Supporting Information For

A Self-Crosslinking Supramolecular Polymer Network Enabled by Crown Ether-Based Molecular Recognition

Lei Wang[+,†], Lin Cheng[+,†], Guangfeng Li[+,†], Kai Liu[†], Zhaoming Zhang[†], Peitong Li[†], Shengyi Dong[‡], Wei Yu[*,†], Feihe Huang[*,§], and Xuzhou Yan[*,†]

[†]*School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China*

[‡]*College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China.*

[§]*State Key Laboratory of Chemical Engineering, Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China*

[+]*These authors contributed equally to this work.*

Email addresses: wyu@sjtu.edu.cn; fhuang@zju.edu.cn; xzyan@sjtu.edu.cn

Table of contents

1. Materials and methods

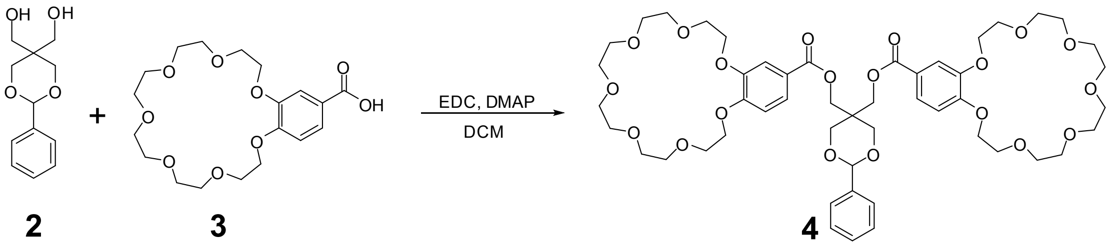
All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds **2**[S1], **3**[S2] and **9**[S2] were prepared according to the literature procedures. NMR spectra were recorded with a Bruker Avance DMX 400 and 500 spectrophotometers with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Viscosity measurements were performed with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in CH_3CN. Monomer **1** was measured with a 0.30 mm inner diameter viscometer. The thermal stability analysis was conducted using a TA Instruments Q500 Thermogravimetric analyzer (TGA) under the nitrogen. Each sample (~5 mg) was heated from 50 to 800 °C with a rate of 20 °C min^{-1}. Transition temperatures of materials determined on a TA Instruments Q2000 differential scanning calorimetry (DSC) under the nitrogen. Each sample (~5 mg) was heated from −70 to 150 °C with a rate of 20 °C min^{-1}. Scanning Electron Microscopy (SEM) images were recorded on a Phenom Pro under vacuum. Rheological experiments were carried out using a TA Instruments ARES G2 stress-controlled rheometer with an 8 mm parallel plate attachment. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on a Thermo-iCAP 7600 Series instrument.

Xerogel preparation for SEM: the concentrated (80 mM) SPN solution was dropped on silicon slice, which was then frozen in liquid nitrogen about 1 hour before drying under vacuum overnight to generate the xerogel sample for SEM test.

Film preparation for rheological property test: SPN powder was filled in the rounded mold, and then was heated at 70 °C to form viscous fluids. After cooling to ambient temperature, the rounded film was prepared. The same procedure was used to prepare other shaped films.

2. *Synthesis of monomer 1*

*2.1. Synthesis of compound **4***



2 **3** **4**

A solution of **2** (2.80 g, 12.5 mmol), **3** (15.0 g, 37.5 mmol), and 4-dimethylaminopyridine (DMAP) (1.53 g, 12.5 mmol) in dichloromethane (300 mL) was stirred for 10 minutes at 0 °C. To this solution was added *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC) (4.79 g, 25.0 mmol). The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a pale yellow oil, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v*/*v*) to afford **4** as a colorless oil (9.78 g, 79%). The ^{1}H NMR spectrum of **4** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.55 (d, J = 7 Hz, 2H), 7.41–7.48 (m, 4H), 7.26–7.33 (m, 3H), 6.75–6.82 (m, 2H), 5.44 (s, 1H), 4.73 (s, 2H), 4.24 (d, J = 9 Hz, 2H), 4.17 (s, 2H), 4.09–4.16 (m, 8H), 3.95 (d, J = 9 Hz, 2H), 3.81–3.89 (m, 8H), 3.70–3.76 (m, 8H), 3.63–3.69 (m, 8H), 3.56–3.62 (m, 12H). The ^{13}C NMR spectrum of **4** is shown in Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$, room temperature) δ (ppm): 28.67, 36.80, 62.00, 62.75, 68.06, 68.09, 68.30, 68.44, 68.61, 68.77, 69.56, 69.97, 70.04, 70.08, 70.17, 70.28, 101.22, 111.25, 111.29, 113.60, 113.69, 121.06, 121.59, 122.93, 123.00, 125.13, 127.37, 128.18, 136.65, 147.32, 147.42, 152.10, 152.32, 164.84, 164.90. LRESIMS is shown in Figure S3: *m*/*z* 989.5 $[M + H]^+$, 1007.6 $[M + H_3O]^+$, 1011.5 $[M + Na]^+$. HRESIMS: *m*/*z* calcd for $C_{50}H_{68}NaO_{20}$, 1011.4202; found 1011.4112, error −1.6 ppm.

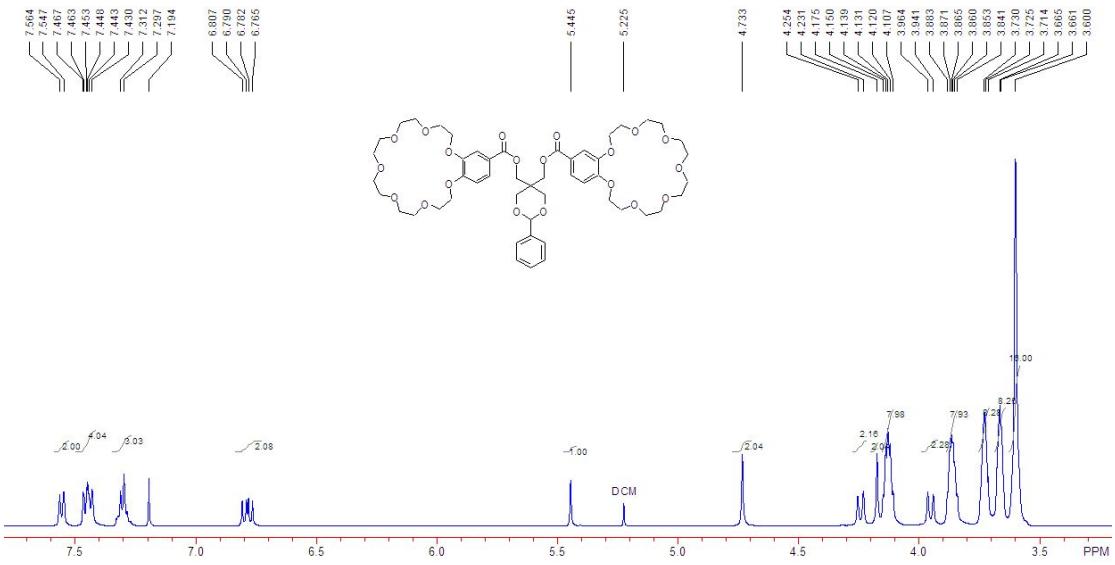


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **4**.

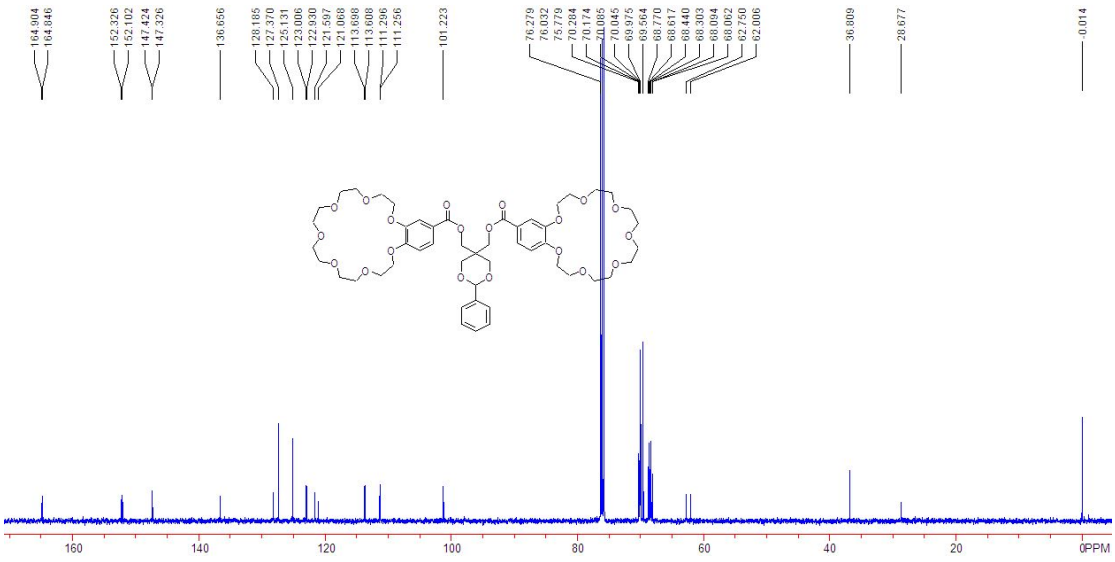


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **4**.

