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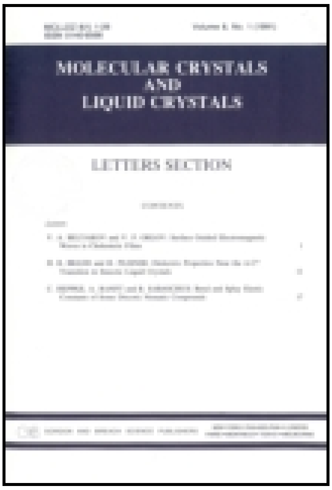

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Synthesis of Fréchet-type Dendrimer Using Glaser-type Coupling Reaction of the Terminal Alkyne-focal Dendrons

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Synthesis of Fréchet-type Dendrimer Using Glaser-type Coupling Reaction of the Terminal Alkyne-focal Dendrons

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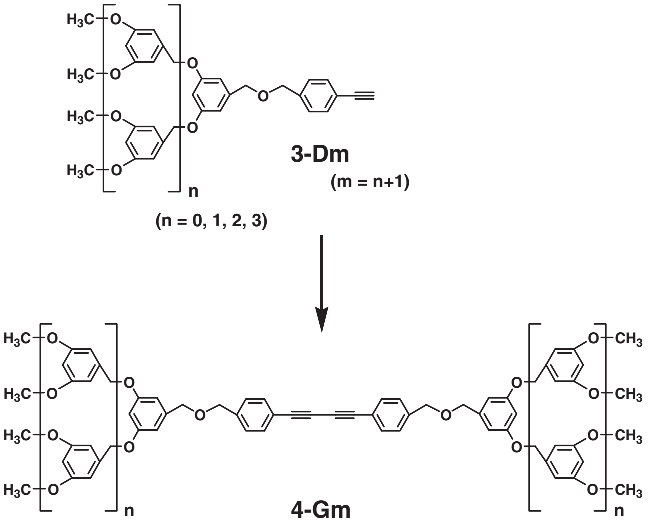
Graphical Abstract



General, fast, and efficient fusion methods for the synthesis of dendrimers with 1,4-diphenylbuta-1,3-diyne at a core were developed. The synthetic strategy was employed the fusion method of the terminal alkyne via CuI/NBS/DIPEA-mediated Glaser-type coupling reaction. Glaser-type coupling reaction under CuI/NBS/DIPEA promoting system could be completed under ambient temperature without exclusion of air and moisture. The fusion of the terminal alkyne-focal Fréchet-type dendrons ***3-Dm*** *by homo-coupling of terminal alkyne lead to the formation of symmetric Fréchet-type dendrimers* ***4-Gm***

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with 1,4-diphenylbuta-1,3-diyne at core. Their structure of dendrimers was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, mass spectrometry, and GPC analysis.

Keywords Alkyne; homo-coupling; Glaser-type coupling; dendrimer

Introduction

Terminal alkynes are versatile intermediates in synthetic organic and material chemistry due to their characteristic reactions such as metal-catalyzed coupling reactions including sonogashira coupling reaction and oxidative homo-coupling, and so on [1]. Homocoupling reaction of terminal alkynes to give 1,3-diynes is highly important for a number of applications, particularly in the construction of linearly π-conjugated acetylenic oligomers and polymers [2], natural products [3], supramolecular materials [4], and molecular recognition processes [5]. Conjugate 1,3-diyne derivatives are one of the most versatile building block materials, particularly for the synthesis of natural products [6], pharmaceuticals [7], dendrimers [8], and polymers [2]. Since the first discovery of oxidative coupling of copper acetylides by Glaser [9], oxidative alkyne–alkyne coupling has become a standard strategy for the synthesis of 1,3-diyne derivatives [10]. A relatively few applications using the alkyne-functionalized dendrons in dendrimer synthesis have been reported. An effective convergent synthesis of dendrons and dendrimers requires a monomer that can undergo the activation and coupling steps in high yield and whose products can be readily isolated from excess starting material and byproducts [11]. In addition, the coupling step must be very efficient to enable complete reaction even when involving sterically demanding high generation dendrons. In continuation with our research on the synthesis of dendrimers via click chemistry using alkyne derivatives, we were fascinated to develop the new click chemistry for the construction of dendrimers using oxidative homo-coupling reaction of the terminal acetylene. Recently, we have developed the fusion methods for the synthesis of the symmetric dendrimers from Fréchet type dendrons and poly(amido amine) (PAMAM) dendrons containing alkyne moiety at their focal point by oxidative homo-coupling of terminal alkyne [8]. Because dendrimers contain three distinct structural parts that are the core, end-groups, and branched units connecting core and periphery, we became interested in the synthesis of self-emissive dendrimer with a fluorescent probe in core region. Herein, we report a feasible route to synthesize the self-emissive dendrimers by fusion method through homo-coupling of dendrons with a profluorophore at core.

