JOC Article

Synthesis of Conjugated Dendrons with Nonlinear Optical Activity

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New dipolar conjugated dendrons with electron-withdrawing groups on the periphery and electron-donating groups distributed at the core and throughout the dendritic skeleton have been conveniently synthesized. The π-conjugated dendritic skeleton provides extended conjugation between each electron donor−acceptor pair, resulting in numerous traditional nonlinear optically active chromophores in one single dendron.

Introduction

Dendrimers have been extensively studied in the past decade.[1] Not only have general synthetic methodologies been well-established and applied for the synthesis of a huge number of dendrimers, but interesting properties associated with the unique dendritic structures have been explored as well.[2] Along with flexible backbone dendrimers, conjugated dendrimers with rigid structures have also been developed in recent years.[3] These shape-persistent molecules have found applications as light-emitting diodes[4] and fluorescence sensors[5] and in other photonic devices.[6]

Organic nonlinear optically (NLO) active chromophores are usually composed of an electron donor and an electron acceptor linked by a π-conjugated bridge.[7] Such linear chromophores, particularly those with high dipole moments, exhibit poor dipole alignment stability due to the strong intermolecular electrostatic interactions.[8] It is known that spherical molecules have weaker intermolecular dipole−dipole interactions,[9] which points to the importance of dendritic chromophores. Indeed, efforts such as introducing dendrons as substituents to a linear chromophore[10] or linking multiple chromophores to the periphery of a dendrimer[11] have been made and promising results have been achieved. However, the dendrimers in these chromophores all have flexible backbone structures and merely play the role of site-isolator. Chromophores based on rigid dendrimers with a donor−acceptor pair in conjugation have not yet been reported.[12] This is not surprising since very few dendrimers exhibit π-conjugation beyond its branching units. We have previously reported an unsymmetrical conjugated dendrimer that allows extended conjugation even from the periphery to the core.[13] Herein, we report that such a unique dendritic skeleton can serve as the π-linker for numerous electron donor−acceptor pairs, resulting in dipolar NLO active dendrimers.

Results and Discussion

Chart 1 shows the structures of the two sets of dendrons, one with cyano and one with ester as the electron-withdrawing group. The dendritic skeleton is

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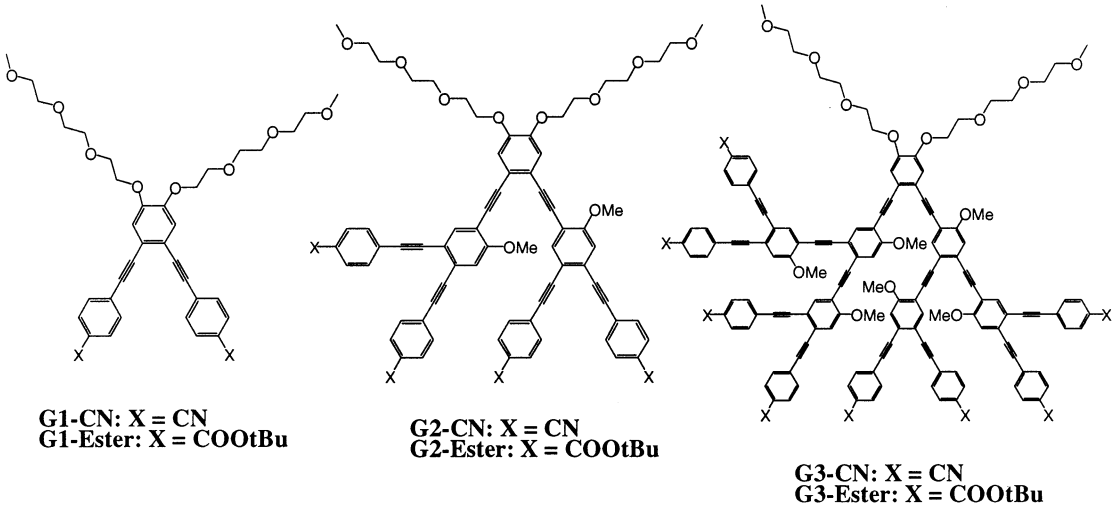
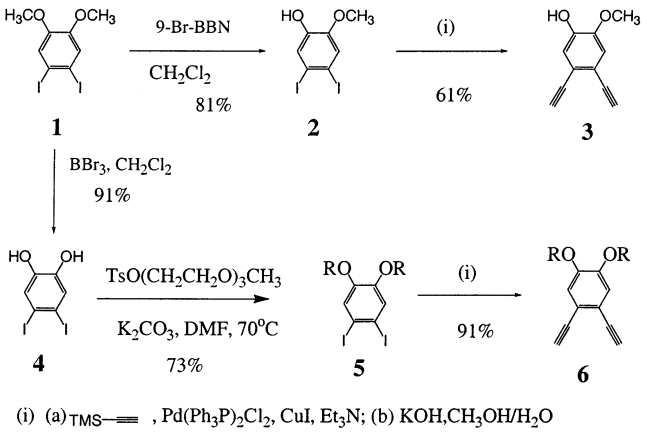
CHART 1. Structures of NLO-Active Dendrons



