Well-Defined Supramolecular Polymers Based on Orthogonal Hydrogen Bonding and Host–Guest Interactions

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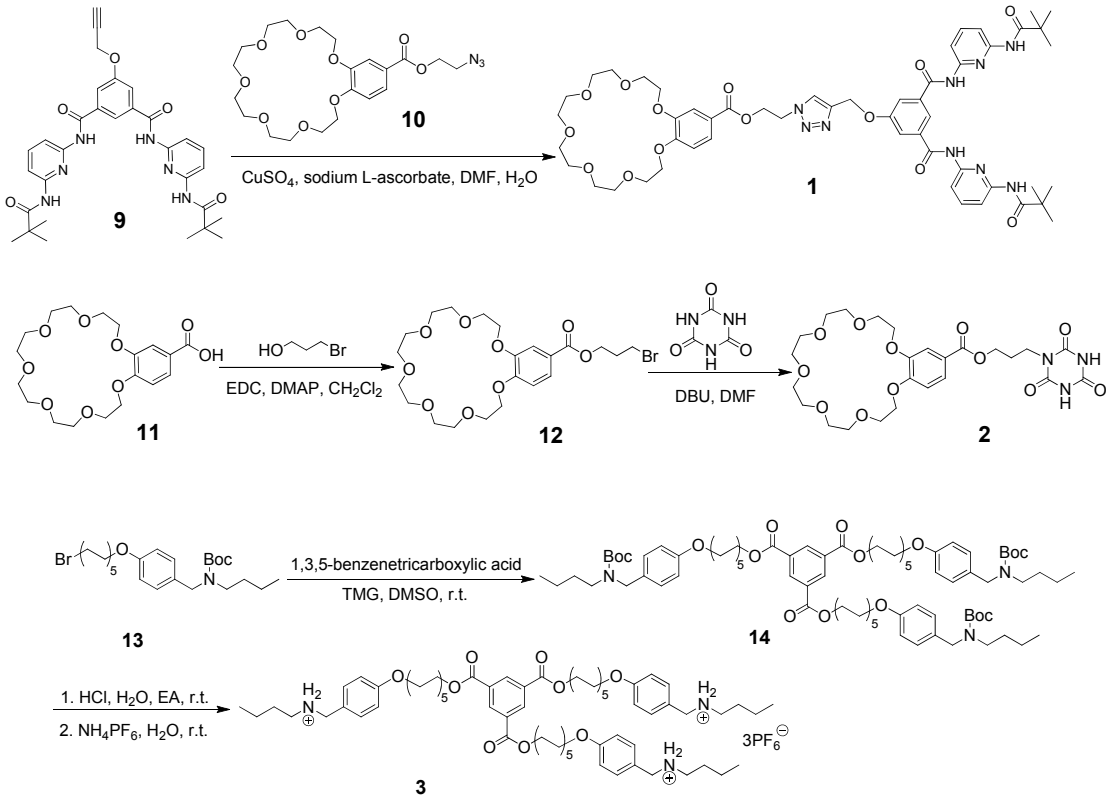
Supporting Information

1. Materials and Methods

Tosyl chloride, copper sulfate pentahydrate, sodium ascorbate, 5-amino-1-pentanol, 3-bromopropan-1-ol, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl), 4-dimethylamino pyridine (DMAP), cyanuric acid, 1,8-Diazabicyclo[5.4.0]undec-7-ene are reagent grade and used as received. Compounds **9**,[S1] **10**,[S2] **11**,[S2] and **13**[S3] were synthesized according to the previously reported procedures. Other reagents and solvents were employed as purchased.

