 + E_{\text{ox}}^{\text{onset}})$ . <sup>c</sup>LUMO = HOMO +  $E_g$ . <sup>d</sup> $E_g$  (optical energy gap) calculated from the low-energy absorption edge.

energy gap in comparison to the corresponding chromophores **1–3**.

**Two-Photon Absorption Characteristics of 1–6.** 2PA spectra of the chromophores **1–6** were recorded in toluene and THF by two-photon excited fluorescence (2PEF) measurements in the range of 740–860 nm (Figure 6 and in the SI Figure S2). The 2PEF spectra of these samples were compared with a reference solution of fluorescein at the corresponding excitation wavelengths.<sup>21</sup> All six chromophores exhibited maximum 2PA cross-section ( $\sigma_2$ ) ranging from 280 GM to 1620 GM in the two solvents (Table 1). A quadratic dependence of the 2PEF on the incident power was observed (Figure S5, SI), indicating a two-photon absorption process.

A discernible trend of the two-photon absorption cross-section ( $\sigma_2$ ) was observed for chromophores **1–3**: the values in toluene increase from **1** to **3** with the maxima 2PA cross-section increasing from 730 GM to 1050 GM (Figure 6a). A similar trend was observed in THF (Figures S2 and S4, SI). Since **1–3** have a common TAT core with the same electron-donating effect, such a difference must be due to the varied electron-withdrawing groups and the different effective  $\pi$ -conjugation length. Although the dicyanomethylene group shows the strongest electron-withdrawing property, **2** and **3** have more extended conjugation length than **1**, which results in larger 2PA cross-sections than **1**. Chromophores **2** and **3** have a similar conjugation length, while **3** has the  $-\text{CN}$  groups at the terminal sites which may cause **3** to have larger two-photon absorptivity than **2**.<sup>7u,8j</sup>

Compounds **4–6** in toluene show their maxima 2PA cross-section ( $\sigma_2$ ) of 540 GM at 770 nm, 1620 GM at 740 nm, and 1050 GM at 740 nm, respectively, which are larger than those of **1–3** (Figure S4, SI). This trend could be explained as due

to extended effective  $\pi$ -conjugation length after incorporating a thienylene vinylene unit into the each branch. The longer  $\pi$ -conjugated compound may have a larger number of density of states which could provide more effective coupling channels between the ground states and two-photon allowed states, which in turn will enhance the 2PA cross-section.<sup>8j</sup> Chromophores **1–3** showed their 2PA cross-section maxima in the sequence **3** > **2** > **1**, and chromophores **5** and **6** exhibited comparable 2PA cross-section values with both larger than that for **4**.

It is clear to see the trend of 2P action cross-section maximum values of the six chromophores as **3** > **2** > **1**, **6** > **5** > **4** in toluene as well as in THF (Figure 7, and in the SI Figure S3). The 2P action cross-section maxima of **2** and **3** are almost the same and much larger than that of **1**, and this is due to the relatively low quantum yield of **1**. In the measurement range from 740 to 860 nm, the 2P action cross-section of **6** is a little bit larger than that of **5**, and much larger than that of **4**. In addition, the 2P action cross-section of **2**, **3**, **5**, and **6** are larger in THF than those in toluene. It is worth noting that compared with rhodamine B, one common commercial fluorophore with a 2PA cross-section value of 200 GM and 2P action cross-section ( $\sigma_2\Phi$ ) of 140 GM at 840 nm in MeOH,<sup>22</sup> both compounds **5** and **6** have much higher 2PA cross-section and 2P action cross-section values. Thus, compounds **5** and **6** could be potential efficient two-photon fluorescent probes.

There have been few theoretical studies to address the solvent effect, and unfortunately the published results still lack consensus.<sup>23</sup> One recent experimental study by using vinylbenzene<sup>24a</sup> and vinylfluorene<sup>24b</sup> derivatives revealed that, unlike one-photon transition, two-photon transition does not correlate with the polarity of the solvent. However, Bazan et al.<sup>25</sup> reported

(22) Xu, C.; Williams, R. M.; Zipfel, W.; Webb, W. W. *Bioimaging* **1996**, *4*, 198.

(23) (a) Luo, Y.; Norman, P.; Macak, P.; Agren, H. *J. Phys. Chem. A* **2000**, *104*, 4718. (b) Wang, C.-K.; Zhao, K.; Su, Y.; Ren, Y.; Zhao, X.; Luo, Y. *J. Chem. Phys.* **2003**, *119*, 1208. (c) Ray, P. C.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 6689. (d) Terenziani, F.; Painelli, A.; Katan, C.; Charlot, M.; Blanchard-Desce, M. *J. Am. Chem. Soc.* **2006**, *128*, 15742. (e) Paterson, M. J.; Kongsted, J.; Christiansen, O.; Mikkelsen, K. V.; Nielsen, C. B. *J. Chem. Phys.* **2006**, *125*, 184501. (f) Zhao, K.; Ferrighi, L.; Frediani, L.; Wang, C.-K.; Luo, Y. *J. Chem. Phys.* **2007**, *126*, 204509. (g) Easwaramoorthi, S.; Shin, J. Y.; Cho, S.; Kim, P.; Inokuma, Y.; Tsurumaki, E.; Osuka, A.; Kim, D. *Chem.—Eur. J.* **2009**, *15*, 12005.

(24) (a) Johnsen, M.; Ogilby, P. R. *J. Phys. Chem. A* **2008**, *112*, 78319. (b) Fitisil, I.; Fakis, M.; Polyzos, I.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *J. Phys. Chem. A* **2008**, *112*, 4742.

