Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A Novel Supramolecular Polymer Network Based on A Catenane-Type Crosslinker

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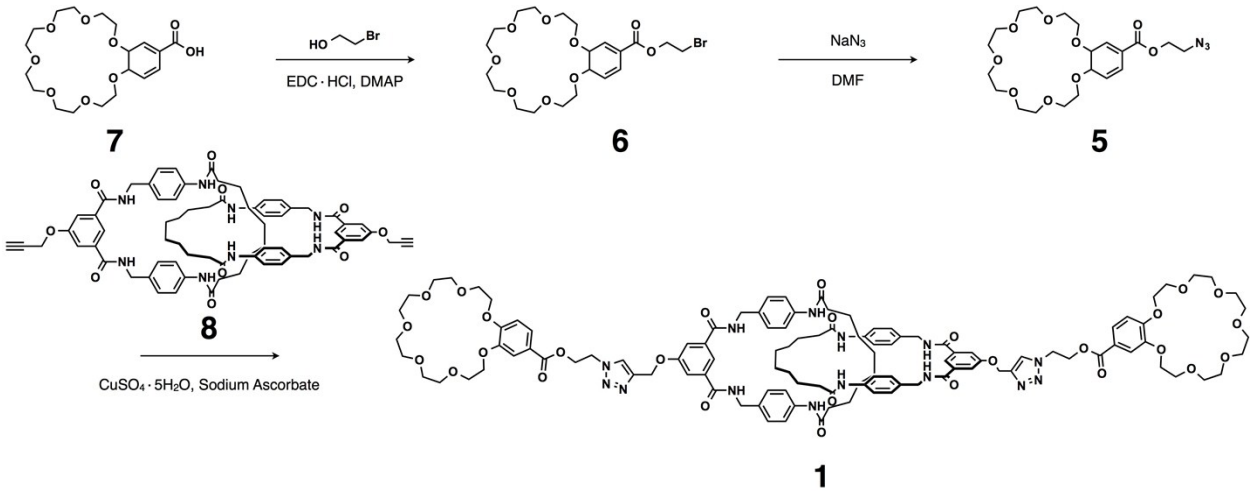
1. General

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **3**,[S1] **4**,[S2] **7**[S3], **8**[S4] were prepared according to the published procedures. NMR spectra were collected on a Bruker AVANCE DMX-500 spectrometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal standard. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an 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 carried out with Ubbelohde micro dilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 and 0.70 mm inner diameter) at 25 °C in chloroform. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Rheological data were obtained by using a Physical MCR301 rheometer (Anton Paar) with cone-plate geometry (diameter of 25 mm, 2° cone, truncation height is 103 μm. Oscillatory frequency sweep experiments were performed from 0.1 rad/s to 1000 rad/s with a strain in the linear region at 25 °C.

2. Synthesis

2.1. Synthesis of crosslinker 1



Scheme S1. Synthetic route to crosslinker **1**.

Compound 6. To a dichloromethane solution (100 mL) of **7** (1.60 g, 4.00 mmol) was added bromoethanol (3.40 g, 27.00 mmol), 4-dimethylaminopyridine (DMAP) (0.24 g, 2.00 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (1.53 g, 8.00 mmol). The resulting mixture was stirred overnight. The excess solvent was removed on a rotary evaporator at reduced pressure and the residue was subjected to silica gel chromatography (CH_2Cl_2/CH_3OH, 100:1 *v*/*v*) to give **6** (1.32 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.71–7.68 (m, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 6.90–6.88 (d, *J* = 10 Hz, 1H), 4.61–4.58 (t, *J* = 7.5 Hz, 2H), 4.23–4.20 (m, 4H), 3.96–3.93 (m, 4H), 3.83–3.80 (m, 4H), 3.76–3.73 (m, 4H), 3.70–3.67 (m, 8H), 3.65–3.62 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.77, 153.22, 148.31, 124.20, 122.26, 114.63, 112.24, 71.37, 71.25, 71.16, 71.12, 71.03, 71.01, 70.66, 70.59, 70.56, 69.82, 69.63, 69.47, 69.33, 69.13, 66.63, 64.03, 28.93, 15.17.

Compound 5. To a dimethylformamide solution (60 mL) of **6** (0.40 g, 0.79 mmol) was added a water solution (10 mL) of sodium azide (NaN_3) (0.25 g, 3.95 mmol). The resulting mixture was heated to 80 °C and stirred overnight. The excess solvent was removed on a rotary evaporator at reduced pressure and the residue was subjected to silica gel chromatography (CH_2Cl_2/CH_3OH, 100:1 *v*/*v*) to give **5** (0.34 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.70–7.68 (m, 1H), 7.56–7.55 (d, *J* = 5 Hz, 1H), 6.90–6.88 (d, *J* = 10 Hz, 1H), 4.49–4.46 (t, *J* = 7.5 Hz, 2H), 4.23–4.19 (m, 4H), 3.96–3.92 (m, 4H), 3.83–3.79 (m, 4H), 3.76–3.74 (m, 4H), 3.68 (s, 8H), 3.66–3.65 (d, *J* = 5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.92, 153.15,

148.29, 124.18, 122.13, 114.38, 112.24, 71.33, 71.22, 71.11, 71.09, 70.98, 70.64, 70.55, 69.80, 69.58, 69.45, 69.21, 69.09, 66.62, 63.65, 60.38, 50.04, 30.92, 21.04, 15.14, 14.19.

Compound 1. To a DMF solution (10 mL) of **5** (0.17 g, 0.37 mmol) and **8** (0.20 g, 0.17 mmol) was added a water solution (1 mL) of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) (8.40 mg, 0.03 mmol) and sodium ascorbate (16.80 mg, 0.08 mmol). The resulting mixture was heated to 80 °C and stirred for 24 hours under nitrogen atmosphere. The excess solvent was removed on a rotary evaporator at reduced pressure and the residue was subjected to silica gel chromatography (CH_2Cl_2/CH_3OH, 100:1 *v*/*v*) to give **1** (0.31 g, 86%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K): δ (ppm) 9.73 (s, 4H), 8.45 (s, 4H), 8.37 (s, 2H), 7.74 (s, 2H), 7.51 (s, 6H), 7.37 (d, J = 1.5 Hz, 2H), 7.34–7.32 (d, J = 10 Hz, 8H), 7.06–7.04 (d, J = 10 Hz, 2H), 6.94–6.92 (d, J = 10 Hz, 8H), 5.04 (s, 4H), 4.82–4.80 (d, J = 10 Hz, 4H), 4.63–4.60 (t, J = 7.5Hz, 4H), 4.16–4.10 (m, 18H), 3.76–3.72 (m, 8H), 3.60–3.51 (m, 8H), 3.49–3.48 (d, J = 5 Hz, 16H), 2.13 (s, 8H), 1.27 (s, 12 H), 0.78 (s, 16H). ^{13}C NMR (125 MHz, d_6-DMSO, 298 K): δ (ppm) 171.39, 165.70, 164.93, 157.82, 152.45, 147.55, 142.39, 138.08, 136.30, 128.13, 125.05, 123.33, 121.31, 118.74, 112.98, 112.11, 70.34, 70.25, 70.20, 70.17, 70.12, 70.10, 69.85, 68.73, 68.63, 68.41, 68.28, 62.87, 48.65, 36.01, 28.99, 27.92, 25.25. LRESIMS for **1**: *m*/*z* 1064.8 $[M + 2H]^{2+}$ and 2146.0 $[M + H_2O + H]^+$. HRESIMS for **1**: *m*/*z* calcd for $[M]^+$ $C_{112}H_{138}N_{14}O_{28}$ 2126.9805; found 2126.9811; error 0.2 ppm.

