

**Formation of linear main-chain polypseudorotaxanes with
supramolecular polymer backbones *via* two self-sorting host-guest
recognition motifs**

Feng Wang, Bo Zheng, Kelong Zhu, Qizhong Zhou, Chunxi Zhai, Shijun Li, Ning Li,
and Feihe Huang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Fax: +86-571-8795-1895; Tel: +86-571-8795-3189; Email address: fhuang@zju.edu.cn.

Electronic Supplementary Information (16 pages)

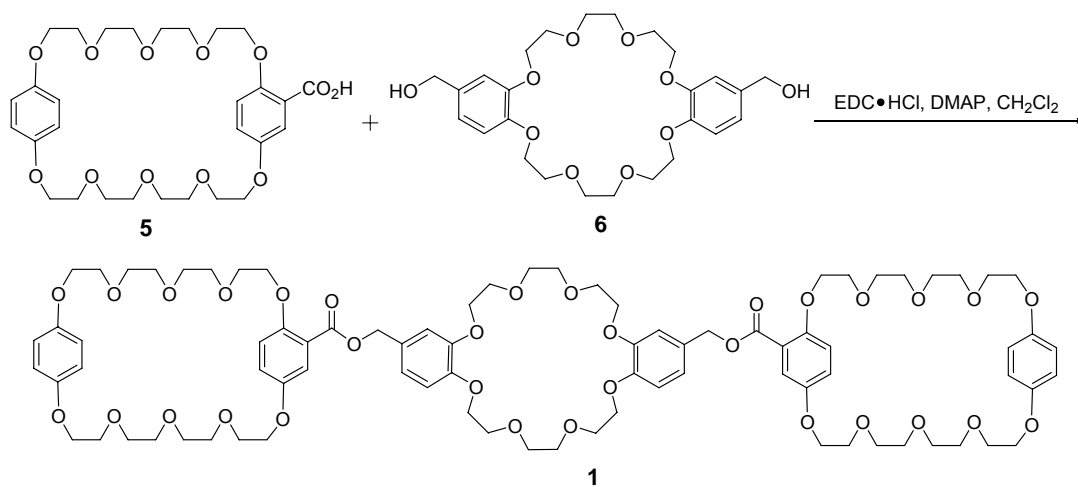
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1. Materials and methods

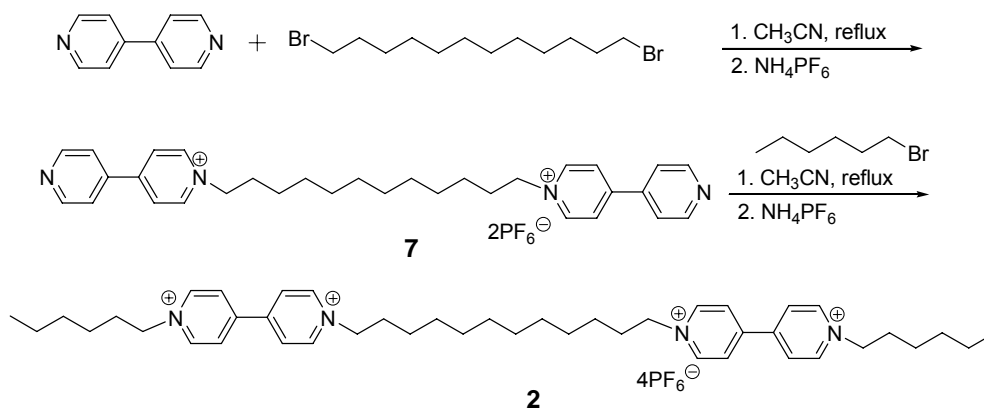
1,12-Dibromododecane, 1-bromohexane, 4-dimethylaminopyridine (DMAP), 4,4'-bipyridine, 1-ethyl-3-[3-(dimethylamino) propyl] carbodiimide (EDC•HCl), and ammonium hexafluorophosphate (NH₄PF₆) were reagent grade and used as received. The intermediates bis(*p*-phenylene)-34-crown-10 acid **5**,^{S1} *trans*-bis(hydroxymethylbenzo)-24-crown-8 **6**^{S2} were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR spectra were collected on Varian Unity INOVA-400 spectrometer with internal standard TMS. ¹³C NMR spectra were recorded on Varian Unity INOVA-400 spectrometry at 100 MHz. Low-resolution electrospray ionization mass spectra (LRESIMS) were obtained on a Bruker Esquire 3000plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESIMS) were obtained on a Bruker 7-tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). Viscosity measurements were carried out on Cannon-Ubbelohde semi-micro dilution viscometers at 25 °C in chloroform/acetonitrile (1/1, v/v). Scanning electron microscopy investigations were carried out on a XL30-ESEM instrument operating at an energy of 10 Kev. All observations were performed from low to high magnification up to 20000×.

