Stepwise radial complexation from the outer layer to the inner layer of the dendritic ligand: a phenylazomethine dendrimer with an inverted coordination sequence

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Electronic Supplementary Information

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1. Experimental section

Chemicals. The *para*-substituted phenylazomethine dendrons,[1] dendrimers (**pG*n*A**)[2] and aminophenylferrocenes[3] were synthesized according to a literature method. $GaCl_3$ was purchased from Alfa Aesar, and all other chemicals were purchased from Kanto Kagaku Co., Ltd. or Aldrich, and used without further purification (solvents for the UV-vis titration and electrochemical measurements were of the dehydrated grade.). The silica gel for column chromatography was the neutral grade (Kanto Kagaku Co., Ltd.).

General. The NMR spectra were obtained using a Bruker AVANCE Ⅲ 400 (400MHz), and JEOL JNM-GX400 (400MHz). ^1H NMR and ^{13}C NMR was measured with TMS as the internal standard, and the ^{15}N NMR was measured with CD_3NO_2 as external standard (a capillary with neat CD_3NO_2 was inserted to the NMR tube). The MALDI TOF-MS data were obtained using Shimadzu/ Kratos AXIMA CFR plus in the linear positive ion mode. Dithranol was used as the matrix. The UV-vis spectra were recorded using a Shimadzu UV-3150 spectrometer with a quartz cell having a 1cm optical length at 20ºC. The elemental analysis was performed at the Center for Advanced Materials Analysis, Technical Department, TIT. The electrochemical measurements were done using a conventional three-electrode configuration with an ALS Chi660 electrochemical analyzer. The working, counter and reference electrodes were a glassy carbon ($0.09mm^2$), Pt wire, and Ag/Ag^+, respectively. The solvent was benzonitrile, the concentration of the sample was 0.5mM, the supporting electrolyte was 0.2M tetra-n-butylammonium perchlorate (TBAP), and the scan rate was 0.1V/s. Analytical size-exclusion chromatography (SEC) was performed using an HPLC (Shimadzu, LC-10AP) equipped with a TSK-GEL CMHXL (Tosoh) at 40ºC. Tetrahydrofuran (THF) was used as the eluent at the flow rate of 1 mL/min. The detection line was connected to a triple detector (refractive index, light scattering, and viscosity. Viscotek, TriSEC model 302). A preparative scale gel permeation chromatograph, LC-908 (Japan Analytical Industry Co., Ltd.), was used to isolate each compound with chloroform as the eluent.

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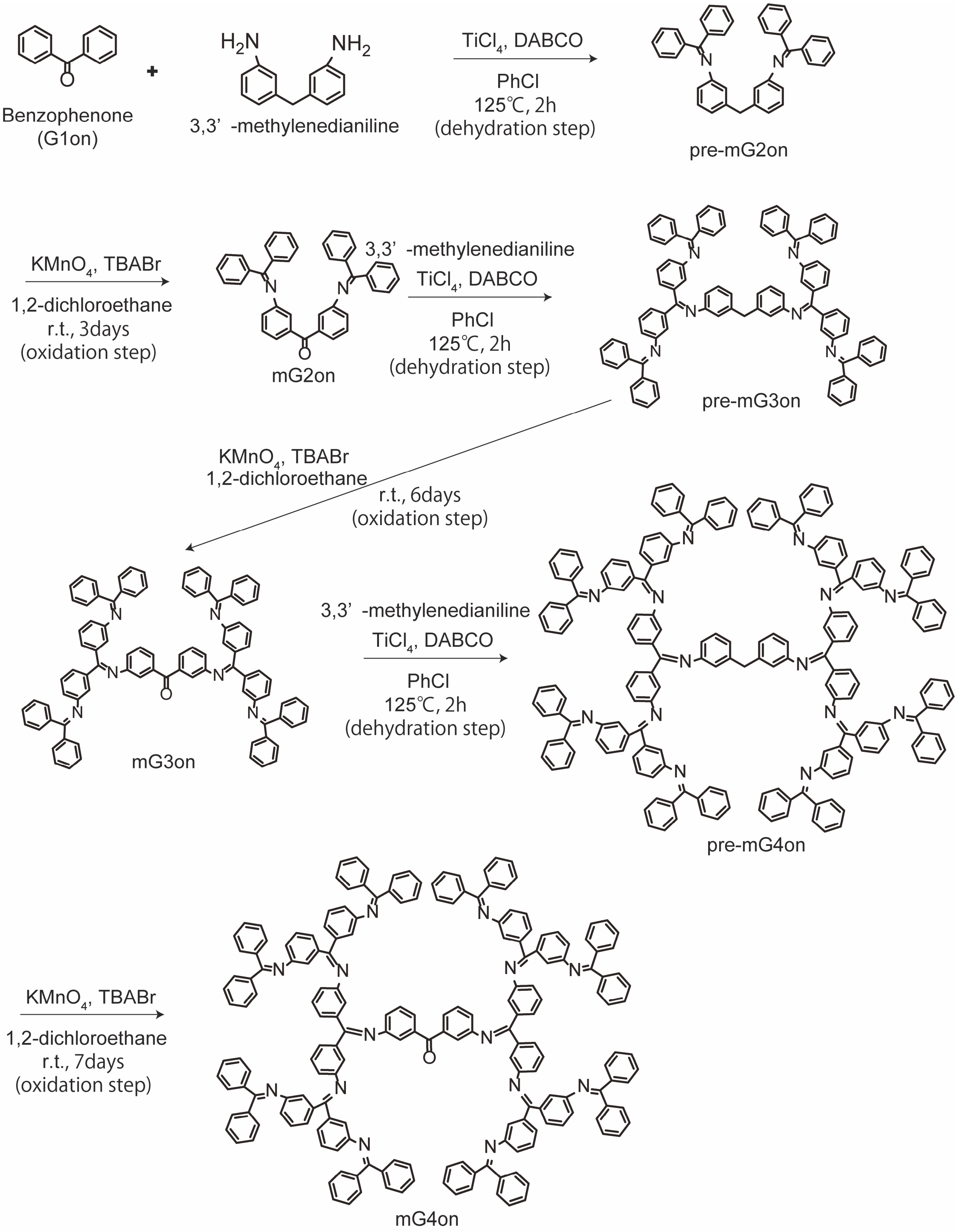
(1) Takanashi, K.; Chiba, H.; Higuchi, M.; Yamamoto, K. *Org. Lett.* **2004**, *6*, 1709.

(2)Yamamoto, K.; Higuchi, M.; Kimoto, A.; Imaoka, T.; Masachika, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 349.

(3) (a) Weinmayr, V. *J. Am. Chem. Soc.* **1955**, *77*, 3012. (b)Ping, H.; Zhao, K.; Xu, H. *Molecules* **2001**, *6*, M250.

2. Synthesis



Scheme S1. Synthesis of *meta*-substituted phenylazomethine dendrons.

Pre-mG2on (general procedure for dehydration reaction with $TiCl_4$)

Benzophenone (3.48 g, 19.1 mmol), 3,3'-methylenedianiline (1.87 g, 9.45 mmol), and 4-diazabicyclo[2.2.2]octane(DABCO) (6.4 g, 57.1 mmol) were dissolved in chlorobenzene (50mL), and heated to 75ºC. $TiCl_4$ (1.56 ml, 14.2 mmol) dissolved in 10ml of chlorobenzene was dropwise added, and the addition funnel was then rinsed with 5ml of chlorobenzene. The mixture was heated to 125 ºC and stirred for 2h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and stirred for 2h in air and then filtered through celite. The filtrate was concentrated and the product was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate = 5: 5: 1 with 2% Et_3N). Yield: 70% (3.49 g, 6.62 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.0 ºC, TMS):

δ= 7.74 (4H, t, *J* = 4.2 Hz), 7.49-7.42 (2H, m), 7.39 (4H, dd, *J* = 11.7, 4.4 Hz), 7.23-7.19 (6H, m), 7.03-7.00 (6H, m), 6.52 (4H, t, *J* = 7.8 Hz), 6.40 (2H, s), 3.65 (2H, s).

^{13}C NMR (100 MHz, $CDCl_3$, 22.5 ºC, TMS):

δ = 168.00, 151.19, 141.16, 139.53, 136.08, 130.57, 129.3, 129.16, 128.35, 128.33, 128.08, 127.77, 123.69, 121.48, 118.36, 41.54.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 527.24($[M+H]^+$), Found: 527.33.

Anal. Calcd. for $C_{39}H_{30}N_2$: C, 88.94; H, 5.74; N, 5.32. Found: C,89.14; H, 5.72; N, 5.19.

mG2on (general procedure for oxidation reaction with $KMnO_4$)

Pre-mG2 (2.84 g, 5.39 mmol), and TBABr (5.2 g, 15.8 mmol) were dissolved in 1,2-dichloroethane (40ml). $KMnO_4$ (2.54 g, 16.0 mmol) was then added to the solution and stirred for 72h at room temperature. The reaction was quenched with aqueous sodium bisulfite. The organic layer was washed with water and brine, then dried over sodium sulfite and concentrated. The product (**mG2)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 10: 5: 1 with 2% Et_3N). Yield: 88% (2.58g, 4.77 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.2ºC, TMS):

δ= 7.74 (4H, d, *J* = 7.8 Hz), 7.48 (2H, t, *J* = 7.3 Hz), 7.41 (4H, t, *J* = 7.3 Hz), 7.25 (6H, d, *J* = 3.4 Hz), 7.19 (2H, t, *J* = 7.8 Hz), 7.14-7.09 (6H, m), 7.03 (2H, s), 6.91 (2H, d, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, 22.3ºC, TMS):

δ=196.03, 169.1, 151.11, 139.18, 137.8, 135.66, 130.91, 129.36, 129.29, 128.67, 128.39, 128.18, 128.01, 124.71, 124.67, 122.11

MALDI TOF-MS (Matrix: Dithranol): Calcd: 541.22($[M+H]^+$), Found: 541.39.

Anal. Calcd. for $C_{39}H_{28}N_2O$: C, 86.64; H, 5.22; N, 5.18. Found: C, 86.31; H, 4.98; N, 5.22.

Pre-mG3on

As per the general procedure for the dehydration reaction, the **mG2on** (432 mg, 0.79 mmol), 3,3'-methylenedianiline (78 mg, 0.39 mmol) and DABCO (466 mg, 4.15mmol) were dissolved in chlorobenzene (30mL). $TiCl_4$ (64 μl, 0.58 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**pre-mG4on)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 3: 3: 1 with 2% Et_3N). Yield: 97% (470 g, 0.38 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 23.2 ºC, TMS):

δ = 7.79-7.58 (8H, m), 7.48-7.28 (14H, m), 7.28-7.18 (6H, m), 7.18-7.07 (8H, m), 7.06-6.97 (4H, m), 6.96-6.81 (10H, m), 6.81-6.70 (2H, m), 6.62-6.53 (2H, m), 6.53-6.32 (8H, m), 6.17 (2H, m), 3.66 (2H, s).

^{13}C NMR (100 MHz, $CDCl_3$, 24.3 ºC, TMS):

δ = 168.76, 168.63, 167.63, 151.16, 151.01, 150.98, 141.13, 139.7, 139.44, 139.27, 136.57, 135.93, 135.74, 130.82, 130.75, 129.39, 129.32, 129.27, 128.53, 128.48, 128.34, 128.28, 128.15, 127.98, 127.91, 124.04, 123.68, 123.59, 122.99, 122.52, 121.88, 121.54, 120.32, 117.98, 41.61

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1243.53($[M+H]^+$), Found: 1243.67.

Anal. Calcd. for $C_{91}H_{66}N_6$: C, 87.89; H, 5.35; N, 6.76. Found: C, 87.89; H, 5.19; N, 6.72.

mG3on

As per the general procedure for oxidation reaction, **pre-mG3on** (470 mg, 0.38 mmol) , and TBABr (1934 mg, 6.0 mmol) were dissolved in 1,2-dichloroethane (20ml). $KMnO_4$ (1010 mg, 6.4 mmol) was then added and stirred for 6 days. The product (**mG3on)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 5: 5: 1 with 2% Et_3N). Yield: 70% (345 mg, 0.27 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.7 ºC, TMS):

δ = 7.74 (4H, d, *J* = 6.8 Hz), 7.68 (4H, d, *J* = 7.3 Hz), 7.48-7.30 (14H, m), 7.24 (6H, t, *J* = 5.6 Hz), 7.19-7.12 (12H, m), 7.07 (2H, s), 7.03 (4H, dd, *J* = 6.8, 2.4 Hz), 6.95-6.88 (8H, m), 6.80 (2H, dd, *J* = 7.8, 1.0 Hz), 6.64 (2H, d, *J* = 7.8 Hz), 6.50-6.42 (6H, m).

^{13}C NMR (100 MHz, $CDCl_3$, 22.8 ºC, TMS):

δ = 195.95, 180.06, 168.81, 168.64, 168.59, 151.09, 151.01, 150.96, 139.29, 139.22, 139.08, 137.69, 136.11, 135.8, 135.58, 130.81, 130.75, 129.3, 129.21, 129.16, 128.55, 128.47, 128.3, 128.11, 127.94, 127.89, 124.76, 124.36, 123.91, 123.59, 123.31, 122.55, 122.35, 121.42, 120.58

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1257.51($[M+H]^+$), Found: 1257.64.

Anal. Calcd. for $C_{91}H_{64}N_6O$: C, 86.91; H, 5.13; N, 6.68. Found: C, 86.55; H, 5.01; N, 6.63.

pre-mG4on

As per the general procedure for the dehydration reaction, the **mG3on** (6.08 g, 4.84 mmol), 3,3’-methylenedianiline (0.439g, 2.21 mmol) and DABCO (2.56 g, 22.8 mmol) were dissolved in chlorobenzene (50mL). $TiCl_4$ (0.536 ml, 4.90 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**pre-mG4on)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 3: 3: 1 with 2% Et_3N). Yield: 76% (4.50 g, 1.68 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.6 ºC, TMS):

δ = 7.84-7.56 (16H, m), 7.54-7.26 (26H, m), 7.26-6.96 (44H, m), 6.96-6.65 (26H, m), 6.64-6.34 (16H, m), 6.34-6.28 (2H, m), 6.28-6.19 (2H, m), 6.19-6.00 (4H, m), 3.61 (2H, s).

^{13}C NMR (100 MHz, $CDCl_3$, 22.4 ºC, TMS):

δ = 168.88, 168.83, 168.72, 168.7, 168.24, 167.55, 151.16, 151.13, 151.03, 150.87, 141.22, 139.65, 139.48, 139.42, 139.29, 139.18, 136.54, 136.48, 136.05, 135.92, 135.78, 135.75, 130.91, 130.84, 129.38, 129.33, 129.26, 128.58, 128.54, 128.35, 128.25, 128.21, 128.04, 124.02, 123.73, 123.23, 123.15, 122.74, 122.65, 122.57, 122.14, 121.8, 121.49, 121.19, 120.93, 120.33, 120.22, 118.14, 41.73.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2678.13($[M+H]^+$), Found: 2677.50.