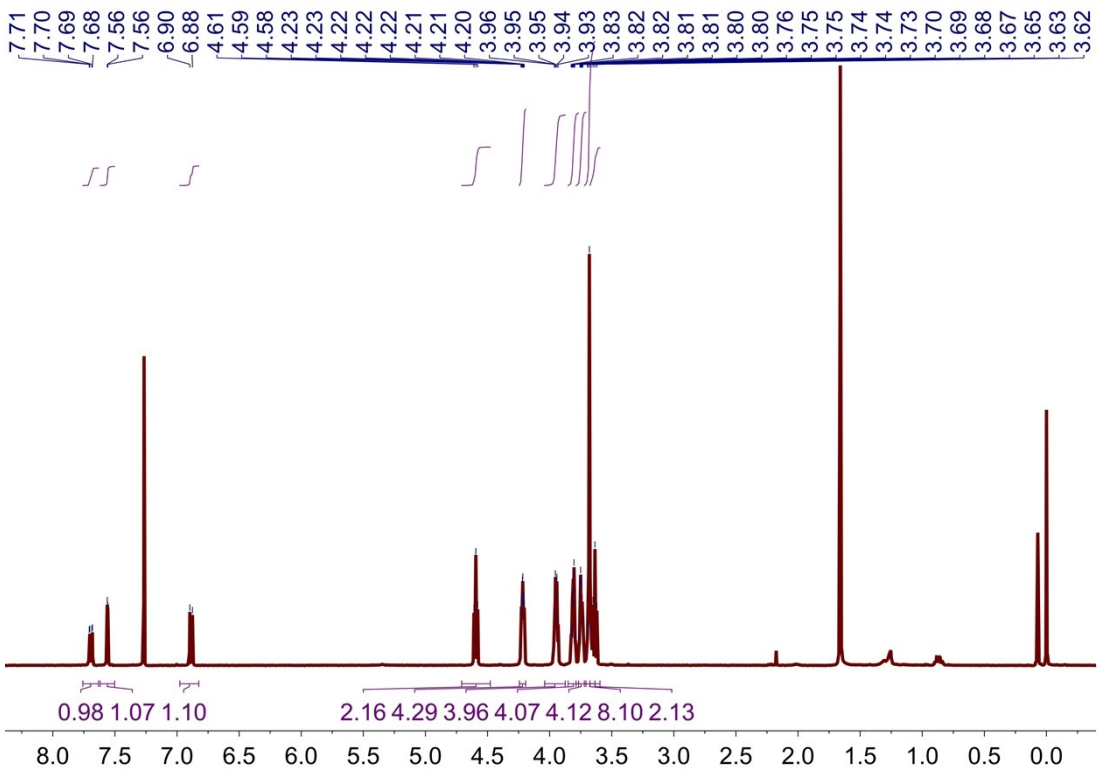


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of compound **6**.

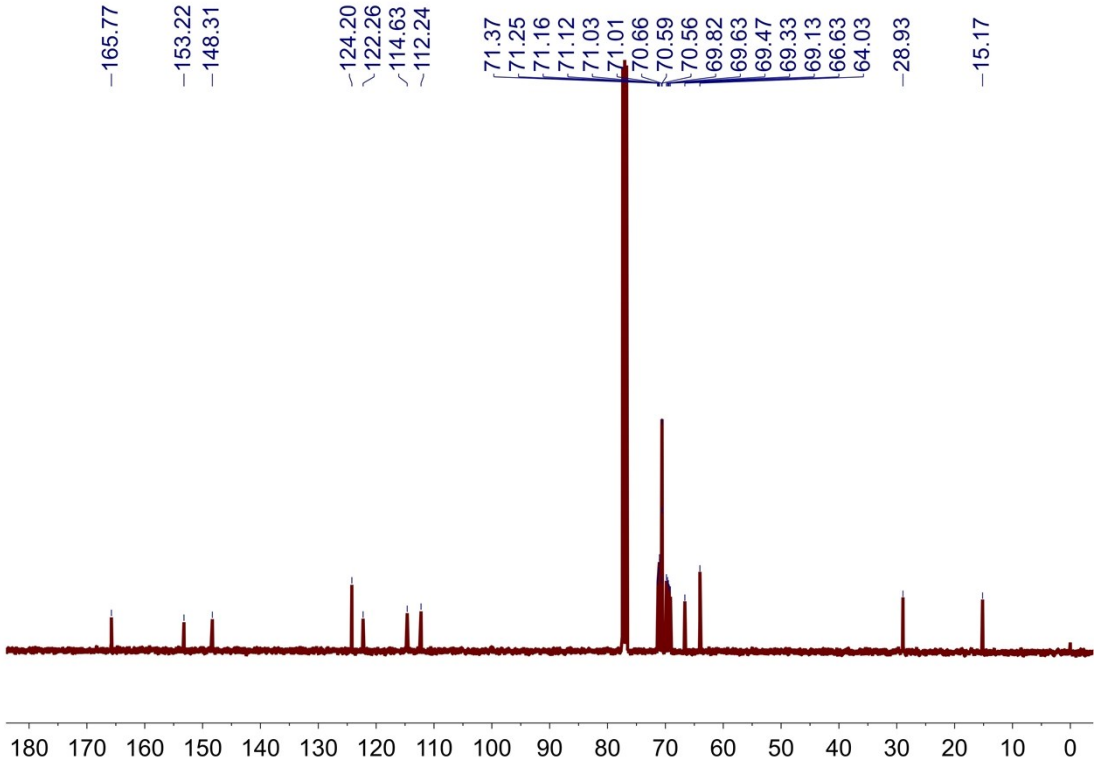


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of compound **6**.

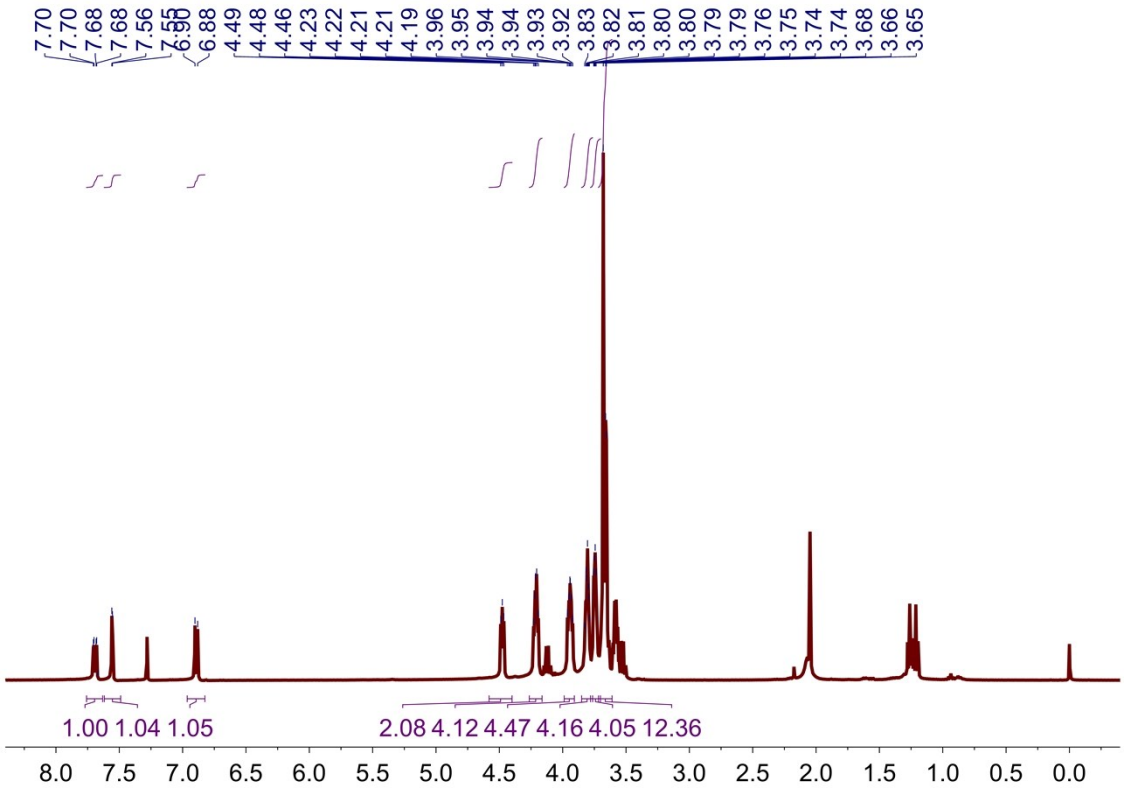


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of compound **5**.