Experimental

General Methods

^{1}H-NMR spectra were recorded on a 500 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; d of d, doublet of a doublet; m, multiplet; br, broad. ^{13}C-NMR spectra were proton decoupled and recorded on a 125 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. FAB and MALDI 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. 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. Polydispersity (PDI) of dendrimers was determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5μm MIXED-C, refractive index detector) in THF solution.

General Procedure for the Synthesis of Dendrons 3-Dm. 4-Ethynylbenzyl alcohol **2** (1.1 mmol) was added to a THF (10 mL) solution of sodium hydride (2 mmol). After stirred under nitrogen for 30 min, dendritic benzyl iodide (1 mmol) was added and the mixture was stirred for ~6 h. The reaction mixture was poured slowly into cold 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 (EtOAc/Hex system) to afford the desired product **3-Dm.**

Compound 3-D1. R_f = 0.5 (EA/Hex = 1:4); A yellow solid; mp 71-73°C; 93% yield; IR 3280, 3000, 2940, 2840, 2110, 1600, 1460, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.09$ (s, 1H), 3.80 (s, 6H), 4.51 (s, 2H), 4.55 (s, 2H), 6.41 (s, 1H), 6.54 (d, $J = 1.0$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 71.5, 72.2, 77.2, 83.5, 99.7, 105.4, 121.3, 127.5, 132.1, 139.1, 140.4, 160.9; MS (EI): *m/z* 282 [M$^+$]; HRMS (EI) Calcd for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1258 [M$^+$], 283.1283 [M$^+$+H].

Compound 3-D2. R_f = 0.4 (EA/Hex = 1:2); A yellowish oil; 90% yield; IR 3280, 3000, 2940, 2840, 2110, 1600, 1460, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.11$ (s, 1H), 3.80 (s, 12H), 4.51 (s, 2H), 4.53 (s, 2H), 5.00 (s, 4H), 6.44 (s, 2H), 6.60 (m, 5H), 6.64 (m, 2H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.2$, 69.9, 71.4, 72.0, 77.2, 83.5, 99.8, 101.4, 105.1, 106.5, 121.2, 127.4, 132.1, 139.0, 139.1, 140.4, 159.9, 160.9; MS (EI): *m/z* 554 [M$^+$]; HRMS (EI) Calcd for $C_{34}H_{34}O_7$: 554.2305. Found: 554.2302 [M$^+$], 555.2383 [M$^+$+H].

Compound 3-D3. R_f = 0.25 (EA/Hex = 1:2); A yellow gum; 89% yield; IR 3280, 3000, 2940, 2840, 2110, 1600, 1460, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.08$ (s, 1H), 3.79 (s, 24H), 4.50 (s, 2H), 4.53 (s, 2H), 4.98 (s, 12H), 6.43 (s, 4H), 6.59-6.62 (m, 13H), 6.69 (m, 4H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.49 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 69.9, 70.0, 71.5, 72.1, 77.2, 83.5, 99.9, 101.4, 101.5, 105.2, 106.3, 106.6, 121.2, 127.5, 132.1, 139.0, 139.1, 139.3, 140.5, 159.9, 160.0, 160.9; MS (FAB): *m/z* 1098.1 [M$^+$]; HRMS (FAB) Calcd for $C_{66}H_{66}O_{15}$: 1098.4402. Found: 1098.4399 [M$^+$], 1099.4484 [M$^+$+H].

