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Synthesis of Triphenylamine-Cored Dendritic Two-Photon Absorbing Chromophores

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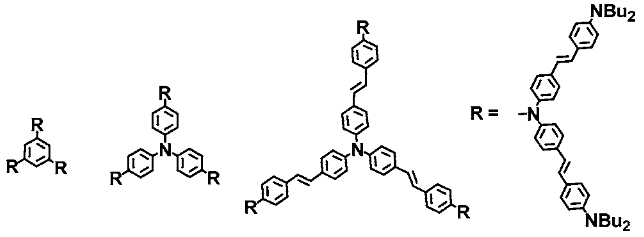
ABSTRACT



A new series of dendritic two-photon absorbing chromophores containing triphenylamine moiety as a core or branching points have been synthesized through a convergent synthetic strategy. One-photon and two-photon optical properties of these molecules were characterized. In the nanosecond time domain, these molecules exhibited large two-photon absorption (TPA) cross sections up to $7.56–12.2 \times 10^{-44}$ s cm^4 at 800 nm, indicating that these molecular structures were viable candidates for various two-photon related applications.

Two-photon absorption (TPA) has potential applications in many important technological areas including optical power limiting,[1] three-dimensional (3-D) storage media,[2] two-photon dynamic therapy,[3] up-converted lasing,[4] and two-photon fluorescence microscopy.[5] The realization of these technological applications relies greatly on the development of organic molecules with large TPA cross sections. Extensive studies have been conducted, and great progress has been made on the relationship between molecular structure and TPA cross section.[6−9] Some basic structural motifs have been revealed to be important regarding TPA molecular construction.[3b,6] Molecular structures containing a π-center with electron donors or acceptors on the terminal sites of the conjugation system are expected to exhibit good TPA

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(1) (a) Enrlich, J. E.; Wu, X. L.; Lee, L. Y. S.; Hu, Z. Y.; Rockel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett*. **1997**, *22*, 1843−1845. (b) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041−1070.

(2) (a) 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.; Röckel, H.; Rumi, M.; Wu, S. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51−54. (b) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843−845.

(3) (a) Prasad, P. N.; Bhawalkar, J. D.; Kumar, N. D.; Lal, M. *Macromol. Symp*. **1997**, *118*, 467−472. (b) Bhawalkar, J. D.; Kumar, N. D.; Zhao, C. F.; Prasad, P. N. *J. Clin. Laser Med. Surg.* **1997**, *15*, 201−204.

(4) (a) Mukherjee, A. *Appl. Phys. Lett*. **1993**, *62*, 3423−3425. (b) Zhao, C. F.; He, G. S.; Bhawalkar, J. D.; Park, C. K.; Prasad, P. N. *Chem. Mater*. **1995**, *7*, 1979−1983.

(5) (a) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73−76. (b) Denk, K.; Svoboda, K. *Neuron* **1997**, *18*, 351−357.

(6) (a) Kannan, R.; He, G. S.; Yuan, L. X.; Xu, F. M.; Prasas, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L. S. *Chem. Mater*. **2001**, *13*, 1896−1904. (b) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J. *Chem. Mater*. **1998**, *10*, 1863−1874.

(7) 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.; Bredas, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9500−9510.

(8) (a) Kim, O. K.; Lee, K. S.; Woo, H. Y.; Kim, K. S.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *Chem. Mater*. **2000**, *12*, 284−286. (b) Albota, M.; Beljonne, D.; Bredas, 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.; Rockel, H.; Rumi, M.; Subramaniam, C.; Webb, W. W.; Wu, I. L.; Xu, C. *Science* **1998**, *281*, 1653−1656.