2. Syntheses of the monomers

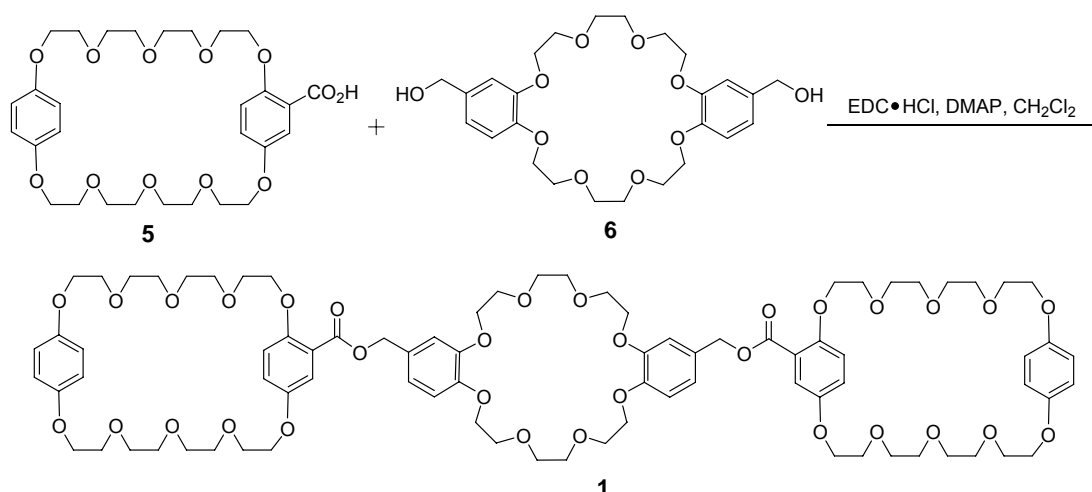
Scheme S1. Synthesis of Monomer 1



Scheme S2. Synthesis of Monomer 2



2.1. Synthesis of Compound **1**



Into a 250 mL three-necked, round-bottomed flask equipped with a septum and a N₂ inlet were added the BPP34C10 monoacid **5** (1.45 g, 2.50 mmol), *trans*-DB24C8 diol **6** (0.64 g, 1.25 mmol), EDC•HCl (1.92 g, 10.0 mmol), DMAP (0.31 g, 2.50 mmol) and 120 mL of CH₂Cl₂. The solution was stirred for two days. After evaporation of the solvent, the purification of the crude product was performed by flash column chromatography (CH₂Cl₂/acetone 2/1→1/2 v/v) on silica gel to afford **1** as a colorless oil (1.05 g, 51%). The proton NMR spectrum of **1** is shown in Figure S1. ¹H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 7.32 (d, J = 2.8 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.96 (s, 2H), 6.92 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 2H), 6.84 (t, J = 8.0 Hz, 4H), 6.75 (s, 8H), 5.22 (s, 4H), 4.16 (br s, 8H), 4.04 (t, J = 4.4 Hz, 4H), 3.96–4.00 (m, 12H), 3.93 (br s, 8H), 3.78–3.84 (m, 24H), 3.66–3.70 (m, 32H). The ¹³C NMR spectrum of **1** is shown in Figure S2. ¹³C NMR (100 MHz, chloroform-*d*, room temperature) δ (ppm): 165.3, 152.5, 152.1, 148.4, 148.3, 128.7, 121.3, 120.8, 119.7, 116.4, 116.2, 115.0, 114.0, 113.2, 70.7, 70.3, 70.2, 69.6, 69.3, 69.2, 69.1, 68.9, 67.7, 67.6, 66.1. LRESIMS is shown in Figure S3: m/z 1671.5 [M + K]⁺ (31%), 1655.7 [M + Na]⁺ (100%). HRESIMS: m/z calcd for [M + Na]⁺ C₈₄H₁₁₂NaO₃₂, 1655.7029, found 1655.7048, error 1.1 ppm.

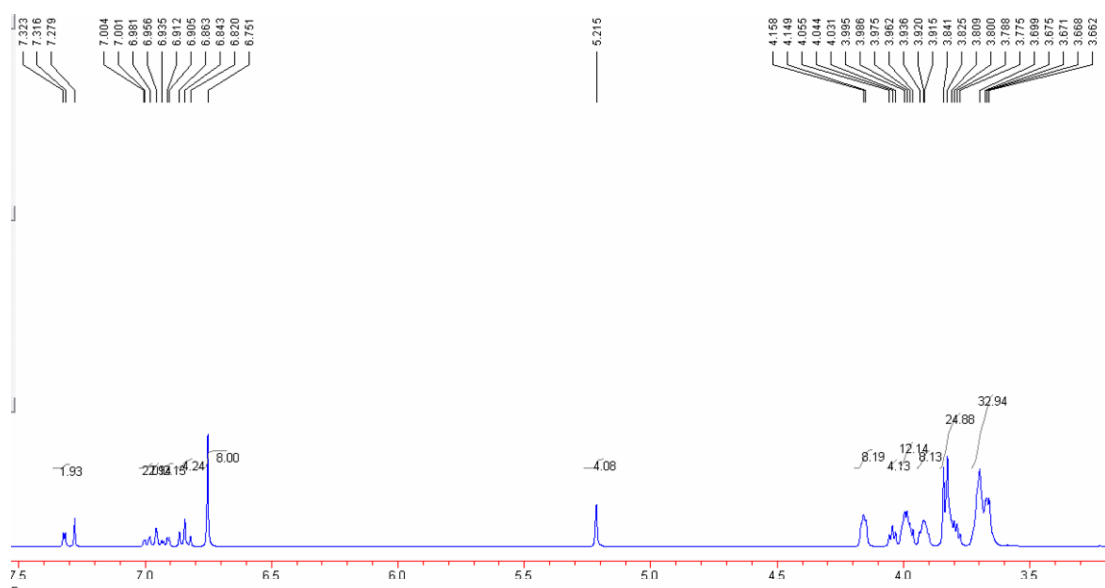


Figure S1. ^1H NMR spectrum (400 MHz, chloroform- d , room temperature) of **1**.

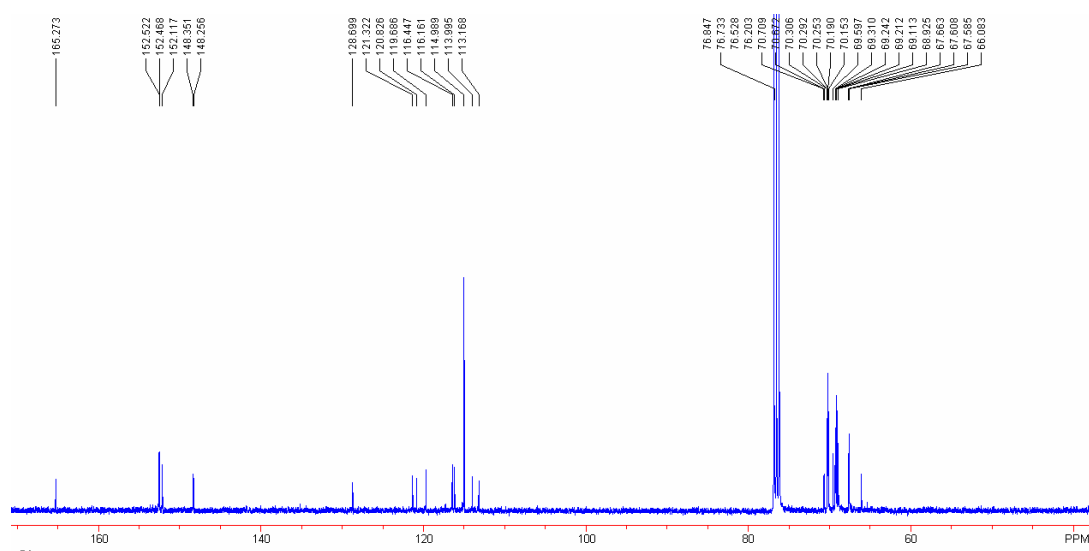


Figure S2. ^{13}C NMR spectrum (100 MHz, chloroform- d , room temperature) of **1**.

wfb50_2

WFB50_2 56 (1.040) Sm (SG, 2x3.00); Sb (1,40.00); Cm (56:71)

