A Click Approach to Chiral Dendronized Polyfluorene Derivatives

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1. General Experimental

Materials. All chemicals were purchased from Acros or Aldrich and used as received without further purification. (S)-6,6’-Dibromo-2,2’-bis(methoxylmethyl)-1,1’-dinaphthol (M1),[1] 2,7-dibromo-9-fluorene (S2),[2] 2,7-dibromo-9,9-dihexylfluorene (M2),[2] 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (M3),[2] Fréchet’s dendritic bromides[3] and azides (G1-N3 ~ G3-N3 and G’1-N3 ~ G’3-N3)[4] were synthesized according to the published methods. All reactions were carried out under dry nitrogen atmosphere. All solvents used were dried using standard, published methods and were distilled under nitrogen atmosphere before use.

Characterization. The $^1$H and $^{13}$C NMR spectra were recorded on a BRUKER Model ADVANCE DPX 300 spectrometer (300 MHz $^1$H and 75 MHz $^{13}$C) using tetramethylsilane as an internal standard. All signals are reported in parts per million unit (ppm). IR spectra were recorded on a JASCO FT/IR-480 plus fourier transform infrared spectrometer. Optical rotations were measured with Perkin-Elmer341 digital polarimeter in tetrahydrofuran (THF) with sodium D light at room temperature. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. The gel permeation chromatography (GPC) measurements were performed on Waters 410 system with RI (refractive index) detector against polystyrene standards with THF as an eluent. The polymers were also measured through a multidetector GPC apparatus equipped with a Postnava PN 1011 pump, a 5-μm mixed-bed C column (Polymer Lab), and a Precision PD 2100 detector system [including an RI detector, two-angle static laser light scattering (TALLS) detectors at 15 and 90 degree, and a dynamic laser light scattering detector] with THF as the eluent at a flow rate of 1mL/min at 25 °C. Electronic absorption spectra were obtained on a Shimadzu UV-vis spectrometer model UV-1601PC. Fluorescence emission spectra were recorded in THF at 293K with a Hitachi F4500 fluorescence spectrophotometer. Fluorescence quantum yields ($\Phi_F$) of the samples in toluene were measured by using 9, 10-diphenylanthracene ($\Phi_F = 0.9$ in cyclohexane)[5] as standard. The films on quartz used for PL measurements were prepared by spin-coating with 10 mg/mL toluene solution at 2000 rpm. TGA
(NETZSCH STA 409C) and DSC (Perkin-Elmer 7 series thermal analyzers) measurements were performed under nitrogen atmosphere at a heating rate of 10 °C/min, respectively.

2. Synthesis.

Scheme S1. Synthetic routes to the monomers and other reaction mediates:

\[ \text{(S)-BINOL} \begin{align*} \text{Br}_2 & \text{Br} \quad \text{-78°C} \\ \end{align*} \text{(s)-6',6'-Dibromo-BINOL} \begin{align*} \text{OCl} & \text{NaH} \quad \text{M1} \\ \end{align*} \]

\[ \text{S1} \begin{align*} \text{Br} & \text{Br} \quad \text{S2} \begin{align*} \text{NaOH} & \text{M2} \\ \text{H}_2\text{SO}_4(50\%) \text{HO} & \text{reflux} \quad \text{M3} \\ \end{align*} \]

\[ \text{Mg} \quad \text{B(OCH}_3\text{)}_3 \quad \text{Br} \quad \text{-78°C to rt} \]

\[ \text{NaN}_3 \quad \text{DMSO} \]

\[ R= \quad \text{Ph} \quad \text{G}_1\cdot\text{N}_3 (m = 0); \text{G}_2\cdot\text{N}_3 (m = 1); \text{G}_3\cdot\text{N}_3 (m = 2) \]