(25) Woo, H. Y.; Liu, B.; Kohler, B.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 14721.

(21) (a) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481. (b) Tian, N.; Xu, Q.-H. *Adv. Mater.* **2007**, *19*, 1988.

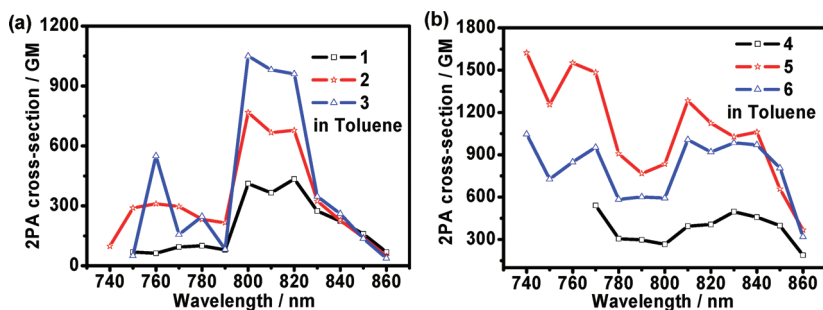


FIGURE 6. 2PA spectra of compounds 1–6 in toluene.

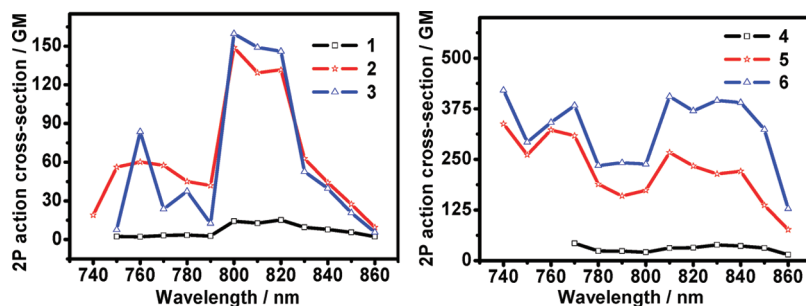


FIGURE 7. 2P action cross-section spectra ( $\sigma_2\Phi$ ) of the compounds 1–6 in toluene.

that the 2PA cross-section value of distyrylbenzene chromophores was solvent-dependent and nonmonotonic, and the maxima 2PA cross-section values were observed in the solvent with intermediate polarity. On the other hand, the 2PA cross-section values of octupolar molecules are expected to show little solvent dependence on account of lack of permanent dipole moment. However, theoretical and computational studies indicate the influence of dipolar, quadrupolar, octupolar, and higher-order interactions with the solvent.<sup>23c</sup> In our TAT-based chromophores, no clear trend of the solvent dependence was observed. In the nonpolar solvent such as toluene, the  $\sigma_2\Phi$  values are slightly smaller than those in polar solvents such as THF. The difference should be related to the conformation of the chromophore molecules in excited states and solvation effect in different solvents. The small difference may be due to the rigid and planar core structure of these TAT-based chromophores.

**Thermal Properties.** The thermal stability is one of the key requirements for some practical applications of organic chromophores used in a solid matrix. The thermal stability of the compounds is examined by thermogravimetric analysis (TGA) in  $N_2$  at a heating rate of 10 deg/min, and all the compounds have high thermal stability, with decomposition temperatures ( $T_d$ , corresponding to a 5% weight loss) at 330, 347, 378, 352, 393, and 420 °C for compounds 1–6, respectively (Figure 8). These results confirm that the triazatruxene-containing chromophores are thermally stable.

**Photostability Test.** The photostability of a chromophore is of great importance regarding potential application for two-photon fluorescent microscopy (2PFM) probes. Herein the

photostability and 2PA cross-sections of chromophores 1–6 were compared with the commercially available Fluorescein via photodecomposition experiments using the absorption method (Figure 9 and in the SI Figure S6).<sup>26</sup> A figure of merit ( $F_M$ )<sup>26b,c</sup> by which probes for 2PFM was defined as two-photon action cross-section ( $\Phi\sigma_2$ ) normalized by their photodecomposition quantum yields ( $\eta$ , see the SI), i.e.,  $F_M = \Phi\sigma_2/\eta$ . The data are shown in Table 3. The  $F_M$  values of all chromophores are 1–3 orders of magnitude higher than that of fluorescein, providing strong support for the fidelity of chromophore 5 and 6 relative to commercial fluorescein probes for 2PFM biological imaging.

## Conclusions

A new synthetic route was developed to prepare six new star-shaped octupolar compounds based on triazatruxene. The synthesis of the trisformylated precursor 10 was the key for the synthesis of 1, 2, 3, and 15. Direct formylation introduced three aldehyde groups onto 15, which was the key intermediate to synthesize 4, 5, and 6. In general, all six chromophores were readily obtained with a good overall yield from the starting material 7. Solvent polarity has little effect on the UV–vis absorption spectra, while significant bathochromic shift of the emission spectra was observed together with a larger Stokes shift in polar solvents due to intramolecular charge transfer. Chromophores 1–6 show high two-photon absorptivity with the maxima 2PA cross-section ranging from 280 GM to 1620 GM. At the same time, 5 and 6 exhibit the large 2P action cross-section ( $\sigma_2\Phi$ ) and the figure of merit ( $F_M$ ), so they could be the potential 2P fluorescent probes. In addition, all chromophores show good thermal stability and photostability. We can also expect that more modifications can be done on this TAT core to further tune their 2PA properties by introducing multiple branched or dendritic structures with more extended  $\pi$ -conjugation in the future. Construction of dendrimers based on TAT is underway in our laboratories.

