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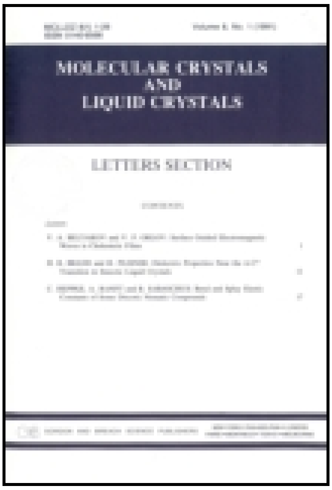

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Efficient Synthesis of Carbazole Core Diblock Dendrimer by Double Click Chemistry

Seung Choul Han[a], In-Hwa Choi[a], Sung-Ho Jin[b] & Jae Wook Lee[a]
[a] Department of Chemistry, Dong-A University, Busan, Korea
[b] Department of Chemistry Education, Pusan National University, Busan, Korea

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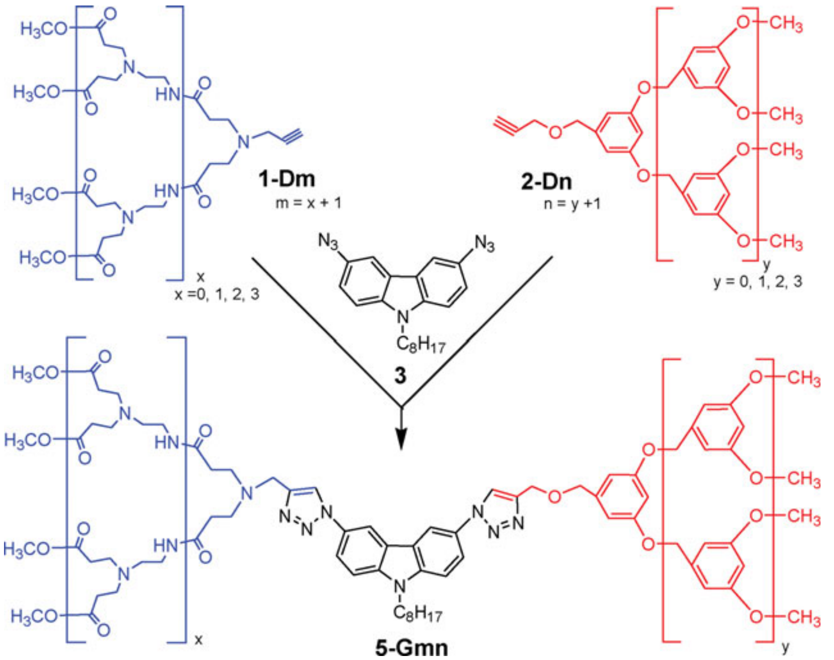
Efficient Synthesis of Carbazole Core Diblock Dendrimer by Double Click Chemistry

SEUNG CHOUL HAN,[1] IN-HWA CHOI,[1] SUNG-HO JIN,[2,*]
AND JAE WOOK LEE[1,*]

[1]Department of Chemistry, Dong-A University, Busan, Korea
[2]Department of Chemistry Education, Pusan National University, Busan, Korea

Graphical Abstract



Efficient double click methods for the synthesis of carbazole core diblock codendrimers were developed. The synthetic strategy involved the sequential double click reactions between an alkyne and an azide. The chromophore building block, N-octyl-*3,6-diazidocarbazole, was chosen to serve as the azide functionalities for dendrimer growth via double click reactions with the alkyne-functionalized PAMAM dendrons as hydrophilic dendron and alkyne-functionalized Fréchet-type dendrons as hydrophobic*

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[*] Address correspondence to Sung-Ho Jin, Department of Chemistry Education, Graduate Department of Chemical Materials, and Institute for Plastic Information and Energy Materials, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr and Jae Wook Lee, Department of Chemistry, Dong-A University, Busan 604-714, Korea. E-mail: jlee@donga.ac.kr.

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dendron. The structure of diblock codendrimers was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, mass spectrometry, and GPC analysis.