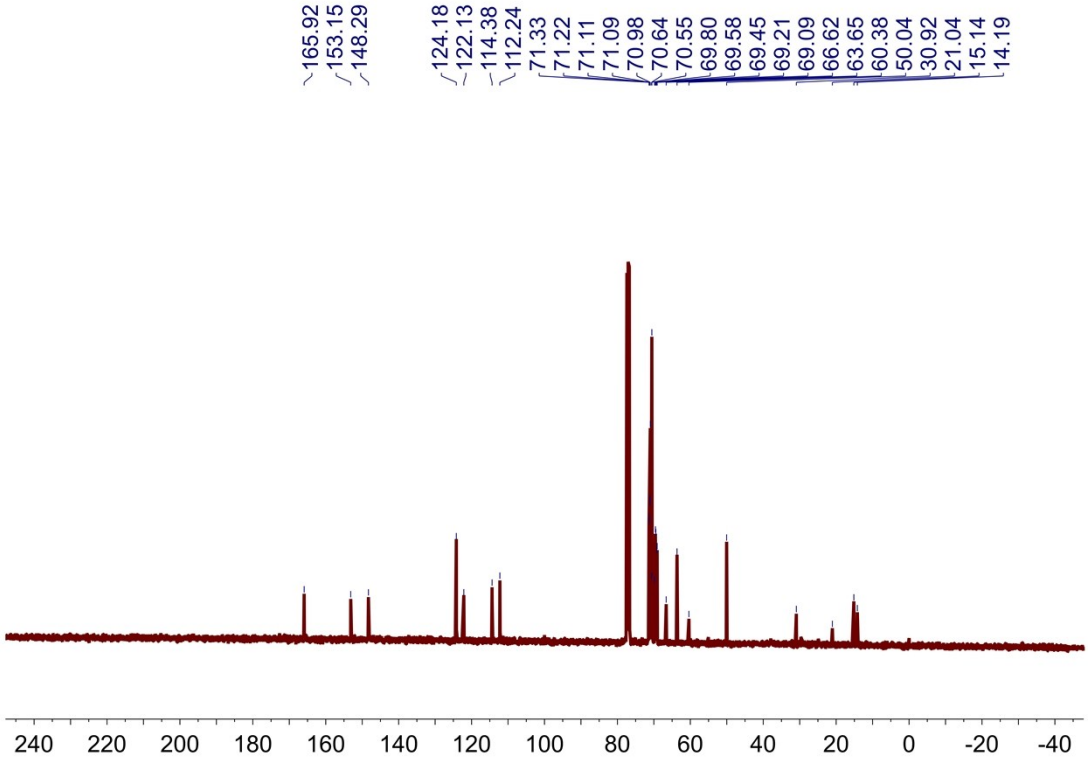


Figure S4. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of compound **5**.

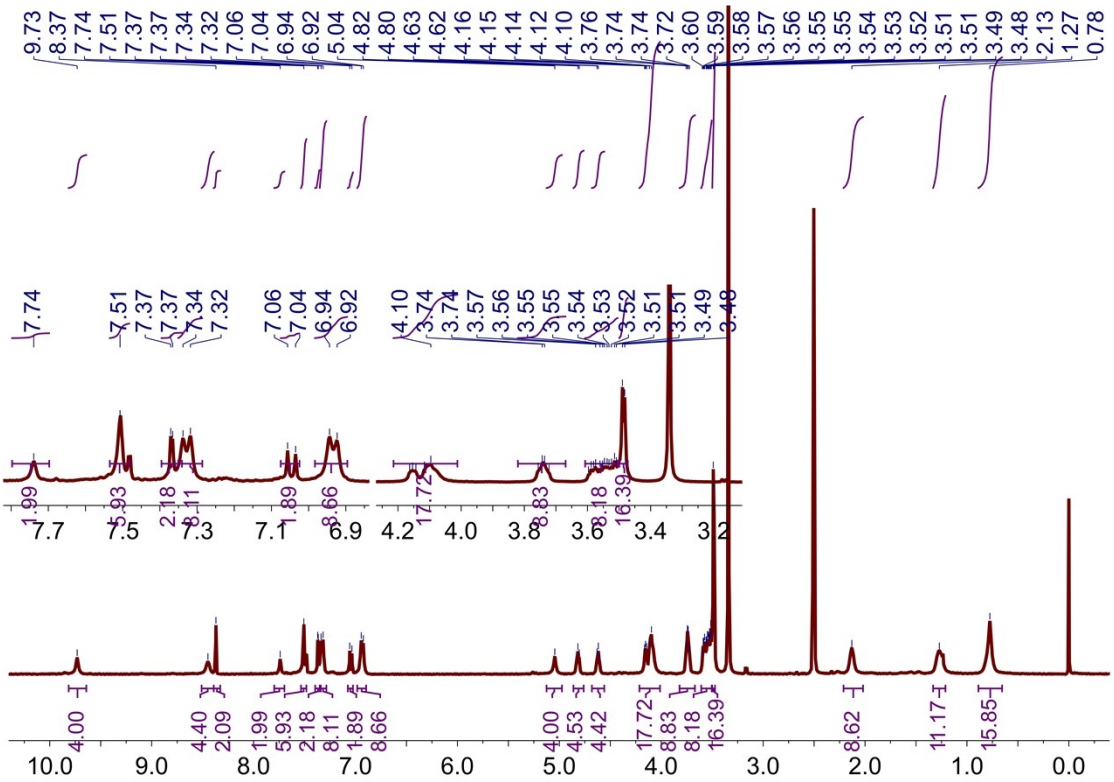


Figure S5. [1]H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of compound **1**.

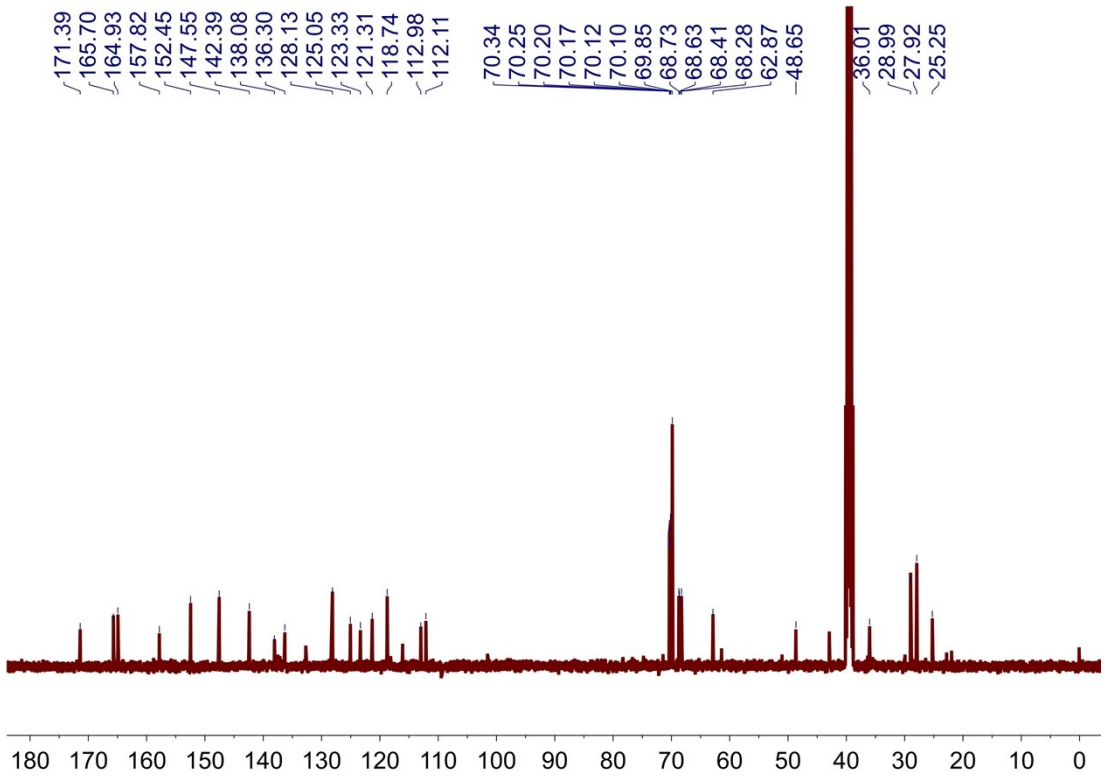


Figure S6. [13]C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of compound **1**.

