Electronic Supplementary Material (ESI) for Chemical Communications

Supramolecular Polymer Nanofibers *via* Electrospinning of a Heteroditopic Monomer

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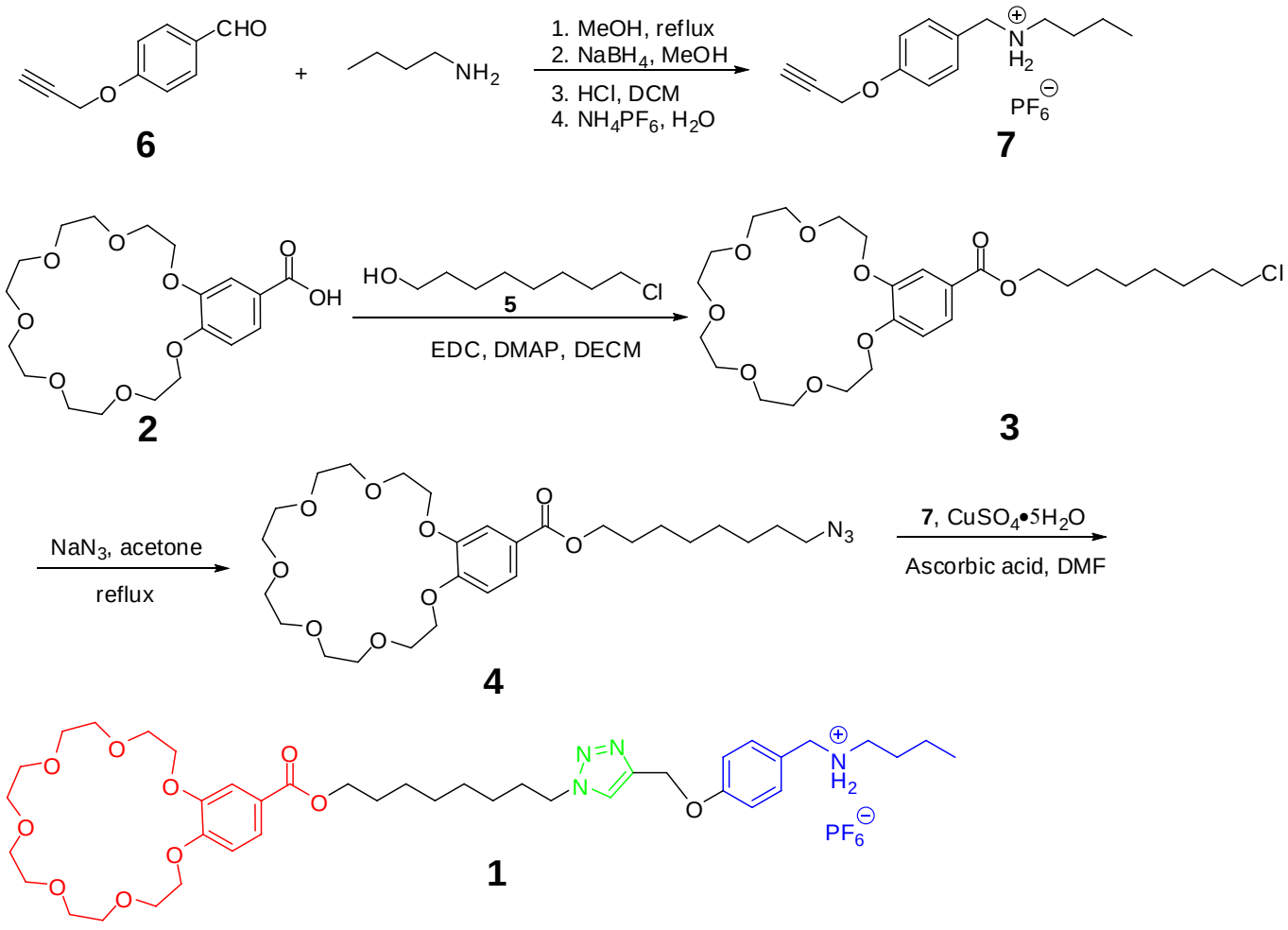
Electronic Supplementary Information (24 pages)

1. Materials and methods

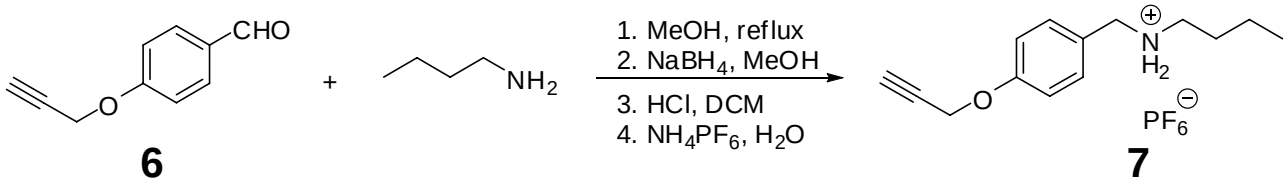
All reagents were commercially available and used as supplied without further purification. Compounds **2**[S1] and **6**[S2] were prepared according to the published procedures. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in chloroform. The two-dimensional diffusion-ordered NMR spectra were recorded on a Bruker DRX500 spectrometer. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. Transmission electron microscopy investigations were carried out on a JEM-1200EX instrument. Atomic force microscopy investigations were carried out on a SPI-3800N instrument. Electrospun supramolecular polymer nanofibers were obtained under the following conditions, 25 kV, 2.0 mL/h syringe flow rate, and 10 cm working distance, from a concentrated solution (250 mM) of 1 in chloroform.

*2. Synthesis of monomer **1***

Scheme S1. Synthesis of monomer **1**.



2.1. Synthesis of compound ***7***



6 **7**

A solution of butylamine (9.36 mL, 93.7 mmol) and compound **6** (15.0 mL, 93.7 mmol) was heated under reflux overnight in MeOH (300 mL). After the reaction mixture was cooled to ambient temperature, $NaBH_4$ (7.10 g, 187 mmol) was added portionwise to the stirring solution over a period of 0.5 h. Stirring was maintained under ambient conditions for further 24 h, after which time 5 M HCl was added to neutralize excess $NaBH_4$. The mixture was filtered and MeOH was removed with a rotaevaporator. The residue was extracted with ethyl acetate and the extract was concentrated to get a yellow oil. After the oil was added to a hydrochloric acid solution and stirred for a moment, a white precipitate formed. The mixture was filtered and the solid was dissolved in water to get a saturated solution. The solution was added to a saturated aqueous NH_4PF_6 solution to produce a precipitate, which was collected by suction filtration and recrystallized from deionized water to afford **7** (20.2 g, 59%) as a white solid. mp 183.6–185.3 °C. The ^{1}H NMR spectrum of compound **7** is shown in Figure S1. ^{1}H NMR (400 MHz, acetonitrile-d_3, room temperature) δ (ppm): 7.43 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 4.79 (d, J = 2.0 Hz, 2H), 4.12 (s, 2H), 3.03 (t, J = 7.6 Hz, 2H), 2.85 (t, J = 2.4 Hz, 1H), 1.60–1.68 (m, 2H), 1.34–1.43 (m, 2H)，0.95 (t, J = 7.6 Hz, 3H). The ^{13}C NMR spectrum of **7** is shown in Figure S2. ^{13}C NMR (125 MHz, acetonitrile-d_3, room temperature) δ (ppm): 13.74, 20.27, 28.51, 48.76, 52.04, 56.60, 77.15, 79.48, 116.25, 124.40, 132.74, 159.47. LRESIMS is shown in Figure S3: m/z 218.2 $[M - PF_6]^+$ (100%), 219.1 $[M - PF_6 + H]^+$ (15%). HRESIMS: m/z calcd for $[M - HPF_6]^+$ $C_{14}H_{19}NO^+$, 217.1467; found 217.1465, error –0.9 ppm.

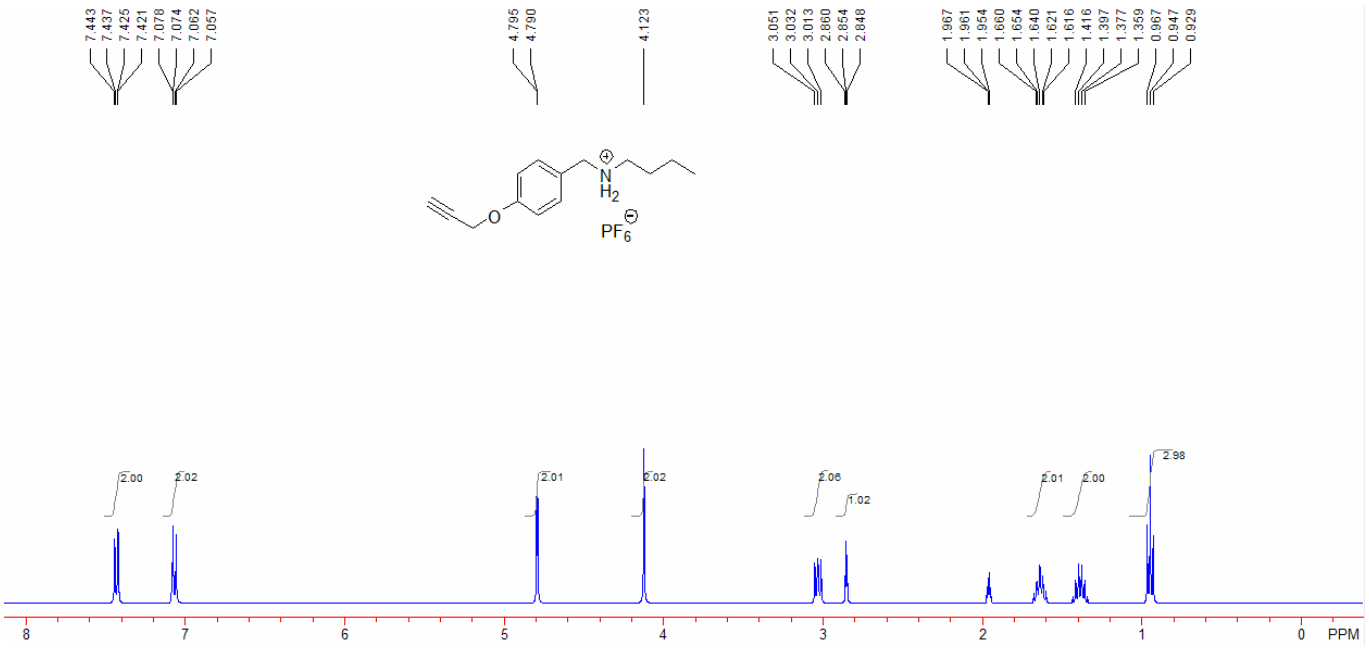


Figure S1. ^{1}H NMR spectrum (400 MHz, acetonitrile-d_3, room temperature) of **7**.

