π-Conjugated Dendritic Nanosized Chromophore with Enhanced Two-Photon Absorption

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A novel π-conjugated dendritic nanosized chromophore, 1,3,5-tris(7,12-bis(2-{4-[2-(7-diphenylamino-9,9-dibutyl-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-5,5 ,10,10,15,15-hexabutyl-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluoren-2-yl)-benzene (**3**), was synthesized and characterized, together with its corresponding one- and three-branched units. Two-photon absorption (TPA) spectra for these chromophores were measured by the nonlinear transmission spectral technique which utilizes a femtosecond white-light continuum. The TPA peak value for the dendritic chromophore is 5.47×10^{-20} cm^4/GW, 15.6 times larger than that for the one-branched dipolar chromophore (0.35×10^{-20} cm^4/GW), [9,9-dibutyl-7-(2-{4-[2-(9,9-dibutyl-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-9*H*-fluoren-2-yl]-diphenylamine (**1**). The three-branched chromophore, 2,7,12-tris(2-{4-[2-(9,9-dibutyl-7-diphenylamino-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-5,5,10,10,15,15-hexabutyl-10,15-dihydro-5H-diindeno[1,2-a;1′,2′-c]fluorene (**2**) has a TPA peak value of 2.28×10^{-20} cm^4/GW, 6.5 times as large as that for compound **1**. The enhanced two-photon absorption found in these two multibranched chromophores is attributed to the fact that the dendritic or the three-branched chromophore has both an extended π-conjugated system and an increased intramolecular charge redistribution compared to the one-branched chromophore. With use of comparable structure unit based concentrations, the two-photon excited (TPE) fluorescence intensity for this dendritic chromophore (0.0033 M solution) was found to be enhanced by a factor of 2.9 compared to that for chromophore **1** (0.02 M solution), which would offer a major advantage in TPE fluorescence related applications.

1. Introduction

Over the past decade, two-photon absorption (TPA) has been a subject of numerous research efforts due to its potential applications in photonics and biophotonics,[1−5] such as optical data storage, optical power limiting, three-dimensional fluorescence imaging, and photodynamic therapy. To fully explore these applications, chromophores with large TPA are in great demand. It has been known that a large TPA can be attributed to an extended π-conjugated system and an increased charge transfer within a molecule. Recently, dendrimers have been introduced into the field of organic nonlinear optics due to their well-defined and controllable architectures.[6] Dendritic structures can afford the advantages of increasing the molecular density without causing aggregation and the ease of chemical modification toward different functionalities. Nonconjugated two-photon absorbing dendritic chromophores have been developed by Fréchet and co-workers.[6a,b] In this work, a linear enhancement in two-photon absorption was found in going from a generation to next. However, with use of a π-conjugated dendritic architecture, a significant increase in two-photon absorption may be expected. So far, a few types of π-conjugated dendrimers with rigid structures have been reported.[7] Among them, Pei and co-workers reported synthesis of dendrimers containing 10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (truxene), a polycyclic aromatic system with C_3 symmetry.[7c] The structure of truxene involves three fluorenes sharing a central benzene ring. Not surprisingly, truxene π-system will have properties similar to the fluorene π-system, which has been proven to be an efficient building block for chromophores

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with high two-photon absorptivities, as well as excellent thermal and photochemical stabilities.[8] Unlike fluorene, which can only be used for building one-dimensional quadrupolar chromophores, the truxene can readily be functionalized in three directions in space to serve as an excellent building block for octupolar or dendritic chromophores.

One- and three-branched chromophores (**1** and **2**) and a dendritic chromophore (**3**) are specially designed; their structures are shown in Figure 1. Diphenylamine was chosen as an electron donor in our design strategy and butyl groups were introduced for increasing chromophore solubility in organic solvents. We report here a new approach to the development of highly soluble π-conjugated dendritic chromophores with large two-photon absorption. The linear and two-photon absorption properties, as well as the one- and two-photon excited fluorescence properties, for these chromophores were investigated.

2. Results and Discussions

2.1. Synthesis. The synthetic routes for these targeted chromophores are shown in Scheme 1. Compounds **2**−**3** were obtained by multifold Heck reactions of aryl iodides with an excess amount of vinylated intermediate (**5**) in 80−85% yields. Compound **5** was prepared via Horner-Emmons Wittig coupling reaction between 9,9-dibutyl-7-diphenylamino-9*H*-fluorene-2-carbaldehyde (**4**) and (4-vinyl-benzyl)-diethyl phosphonate using sodium *tert*-butoxide as a base in THF at 0 °C. Compound **7** was obtained by 3-fold electrophilic iodination of compound **6** using controlled amounts of iodine and iodic acid. Friedel−Crafts acylation of compound **6** produced compound **8** with 80% yield. Two-fold iodination of compound **8** in the presence of bis(trifluoroacetoxy) iodobenzene and iodine at room temperature afforded compound **9** in 85% yield. Cyclotrimerization[9] of compound **9** by using a large excess of $SiCl_4$ (20 equiv) in toluene/ethanol (1/4) yielded compound **10** (91%). For comparison purposes, the one-branched compound (**1**) was also synthesized by Heck reaction between 2-bromo-9,9-dibutyl-9*H*-fluorene and compound **5**. All new compounds have been fully characterized by a variety of spectroscopic techniques including ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, HRMS, and elemental analysis.

2.2. Linear Absorption and Emission. Linear absorption spectra for compounds **1**−**3** were recorded on a Shimadzu UV-3101 PC spectrophotometer using chloroform dilute solutions (10^{-5} M for **1**, 3.3×10^{-6} M for **2**, and 1.67×10^{-6} for **3**). One-photon excited (OPE) fluorescence was measured in $CHCl_3$ dilute solutions (1×10^{-6} M for **1**, 3.3×10^{-7} M for **2**, and 1.67×10^{-7} for **3**) by using a Jobin-Yvon Fluorolog FL-311 spectrofluorometer. The linear absorption and emission spectra for compounds **1**−**3** in $CHCl_3$ are shown in Figure 2. For linear fluorescence quantum efficiency measurements in solution, an external reference of Coumarin 152 ($\phi_f = 0.21$ in ethanol) was used.[10] The fluorescence lifetimes for chromophores **1**−**3** were measured by utilizing a high-speed streak camera with a resolution of 20 ps.