SCHEME 1. Synthesis of Building Block and Core Units



based on para- and meta-branched phenylacetylenes.[13] A unique feature for these dendrons is that for each electron-withdrawing group, there is an electron-donating alkoxy group in direct conjugation with it. As a result, a G1 dendron contains two chromophores, while a G2 dendron contains four chromophores and a G3 dendron eight chromophores. The chromophores in one dendron may have different conjugation lengths. For example, the eight chromophores in the G3 dendron have three different conjugation lengths. Furthermore, these chromophores are electronically cross-conjugated as one chromophore always shares at least one phenyl ring with other chromophores. It will be interesting to study how such a π-interaction will contribute to the overall nonlinearity and how the nonlinearity of the dendrimer depends on its size, conformation, and donor−acceptor combinations, which is the ultimate goal of this research.

Scheme 1 shows the synthesis of the building block molecule **3**. We have previously reported using BBr_3 as the monodemethylation agent to convert compound **1** to **2**,[13] which gave only about 40% yield. When *B*-bromo-9-BBN was used, however, selective demethylation of one of the methoxy groups can be achieved in over 80% yield.[14] The reaction is clean and no chromatography separation is required. This improvement allows the synthesis of compound **2** in large quantities in one batch.

To improve the solubility of the NLO dendrons, two oligoethylene glycol chains are introduced to the core phenyl ring, whose synthesis is also shown in Scheme 1. Demethylation of **1** with BBr_3 gives compound **4** in 91% yield.[15] Long-chain substituents are then introduced by the nucleophilic substitution of **4** with 2-(2-(2-methoxyethoxy)ethoxyl)ethyl-*p*-tolunesulfonate.[16] Palladium-catalyzed coupling (Sonogashira reaction[17]) of **4** with trimethylsilylacetylene, followed by desilylation with potasium hydroxide, generates core unit **6** in 91% yield. The iterative synthesis of the NLO-active dendrons is shown in Scheme 2. The mode of synthesis is convergent. 4-Ethynylbenzonitrile (**7a**)[18] and *tert*-butyl 4-ethynylbenzoate (**7b**)[19] were prepared according to literature procedures. Palladium-catalyzed coupling of **7a** or **7b** with **5** gave **G1-CN** or **G1-Ester** in 42% and 87% yield, respectively. To build higher generation dendrons, **7a** or **7b** was coupled with **2** to give **8a** or **8b**, whose hydroxy group was then converted to a triflate (**9a** or **9b**). The cross coupling of triflate with acetylene between **9a** or **9b** with core molecule **6** yielded **G2-CN** or **G2-Ester**.[20] The yields for **G2-CN** and **G2-Ester** are 44% and 92%, respectively. **9a** or **9b** can react with building block molecule **3** to yield **10a** or **10b**. Further conversion of the

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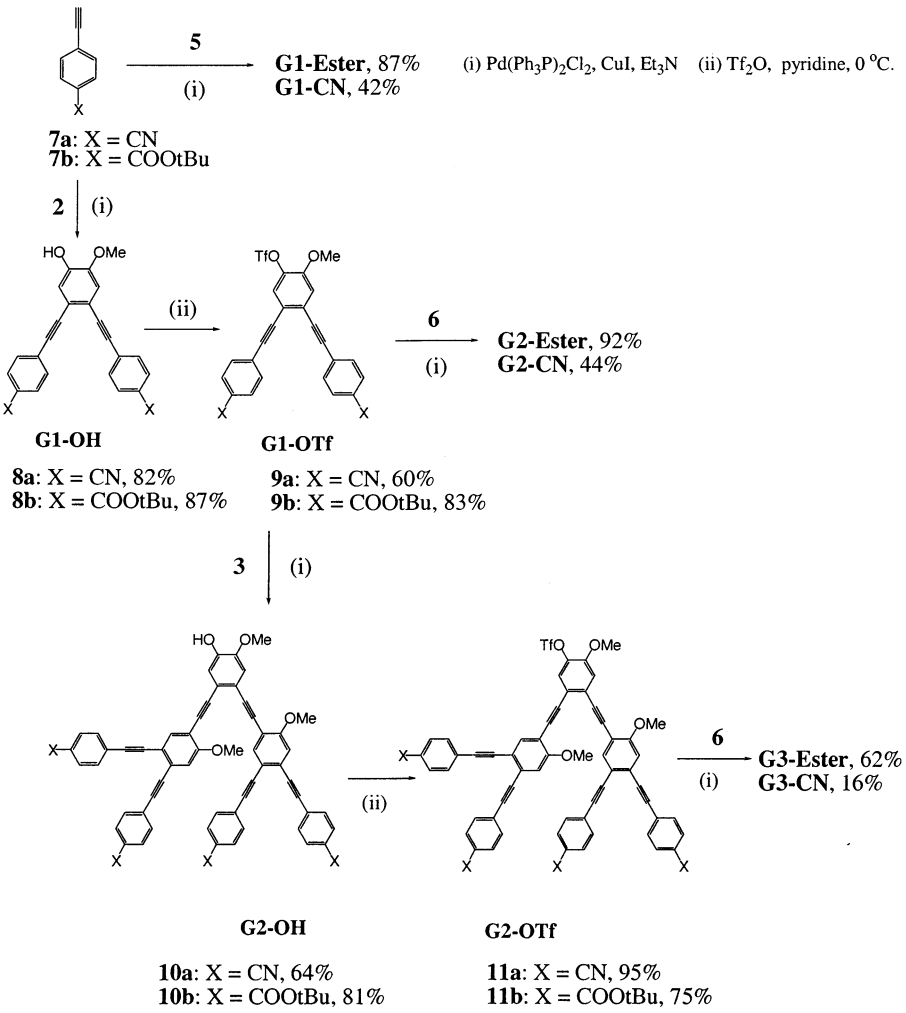
SCHEME 2. Iterative Syntheses of NLO-Active Dendrons