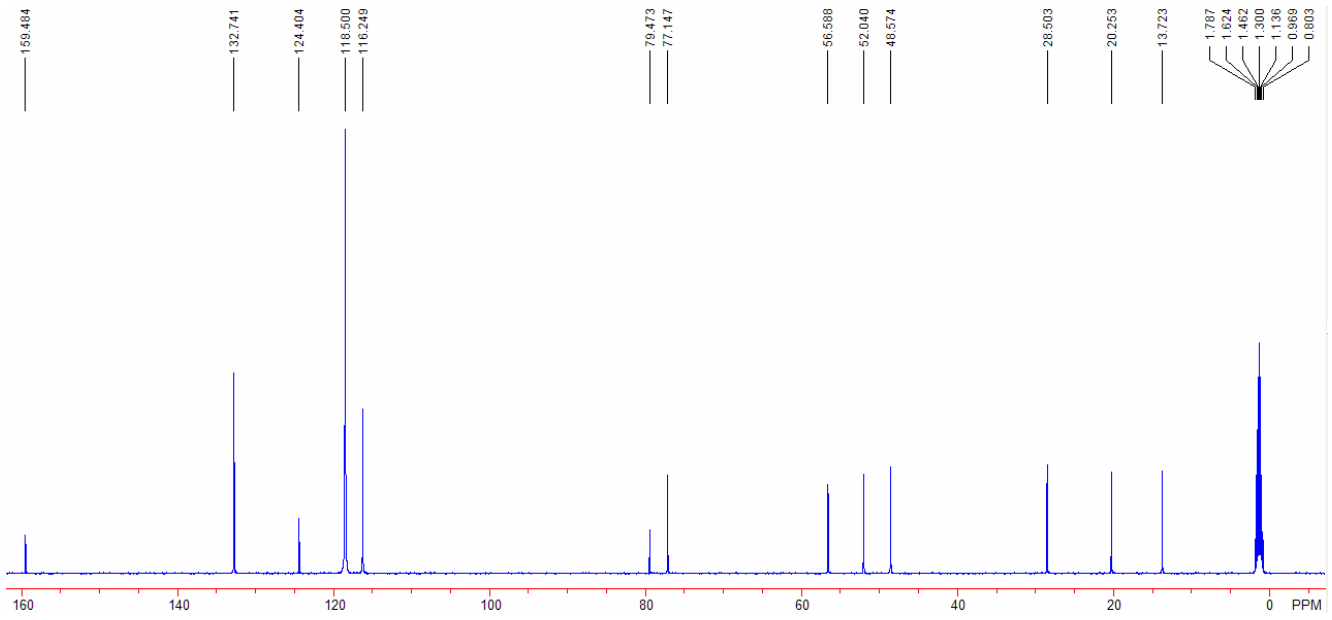


Figure S2. ^{13}C NMR spectrum (125 MHz, acetonitrile-d_3, room temperature) of **7**.

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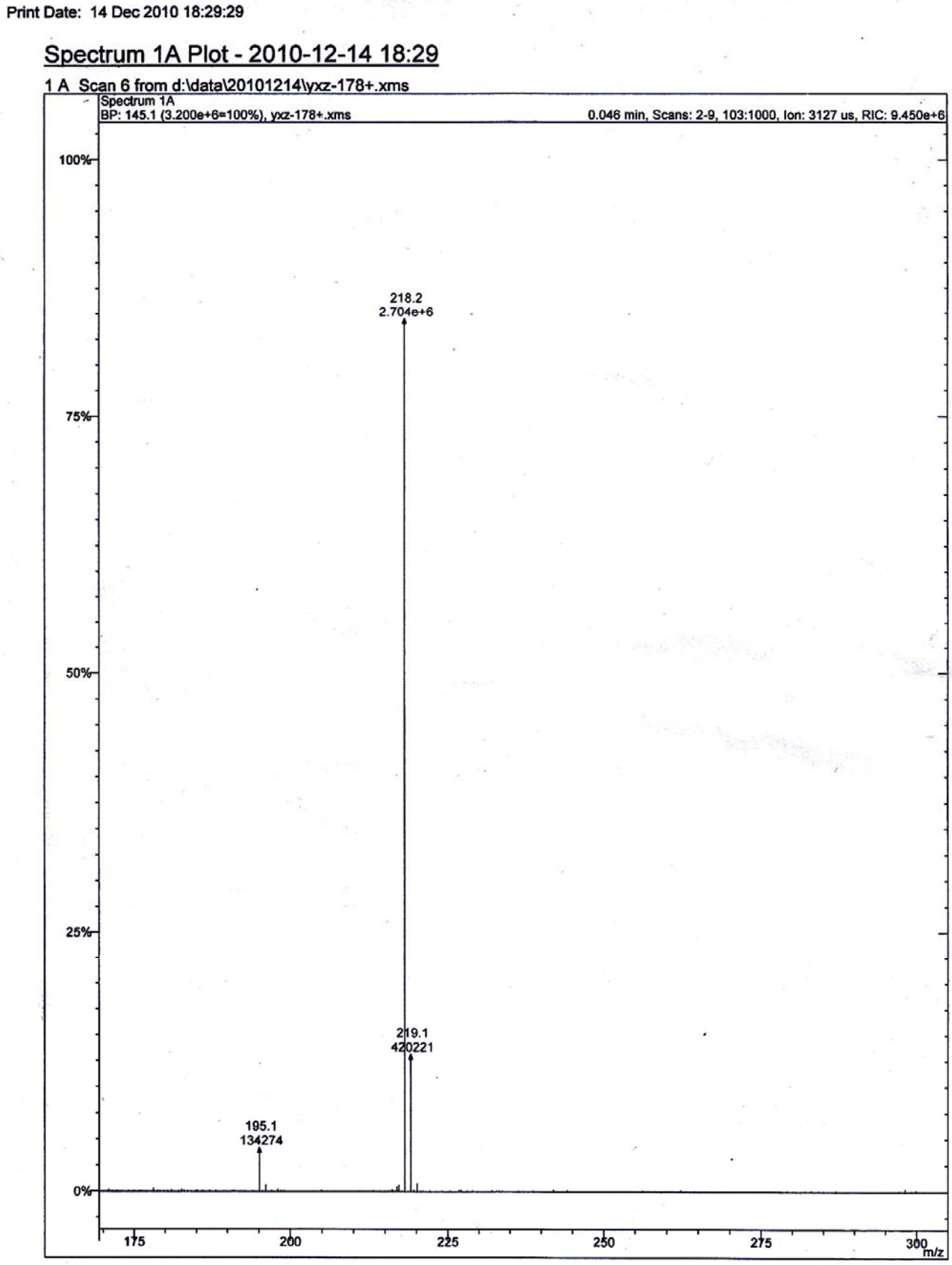
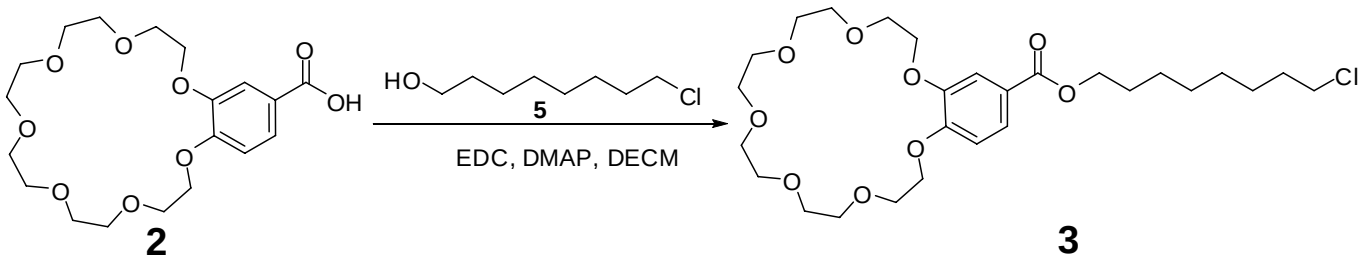


Figure S3. Electrospray ionization mass spectrum of **7**.

2.2. Synthesis of compound ***3***



2 **3**

A solution of **2** (8.74 g, 21.8 mmol), **5** (3.59 g, 21.8 mmol) and 4-dimethylaminopyridine (DMAP) (1.22 g, 9.99 mmol) in dichloromethane (200 mL) was stirred for 10 minutes at 0 °C. To this solution was added EDC (8.73 g, 45.5 mmol). The reaction mixture was stirred for 48 h at room temperature, filtered, and concentrated to give a pale yellow oil, which was purified by flash column chromatography (ethyl acetate/petroleum ether, 2:1 *v*/*v*) to afford **3** as a pale yellow oil (6.33 g, 53%). The ^{1}H NMR spectrum of **3** is shown in Figure S4. ^{1}H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 7.64–7.67 (m, 1H), 7.55 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 6.8 Hz, 1H), 4.28 (t, J = 5.4 Hz, 2H), 4.19–4.23 (m, 4H), 3.92–3.97 (m, 4H), 3.78–3.83 (m, 4H), 3.72–3.77 (m, 4H), 3.64–3.70 (m, 8H), 3.53 (t, J = 5.4 Hz, 2H), 1.71–1.81 (m, 4H), 1.40–1.50 (m, 4H), 1.30–1.40 (m, 4H). The ^{13}C NMR spectrum of **3** is shown in Figure S5. ^{13}C NMR (125 MHz, chloroform-*d*, room temperature) δ (ppm): 26.15, 27.00, 28.96, 29.32, 32.80, 45.34, 65.10, 69.34, 69.56, 69.73, 69.88, 70.79, 71.25, 71.36, 71.44, 71.57, 112.51, 114.88, 123.51, 124.07, 148.49, 153.09, 166.62. LRESIMS is shown in Figure S6: *m*/*z* 564.2 $[M + H_2O]^+$ (100%), 569.2 $[M + Na]^+$ (60%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{27}H_{43}ClO_9$, 546.2596; found 546.2587, error –1.6 ppm.