The linear absorption and emission properties for these chromophores are listed in Table 1. Chromophore **3** exhibits a red-shifted absorption band compared to chromophore **1** due to its extended π-conjugated system. As the linear absorption bands for these three chromophores are around 400 nm, their two-photon absorption bands are expected to be centered around 800 nm. All of the three chromophores are highly fluorescent and their fluorescence quantum yields are in the range of 0.73−0.78 (0.78 for **1,** 0.74 for **2**, and 0.73 for **3**). The dendritic chromophore **3** exhibits a small decrease in fluorescence lifetime probably due to interbranch interactions in the excited state.

2.3. Two-Photon Absorption. TPA spectra were obtained by using a single femtosecond white-light continuum generation and the direct degenerate-TPA measurement technique. The pump source for continuum generation is a focused ultrashort pulsed laser beam from a Ti:sapphire laser/amplifier system (model CPA-2010 from Clark-MXR). The continuum was generated in a 10-cm heavy water cell pumped by ∼775-nm and ∼160-fs laser pulses (180 μJ) at 1-kHz repetition rate. A reference chromophore (AF350) was chosen for TPA spectra measurements.[11] Under these conditions, the peak value for AF350 was 0.8×10^{-20} cm^4/GW (206 GM at 770 nm). The concentrations for **1**, **2**, and **3** were 0.02, 0.00667, and 0.00333 M in chloroform, respectively. The underlying principle and technical details of this TPA spectral measurement technique have been previously described.[11,12]

The measured TPA spectra for these chromophores are shown in Figure 3, and the TPA peaks and peak values are listed in Table 1. As shown in Figure 3, the dendritic

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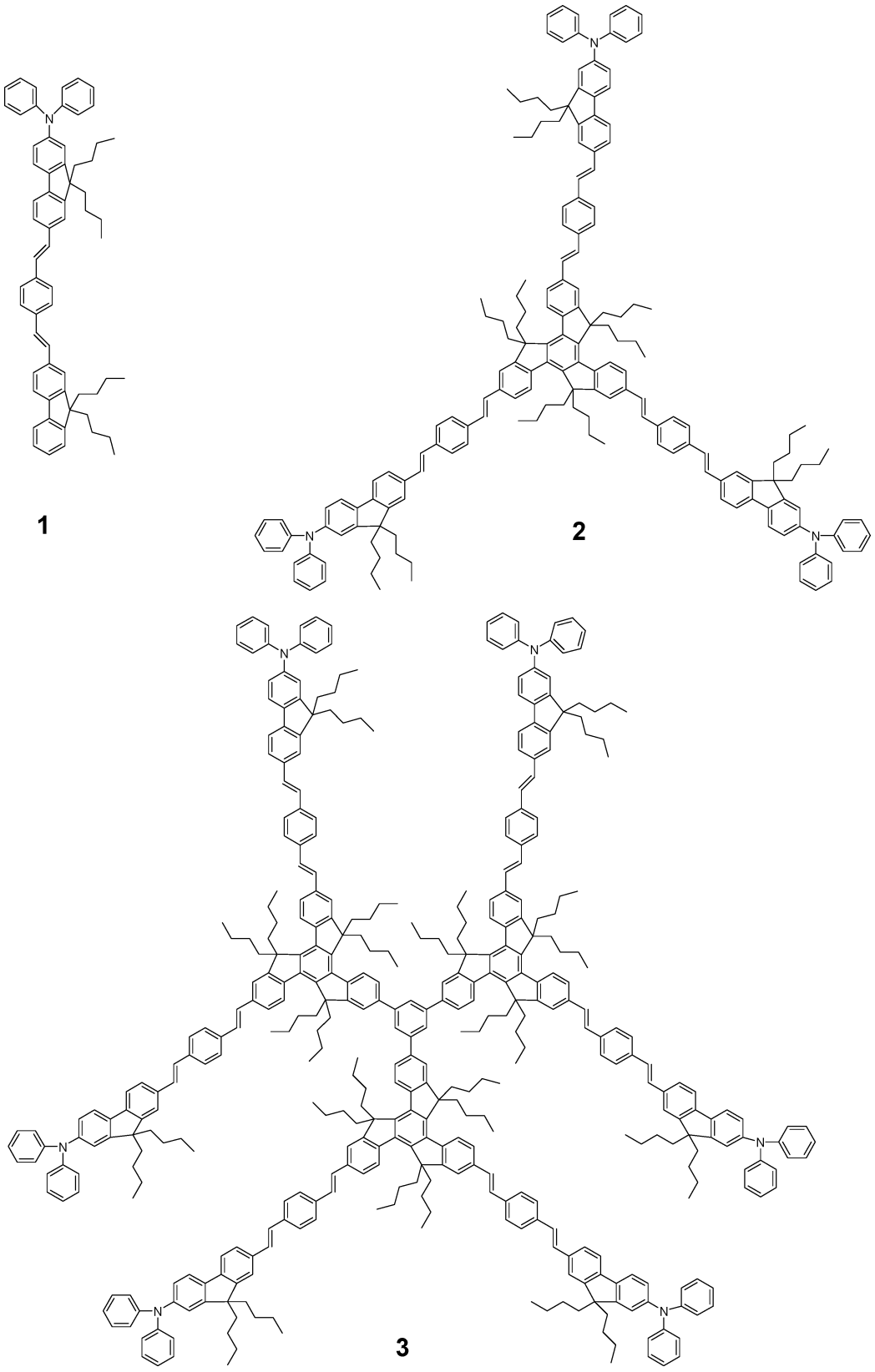
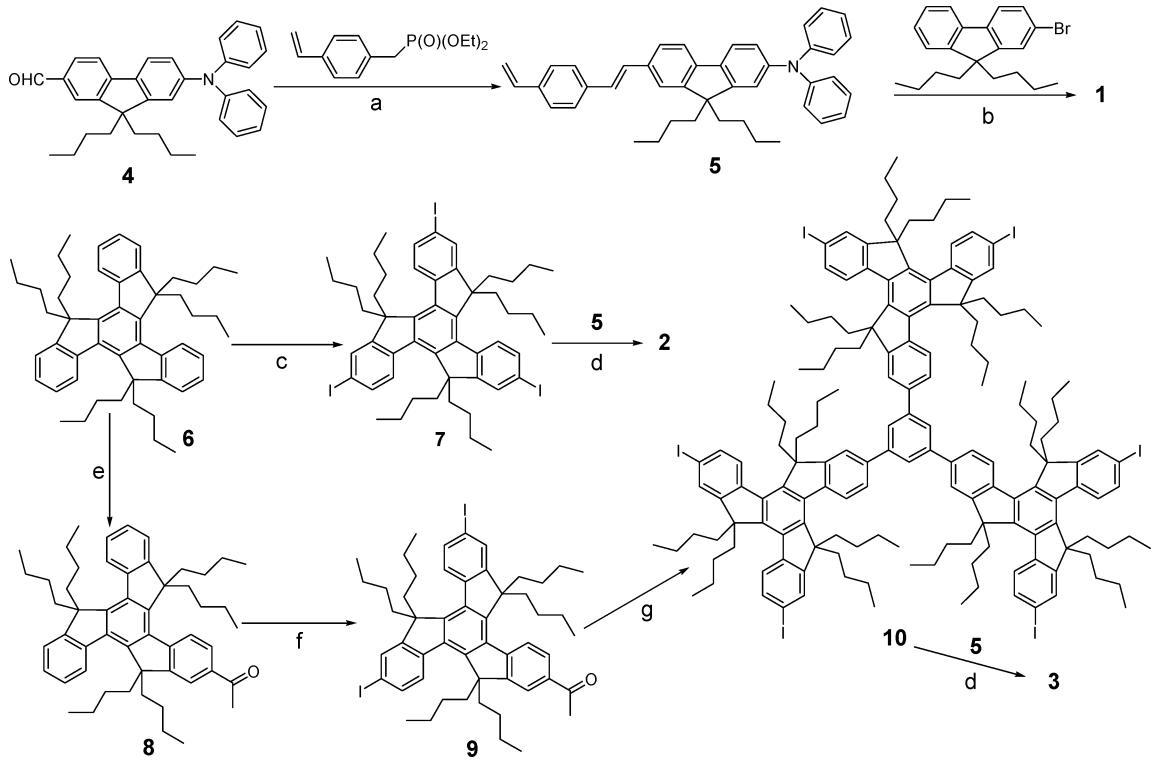