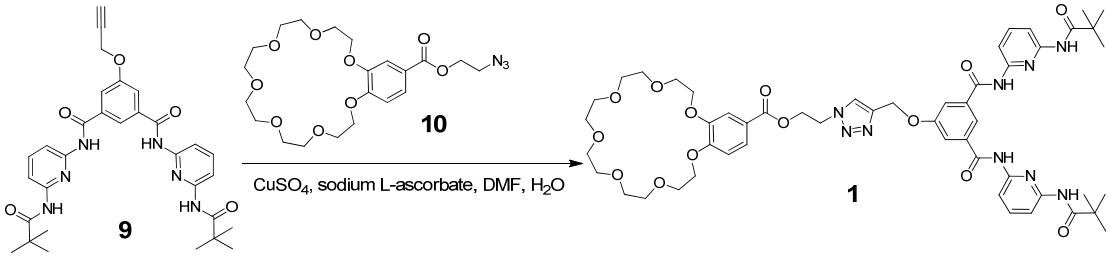
^{1}H NMR spectra were collected on a Varian Unity INOVA-300 or INOVA-400 spectrometer with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometer at 100 MHz. Two-dimensional DOSY experiments were performed on a Varian Unity INOVA-400 MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and ion trap analyzer. Time-of-flight mass spectra (TOF-MS) were obtained on matrix-assisted laser desorption/ionization TOF/TOF MS (autoflex speed TOF/TOF, Bruker). Viscosity measurements were carried out with Ubbelohde semi-micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.47 mm inner diameter) at 25 °C in 2 : 1 chloroform : acetonitrile solution. SEM spectra were observed on SEM-Sirion 200.

*2. Synthetic routes to the targeted monomers **1–3***



Scheme S1. Synthetic routes to the targeted monomers **1**–**3**.

*2.1. Synthesis of monomer **1***



Compound **9** (3.02 g, 5.28 mmol) and **10** (2.20 g, 4.68 mmol) were dissolved in DMF (20 mL). An aqueous solution of mono-sodium L-ascorbate (92.8 mg, 0.47 mmol) and $CuSO_4$•$5H_2O$ (59.5 mg, 0.23 mmol) was then added. The resulting mixture was heated at 60 °C and stirred for 24 hours. The solvent was then removed with a rotary evaporator and the residue was extracted with H_2O/EA. The combined organic extracts were dried over anhydrous Na_2SO_4 and removed with a rotary evaporator.

The crude product was purified by flash column chromatography (CH_2Cl_2/CH_3OH, 30 : 1 *v*/*v* as the eluent) to afford monomer **1** as a white solid (3.22 g, 68%). The ^1H NMR spectrum of compound **1** is shown in Figure S1. ^1H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 8.48 (s, 2H), 8.10–7.95 (m, 5H), 7.89 (s, 2H), 7.83–7.68 (m, 5H), 7.54 (d, J = 7.6 Hz, 1H), 7.44 (s, 1H), 6.84 (d, J = 8.5 Hz, 1H), 5.37 (s, 2H), 4.75 (d, J = 24.8 Hz, 4H), 4.16 (s, 4H), 3.90 (s, 4H), 3.76 (s, 4H), 3.68 (d, J = 19.3 Hz, 12H), 1.34 (s, 18H). The ^{13}C NMR spectrum of compound **1** is shown in Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 177.19, 171.34, 165.75, 164.15, 159.03, 153.60, 150.13, 149.40, 148.49, 143.37, 141.06, 136.36, 124.08, 121.75, 118.37, 117.53, 114.70, 112.33, 110.17, 109.69, 71.74, 70.87, 70.68, 69.48, 62.56, 62.20, 61.51, 60.58, 49.64, 39.98, 27.59. ESI–MS m/z: $[M + H]^+$ = 1040.47168.

