

Supporting Information

Size-tunable fluorescent dendrimersomes via aggregation-induced emission

Marilyne Bélanger-Bouliga,[‡] Brandon Andrade-Gagnon,[‡] Diep Thi Hong Nguyen and Ali Nazemi*

Department of Chemistry, NanoQAM, Quebec Centre for Advanced Materials,
Université du Québec à Montréal, C.P. 8888, Succursale Centre-Ville, Montréal, QC, H3C
3P8 Canada

[‡] These authors contributed equally to this work.

General Procedure and Materials:

Dendrons **1-3**¹ and compounds **4**² and **11**³ were synthesized according to previously published procedures. All chemicals were purchased from Sigma-Aldrich or Alfa Aesar and were used without further purification unless otherwise noted. Anhydrous tetrahydrofuran (THF) and anhydrous dichloromethane (CH₂Cl₂) were obtained from a solvent purification system using aluminum oxide columns. The reactions were mostly performed under argon using Schlenk line techniques and anhydrous THF/CH₂Cl₂. ¹H- and ¹³C-NMR spectra were recorded at 300 and 150 MHz, respectively, using CDCl₃ as solvent. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm). Coupling constants (J) are expressed in hertz (Hz). Dialyses were performed using Spectra/Por regenerated cellulose membranes with a 12000 – 14000 g mol⁻¹ molecular weight cut-off (MWCO). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity indices (D) of dendrons and dendrimers were determined by size exclusion chromatography (SEC) using an EcoSEC HLC-8320 (Tosoh Bioscience, Tokyo, Japan) instrument equipped with two TSKgel Alpha-M, 13 μ m columns (7.8 mm ID x 30 cm L) and a TSKgel Alpha Guardcolumn (6.0 mm ID x 4 cm L) calibrated with poly(methyl methacrylate) standards in DMF at 50 °C. The samples were prepared at a concentration of 2 mg/mL in DMF and filtered through a 0.22 μ m PTFE syringe filter prior to injection. The data were acquired at a flow rate of 0.6 mL/min at 50 °C. Dynamic light scattering (DLS) data were obtained using a Zetasizer Nano ZS instrument from Malvern Instruments (Malvern, UK) at a dendrimer concentration of 17 μ M. UV-vis spectroscopy was conducted using a PerkinElmer Lambda 750 spectrometer. Samples were analyzed at a concentration of 17 μ M within a range of 250 - 800 nm. Fluorescence spectroscopy was performed with a Perkin Elmer LS45 Spectrofluorometer (Waltham, MA, USA). Samples were analyzed at a dendrimer concentration of 17 μ M. The excitation wavelength for acquiring the emission spectra was set at 320 nm. Differential scanning calorimetry (DSC) data were obtained using a DSC1 Mettler Toledo instrument (Columbus, OH, USA) with a heating/cooling rate of 10 °C/min between -50 and 200 °C under nitrogen atmosphere. The midpoint glass transition temperature (T_g) values were extracted from the second heating cycle. Samples for transmission electron microscopy (TEM) were prepared by drop casting 5.0 μ L of each solution on a TEM grid, being held by a twizzler, and set to dry for 45-60 minutes. After grid was dry, 5.0 μ L of the uranyl formate stain solution was cast on the grid. After waiting for 60 seconds, the solution was blotted off using a filter paper. The measurements were performed on a Joel JEM-2100F instrument (Tokyo, Japan) at 80 kV. High-resolution mass spectrometry (HRMS) was performed using a Liquid Chromatography Mass Spectrometry Time of Flight (LC-MS TOF) mass analyzer (Agilent Technologies Santa Clara, CA, USA) in the electrospray mode.

Synthesis of first-generation TPE-conjugated dendron (5):

In a vial, **1** (0.41 g, 2.0 mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **4** (2.0 g, 5.0 mmol, 2.4 equiv.) was dissolved in THF and added to the stirred solution. Sodium ascorbate (0.76 g, 4.0 mmol, 2.0 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (0.48 g, 2.0 mmol, 1.0 equiv.) was separately dissolved in water and transferred to the solution (changing colors from opaque green to opaque orange to opaque yellow), where the reaction stirred at room temperature for 24 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 30 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (5% MeOH in CH₂Cl₂). Pure product is a white fluffy solid (1.4 g, yield = 70%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.59 (s, 2H), 7.14-6.98 (m, 30H), 6.91 (d, *J* = 8.8 Hz, 4H), 6.62-6.55 (m, 7H), 5.16 (s, 4H), 4.60 (d, *J* = 6.1 Hz), 4.54 (t, *J* = 6.9 Hz), 3.90 (t, *J* = 5.7 Hz, 4H), 2.35 (q, *J* = 12 Hz, 4H), 1.76 (t, *J* = 6.0 Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.4, 156.9, 144.3, 143.9, 143.8, 140.3, 140.2, 136.6, 132.6, 131.3, 127.7, 127.6, 126.4, 126.3, 123.4, 113.6, 105.7, 101.1, 64.6, 63.9, 61.8, 47.2, 29.9. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₇₁H₆₂N₆O₅: 1079.4782, found 1079.4854.

Synthesis of second-generation TPE-conjugated dendron (6):

In a vial, **2** (0.20 g, 0.40 mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **4** (0.77 g, 2.0 mmol, 4.8 equiv.) was dissolved in THF and added to the stirred solution. Sodium ascorbate (0.30 g, 2.0 mmol, 4.0 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (0.19 g, 0.80 mmol, 2.0 equiv.) was separately dissolved in water and transferred to the solution (changing colors from opaque green to opaque orange to opaque yellow), where the reaction stirred at room temperature for 48 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 30 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (5% MeOH in CH₂Cl₂). Pure product is a white fluffy solid (0.67 g, yield = 79%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.58 (s, 4H), 7.14-6.98 (m, 60H), 6.92 (d, *J* = 8.8 Hz, 8H), 6.67 (d, *J* = 2.2 Hz, 4H), 6.61-6.58 (m, 12H), 6.46 (t, *J* = 2.2 Hz, 1H), 5.14 (s, 8H), 4.96 (s, 4H), 4.60 (d, *J* = 5.9 Hz, 2H), 4.52 (t, *J* = 6.9 Hz, 8H), 3.89 (t, *J* = 5.7 Hz, 8H), 2.33 (q, *J* = 12 Hz, 8H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.8, 159.6, 156.9, 144.1, 144.0, 143.9, 143.8, 140.4, 140.3, 136.6, 132.6, 131.3, 127.8, 127.7, 126.4, 126.4, 123.4, 113.6, 106.5, 105.8, 101.5, 101.2, 69.7, 64.8, 64.0, 62.0, 47.3, 30.0. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₁₄₉H₁₂₈N₁₂O₁₁: 2260.9826, found 2260.9809.

Synthesis of third generation TPE-conjugated dendron (7):

In a vial, **3** (0.16 g, 0.10 mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **4** (0.55 g, 1.0 mmol, 9.6 equiv.) was dissolved in THF and added to the stirred solution. Sodium ascorbate (0.21 g, 1.0 mmol, 8.0 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (0.13 g, 0.50 mmol, 4.0 equiv.) was separately dissolved in water and transferred to the solution (changing colors from opaque green to opaque orange to opaque yellow), where the reaction stirred at room temperature for 72 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 30 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (2% MeOH in CH₂Cl₂). Pure product is a white fluffy solid (0.50 g, yield = 82%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.59 (s, 8H), 7.07-6.97 (m, 120H), 6.91 (d, *J* = 8.8 Hz, 16H), 6.64-6.42 (m, 37H), 5.12 (s, 16H), 4.93 (s, 12H), 4.56 (d, *J* = 5.9 Hz, 2H), 4.49 (t, *J* = 6.9 Hz, 16H), 3.87 (t, *J* = 5.7 Hz, 16H), 2.30 (q, *J* = 12 Hz, 16H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.9, 159.5, 156.9, 144.2, 143.9, 143.8, 140.3, 140.2, 139.6, 136.5, 132.6, 131.3, 130.9, 127.7, 127.6, 126.4, 126.3, 113.6, 106.4, 101.4, 64.0, 47.4, 29.9, 29.7. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₃₀₅H₂₆₀N₂₄O₂₃: 4625.9913, found 4625.9921.

Synthesis of first-generation azido-functionalized TPE-conjugated dendron (8):

In a Schlenk flask, **5** (1.4 g, 1.3 mmol, 1.0 equiv.) was dissolved in 20 mL anhydrous THF and stirred under argon. 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.33 g, 2.2 mmol, 1.7 equiv.) was added, followed by diphenyl phosphoryl azide (DPPA) (0.57 g, 2.2 mmol, 1.7 equiv.). Solution was placed under reflux at 65 °C overnight. The reaction completion was confirmed by TLC, quenched with saturated ammonium chloride, and extracted with CH₂Cl₂ (3 x 20 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (2% MeOH in CH₂Cl₂). Pure product is a brown fluffy solid (1.3 g, yield = 92%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.61 (s, 2H), 7.11-6.99 (m, 30H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.61-6.56 (m, 7H), 5.18 (s, 4H), 4.55 (t, *J* = 6.9 Hz, 4H), 4.24 (s, 2H), 3.91 (t, *J* = 5.7 Hz, 4H), 2.36 (q, *J* = 12 Hz, 4H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.6, 156.2, 143.8, 143.7, 140.2, 140.1, 137.7, 136.5, 132.4, 131.1, 131.0, 127.6, 127.4, 127.3, 126.2, 126.1, 126.0, 113.4, 107.3, 101.6, 67.7, 63.8, 61.8, 54.4, 47.0, 29.7, 25.4. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₇₁H₆₁N₉O₄: 1104.4847, found 1104.4927. IR (cm⁻¹): 3048, 2933, 2869, 2094, 1595, 1505, 1442, 1239, 1152, 1043, 697.