Keywords Carbazole; click reaction; diblock dendrimer; triazole

Introduction

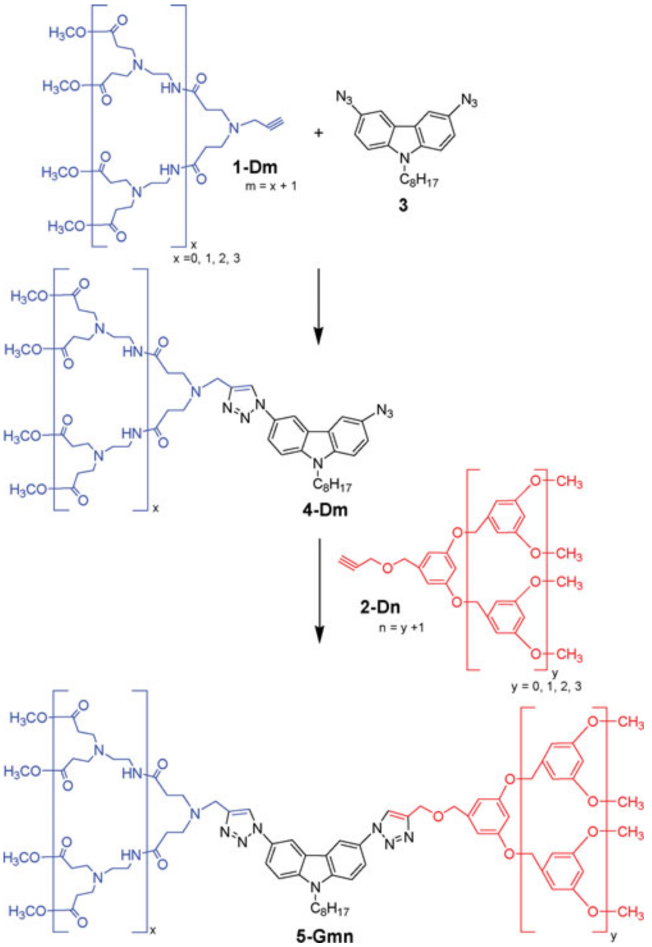
Dendrimers and dendrons can be considered as unique quantized building blocks for nanoscience and have served as functional objects in nanotechnology and nano-materials science [1]. The amphiphilic dendrimers consisting of both hydrophobic and hydrophilic regions in the same molecule appear as an important issue throughout the physical and life sciences and can be considered unimolecular micelles [2, 3]. The diblock codendrimer composed of two different dendrons is also intriguing macromolecule, which offers challenge and fascination as purely synthetic objects at the boundary of organic and polymer chemistry and as promising materials for diverse advanced applications. Relatively few diblock codendrimers have been reported so far. Most of the diblock codendrimers are the surface-modified block dendrimers [4]. Future applications of dendrimers rely on efficient and practical synthetic procedures. Therefore, a general strategy for the facile synthesis of diblock codendrimers from distinct component blocks is still needed.

The synthetic methods in dendrimer chemistry have recently been upgraded by the click chemistry which is the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide explored by Sharpless and Tornøe [5, 6]. This chemistry have seen tremendous growth in many fields including organic chemistry and polymer chemistry in recent years and is considered as efficient, simple and greener routes to design dendrimers [7]. We have the first recognized that the click reaction 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 the years [8, 9]. Taking advantage of this fact, herein we present the efficient synthetic method for the chromophore core diblock codendrimers by sequential double click reactions which involved double stitching methods of different dendrons with a carbazole core (Scheme 1).

Experimental

General Methods

^{1}H-NMR spectra were recorded on a 300 or 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 75 or 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 5 μm MIXED-C, refractive index detector) in THF solution.



Scheme 1. Synthesis of diblock codendrimers **5-Gmn**. *Reagents and conditions:* 5 mol% of $CuSO_4 \cdot 5H_2O$/10 mol% of sodium ascorbate, THF/H_2O (4:1).

General procedure for the preparation of azide-focal PAMAM dendrons 4-Dm from alkyne-focal PAMAM dendrons 1-Dm and *N*-octyl-3,6-diazidocarbazole 3. A mixture of alkyne-functionalized PAMAM dendrons **1-Dm** (0.1 mmol) and *N*-octyl-3,6-diazidocarbazole **3** (1.5 mmol) in THF-H_2O (4:1, 1 mL) in the presence of 5 mol% $CuSO_4 \cdot 5H_2O$ with 10 mol% sodium ascorbate was stirred at rt for ~4.5 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 product **4-Dm.**

Compound 4-D1. $R_f = 0.5$ (EA/Hexane = 2:1); A yellowish oil; 99% yield; IR : 2951, 2928, 2855, 2110, 1736, 1497, 1474, 1300, 1227, 1204, 1173, 1042 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.84$ (t, $J = 6.5$ Hz, 3H), 1.22 (m, 6H), 1.31 (m, 4H), 1.85 (quin, $J = 6.5$ Hz, 2H), 2.58 (t, $J = 6.9$ Hz, 4H), 2.91 (t, $J = 6.9$ Hz, 4H), 3.67 (s, 6H), 3.93 (s, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 1H), 7.38 (d, $J = 8.7$ Hz, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 7.73 (s, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 8.03 (s, 1H), 8.35 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 22.5, 27.2, 28.9, 29.1, 29.2, 31.7, 32.5, 43.5, 48.8, 49.0, 51.6, 109.6, 110.2, 110.5, 113.2, 118.3, 119.4, 121.6, 122.2, 123.3, 129.6, 131.8, 138.7, 140.5, 145.1, 172.7; MS (FAB): *m/z* 589.44 [M$^+$+H]; HRMS (FAB): Calcd for $C_{31}H_{40}N_8O_4$: 588.3173. Found: 589.3256 [M$^+$+H].