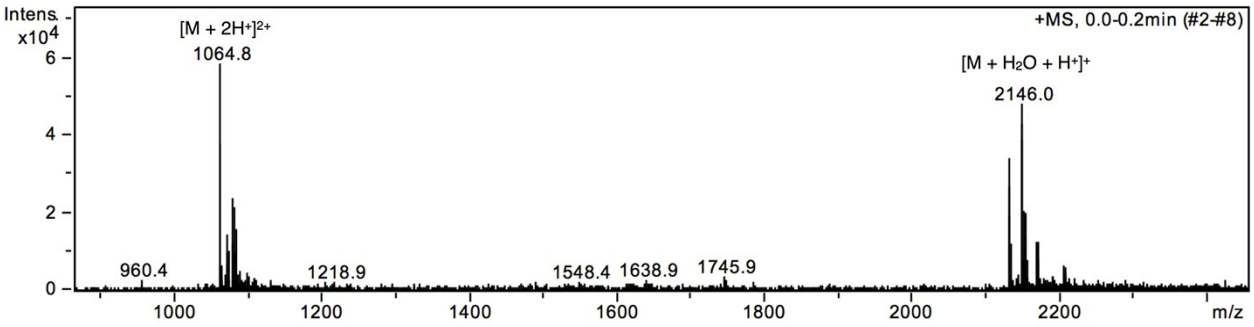
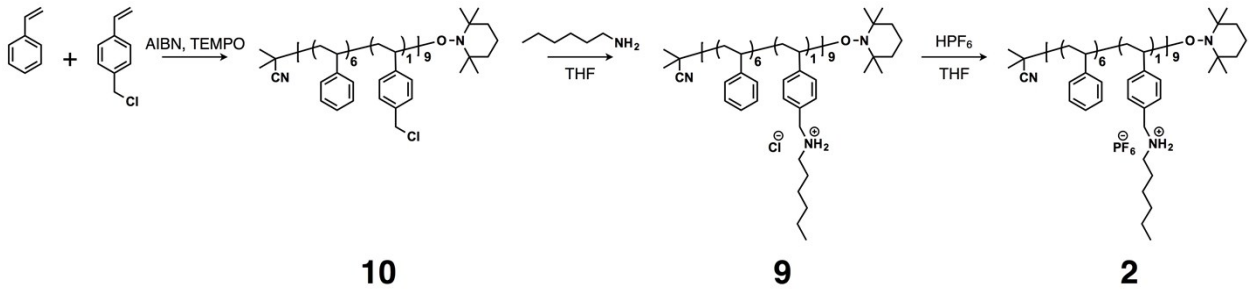


Figure S7. LRESIMS spectrum of compound **1**.

2.2. Synthesis of polymer 2



Scheme S2. Synthetic route to polymer **2**.

Polymer 10. A stirred mixture of styrene (22.65 g, 191.40 mmol), 4-vinylbenzyl chloride (2.49 g, 12.75 mmol), azobisisobutyronitrile (AIBN) (0.21 g, 1.27 mmol), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.49 g, 3.19 mmol) in *o*-xylene (25 mL) under nitrogen atmosphere was maintained at 125 °C in an oil bath for 3 days. The reaction mixture was precipitated into methanol; the solid was reprecipitated several times and vacuum dried to afford **10** as a white solid (11.54 g, 46%). The chemical structure of polymer **10** was determined by ^{1}H NMR spectroscopy (Figure S8). The number-average molecular weight (M_n = 6927) and polydispersity value (PDI = 1.17) could be calculated from the GPC data (Figure S9) of polymer **10**.

Polymer 9. A mixture of **10** (7.61 g, 1.10 mmol) and hexylamine (64.70 mL, 490 mmol) in tetrahydrofuran (THF) (400 mL) was stirred for 24 hours at room temperature. The resulting solution was concentrated and precipitated into methanol to afford **9** as a white solid (7.55 g, 87%). The chemical structure of polymer **9** was determined by ^{1}H NMR spectroscopy (Figure S10). By comparing the ^{1}H NMR spectra of polymer **10** and **9**, this conversion was complete.

Polymer 2. A mixture of **9** (6.28 g, 0.81 mmol) and hexafluorophosphoric acid (HPF_6) (5.26 mL, 35.70 mmol) in THF (400 mL) was stirred for 4 hours at room temperature. The excess THF was removed on a rotary evaporator at reduced pressure and the residue was precipitated in methanol/H_2O (1:9, *v*/*v*) to afford **2** as a white solid (6.39 g, 90%). The chemical structure of polymer **2** was determined by ^{1}H NMR spectroscopy (Figure S11). By comparing the ^{1}H NMR spectra of polymer **9** and **2**, this conversion was complete.

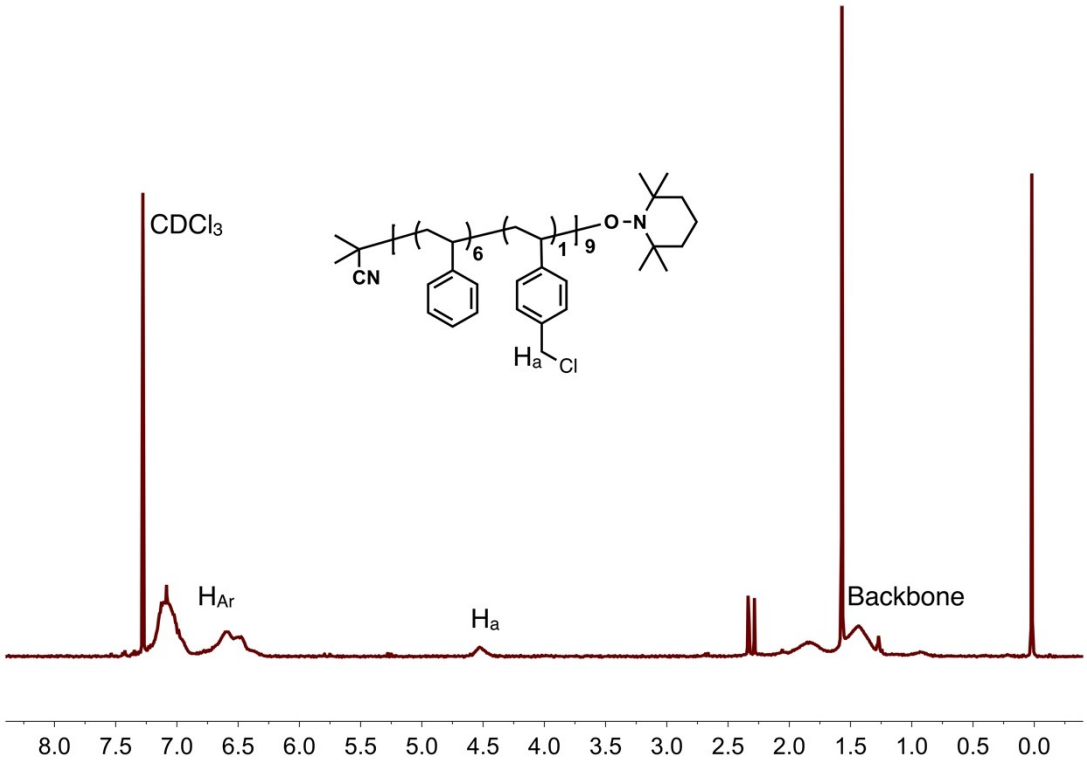


Figure S8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of polymer **10**.

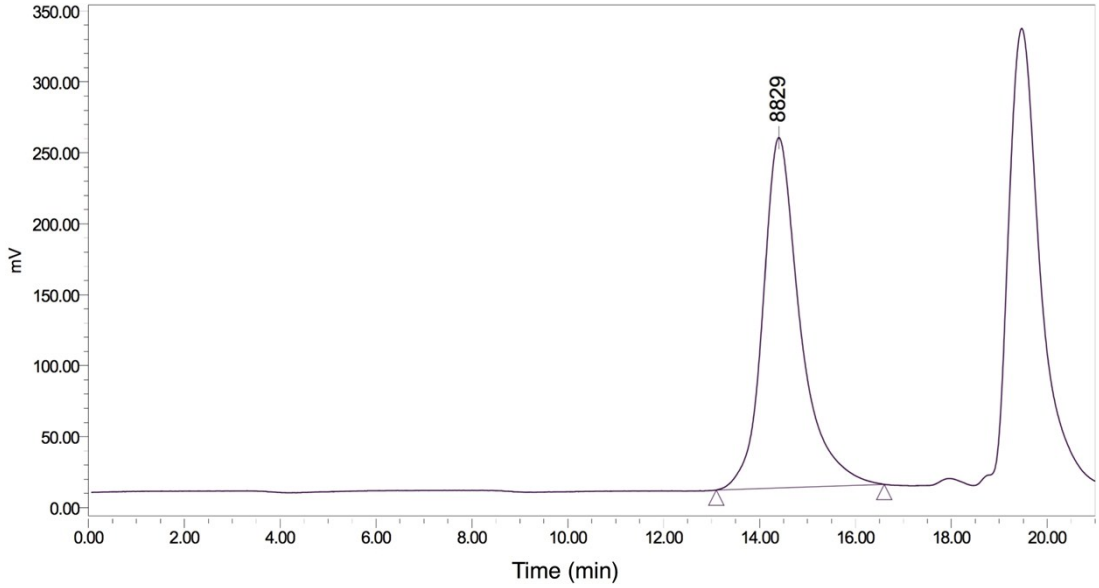


Figure S9. GPC spectrum of polymer **10**.