Synthesis of second-generation azido-functionalized TPE-conjugated dendron (9):

In a Schlenk flask, **6** (0.67 g, 0.30 mmol, 1.0 equiv.) was dissolved in 20 mL anhydrous THF and stirred under argon. DBU (76 mg, 0.50 mmol, 1.7 equiv.) was added, followed by DPPA (0.14 g, 0.50 mmol, 1.7 equiv.). Solution was placed under reflux at 65 °C overnight. The reaction completion was confirmed by TLC, quenched with saturated ammonium chloride, and extracted with CH₂Cl₂ (3 x 20mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (2% MeOH in CH₂Cl₂). Pure product is a brown fluffy solid (0.62 g, yield = 91%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.67 (s, 4H), 7.11-6.98 (m, 60H), 6.92 (d, *J* = 8.8 Hz, 8H), 6.68-6.53 (m, 17H), 5.19 (s, 8H), 5.00 (s, 4H), 4.59 (t, *J* = 6.9 Hz, 8H), 4.27 (s, 2H), 3.93 (t, *J* = 5.7 Hz, 8H), 2.38 (q, *J* = 12 Hz, 8H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.9, 159.5, 156.8, 143.8, 143.7, 143.5, 140.2, 140.1, 139.2, 136.4, 132.4, 131.2, 131.1, 127.6, 127.5, 126.2, 126.1, 123.2, 113.5, 107.2, 106.4, 101.7, 101.4, 69.7, 63.9, 61.9, 54.5, 47.1, 29.8. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₁₄₉H₁₂₇N₁₅O₁₀: 2289.9890, found 2289.9889. IR (cm⁻¹): 3050, 2950, 2870, 2096, 1594, 1505, 1444, 1241, 1154, 1045, 698.

Synthesis of third generation azido-functionalized TPE-conjugated dendron (10):

In a Schlenk flask, **7** (0.45 g, 9.7×10⁻² mmol, 1.0 equiv.) was dissolved in 20 mL anhydrous THF and stirred under argon. DBU (25 mg, 0.20 mmol, 1.7 equiv.) was added, followed by DPPA (46 mg, 0.20 mmol, 1.7 equiv.). Solution was placed under reflux at 65 °C overnight. The reaction completion was confirmed by TLC, quenched with saturated ammonium chloride, and extracted with CH₂Cl₂ (3 x 20 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (2% MeOH in CH₂Cl₂). Pure product is a brown fluffy solid (0.31 g, yield = 68%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.60 (s, 8H), 7.09-6.97 (m, 120H), 6.92 (d, *J* = 8.8 Hz, 16H), 6.66-6.51 (m, 37H), 5.18 (s, 16H), 4.96 (s, 12H), 4.53 (t, *J* = 6.9 Hz, 16H), 4.22 (s, 2H), 3.90 (t, *J* = 5.7 Hz, 16H), 2.34 (q, *J* = 12 Hz, 16H). ¹³C-NMR (150 MHz, CDCl₃, δ): 159.9, 159.5, 156.8, 143.9, 143.8, 143.6, 140.3, 140.2, 136.4, 132.5, 131.2, 131.1, 129.8, 127.7, 127.5, 126.3, 126.2, 126.1, 123.2, 120.0, 113.5, 106.4, 101.4, 69.7, 63.9, 61.9, 47.1, 29.8. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₃₀₅H₂₅₉N₂₇O₂₂: 4650.9978, found 4650.9982. IR (cm⁻¹): 3100, 2970, 2868, 2096, 1592, 1508, 1440, 1237, 1155, 1046, 699.

Synthesis of first-generation amphiphilic Janus dendrimer (AJD-G1):

In a vial, **11** (0.23 g, 0.40 mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **8** (0.50 g, 0.50 mmol, 1.3 equiv.) was dissolved in THF and added to the stirred solution.

Sodium ascorbate (83 mg, 0.40 mmol, 1.2 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (61 mg, 0.20 mmol, 0.70 equiv.) was separately dissolved in water and transferred to the solution, where the reaction stirred at room temperature for 24 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 10 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (10% MeOH in EtOAc). Pure product is a fluffy solid (0.53 g, yield = 86%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.72 (s, 3H), 7.28 (s, 2H), 7.14-6.98 (m, 30H), 6.92 (d, *J* = 8.6 Hz, 4H), 6.60 (d, *J* = 8.6 Hz, 7H), 5.42 (s, 4H), 5.12 (t, *J* = 6.0 Hz, 4H), 4.57 (t, *J* = 6.7 Hz, 4H), 4.20 (m, 6H), 3.91 (t, *J* = 5.4 Hz, 3H), 3.84 (t, *J* = 9.8 Hz, 4H), 3.74-3.61 (m, 21H), 3.53 (m, 6H), 3.36 (s, 9H), 2.39 (q, *J* = 12 Hz, 4H). ¹³C-NMR (150 MHz, CDCl₃, δ): 165.6, 159.6, 156.7, 152.0, 143.7, 143.6, 142.6, 140.1, 140.0, 136.7, 136.3, 132.3, 131.1, 131.0, 127.5, 127.4, 126.2, 126.1, 126.0, 124.3, 113.4, 108.9, 107.2, 101.7, 72.2, 71.6, 70.5, 70.4, 70.3, 70.2, 70.1, 69.3, 68.7, 63.8, 61.6, 58.7, 57.8, 47.1, 29.6. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₁₀₂H₁₁₁N₉O₁₈: 1749.8047, found 1749.8086. IR (cm⁻¹): 2800, 2642, 2621, 1461, 1344, 1255, 1178, 991, 852, 447.

Synthesis of second-generation amphiphilic Janus dendrimer (AJD-G2):

In a vial, **11** (0.11 g, 0.20 mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **9** (0.50 g, 0.20 mmol, 1.3 equiv.) was dissolved in THF and added to the stirred solution. Sodium ascorbate (40 mg, 0.20 mmol, 1.2 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (29 mg, 0.10 mmol, 0.70 equiv.) was separately dissolved in water and transferred to the solution, where the reaction stirred at room temperature for 24 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 10 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (10% MeOH in EtOAc). (0.34 g, yield = 70%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.69 (s, 5H), 7.35 (s, 2H), 7.12-7.01 (m, 60H), 6.94 (d, *J* = 8.6 Hz, 8H), 6.62 (d, *J* = 8.6 Hz, 17H), 5.46 (s, 4H), 5.19 (t, *J* = 6.0 Hz, 8H, triazole-CH₂), 4.96 (s, 4H, Ar-O-CH₂), 4.59 (t, *J* = 6.7 Hz, 8H, Ar-O-CH₂), 4.22 (m, 6H), 3.93 ppm (t, *J* = 5.4 Hz, 3H), 3.87 (t, *J* = 9.8 Hz, 8H), 3.85-3.63 (m, 21H), 3.54 (m, 6H), 3.39 (s, 9H), 2.43 ppm (q, *J* = 12 Hz, 8H). ¹³C-NMR (150 MHz, CDCl₃, δ): 165.7, 160.0, 159.4, 156.7, 152.1, 143.7, 143.6, 143.0, 140.2, 140.0, 139.0, 136.3, 132.4, 131.1, 131.0, 127.6 ppm, 127.5, 127.4, 126.2, 126.1, 126.0, 124.3, 114.0, 109.0, 107.1, 106.3, 102.1, 100.9, 72.2, 71.7, 70.6, 70.5, 70.4, 70.3, 69.4, 68.7, 63.8, 58.8, 47.4, 29.7. HRMS (EI, *m/z*): [M+H]⁺ calculated for C₁₈₀H₁₇₇N₁₅O₂₄: 2932.3091, found 2932.3069. IR (cm⁻¹): 3047, 2919, 2867, 1594, 1508, 1446, 1243, 1148, 1044, 695.

Synthesis of third-generation amphiphilic Janus dendrimer (AJD-G3):

In a vial, **11** (23 mg, 3.6×10^{-2} mmol, 1.0 equiv.) was dissolved in 10 mL THF. Separately, **28** (0.22 g, 4.7×10^{-2} mmol, 1.3 equiv.) was dissolved in THF and added to the stirred solution. Sodium ascorbate (8.6 mg, 4.3×10^{-2} mmol, 1.2 equiv.) was dissolved in 2 mL water and transferred to the solution. Lastly, copper sulfate (6.3 mg, 2.5×10^{-2} mmol, 0.70 equiv.) was separately dissolved in water and transferred to the solution, where the reaction stirred at room temperature for 24 hours. After the reaction was completed, THF was removed by rotary evaporation. Product was dissolved in water/CH₂Cl₂, extracted with CH₂Cl₂ (3 x 10 mL), and the accumulated organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. Crude product was purified by column (10% MeOH in EtOAc). (0.11 g, yield = 60%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.62 (s, 9H), 7.32 (s, 2H), 7.09-6.90 (m, 120H), 6.63 (d, $J = 8.6$ Hz, 16H), 6.49 (d, $J = 8.6$ Hz, 37H), 5.40 (s, 4H), 5.13 (t, $J = 6.0$ Hz, 16H), 4.92 (d, $J = 11$ Hz, 12H), 4.51 (t, $J = 6.7$ Hz, 16H), 4.22 (m, 6H), 3.88 (t, $J = 5.4$ Hz, 3H), 3.83 (t, $J = 9.8$ Hz, 16H), 3.81-3.60 (m, 21H), 3.52 (m, 6H), 3.35 (s, 9H), 2.32 (q, $J = 12$ Hz, 16H). ¹³C-NMR (150 MHz, CDCl₃, δ): 165.9, 160.2, 160.0, 159.6, 156.9, 151.9, 143.9, 143.8, 140.3, 140.2, 136.5, 132.6, 131.4, 131.3, 127.7, 127.6, 127.5, 126.4, 126.3, 126.2, 113.6, 109.1, 107.3, 106.5, 102.0, 101.7, 101.4, 72.4, 71.9, 70.8, 70.6, 70.5, 70.4, 69.6, 68.9, 64.0, 62.3, 59.0, 47.4, 29.9. HRMS (EI, m/z): [M+H]⁺ calculated for C₃₃₆H₃₀₉N₂₇O₃₆: 5297.3179, found 5297.3188. IR (cm⁻¹): 3048, 2921, 2874, 1598, 1500, 1441, 1238, 1147, 1040, 700.

Self-assembly procedure:

(a) Self-assembly under thermodynamic control

Water and dimethyl sulfoxide (DMSO) were filtered using 0.2 μ m filters (PTFE and TF filters, respectively) before proceeding to the self-assembly. A solution of the amphiphilic Janus dendrimer (AJD) was prepared at a concentration of 205 μ M in DMSO (250 μ L). Water (2.75 mL) was then added dropwise into the DMSO solution of the AJD while stirring vigorously. The final concentration of the nano-assemblies was 17 μ M. Each sample was then stirred overnight at room temperature and then dialyzed against deionized (DI)-water with three dialysate changes to remove the organic solvent using a 12-14K MWCO membrane.

