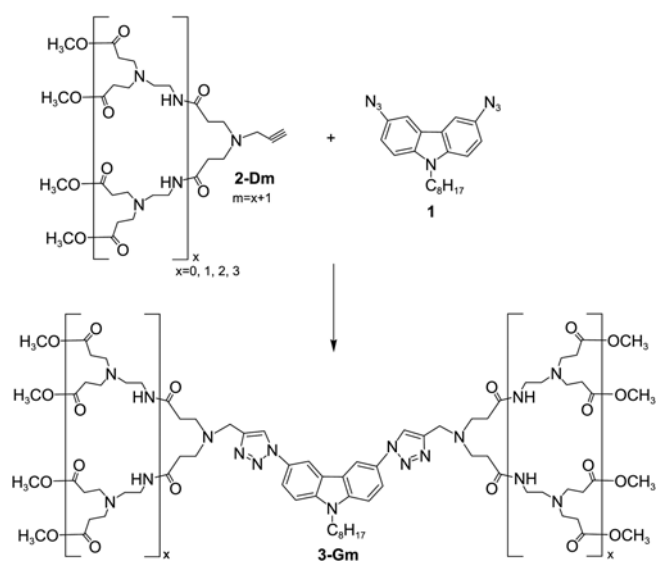


Convergent Synthesis of Carbazole Core PAMAM Dendrimer *via* Click ChemistryJae Wook Lee,<sup>\*</sup> Seung Choul Han, Seong-Hee Yun, and Sung-Ho Jin<sup>†,\*</sup>*Department of Chemistry, Dong-A University, Busan 604-714, Korea. \*E-mail: jlee@donga.ac.kr**†Department of Chemistry Education, Pusan National University, Busan 609-735, Korea. \*E-mail: shjin@pusan.ac.kr**Received December 5, 2012, Accepted December 18, 2012***Key Words :** Alkyne, Azide, Carbazole, Click chemistry, PAMAM Dendrimer

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.<sup>1</sup> Dendrimers and dendrons can be considered as unique quantized building blocks for nanoscience and have served as functional objects in nanotechnology and nano-materials science.<sup>2,3</sup> As synthetic nanoscale objects, the structures and properties of the individual dendritic building blocks are hugely versatile. Unlike many other nanoscale objects, dendrimers are inherently synthetically versatile. Therefore dendrimers and dendrons have hugely wide ranging potential applications across a wide range of areas of interdisciplinary science. The two most widely studied dendrimer families are the Fréchet-type polyether and the Tomalia-type poly(amidoamine) (PAMAM) dendrimers.<sup>1</sup> PAMAM dendrimers are synthesized by the divergent approach.<sup>4</sup> This methodology involves building the dendrimers from the core by an iterative synthetic procedure. The convergent approach to dendrimer synthesis introduced by Fréchet and co-workers revolutionized the synthetic approaches to monodisperse dendrimers.<sup>5</sup> The convergent methodology installs the core in the final step, enabling the incorporation of functionalities. It provides greater structural control than the divergent approach due to its relatively low number of coupling reactions at each growth step.

The ability to prepare well-defined (un)symmetrical dendrimers is the most attractive features of the convergent synthesis. Future applications of dendrimers rely on efficient and practical synthetic procedures. Therefore, the innovative strategy different from conventional convergent and divergent routes has been required to simplify dendrimer synthesis. The synthetic methods in dendrimer chemistry have recently been upgraded to allow easier access to high-quality dendritic products. These advances have taken advantage of widely-applied approaches such as the click chemistry.<sup>6,7</sup> This has allowed dendritic architectures to be incorporated into ever more elaborate nanostructures.<sup>8</sup> The representative click chemistry is the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide explored by Sharpless and Tornøe.<sup>9,10</sup> We were among the first to recognize that the click chemistry between alkyne and azide possess high value for convergent synthetic strategy of dendrimer. As a result, the fusion and stitching methods for the convergent synthesis of dendrimers using click chemistry between an alkyne and an azide have been developed over



**Scheme 1.** Synthesis of dendrimers **3-Gm**. Reagents and conditions: CuI, DMF, rt.

the years.<sup>11,12</sup> Taking advantage of this fact, herein we report the convergent synthesis of carbazole core PAMAM dendrimers by stitching method of PAMAM dendrons with a carbazole core (Scheme 1).