\[ R= \quad \text{(CH}_2\text{)}_3 \quad \text{G}^{1'}\cdot\text{N}_3 (m = 0); \text{G}^{2'}\cdot\text{N}_3 (m = 1); \text{G}^{3'}\cdot\text{N}_3 (m = 2) \]
**Synthesis of M1.** Under nitrogen, to a solution of NaH (429 mg, 70 wt%, 12.5 mmol) in THF (30 mL) was slowly added (S)-6,6’-dibromo-1,1’-bi-2-naphthol (2.143 g, 4.9 mmol) at 0 °C. After 5 min, chloromethyl methyl ether (0.9 mL, 12.4 mmol) was added. The mixture was stirred at rt for 12 h. A small amount of water was then slowly added to quench the reaction and the mixture was extracted with ethyl acetate. The organic layer was washed with brine. After removal of solvent by rotary evaporation, the product was recrystallized from hexane to afford **M1** (2.271 g, 70%) as a white solid.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.03 (d, $J = 1.9$ Hz, 2H, Ar-H), 7.86 (d, $J = 9.1$ Hz, 2H, Ar-H) 7.59 (d, $J = 9.1$ Hz, 2H, Ar-H), 7.29 (dd, $J = 9.0$ Hz, 2.0 Hz, 2H, Ar-H), 6.98 (d, $J = 9.0$ Hz, 2H, Ar-H), 5.09 (d, $J = 6.9$ Hz, 2H, OCH$_2$O), 4.98 (d, $J = 6.9$ Hz, 2H, OCH$_2$O), 3.15 (s, 6H, OCH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 153.0, 132.4, 130.9, 129.9, 129.7, 128.7, 127.2, 120.7, 118.1, 118.0, 95.0, 55.9.

**Synthesis of S2.** To a stirred solution of **S1** (20.058 g, 120 mmol) and I$_2$ (about 0.1 g) in CH$_2$Cl$_2$ (400 mL) was slowly added bromine (52.870 g, 334 mmol) in CH$_2$Cl$_2$ (100 mL) at room temperature. Because it is an exothermic reaction, any rapid addition of bromine should be avoided. The solution was stirred at room temperature for 24 h in the dark, and then aqueous Na$_2$SO$_3$ was added. Vigorous stirring was applied until the red color disappeared. The organic layer was separated, washed with water, NaHCO$_3$ aq and brine, and finally dried over anhydrous Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the product was purified by recrystallization from petroleum ether to yield a white crystalline product of **S2** (38.520 g, 99%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.65 (s, 2H, Ar-H), 7.59 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.49 (d, $J = 8.2$ Hz, 2H, Ar-H), 3.85 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 144.8, 139.7, 130.1, 128.3, 121.2, 121.0, 36.6.

**Synthesis of M2.** A mixture of **S2** (38.520 g, 118 mmol) and tetrabutylammonium iodide (2.6 g) in DMSO (160 mL) and aqueous NaOH (80 mL, 50%, w/w) was purged with nitrogen. 1-Bromohexane
(80.360 g, 416 mmol) was then added to the mixture using a syringe. The resulting solution was stirred at 35 °C for 24 h before 160 mL of H₂O was added. The solution was then extracted with diethyl ether (2 x 200 mL). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using petroleum ether as eluent to yield a colorless oil of M₂ (53.814 g, 80%).

¹H NMR (300 MHz, CDCl₃): δ = 7.52 (dd, J = 6.7 Hz, 1.9 Hz, 2H, Ar-H), 7.49 (s, 2H, Ar-H), 7.45 (dd, J = 6.7 Hz, 1.8 Hz, 2H, Ar-H), 1.94-1.86 (m, 4H), 1.13-1.03 (m, 12H), 0.78 (t, J = 7.0 Hz, 6H), 0.60-0.55 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ = 152.6, 139.1, 130.2, 126.2, 121.5, 121.1, 55.7, 40.2, 31.5, 29.6, 23.7, 22.6, 14.0.

Synthesis of M₃. In a two-necked flask was charged with M₂ (22.406 g, 46 mmol), magnesium turnings (2.295 g, 96 mmol) and dry THF (100 mL) under nitrogen. The reaction was initiated by the addition of minimal iodine. The resulting mixture was heated under reflux for 2 h and then added to a solution of trimethyl borate (14.340 g, 138 mmol) in dry THF (50 mL) which was already cooled to -78 °C. This reaction mixture was stirred at room temperature for 24 h. Then, H₂SO₄ (50 mL, 50 %) was added to the mixture carefully. The organic layer was separated and dried over anhydrous Na₂SO₄. Purification was performed by a silica gel column eluting with acetone/petroleum ether from 1/9 to 1/3 (v/v) to give the boric acid. Then, esterification was carried out by reacting the resulting boric acid with 1,3-propanediol (7.388 g, 97 mmol) in 150 mL toluene at refluxing temperature for 24 h. After the solvent was distilled, the residue was extracted with diethyl ether (200 mL). The solvent was evaporated to afford M₃ (12.666 g, 56%) as a white solid without further purification.