Compound 3-D4. R_f = 0.15 (EA/Hex = 1:2); A white gum; 84% yield; IR 3280, 3000, 2940, 2840, 2110, 1600, 1460, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta =$ 3.07 (s, 1H), 3.78 (s, 48H), 4.49 (s, 2H), 4.52 (s, 2H), 4.97 (s, 28H), 6.42 (s, 8H), 6.58-6.62 (m, 25H), 6.68 (m, 12H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 69.9, 70.0, 71.5, 72.1, 77.2, 83.5, 99.9, 101.3, 101.5, 101.6, 105.2, 106.3, 106.6, 121.2, 127.5, 132.1, 139.0, 139.08, 139.14, 139.3, 140.5, 159.9, 160.0, 160.9; MS (MALDI): Calcd for $C_{130}H_{130}O_{31}$: 2186.8596. Found: 2209.7849 [M$^+$+Na].

General Procedure for the Synthesis of Dendrimers 4-Gm. A solution of terminal acetylenic Fréchet-type dendrons **3-Dm** (0.1 mmol), CuI (0.1 mol%), and diisopropyl ethyl amine (2 equiv) in acetonitrile (0.2M) was stirred at room temperature for the specified time. After stirred for 30min, NBS (0.1 mol%) was added and the mixture was stirred for ~6 h. The resulting mixture was diluted with EtOAc (30 mL). The organic phase was washed with brine, dried over Na_2SO_4, and filtered and the filtrate was concentrated. The crude product was purified by column chromatography (EtOAc/Hex/CH_2Cl_2) to afford the desired product **4-Gm**.

Compound 4-G1. R_f = 0.2 (EA/Hex = 1:4); A yellow solid; mp 72-74°C; 92% yield; IR 3000, 2940, 2840, 1600, 1460, 1360, 1210, 1160, 1070 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.80$ (s, 12H), 4.52 (s, 4H), 4.56 (s, 4H), 6.41 (s, 2H), 6.53 (s, 4H), 7.35

(d, $J = 7.5$ Hz, 4H), 7.52 (d, $J = 8.0$ Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 71.5, 72.3, 73.9, 81.5, 99.7, 105.4, 120.9, 127.6, 132.5, 139.6, 140.4, 160.9; MS (EI): *m/z* 562 [M^+]; HRMS (EI) Calcd for $C_{36}H_{34}O_6$: 562.2355. Found: 562.2359 [M^+], 564.2439 [M^++H]. PDI: 1.01.

Compound 4-G2. $R_f = 0.2$ (EA/Hex = 1:2); A yellow oil; 90% yield; IR 3000, 2930, 2840, 1600, 1460, 1370, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.80$ (s, 24H), 4.50 (s, 4H), 4.53 (s, 4H), 4.98 (s, 8H), 6.42 (s, 4H), 6.58-6.61 (m, 14H), 7.31 (d, $J = 7.5$ Hz, 4H), 7.51 (d, $J = 8.0$ Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.4$, 70.0, 71.5, 72.2, 73.9, 81.5, 99.9, 101.5, 105.2, 106.7, 120.9, 127.6, 132.6, 139.2, 139.6, 140.4, 160.0, 161.0; MS (FAB): *m/z* 1106.1 [M^+]; HRMS (FAB) Calcd for $C_{68}H_{66}O_{14}$: 1106.4453. Found: 1106.4459 [M^+], 1107.4528 [M^++H]. PDI: 1.01.