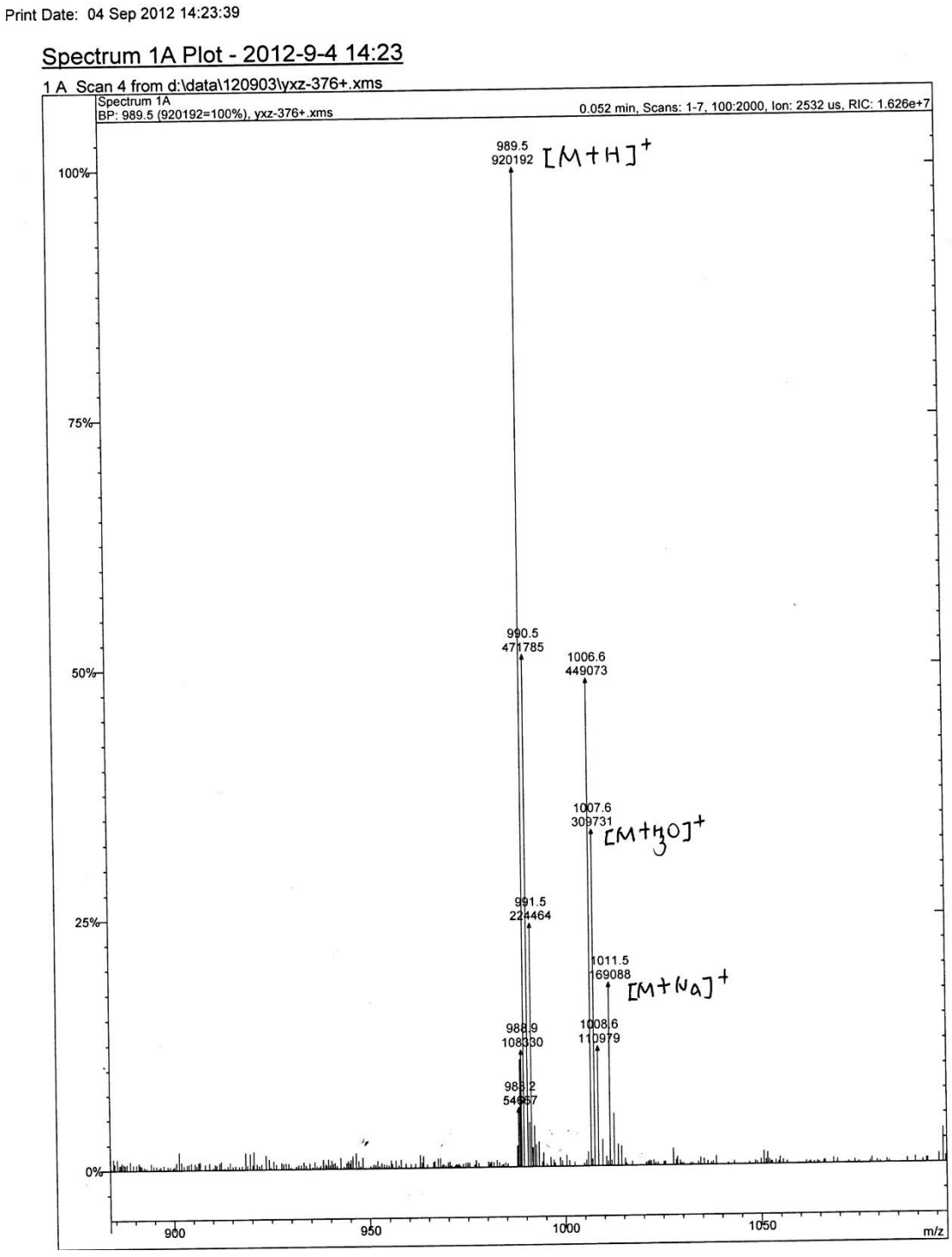
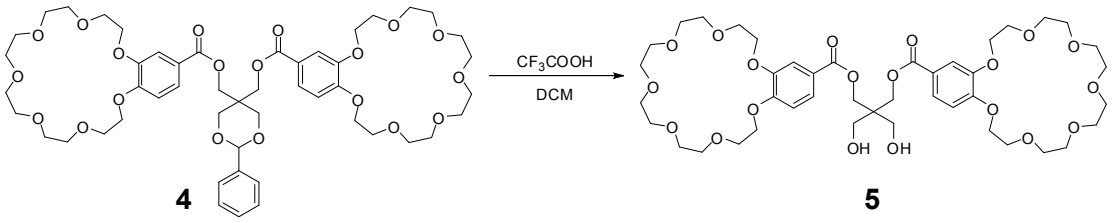


Figure S3. Electrospray ionization mass spectrum of **4**.

2.2. Synthesis of compound ***5***



4 **5**

Into a 250 mL round-bottomed flask were added **4** (9.10 g, 9.20 mmol) in 100 mL of dichloromethane and 50.0 mL of CF_3COOH (TFA). After stirring at room temperature for 4 h, water was added slowly to quench the reaction. Then, the solution was extracted with CH_2Cl_2 three times. The organic phases were combined, washed with water and brine, and then dried over Na_2SO_4 overnight. After filtration and solvent evaporation, compound **5** was obtained as a pale yellow oil (6.94 g, 84%). The ^{1}H NMR spectrum of **5** is shown in Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.62–7.69 (m, 2H), 7.54 (d, J = 2 Hz, 2H), 6.87 (d, J = 9 Hz, 2H), 4.45 (s, 4H), 4.17–4.27 (m, 8H), 3.89–3.99 (m, 8H), 3.78–3.84 (m, 8H), 3.72–3.77 (m, 12H), 3.63–3.71 (m, 16H). The ^{13}C NMR spectrum of **5** is shown in Figure S5. ^{13}C NMR (125 MHz, $CDCl_3$, room temperature) δ (ppm): 13.16, 20.02, 44.74, 59.38, 61.76, 61.94, 68.08, 68.30, 68.48, 68.64, 69.50, 69.92, 69.98, 70.02, 70.09, 70.22, 111.38, 113.81, 121.10, 123.28, 147.40, 152.40, 165.83. LRESIMS is shown in Figure S6: m/z 901.4 $[M + H]^+$, 918.6 $[M + H_3O]^+$, 923.5 $[M + Na]^+$. HRESIMS: m/z calcd for $C_{43}H_{64}NaO_{20}$, 923.3889; found 923.3878, error −1.2 ppm.

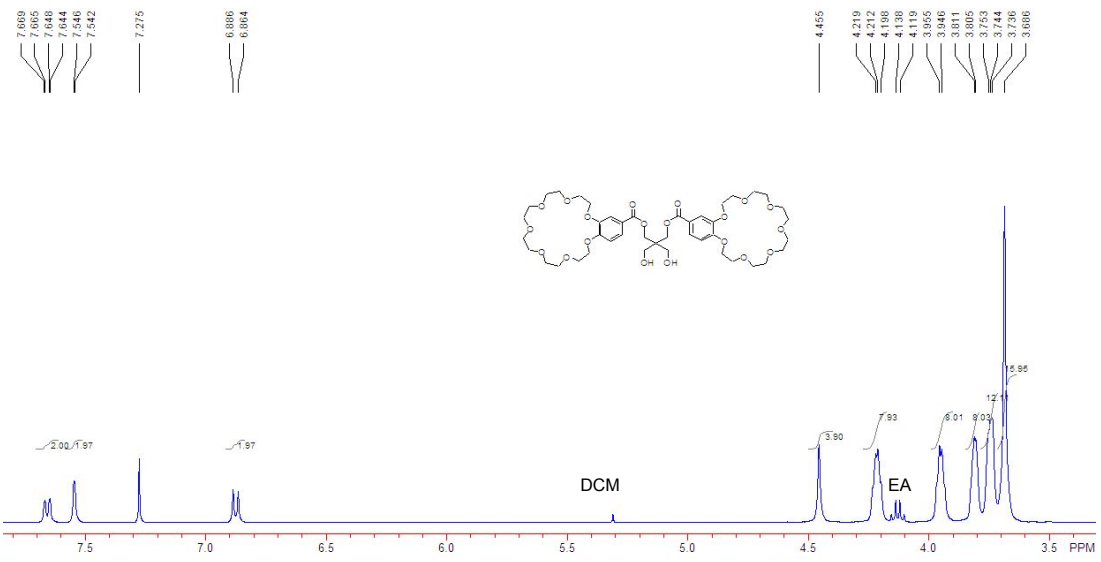


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **5**.

