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[^1], 1[^2] 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 rotavaporator. 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$_4$PF$_6$ 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%).[^3]

[^1]: $^1$H NMR (400 MHz, CD$_3$COCD$_3$, 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).

[^2]: $^{13}$C NMR (101 MHz, CD$_3$COCD$_3$, 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$_2$O$_2$]$^+$, 441.3497, error +4.78ppm.
Figure S1. $^1$H NMR spectra (400 MHz, CD$_3$COCD$_3$, room temperature) of 2

Figure S2. $^{13}$C NMR spectra (101 MHz, CD$_3$COCD$_3$, 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$_3$CN, 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$_3$CN, 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$_3$CN, 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$_3$CN, 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$_3$CN, 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
10. Information of Supplementary Video

Soft viscous fibers were pulled from cross-linked supramolecular polymers (CHCl$_3$/CH$_3$CN, 3/1, v/v, room temperature) at TC7 concentration of 160 mM.

11. References