Compound 4-D2. R$_f$ = 0.3 (EA/MeOH = 7:1); A brownish oil; 99% yield; IR : 3333, 2951, 2928, 2855, 2110, 1736, 1655, 1497, 1470, 1439, 1296, 1204, 1045 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.4$ Hz, 3H), 1.24 (m, 6H), 1.32 (m, 4H), 1.87 (quin, $J = 6.8$ Hz, 2H), 2.41 (t, $J = 6.6$ Hz, 8H), 2.50 (t, $J = 6.6$ Hz, 4H), 2.54 (t, $J = 6.0$ Hz, 4H), 2.73 (t, $J = 6.6$ Hz, 8H), 2.90 (t, $J = 6.5$ Hz, 4H), 3.30 (q, $J = 5.6$ Hz, 4H), 3.64 (s, 12H), 3.95 (s, 2H), 4.31 (t, $J = 7.1$ Hz, 2H), 7.17-7.19 (m, 3H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 2.0$ Hz, 1H), 7.85 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H), 8.12 (s, 1H), 8.41 (d, $J = 1.9$ Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 22.5, 27.2, 28.9, 29.1, 29.3, 31.7, 32.7, 33.8, 37.2, 43.5, 48.0, 49.3, 49.5, 51.6, 52.9, 109.6, 110.2, 110.6, 113.1, 118.3, 119.4, 121.5, 122.3, 123.4, 129.6, 131.8, 138.7, 140.5, 144.9, 172.2, 173.0; MS (FAB): *m/z* 990.0 [M$^+$+H]; HRMS (FAB): Calcd for $C_{49}H_{72}N_{12}O_{10}$: 988.5494. Found: 988.5433 [M$^+$], 989.5562 [M$^+$+H].

Compound 4-D3. R$_f$ = 0.45 (EA/MeOH = 1:1); A brownish oil; 97% yield; IR : 3291, 2951, 2924, 2855, 2106, 1736, 1651, 1543, 1462, 1439, 1296, 1200, 1045 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.5$ Hz, 3H), 1.24 (m, 6H), 1.33 (m, 4H), 1.87 (quin, $J = 6.5$ Hz, 2H), 2.36–2.42 (m, 24H), 2.50 (t, $J = 5.4$ Hz, 12H), 2.59 (t, $J = 5.5$ Hz, 4H), 2.72 (t, $J = 6.4$ Hz, 16H), 2.80 (t, $J = 6.2$ Hz, 8H), 2.88 (t, $J = 6.3$ Hz, 4H), 3.26 (q, $J = 5.3$ Hz, 12H), 3.64 (s, 24H), 3.95 (s, 2H), 4.31 (t, $J = 7.0$ Hz, 2H), 7.07 (t, $J = 5.0$ Hz, 4H), 7.18 (d, $J = 8.7$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 1H), 7.79 (m, 3H), 7.85 (d, $J = 8.7$ Hz, 1H), 8.20 (s, 1H), 8.43 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta =$ 14.0, 22.5, 27.2, 29.0, 29.1, 29.3, 31.7, 32.6, 33.8, 33.9, 37.2, 37.5, 43.5, 47.7, 49.2, 49.3, 49.9, 51.6, 52.5, 52.9, 109.7, 110.2, 110.7, 113.2, 118.2, 119.5, 121.8, 122.3, 123.4, 129.6, 131.8, 138.7, 140.5, 144.6, 172.4, 173.0; MS (FAB): *m/z* 1790.1 [M$^+$+H]; HRMS (FAB): Calcd for $C_{85}H_{136}N_{20}O_{22}$: 1789.0138. Found: 1789.0198 [M$^+$], 1790.0201 [M$^+$+H].