Anal. Calcd. for $C_{195}H_{138}N_{14}$: C, 87.48; H, 5.20; N, 7.32. Found: C, 87.13; H, 4.98; N, 7.30.

mG4on

As per the general procedure for oxidation reaction, **pre-mG4on** (3.71 g, 1.38 mmol）, and TBABr (7.73 g, 24.0 mmol) were dissolved in 1,2-dichloroethane (120ml). $KMnO_4$ (3.80 g, 24.0 mmol) was then added and stirred for 1 week. Same amount of TBABr and $KMnO_4$ was added and stirred for 4days. The product (**mG4on)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 3: 3: 1 with 2% Et_3N) and purified by preparative scale GPC (eluent: chloroform). Yield: 73% (2.71 g, 1.01 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.5 ºC, TMS):

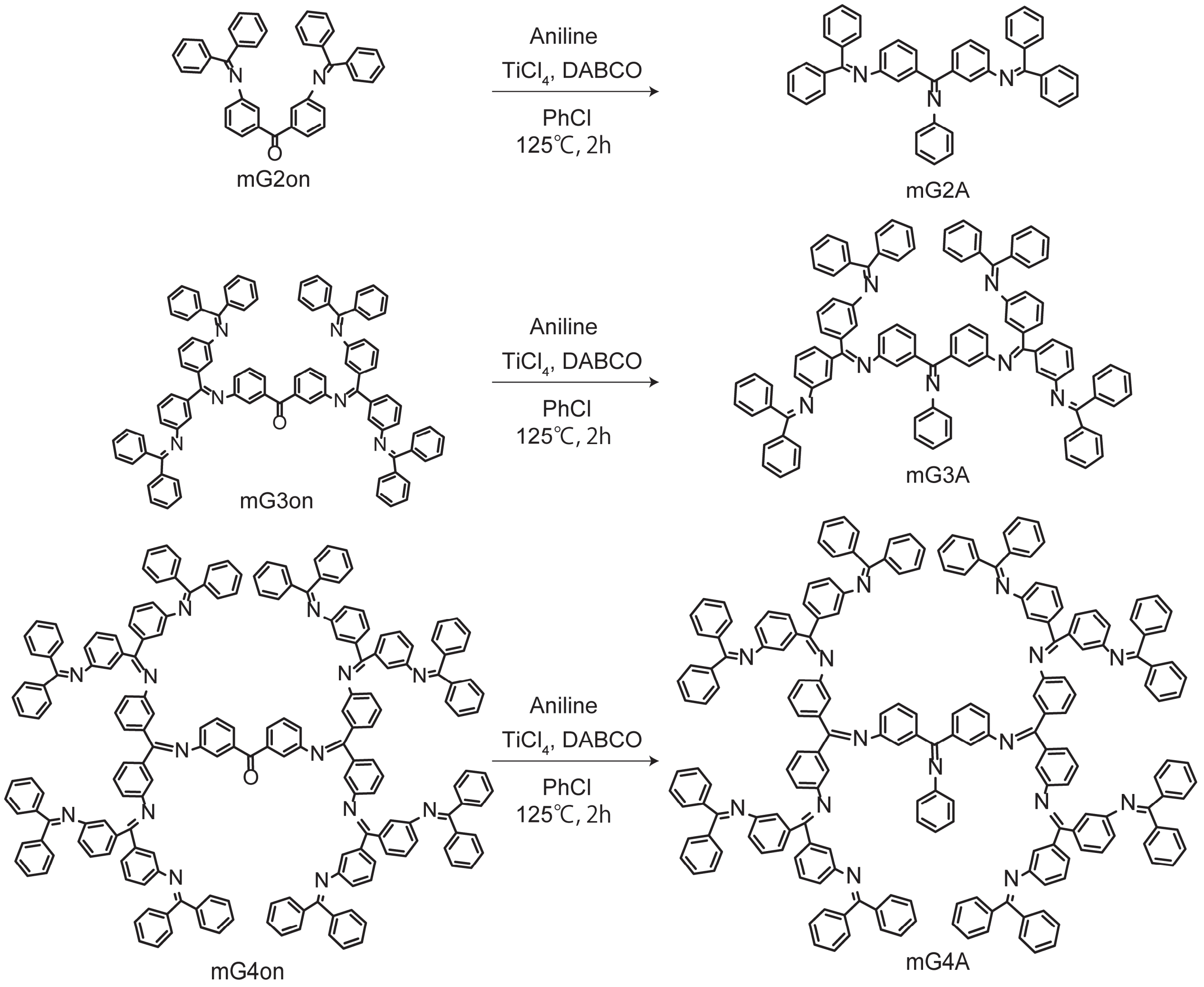
δ = 7.80-7.64 (16H, m), 7.53-7.29 (28H, m), 7.27-6.96 (48H, m), 6.95-6.70 (22H, m), 6.64-6.56 (2H, m), 6.54-6.41 (12H, m), 6.37 (2H, m), 6.29 (2H, s), 6.17 (4H, m).

^{13}C NMR (100 MHz, $CDCl_3$, 22.6 ºC, TMS):

δ = 196.18, 168.83, 168.81, 168.65, 168.61, 168.3, 168.29, 151.11, 151.03, 150.96, 139.37, 139.29, 139.17, 139.05, 137.77, 136.36, 136.05, 135.91, 135.83, 135.69, 135.66, 130.85, 130.74, 129.33, 129.3, 129.25, 129.13, 128.58, 128.53, 128.5, 128.47, 128.36, 128.29, 128.17, 128.14, 127.96, 124.92, 124.35, 123.9, 123.76, 123.62, 123.56, 123.2, 123.12, 122.84, 122.75, 122.66, 122.6, 122.51, 121.6, 121.37, 121.03, 120.93, 120.45, 120.28

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2692.11 ($[M+H]^+$), Found: 2691.61.

Anal. Calcd. for $C_{195}H_{136}N_{14}O$: C, 87.03; H, 5.09; N, 7.29. Found: C, 86.86; H, 5.13; N, 7.23.



Schem S2. Synthesis of *meta*-substituted phenylazomethine dendrimers.

mG2A

As per the general procedure for the dehydration reaction, the **mG2on** (352 mg, 0.65 mmol), aniline (0.089 ml, 0.97 mmol) and DABCO (0.59 g, 5.26 mmol) were dissolved in chlorobenzene (25mL). $TiCl_4$ (0.14 ml, 1.29 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**mG2A)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 5: 5: 1 with 2% Et_3N). Yield: 54% (218 mg, 0.353 mmol).

^1H NMR (400 MHz, $CDCl_3$, 21.5 ºC, TMS),

δ= 7.75 (2H, m), 7.70 (3H, d, J = 17.6 Hz), 7.51-7.43 (2H, m), 7.43-7.32 (5H, m), 7.29-7.23 (3H, m), 7.23-7.19 (3H, m), 7.19-7.08 (3H, m), 7.08-7.02 (2H, m), 6.97-6.85 (5H, m), 6.81 (1H, m), 6.56 (2H, m), 6.51-6.38 (3H, m).

^{13}C NMR (100 MHz, $CDCl_3$, 22.3 ºC, TMS):

δ= 168.9, 168.7, 167.82, 151.16, 151.09, 151.04, 139.66, 139.45, 139.23, 136.64, 135.99, 135.77, 130.88, 130.78, 129.41, 129.29, 128.54, 128.48, 128.34, 128.2, 128.17, 128.14, 128, 127.92, 124.01, 123.63, 123.15, 122.93, 122.56, 121.73, 120.89, 120.35

MALDI TOF-MS (Matrix: Dithranol): Calcd: 616.27($[M+H]^+$), Found: 616.52.

Anal. Calcd. for $C_{45}H_{33}N_3$: C, 87.77; H, 5.40; N, 6.82. Found: C,87.54; H, 5.40; N, 6.74.

mG3A

As per the general procedure for the dehydration reaction, the **mG3on** (283 mg, 0.225 mmol), aniline (0.031 ml, 0.34 mmol) and DABCO (0.51 g, 4.55 mmol) were dissolved in chlorobenzene (20mL). $TiCl_4$ (0.1 ml, 0.91 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**mG3A)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 5: 5: 1 with 2% Et_3N). Yield: 74% (222 mg, 0.167 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 22.3 ºC, TMS),

δ= 7.72 (8H, m), 7.46-7.31 (14H, m), 7.25-7.01 (24H, m), 6.96-6.83 (10H, m), 6.76 (2H, d, J = 6.8 Hz), 6.59-6.39 (8H, m), 6.28 (1H, d, J = 1.5 Hz), 6.15 (2H, t, J = 9.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, 23.4 ºC, TMS):

δ= 168.82, 168.67, 168.3, 167.7, 151.13, 151.1, 151.06, 151.02, 151, 150.81, 139.54, 139.41, 139.37, 139.24, 139.12, 136.51, 136.46, 136.02, 135.89, 135.77, 130.92, 130.86, 130.81, 130.77, 129.37, 129.27, 129.23, 128.56, 128.52, 128.48, 128.38, 128.3, 128.2, 127.97, 124.16, 123.99, 123.95, 123.73, 123.63, 123.58, 123.2, 123.14, 122.94, 122.7, 122.59, 122.52, 122, 121.46, 121.14, 120.99, 120.86, 120.31, 120.19.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1333.56([M+H]$^+$), Found: 1333.75.

Anal. Calcd. for $C_{18}H_{14}N_2$: C, 87.42; H, 5.22; N, 7.36. Found: C, 87.15; H, 5.20; N, 7.29.

mG4A

As per the general procedure for the dehydration reaction, the **mG4on** (484 mg, 0.180 mmol), aniline (0.080 ml, 0.88 mmol) and DABCO (0.41 g, 3.67 mmol) were dissolved in chlorobenzene (20mL). $TiCl_4$ (0.08 ml, 0.73 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**mG4A)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 3: 3: 1 with 2% Et_3N). Yield: 69% (341 mg, 0.123 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 21.2 ºC, TMS),

δ= 7.73-7.67 (16H, m), 7.42-7.36 (28H, m), 7.29-7.00 (46H, m), 6.96-6.74 (26H, m), 6.62-6.53 (4H, m), 6.47-6.43 (10H, m), 6.35-6.33 (4H, m), 6.27-6.26 (2H, m), 6.18-6.13 (5H, m).

^{13}C NMR (100 MHz, $CDCl_3$, 23.0 ºC, TMS):

δ= 168.83, 168.67, 168.25, 168.19, 167.84, 151.19, 151.09, 151.02, 150.96, 150.9, 150.75, 139.57, 139.38, 139.32, 139.27, 139.21, 139.16, 139.07, 136.47, 136.37, 136.32, 135.95, 135.83, 135.8, 135.72, 135.66, 130.88, 130.78, 129.31, 129.26, 129.15, 128.63, 128.57, 128.51, 128.48, 128.39, 128.29, 128.19, 128.15, 127.97, 124.16, 124.03, 123.95, 123.9, 123.61, 123.18, 123.12, 122.84, 122.7, 122.62, 122.52, 121.56, 121.35, 121.11, 120.92, 120.84, 120.43, 120.27, 120.17

Anal. Calcd. for $C_{18}H_{14}N_2$: C, 87.27; H, 5.14; N, 7.59. Found: C, 87.06; H, 5.14; N, 7.51.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2767.16 ([M+H]$^+$), Found: 2767.67.

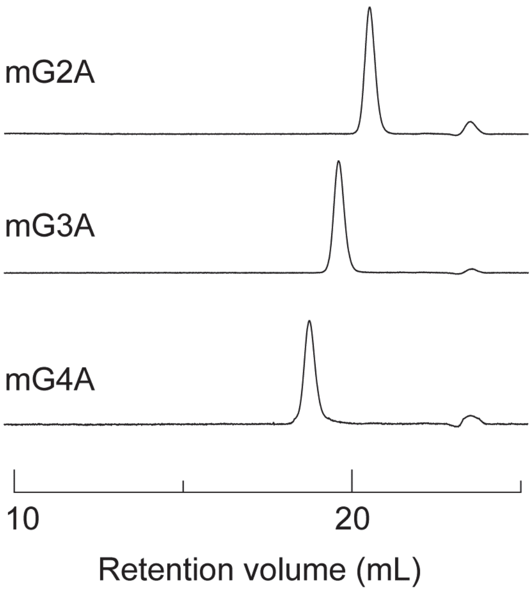
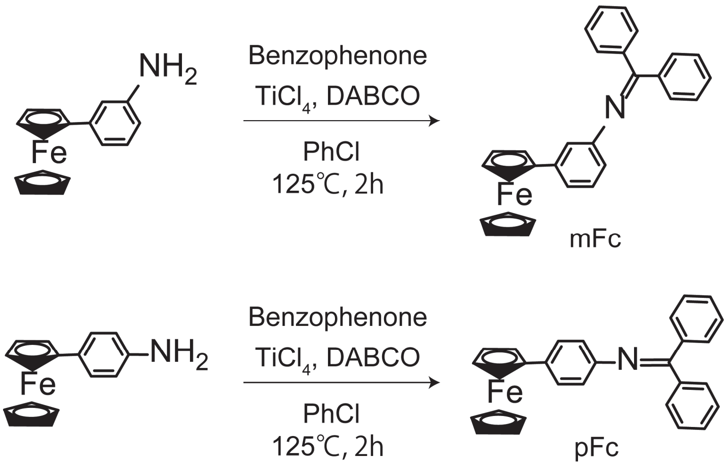


Figure S1. DP (differential pressure) Chromatogram of **mG*n*A**.



Scheme S3. Synthesis of ferrocene substituted phenylazomethines.

mFc

As per the general procedure for the dehydration reaction, the benzophenone (833 mg, 4.57 mmol), 3-aminophenyl ferrocene (259 mg, 0.93 mmol) and DABCO (2.60 g, 23.2 mmol) were dissolved in chlorobenzene (20mL). $TiCl_4$ (0.49 ml, 4.51 mmol) was added and the mixture was stirred for 2h at 125ºC. The product (**mFc)** was isolated by silica gel column chromatography (toluene: hexane = 4: 1 with 2% Et_3N) and purified by preparative scale GPC (eluent: chloroform). Yield: 63% (259 mg, 0.59 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 28.9 ºC, TMS),

δ= 7.78-7.77 (2H, m), 7.48 (1H, t, J = 7.3 Hz), 7.42 (2H, t, J = 7.3 Hz), 7.30-7.29 (3H, m), 7.20-7.18 (2H, m), 7.10-7.02 (2H, m), 6.82 (1H, t, J = 1.8 Hz), 6.60 (1H, dt, J = 7.5, 1.7 Hz), 4.50 (2H, t, J = 1.9 Hz), 4.24 (2H, t, J = 1.8 Hz), 3.89 (5H, s).

^{13}C NMR (100 MHz, $CDCl_3$, 23.0 ºC, TMS):

δ= 168.40, 151.47, 139.76, 139.50, 136.50, 130.76, 129.56, 129.39, 128.70, 128.47, 128.24, 128.02, 120.84, 118.91, 118.04, 84.85, 69.58, 68.86, 66.24

Anal. Calcd. for $C_{29}H_{23}FeN$: C, 78.92; H, 5.25; N, 3.17. Found: C, 78.68; H, 5.08; N, 3.21.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 441.12 ([M]$^+$), Found: 441.71.

pFc

As per the general procedure for the dehydration reaction, the benzophenone (487 mg, 2.67 mmol), 4-aminophenyl ferrocene (151 mg, 0.54 mmol) and DABCO (760 mg, 6.78 mmol) were dissolved in chlorobenzene (10mL). $TiCl_4$ (0.15 ml, 1.35 mmol) was added and the mixture was stirred for 1.5h at 125ºC. The product (**pFc)** was isolated by silica gel column chromatography (hexane: chloroform: ethyl acetate= 10: 10: 1 with 2% Et_3N) and purified by preparative scale GPC (eluent: chloroform). Yield: 79% (189 mg, 0.43 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 28.5 ºC, TMS),

δ= 7.76 (2H, dt, J = 6.7, 1.6 Hz), 7.47 (1H, t, J = 7.3 Hz), 7.41 (2H, t, J = 7.3 Hz), 7.27-7.24 (5H, m), 7.15-7.14 (2H, m), 6.65 (2H, d, J = 8.5 Hz), 4.56 (2H, t, J = 1.9 Hz), 4.25 (2H, t, J = 1.9 Hz), 3.96 (5H, s).