1: TOF MS ES+
38.4

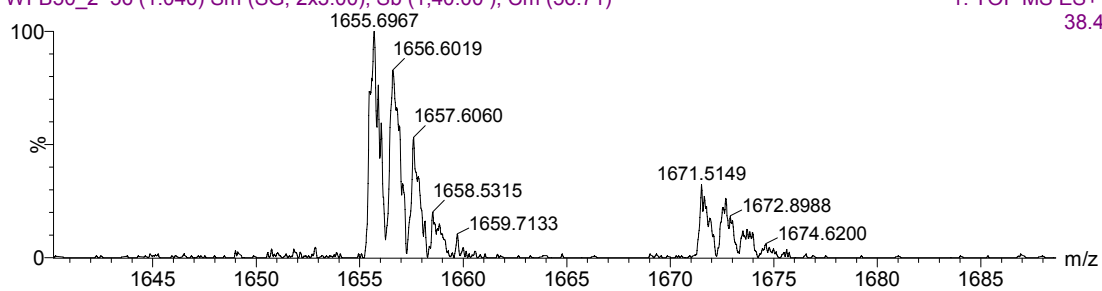
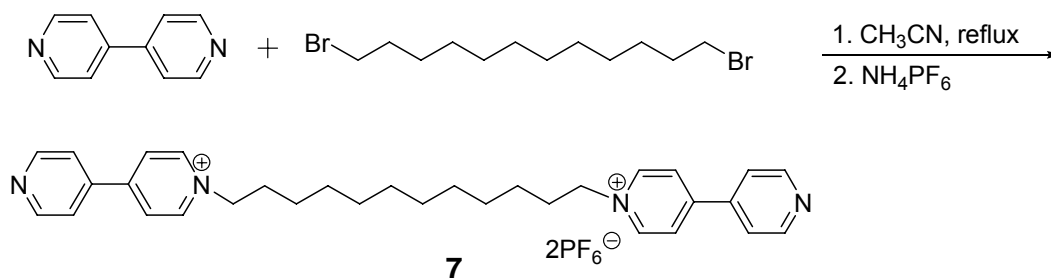


Figure S3. Electrospray ionization mass spectrum of **1**. Assignment of main peaks: m/z 1671.5 $[\text{M} + \text{K}]^+$ (31%), 1655.7 $[\text{M} + \text{Na}]^+$ (100%).

2.2. Synthesis of Compound 7



A solution of 1,12-dibromododecane (6.20 g, 18.9 mmol) in CH_3CN (180 mL) was added dropwise into a stirred and refluxed solution of 4,4'-bipyridine (16.7 g, 0.107 mol) in CH_3CN (210 mL) over 24 hours. After addition, the mixture was further stirred and refluxed for 36 hours. After it had cooled, the suspension was filtered. The solid was washed with CH_3CN and then dried in an oven to afford a pale green solid. It was dissolved in minimum deionized water and aqueous NH_4PF_6 (16.8 g, 0.103 mol) was added to precipitate a white solid. The resulting solid was filtered and washed with water to afford the desired product **7** (13.4 g, 91%).^{S3} The proton NMR spectrum of **7** is shown in Figure S4. ^1H NMR (400 MHz, acetone- d_6 , room temperature) δ (ppm): 9.24 (d, $J = 7.2$ Hz, 4H), 8.88 (br s, 4H), 8.64 (d, $J = 7.2$ Hz, 4H), 8.00 (d, $J = 6.0$ Hz, 4H), 4.87 (t, $J = 7.6$ Hz, 4H), 2.13–2.21 (m, 4H), 1.29–1.47 (m, 16H).

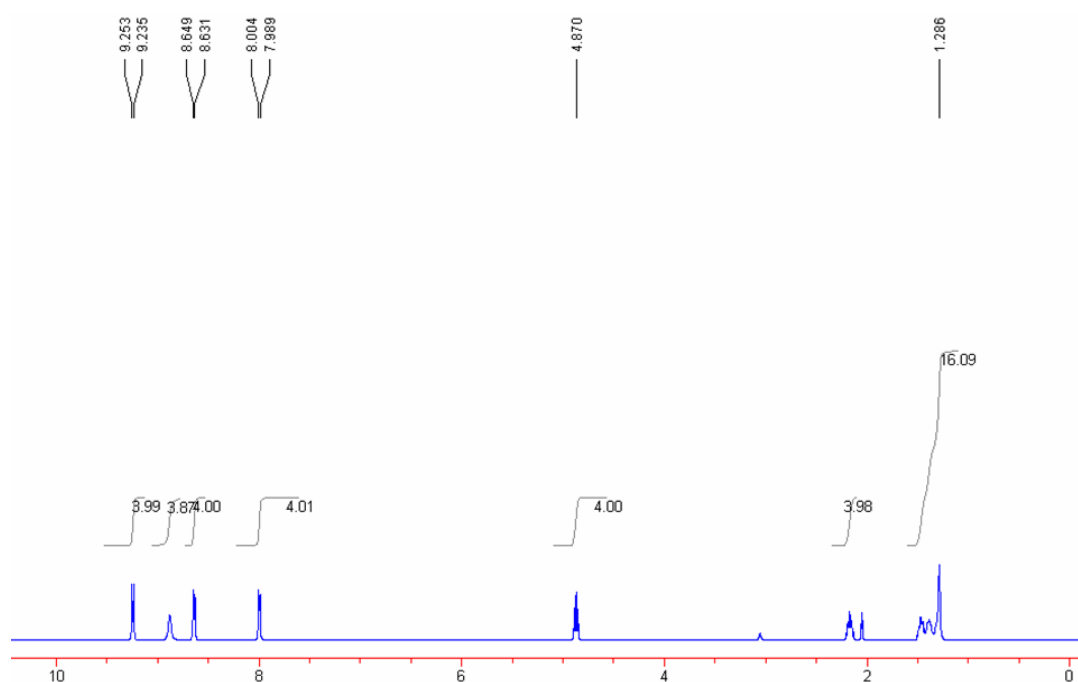
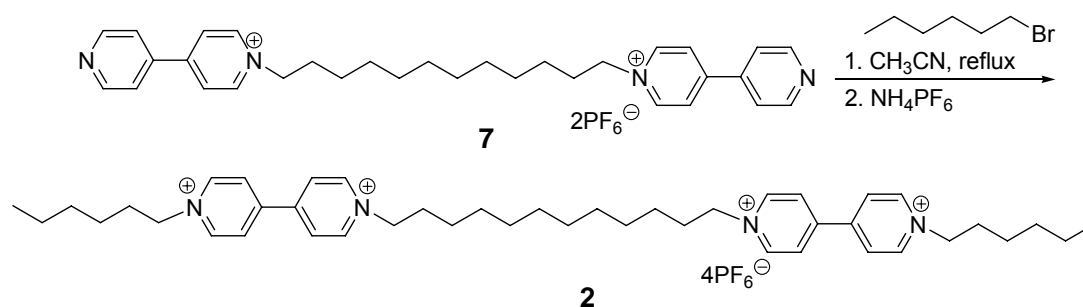


