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Supporting Information For

Preparation of cross-linked supramolecular polymers based on benzo-21-crown-7/secondary ammonium salt host-guest interactions

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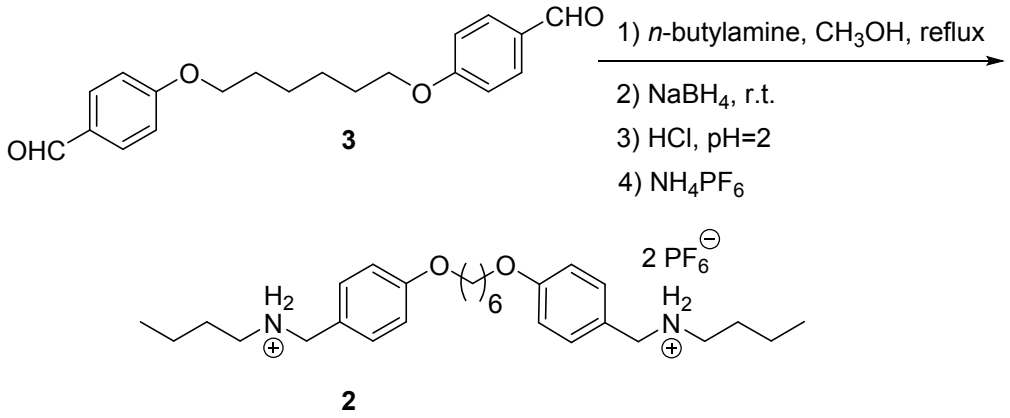
1. Materials and Methods

TC7[S1], **1**[S2] were synthesized according to the previously reported procedures. Other reagents and solvents are commercially available. ^{1}H NMR spectra were collected on a Varian Unity INOVA-400 or Bruker-AV400 with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Bruker-AV400 spectrometer at 101 MHz. Two-dimensional DOSY experiments were performed on a Bruker-AV500 MHz spectrometer. Viscosity measurements were carried out with Ubbelohde semi-micro dilution viscometer (0.47 mm inner diameter). Dynamic light scattering (DLS) measurements were carried out on a Malvern Zetasizer Nano ZS.

2. Synthesis of 2



A solution of **3** (1.50 g, 4.60 mmol) and *n*-butylamine (0.700 g, 9.70 mmol) was heated under reflux overnight in MeOH (30.0 mL). After the reaction mixture was cooled to ambient temperature, $NaBH_4$ (0.900 g, 23.7 mol) was added portionwise to the stirring solution over a period of 0.5 h. Stirring was maintained under ambient conditions for a further 24 h, after which time 5.0 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 white 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 NH_4PF_6 solution to produce a precipitate. It was collected by suction filtration and recrystallized from deionized water three times. **2** was obtained as a white solid (3.10 g, 92.0%).[S3]

^{1}H NMR (400 MHz, CD_3COCD_3, room temperature) δ 7.49 (d, J = 8.0 Hz, 4H), 7.00 (d, J = 8.0 Hz, 4H), 4.46 (s, 4H), 4.04 (t, J = 6.0 Hz, 4H), 3.41 – 3.29 (m, 4H), 1.82 (m, 8H), 1.55 (s, 4H), 1.44 (m, 4H), 0.93 (t, J = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, CD_3COCD_3, room temperature) δ 160.86, 132.33, 123.46, 115.49, 68.38, 52.03, 48.37, 29.58, 28.53, 26.23, 20.04, 13.51. ESI-HR-MS: m/z 441.3476 [**2**-HPF_6-PF_6]$^{+}$, calcd. for $[C_{28}H_{45}N_2O_2]^{+}$, 441.3497, error +4.78ppm.

