Electronic Supplementary Information

Neutral linear supramolecular polymers constructed by the triple different interactions

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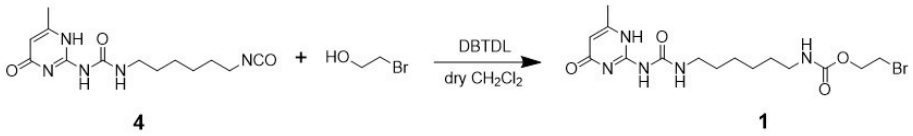
Table of Contents

1. *Materials and methods*

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **2**[S1], **3**[S2] and **4**[S3] were prepared according to literature procedure. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. DOSY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. *Synthesis of **1***



4 1

Scheme S1 Synthesis of **1**.

4 (0.10 g, 0.34 mmol), 2-bromoethanol (0.13 g, 1.02 mmol), and dibutyltin dilaurate (DBTDL, cat.) were dissolved in dry CH_2Cl_2 (20 mL) under nitrogen gas protection. The mixture was stirred at room temperature for 24 h. The mixture was filtered and the filtrate was removed by rotary evaporation to give **1** as a white solid (0.10g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 13.14 (s, 1H), 11.86 (s, 1H), 10.12 (s, 1H), 5.86 (s, 1H), 5.16 (s, 1H), 4.36 (t, J = 6.0 Hz, 2H), 3.51 (t, J = 6.0 Hz, 2H), 3.28−3.23 (m, 2H), 3.19−3.14 (m, 2H), 2.23 (s, 3H), 1.63−1.57 (m, 2H), 1.53−1.50 (m, 2H), 1.38−1.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 173.3, 156.7, 156.0, 154.8, 148.4, 106.8, 64.2, 40.8, 39.6, 29.9, 29.7, 29.4, 26.2, 26.1, 19.1. LR-ESI-MS: *m/z* calcd. for $[M + H]^+$ = 418.11, 420.11, found 418.10 (66%), 420.10 (60%); $[M + Na]^+$ = 440.09, 442.09, found 440.10 (100%), 442.10 (100%). HR-ESI-MS: *m/z* calcd. for $[M + Na]^+$ = 440.0909, found 440.0903.

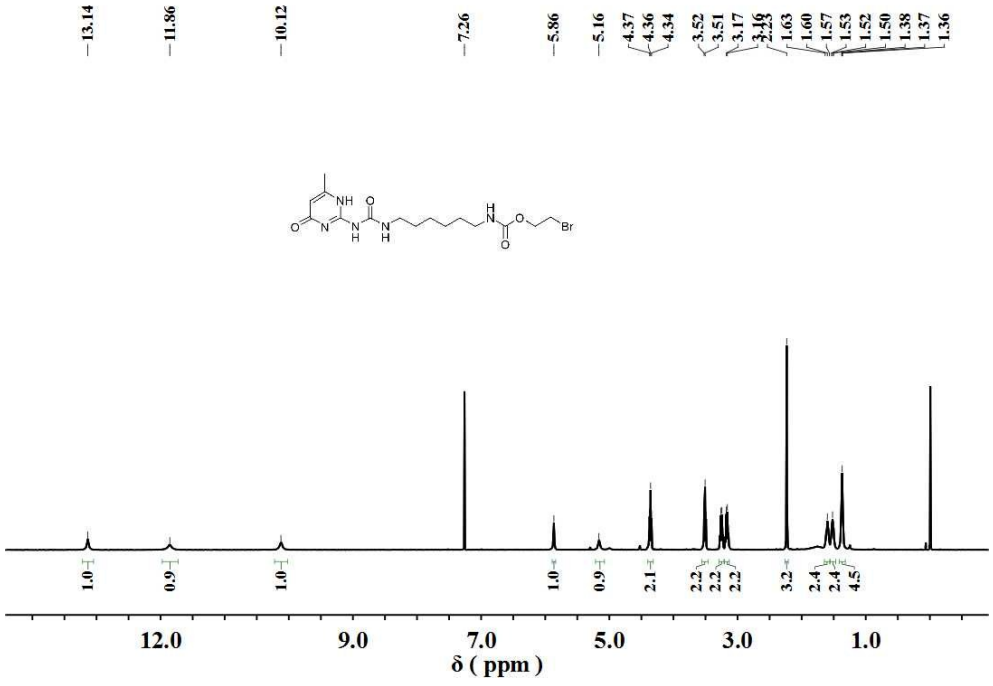


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**.

