

Reversible formation of supramolecular polymer networks via orthogonal pillar[10]arene-based host–guest interactions and metal ion coordinations

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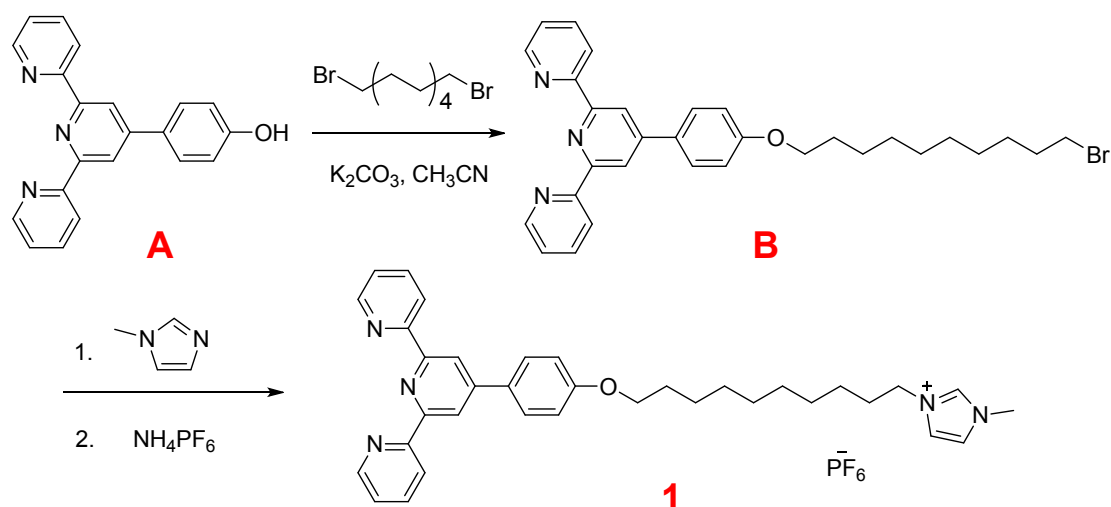
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. **P**₁₀ was prepared according previous relevant reports.^{S1} ¹H or ¹³C NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. 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. HRMS were obtained on a WATERS GCT Premier mass spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25.0 °C in acetonitrile. Scanning electron microscopy investigation was carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer. UV–Vis spectra were taken on a Perkin-Elmer Lambda 35 UV–Vis spectrophotometer.

2. Synthesis of ligand 1



Scheme S1. Synthesis route to ligand 1.

In a 500 mL round-bottom flask, compound **A** (3.25 g, 10.0 mmol), K₂CO₃ (3.31 g, 24.0 mmol), 1,10-dibromodecane (5.40 g, 18.0 mmol) and acetonitrile (300 mL) were added. The reaction mixture was stirred at reflux for 48 hours. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl₃ (200 mL) and washed twice with H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was recrystallized with CH₃CN to give the intermediate **B** as a white solid (4.35 g, 80.0 %) as a white solid. The proton NMR spectrum of **B** is shown in Fig. S1. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 8.73-8.66 (m, 6H), 7.88-7.86 (t, *J* = 4 Hz, 4H), 7.36-7.33 (m, 2H), 7.03-7.01 (d, *J* = 8 Hz, 2H), 4.04-4.01 (d, *J* = 12 Hz, 2H), 3.43-3.40 (d, *J* = 12 Hz, 2H), 1.90-1.79 (m, 4H), 1.59-1.33 (m, 12H).