Compound 4-D4. R$_f$ = 0.25 (MeOH); A brownish oil; 94% yield; IR : 3294, 2951, 2932, 2851, 2110, 1736, 1647, 1547, 1462, 1439, 1258, 1200, 1045 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.84$ (t, $J = 6.6$ Hz, 3H), 1.23 (m, 6H), 1.32 (m, 4H), 1.86 (quin, $J = 6.4$ Hz, 2H), 2.33-2.42 (m, 56H), 2.49-2.52 (m, 32H), 2.70–2.77 (m, 56H), 2.84-2.86 (m, 4H), 3.24-3.25 (m, 28H), 3.63 (s, 48H), 3.94 (s, 2H), 4.31 (t, $J = 6.6$ Hz, 2H), 7.07 (t, $J = 4.9$ Hz, 8H), 7.16 (d, $J = 8.7$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.50 (d, $J = 8.7$ Hz, 1H), 7.65 (t, 4H), 7.80 (s, 1H), 7.85 (d, $J = 9.1$ Hz, 1H), 7.88 (br, 2H), 8.24 (s, 1H), 8.44 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 22.5, 27.1, 28.9, 29.0, 29.2, 31.6, 32.6, 33.7, 37.1, 37.4, 43.5, 47.4, 49.2, 49.7, 50.0, 51.5, 52.4, 52.8, 109.7, 110.2, 110.7, 113.2, 118.1, 119.4, 121.9, 122.2, 123.3, 129.6, 131.7, 138.6, 140.4, 144.4, 172.3, 172.4, 173.0; MS (MALDI): Calcd for $C_{157}H_{264}N_{36}O_{46}$: 3389.9426. Found: 3390.1411 [M$^+$].

General procedure for the preparation of diblock codendrimers 5-Gmn from azide-focal dendrons 4-Dm and alkyne-focal dendrons 2-Dn. A mixture of **4-Dm** (0.10 mmol) and **2-Dn** (1.05 mmol) in THF-H_2O (4:1, 1 mL) in the presence of 5 mol% $CuSO_4{\cdot}5H_2O$ with 10 mol% sodium ascorbate was stirred at rt for ~6 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 diblock codendrimers **5-Gmn.**

Compound 5-G11. R$_f$ = 0.4 (EA/Hexane = 10:1); A yellowish oil; 97% yield; IR 2951, 2928, 2855, 1736, 1597, 1504, 1462, 1319, 1204, 1157, 1045 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.6$ Hz, 3H), 1.24 (m, 6H), 1.34 (m, 4H), 1.91 (quin, $J = 6.9$ Hz, 2H), 2.60 (t, J = 6.4 Hz, 4H), 2.93 (t, J = 6.6 Hz, 4H), 3.67 (s, 6H), 3.79 (s, 6H), 3.96 (s, 2H), 4.37 (t, J = 7.0 Hz, 2H), 4.63 (s, 2H), 4.80 (s, 2H), 6.40 (t, J = 2.2 Hz, 1H), 6.56 (d, J = 2.2 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.86 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.90 (dd, J_1 = 8.9 Hz, J_2 = 2.1 Hz, 1H), 8.07 (s, 2H), 8.40 (d, J = 1.9 Hz, 1H), 8.43 (d, J = 1.9 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.5, 27.2, 28.9, 29.0, 29.2, 31.6, 32.4, 43.6, 48.7, 49.0, 51.6, 55.3, 63.7, 72.6, 99.8, 105.5, 109.9, 113.2, 113.3, 119.8, 121.4, 121.6, 122.6, 126.7, 129.8, 130.0, 140.1, 140.6, 140.7, 145.7, 160.8, 172.7; MS (FAB): *m/z* 795.5 [M^++H]; HRMS (FAB): Calcd for $C_{43}H_{54}N_8O_7$: 794.4115. Found: 755.4200 [M^++H]. PDI: 1.01.

Compound 5-G22. R_f = 0.3 (EA/MeOH = 5:1); A yellowish oil; 94% yield; IR 3364, 2951, 2928, 2851, 1736, 1655, 1597, 1458, 1319, 1204, 1157, 1045 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.6 Hz, 3H), 1.24 (m, 6H), 1.35 (m, 4H), 1.91 (quin, J = 6.8 Hz, 2H), 2.40 (t, J = 6.4 Hz, 8H), 2.50-2.55 (m, 8H), 2.73 (t, J = 6.5 Hz, 8H), 2.90 (t, J = 6.2 Hz, 4H), 3.30 (q, J = 5.2 Hz, 4H), 3.63 (s, 12H), 3.76 (s, 12H), 3.95 (s, 2H), 4.38 (t, J = 7.0 Hz, 2H), 4.62 (s, 2H), 4.77 (s, 2H), 4.97 (s, 4H), 6.38 (m, 2H), 6.56 (m, 5H), 6.65 (m, 2H), 7.16 (m, 2H), 7.54 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 8.06 (s, 1H), 8.12 (s, 1H), 8.45 (s, 1H), 8.49 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.8, 22.3, 27.0, 28.7, 28.9, 29.0, 31.5, 32.4, 33.6, 36.9, 43.4, 47.8, 49.0, 49.2, 51.4, 52.7, 55.1, 63.5, 69.8, 72.3, 99.7, 101.3, 104.9, 106.5, 109.7, 113.0, 113.3, 119.7, 121.2, 122.5, 122.6, 129.7, 129.9, 139.0, 140.0, 140.5, 144.8, 145.4, 159.7, 160.7, 171.9, 172.8; MS (FAB): *m/z* 1467.7 [M^++H]; HRMS (FAB): Calcd for $C_{77}H_{102}N_{12}O_{17}$: 1466.7486. Found: 1466.7441 [M^+], 1467.7574 [M^++H]. PDI: 1.01.