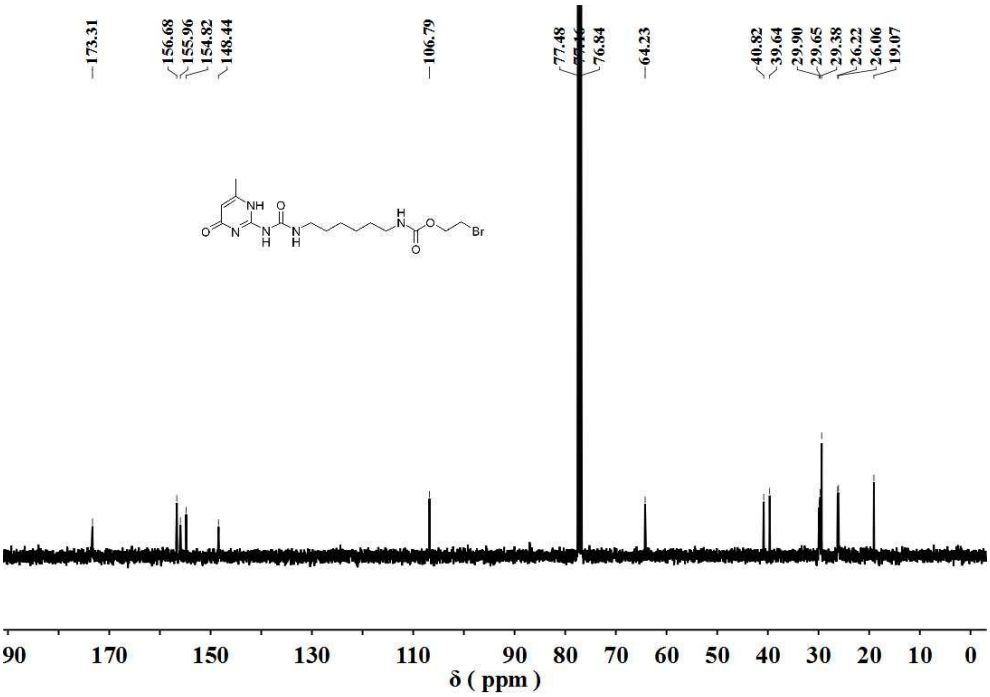


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1**.

