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Synthesis of Unsymmetrical Fréchet-type Dendrimers *via* Double Click Chemistry

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Dendrimers are highly branched and regular macromolecules with well-defined structures which are prepared by repetition of a given set of reactions using either divergent or convergent strategies.[1] The convergent approach to dendrimer synthesis introduced by Fréchet and co-workers revolutionized the synthetic approaches to monodisperse dendrimers.[2] 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. Future applications of dendrimers rely on efficient and practical synthetic procedures. Therefore, development of a versatile methodology to render the synthesis of dendrimers more adaptable to specific needs is necessary. The last decade has witnessed the rapid growth of the click chemistry which is the copper-catalyzed azide-alkyne cycloaddition reaction developed by Sharpless and Tornøe.[3,4] Owing to its remarkable features, click reaction has been widely used in the synthesis of dendrimers and now appears to offer a simple, reliable, and productive dendrimer synthesis method.[5,6] Because of the high yields and lack of byproducts provided by the click chemistry, we have focused on the development of convergent synthetic method for the construction of dendrimers. The most attractive features of the convergent synthesis are abilities to prepare well-defined (un)symmetrical dendrimers. Therefore we have developed the stitching method[7,8] using alkyne-dendrons and multiple-azides core unit or *vice versa* and the fusion method[8,9] between an alkyne-dendron and an azide-dendron for the convergent synthesis of dendrimers using click chemistry between an alkyne and an azide. The former provided only the symmetric dendrimers and various dendrimers having functional building block at core which could be shown the characteristic behaviors, the latter yielded the symmetric and unsymmetric dendrimers according to selection of dendrons. Because of our interest in developing new functional dendrimers, we became involved in exploring double click reactions for the stitching method that provides an easy access to the unsymmetric dendrimers. Herein we report preliminary result in synthesis of unsymmetric Fréchet-type dendrimers using double click chemistry with a bis-azides core.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 MHz NMR spectrometer. Mass spectra were obtained from Korea Basic Science Institute (KBSI) in Daejeon. Flash chromatography was performed with 37-75 μm silica gel. Polydispersity (PDI) of dendrimers was determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5 μm MIXED-C, refractive index detector) in THF solution.

General Procedure for the Preparation of Azide-focal Dendrons 3-Dm from Alkyne-focal Dendrons 1-Dm and *p*-xylylenediazide 2. A mixture of dendrons **1-Dm** (0.127 mmol) and *p*-xylylenediazide **2** (1.91 mmol) in DMF-H_2O (4:1, 1.27 mL) in the presence of 5 mol % $CuSO_4·5H_2O$ with 10 mol % sodium ascorbate was stirred at 50 °C for ~1 h. The reaction mixture was poured into brine (30 mL) and the resulting solution was extracted with EtOAc (30 mL × 3). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography to afford the desired product **3-Dm**.

Compound 3-D1: A yellowish oil; 99% yield; IR 3001, 2928, 2859, 2099, 1597, 1462, 1323, 1204, 1153, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 6H), 4.32 (s, 2H), 4.51 (s, 2H), 4.64 (s, 2H), 5.49 (s, 2H), 6.36 (s, 1H), 6.48 (s, 2H), 7.26 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.6, 54.1, 55.2, 63.5, 72.4, 99.7, 105.4, 122.4, 128.4, 128.7, 134.6, 136.0, 140.0, 145.5, 160.8; MS (FAB): *m/z* 395.3 [M$^+$ + H]; HRMS (FAB) Calcd for $C_{20}H_{22}N_6O_3$: 394.1753. Found: 395.1830 [M$^+$ + H].