Figure 1. Molecular structures of targeted chromophores.

chromophore **3** has extremely large two-photon absorption around 800 nm in a femtosecond regime (5.47×10^{-20} cm^4/GW). Hence, one may find in Figure 3 that the TPA cross-section peak value increases by a factor of 6.5 and 15.6 when going from **1**, to **2** and **3**, respectively. Considering that compounds **1**, **2**, and **3** have one, three, and six branches, respectively, there is a 160% TPA enhancement on going from **1** to **3,** a 117% enhancement on going from **1** to **2**, and a 20% enhancement on going from **2** to **3**. This dramatic enhancement in TPA can be attributed to the extended π-conjugated system in compounds **2** and **3** as we expected. At the same time, compounds **2** and **3** show red-shifted two-

Scheme 1[a]



[a] Reaction conditions: (a) t-BuONa, THF, 0−20 °C, 12 h, 90%; (b) $Pd(OAc)_2$, Et_3N, P(*o*-tolyl)$_3$, CH_3CN, 82 °C, 24 h, 90%; (c) I_2, HIO_3, H_2SO_4−CH_3COOH−H_2O, 70 °C, 12 h, 93%; (d) $Pd(OAc)_2$, K_2CO_3, NBu_4Br, DMA, 140 °C, 48 h, 85% for **2**, 80% for **3**; (e) $AlCl_3$, $(CH_3CO)_2O$, CH_2Cl_2, 0−20 °C, 5 h, 80%; (f) I_2, $PhI(O_2CCF_3)_2$, CH_2Cl_2, 0−20 °C, 10 h, 85%; (g) $SiCl_4$, Tol/ethanol, 80 °C, 24 h, 91%.