Compound 5-G33. R_f = 0.18 (EA/MeOH = 2:1); A yellowish oil; 83% yield; IR 3314, 2951, 2936, 2843, 1736, 1651, 1597, 1458, 1373, 1204, 1157, 1049 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, J = 6.8 Hz, 3H), 1.24 (m, 6H), 1.35 (m, 4H), 1.90 (quin, J = 6.8 Hz, 2H), 2.39 (t, J = 6.7 Hz, 24H), 2.50 (t, J = 5.6 Hz, 12H), 2.58 (t, J = 5.5 Hz, 4H), 2.71 (t, J = 6.6 Hz, 16H), 2.79 (t, J = 6.1 Hz, 8H), 2.87 (t, J = 5.1 Hz, 4H), 3.25–3.32 (m, 12H), 3.63 (s, 24H), 3.75 (s, 24H), 3.94 (s, 2H), 4.36 (t, J = 7.0 Hz, 2H), 4.62 (s, 2H), 4.76 (s, 2H), 4.94 (s, 8H), 4.97 (s, 4H), 6.37 (t, J = 2.0 Hz, 4H), 6.54 (m, 11H), 6.64 (d, J = 1.9 Hz, 2H), 6.66 (d, J = 1.9 Hz, 4H), 7.06 (t, J = 5.0 Hz, 4H), 7.51 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 8.9 Hz, 1H), 7.79–7.83 (m, 3H), 7.90 (dd, J_1 = 8.8 Hz, J_2 = 1.9 Hz, 1H), 8.08 (s, 1H), 8.20 (s, 1H), 8.49 (d, J = 1.8 Hz, 1H), 8.51 (d, J = 1.8 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.5, 27.2, 28.9, 29.0, 29.2, 31.6, 32.6, 33.7, 33.8, 37.1, 37.4, 43.6, 47.6, 49.1, 49.3, 49.8, 51.5, 52.4, 52.8, 55.2, 63.5, 69.8, 69.9, 72.4, 99.8, 101.5, 105.1, 106.3, 106.7, 109.8, 109.9, 113.3, 113.5, 119.8, 121.4, 121.7, 122.7, 122.8, 129.8, 130.0, 139.0, 139.2, 140.2, 140.7, 144.7, 145.5, 159.89, 159.94, 160.9, 172.2, 172.3, 172.9; MS (MALDI): Calcd for $C_{145}H_{198}N_{20}O_{37}$: 2811.4227. Found: 2834.5749 [M^++Na]. PDI: 1.01.

Compound 5-G44. R_f = 0.2 (CH_2Cl_2/MeOH = 1:1); A brownish oil; 87% yield; IR 3291, 2951, 2932, 2843, 1736, 1651, 1597, 1458, 1373, 1204, 1157, 1049 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, J = 6.8 Hz, 3H), 1.22 (m, 6H), 1.31 (m, 4H), 1.87 (br, 2H), 2.34-2.40 (m, 56H), 2.51 (m, 32H), 2.72-2.76 (m, 56H), 2.84 (br, 4H), 3.25 (m, 28H), 3.63 (s, 48H), 3.73 (s, 48H), 3.93 (s, 2H), 4.33 (br, 2H), 4.61 (s, 2H), 4.75 (s, 2H), 4.92 (s, 24H), 4.96 (s, 4H), 6.36 (m, 8H), 6.53 (m, 23H), 6.64 (m, 14H), 7.08 (br, 8H), 7.46 (br, 1H), 7.54 (br, 1H), 7.67 (br, 4H), 7.76 (br, 1H), 7.88 (br, 1H), 7.98 (br, 2H), 8.09 (s, 1H), 8.22 (s, 1H), 8.51 (br, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.5, 27.2, 28.9, 29.1, 29.2, 31.6, 32.6, 33.8, 37.1, 37.5, 43.7, 47.6, 49.2, 49.8, 50.4, 51.6, 52.5, 52.8, 55.2, 63.5, 69.9, 72.5, 99.9, 101.6, 105.1, 106.3, 106.8, 109.9, 109.9, 113.3, 113.5, 119.8, 122.0, 122.8, 129.8, 139.06, 139.14, 139.2, 140.3, 140.7, 144.8, 145.6, 159.9, 160.0, 160.9, 172.2, 172.3, 173.0; MS (MALDI): Calcd for $C_{281}H_{390}N_{36}O_{77}$: 5500.7709. Found: 5523.6389 [M^++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 and physical property. Carbazole, as a kind of rigid plane biphenyl compound with wide band gap, high luminescent efficiency and high flexibility to modify the molecule skeleton, has been a key chromophore in organic EL materials and electrochromic displays, and so on in many fields. By careful structural design, dendrimers will have the potential applications across a wide range of areas of interdisciplinary science. Keeping in mind, we were intrigued to develop the sequential double click reactions for the synthesis of carbazole-based chromophore diblock codendrimer which are characterized by half hydrophobic and half hydrophilic dendrons.