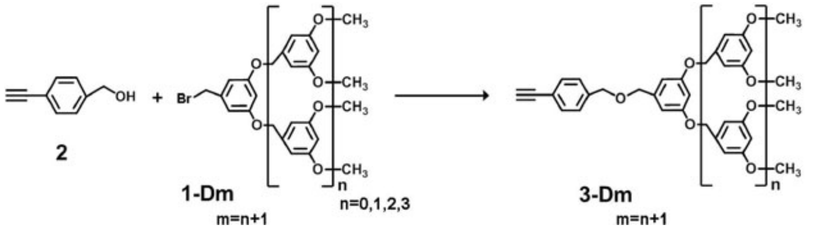
Compound 4-G3. $R_f = 0.12$ (EA/Hex = 1:2); A yellow gum; 88% yield; IR 3000, 2940, 2840, 1600, 1460, 1370, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta =$ 3.79 (s, 48H), 4.50 (s, 4H), 4.53 (s, 4H), 4.98 (s, 24H), 6.41 (s, 8H), 6.57-6.60 (m, 26H), 6.68 (m, 8H), 7.31 (d, $J = 7.5$ Hz, 4H), 7.50 (d, $J = 7.5$ Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 69.9, 70.0, 71.5, 72.2, 73.9, 81.5, 99.9, 101.4, 101.5, 105.2, 106.3, 106.6, 120.9, 127.6, 132.5, 139.1, 139.3, 139.6, 140.4, 159.9, 160.0, 160.9; MS (MALDI): Calcd for $C_{132}H_{130}O_{30}$: 2194.8647. Found: 2217.7933 [M^++Na]. PDI: 1.01.

Compound 4-G4. $R_f = 0.4$ (EA/Hex = 2:1); A white gum; 80% yield; IR 3000, 2940, 2840, 1600, 1460, 1380, 1210, 1160, 1050 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.76$ (s, 96H), 4.48 (s, 4H), 4.50 (s, 4H), 4.95 (s, 56H), 6.39 (s, 16H), 6.55-6.60 (m, 50H), 6.66 (m, 24H), 7.28 (d, $J = 8.0$ Hz, 4H), 7.46 (d, $J = 7.5$ Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 55.3$, 69.9, 70.0, 71.5, 72.2, 74.0, 81.5, 99.9, 101.3, 101.5, 101.6, 105.2, 106.4, 106.6, 120.9, 127.5, 132.5, 139.1, 139.2, 139.3, 139.6, 140.5, 159.96, 160.03, 160.9; MS (MALDI): Calcd for $C_{260}H_{258}O_{62}$: 4371.7036. Found: 4394.6456 [M^++Na]. PDI: 1.01.

Results and Discussion

The palladium-catalyzed coupling of terminal acetylenes to aromatic bromides or iodides in basic amines have been well known since 1975 [12]. Palladium-assisted Glaser-type coupling reactions mediated by Pd (0) or Pd (II), are arguably the most mild, efficient, and selective methods for the synthesis of 1,3-diynes [13]. However palladium reagents are expensive, and often required air-sensitive and poisonous ligands. Recently, the homocoupling of terminal alkyne under the CuI/NBS/DIPEA promoting system was developed by Zhang et al [14]. Glaser-type coupling reaction under CuI/NBS/DIPEA promoting system could be completed under ambient temperature without exclusion of air and moisture. Taking advantage of this fact, we report a feasible route to synthesize the symmetric Fréchet-type dendrimers from Fréchet-type dendrons containing alkyne moiety at their focal point by Glaser-type coupling reaction under CuI/NBS/DIPEA.

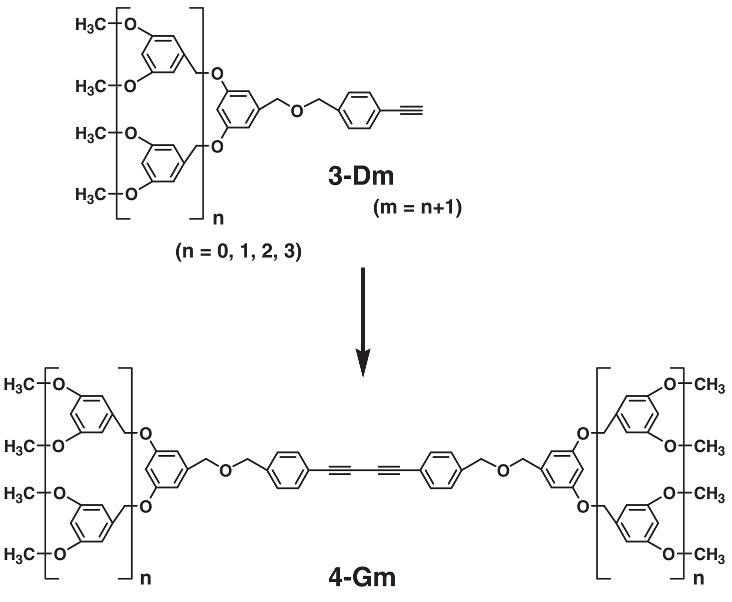
The synthetic strategy for Fréchet-type dendrimers, linked by 1,4-diphenylbuta-1,3-diyne, utilized a convergent method using the alkyne-functionalized Fréchet-type dendrons **3-Dm**. The alkyne-functionalized Fréchet-type dendrons **3-Dm** ($m = 1$–4: generation of Dendron) was synthesized by *O*-alkylation of the corresponding dendritic benzyl bromides **1-Dm** [15] with 4-ethynylbenzyl alcohol **2** (Scheme 1). The reaction of alkyne-focal dendron **1-D1** and 1.1 equiv of **2** in the presence of NaH in THF at room temperature gave the terminal alkyne-focal dendron **3-D1** in 93% yield after 2h. Given the success in the synthesis of first-generation dendron, therefore we expanded this reaction to get higher-generation dendrons. Reactions of 4-ethynylbenzyl alcohol **2** with **1-D2**, **1-D3**, and **1-D4** under same condition gave the terminal alkyne-focal dendron **3-D2**, **3-D3**, and **3-D4** in yields of 90,