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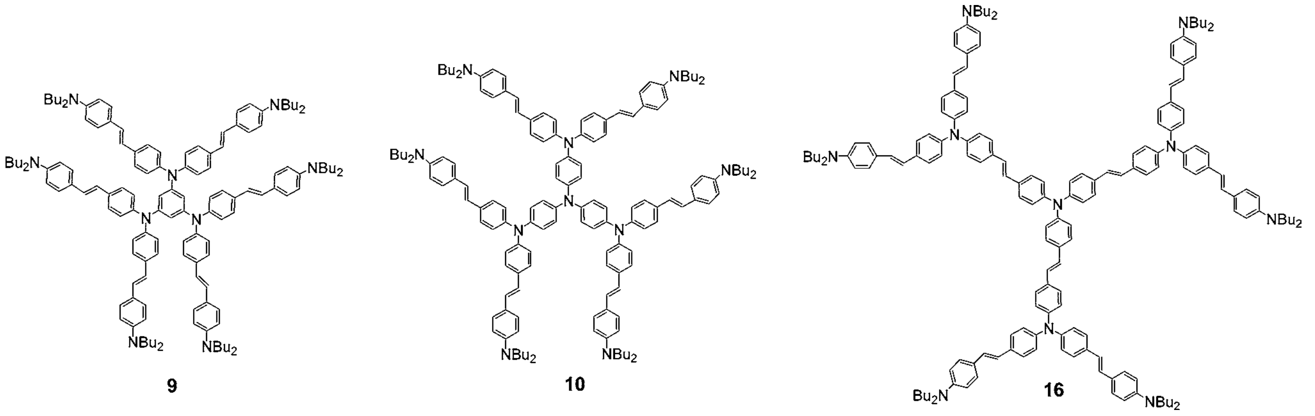

Figure 1. Structures of dendritic TPA molecules **9**, **10**, and **16**.

response.[1a,7] Particularly, the conjugation length, π-electron center, and chemical functional groups at the end of electron conjugation are recognized as three important factors for structure−property optimization.[6b,8] Quadrupolar molecules have received considerable attention in earlier studies,[1a,3b,7] whereas many recent studies have focused on octupolar, multibranched structures whose TPA cross sections have been greatly enhanced as a result of higher molecular symmetry and multidimensionality.[9] Quantum mechanic calculations have further elucidated the newly developed structure−property relationship based on the symmetric and multibranched π-electron conjugation framework.[10]

The concept of multidimensionality has further been extended to the construction of dendritic and polymeric TPA structures.[11] Because of their compact size and exponentially increased number of branches, dendritic structures possess effective geometric sizes less than their corresponding linear polymers and constitute a new class of TPA molecules with drastic increase of both the conjugation length and the density of chromophores achieved in a single molecular structure.[11c] As such, dendritic TPA molecules are expected to display much greater TPA cross sections than their linear or branched counterparts.

In this letter, we report the design, novel synthesis, characterization, and nonlinear optical properties of three representative new dendritic molecular structures having either a phenyl ring or triphenylamine as the π-center with three branches extending outward connected by phenylenevinylene units (Figure 1). The triphenylamine moiety is carefully chosen and intensely employed in each structure as either the core or branching points, since triphenylamine has been shown to be a good framework in enhancing nonlinear responses.[12] Because triphenylamine displays good coplanarity of the central nitrogen and the three surrounding carbon atoms connecting to it, the triphenylamine unit can maintain uninterrupted conjugation between central nitrogen lone pair electrons and the arms,[13] as well as function as a strong electron donor to the conjugation system. The peripherally substituted amino groups further modulate the solubility of the molecule and provide more electron density to the structure. Their one-photon optical properties were characterized by UV−vis and fluorescent emission, and their TPA cross sections were determined using nonlinear optical transmission[14] and two-photon induced fluorescent emission measurements.

The synthesis of dendritic structures **9**, **10**, and **16** was accomplished using convergent strategy in which the dendron/branch molecule **8** was first synthesized and then coupled with different central units. Central units include tribromobenzene, tris(4-bromophenyl)amine, or tribromo species **15** (Scheme 1). Heck coupling reaction and Horner−Wittig reaction were extensively utilized to construct the trans double bond in each phenylenevinylene conjugation unit. Palladium-catalyzed amination was employed for carbon−nitrogen bond construction. The branch molecule **8** was prepared from diphenylamine **1**, which was protected by benzyol chloride.[15] The resulting species **2** was brominated

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(9) (a) Kannan, R.; He, G. S.; Lin, T. C.; Prasad, P. N.; Vaia, R. A.; Tan, L. S. *Chem. Mater*. **2004**, *16*, 185−194. (b) Chung, S. J.; Kim, K. S.; Lin, T. C.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741−10745. (c) Yan, Y. X.; Tao, X. T.; Sun, Y. H.; Wang, C. K.; Xu, G. B.; Yang, J. X.; Ren, Y.; Zhao, X.; Wu, Y. Z.; Yu, X. Q.; Jiang, M. H. *J. Mater. Chem*. **2004**, *14*, 2995−3000. (d) Varnavski, O.; Samuel, I. D. W.; Palsson, L. O.; Beavington, R.; Burn, P. L.; Goodson, T. *J. Chem. Phys.* **2002**, *116*, 8893−8903.