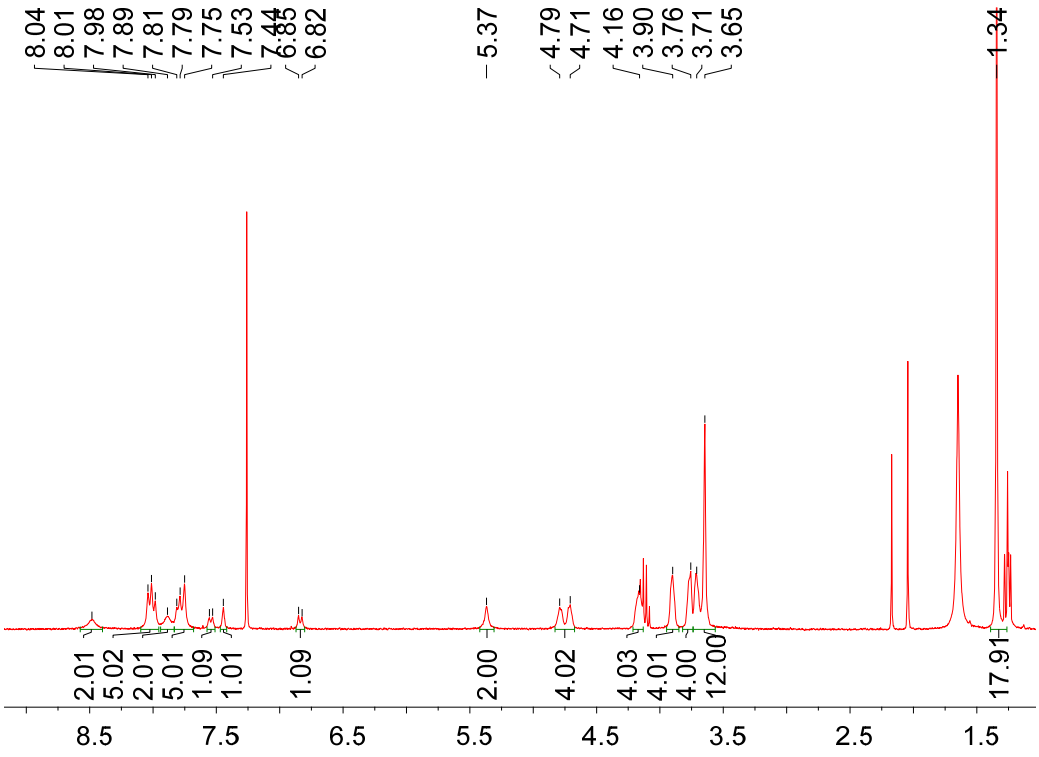


Figure S1. ^1H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of monomer **1**.

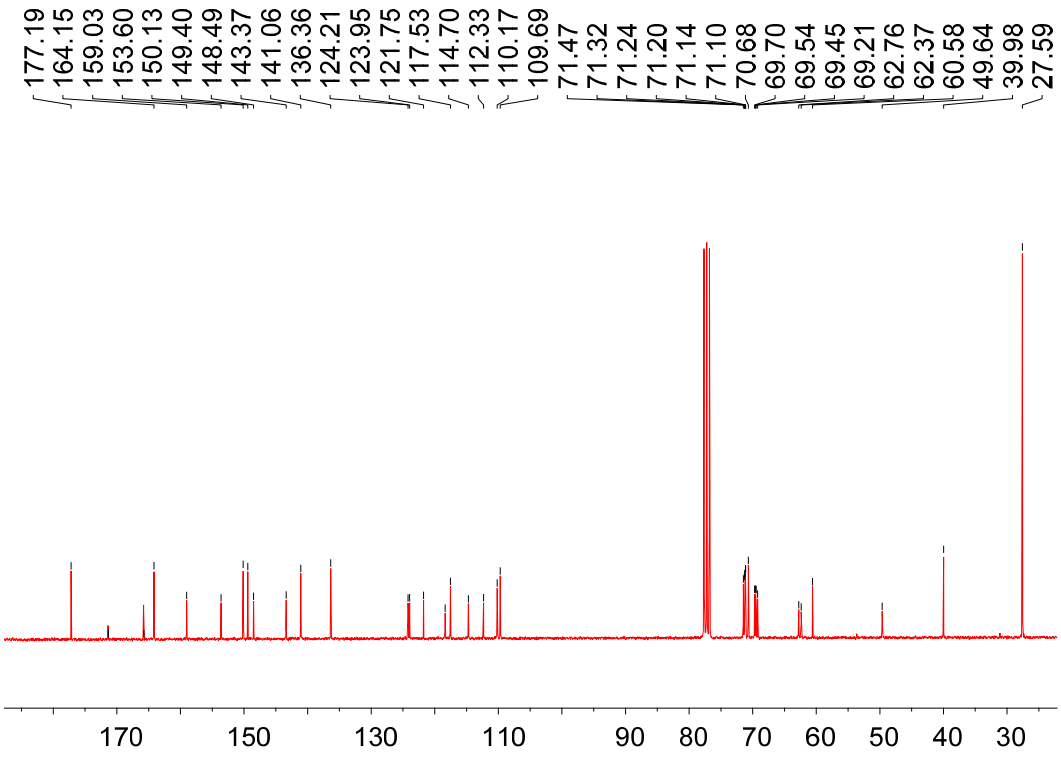


Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of monomer **1**.