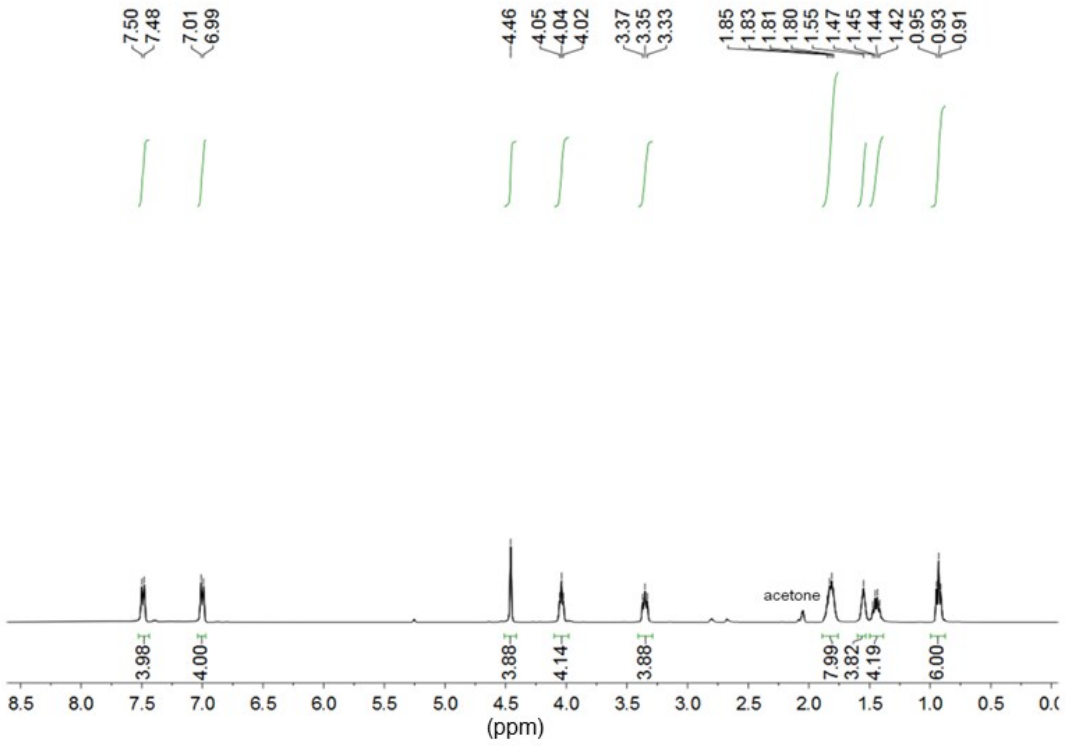


Figure S1. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of **2**

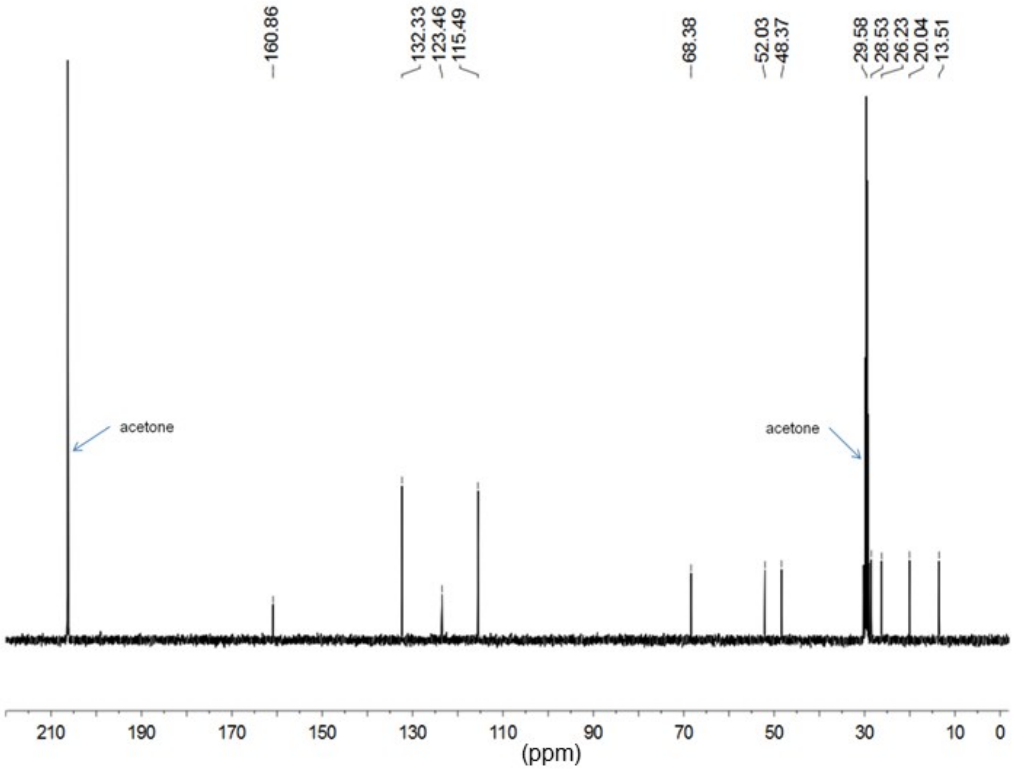


Figure S2. ^{13}C NMR spectra (101 MHz, CD_3COCD_3, room temperature) of **2**