^{13}C NMR (100 MHz, $CDCl_3$, 28.5 ºC, TMS):

δ= 168.14, 149.38, 139.81, 136.47, 134.02, 130.67, 129.65, 129.34, 128.59, 128.21, 127.93, 125.91, 121.27, 85.21, 69.62, 68.76, 66.01

Anal. Calcd. for $C_{29}H_{23}FeN$: C, 78.92; H, 5.25; N, 3.17. Found: C, 78.93; H, 5.04; N, 3.21.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 441.12 ([M]$^+$), Found: 441.68.

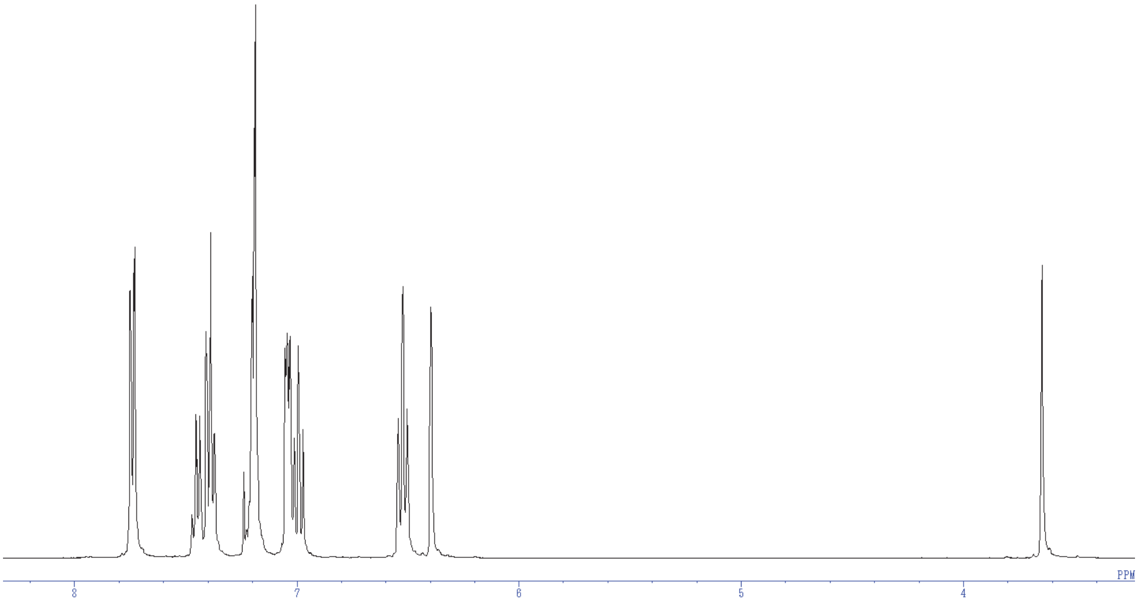


Figure S2. ^{1}H NMR spectra of **pre-mG2on**.

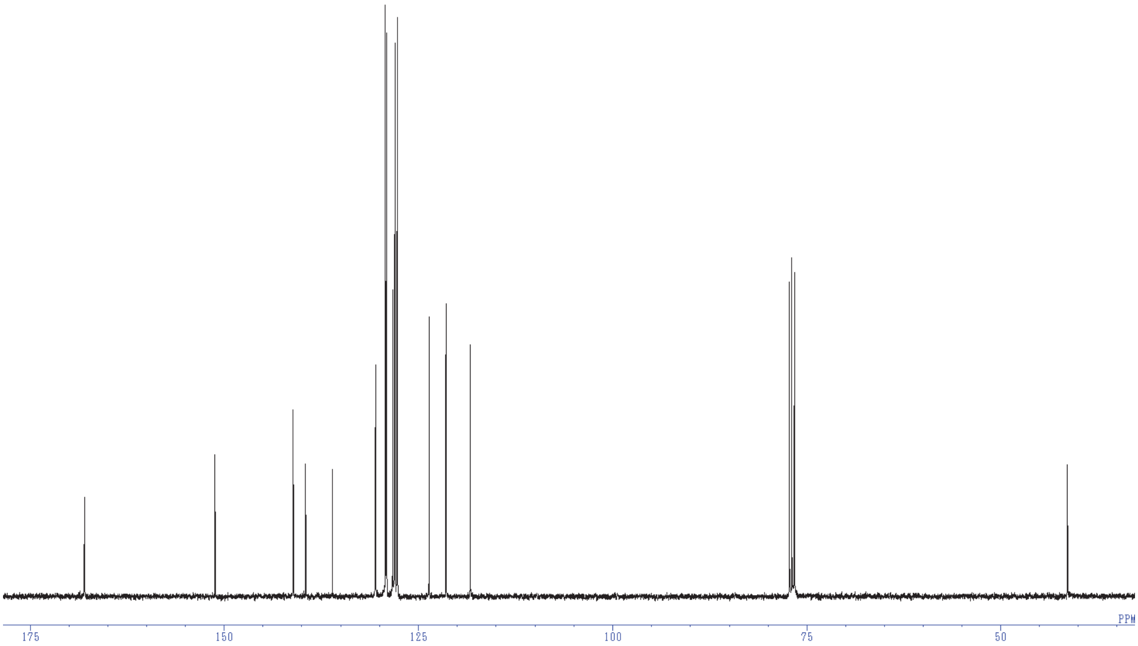


Figure S3. ^{13}C NMR spectra of **pre-mG2on**.

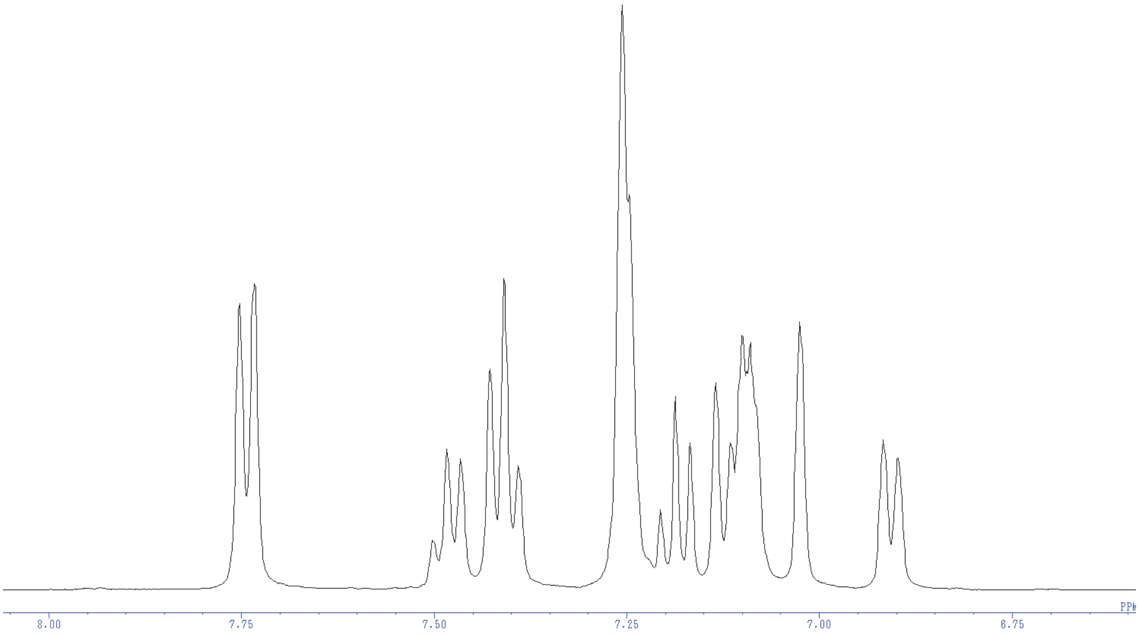


Figure S4. ^{1}H NMR spectra of **mG2on**.

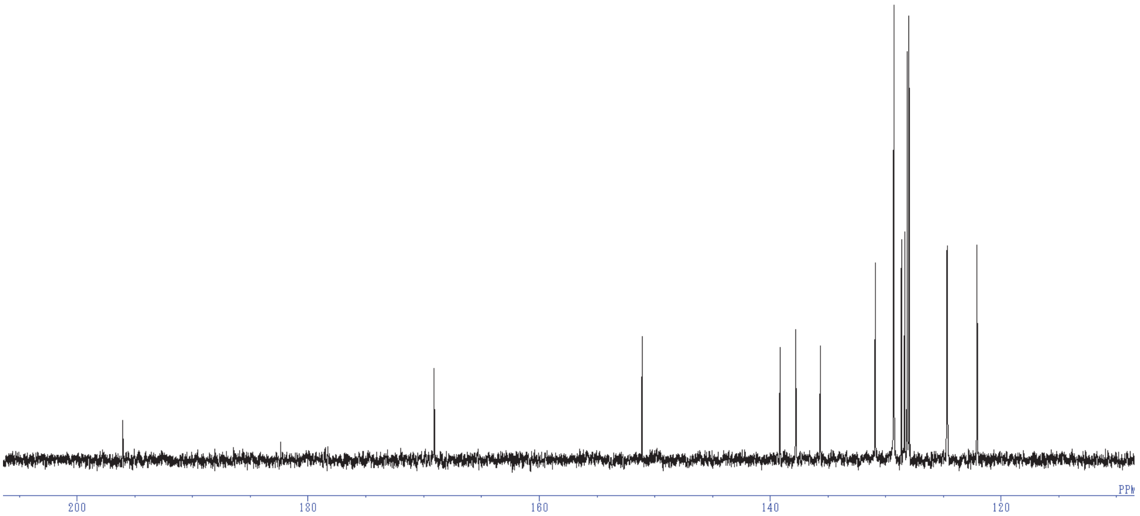


Figure S5. ^{13}C NMR spectra of **mG2on**.

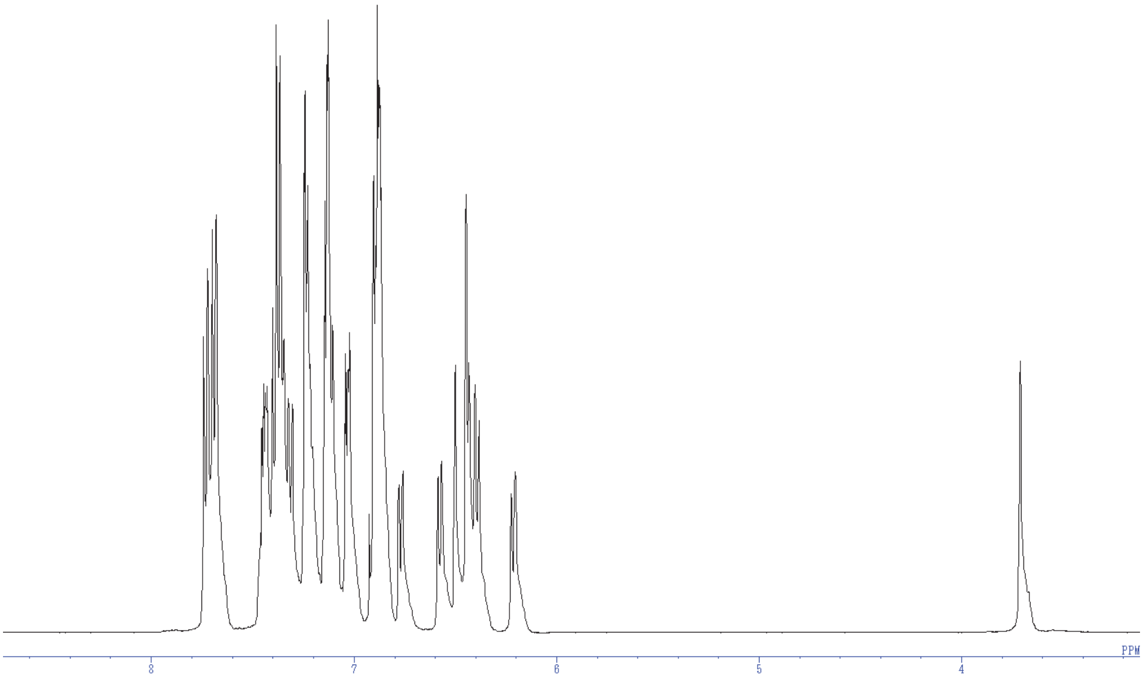


Figure S6. ^{1}H NMR spectra of **pre-mG3on**.

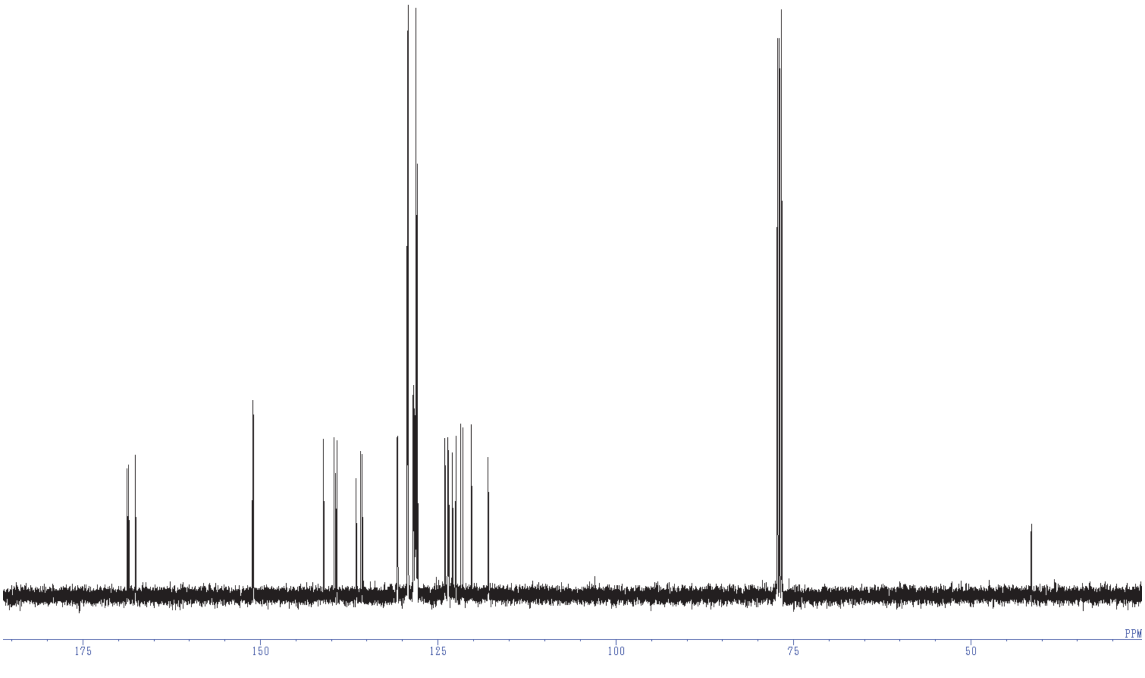


Figure S7. ^{13}C NMR spectra of **pre-mG3on**.