(26) (a) Corredor, C. C.; Belfield, K. D.; Bondar, M. V.; Przhonska, O. V.; Yao, S. *J. Photochem. Photobiol., A* **2006**, *184*, 105. (b) Wang, X.; Nguyen, D. M.; Yanez, C. O.; Rodriguez, L.; Ahn, H.-Y.; Bondar, M. V.; Belfield, K. D. *J. Am. Chem. Soc.* **2010**, *132*, 12237. (c) Wang, X.; Yao, S.; Ahn, H.-Y.; Zhang, Y.; Bondar, M. V.; Torres, J. A.; Belfield, K. D. *Biomed. Opt. Express* **2010**, *1*, 453.

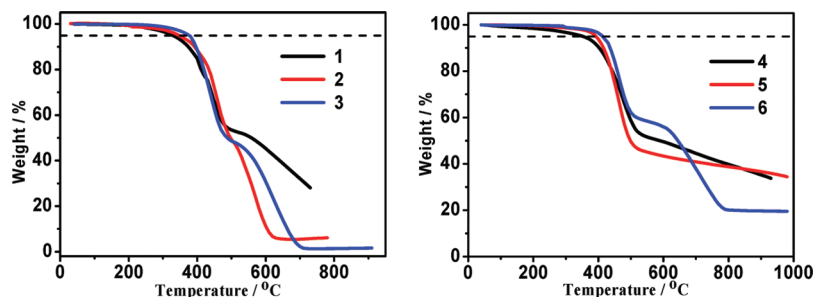


FIGURE 8. TGA curves of compounds 1–6. TGA was obtained under  $N_2$  at a heating rate of 10 deg/min.

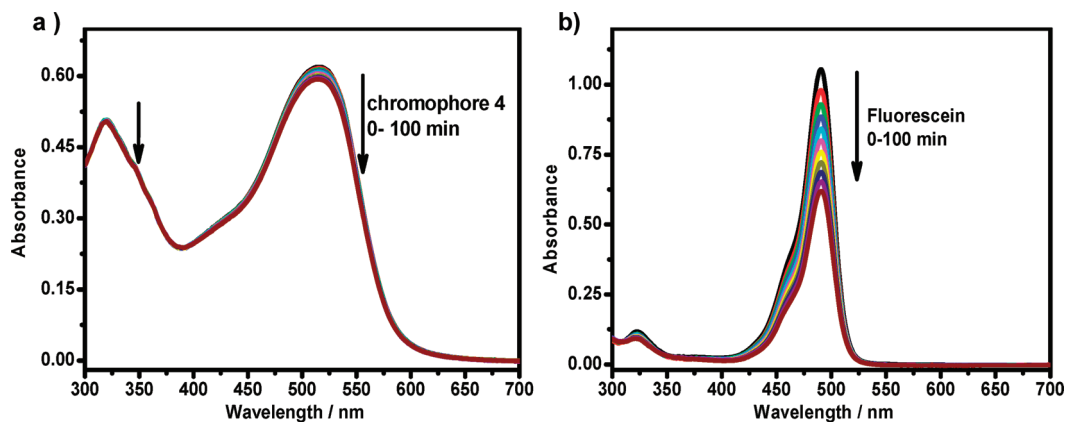


FIGURE 9. Absorption spectra of 4 in toluene (a) and fluorescein in 0.1 M NaOH (aq) (b) recorded after irradiation with a 457 nm diode laser at 20 mW for different periods of time.

TABLE 3. Photophysical Data for 1–6 and Fluorescein

compd	$10^6\eta^a$	$\Phi\sigma_2^b$	$10^{-6}F_M^c$
1	0.04	22	550
2	1.22	146	120
3	9.0	158	18
4	0.28	43	154
5	0.07	340	4857
6	0.87	357	410
fluorescein	7.16	33	5

<sup>a</sup>Photobleaching decomposition quantum yield; the experimental uncertainty is  $\pm 15\%$ . <sup>b</sup> $2P$  action cross-section maximum in the measurable range in GM. <sup>c</sup>Figure of merit in GM,  $F_M = \Phi\sigma_2/\eta$ .

## Experimental Section

**Materials.** Anhydrous tetrahydrofuran (THF) and DCM were obtained by distillation over sodium and  $CaH_2$ , respectively. Hexabromotriazatruxene (7),<sup>11a</sup> diethyl (benzothiazol-2-yl)-methylphosphonate (12),<sup>14c</sup> diethyl (4-cyanophenyl)methylphosphonate (13),<sup>16</sup> and diethyl (thiophen-2-yl)methylphosphonate (14)<sup>17</sup> were prepared according to the literature procedure. All other chemicals were purchased from commercial supplies and used without further purification. Deuterated solvents for NMR spectroscopic analyses were used as received.

**Characterizations.**  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded in  $CDCl_3$  or  $CDCl_2CDCl_2$ . All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. MS were recorded in either EI mode or FAB mode and high resolution mass spectrometry were recorded with a FAB ionization source. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis was performed by using dithranol as matrix. UV-vis absorption and fluorescence spectra were recorded in HPLC pure solvents. Melting points were checked on the Buchi Melting Point B-540 instrument

by using the capillary method and the data are not calibrated. Cyclic voltammetry was performed on an electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) dissolved in dry DCM at a scan rate of  $50\text{ mV s}^{-1}$ . A gold electrode with a diameter of 2 mm, a Pt wire, and an Ag/AgCl electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium couple. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 deg/min under nitrogen flow.

