

## Synthesis of Dendrimer Containing Dialkylated-fluorene Unit as a Core Chromophore *via* Click Chemistry

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The convergent synthetic strategy for the emissive dendrimers having the chromophore at core *via* the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide was described. 2,7-Diazido-9,9-dioctyl-9H-fluorene, designed to serve as the core in dendrimer, was stitched with the alkyne-functionalized Fréchet-type and PAMAM dendrons by the click chemistry leading to the formation of the corresponding fluorescent dendrimers in high yields. The preliminary photoluminescence studies indicated that 2,7-diazido-9,9-dioctyl-9H-fluorene showed no fluorescence due to the quenching effect from the electron-rich  $\alpha$ -nitrogen of the azido group but the dendrimers fluoresced due to the elimination of the quenching through the formation of the triazole ring.

**Key Words** : Click chemistry, 1,3-Dipolar cycloaddition, Fluorene, Dendrimer

### Introduction

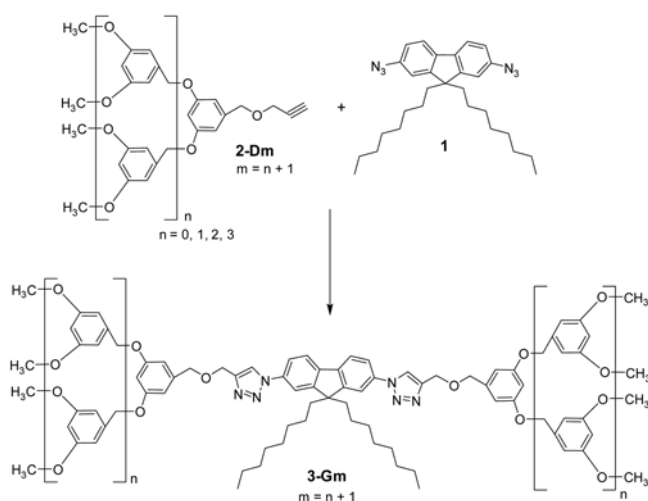
Dendrimers, which are prepared by repetition of a given set of reactions using either divergent or convergent strategies, are highly branched and regular macromolecules with well-defined structures and have served as functional objects in nanotechnology and nanoscience.<sup>1</sup> Although recent research emphasis seems to shift from the synthesis of novel dendrimers to their properties and potential applications, future more expanded applications of dendrimers rely on efficient and practical synthetic procedures. Recent solid chemistry is the click chemistry which is the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide developed by Sharpless and Tornøe.<sup>2</sup> This reaction, characterized by very high yields, mild and simple reaction conditions, oxygen and water tolerance, and simple product isolations, is highly chemoselective affording reliable 1,4-regiospecific 1,2,3-triazole even in the presence of a large variety of other functional groups. This reaction is clearly a breakthrough in the synthesis of dendrimers<sup>3,4</sup> and dendritic and polymer materials.<sup>5,6</sup> We have developed the fusion and stitching methods for the synthesis of various dendrimers using click chemistry between an alkyne and an azide.<sup>4</sup> Overall, this method was found to be a straightforward strategy for the synthesis of triazole-based dendrimers. In continuation with our research on the synthesis of dendrimers *via* click chemistry, we were intrigued to apply this methodology for the synthesis of emissive dendrimers having a chromophore at core. Taking advantage of this fact, herein we report a feasible route for the synthesis of Fréchet-type and PAMAM dendrimers having a fluorine unit at core, which will be soluble in common organic solvents and easily spin-coated with high quality optical thin films. Because of the high yields and lack of byproducts provided by the click

chemistry for stitching together dendrons and core unit, the various emissive dendrimers could be obtained easily and shown the characteristic behaviors.

### Results and Discussion

The convergent approach to dendrimer synthesis introduced by Fréchet and co-workers revolutionized the synthetic approaches to monodisperse dendrimers.<sup>7,8</sup> The convergent methodology installs the core in the final step, enabling the incorporation of functionalities. The ability to prepare well-defined symmetrical dendrimers is the most attractive features of the convergent synthesis. The convergent approach allows for a large degree of chemical diversity such that functional groups can be incorporated at nearly central position in the dendritic architecture. The inward growth employed by the convergent synthesis is ideally suited for the synthesis of dendrimers having a chromophore at core. 2,7-Diazido-9,9-dioctyl-9H-fluorene **1** was designed to serve as an emissive building block and the azide functionalities for dendrimer growth *via* click reactions with the alkyne-dendrons. Compound **1** was prepared from the reaction of 2,7-dibromo-9,9-dioctylfluorene with  $\text{NaN}_3$  in the presence of *N,N'*-dimethylethylenediamine and copper(II) iodide and sodium ascorbate.