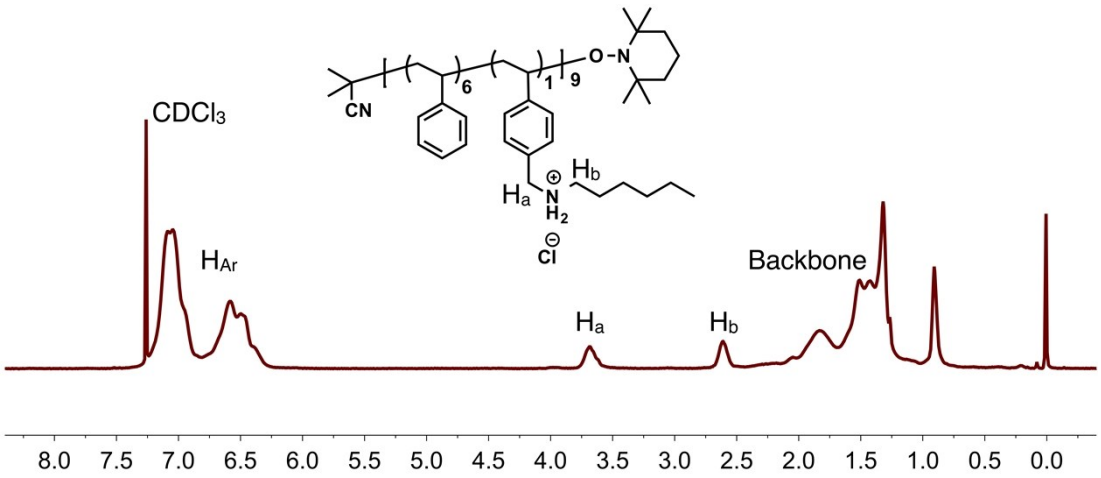


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of polymer **9**.

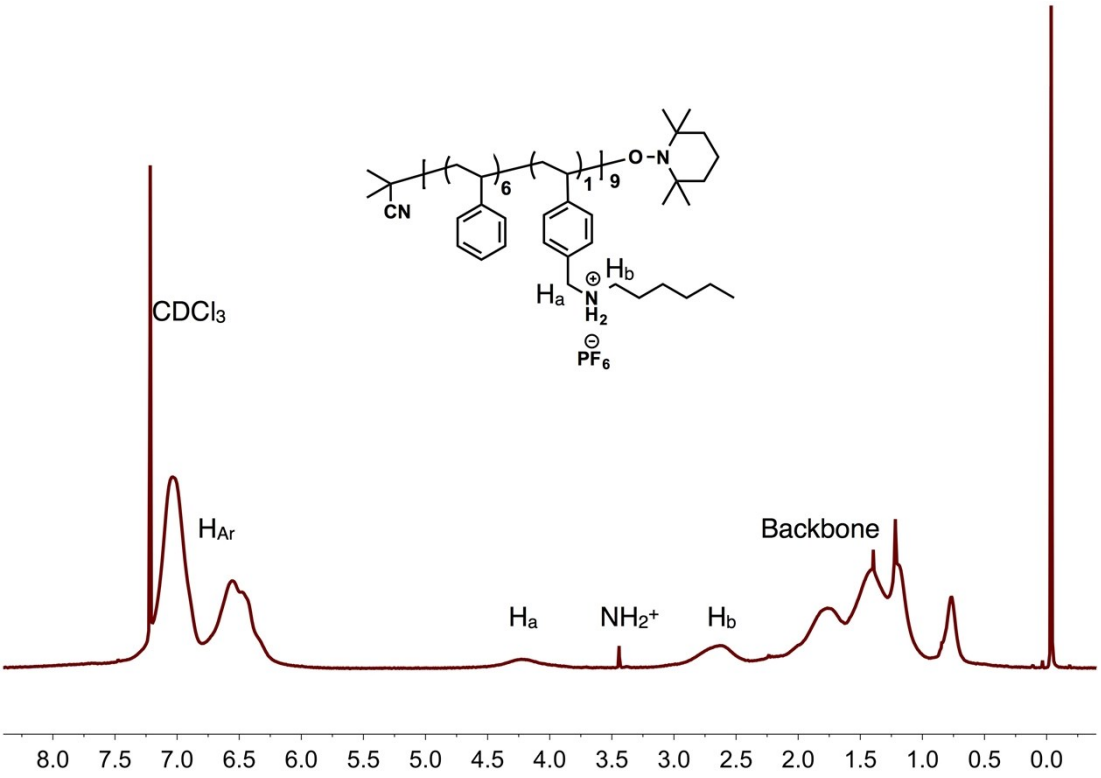


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of polymer **2**.

2.3. NMR spectra of crosslinker 3 and model guest 4

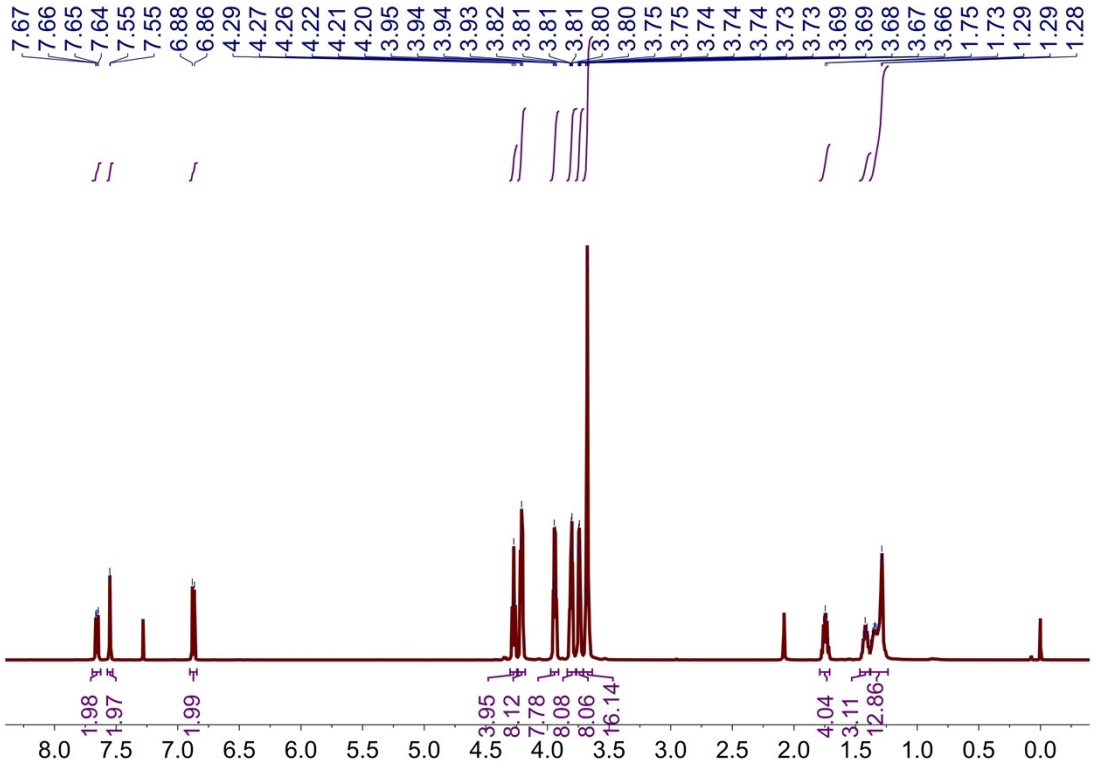


Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of crosslinker **3**.