3. Concentration-dependent ^{1}H NMR measurements of TC7

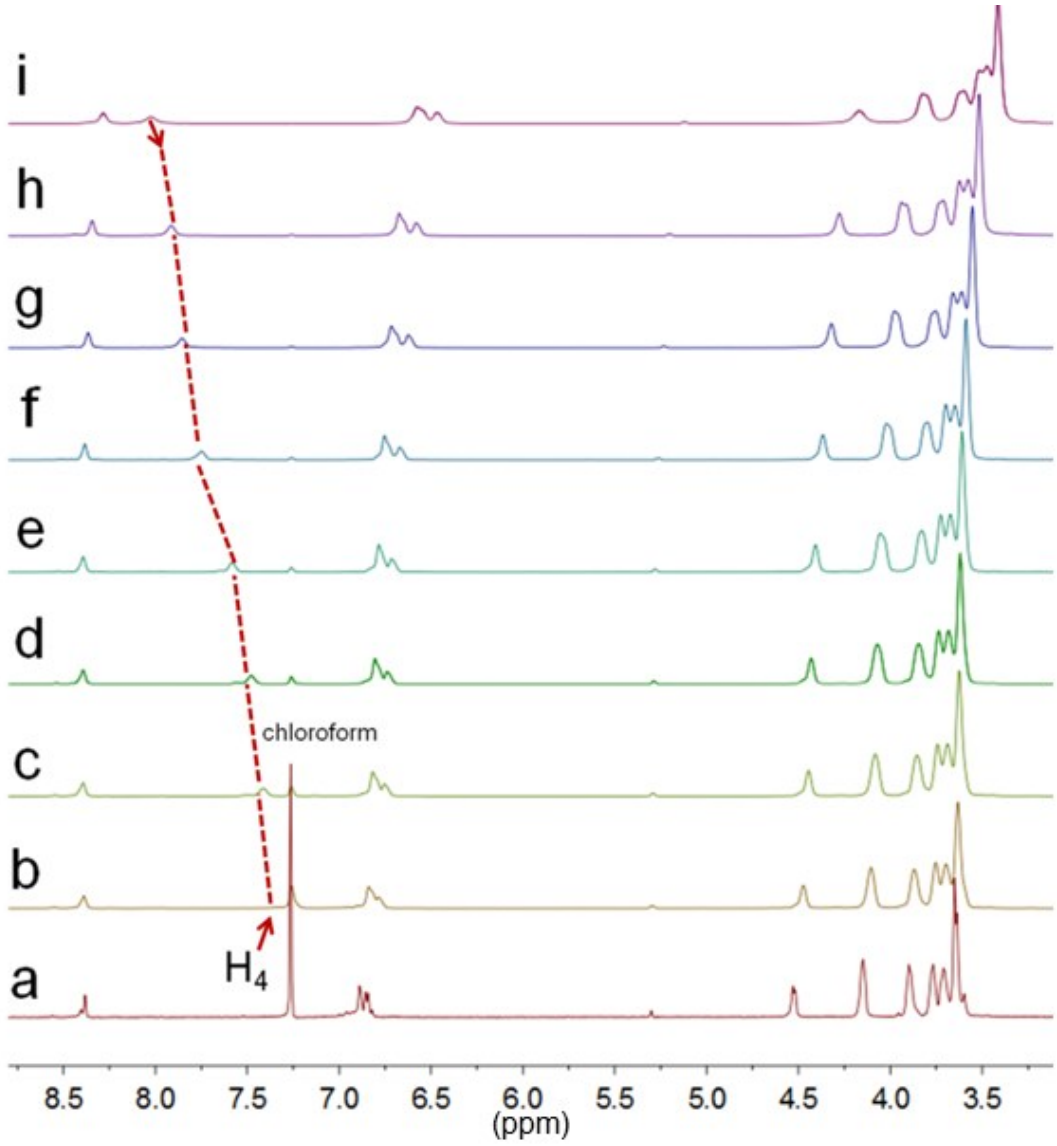


Figure S3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, room temperature) of **TC7** (a) 1.0 mM (b) 8.0 mM (c) 16 mM, (d) 24 mM, (e) 40 mM, (f) 80 mM, (g) 160 mM, (h) 240 mM, (i) 400 mM.