(10) (a) Zyss, J. *J. Chem. Phys.* **1993**, *98*, 6583−6599. (b) Zyss, J.; Ledoux, I. *Chem. Rev*. **1994**, *94*, 77−105.

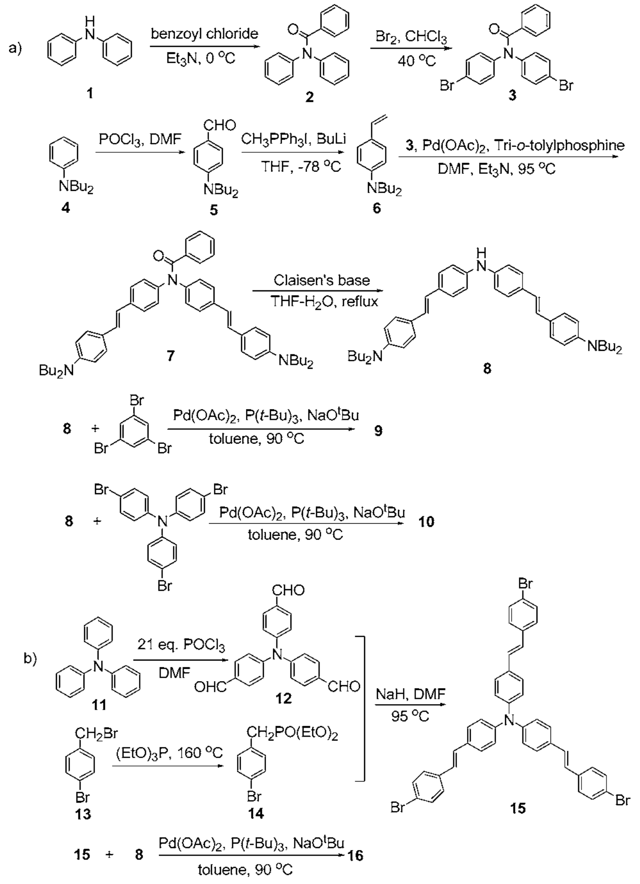
(11) (a) Cho, B. R.; Piao, M. J.; Son, K. H.; Lee, S. H.; Yoon, S. J.; Jeon, S. J.; Cho, M. *Chem. Eur. J*. **2002**, *8*, 3907−3916. (b) Hua, J. L.; Li, B.; Meng, F. S.; Ding, F.; Qian, S. X.; Tian, H. *Polymer* **2004**, *45*, 7143−7149. (c) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A. *J. Phys. Chem. B* **2003**, *107*, 7540−7543. (d) Ranasinghe, M. I.; Varnavski, O. P.; Pawlas, J.; Hauck, S. I.; Louie, J.; Hartwig, J. F.; Goodson, T. *J. Am. Chem. Soc.* **2002**, *124*, 6520−6521.

(12) (a) Lee, H. J.; Sohn, J.; Hwang, J.; Park, S. Y.; Choi, H.; Cha, M. *Chem. Mater*. **2004**, *16*, 456−465. (b) Yan, Y. X.; Tao, X. T.; Sun, Y. H.; Xu, G. B.; Wang, C. K.; Yang, T. X.; Zhao, X.; Wu, Y. Z.; Ren, Y.; Jiang, M. H. *Mater. Chem. Phys.* **2005**, *90*, 139−143.

(13) (a) Wang, X. M.; Wang, D.; Zhou, G. Y.; Yu, W. T.; Zhou, Y. F.; Fang, Q.; Ji, M. H. *J. Mater. Chem*. **2001**, *11*, 1600−1605. (b) Lupton, J. M.; Sameul, I. D.; Burn, P. L.; Mukamel, S. *J. Phys. Chem. B* **2002**, *106*, 7647−7653. (c) Yang, J. S.; Chiou, S. Y.; Liau, K. L. *J. Am. Chem. Soc.* **2002**, *124*, 2518−2527. (d) Sander, R.; Stumpflen, V.; Wendorff, J. H.; Greiner, A. *Macromolecules* **1996**, *29*, 7705−7708.