The synthetic strategy for diblock codendrimers, linked by the triazole units, utilized double click methods using the alkyne-functionalized PAMAM dendrons **1-Dm** and alkyne-functionalized Fréchet-type dendrons **2-Dn** (Scheme 1). *N*-Octyl-3,6-diazidocarbazole **3** was designed to serve as an chromophore building block and the azide functionalities for dendrimer growth via click reactions with the alkyne-dendrons. The propargyl-functionalized PAMAM dendrons **1-Dm** ($m = 1\sim4$: generation of dendron) as hydrophilic dendron are synthesized by the divergent approach using propargyl amine as a propargyl focal point [9d]. The Fréchet-type alkyne-dendrons **2-Dn** ($n = 1\sim4$: generation of dendron) as hydrophobic dendron were prepared by the propargylation of the corresponding dendritic benzyl alcohols with propargyl bromide [8d].

Considering product isolation viewpoint, we first have investigated the reaction of the alkyne-functionalized PAMAM dendrons **1-Dm** and bis(azide) core **3** to provide the mono-dendritic compounds **4-Dm** with one more reactive azide focal group. Reaction of alkyne-focal dendron **1-D1** and 15 equiv of **3** in the presence of 5 mol% $CuSO_4{\cdot}5H_2O$ with 10 mol% sodium ascorbate in a 4:1 solvent ratio of THF to H_2O at rt gave the azide-focal dendron **4-D1** in 99% yield after 1 h. Given the success in the synthesis of first-generation dendron, therefore we expanded this reaction to get higher-generation dendrons. Reactions of alkyne-focal dendrons **1-D2**, **1-D3**, and **1-D4** and 15 equiv of **3** under same condition afforded the azide-focal dendrons **4-D2**, **4-D3**, and **4-D4** in yields of 97, 96, and 94% after 2, 3.5, and 4.5 h, respectively. The disappearance of dendron **1-Dm** and generation of the mono-triazole derivative **4-Dm** were observed by TLC runs of the reaction mixture. The azide-focal dendrons **4-Dm** was purified by column chromatography and the structure of **4-Dm** was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, and mass spectra. Structural characterization of the dendrons **4-Dm** with ^{1}H-NMR and IR spectroscopy showed complete stitching of dendrons. The IR spectra showed the disappearance of the acetylene peak at 3277∼3298 cm^{-1} and the appearance of azide peak at 2110 cm^{-1} in dendron **4-Dm**, while the ^{1}H-NMR revealed no alkyne peak at around δ 2.19 ppm. The ^{1}H-NMR signals of the triazole proton and the methylene protons adjacent to the nitrogen of triazole in dendrons **4-Dm** were observed at 8.03 and 3.93 ppm for **4-D1**, 8.12 and 3.95 ppm for **4-D2**, 8.20 and 3.95 ppm for **4-D3**, and 8.24 and 3.94 ppm for **4-D4**, respectively. As the dendron generation increased, the peaks of the triazole proton shifted gradually to down-field which may be influenced by the dendritic microenvironment effect.[15] The peaks of the amide protons (NH) in the ^{1}H-NMR spectra were found at 7.17 ppm for **4-D2**, 7.07 and 7.79 ppm for **4-D3**, and 7.07, 7.65, and 7.88 ppm for **4-D4**, respectively. Their FAB or MALDI mass spectra for dendrimer exhibited very good correlation with the calculated molecular masses.