4. ^{1}H NMR spectra of host-guest complexation between TC7 and 1

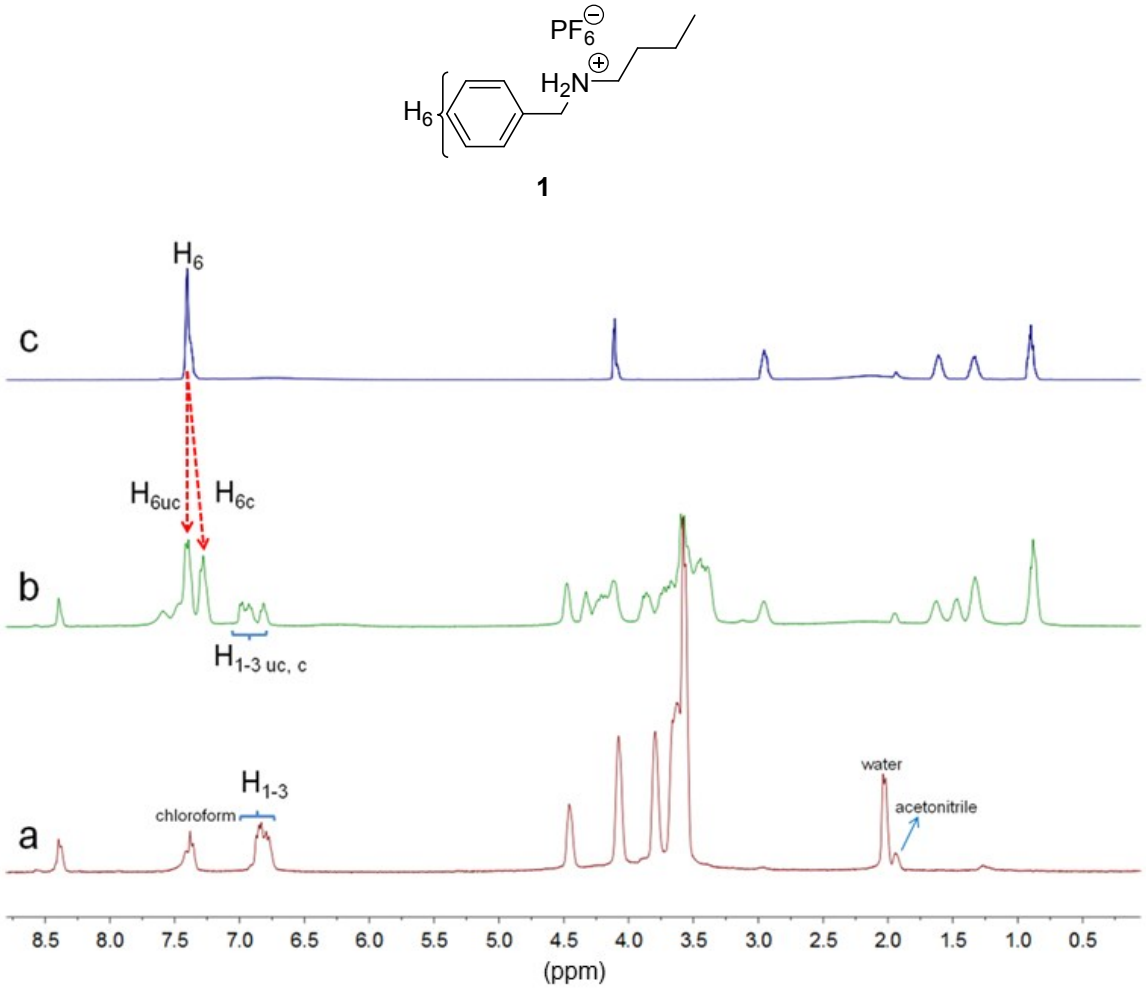


Figure S4. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 3/1, *v*/*v*, room temperature) of (a) **TC7** at 8.0 mM, (b) mixture of 8.0 mM **TC7** and 24 mM **1**, (c) **1** at 24 mM. Here ‘‘c’’ and ‘‘uc’’ denote the complexed and uncomplexed crown ether and secondary ammonium salts, respectively.