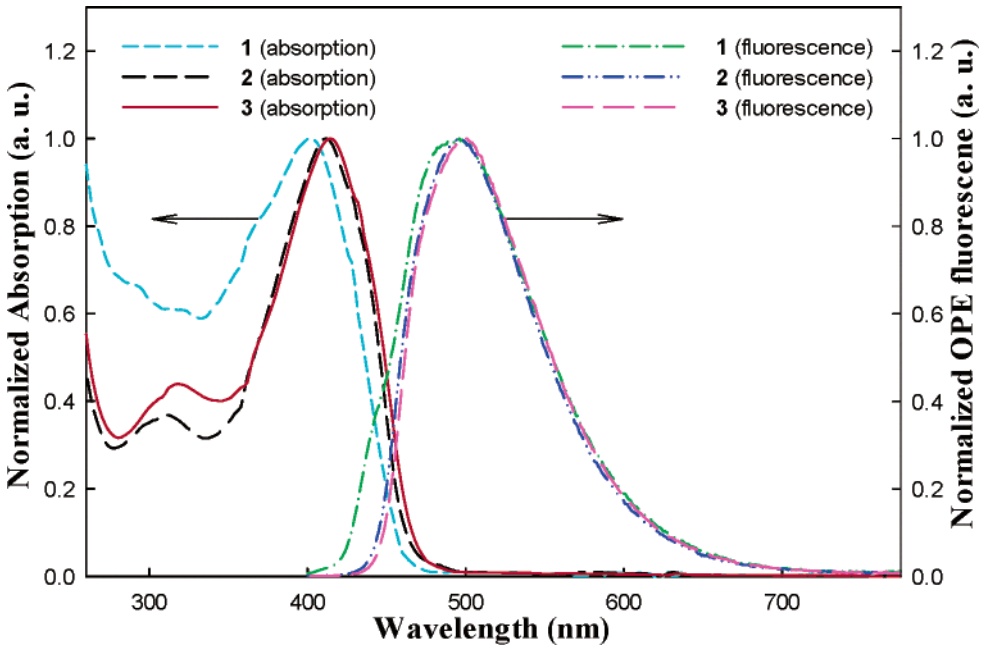


Figure 2. Linear absorption and emission spectra for compounds **1**−**3**.

photon absorption bands compared to compound **1,** due to their extended π-conjugated systems.

2.4. Two-Photon Excited Fluorescence. To demonstrate the advantages large two-photon absorbing chromophores would provide, we investigated their relative two-photon excited (TPE) fluorescence intensities using comparable structure unit based concentrations.

The pump source for two-photon excitation was a focused ultra-short pulsed laser beam from a Ti:sapphire laser oscillator/amplifier system like that used for TPA spectra measurements. This beam was focused by an $f = 10$ cm lens, and the solution sample in a fluorimeter cuvette (four optically clear windows) was placed at a fixed distance of ~13.5 cm from the focusing lens. Under these conditions, the intensity for two-photon excitation was in an excitation regime, where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon induced emission (Figure 4). The

Table 1. Photophysical Properties for Chromophores 1−3

	one-photon absorption		one-photon excited fluorescence			two-photon absorption[d]		
compd[a]	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϕ_f[b]	τ[c] (ns)	λ_{max} (nm)	σ_2 (σ_2/n)[e]	σ_2'(GM)
1	402	6.8×10^4	496	0.78	1.40	740	0.35 (0.35)	93.8
2	412	2.77×10^5	497	0.74	1.21	752	2.28 (0.76)	603
3	413	5.76×10^5	497	0.73	1.15	770	5.47 (0.91)	1412

[a] The concentrations of compounds **1**−**3** solutions for linear absorption measurements were 10^{-5}, 3.3×10^{-6}, and 1.67×10^{-6} M, respectively. The concentrations of compounds **1**−**3** solutions for emission measurements were 10^{-6}, 3.3×10^{-7}, and 1.67×10^{-7} M, respectively. The concentrations of compounds **1**−**3** solutions for TPA measurements were 0.02, 0.0067, and 0.0033 M, respectively. All samples were dissolved in $CHCl_3$. [b] Quantum efficiency (ϕ_f) at room temperature was determined with coumarin 152 ($\phi_f = 0.21$ in ethanol) as a reference. [c] Fluorescence lifetime. [d] The estimated uncertainty is ±15%. [e] In unit of 10^{-20} cm^4/GW, $n = 1$ for compound **1**, $n = 3$ for compound **2**, and $n = 6$ for compound **3**.

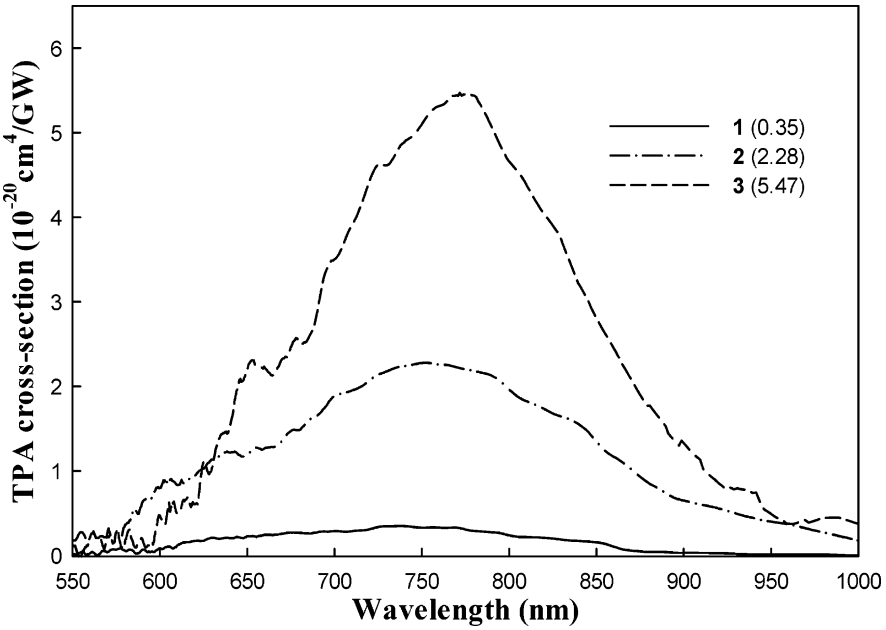


Figure 3. Two-photon absorption spectra for chromophores **1**−**3**.