¹H NMR (300 MHz, CDCl₃): δ = 7.77-7.68 (m, 6H, Ar-H), 4.20 (t, J = 5.4 Hz, 8H), 2.13-2.05 (m, 4H), 2.02-1.97 (m, 4H), 1.12-1.05, (m, 12H), 0.75 (t, J = 7.0 Hz, 6H), 0.58-0.56 (m, 4H).
General Procedure for the Synthesis of Dendritic Azides

A mixture of the corresponding dendronized bromide and NaN₃ in DMSO was heated to 55 °C under nitrogen and stirred overnight. The reaction mixture was cooled, then poured into water, and extracted with dichloromethane. The combined organic layer was dried with anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by flash column chromatography.

Preparation of G₁-N₃. G₁-Br (1 g, 2.61 mmol) and NaN₃ (1.531g, 23.63 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH₂Cl₂/petroleum ether (1/2) to afford G₁-N₃ (0.782 g, 87%) as a white solid.

¹H NMR (300 MHz, CDCl₃): δ = 7.48-7.37 (m, 10H, Ph-H), 6.64-6.60 (m, 3H, Ar-H), 5.07 (s, 4H, PhCH₂O), 4.29 (s, 2H, ArH₂N₃).

¹³C NMR (75 MHz, CDCl₃): δ = 160.3, 137.7, 136.7, 128.7, 128.1, 127.6, 107.3, 101.9, 70.2, 54.9.

IR (thin film): 3064, 3033, 2929, 2873, 2098 (ν N₃), 1955, 1875, 1811, 1598, 1496, 1450, 1377, 1347, 1293, 1214, 1157, 1057, 986, 908, 835, 738, 698, 634.

Preparation of G₂-N₃. G₂-Br (0.3 g, 0.37 mmol) and NaN₃ (0.145 g, 2.2 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH₂Cl₂/petroleum ether (1/2) to afford G₂-N₃ (0.232 g, 81%) as a white foam.

¹H NMR (300 MHz, CDCl₃): δ = 7.44-7.30 (m, 20H, Ph-H), 6.68-6.54 (m, 9H, Ar-H), 5.04 (s, 8 H, PhCH₂O), 4.98 (s, 4H, ArCH₂O), 4.26 (s, 2H, ArCH₂N₃).

¹³C NMR (75 MHz, CDCl₃): δ = 160.2, 160.2, 139.1, 137.7, 136.8, 128.6, 128.0, 127.6, 107.2, 106.4, 101.9, 101.6, 70.1, 70.0, 54.8.
IR (thin film): 3032, 2924, 2872, 2098 (νN₃), 1814, 1726, 1596, 1531, 1448, 1345, 1296, 1212, 1156, 1052, 833, 737, 698, 659, 634.

**Preparation of G₃-N₃.** G₃-Br (0.5 g, 0.3 mmol) and NaN₃ (0.177 g, 2.7 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH₂Cl₂/petroleum ether (2/3) to afford G₃-N₃ (0.400 g, 82%) as a white foam.

^1^H NMR (300 MHz, CDCl₃): δ = 7.42-7.30 (m, 40H, Ph-H), 6.68-6.54 (m, 21H, Ar-H), 5.02 (s, 16H, PhCH₂O), 4.96-4.92 (m, 12H, ArCH₂O), 4.23 (s, 2H, ArCH₂N₃). ^1^C NMR (75 MHz, CDCl₃): δ = 160.2, 160.2, 139.3, 139.2, 137.8, 136.9, 128.6, 128.3, 128.2, 128.0, 127.8, 127.6, 107.3, 106.5, 101.9, 101.7, 70.2, 70.1, 54.8.

IR (thin film): 3050, 2934, 2874, 2098 (νN₃), 1889, 1771, 1597, 1483, 1456, 1377, 1330, 1297, 1266, 1238, 1161, 1058, 928, 835, 750, 726, 617.

**Preparation of G′₁-N₃.** G′₁-Br (0.333 g, 0.5 mmol) and NaN₃ (0.302 g, 4.6 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH₂Cl₂/petroleum ether (2/3) to afford G′₁-N₃ (0.231 g, 83%) as a white solid.

^1^H NMR (300 MHz, CDCl₃): δ = 8.09 (d, J = 7.7 Hz, 4H, carbazole Ar-H), 7.48-7.39 (m, 8H, carbazole Ar-H), 7.25-7.19 (m, 4H, carbazole Ar-H), 6.38-6.31 (m, 3H, Ar-H), 4.39 (t, J = 7.0 Hz, 4H, ArOCH₂), 4.21 (s, 2H, CH₂N₃), 3.91 (t, J = 6.1 Hz, 4H, ArNCH₂), 2.13-2.03 (m, 4H, CH₂), 1.88-1.79 (m, 4H, CH₂).