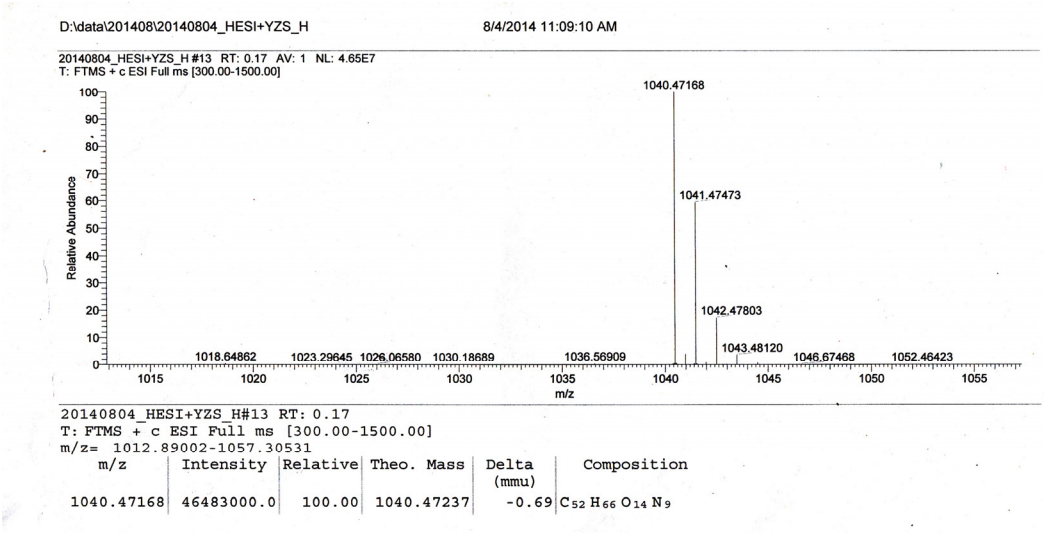
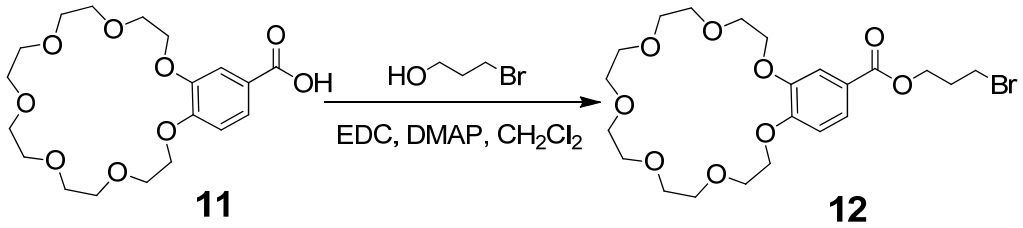


Figure S3. Electrospray ionization spectrum of monomer **1**.

*2.2. Synthesis of compound **12***



Compounds **11** (3.00 g, 7.50 mmol), 3-bromo-1-propanol (3.13 g, 22.5 mmol) and DMAP (0.23 g, 1.88 mmol) in 80 mL CH_2Cl_2 were stirred at 0 °C for 10 minutes. EDC•HCl (1.37 g, 11.3 mmol) was then added to this solution. The mixture was stirred at room temperature for 48 h. When the reaction was completed, the solvent was extracted with H_2O/CH_2Cl_2. The organic extracts were combined and concentrated to provide a pale yellow oil, which was purified by flash column chromatography (petroleum ether/ethyl acetate, 1 : 2 *v*/*v*) to give **12** as a pale yellow oil (2.35 g, 60%).[S4] The ^{1}H NMR spectrum of compound **12** is shown in Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 7.65 (m, J = 8.4, 2.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 4.47–4.39 (t, 2H), 4.20 (m, J = 6.2, 2.7 Hz, 4H), 3.97–3.90 (m, 4H), 3.84–3.78 (m, 4H), 3.76–3.71 (m, 4H), 3.70–3.64 (m, 8H), 3.54 (t, J = 6.6 Hz, 2H), 2.31 (m, J = 6.3 Hz, 2H). The ^{13}C NMR spectrum of compound **12** is shown in Figure S5.^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 165.65, 152.54, 147.72, 123.45, 122.22, 114.04, 111.70, 70.66, 70.07, 68.87, 62.05, 61.06, 40.89, 31.36, 29.05.