(14) He, G. S.; Yuan, L. X.; Cheng, N.; Bhawalkar, J. D.; Prasad, P. N.; Brott, L. L.; Clarson, S. J.; Reinhardt, B. A. *J. Opt. Soc. Am. B* **1997**, *14*, 1079−1087.

Scheme 1: Synthesis of Dendritic Molecules **9**, **10**, and **16**



in the presence of bromine in chloroform at 40 °C [16] to afford **3** in 95% yield for further Heck coupling reactions. The 4-dibutylaminostyrene **6** was prepared in two steps from *N*,*N*′-dibutylaminobenzene **4** via the Vilsmeier reaction to yield the aldehyde **5**, followed by Wittig reaction with methyltriphenylphosphine iodide. Heck coupling reaction of **3** and **6** produced **7** in 85% yield. Compound **7** was hydrolyzed in Claisen's base[17] in $\text{THF}-\text{H}_2\text{O}$ to yield the secondary amine as the branch molecule **8**. Finally, the dendritic structures **9** and **10** were synthesized in high yields (95% and 91%) through palladium-catalyzed amination[18] of the branch molecule **8** with 1,3,5-tribromobenzene and tris-(4-bromophenyl)amine, respectively.

To construct molecule **16** (Scheme 1b), a more complex central unit (**15**) was employed using the same strategy. The tris(4-formylphenyl)amine **12** was prepared in 35% yield from triphenylamine **11** under Vilsmeier conditions.[19] The resulting compound **12** further underwent the Horner−Wittig reaction with **14** to furnish the core species **15** in 39% yield. Reaction of **15** with the branch molecule **8** under palladium-catalyzed conditions afforded the species **16** in 57% yield. All structures were carefully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry.[20]

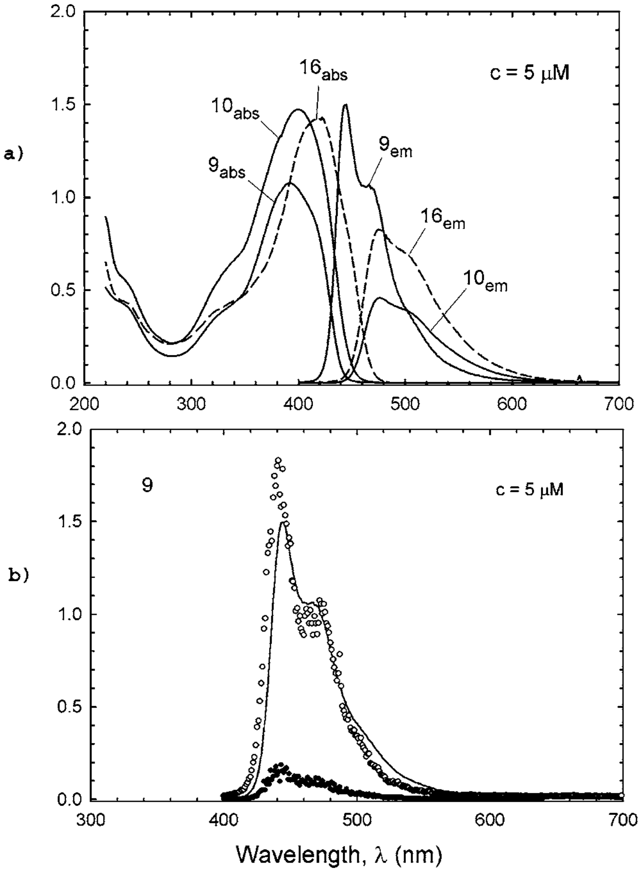


Figure 2. (a) One-Photon absorption and fluorescent emission of **9**, **10**, and **16** in THF. (b) One-photon (solid line) and two-photon (660 nm, filled circles; 800 nm, open circles) emission of **9**.

