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Electronic Supplementary Information

Mechanochromic dendrimers: The relationship between primary structure and mechanochromic properties in the bulk

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Materials

All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, and Kanto Chemical and used as received, unless otherwise noted. **DABBF-dialkyne**,[1] **DABBF-tetraalkyne**,[1] and Fréchet-type dendrons[2] were synthesized according to previously published methods. Copper(I) bromide (CuBr) was washed with acetic acid and with methanol, and dried in vacuo.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD500 spectrometer. IR spectra were recorded on a JEOL FT/IR-4100 Fourier transform infrared spectrometer as thin films with KBr and cast on NaCl. Analytical gel permeation chromatographic (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. MALDI-TOF MS spectrometry was performed on a SHIMADZU AXIMA Performance MALDI-TOF mass spectrometer operating in linear mode, using dithranol or *trans*-2-[3-(4-*tert*-butylphenyl)- 2-methyl-2-propenylidene]malononitrile (DCTB) in combination with sodium trifluoroacetate. DSC measurements were carried out using a SHIMADZU DSC-60A Plus with a heating rate 10 °C/min. Preparative HPLC was performed on JAI LC-9104 eluted with chloroform.

Measurements

Grinding tests and electron paramagnetic resonance (EPR) spectroscopy

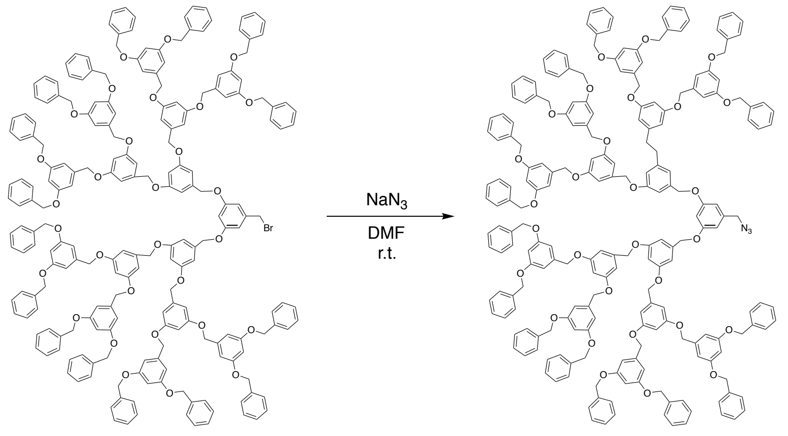
Grinding tests were performed on a Retsch Mixer Mill MM 400. The applied force was controlled by vibrational frequency and grinding time. A powdered sample (50 mg) was placed in the grinding jar and ground for 10 min at 30 Hz. The ground samples were transferred into an EPR 5 mm glass capillary, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The spectra of ground samples were measured using a microwave power of 0.199 mW, field modulation of 0.1 mT with a time constant of 0.03 s, a sweep rate of 0.125 mT/s at 25 °C, and integrated for 16 times. The concentration of the radicals formed from the cleavage of DABBF was determined by comparing the area of the observed integral spectrum with a 0.05 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in benzene under the same experimental condition. The Mn^{2+} signal was used as an auxiliary standard. The *g* value was calculated according to the following equation: $g = h\nu/\beta H$ where *h* is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and *H* is the magnetic field.

Synthesis

Synthesis of azide-terminated Fréchet-type dendrons

Azide-terminated Fréchet-type dendrons from first to third generations (**[G-1]-N$_3$~[G-3]-N$_3$**) were prepared according to previously reported method.[3]

Synthesis of azide-terminated 4th generation dendron ([G-4]-N$_3$)



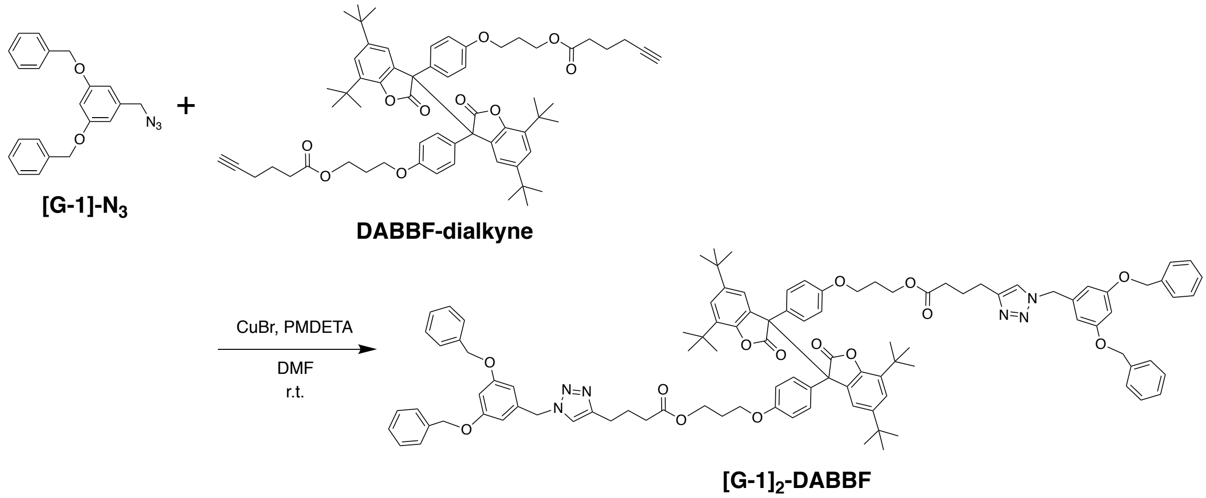
[G-4]-Br **[G-4]-N$_3$**

Under a nitrogen atmosphere, **[G-4]-Br** (1.71 g, 0.508 mmol) and sodium azide (0.333 g, 5.13 mmol) in anhydrous DMF (15 mL) were stirred at r.t. for 1 day. The reaction mixture was precipitated into water. Following filtration, the product was dried in vacuo to afford **[G-4]-N$_3$** as a white solid (1.66 g, 98%)

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.26–7.38 (m, 80H, aromatic), 6.63–6.64 (m, 28H, aromatic), 6.50–6.54 (m, 15H, aromatic), 6.49 (d, *J* = 2.1 Hz, 2H, aromatic), 4.97 (s, 32H, CH$_2$), 4.91 (s, 28H, CH$_2$), 4.16 (s, 2H, CH$_2$); ^{13}C NMR (125 MHz, CDCl$_3$) : δ / ppm 160.18, 160.12, 160.09, 139.24, 139.18, 137.72, 136.80, 128.64, 128.06, 127.63, 107.31, 106.45, 106.41, 101.77, 101.60, 70.10, 69.99, 54.75; FT-IR (KBr, cm^{-1}) : 3033, 2925, 2872, 2099, 1598, 1450, 1374, 1298, 1156, 1051, 834, 740, 696; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 3335.3, found: 3337.8.

Synthesis of series of mechanochromic dendrimers

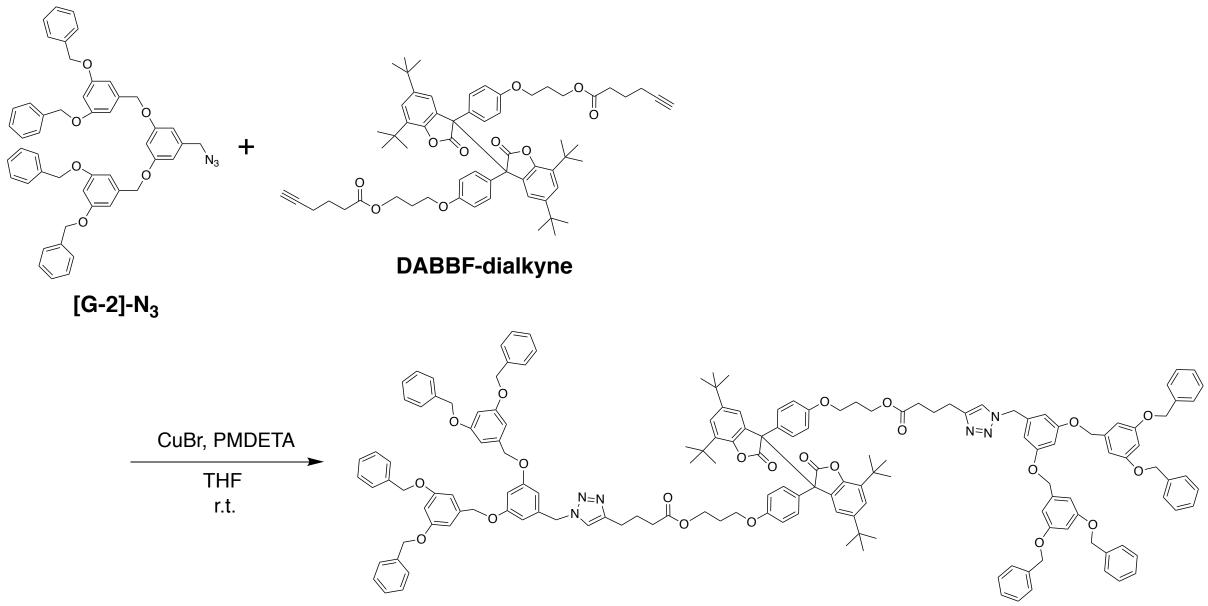
Synthesis of [G-1]$_2$-DABBF



Under a nitrogen atmosphere, *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDETA) (0.725 mL, 3.47 mmol) was added to a solution of **DABBF-dialkyne** (0.367 g, 0.374 mmol), **[G-1]-N$_3$** (0.424 g, 1.23 mmol), Cu (77.8 mg, 1.22 mmol), and CuBr (164 mg, 1.14 mmol) in anhydrous DMF (15 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 1 day. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation and pouring into water, the resulting emulsion was centrifuged to separate a precipitate. The mixture was diluted with THF and dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was subsequently purified by flash chromatography (ethyl acetate : hexane = 1:1) and freeze-drying using benzene as a solvent to give the product as a white solid (0.259 g, 42%).

^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.28–7.39 (m, 22H, aromatic and CH), 7.19 (s, 6H, aromatic), 6.78 (d, *J* = 7.8 Hz, 6H, aromatic), 6.57 (t, *J* = 2.2 Hz, 2H, aromatic), 6.47 (d, *J* = 2.2 Hz, 4H, aromatic), 5.38 (s, 4H, CH_2), 4.98 (s, 8H, CH_2), 4.24 (t, *J* = 6.4 Hz, 4H, CH_2), 4.04 (m, 4H, CH_2), 2.73 (t, *J* = 7.6 Hz, 4H, CH_2), 2.38 (t, *J* = 7.5 Hz, 4H, CH_2), 2.09 (quin, *J* = 6.3 Hz, 4H, CH_2), 1.98 (quin, *J* = 7.5 Hz, 4H, CH_2), 1.30 (br, 18H, CH_3), 1.16 (br, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ / ppm 174.37, 173.22, 160.33, 158.81, 149.10, 147.54, 145.70, 137.02, 136.42, 133.48, 132.24, 128.60, 128.08, 127.51, 123.96, 120.85, 113.12, 107.07, 102.01, 70.10, 64.29, 61.18, 53.97, 34.69, 34.34, 33.49, 31.59, 31.52, 29.65, 28.51, 24.97, 24.50; FT-IR (KBr, cm^{-1}): 2959, 2873, 1794, 1733, 1602, 1507, 1458, 1367, 1298, 1254, 1159, 1088, 1053, 824, 741, 699; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 1691.8, found: 1691.8.

Synthesis of [G-2]$_2$-DABBF



[G-2]-N$_3$

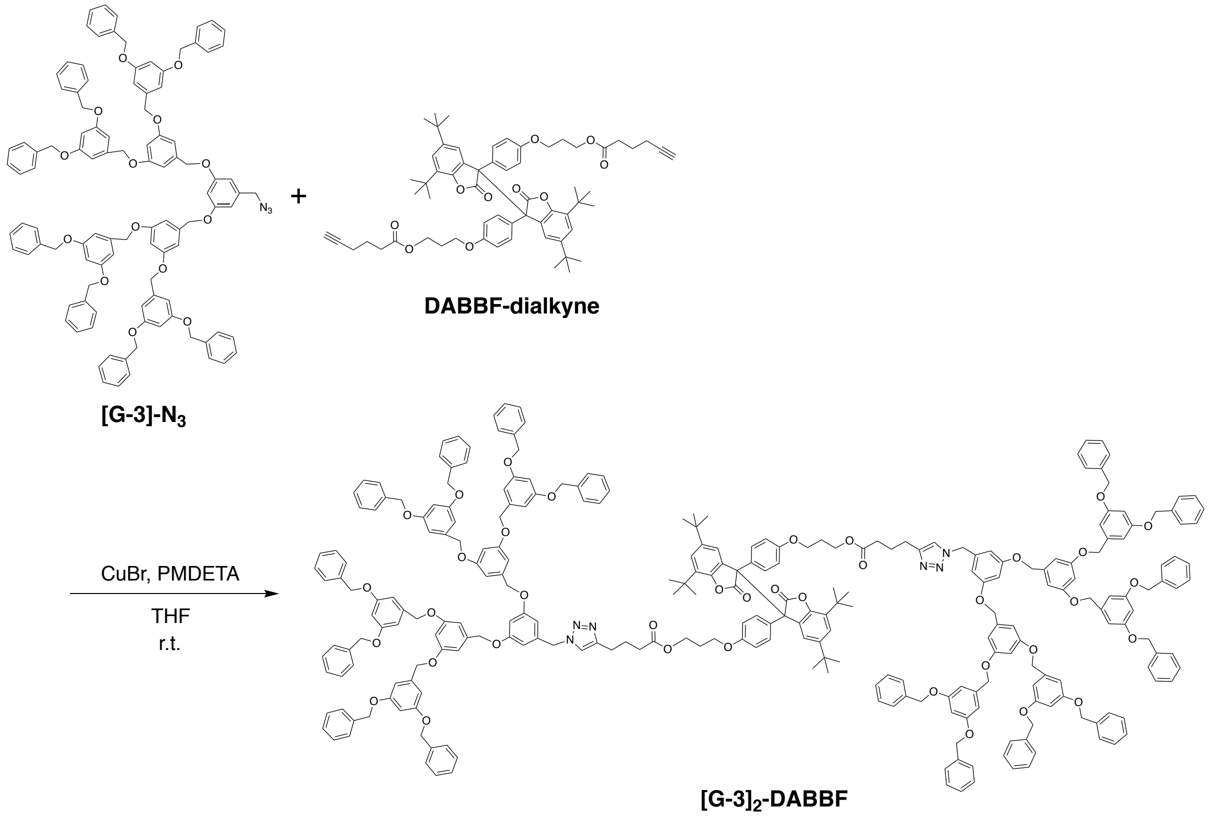
DABBF-dialkyne

[G-2]$_2$-DABBF

Under a nitrogen atmosphere, PMDETA (0.407 mL, 1.95 mmol) was added to a solution of **DABBF-dialkyne** (0.213 g, 0.218 mmol), **[G-2]-N$_3$** (0.502 g, 0.651 mmol), Cu (86.3 mg, 1.35 mmol), and CuBr (94.1 mg, 0.656 mmol) in anhydrous THF (10 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 6 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by flash chromatography (dichloromethane/ethyl acetate gradient, 0–25% ethyl acetate) and freeze-drying using benzene as a solvent to give the product as a white solid (0.473 g, 86%).

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.27–7.41 (m, 42H, aromatic and CH), 7.19 (s, 6H, aromatic), 6.77 (d, *J* = 7.9 Hz, 6H, aromatic), 6.64 (d, *J* = 2.3 Hz, 8H, aromatic), 6.56 (t, *J* = 2.3 Hz, 4H, aromatic), 6.53 (t, *J* = 2.2 Hz, 2H, aromatic), 6.44 (d, *J* = 2.2 Hz, 4H, aromatic), 5.36 (s, 4H, CH$_2$), 5.02 (s, 16H, CH$_2$), 4.91 (s, 8H, CH$_2$), 4.22 (t, *J* = 6.3 Hz, 4H, CH$_2$), 4.02 (m, 4H, CH$_2$), 2.71 (t, *J* = 7.6 Hz, 4H, CH$_2$), 2.35 (t, *J* = 7.5 Hz, 4H, CH$_2$), 2.07 (quin, *J* = 6.3 Hz, 4H, CH$_2$), 1.96 (quin, *J* = 7.5 Hz, 4H, CH$_2$), 1.30 (br, 18H, CH$_3$), 1.16 (br, 18H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ / ppm 173.22, 160.26, 160.16, 158.82, 149.11, 147.62, 138.86, 137.05, 136.70, 133.50, 132.28, 128.58, 128.03, 127.56, 124.02, 120.87, 113.14, 107.08, 106.33, 101.97, 101.59, 70.09, 69.99, 64.30, 61.20, 53.98, 34.70, 34.35, 33.50, 31.59, 31.53, 29.66, 28.52, 24.97, 24.51; FT-IR (KBr, cm^{-1}): 3033, 2957, 2872, 1794, 1732, 1600, 1453, 1371, 1298, 1156, 1051, 832, 740, 697; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 2540.2, found: 2534.6.

