

Synthesis of Dendrimer Containing Carbazole Unit as a Core Chromophore

Seung Choul Han, Sung-Ho Jin,^{†,*} and Jae Wook Lee^{*}

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

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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 nano-materials science.¹ Following conventional organic small molecules and polymers, dendrimers are now regarded as the third class of materials for use in organic light-emitting diodes (OLEDs) and have attracted much attention due to their distinguished properties.² Dendrimers contain three distinct structural parts that are the core, end-groups, and branched units connecting core and periphery. For light-emitting dendrimers, the core is usually selected as the luminescent chromophore, and the dendrons and their periphery are charge transporting units and can also tune the solubility. In contrast to linear polymers, dendrimers are sphere-like with dimensions of the order of nanometers depending on the generation number. By careful structural design, dendrimers combine the potential advantages of both small molecules and polymers. Therefore, the innovative strategy different from conventional convergent and divergent routes has been required to simplify dendrimer synthesis.

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.^{3,4} This reaction has many advantages: very high yields, mild and simple reaction conditions, oxygen and water tolerance, and easy isolation of product. This reaction is clearly a breakthrough in the synthesis of dendrimers⁵ and dendritic and polymer materials.^{6,7} We have developed the fusion and stitching methods for the synthesis of various dendrimers using click chemistry between an alkyne and an azide.^{8,9} 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 a feasible route for the synthesis of Fréchet-type dendrimers having a carbazole unit at core, which will be soluble in common organic solvents and easily spin-coated with high quality optical thin films.

Experimental Section

General. ¹H NMR and ¹³C NMR spectra were recorded on 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 μ 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 μ 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 Fréchet-type Dendrimers 3-Gm. A mixture of alkyne-functionalized Fréchet-type dendrons **2-Dm** (0.22 mmol) and *N*-octyl-3,6-diazidocarbazole **1** (0.10 mmol) in DMF-H₂O (4:1, 1 mL) in the presence of 20 mol % CuSO₄·5H₂O with 10 mol % sodium ascorbate was stirred at 50 °C for ~4 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: A yellowish oil; 97% yield; IR 2997, 2928, 2855, 1597, 1466, 1319, 1204, 1153, 1045 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.22-1.25 (m, 6H), 1.32 (m, 4H), 1.86 (quin, *J* = 6.5 Hz, 2H), 3.77 (s, 12H), 4.30 (t, *J* = 6.8 Hz, 2H), 4.61 (s, 4H), 4.78 (s, 4H), 6.38 (t, *J* = 2.0 Hz, 2H), 6.56 (d, *J* = 2.5 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.81 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.0 Hz, 2H), 8.06 (s, 2H), 8.33 (d, *J* = 2.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 22.4, 27.1, 28.8, 29.0, 29.2, 31.6, 43.5, 55.2, 63.6, 72.5, 99.7, 105.5, 109.9, 113.1, 119.7, 121.3, 122.5, 129.8, 140.1, 140.6, 145.6, 160.8; MS(FAB): *m/z* 774.1 [M⁺]; HRMS (FAB) Calcd for C₄₄H₅₁N₇O₆: 773.3901. Found: 774.3982 [M⁺ + H]. PDI: 1.01

Compound 3-G2: A yellowish oil; 94% yield; IR 3001, 2932, 2855, 1597, 1458, 1323, 1204, 1157, 1053 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.86 (t, *J* = 6.5 Hz, 3H), 1.25-1.27 (m, 6H), 1.34-1.36 (m, 4H), 1.91 (quin, *J* = 6.8 Hz, 2H), 3.76 (s, 24H), 4.36 (t, *J* = 6.5 Hz, 2H), 4.63 (s, 4H), 4.79 (s, 4H), 4.97 (s, 8H), 6.39 (m, 4H), 6.57 (m, 8H+2H), 6.67 (m, 4H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 8.03 (s, 2H), 8.39 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 22.5, 27.2, 28.9, 29.1, 29.2, 31.7, 43.6, 55.2, 63.7, 69.9, 72.5, 99.8, 101.5, 105.1, 106.7, 109.9, 113.3, 119.9, 121.4, 122.7,

129.9, 139.1, 140.3, 140.7, 145.7, 159.9, 160.9; MS (FAB): m/z 1318.1 [M^+]; HRMS (FAB) Calcd for $C_{76}H_{83}N_7O_{14}$: 1317.5998. Found: 1318.6082 [$M^+ + H$]. PDI: 1.01.