One-photon absorption and one-photon fluorescent emission spectra of molecule **9**, **10**, and **16** are shown in Figure 2a. The concentrations of **9**, **10**, and **16** used for optical measurement were 5×10^{-6} M in THF. The UV−vis peak absorption maximum occurred at 392, 400, and 420 nm, respectively, for molecule **9**, **10**, and **16**. This systematic shift in peak absorbance wavelength can be explained using one- or two-dimensional quantum well model where longer conjugation length usually leads to smaller energy gap between HOMO and LUMO. This systematic shift supports the notion that triphenylamine moiety serves as π-electron bridge for extended electron conjugation within the molecules.[11c,13d]

The emission peak maximum of molecule **9** appears at 440 nm, while that of molecules **10** and **16** appears at 476 nm. In Figure 2a, the relative emission peak heights of the three molecules reflect their fluorescent emission quantum yields (*Q*), as calibrated using dye molecules with well-established fluorescent emission quantum yields such as Rhodamine-6G. The wavelength of one-photon absorption

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(15) Horner, L.; Singer, R. J. *Tetrahedron Lett.* **1969**, *10*, 1545−1547.

(16) Calo, V.; Ciminale, F.; Lopez, L.; Todesco, P. E. *J. Chem. Soc. C* **1971**, *21*, 3652−3653.

(17) Rosenfeld, J. *Anal. Lett.* **1977**, *10*, 917−930.

(18) (a) Louie, J.; Hartwig, J. F.; Fry, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 11695−11696. (b) Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861−2873. (c) Meier, H.; Hanold, N.; Kalbitz, H. *Synthesis* **1997**, *3*, 276−8.

(19) Lai, G.; Bu, X. R.; Santos, J.; Mintz, E. A. *Synlett* **1997**, 1275−1276.

Table 1. Linear and Nonlinear Optical Properties of Dendritic Molecules **9**, **10**, and **16**

compd	λ_{abs} (nm)	λ_{em} (nm)	quantum yield (Q)	$\sigma \times 10^{-44}$ (s cm^4) 660 nm	$\sigma \times 10^{-44}$ (s cm^4) 800 nm
9	392	440	0.48	0.54	7.56
10	400	476	0.15	0.32	12.2
16	420	476	0.28	0.38	9.61

peak maximum (λ_{abs}), one-photon emission peak maximum (λ_{em}), and one-photon emission quantum yield (Q) of the three molecules are summarized in Table 1.

Also shown in Table 1 are TPA cross sections (σ, ±15% uncertainty) of the three molecules at 660 and 800 nm using a Quanta-Ray MOPO-730 laser. At 660 nm, the TPA cross sections are 0.54×10^{-44}, 0.32×10^{-44}, and 0.38×10^{-44} s cm^4 for molecules **9**, **10**, and **16**, respectively, as determined using transmission two-photon absorption measurements.[14] At 800 nm, the TPA cross sections were obtained using two-photon induced fluorescent emission.[21] A typical spectra of two-photon induced fluorescent emission of molecule **9** is shown in Figure 2b. The filled circles depict the two-photon emission spectrum obtained with 660 nm excitation, and open circles depict that obtained with 800 nm excitation. The corresponding one-photon emission spectrum (solid curve) is also shown in Figure 2b for comparison. The two-photon and one-photon emission spectra resemble each other in both shape and wavelength, indicating a similar emission relaxation path for the two very different excitation mechanisms.[22] The values of σ at 800 nm are 7.56×10^{-44}, 12.2×10^{-44}, and 9.61×10^{-44} s cm^4 for molecule **9**, **10**, and **16**, respectively. These are among the best values ever reported.[6a,8a,9a] It is interesting to note that the TPA cross sections have increased 14-, 38-, and 25-fold for molecules **9**, **10**, and **16**, respectively, when the excitation wavelength is changed from 660 to 800 nm. The dramatic change in TPA cross sections cannot be explained solely on the basis of resonance effect, since the corresponding one-photon absorbance has increased only by a factor of 3−4 when the wavelength is changed from 330 to 400 nm. This seems to suggest that the two-photon transition may have a narrow intrinsic band profile that does not follow the absorption contour of its one-photon counterpart. Also, it is unclear at present why molecule **10** has a larger TPA cross-section than **9** and **16**. This structure−function relationship is the subject of our current investigation.