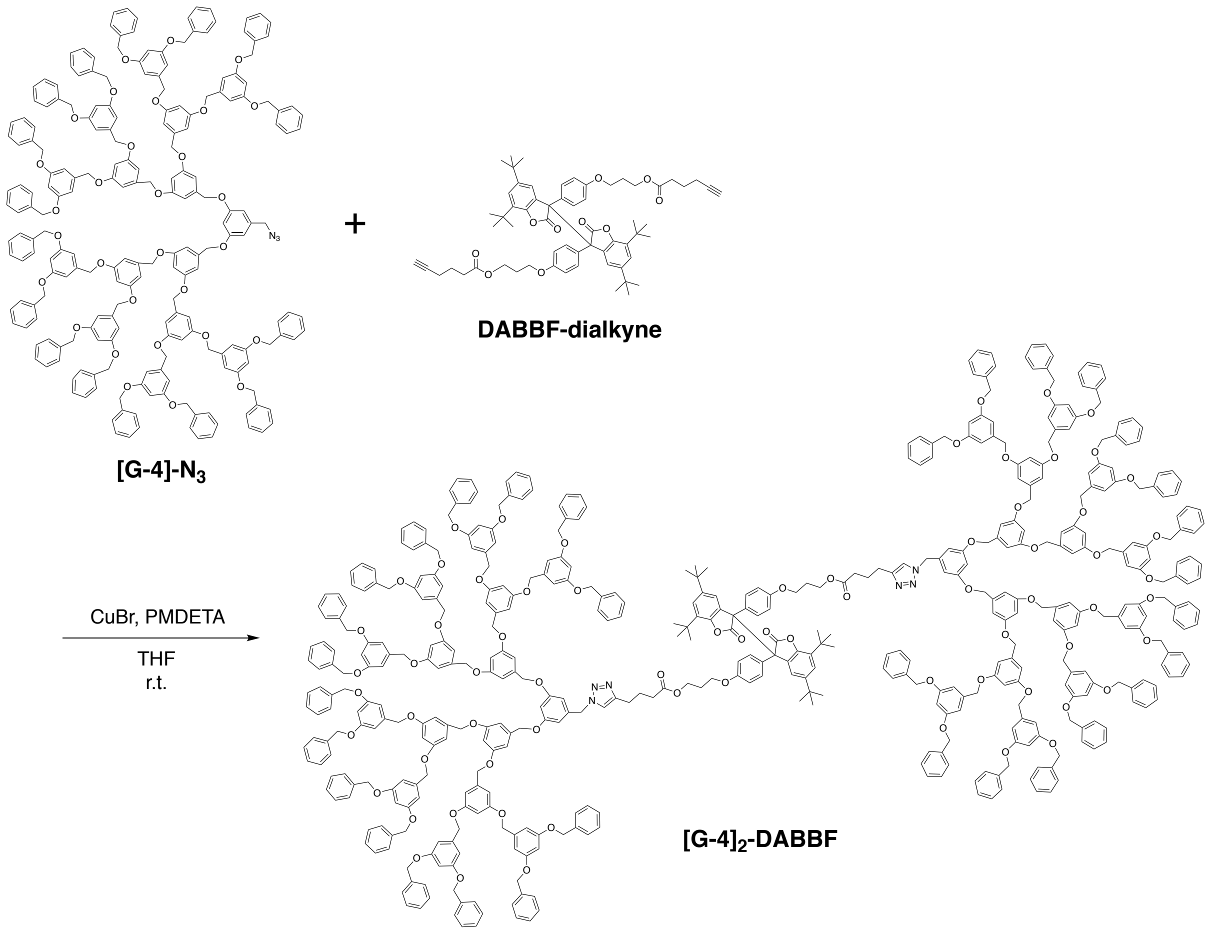
Synthesis of [G-3]$_2$-DABBF



Under a nitrogen atmosphere, PMDETA (0.232 mL, 1.11 mmol) was added to a solution of **DABBF-dialkyne** (0.122 g, 0.124 mmol), **[G-3]-N$_3$** (0.600 g, 0.371 mmol), Cu (47.5 mg, 0.748 mmol), and CuBr (53.6 mg, 0.374 mmol) in anhydrous THF (15 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 1 day. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by preparative HPLC and freeze-drying using benzene as a solvent to give the product as a white solid (0.164 g, 31%).

^{1}H NMR (500 MHz, CDCl$_3$): δ/ ppm 7.27–7.39 (m, 82H, aromatic), 7.17 (s, 6H, aromatic), 6.76 (d, *J* = 6.7 Hz, 6H, aromatic), 6.65 (d, *J* = 2.3 Hz, 16H, aromatic), 6.61 (d, *J* = 2.2 Hz, 8H, aromatic), 6.54 (m, 12H, aromatic), 6.52 (t, *J* = 2.3 Hz, 2H, aromatic), 6.43 (d, *J* = 2.1 Hz, 4H, aromatic), 5.31 (s, 4H, CH$_2$), 4.99 (s, 32H, CH$_2$), 4.93 (s, 16H, CH$_2$), 4.88 (s, 8H, CH$_2$), 4.21 (t, *J* = 6.2 Hz, 4H, CH$_2$), 4.00 (m, 4H, CH$_2$), 2.69 (t, *J* = 7.6 Hz, 4H, CH$_2$), 2.34 (t, *J* = 7.5 Hz, 4H, CH$_2$), 2.06 (quin, *J* = 6.1 Hz, 4H, CH$_2$), 1.95 (quin, *J* = 7.4 Hz, 4H, CH$_2$), 1.30 (br, 18H, CH$_3$), 1.16 (br, 18H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ/ ppm 173.19, 160.26, 160.13, 160.04, 158.81, 149.11, 147.61, 139.15, 138.85, 137.11, 136.72, 133.48, 132.28, 128.56, 127.99, 127.55, 123.98, 120.89, 113.13, 107.07, 106.37, 101.89, 101.61, 101.52, 70.06, 69.99, 69.95, 64.29, 61.19, 53.90, 34.69, 34.34, 33.49, 31.53, 29.65, 28.51, 24.97, 24.51; FT-IR (KBr, cm^{-1}): 3033, 2956, 1794, 1732, 1599, 1452, 1372, 1299, 1156, 1052, 834, 740, 696; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 4236.8, found: 4236.0.

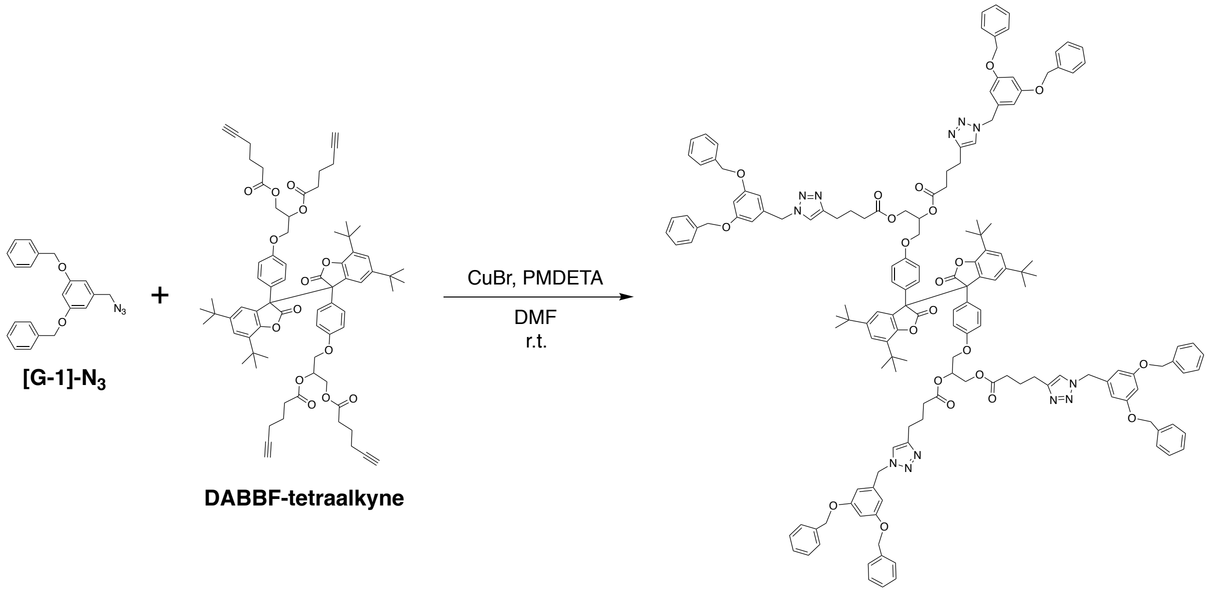
Synthesis of [G-4]$_2$-DABBF



Under a nitrogen atmosphere, PMDETA (0.132 mL, 0.633 mmol) was added to a solution of **DABBF-dialkyne** (71.3 mg, 72.8 μmol), **[G-4]-N$_3$** (0.700 g, 0.211 mmol), Cu (27.8 mg, 0.438 mmol), and CuBr (37.7 mg, 0.263 mmol) in anhydrous THF (15 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 3 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by flash chromatography (dichloromethane/ethyl acetate gradient, 0–20% ethyl acetate) and freeze-drying using benzene as a solvent to give the product as a white solid (0.430 g, 78%).

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.24–7.36 (m, 164H, aromatic), 7.13 (s, 6H, aromatic), 6.74 (d, *J* = 6.8 Hz, 6H, aromatic), 6.62 (d, *J* = 2.2 Hz, 32H, aromatic), 6.61 (d, *J* = 2.3 Hz, 16H, aromatic), 6.60 (d, *J* = 2.0 Hz, 8H, aromatic), 6.52 (t, *J* = 2.2 Hz, 20H, aromatic), 6.49 (t, *J* = 2.1 Hz, 10H, aromatic), 6.40 (d, *J* = 2.0 Hz, 4H, aromatic), 5.25 (s, 4H, CH_2), 4.94 (s, 64H, CH_2), 4.88 (s, 48H, CH_2), 4.83 (s, 8H, CH_2), 4.18 (t, *J* = 6.4 Hz, 4H, CH_2), 3.97 (m, 4H, CH_2), 2.65 (t, *J* = 7.6 Hz, 4H, CH_2), 2.31 (t, *J* = 7.4 Hz, 4H, CH_2), 2.03 (quin, *J* = 6.3 Hz, 4H, CH_2), 1.91 (quin, *J* = 7.6 Hz, 4H, CH_2), 1.28 (br, 18H, CH_3), 1.14 (br, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ / ppm 173.16, 160.23, 160.10, 160.03, 160.01, 158.79, 149.11, 147.59, 139.16, 138.90, 137.13, 136.72, 133.47, 128.55, 128.33, 127.97, 127.54, 120.87, 113.14, 107.11, 106.40, 106.34, 101.79, 101.52, 70.02, 69.91, 64.28, 61.19, 53.84, 34.69, 34.34, 33.47, 31.53, 29.64, 28.50, 24.97, 24.51; FT-IR (KBr, cm^{-1}): 3032, 2932, 2871, 1794, 1732, 1596, 1451, 1374, 1322, 1296, 1157, 1052, 833, 738, 697; MALDI-TOF: *m*/*z* $[M+Na]^+$ calcd: 7630.2, found: 7628.5.

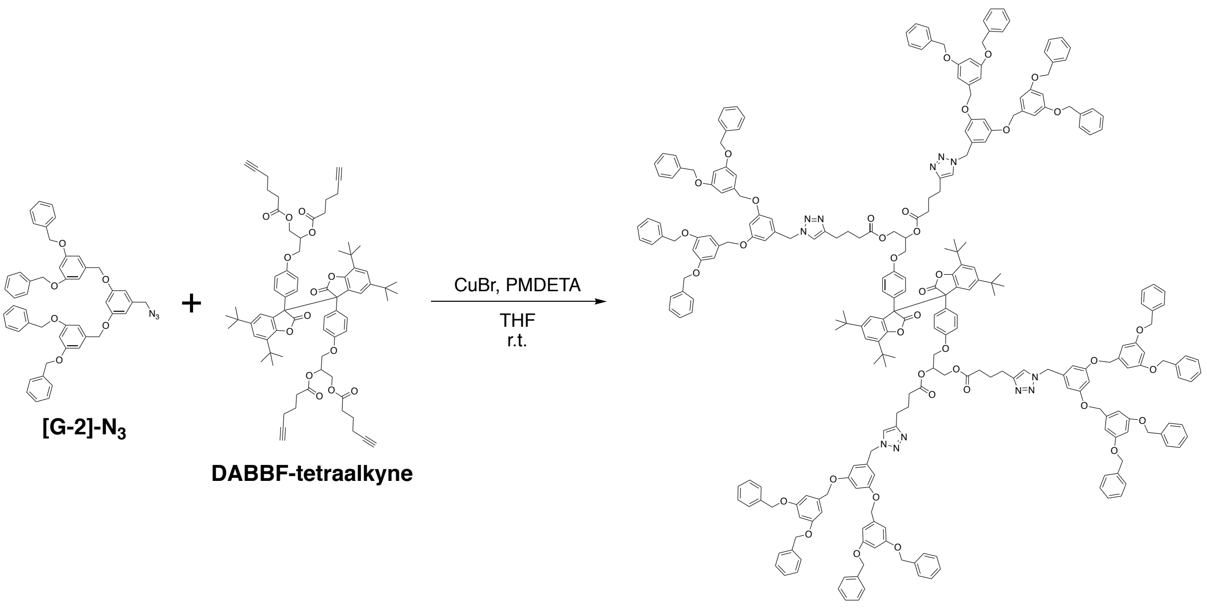
Synthesis of [G-1]$_4$-DABBF



Under a nitrogen atmosphere, PMDETA (0.806 mL, 3.86 mmol) was added to a solution of **DABBF-tetraalkyne** (0.287 g, 0.239 mmol), **[G-1]-N$_3$** (0.523 g, 1.51 mmol), Cu (151 mg, 2.37 mmol), and CuBr (206 mg, 1.44 mmol) in anhydrous DMF (15 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 1 day. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation and pouring into water, the resulting emulsion was centrifuged to separate a precipitate. The mixture was diluted with THF and dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was subsequently purified by flash chromatography (ethyl acetate/hexane gradient, 60–100% ethyl acetate) and freeze-drying using benzene as a solvent to give the product as a white solid (0.234 g, 38%).

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.28–7.39 (m, 44H, aromatic and CH), 7.20 (d, *J* = 5.0 Hz, 6H, aromatic), 6.78 (br, 6H, aromatic), 6.55 (s, 4H, aromatic), 6.46 (d, *J* = 1.9 Hz, 8H, aromatic), 5.38 (m, 2H, CH), 5.35 (s, 8H, CH$_2$), 4.96 (s, 16H, CH$_2$), 4.21–4.45 (m, 4H, CH$_2$), 4.07 (m, 4H, CH$_2$), 2.69 (q, *J* = 7.3 Hz, 8H, CH$_2$), 2.37 (m, 8H, CH$_2$), 1.95 (m, 8H, CH$_2$), 1.29 (br, 18H, CH$_3$), 1.16 (br, 18H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ / ppm 172.82, 172.50, 160.33, 158.27, 149.10, 147.44, 147.40, 137.08, 136.44, 133.57, 132.32, 128.60, 128.09, 127.54, 124.15, 120.99, 120.96, 113.24, 107.09, 101.99, 70.10, 69.48, 66.00, 62.45, 53.94, 34.71, 34.36, 33.47, 33.29, 31.53, 29.65, 24.90, 24.86, 24.42; FT-IR (KBr, cm^{-1}): 3034, 2958, 1793, 1739, 1601, 1506, 1456, 1369, 1298, 1226, 1158, 1088, 1053, 828, 741, 699; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 2602.2, found: 2601.2.

Synthesis of [G-2]$_4$-DABBF



[G-2]-N$_3$

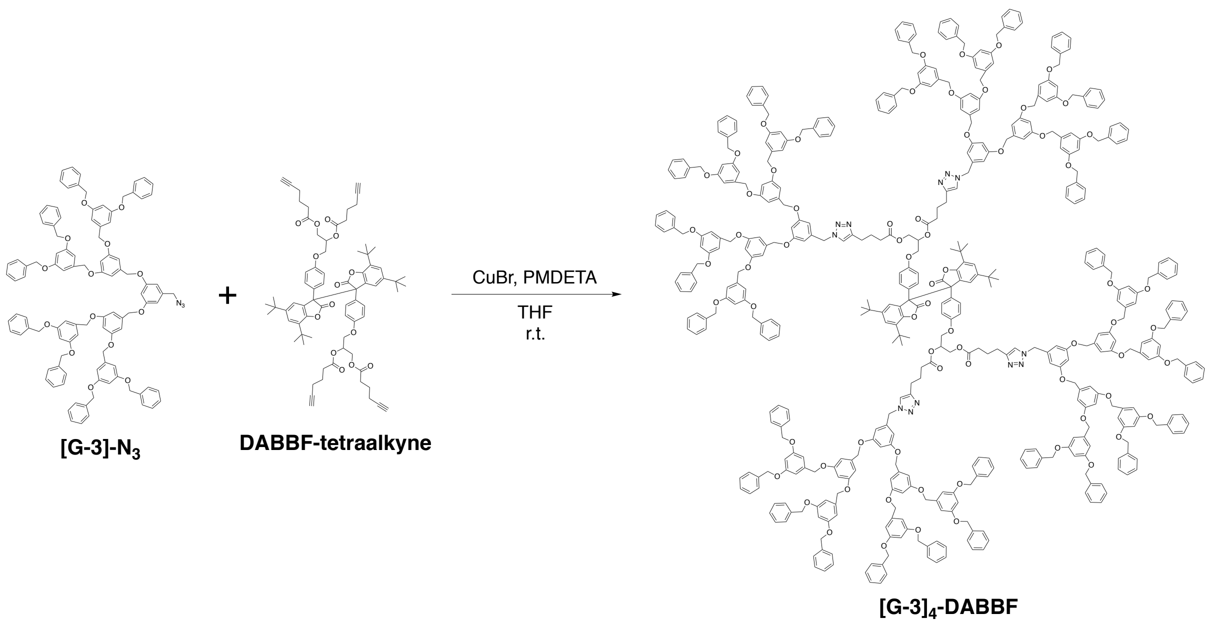
DABBF-tetraalkyne

[G-2]$_4$-DABBF

Under a nitrogen atmosphere, PMDETA (0.361 mL, 1.73 mmol) was added to a solution of **DABBF-tetraalkyne** (0.131 g, 0.109 mmol), **[G-2]-N$_3$** (0.500 g, 0.650 mmol), Cu (70.8 mg, 1.11 mmol), and CuBr (97.6 mg, 0.680 mmol) in anhydrous THF (20 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 9 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by flash chromatography (dichloromethane/methanol gradient, 0–2% methanol) and freeze-drying using benzene as a solvent to give the product as a white solid (0.272 g, 58%).