Compound 3-G3: A yellowish oil; 90% yield; IR 3005, 2932, 2939, 1597, 1458, 1323, 1204, 1153, 1053 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.26–1.29 (m, 6H), 1.34–1.36 (m, 4H), 1.89 (quin, $J = 6.8$ Hz, 2H), 3.76 (s, 48H), 4.33 (t, $J = 6.5$ Hz, 2H), 4.64 (s, 4H), 4.79 (s, 4H), 4.94 (s, 16H), 4.98 (s, 8H), 6.39 (t, $J = 2.0$ Hz, 8H), 6.55–6.56 (m, 16H+4H+2H), 6.67 (d, $J = 2.0$ Hz, 4H), 6.68 (d, $J = 2.0$ Hz, 8H), 7.50 (d, $J = 9.0$ Hz, 2H), 7.85 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz, 2H), 8.01 (s, 2H), 8.37 (d, $J = 1.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 27.2, 28.9, 29.0, 29.2, 31.6, 43.5, 55.2, 63.6, 69.8, 69.9, 72.5, 99.8, 101.5, 105.1, 106.3, 106.7, 109.9, 113.2, 119.8, 121.3, 122.6, 129.8, 139.0, 139.2, 140.3, 140.6, 145.6, 159.88, 159.94, 160.9; MS (FAB): m/z 2407.7 [M^+]; HRMS (FAB) Calcd for $C_{140}H_{147}N_7O_{30}$: 2406.0192. Found: 2407.0288 [$M^+ + H$]. PDI: 1.01.

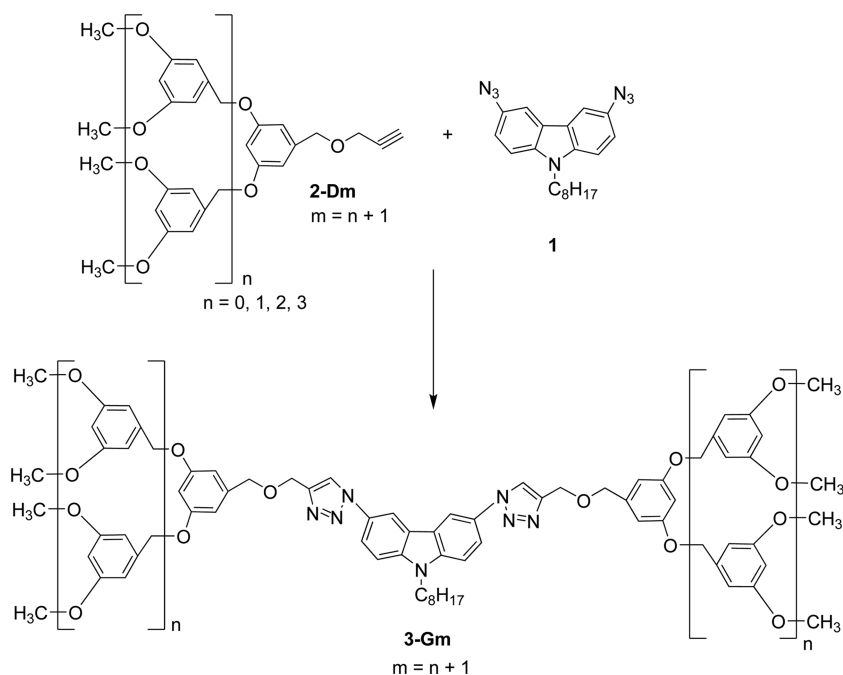
Compound 3-G4: A yellowish oil; 87% yield; IR 3005, 2934, 2839, 1597, 1458, 1323, 1204, 1153, 1053 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, $J = 6.5$ Hz, 3H), 1.24 (m, 6H), 1.33 (m, 4H), 1.86 (m, 2H), 3.75 (m, 96H), 4.28 (m, 2H), 4.61 (s, 4H), 4.75 (s, 4H), 4.93 (s, 32H+16H), 4.97 (s, 8H), 6.39 (s, 16H), 6.54–6.55 (m, 32H+8H+4H+2H), 6.65–6.67 (m, 16H+8H+4H), 7.47 (d, $J = 9.0$ Hz, 2H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.97 (s, 2H), 8.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 27.2, 28.9, 29.1, 29.2, 31.7, 43.6, 55.2, 63.6, 69.9, 72.5, 99.8, 101.5, 105.1, 106.3, 106.7, 109.9, 113.3, 119.9, 121.4, 122.6, 129.8, 139.07, 139.14, 139.3, 140.3, 140.7, 145.6, 160.0, 160.9; MS (MALDI): Calcd for $C_{268}H_{275}N_7O_{62}$: 4582.8581. Found: 4583.7410 [$M^+ + H$], 4605.8021 [$M^+ + Na$]. PDI: 1.01.