^1^C NMR (75 MHz, CDCl₃): δ = 160.4, 140.4, 137.6, 125.7, 122.9, 120.4, 118.9, 108.6, 106.7, 101.1, 67.6, 54.8, 42.7, 27.0, 25.9.

IR (thin film): 3051, 2940, 2875, 2098 (νN₃), 1890, 1771, 1598, 1484, 1457, 1383, 1330, 1295, 1240, 1165, 1124, 1165, 1124, 1063, 999, 927, 835, 750, 725, 617.
Preparation of G’2-N3. G’2-Br (0.496 g, 0.37 mmol) and NaN3 (0.145 g, 2.2 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH2Cl2/petroleum ether (1/1) to afford G’2-N3 (0.412 g, 86%) as a white foam.

1H NMR (300 MHz, CDCl3): δ = 8.08 (d, J = 7.7 Hz, 8H, carbazole Ar-H), 7.47-7.38 (m, 16H, carbazole Ar-H), 7.23-7.19 (m, 8H, carbazole Ar-H), 6.51-6.31 (m, 9H, Ar-H), 4.90 (s, 4H, ArCH2O), 4.37 (t, J = 6.9 Hz, 8H, ArOCH2), 4.22 (s, 2H, ArCH2N3), 3.89 (t, J = 5.9 Hz, 8H, ArNCH2), 2.08-2.01 (m, 8H, CH2), 1.83-1.78 (m, 8H, CH2).

13C NMR (75 MHz, CDCl3): δ = 160.3, 160.2, 140.4, 139.0, 137.9, 137.7, 125.7, 122.9, 120.4, 118.9, 108.7, 107.2, 105.9, 101.9, 101.0, 70.1, 67.6, 54.8, 42.7, 27.0, 25.9.


Preparation of G’3-N3. G’3-Br (0.5 g, 0.18 mmol) and NaN3 (0.152 g, 2.3 mmol) were used. The crude product was purified by a silica gel column chromatography eluting with CH2Cl2 to afford G’3-N3 (0.358 g, 73%) as a white foam.

1H NMR (300 MHz, CDCl3): δ = 8.06 (d, J = 7.7 Hz, 16H, carbazole Ar-H), 7.45-7.35 (m, 32H, carbazole Ar-H), 7.22-7.17 (m, 16H, carbazole Ar-H), 6.64-6.29 (m, 21H, Ar-H), 4.89 (s, 12H, ArCH2O), 4.32 (t, J = 7.0 Hz, 16H, ArOCH2), 4.16 (s, 2H, CH2N3), 3.84 (t, J = 6.0 Hz, 16H, ArNCH2), 2.06-1.96 (m, 16H, CH2), 1.81-1.72 (m, 16H, CH2).

13C NMR (75 MHz, CDCl3): δ = 160.4, 160.3, 140.5, 139.2, 137.8, 126.2, 125.8, 123.0, 120.5, 119.3, 119.0, 108.8, 107.3, 106.6, 106.0, 102.0, 101.8, 101.0, 70.2, 67.6, 54.8, 42.7, 27.0, 25.9.

IR (thin film): 3050, 2397, 2874, 2098 (ν N3), 1890, 1770, 1597, 1483, 1456, 1377, 1330, 1297, 1265, 1268, 1161, 1058, 929, 835, 750, 727, 618.

Synthesis of Dendritic Model Monomer M5
Synthesis of M4. To a solution of (S)-6,6'-dibromo-BINOL (0.500 g, 1.1 mmol) and K₂CO₃ (0.932 g, 6.8 mmol) in acetone was added propargyl bromide (0.25 mL, 2.4 mmol). The mixture was refluxed for 12 h till the reaction was completed (monitored by TLC). After most of the solvent was evaporated under reduced pressure, water was added to the mixture. The aqueous layer was extracted with CH₂Cl₂ three times, and the combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. Purification was performed by a silica gel column eluting with petroleum ether, and then AcOEt/petroleum ether (1/5) to afford M4 (0.352 g, 60%) as a white solid.

¹H NMR (300 MHz, CDCl₃): δ = 8.03 (s, 2H, Ar-H), 7.89 (d, J = 9.0 Hz, 2H, Ar-H), 7.58 (d, J = 9.0 Hz, 2H, Ar-H), 7.28 (d, J = 9.2 Hz, 2H, Ar-H), 6.97 (d, J = 9.0 Hz, 2H, Ar-H), 4.67-4.55 (m, 4H, ArOCH₂), 2.40 (s, 2H, terminal alkyne CH)

¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 132.3, 130.8, 129.9, 129.9, 128.7, 127.2, 120.1, 118.0, 116.7, 78.9, 75.6, 57.0.