Figure S4. ^1H NMR spectrum (400 MHz, acetone- d_6 , room temperature) of **7**

2.3. Synthesis of Compound 2



A solution of compound **7** (13.3 g, 17.1 mmol) and 1-bromohexane (5.65 g, 34.2 mmol) in CH_3CN (150 mL) was heated at reflux for 36 hours. After it cooled, the mixture was filtered. The solid was washed with CH_3CN . Then excess aqueous NH_4PF_6 (16.8 g, 0.103 mmol) was added to the solution of this solid in minimal deionized water. The suspension was heated at reflux for 24 hours. After it cooled, the mixture was filtered. The solid was washed with water and dried in an oven to afford a white solid (6.31 g, 30%). The proton NMR spectrum of **2** is shown in Figure S5. ^1H NMR (400 MHz, acetone- d_6 , room temperature) δ (ppm): 9.39 (t, $J = 6.8$ Hz, 8H), 8.79 (s, 8H), 4.92 (q, $J = 6.4$ Hz, 8H), 2.16–2.19 (m, 8H), 1.28–1.48 (m, 28H), 0.86 (t, $J = 7.2$ Hz, 6H). LR MALDI-TOF MS is shown in Figure S6: m/z 940.7 $[\text{M} - 2\text{PF}_6]^+$ (22%), 796.4 $[\text{M} - 3\text{PF}_6]^+$ (66%), 711.3 $[\text{M} - 3\text{PF}_6 - \text{C}_6\text{H}_{12}]^+$ (25%), 651.3 $[\text{M} - 4\text{PF}_6]^+$ (100%). HR MALDI-TOF MS: m/z calcd for $[\text{M} - 4\text{PF}_6]^+ \text{C}_{44}\text{H}_{66}\text{N}_4$, 650.5266, found 650.5282, error 2.5 ppm.

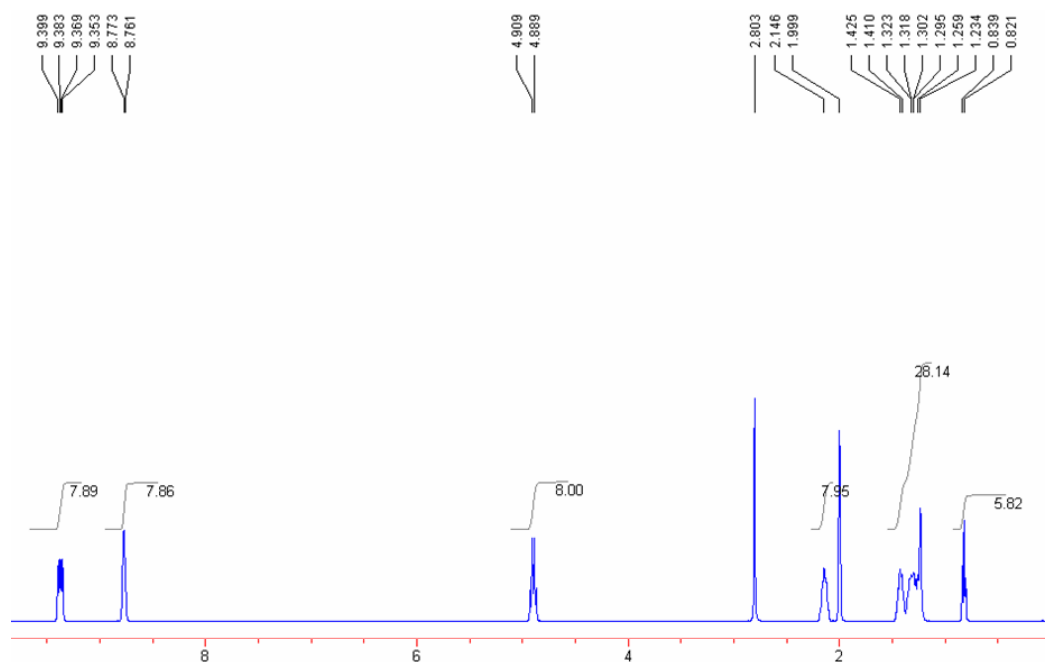


Figure S5. ^1H NMR spectrum (400 MHz, acetone- d_6 , room temperature) of **2**.

