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Jae Wook Lee [a] , Byoung-Ki Kim [a] , Seung Choul Han [a] , Un Yup Lee [a] , Ji Hyeon Kim [b] , Jinho Oh [c] & Sung-Ho Jin [d]

[a] Department of Chemistry and Department of Medical Bioscience, Dong-A University, Busan, Korea

[b] Department of Chemical & Bio Engineering, Kyungwon University, Seonynam, Korea

[c] Institute for Gifted Students, Korea Advanced Institute of Science and Technology, Daejeon, Korea

[d] Department of Chemistry Education & Center for Plastic Information System, Pusan National University, Busan, Korea

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# Synthesis and Characterization of Poly(benzyl ether) Dendrimer Containing Fluorene as a Core Chromophore

## Jae Wook Lee[1], Byoung-Ki Kim[1], Seung Choul Han[1], Un Yup Lee[1], Ji Hyeon Kim[2], Jinho Oh[3], and Sung-Ho Jin[4]

[1]Department of Chemistry and Department of Medical Bioscience, Dong-A University, Busan, Korea
[2]Department of Chemical & Bio Engineering, Kyungwon University, Seonynam, Korea
[3]Institute for Gifted Students, Korea Advanced Institute of Science and Technology, Daejeon, Korea
[4]Department of Chemistry Education & Center for Plastic Information System, Pusan National University, Busan, Korea

*The convergent synthetic strategy for the emissive poly(benzyl ether) dendrimers having the chromophore at core via the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide was described. 2,7-Diazido-9H-fluorene, designed to serve as the core in dendrimer, was stitched with the alkyne-functionalized poly(benzyl ether) dendrons by the click chemistry leading to the formation of fluorescent poly(benzyl ether) dendrimers in high yields. The absorption and emission of the dendrimers were investigated. Their photophysical studies indicated that 2,7-diazido-9H-fluorene showed no fluorescence due to the quenching effect from the electron-rich α-nitrogen of the azido group but the dendrimers fluoresced due to the elimination of the quenching through the formation of the triazole ring.*

**Keywords:** 1,3-dipolar cycloaddition; click chemistry; dendrimer; fluorene

## 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 [1]. 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. Recently, click chemistry, the copper-catalyzed 1,3-dipolar cycloaddition reaction between an alkyne and an azide,has attracted much attention [2]. This type of reaction, characterized by high yields, mild and simple reaction conditions, oxygen and water tolerance, and simple work-up of products, is highly chemoselective in the formation of the desired 1,4-disubstituted 1,2,3-triazole even presence of a large variety of functional groups.

Polymer chemists have employed click chemistry to construct dendritic and linear macromolecules [2b]. However, the synthesis of emissive dendrimers by 1,3-cycloadditions has been conspicuously absent. We have been interested in the construction of new pathway for synthesis of novel fluorene-based dendrimers *via* click reaction, which will be soluble in common organic solvents and easily spin-coated with high quality optical thin films. In our previous work, we have synthesized various types of convergent Fréchet- and PAMAM-type dendrimers using click chemistry [3–5]. Overall, this method was found to be a straightforward strategy for the synthesis of triazole-based dendrimers. Taking advantage of this fact, herein we report the first general and efficient strategy for the synthesis of Fréchet-type poly(benzyl ether) dendrimers having a chromophore at core.

## EXPERIMENTAL

### General Methods

$^1$H- and $^{13}$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 μm silica gel. 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. Solid

state emission measurements were carried out by supporting each film on a quartz substrate that was mounted to receive front-face excitation at an angle of less than $45^\circ$. The polymer films were prepared through spin casting of polymer solution containing 0.1 wt% chloroform. The polydispersity of the dendrimer was determined by gel permeation chromatography (GPC) using PLgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards.