Next, the second click reaction was tried to obtain the diblock codendrimers by stitching with different dendron. The reaction of first generation azido-focal PAMAM dendron **4-D1** with alkyne-functionalized Fréchet-type dendron **2-D1** in the presence of 5 mol% $CuSO_4{\cdot}5H_2O$ with 10 mol% sodium ascorbate in a 4:1 solvent ratio of DMF to H_2O at 50μm afforded the dendrimer **5-G11** in yield of 97% after 1 h. The disappearance of two dendrons as well as generation of product could be 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 reaction of second generation azido-focal dendron **4-D2** with alkyne-focal dendron **2-D2** under same condition gave the dendrimer **5-G22** in yield of 94% after 2.5 h. The reaction of **4-D3** with **2-D3** provided the diblock codendrimer **5-G33** in 87% yield after 4 h. Finally, the diblock codendrimer **5-G44** was obtained in 83% yield from reaction of **4-D4** with **2-D4** after 6 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 by click chemistry between an azide and an alkyne is found to be an efficient connector to construct the generation-symmetric diblock codendrimers from different kinds of dendrons. All diblock codendrimers **5-Gmn** were also confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, IR spectroscopy, and mass spectra. From the ^{1}H-NMR spectra ($CDCl_3$), the peaks of two triazole protons in dendrimers **5-Gmn** were found around 8.07 ppm for **5-G11**, 8.06 and 8.12 ppm for **5-G22**, 8.08 and 8.20 ppm for **5-G33**, and 8.09 and 8.22 ppm for **5-G44**, respectively (Fig. 1). As the dendrimer generation increased,

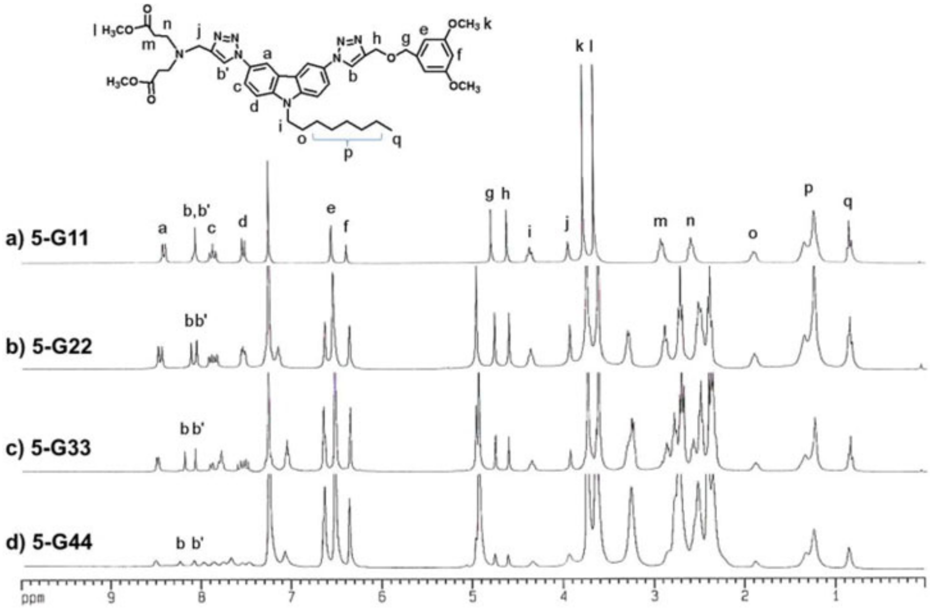


Figure 1. ^{1}H-NMR spectra for a) **5-G11**, b) **5-G22**, c) **5-G33**, and d) **5-G44**.

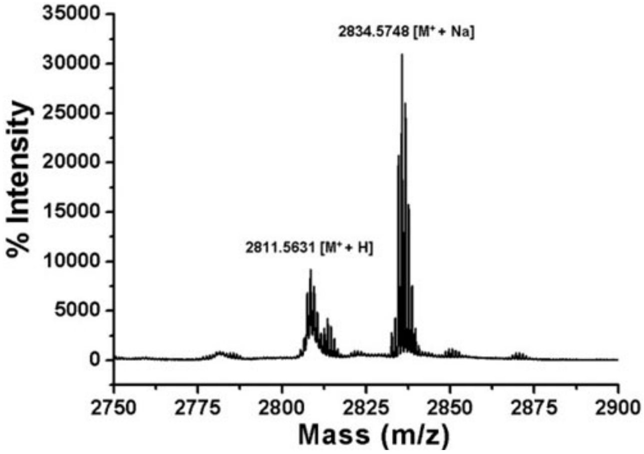


Figure 2. MALDI-TOF mass spectrum of diblock codendrimers **5-G33**.

the peaks of the triazole protons shifted gradually to down-field which may be influenced by the dendritic microenvironment effect [10]. The ^{1}H-NMR revealed no alkyne peak at around δ 2.47 ppm and IR data also confirmed that neither azide ($\sim$2110 cm^{-1}) nor alkyne ($\sim$3285 cm^{-1}) residues remain in the final dendrimer. Their FAB or MALDI mass spectra (Fig. 2) for dendrimer exhibited very good correlation with the calculated molecular masses. From the analysis of gel-permeation chromatography (Fig. 3), the dendrimers showed very low polydispersity values (PDI = 1.01–1.02). All diblock codendrimers are soluble in a vast range of organic solvents excluding nonpolar solvent such as n-hexane and are not soluble in water.