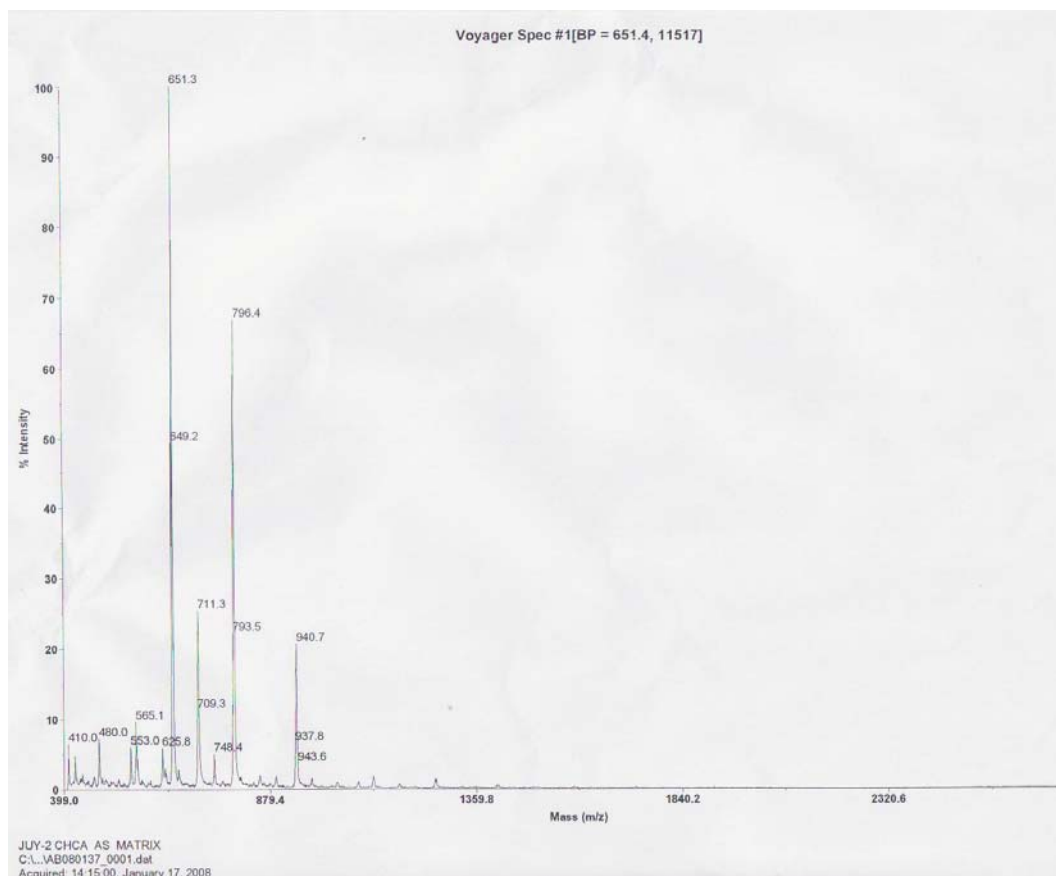


Figure S6. MALDI-TOF mass spectrum of **2**. Assignment of main peaks: m/z 940.7 $[\text{M} - 2\text{PF}_6]^+$ (22%), 796.4 $[\text{M} - 3\text{PF}_6]^+$ (66%), 711.3 $[\text{M} - 3\text{PF}_6 - \text{C}_6\text{H}_{12}]^+$ (25%), 651.3 $[\text{M} - 4\text{PF}_6]^+$ (100%).

3. ^1H NMR spectra of equimolar solutions of **1** and **2**

The ^1H NMR spectra of equimolar solutions of **1** and **2** were concentration-dependent (Figure S7). As the concentration increased, significant upfield shifts were observed for the aromatic protons of BPP34C10 and paraquat groups. The shifts were accompanied by a progressive broadening of the resonances, revealing the formation of high-molecular-weight aggregates at high concentrations. The chemical shift of the H^1 located on the BPP34C10 group was monitored by ^1H NMR spectroscopy. From the relationship between the chemical shift of H^1 and the BPP34C10 concentration (Figure S8), it is obvious that the percentage of complexed BPP34C10 moieties increased with increasing concentration, suggesting the formation of linear supramolecular polymers.

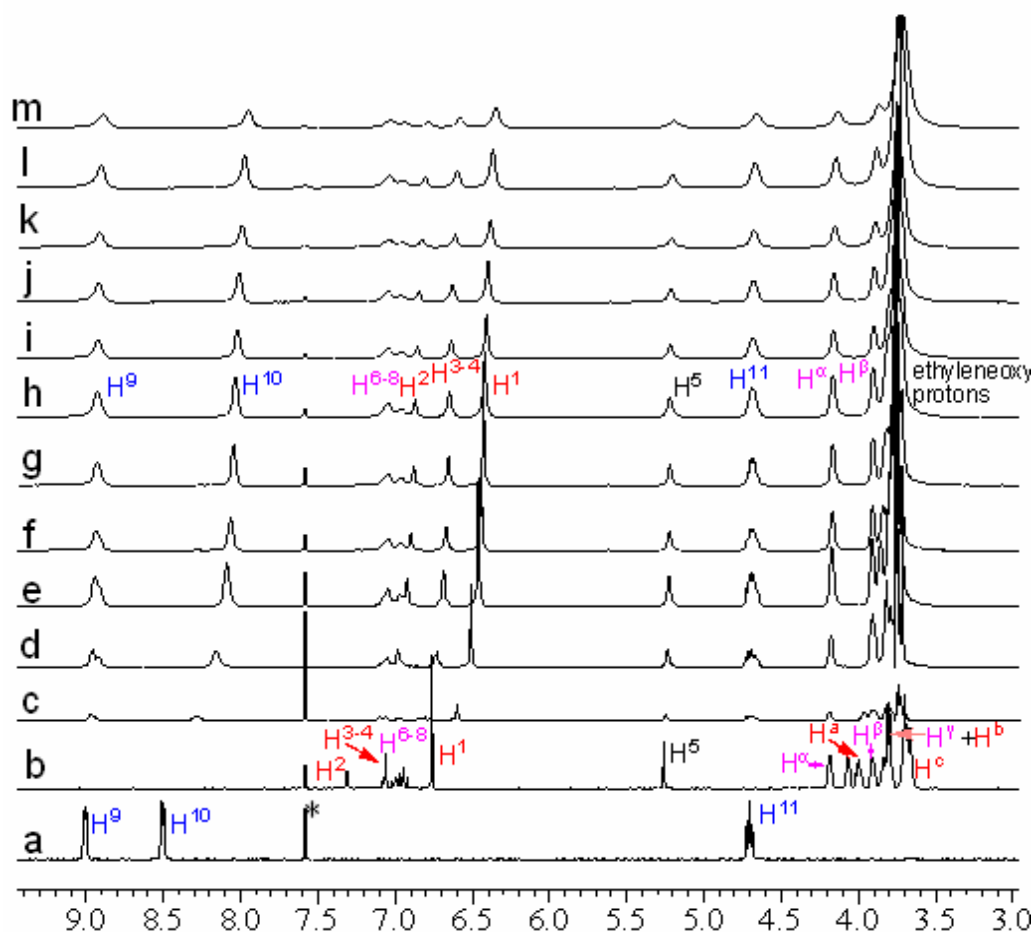


Figure S7. ^1H NMR spectra (400 MHz, chloroform- d /acetonitrile- d_3 (1/1, v/v), 20 $^\circ\text{C}$) of (a) **2**; (b) **1**; equimolar mixtures of **1** and **2** at different BPP34C10 crown unit concentrations ($= 2$ [**1**] $_0$): (c) 1.84 mM, (d) 11.5 mM, (e) 38.3 mM, (f) 57.4 mM, (g) 76.5 mM, (h) 92.0 mM, (i) 115 mM, (j) 131 mM, (k) 184 mM, (l) 230 mM, (m) 306 mM. Signals affiliated with solvents are denoted by star symbols.