phenolic hydroxy group in **10a** or **10b** to triflate (**11a** and **11b**) followed by the coupling with **6** gave the third-generation dendrons.

Both sets of dendrons are soluble in common organic solvents such as methylene chloride, chloroform, THF, DMF and DMSO. With the presence of two long oligo(ethylene glycol) chains at the core, these dendrons show solubility in acetonitrile and methanol as well. In general, the Gn-Ester dendrons exhibit better solubility than CN-bearing dendrons. Their structures are confirmed by ^{1}H and ^{13}C NMR and elemental analysis (see Experimental Section). The ^{1}H NMR spectra of up to the second-generation dendrons show clearly resolved signals which can all be ambiguously assigned. Figure 1 shows the ^{1}H NMR spectra of **G2-CN** and **G2-Ester**. The *tert*-butyl protons show two singlets at 1.56 and 1.61 ppm. Both dendrons show nearly identical signals between 3.4 and 4.2 ppm, which are attributed to the protons of the two long chains and of methoxy groups. In the aromatic region, both dendrons show clearly four doublets (labeled j, k, m, and n in Figure 1), which are assigned to the peripheral phenyl rings, and three singlets (peaks h, i, and l in Figure 1), which belong to protons in the core and middle-layer phenyl rings. The signals for the aromatic protons in **G3-CN** and **G3-Ester** are severely overlapped. Directed assignments of these proton signals have thus not been possible. However, the integration

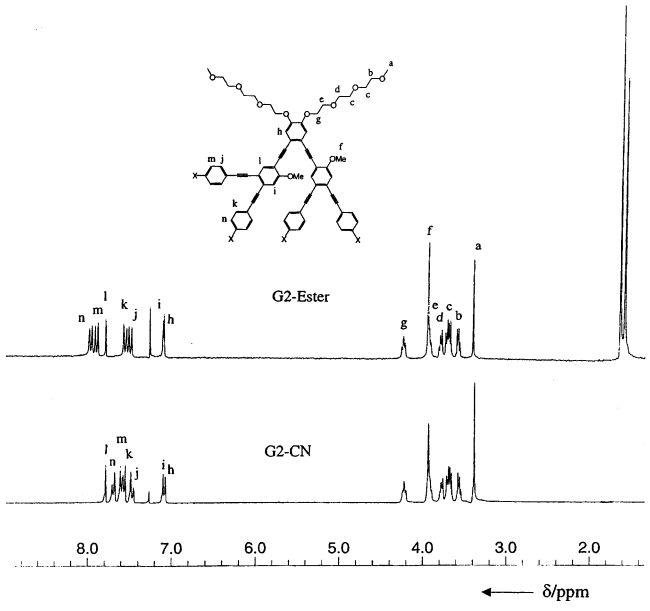


FIGURE 1. ^{1}H NMR spectra of **G2-CN** and **G2-Ester**.

ratio of the signals due to the aromatic protons vs that of the alkoxyl protons of 1:1 is in good agreement with the structures. Excellent elemental analysis results (see