The two-photon excited fluorescence (2PEF) method was used to measure the 2PA cross-sections.<sup>21</sup> The excitation source was a femtosecond Ti:sapphire oscillator pumped by a 532 nm diode laser. The output laser pulses have pulse duration of 50 fs, a repetition rate of 80 MHz, and a center wavelength at 800 nm. The power of the laser beam before the samples was adjusted to 100 mW by using neutral density filters for most measurements. The samples were excited by directing a tightly collimated, high intensity laser beam onto the sample. The emission from the sample was collected at a  $90^\circ$  angle by a pair of lens and optical fibers and directed to the spectrometer, which was a monochromator coupled CCD system. To avoid internal filter effects, the excitation volume was located near the cell wall on the collection optics side. This configuration minimizes the fluorescence path inside the sample cell and thus reduces self-absorption. A short pass filter with cutoff wavelength at 700 nm was placed before the spectrometer to minimize the intensity of pumping light scattering. Samples were dissolved in toluene and THF at the same concentration of  $5 \times 10^{-6}\text{ M}$  and the two-photon induced fluorescence intensity was measured at 740–860 nm by using Fluorescein ( $5 \times 10^{-6}\text{ M}$  in water, pH 11) as the reference. The intensities of the two-photon-induced fluorescence spectra of the reference and sample under the same measurement conditions



were determined and compared. The 2PA cross-section of sample  $\delta_s$ , measured by using the two-photon-induced fluorescence measurement technique, can be calculated by using the equation

$$\delta_s = \frac{F_s \Phi_r C_r n_s^2}{F_r \Phi_s C_s n_r^2} \delta_r$$

where the subscripts s and r stand for the sample and reference molecules, respectively.  $F$  is the integral area of the two-photon fluorescence;  $\Phi$  is the fluorescence quantum yield; and  $C$  is the number density of the molecules in solution.  $\delta_r$  is the 2PA cross-section of the reference molecule;  $n$  is the refractive indices of the solvents. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the excitation intensity, as expected for two-photon-induced emission.

The photostability of all the chromophores was determined by the absorption method.<sup>26</sup> For chromophores **1**, **4**, **5**, and **6**, a solution in toluene was irradiated in 1 mm path length quartz cuvettes with a 457 nm diode laser at 20 mW, and fluorescein in 0.1 M NaOH(aq) was tested under the same condition; for compounds **2** and **3**, a solution in toluene was irradiated in 1 mm path length quartz cuvettes with a 400 nm diode laser at 20 mW.

**Synthesis. 2,3,7,8,12,13-Hexabromo-5,10,15-tridodecyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (8).** A mixture of hexabromotriazatruxene **7** (2.45 g, 3.00 mmol) and KOH (1.68 g, 30.00 mmol) was heated to reflux in THF (30 mL) for 30 min. Then, 1-bromododecane (3.50 mL, 13.5 mmol) was added and the mixture was refluxed for 13 h before it was cooled to room temperature. The mixture was diluted with DCM (50 mL) and washed with 10% aqueous HCl solution (2 × 50 mL) and with saturated aqueous NaCl solution (2 × 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuum. The residue was purified by silica gel column chromatography with hexane as the eluent to give **8** as a yellow solid (2.3 g, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.95 (s, 3H), 7.49 (s, 3H), 3.97 (t,  $J = 7.5$  Hz, 6H), 1.71 (br, 6H), 1.31–1.22 (m, 54H), 0.90 (t,  $J = 7.0$  Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 140.0, 138.6, 124.8, 122.7, 118.5, 115.2, 114.4, 101.2, 46.8, 32.0, 30.2, 29.69, 29.67, 29.60, 29.58, 29.4, 29.3, 26.5, 22.7, 14.1; FAB-MS ( $m/z$ ) calcd for C<sub>60</sub>H<sub>81</sub>Br<sub>6</sub>N<sub>3</sub> 1323.15, found 1323.0 (M<sup>+</sup>), 1243.1 (M<sup>+</sup>–Br). Elemental Anal. Calcd for C<sub>60</sub>H<sub>81</sub>–Br<sub>6</sub>N<sub>3</sub>: C, 54.44; H, 6.17; N, 3.17. Found: C, 54.54; H, 6.01; N, 3.17.

**5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (9).** A mixture of **8** (0.662 g, 0.50 mmol), Et<sub>3</sub>N (0.55 mL, 4.00 mmol), HCOOH (0.16 mL, 4.00 mmol), and 10% Pd/C (160 mg, 0.15 mmol) in THF (10 mL) was heated at 70 °C overnight. The mixture was filtered through Celite, and the filtrate was diluted with DCM (30 mL), washed with 10% aqueous HCl (3 × 30 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with pure hexane as eluent to give **9** as a white solid (0.404 g, 95%). Mp 63–65 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.29 (d,  $J = 8.0$  Hz, 3H), 7.64 (d,  $J = 8.0$  Hz, 3H), 7.46 (t,  $J = 8.0$  Hz, 3H), 7.35 (t,  $J = 8.0$  Hz, 3H), 4.92 (t,  $J = 8.0$  Hz, 6H), 2.00 (quin, 6H), 1.29–1.18 (m, 54H), 0.89 (t,  $J = 8.0$  Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 141.0, 138.9, 123.5, 122.6, 121.5, 119.6, 110.5, 103.2, 47.0, 31.9, 29.8, 29.59, 29.58, 29.5, 29.4, 29.3, 29.2, 26.7, 22.7, 14.1; EI-MS ( $m/z$ ) calcd for C<sub>60</sub>H<sub>87</sub>N<sub>3</sub> 849.69, found 849.9 (M<sup>+</sup>). Elemental Anal. Calcd for C<sub>60</sub>H<sub>87</sub>N<sub>3</sub>: C, 84.75; H, 10.31; N, 4.94. Found: C, 84.85; H, 10.20; N, 4.82.