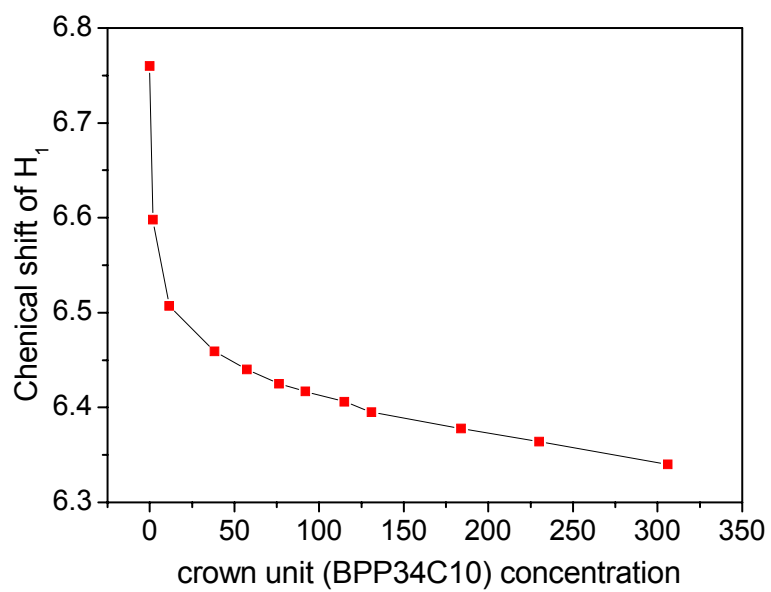


Figure S8. The chemical shift of H₁ on **1** as a function of BPP34C10 concentration.

4. ^1H NMR spectra of equimolar solutions of **1** and **2** at 230 mM with gradual addition of **3**

The feed-ratio effect of DBA on the formation of supramolecular polypseudorotaxanes was also studied by gradual addition of **3** into equimolar mixtures of **1** and **2** at a BPP34C10 concentration of 230 mM (Figure S9). At this concentration the linear species played a more prominent role than the case of 98.0 mM. Unlike the spectra at 98.0 mM in which two sets of signals existed at the same time, at this higher concentration all the protons demonstrated only one set of signals, indicating the essentially complete conversion of the linear supramolecular polymer to the supramolecular polypseudorotaxane. Moreover, a slight downfield shift was observed for the protons H^{10} on the paraquat groups. Therefore, it was demonstrated that the concentration also played an important role on the formation of supramolecular polypseudorotaxane **4**.

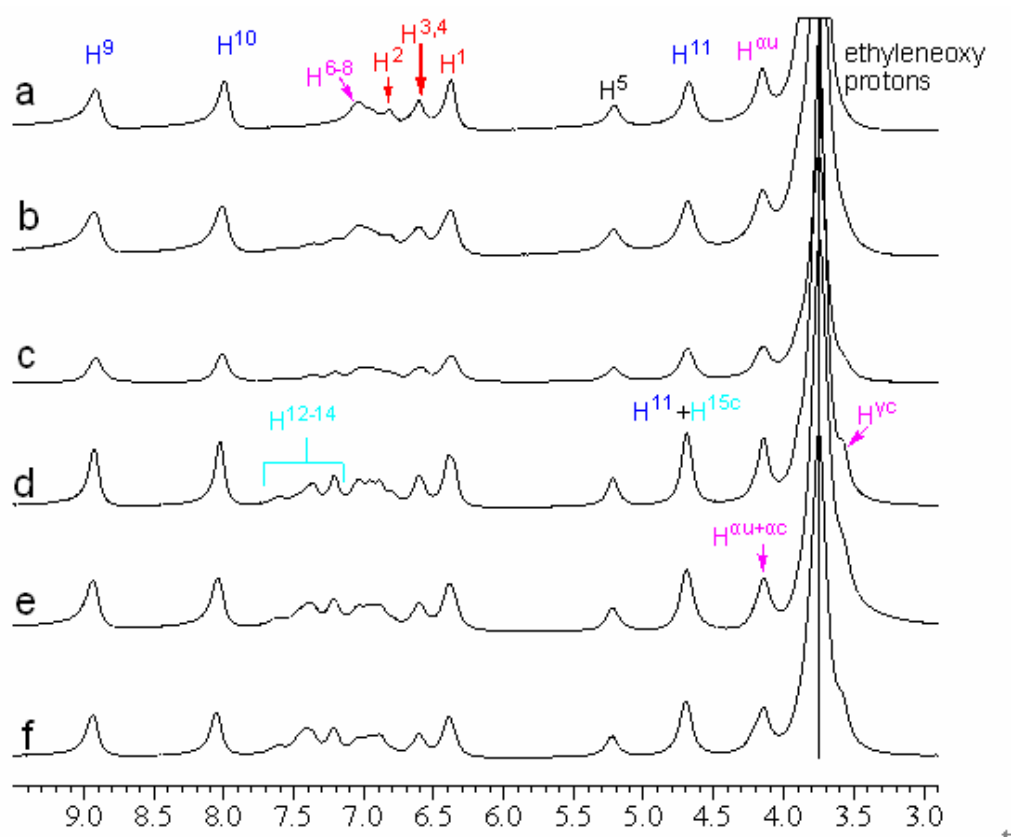


Figure S9. Partial ^1H NMR (400 MHz, chloroform- d /acetonitrile- d_3 (1/1, v/v), 20 $^\circ\text{C}$) spectra of equimolar mixtures of **1** and **2** upon addition of **3**: (a) 0; (b) 0.2 equiv; (c) 0.4 equiv; (d) 0.6 equiv; (e) 0.8 equiv; and (f) 1 equiv of **3**. $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 115$ mM. (“c” and “u” denote complexed and uncomplexed moieties, respectively).

5. NOESY spectrum of an equimolar solution of **1** and **2** at the BPP34C10 concentration of 31.4 mM

The two-dimensional NOESY NMR spectrum (Figure S10) of an equimolar solution of **1–2** at the BPP34C10 concentration of 31.4 mM showed the proton H⁹ was correlated with the protons H¹⁰ and H¹¹ on the paraquat groups. Similar correlations were observed for the DB24C8 moiety (H^{6–8} with H⁵ and H^α) and BPP34C10 moiety (ethyleneoxy protons with H¹, H², H^{3–4}). Hence, the protons in the ¹H NMR spectra (Figure S7) could be accurately assigned. However, the correlation peaks between the peaks of the BPP34C10 protons and the paraquat protons were not observed probably due to the relatively low concentration. An equimolar solution of **1–3** at a higher concentration was then studied.