The synthetic strategy for emissive Fréchet-type dendrimers, linked by the triazole units, utilized a convergent method using the alkyne-functionalized Fréchet-type dendrons **2-Dm** and 2,7-diazido-9,9-dioctyl-9H-fluorene **1** (Scheme 1). The propargyl-functionalized Fréchet-type dendrons **2-Dm** ( $m = 1-4$ : generation of dendron) were synthesized by the propargylation of the corresponding dendritic benzyl alcohols with propargyl bromide.<sup>4c</sup> To efficiently connect the propargyl focal point Fréchet-type dendrons

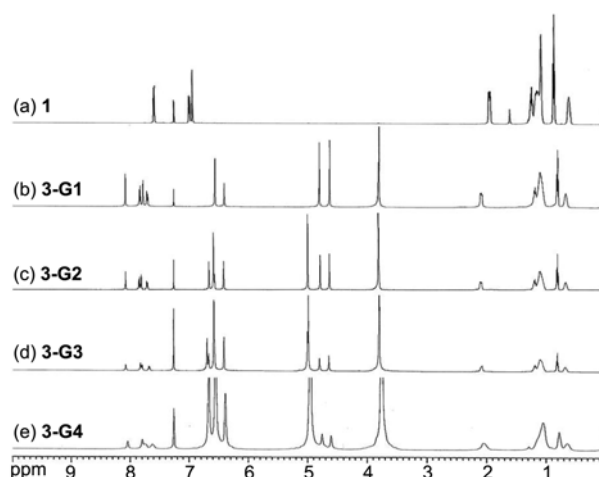


**Scheme 1.** Synthesis of dendrimers **3-Gm**. *Reagents and conditions:* 20 mol % of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /10 mol % of sodium ascorbate, DMF/ $\text{H}_2\text{O}$  (4:1).

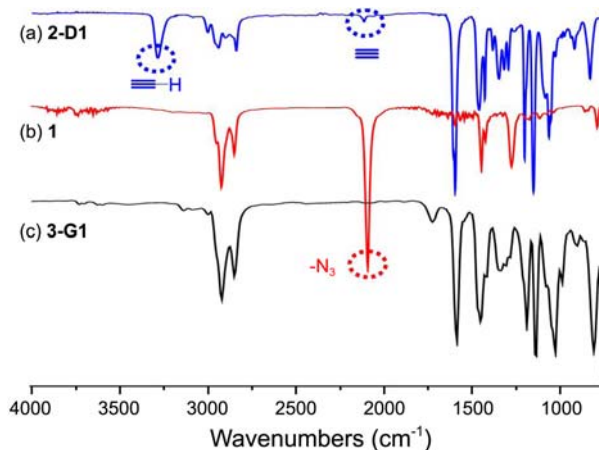
with 2,7-diazo-9,9-dioctyl-9H-fluorene **1**, the synthetic approach selected is based on the click condition using Cu(I) species.<sup>9</sup>

The efficiency of the click reaction between the alkyne-dendrons and bis(azides) was evaluated by performing the model coupling reactions between alkyne-dendron **2-D1** and compound **1**. Click reaction was carried out in a 4:1 solvent ratio of DMF to  $\text{H}_2\text{O}$  using 10 mol %  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with 5 mol % sodium ascorbate with respect to alkyne as the in situ reducing agent to generate the active Cu(I) species. The reaction of 2,7-diazo-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendron **2-D1** afforded the desired product **3-G1** in a yield of 96% after 10 min at 50 °C which was separated by column chromatography. The disappearance of bis(azides) as well as generation and disappearance of the mono-triazole derivative were monitored by TLC runs of the reaction mixture. Given the success in the synthesis of first-generation dendrimer, therefore we expanded this reaction to get higher-generation dendrimers. The reactions of 2,7-diazo-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendrons **2-D2** and **2-D3** afforded the dendrimers **3-G2** and **3-G3** in yields of 94 and 93%, respectively, after 10 min at 50 °C. Finally, reaction of 2,7-diazo-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendron **2-D4** gave the dendrimer **3-G4** in a yield of 93% after 10 min at 50 °C. This result showed that the formation of triazole can be regarded as an efficient connector to stitch the dendrons with a chromophore. Therefore this approach may provide facile methodological insight into introduction of various fluorescent cores and would greatly contribute to researches on the application side.