## Experimental Section

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on 300 or 500 MHz NMR spectrometers. Mass spectra were obtained from Korea Basic Science Institute (KBSI) in Daegu and POSTECH. Flash chromatography was performed with 37-75  $\mu$ m silica gel. Polydispersity (PDI) of dendrimers was determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5  $\mu$ m MIXED-C, refractive index detector) in THF solution. 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.

**General Procedure for the Synthesis of PAMAM Dendrimers 3-Gm.** A mixture of alkyne-functionalized PAMAM dendrons **2-Dm** (0.21 mmol) and *N*-octyl-3,6-diazidocarbazole **1** (0.10 mmol) in DMF (1 mL) in the presence of CuI

was stirred at rt for ~48 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 **3-Gm**.

**Compound 3-G1:**  $R_f = 0.15$  (EtOAc/Hex = 1:1); A brownish oil; 97% yield; IR 3140, 2951, 2928, 2855, 1736, 1504, 1439, 1204, 1042  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $J = 6.8$  Hz, 3H), 1.23 (m, 6H), 1.34 (m, 4H), 1.91 (quin,  $J = 6.6$  Hz, 2H), 2.56 (t,  $J = 6.9$  Hz, 8H), 2.89 (t,  $J = 6.9$  Hz, 8H), 3.67 (s, 12H), 3.92 (s, 4H), 4.37 (t,  $J = 6.9$  Hz, 2H), 7.54 (d,  $J = 8.8$  Hz, 2H), 7.89 (d,  $J = 8.8$  Hz, 2H), 8.02 (s, 2H), 8.44 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.4, 27.1, 28.8, 29.0, 29.2, 31.6, 32.6, 43.5, 48.7, 48.9, 51.5, 109.8, 113.1, 119.7, 121.3, 122.6, 129.9, 140.6, 145.4, 172.7; MS (FAB):  $m/z$  816.5 [ $\text{M}^+\text{+H}$ ]; HRMS (FAB) Calcd for  $\text{C}_{42}\text{H}_{57}\text{N}_9\text{O}_8$ : 815.4330. Found: 816.4408 [ $\text{M}^+\text{+H}$ ]. PDI: 1.01.

**Compound 3-G2:**  $R_f = 0.2$  (EtOAc/MeOH = 4:1); A brownish oil; 87% yield; IR 3318, 3071, 2951, 2932, 2847, 1736, 1651, 1539, 1439, 1200, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.82 (t,  $J = 6.8$  Hz, 3H), 1.21 (m, 6H), 1.33 (m, 4H), 1.89 (quin,  $J = 6.6$  Hz, 2H), 2.39 (t,  $J = 6.4$  Hz, 16H), 2.46-2.53 (m, 16H), 2.71 (t,  $J = 6.4$  Hz, 16H), 2.88 (t,  $J = 5.9$  Hz, 8H), 3.28 (q,  $J = 5.3$  Hz, 8H), 3.61 (s, 24H), 3.94 (s, 4H), 4.36 (t,  $J = 6.9$  Hz, 2H), 7.14 (t,  $J = 4.9$  Hz, 4H), 7.53 (d,  $J = 8.7$  Hz, 2H), 7.87 (d,  $J = 8.8$  Hz, 2H), 8.12 (s, 2H), 8.48 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 22.3, 26.9, 28.7, 28.8, 29.0, 31.4, 32.4, 33.5, 36.9, 43.3, 47.7, 49.0, 49.2, 51.3, 52.7, 109.7, 113.0, 119.4, 121.4, 122.5, 129.8, 140.4, 144.5, 171.8, 172.7; MS (FAB):  $m/z$  1616.8 [ $\text{M}^+\text{+H}$ ]; HRMS (FAB) Calcd for  $\text{C}_{78}\text{H}_{121}\text{N}_{17}\text{O}_{20}$ : 1615.8974. Found: 1616.9060 [ $\text{M}^+\text{+H}$ ]. PDI: 1.01.