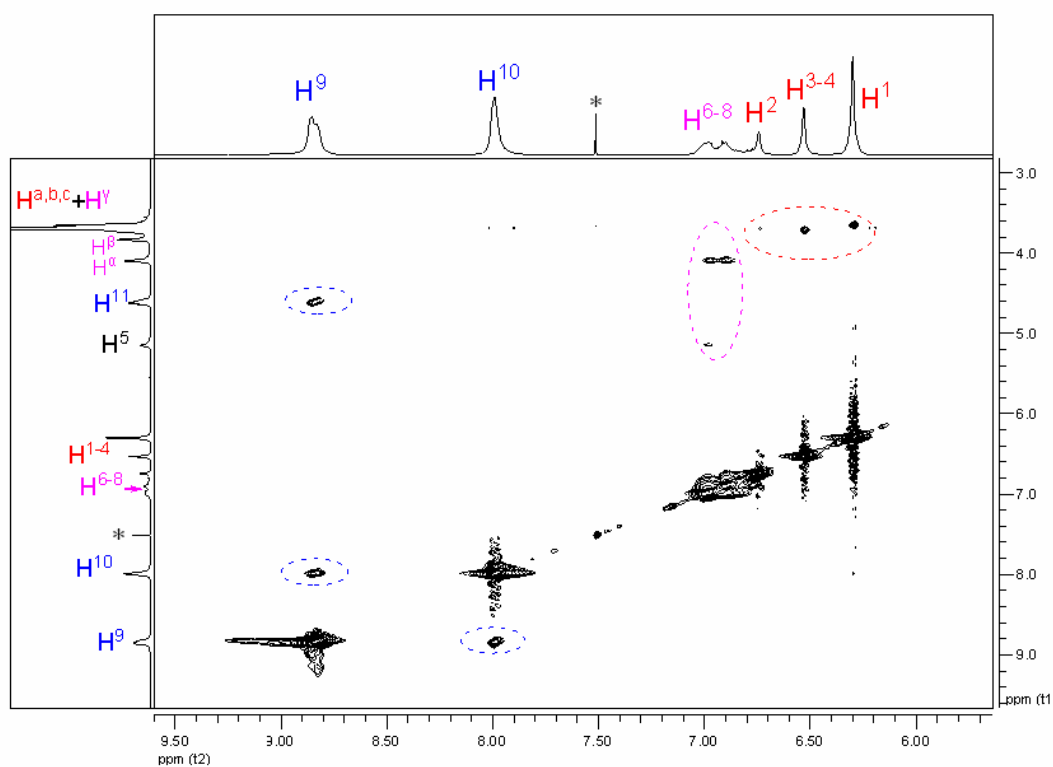
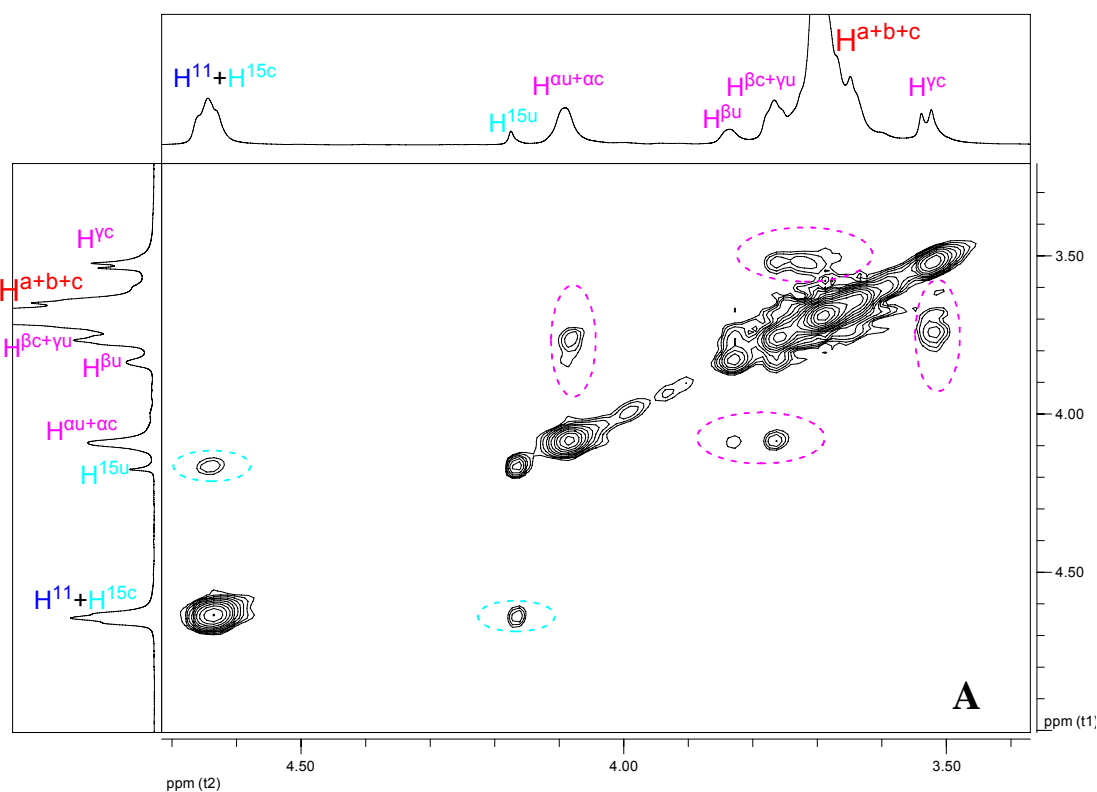


Figure S10. Partial NOESY NMR (500 MHz, chloroform-*d*/acetonitrile-*d*₃ (1/1, v/v), 20 °C) spectrum of an equimolar solution of **1–2** at the BPP34C10 concentration of 31.4 mM. Signals affiliated with solvents are denoted by star symbols.

6. NOESY spectrum of an equimolar solution of **1–3** at the BPP34C10 concentration of 64.0 mM

The two-dimensional NOESY NMR spectrum of an equimolar solution of **1–3** at a BPP34C10 concentration of 64.0 mM is shown in Figure S11. From Figure S11A we could assign the ethyleneoxy protons on BPP34C10 and DB24C8 moieties. The aromatic protons were then determined based on correlation signals between aromatic and ethyleneoxy peak regions (Figure S11B). Furthermore, the peaks of H⁹ and H¹⁰ on the paraquat moiety were correlated with the ethyleneoxy protons on the BPP34C10 moiety, while no correlation peaks between H⁹ or H¹⁰ and ethyleneoxy protons on DB24C8 moiety were observed, which supported the existence of the self-sorting organization of the two host-guest recognition pairs.