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.27–7.40 (m, 84H, aromatic and CH), 7.20 (d, *J* = 6.9 Hz, 6H, aromatic), 6.76 (br, 6H, aromatic), 6.61 (d, *J* = 1.9 Hz, 16H, aromatic), 6.54 (s, 8H, aromatic), 6.50 (s, 4H, aromatic), 6.42 (s, 8H, aromatic), 5.35 (s, 2H, CH), 5.31 (s, 8H, CH$_2$), 4.97 (s, 32H, CH$_2$), 4.86 (s, 16H, CH$_2$), 4.19–4.41 (m, 4H, CH$_2$), 4.04 (m, 4H, CH$_2$), 2.66 (q, *J* = 7.5 Hz, 8H, CH$_2$), 2.34 (m, 8H, CH$_2$), 1.93 (m, 8H, CH$_2$), 1.27 (br, 18H, CH$_3$), 1.16 (br, 18H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ / ppm 172.84, 172.52, 160.27, 160.18, 158.33, 149.14, 147.52, 147.49, 138.92, 137.20, 136.75, 133.60, 128.61, 128.05, 127.60, 121.09, 121.05, 113.28, 107.10, 106.38, 101.95, 101.62, 70.10, 69.99, 69.51, 66.04, 62.50, 53.93, 34.75, 34.39, 33.52, 33.33, 31.58, 29.70, 24.92, 24.89, 24.46; FT-IR (KBr, cm^{-1}): 3033, 2955, 2872, 1794, 1739, 1599, 1504, 1453, 1372, 1299, 1156, 1051, 834, 740, 697; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 4298.9, found: 4297.9.

Synthesis of [G-3]$_4$-DABBF

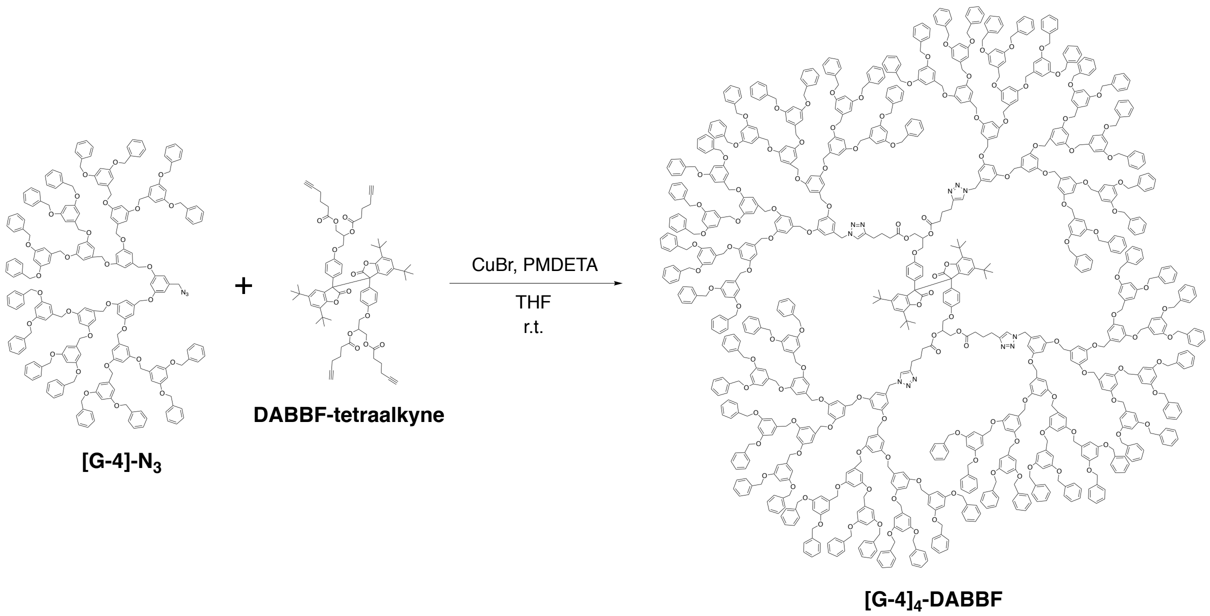


Under a nitrogen atmosphere, PMDETA (0.195 mL, 0.933 mmol) was added to a solution of **DABBF-tetraalkyne** (70.0 mg, 58.4 μmol), **[G-3]-N$_3$** (0.567 g, 0.350 mmol), Cu (36.2 mg, 0.570 mmol), and CuBr (50.1 mg, 0.349 mmol) in anhydrous THF (15 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 2.5 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by preparative HPLC and freeze-drying using benzene as a solvent to give the product as a white solid (0.306 g, 68%).

^{1}H NMR (500 MHz, CDCl$_3$): δ / ppm 7.24–7.37 (m, 164H, aromatic and CH), 7.19 (d, *J* = 9.9 Hz, 6H, aromatic), 6.74 (br, 6H, aromatic), 6.62 (d, *J* = 2.0 Hz, 32H, aromatic), 6.57 (d, *J* = 1.9

Hz, 16H, aromatic), 6.52 (s, 16H, aromatic), 6.48 (s, 12H, aromatic), 6.40 (s, 8H, aromatic), 5.33 (s, 2H, CH), 5.24 (s, 8H, CH_2), 4.94 (s, 64H, CH_2), 4.86 (s, 32H, CH_2), 4.80 (s, 16H, CH_2), 4.17–4.40 (m, 4H, CH_2), 4.02 (m, 4H, CH_2), 2.63 (q, J = 8.1 Hz, 8H, CH_2), 2.30 (m, 8H, CH_2), 1.90 (m, 8H, CH_2), 1.27 (br, 18H, CH_3), 1.15 (br, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ / ppm 172.77, 172.46, 160.20, 160.09, 159.99, 158.25, 149.08, 147.44, 147.41, 139.15, 138.86, 137.24, 136.72, 133.53, 128.54, 127.96, 127.54, 121.09, 121.06, 113.24, 107.01, 106.35, 101.76, 101.56, 101.49, 70.00, 69.88, 69.44, 65.98, 62.45, 53.78, 34.68, 34.33, 33.47, 33.27, 31.52, 29.64, 24.86, 24.45, 24.40; FT-IR (KBr, cm^{-1}): 3033, 2946, 2871, 1794, 1739, 1598, 1451, 1373, 1299, 1156, 1050, 834, 740, 696; MALDI-TOF: *m/z* [M+Na]$^+$ calcd: 7692.2, found: 7691.9.

Synthesis of [G-4]$_4$-DABBF



Under a nitrogen atmosphere, PMDETA (0.117 mL, 0.563 mmol) was added to a solution of **DABBF-tetraalkyne** (42.5 mg, 35.4 μmol), **[G-4]-N$_3$** (0.700 g, 0.211 mmol), Cu (22.3 mg, 0.351 mmol), and CuBr (30.3 mg, 0.211 mmol) in anhydrous THF (12 mL) bubbled with nitrogen for 20 minutes. After being bubbled with nitrogen for another 20 minutes, the resulting solution was allowed to stir at r.t. for 1 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. Following evaporation, the crude product was subsequently purified by flash chromatography (dichloromethane/ethyl acetate gradient, 0-20% ethyl acetate) and freeze-drying using benzene as a solvent to give the product as a white solid (0.271 g, 53%).

^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.21–7.35 (m, 324H, aromatic and CH), 7.15 (d, J = 12.7

Hz, 6H, aromatic), 6.73 (br, 6H, aromatic), 6.58 (m, 96H, aromatic), 6.55 (s, 16H, aromatic), 6.48 (s, 32H, aromatic), 6.45 (s, 24H, aromatic), 6.42 (s, 4H, aromatic), 6.36 (s, 8H, aromatic), 5.31 (s, 4H, CH), 5.17 (s, 8H, CH_2), 4.88 (s, 128H, CH_2), 4.80 (s, 64H, CH_2), 4.78 (s, 32H, CH_2), 4.71 (s, 16H, CH_2), 4.15–4.38 (m, 4H, CH_2), 3.98 (m, 4H, CH_2), 2.58 (m, 8H, CH_2), 2.27 (m, 8H, CH_2), 1.86 (m, 8H, CH_2), 1.26 (br, 18H, CH_3), 1.13 (br, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ / ppm 172.73, 172.41, 160.16, 160.05, 159.96, 147.41, 139.16, 138.90, 137.28, 136.72, 136.48, 128.51, 128.33, 127.92, 127.52, 121.07, 107.01, 106.38, 106.32, 101.48, 69.94, 69.82, 53.70, 34.31, 33.47, 33.26, 31.51, 29.61, 24.86, 24.46, 24.40; FT-IR (KBr, cm^{-1}): 3063, 3032, 2931, 2871, 1793, 1739, 1596, 1497, 1451, 1374, 1321, 1296, 1157, 1053, 832, 738, 697; MALDI-TOF: *m*/*z* [M+Na]$^+$ calcd: 14479, found: 14480.

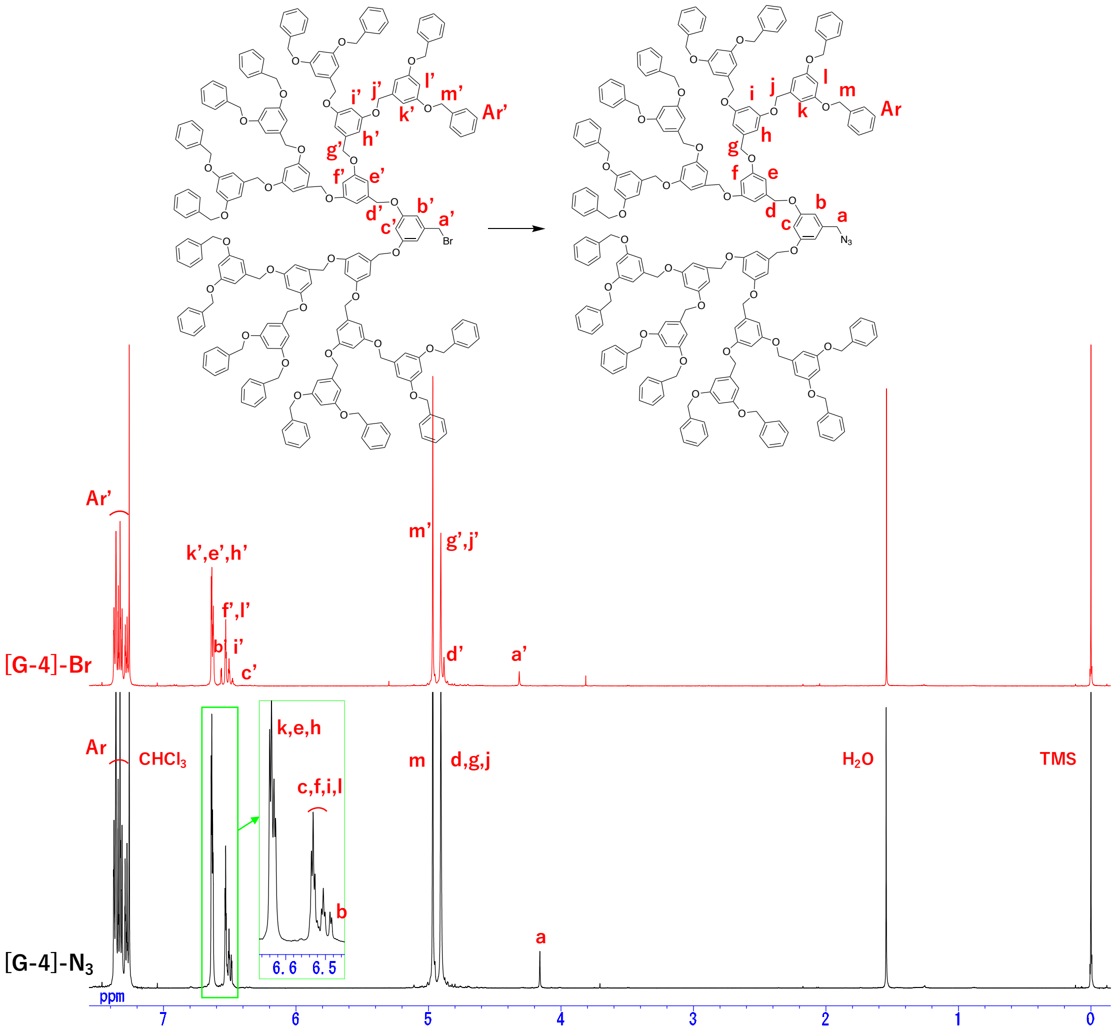


Figure S1. ^{1}H NMR spectra of **[G-4]-N$_3$** (black) and **[G-4]-Br** (red) (500 MHz, CDCl$_3$).

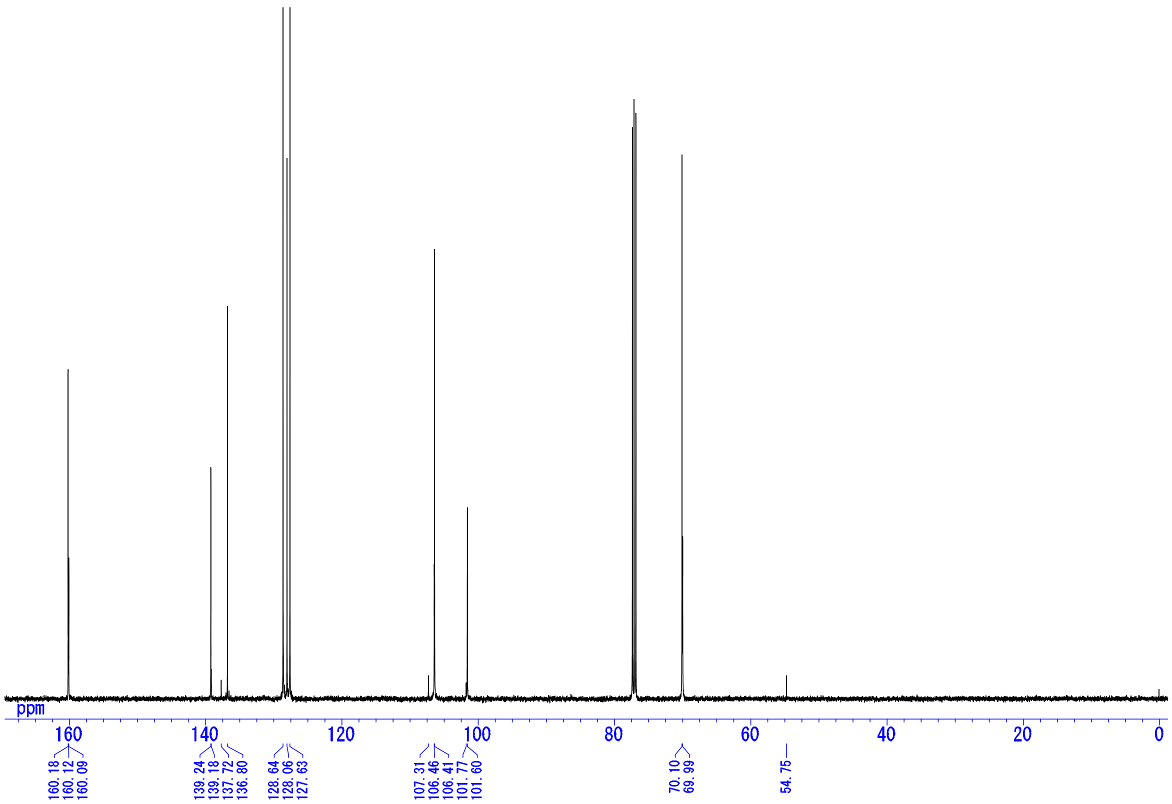


Figure S2. ^{13}C NMR spectrum of **[G-4]-N$_3$** (500 MHz, CDCl$_3$).

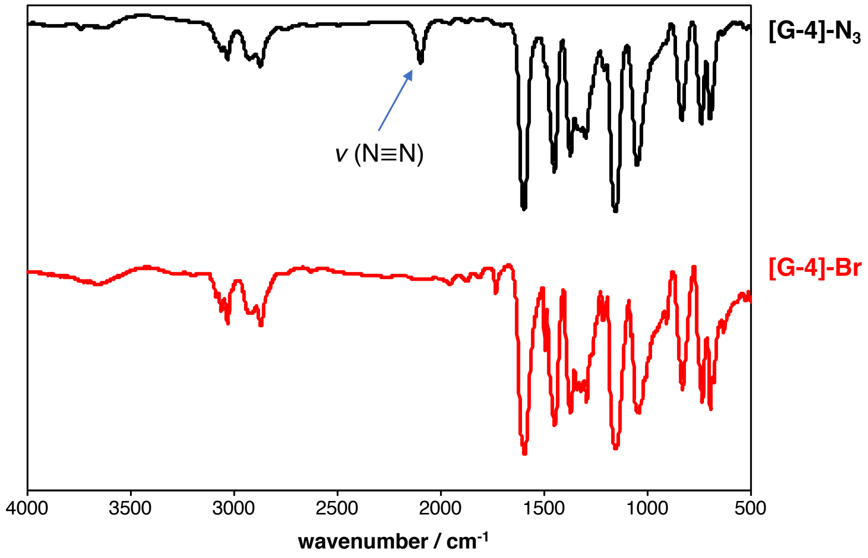


Figure S3. IR spectra of **[G-4]-N$_3$** (black) and **[G-4]-Br** (red) (KBr).