**5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole-3,8,13-tricarbaldehyde (10).** Compound **9** (1.360 g, 1.60 mmol) was dissolved in dry DCM (10.0 mL) and cooled to 0 °C under an N<sub>2</sub> atmosphere. SnCl<sub>4</sub> (0.57 mL, 5.20 mmol, 3.25 equiv) was added dropwise with stirring, followed by slow addition of dichloromethyl methyl ether (0.47 mL, 5.20 mmol, 3.25 equiv).

After 30 min at 0 °C the solution was warmed to room temperature and stirred for another 36 h. The dark solution was poured into a separatory funnel filled with 10 g of ice and shaken thoroughly. The layers were separated, and the aqueous phase was diluted with water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with water (2 × 50 mL) and saturated aq NaHCO<sub>3</sub> (2 × 50 mL), diluted with ether (75 mL), and washed with brine (3 × 50 mL). The solution was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvents were removed under reduced pressure to give the crude product as a dark oil. Purification by flash chromatography (silica gel, hexane/EtOAc = 8:1) gave a deep-red solid (0.83 g, 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 10.13 (s, 3H), 8.66 (s, 3H), 7.97 (d,  $J = 8.8$  Hz, 3H), 7.63 (d,  $J = 8.8$  Hz, 3H), 4.80 (t,  $J = 8.2$  Hz, 6H), 1.97 (quin, 6H), 1.31–1.14 (m, 54H), 0.86 (t,  $J = 7.0$  Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 191.6, 144.4, 139.4, 129.5, 125.9, 124.07, 122.7, 110.7, 103.7, 47.2, 31.9, 30.1, 29.6, 29.5, 29.4, 29.32, 29.28, 26.5, 22.7, 14.1; EI-MS ( $m/z$ ) calcd for C<sub>63</sub>H<sub>87</sub>N<sub>3</sub>O<sub>3</sub> 933.67, found 933.9 (M<sup>+</sup>). Elemental Anal. Calcd for C<sub>63</sub>H<sub>87</sub>N<sub>3</sub>O<sub>3</sub>: C, 80.98; H, 9.38; N, 4.50. Found: C, 81.09; H, 9.26; N, 4.35.

**5,10,15-Tridodecyl-3,8,13-tris((*E*)-2-(thiophen-2-yl)vinyl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (15).** Under N<sub>2</sub> atmosphere, *t*-BuOK (561 mg, 5.0 mmol, 5 equiv) was added in a small portion to a solution of **14** (1.173 g, 5.0 mmol, 5 equiv) and **10** (0.934 g, 1.0 mmol) in dry THF (60 mL). After adding *t*-BuOK, the reaction solution turned red. The mixture was stirred at 65 °C overnight. After cooling to room temperature, the reaction solution was diluted with DCM (60 mL) and washed with water (2 × 60 mL) and brine (2 × 60 mL), then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents, the residue was purified by column chromatography (silica gel, hexane/CHCl<sub>3</sub> = 4:1 to 3:1) to give the title compound **15** as a yellow solid (1.00 g, 85%). Mp 137–139 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.10 (s, 3H), 7.59 (d,  $J = 7.6$  Hz, 3H), 7.48 (d,  $J = 8.2$  Hz, 3H), 7.26 (d,  $J = 16.4$  Hz, 3H), 7.20 (d,  $J = 5.0$  Hz, 3H), 7.14 (d,  $J = 15.7$  Hz, 3H), 7.10 (d,  $J = 3.2$  Hz, 3H), 7.06–7.04 (m, 3H), 4.67 (t,  $J = 8.2$  Hz, 6H), 1.99 (quin, 6H), 1.29–1.16 (m, 54H), 0.88 (t,  $J = 7.0$  Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 143.70, 140.74, 139.1, 130.0, 128.9, 127.6, 125.1, 123.5, 123.4, 120.8, 120.5, 119.4, 110.6, 103.1, 47.1, 31.9, 30.2, 29.7, 29.6, 29.5, 29.4 26.9, 22.7, 14.1; HR-FAB-MS ( $m/z$ ) calcd for C<sub>78</sub>H<sub>99</sub>N<sub>3</sub>S<sub>3</sub> (M<sup>+</sup>) 1173.7001, found 1173.6952 (error: –4.2 ppm); MALDI-TOF MS ( $m/z$ ) calcd for C<sub>78</sub>H<sub>99</sub>N<sub>3</sub>S<sub>3</sub> 1173.700, found 1174.776 (M + H)<sup>+</sup>. Elemental Anal. Calcd for C<sub>78</sub>H<sub>99</sub>N<sub>3</sub>S<sub>3</sub>: C, 79.74; H, 8.49; N, 3.58; S, 8.19. Found: C, 79.96; H, 8.27; N, 3.35; S, 8.36.