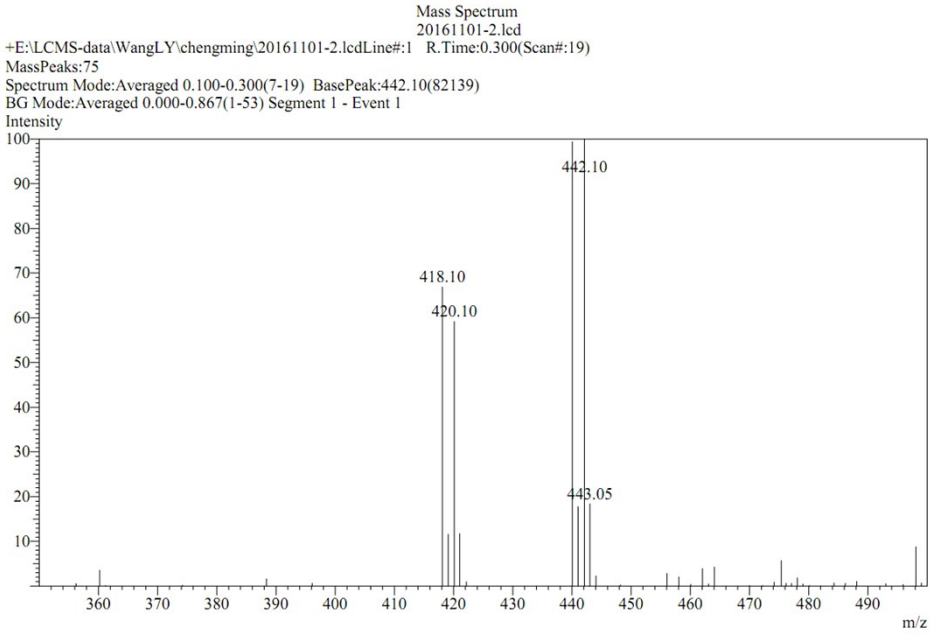


Fig. S3 LR-ESI-MS spectrum of **1**.

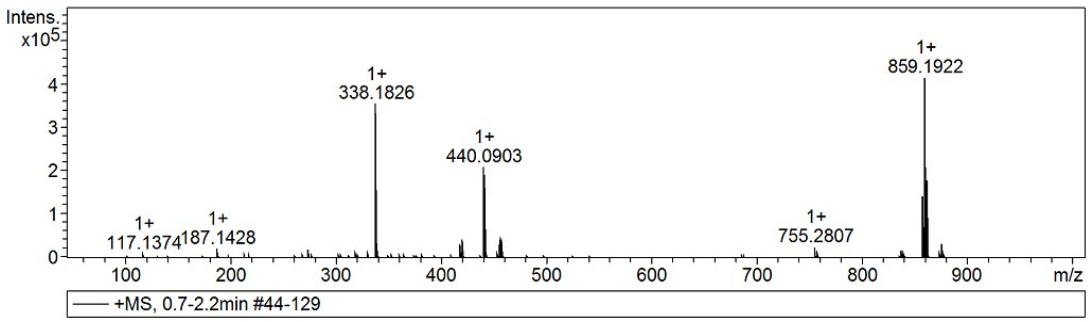


Fig. S4 HR-ESI-MS spectrum of **1**.