In a 50 mL round-bottom flask, compound **B** (1.09 g, 2.0 mmol), methylimidazole (0.82 g, 10.0 mmol), and toluene (20 mL) were added. The reaction mixture was stirred at reflux for 24 hours. Then the solvent was removed. The solid was dissolved in water (20 mL). Then upon addition of aqueous solution of NH₄PF₆, a white precipitate **1** (1.24g, 90%) was prepared. The proton NMR spectrum of **1** is shown in Fig. S2. ¹H NMR (400 MHz, CD₃CN, 298K) δ (ppm): 8.72-8.64 (m, 6H), 8.34 (s, 1H), 7.98-7.89 (m, 2H), 7.84 (s, 2H), 7.45-7.42 (t, *J* = 4 Hz, 2H), 7.34-7.31 (d, *J* = 8 Hz, 2H), 7.15-7.12 (t, *J* = 6 Hz, 2H), 7.06 (s, 1H), 7.04 (s, 2H), 4.09-4.03 (m,

4H), 4.00 (s, 3H), 1.94-1.75 (m, 4H), 1.47-1.43 (m, 2H), 1.31 (s, 12H). The ^{13}C NMR spectrum of **1** is shown in Fig. S3. The ^{13}C NMR (100 MHz, CD_3CN , 298K) δ (ppm): 160.12, 156.43, 155.83, 149.11, 136.86, 128.50, 123.76, 121.39, 118.26, 114.87, 68.12, 34.06, 32.84, 29.45, 29.37, 29.26, 28.76, 28.18, 26.04. LRESIMS is shown in Fig. S4: m/z 546.7 [**1** - PF_6] $^+$. HRESIMS: m/z calcd for [**1** - PF_6] $^+$ $\text{C}_{35}\text{H}_{40}\text{N}_5\text{O}$, 546.3200; found, 546.3200; error 0 ppm.

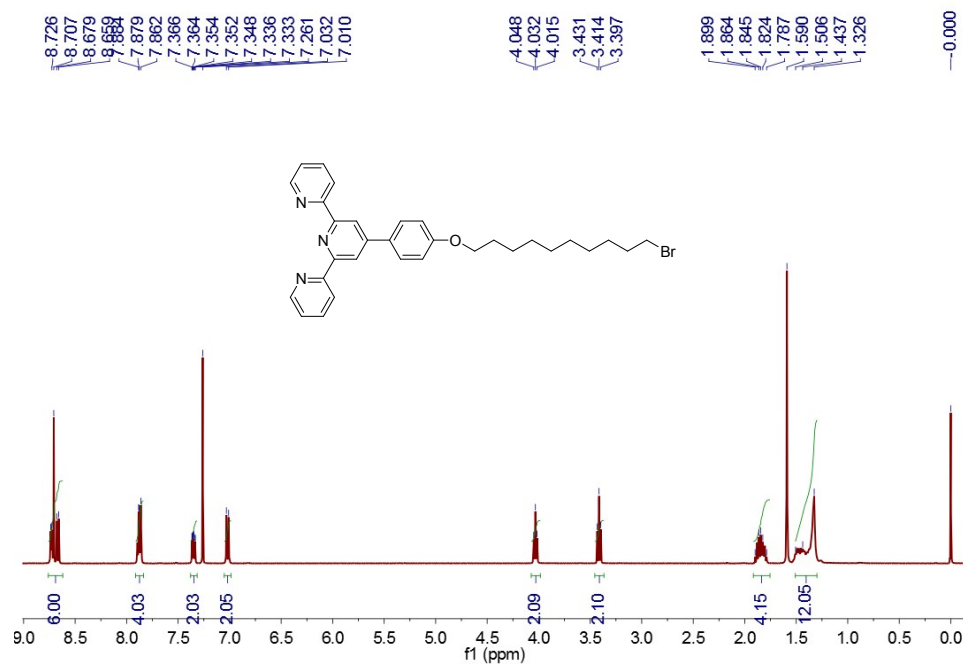


Fig. S1 ^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of **B**.