*General Procedure for the Synthesis of Fréchet-type poly(benzyl ether) Dendrimers 3-Gm.* A mixture of alkyne-functionalized poly (benzyl ether) dendrons **1-Dm** (0.22 mmol) and 2,7-diazido-9H-fluorene **2** (0.10 mmol) in DMF-$H_2O$ (4:1, 1 mL) in the presence of 10 mol% $CuSO_4 \cdot 5H_2O$ with 20 mol% sodium ascorbate was stirred at 50°C for $\sim$30 min. The reaction mixture was poured into brine (20 mL) and the resulting solution was extracted with EtOAc (20 mL × 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.* $R_f$ 0.4 (EtOAc/hexane = 3:2); 94% yield. A yellow solid; IR: 3016, 2962, 2862, 1720, 1597, 1462, 1215, 1153, 1041 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.79 (s, 12H), 4.07 (s, 2H), 4.61 (s, 4H), 4.78 (s, 4H), 6.40 (s, 2H), 6.56 (d, $J = 1.5$ Hz, 4H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.91 (d, $J = 7.9$ Hz, 4H), 7.96 (s, 2H), 8.05 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 37.6, 55.8, 64.1, 73.1, 100.3, 106.1, 118.1, 120.2, 121.3, 121.6, 136.6, 140.5, 141.4, 145.5, 146.5, 161.4; MS (FAB): $m/z$ 660.4 [M$^+$], 661.4 [M$^+$ + H]; HRMS (FAB) Calcd for C$_{37}$H$_{36}$N$_6$O$_6$: 660.2696. Found: 661.2772 [M$^+$ + H]. PDI: 1.01.

*Compound 3-G2.* $R_f$ 0.45 (EtOAc/hexane = 3:2); 94% yield; A yellowish oil; IR 3000, 2931, 2839, 1720, 1597, 1458, 1203, 1153, 1045 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.78 (s, 24H), 4.07 (s, 2H), 4.61 (s, 4H), 4.77 (s, 4H), 4.98 (s, 8H), 6.40 (s, 4H), 6.55 (s, 2H), 6.57 (d, $J = 1.8$ Hz, 8H), 6.65 (d, $J = 1.7$ Hz, 4H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.91 (d, $J = 8.2$ Hz, 2H), 7.97 (s, 2H), 8.02 (s, 2H); $^{13}$C NMR (125 MHz, MHz, CDCl$_3$) δ 37.6, 55.8, 64.1, 70.5, 73.1, 100.3, 102.0, 105.7, 107.3, 118.0, 120.1, 121.3, 121.6, 136.6, 139.6, 140.7, 141.4, 145.5, 146.4, 160.5, 161.4; MS (FAB): $m/z$ 1205.1 [M$^+$ + H]; HRMS (FAB) Calcd for C$_{69}$H$_{68}$N$_6$O$_{14}$: 1204.4794. Found: 1205.4877 [M$^+$ + H]. PDI: 1.01.

*Compound 3-G3.* $R_f$ 0.35 (EtOAc/hexane = 3:2); 95% yield; A yellowish oil; IR 3012, 2935, 2839, 1735, 1597, 1458, 1203, 1157, 1049 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.77 (s, 48H), 3.99 (s, 2H), 4.62 (s, 4H), 4.76 (s, 4H), 4.96 (s, 16H), 4.98 (s, 8H), 6.39 (s, 8H),

6.56 (br m, 22H), 6.64 (s, 4H), 6.68 (s, 8H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.85 (d, $J = 8.2$ Hz, 2H), 7.90 (s, 2H), 7.97 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 37.6, 55.8, 64.1, 70.4, 70.5, 73.1, 100.3, 102.0, 105.7, 106.8, 107.2, 118.0, 120.1, 121.3, 121.5, 136.6, 139.5, 139.8, 140.7, 141.3, 145.5, 146.4, 160.4, 160.5, 161.4; MS (MALDI): Calcd for C$_{133}$H$_{132}$N$_6$O$_{30}$: 2292.8988. Found: 2315.9252 [M$^+$ + Na]. PDI: 1.01.

*Compound 3-G4.* R$_f$ 0.2 (EtOAc/ hexane/ dichloromethane = 1:2:6); 91% yield; A yellowish oil; IR 3008, 2939, 2839, 1728, 1593, 1454, 1203, 1149, 1049 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.75 (s, 96H), 3.90 (s, 2H), 4.60 (s, 4H), 4.72 (s, 4H), 4.93 (s, 48H), 4.98 (s, 8H), 6.38 (s, 16H), 6.53–6.55 (br m, 46H), 6.65–6.66 (br m, 28H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.84 (s, 2H), 7.93 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 37.0, 55.3, 63.6, 70.0, 72.6, 99.88, 99.92, 101.6, 105.2, 106.4, 106.8, 106.9, 117.4, 119.5, 120.8, 121.0, 136.0, 139.1, 139.2, 139.3, 140.2, 140.8, 145.1, 145.8, 159.98, 160.02, 160.9; MS (MALDI): Calcd for C$_{261}$H$_{260}$N$_6$O$_{62}$: 4469.7377. Found: 4492.7363 [M$^+$ + Na]. PDI: 1.01.