**Compound 3-G3:**  $R_f = 0.15$  (EtOAc/MeOH = 1:1); A brownish oil; 80% yield; IR 3287, 3078, 2955, 2851, 1736, 1647, 1551, 1439, 1219, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $J = 6.8$  Hz, 3H), 1.23 (m, 6H), 1.33-1.37 (m, 4H), 1.90 (m, 2H), 2.36 (m, 16H), 2.40 (t,  $J = 6.3$  Hz, 32H), 2.51 (m, 24H), 2.59 (m, 8H), 2.72 (t,  $J = 6.4$  Hz, 32H), 2.80 (m, 16H), 2.87 (m, 8H), 3.27 (m, 16H), 3.31 (m, 8H), 3.64 (s, 48H), 3.95 (s, 4H), 4.39 (t,  $J = 6.8$  Hz, 2H), 7.07 (m, 8H), 7.57 (d,  $J = 8.5$  Hz, 2H), 7.79 (m, 4H), 7.89 (d,  $J = 8.6$  Hz, 2H), 8.21 (s, 2H), 8.54 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 27.2, 29.0, 29.1, 29.3, 31.7, 32.6, 33.7, 33.8, 37.1, 37.5, 43.6, 47.6, 49.2, 49.9, 51.6, 52.5, 52.9, 109.9, 113.4, 119.7, 121.7, 122.8, 130.0, 140.7, 144.5, 172.2, 172.3, 173.0; MS (MALDI): Calcd for  $\text{C}_{150}\text{H}_{249}\text{N}_{33}\text{O}_{44}$ : 3216.8261. Found: 3239.6764 [ $\text{M}^+\text{+Na}$ ]. PDI: 1.01.

**Compound 3-G4:**  $R_f = 0.1$  (MeOH); A brownish oil; 84% yield; IR 3298, 3082, 2951, 2843, 1736, 1647, 1547, 1439, 1200, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t,  $J = 6.8$  Hz, 3H), 1.24 (m, 6H), 1.33-1.38 (m, 4H), 1.91 (m, 2H), 2.39-2.46 (m, 120H), 2.54-2.57 (m, 56H), 2.71-2.78 (m, 120H), 3.27 (m, 56H), 3.66 (s, 96H), 3.97 (s, 4H), 4.40 (br, 2H), 7.13 (m, 16H), 7.58 (d,  $J = 8.8$  Hz, 2H), 7.72 (m, 8H), 7.88 (d,  $J = 8.8$  Hz, 2H), 7.94 (m, 4H), 8.26 (s, 2H), 8.57 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.7, 22.3, 27.0, 28.8,

29.0, 29.3, 31.4, 32.3, 33.4, 36.8, 37.1, 43.4, 47.6, 48.9, 49.4, 49.7, 51.3, 52.1, 52.5, 109.8, 113.2, 119.4, 121.5, 122.5, 129.9, 140.4, 144.5, 172.0, 172.2, 172.7; MS (MALDI): Calcd for  $\text{C}_{294}\text{H}_{505}\text{N}_{65}\text{O}_{92}$ : 6418.6836. Found: 6441.2371 [ $\text{M}^+\text{+Na}$ ]. PDI: 1.02.

## Results and Discussion

Dendrimers contain three distinct structural parts that are the core, end-groups, and branched units connecting core and periphery. When the core is selected as the luminescent chromophore, the dendrons and their periphery indeed isolate the chromophore core and can also tune the solubility. By careful structural design, dendrimers will have the potential applications across a wide range of areas of interdisciplinary science. Since the convergent approach installs the core in the final reaction step, it can allow various functional groups to be incorporated in dendrimers. Moreover, the approach enables the preparation of ordered and symmetrical dendrimeric structures, which is very attractive in terms of dendrimer syntheses. These characteristics of the convergent synthesis are ideal for the synthesis of dendrimers whose the luminescent chromophore unit is located at the core region. This method, however, could be limited to obtain the core-functional PAMAM dendrimers which are mainly prepared by the divergent approach. To overcome this limitation, we were intrigued to investigate the stitching method for the convergent synthesis of chromophore core PAMAM dendrimers. *N*-Octyl-3,6-diazidocarbazole **1** was designed to serve as an chromophore building block and the azide functionalities for dendrimer growth *via* click reactions with the alkyne-dendrons. Compound **1** was prepared from the reaction of *N*-octyl-3,6-dibromocarbazole with  $\text{NaN}_3$  in the presence of *N,N'*-dimethylethylenediamine and copper(II) iodide and sodium ascorbate.