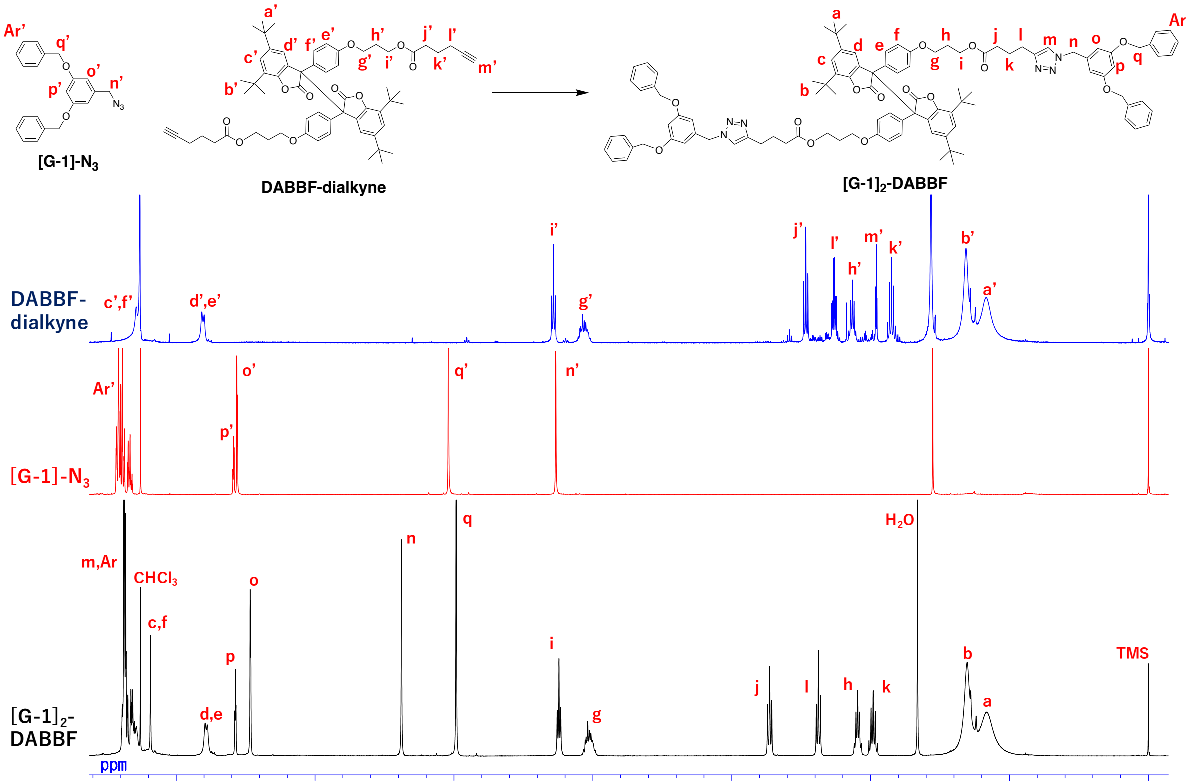


Figure S4. ^{1}H NMR spectra of **[G-1]$_2$-DABBF** (black), **[G-1]-N$_3$** (red), and **DABBF-dialkyne** (blue) (500 MHz, CDCl$_3$).

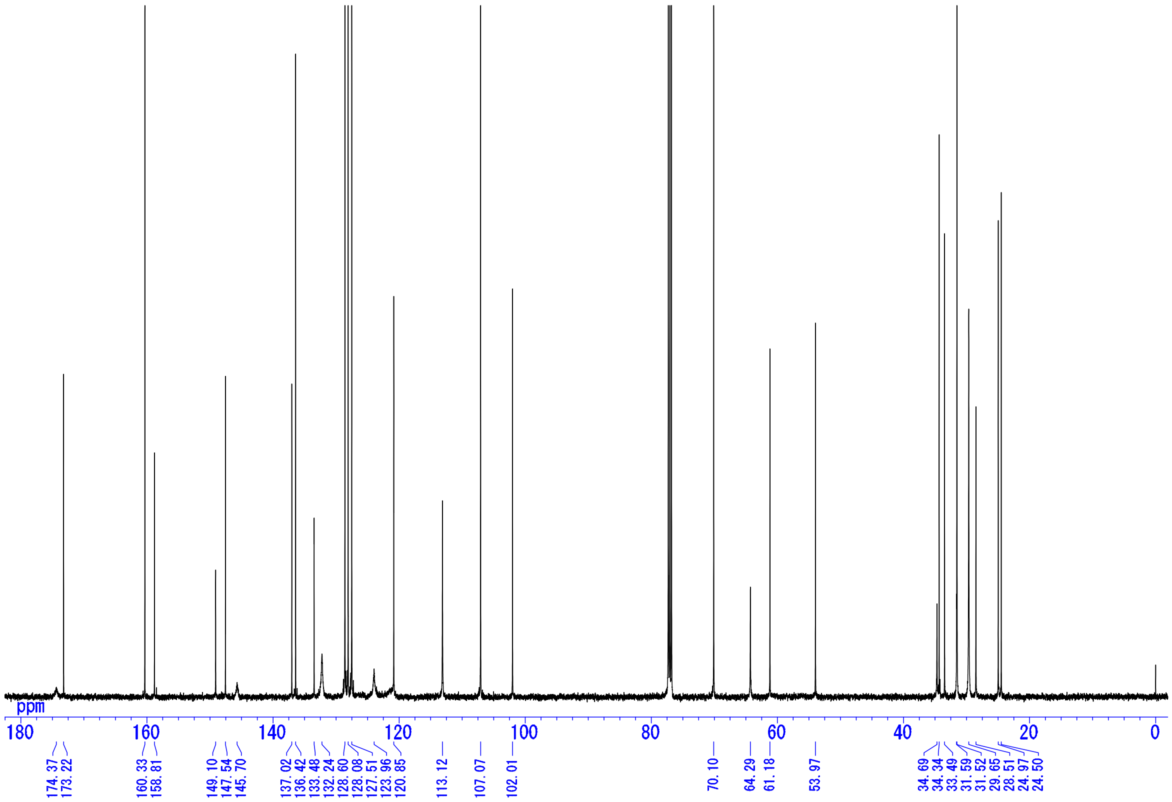


Figure S5. ^{13}C NMR spectrum of **[G-1]$_2$-DABBF** (500 MHz, CDCl$_3$).

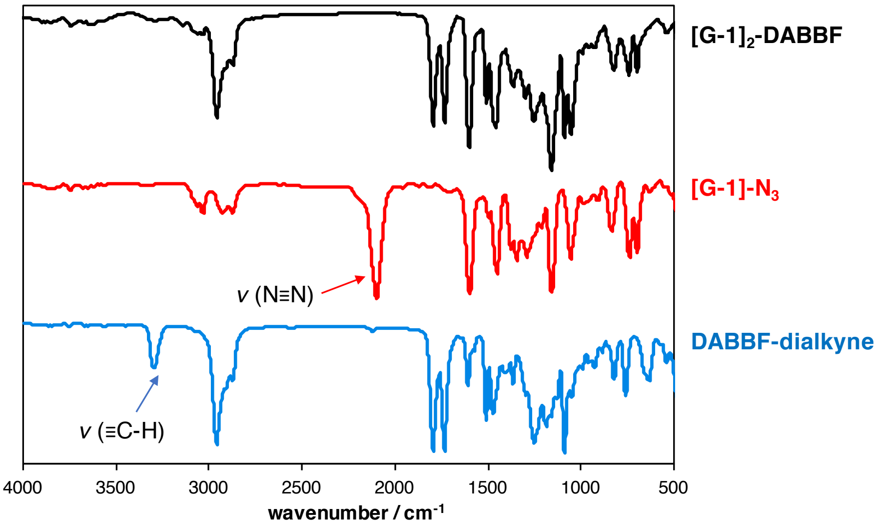


Figure S6. IR spectra of **[G-1]$_2$-DABBF** (black, KBr), **[G-1]-N$_3$** (red, NaCl), and **DABBF-dialkyne** (blue, KBr).

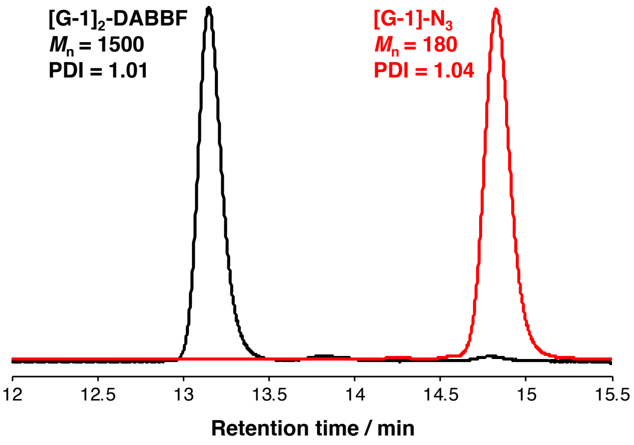


Figure S7. Overlay of GPC traces for **[G-1]$_2$-DABBF** (black) and **[G-1]-N$_3$** (red) (RI).

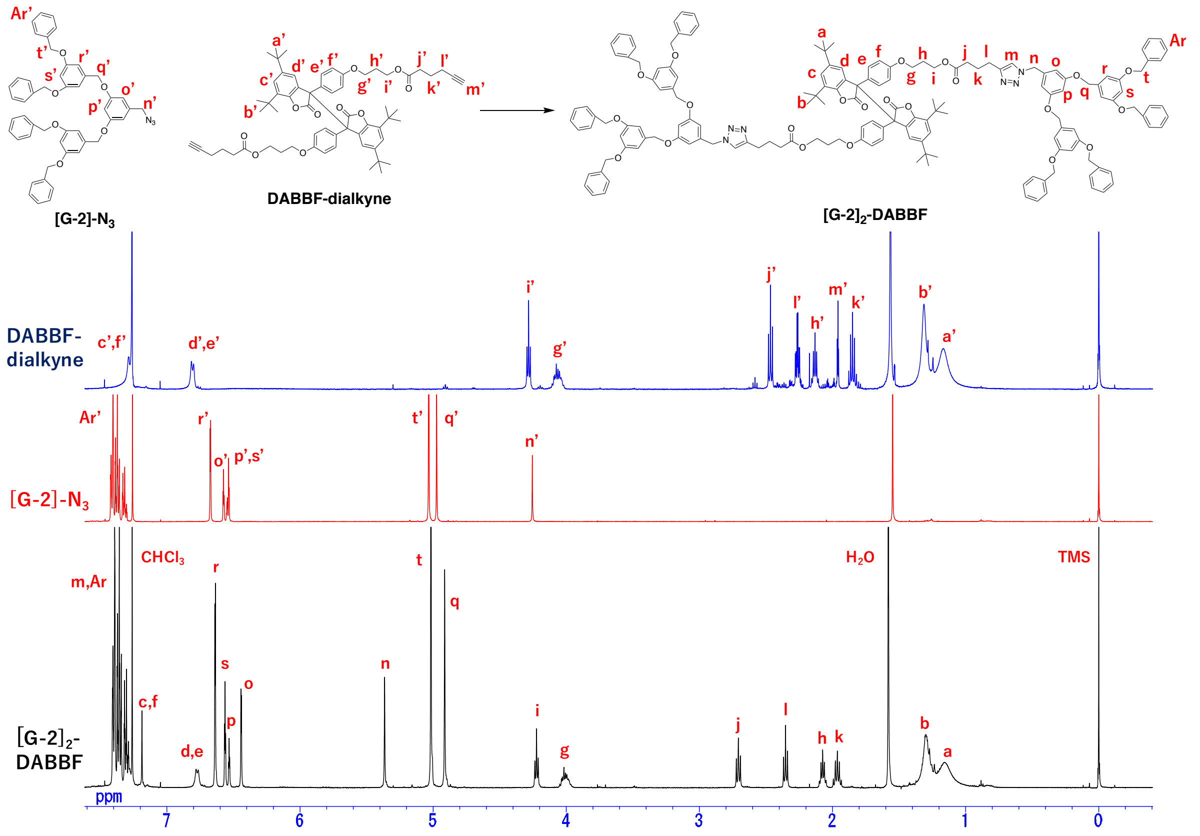


Figure S8. ^{1}H NMR spectra of **[G-2]$_2$-DABBF** (black), **[G-2]-N$_3$** (red), and **DABBF-dialkyne** (blue) (500 MHz, CDCl$_3$).

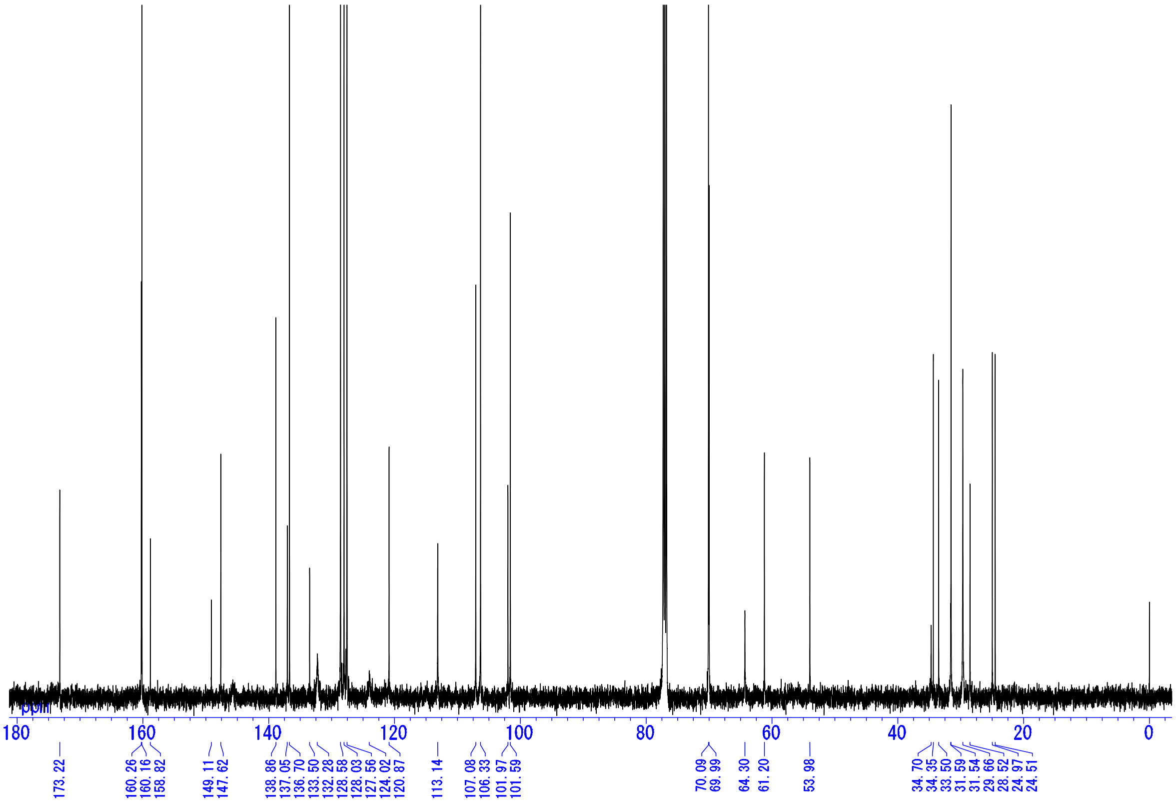


Figure S9. ^{13}C NMR spectrum of **[G-2]₂-DABBF** (500 MHz, CDCl₃).

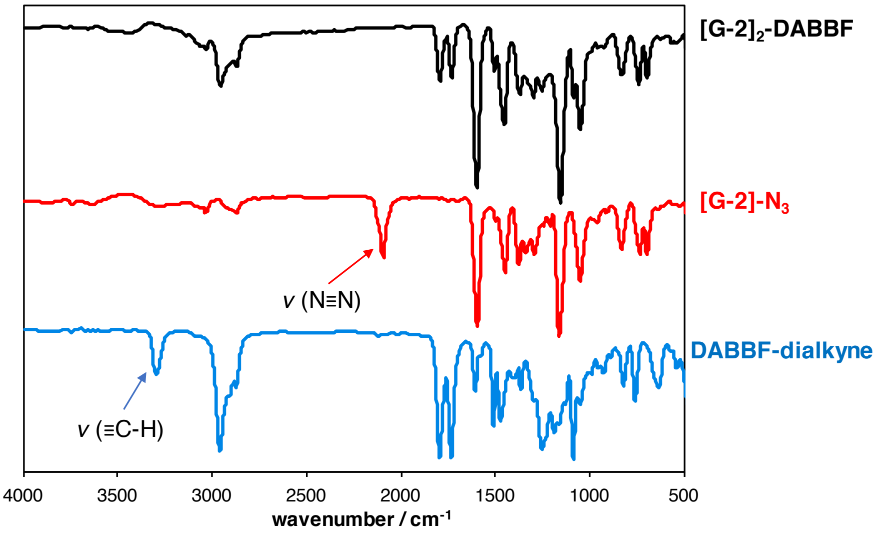


Figure S10. IR spectra of **[G-2]$_2$-DABBF** (black), **[G-2]-N$_3$** (red), and **DABBF-dialkyne** (blue) (KBr).