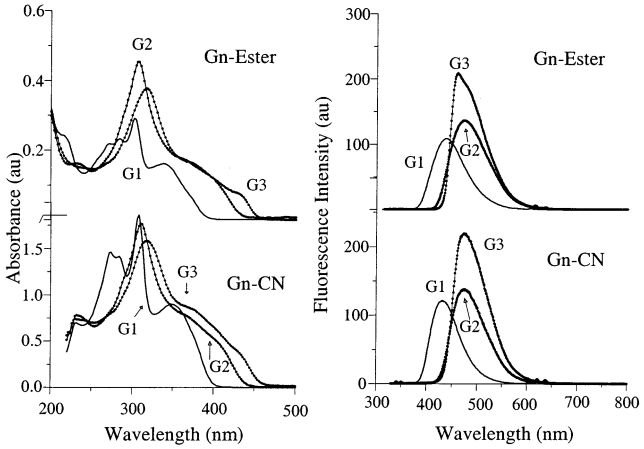


FIGURE 2. UV/vis absorption (left) and fluorescence emission spectra (right) of NLO dendrons in methylene chloride solutions.

Experimental Section) have also confirmed the purity of these dendrons.

A preliminary investigation of the optical properties of these dipolar dendrons was conducted by UV/vis and fluorescence spectroscopy. As shown in Figure 2, similar to our previous observations, the lowest excitation energy shifts to the red as generation increases. The absorption edges for the **Gn-Ester** series are 390, 432, and 452 nm, respectively. The absorption edges for the **Gn-CN** series are slightly red shifted at 400, 440, and 460 nm. When excited, these dendrons exhibit fluorescence emissions. As shown in Figure 2, the fluorescence emissions of **G2-CN** and **G2-Ester** are significantly red shifted compared to that of their **G1** analogues. However, the emissions of **G3-CN** and **G3-Ester** have nearly identical maximum wavelengths to that of their respective G2 analogues, which is in contrast to the observations on unsymmetrical dendrimers without electron-withdrawing groups at the peripheral phenyl rings, where red-shifted emissions are observed up to the forth generation.[13] The emissions from these NLO dendrons likely originated from the low-lying charge-transfer states involving the longest D−π−*A* chromophores. Detailed studies of the absorption and emissions of NLO dendrons in various solvents with different dielectric constants and the measurements of their linear hyperpolarizabilities are in progress and will be reported shortly.

Conclusions

The first dipolar conjugated dendrons with donor−acceptor pairs in direct conjugation have been successfully synthesized through a convergent approach. These dendrons exhibit UV/vis absorption spectra similar to, but fluorescence behaviors different from those of unsymmetrical conjugated dendrimers without electron-withdrawing groups. It should be noted that the surface ester and the cyano groups can undergo further conversions, for example, to carboxylic acids (ester hydrolysis)[21] and hydroxymethyl (ester reduction)[22] and aminomethyl (cyano reduction with $LiAlH_4$) groups, allowing further assembly of functional units to the dendrimer surface.

Experimental Section

Compounds **1**,[23] **3**,[13] **4**,[15] **7a**,[18] **7b**,[19] and 2-(2-(2-methoxyethoxy)ethoxy)ethyl *p*-toluenesulfonate[16] were prepared according to literature procedures.

4,5-Diiodo-1,2-bis(1,4,7,10-tetraoxaundecyl)benzene (5). Diiodocatechol **4** (3.62 g, 10 mmol) was added to a solution of K_2CO_3 (4.14 g, 30 mmol) in DMF (50 mL) and stirred at 60 °C for 15 min under N_2. To the resulting yellow solution was added 2-(2-(2-methoxyethoxy)ethoxy)ethyl *p*-toluenesulfonate (6.36 g, 20 mmol). The mixture was stirred at 60 °C for 7 h and further stirred for an additional 12 h at room temperature. The reaction mixture was filtered, and the filter remainder was washed with diethyl ether. Upon addition of 500 mL of water, the phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were extracted with small amounts of diluted NaOH solution and washed several times with brine. After drying over Na_2SO_4, the solvent was evaporated. The crude product was purified by flash column chromatography eluting with 5:5:1 hexane/ethyl acetate/MeOH to yield the title compound as a colorless oil (4.8 g, 73%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.32 (s, 2H), 4.11 (t, J = 5.0 Hz, 4H), 3.85 (t, J = 5.0 Hz, 4H), 3.72−3.64 (m, 12H), 3.54 (t, J = 5.0 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 149.6, 124.8, 96.8, 72.0, 70.9, 70.7, 70.6, 69.6, 69.2, 59.1. Anal. Calcd for $C_{20}H_{32}I_2O_8$: C, 36.71; H, 4.93. Found: C, 36.55; H, 5.08.