(b) Kinetic control

Water and DMSO were filtered with 0.2 μ m filters (PTFE and TF filters, respectively) before proceeding to the self-assembly. A solution of the amphiphilic Janus dendrimer (AJD) was prepared at a concentration of 205 μ M in DMSO (250 μ L). The AJD solution was then added rapidly into 2.75 mL of DI-water with vigorous stirring. The final concentration of the nano-assemblies was 17 μ M. Each sample was then stirred overnight

at room temperature and then dialyzed against DI-water with three dialysate changes) to remove the organic solvent using a 12-14K MWCO membrane.

Fluorescence quantum yield (QY) measurement:

A solution of 9,10-diphenylanthracene at a concentration of 1 µg/mL in ethanol ($n_d = 1.361$)⁴ was used as the reference for the determination of the fluorescence quantum yield of the dendrimersomes. The quantum yield of 9,10-diphenylanthracene in the above-mentioned conditions is 0.96 based on the literature.¹ The fluorescence quantum yields of the dendrimersomes (AJD-G1, AJD-G2, and AJD-G3 under thermodynamic control as well as the AJD-G1 under kinetic control) were measured at a concentration of 1 µM in water ($n_d = 1.343$)⁵ in order to respect the 0.1 absorbance of the maximum for each generation. Solutions of the dendrimersomes at the concentration of 1 µM were prepared from their initial self-assembled samples at a concentration of 17 µM in DI-water. The fluorescence spectra of the dendrimersome solutions and the reference were measured using 354 nm as the excitation wavelength in presence of a 2% filter. The fluorescence quantum yield of each dendrimersomes was calculated using this equation:

$$\Phi_{sample} = \Phi_{ref} \times \frac{n_{sample}^2}{n_{ref}^2} \times \frac{F_{sample}}{F_{ref}} \times \frac{A_{ref}}{A_{sample}}$$

Φ : Fluorescence quantum yield of substance

n : Refractive index at 20 °C

F : Integrated fluorescence intensity (area under spectrum)

A : Absorbance at 354 nm

Critical aggregation concentration (CAC) measurement:

The self-assembly procedure under thermodynamic control was repeated for each AJD at an initial concentration of 25 µM. The newly formed assemblies were then purified by dialysis against DI-water with three dialysate changes using a 12-14K MWCO membrane. The optical transmittance spectrum was obtained for the initial solution (25 µM) in water and then at each subsequent series of dilutions until reaching the desired concentration. The CAC was then calculated after plotting the optical transmittance at 500 nm versus the concentration of the AJDs. Same procedure was repeated for the assemblies based on AJD-G1 obtained under kinetic control.

Solvent-composition dependent AIE behaviour of the AJDs:

The solvent-composition dependent photoluminescence (PL) profile of all dendrimersomes was determined at a concentration of 17 µM in a mixture of H₂O/DMSO of varying

compositions. All fluorescence spectra were obtained using 320 nm as the excitation wavelength and collected from 390 nm to 650 nm. Fluorescence spectra were collected at different water contents starting at 0% up to 100% with increments of 5% from up to 30% followed by increments of 10% from 30% up to 100%, resulting in 14 fluorescence spectra.

Table S1: Summary of SEC and DSC analysis for each dendron/dendrimer.

Dendron/Dendrimer	M_n (g/mol)	\mathcal{D}	T_g (°C)
G1-N ₃ (8)	1600	1.07	72
AJD-G1	2200	1.08	25
G2-N ₃ (9)	2500	1.12	102
AJD-G2	3300	1.01	58
G3-N ₃ (10)	4400	1.14	99
AJD-G3	4700	1.08	77

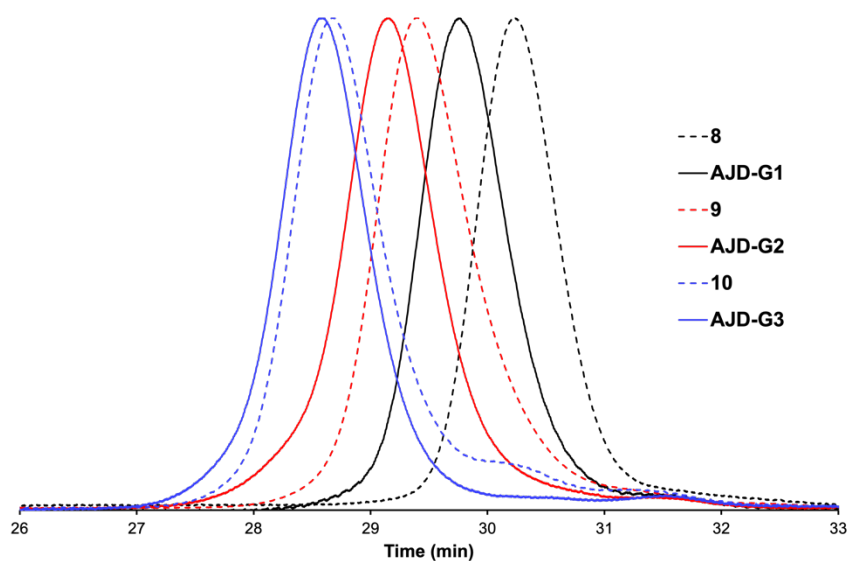


Fig. S1 SEC refractive index (RI) traces of TPE-conjugated dendrons (dashed lines) and amphiphilic Janus dendrimers (solid lines).

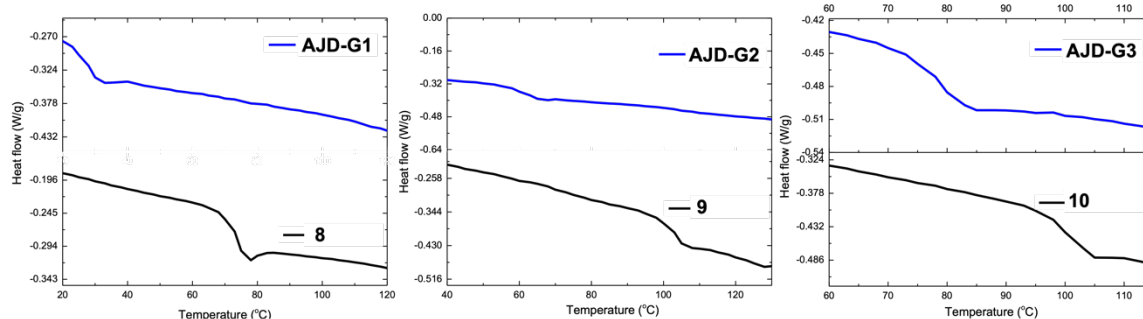


Fig. S2 DSC analysis of dendrons **8-10** and AJDs-G1-3.

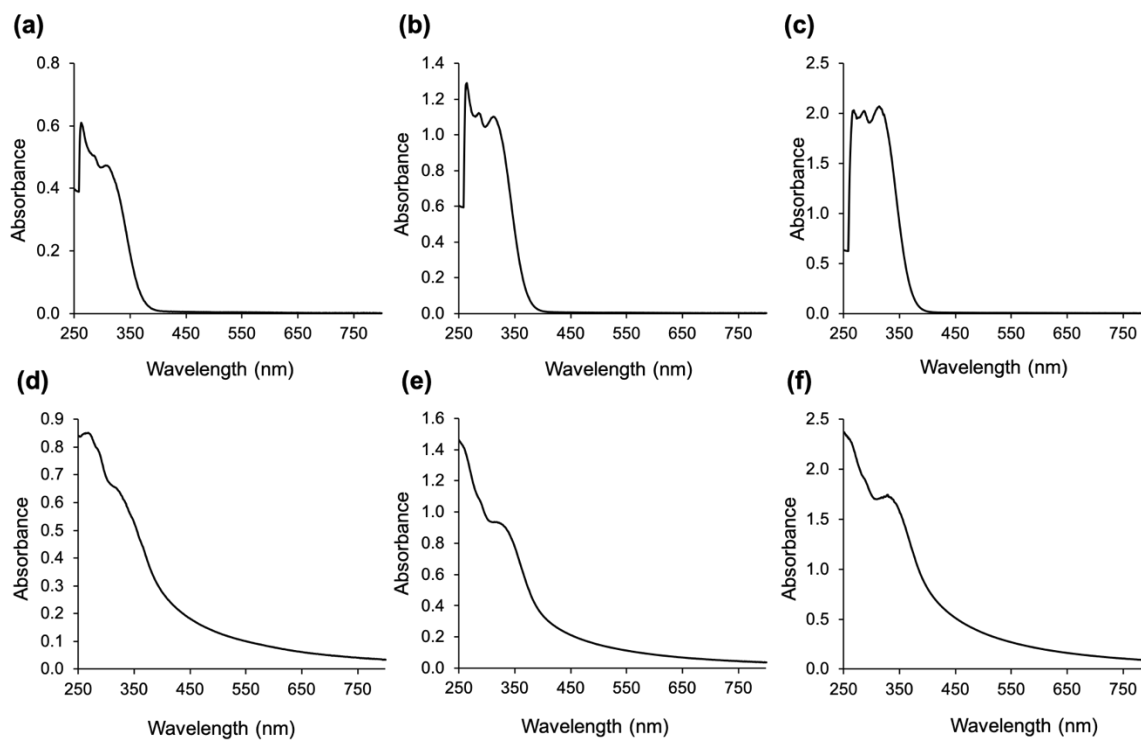


Fig. S3 (a-c) UV-vis absorption spectra of AJDs G1-3 in DMSO (17 μ M), respectively. (d-f) UV-vis absorption of AJDs G1-3 after dilution in DI-water (17 μ M), respectively.