3. *[1]H NMR spectra of **1** in the absence and presence of **2***

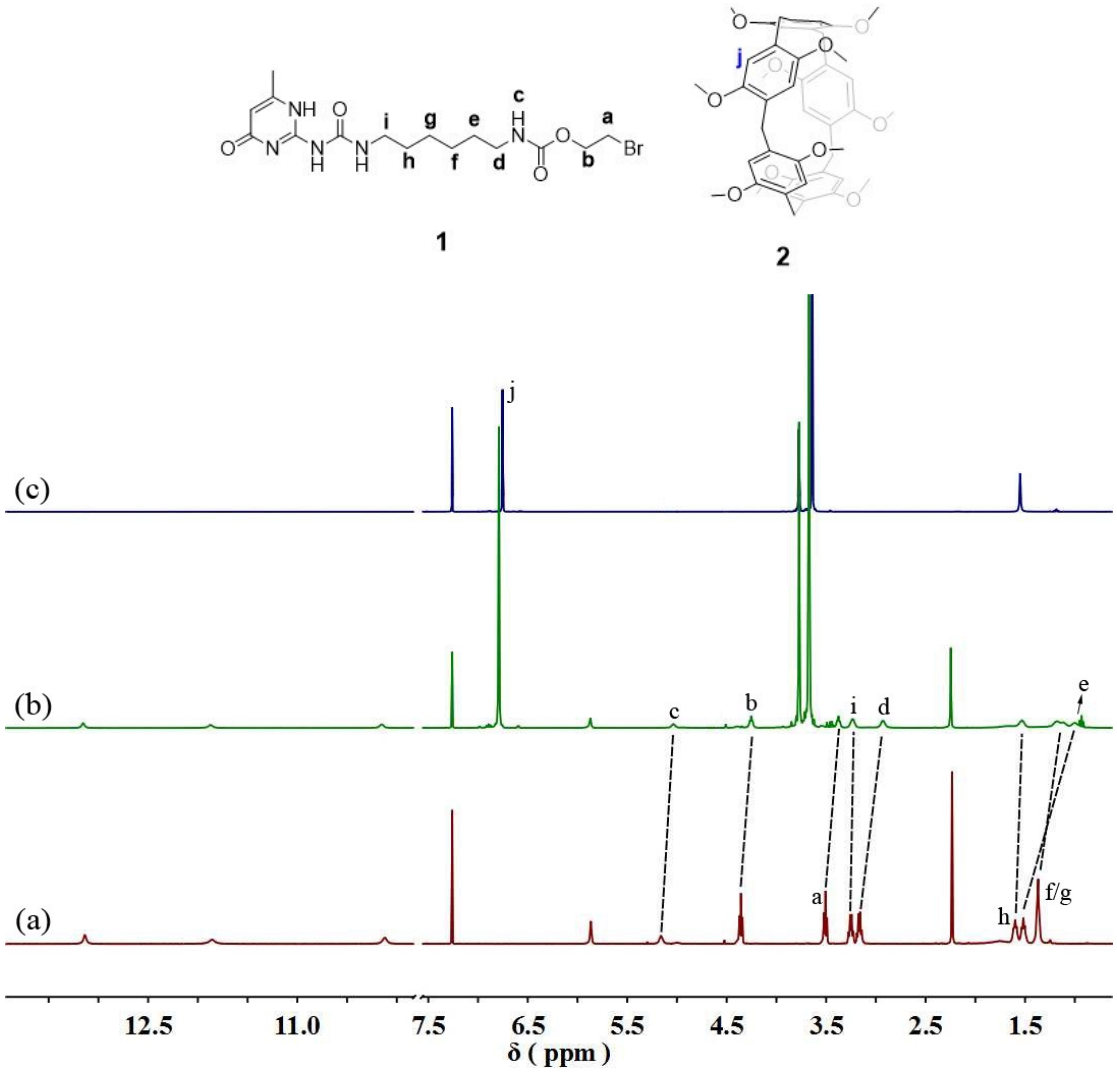


Fig. S5 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K): (a) **1** (8.00 mM); (b) **1** (8.00 mM) and **2** (12.00 mM); (c) **2** (12.00 mM).