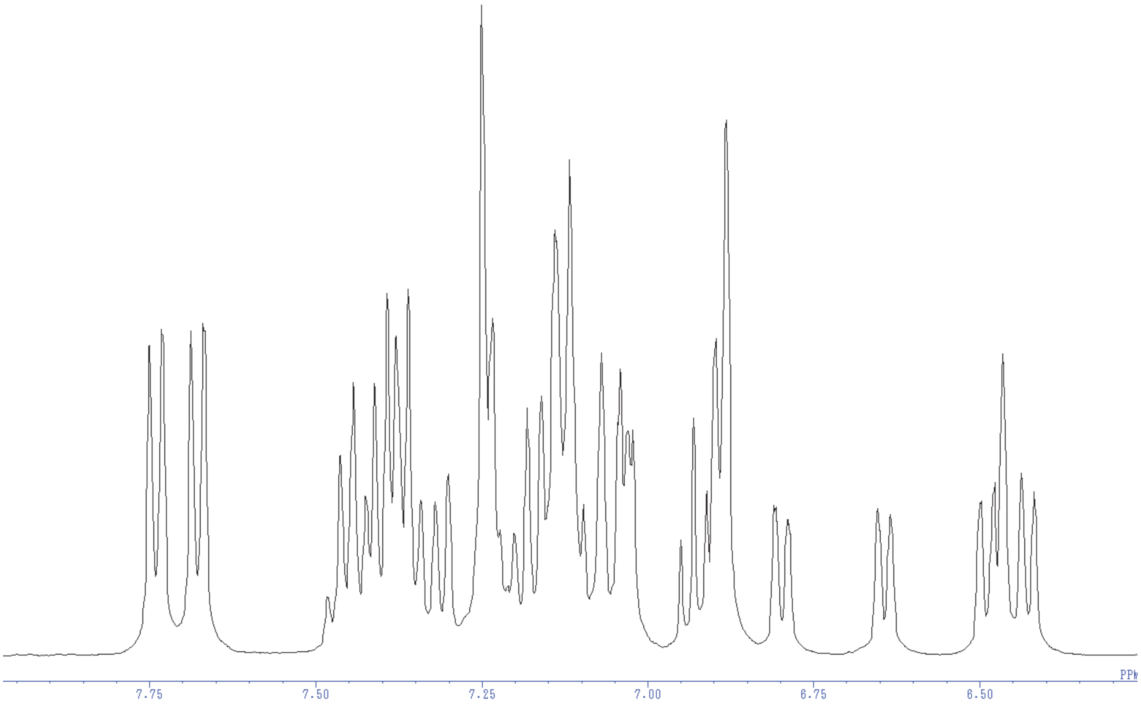


Figure S8. ^{1}H NMR spectra of **mG3on**.

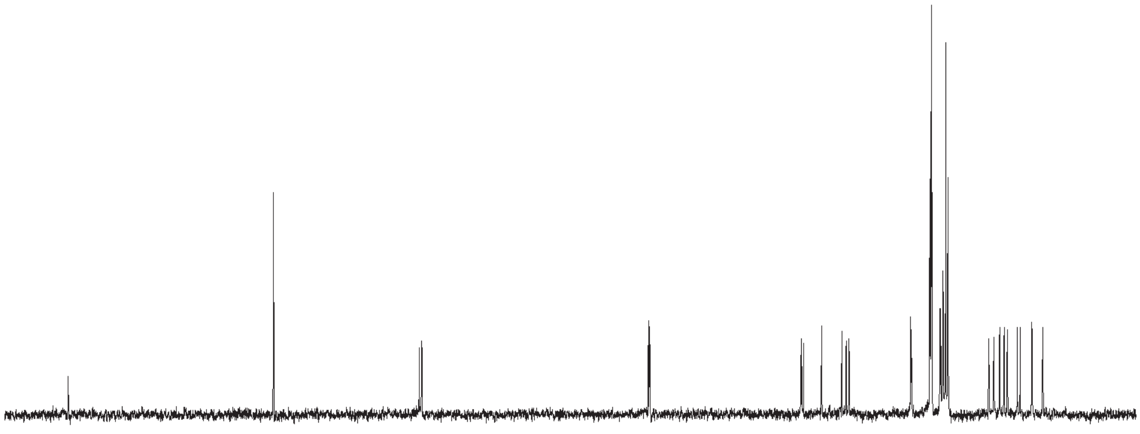


Figure S9. ^{13}C NMR spectra of **mG3on**.

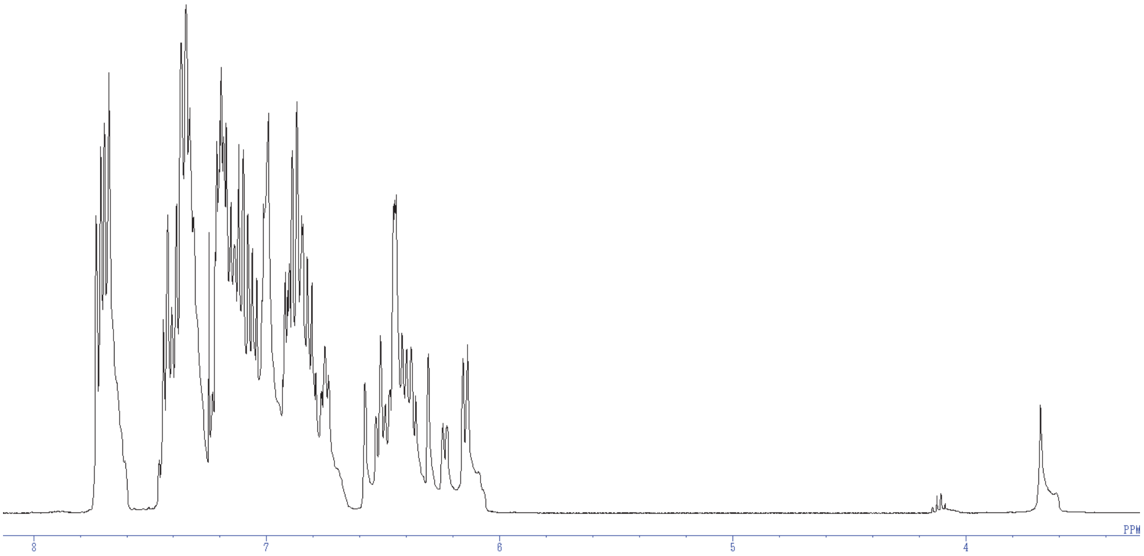


Figure S10. ^{1}H NMR spectra of **pre-mG4on**.

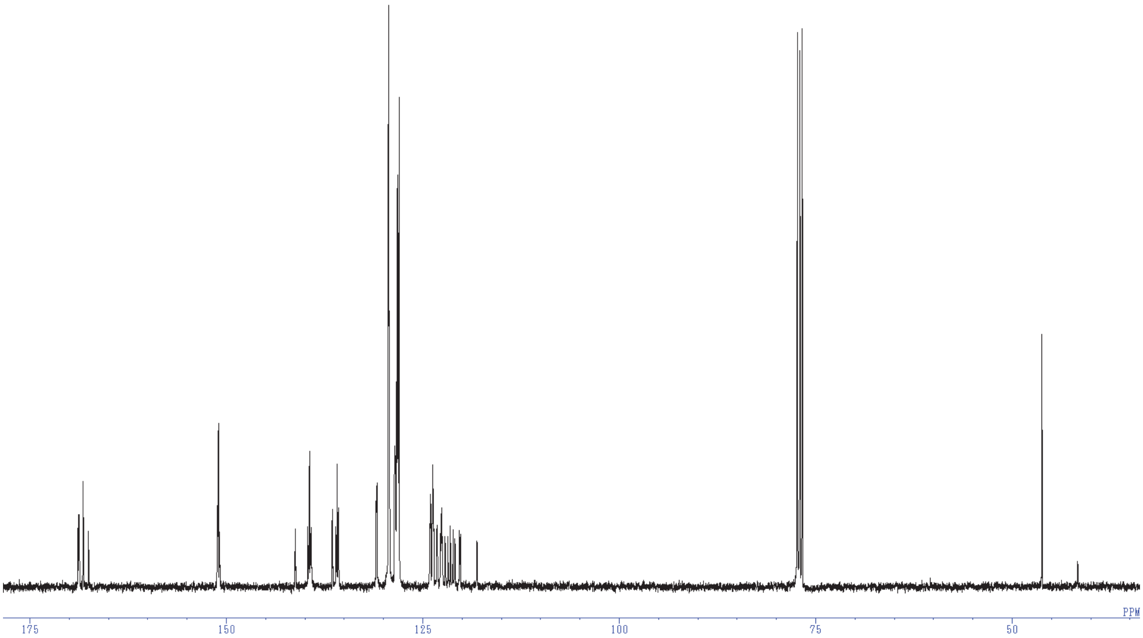


Figure S11. ^{13}C NMR spectra of **pre-mG4on**.

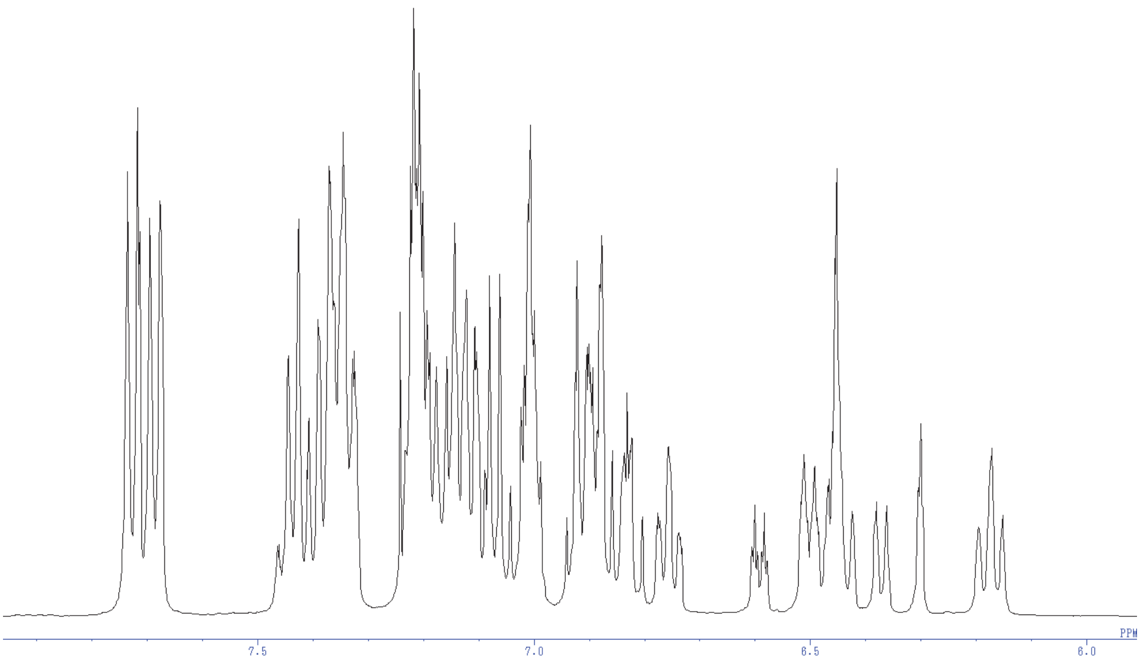


Figure S12. ^{1}H NMR spectra of **mG4on**.

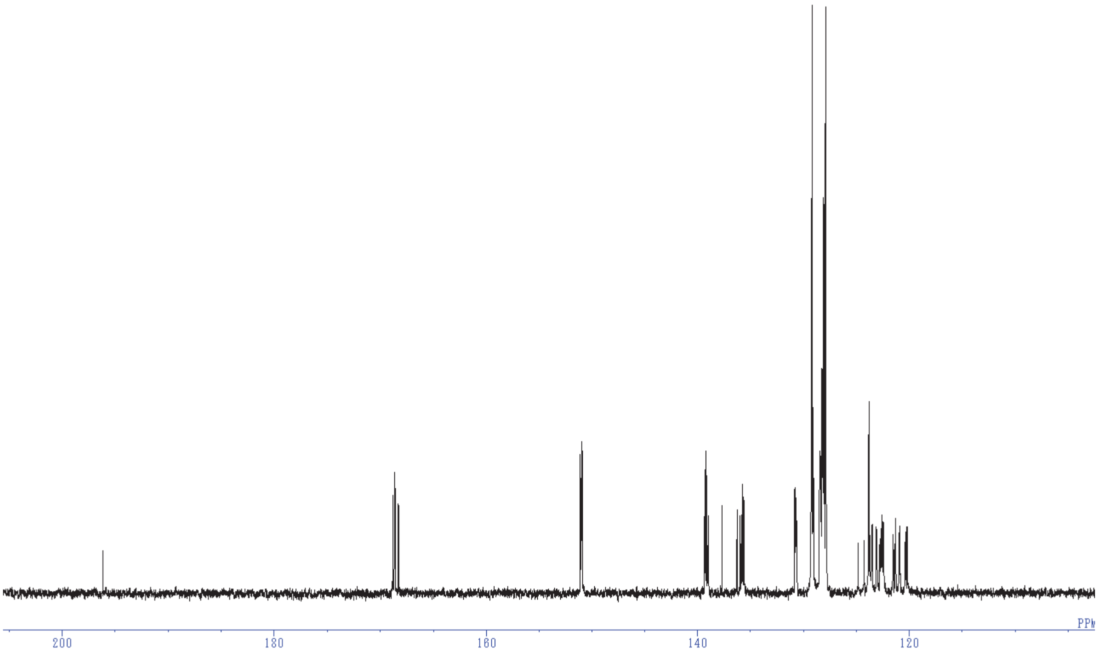


Figure S13. ^{13}C NMR spectra of **mG4on**.

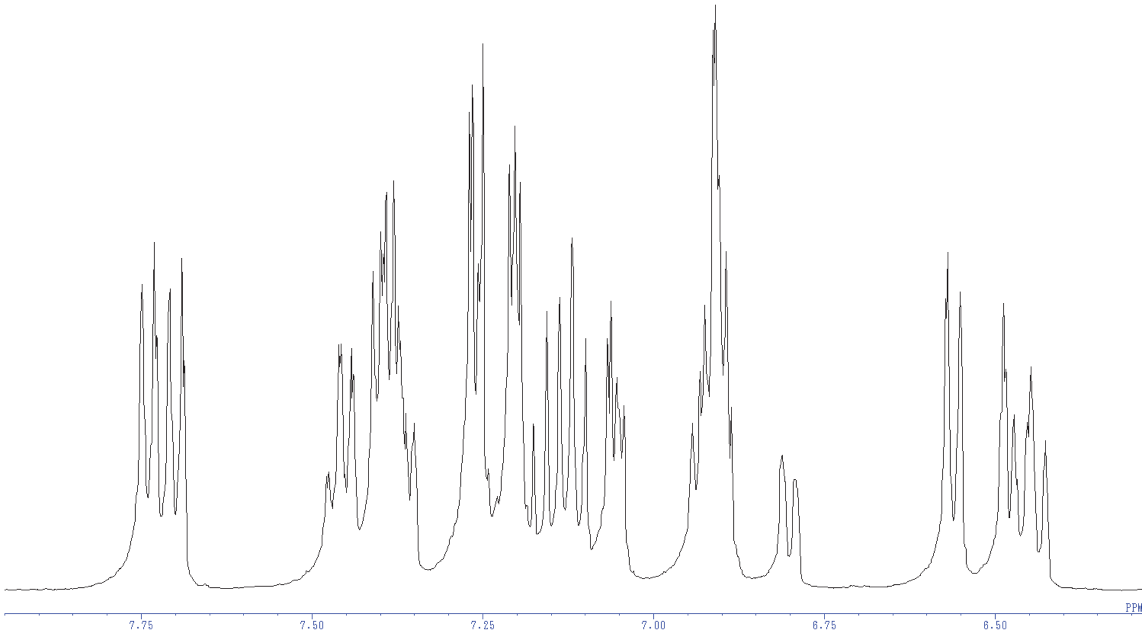


Figure S14. ^{1}H NMR spectra of **mG2A**.