Scheme 1. Synthesis of terminal alkyne-focal dendrons **3-Dm**. *Reagents and conditions*: NaH, THF, rt.

89, and 84% after 3.5, 4, and 6 h, respectively. The disappearance of dendrons **1-Dm** and generation of the terminal alkyne-focal dendrons **3-Dm** were observed by TLC runs of the reaction mixture. The alkyne-focal dendrons **3-Dm** was purified by column chromatography and the structure of **3-Dm** was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, and mass spectra.

A coupling reaction in organic chemistry is a catch-all for a range of reactions in organometallic chemistry where two hydrocarbon fragments are coupled with the aid of a metal catalyst supported by suitable ligands. The Glaser-type coupling reaction is one of the few C–C bond forming reaction which takes place under very mild conditions in aqueous solutions and in the presence of oxygen. We investigated the Glaser-type coupling reaction for the synthesis of Fréchet-type dendrimers from the terminal alkyne-focal dendrons **3-Dm** (Scheme 2). The reaction of terminal alkyne-focal dendron **3-D1** in acetonitrile (0.2 M) in the presence of 1 equiv of CuI/1 equiv of NBS and 2 equiv of diisopropyl ethyl amine for 1 h 30 min at room temperature afforded the desired product **4-G1** in yield of 92%.



Scheme 2. Synthesis of dendrimers by Glaser-type coupling of the terminal alkyne-focal dendrons. *Reagents and conditions:* NBS/CuI, diisopropyl ethyl amine, acetonitrile, rt.

The disappearance of **3-D1** and the appearance of new spot were observed from TLC analysis. The dendrimer **4-G1** was purified by column chromatography and the structure of dendrimer was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, and FAB mass spectra. The proton peak in terminal alkyne did not show at 3.09 ppm in the ^{1}H-NMR spectrum of dendrimer **4-G1** and the carbon peaks for the ethynylene carbons of dendrimer **4-G1** are at 73.9 and 81.5 ppm. IR data also confirmed that neither 3280 cm^{-1} for the H-C≡ bond stretching frequency nor 2110 cm^{-1} for the C≡C bond stretching absorption remain in the final dendrimer. Given the success in the synthesis of first generation dendrimer, we expanded this reaction to get higher generation dendrimers. Reactions of dendron **3-D2** and **3-D3** afforded the dendrimers **4-G2** and **4-G3** in yields of 90 and 88% after 2 h and 4 h, respectively, which were separated by column chromatography. Finally, reaction of dendron **3-D4** gave the dendrimer **4-G4** in a yield of 80% after 6 h. As the generation of dendrons increases, the steric hindrance between dendrons will affect the reaction more significantly. Therefore, the higher generation dendron takes longer time than the lower generation dendron.