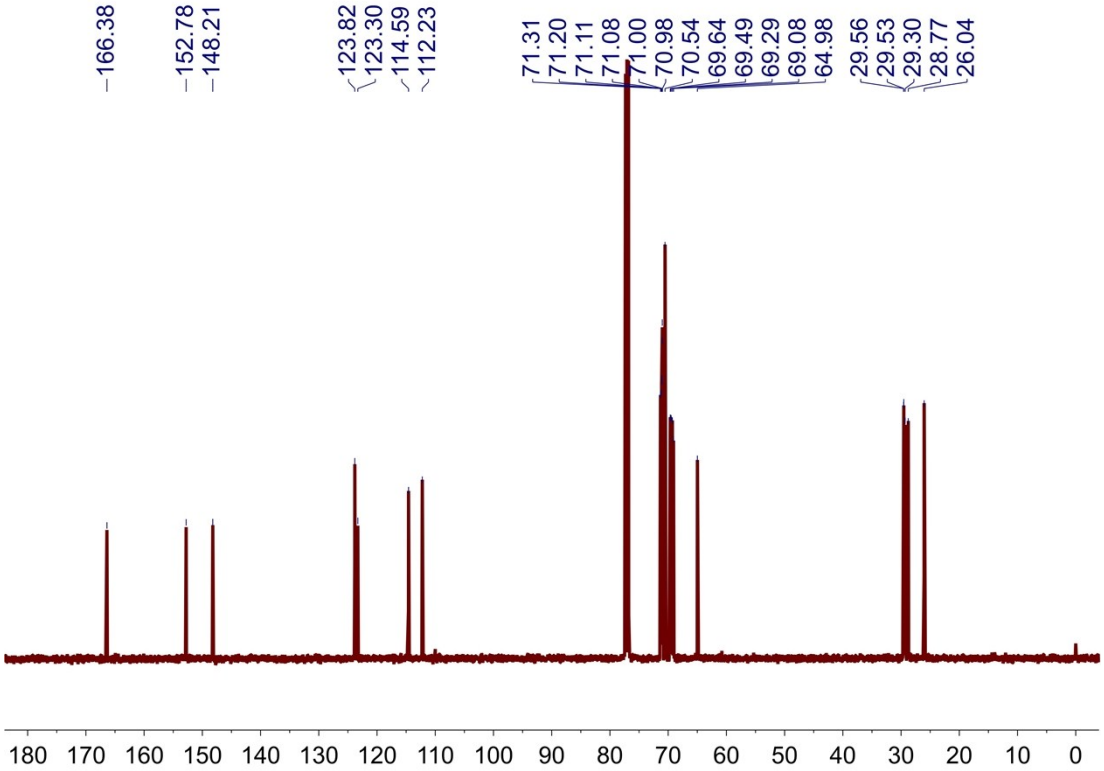


Figure S13. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of crosslinker **3**.

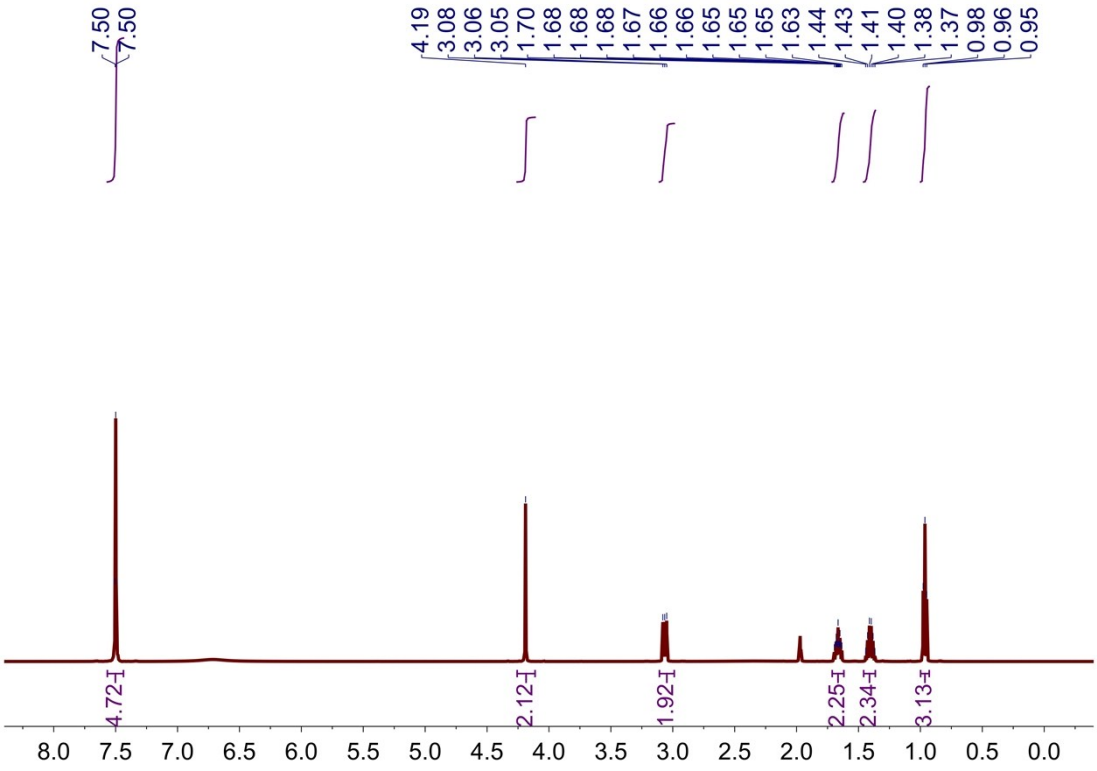


Figure S14. ^{1}H NMR spectrum (500 MHz, d_6-acetone, 298 K) of model guest **4**.

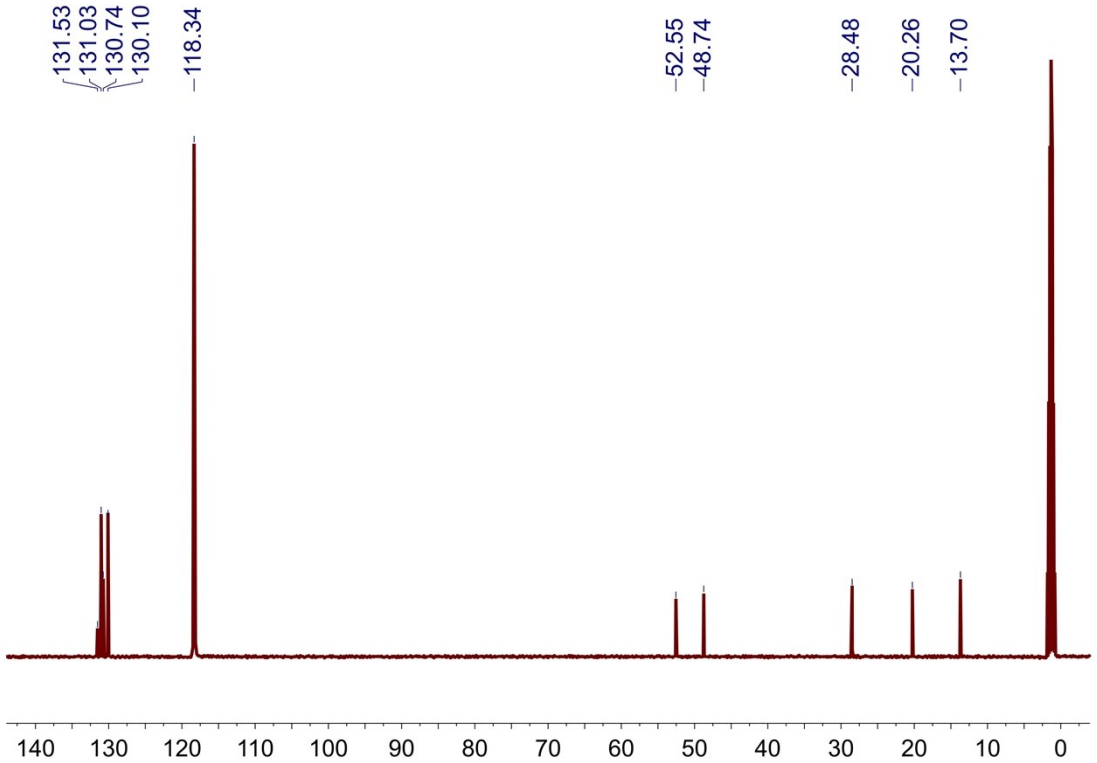


Figure S15. ^{13}C NMR spectrum (125 MHz, d_6-acetone, 298 K) of model guest **4**.