4. *Partial 2D NOESY spectrum of **2⊃1***

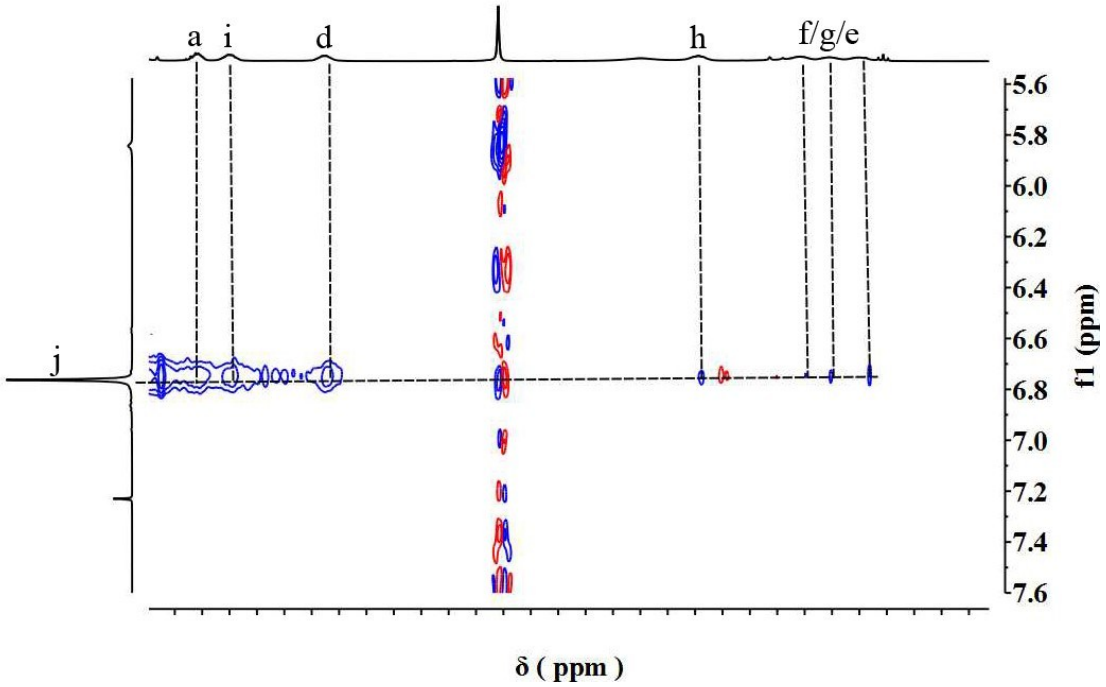


Fig. S6 Partial NOESY NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2⊃1** (**1** = 8.00 mM, **2** = 12.00 mM).

5. *Job plot for the complex of **2⊃1***

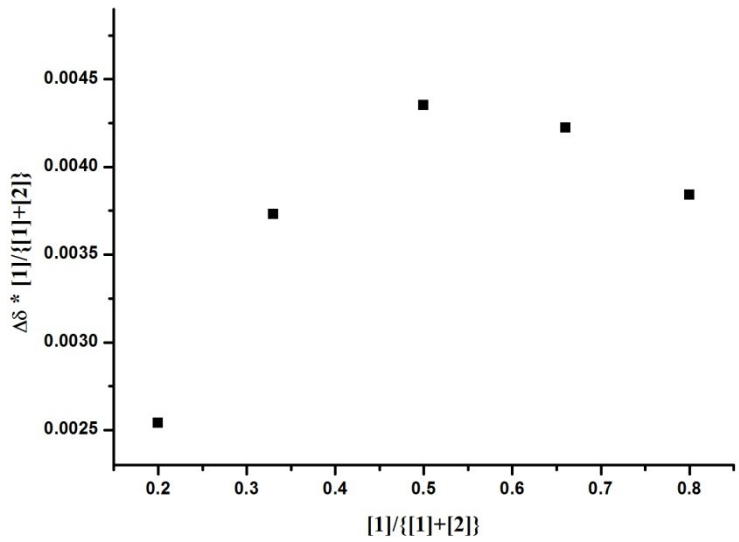


Fig. S7 Job Plot showing the 1:1 stoichiometry of the complexation between **1** and **2** in $CDCl_3$.

6. *Determination of the association constant of **2**⊃**1** by ^{1}H NMR*

^{1}H NMR titrations were performed with a constant concentration of guest (2.00 mM) and varying concentrations of host in the range of 1.0 - 30.0 mM. Using a non-linear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation:

$$\Delta\delta = (\Delta\delta_\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5\ ([H]_0^2 + (2[H]_0(1/K_a - [G]_0)) + (1/K_a + [G]_0)^{\ 2})^{\ 0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of H_a on G at $[H]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_a when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the initial concentration of the host.