## RESULTS AND DISCUSSION

The convergent methodology in the synthesis of dendrimers installs the core in the final step and allows for a large degree of chemical diversity such that functional groups can be incorporated at nearly central position in the dendritic architecture [6]. Because of the high yields and lack of byproducts provided by the click chemistry for stitching together dendrons and core unit, the various dendrimers having functional building block at core could be obtained easily and shown the characteristic behaviors. 2,7-Diazido-9H-fluorene **2** was designed to serve as an emissive building block and the azide functionalities for dendrimer growth via click reactions with the alkyne-dendrons. Compound **2** was prepared from the reaction of 2,7-diaminofluorene with triflyl azide (TfN$_3$) in the presence of triethylamine and copper(II) sulfate according to previously reported procedure [7].

The synthetic strategy for emissive Fréchet-type poly(benzyl ether) dendrimers, linked by the triazole units, utilized a convergent method using the alkyne-functionalized Fréchet-type poly(benzyl ether) dendrons **1-Dm** and 2,7-diazido-9H-fluorene **2** (Scheme 1). The propargyl-functionalized Fréchet-type poly(benzyl ether) dendrons **1-Dm** (m = 1 ∼ 4: generation of dendron) were synthesized by the propargylation of the corresponding dendritic benzyl alcohols with propargyl bromide [3e]. To efficiently connect the propargylfocal point
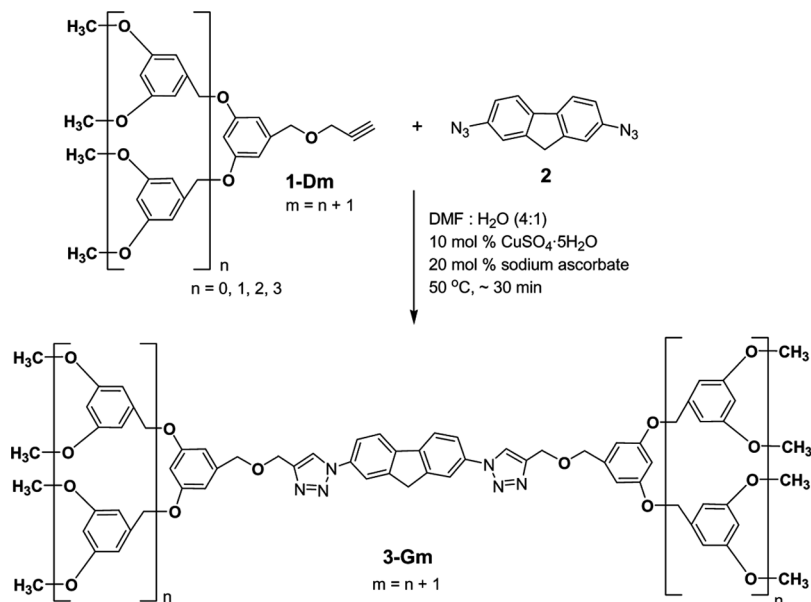
**SCHEME 1** Synthesis of dendrimers containing fluorene.

Fréchet-type dendrons with 2,7-diazido-9H-fluorene **2**, the synthetic approach selected is based on the click condition using Cu (I) species [8].