All dendrimer were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy. From their ^{1}H-NMR spectra ($CDCl_3$), the peaks of the methylene protons of core and the inside benzylic protons in dendrimers **4-Gm** were found at 4.52 and 4.56 ppm for **4-G1**, 4.50 and 4.53 ppm for **4-G2**, 4.50 and 4.53 ppm for **4-G3**, and 4.48 and 4.50 ppm for **4-G4**, respectively (Figure 1). As the dendrimer generation increased, the peaks of the discussed protons showed up-field shift which may be influenced by the dendritic microenvironment effect [16]. The IR spectra show the disappearance of the H-C≡ bond stretching frequencies around 3280 cm^{-1} and the C≡C bond stretching absorptions around 2110 cm^{-1} in the final dendrimer (Figure 2). Analysis of the dendrimers by FAB or MALDI mass spectrometry as well as by gel-permeation chromatography (Figure 3) provides no signs of products with defects that would arise from incomplete coupling. As expected, the obtained dendrimer

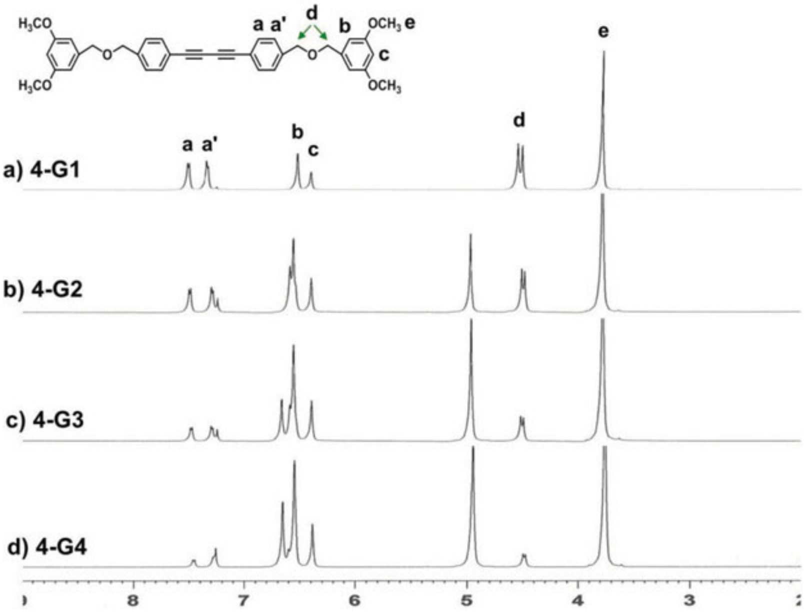


Figure 1. ^{1}H-NMR spectra for a) **4-G1**, b) **4-G2**, c) **4-G3**, and d) **4-G4**.

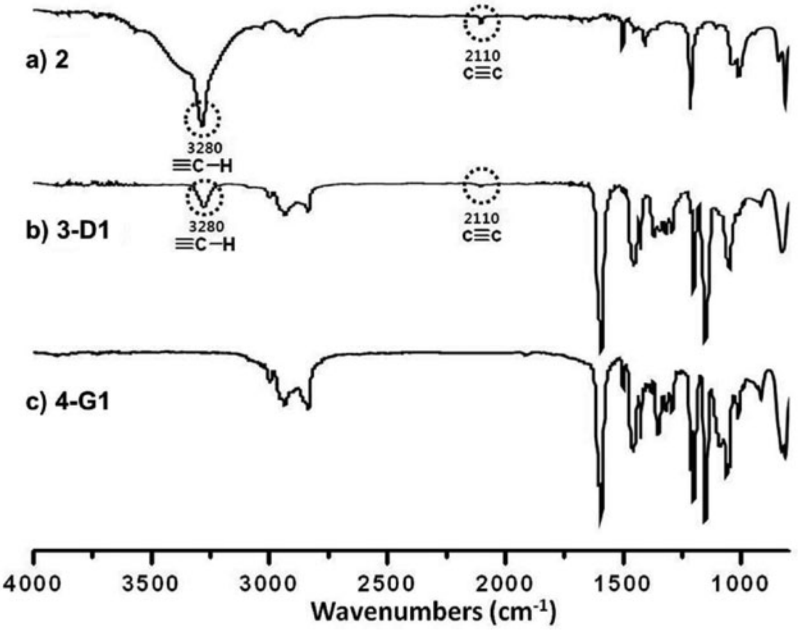


Figure 2. IR spectra for a) **2**, b) **3-D1**, and c) **4-G1**.

possessed a very well-defined molecular structure with very low polydispersity values (PDI = 1.01).