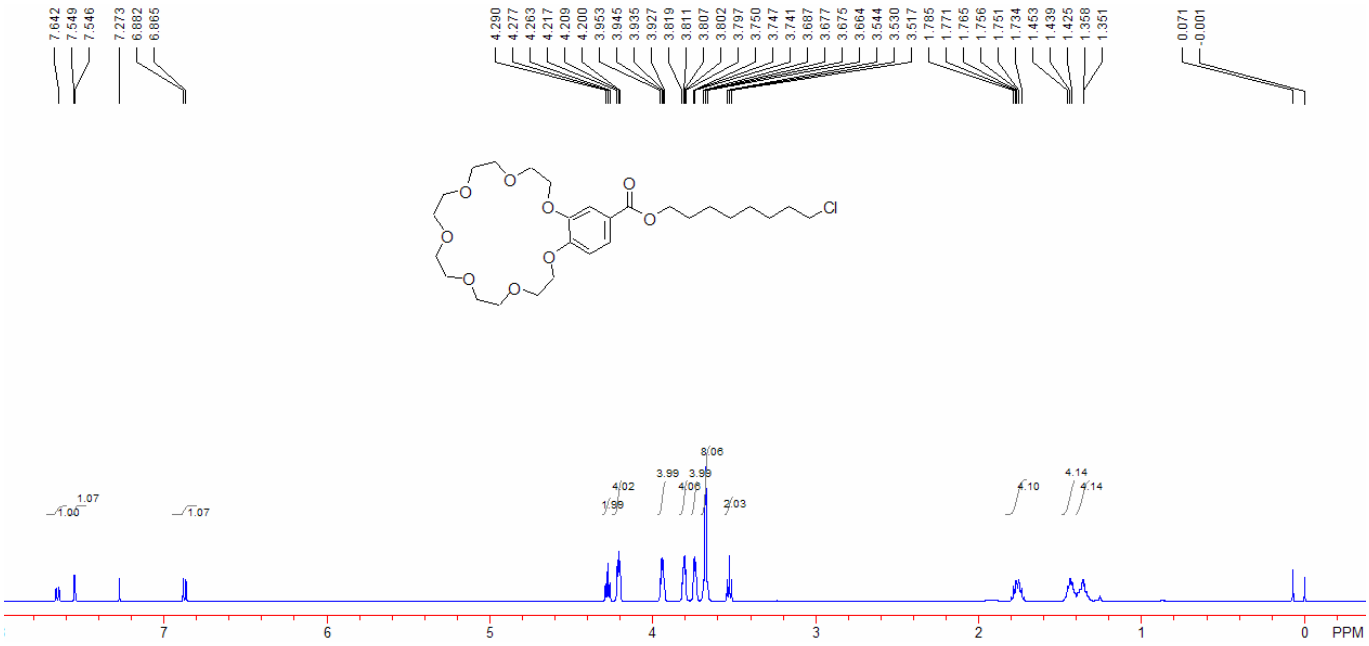


Figure S4. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **3**.

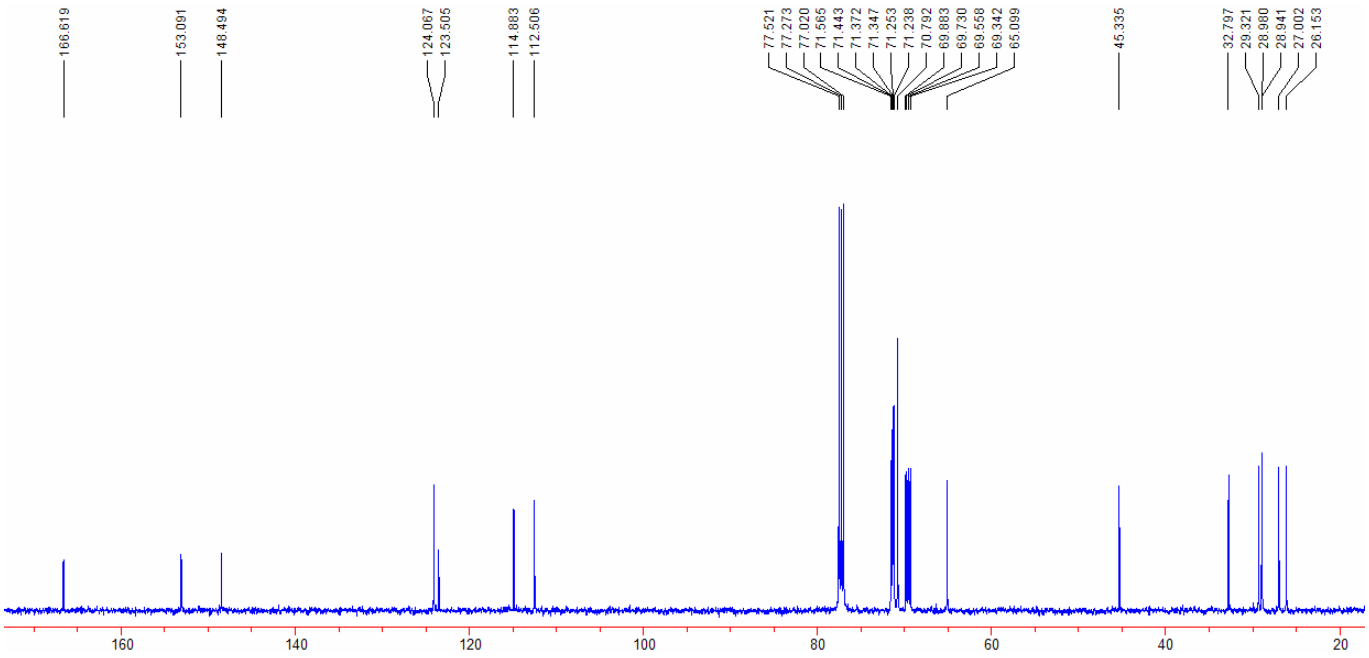


Figure S5. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **3**.

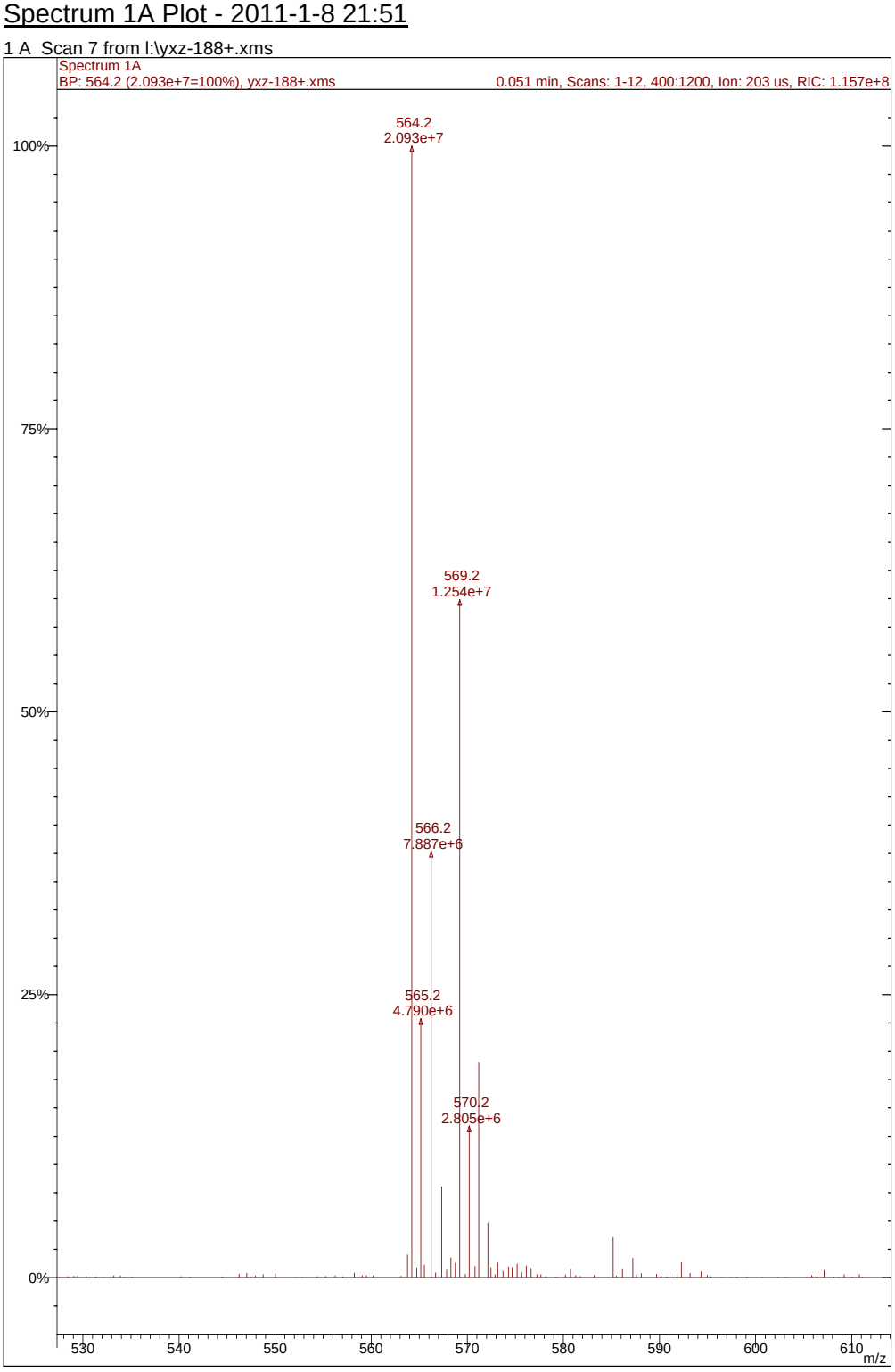
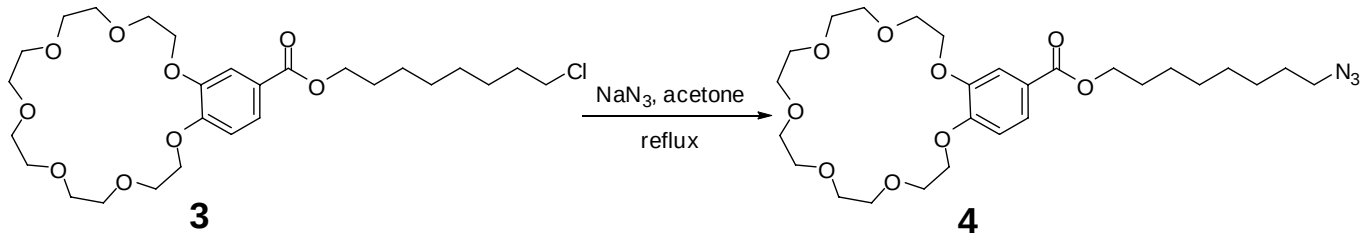


Figure S6. Electrospray ionization mass spectrum of **3**.