5. ^{1}H NMR titration experiments between TC7 and 2

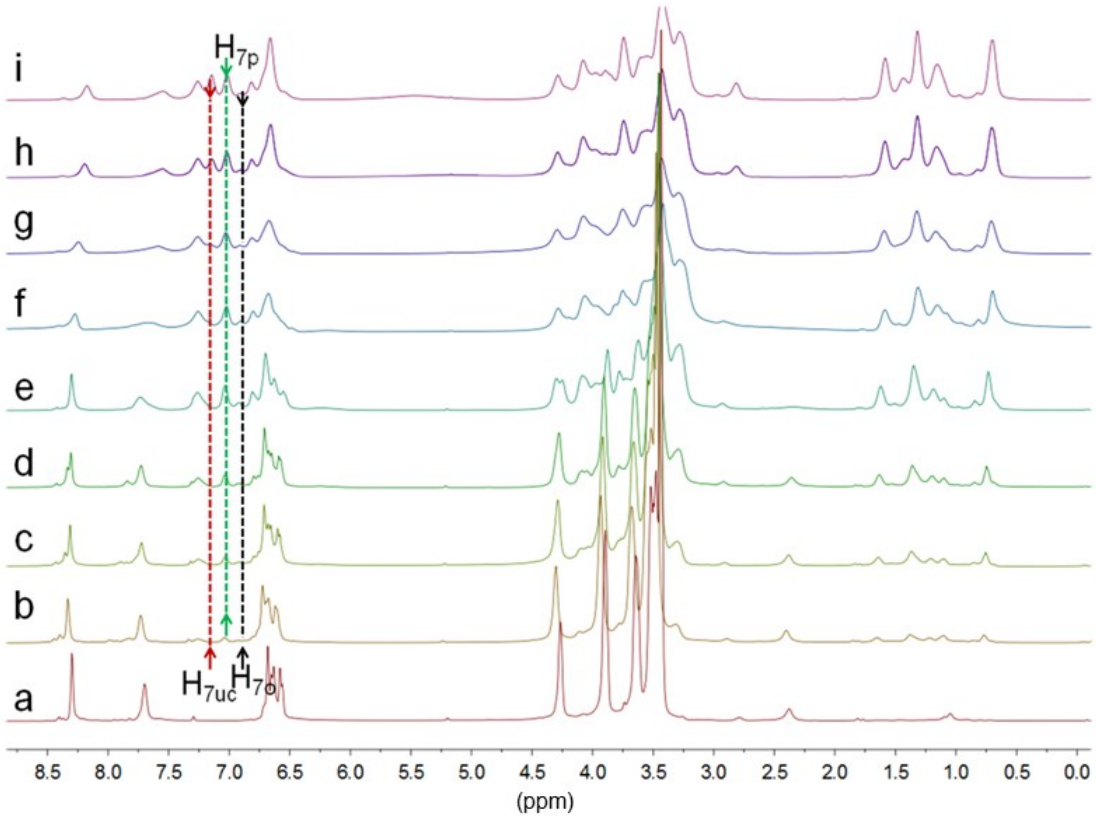


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3/CD_3CN$, 3/1, *v*/*v*, room temperature) titration experiment was performed between **TC7** and **2**, for which the concentration of **TC7** was kept constant at 120 mM, while concentration of **2** was systematically varied: (a) 12 mM, (b) 24 mM, (c) 36 mM, (d) 84 mM, (e) 120 mM, (f) 144 mM, (g) 180 mM, (h) 216 mM, (i) 240 mM. Herein, peaks of uncomplexed monomers, cyclic oligomers, and the cross-linked polymers, are designated as uc, o, and p, respectively.