Compound 3-D2: A yellowish oil; 97% yield; IR 3001, 2936, 2839, 2099, 1597, 1458, 1323, 1204, 1157, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 12H), 4.32 (s, 2H), 4.52 (s, 2H), 4.64 (s, 2H), 4.95 (s, 4H), 5.51 (s, 2H), 6.41 (t, J = 2.0 Hz, 2H), 6.53 (t, J = 2.0 Hz, 1H), 6.57 (d, J = 2.0 Hz, 4H), 6.59 (d, J = 4.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.6, 54.2, 55.3, 63.6, 69.9, 72.4, 99.9, 101.4, 105.2, 106.7, 122.4, 128.5, 128.8, 134.6, 136.1, 139.2, 140.2, 145.6, 159.9, 160.9; MS (FAB): *m/z* 667.4 [M$^+$ + H]; HRMS (FAB) Calcd for $C_{36}H_{38}N_6O_7$: 666.2802. Found:

667.2884 [M$^+$ + H].

Compound 3-D3: A yellowish oil; 95% yield; IR 3005, 2940, 2839, 2099, 1597, 1458, 1323, 1204, 1157, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 24H), 4.30 (s, 2H), 4.52 (s, 2H), 4.64 (s, 2H), 4.95 (s, 4H), 4.97 (s, 8H), 5.49 (s, 2H), 6.41 (t, J = 2.0 Hz, 4H), 6.52 (m, 1H), 6.55 (m, 2H), 6.57 (m, 8H+2H), 6.67 (d, J = 2.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.44 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.7, 54.2, 55.3, 63.7, 69.9, 70.1, 72.5, 99.9, 101.4, 101.6, 105.2, 106.4, 106.7, 122.4, 128.5, 128.8, 134.7, 136.1, 139.1, 139.3, 140.2, 145.6, 159.9, 160.1, 161.0; MS (FAB): *m/z* 1210.7 [M$^+$]; HRMS (FAB) Calcd for $C_{68}H_{70}N_6O_{15}$: 1210.4899. Found: 1211.4968 [M$^+$ + H].

General Procedure for the Preparation of Dendrimers 4-Gmm from Azide-focal Dendrons 3-Dm and Alkyne-focal Dendrons 1-Dm. A mixture of **3-Dm** (0.057 mmol) and **1-Dm** (0.068 mmol) in DMF-H_2O (4:1, 0.57 mL) in the presence of 10 mol % $CuSO_4{\cdot}5H_2O$ with 20 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 × 3). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography to afford the desired unsymmetric dendrimers **4-Gmm**.

Compound 4-G12: A yellowish oil; 94% yield; IR 3001, 2940, 2839, 1597, 1458, 1323, 1204, 1153, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 6H), 3.78 (s, 12H), 4.51 (s, 4H), 4.629 (s, 2H), 4.632 (s, 2H), 4.95 (s, 4H), 5.47 (s, 2H), 5.49 (s, 2H), 6.37 (t, J = 2.0 Hz, 1H), 6.40 (t, J = 2.0 Hz, 2H), 6.48 (d, J = 2.0 Hz, 2H), 6.52 (d, J = 2.0 Hz, 1H), 6.56 (d, J = 2.0 Hz, 4H), 6.58 (d, J = 1.5 Hz, 2H), 7.25 (s, 4H), 7.445 (s, 1H), 7.449 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.5, 55.28, 55.31, 63.6, 70.0, 72.4, 72.5, 99.7, 99.9, 101.4, 105.2, 105.5, 106.7, 122.4, 122.5, 128.68, 128.71, 135.2, 135.3, 139.2, 140.1, 140.2, 145.7, 159.9, 160.8, 160.9; MS (FAB): *m/z* 873.4 [M$^+$ + H]; HRMS (FAB) Calcd for $C_{48}H_{52}N_6O_{10}$: 872.3745. Found: 873.3828 [M$^+$ + H]. PDI: 1.01.