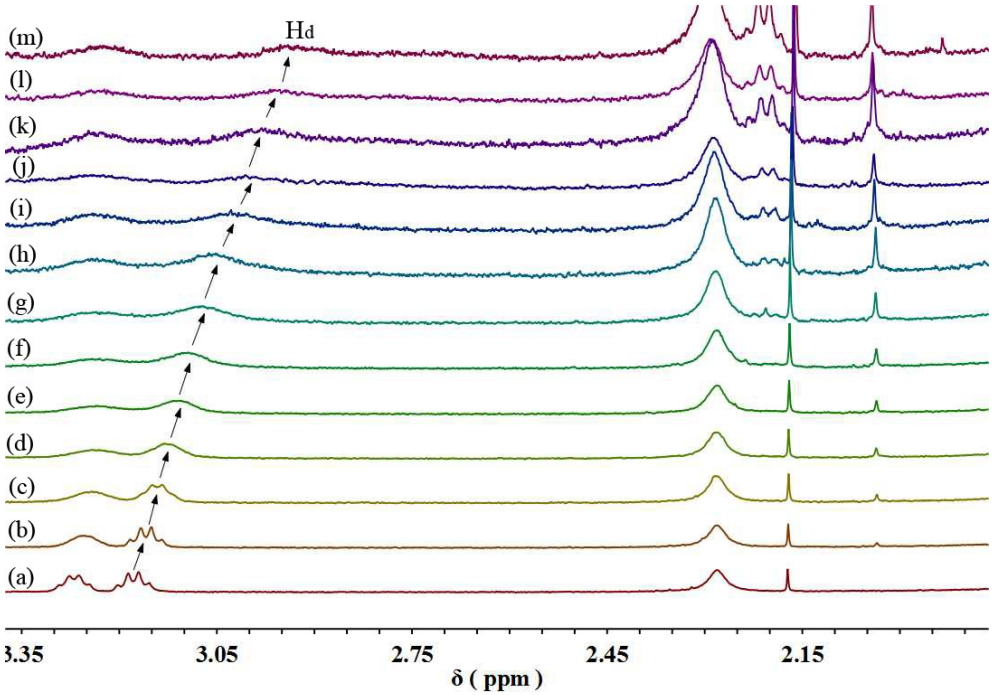


Fig. S8 Partial ^{1}H NMR spectral changes (400 MHz, $CDCl_3$, 298 K) of **1** at a concentration of 2.00 mM upon gradual addition of **2**: (a) 0.00; (b) 1.00; (c) 2.00; (d) 3.00; (e) 4.00; (f) 5.00; (g) 7.00; (h) 9.00; (i) 13.00; (j) 17.00; (k) 20.00; (l) 24.00; (m) 30.00 mM.

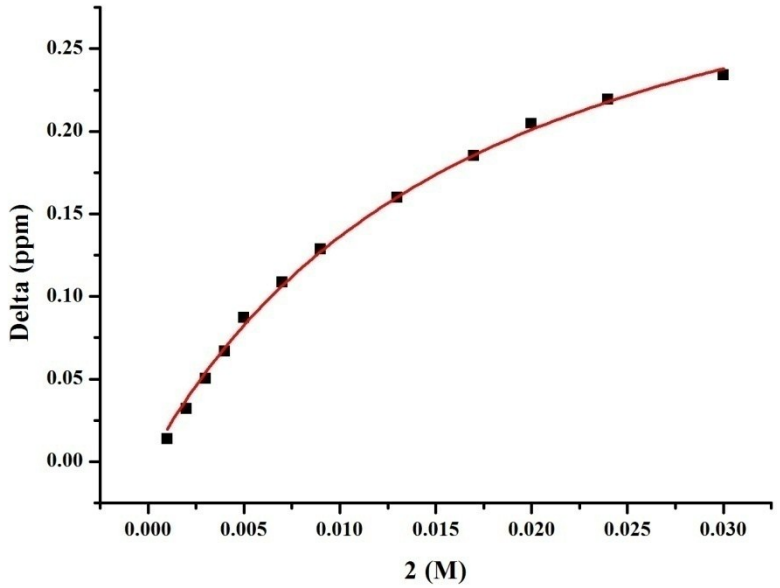


Fig. S9 The chemical shift changes of H_d on **1** upon addition of **2**. The red solid line was obtained from the non-linear curve-fitting (K_a = 85 ± 4.1 M^{-1}, R^2= 0.9975).