Structural characterization of the dendrimers **3-Gm** with  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and IR spectroscopy showed complete stitching of dendrons. From the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ), the peaks of the triazole proton, the methylene protons adjacent to the carbon of triazole, and the benzylic protons of dendritic part in dendrimers **3-Gm** were found at 8.08,



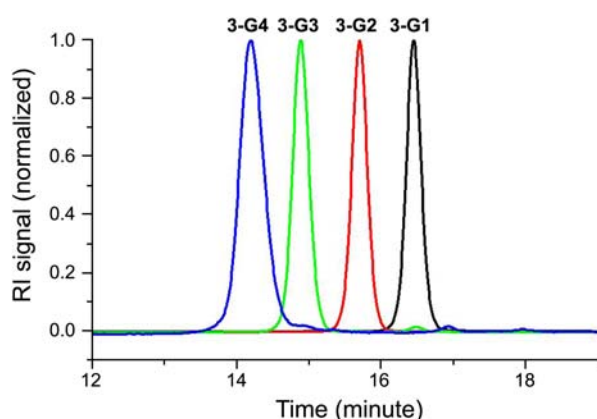
**Figure 1.**  $^1\text{H}$ -NMR spectra for (a) **1**, (b) **3-G1**, (c) **3-G2**, (d) **3-G3**, and (e) **3-G4**.



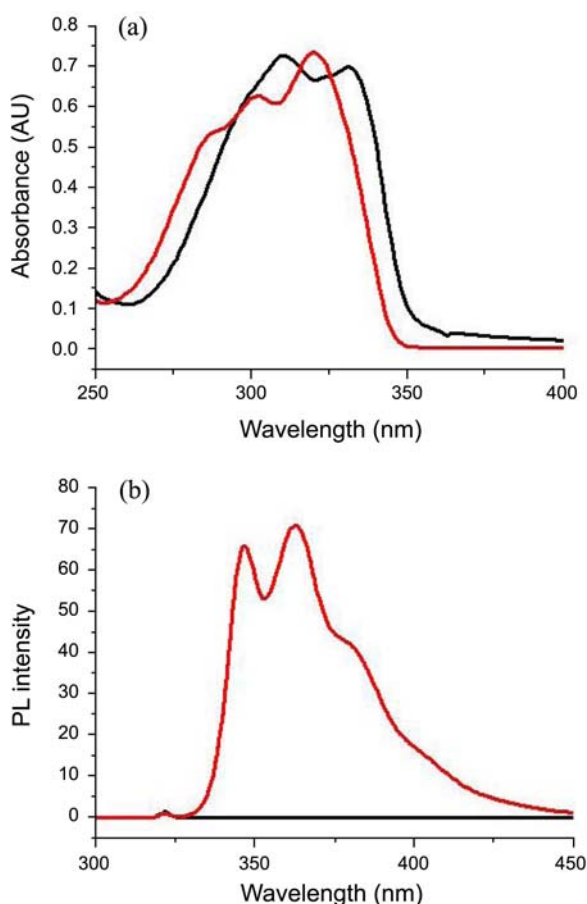
**Figure 2.** IR spectra for (a) **2-D1**, (b) **1**, and (c) **3-G1**.