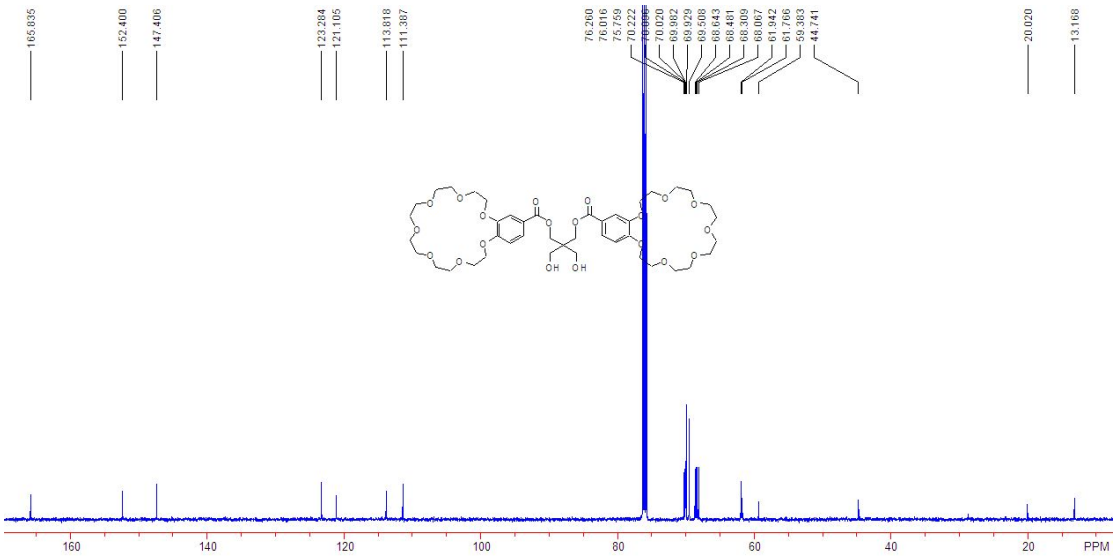


Figure S5. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **5**.

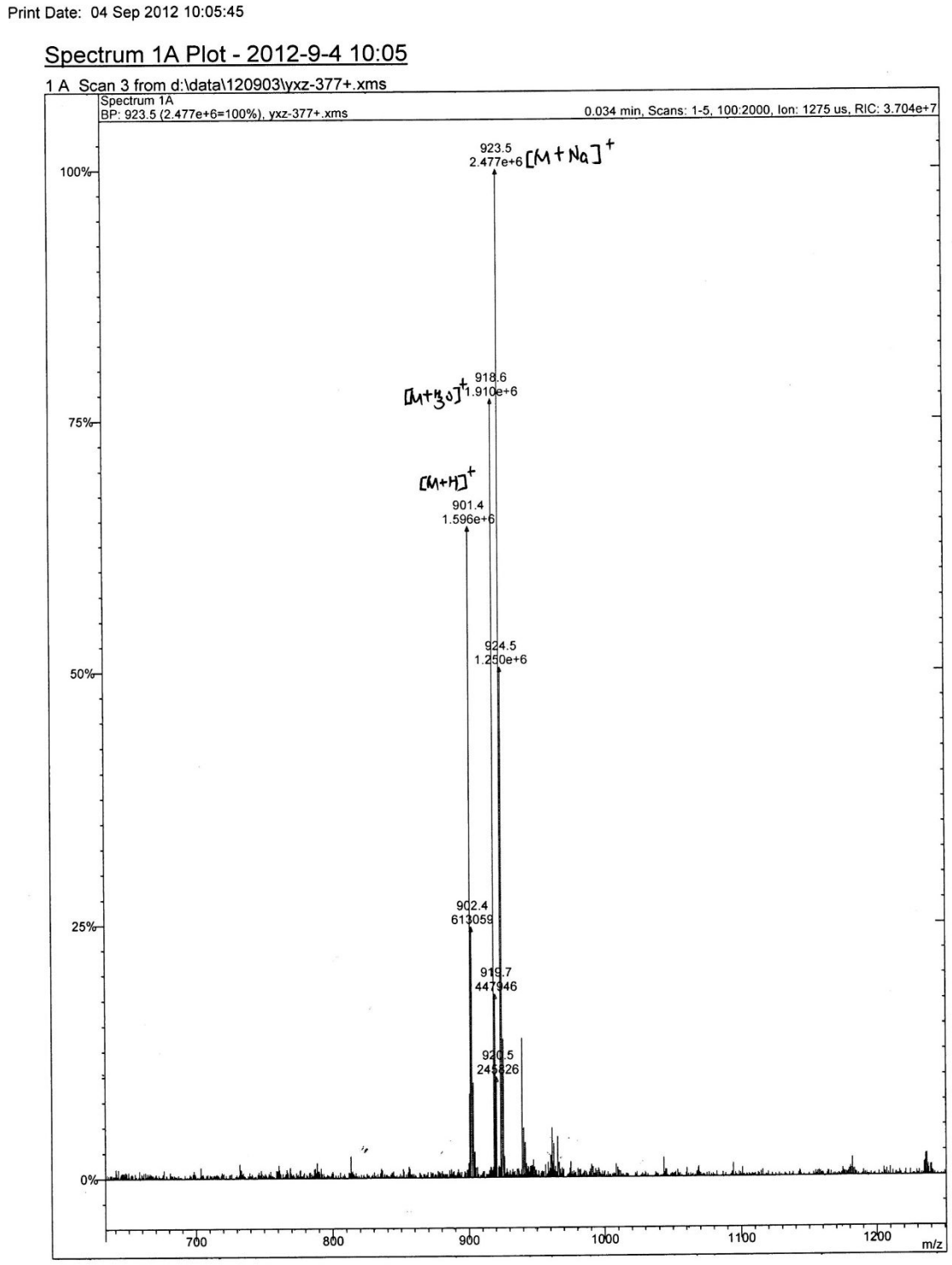
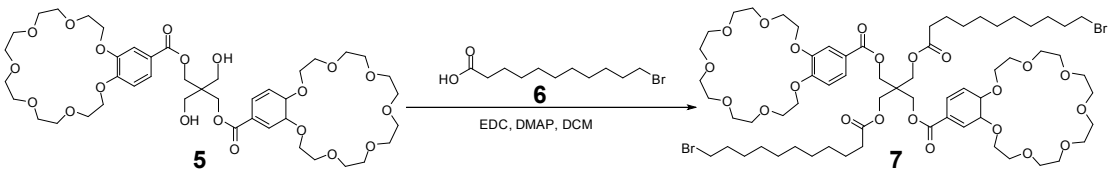


Figure S6. Electrospray ionization mass spectrum of **5**.

2.3. Synthesis of compound 7



A solution of **5** (6.90 g, 7.66 mmol), **6** (8.13 g, 30.6 mmol) and 4-dimethylaminopyridine (DMAP) (0.94 g, 7.66 mmol) in dichloromethane (200 mL) was stirred for 10 minutes at 0 °C. To this solution was added *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) (2.94 g, 15.3 mmol). The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a pale yellow oil, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v*/*v*) to afford **7** as a pale yellow oil (8.50 g, 80%). The ^{1}H NMR spectrum of **7** is shown in Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.58 (d, J = 7 Hz, 2H), 7.48 (s, 2H), 6.83 (d, J = 7 Hz, 2H), 4.41 (s, 4H), 4.27 (s, 4H), 4.14–4.22 (m, 8H), 3.87–3.95 (m, 8H), 3.76–3.82 (m, 8H), 3.69–3.75 (m, 8H), 3.62–3.68 (m, 16H), 3.38 (t, J = 5 Hz, 4H), 2.28 (t, J = 6 Hz, 4H), 1.78–1.87 (m, 4H), 1.51–1.60 (m, 4H), 1.35–1.42 (m, 4H), 1.18–1.89 (m, 20H). The ^{13}C NMR spectrum of **7** is shown in Figure S8. ^{13}C NMR (125 MHz, $CDCl_3$, room temperature) δ (ppm): 23.81, 27.11, 27.68, 28.04, 28.13, 28.25, 28.32, 31.80, 33.00, 33.65, 41.45, 61.48, 61.85, 68.14, 68.36, 68.44, 68.60, 69.55, 69.99, 70.12, 70.13, 70.23, 70.34, 111.28, 113.56, 121.11, 122.99, 147.43, 152.29, 164.69, 172.27. LRESIMS is shown in Figure S9: m/z 1397.5 $[M + H]^+$, 1414.6 $[M + H_2O]^+$, 1419.6 $[M + Na]^+$. HRESIMS: m/z calcd for $C_{65}H_{104}Br_2NaO_{22}$, 1419.5263; found 1419.5214, error −3.5 ppm.

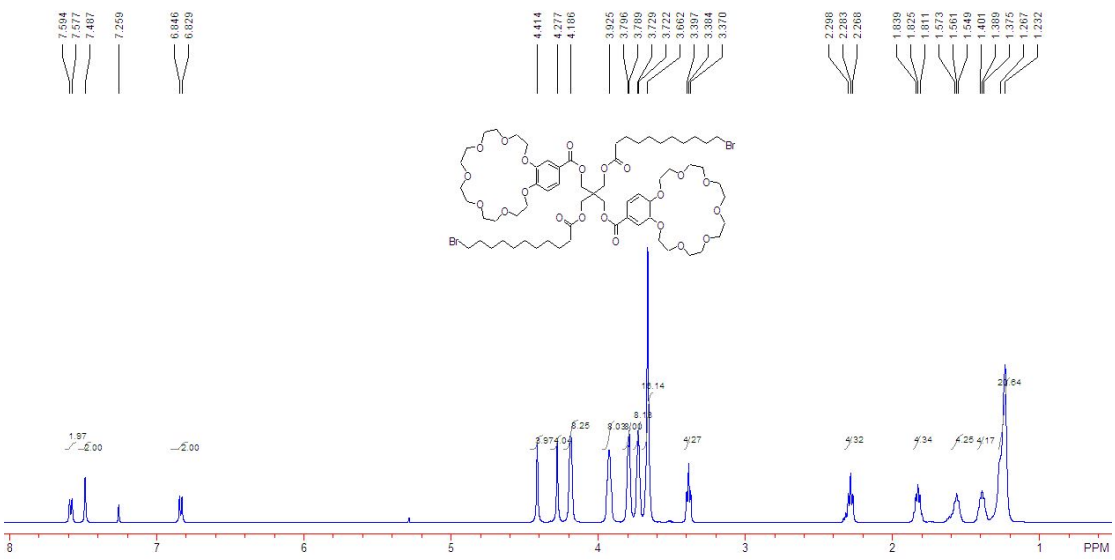


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **7**.