Results and Discussion

A convergent approach introduced by Fréchet and co-workers revolutionized the synthetic approaches to monodisperse dendrimers.¹⁰ Since the synthetic 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. *N*-Octyl-3,6-diazidocarbazole (**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 *N*-octyl-3,6-dibromocarbazole with NaN_3 in the presence of *N,N'*-dimethylethylenediamine and copper(II) iodide and sodium ascorbate.

The synthetic strategy for emissive dendrimers, linked by the triazole units, utilized a convergent method using the alkyne-functionalized Fréchet-type dendrons **2-Dm** and *N*-octyl-3,6-diazidocarbazole **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.^{8d} To efficiently connect the propargyl focal point Fréchet-type dendrons with *N*-octyl-3,6-diazidocarbazole (**1**), the synthetic approach selected is based on the click condition using Cu(I) species.¹¹

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



Scheme 1. Synthesis of dendrimers **3-Gm**. Reagents and conditions: 20 mol % of $CuSO_4 \cdot 5H_2O$ /10 mol % of sodium ascorbate, DMF/ H_2O (4:1).

compound **1**. Click reaction was carried out in a 4:1 solvent ratio of DMF to H₂O using 10 mol % CuSO₄·5H₂O with 5 mol % sodium ascorbate with respect to alkyne as the in situ reducing agent to generate the active Cu(I) species.¹¹ The reaction of *N*-octyl-3,6-diazidocarbazole (**1**) and 2.2 equiv of alkyne-dendron **2-D1** afforded the desired product **3-G1** in a yield of 97% after 1 h 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 *N*-octyl-3,6-diazidocarbazole (**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 90%, respectively, after 1.5 and 2.5 h at 50 °C. Finally, reaction of *N*-octyl-3,6-diazidocarbazole **1** and 2.2 equiv of alkyne-dendron **2-D4** gave the dendrimer **3-G4** in a yield of 87% after 4 h 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 ¹H NMR, ¹³C NMR, and IR spectroscopy showed complete stitching of dendrons. From the ¹H NMR spectra (CDCl₃), 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 8.06, 4.78, and 4.61 ppm for **3-G1**, 8.03, 4.79, and 4.63 ppm for **3-G2**, 8.01, 4.79, and 4.64 ppm for **3-G3**, and 7.97, 4.75, and 4.61 ppm for **3-G4**, respectively. The IR spectra showed that neither alkyne (~3285 cm⁻¹) nor azide (2114 cm⁻¹) residues remain in the final dendrimer (Figure 1). 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 2).

The UV-visible absorption and photoluminescence (PL)

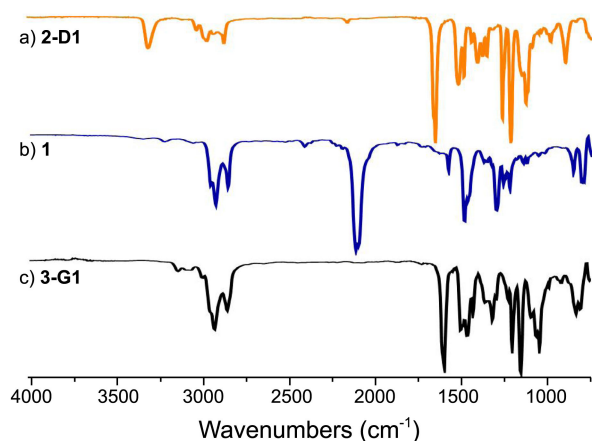


Figure 1. IR spectra for (a) **2-D1**, (b) **1**, and (c) **3-G1**.

spectra of **3-Gm** and **1** in chloroform solutions were investigated (Figure 3). Compound **1** exhibited the maximum absorption at 251 and 292 nm. Dendrimers showed absorption maxima at 253 and 285, 241 and 284, 241 and 282, and 243 and 276 nm for **3-G1–G4**, respectively which are mainly attributed by the dendrons and the carbazole unit is buried