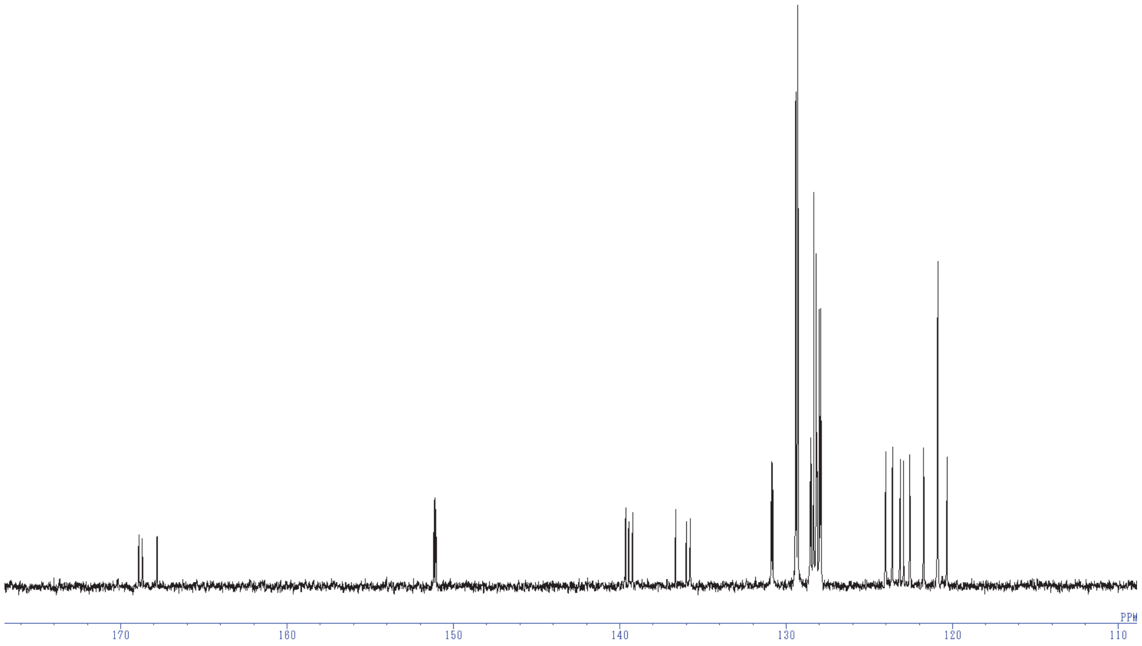


Figure S15. ^{13}C NMR spectra of **mG2A**.

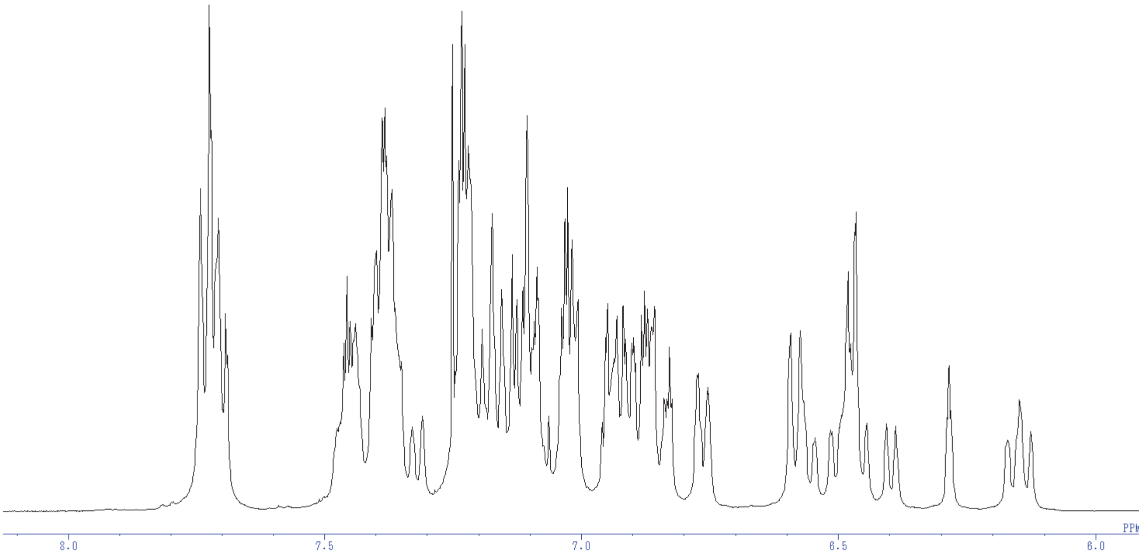


Figure S16. ^1H NMR spectra of **mG3A**.

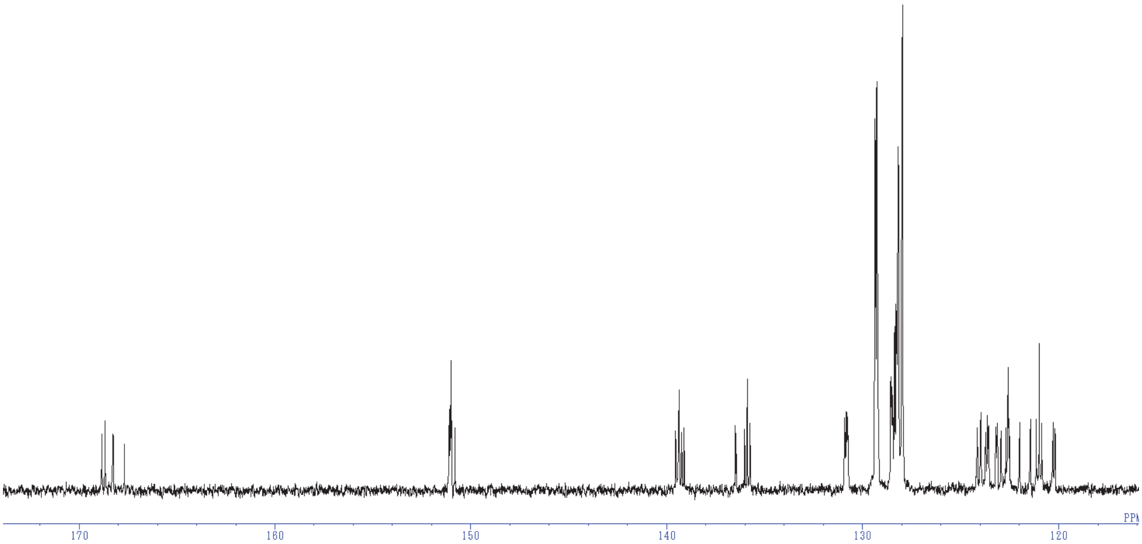


Figure S17. ^{13}C NMR spectra of **mG3A**.

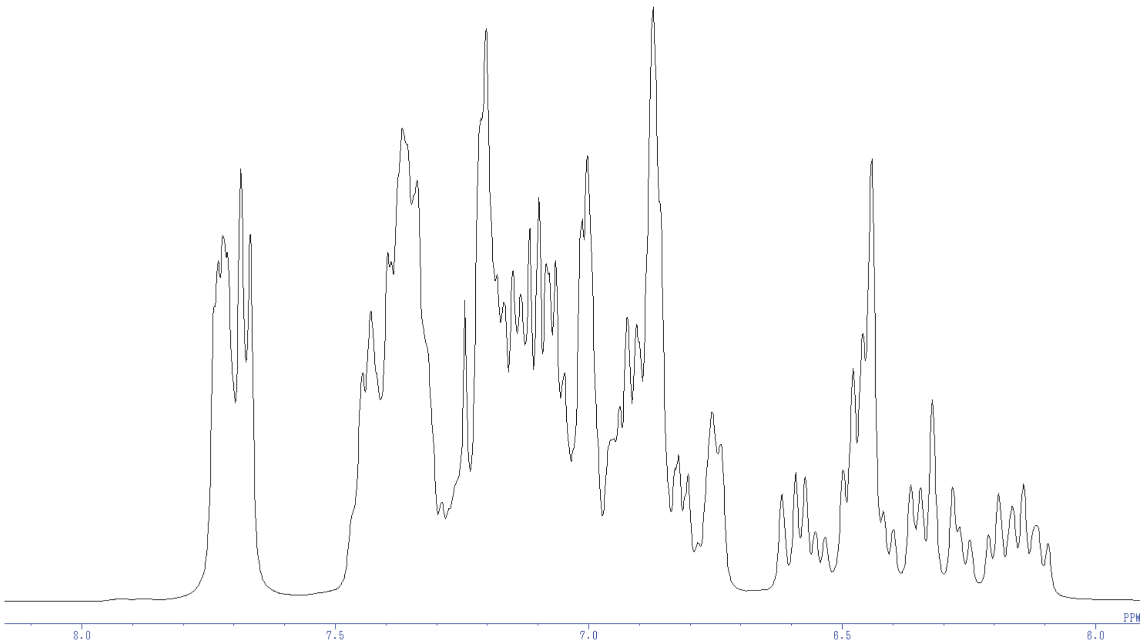


Figure S18. ^{1}H NMR spectra of **mG4A**.

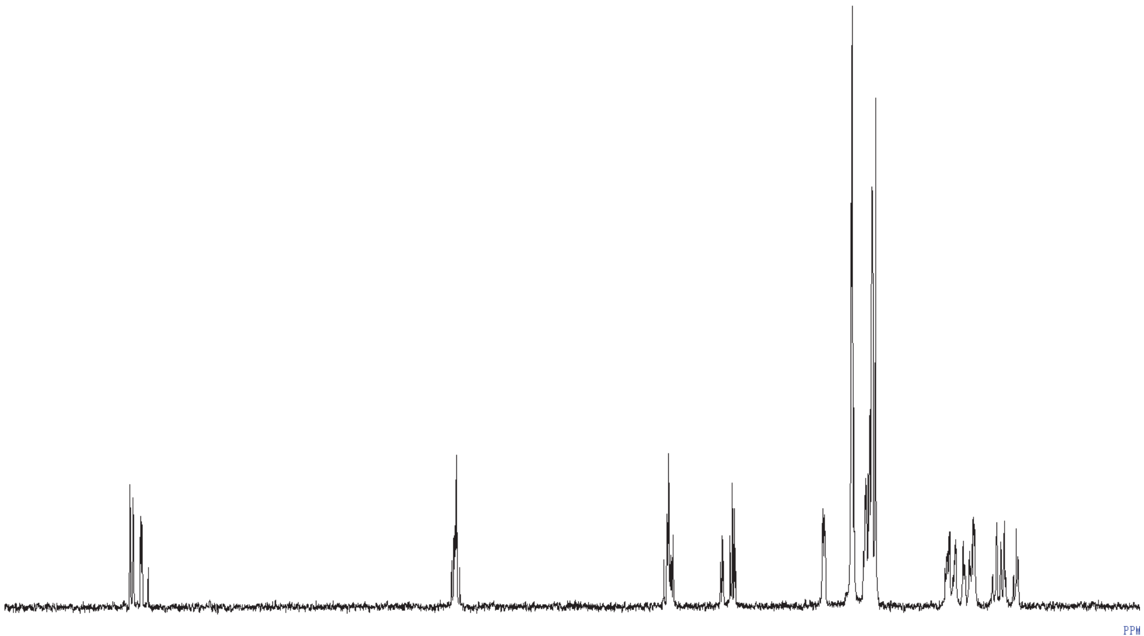


Figure S19. ^{13}C NMR spectra of **mG4A**.

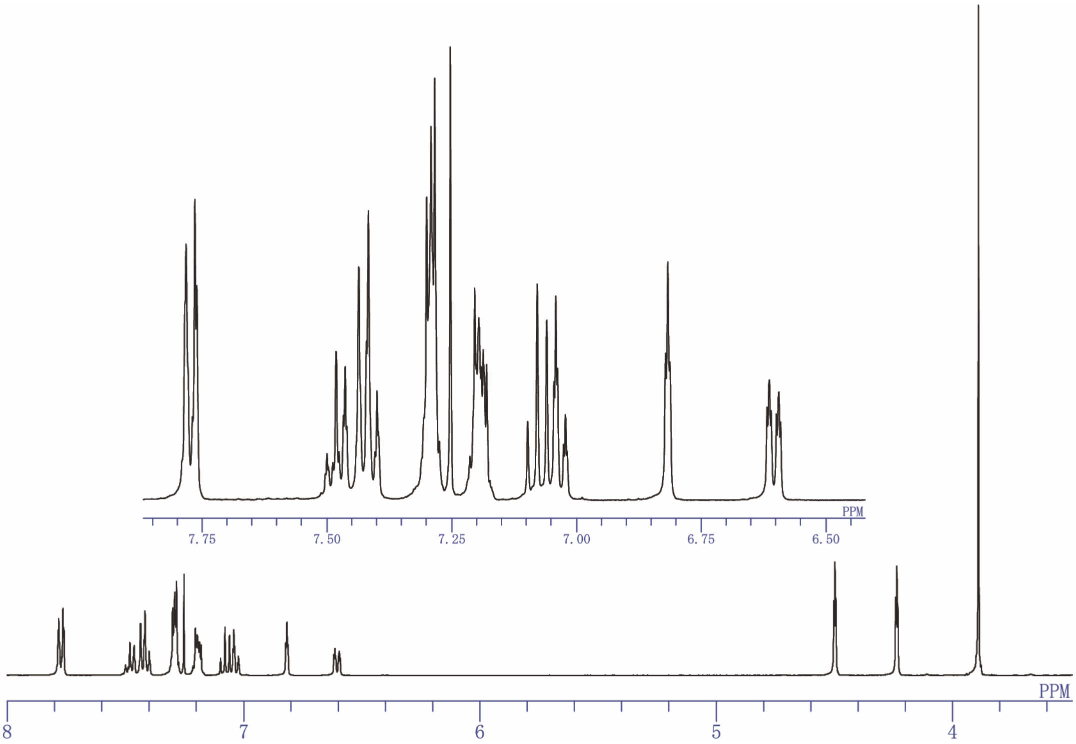


Figure S20. ^{1}H NMR spectra of **mFc**.