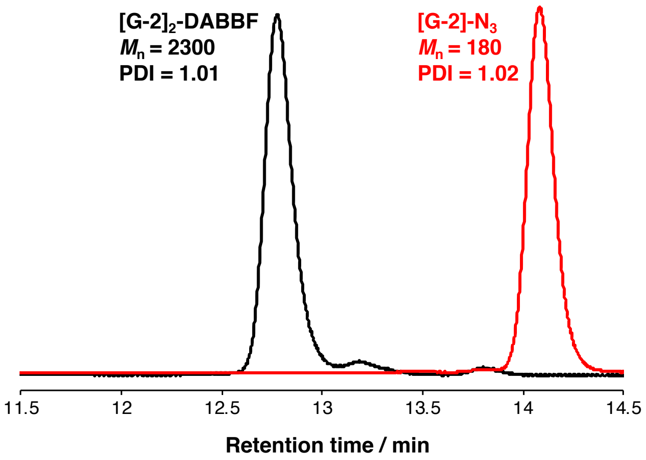


Figure S11. Overlay of GPC traces for **[G-2]$_2$-DABBF** (black) and **[G-2]-N$_3$** (red) (RI).

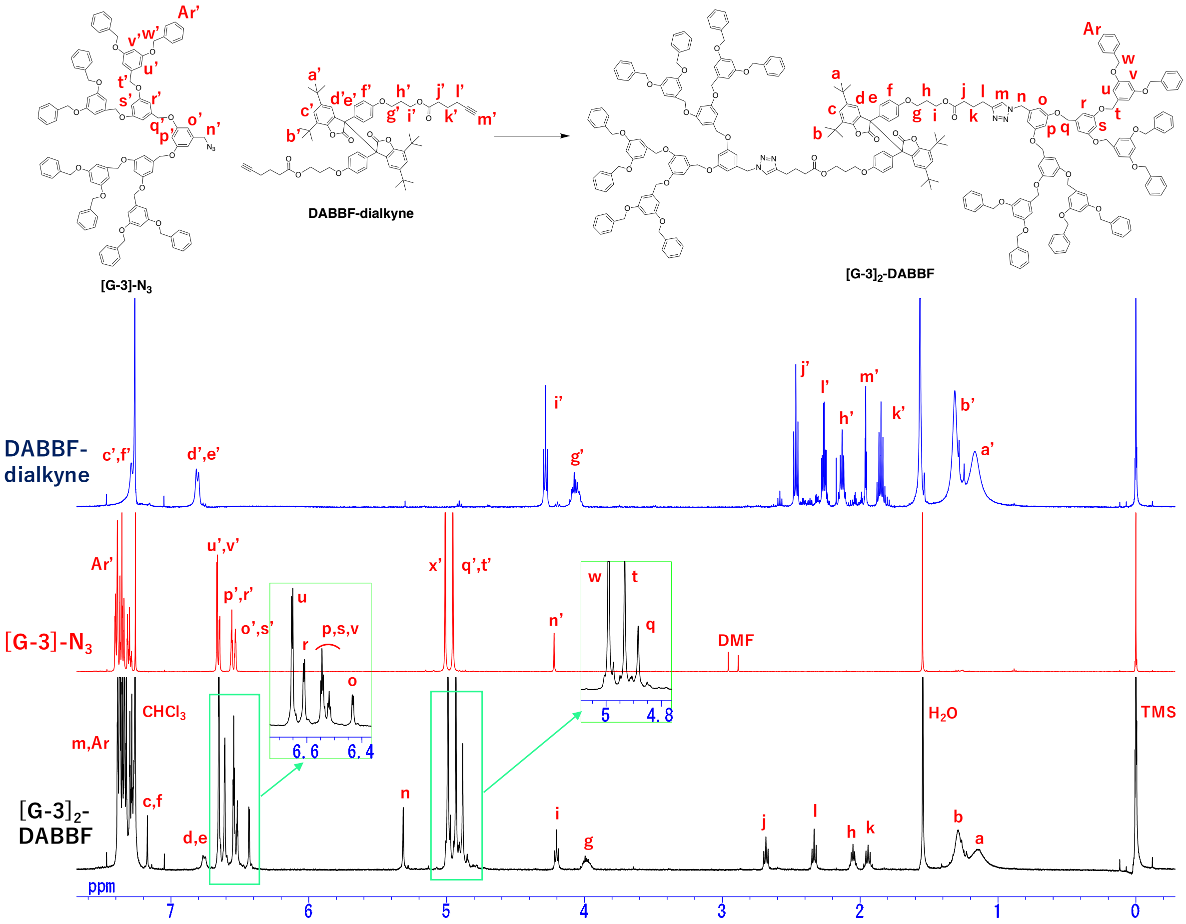


Figure S12. ^{1}H NMR spectra of **[G-3]$_2$-DABBF** (black), **[G-3]-N$_3$** (red), and **DABBF-dialkyne** (blue) (500 MHz, CDCl$_3$).

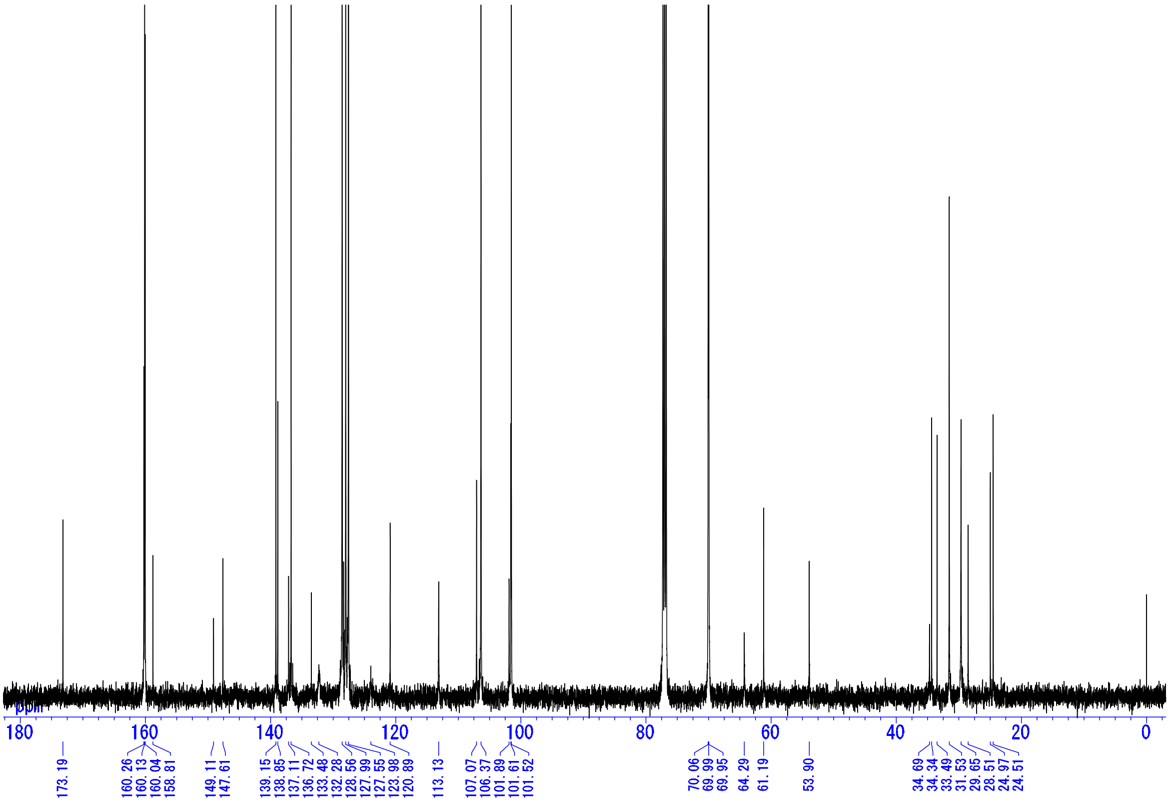


Figure S13. ^{13}C NMR spectrum of **[G-3]$_2$-DABBF** (500 MHz, $CDCl_3$).

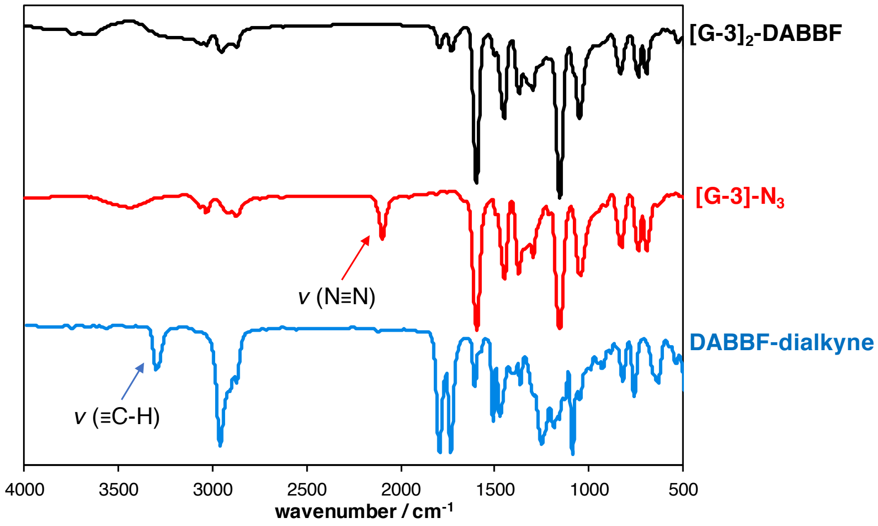


Figure S14. IR spectra of **[G-3]$_2$-DABBF** (black), **[G-3]-N$_3$** (red), and **DABBF-dialkyne** (blue) (KBr).

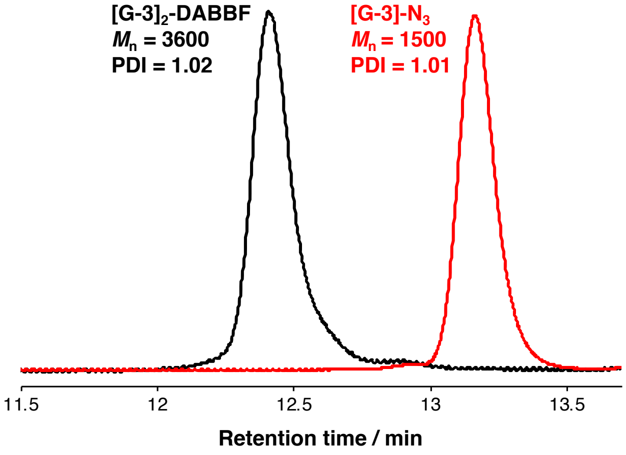


Figure S15. Overlay of GPC traces for **[G-3]$_2$-DABBF** (black) and **[G-3]-N$_3$** (red) (RI).

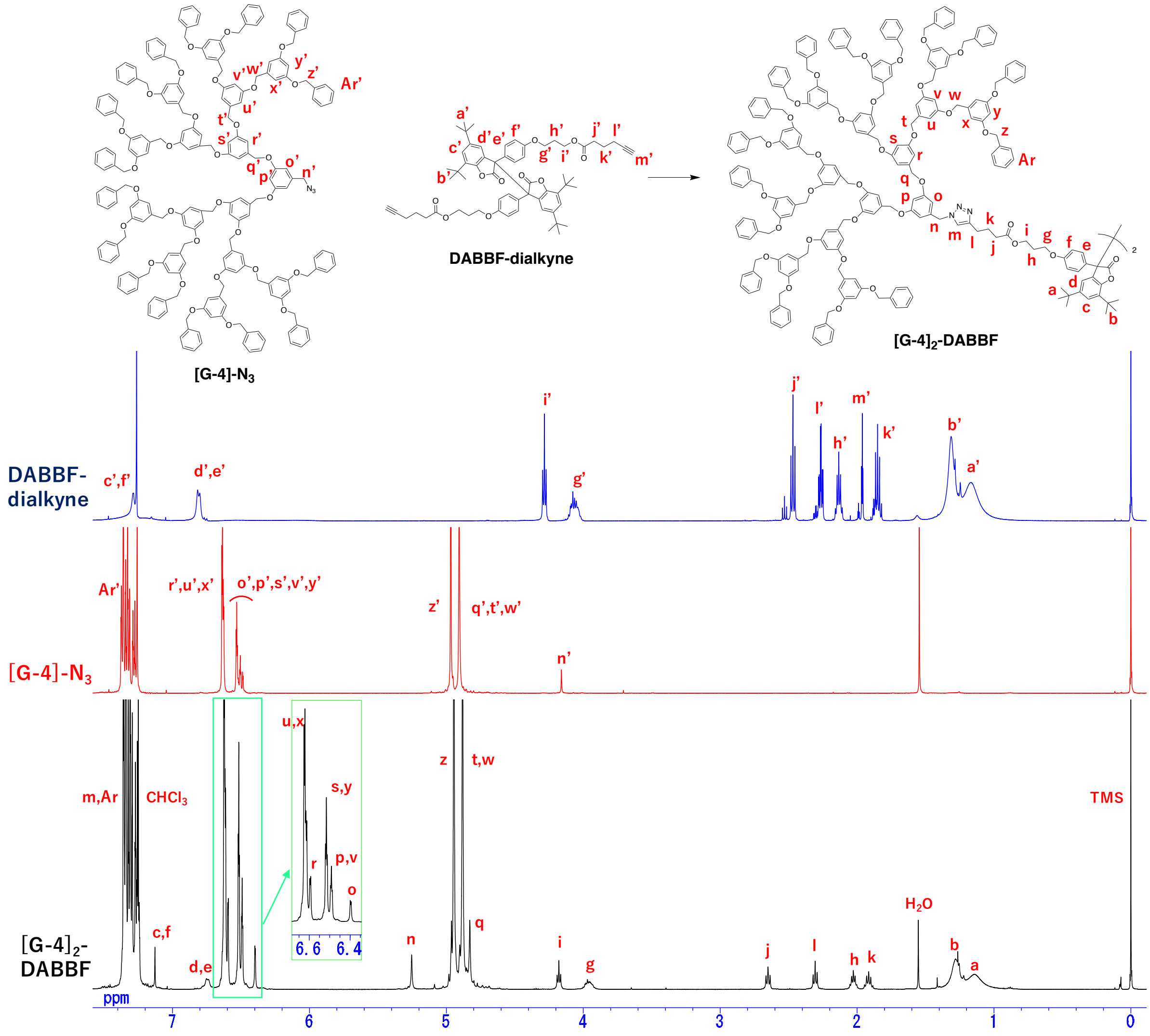


Figure S16. ^{1}H NMR spectra of **[G-4]$_2$-DABBF** (black), **[G-4]-N$_3$** (red), and **DABBF-dialkyne** (blue) (500 MHz, $CDCl_3$).

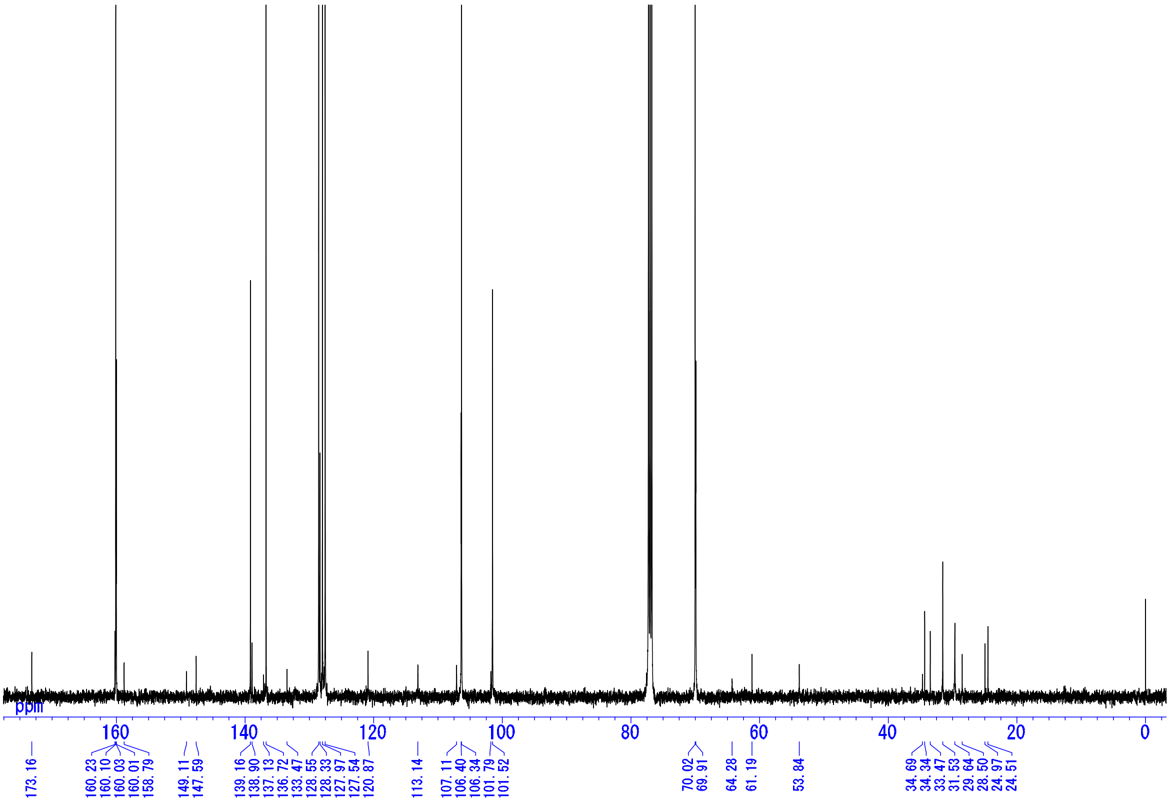


Figure S17. ^{13}C NMR spectrum of **[G-4]$_2$-DABBF** (500 MHz, $CDCl_3$).