4,5-Bis(trimethylsilylethynyl)-1,2-bis(1,4,7,10-tetraoxaundecyl)benzene. A 1.69-g (17.2 mmol) sample of trimethylsilylacetylene was added to a mixture containing compound **5** (3.75 g, 5.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.16 g, 0.23 mmol), CuI (0.087 g, 0.46 mmol), and triethylamine (30 mL) at room temperature. The resulting mixture was stirred for 5 h and then the solids were separated from the solution by filtration. The filtrate was concentrated and then dissolved in CH_2Cl_2. The resulting solution was washed with an aqueous HCl solution and then with water. The organic layer was separated and dried over Na_2SO_4. The crude product was purified by flash column chromatography eluting with 10:10:1 hexane/ethyl acetate/MeOH to yield 3.25 g of the title compound (96%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.92 (s, 2H), 4.11 (t, J = 5.0 Hz, 4H), 3.84 (t, J = 5.0 Hz, 4H), 3.71 (t, J = 5.0 Hz, 4H), 3.66−3.61 (m, 8H), 3.53 (t, J = 5.0 Hz, 4H), 3.36 (s, 6H), 0.24 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 148.9, 119.3, 116.9, 103.4, 96.9, 72.0, 71.0, 70.8, 70.7, 69.6, 68.7, 59.1. Anal. Calcd for $C_{30}H_{50}O_8Si_2$: C, 60.57; H, 8.47. Found: C, 60.44; H, 8.55.

4,5-Diethynyl-1,2-bis(1,4,7,10-tetraoxaundecyl)benzene (6). A 30-mL sample of aqueous KOH solution (1 N) was added to the solution containing 3.63 g (6.1 mmol) of 4,5-bis-(trimethylsilylethynyl)-1,2-bis(1,4,7,10-tetraoxaundecyl)benzene and 30 mL of MeOH at room temperature. The mixture was stirred at room temperature for 1 h. After removal of the majority of the solvent, the residue was treated with an aqueous HCl solution. The resulting solution was extracted with CH_2Cl_2. The organic layer was collected. After drying over Na_2SO_4, the solvent was evaporated. The crude product was purified by flash column chromatography eluting with 10:10:1 hexane/ethyl acetate/MeOH to yield the title compound as a light yellow oil (2.61 g, 95%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.87 (s, 2H), 5.18 (s, 2H), 4.03 (t, J = 5.0 Hz, 4H), 3.74 (t, J = 5.0 Hz, 4H), 3.60 (t, J = 5.0 Hz, 4H), 3.54−3.51 (m, 8H), 3.40 (t, J = 5.0 Hz, 4H), 3.24 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 149.2, 118.4, 117.4, 82.0, 79.9, 72.0, 70.9, 70.7, 70.6, 69.5, 68.8, 59.1. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 64.00; H, 7.63.

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G1-Ester. A mixture consisting of compounds **5** (0.387 g, 0.59 mmol), **7b** (0.238 g, 1.18 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.023 mmol), and CuI (0.009 g, 0.047 mmol) in 5 mL of anhydrous triethylamine was stirred at room temperature under N_2. After 12 h, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2. The resulting solution was washed with an aqueous HCl solution and then with water. The organic layer was separated and dried over Na_2SO_4. After removal of solvent, the brown residue was flash chromatographed on a column of silica gel eluting with 5:5:1 hexane/ethyl acetate/MeOH to give the compound **G1-Ester** as a colorless oil (0.412 g, 87%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.97 (d, J = 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H), 7.10 (s, 2H), 4.17 (t, J = 5.0 Hz, 4H), 3.89 (t, J = 5.0 Hz, 4H), 3.79−3.64 (m, 12H), 3.56 (t, J = 5.0 Hz, 4H), 3.38 (s, 6H), 1.61 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.3, 149.4, 131.6, 131.3, 129.6, 129.5, 127.7, 124.9, 123.9, 119.0, 117.8, 116.7, 92.1, 91.0, 81.5, 72.1, 71.1, 70.9, 70.7, 69.7, 69.0, 59.2, 28.4. Anal. Calcd for $C_{46}H_{58}O_{12}$: C, 68.81; H, 7.28. Found: C, 68.63; H, 7.14. Calcd MALDI-TOF for $C_{46}H_{58}O_{12}$ 802.95, found 802.86.

G1-OH (8b): The synthetic procedure for **8b** is similar to that of **G1-Ester**. Yield: 87%. Mp: 180−182 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.97 (d, J = 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H), 7.13 (s, 1H), 7.05 (s, 1H), 5.87 (s, 1H), 3.95 (s, 3H), 1.61 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 147.1, 146.4, 131.5, 131.4, 131.3, 129.6, 127.7, 119.5, 118.1, 117.9, 113.8, 92.0, 91.7, 91.2, 90.9, 81.5, 56.3, 28.4. Anal. Calcd for $C_{33}H_{32}O_6$: C, 75.55; H, 6.15. Found: C, 75.38; H, 6.27.