2.3. Synthesis of compound ***4***



3 **4**

Into a 250 mL round-bottomed flask were added **3** (5.37 g, 7.86 mmol) and sodium azide (1.02 g, 15.7 mmol) in 100 mL of acetone and 10 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 **4** was obtained as a pale yellow oil (5.33 g, 98%). The ^{1}H NMR spectrum of **4** is shown in Figure S7. ^{1}H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 7.65–7.67 (m, 1H), 7.55 (d, J = 1.6 Hz, 1H), 6.87 (d, J = 6.8 Hz, 1H), 4.28 (t, J = 5.4 Hz, 2H), 4.18–4.24 (m, 4H), 3.92–3.97 (m, 4H), 3.79–3.84 (m, 4H), 3.72–3.77 (m, 4H), 3.64–3.70 (m, 8H), 3.26 (t, J = 5.6 Hz, 2H), 1.71–1.81 (m, 2H), 1.56–1.64 (m, 2H), 1.29–1.48 (m, 8H). The ^{13}C NMR spectrum of **4** is shown in Figure S8. ^{13}C NMR (125 MHz, chloroform-*d*, room temperature) δ (ppm): 26.13, 26.82, 28.95, 29.27, 29.47,51.62, 65.05, 69.32, 69.54, 69.69, 69.85, 70.74, 71.22, 71.34, 71.44, 71.55, 112.45, 114.85, 123.44, 124.03, 148.46, 153.05, 166.58. LRESIMS is shown in Figure S9: m/z 576.3 $[M + Na]^+$ (100%), 592.3 $[M + K]^+$ (35%). HRESIMS: m/z calcd for $[M]^+$ $C_{27}H_{43}N_3O_9$, 553.2999; found 553.2985, error –2.5 ppm.

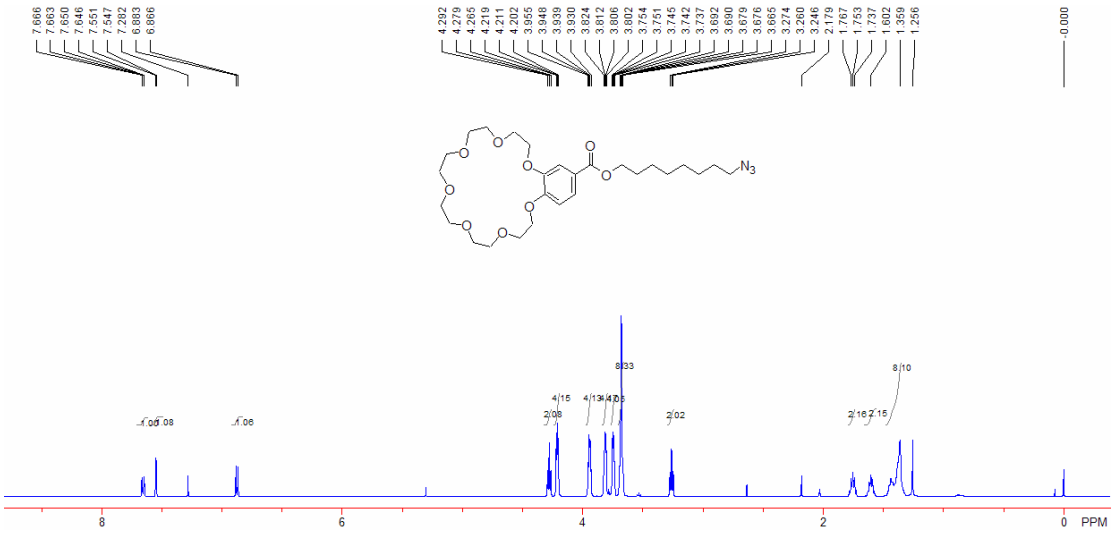


Figure S7. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **4**.

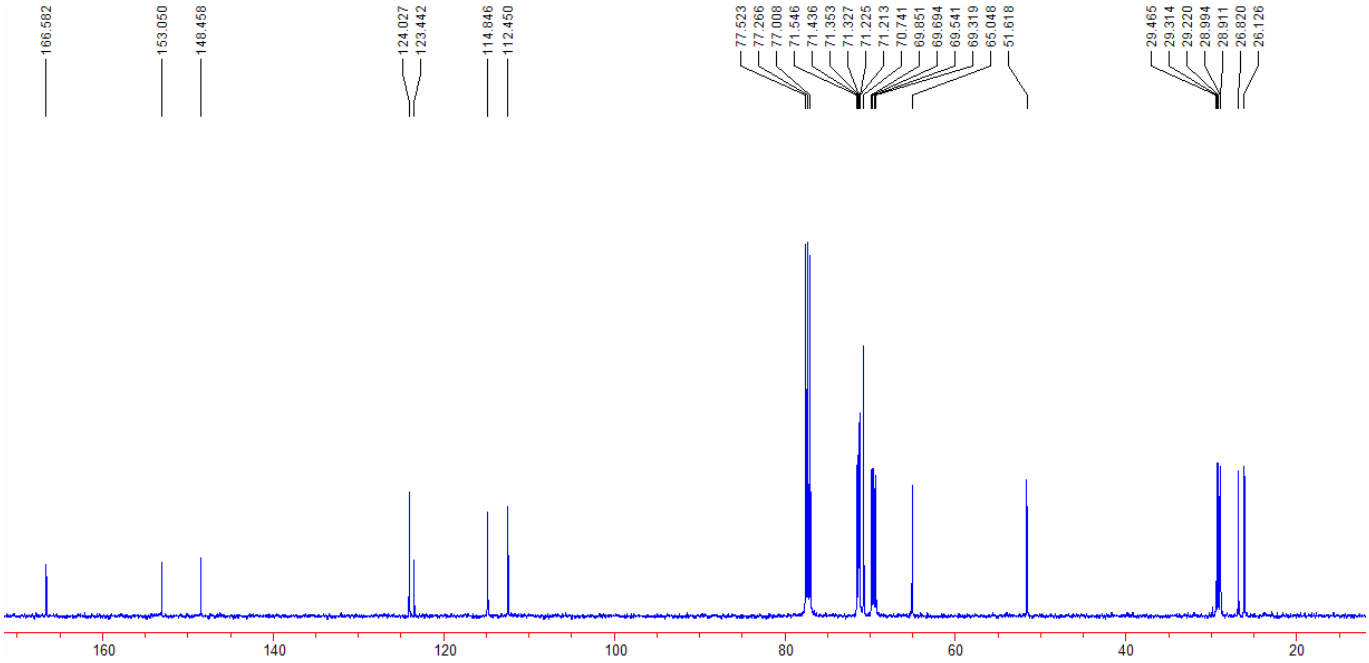


Figure S8. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **4**.