6. Concentration-dependent ^{1}H NMR measurements of cross-linked supramolecular polymers

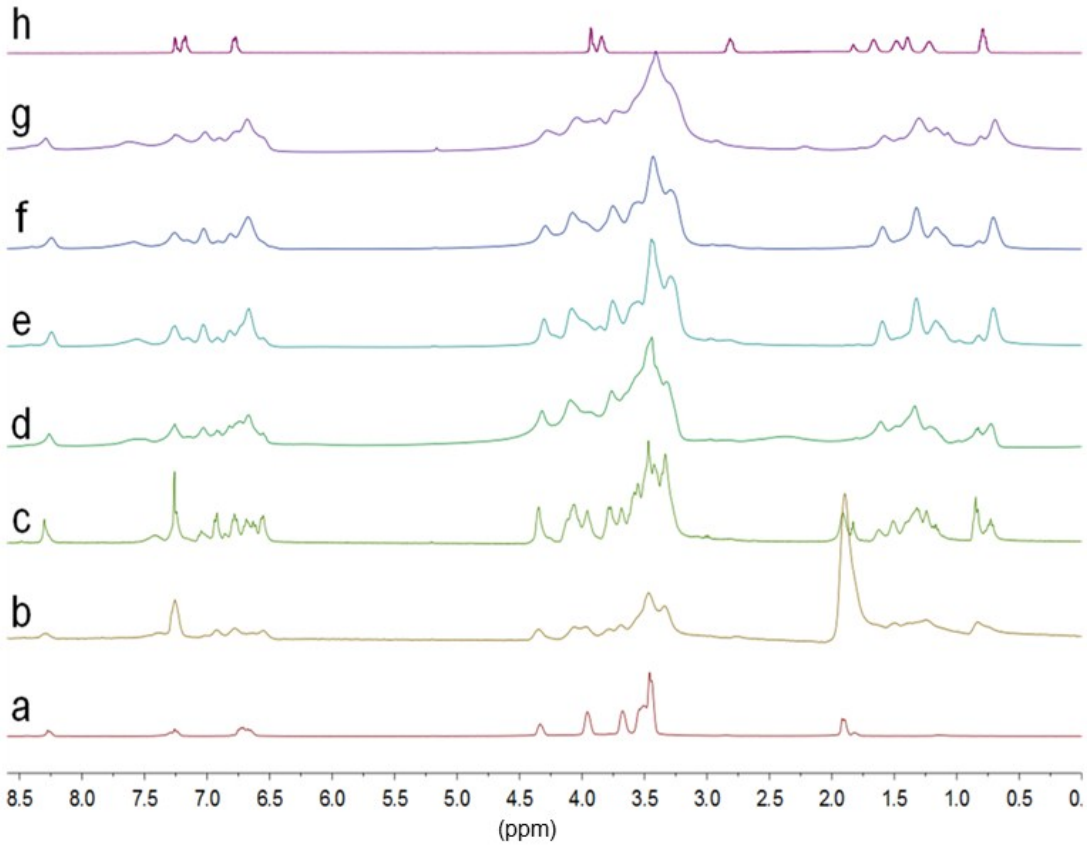


Figure S6. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 3/1, *v*/*v*, room temperature) of (a) **TC7** at 8.0 mM, (h) **2** at 12 mM; mixtures of **TC7** and 1.50 equiv. **2** at different concentrations of **TC7**: (b) 1.0 mM, (c) 8.0 mM, (d) 40 mM, (e) 80 mM, (f) 120 mM, (g) 160 mM.