Synthesis of M5. To a suspension of M4 (0.2 g, 0.38 mmol) and G₁N₃ (0.266 g, 0.77 mmol) in a mixture of water (5 mL) and THF (5 mL) was added sodium ascorbate (26 mg, 30 mol%), and followed
by CuSO\(_4\cdot5\)H\(_2\)O (30 mg, 15 mol%). The resulting solution was stirred for 5 h, and then extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using petroleum ether/CH\(_2\)Cl\(_2\) (1/2) as eluent to yield a white foam of M\(_5\) (444 mg, 96%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.91\) (d, \(J = 1.9\) Hz, 2H, binaphthyl Ar-H), 7.74 (d, \(J = 9.0\) Hz, 2H, binaphthyl Ar-H), 7.45-7.32 (m, 22H, 2H for binaphthyl Ar-H and 20H for dendron Ph-H), 7.20 (dd, \(J = 9.0\) Hz, 2.0 Hz, 2H, binaphthyl Ar-H), 6.90 (d, \(J = 9.0\) Hz, 2H, binaphthyl Ar-H), 6.61 (s, 4H, 2H for dendron Ar-H and 2H for CH\(_2\)), 6.36 (d, \(J = 2.1\) Hz, 4H, dendron Ar-H), 5.24-5.12 (m, 4H, ArOCH\(_2\)), 5.10-5.06 (m, 4H, ArCH\(_2\)O), 4.96 (s, 8H, ArCH\(_2\)N).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.86-7.83\) (br, m, 2H, Ar-H), 7.71-7.60 (br, m, 4H, Ar-H), 7.13 (br, 4H, CH\(_2\)), 1.14 (br, m, 12H, CH\(_2\)), 0.82-0.78 (br, m, 10H, CH\(_2\) and CH\(_3\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 151.8, 140.5, 140.0, 126.2, 121.5, 120.0, 55.3, 40.4, 31.5, 29.7, 23.9, 22.6, 14.0.\)

**Preparation of Polyfluorene (PF).** For comparison, PF was also synthesized. To a mixture of monomers M\(_1\) (280 mg, 0.57 mmol), M\(_2\) (290 mg, 0.57 mmol) in toluene (20 mL) was added Aliquate336, aqueous sodium carbonate (2 M, 12 mL) and Pd(PPh\(_3\))\(_4\) (13.0 mg) under nitrogen atmosphere. The reaction mixture was heated at 90 °C and stirred under nitrogen for 3-5 days. The mixture was poured into a stirred mixture of methanol and water (10:1, v/v) to precipitate the solid product. The product was collected by filtration and washed with methanol and water. Then the polymer was extracted by acetone in Soxhlet for 24 h and dried under vacuum at 50 °C, giving PF (280 mg, 76%) as a light yellow solid.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.86-7.83\) (br, m, 2H, Ar-H), 7.71-7.60 (br, m, 4H, Ar-H), 2.13 (br, 4H, CH\(_2\)), 1.14 (br, m, 12H, CH\(_2\)), 0.82-0.78 (br, m, 10H, CH\(_2\) and CH\(_3\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 151.8, 140.5, 140.0, 126.2, 121.5, 120.0, 55.3, 40.4, 31.5, 29.7, 23.9, 22.6, 14.0\).
**Preparation of PFMOM.** A mixture of the respective monomers M1 (0.355 g, 0.667 mmol, 1 eqiv), M2 (0.656 g, 1.333 mmol, 2 eqiv), M3 (1.0046 g, 2.000 mmol, 3 eqiv), Aliquate (methyltrioctylammonium chloride, CH$_3$N[(CH$_2$)$_7$CH$_3$]$_2$Cl), toluene (25 mL), and aqueous potassium carbonate solution (2M, 12 mL) were degassed, and then Pd(PPh$_3$)$_4$ (40.8 mg, 2 mol %) was added under nitrogen atmosphere. The reaction mixture was heated at 90 °C and stirred under nitrogen for 3 days. The mixture was poured into a stirred mixture of methanol and water (10:1, v/v) to precipitate the solid product. The solid was collected by filtration and washed with methanol and water. Then the polymer was extracted by acetone in Soxhlet for 24 h and dried under vacuum at 50 °C to afford brown solid (1.302 g, 96% yield).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.20 (br, m, 0.4H, binaphthyl Ar-H), 8.10-8.07 (br, m, 0.4H, binaphthyl Ar-H), 7.84-7.82 (br, m, 2H, fluorene Ar-H), 7.68-7.61 (br, m, 4.8H, binaphthyl and fluorene Ar-H), 5.16-5.07 (br, m, 0.8H, ArOCH$_2$O), 3.25-3.19 (br, m, 1.2H, CH$_2$O), 2.17-2.11 (br, m, 4H, CH$_2$), 1.26-1.14 (br, m, 12H, CH$_2$ and CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 152.9, 151.8, 140.6, 140.0, 139.9, 137.3, 133.3, 130.3, 129.8, 128.8, 127.2, 126.2, 125.6, 121.6, 121.3, 120.0, 117.9, 95.5, 68.0, 55.9, 55.4, 40.4, 31.5, 29.7, 25.6, 23.9, 22.6, 14.0.