7. *Solution colors of the supramolecular polymers at different concentrations*

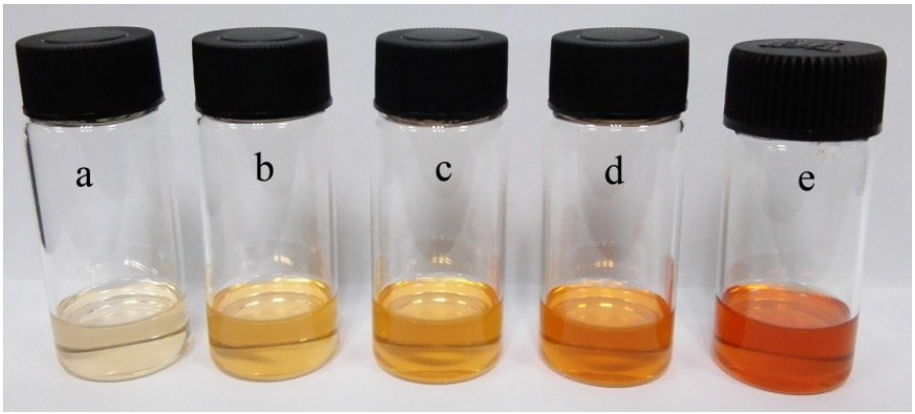


Fig. S10 Concentration-dependent color changes ($CHCl_3$) of the mixed solution of **1**, **2**, and **3** in a 2 : 2 : 1 molar ratio at different **3** concentrations: (a) 12; (b) 20; (c) 24; (d)32; and (e) 48 mM.

8. *Concentration-dependent ^{1}H NMR spectra*

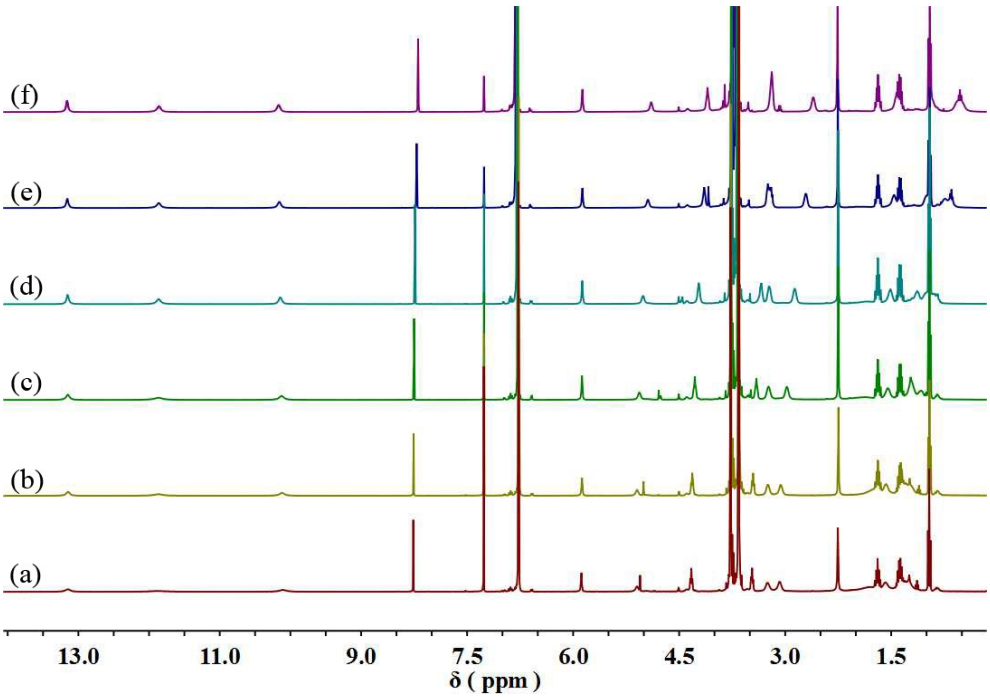


Fig. S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the mixed solution of **1**, **2**, and **3** in a 2 : 2 : 1 molar ratio at different **3** concentrations: (a) 3; (b) 5; (c) 10; (d) 20; (e) 40; and (f) 50 mM.