G1-OTf (9b). A 0.42-g sample of trifluoromethanesulfonic anhydride (1.5 mmol, 1.5 equiv) was added slowly to the solution of compound **8b** (0.52 g, 1.0 mmol) in 10 mL of anhydrous pyridine at 0 °C. The resulting mixture was warmed to room temperature and stirred for 4 h, then poured into 50 mL of water. The aqueous solution was extracted with CH_2Cl_2. The organic layer was washed with an aqueous HCl solution and then dried over Na_2SO_4. After the solvent was stripped off, the residue was purified by flash column chromatography eluting with 6:1 hexane/ethyl acetate to yield the title compound as a white solid (0.54 g, 83%). Mp: 175−177 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.99 (d, J = 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H), 7.43 (s, 1H), 7.21 (s, 1H), 3.99 (s, 3H), 1.61 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.3, 165.2, 151.6, 138.4, 132.3, 132.0, 131.6, 131.5, 129.7, 127.1, 127.0, 126.6, 125.9, 121.4, 118.9, 116.3, 116.1, 94.7, 93.4, 89.3, 89.0, 81.7, 81.6, 56.7, 28.4. Anal. Calcd for $C_{34}H_{31}F_3O_8S$: C, 62.19; H, 4.76. Found: C, 62.13; H, 4.91.

G2-Ester. A solution of **6** (0.38 g, 0.75 mmol) in 2 mL of DMF was added slowly by portion within 1 h to the mixture of compound **9b** (0.656 g, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.021 g, 0.03 mmol), CuI (0.012 g, 0.06 mmol), anhydrous triethylamine (0.21 g, 2.0 mmol), and 5 mL of DMF at 75−80 °C under N_2. The resulting mixture was stirred under this temperature for an additional 4 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with an aqueous HCl solution and then dried over Na_2SO_4. After removal of the solvent, the brown residue was flash chromatographed on a column of silica gel eluting with 5:5:1 hexane/ethyl acetate/MeOH to give the compound **G2-Ester** as a bright yellow solid (0.67 g, 92%). Mp: 121−123 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.98 (d, J = 8.5 Hz, 4H), 7.92 (d, J = 8.5 Hz, 4H), 7.80 (s, 2H), 7.57 (d, J = 8.5 Hz, 4H), 7.51 (d, J = 8.5 Hz, 4H), 7.11 (s, 2H), 7.01 (s, 2H), 4.22 (t, J = 5.0 Hz, 4H), 3.93 (m, 10H), 3.78 (t, J = 5.0 Hz, 4H), 3.72−3.66 (m, 8H), 3.56 (t, J = 5.0 Hz, 4H), 3.39 (s, 6H), 1.61 (s, 18H), 1.56 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.3, 159.5, 149.2, 137.4, 132.0, 131.6, 131.3, 129.7, 129.6, 127.5, 127.0, 126.5, 119.4, 118.4, 116.5, 114.2, 113.8, 94.9, 94.7, 92.4, 90.8, 90.2, 88.0, 81.6, 81.4, 72.1, 71.1, 70.9, 70.7, 69.7, 68.8, 59.2, 56.3, 28.3. Anal. Calcd for $C_{90}H_{94}O_{18}$: C, 73.85; H, 6.47. Found: C, 73.69; H, 6.53. Calcd MALDI-TOF for $C_{90}H_{94}O_{18}$ 1463.70, found 1462.18.

Compound 10b. The synthetic procedure is similar to that of **G2-Ester**. Yield: 81%. Mp: 113−115 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.99 (d, J = 8.5 Hz, 4H), 7.92 (d, J = 8.5 Hz, 4H), 7.79 (s, 2H), 7.56 (d, J = 8.5 Hz, 4H), 7.50 (d, J = 8.5 Hz, 4H), 7.15 (s, 2H), 7.08 (s, 2H), 6.22 (s, 1H), 3.95−3.91 (m, 9H), 1.61 (s, 18H), 1.56 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.3, 162.7, 159.5, 159.4, 147.1, 146.4, 137.4, 132.0, 131.6, 131.3, 129.7, 129.6, 127.5, 127.0, 126.5, 119.8, 118.4, 117.9, 114.3, 113.8, 95.2, 94.8, 94.7, 92.3, 90.8, 90.2, 87.9, 87.6, 81.6, 81.4, 56.3, 28.3. Anal. Calcd for $C_{77}H_{68}O_{12}$: C, 78.02; H, 5.78. Found: C, 77.93; H, 5.91.