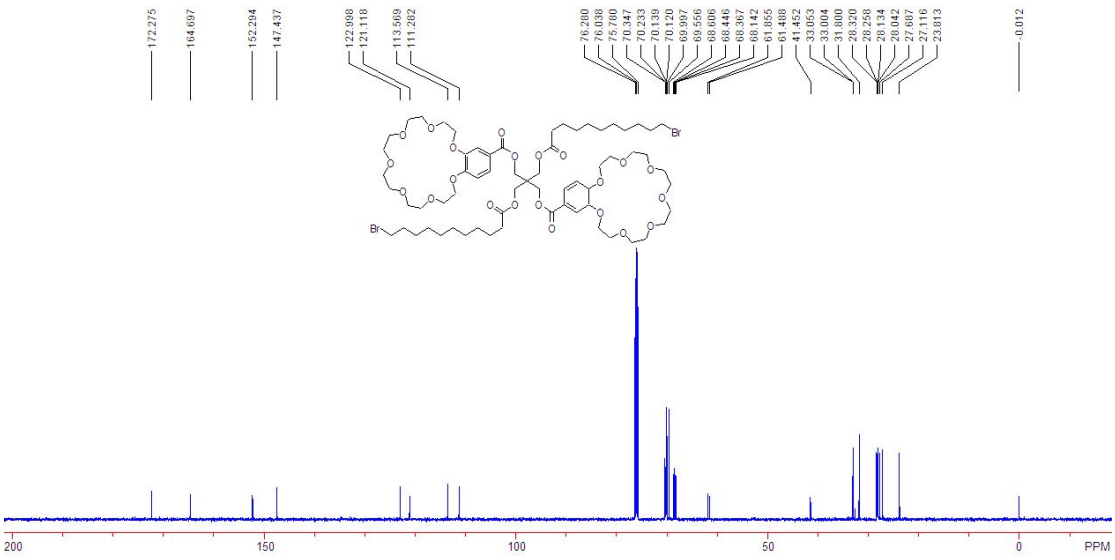


Figure S8. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **7**.

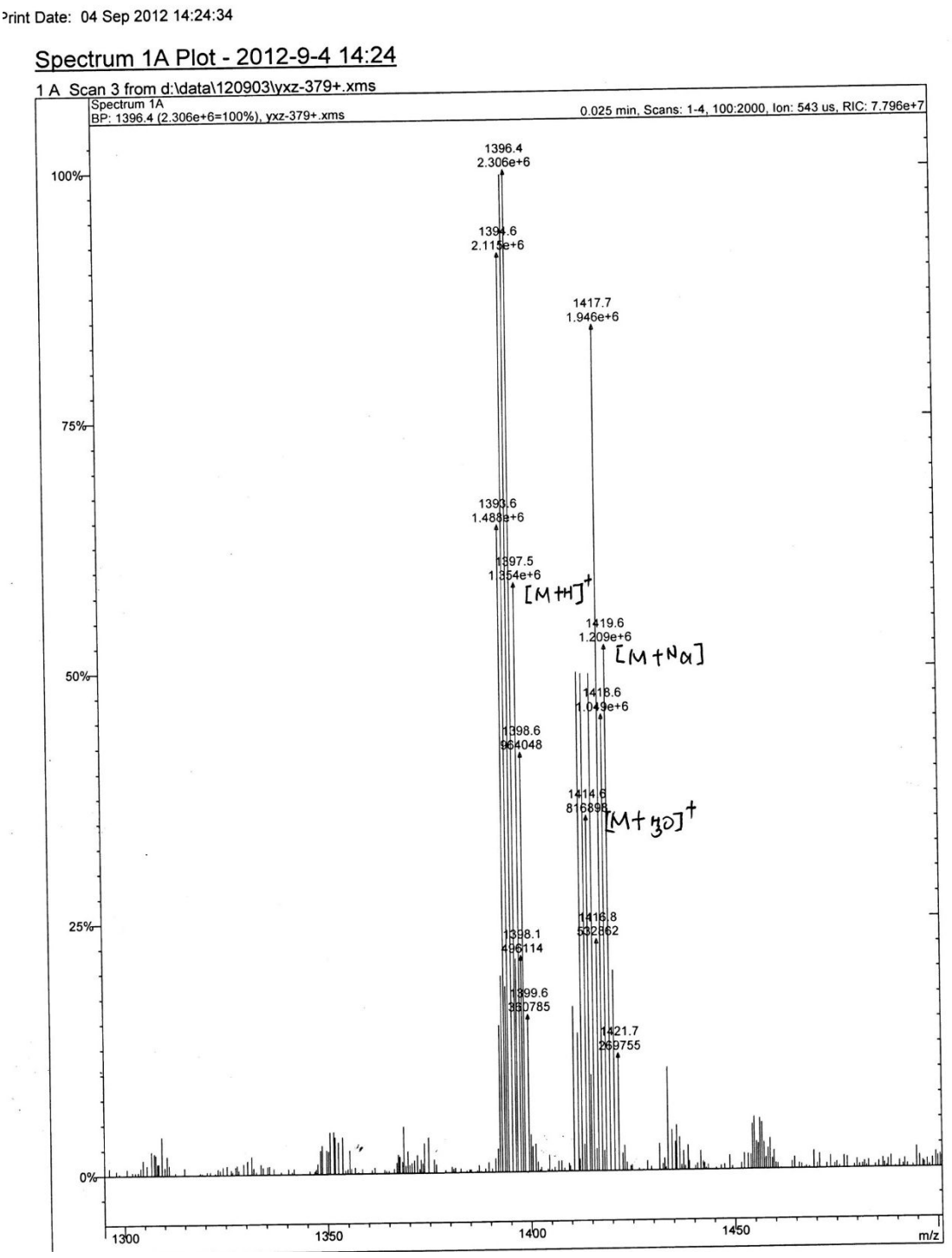
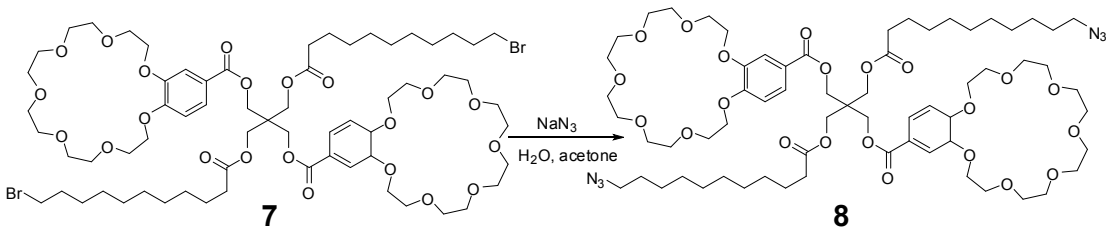


Figure S9. Electrospray ionization mass spectrum of **7**.

*2.4. Synthesis of compound **8***



7 **8**

Into a 250 mL round-bottomed flask were added **7** (7.50 g, 5.37 mmol) and sodium azide (2.10 g, 32.2 mmol) in 150 mL of acetone and 15 mL of H_2O. After heating at reflux for 48 h, water was added to quench the reaction. After removal of acetone, the solution was extracted with CH_2Cl_2 three times. The organic phases were combined, washed with water and brine, and then dried over Na_2SO_4 overnight. After filtration and solvent evaporation, compound **8** was obtained as a pale yellow oil (6.95 g, 98%). The ^{1}H NMR spectrum of **8** is shown in Figure S10. ^{1}H NMR (400 MHz, [D]chloroform, room temperature) δ (ppm): ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.59 (d, J = 7 Hz, 2H), 7.50 (s, 2H), 6.85 (d, J = 7 Hz, 2H), 4.42 (s, 4H), 4.29 (s, 4H), 4.15–4.24 (m, 8H), 3.89–3.98 (m, 8H), 3.77–3.83 (m, 8H), 3.71–3.76 (m, 8H), 3.63–3.70 (m, 16H), 3.24 (t, J = 6 Hz, 4H), 2.29 (t, J = 6 Hz, 4H), 1.52–1.65 (m, 8H), 1.17–1.37 (m, 24H). The ^{13}C NMR spectrum of **8** is shown in Figure S11. ^{13}C NMR (125 MHz, $CDCl_3$, room temperature) δ (ppm): 24.81, 26.66, 28.81, 29.04, 29.07, 29.14, 29.25, 29.35, 34.06, 42.48, 51.46, 62.49, 62.87, 69.07, 69.28, 69.44, 69.60, 70.55, 70.96, 71.04, 71.05, 71.16, 71.27, 112.27, 114.53, 122.13, 124.00, 148.40, 153.26, 165.70, 173.28. LRESIMS is shown in Figure S12: m/z 1321.8 $[M + H]^+$, 1338.8 $[M + H_3O]^+$, 1343.8 $[M + Na]^+$, 1357.8 $[M + K]^+$. HRESIMS: m/z calcd for $C_{65}H_{104}N_6NaO_{22}$, 1343.7101; found 1343.7118, error 1.3 ppm.