**5,5',5''-(1*E*,1'*E*,1''*E*)-2,2',2''-(5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)trithiophene-2-carbaldehyde (16).** To a three-necked flask were added POCl<sub>3</sub> (0.118 mL, 1.2 mmol) and dry DMF (0.116 mL, 1.5 mmol) dropwise to dry dichloroethane (DCE) (20 mL) at 0 °C with stirring. The mixture was warmed to room temperature, stirred for another 30 min, and cooled back to 0 °C. A cooled solution of **15** (117.5 mg, 0.1 mmol) in DMF (2 mL) was added dropwise over 5 min with stirring. The reaction mixture was heated to 85 °C for 10 h and poured into a stirred solution of brine and crushed ice (30 mL). After 30 min, the whole was extracted with DCM (3 × 30 mL) and the combined organic extracts were washed with brine (30 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. Purification by flash chromatography on silica gel (ethyl acetate/hexane, 1:4) gave the title compound **16** as a red solid (117 mg, 93%). Mp > 350 °C (the sample decomposes when the temperature is higher than 350 °C, and the color of the solid changes from red to black); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.88 (s, 3H), 8.03 (s, 3H), 7.68 (d,  $J = 3.8$  Hz, 3H), 7.62 (d,  $J = 8.8$  Hz, 3H), 7.48 (d,  $J = 8.8$  Hz, 3H), 7.30 (d,  $J = 15.8$  Hz, 3H), 7.19 (d,  $J = 15.8$  Hz, 3H), 7.12 (d,  $J = 3.8$  Hz, 3H), 4.62 (br, 6H), 1.93 (br, 6H), 1.25–1.12 (m, 54H), 0.85 (t,  $J = 7.5$  Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 182.2, 153.3, 141.0, 138.6, 137.3, 134.4, 127.7, 125.7, 123.0, 121.5, 121.1, 118.1, 110.6, 102.8, 46.9, 31.9, 30.2, 29.72, 29.66, 29.61,

29.5, 29.3, 26.9, 22.7, 14.1; MALDI-TOF MS ( $m/z$ ) calcd for 1257.685, found 1258.737 ( $M^+ + H$ ). Elemental Anal. Calcd for  $C_{81}H_{99}N_3O_3S_3$ : C, 77.28; H, 7.93; N, 3.34; O, 3.81; S, 7.6. Found: C, 77.58; H, 7.84; N, 3.41; S, 7.81.

**2,2',2''-(5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(methan-1-yl-1-ylidene)trimalononitrile (1).** Compound **10** (187 mg, 0.20 mmol) and malononitrile (**11**, 0.08 mL, 1.20 mmol, 6 equiv) were dissolved in DCM (10 mL) under nitrogen atmosphere and then  $TiCl_4$  (0.14 mL, 1.20 mmol, 6 equiv) and pyridine (0.20 mL, 2.40 mmol, 12 equiv) were slowly added at room temperature. The reaction mixture was heated to reflux and the reaction was monitored by TLC. After 12 h the reaction was cooled to room temperature and the mixture was poured into water (80 mL) and extracted with DCM (3  $\times$  80 mL). The organic layer was dried over  $Na_2SO_4$ , and the solvent was removed under vacuum. The crude concentrated extract was dropped into a large amount of  $CH_3OH$  to give the title compound as a red precipitate (180 mg, 83%). Mp 179–180 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.93 (s, 3H), 7.95 (d,  $J = 8.8$  Hz, 3H), 7.92 (s, 3H), 7.77 (d,  $J = 8.8$  Hz, 3H), 5.07 (t,  $J = 8.0$  Hz, 6H), 1.80 (quin, 6H), 1.26–1.01 (m, 54H), 0.85 (t,  $J = 7.5$  Hz, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  (ppm) 160.2, 144.7, 139.9, 128.2, 124.7, 123.7, 123.6, 114.7, 114.1, 112.1, 104.3, 77.9, 47.4, 31.8, 29.52, 29.47, 29.37, 29.26, 29.0, 26.4, 22.6, 14.1; HR-FAB-MS ( $m/z$ ) calcd for  $C_{72}H_{87}N_9$  ( $M + H$ )<sup>+</sup> 1078.7163, found 1078.7172 (error: 0.83 ppm); MALDI-TOF MS ( $m/z$ ) found 1078.571. Elemental Anal. Calcd for  $C_{72}H_{87}N_9$ : C, 80.18; H, 8.13; N, 11.69. Found: C, 80.35; H, 8.11; N, 11.51.

**2,2',2''-(1E,1'E,1''E)-2,2',2''-(5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)tribenzo[d]thiazole (2).** Under  $N_2$  atmosphere, potassium *tert*-butoxide (100 mg, 1.125 mmol, 9 equiv) was added in portion to a solution of diethyl (benzo[d]thiazol-2-yl)methylphosphonate **12** (178 mg, 0.625 mmol, 5 equiv) and **10** (117 mg, 0.125 mmol) in dry THF (20 mL). After adding potassium *tert*-butoxide, the reaction solution turned red. The mixture was stirred at 65 °C overnight. After cooling to room temperature, the reaction solution was diluted with DCM (30 mL) and the organic layer was washed with water (2  $\times$  30 mL) and brine (2  $\times$  30 mL) and dried over  $Na_2SO_4$ , then the solution was concentrated under reduced pressure. The crude concentrated extract was dropped into a large amount of  $CH_3OH$  to give the title compound as an orange powder (140 mg, 84%). Mp 190–191 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.25 (s, 3H), 8.01 (d,  $J = 8.0$  Hz, 3H), 7.83 (d,  $J = 8.0$  Hz, 3H), 7.74–7.67 (m, 6H), 7.57 (d,  $J = 8.0$  Hz, 3H), 7.49–7.46 (m, 6H), 7.36 (t,  $J = 7.5$  Hz, 3H), 4.77 (br, 6H), 1.99 (br, 6H), 1.29–1.11 (m, 54H), 0.83 (t,  $J = 7.8$  Hz, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  (ppm) 167.6, 154.0, 141.55, 139.2, 138.9, 134.2, 127.4, 126.2, 125.0, 123.1, 122.7, 122.0, 121.8, 121.4, 119.7, 110.8, 103.1, 47.1, 31.9, 30.3, 29.86, 29.77, 29.74, 29.71, 29.66, 29.64, 29.4, 27.0, 14.1; HR-FAB-MS ( $m/z$ ) calcd for  $C_{87}H_{102}N_6S_3$  ( $M + H$ )<sup>+</sup> 1327.7406, found 1327.7387 (error: -1.4 ppm); MALDI-TOF MS ( $m/z$ ) found 1327.793. Elemental Anal. Calcd for  $C_{87}H_{102}N_6S_3$ : C, 78.69; H, 7.74; N, 6.33; S, 7.24. Found: C, 78.86; H, 7.62; N, 6.18; S, 7.16.