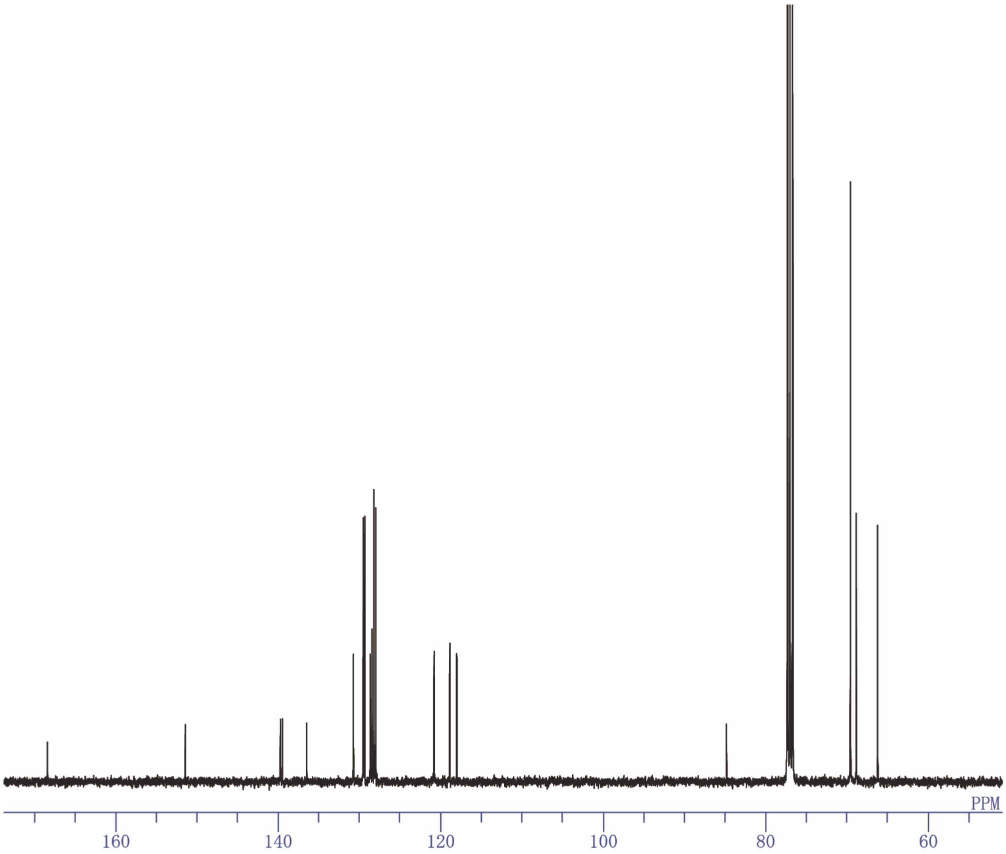


Figure S21. ^{13}C NMR spectra of **mFc**.

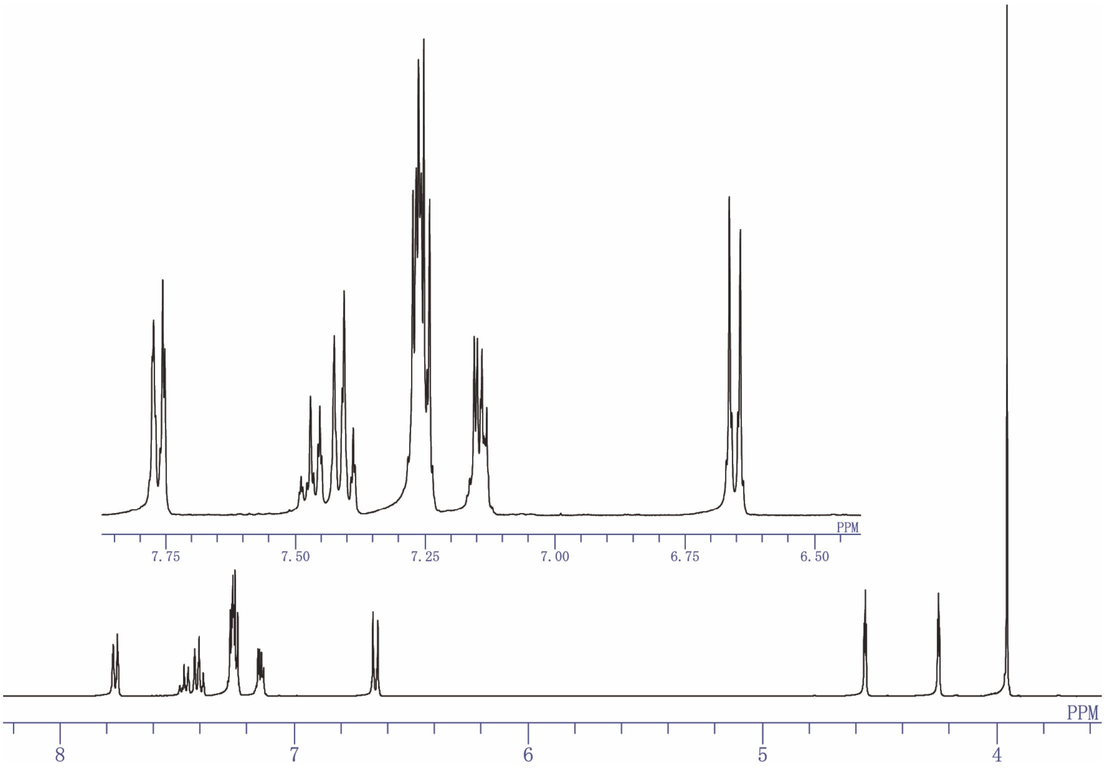


Figure S22. ^{1}H NMR spectra of **mFc**.

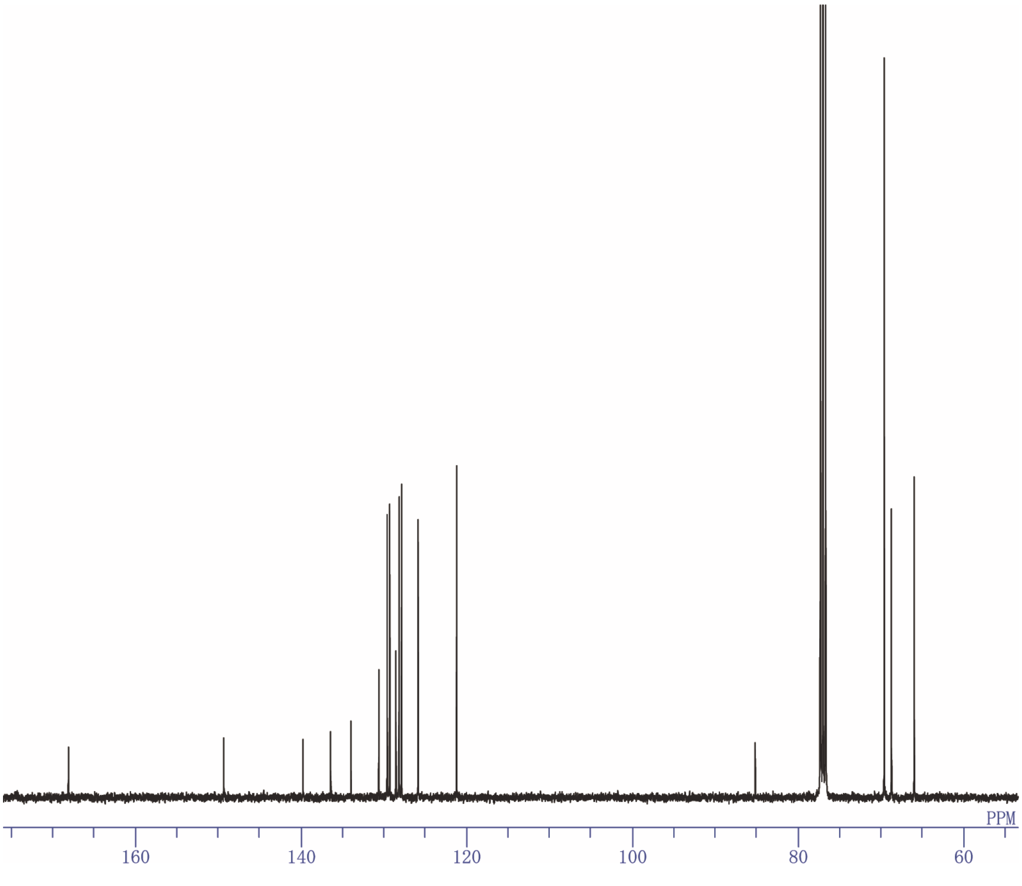


Figure S23. ^{13}C NMR spectra of **pFc**.

3. UV-vis spectra

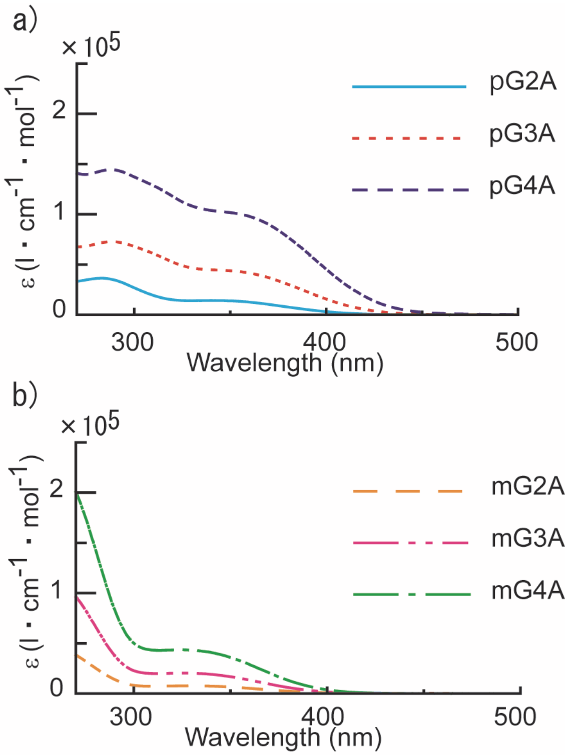


Figure S24. UV-vis spectra of a) **pG*n*A**, and b) **mG*n*A** in CH_3CN: $CHCl_3$= 1: 1 solvent.

4. Mark-Houwink-Sakurada plot

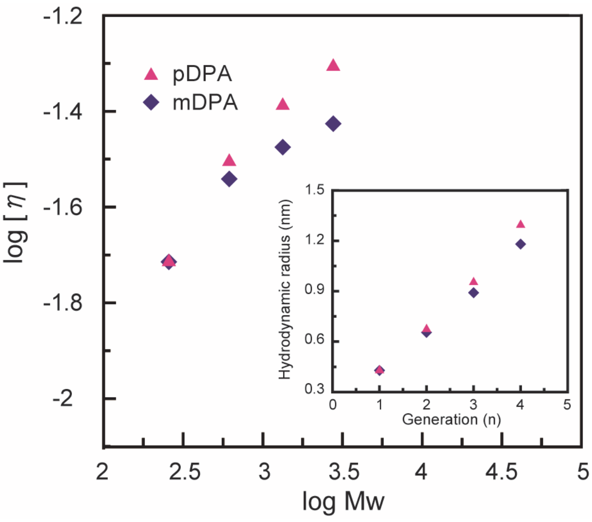


Figure S25. Mark-Houwink-Sakurada plot of **pDPA** and **mDPA** (inset is generation-hydrodynamic radius plot).

5. Molecular models

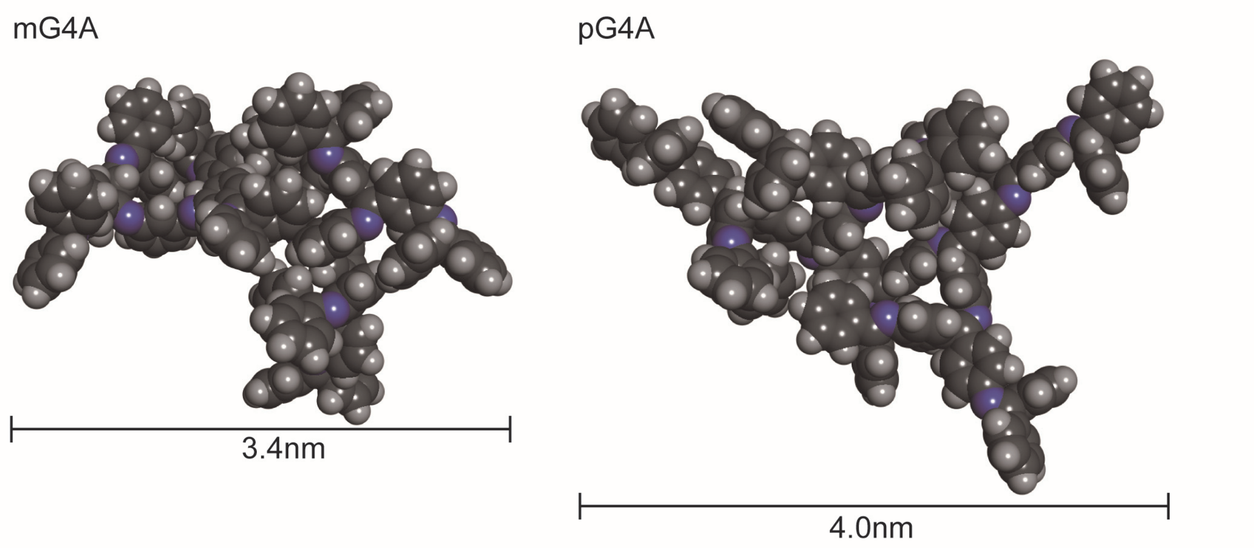


Figure S26. Molecular model of **mG4A** and **pG4A** (optimized with semi-empirical calculation with AM1 hamiltonian on Gaussian 09, Revision C.01[4] on the nodes of a supercomputer (TSUBAME2, Tokyo Institute of Technology).).

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(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, J. J.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2010.