The efficiency of the click reaction between the alkyne-dendrons and bis(azides) was evaluated by performing the model coupling reactions between alkyne-dendron **1-D1** and compound **2**. Click reaction was carried out in a 4:1 solvent ratio of DMF to $H_2O$ using $5 \, mol\%$ $CuSO_4 \cdot 5H_2O$ with $10 \, mol\%$ 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-9H-fluorene **2** and 2.2 equiv of alkyne-dendron **1-D1** afforded the desired product **3-G1** in a yield of 94% 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-diazido-9H-fluorene **2** and 2.2 equiv of alkyne-dendrons **1-D2** and **1-D3** afforded the dendrimers **3-G2** and **3-G3** in yields of 94 and 95%, respectively, after 30 min at 50°C. Finally, reaction of 2,7-diazido-9H-fluorene **2** and 2.2 equiv of alkyne-dendron **1-D4** gave the dnedrimer **3-G4** in a
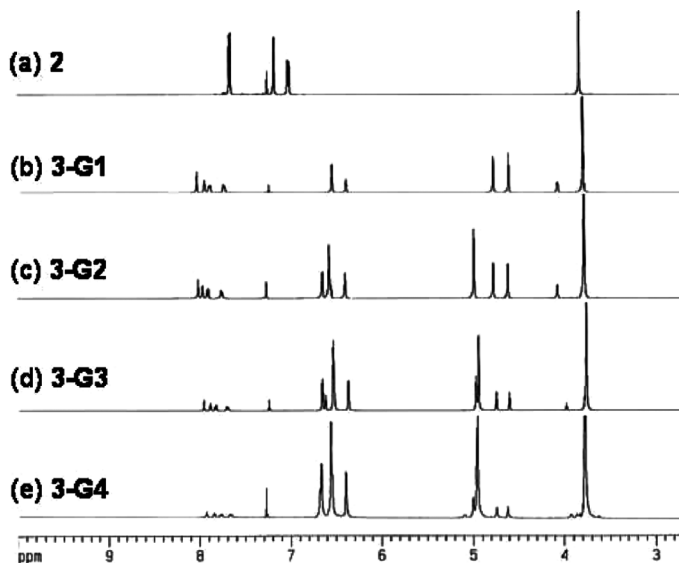
**FIGURE 1** $^1$H-NMR spectra for (a) **2**, (b) **3-G1**, (c) **3-G2**, (d) **3-G3**, and (e) **3-G4**.

yield of 91% after 30 min at 50°C. This result showed that the formation of triazole can be regarded as a new connector to stitch the dendrons with a chromophore. Therefore this approach may provide new 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 $^1$H NMR, $^{13}$C NMR, and IR spectroscopy showed complete stitching of dendrons. From the $^1$H NMR spectra (CDCl$_3$), the peaks of the methylene protons of fluorene moiety and the triazole proton in dendrimers **3-Gm** were found at 4.07 and 8.05 ppm for **3-G1**, 4.07 and 8.02 ppm for **3-G2**, 3.99 and 7.97 ppm for **3-G3**, and 3.90 and 7.93 ppm for **3-G4**, respectively (Fig. 1). As the dendrimer generation increased, the peaks of the methylene protons of fluorene moiety and the triazole proton shifted gradually to up-field which may be influenced by the dendritic microenvironment effect [9]. In the $^1$H NMR spectra, all the signals corresponding to the fluorene unit of the dendrimers **3-Gm** shifted to lower field than that of compound **2**. The IR spectra showed that neither alkyne ($\sim$3285 cm$^{-1}$) nor azide (2116 cm$^{-1}$) residues remain in the final dendrimer. Their FAB or MALDI mass spectra for dendrimer exhibited very good correlation with the calculated molecular masses. Analysis of the dendrimers by gel-permeation
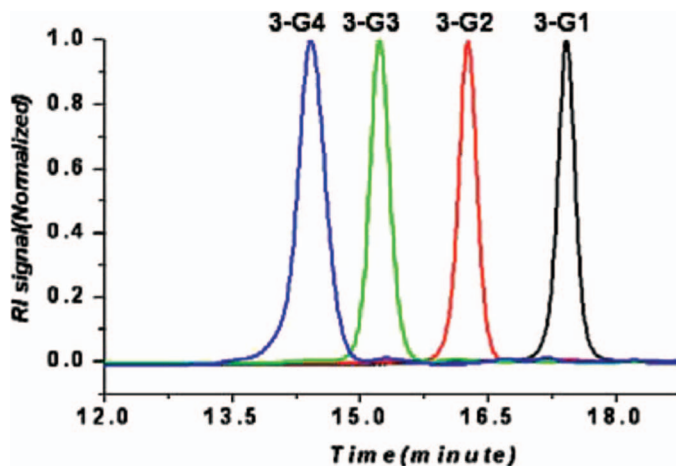
**FIGURE 2** GPC diagrams of dendrimers **3-Gm** obtained from THF eluent.

chromatography (GPC) shows very low polydispersity values, $PDI = 1.01$ for all dendrimers (Fig. 2).