4.79, and 4.62 ppm for **3-G1**, 8.07, 4.78, and 4.62 ppm for **3-G2**, 8.08, 4.80, and 4.64 ppm for **3-G3**, and 8.05, 4.76, and 4.61 ppm for **3-G4**, respectively (Figure 1). In the  $^1\text{H}$  NMR spectra, all the signals corresponding to the fluorene unit of the dendrimers **3-Gm** shifted to lower field than that of compound **1**. The IR spectra showed that neither alkyne ( $\sim 3285\text{ cm}^{-1}$ ) nor azide ( $2116\text{ cm}^{-1}$ ) residues remain in the final dendrimer (Figure 2). Their FAB or MALDI mass spectra for dendrimer exhibited very good correlation with the calculated molecular masses. Analysis of the dendrimers by gel-permeation chromatography (GPC) shows very low polydispersity values, PDI = 1.01 for all dendrimers (Figure 3).

The preliminary UV-visible absorption and photoluminescence (PL) spectra of **3-G1** and **1** in chloroform solutions were investigated (Figure 4). Compound **1** exhibited the maximum absorption at 310 nm. **3-G1** showed absorption maximum at 320 nm. Linkage of fluorene unit to the dendrimer showed red shift relative to the corresponding bands for compound **1** which may be caused by the conjugation effect according to the formation of the triazole rings. The photoluminescence (PL) spectra of compound **1** and **3-G1** in



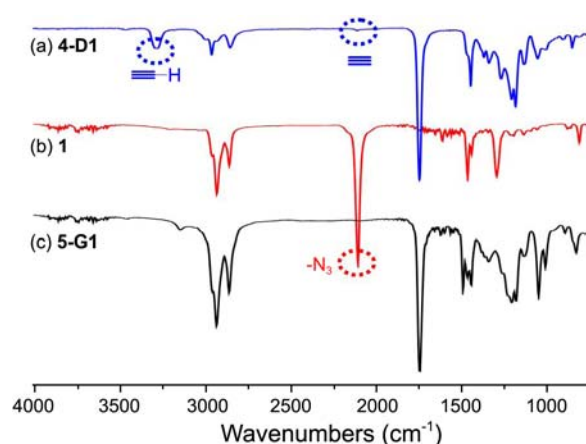
**Figure 3.** GPC diagrams of dendrimers **3-Gm** obtained from THF eluent.



**Figure 4.** (a) UV-vis spectra in  $\text{CHCl}_3$  (conc. =  $2.5 \times 10^{-5}$  M) and (b) PL spectra in  $\text{CHCl}_3$  ( $\lambda_{\text{ex}}$  = 320 nm, conc. =  $1.0 \times 10^{-5}$  M) for **1** (black) and **3-G1** (red).

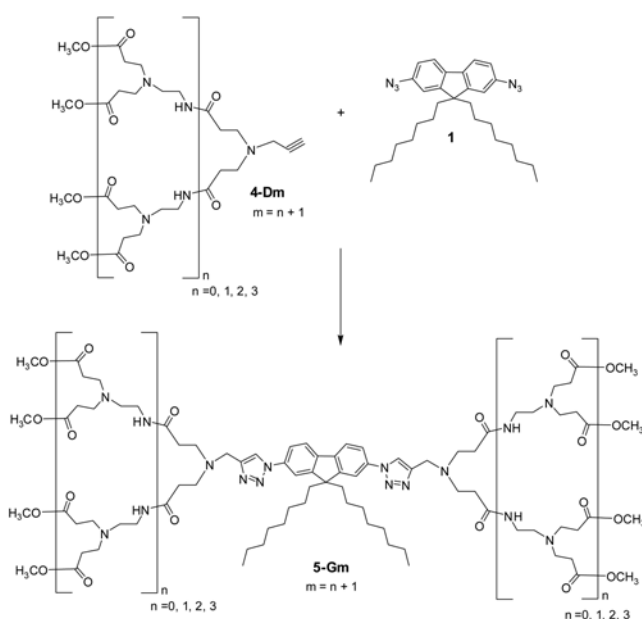
chloroform solutions were obtained. Compound **1** showed no fluorescence due to the quenching effect from the electron-rich  $\alpha$ -nitrogen of the azido group.<sup>10</sup> The maximum emission peak for **3-G1** showed at 363 nm due to the elimination of the quenching through the formation of the triazole ring. Our results demonstrate that potentially luminescent dendrimers can be obtained by incorporating a profluorophore unit with dendrons.