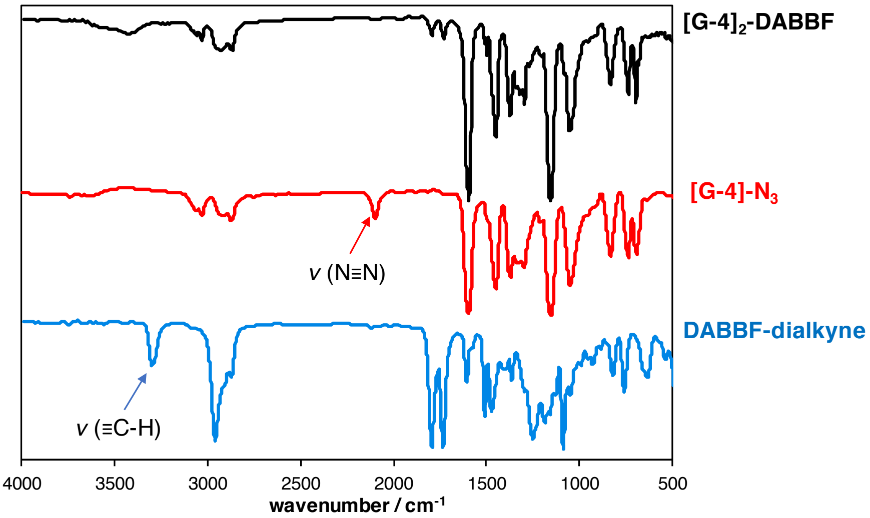


Figure S18. IR spectra of **[G-4]$_2$-DABBF** (black), **[G-4]-N$_3$** (red), and **DABBF-dialkyne** (blue) (KBr).

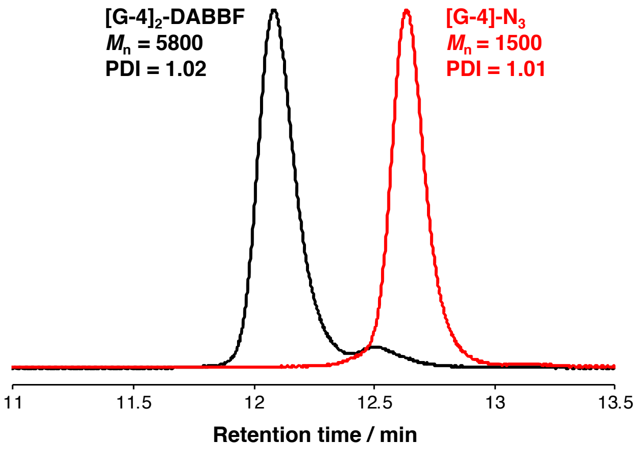


Figure S19. Overlay of GPC traces for **[G-4]$_2$-DABBF** (black) and **[G-4]-N$_3$** (red) (RI).

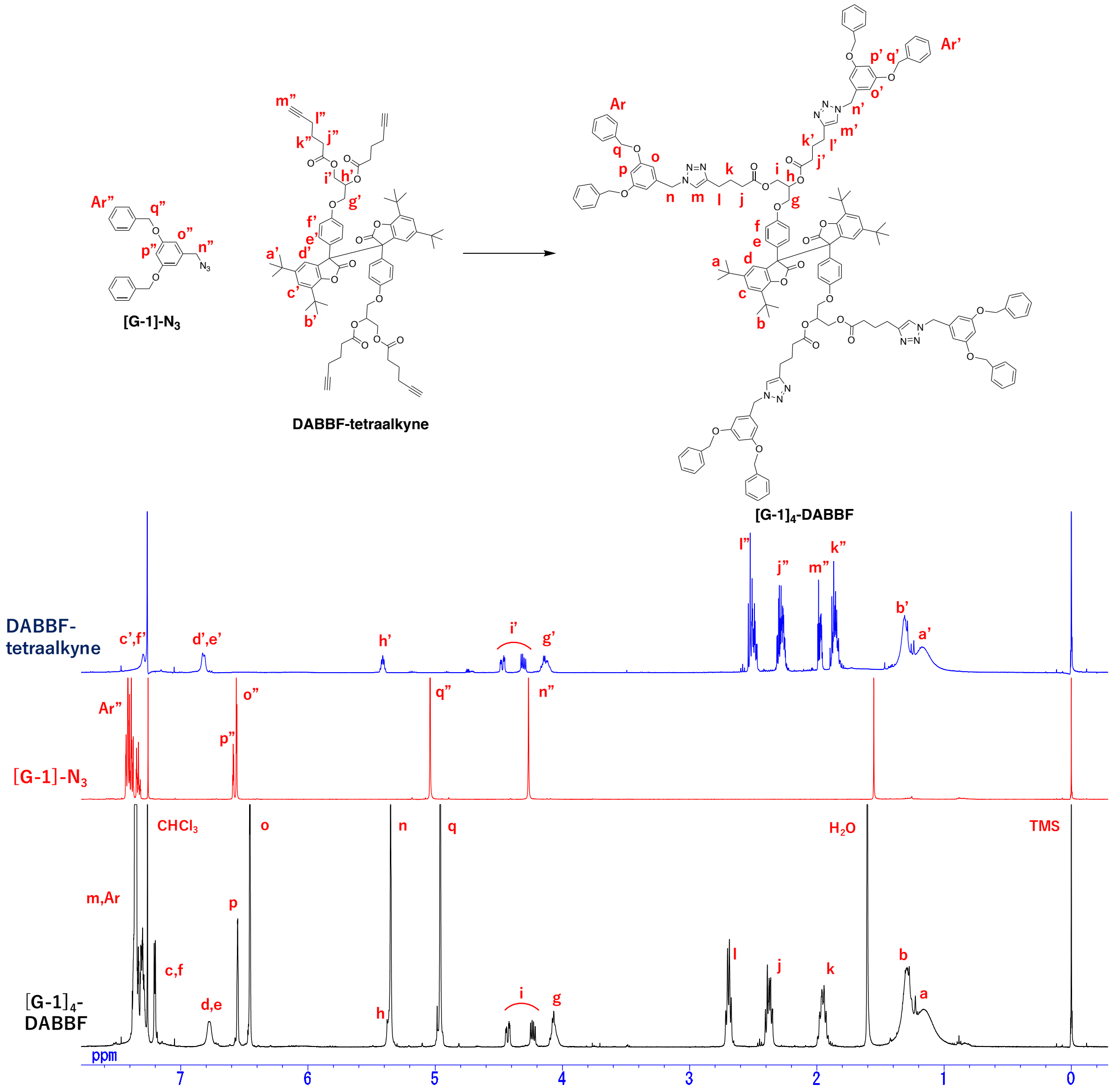


Figure S20. ^{1}H NMR spectra of **[G-1]$_4$-DABBF** (black), **[G-1]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (500 MHz, $CDCl_3$).

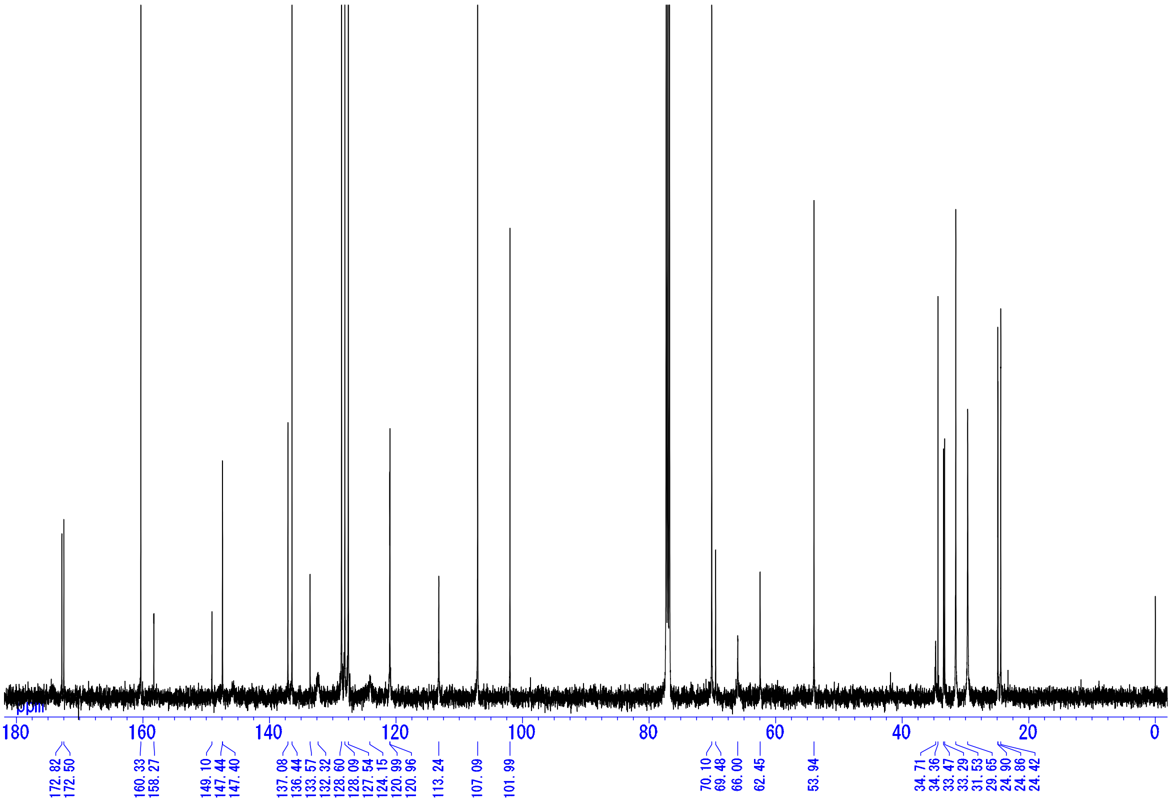


Figure S21. ^{13}C NMR spectrum of **[G-1]$_4$-DABBF** (500 MHz, $CDCl_3$).

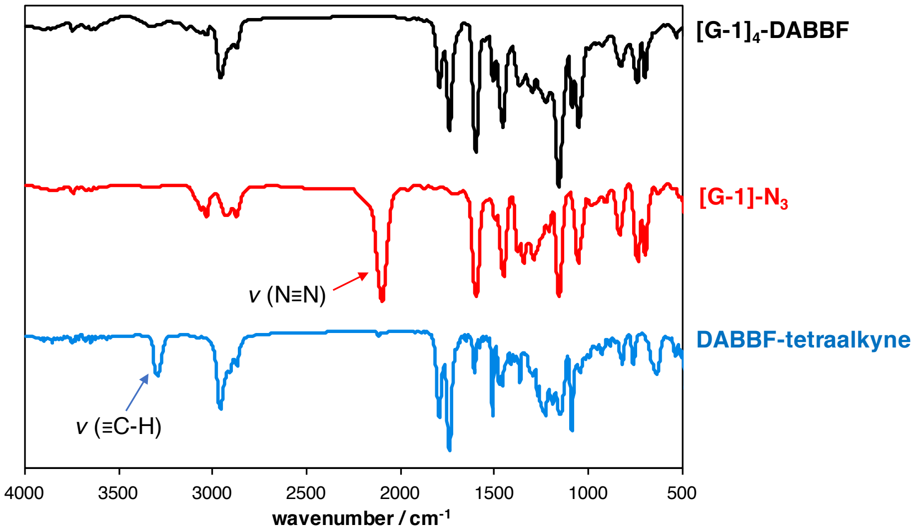


Figure S22. IR spectra of **[G-1]$_4$-DABBF** (black), **[G-1]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (KBr).

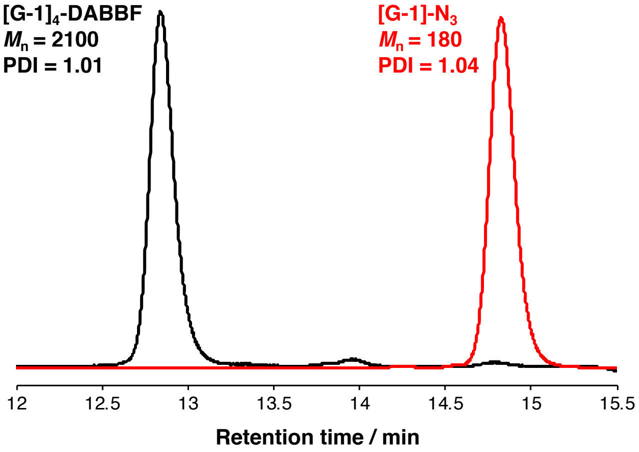


Figure S23. Overlay of GPC traces for **[G-1]$_4$-DABBF** (black) and **[G-1]-N$_3$** (red) (RI).

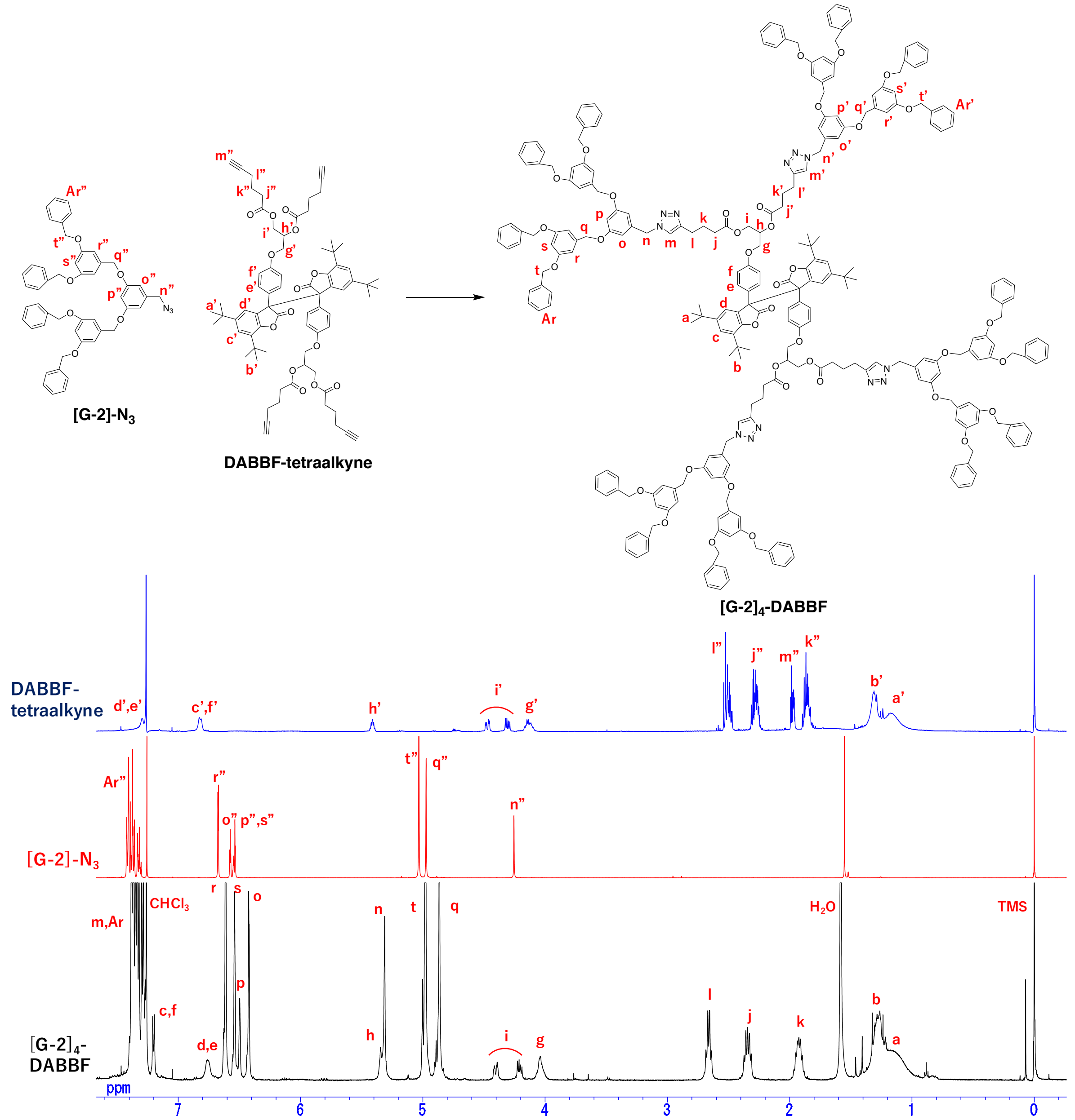


Figure S24. ^{1}H NMR spectra of **[G-2]$_4$-DABBF** (black), **[G-2]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (500 MHz, $CDCl_3$).