**4,4',4''-(1E,1'E,1''E)-2,2',2''-(5,10,15-Tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)tribenzonitrile (3).** Under  $N_2$  atmosphere, *t*-BuOK (200 mg, 2.25 mmol, 9 equiv) was added in a small portion to a solution of diethyl (4-cyanophenyl)methylphosphonate **13** (200 mg, 1.25 mmol, 5 equiv) and **10** (234 mg, 0.25 mmol) in dry THF (30 mL). After adding *t*-BuOK, the reaction solution turned red. The mixture was stirred at 65 °C overnight. After cooling to room temperature, the reaction solution was diluted with DCM (30 mL) and washed with water (2  $\times$  30 mL) and brine (2  $\times$  30 mL), then the organic layer was dried over  $Na_2SO_4$  and concentrated to afford a crude solid. The crude extract was dropped into  $CH_3OH$  to give the title compound as a yellow powder (220 mg, 72%). Mp 200–201 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.30 (s, 3H), 7.73–7.61 (m, 18H), 7.44 (d,  $J = 16.4$  Hz, 3H), 7.13 (d,  $J = 16.4$  Hz, 3H), 4.89 (t,  $J = 7.5$  Hz,

6H), 2.05 (quin, 6H), 1.26–1.12 (m, 54H), 0.86 (t,  $J = 7.0$  Hz, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  (ppm) 142.4, 141.3, 139.2, 133.7, 132.5, 128.5, 126.5, 124.3, 123.5, 121.5, 121.3, 119.1, 110.9, 110.0, 103.4, 47.2, 31.9, 30.1, 29.7, 29.64, 29.61, 29.58, 29.47, 29.3, 26.9, 22.7, 14.1; HR-FAB-MS ( $m/z$ ) calcd for  $C_{87}H_{102}N_6$  ( $M^+$ ) 1230.8166, found 1230.8187 (error: 1.7 ppm); MALDI-TOF MS ( $m/z$ ) found 1232.139. Elemental Anal. Calcd for  $C_{87}H_{102}N_6$ : C, 84.83; H, 8.35; N, 6.82. Found: C, 84.79; H, 8.27; N, 6.67.

**2,2',2''-(5,5',5''-(1E,1'E,1''E)-2,2',2''-(5,10,15-tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)tris(thiophene-5,2-diyl)tris(methan-1-yl-1-ylidene)trimalononitrile (4).** Compound **16** (377 mg, 0.30 mmol) and malononitrile (**11**, 119 mg, 1.80 mmol, 6 equiv) were dissolved in dry dichloroethane (DCE) (20 mL) under nitrogen atmosphere and then  $TiCl_4$  (0.2 mL, 1.80 mmol, 6 equiv) and pyridine (0.29 mL, 3.60 mmol, 12 equiv) were slowly added at room temperature. The reaction mixture was heated at 85 °C and the reaction was monitored by TLC. After 24 h the reaction was cooled to room temperature and the mixture was poured into water (200 mL) and extracted with DCM. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give the crude product as a red solid. Then 1.0 mL of  $CHCl_3$  was added to dissolve the solid, followed by the addition of 15.0 mL of  $CH_3OH$ . The pure product was precipitated out as a purple-red solid (316 mg, 75%). Mp 219–220 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ , 323 K)  $\delta$  (ppm) 8.12 (s, 3H), 7.72–7.66 (m, 6H), 7.62–7.55 (m, 6H), 7.39 (d,  $J = 15.8$  Hz, 3H), 7.23 (d,  $J = 15.8$  Hz, 3H), 7.16 (d,  $J = 4.4$  Hz, 3H), 4.75 (t,  $J = 7.5$  Hz, 6H), 1.88 (br, 6H), 1.28–1.09 (m, 54H), 0.85 (t,  $J = 7.0$  Hz, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , 323 K)  $\delta$  (ppm) 155.8, 149.8, 141.9, 140.1, 139.1, 136.4, 133.2, 127.9, 126.2, 123.5, 122.2, 121.9, 117.8, 114.4, 113.8, 111.2, 103.7, 75.5, 47.2, 31.9, 29.8, 29.7, 29.59, 29.57, 29.5, 29.28, 29.26, 26.7, 22.6, 14.0; HR-FAB-MS ( $m/z$ ) calcd for  $C_{90}H_{99}N_9S_3$  ( $M + H$ )<sup>+</sup> 1402.7264, found 1402.7224 (error: -2.9 ppm); MALDI-TOF MS ( $m/z$ ) found 1402.762. Elemental Anal. Calcd for  $C_{90}H_{99}N_9S_3$ : C, 77.05; H, 7.11; N, 8.99; S, 6.86. Found: C, 77.16; H, 6.98; N, 8.76; S, 6.61.