9. *TEM study of the supramolecular polymers*

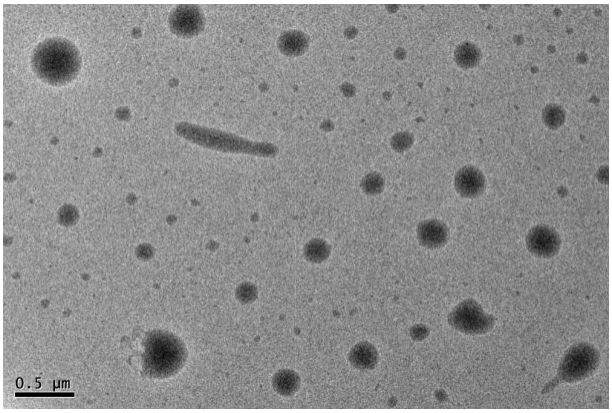


Fig. S12 Representative TEM image of the supramolecular polymers.

10. *Disassembly of the supramolecular polymers by addition of competitive guest*

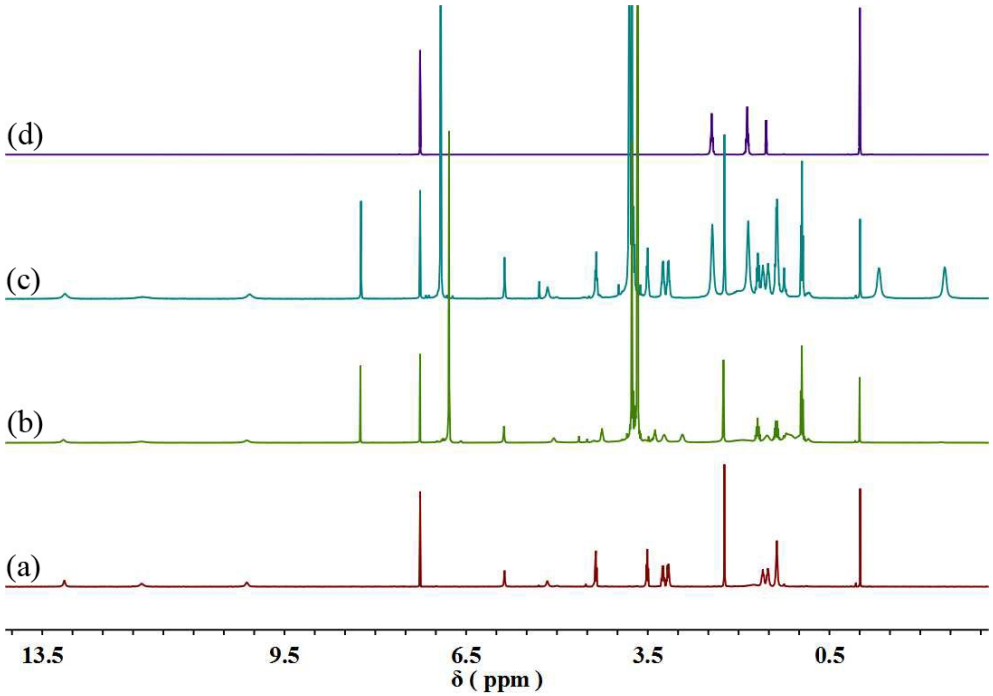


Fig. S13 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) **1**; (b) **3** (10 mM) with 2 equiv. **1** and **2**; (c) after addition of 2.5 equiv. adiponitrile to (b); and (d) adiponitrile.

References

S1. T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022-5023.

S2. S. De and S. Ramakrishnan, *Macromolecules*, 2009, **42**, 8599-8603.

S3. H. Hofmeier, A. El-ghayoury, A. P. H. J. Schenning and U. S. Schubert, *Chem. Commun.*, 2004, 318-319.