The synthetic strategy for the chromophore core PAMAM dendrimers, linked by the triazole units, utilized a convergent method using the alkyne-functionalized PAMAM dendrons **2-Dm** and *N*-octyl-3,6-diazidocarbazole **1** (Scheme 1). The propargyl-functionalized PAMAM dendrons **2-Dm** ( $m = 1-4$ : generation of dendron) were synthesized by the divergent approach using propargyl amine as a propargyl focal point.<sup>12d</sup> To efficiently connect the propargyl focal point PAMAM dendrons with *N*-octyl-3,6-diazidocarbazole **1**, the synthetic approach selected is based on the click condition using Cu(I) species.<sup>13</sup>

To test the effectiveness of the click reaction between the bis(azide) core **1** and alkyne-dendrons **2-Dm**, we have screened several conditions using various Cu(I) sources in different solvents.<sup>13</sup> We have found that the reaction of *N*-octyl-3,6-diazidocarbazole **1** and 2.1 equiv of alkyne-dendrons **2-D1** in the presence of 0.1 equiv of CuI in DMF at room temperature for 5 h afforded the desired product **3-G1** in 97% yield. The disappearance of **1** as well as generation and disappearance of the mono-triazole derivative were monitored by TLC runs of the reaction mixture. It was observed that the desired product was obtained from only

catalytic amount of CuI without amine additive even at room temperature which may potentially be explained by anchimeric assistance due to the amino ester part. Given the success in the synthesis of first-generation dendrimer, therefore we expanded this reaction to get higher-generation dendrimers. The reaction of **1** and 2.1 equiv of **2-D2** in the presence of 0.1 equiv of CuI in DMF at rt for 10 h gave the dendrimer **3-G2** in 87% yield. The reactions of *N*-octyl-3,6-diazidocarbazole **1** and 2.1 equiv of alkyne-dendrons **2-D3** and **2-D4** in the presence of 0.5 equiv of CuI in DMF afforded the dendrimers **3-G3** and **3-G4** in yields of 80 and 84%, respectively, after 24 and 48 h at rt. For completion of the reaction between the alkyne-dendrons and the core, the higher generation dendron takes longer time than the lower generation dendron which could be differentiated by the accessibility of acetylide due to the steric hindrance (bulkiness) of dendron and spatial congestion of focal region. This result showed that the formation of triazole by click reaction can be regarded as an efficient connector to construct the symmetric chromophore core PAMAM dendrimers from the stitching 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 and the methylene protons adjacent to the carbon of triazole in dendrimers **3-Gm** were found at 8.02 and 3.92 ppm for **3-G1**, 8.12 and 3.94 ppm for **3-G2**, 8.21 and 3.95 ppm for **3-G3**, and 8.26 and 3.97 ppm for **3-G4**, respectively. As the dendrimer generation increased, the peaks of the triazole protons shifted gradually to down-field which may be influenced by the dendritic micro-environment effect.<sup>14</sup> The peaks of the amide protons (NH) in the  $^1\text{H}$ -NMR spectra were found at 7.14 ppm for **3-D2**, 7.07 and 7.79 ppm for **3-D3**, and 7.13, 7.72, and 7.94 ppm for **3-D4**, respectively. The IR spectra showed the disappearance of the acetylene peak at  $3283\text{--}3299\text{ cm}^{-1}$  and the azide peak at  $2114\text{ cm}^{-1}$  in the final dendrimer (Figure 1), while the  $^1\text{H}$  NMR revealed no alkyne peak around  $\delta$  2.19

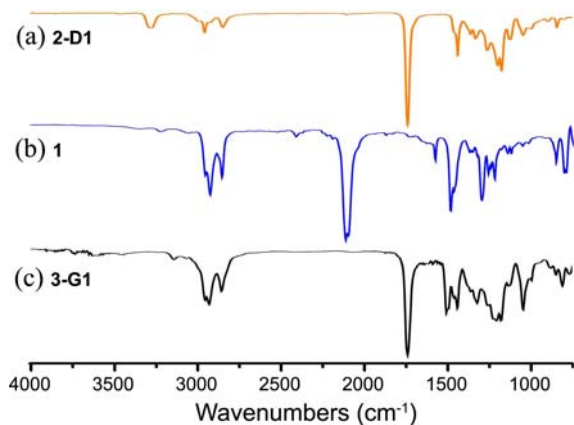


Figure 1. IR spectra for (a) **2-D1**, (b) **1**, and (c) **3-G1**.