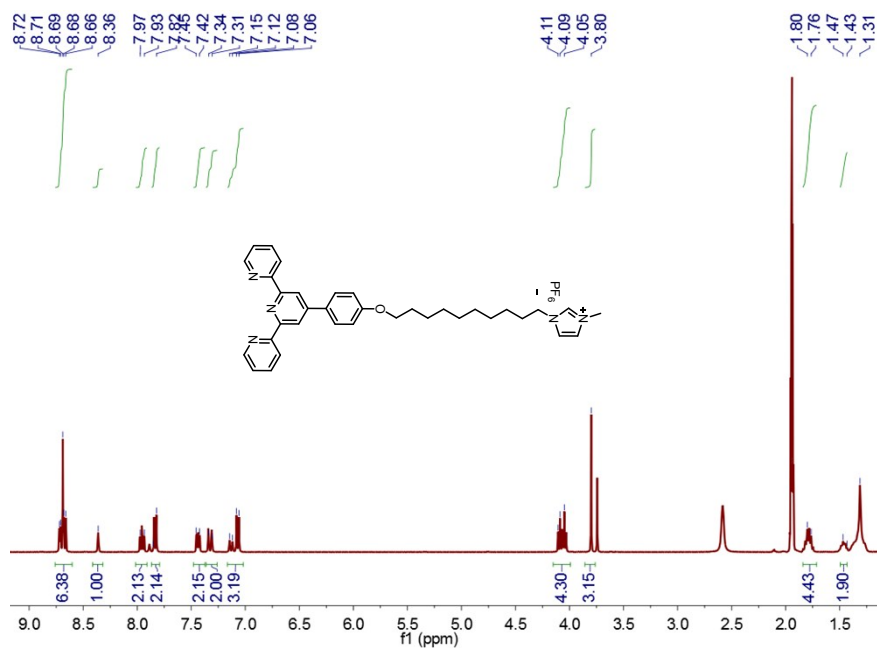


Fig. S2 ^1H NMR spectrum (400 MHz, CD_3CN , 298K) of ligand **1**.