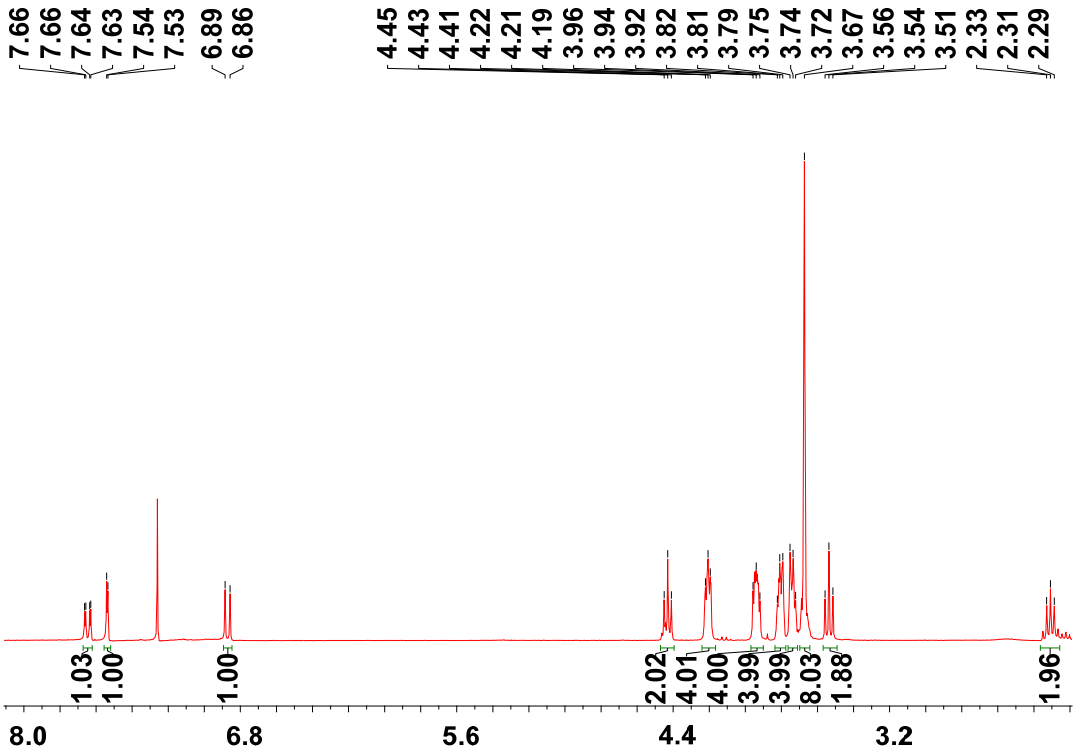


Figure S4. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of **12**.