6. UV-vis titration with $GaCl_3$

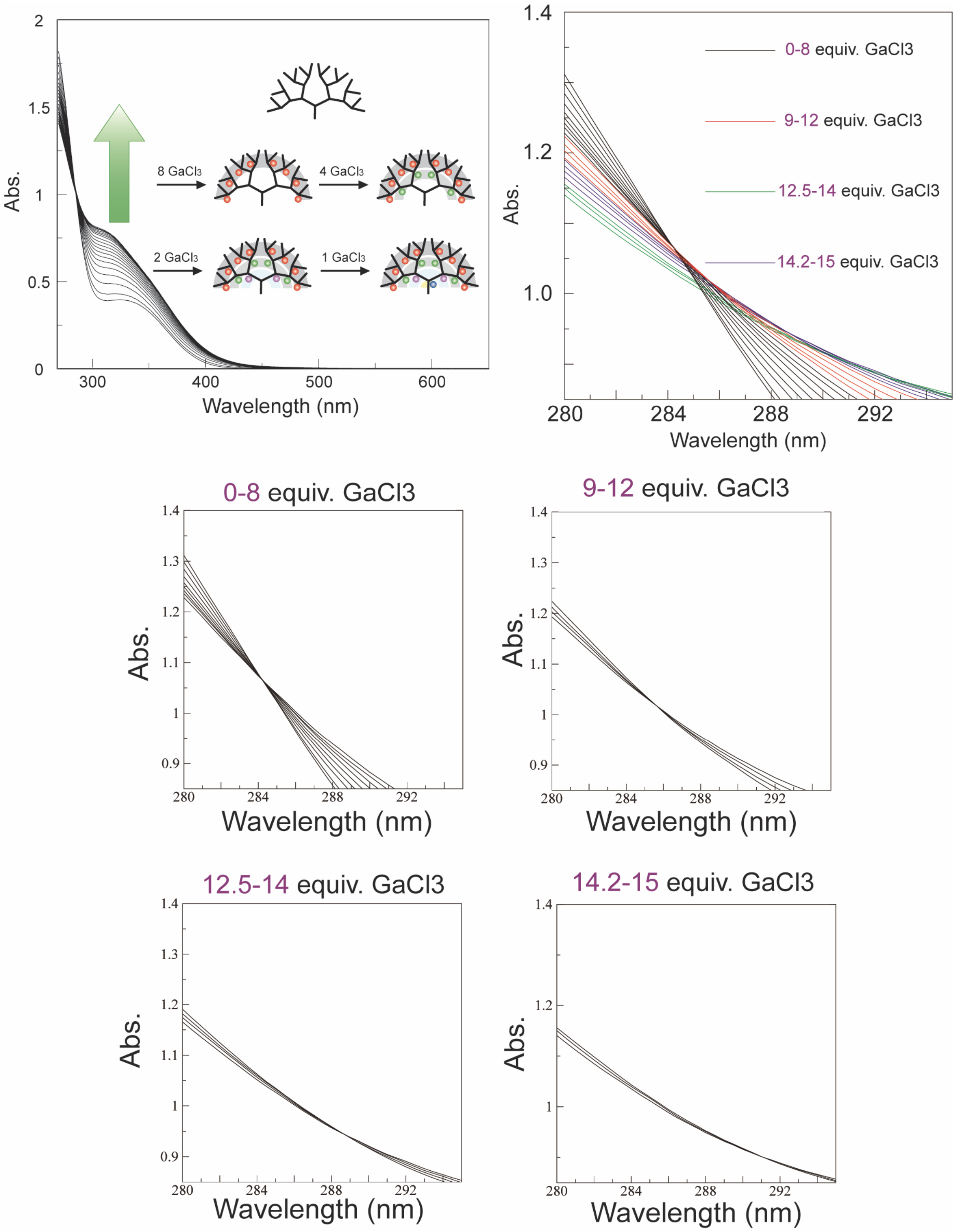


Figure S27. UV-vis spectra of **mG4A** during the addition of $GaCl_3$ in chloroform: acetonitrile = 1: 1 solution.

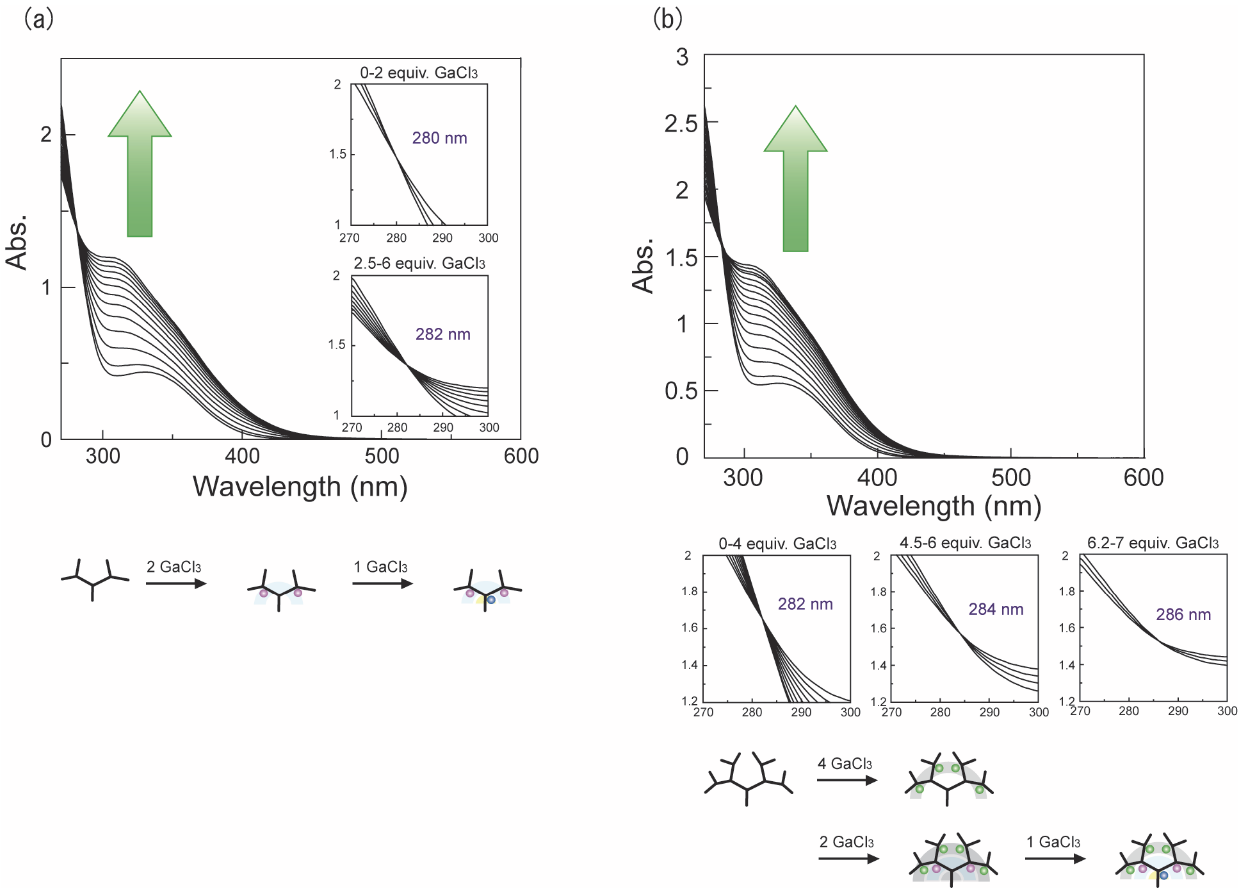


Figure S28. UV-vis spectra of (a) **mG2A** (b) **mG3A** during the addition of $GaCl_3$ in chloroform: acetonitrile = 1: 1 solution.

7. UV-vis titration with BF_3 O(Et)$_2$

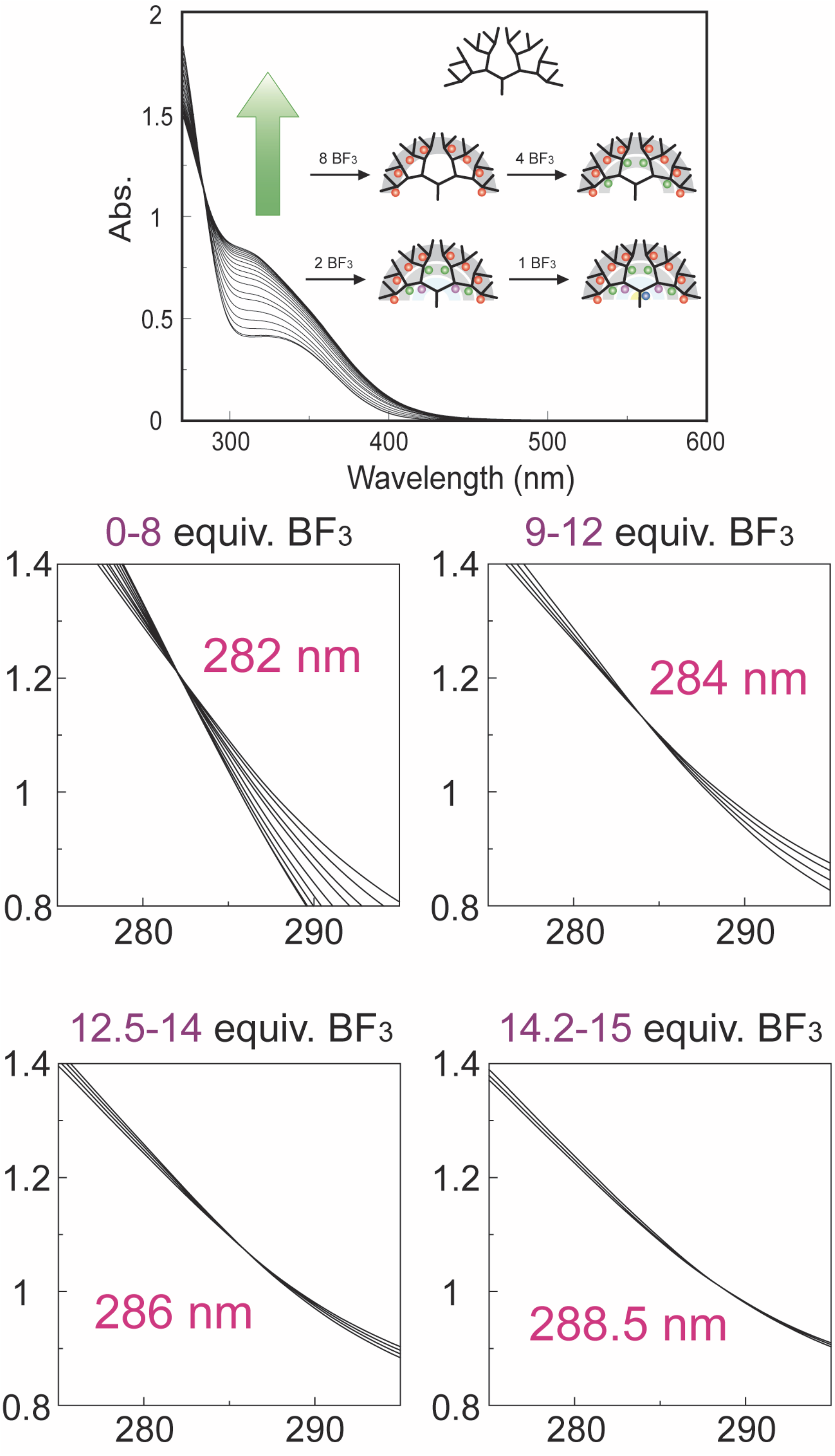
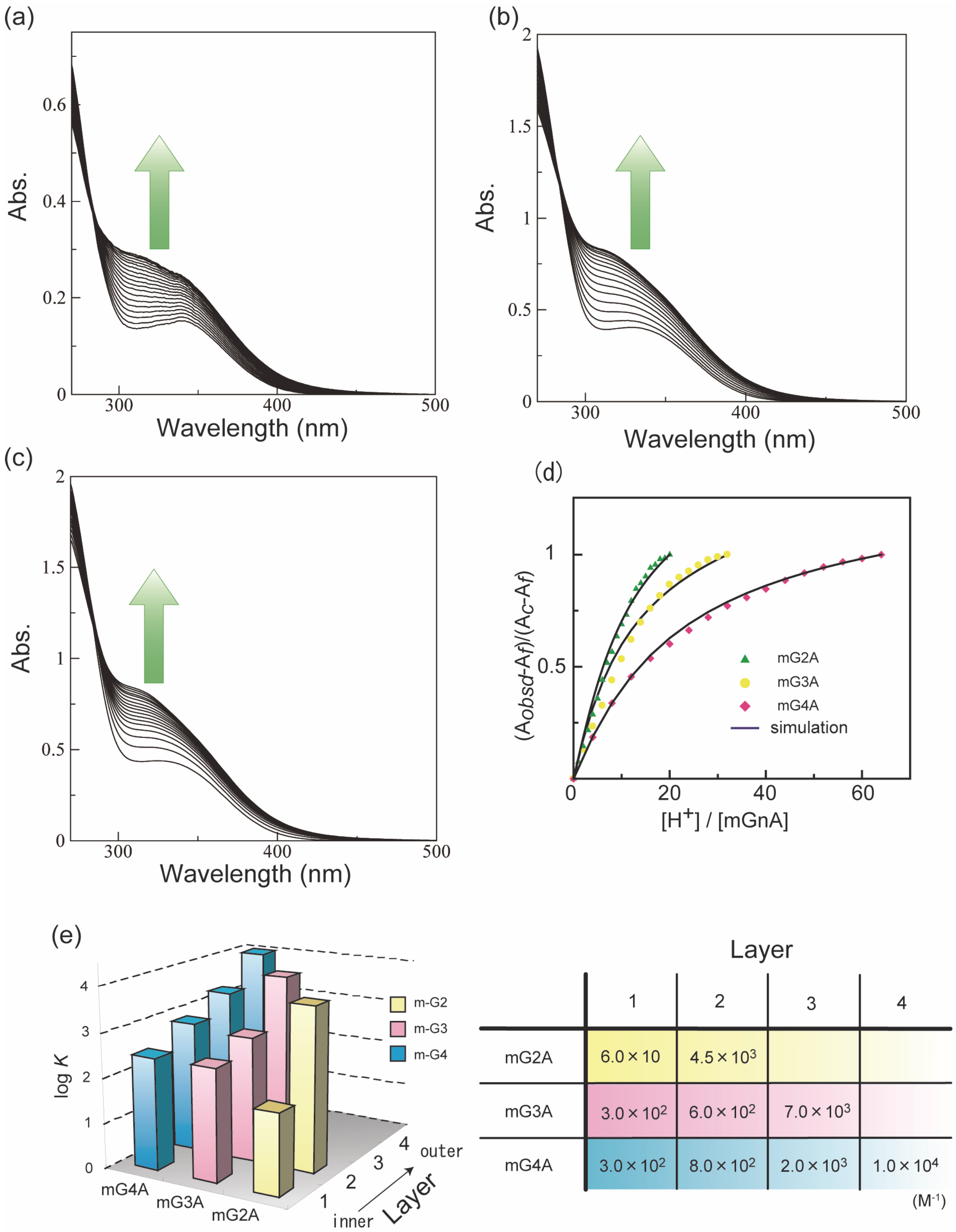


Figure S29. UV-vis spectra of **mG4A** during the addition of $BF_3O(Et)_2$ in chloroform: acetonitrile = 1: 1 solution.

8. UV-vis titration with TFA(H^+)



Layer

	1	2	3	4
mG2A	6.0×10	4.5×10^3		
mG3A	3.0×10^2	6.0×10^2	7.0×10^3	
mG4A	3.0×10^2	8.0×10^2	2.0×10^3	1.0×10^4

(M^{-1})

Figure S30. UV-vis spectra of (a) **mG2A**, (b) **mG3A**, (c) **mG4A** during the addition TFA in dichloromethane, (d) Titration curve and the theoretical fitting curve (the wavelength that was used were 360(**mG2A**), 350(**mG3A**), and 350nm(**mG4A**)), and (e) Binding constants of each layer of **mG*n*A** with TFA(H^+).

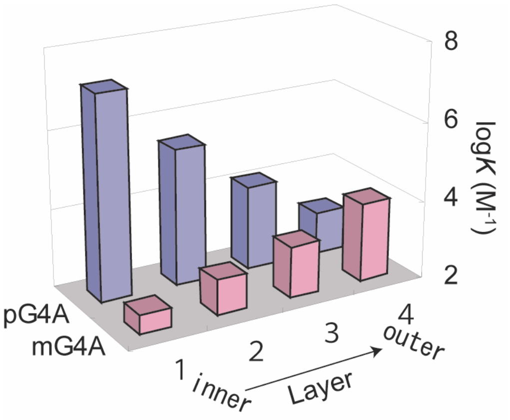


Figure S31. Binding constants of each layer of **pG4A** and **mG4A** with TFA(H^+).