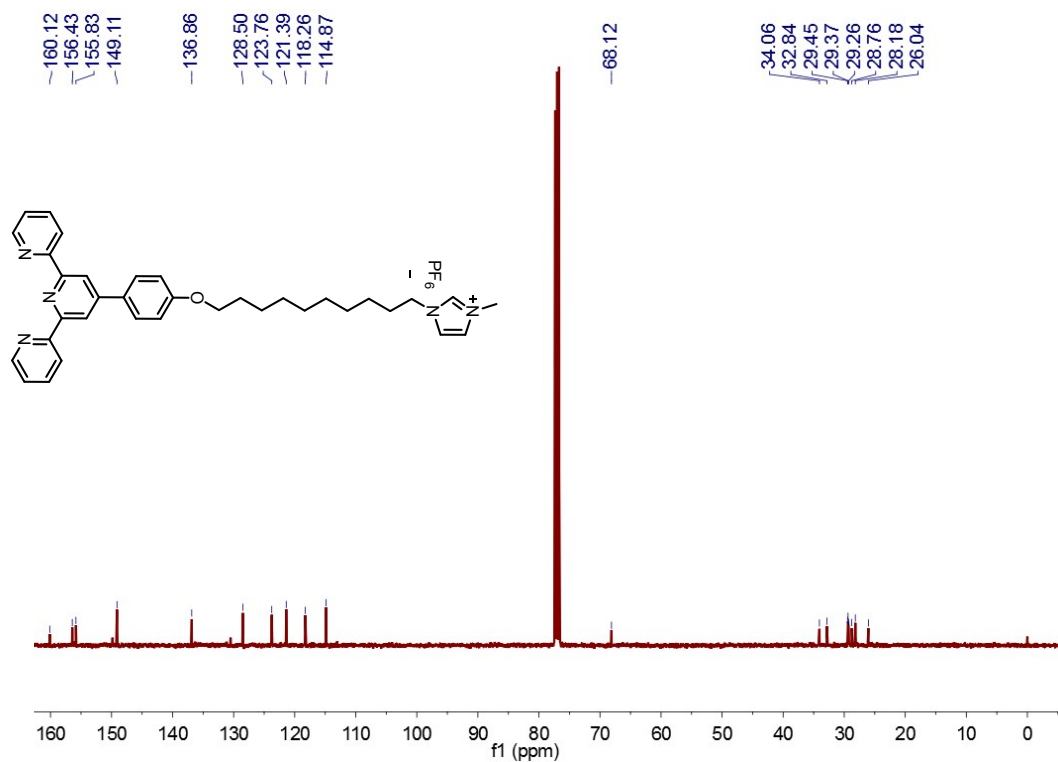


Fig. S3 ^{13}C NMR spectrum (100 MHz, CD_3CN , 298K) of ligand **1**.

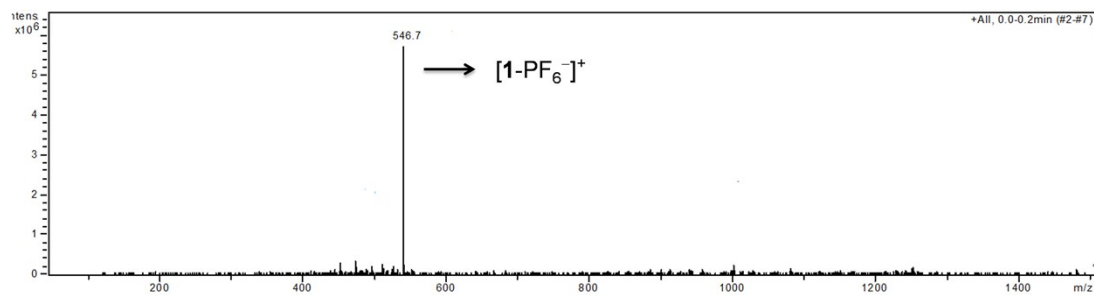


Fig. S4 Electrospray ionization mass spectrum of ligand **1**. Assignment of the main peak: m/z 546.7 $[1-\text{PF}_6]^+$.