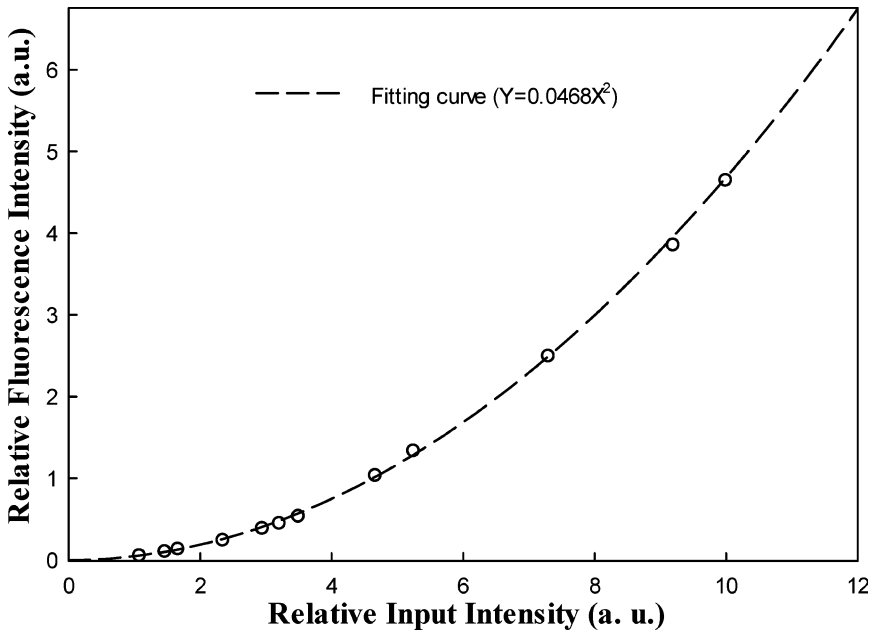


Figure 4. Measured intensity dependence of two-photon excited fluorescence on the relative input intensity of ~775 nm laser pulses for compound **3** solution (6.7×10^{-3} M in $CHCl_3$). The dashed line corresponds to a fitting curve following the square law.

concentrations for **1**, **2**, and **3** were 0.02, 0.00667, and 0.00333 M in chloroform, respectively. The collection of the two-photon excited fluorescence signal was performed by using a HoloSpec CCD-array spectrometer in conjunction with a fiber coupler head.

As shown in Figure 5, the relative TPE fluorescence intensities for **1**, **2**, and **3** are 0.344, 0.810, and 1, respectively. There is a 190% increased emission on going from compound **1** to compound **3** and a 135% increased emission on going from compound **1** to compound **2**. This enhance-

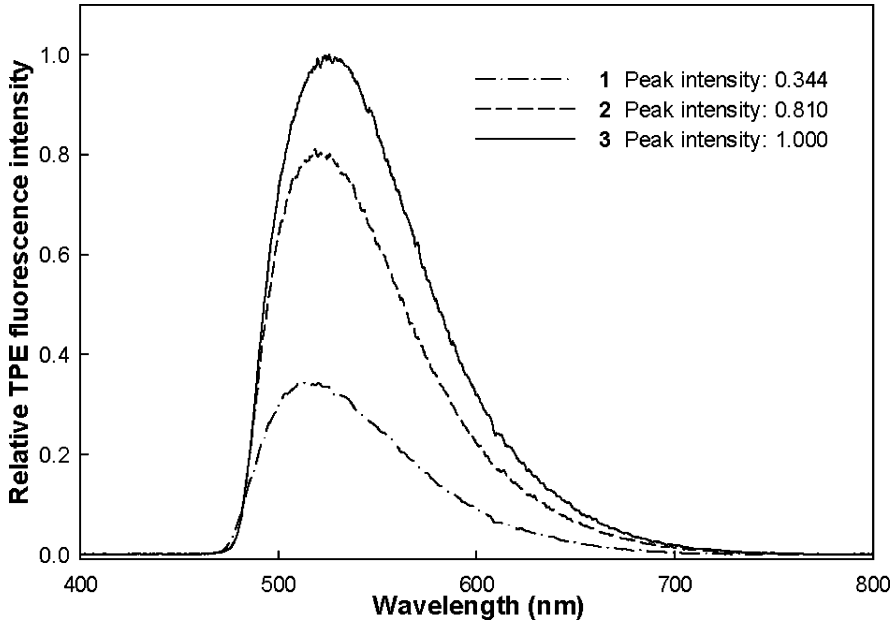


Figure 5. Relative two-photon excited fluorescence spectra for chromophores **1**−**3** (the concentration ratio of **1** to **2** to **3** was 6:2:1).

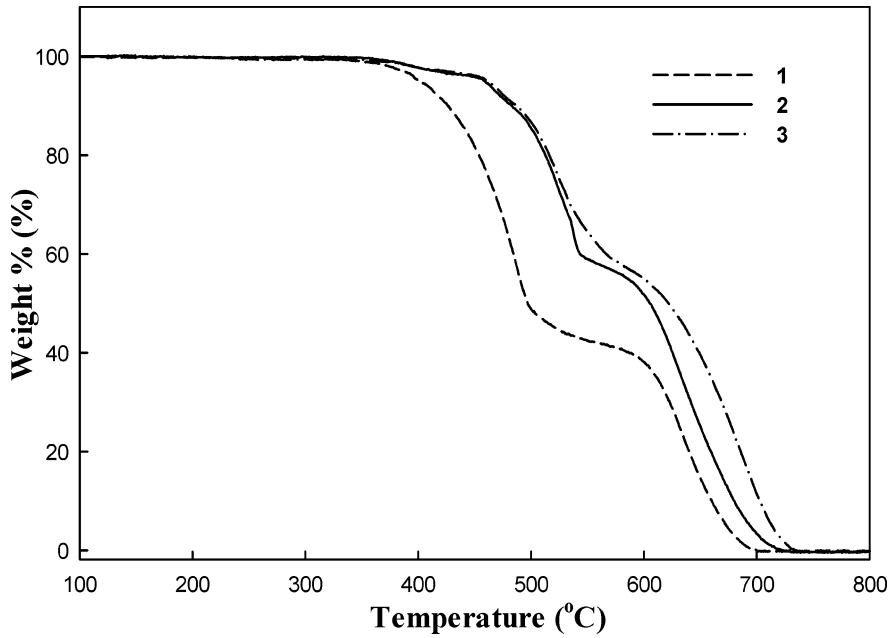


Figure 6. TGA spectra of compounds **1**−**3**, heated from 100 to 800 °C at a rate of 10 °C/min.

ment of TPE emission in the dendritic chromophore (**3**) implies that, in TPE fluorescence related applications, the dendritic compound will offer less laser power needed, less photodamage, and an increased signal-to-noise ratio.