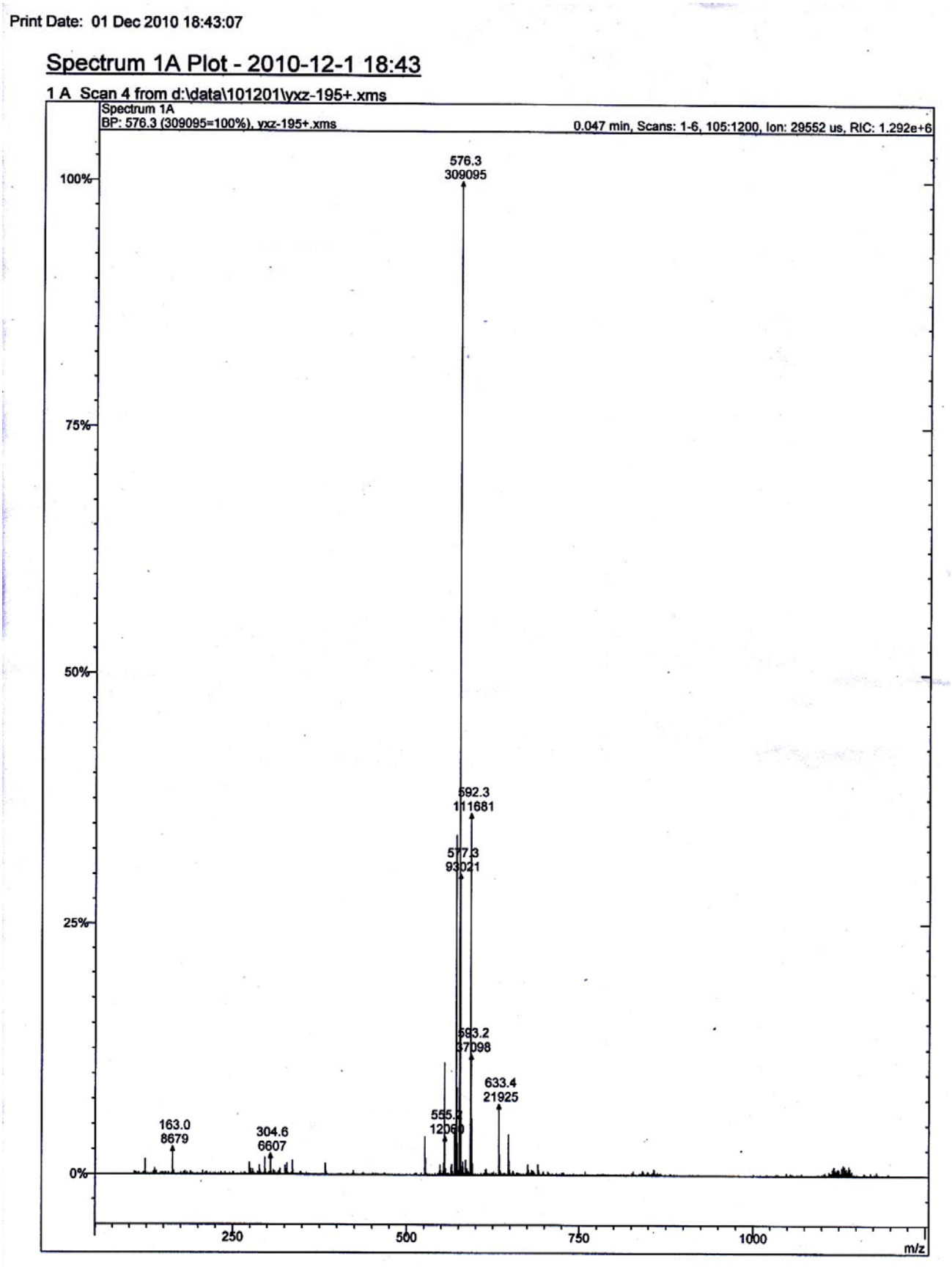
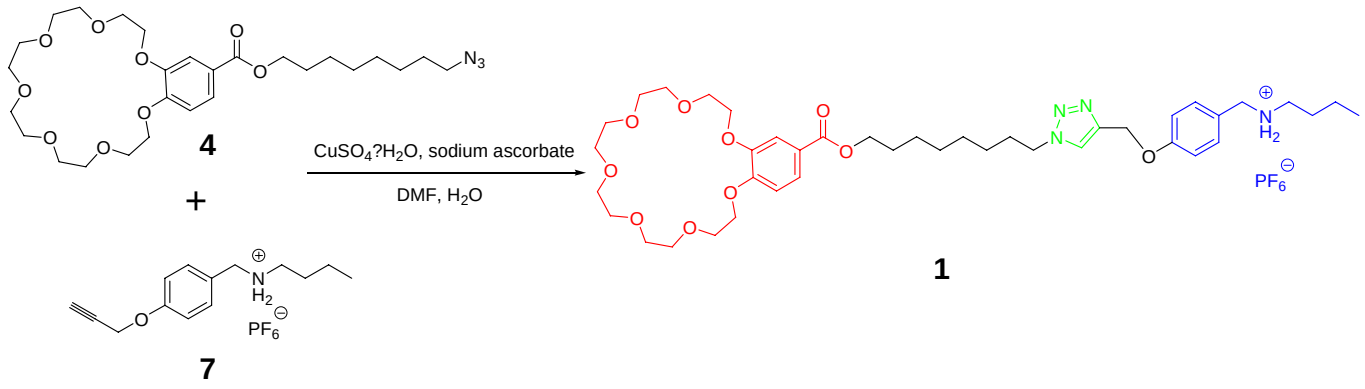


Figure S9. Electrospray ionization mass spectrum of **4**.

2.4. Synthesis of compound ***1***



A mixture of **4** (0.69 g, 1.3 mmol) and **7** (0.43 g, 1.3 mmol) in a mixture of DMF and H_2O (4:1, 30 mL) in the presence of $CuSO_4$•$5H_2O$ (31.2 mg, 0.13 mmol) with sodium ascorbate (49.5 mg, 0.26 mmol) was stirred at 50 ºC for 24 h. The reaction mixture was poured into saturated brine (100 mL) and the resulting solution was extracted with chloroform (50 mL × 3). The combined organic phase was concentrated and purified by flash column chromatography (MeOH/CH_2Cl_2, 50:1 *v*/*v*) to afford compound **1** as a white solid (0.54 g, 48%). mp 97.6–99.4 ºC. The ^{1}H NMR spectrum of **1** is shown in Figure S10. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 8.23 (s, 1H) 7.54–7.57 (m, 1H), 7.43 (d, J = 1.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 1H), 5.14 (s, 2H), 4.34 (t, J = 6.6 Hz, 2H), 4.21 (t, J = 6.6 Hz, 2H), 4.11–4.17 (m, 4H), 4.06 (s, 2H), 3.74–3.79 (m, 4H), 3.58–3.63 (m, 4H), 3.52–3.57 (m, 4H), 3.48–3.51 (m, 8H), 2.87 (t, J = 8.0 Hz, 2H), 1.76–1.85 (m, 2H), 1.63–1.72 (m, 2H), 1.51–1.61 (m, 2H), 1.20–1.41 (m, 10H), 0.88 (t, J = 7.2 Hz, 3H). The ^{13}C NMR spectrum of **1** is shown in Figure S11. ^{13}C NMR (125 MHz, DMSO-d_6, room temperature) δ (ppm): 13.99, 19.78, 25.89, 26.25, 27.91, 28.71,28.99, 30.18, 46.56, 49.92, 61.92, 64.89, 68.93, 69.20, 69.31, 70.40, 70.69, 70.75, 70.80, 70.90, 112.70, 113.52, 115.34, 122.58, 123.70, 124.59, 124.99, 132.01, 142.87, 148.17, 152.83, 159.07, 166.00. LRESIMS is shown in Figure S12: m/z 771.7 $[M - PF_6]^+$ (100%). HRESIMS: m/z calcd for $[M - PF_6]^+$ $C_{41}H_{63}N_4O_{10}^+$, 771.4544; found 771.4537, error –0.9 ppm.

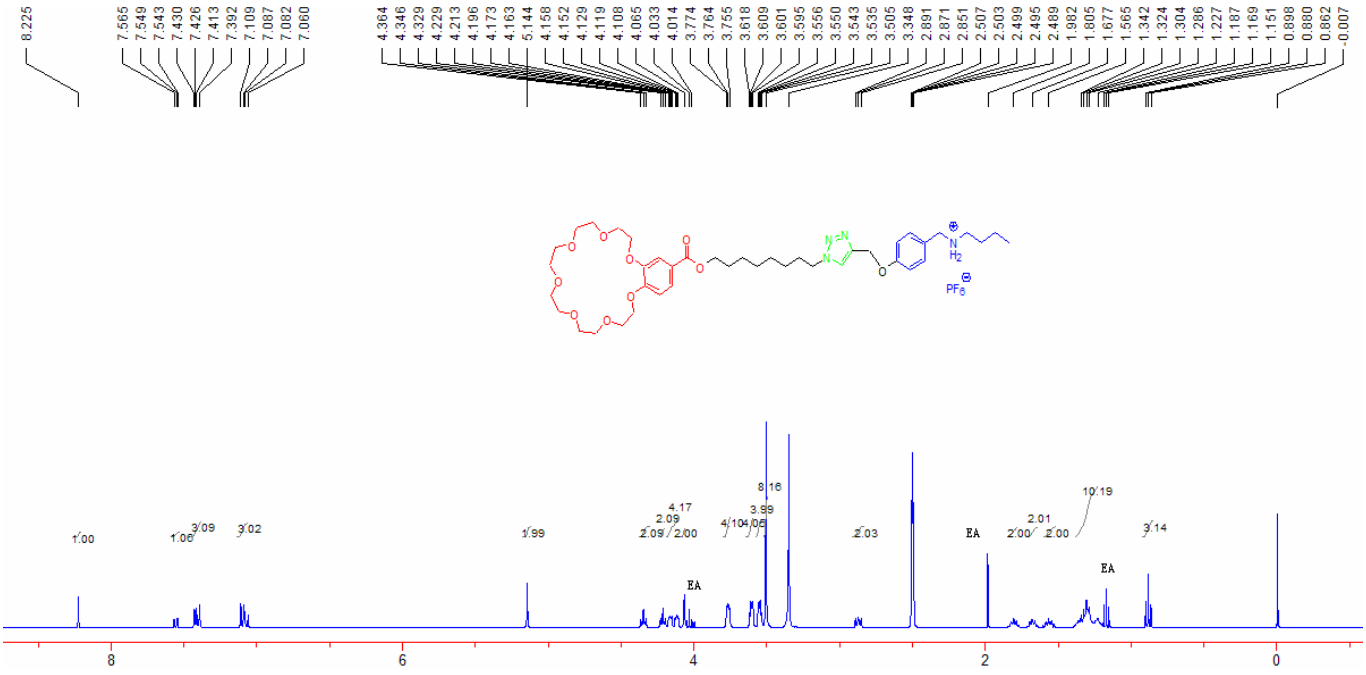


Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **1**.