3. Synthesis of dimeric complex 3

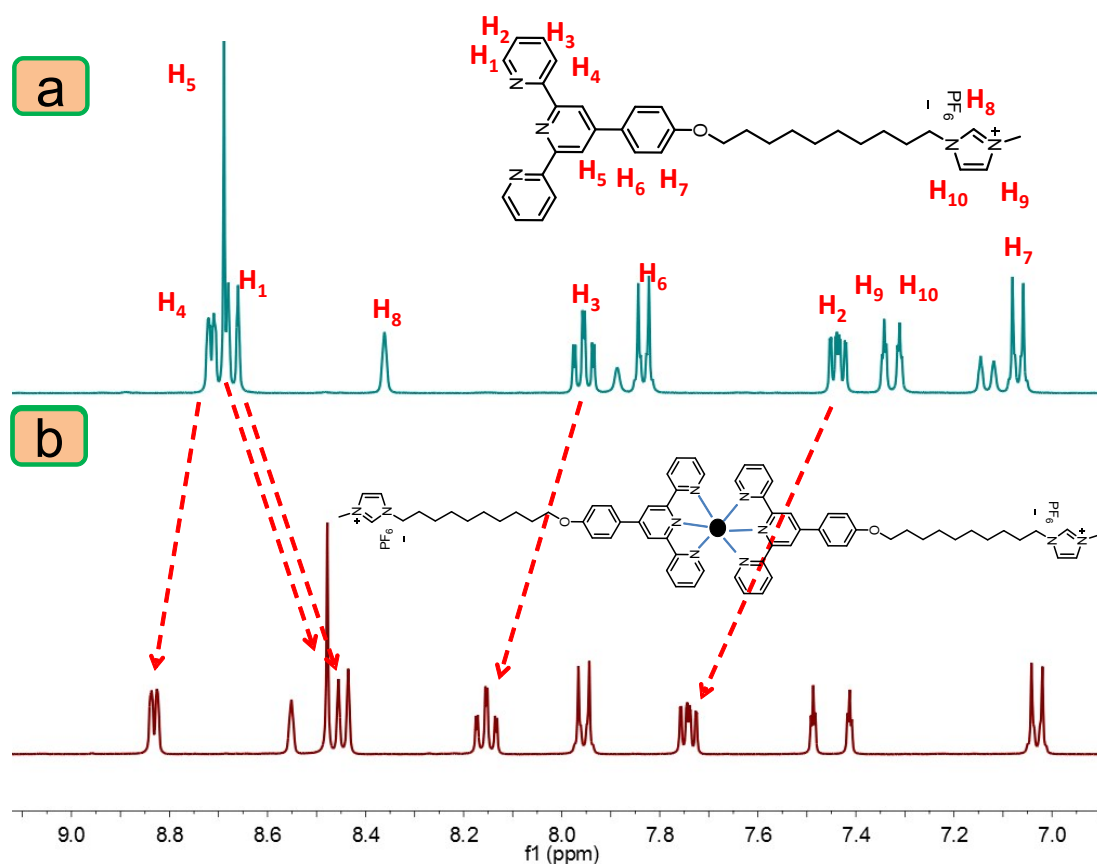


Fig. S5 partial ^1H NMR spectrum (400 MHz, CD_3CN , 25 $^\circ\text{C}$) of (a) ligand **1** and (b) dimeric complex **3**.

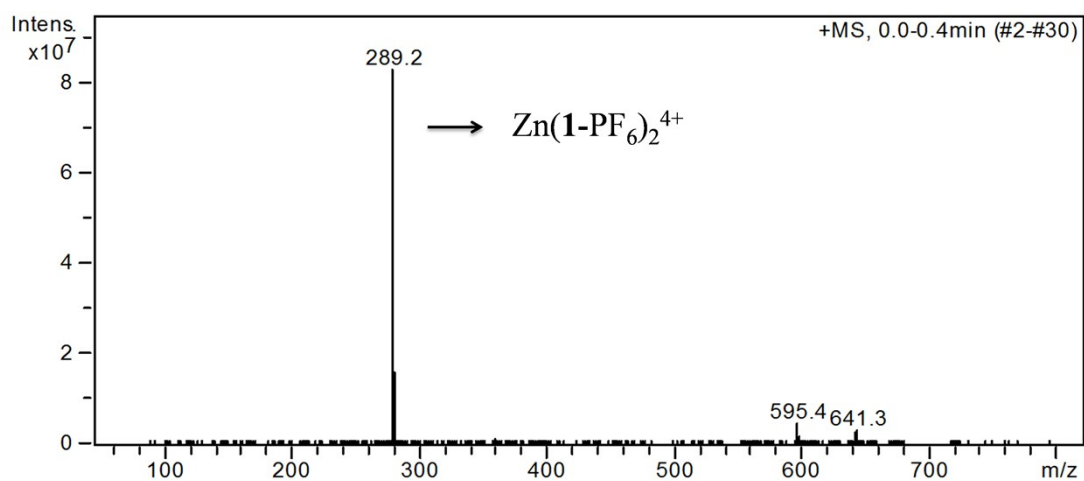


Fig. S6 Electrospray ionization mass spectrum of dimeric complex **3**. Assignment of the main peak: m/z 289.2 $[\text{Zn}(\mathbf{1} - \text{PF}_6)_2]^{4+}$.