**2,2',2''-(1E,1'E,1''E)-2,2',2''-(5,5',5''-(1E,1'E,1''E)-2,2',2''-(5,10,15-tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)tris(thiophene-5,2-diyl)tris(ethene-2,1-diyl)tribenzo[d]thiazole (5).** Under  $N_2$  atmosphere, potassium *tert*-butoxide (253 mg, 2.25 mmol, 9 equiv) was added in one portion to a solution of diethyl (benzo[d]thiazol-2-yl)methylphosphonate **12** (357 mg, 1.25 mmol, 5 equiv) and **16** (315 mg, 0.25 mmol) in dry THF (30 mL). After adding potassium *tert*-butoxide, the reaction solution turned red. The mixture was stirred at 85 °C overnight. After cooling to room temperature, the reaction solution was diluted with DCM, then washed with water and brine. The organic layer was dried over  $Na_2SO_4$  and the solution was concentrated under reduced pressure. The crude concentrated extract was dropped into a large amount of  $CH_3OH$  to give the title compound as a red powder (338 mg, 82%). Mp 231–233 °C;  $^1H$  NMR (500 MHz,  $Cl_2CDCDCCl_2$ , 313 K)  $\delta$  (ppm) 8.17 (s, 3H), 7.99 (d,  $J = 8.0$  Hz, 3H), 7.85 (d,  $J = 8.0$  Hz, 3H), 7.67–7.55 (m, 9H), 7.48 (t,  $J = 8.0$  Hz, 3H), 7.37 (t,  $J = 8.0$  Hz, 3H), 7.20–7.15 (m, 12H), 7.04 (d,  $J = 3.65$  Hz), 4.76 (br, 6H), 2.09 (br, 6H), 1.37–1.18 (m, 54H), 0.82 (t,  $J = 7.1$  Hz, 9H);  $^{13}C$  NMR (125 MHz,  $CCl_2CDCDCCl_2$ )  $\delta$  (ppm) 165.8, 154.1, 145.5, 141.2, 139.1, 138.7, 134.5, 131.6, 129.8, 129.6, 128.8, 125.9, 125.7, 124.8, 123.6, 122.7, 121.3, 121.1, 120.5, 119.0, 110.6, 103.6, 47.2, 31.5, 29.7, 29.24, 29.21, 29.20, 29.1, 28.9, 26.6, 22.2, 13.5; HR-FAB-MS ( $m/z$ ) calcd for  $C_{105}H_{114}N_6S_6$  ( $M^+$ ) 1651.7463, found 1651.7460 (error: -0.2 ppm); MALDI-TOF MS ( $m/z$ ) found 1652.788. Elemental Anal. Calcd for  $C_{105}H_{114}N_6S_6$ : C, 76.32; H, 6.95; N, 5.09; S, 11.64. Found: C, 76.22; H, 6.72; N, 4.95; S, 11.56.

**4,4',4''-(1E,1'E,1''E)-2,2',2''-(5,5',5''-(1E,1'E,1''E)-2,2',2''-(5,10,15-tridodecyl-10,15-dihydro-5H-diindolo[3,2- $\alpha$ :3',2'-c]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl)tris(thiophene-5,2-diyl)tris(ethene-2,1-diyl)tribenzonitrile (6).** Under  $N_2$  atmosphere,

potassium *tert*-butoxide (240 mg, 2.0 mmol, 10 equiv) was added in a small portion to a solution of diethyl (4-cyanophenyl)methylphosphonate **13** (254 mg, 1.0 mmol, 5 equiv) and **16** (252 mg, 0.2 mmol) in dry THF (30 mL). After adding potassium *tert*-butoxide, the reaction solution turned red. The mixture was stirred at 85 °C overnight. After cooling to room temperature, the reaction solution was diluted with DCM and washed with water and brine, then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford a crude solid. The crude extract was dropped into CH<sub>3</sub>OH to give the title compound as an orange powder (264.2 mg, 85%). Mp 246–248 °C; <sup>1</sup>H NMR (500 MHz, Cl<sub>2</sub>CDCDCCl<sub>2</sub>, 343 K) δ (ppm) 8.30 (s, 3H), 7.69–7.62 (m, 12H), 7.55 (d, *J* = 8.85 Hz, 6H), 7.32–7.25 (m, 9H), 7.11 (d, *J* = 3.75 Hz, 3H), 7.05 (d, *J* = 3.75 Hz, 3H), 6.91 (d, *J* = 15.75 Hz, 3H), 4.92 (t, *J* = 7.0 Hz, 6H), 2.13 (br, 6H), 1.42–1.21 (m, 54H), 0.87 (t, *J* = 7.0 Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 323 K) δ (ppm) 144.4, 141.6, 141.1, 139.9, 139.2, 132.4, 131.1, 128.9, 128.8, 126.5, 126.0, 125.7, 125.5, 123.7, 121.2,

120.7, 119.3, 118.8, 110.7, 110.5, 103.5, 47.3, 31.8, 30.1, 29.63, 29.58, 29.4, 29.31, 29.26, 29.20, 26.9, 22.6, 13.9; HR-FAB-MS (*m/z*) calcd for C<sub>105</sub>H<sub>114</sub>N<sub>6</sub>S<sub>3</sub> (M + H)<sup>+</sup> 1556.8379, found 1556.8376 (error: –0.2 ppm); MALDI-TOF MS (*m/z*) found 1556.890. Elemental Anal. Calcd for C<sub>105</sub>H<sub>114</sub>N<sub>6</sub>S<sub>3</sub>: C, 81.04; H, 7.38; N, 5.40; S, 6.18. Found: C, 80.93; H, 7.21; N, 5.28; S, 6.34.

**Acknowledgment.** This work is financially supported by the National University of Singapore under MOE AcRF FRC grants R-143-000-444-112, R-143-000-412-112, and R-143-000-403-112.

**Supporting Information Available:** Characterization data of all of compounds and photophysical data of compounds **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.