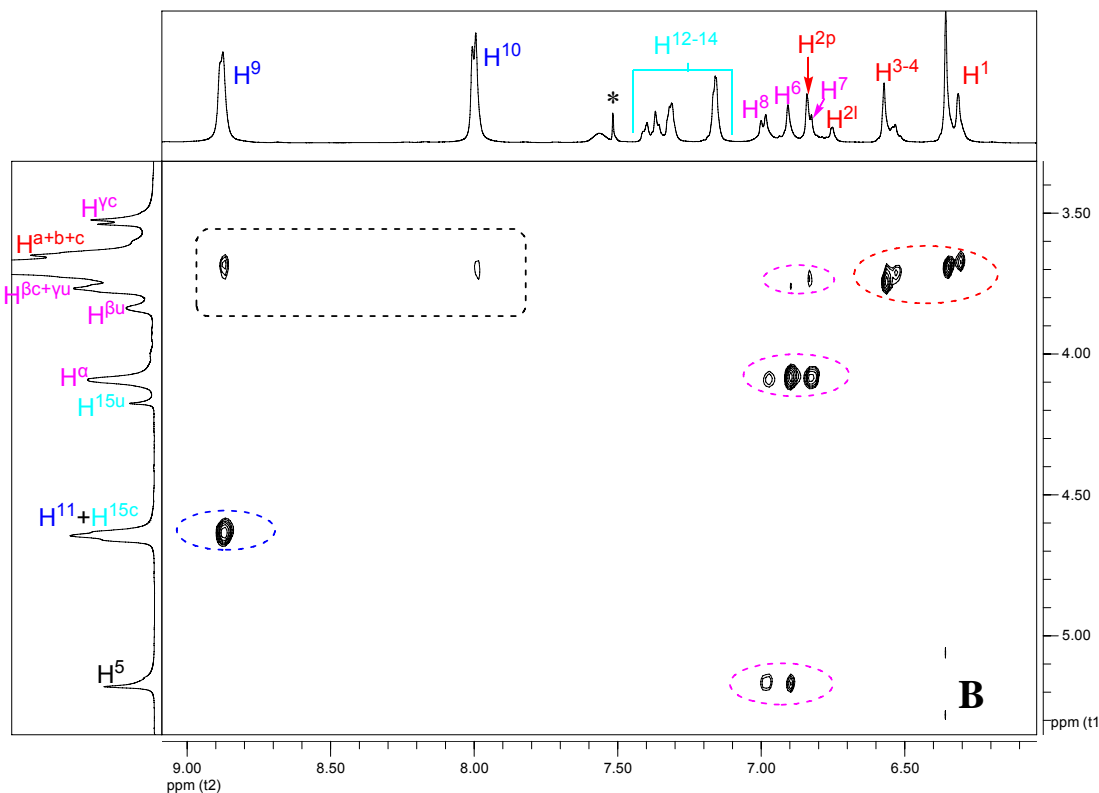


Figure S11. Partial NOESY NMR (500 MHz, chloroform-*d*/acetonitrile-*d*₃ (1/1, v/v), 20 °C) spectrum of an equimolar solution of **1–3** at a BPP34C10 concentration of 64.0 mM. (“c” and “u” denote complexed and uncomplexed moieties, respectively, while “p” and “l” denote the DBA-threaded and DBA-unthreaded monomer **1**, respectively). Signals affiliated with solvents are denoted by star symbols. The rounded rectangle frame and the ellipse frame denote the correlation signals of intermolecular and intramolecular interactions, respectively.

7. UV-Vis spectra of equimolar solutions of **1–3**

Figure S12 displays the UV-Vis absorption spectra of the individual compounds **1–3** and the equimolar mixtures of them (1.8 mM for each monomer) from 290 nm to 600 nm in chloroform/acetonitrile (1/1, v/v). No absorbance was observed for single compound and the mixtures between compounds of compounds **1** with **3** and **2** with **3**. In contrast, the absorption spectra of both of equimolar mixtures of **1–2** and **1–3** showed an identical band around 422 nm, which is characteristic for the charge-transfer interactions between BPP34C10 and paraquat groups. Addition of DBA **3** did not lead to any shift for this wavelength, hence, also confirming the self-sorting organization of these two host-guest recognition pairs.

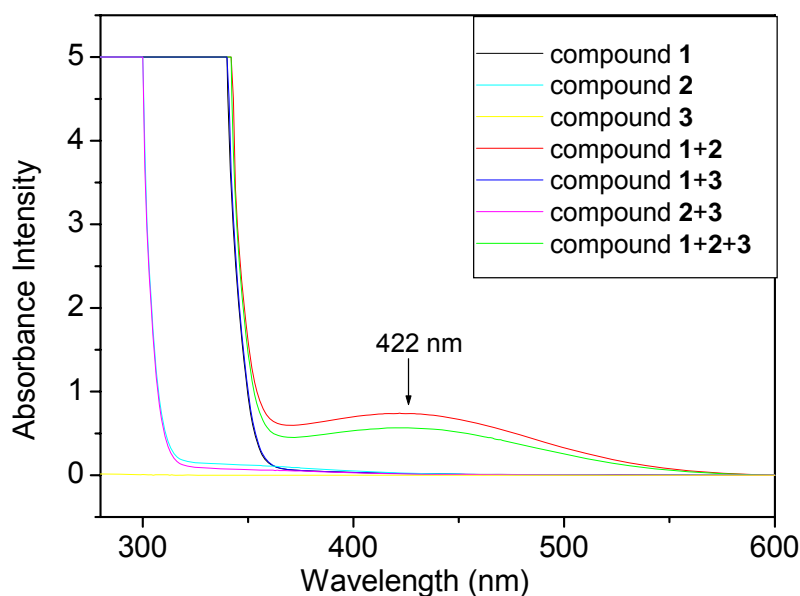


Figure S12. UV-Vis absorption spectra of the compounds **1–3** and the equimolar mixtures of these compounds (1.8 mM for each compound) in chloroform/acetonitrile (1/1, v/v).

References:

- S1. X.-B. Shao, X.-K. Jiang, X.-Z. Wang, Z.-T. Li and S.-Z. Zhu, *Tetrahedron*, 2003, **59**, 4881–4889.
- S2. H. W. Gibson, H. Wang, C. Slebodnick, J. Merola, W. S. Kassel and A. L. Rheingold, *J. Org. Chem.*, 2007, **72**, 3381–3393.
- S3. Y. Kawaguchi and A. Harada, *Org. Lett.*, 2000, **2**, 1353–1356.