3. Host–guest interaction between crosslinker 1 and model guest 4

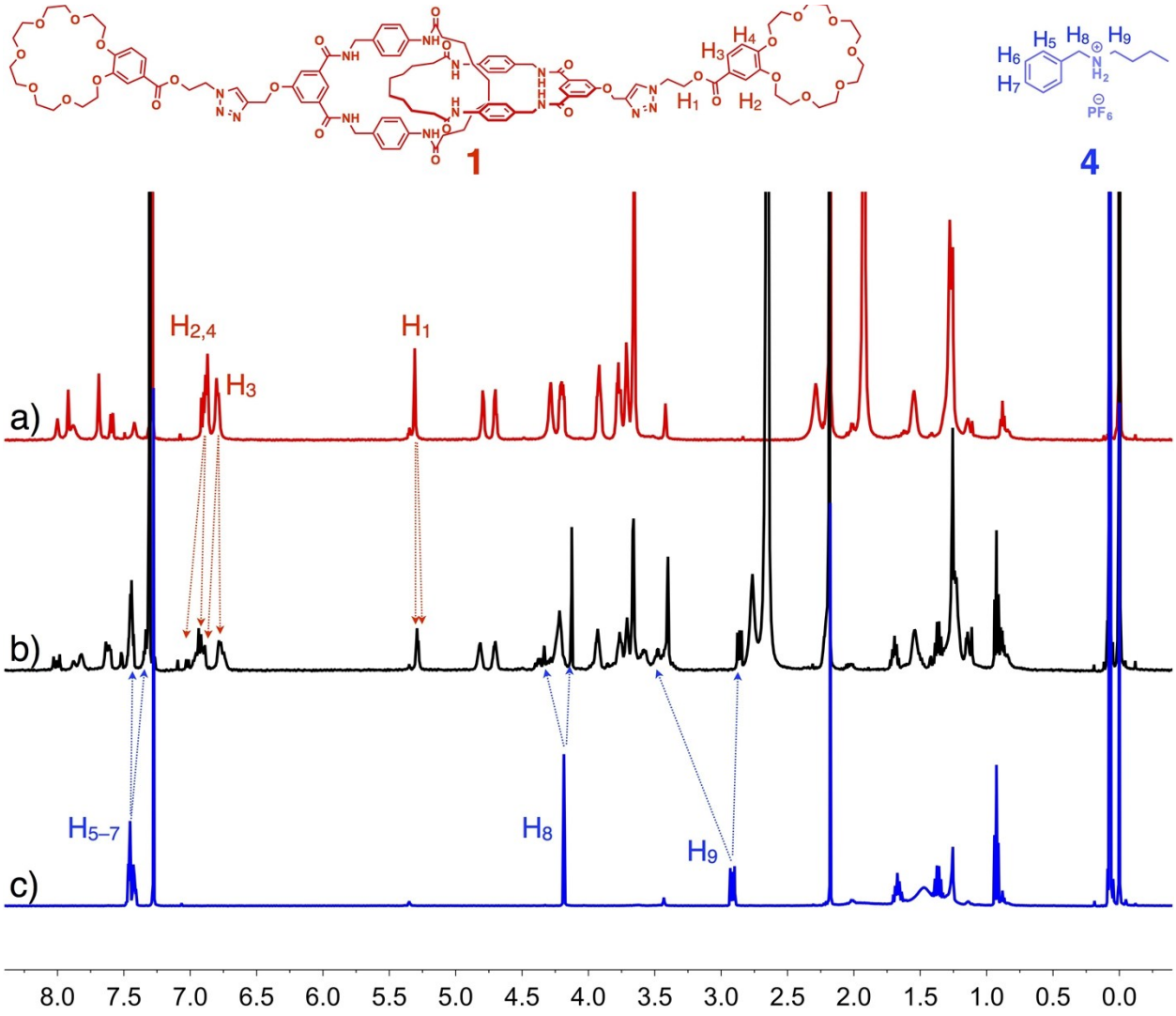


Figure S16. Proton NMR spectra (500 MHz, $CDCl_3$, 298 K) of a) 1.00 mM **1**, b) 1:2 equimolar mixture of 1.00 mM **1** and 2.00 mM **4**, and c) 2.00 mM **4**.

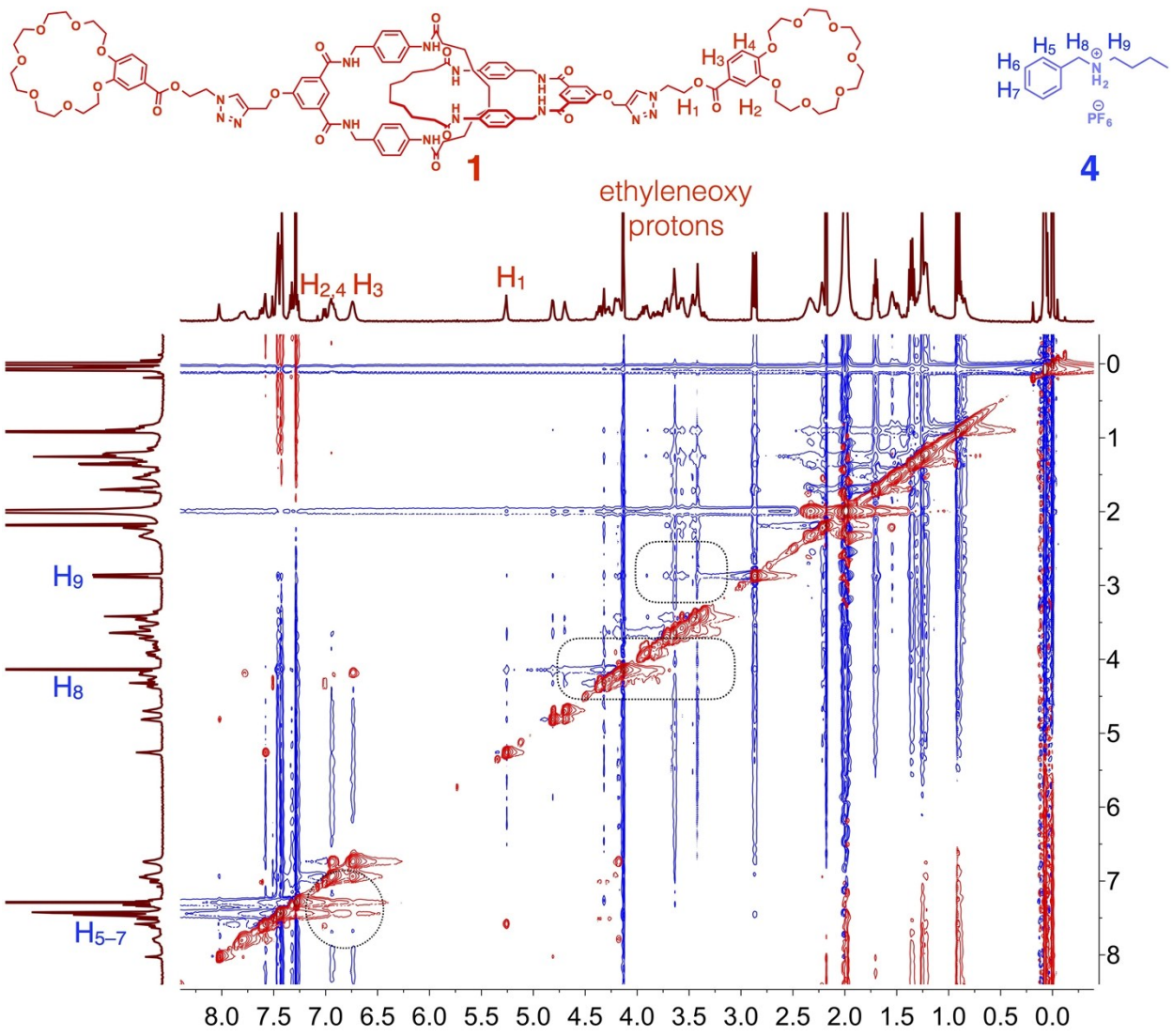


Figure S17. NOESY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a 1:2 equimolar mixture of 1.00 mM **1** and 2.00 mM **4**.