Compound 11b. The synthetic procedure is similar to that of compound **9b**. Yield: 75%. Mp 137−139 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.98 (d, J = 8.5 Hz, 4H), 7.90 (d, J = 8.5 Hz, 4H), 7.78 (s, 2H), 7.56 (d, J = 8.5 Hz, 4H), 7.49 (d, J = 8.5 Hz, 4H), 7.23 (s, 2H), 7.11 (s, 2H), 3.99 (s, 3H), 3.92 (s, 6H), 1.62 (s, 18H), 1.55 (s, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.3, 159.6, 151.5, 138.3, 137.6, 137.4, 132.2, 131.7, 131.4, 129.7, 129.6, 127.5, 127.4, 127.0, 125.8, 119.3, 118.5, 116.0, 113.9, 113.6, 95.2, 95.0, 93.2, 92.9, 92.6, 92.5, 90.9, 90.7, 90.6, 90.0, 89.9, 89.5, 81.7, 81.5, 56.8, 56.3, 28.4. Anal. Calcd for $C_{78}H_{67}F_3O_{14}S$: C, 71.11; H, 5.13. Found: C, 70.97; H, 5.21.

G3-Ester. The synthetic procedure is similar to that of **G2-Ester**. Yield: 62%. Mp: 135−137 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.99−7.84 (m, 16H), 7.78 (s, 1H), 7.72 (s, 1H), 7.55−7.43 (m, 16H), 7.29−7.26 (m, 4H), 7.13−7.03 (m, 8H), 4.24 (t, J = 5.0 Hz, 4H), 3.95−3.91 (m, 22H), 3.78 (t, J = 5.0 Hz, 4H), 3.72−3.69 (m, 8H), 3.57 (t, J = 5.0 Hz, 4H), 3.39 (s, 6H), 1.68−1.55 (m, 72H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.2, 159.6, 159.4, 149.2, 137.6, 137.3, 132.1, 131.9, 131.6, 131.3, 129.7, 129.6, 129.5, 127.6, 127.4, 127.0, 126.9, 126.8, 126.6, 119.5, 118.7, 118.5, 116.7, 114.1, 113.9, 113.8, 113.6, 95.0, 94.9, 94.6, 94.0, 92.5, 92.3, 90.9, 90.8, 90.7, 90.4, 90.1, 88.4, 88.3, 81.6, 81.5, 81.3, 72.1, 71.1, 70.9, 70.8, 69.7, 68.9, 59.2, 56.3, 28.3. Anal. Calcd for $C_{178}H_{166}O_{30}$: C, 76.76; H, 6.01. Found: C, 76.66; H, 5.97. Calcd MALDI-TOF for $C_{178}H_{166}O_{30}$ 2785.20, found 2784.81.

The synthetic procedures for **G1-CN, G2-CN**, and **G3-CN** are similar to those of **G1-Ester**, **G2-Ester**, and **G3-Ester**, respectively. The procedures for the synthesis of **8a**, **9a**, **10a**, and **11a** are similar to those of **8b**, **9b**, **10b**, and **11b**, respectively.

G1-CN. Yield: 42%. Mp: 70−71 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.69−7.43 (m, 8H), 7.08 (s, 2H), 4.24 (t, J = 5.0 Hz, 4H), 3.90 (t, J = 5.0 Hz, 4H), 3.76 (t, J = 5.0 Hz, 4H), 3.66 (m, 8H), 3.54 (t, J = 5.0 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 149.8, 132.4, 132.0, 128.4, 118.6, 118.5, 116.8, 111.7, 92.6, 91.0, 72.1, 71.1, 70.9, 70.8, 69.7, 69.0, 59.2. Anal. Calcd for $C_{38}H_{40}N_2O_8$: C, 69.92; H, 6.18. Found: C, 70.10; H, 6.22.

G1-OH (8a). Yield: 82%. Mp: 190−192 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.66−7.57 (m, 8H), 7.14 (s, 1H), 7.05 (s, 1H), 6.10 (s, 1H), 3.97 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 147.6, 146.9, 135.5, 134.1, 133.2, 132.1, 132.0, 130.5, 128.4, 127.9, 119.0, 118.7, 118.3, 118.1, 117.6, 114.0, 111.7, 92.8, 92.5, 90.9, 90.6, 56.4. Anal. Calcd for $C_{25}H_{14}N_2O_2$: C, 80.20; H, 3.77. Found: C, 80.11; H, 3.63.

G1-OTf (9a). Yield: 60%. Mp: 200−201 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.70−7.62 (m, 8H), 7.46 (s, 1H), 7.23 (s, 1H), 4.01 (s, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 152.1, 138.7, 133.2, 132.7, 132.5, 132.3, 132.2, 127.7, 127.3, 126.6, 126.3, 121.4, 118.5, 118.4, 116.4, 112.7, 112.4, 93.4, 92.3, 90.7, 90.5, 56.9. Anal. Calcd for $C_{26}H_{13}F_3N_2O_4S$: C, 61.66; H, 2.59. Found: C, 61.58; H, 2.64.