Compound 4-G13: A yellowish oil; 98% yield; IR 3001, 2940, 2839, 1597, 1458, 1323, 1204, 1153, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.78 (s, 24H), 4.51 (s, 2H), 4.52 (s, 2H), 4.627 (s, 2H), 4.634 (s, 2H), 4.95 (s, 4H), 4.96 (s, 8H), 5.45 (s, 2H), 5.47 (s, 2H), 6.37 (t, J = 2.0 Hz, 1H), 6.40 (t, J = 2.0 Hz, 4H), 6.48 (d, J = 2.5 Hz, 2H), 6.52 (t, 1H), 6.55 (d, J = 2.0 Hz, 2H), 6.57 (m, 8H+2H), 6.66 (d, J = 2.0 Hz, 4H), 7.23 (s, 4H), 7.43 (s, 1H), 7.44 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.5, 55.28, 55.32, 63.6, 69.9, 70.0, 72.4, 72.5, 99.7, 99.9, 101.4, 101.5, 105.2, 105.6, 106.4, 106.7, 122.4, 122.5, 128.68, 128.71, 135.2, 135.3, 139.1, 139.3, 140.1, 140.2, 145.65, 145.67, 159.9, 160.0, 160.9, 161.0; MS (FAB): *m/z* 1417.9 [M$^+$ + H]; HRMS (FAB) Calcd for $C_{80}H_{84}N_6O_{18}$: 1416.5842. Found: 1417.5916 [M$^+$ + H]. PDI: 1.01.

Compound 4-G14: A yellowish oil; 98% yield; IR 3001, 2936, 2839, 1597, 1458, 1323, 1204, 1153, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 6H), 3.77 (s, 48H), 4.50 (s, 2H), 4.51 (s, 2H), 4.616 (s, 2H), 4.622 (s, 2H), 4.96 (s, 16H+8H+4H), 5.42 (s, 2H), 5.43 (s, 2H), 6.36 (t, J = 2.0 Hz, 1H), 6.40 (t, J = 2.0 Hz, 8H), 6.48 (d, J = 2.0 Hz, 2H), 6.55-6.58 (m, 16H+4H+2H+2H+1H), 6.67 (m, 8H+4H), 7.21 (s, 4H), 7.41 (s, 1H), 7.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.5, 55.3, 63.6, 69.9, 70.0, 72.4, 72.5, 99.7, 99.9, 101.5, 101.6, 105.2, 105.5, 106.4, 106.7, 122.4, 122.5, 128.65, 128.68, 135.2, 135.3, 139.1, 139.2, 139.3, 140.1, 140.2, 145.62, 145.64, 159.9, 160.0, 160.8, 160.9; MS (MALDI): Calcd for $C_{144}H_{148}N_6O_{34}$: 2505.0037. Found: 2527.9084 [M$^+$ + Na]. PDI: 1.01.