The UV-visible absorption spectra of **4-Gm** in chloroform solutions were investigated. Dendrimers exhibited the absorption at 314 and 336 ppm for **4-G1**, 314 and 337 nm for **4-G2**, 315 and 337 nm for **4-G3**, and 315 and 337 nm for **4-G4**, respectively. The photoluminescence (PL) spectra of dendron **3-D1**, dendrimers **4-G1** and **4G-4** in chloroform solutions were obtained (Figure 4). The emission peaks of dendrimer **4-G1** low more than

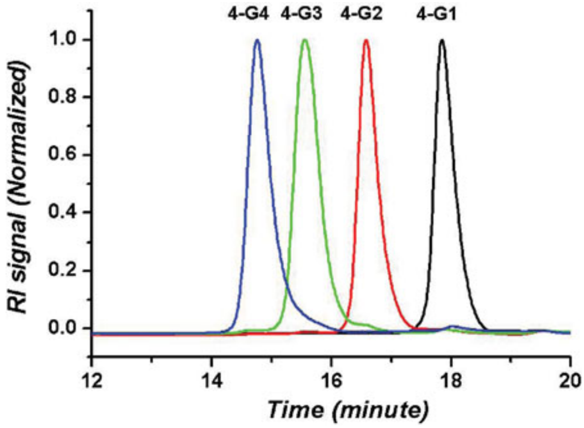


Figure 3. GPC diagrams of dendrimers **4-Gm** obtained from THF eluent.

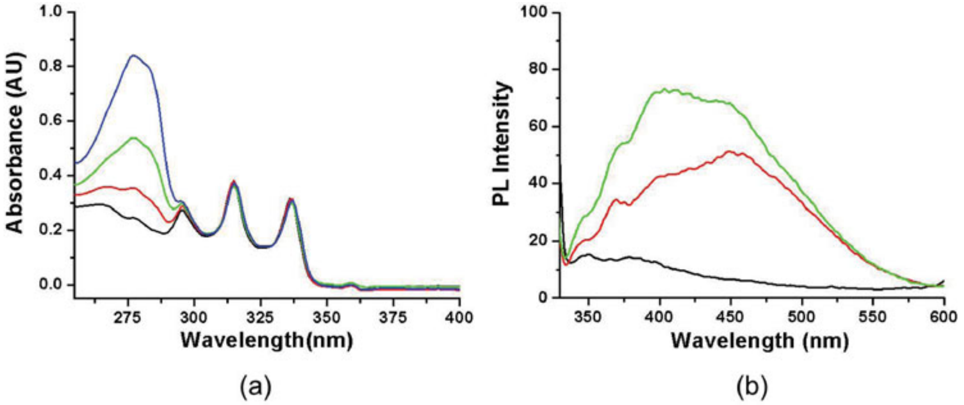


Figure 4. (a) UV-vis spectra in $CHCl_3$ (conc. = 1.0×10^{-5} M) for **4-G1** (black), **4-G2** (red), **4-G3** (green), and **4-G4** (blue). (b) PL spectra in $CHCl_3$ (λ_{ex} = 315 nm, conc. = 1.0×10^{-6} M) for **3-D1** (black), **4-G1** (red), and **4-G4** (green).

4-G4. When the dendrimer generation increases, the fluorescence intensity increases. The maximum emission intensity of dendrimer showed at 403 nm for **4-G4**.

Conclusion

We have successfully synthesized of the self-emissive dendrimers with a fluorescent probe at core by fusion method through Glaser-type coupling of terminal alkyne-focal dendrons. CuI/NBS/DIPEA-mediated Glaser-type coupling reaction could be completed under ambient temperature without exclusion of air and moisture. The homo-coupling reaction of terminal alkyne-focal dendrons **3-Dm** was allowed to provide first through fourth generation dendrimers **4-Gm** with 1,4-diphenylbuta-1,3-diyne at core. Our results demonstrate that luminescent dendrimers can be obtained by fusion method through homo-coupling of dendrons with a profluorophore at core. 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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References and Notes

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