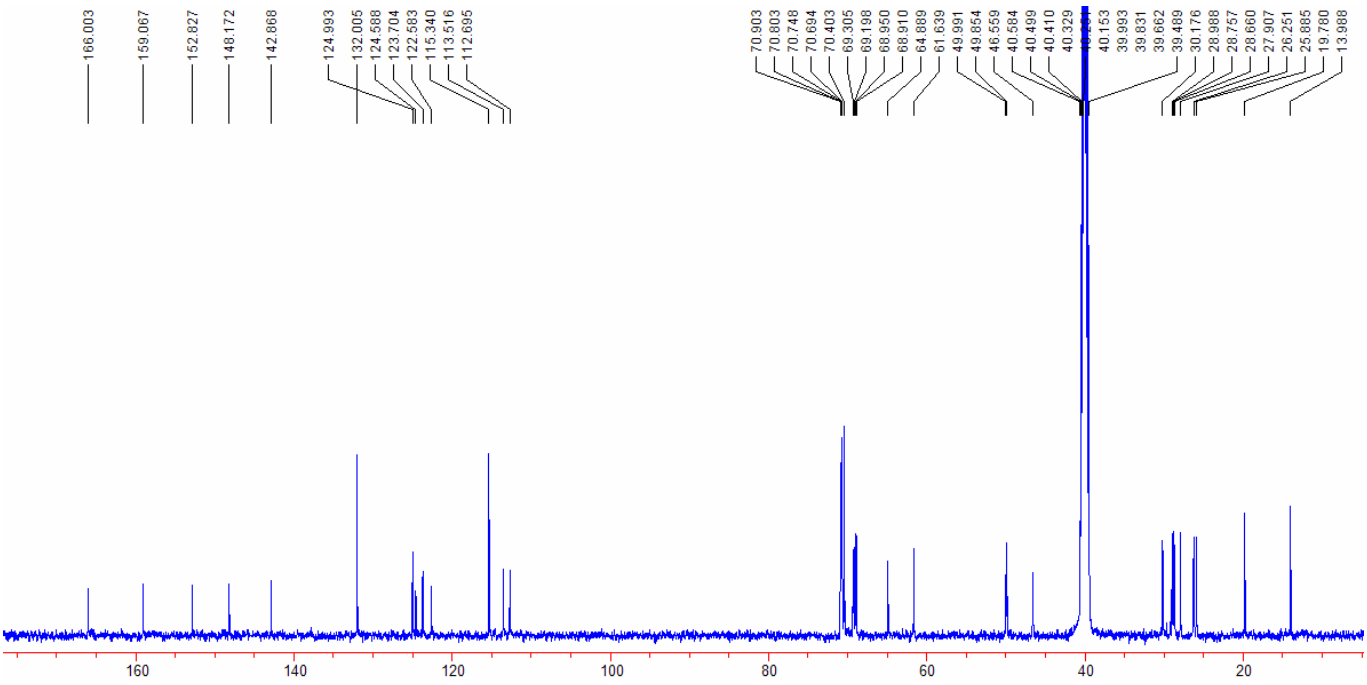


Figure S11. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of **1**.

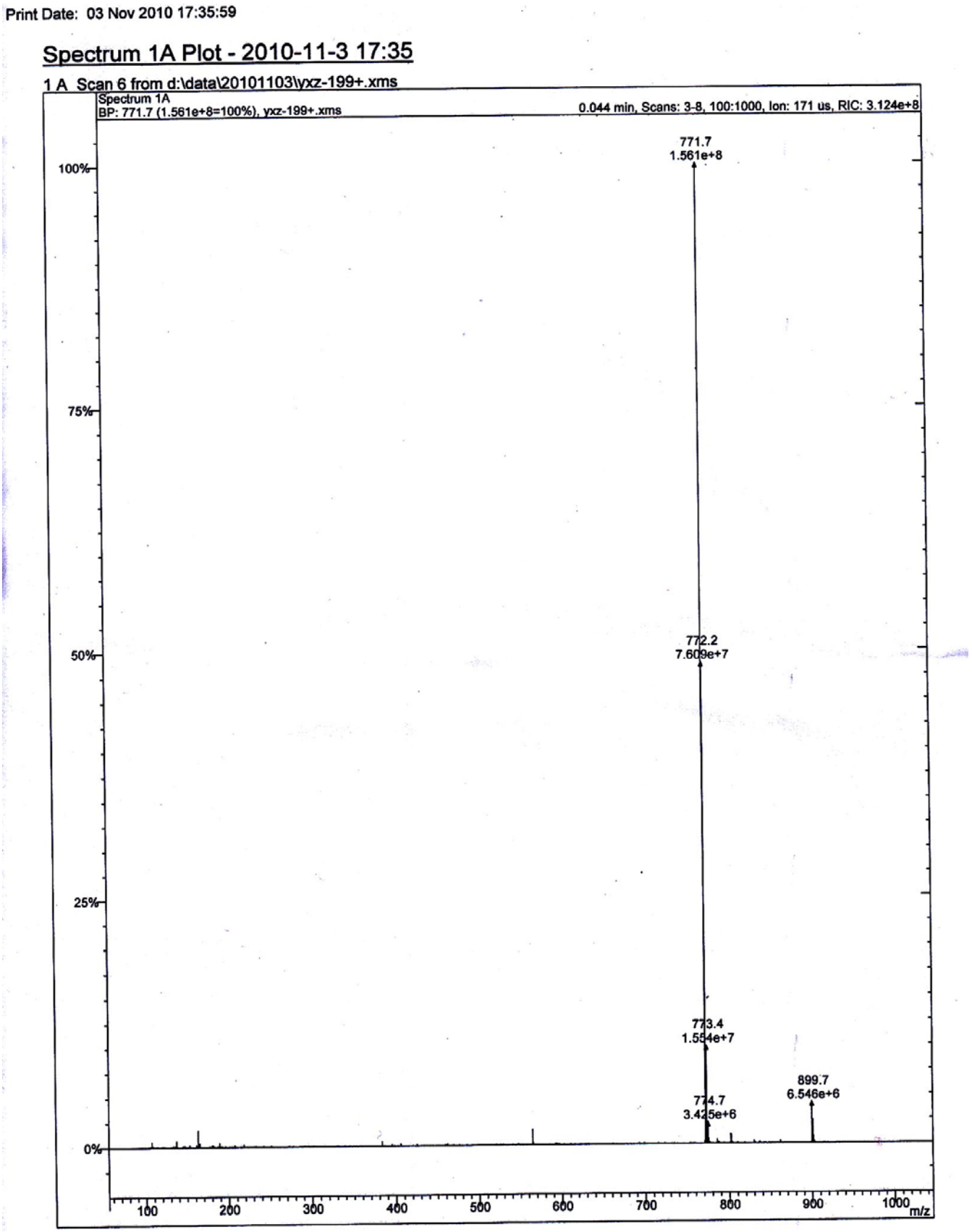


Figure S12. Electrospray ionization mass spectrum of **1**.

3. Partial COSY NMR spectrum of ***1***

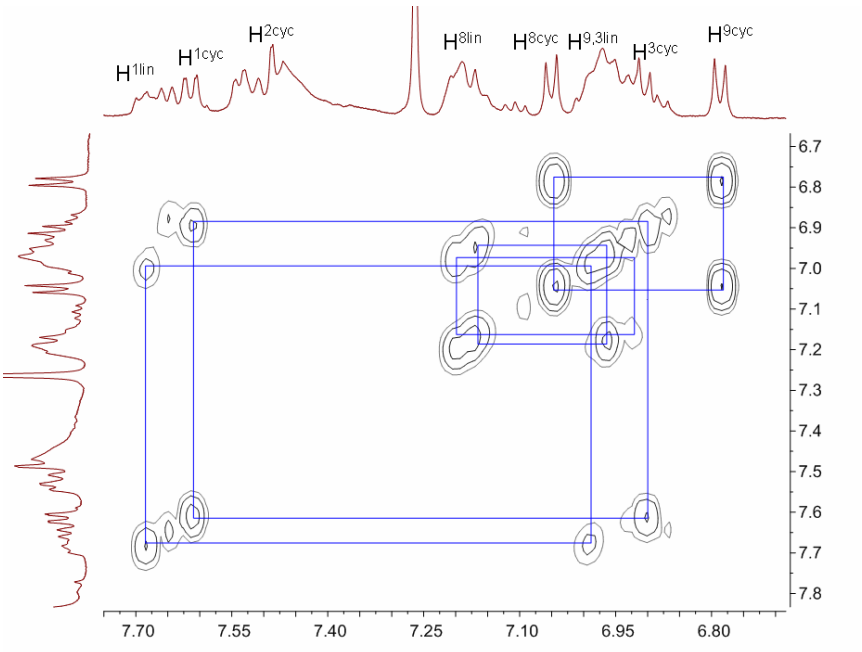


Figure S13. Partial COSY NMR (500 MHz, chloroform-*d*, 293 K) spectrum of a solution of **1** at a concentration of 50.0 mM.

From the 2D COSY NMR spectrum, strong correlations were observed between the correlative aromatic protons H_{8cyc} and H_{9cyc}, as well as H_{1cyc} and H_{3cyc}. Meanwhile, the linear correlative peaks between H_{1lin} and H_{3lin}, as well as H_{8lin} and H_{9lin} were also observed as shown in Figure S14. On the basis of the elaborate analysis mentioned above, the assignments of the complicated concentration-dependent ^{1}H NMR (Figure 1) and the formation of supramolecular polymer were made.

*4. Specific viscosity and Concentration dependence of diffusion coefficient D ofchloroform solution of monomer **1***