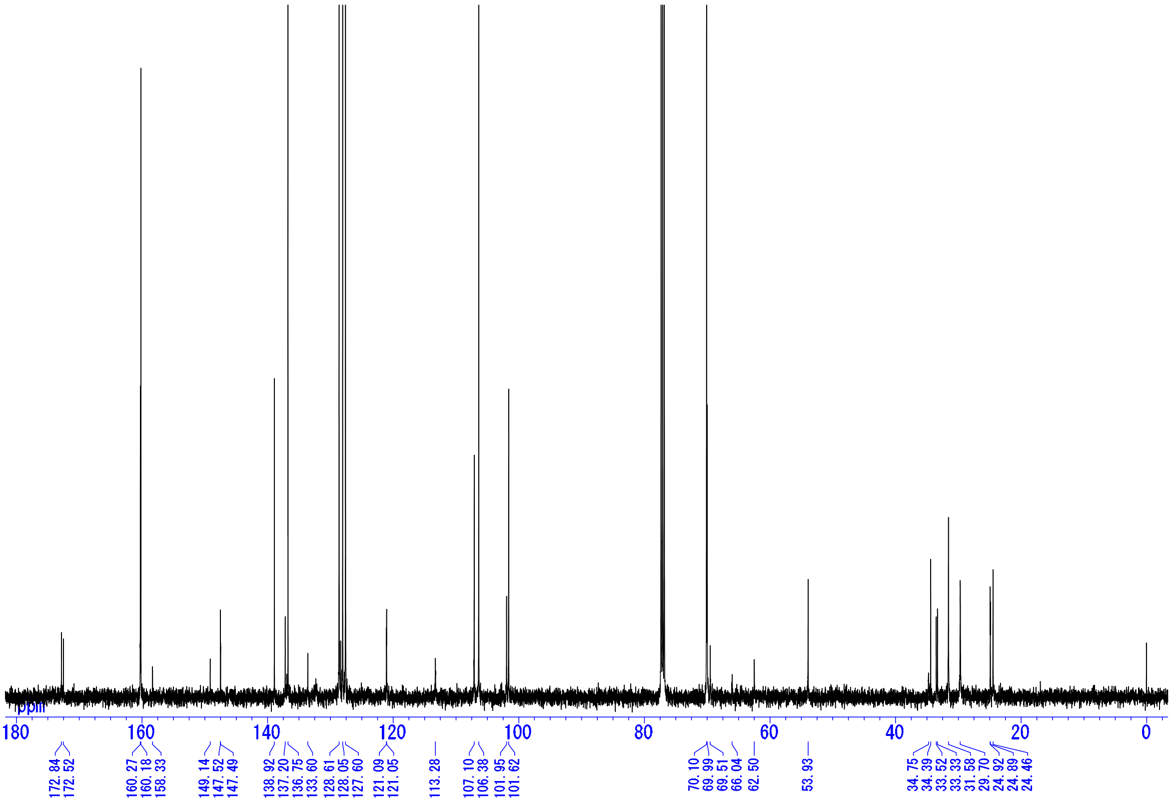


Figure S25. ^{13}C NMR spectrum of **[G-2]$_4$-DABBF** (500 MHz, $CDCl_3$).

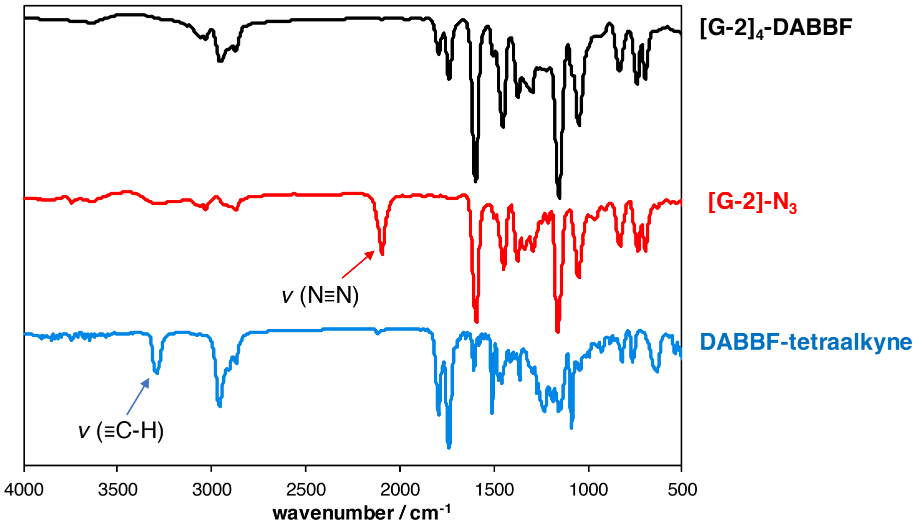


Figure S26. IR spectra of **[G-2]$_4$-DABBF** (black), **[G-2]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (KBr).

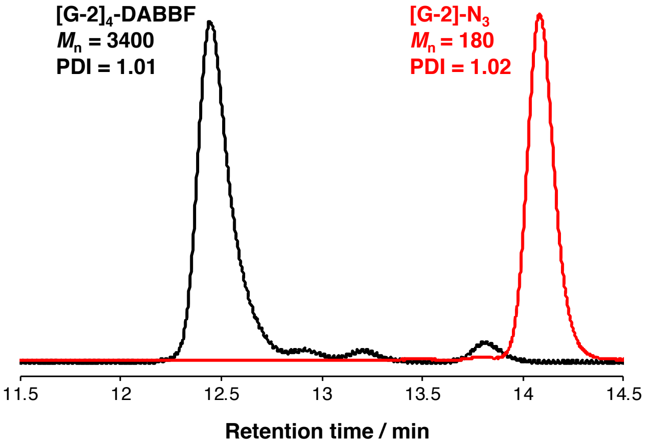


Figure S27. Overlay of GPC traces for **[G-2]$_4$-DABBF** (black) and **[G-2]-N$_3$** (red) (RI).

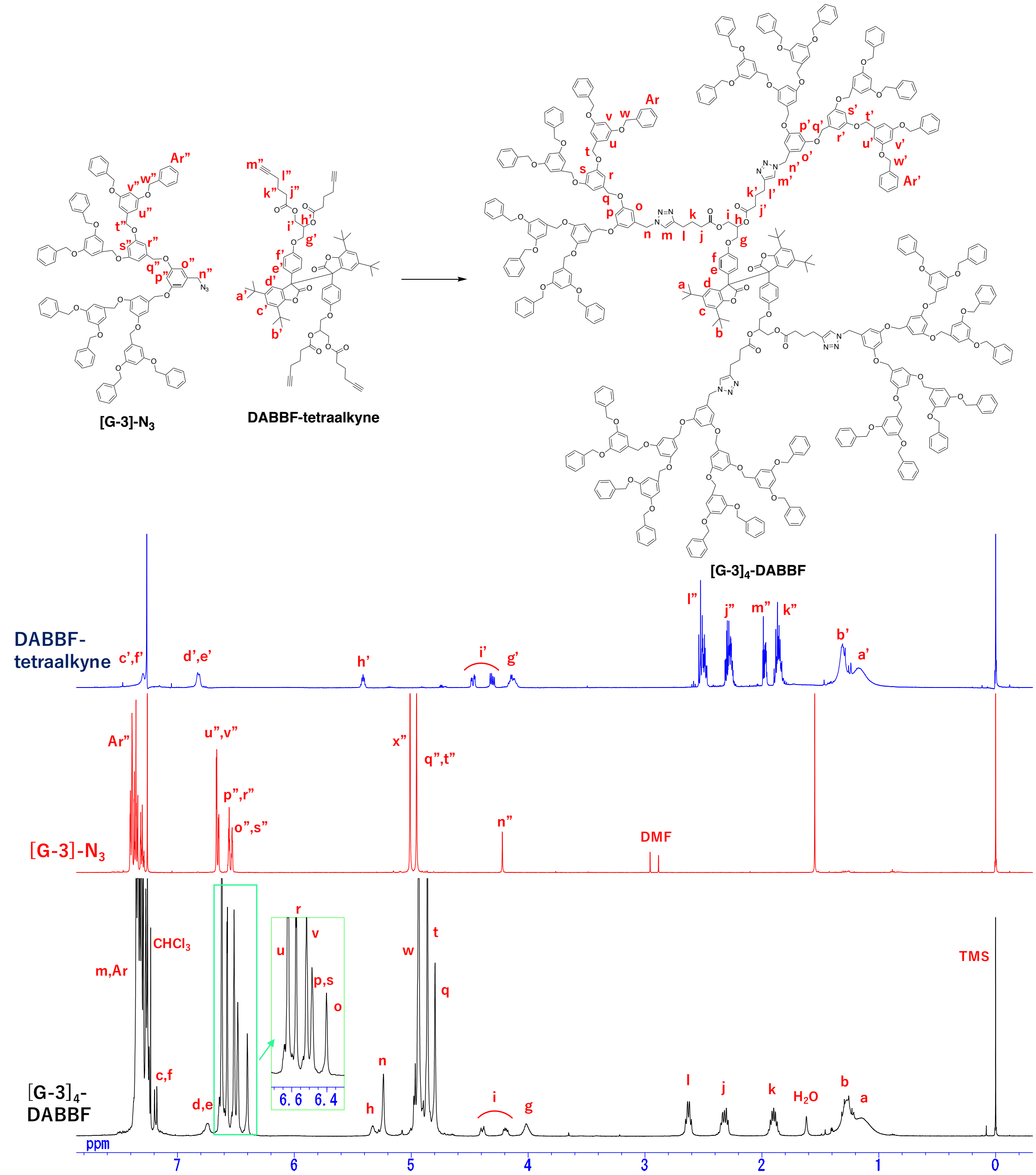


Figure S28. ^{1}H NMR spectra of **[G-3]$_4$-DABBF** (black), **[G-3]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (500 MHz, CDCl$_3$).

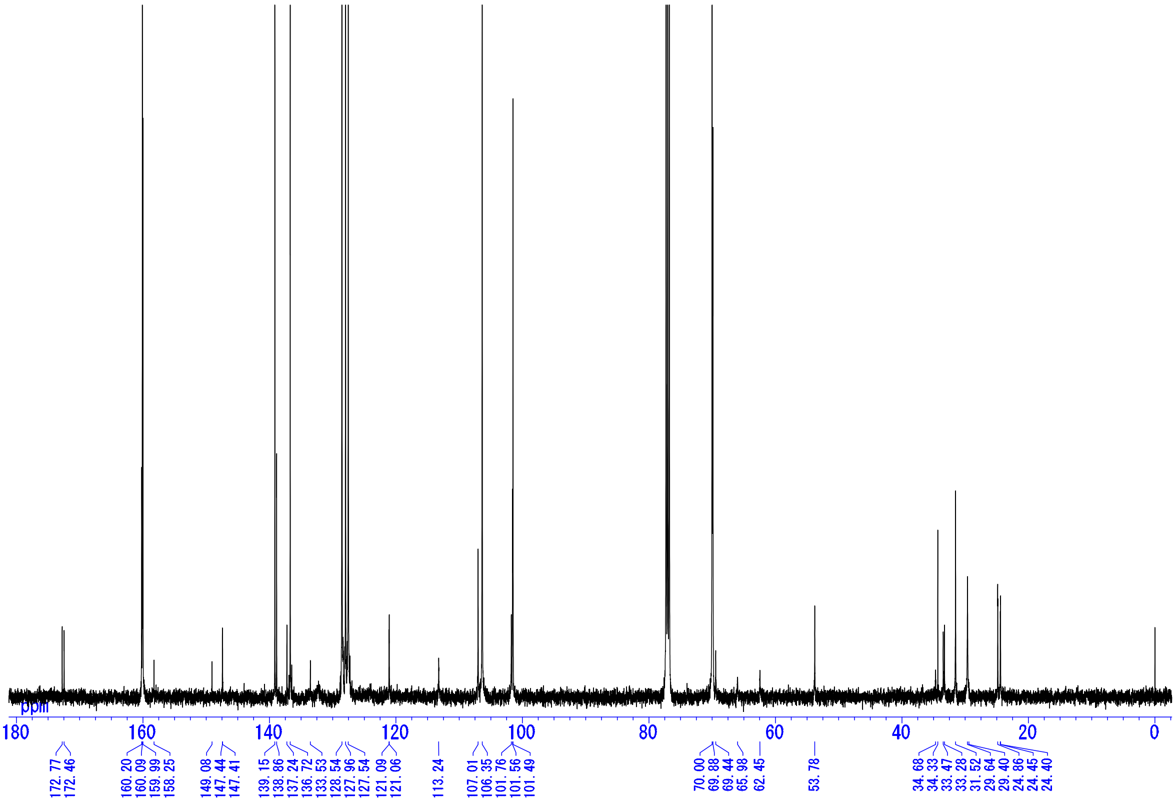


Figure S29. ^{13}C NMR spectrum of **[G-3]$_4$-DABBF** (500 MHz, $CDCl_3$).

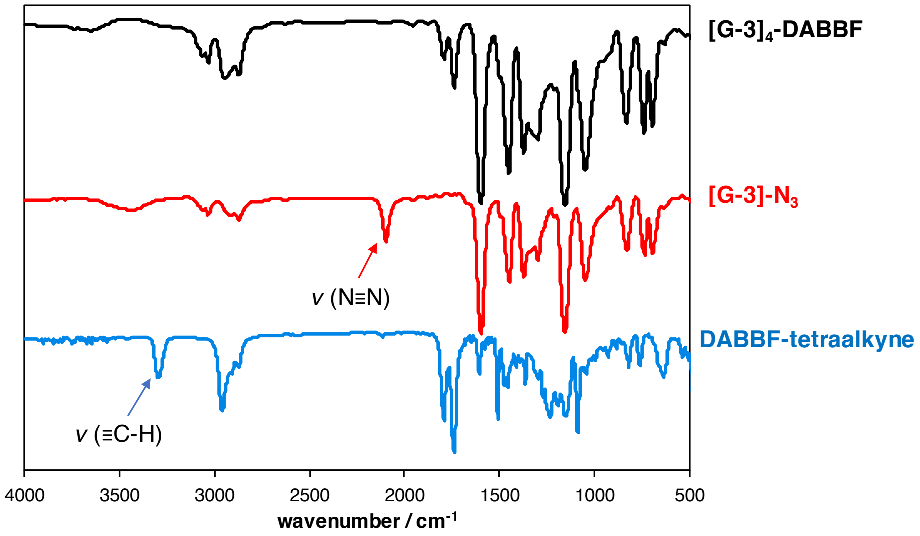


Figure S30. IR spectra of **[G-3]$_4$-DABBF** (black), **[G-3]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (KBr).

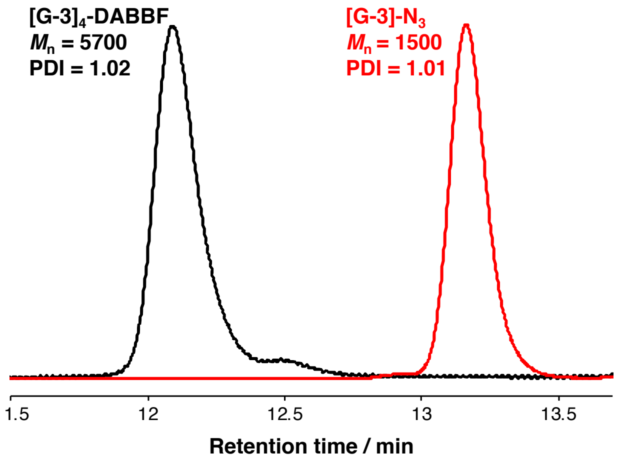


Figure S31. Overlay of GPC traces for **[G-3]$_4$-DABBF** (black) and **[G-3]-N$_3$** (red) (RI).

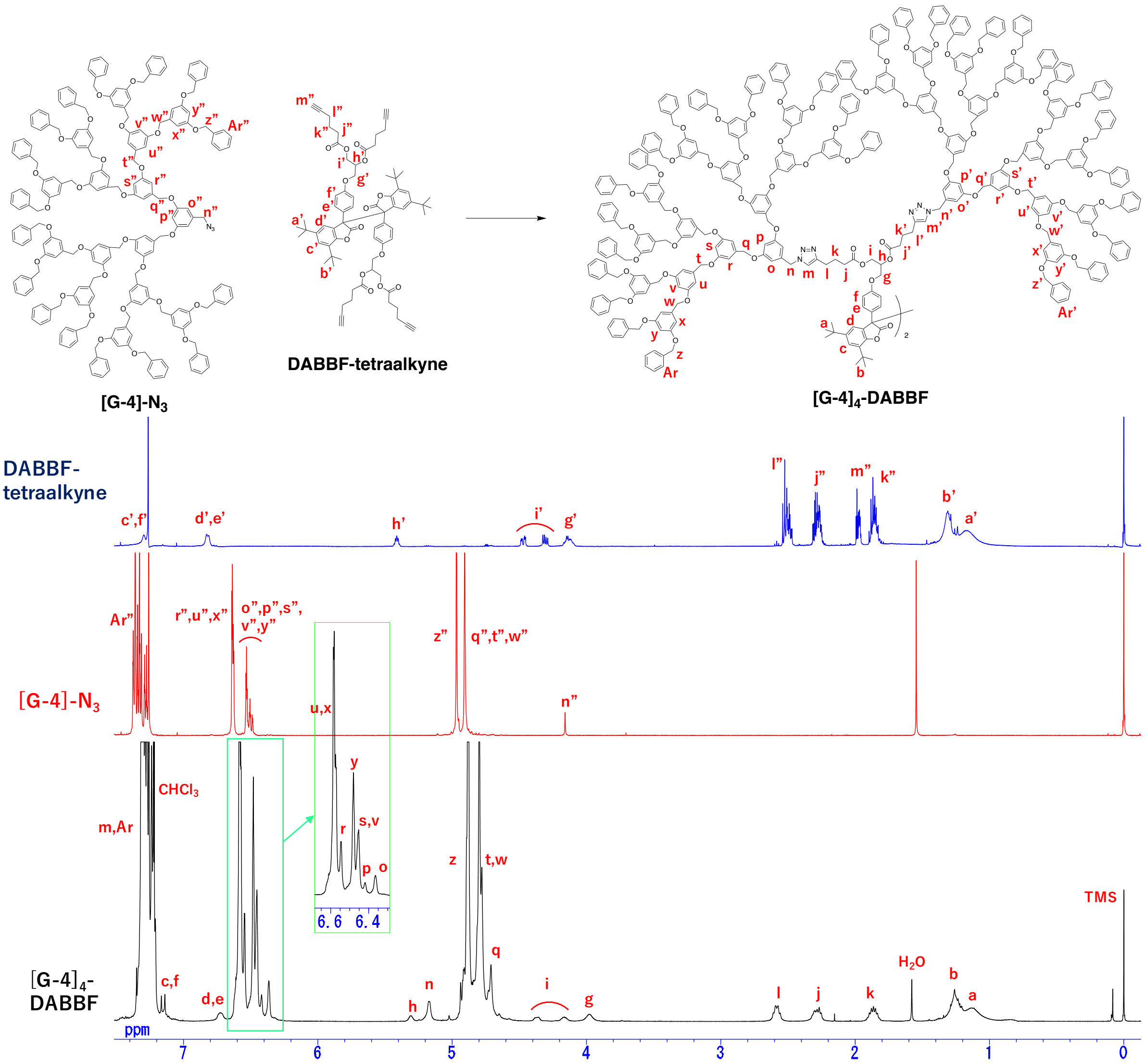


Figure S32. ^{1}H NMR spectra of **[G-4]$_4$-DABBF** (black), **[G-4]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (500 MHz, CDCl$_3$).