The UV-visible absorption and photoluminescence (PL) spectra of **5-Gmn** and **3** in chloroform solutions were investigated (Fig. 4). Compound **3** exhibited the maximum absorption at 251 and 292 nm. Dendrimers showed absorption maxima at 252 and 286, 253 and 286, 243 and 284, and 243 and 283 nm for **5-Gmn**, respectively. Linkage of carbazole unit to the dendrimer showed blue shift relative to the corresponding bands for compound

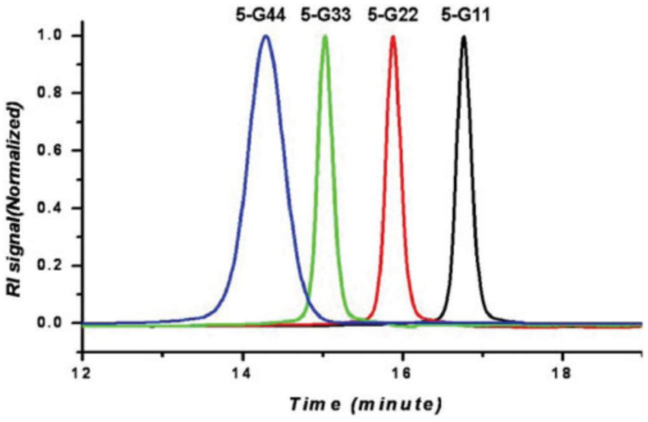
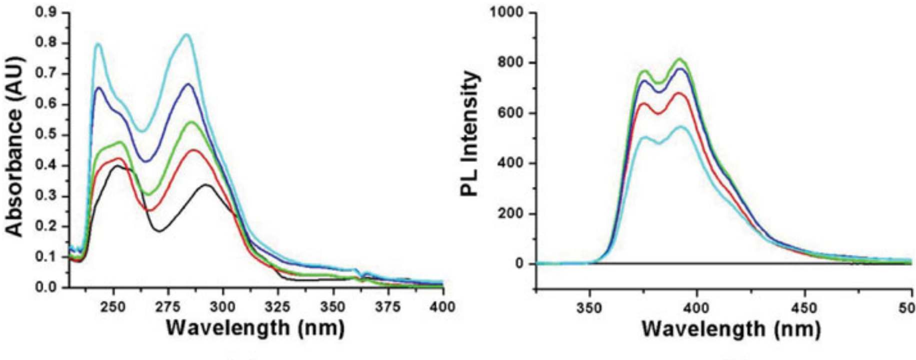


Figure 3. GPC diagrams of generation-symmetric diblock codendrimers **5-Gmn** obtained from THF eluent.



(a) (b)

Figure 4. (a) UV-vis spectra in $CHCl_3$ (conc. = 1.0×10^{-5} M) and (b) PL spectra in $CHCl_3$ (λ_{ex} = 285 nm, conc. = 1.0×10^{-6} M) for **3** (black), **5-G11** (red), **5-G22** (green), **5-G33** (blue), and **5-G44** (cyan).

3. The absorbance of the dendrimers **5-Gmn** are increased with increasing the generation number. The photoluminescence (PL) spectra of compound **3** and **5-Gmn** in chloroform solutions were obtained. Compound **3** showed no fluorescence due to the quenching effect from the electron-rich α-nitrogen of the azido group [11]. Dendrimers **5-Gmn** fluoresces at 392 nm due to the elimination of the quenching through the formation of the triazole ring. And these dendrimers have shoulder emission peaks at 375 nm. Our results demonstrate that potentially luminescent dendrimers can be obtained by incorporating a profluorophore unit with dendrons.

Conclusion

We have developed for the first time the efficient synthetic method for the carbazole-based chromophore diblock codendrimers which are characterized by half hydrophobic and half hydrophilic dendrons. The successive click reactions between a carbazole core unit and different polar dendrons (the Fréchet-type polyether and the Tomalia-type PAMAM dendrons) afford the component differenciated diblock codendrimers. Therefore double click reactions can be applied for the fast synthesis of specific dendrimers and may then provide an insight into designing dendrimers, which will have the potential applications across a wide range of areas of interdisciplinary science. We are currently working toward the formation of micelles by self-assembly of the amphiphilic codendrimers for various applications.

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