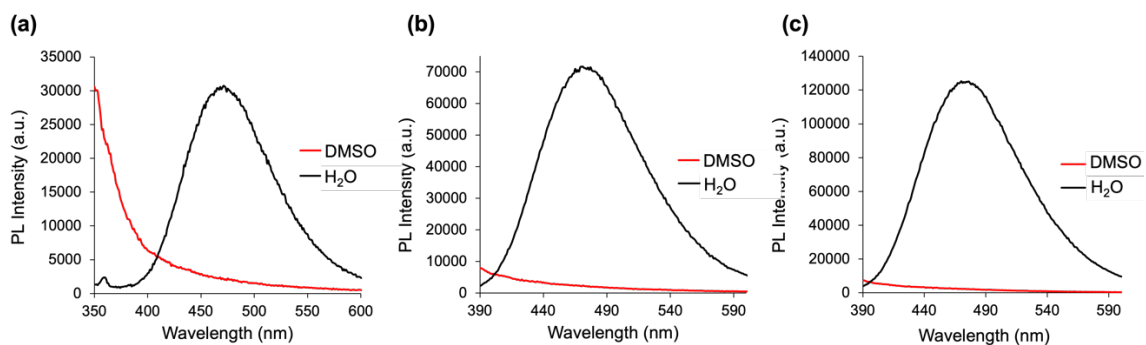


Fig. S4 PL spectra of (a) AJD-G1, (b) AJD-G2, and (c) AJD-G3 in DMSO and DI-water at the concentration of 17 μM .

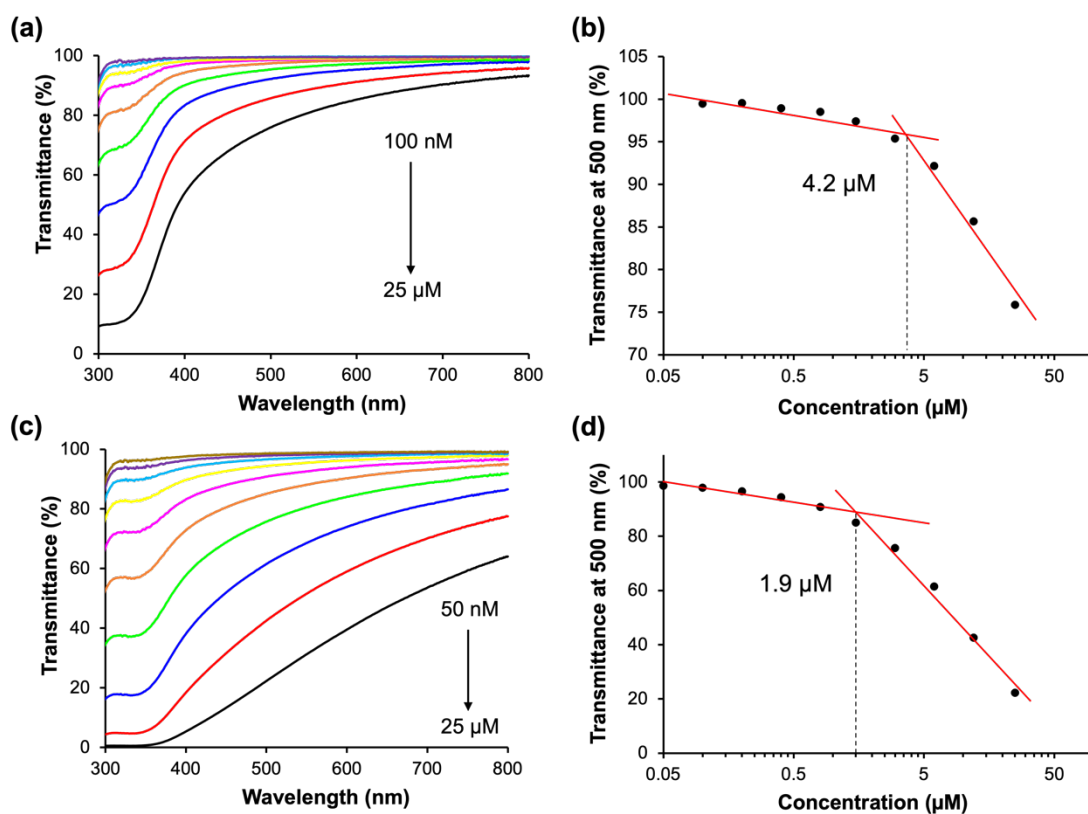


Fig. S5 (a) Concentration-dependent optical transmittance spectra and (b) its evolution at 500 nm of AJD-G1 in DI-water. (c) Concentration-dependent optical transmittance spectra and (d) its evolution at 500 nm of AJD-G2 in DI-water.

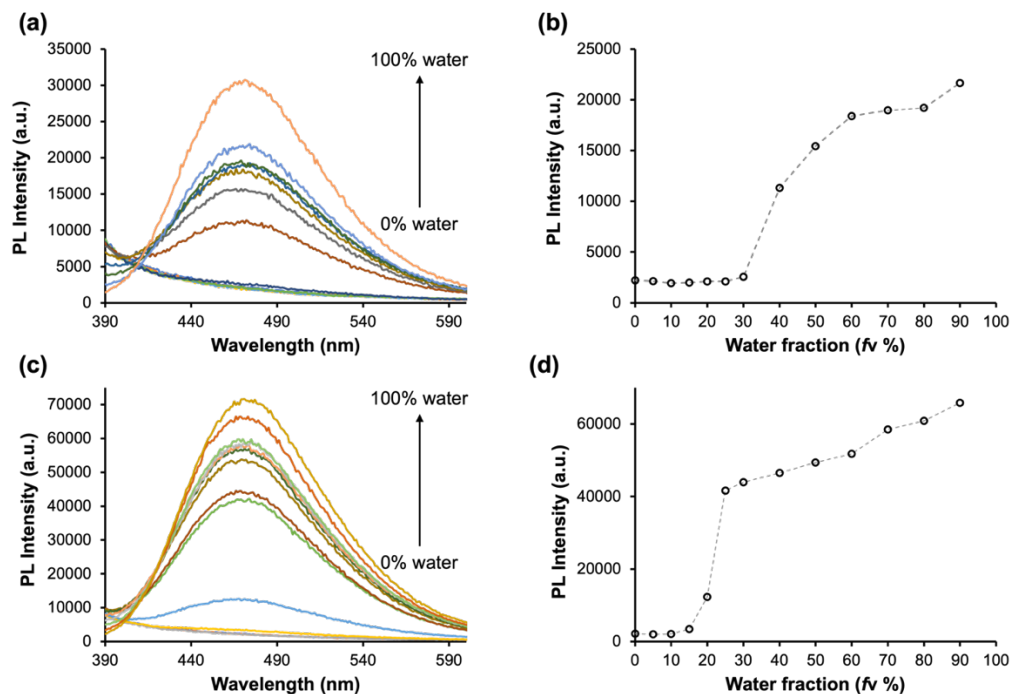


Fig. S6 (a) PL spectra of AJD-G1 (17 μ M) in DMSO/H₂O mixtures with varying water fractions. (b) Evolution of PL intensity of AJD-G1 at 474 nm as a function of water content in DMSO/H₂O mixtures. (c) PL spectra of AJD-G2 (17 μ M) in DMSO/H₂O mixtures with varying water fractions. (d) Evolution of PL intensity of AJD-G2 at 474 nm as a function of water content in DMSO/H₂O mixtures. Excitation wavelength: 320 nm in (c) and (d).

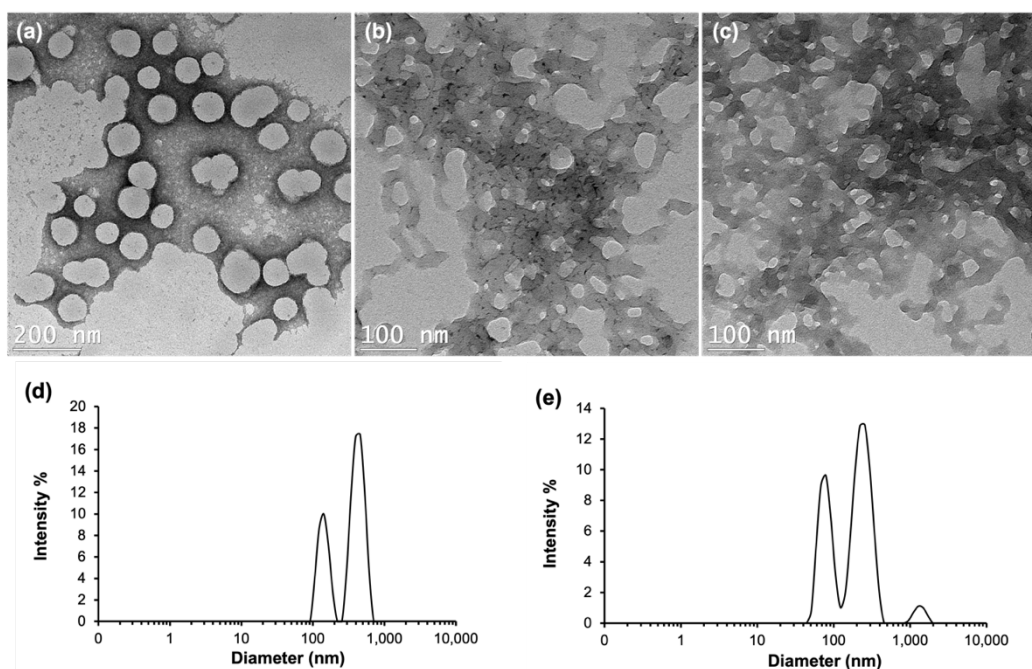


Fig. S7 Supplementary TEM images of assemblies formed by (a) AJD-G1, (b) AJD-G2, and (c) AJD-G3 under kinetic control. DLS size distribution of assemblies formed by AJD-G2 (d) and AJD-G3 (e).

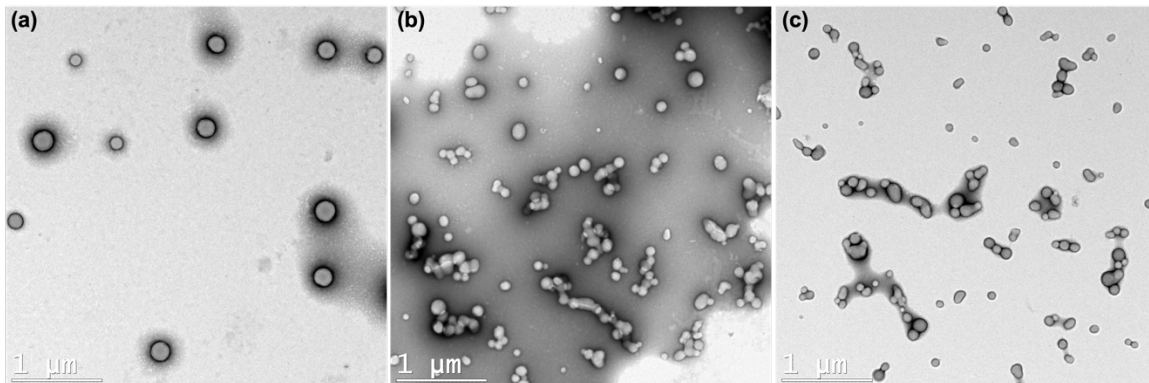


Fig. S8 Supplementary TEM images of assemblies formed by (a) AJD-G1, (b) AJD-G2, and (c) AJD-G3 under thermodynamic control.