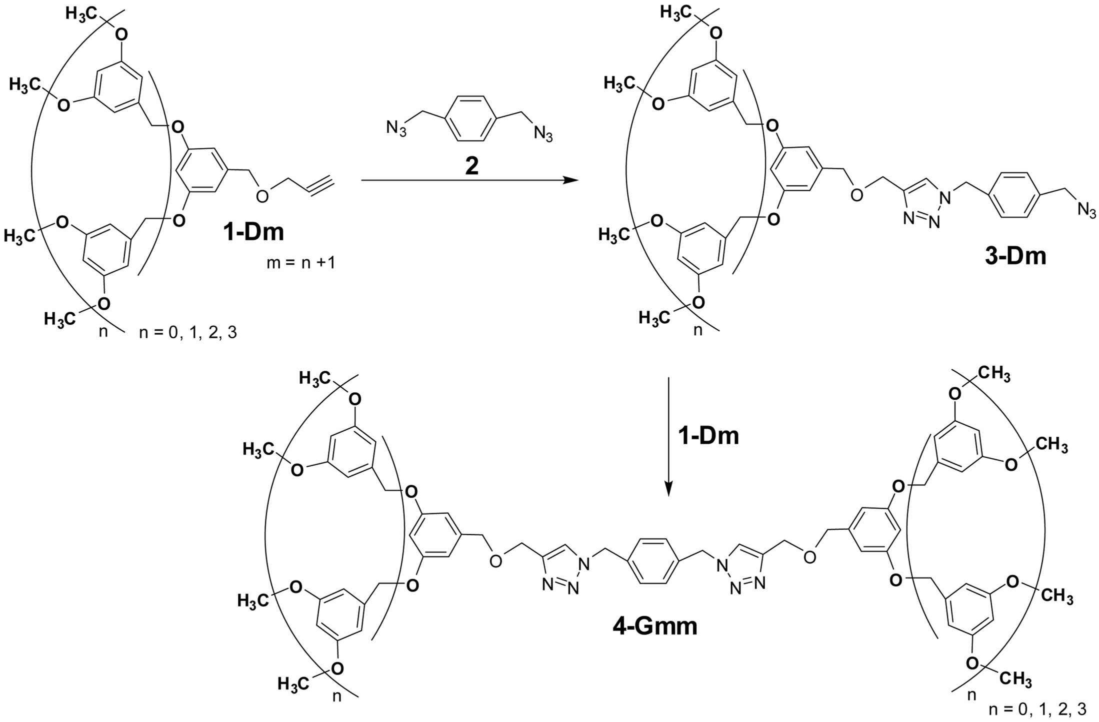
Compound 4-G23: A yellowish oil; 98% yield; IR 3005, 2940, 2839, 1597, 1458, 1323, 1204, 1157, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 12H), 3.78 (s, 24H), 4.50 (s, 2H), 4.52 (s, 2H), 4.62 (s, 2H), 4.63 (s, 2H), 4.94 (s, 4H), 4.95 (s, 4H), 4.96 (s, 8H), 5.45 (s, 4H), 6.40 (m, 4H+2H), 6.52 (m, 2H), 6.56-6.58 (m, 8H+4H+2H+2H+1H+ 1H), 6.67 (d, J = 2.0 Hz, 4H), 7.23 (s, 4H), 7.42 (s, 1H), 7.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.5, 55.3, 63.6, 69.87, 69.94, 70.01, 72.4, 99.8, 99.9, 101.4, 101.5, 105.2, 106.4, 106.7, 122.5, 128.7, 135.3, 139.1, 139.2, 139.3, 140.18, 140.20, 145.61, 145.62, 159.9, 160.0, 160.9; MS (FAB): *m/z* 1690.3 [M$^+$ + H]; HRMS (FAB) Calcd for $C_{96}H_{100}N_6O_{22}$: 1688.6891. Found: 1688.6770 [M$^+$], 1689.6976 [M$^+$ + H]. PDI: 1.01.

Compound 4-G24: A yellowish oil; 96% yield; IR 3001, 2932, 2839, 1597, 1458, 1323, 1204, 1157, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 12H), 3.76 (s, 48H), 4.49 (s, 2H), 4.50 (s, 2H), 4.60 (s, 2H), 4.61 (s, 2H), 4.93 (s, 4H), 4.95 (s, 28H), 5.413 (s, 2H), 5.416 (s, 2H), 6.39 (m, 8H+2H), 6.52-6.56 (m, 32H), 6.65-6.66 (m, 8H+4H), 7.20 (s, 4H), 7.40 (s, 1H), 7.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.5, 55.3, 63.6, 69.93, 69.96, 70.00, 70.02, 72.4, 99.9, 101.4, 101.5, 101.6, 105.2, 106.4, 106.71, 106.74, 122.5, 128.7, 128.6, 135.3, 139.1, 139.2, 139.3, 140.3, 145.6, 159.9, 160.03, 160.05, 161.0; MS (MALDI): Calcd for $C_{160}H_{164}N_6O_{38}$: 2777.1085. Found: 2800.1043 [M$^+$ + Na]. PDI: 1.01.