Encouraged by this successful proof of concept, we decid-



**Figure 5.** IR spectra for (a) **4-D1**, (b) **1**, and (c) **5-G1**.

ed to apply this methodology into the synthesis of another dendrimer so that we next turned our attention toward the alkyne-PAMAM dendron which is more hydrophilic than Fréchet type dendrons. The synthetic strategy for emissive PAMAM dendrimers, linked by the triazole units, utilized a convergent method using the alkyne-functionalized PAMAM dendrons **4-Dm** (Scheme 2). The propargyl-functionalized PAMAM dendrons **4-Dm** ( $m = 1-4$ : generation of dendron) were synthesized by the divergent approach using propargylamine as an alkyne-focal points.<sup>4f</sup> Based on optimizations for the synthesis of the dendrimers **3-Gm**, the reaction have been screened at rt. Click reaction was carried out in a 4:1 solvent ratio of DMF to  $\text{H}_2\text{O}$  using 10 mol %  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with 5 mol % sodium ascorbate with respect to alkyne as the in situ reducing agent to generate the active Cu(I) species. The reaction of 2,7-diazido-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendron **4-D1** afforded the desired product **5-G1** in a yield of 95% after 2 h 30 min at rt which



**Scheme 2.** Synthesis of dendrimers **5-Gm**. Reagents and conditions: 20 mol % of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /10 mol % of sodium ascorbate, DMF/ $\text{H}_2\text{O}$  (4:1).

was separated by column chromatography. The disappearance of bis(azides) as well as generation and disappearance of the mono-triazole derivative were monitored by TLC runs of the reaction mixture. Given the success in the synthesis of first-generation dendrimer, therefore we expanded this reaction to get higher-generation dendrimers. The reactions of 2,7-diazido-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendrons **4-D2** and **4-D3** afforded the dendrimers **5-G2** and **5-G3** in yields of 96 and 80%, respectively, after 3 h and 3 h 30 min at rt. Finally, reaction of 2,7-diazido-9,9-dioctyl-9H-fluorene **1** and 2.2 equiv of alkyne-dendron **4-D4** gave the dendrimer **5-G4** in a yield of 86% after 12 h at 50 °C.

From the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ), the peaks of the triazole proton and the methylene protons adjacent to the nitrogen of triazole in dendrimers **5-Gm** were found at 8.08 and 3.68 ppm for **5-G1**, 8.14 and 3.95 ppm for **5-G2**, 8.23 and 3.96 ppm for **5-G3**, and 8.25 and 3.97 ppm for **5-G4**, respectively. As the dendrimer generation increased, the peaks of the triazole proton and the methylene protons adjacent to the nitrogen of triazole shifted gradually to downfield which may be influenced by the dendritic micro-environment effect.<sup>11</sup> In the  $^1\text{H}$  NMR spectra, all the signals corresponding to the fluorene unit of the dendrimers **5-Gm** shifted to lower field than that of compound **1**. The IR spectra showed that neither alkyne ( $\sim 3277\text{ cm}^{-1}$ ) nor azide ( $2116\text{ cm}^{-1}$ ) residues remain in the final dendrimer (Figure 5). Their FAB or MALDI mass spectra for dendrimer exhibited very good correlation with the calculated molecular masses. Analysis of the dendrimers by gel-permeation chromatography (GPC) shows very low polydispersity values, PDI = 1.01-1.02 for all dendrimers. The preliminary UV-visible absorption and photoluminescence spectra of **5-G1** and **1** in chloroform solutions were similar with those of **3-G1**. The details for the UV-visible absorption and photoluminescence spectra of dendrimers **3-Gm** and **5-Gm** in solution and film and the dendritic generations are currently in progress.

In summary, we have successfully synthesized a series of novel soluble fluorene-based functional dendrimers by copper-catalyzed 1,3-dipolar click chemistry between azide and alkyne. The profluorophore-diazide building block, designed to serve as the core in dendrimer, was stitched together with the propargyl-functionalized Fréchet-type and PAMAM dendrons leading to the formation of fluorescent Fréchet-type and PAMAM dendrimers in high yields. This strategy will lead to the convenient synthesis of other fluorescent nanomaterials with specific structures and properties in conjunction with their applications in nanotechnology. Our results demonstrated that potentially luminescent dendrimers can be obtained by incorporating a profluorophore unit with dendrons.