G2-CN. Yield: 44%. Mp: 165−166 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.79 (s, 2H), 7.70 (d, J = 8.5 Hz, 4H), 7.61−7.55 (m, 8H), 7.47 (d, J = 8.5 Hz, 4H), 7.10 (s, 2H), 7.08 (s, 2H), 4.23 (t, J = 5.0 Hz, 4H), 3.93 (m, 10H), 3.77 (t, J = 5.0 Hz, 4H), 3.71−3.66 (m, 8H), 3.56 (t, J = 5.0 Hz, 4H), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.8, 149.4, 137.7, 132.5, 132.3, 132.1, 132.0, 128.1, 127.5, 125.8, 119.2, 118.5, 118.4, 117.8, 116.6, 114.9, 114.0, 112.6, 111.8, 95.5, 93.5, 92.1, 91.8, 91.2, 87.7, 72.1, 71.1, 70.9, 70.8, 69.7, 68.9, 59.2, 56.4. Anal. Calcd for $C_{74}H_{58}N_4O_{10}$: C, 76.40; H, 5.03. Found: C, 76.31; H, 5.14.

G2-OH (10a). Yield: 64%. Mp: 246−248 °C. ^{1}H NMR (DMSO, ppm): δ 7.94 (d, J = 8.5 Hz, 4H), 7.79−7.68 (m, 10H), 7.56 (d, J = 8.5 Hz, 4H), 7.42 (s, 2H), 7.15 (s, 2H), 7.00 (s, 2H), 3.94 (s, 6H), 3.89 (s, 3H). ^{13}C NMR (DMSO, ppm): δ 159.5, 159.4, 148.7, 147.9, 133.4, 133.2, 132.9, 132.7, 132.6, 132.5, 132.1, 132.0, 131.8, 131.7, 126.9, 126.5, 125.4, 125.3, 118.4, 118.3, 117.9, 116.7, 116.3, 114.9, 113.8, 113.7, 111.6, 110.9, 95.3, 94.8, 93.5, 91.5, 91.2, 90.9, 87.0, 56.4, 55.9. Anal. Calcd for $C_{61}H_{32}N_4O_4$: C, 82.79; H, 3.64. Found: C, 82.66; H, 3.71.

G2-OTf (11a). Yield: 95%. Mp: 226−228 °C. ^{1}H NMR (DMSO, ppm): δ 7.93 (d, J = 8.5 Hz, 4H), 7.76 (s, 2H), 7.66 (d, J = 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H), 7.43 (s, 2H), 7.39 (s, 2H), 4.01 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (DMSO, ppm): δ 159.7, 159.6, 151.2, 137.7, 136.8, 136.7, 136.6, 135.5, 135.2, 135.0, 134.7, 134.1, 133.9, 133.6, 133.5, 133.0, 132.8, 132.6, 132.4, 132.0, 131.8, 126.9, 126.6, 126.4, 126.0, 120.7, 118.3, 117.7, 116.7, 115.0, 112.9, 112.6, 111.6, 110.9, 93.9, 93.7, 92.9, 92.7, 91.3, 90.8, 90.7, 89.0, 57.1, 56.5. Anal. Calcd for $C_{62}H_{31}F_3N_4O_6S$: C, 73.22; H, 3.07. Found: C, 73.34; H, 3.21.

G3-CN. Yield: 16%. Mp: 205−207 °C. ^{1}H NMR (DMSO, ppm): δ 7.86 (s, 2H), 7.80−7.41 (m, 32H), 7.27 (s, 4H), 7.11 (m, 4H), 7.05 (s, 2H), 7.01 (s, 2H), 4.24 (t, J = 5.0 Hz, 4H), 3.99−3.88 (m, 22H), 3.78 (t, J = 5.0 Hz, 4H), 3.72−3.69 (m, 8H), 3.66 (t, J = 5.0 Hz, 4H), 3.38 (s, 6H). ^{13}C NMR (DMSO, ppm): δ 159.3, 159.2, 149.1, 137.6, 137.4, 132.1, 131.9, 131.6, 131.3, 129.7, 129.6, 129.5, 127.8, 127.6, 127.1, 126.9, 126.8, 126.6, 119.5, 118.7, 118.5, 116.7, 114.1, 113.9,113.8, 113.6, 95.0, 94.8, 94.6, 94.0, 92.5, 92.3, 90.9, 90.8, 90.7, 90.4, 90.1, 88.4, 88.3, 81.6, 81.2, 72.4, 71.1, 71.0, 70.7, 69.6, 69.0, 59.4, 56.4. Anal. Calcd for $C_{146}H_{94}N_8O_{14}$: C, 80.28; H, 4.34. Found: C, 80.42; H, 4.53.

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