**Preparation of PFOH.** To a solution of PFMOM (1.302 g, 0.6 mmol for repeating unit) in CH$_2$Cl$_2$ (40 mL) was slowly added trifluoroacetic acid (TFA, 2.4 mL) at room temperature. The reaction mixture was stirred overnight, and then aqueous NaHCO$_3$ was added. The mixture was poured into a stirred mixture of methanol and water (5:1, v/v) to precipitate the solid product. The solid was collected by filtration and washed with methanol and water. Then the polymer was dried under vacuum at 50 °C to afford a fibroid gray solid (1.208 g, 96% yield).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.21 (br, m, 0.4H, binaphthyl Ar-H), 8.13-8.11 (br, m, 0.4H, binaphthyl Ar-H), 7.83-7.77 (br, m, 2H, fluorene Ar-H), 7.68-7.61 (br, m, 4.4H, binaphthyl and fluorene...
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.19-8.10 (br, m, 0.8H, binaphthyl Ar-H), 7.83-7.81 (br, m, 2H, fluorene Ar-H), 7.67-7.61 (br, m, 4.8H, binaphthyl and fluorene Ar-H), 7.49-7.31 (br, m, 0.4H, binaphthyl Ar-H), 4.68 (br, m, 0.8H, binaphthyl ArOCH$_2$), 2.45 (br, m, 0.4H, CH), 2.26-2.04 (br, m, 4H, CH$_2$), 1.25-0.95 (br, m, 12H, CH$_2$), 0.79-0.77 (br, m, 10H, CH$_2$ and CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 151.8, 140.5, 140.0, 137.3, 132.3, 126.2, 121.5, 120.6, 120.0, 79.3, 75.3, 57.4, 55.3, 40.4, 31.5, 29.7, 23.8, 22.6, 14.0.

IR (thin film): 3305 ( $\nu = $C-H), 2925, 2855, 2123 ( $\nu $ $\equiv$C-H), 1892, 1596, 1459, 1372, 1340, 1273, 1220, 1141, 1094, 1054, 938, 886, 815, 751, 669, 629.
**General procedure for the synthesis of PFG$_2$ and PFG$_3$**

The corresponding dendritic azide $G_m$-$N_3$ and PFYNE were dissolved in THF (1 mL per about 20 mg of reaction mixture). To this solution, a little amount of water was added while stirring vigorously at 25°C. Sodium ascorbate (10 mol%) and CuSO$_4$·5H$_2$O (5 mol%) were then added to the reaction mixture from freshly prepared aqueous solutions (1.0 M). The reaction mixture was stirred for 1 day (PFG$_2$) or 2 days (PFG$_3$). The crude product was evaporated to dryness and washed with water for times. The dendronized polymer was precipitated into hexane from THF for several times to remove excess dendritic azide.

**Preparation of PFG$_2$.** $G_2$-$N_3$ (23.0 mg, 0.030 mmol) and PFYNE (30.0 mg, 0.015 mmol) were used to afford a yellow solid (46.7 mg, 87% yield). [α]$^\text{20}_D = +110.2$ (c 0.27 THF)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.21$-8.11 (br, m, 0.8H, binaphthyl Ar-$H$), 7.83 (br, m, 2H, fluorene Ar-$H$), 7.67 (br, m, 5.2H, 4H for fluorene and 1.2H binaphthyl Ar-$H$), 7.35-7.30 (br, m, 8H, dendron Ph-$H$), 6.84 (br, m, 0.4H, triazole $CH$), 6.69 – 6.35 (br, m, 3.6 H, dendron Ar-$H$), 5.29-4.80 (br, m, 6.4H, 0.8H for binaphthyl ArOCH$_2$, 0.8H for ArCH$_2$N and 4.8H for ArCH$_2$O), 2.32-1.91 (br, m, 4H, CH$_2$), 1.12 (br, m, 12H, CH$_2$), 0.79 (br, m, 10H, CH$_2$ and CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 160.0,$ 151.7, 140.4, 139.8, 136.6, 128.4, 127.8, 127.4, 126.0, 121.4, 119.8, 106.2, 101.4, 69.9, 55.2, 40.2, 31.3, 29.5, 23.7, 22.4, 13.9.