2.5. Thermal Stability. The thermal stability is one of the key requirements for some practical applications of organic chromophores used in a solid matrix. The thermal properties of compounds **1**−**3** were investigated by thermogravimetric analysis (TGA) at the heating rate of 10 °C/min under a nitrogen atmosphere. The sample weight was fixed at ∼2.1 mg per load. As shown in Figure 6, compounds **1**−**3** are relatively robust and no degradation was found below 420 °C in an argon atmosphere. The decomposing temperatures for **1**, **2**, and **3** are 420, 450, and 453 °C, respectively. Enhanced thermal stability was found, on going from **1** to **2** or from **1** to **3**. These results confirmed that the truxene-containing chromophores are thermally stable.

3. Conclusions

A novel dendritic chromophore with enhanced TPA has been designed, synthesized, and characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis, together with its one- and three-branched units. Two-photon absorption spectra for these chromophores were measured by a nonlinear transmission spectral technique, which utilizes a femtosecond white-light continuum. The TPA peak value for chromophore **3** is 5.47×10^{-20} cm^4/GW, 15.6 times larger than that for **1** (0.35×10^{-20} cm^4/GW). Chromophore **2** has a TPA peak value of 2.28×10^{-20} cm^4/GW, 6.5 times as large as that for **1**. The enhanced two-photon absorption

found in these two multibranched chromophores is attributed to the fact that the dendritic or the three-branched chromophore has both an extended π-conjugated system and an increased intramolecular charge redistribution compared to the one-branched dipolar chromophore (**1**). With use of comparable structure unit based concentrations, the two-photon excited (TPE) fluorescence intensity for this dendritic chromophore (**3**) (0.0033 M solution) was found to be enhanced by a factor of 2.9 compared to that for chromophore **1** (0.02 M solution), which would offer a major advantage in TPE fluorescence related applications. Truxene was proved to be an excellent building block for two-photon absorbing dendritic chromophores. Together with their high fluorescence quantum yields, this type of dendritic chromophores would be very useful for TPE fluorescence based applications. Hence, the dendritic and the three-branched chromophores are thermally stable as we expected.

4. Experimental Section

Reagents were purchased from Aldrich Inc. and Lancaster Synthesis Ltd. and used without further purification unless otherwise stated. (7-Bromo-9,9-dibutylfluoren-2-yl)diphenylamine, 2-bromo-9,9-dibutyl-fluorene, and truxene were prepared according to the literature procedures.[7c,8c,13,14] Column chromatography was conducted with silica gel 60 (400 mesh). ^{1}H NMR spectra were recorded either at 300, 400, or 500 MHz. ^{13}C NMR spectra were recorded either at 75 or 125 MHz. MALDI-TOF MS spectra were recorded on a Bruker Biflex IV MS spectrometer with dithranol as a matrix. Electrospray ionization (ESI) mass spectra were obtained on a Themo Finnigan LCQ Advantage mass spectrometer. EI mass spectra were measured at 70 eV. Elemental analysis was carried by Atlantic Analysis Inc., Norcross, GA.

{9,9-Dibutyl-7-[2-(4-vinyl-phenyl)-vinyl]-9*H*-fluoren-2-yl}-diphenyl-amine (5). To (4-vinyl-benzyl)diethyl phosphonate (1.78 g, 7.0 mmol) in 50 mL of dry THF was added sodium *tert*-butoxide (1.34 g, 14.0 mmol). The reaction mixture was cooled to 0 °C in an ice bath. 9,9-Dibutyl-7-diphenylamino-9*H*-fluorene-2-carboxaldehyde (2.37 g, 5.0 mmol) was added to the solution, the ice bath was removed, and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into 200 mL of water and then THF was removed. The crude product was collected by filtration and further purified by column chromatography with hexane/toluene (4/1), affording 2.6 g of **5** (90% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ [ppm]: 7.62−7.41 (9H, m), 7.27−7.11 (10H, m), 7.03−6.97 (3H, m), 6.76−6.67 (1H, dd, J_1 = 11.1 Hz, J_2 = 17.7 Hz), 5.76 (1H, d, J = 17.7 Hz), 5.24 (1H, d, J = 11.1 Hz), 1.97−1.85 (4H, m), 1.12−1.03 (4H, m), 0.73−0.67 (10H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 152.41, 151.16, 147.95, 147.19, 140.84, 137.18, 136.65, 136.50, 135.95, 135.49, 129.35, 129.15, 127.16, 126.56, 125.72, 123.84, 123.44, 122.52, 120.60, 120.34, 119.30, 119.26, 113.55, 54.90, 40.06, 26.03, 23.01, 13.87. MS (ESI): m/z 574.5 (M + H$^+$). HRMS (ESI) calcd for (M + H)$^+$ $C_{43}H_{44}N$, 574.3468; found, 574.3480.

5,5,10,10,15,15-Hexabutyl-2,7,12-triiodo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (7). A mixture of compound **6** (2.00 g, 2.95 mmol) and 15 mL of solvent (CH_3COOH:H_2SO_4:H_2O = 100:20:3) was heated to 60 °C with vigorous stirring, followed by addition of $CHCl_3$ (3 mL), HIO_3 (0.58 g, 2.5 mmol), and I_2 (1.25 g, 4.92 mmol). The mixture was stirred at 70 °C under a nitrogen atmosphere for 12 h. After the mixture was cooled to room temperature and 75 mL of water was added, the brown precipitate was filtered and purified by recrystallization twice from ethanol to afford the title compound as a white solid (2.9 g, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ [ppm]: 8.04 (3H, d, J = 8.4 Hz), 7.74 (3H, s), 7.69 (3H, d, J = 8.4 Hz), 2.86−2.80 (6H, m), 2.04−1.96 (6H, m), 0.92−0.81 (12H, m), 0.50−0.36 (30H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 155.96, 145.11, 139.52, 137.69, 135.32, 131.58, 126.31, 92.66, 55.86, 36.43, 26.45, 22.74, 13.77. MS (EI): m/z 1055.8 (M$^+$), 998.6 ([M-57]$^+$). HRMS (EI) calcd for M$^+$ $C_{51}H_{63}I_3$, 1056.2058; found,1056.2007.