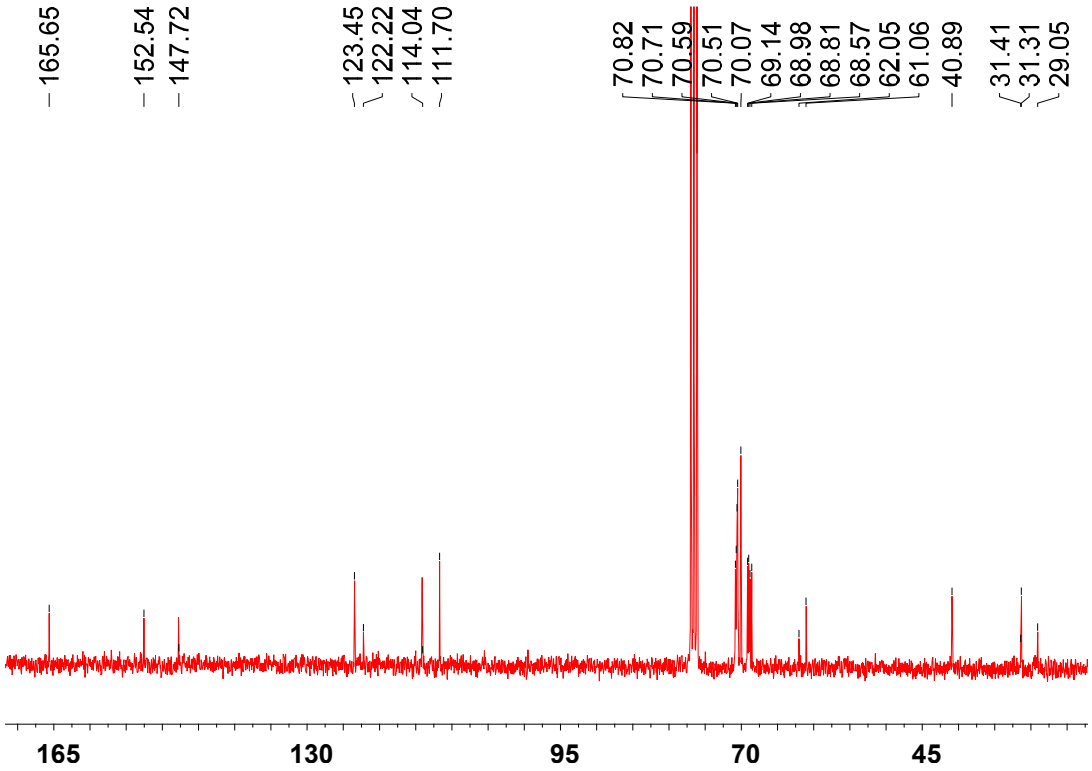
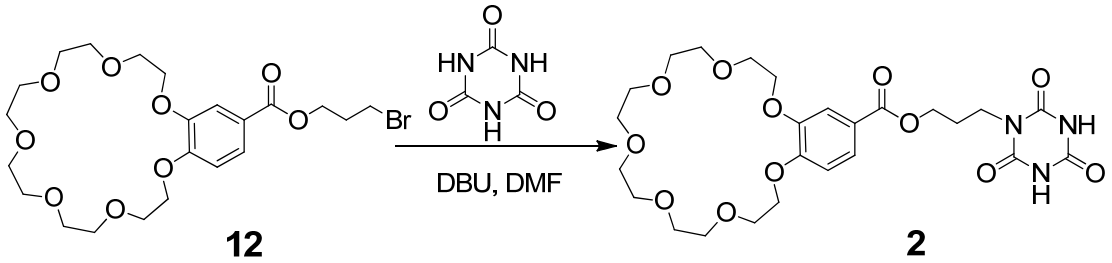


Figure S5. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of **12**.

*2.3. Synthesis of monomer **2***



A solution of compound **12** (2.35 g, 4.51 mmol), cyanuric acid (2.91 g, 22.5 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.69 g, 4.51 mmol) in DMF (50 mL) was stirred for 48 h at 70 °C. After removal of DMF, the solution was extracted with saturated solution of $NaHSO_3/CH_2Cl_2$, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford a white solid, which was purified by flash column chromatography (ethyl acetate/methyl alcohol, 20 : 1 *v*/*v*) to afford **2** as a white solid (1.79 g, 70%). The ^{1}H NMR spectrum of **2** is shown in Figure S6. ^{1}H NMR (300 MHz, d_6-DMSO, room temperature) δ (ppm): 11.39 (s, 2H), 7.57–7.54 (m, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 4.23 (t, J = 5.9 Hz, 2H), 4.15 (m, 4H), 3.82 (t, J = 6.7 Hz, 2H), 3.77 (s, 4H), 3.61 (d, J = 4.6 Hz, 4H), 3.56 (d, J = 5.2 Hz, 4H), 3.51 (s, 8H), 2.02–1.93 (m, 2H). The ^{13}C NMR spectrum of monomer **2** is shown in Figure S7. ^{13}C NMR (75 MHz, d_6-DMSO, room temperature) δ (ppm): 165.45, 152.36, 150.04, 148.78, 147.74, 123.22, 122.12, 112.66, 112.13–111.21, 71.12–70.18, 70.00, 68.68, 58.72, 54.89–54.22, 37.90. ESI–MS m/z: $[M + H]^+$ = 570.22894.