IR (thin film): 3063, 3032, 2952, 2926, 2855, 1733, 1596, 1496, 1457, 1375, 1342, 1295, 1252, 1216, 1157, 1049, 884, 815, 736, 696, 631.

**Preparation of PFG$_3$.** $G_3$-$N_3$ (48.3 mg, 0.030 mmol) and PYNE (30.0 mg, 0.015 mmol) were used to afford a yellow solid (43.7 mg, 75% yield). [α]$^\text{20}_D = +72.0$ (c 0.25 THF)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.06$-8.04 (br, m, 0.8H, binaphthyl Ar-$H$), 7.93-7.83 (br, m, 2H, fluorene Ar-$H$), 7.67-7.55 (br, m, 5.2H, 4H for fluorene and 1.2H binaphthyl Ar-$H$), 7.31-7.06 (br, m, 16H, dendron Ph-$H$), 6.91 (br, m, 0.4H, triazole $CH$), 6.61 (br, m, 4.8H, dendron Ar-$H$), 6.50 (br, m,
2.8H, dendron Ar-H), 6.38 – 6.31 (br, m, 0.8 H, dendron Ar-H), 5.10-4.86 (br, m, 12.8H, 0.8H for binaphthyl ArOCH₂, 0.8H for ArCH₂N and 11.2H for ArCH₂O), 2.17-2.09 (br, m, 4H, CH₂), 1.13 (br, m, 12H, CH₂), 0.79-0.72 (br, m, 10H, CH₂ and CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 160.1, 160.0, 151.8, 140.0, 139.2, 136.7, 128.5, 128.0, 127.6, 126.2, 121.5, 106.4, 101.5, 70.0, 68.0, 55.3, 31.5, 29.7, 25.6, 23.9, 22.6, 14.0.


**General procedure for the synthesis of PFG’ and PFG’₃**

The corresponding dendritic azide G’m-N₃ and PFYNE were dissolved in THF (1 mL per about 20 mg of reaction mixture). To this solution, bromotris(triphenylphosphine) copper(I) (10 mol% related to dendritic azide) and N,N-diisopropylethylamine (1 eqv. to dendritic azide) were then added while stirring vigorously. The reaction mixture was heated at 35 °C and stirred under nitrogen for 2 days. The crude product was evaporated to dryness and washed with water for several times. The dendronized polymer was precipitated into hexane from THF for times to remove excess dendritic azide.

**Preparation of PFG’₂. G’₂-N₃** (39.2 mg, 0.030 mmol) and PFYNE (30.0 mg, 0.015 mmol) were used to afford a gray solid (56.7 mg, 82% yield). [α]²⁰D = + 56.8 (c 0.25 THF).

¹H NMR (300 MHz, CDCl₃): δ = 8.13-8.03 (br, m, 4H, 3.2H for dendron carbazole Ar-H and 0.8H for binaphthyl Ar-H), 7.90-7.83 (br, m, 2H, fluorene Ar-H), 7.67 (br, m, 5.2H, 4H for fluorene and 1.2H binaphthyl Ar-H), 7.40-7.31 (br, m, 6.4H, carbazole Ar-H), 7.17 (br, m, 3.2H, carbazole Ar-H), 6.44-6.27 (br, m, 4H, 0.4H for triazole CH and 3.6H for dendron Ar-H), 5.01-4.77 (br, m, 3.2H, 0.8H for binaphthyl ArOCH₂, 0.8H for dendron ArCH₂N and 1.6H for ArCH₂O), 4.37-4.27 (br, m, 3.2H, dendron ArOCH₂), 3.89-3.79 (br, m, 3.2H, carbazole ArNCH₂), 2.22-1.96 (br, m, 7.2H, 4H for fluorene CH₂ and 3.2H for dendron CH₂), 1.71 (br, m, 3.2H, dendron CH₂), 1.25-0.93 (br, m, 12H, fluorene CH₂), 0.79-0.71 (br, m, 10H, fluorene CH₂ and CH₃).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 160.2, 151.8, 140.5, 140.3, 126.1, 126.1, 125.6, 122.8, 120.3, 118.8, 108.6, 105.8, 67.4, 55.3, 31.4, 29.6, 25.8, 25.8, 22.5, 14.0.