9. Redox potential of ferrocene derivatives

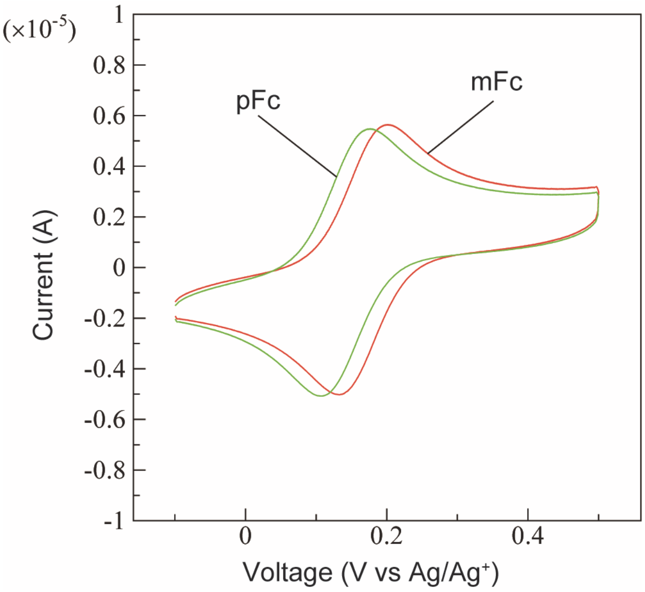


Figure S32. Cyclicvoltammogram of 0.5mM solution of **mFc** and **pFc** in benzonitrile.

10. Assignment of the 13C and 15N NMR spectra

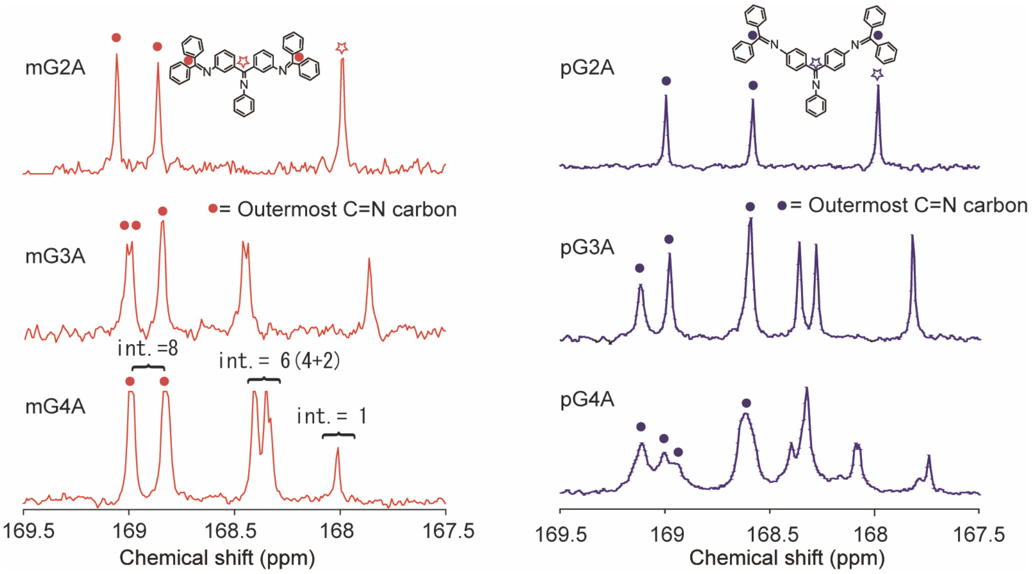


Figure S33. ^{13}C NMR spectra of **mG*n*A** (left) and **pG*n*A** (right) in $CDCl_3$.

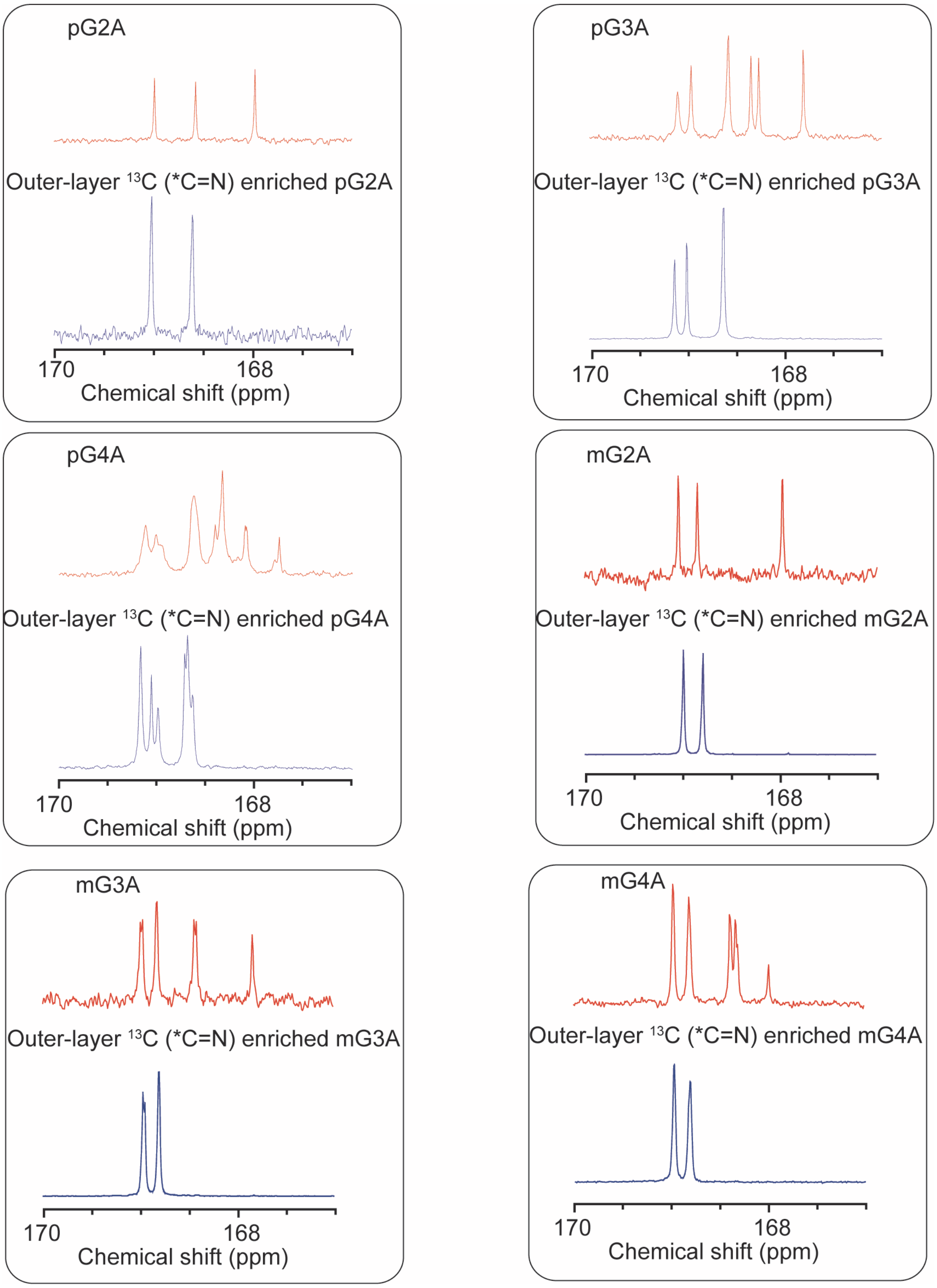


Figure S34. ^{13}C NMR spectra of **pG*n*A**, and **mG*n*A** compared with outer-layer ^{13}C (*C=N) enriched compounds.

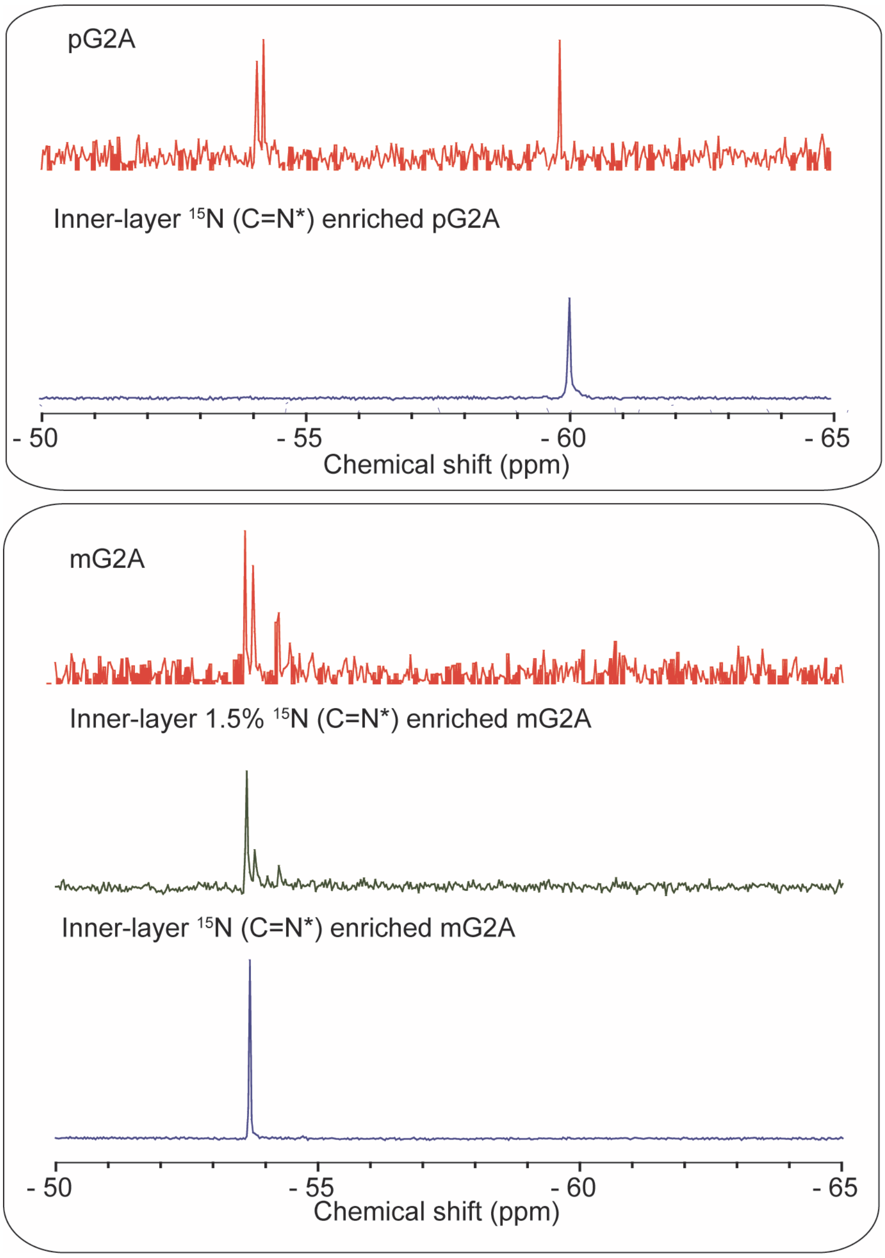


Figure S35. ^{15}N NMR spectra of **pG2A**, and **mG2A** compared with inner-layer ^{15}C (C=N*) enriched compounds.

11. Number and combination of metal salts that can be accumulated

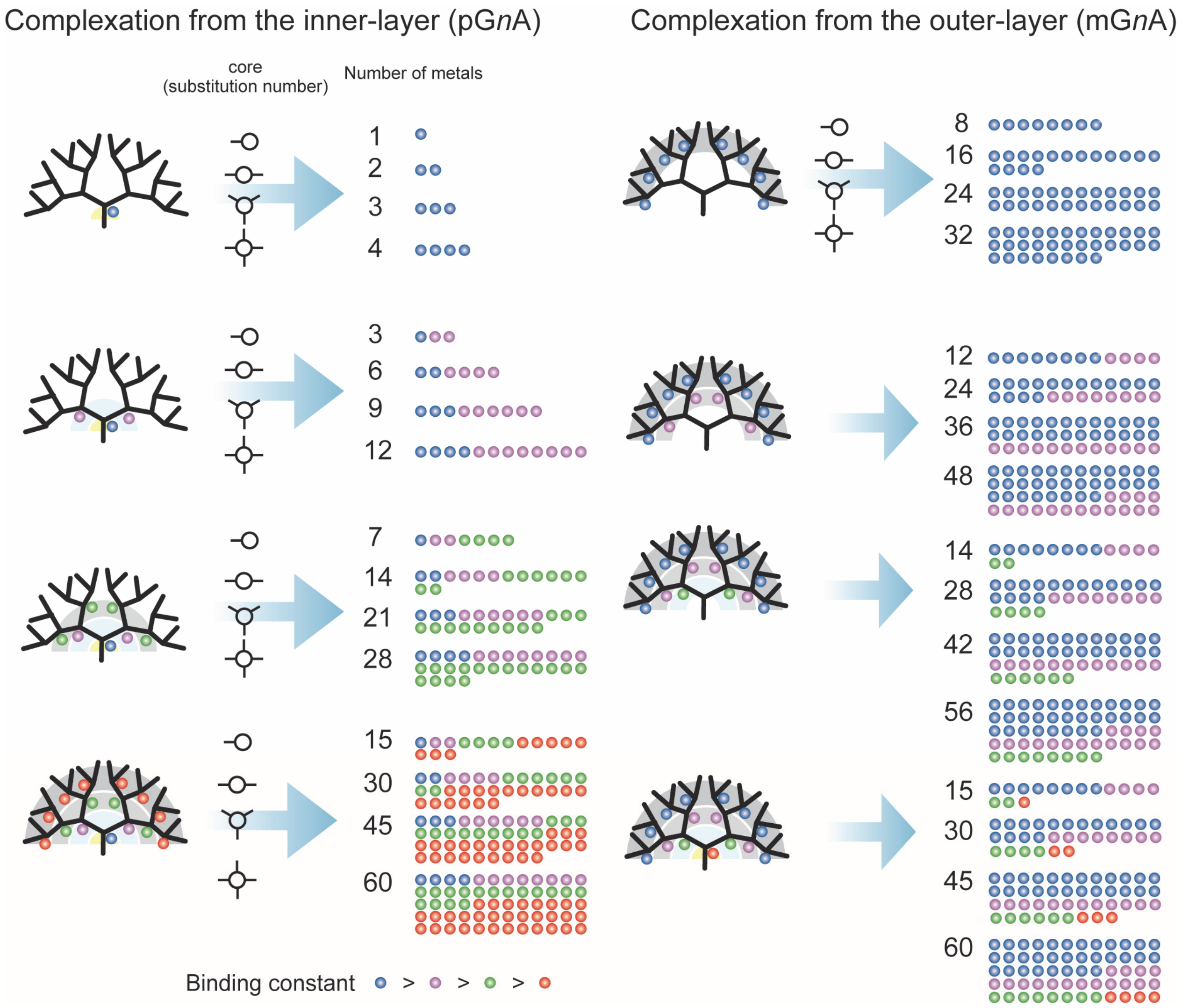


Figure S36. Number and combination of metal salts that are possible to be accumulated into 1 to 4 substituted dendrimers by filling each layer. Actually, other numbers can be also accumulated, but the "closed shell" accumulation that is shown above will have a small statistical distribution compared to other multi ligand systems that have equal binding sites.