### Experimental Section

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AM-500 spectrometer. Mass spectra were obtained from Korea

Basic Science Institute (KBSI) in Daegu or Daejeon and POSTECH. Flash chromatography was performed with 37-75  $\mu\text{m}$  silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using an iodine chamber. The polydispersity of the dendrimer was determined by gel permeation chromatography (GPC) using PLgel 5  $\mu\text{m}$  MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. UV-visible spectra were recorded with a Shimadzu UV-3100 spectrophotometer with a baseline correction and normalization carried out using Microsoft Excel software. The emission spectra for dilute solutions were determined using a Hitachi F-4500 fluorescence spectrophotometer. All chemicals were obtained from commercial sources and used as received, unless otherwise mentioned.

**General Procedure for the Synthesis of Fréchet-type Dendrimers 3-Gm.** A mixture of alkyne-functionalized Fréchet-type dendrons **2-Dm** (0.22 mmol) and 2,7-diazido-9,9-dioctyl-9H-fluorene **1** (0.10 mmol) in DMF- $\text{H}_2\text{O}$  (4:1, 1 mL) in the presence of 20 mol %  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  with 10 mol % sodium ascorbate was stirred at 50 °C for  $\sim 10$  min. The reaction mixture was poured into brine (20 mL) and the resulting solution was extracted with EtOAc (20 mL  $\times$  3). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography to afford the desired product **3-Gm**.

**Compound 3-G1.** A yellowish oil; 96% yield; IR 3001, 2924, 2855, 1597, 1466, 1204, 1150, 1042  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.63 (m, 4H), 0.77 (t,  $J = 7.1$  Hz, 6H), 1.03-1.08 (m, 16H), 1.15 (quin,  $J = 7.0$  Hz, 4H), 2.06 (t,  $J = 8.0$  Hz, 4H), 3.79 (s, 12H), 4.62 (s, 4H), 4.79 (s, 4H), 6.41 (m, 2H), 6.56 (d,  $J = 1.8$  Hz, 4H), 7.71 (dd,  $J = 8.1$  Hz,  $J = 1.4$  Hz, 2H), 7.78 (s, 2H), 7.84 (d,  $J = 8.1$  Hz, 2H), 8.08 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.5, 23.8, 29.1, 29.8, 31.6, 40.2, 55.3, 56.1, 63.7, 72.7, 99.8, 105.6, 115.3, 119.5, 120.8, 121.0, 136.5, 140.1, 140.2, 146.0, 152.9, 160.9; MS (FAB):  $m/z$  885.8 [ $\text{M}^+ + \text{H}$ ]; HRMS (FAB) Calcd for  $\text{C}_{53}\text{H}_{68}\text{N}_6\text{O}_6$ : 884.5200. Found: 885.5285 [ $\text{M}^+ + \text{H}$ ]. PDI: 1.01.

**Compound 3-G2.** A yellowish oil; 94% yield; IR 3001, 2932, 2855, 1597, 1458, 1204, 1150, 1049  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.64 (m, 4H), 0.78 (t,  $J = 7.1$  Hz, 6H), 1.03-1.08 (m, 16H), 1.15 (quin,  $J = 7.0$  Hz, 4H), 2.07 (t,  $J = 8.0$  Hz, 4H), 3.79 (s, 24H), 4.62 (s, 4H), 4.78 (s, 4H), 4.99 (s, 8H), 6.41 (m, 4H), 6.57 (m, 2H), 6.58 (d,  $J = 1.9$  Hz, 8H), 6.66 (d,  $J = 1.8$  Hz, 4H), 7.71 (dd,  $J = 8.1$  Hz,  $J = 1.4$  Hz, 2H), 7.81 (s, 2H), 7.84 (d,  $J = 8.1$  Hz, 2H), 8.07 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 23.8, 29.1, 29.2, 29.8, 31.6, 40.2, 55.3, 56.2, 63.7, 70.0, 72.6, 99.9, 101.5, 105.2, 106.8, 115.3, 119.5, 120.8, 121.0, 136.5, 139.2, 140.1, 140.3, 145.9, 152.9, 160.0, 161.0; MS (FAB):  $m/z$  1429.9 [ $\text{M}^+ + \text{H}$ ]; HRMS (FAB) Calcd for  $\text{C}_{85}\text{H}_{100}\text{N}_6\text{O}_{14}$ : 1428.7298. Found: 1429.7369 [ $\text{M}^+ + \text{H}$ ]. PDI: 1.01.