7. Temperature-dependent ^{1}H NMR measurements of cross-linked supramolecular polymers

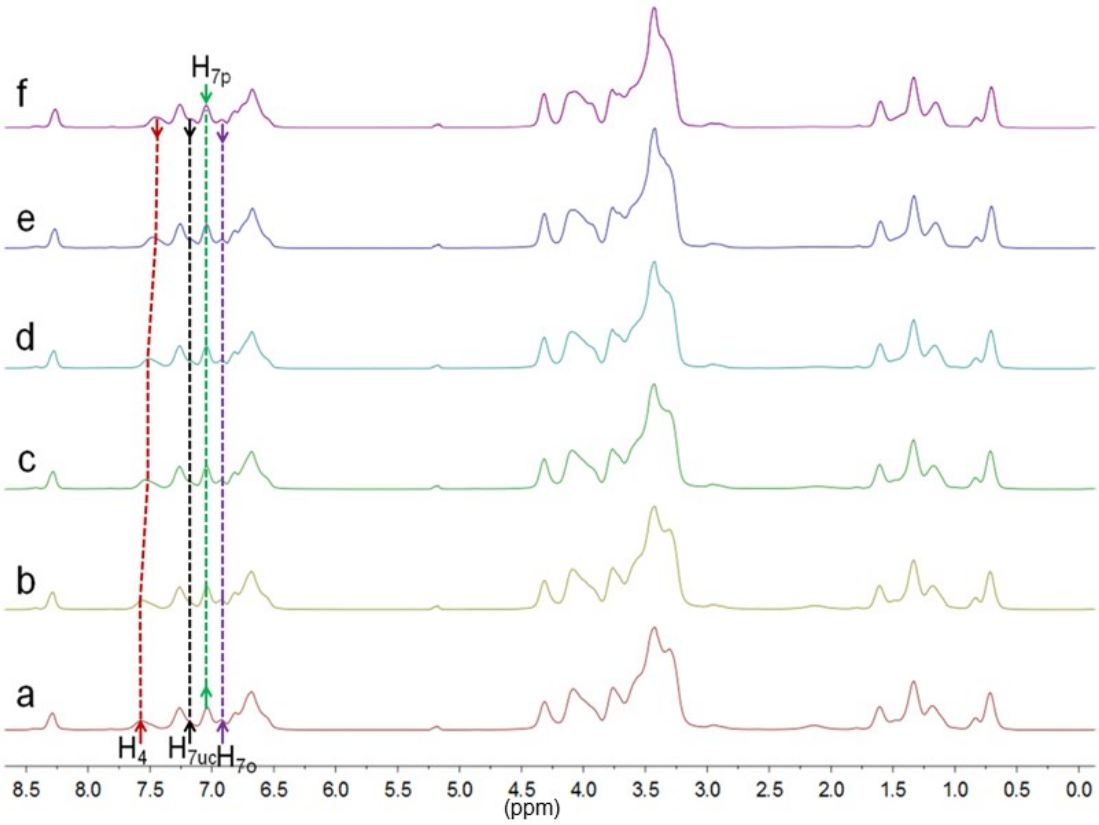


Figure S7. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 3/1, v/v) of 1:1.5 mixture of cross-linked supramolecular polymers at **TC7** concentration of 120 mM: (a) 25 °C, (b) 30 °C, (c) 35 °C, (d) 40 °C, (e) 45 °C, (f) 50 °C. Herein, peaks of uncomplexed monomers, cyclic oligomers, and the cross-linked polymers, are designated as uc, o, and p, respectively.

8. COSY spectra of cross-linked supramolecular polymers

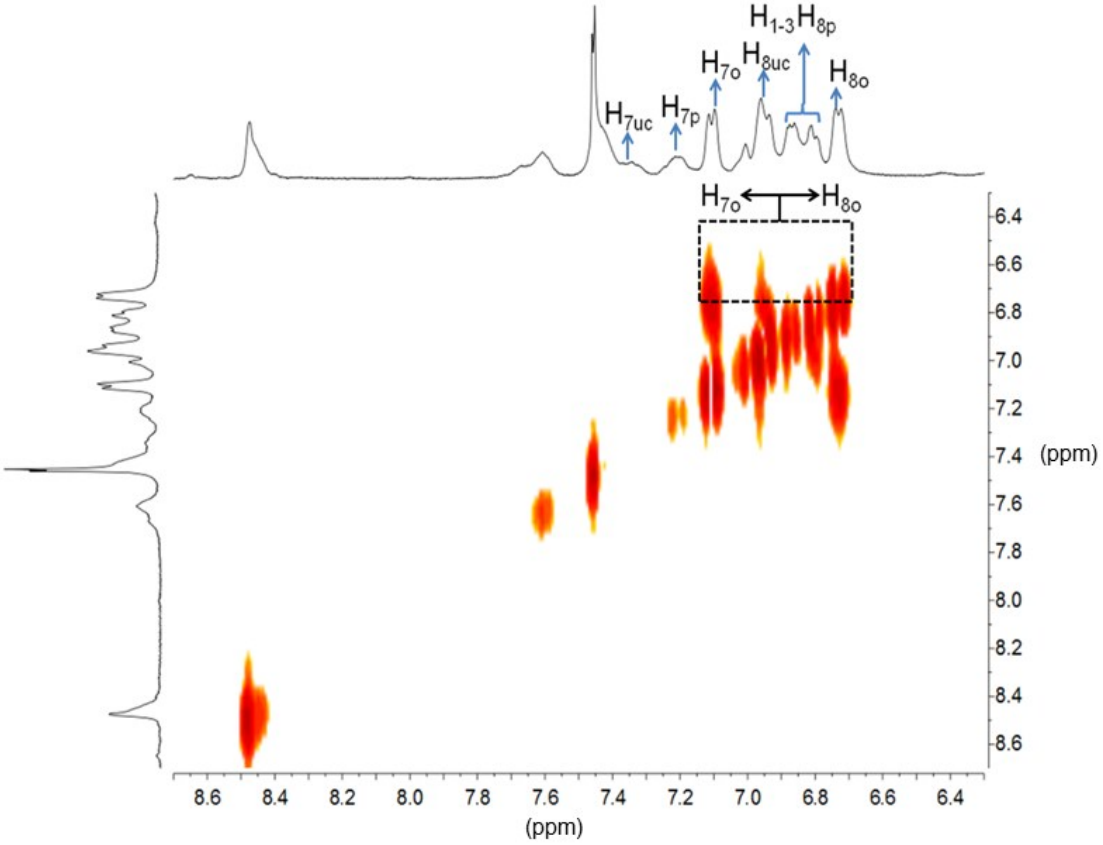


Figure S8. ^{1}H-^{1}H COSY NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 3/1, *v*/*v*, room temperature) of cross-linked supramolecular polymers (at **TC7** concentration of 8.0 mM). Herein, peaks of uncomplexed monomers, cyclic oligomers, and the cross-linked polymers, are designated as uc, o, and p, respectively.