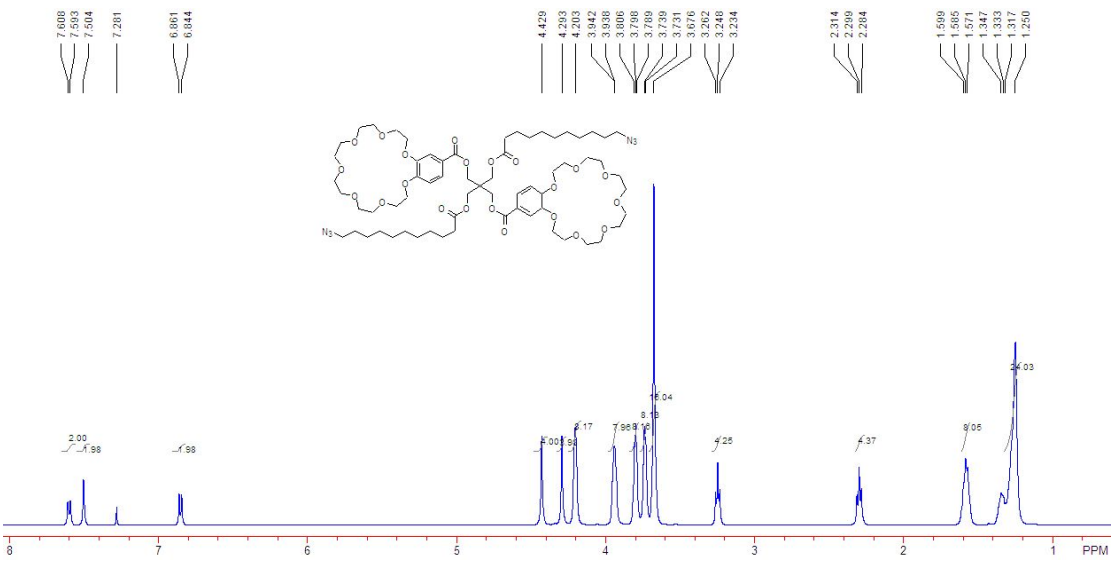


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **8**.

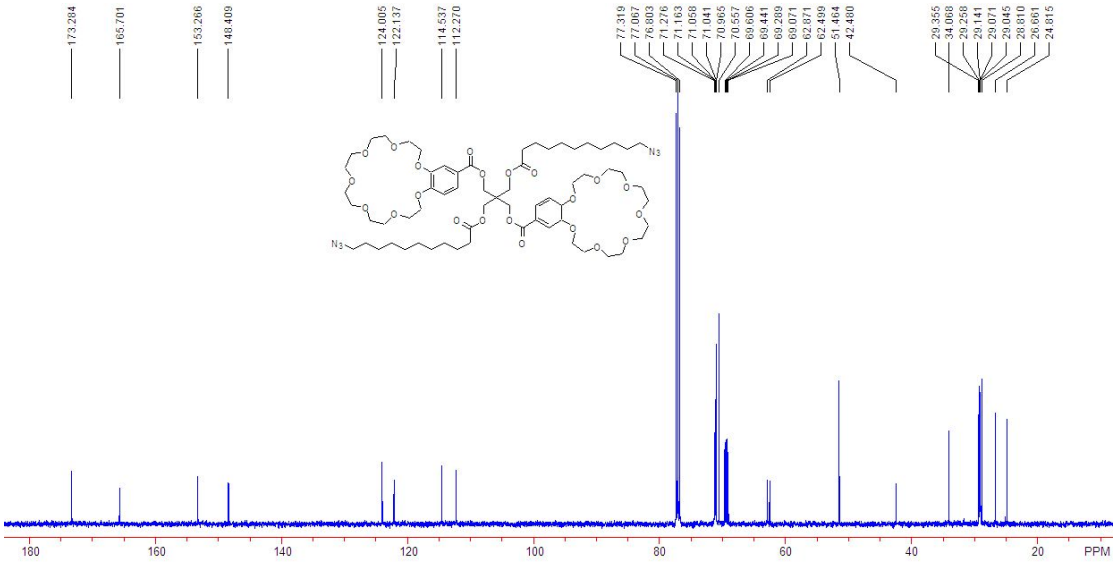


Figure S11. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **8**.

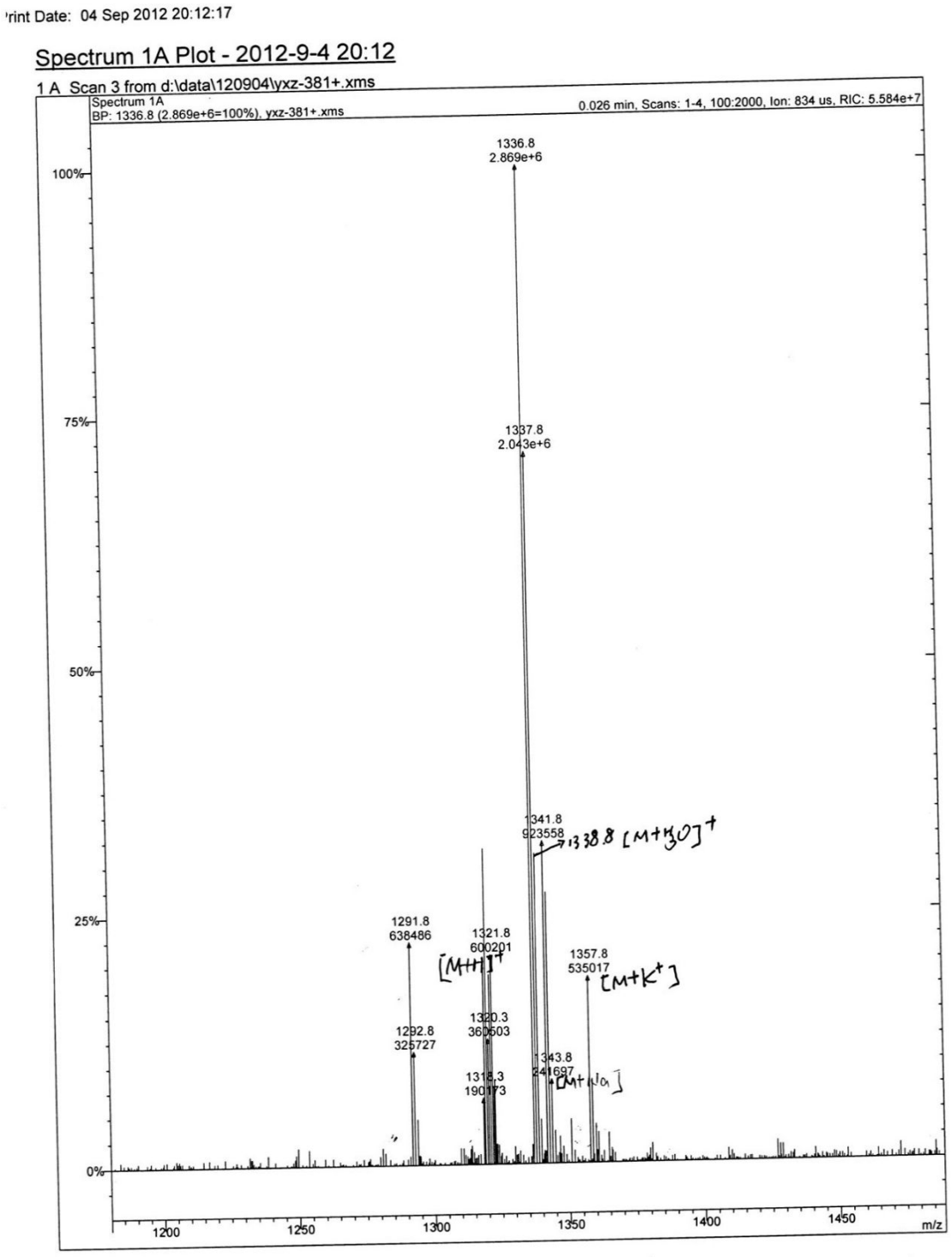
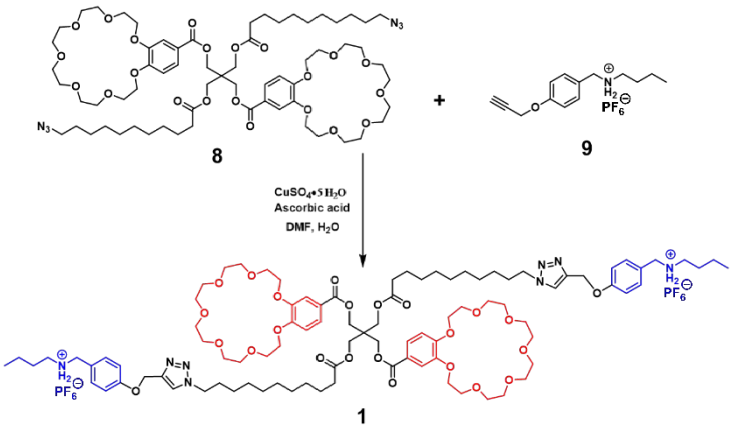


Figure S12. Electrospray ionization mass spectrum of **8**.