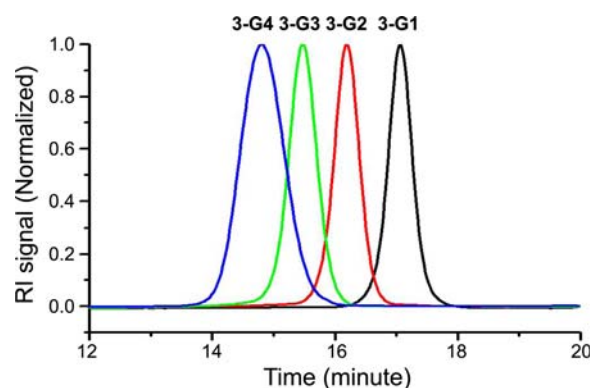


Figure 2. GPC diagrams of dendrimers **3-Gm** obtained from THF eluent.

ppm. 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 (Figure 2).

The UV-visible absorption and photoluminescence (PL) spectra of **3-Gm** and **1** in chloroform solutions were investigated (Figure 3). Compound **1** exhibited the maximum absorption at 252 and 292 nm. Dendrimers showed absorption maxima at 253 and 288, 253 and 289, 252 and 288, and 245 and 288 nm for **3-G1–G4**, respectively. The photolumine-

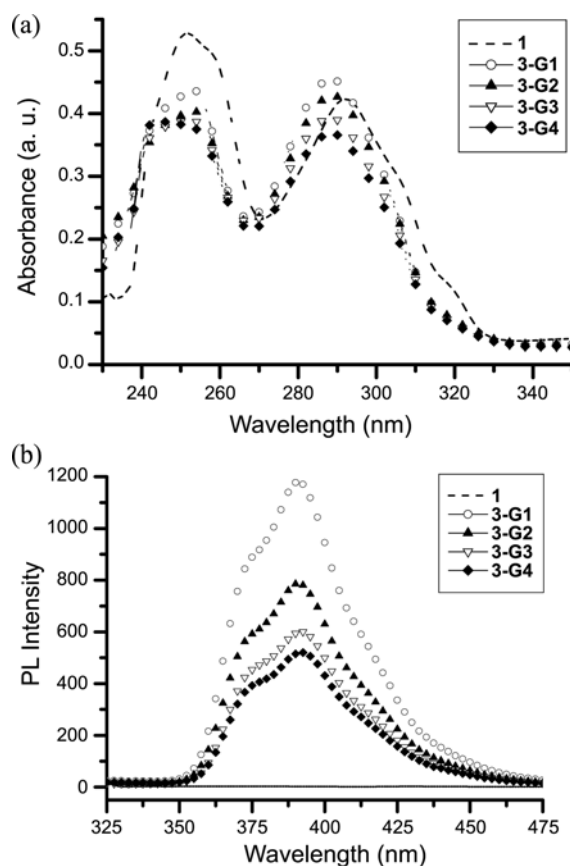


Figure 3. (a) UV-vis spectra in  $\text{CHCl}_3$  (conc. =  $1.0 \times 10^{-5}$  M) and (b) PL spectra in  $\text{CHCl}_3$  ( $\lambda_{\text{ex}} = 290$  nm, conc. =  $1.0 \times 10^{-7}$  M) for **1** (---), **3-G1** (○), **3-G2** (▲), **3-G3** (▽), and **3-G4** (◆).

science (PL) spectra of compound **1** and **3-Gm** in 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>15</sup> The maximum emission peaks of dendrimer showed at 391, 391, 392, and 392 nm for **3-G1–G4**, respectively, due to the elimination of the quenching through the formation of the triazole ring. And these dendrimers have shoulder emission peaks at 375 nm. The PL efficiencies of the dendrimers **3-Gm** are decreased with increasing the generation number. This decrease in PL efficiency is most probably related to molecular aggregation phenomena. Our results demonstrate that potentially luminescent PAMAM dendrimers can be obtained by incorporating a profluorophore unit with PAMAM dendrons.

In summary, we have successfully synthesized the fluorescent core PAMAM dendrimers having a carbazole unit at core by click chemistry between azide and alkyne. *N*-Octyl-3,6-diazidocarbazole as the profluorophore-diazide building block, designed to serve as the core in dendrimer, was stitched together with the propargyl-functionalized PAMAM dendrons leading to the formation of fluorescent core 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 potential applications across a wide range of areas of interdisciplinary science.

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