4. Host-guest complexation between **1** and **P₁₀**

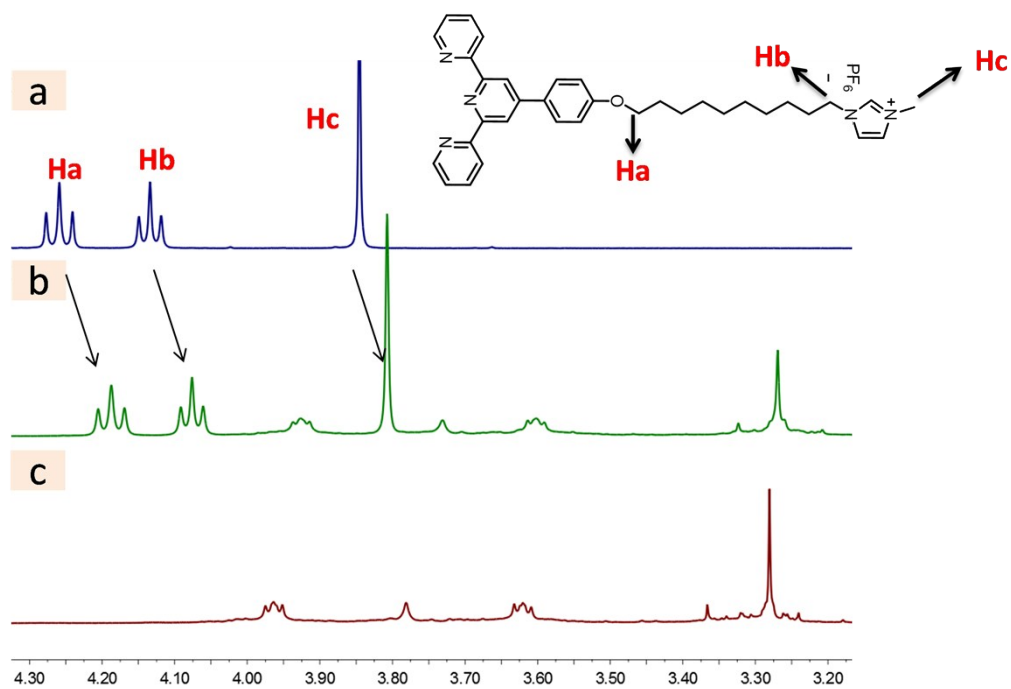


Fig. S7 partial ¹H NMR spectrum (400 MHz, CD₃CN, 25 °C) of (a) ligand **1**, (b) **P₁₀** and ligand **1**, (c) **P₁₀**.

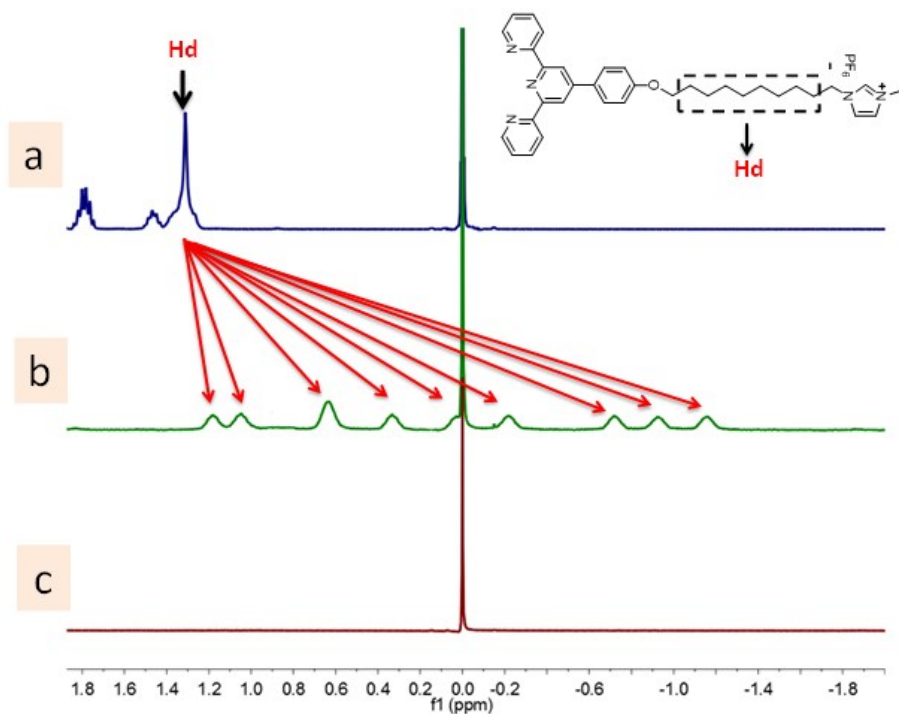


Fig. S8 partial ¹H NMR spectrum (400 MHz, CD₃CN, 25 °C) of (a) ligand **1**, (b) **P₁₀** and ligand **1**, (c) **P₁₀**.