**Compound 3-G3.** A yellowish oil; 93% yield; IR 3009, 2932, 2847, 1597, 1458, 1204, 1150, 1049  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

(500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.65 (m, 4H), 0.78 (t,  $J = 7.1$  Hz, 6H), 1.04–1.07 (m, 16H), 1.15 (quin,  $J = 6.9$  Hz, 4H), 2.05 (m, 4H), 3.79 (s, 48H), 4.64 (s, 4H), 4.80 (s, 4H), 4.98 (s, 16H), 5.00 (s, 8H), 6.42 (m, 8H), 6.58 (m, 22H), 6.67 (m, 4H), 6.70 (m, 8H), 7.68 (d,  $J = 7.8$  Hz, 2H), 7.80 (d,  $J = 8.1$  Hz, 2H), 7.83 (s, 2H), 8.08 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.4, 23.8, 29.06, 29.13, 29.8, 31.6, 40.2, 55.3, 56.1, 63.6, 69.9, 70.0, 72.6, 99.9, 101.5, 105.2, 106.3, 106.8, 115.3, 119.4, 120.8, 121.0, 136.5, 139.1, 139.2, 140.1, 145.9, 152.9, 159.95, 160.01, 160.9; MS (MALDI): Calcd for  $\text{C}_{149}\text{H}_{164}\text{N}_6\text{O}_{30}$ : 2517.1492. Found: 2540.8661 [ $\text{M}^+ + \text{Na}$ ]. PDI: 1.01.

**Compound 3-G4.** A yellowish oil; 93% yield; IR 3009, 2932, 2839, 1597, 1450, 1204, 1150, 1049  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.62 (m, 4H), 0.75 (m, 6H), 1.02 (m, 20H), 2.04 (m, 4H), 3.76 (s, 96H), 4.61 (s, 4H), 4.76 (s, 4H), 4.95 (s, 56H), 6.39 (m, 16H), 6.55 (m, 46H), 6.67 (m, 28H), 7.63 (m, 2H), 7.76 (m, 2H), 7.80 (s, 2H), 8.05 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 23.8, 29.1, 29.2, 29.8, 31.6, 40.2, 55.3, 56.2, 63.6, 70.0, 72.6, 99.9, 101.6, 105.2, 106.4, 106.9, 115.3, 120.9, 121.0, 136.5, 139.1, 139.2, 139.3, 140.2, 145.9, 152.9, 160.1, 161.0; MS (MALDI): Calcd for  $\text{C}_{277}\text{H}_{292}\text{N}_6\text{O}_{62}$ : 4693.9881. Found: 4717.9966 [ $\text{M}^+ + \text{Na}$ ]. PDI: 1.01.

**General Procedure for the Synthesis of PAMAM Dendrimers 5-Gm.** A mixture of alkyne-functionalized PAMAM dendrons **4-Dm** (0.22 mmol) and 2,7-diazido-9,9-dioctyl-9H-fluorene **1** (0.10 mmol) in DMF- $\text{H}_2\text{O}$  (4:1, 1 mL) in the presence of 20 mol %  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with 10 mol % sodium ascorbate was stirred at rt for  $\sim 3.5$  h. The reaction mixture was poured into brine (20 mL) and the resulting solution was extracted with EtOAc (20 mL  $\times$  3). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography to afford the desired product **5-Gm**.

**Compound 5-G1.** A yellowish oil; 95% yield; IR 3140, 2928, 2855, 1736, 1485, 1435, 1200, 1042  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.63 (m, 4H), 0.77 (t,  $J = 6.3$  Hz, 6H), 1.05 (m, 20H), 2.07 (m, 4H), 2.58 (m, 8H), 2.91 (m, 8H), 3.68 (s, 12H), 3.93 (s, 4H), 7.72 (d,  $J = 8.1$  Hz, 2H), 7.83–7.85 (m, 4H), 8.06 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 23.8, 29.17, 29.23, 29.9, 31.7, 32.5, 40.3, 48.9, 49.0, 51.6, 56.2, 115.2, 119.3, 121.0, 136.6, 140.2, 145.7, 152.9, 172.8; MS (FAB):  $m/z$  926.7 [ $\text{M}^+ + \text{H}$ ]; HRMS (FAB) Calcd for  $\text{C}_{51}\text{H}_{74}\text{N}_8\text{O}_8$ : 926.563. Found: 927.57 [ $\text{M}^+ + \text{H}$ ]. PDI: 1.01