1-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluoren-2-yl)-ethanone (8). To a solution of compound **6** (6.79 g, 0.01 mol) in 100 mL of anhydrous methylene chloride was added one portion of aluminum chloride (2.92 g, 0.022 mol). After the mixture was cooled to 0 °C, acetic anhydride (1.02 g, 0.01 mol) in 10 mL of methylene chloride was added dropwise via a syringe pump. Upon completion of addition, the mixture was allowed to warm to room temperature. After the mixture was stirred for 4 h, it was poured into a mixture of ice and concentrated HCl, then extracted with methylene chloride, washed with brine, and dried by anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography with light petroleum−CH_2Cl_2 (3:1) as the eluent. A light yellow crystalline solid was obtained in 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz), δ [ppm]: 8.45 (1H, d, J = 8.0 Hz), 8.38−8.35 (2H, m), 8.07 (1H, d, J = 1.6 Hz), 8.00 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz) 7.47−7.36 (6H, m), 3.02−2.89 (6H, m), 2.71 (3H, s), 2.18−2.06 (6H, m), 0.92−0.81 (12H, m), 0.52−0.38 (30H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 198.17, 154.06, 153.54, 153.43, 146.40, 146.06, 145.90, 145.35, 139.96, 139.87, 138.83, 138.70, 137.19, 134.94, 127.27, 126.65, 126.63, 126.12, 124.78, 124.68, 124.31, 122.30, 122.25, 121.62, 55.76, 55.70, 55.63, 36.78, 36.53, 36.45, 26.80, 26.51, 26.46, 22.81, 22.75, 13.79, 13.77. MS (EI): m/z 720.4 (M$^+$), 663.4 ([M-57]$^+$), HRMS (EI), calcd., for M$^+$ $C_{53}H_{68}O$ 720.5265, found: 720.5250.

1-(5,5,10,10,15,15-Hexabutyl-7,12-diiodo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluoren-2-yl)-ethanone (9). A suspension of **8** (1.00 g, 1.39 mmol), bis(trifluoroacetoxy) iodobenzene (0.717 g, 1.67 mmol), and iodine (0.353 g, 1.39 mmol) in 15 mL of carbon tetrachloride was stirred at room temperature until the color of iodine disappeared. Carbon tetrachloride was removed by rotary evaporation. The residue was washed with ethanol and purified by column chromatography with light petroleum−CH_2Cl_2 (4:1) as the eluent, to give 1.15 g (85% yield) of **9** as a white crystalline solid. ^{1}H NMR ($CDCl_3$, 300 MHz), δ [ppm]: 8.42 (1H, d, J = 8.4 Hz), 8.13−8.01 (4H, m), 7.79−7.20 (4H, m), 2.93−2.87 (6H, m), 2.19−1.99 (6H, m), 0.93−0.83 (12H, m), 0.47−0.41 (30H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 197.90, 155.92, 155.88, 153.86, 146.88, 145.90, 145.81, 144.68, 139.38, 139.39, 137.97, 137.83, 137.47, 135.39, 135.31, 131.58, 127.37, 126.37, 126.33, 124.33, 121.68, 92.79, 55.97, 55.93, 55.84, 36.58, 36.40, 36.33, 26.75, 26.49, 26.45, 22.71, 13.74. MS (EI): m/z 971.8 (M$^+$), 914.5 ([M-57]$^+$). HRMS (EI) calcd for M$^+$ $C_{53}H_{66}OI_2$: 972.3198; found, 972.3162.

1,3,5-Tris(5,5,10,10,15,15-hexabutyl-7,12-diiodo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluoren-2-yl)-benzene (10). Tetrachlorosilane (2.6 g, 15.4 mmol) was added dropwise to a solution of compound **9** (0.75 g, 0.77 mmol) in an anhydrous ethanol−toluene (3:1) mixture (15 mL) under argon at room temperature. After complete addition, the mixture was heated to reflux overnight. The mixture was cooled to room temperature, poured into saturated NH_4Cl solution, and then extracted with ether. The organic layer

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was washed with brine twice, then dried over anhydrous sodium sulfate, and filtered. After the solvent was removed under reduced pressure, a white color crude product was collected and further purified by column chromatography with light petroleum−CH_2Cl_2 (4:1) as the eluent. A white crystalline solid was obtained in 91% yield (0.67 g). ^{1}H NMR ($CDCl_3$, 500 MHz), δ [ppm]: 8.50 (3H, d, J = 8.1 Hz), 8.17−8.09 (9H, m), 7.89 (6H, d, J = 10.8 Hz), 7.80 (6H, d, J = 7.8 Hz), 7.74 (6H, d, J = 7.8 Hz), 3.07−2.85 (18H, m), 2.26−2.03 (18H, m), 0.95−0.90 (36H, m), 0.52−0.45 (90H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 156.13, 156.03, 154.40, 146.03, 145.09, 144.68, 142.54, 139.79, 139.73, 139.59, 139.55, 138.26, 137.83, 137.60, 135.31, 131.62, 126.35, 125.69, 125.23, 125.05, 121.05, 92.57, 55.96, 55.90, 55.86, 36.76, 36.58, 36.52, 26.55, 26.51, 22.86, 22.78, 13.84, 13.80. MALDI-TOF MS calcd for $M^+C_{159}H_{192}I_6$: 2862.93; found, 2863.00.