9. Information of Supplementary Video

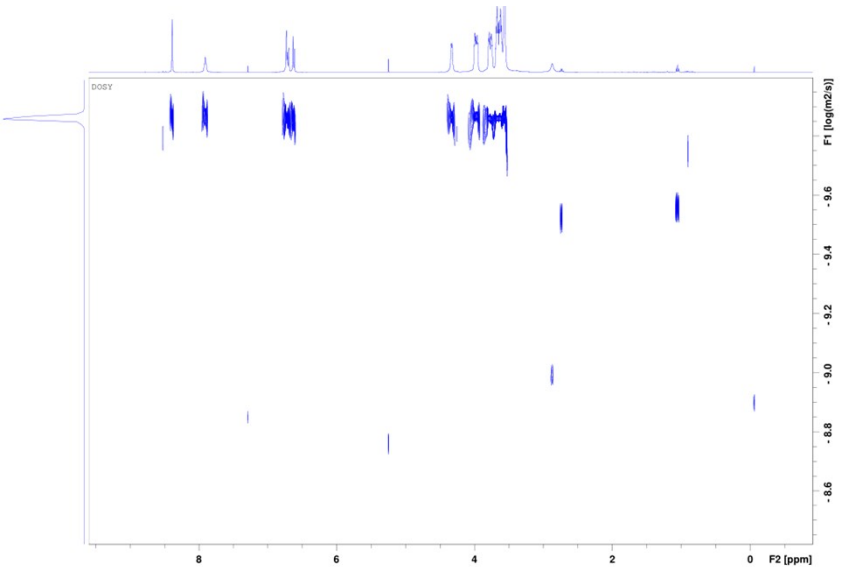


Figure S9. DOSY spectra (400 MHz, $CDCl_3$, room temperature) of linear supramolecular polymers (at **TC7** concentration of 160 mM).

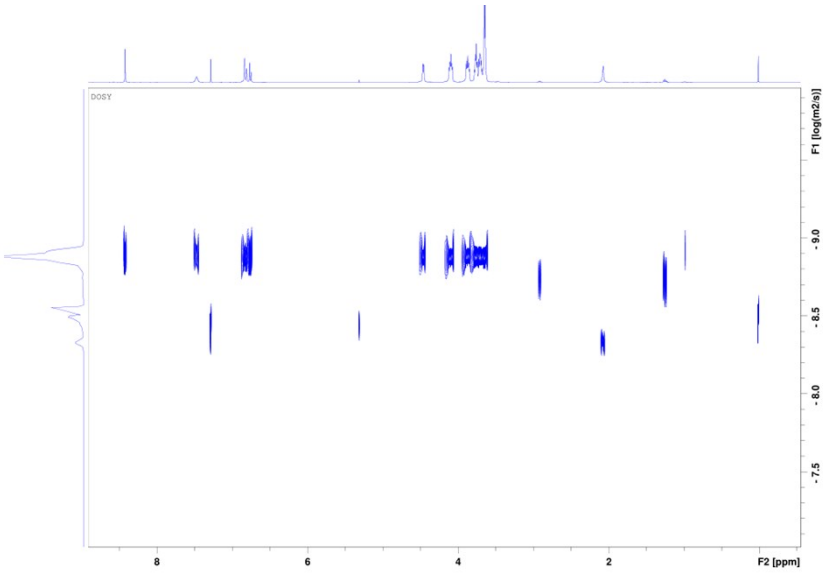


Figure S10. DOSY spectra (400 MHz, $CDCl_3$, room temperature) of linear supramolecular polymers (at **TC7** concentration of 20.0 mM).

10. Information of Supplementary Video

Soft viscous fibers were pulled from cross-linked supramolecular polymers ($CHCl_3$/CH_3CN, 3/1, *v*/*v*, room temperature) at **TC7** concentration of 160 mM.

11. References

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S2. C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li and F. Huang, *Org. Lett.*, 2007, **9**, 5553-5556.

S3. C. Lu, M. Zhang, D. Tang, X. Zhou, Z. Zhang, Z. Zhou, B. Song, H. Wang, X. Li,S. Yin, H. Sepehrpour and P. J. Stang, *J. Am. Chem. Soc*., 2018, **140**, 7674-7680.