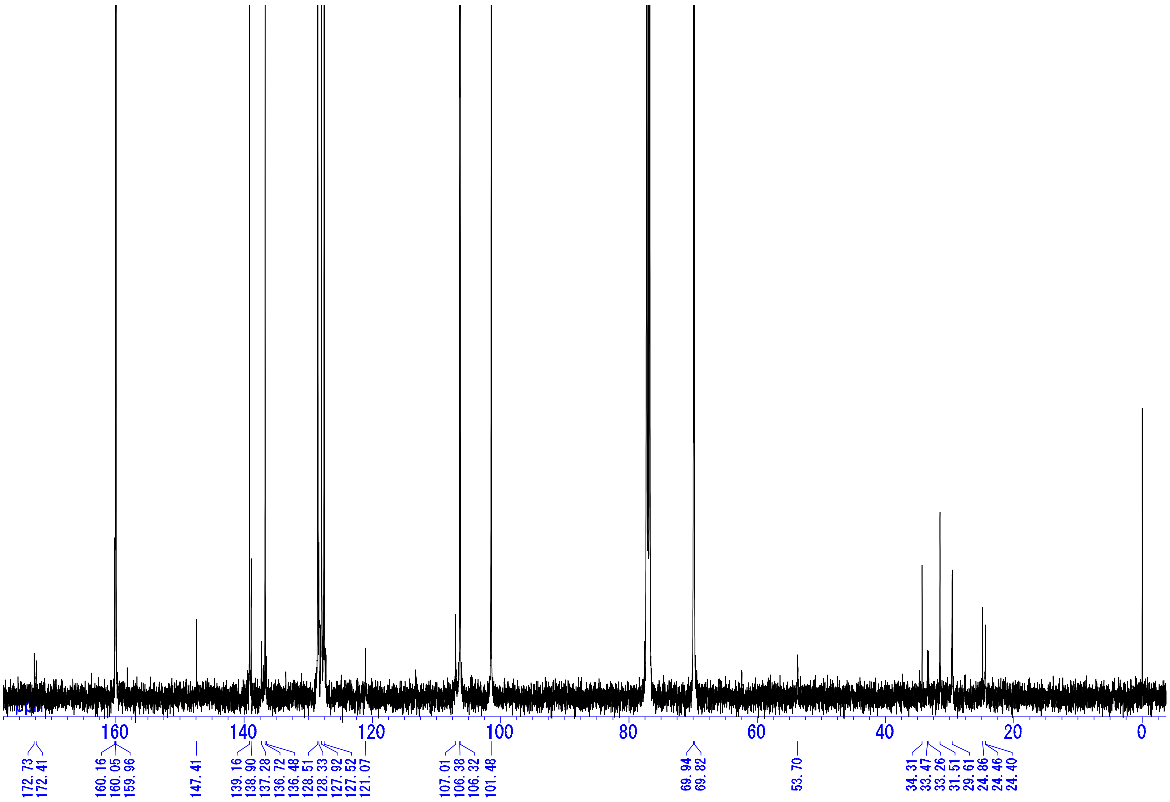


Figure S33. ^{13}C NMR spectrum of **[G-4]₄-DABBF** (500 MHz, CDCl₃).

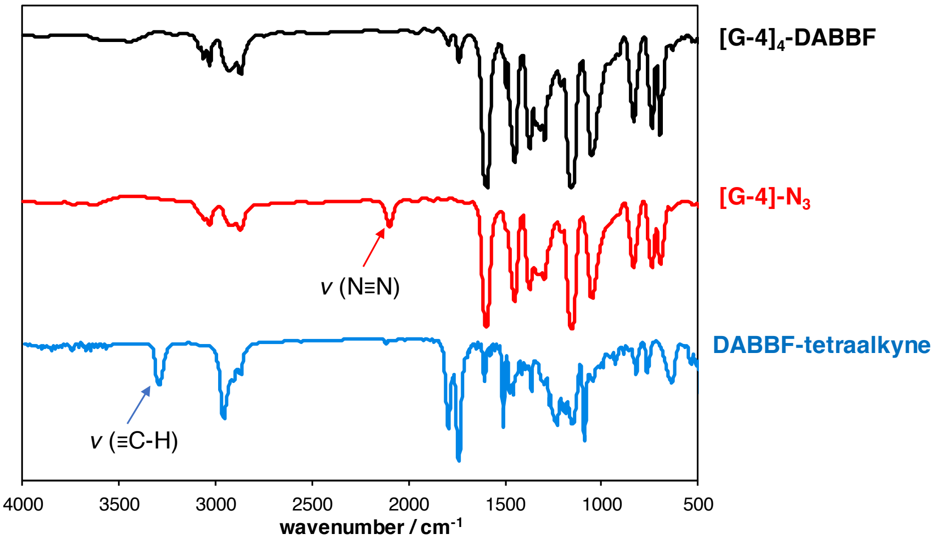


Figure S34. IR spectra of **[G-4]$_4$-DABBF** (black), **[G-4]-N$_3$** (red), and **DABBF-tetraalkyne** (blue) (KBr).

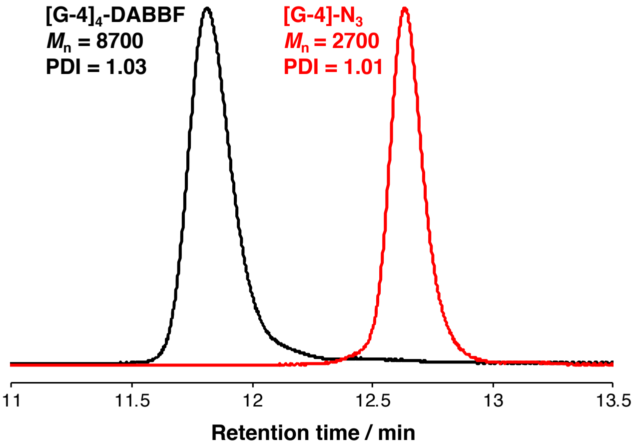


Figure S35. Overlay of GPC traces for **[G-4]$_4$-DABBF** (black) and **[G-4]-N$_3$** (red) (RI).

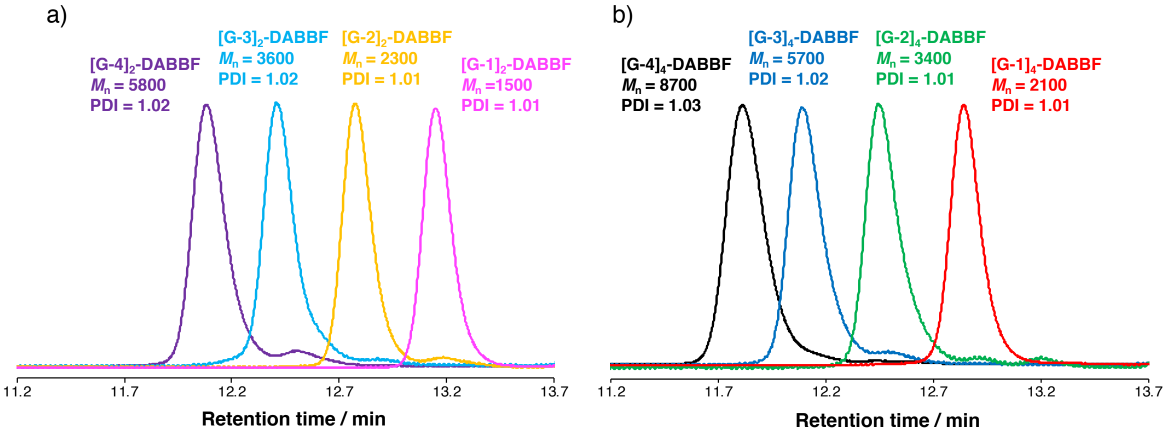


Figure S36. Overlay of GPC traces for (a) **[G-n]$_2$-DABBF**s and (b) **[G-n]$_4$-DABBF**s (RI).

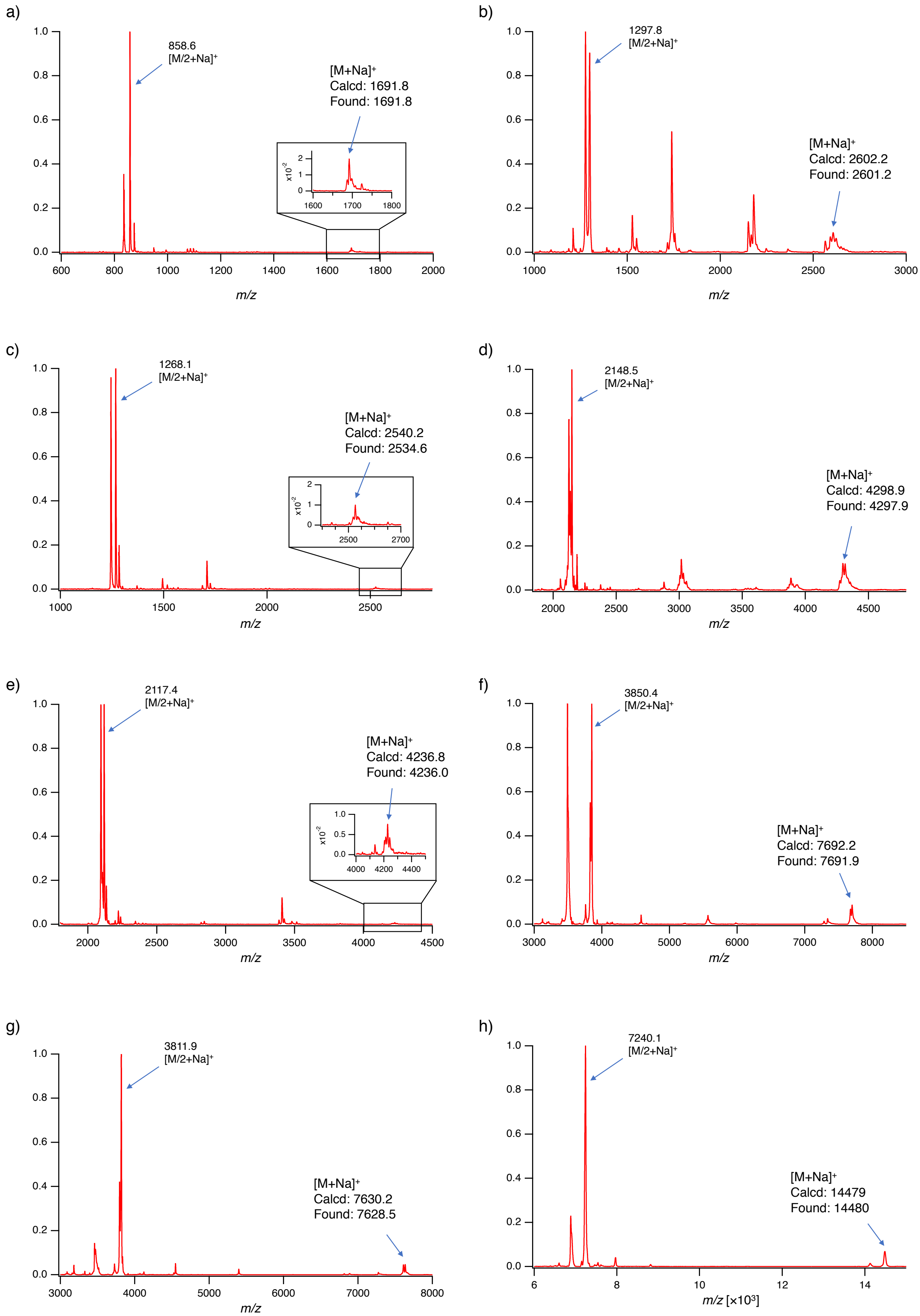


Figure S37. MALDI-TOF-MS spectra of a) **[G-1]$_2$-DABBF**, b) **[G-1]$_4$-DABBF**, c) **[G-2]$_2$-DABBF**, d) **[G-2]$_4$-DABBF**, e) **[G-3]$_2$-DABBF**, f) **[G-3]$_4$-DABBF**, g) **[G-4]$_2$-DABBF**, and h) **[G-4]$_4$-DABBF**.

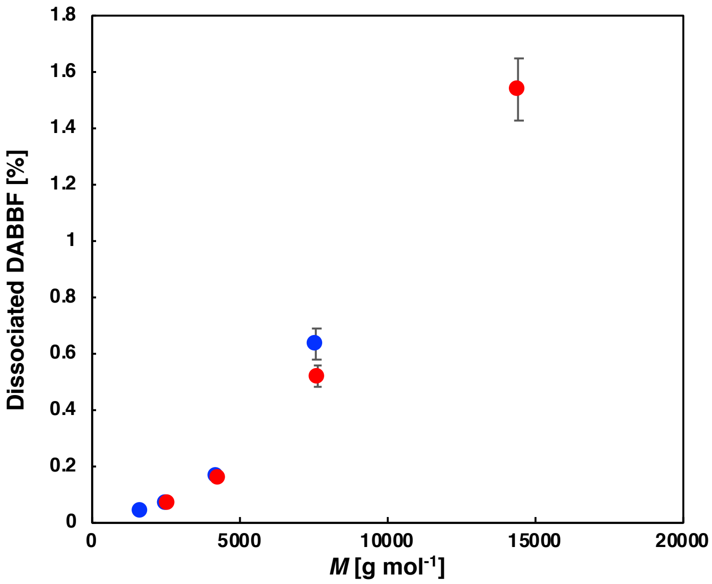


Figure S38. Dissociated DABBF moiety in **[G-n]$_2$-DABBF** (red) and **[G-n]$_4$-DABBF** (blue) as a function of molecular weight.

Table S1. T_g of mechanochromic dendrimers

	T_g [°C]		T_g [°C]
[G-1]$_2$-DABBF	41	**[G-1]$_4$-DABBF**	43
[G-2]$_2$-DABBF	37	**[G-2]$_4$-DABBF**	44
[G-3]$_2$-DABBF	46	**[G-3]$_4$-DABBF**	44
[G-4]$_2$-DABBF	47	**[G-4]$_4$-DABBF**	46

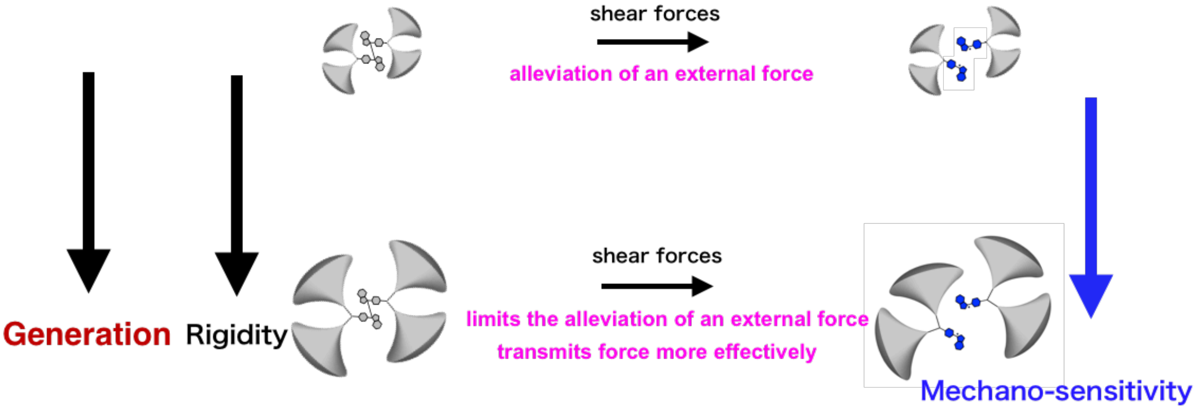


Figure S39. Plausible mechanism of improvement of mechanical sensitivity in higher-generation dendrimers.

SI References

(1) H. Oka, K. Imato, T. Sato, T. Ohishi, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2016**, *5*, 1124–1127.

(2) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

(3) M. Malkoch, K. Schleicher, E. Drockenmuller, C. J. Hawker, T. P. Russell, P. Wu, V. V. Fokin, *Macromolecules* **2005**, *38*, 3663–3678.