Compound 4-G34: A yellowish oil; 90% yield; IR 3005, 2940, 2839, 1597, 1458, 1323, 1204, 1157, 1053 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 24H), 3.77 (s, 48H), 4.50 (s, 4H), 4.61 (s, 4H), 4.93 (s, 12H), 4.95 (s, 28H), 5.38 (s, 4H), 6.39 (m, 8H+4H), 6.51 (d, J = 2.0 Hz, 2H), 6.50-6.57 (m, 36H), 6.65-6.67 (m, 8H+4H+4H), 7.18 (s, 4H), 7.39 (s, 1H), 7.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.4, 55.3, 63.6, 69.86, 69.93, 79.99, 72.4, 99.8, 101.4, 101.5, 101.6, 105.2, 106.4, 106.65, 106.71, 122.5, 128.6, 135.2, 139.1, 139.2, 139.3, 140.2, 145.6, 159.90, 159.92, 160.0, 160.9; MS (MALDI): Calcd for $C_{192}H_{196}N_6O_{46}$: 3321.3182. Found: 3322.2944 [M$^+$ + H], 3344.2509 [M$^+$ + Na]. PDI: 1.01.

Results and Discussion

The inward growth employed by the convergent synthesis is ideally suited for the attachment of diverse core moieties. As a result, building dendrimers *via* the convergent approach allows for the synthesis of symmetric dendrimers and for specific incorporation of function into the dendrimer interior.



Scheme 1. *Reagents and conditions:* $CuSO_4·5H_2O$/sodium ascorbate, DMF/H_2O (4:1), 50 °C.

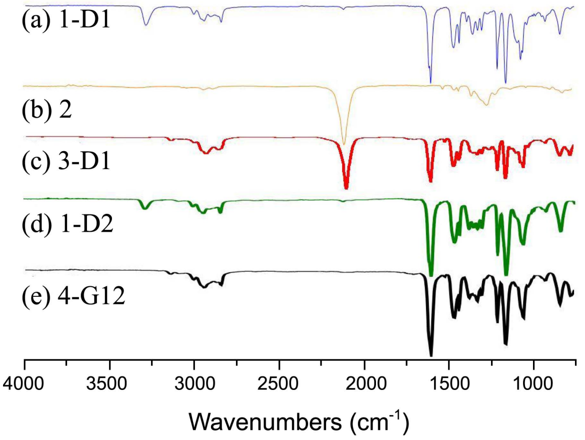


Figure 1. IR spectra for (a) **1-D1**, (b) **2**, (c) **3-D1**, (d) **1-D2**, and (e) **4-G12**.

Then we sought to expand the scope of click chemistry for the convergent synthesis of unsymmetric Fréchet-type dendrimers. Unsymmetric dendrimers were assembled through successive click reactions. In other words, unsymmetric dendrimer growth proceeded *via* an iterative sequence that involved double click reactions of a bis(azide) core with the alkynyl group of the dendron.

The synthetic strategy for unsymmetric Fréchet-type dendrimers, linked by the triazole units, utilized double click methods using the alkyne-functionalized Fréchet-type dendrons **1-Dm** (Scheme 1). The bis(azide) core **2**, designed to present two azide functionalities available for dendrimer growth *via* click reactions with the dendron, was synthesized readily from α,α'-dichloro-*p*-xylene and sodium azide. The alkyne-functionalized Fréchet-type dendrons **1-Dm** (m = 1-4: generation of dendron) was synthesized by the propargylation of the corresponding dendritic benzyl alcohols with propargyl bromide.[8]