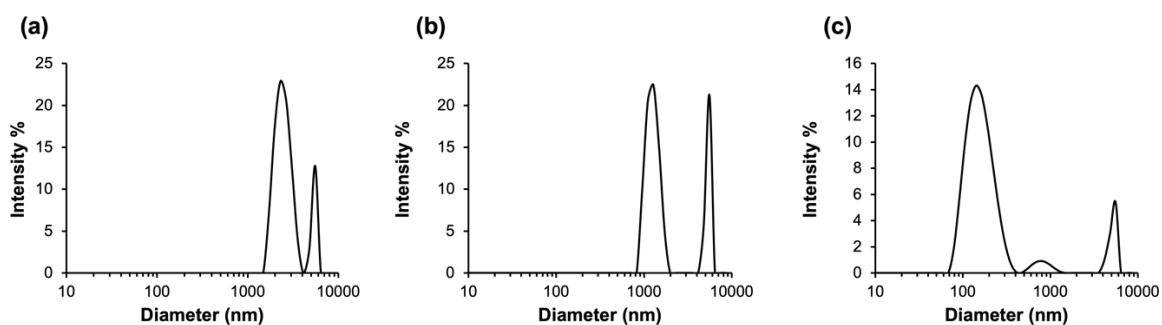


Fig. S9 DLS size distribution of macroscopic aggregates formed by **8** (a), **9** (b), and **10** (c) under thermodynamic control highlighting the importance of the hydrophilic block in the AJDs to in the formation and stabilization of dendrimersomes.

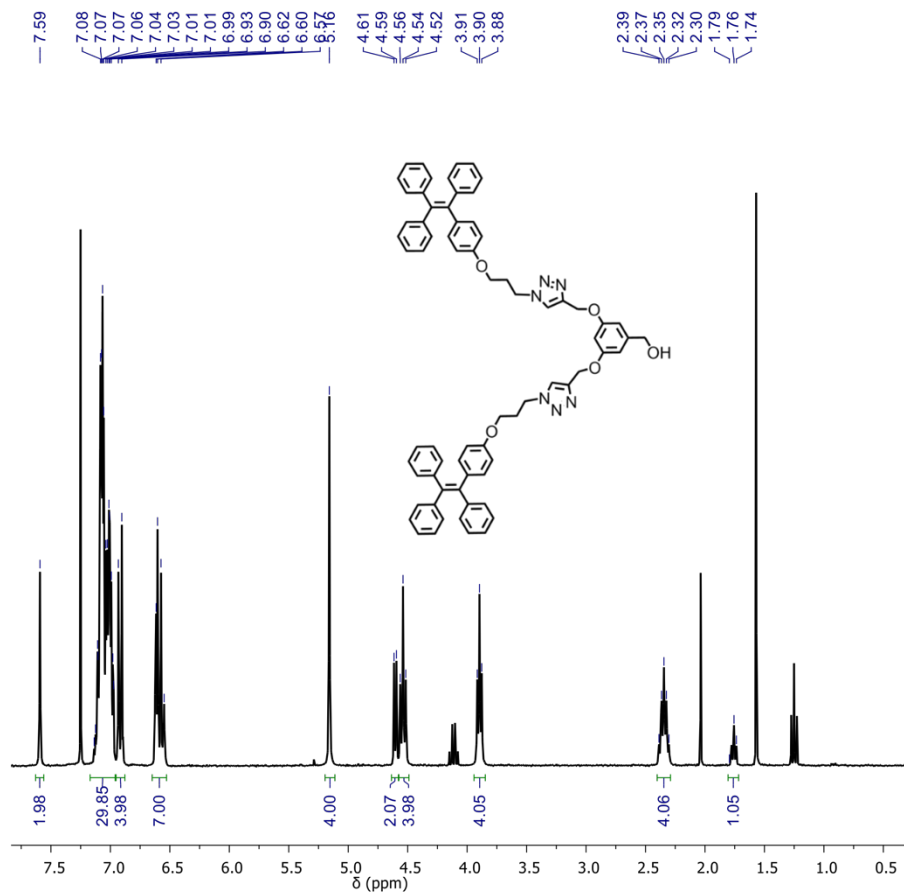


Fig. S10 ^1H NMR spectrum of compound **5** (300 MHz, CDCl_3).

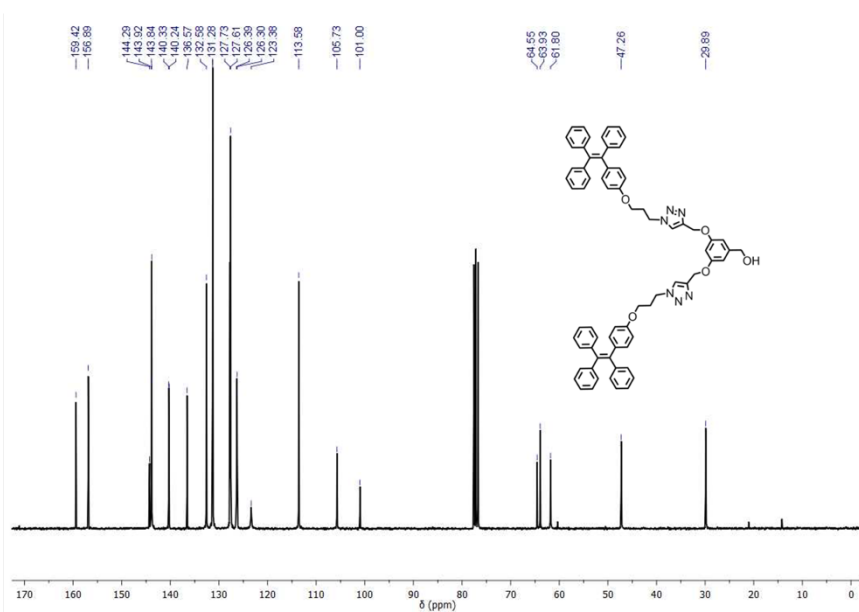


Fig. S11 ^{13}C NMR spectrum of compound **5** (75 MHz, CDCl_3).

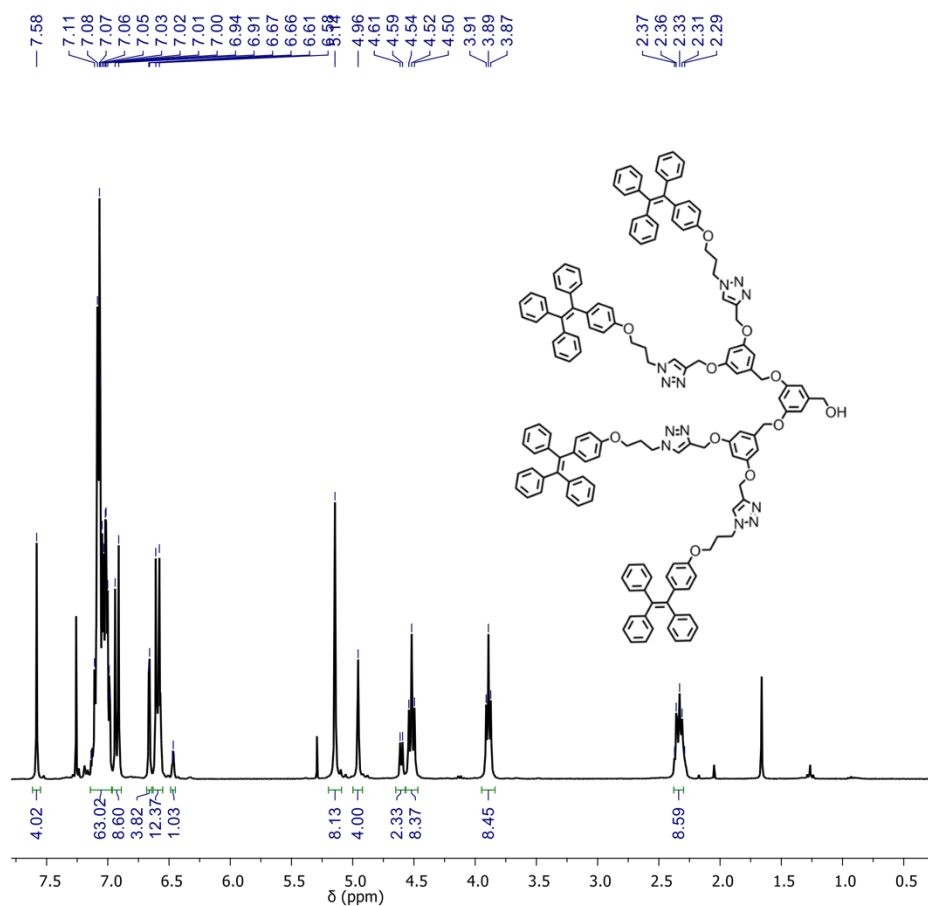


Fig. S12 $^1\text{H NMR}$ spectrum of compound 6 (300 MHz, CDCl_3).