4. Proton NMR spectra of polymer 2 and model crosslinker 3

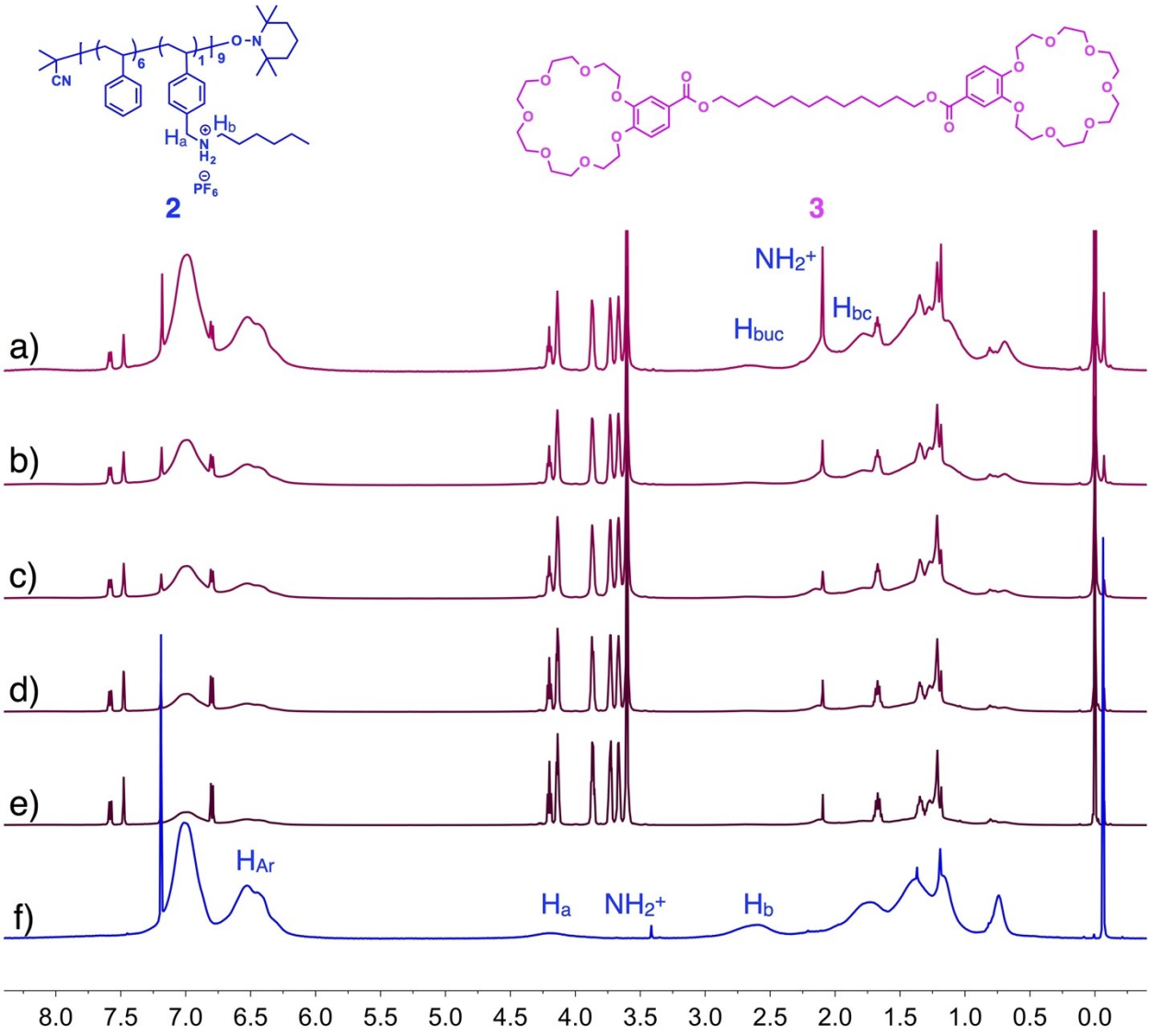


Figure S18. Proton NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5.00 mM **2** upon addition of a) 25.0 mM, b) 20.0 mM, c) 15.0 mM, d) 10.0 mM, e) 5.00 mM, f) 0 mM of **3**.

5. SEM images of supramolecular polymer network CP1

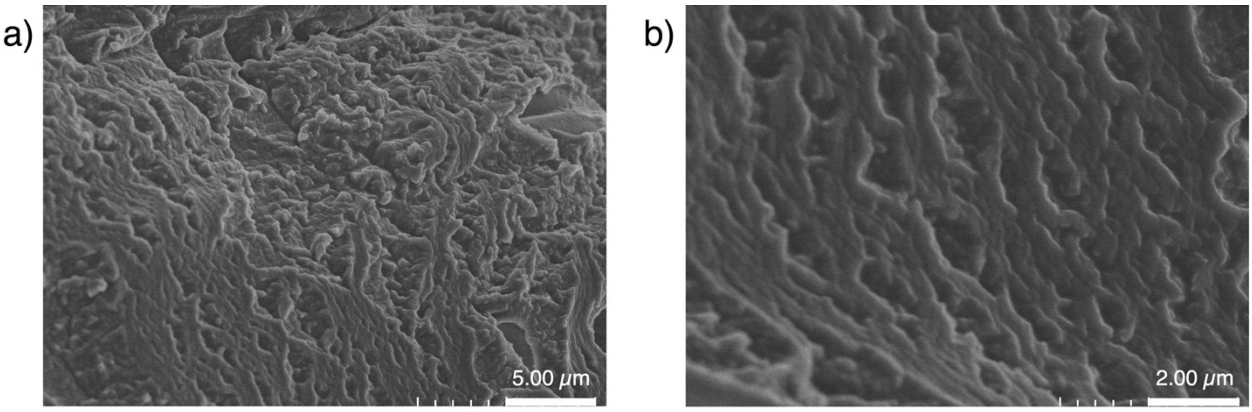


Figure S19. SEM images of supramolecular polymer network **SPN 1** prepared by mixing 22.5 mM **1** and 5.00 mM polymer **2**.

6. Stimuli-responsiveness of supramolecular polymer network SPN 1

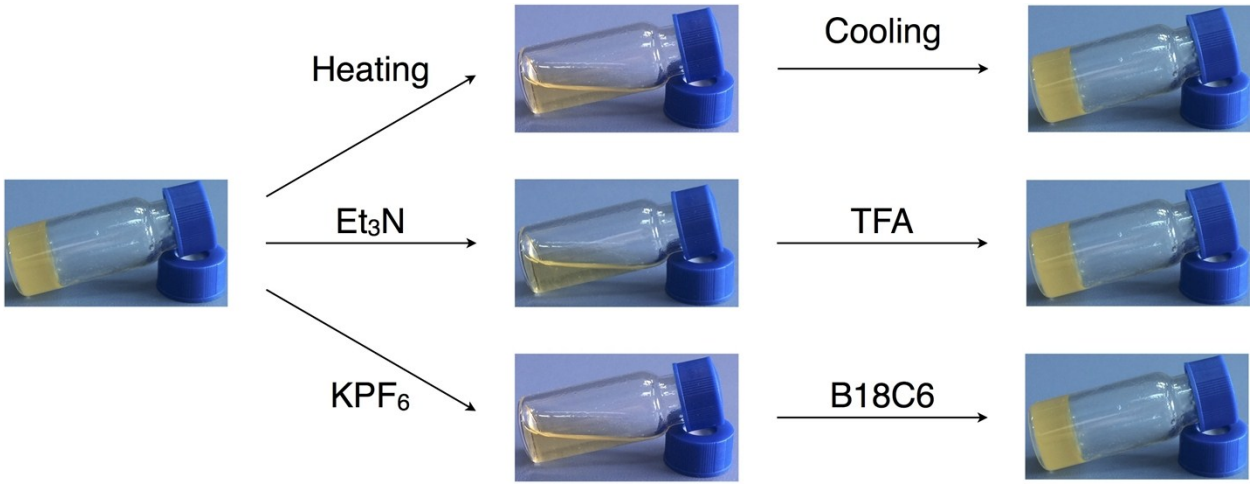


Figure S20. The gel–sol transitions of supramolecular polymer network **SPN 1** triggered by different stimuli.

7. References

S1. X. Yan, D. Xu, J. Chen, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.,* 2013, **4**, 3312.

S2. C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li and F. Huang, *Org. Lett.,* 2007, **9**, 5553.

S3. D. Feng, X. Li, X. Wang, X. Jiang and Z. Li, *Tetrahedron, 2004,* **60**, 6137.

S4. H. Xing and B. Shi, *Polym. Chem.,* 2016, **7**, 6159.