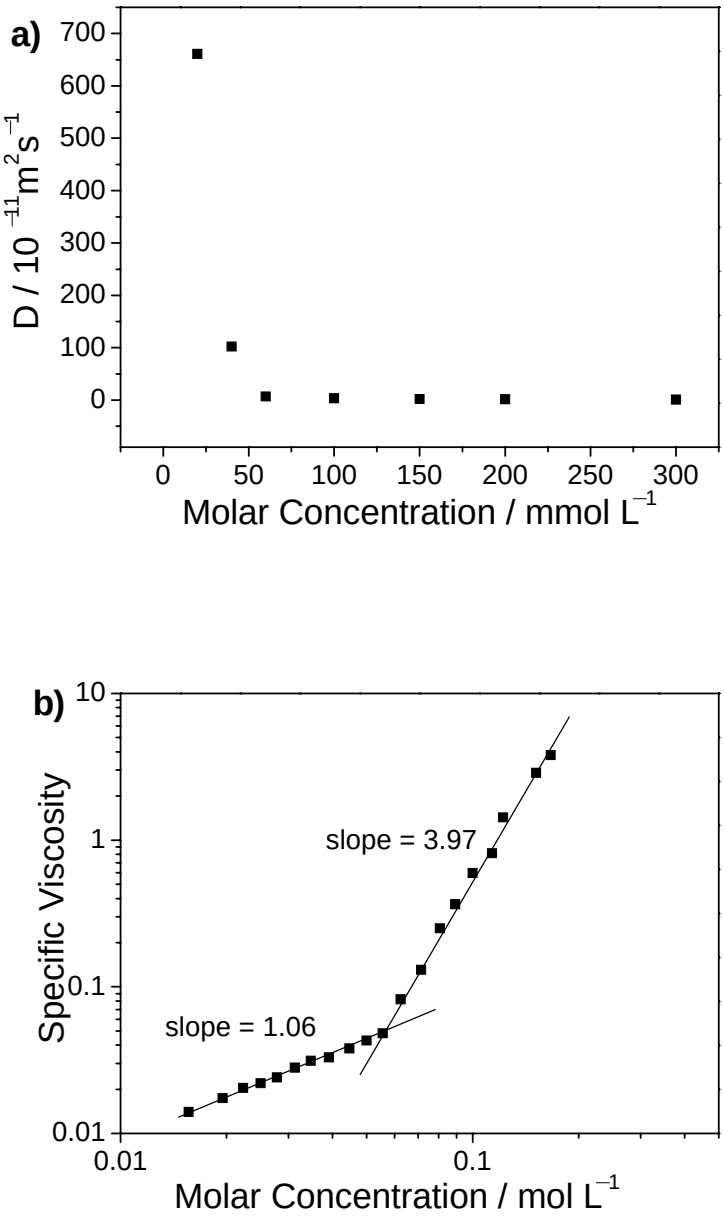
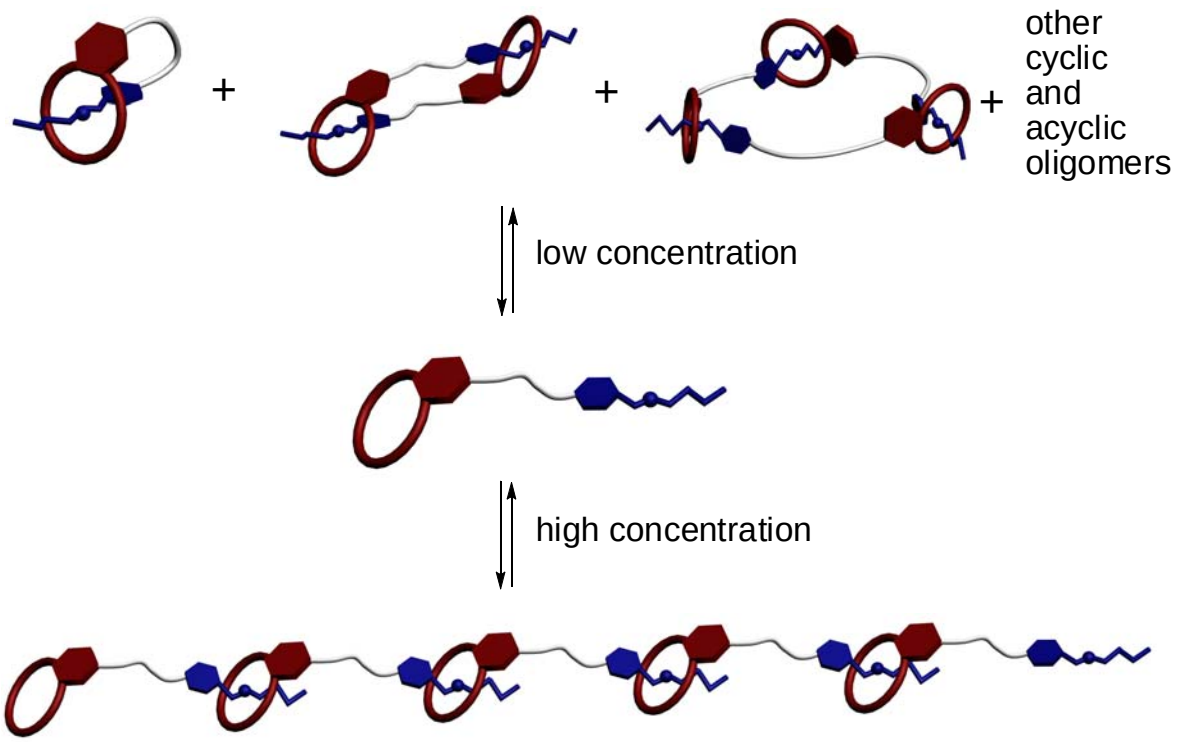


Figure S14. (a) Concentration dependence of diffusion coefficient *D* ($CDCl_3$, 293 K, 500 MHz); (b) Specific viscosity of choloroform solution of monomer **1** at 298 K.

5. Schematic representation of polymerization of monomer ***1***



Scheme S2. Schematic illustration of the formation of cyclic and acyclic oligomers at low concentration and linear supramolecular polymers at high concentration based on the self-organization of monomer **1**.

A log-log plot of the viscosity data at 298 K is shown in Figure 3. In the low monomer concentration range, the curve has a slope of 1.06, demonstrating a linear relationship between specific viscosity and initial monomer concentration, which is characteristic for non-interacting assemblies of constant size; these results indicate the presence of cyclic species in dilute solutions, as also observed in other systems. With increasing initial monomer concentration, a sharp rise in the specific viscosity is observed (slope = 3.97). This stronger concentration dependence of specific viscosity indicates the formation of a linear supramolecular polymer of increasing size. From Figure 3, a critical polymerization concentration, CPC, above which the concentration of cyclic species no longer increases and linear species are produced exclusively,[S3,S4] was determined from the onset of the steeper portion, yielding a value of 55 mM. This value belongs to the range of the CPC values for the crown ether-based systems reported by us (37–80 mM).

6. TEM and AFM images of the electrospun supramolecular polymer nanofibers

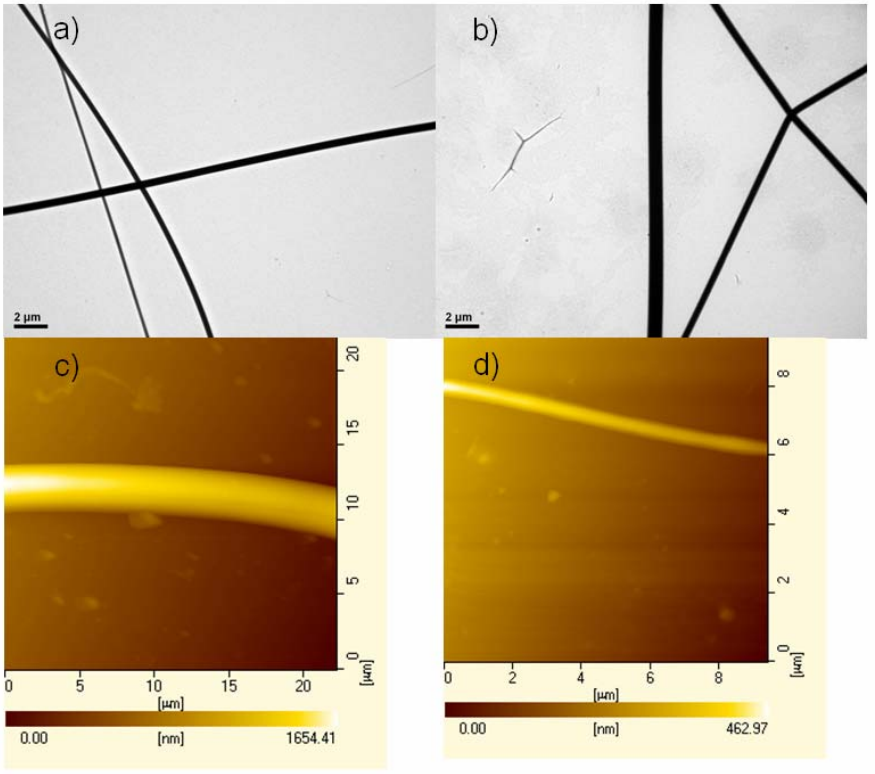
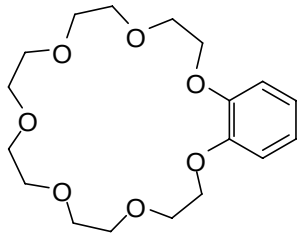


Figure S15. TEM images (a and b) and AFM images (c and d) of the electrospun supramolecular polymer nanofibers.

*7. The estimation of the association constant (K_a) between the **B21C7** host and secondary ammonium salt guest moieties of monomer **1***



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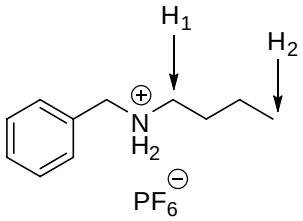

9

Method 1: ITC

Isothermal titration calorimetry (ITC) is a powerful physical technique for measuring solution binding thermodynamics and stoichiometry. ITC measurements were performed in a VP-ITC micro calorimeter (Microcal, USA), which is composed of a reference cell and a sample cell of 1.43 mL. Stock solutions of **9** (1.0 mM, 10 mL), and the titrant **8** (40.0 mM, 10 mL) in chloroform were prepared using volumetric glassware. Before each titration, all the solutions were degassed and kept constant temperature. In a typical run, a 250 μL syringe was full of **8** (40.0 mM) and the cell was loaded with **9** (1.0 mM, 1.43 mL). The titration of **9** with **8** was carried out at 298.15 K with a constant rate of 307 rpm, 34 injections of 8.0 μL, time interval of 240 s and duration of 2 s per μL. The enthalpy change per mole of each added **8** solution in the sample cell was recorded continuously. The control titrations of the **8** solution into chloroform were also completed under the same conditions. The enthalpy changes of the titrations of the blank test were subtracted from the original titration. All the data were analyzed with Microcal Origin 7.0 software provided by the manufacturer. The integration data from the titrations were fit using the "One Set of Sites" model and other stoichiometries yielded unsatisfactory fits of the data.

The determination of the association constant between **8** and **9** in acetonitrile was also performed using ITC.