5. CF₃COOH responsive transformation

As shown in Fig. S9, the signal of imidazolium proton H₈ disappeared, indicating the formation of carbene-Ag complex. More interestingly, the signal of H₈ reappeared by adding CF₃COOH, which is attributed to the stronger binding ability between Ag⁺ and CF₃COOH. However, when we added NaOH into the solution of linear supramolecular polymer **A**, the signal of H₈ remained the same, suggesting that the complexation was not simply pH-reponsive.

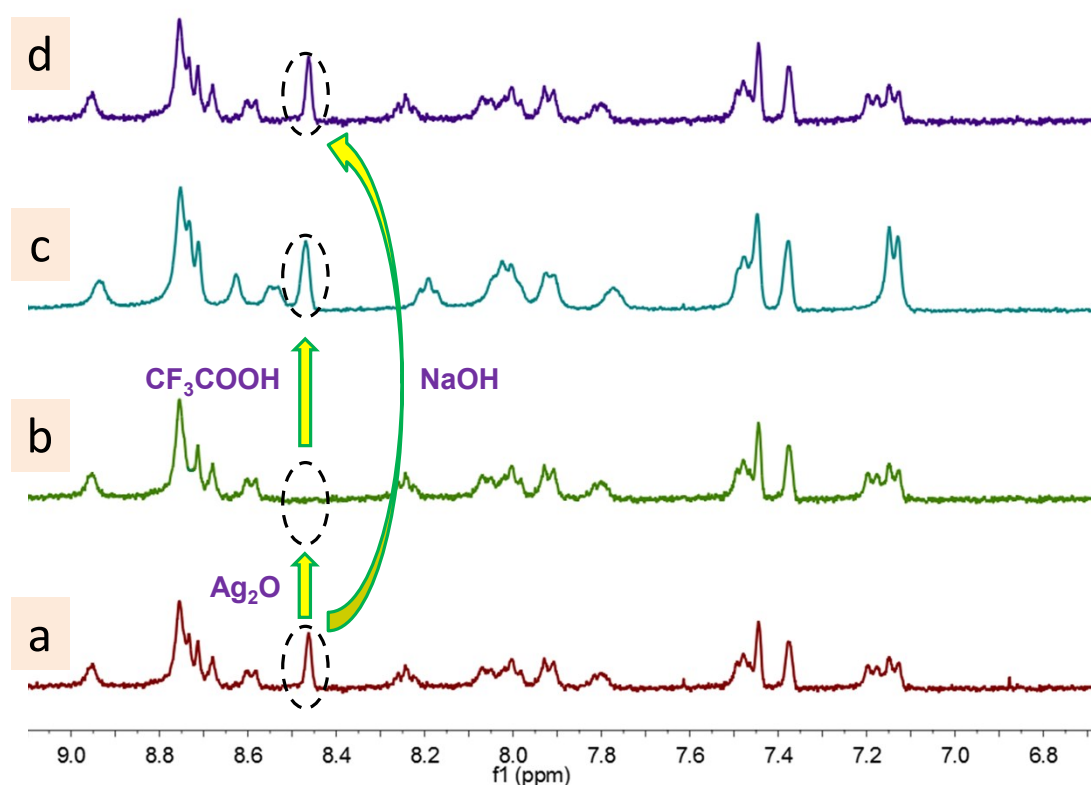


Fig. S9 Partial ¹H NMR spectra (400 MHz, CD₃CN, 25 °C): (a) linear supramolecular polymer **A**; (b) linear supramolecular polymer **A** and excess Ag₂O; (c) after addition of excess CF₃COOH to (b); (d) after addition of excess NaOH to (a).