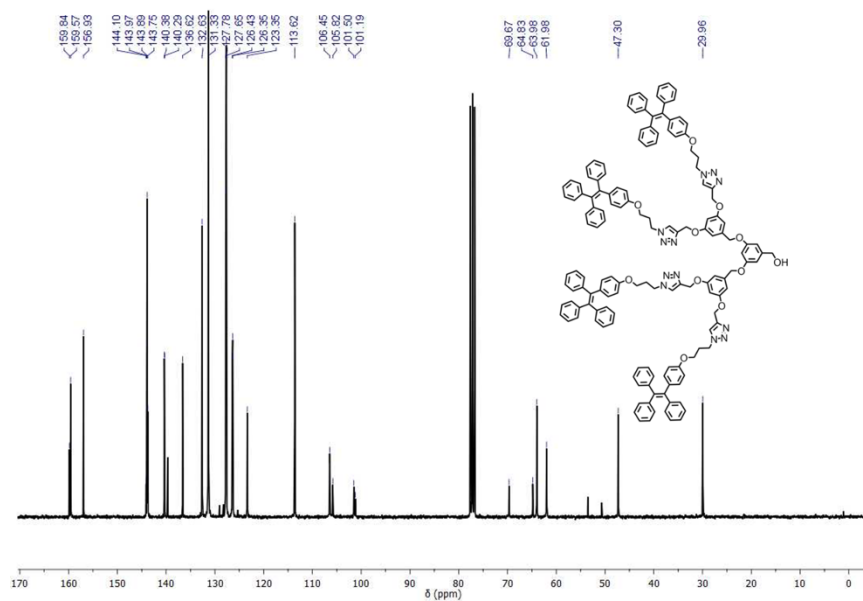


Fig. S13 $^{13}\text{C NMR}$ spectrum of compound 6 (75 MHz, CDCl_3).

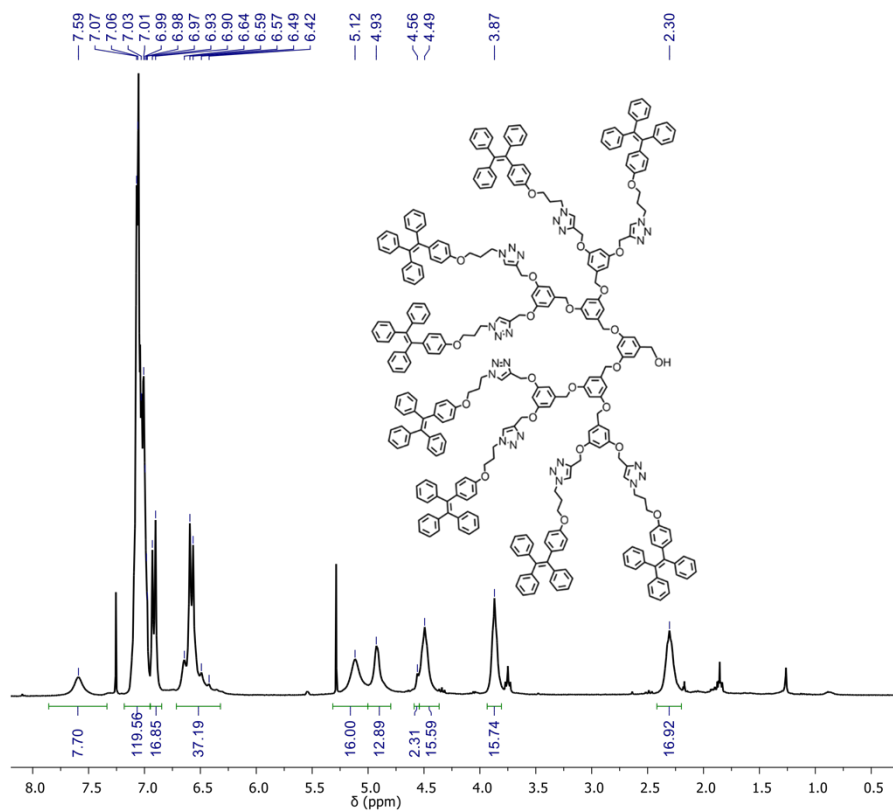


Fig. S14 ^1H NMR spectrum of compound 7 (300 MHz, CDCl_3).

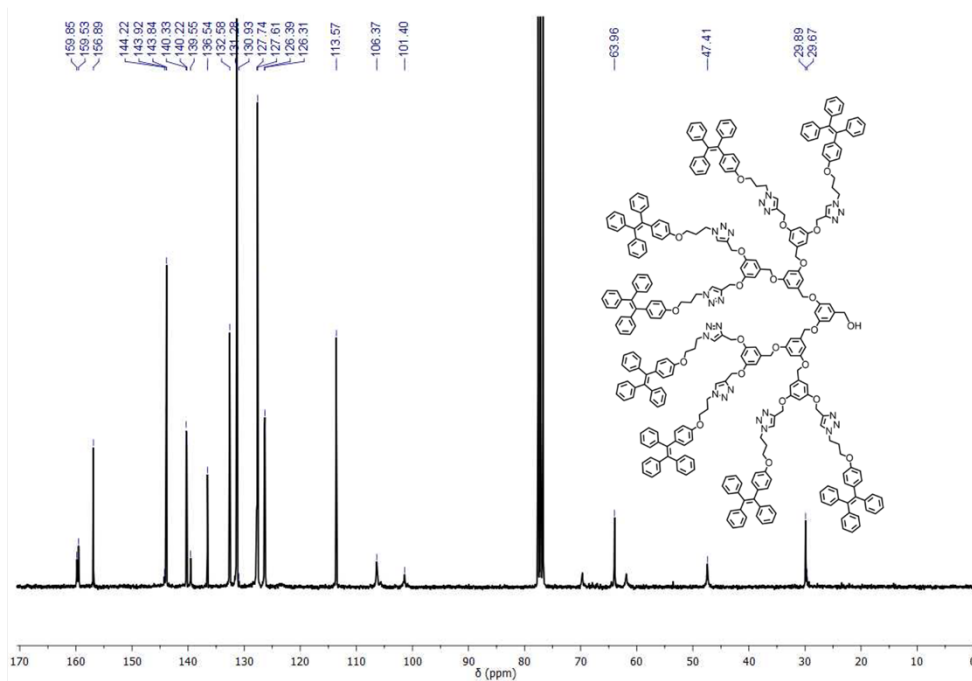


Fig. S15 ^{13}C NMR spectrum of compound 7 (75 MHz, CDCl_3).

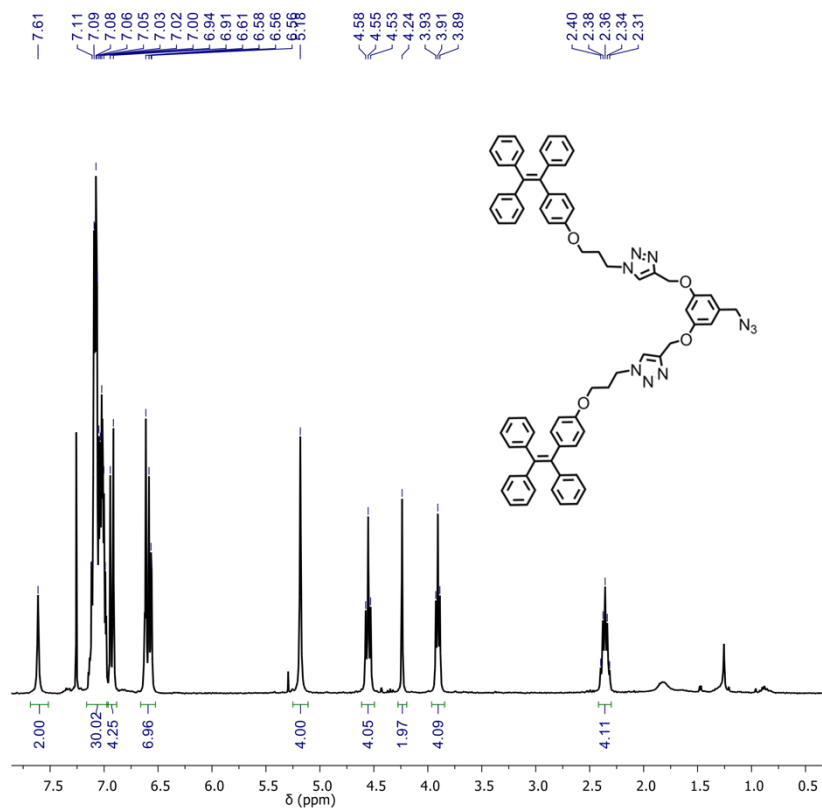


Fig. S16 ^1H NMR spectrum of compound **8** (300 MHz, CDCl_3).

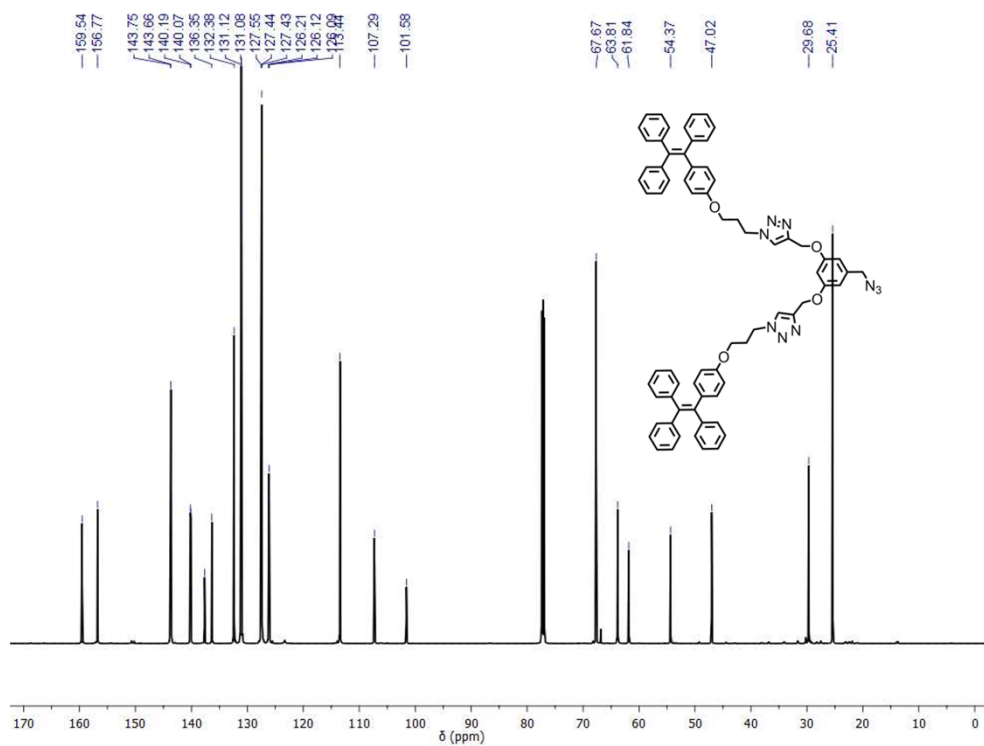


Fig. S17 ^{13}C NMR spectrum of compound **8** (75 MHz, CDCl_3).