In summary, a new series of dendritic two-photon absorbing molecules have been carefully designed, synthesized, and characterized. The preliminary studies show that these new molecules have very large TPA cross sections up to 12.2×10^{-44} s cm^4 (molecule **10**). Given the feasible synthetic routes and superior two-photon absorption properties shown in this communication, it is conceivable that molecules with even larger TPA cross sections could be developed based on the triphenylamine molecular platform. This could further pave the way for the development of new nonlinear optical devices based on two-photon absorption.

Supporting Information Available: Synthetic procedures and NMR characterization of all compounds in Scheme 1 (^{1}H and ^{13}C NMR data and spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) **General Procedure for Palladium-Catalyzed Amination for Compounds 9, 10, and 16.** To a Schlenk tube equipped with a Teflon valve were added **8** (258.6 mg, 0.412 mmol), tris(4-bromophenyl)amine (60.3 mg, 0.125 mmol), Pd(OAc)$_2$ (1.7 mg, 0.007 mmol), tri-*tert*-butyl phosphine (3 mg, 0.014 mmol), and anhydrous toluene (4 mL). The reaction mixture was degassed and refilled with nitrogen three times. The tube was sealed and heated at 95−110 °C for 2 days. The reaction mixture was poured into water and extracted with ethyl acetate. The crude product was purified by column chromatography (silica gel, hexane/methylene chloride = 1:6) to give the pure product as a greenish powder (252.1 mg, yield 95%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 7.40−7.35 (m, 24 H), 7.12 (m, 12 H), 6.98 (d, 6 H), 6.88 (d, 6 H), 6.66 (s, 12 H), 6.59 (s, 3 H), 3.35 (t, 24 H), 1.65 (m, 24 H), 1.43 (m, 24 H), 1.02 (t, 36 H); ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ 149.3, 148.2, 146.0, 133.4, 127.9, 127.3, 125.1, 124.3, 123.3, 112.1, 51.1, 29.9, 20.8, 14.2; *m/z* 1955.6 (M$^+$, 100%). Anal. Calcd for C$_{138}$H$_{171}$N$_9$: C, 84.74; H, 8.81; N, 6.45. Found: C, 84.50; H, 8.86; N, 6.12. Compound **10**: ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 7.43−7.41 (m, 24 H), 7.12−6.93 (m, 36 H), 6.70−6.68 (m, 12 H), 3.36 (t, 24 H), 1.65 (m, 24 H), 1.44 (m, 24 H), 1.05 (t, 36 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 148.0, 133.1, 129.6, 127.9, 127.2, 125.8, 124.2, 123.7, 112.2, 51.3, 32.3, 20.8, 14.5; *m/z* 2122.6 (M$^+$, 100%). Anal. Calcd for C$_{150}$H$_{180}$N$_{10}$: C, 84.86; H, 8.55; N, 6.60. Found: C, 84.48; H, 8.62; N, 6.51. Compound **16**: ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 7.47−7.41 (m, 36 H), 7.13−6.89 (m, 42 H), 6.68 (d, 12 H), 3.35 (t, 24 H), 1.62 (m, 24 H), 1.43 (m, 24 H), 1.02 (t, 36 H); ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ 148.3, 146.2, 133.7, 132.9, 132.3, 128.0, 127.6, 127.1, 124.9, 124.1, 12.32, 112.1, 54.1, 29.9, 20.7, 14.2; *m/z* 2428.9 (M$^+$, 100%). Anal. Calcd for C$_{174}$H$_{198}$N$_{10}$: C, 86.02; H, 8.21; N, 5.77. Found: C, 85.86; H, 8.30; N, 5.43.

(21) The TPA cross section at 800 nm was evaluated using the following equation: $\sigma_{800} = \sigma_{660} \times (R_{800}/R_{660}) \times (\lambda_{660}/\lambda_{800})$, where σ_{660} is the TPA cross section at 660 nm obtained using transmission measurements, R_i is the ratio of two-photon emission peak height to the square of the excitation light intensity at the corresponding wavelength, and the wavelength ratio ($\lambda_{660}/\lambda_{800}$) is for correction of photon energy at different wavelengths. The special excitation beam profiles at the two wavelengths were the same.

(22) Yan, Y. S.; Tao, X. T.; Sun, Y. H.; Xu, G. B.; Wang, C. K.; Yu, X. Q.; Jiang, M. H. *Mater. Sci. Eng. B* **2004**, *113*, 170−174.