[9,9-Dibutyl-7-(2-{4-[2-(9,9-dibutyl-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-9*H*-fluoren-2-yl]-diphenylamine (1). 2-Bromo-9,9-dibutyl-9*H*-fluorene (0.71 g, 2.0 mmol), {9,9-dibutyl-7-[2-(4-vinyl-phenyl)-vinyl]-9*H*-fluoren-2-yl}-diphenylamine (1.15 g, 2.0 mmol), $Pd(OAc)_2$ (25 mg, 0.08 mmol), P(*o*-tolyl)$_3$ (0.38 mg, 0.12 mmol), Et_3N (2.0 mL), and CH_3CN (20 mL) were added to a pressure tube with a plunger valve and a magnetic bar under protecting of argon. The resulting mixture was heated to reflux for 24 h and then cooled to room temperature. The mixture was poured into 50 mL of methanol with vigorous stirring. The precipitate formed was collected on a filter and washed thoroughly with methanol, and the crude product was purified by column chromatography (eluent: toluene/hexane = 1/4) on silica gel affording 1.53 g of the title compound (90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ [ppm]: 7.68−7.44 (9H, m), 7.35−7.11 (18H, m), 7.02−6.98 (4H, m), 2.02−1.90 (8H, m), 1.10−1.05 (8H, m), 0.73−0.66 (20H, m). ^{13}C NMR ($CDCl_3$, 75 MHz), δ [ppm]: 152.43, 151.25, 151.19, 151.12, 151.00, 147.98, 147.20, 142.41, 140.99, 140.82, 136.87, 136.71, 136.31, 135.98, 135.58, 130.00, 129.25, 129.16, 127.56, 127.23, 127.01, 126.80, 126.54, 125.98, 125.72, 125.57, 123.86, 123.78, 123.46, 122.86, 122.53, 120.77, 120.63, 120.35, 119.89, 119.67, 119.28, 54.92, 54.66, 40.29, 40.07, 26.03, 25.96, 23.02, 13.98, 13.81, 13.80. Elemental anal. Calcd: C, 90.41; H, 7.94; N, 1.65. Found: C, 90.19; H, 8.11; N, 1.57. MS (EI): *m*/*z* 849.5 (M^+), 792.5 ([M-57]$^+$). HRMS (EI) calcd for M^+ $C_{64}H_{67}N$: 849.5268; found, 849.5240.

2,7,12-Tris(2-{4-[2-(9,9-dibutyl-7-diphenylamino-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-5,5,10,10,15,15-hexabutyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (2). A mixture of compound 7 (0.53 g, 0.50 mmol), vinylated compound 5 (0.92 g, 1.6 mmol), tetrabutylammonium bromide (1.40 g, 4.4 mmol), potassium carbonate (0.70 g, 5.00 mmol), palladium(II) acetate (20 mg, 90 μmol), and *N*,*N*-dimethylformamide (20 mL) was stirred at 150 °C (oil bath) for 48 h under an atmosphere of argon. After the mixture was cooled, 150 mL of methanol was added, and the precipitate was filtered and washed with methanol. The crude product was purified by column chromatography with hexane−toluene (4:1 to 1:1) as the eluent. Then 1.02 g of yellow crystalline solid (85% yield) was collected after evaporation of the eluent. ^{1}H NMR ($C_2D_2Cl_4$, 500 MHz), δ [ppm]: 8.43 (3H, s, br), 7.68−7.50 (30H, m), 7.37−7.23 (24H, m), 7.18−7.16 (15H, m), 7.05−7.02 (9H, m), 3.05 (6H, s, br), 2.20 (6H, s, br), 1.96−1.90 (12H, m), 1.16−1.11 (12H, m), 0.98−0.91 (12H, m), 0.77−0.74 (36H, m), 0.51−0.49 (24H, m). ^{13}C NMR ($C_2D_2Cl_4$, 75 MHz), δ [ppm]: 154.03, 152.24, 151.09, 147.60, 146.83, 145.16, 140.66, 140.03, 137.98, 136.57, 136.43, 135.64, 135.09, 134.96, 129.18, 128.99, 126.73, 125.40, 123.54, 123.54, 123.32, 120.62, 120.25, 119.23, 55.37, 54.63, 39.72, 26.42, 25.83, 22.85, 22.73, 13.80. Elemental anal. Calcd: C, 90.29; H, 7.96; N, 1.75. Found: C, 90.07; H, 7.89; N, 1.69. MALDI-TOF MS calcd for M^+ $C_{180}H_{188}N_3$: 2392.5; found, 2392.8.

1,3,5-Tris(7,12-bis(2-{4-[2-(7-diphenylamino-9,9-dibutyl-9*H*-fluoren-2-yl)-vinyl]-phenyl}-vinyl)-5,5,10,10,15,15-hexabutyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluoren-2-yl)-benzene (3). The same procedure as described for the preparation of compound 2 was used. Yellow crystalline solid (yield: 80%). ^{1}H NMR (CD_2Cl_2, 500 MHz), δ [ppm]: 8.67 (6H, s, br), 8.51 (6H, s, br), 8.24 (3H, s, br), 8.03 (6H, s, br), 7.79−7.60 (60H, m), 7.41−7.31 (48H, m), 7.22−7.18 (30H, m), 7.10−7.07 (15H, m), 3.19 (18H, s, br), 2.36 (18H, s, br), 2.03 (12H, s, br), 1.97 (12H, s, br), 1.18−1.09 (60H, m), 0.81−0.60 (150H, m). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ [ppm]: 155.11, 154.77, 152.91, 151.71, 148.44, 147.77, 146.01, 145.85, 143.07, 141.38, 140.65, 140.53, 139.79, 138.84, 138.68, 137.46, 137.26, 136.39, 136.08, 129.59, 129.14, 128.27, 127.56, 127.30, 127.23, 126.29, 125.50, 124.31, 123.83, 123.00, 121.03, 120.74, 119.71, 56.38, 56.14, 55.38, 40.46, 37.03, 27.19, 26.56, 23.47, 23.11, 14.18, 14.14, 14.11. Elemental anal. Calcd: C, 90.41; H, 8.08; N, 1.52. Found: C, 90.17; H, 8.13; N, 1.55. MALDI-TOF MS calcd for M + Ag^+ $C_{417}H_{444}AgN_6$: 5647.41; found, 5647.40.

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