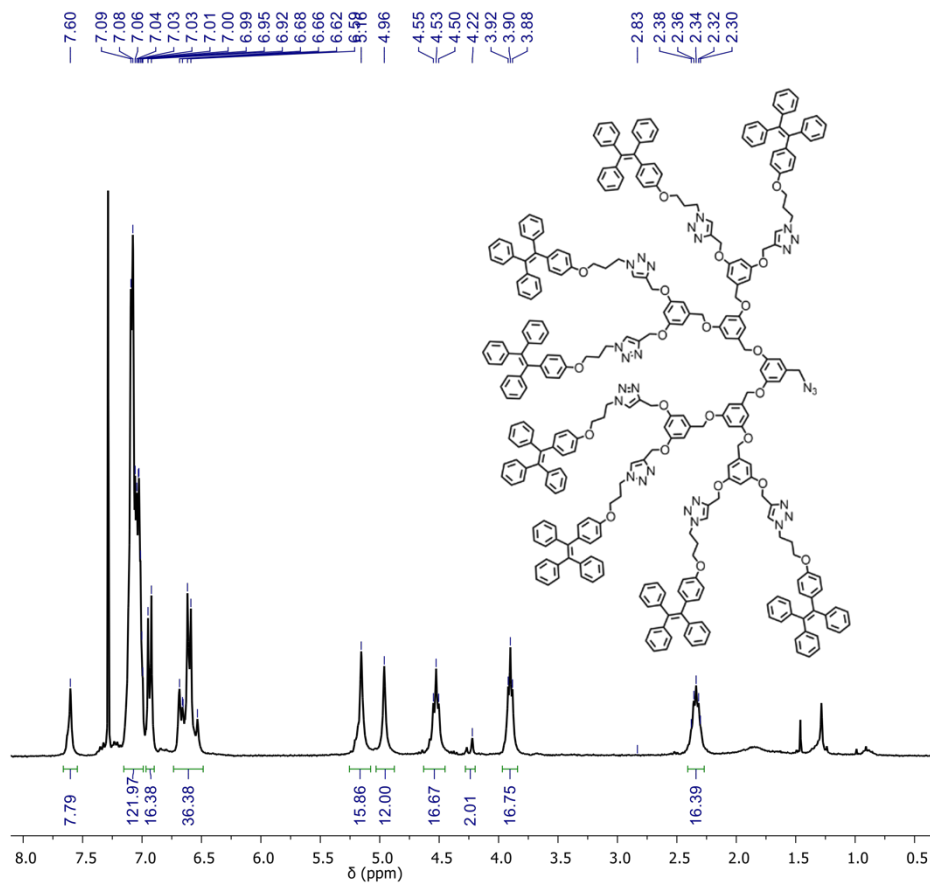


Fig. S20 ^1H NMR spectrum of compound **10** (300 MHz, CDCl_3).

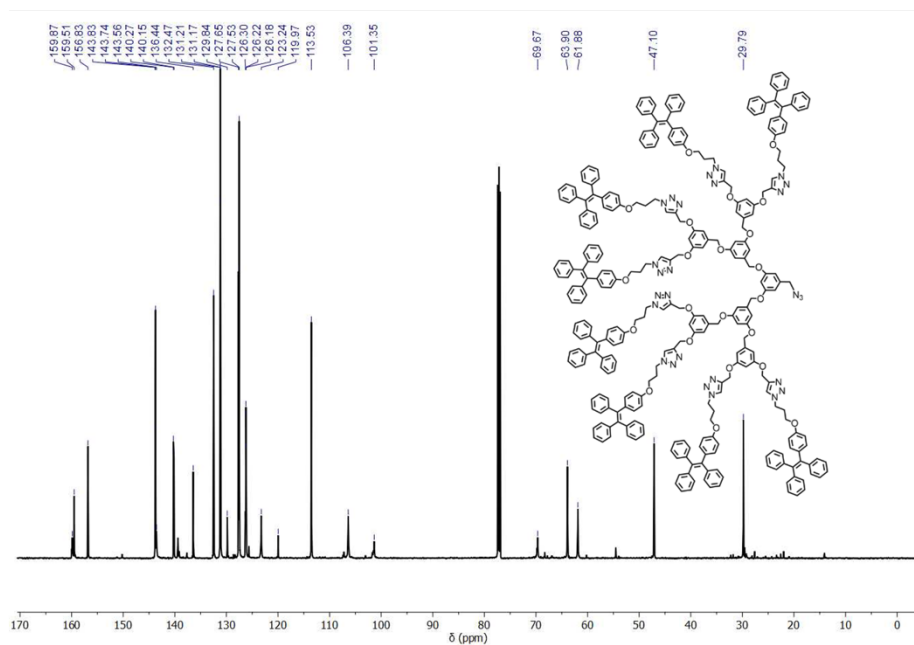


Fig. S21 ^{13}C NMR spectrum of compound **10** (75 MHz, CDCl_3).

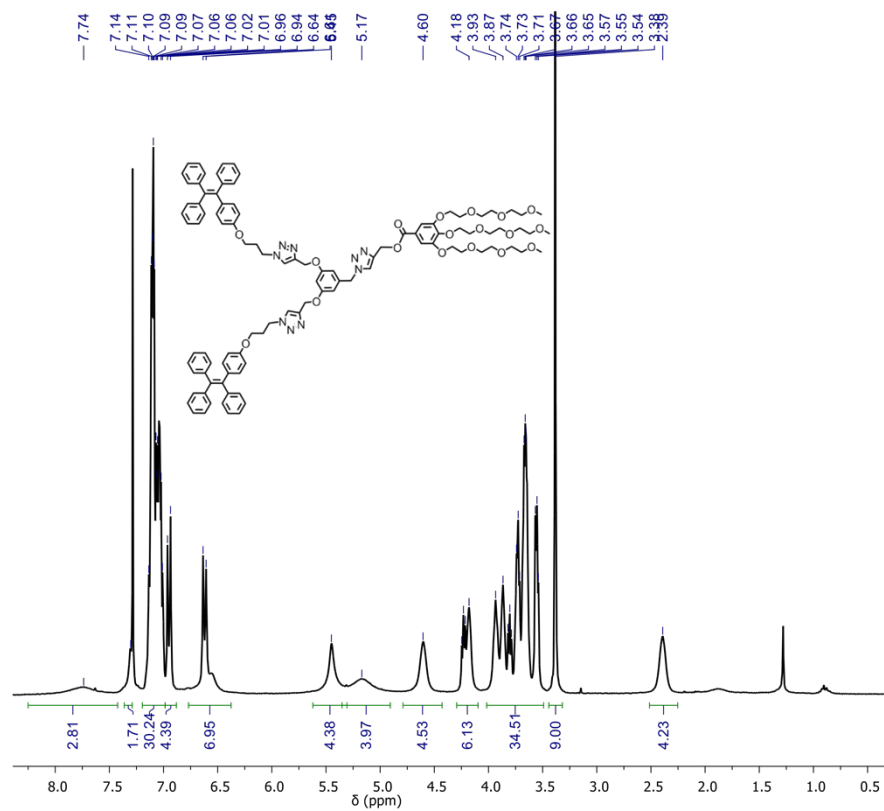


Fig. S22 ^1H NMR spectrum of **AJD-G1** (300 MHz, CDCl_3).

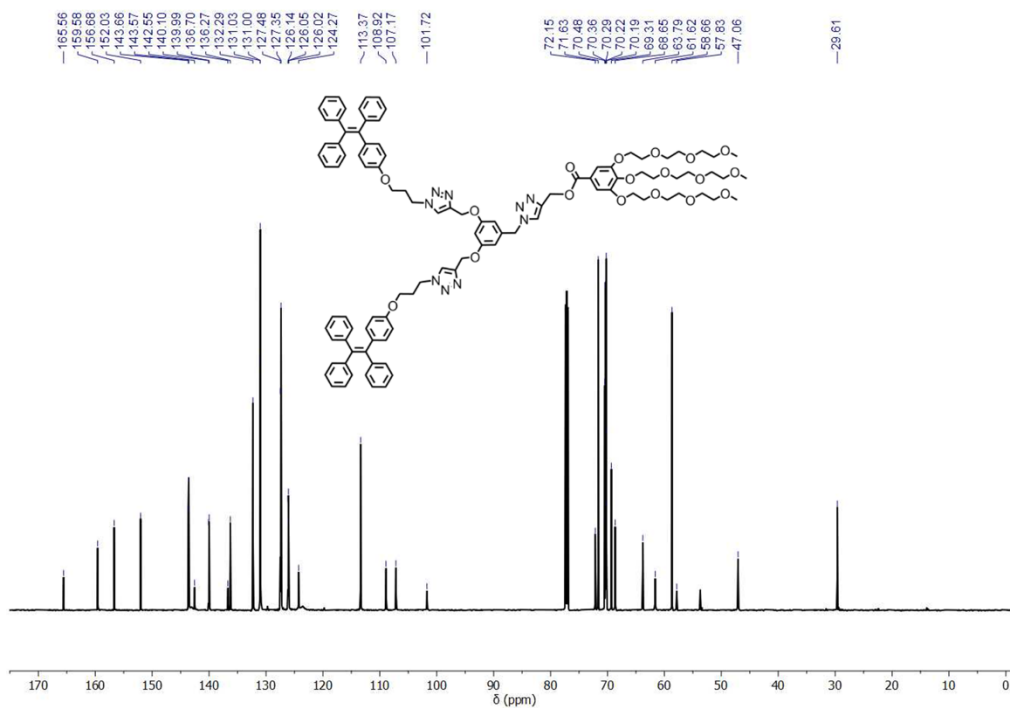


Fig. S23 ^{13}C NMR spectrum of **AJD-G1** (75 MHz, CDCl_3).