6. Competitive host-guest interactions between P10 and 1 or 5

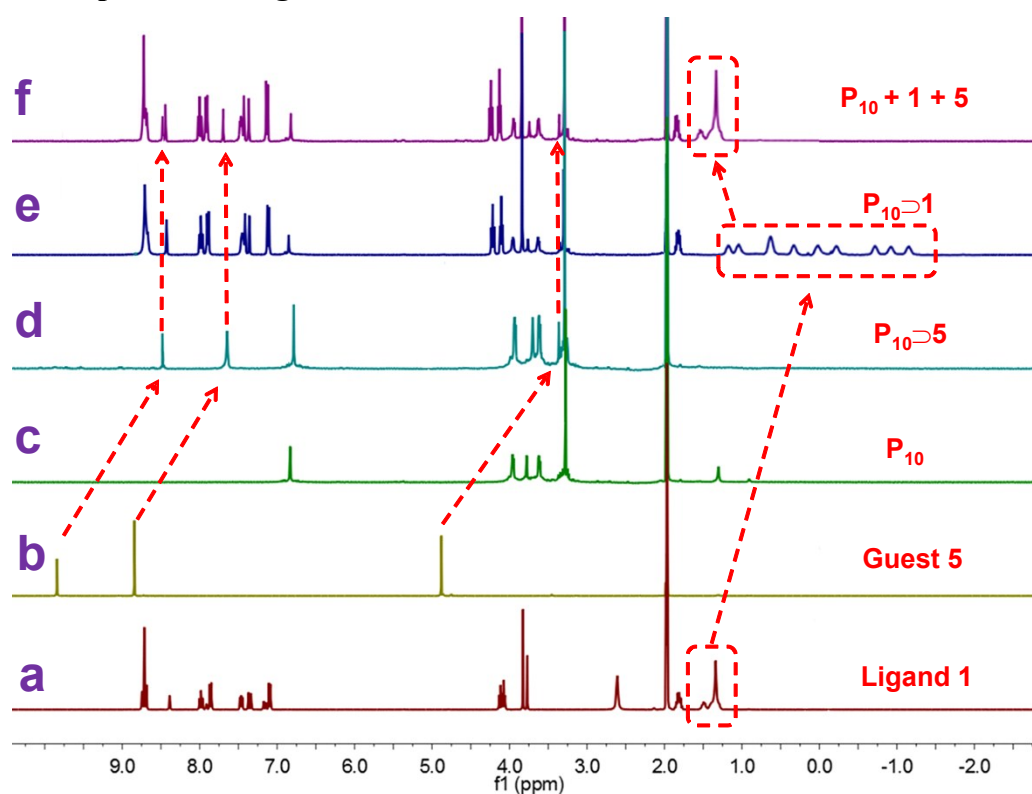


Fig. S10 Partial ¹H NMR spectra (400 MHz, CD₃CN, 25 °C): (a) ligand **1**; (b) guest **5**; (c) P₁₀; (d) P₁₀⊃**5**; (e) P₁₀⊃**1**; (f) P₁₀ + **1** + **5**.

7. References

- S1. (a) T. Ogoshi, T. Aoki, R. Shiga, R. Iizuka, S. Ueda, K. Demachi, D. Yamafuji, H. Kayama, and T.-a. Yamagishi, *J. Am. Chem. Soc.*, 2012, **134**, 20322–20325; (b) X. Chi, and M. Xue, *RSC Adv.*, 2014, **4**, 365–368; (c) G. Yu, J. Zhou, and X. Chi, *Macromol. Rapid Commun.*, 2015, **36**, 23–30.