*2.5. Synthesis of compound **1***



A mixture of **8** (6.18 g, 4.68 mmol) and **9** (3.44 g, 9.46 mmol) in a mixture of DMF and H_2O (4:1, 250 mL) in the presence of $CuSO_4$•$5H_2O$ (0.52 g, 2.06 mmol) with sodium ascorbate (1.00 g, 5.12 mmol) was stirred at 50 ºC for 24 h. The reaction mixture was poured into saturated brine (200 mL) and the resulting solution was extracted with chloroform (70 mL × 3). The combined organic phase was concentrated and purified by flash column chromatography (methanol/dichloromethane, 1:50 *v*/*v*) to afford the compound **1** as a white solid (5.94 g, 62%). mp 97.6–99.4 ºC. The ^{1}H NMR spectrum of **1** is shown in Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 8.54 (s, 4H), 8.22 (s, 2H) 7.56 (d, J = 7 Hz, 2H), 7.37–7.44 (m, 6H), 7.10 (d, J = 6 Hz, 4H), 7.04 (d, J = 7 Hz, 2H), 5.14 (s, 4H), 4.39 (s, 4H), 4.33 (t, J = 6 Hz, 4H), 4.28 (s, 4H), 4.04–4.18 (m, 12H), 3.72–3.79 (m, 8H), 3.58–3.63 (m, 8H), 3.53–3.57 (m, 8H), 3.48–3.52 (m, 16H), 2.25 (t, J = 6 Hz, 4H), 1.74–1.82 (m, 4H), 1.52–1.61 (m, 4H), 1.39–1.49 (m, 4H), 1.28–1.36 (m, 4H), 1.09–1.25 (m, 28H), 0.88 (t, J = 6 Hz, 6H). The ^{13}C NMR spectrum of **1** is shown in Figure S14. ^{13}C NMR (125 MHz, DMSO-d_6, room temperature) δ (ppm):13.40, 19.22, 24.36, 25.79, 27.38, 28.32, 28.34, 28.59, 28.71, 28.26, 29.68, 33.35, 35.71, 42.21, 46.07, 49.33, 49.52, 54.84, 61.14, 62.31, 62.90, 68.44, 68.50, 68.65, 68.77, 69.87, 70.15, 70.19, 70.22, 70.30, 70.37, 112.21, 113.24, 114.81, 121.42, 123.45, 124.07, 124.40, 131.43, 147.67, 152.60, 158.58, 164.97, 172.53. The ^{31}P NMR spectrum of **1** is shown in Figure S15. (162 MHz, DMSO-d_6, room temperature) δ (ppm): –144.20 (hept, J = 711.4 Hz). The ^{19}F NMR spectrum of **1** is shown in Figure S16. (376 MHz, DMSO-d_6, room temperature) δ (ppm): –70.13 (d, J = 711.3 Hz). LRESIMS is shown in Figure S17: m/z 878.0 $[M - 2PF_6]^{2+}$. HRESIMS is shown in Figure S18: m/z calcd for $[M - 2PF_6 + H]^+$ $C_{93}H_{143}N_8O_{24}^+$, 1755.0126; found 1755.0046, error –4.6 ppm.

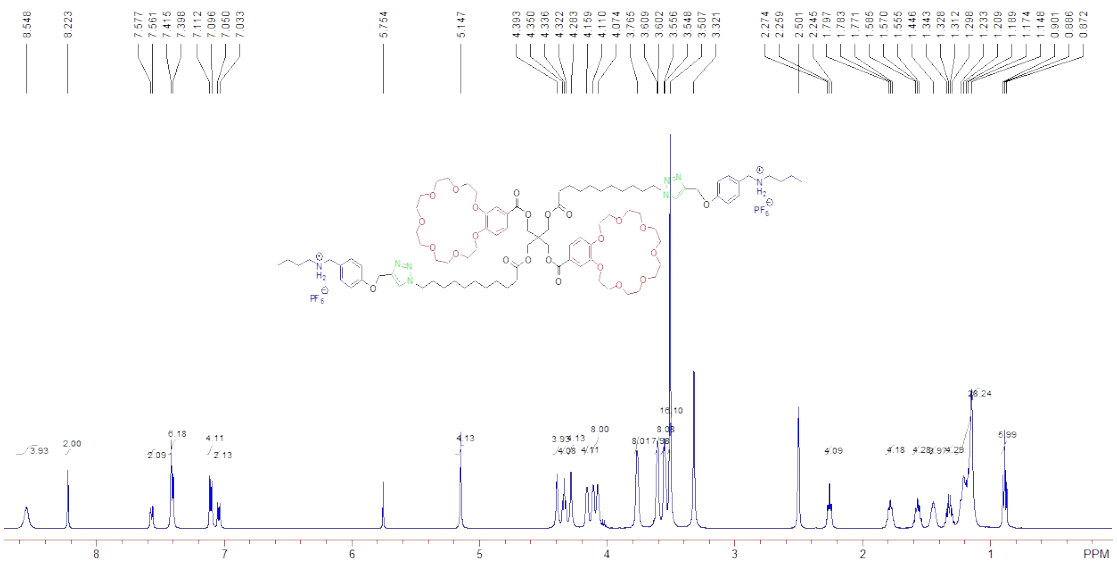


Figure S13. [1]H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **1**.

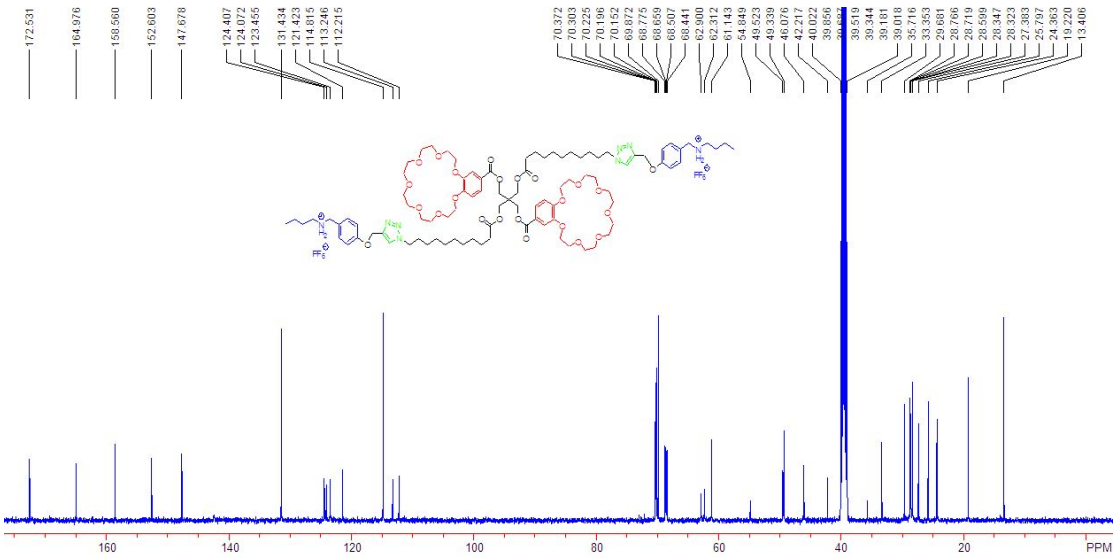


Figure S14. [13]C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of **1**.

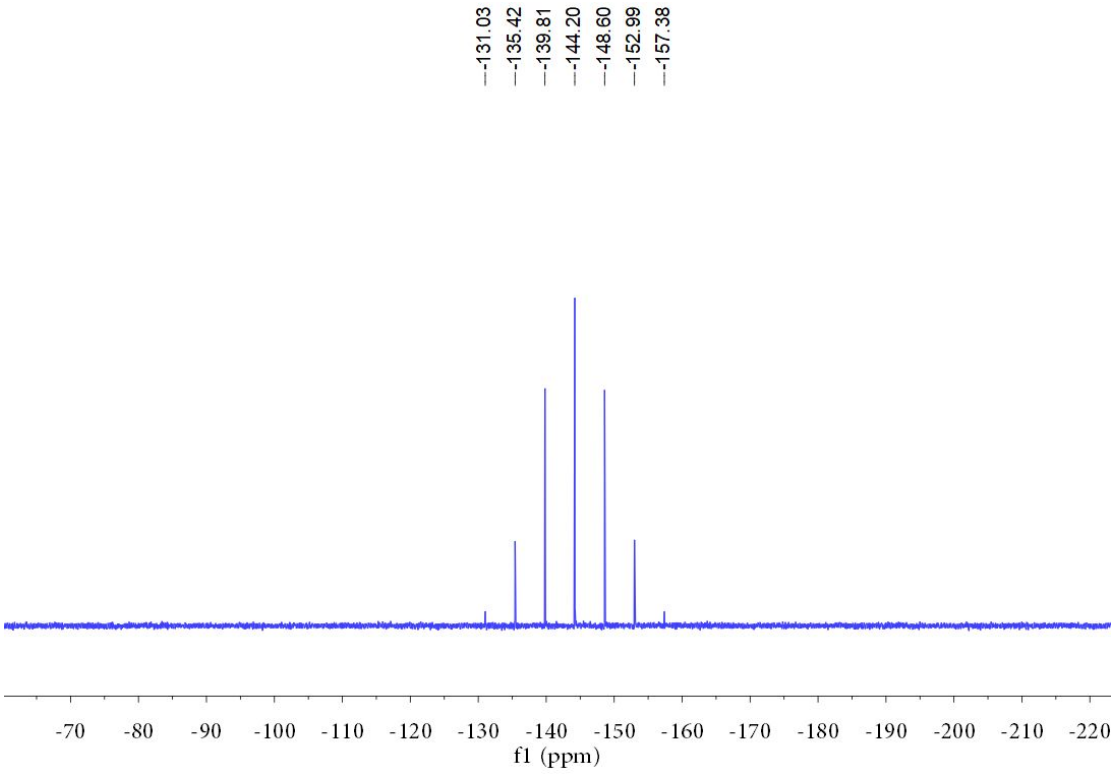


Figure S15. ^{31}P NMR spectrum (162 MHz, DMSO-d_6, room temperature) of **1**.