IR (thin film): 3052, 2925, 2857, 1890, 1598, 1457, 1376, 1332, 1240, 1159, 1055, 885, 817, 747, 617.

Preparation of PFG$^*$$_3$. G$^*$$_3$-N$_3$ (31.8 mg, 0.0149 mmol) and PFYNE (15.0 mg, 0.0074 mmol) were used to afford a gray solid (36.5 mg, 78% yield). [$\alpha$]$^{20}_D = +36.0$ (c 0.26 THF)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.07$-7.99 (br, m, 7.2H, 6.4H for dendron carbazole Ar-H and 0.8H for binaphthyl Ar-H), 7.84 (br, m, 2H, fluorene Ar-H), 7.68 (br, m, 5.2H, 4H for fluorene and 1.2H binaphthyl Ar-H), 7.49-7.29 (br, m, 12.8H, carbazole Ar-H), 7.14 (br, m, 6.4H, carbazole Ar-H), 6.60 (br, m, 2H, 0.4H for triazole CH and 1.6H for dendron Ar-H), 6.50-6.42 (br, m, 5.2H, dendron Ar-H), 6.22 (br, m, 1.6H, dendron Ar-H), 4.81 (br, m, 6.4H, 0.8H for binaphthyl ArOCH$_2$, 0.8H for dendron ArCH$_2$N and 4.8H for ArCH$_2$O), 4.19 (br, m, 6.4H, dendron ArOCH$_2$), 3.70 (br, m, 6.4H, carbazole ArNCH$_2$), 2.04-1.88 (br, m, 10.4H, 4H for fluorene CH$_2$ and 6.4H for dendron CH$_2$), 1.64 (br, m, 6.4H, dendron CH$_2$), 1.19-1.00 (br, m, 12H, fluorene CH$_2$), 0.88-0.69 (br, m, 10H, fluorene CH$_2$ and CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 160.2, 140.3, 139.1, 131.8, 127.4, 125.6, 122.8, 120.3, 118.8, 108.6, 105.9, 70.2, 67.5, 55.3, 42.6, 31.5, 29.7, 26.9, 25.7, 23.9, 22.5, 14.0.

3. Physical Properties of Copolymers

**Figure S1.** GPC elution traces of the copolymers: (a) normalized RI GPC trace; (b) normalized TALLS-RI GPC trace
Table. Molecular Weights of the Copolymers Determined by GPC with RI and LS-Detection

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</table>

Figure S2. TGA curves of the copolymers (Heating rate:10 K/min from 100 °C to 800 °C in nitrogen)
Figure S3. DSC curves of the copolymers (Second-heating DSC curves of the copolymers with a heating rate of 10 K/min in nitrogen).

Figure S4. Photoluminescent spectra of PF in solid films after thermal annealing at 200°C for 0.5 h in air and 2 h in air.

Figure S5. UV-vis absorption and Photoluminescent spectra of PFG1 in solid films after thermal annealing at 200°C for 0.5 h in air and 2 h in air.
Figure S6. UV-vis absorption and Photoluminescent spectra of PFG$_2$ in solid films after thermal annealing at 200 °C for 0.5h in air and 2h in air.

Figure S7. UV-vis absorption and Photoluminescent spectra of PFG$_3$ in solid films after thermal annealing at 200 °C for 0.5 h in air and 2 h in air.
Figure S8. UV-vis absorption and Photoluminescent spectra of PFG$_1$ in solid films after thermal annealing at 200°C for 0.5 h in air and 2 h in air.

Figure S9. UV-vis absorption and Photoluminescent spectra of PFG$_2$ in solid films after thermal annealing at 200°C for 0.5 h in air and 2 h in air.
Figure S11. UV-vis absorption and Photoluminescent spectra of PFG’3 in solid films after thermal annealing at 200 °C for 0.5 h in air and 2 h in air

5. CD Spectra of Dendritic Monomer

Figure S12. CD spectra of the dendritic monomer M5 (10^{-5} M in THF)
6. NMR and IR Spectra of Monomers and Copolymers

Monomer M1
Dendron G$_2$N$_3$
Dendron G₃N₃
Dendron G\textsubscript{1}N\textsubscript{3}
Dendron G'\textsubscript{2}N$_3$
Dendron G'3N3
Monomer M4
Dendritic monomer M5
Polymer PFOH

[Diagram of spectra with labeled peaks: CH of Biphenyl, CH$_2$ of Fluorene, CH$_3$ of Biphenyl, CH$_3$ of Fluorene]
Polymer PFG$_1$
Polymer PFG'$_1$
7. References