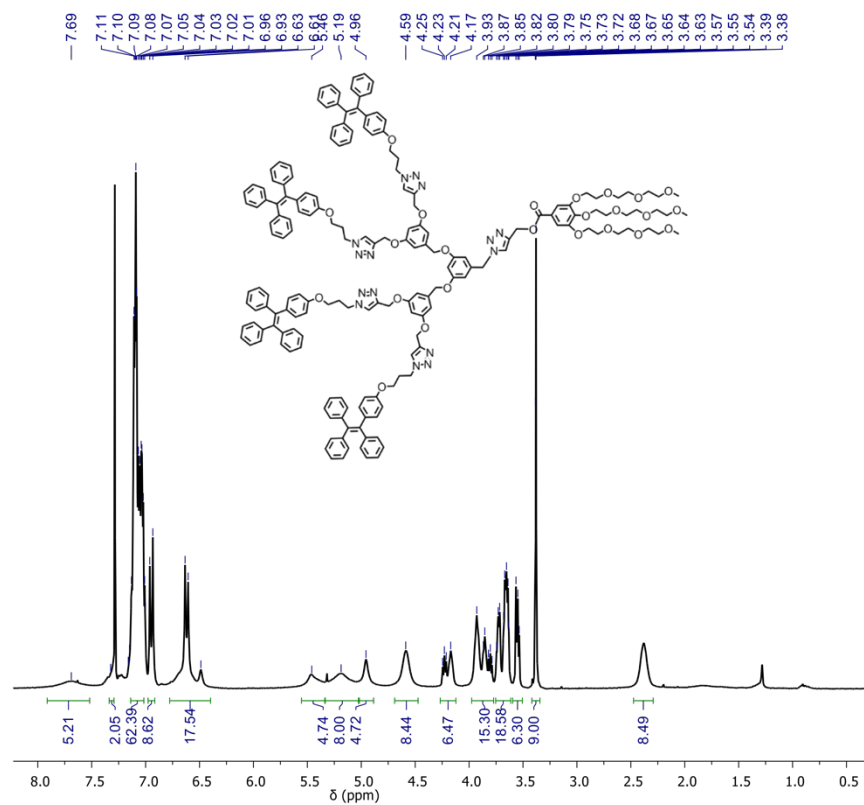


Fig. S24 ^1H NMR spectrum of AJD-G2 (300 MHz, CDCl_3).

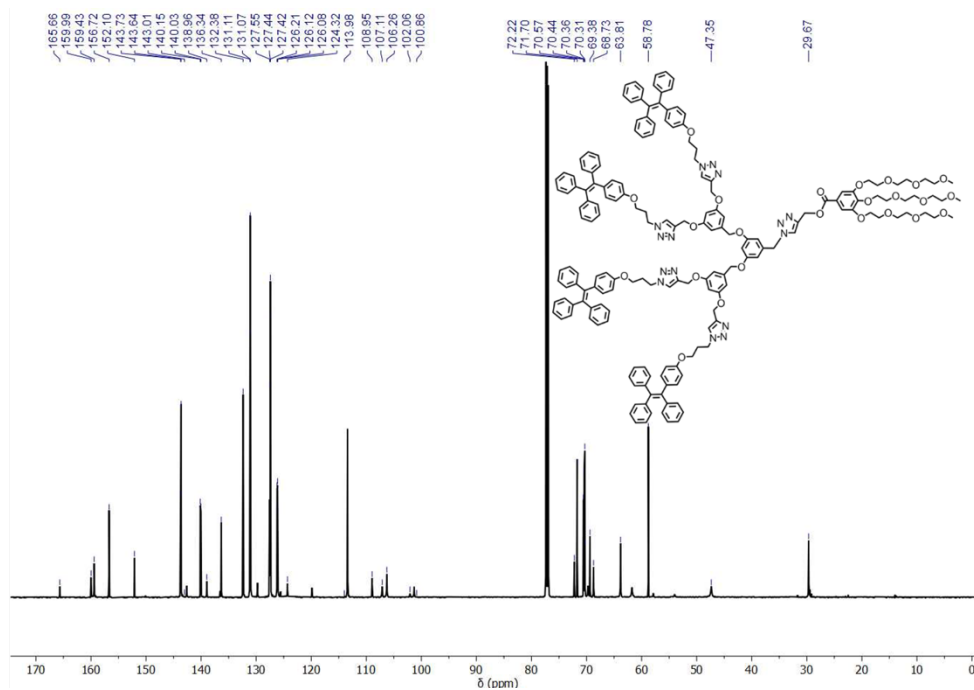


Fig. S25 ^{13}C NMR spectrum of AJD-G2 (75 MHz, CDCl_3).

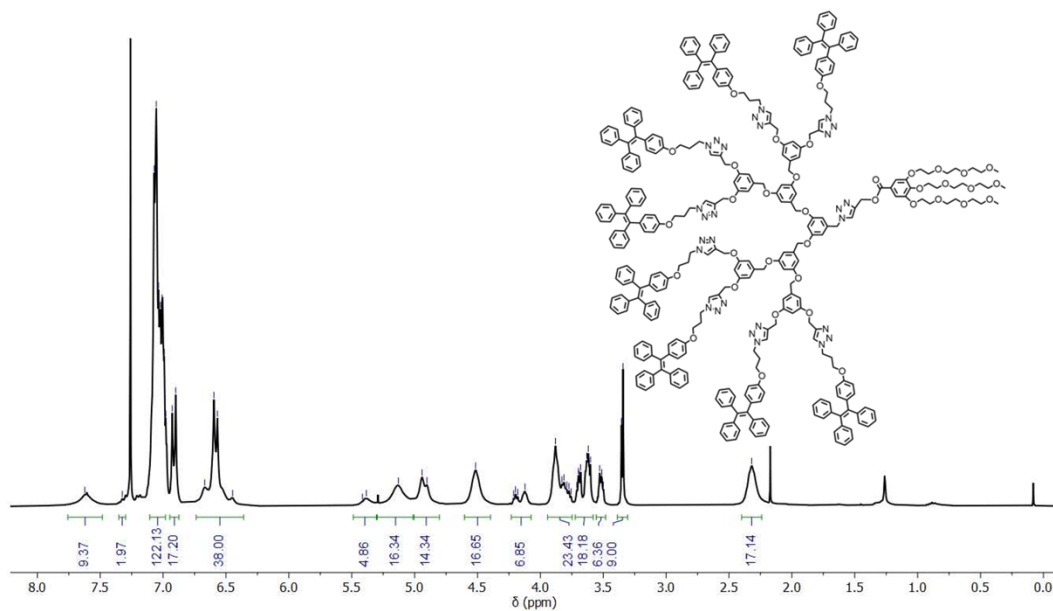


Fig. S26 ^1H NMR spectrum of AJD-G3 (300 MHz, CDCl_3).

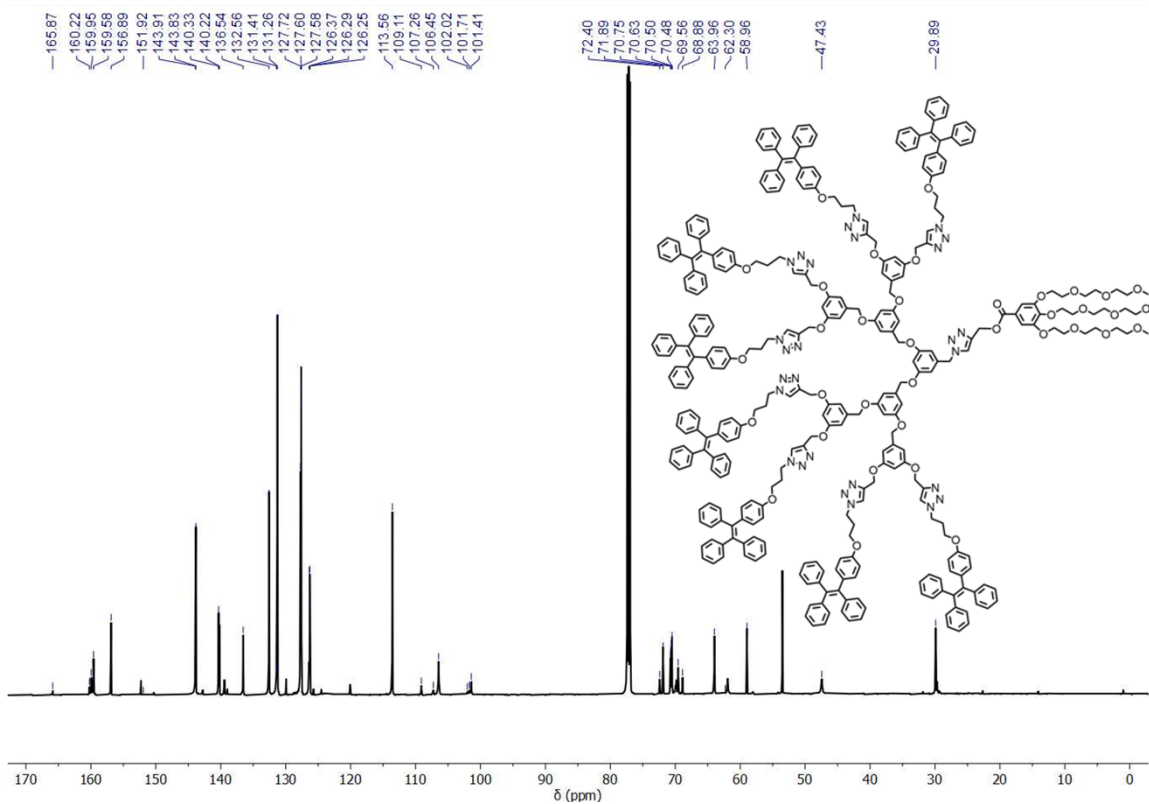


Fig. S27 ^{13}C NMR spectrum of AJD-G2 (75 MHz, CDCl_3).

References:

- (1) M. Malkoch, K. Schleicher, E. Drockenmuller, C. J. Hawker, T. P. Russell, P. Wu and V. V. Fokin, *Macromolecules*, 2005, **38**, 3663-3678.
- (2) R. Singh, A. K. Dwivedi, A. Singh, C.-M. Lin, R. Arumugaperumal, K.-H. Wei and H.-C. Lin, *ACS Appl. Mater. Interfaces*, 2016, **8**, 6751-6762.
- (3) F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung and L.-Z. Wu, *Angew. Chem., Int. Ed.*, 2011, **50**, 3193-3197.
- (4) H. Lu, F. Su, Q. Mei, Y. Tian, W. Tian, R. H. Johnson and D. R. Meldrum, *J. Mater. Chem.* 2012, **22**, 9890–9900.
- (5) D. Masahiko and M. Akira, *Appl. Opt.* 2007, **46**, 3811-20