**Compound 5-G2.** A yellowish oil; 96% yield; IR 3314, 2928, 2851, 1736, 1655, 1539, 1435, 1196, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.61 (m, 4H), 0.75 (t,  $J = 6.8$  Hz, 6H), 1.04 (m, 20H), 2.06 (m, 4H), 2.41 (t,  $J = 5.9$  Hz, 16H), 2.50–2.53 (m, 16H), 2.74 (t,  $J = 5.9$  Hz, 16H), 2.89 (m, 8H), 3.30–3.31 (m, 8H), 3.65 (s, 24H), 3.95 (s, 4H), 7.09 (m, 4H), 7.70–7.73 (m, 2H), 7.81–7.83 (m, 4H), 8.14 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 23.8, 29.17, 29.24, 29.9, 31.6, 32.7, 33.7, 37.1, 40.3, 48.0, 49.2, 49.3, 51.6, 53.0, 56.1, 115.0, 119.1, 120.8, 120.9, 136.6, 140.1, 145.1, 152.8, 172.0, 173.0; MS (FAB):  $m/z$  1728.9 [ $\text{M}^+ + \text{H}$ ]; HRMS

(FAB) Calcd for  $\text{C}_{87}\text{H}_{138}\text{N}_{16}\text{O}_{20}$ : 1727.027. Found: 1728.04 [ $\text{M}^+ + \text{H}$ ]. PDI: 1.01.

**Compound 5-G3.** A yellowish oil; 80% yield; IR 3294, 2928, 2851, 1736, 1651, 1539, 1439, 1200, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.61 (m, 4H), 0.75 (m, 6H), 1.04 (m, 20H), 2.06 (m, 4H), 2.41 (m, 48H), 2.52 (m, 32H), 2.73 (m, 32H), 2.81 (m, 24H), 3.28 (m, 24H), 3.64 (s, 48H), 3.96 (s, 4H), 7.05 (m, 8H), 7.74 (m, 4H), 7.82–7.85 (m, 6H), 8.23 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.4, 23.8, 29.1, 29.2, 29.6, 29.9, 31.6, 31.8, 32.6, 33.5, 37.1, 40.2, 47.3, 49.1, 49.8, 51.5, 52.5, 52.8, 56.1, 114.9, 119.1, 120.9, 121.2, 136.5, 140.0, 144.6, 152.8, 172.2, 172.9; MS (MALDI): Calcd for  $\text{C}_{159}\text{H}_{266}\text{N}_{32}\text{O}_{44}$ : 3327.956. Found: 3351.7794 [ $\text{M}^+ + \text{Na}$ ]. PDI: 1.01

**Compound 5-G4.** A yellowish oil; 86% yield; IR 3291, 2951, 2828, 1736, 1651, 1539, 1435, 1196, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.63 (m, 4H), 0.73–0.78 (m, 6H), 1.05 (m, 20H), 2.03 (m, 4H), 2.36–2.44 (m, 112H), 2.53–2.57 (m, 64H), 2.72–2.80 (m, 56H), 3.65 (s, 96H), 3.97 (s, 4H), 7.08 (m, 16H), 7.67–7.75 (m, 10H), 7.84–7.86 (m, 8H), 8.25 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.4, 22.5, 23.7, 29.05, 29.12, 29.5, 29.8, 31.4, 31.5, 32.6, 33.5, 33.7, 37.1, 37.4, 40.1, 49.0, 49.1, 49.7, 50.0, 51.5, 52.4, 52.8, 56.0, 114.9, 119.1, 120.9, 121.2, 136.5, 140.0, 144.2, 152.7, 172.2, 172.3, 172.9; MS (MALDI): Calcd for  $\text{C}_{303}\text{H}_{522}\text{N}_{64}\text{O}_{92}$ : 6529.814. Found: 6553.3454 [ $\text{M}^+ + \text{Na}$ ]. PDI: 1.02.

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