The UV-visible absorption spectra of **3-Gm** and **2** in chloroform solutions were investigated. Compound **2** exhibited the maximum absorption at 316 nm. Dendrimers showed absorption maxima at 320, 319, 321, and 321 nm for **3-G1–G4**, respectively. Linkage of fluorene unit to the dendrimer showed red shift relative to the corresponding bands for compound **2** which may be caused by the conjugation effect
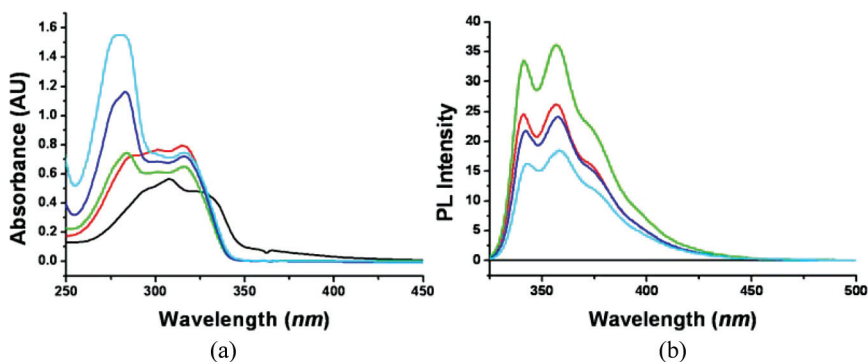


**FIGURE 3** (a) UV-vis spectra in CHCl$_3$ (conc. $= 2.5 \times 10^{-5}$ M) and (b) PL spectra in CHCl$_3$ ($\lambda_{ex} = 310$ nm, conc. $= 3.7 \times 10^{-6}$ M) for **2** (black), **3-G1** (red), **3-G2** (green), **3-G3** (blue), and **3-G4** (cyan).
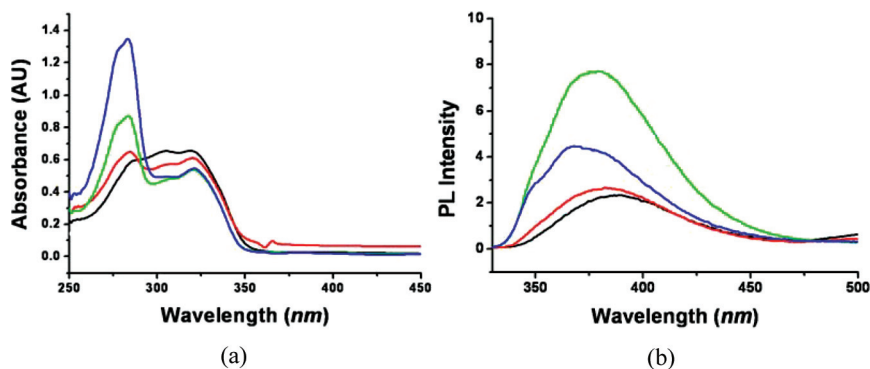
**FIGURE 4** (a) UV-vis spectra and (b) PL spectra in film for **3-G1** (black), **3-G2** (red), **3-G3** (green), and **3-G4** (blue).

according to the formation of the triazole rings. The photoluminescence (PL) spectra of compound **2** and the dendrimers **3-Gm** in chloroform solutions were obtained (Fig. 3). Compound **2** showed no fluorescence due to the quenching effect from the electron-rich $\alpha$-nitrogen of the azido group [10]. The maximum emission peaks of dendrimershowed at 356 nm, 356, 358, and 358 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 341, 341, 342, and 342 nm, respectively. The photoluminescence (PL) spectra of compound **2** and the dendrimers **3-Gm** in the film state were investigated (Fig. 4). Compound **2** showed no emission and the PL efficiencies of the dendrimers **3-Gm** are increased with increasing the generation number. There is a red shift in the PL emission maxima for films compared to solutions of the dendrimers. The maximum emission peaks of dendrimers showed at 389, 383, 378, and 367 nm for **3-G1–G4**, respectively. Our results demonstrate that potentially luminescent dendrimers can be obtained by incorporating a profluorophore unit with dendrons.

## CONCLUSION

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 poly(benzyl ether) dendrons leading to the formation of fluorescent

Fréchet-type poly(benzyl ether) 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.

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