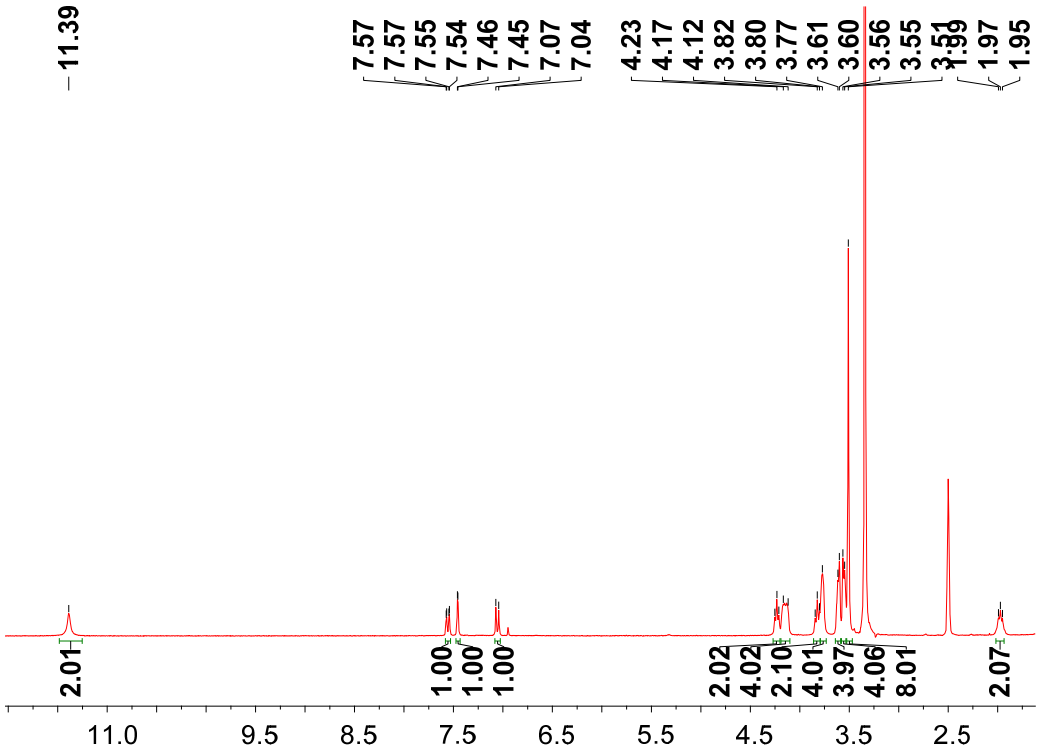


Figure S6. ^{1}H NMR spectrum (300 MHz, d_6-DMSO, room temperature) of **2**.

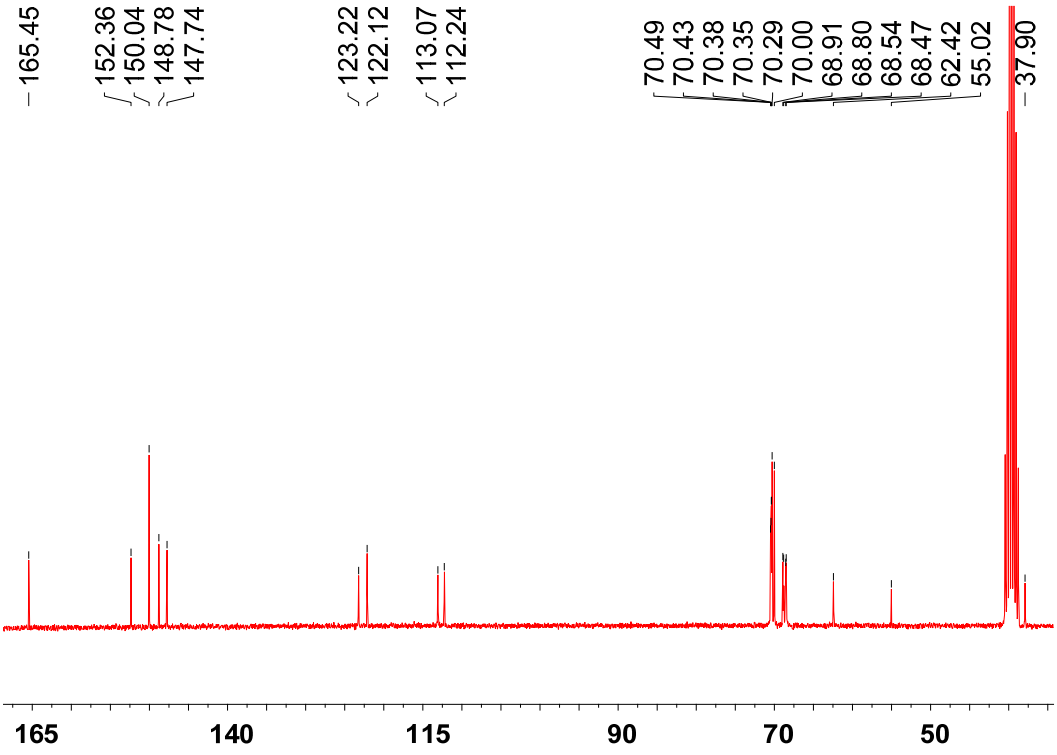


Figure S7. ^{13}C NMR spectrum (75 MHz, d_6-DMSO, room temperature) of **2**.