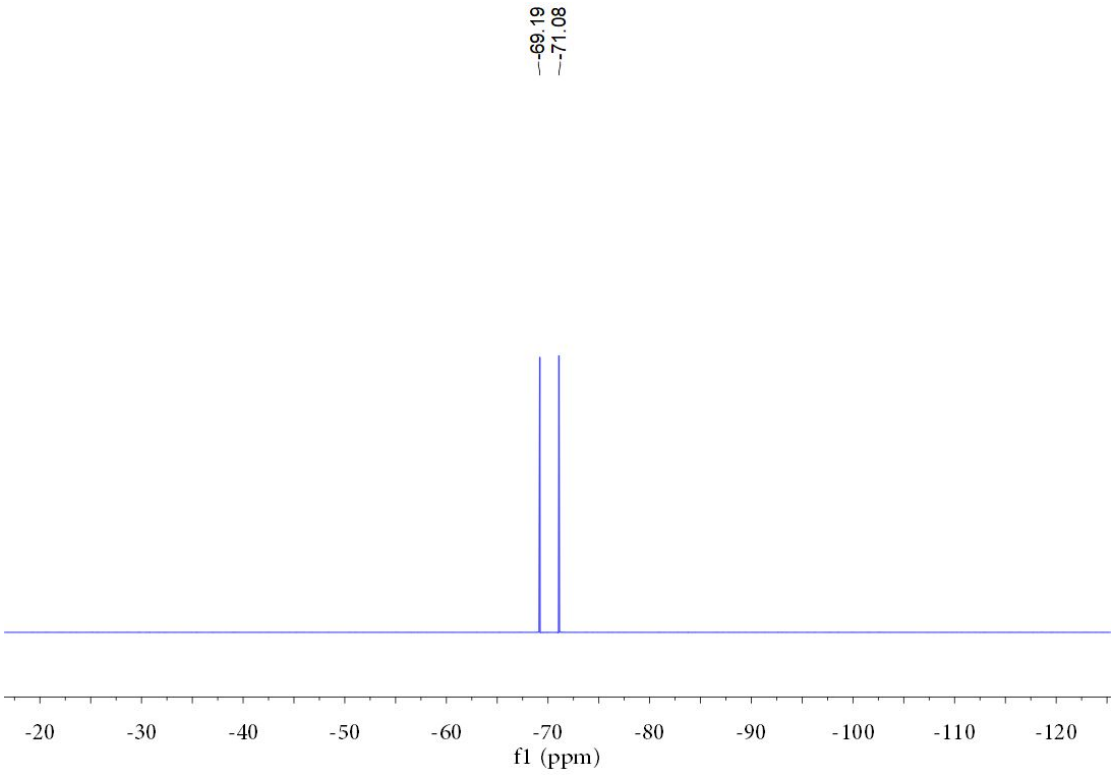


Figure S16. ^{19}F NMR spectrum (376 MHz, DMSO-d_6, room temperature) of **1**.

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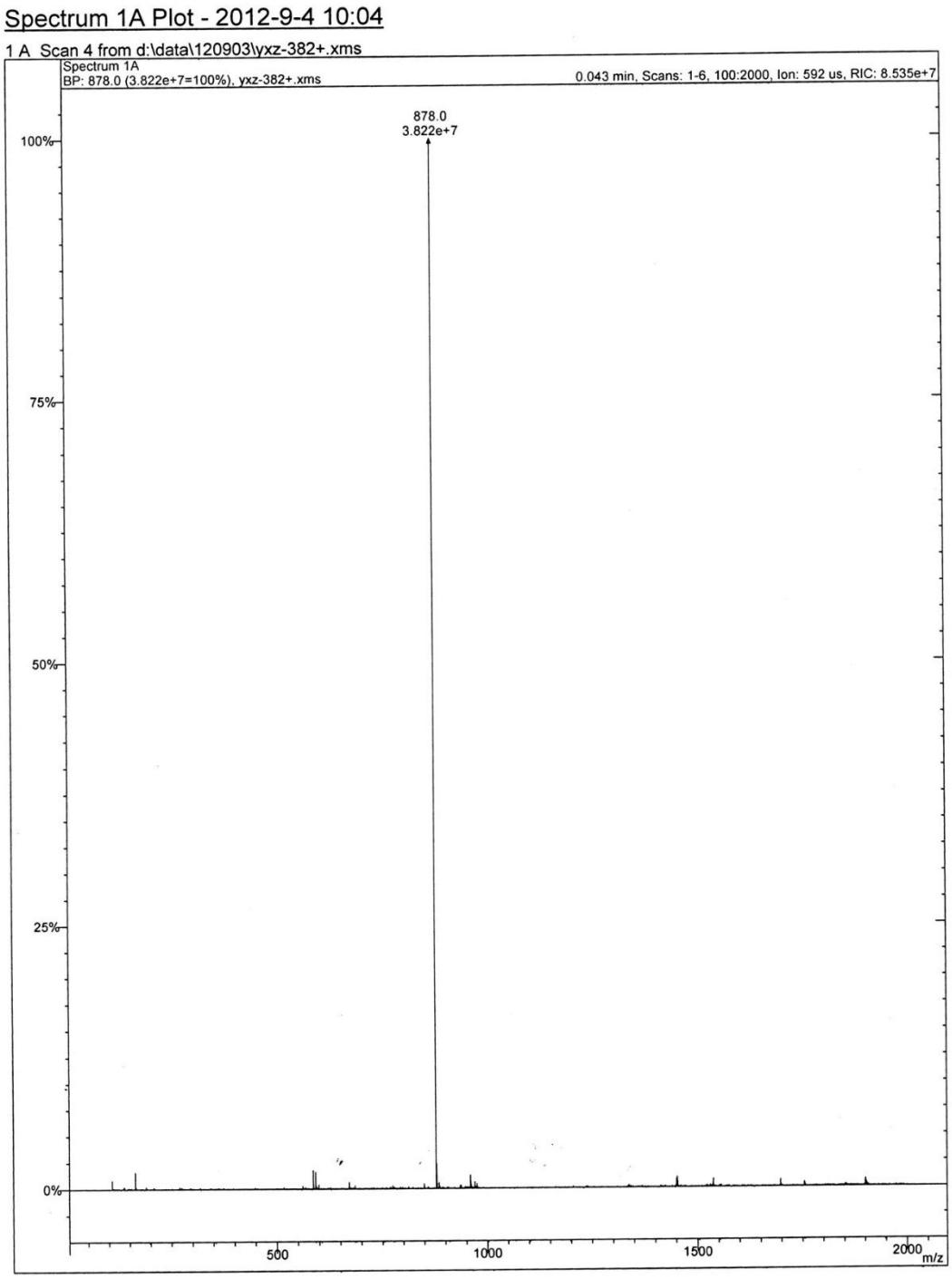

Figure S17. Electrospray ionization mass spectrum of **1**.

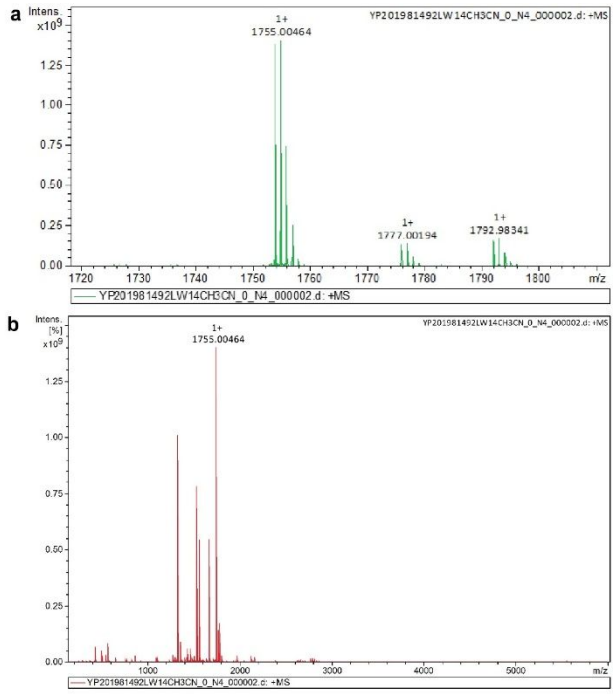

Figure S18. Partial (a) and whole (b) high-resolution electrospray ionization mass spectra of **1**.