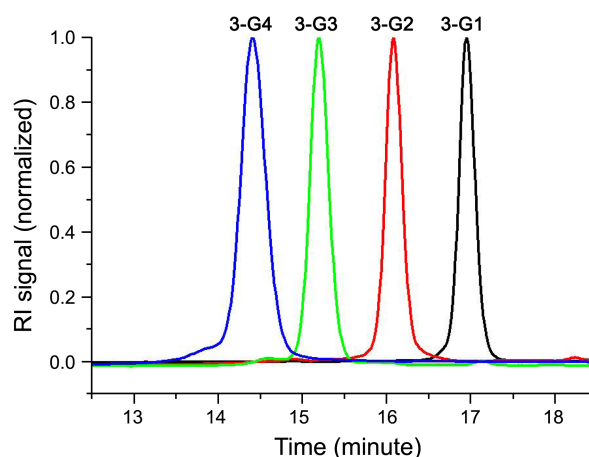


Figure 2. GPC diagrams of dendrimers **3-Gm** obtained from THF eluent.

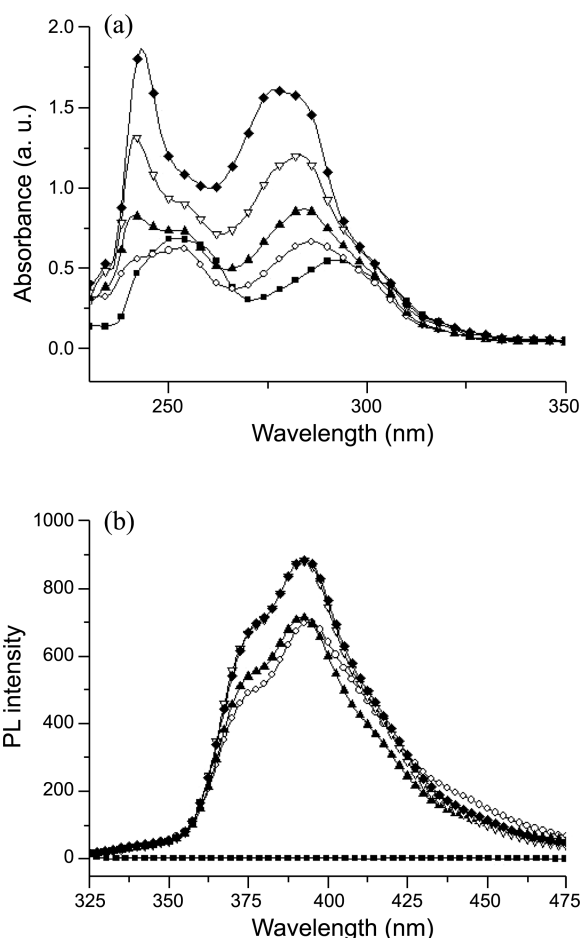


Figure 3. (a) UV-vis spectra in CHCl₃ (conc. = 2.5×10^{-5} M) and (b) PL spectra in CHCl₃ (λ_{ex} = 280 nm, conc. = 1.0×10^{-7} M) for **1** (■), **3-G1** (○), **3-G2** (▲), **3-G3** (▼), and **3-G4** (◆).

under the dendron regions. As the result, the absorbance of the dendrimers **3-Gm** are increased with increasing the generation number. Although linkage of carbazole unit to the dendrimer showed blue shift relative to the corresponding bands for compound **1**, it could be characterized by the presence of the different dendron generations. The photoluminescence (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 α -nitrogen of the azido group.¹² The maximum emission peaks of dendrimer showed at 394, 392, 391, and 393 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 which may be originated from the excimers. The PL efficiencies of the dendrimers **3-Gm** are increased with increasing the generation number due to the size effect of dendrons. The bulky dendrons would increase steric hindrance and prevent the self-aggregation between chromophore and thus reduce self-quenching. The dendrons effect in **3-G1** and **3-G2** would be similar in the factor of steric hindrance and is discriminated from one in **3-G3** and **3-G4** which are almost same. Our results demonstrate that potentially luminescent dendrimers can be obtained by incorporating a profluorophore unit with dendrons.

In summary, we have successfully synthesized the fluorescent dendrimers having a carbazole unit at core by click chemistry between azide and alkyne. *N*-Octyl-3,6-diazido-carbazole as the profluorophore-diazide building block, designed to serve as the core in dendrimer, was stitched together with the propargyl-functionalized Fréchet-type dendrons leading to the formation of fluorescent 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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