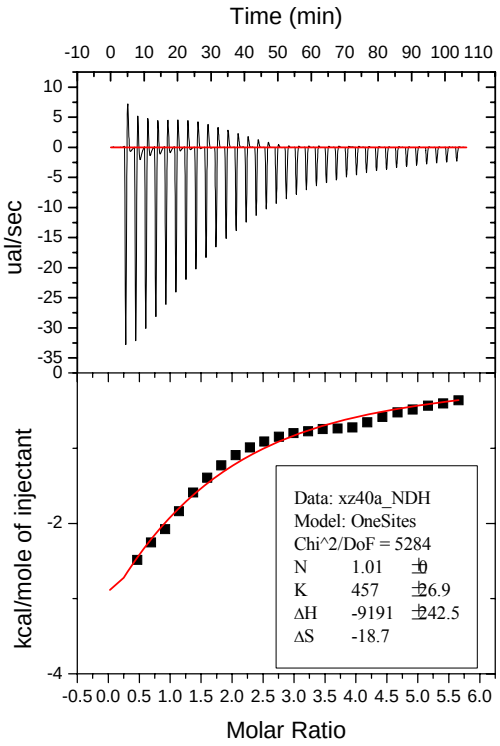

Figure S16. Titration of **9** (1.0 mM) with **8** (40.0 mM) in chloroform at 298 K.

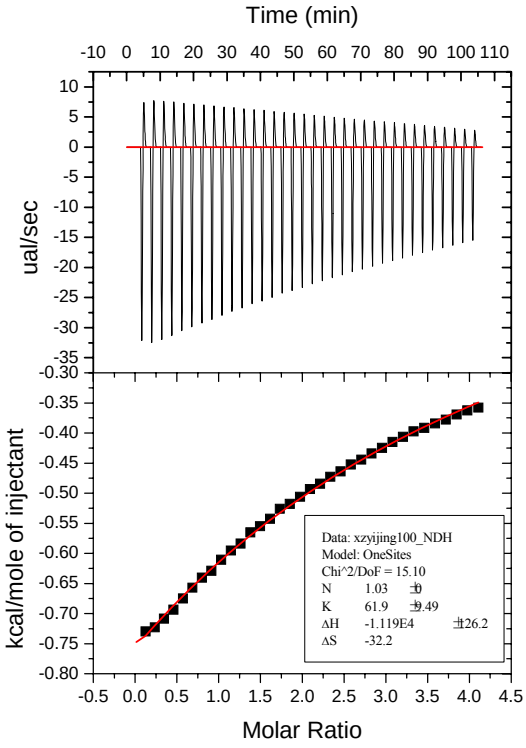

Figure S17. Titration of **9** (5.0 mM) with **8** (100 mM) in acetonitrile at 298 K.

Method 2: ^{1}H NMR

The ^{1}H NMR spectra of an equimolar solution of **8** and **9** in chloroform (or acetonitrile) shows three sets of resonances for uncomplexed **8**, uncomplexed **9**, and the complex between **8** and **9**, indicating slow-exchange complexation on the ^{1}H NMR time scale. The K_a values were calculated from integrations of complexed and uncomplexed peaks.

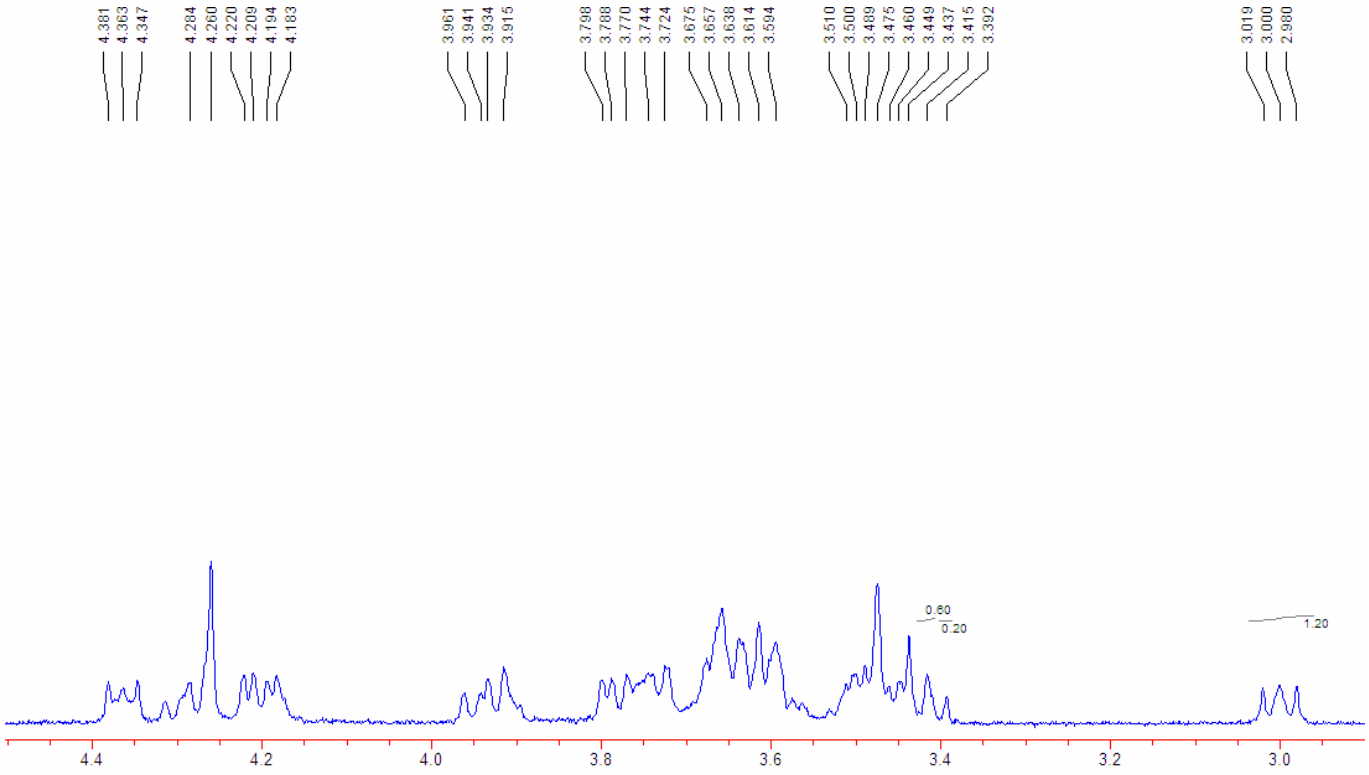

Figure S18. ^{1}H NMR spectrum of (400 MHz, chloroform-*d*, room temperature) of 2.50 mM **8** and **9**. The association constant $K_{a,\mathbf{8}\bullet\mathbf{9}}$ value calculated from integrations of complexed and uncomplexed peaks of H_1 of **9** is $[(0.80/2.0) \times 2.5 \times 10^{-3}]/[(1 - 0.80/2.0) \times 2.5 \times 10^{-3}]^2 = 444\ M^{-1}$.

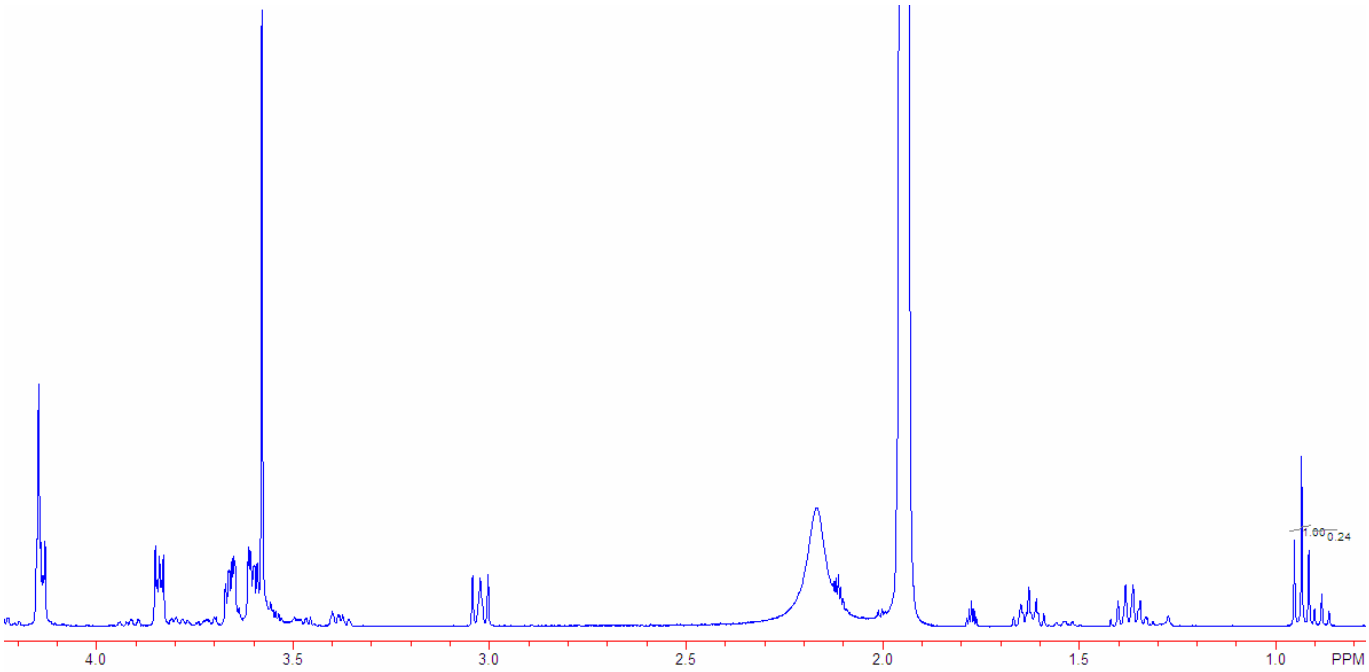

Figure S19. ^{1}H NMR spectrum of (400 MHz, acetonitrile-d_3, room temperature) of 5.0 mM **8** and **9**. The association constant $K_{a,\mathbf{8}\bullet\mathbf{9}}$ value calculated from integrations of complexed and uncomplexed peaks of H_2 of **9** is $[(0.24/1.24) \times 5.0 \times 10^{-3}]/[(1 - 0.24/1.24) \times 5.0 \times 10^{-3}]^2 = 60\ M^{-1}$.

By comparison, the K_a values between **8** and **9** produced by ITC and NMR are close.

*8. Glue-like viscous liquids pulled from a supramolecular polymer chloroform solution at 970 mM of monomer **1***

Figure S20. Glue-like viscous liquids pulled from a supramolecular polymer chloroform solution at 970 mM of monomer **1**.

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