3. Partial COSY NMR spectrum of 1

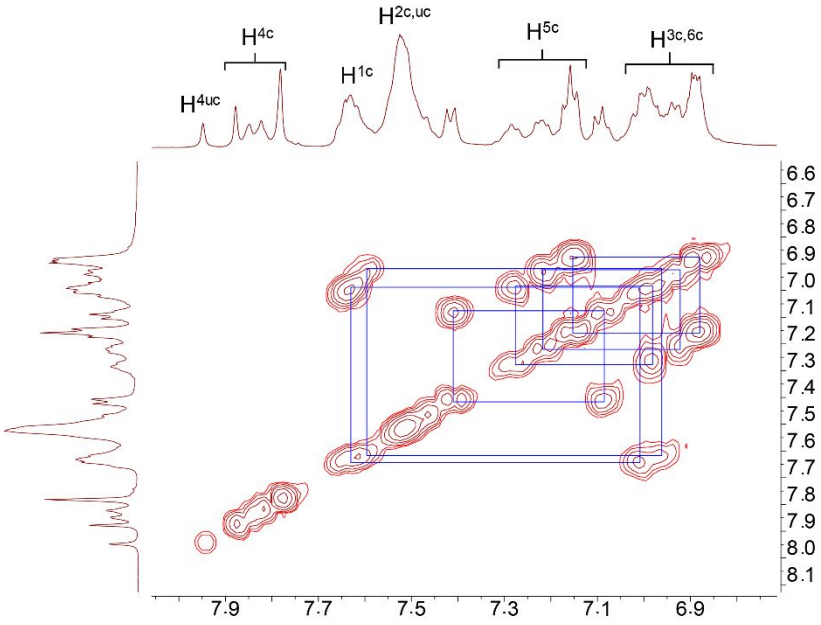

Figure S19. Partial COSY NMR spectrum (500 MHz, CD_3CN, room temperature) of **1** at a concentration of 80 mM. Letters "c" and "uc" denote complexed and uncomplexed species, respectively.

4. Inductively coupled plasma optical emission spectrometry analysis of the SPN

1	Unk: YP201981539 LW-14 2020/1/2 11:47:21 CONC x.0999
	P_1774
Units	%
Avg	**3.135**
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% RSD	.0049
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Rep #2	3.135
Rep #3	3.135

Figure S20. Inductively coupled plasma optical emission spectrometry analysis of SPN. The P element content was estimated to be 3.135%, which is consistent with that in theory.

5. pH-responsive experiments on the SPN

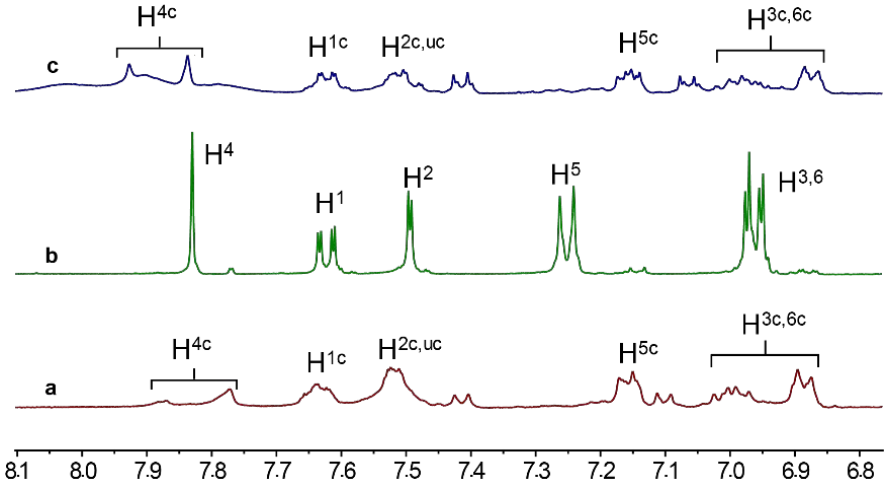

Figure S21. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature) of: (a) 50 mM **1**; (b) after addition of 13 μL (1.5 equiv.) of Et_3N to a; (c) after addition of 8.0 μL (1.8 equiv.) of TFA to b. Letters "c" and "uc" denote complexed and uncomplexed species, respectively.

6. Shift factors for master curves of the SPN

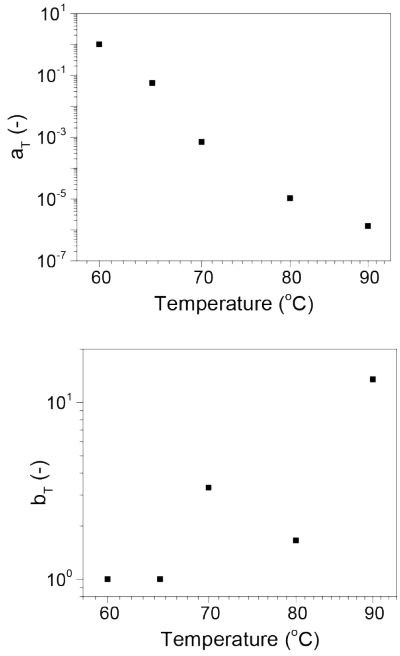

Figure S22. Temperature dependence of viscoelastic shift factors a_T and b_T of master curves at a reference temperature of 60 ºC.

7. *Frequency sweep tests of the SPN at different temperatures*

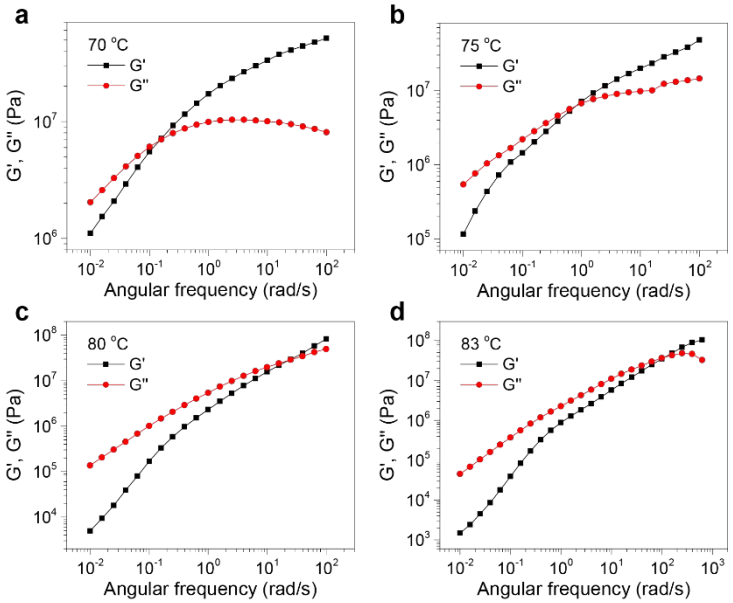

Figure S23. Frequency sweep tests of SPN at (a) 70 ºC, (b) 75 ºC, (c) 80 ºC, and (d) 83 ºC.

8. *Frequency-dependent changes of moduli and viscosities of the SPN at different temperatures*

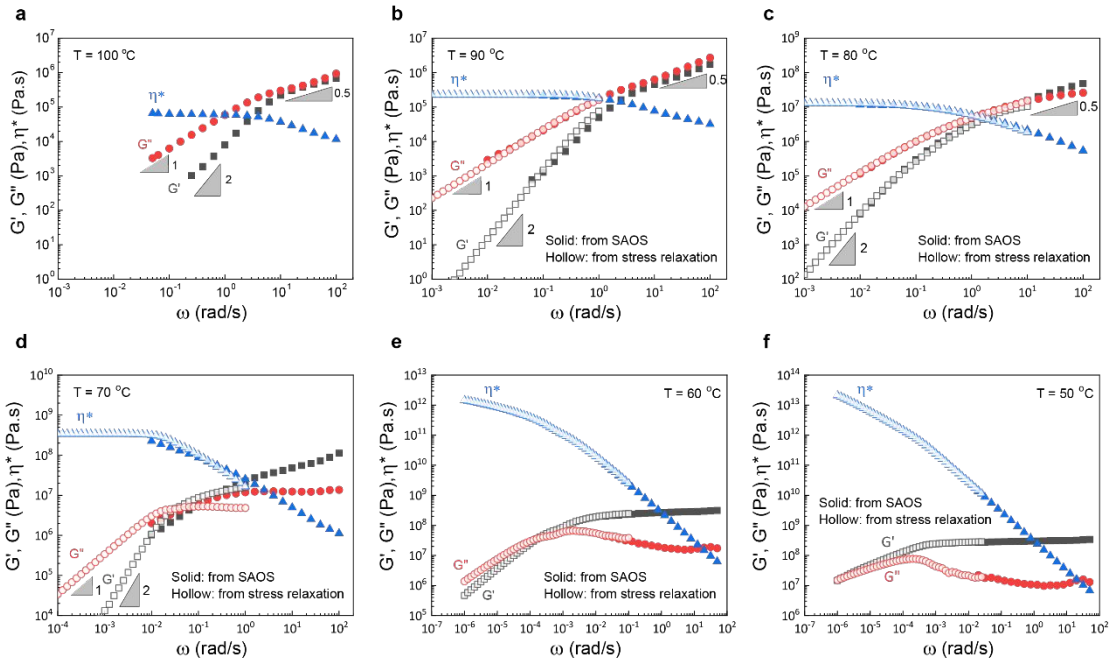

Figure S24. G', G'' and viscosity η varied with ω at (a) 100 °C, (b) 90 °C, (c) 80 °C, (d) 70 °C, (e) 60 °C, and (f) 50 °C obtained from both frequency sweep and relaxation modulus by fast Fourier transforms (FFT).

References:

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S2. X. Yan, M. Zhou, J. Chen, X. Chi, S. Dong, M. Zhang, X. Ding, Y. Yu, S. Shao, F. Huang, *Chem. Commun.* **2011**, *47*, 7086–7088.