We first have investigated the reaction of the alkyne-functionalized Fréchet-type dendrons **1-Dm** and bis(azide) core **2** to provide the mono-dendritic compounds **3-Dm** with one more reactive azide focal group. Reactions of alkyne-focal dendrons **1-D1**, **1-D2**, **1-D3** and 15 equiv of *p*-xylylenediazide **2** in the presence of 5 mol % $CuSO_4·5H_2O$ with 10 mol % sodium ascorbate in a 4:1 solvent ratio of DMF to H_2O at 50 °C gave the azide-focal dendron **3-D1**, **3-D2**, and **3-D3** in yields of 99, 97, and 95% after 15 min, 30 min, and 1 h, respectively. The disappearance of dendrons **1-Dm** and generation of the mono-triazole derivative **3-Dm** were monitored by TLC runs of the reaction mixture. The azide-focal dendron **3-Dm** was purified by column chromatography and the structure of **3-Dm** was confirmed by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectra. The IR spectra showed the disappearance of the acetylene peak at ~3277 cm^{-1} and the appearance of azide peak at 2099 cm^{-1} in dendron **3-Dm** (Figure 1), while the ^1H NMR revealed no alkyne peak at around δ 2.47 ppm and the ^1H NMR signals of the triazole proton and the methylene protons adjacent to the azide in dendron **3-Dm** were observed at 7.47 and 4.32 ppm for **3-D1**, 7.45 and 4.32 ppm for **3-D2**, and 7.44 and 4.30 ppm for **3-D3**, respectively.

Next, we tried the second click reaction to obtain the unsymmetric dendrimers by stitching of core unit with dendrons. The reaction of first generation azido-focal dendron **3-D1** with **1-D2**, **1-D3**, and **1-D4** in the presence of 10 mol % $CuSO_4·5H_2O$ with 20 mol % sodium ascorbate in a 4:1 solvent ratio of DMF to H_2O at 50 °C afforded the

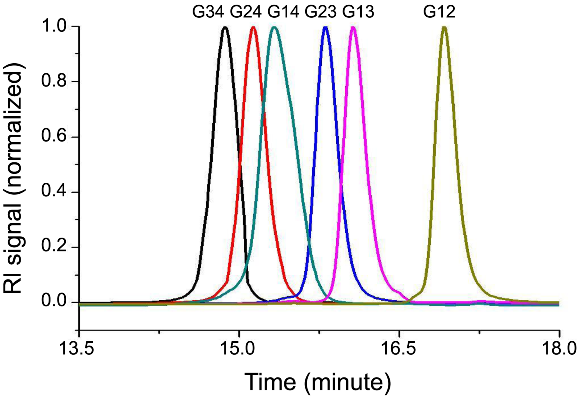


Figure 2. GPC diagrams of dendrimers **4-Gmm** obtained from THF eluent.

unsymmetrical dendrimers **4-G12**, **4-G13**, and **4-G14** in yields of 94, 98 and 98%, respectively, after 15, 30, and 30 min. The reaction of second generation azido-focal dendron **3-D2** with **1-D3** and **1-D4** under same condition gave the unsymmetrical dendrimers **4-G23** and **4-G24** in yields of 98% and 96%, respectively, after 1 h and 2 h. Finally, The reaction of **3-D3** with **1-D4** provided the unsymmetrical dendrimers **4-G34** in 90% yield after 4 h. For completion of the reaction, the higher generation dendron takes longer time than the lower generation dendron which could be caused by the limitation of the accessibility of acetylide due to the steric hindrance (bulkiness) of dendron. This result showed that the successive formation of triazole is found to be an efficient connector to construct the unsymmetric Fréchet-type dendrimers from dendrons. We are currently investigated the synthesis of various unsymmetric functional dendrimers using the different kinds of dendrons. All unsymmetric dendrimers were also confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectra. The ^{1}H NMR revealed no alkyne peak at around δ 2.47 ppm and methylene peak adjacent to the azide at ~ δ 4.30 in the final dendrimer. IR data also confirmed that neither azide (~2099 cm^{-1}) nor alkyne (~3277 cm^{-1}) residues remain in the final dendrimer (Figure 1). From the analysis of gel-permeation chromatography (Figure 2), the dendrimers showed very low polydispersity values (PDI = 1.01).

In summary, we have demonstrated for the first time that successive click reactions between dendrons of different generations and a core unit afford unsymmetrical Fréchet-type dendrimers. Therefore double click reactions can be applied for the fast synthesis of specific dendrimers with different lengths (spacers) at core and may then provide an insight into designing various unsymmetrical dendrimers such as amphiphilic dendrimers. We are currently working toward synthesis of various functional dendrimers using this strategy for various applications.

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