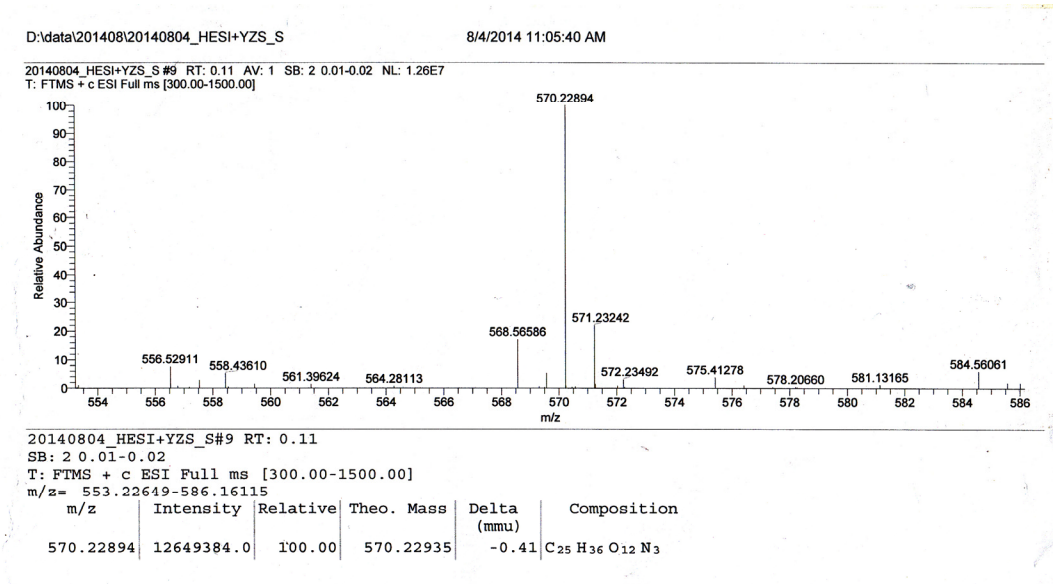
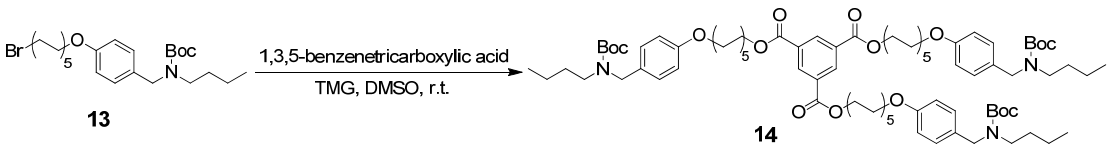


Figure S8. Electrospray ionization spectrum of **2**.

*2.4. Synthesis of compound **14***



Compound **13** (5.07 g, 10.2 mmol), 1,3,5-benzenetricarboxylic acid (0.53 g, 2.51 mmol) and 1,1,3,3-tetramethylguanidine (0.87 g, 7.53 mmol) in 60 mL DMSO were stirred at room temperature for 48 hours. After removal of DMSO, the solution was extracted with H_2O/CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered, and concentrated to give a colorless oil, which was purified by flash column chromatography (petroleum ether/CH_2Cl_2, 1 : 1 *v*/*v* as the eluent) to afford compound **14** as a colorless oil (2.73 g, 74%).[S3] The ^{1}H NMR spectrum of compound **14** is shown in Figure S9. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 8.84 (s, 3H), 7.12 (br, 6H), 6.83 (d, J = 8.5 Hz, 6H), 4.36 (t, J = 6.7 Hz, 12H), 3.92 (t, J = 6.5 Hz, 6H), 3.12 (br, 6H), 1.84–1.71 (m, 12H), 1.46 (s, 42H), 1.37–1.22 (m, 34H), 0.88 (t, J = 7.3 Hz, 12H). The ^{13}C NMR spectrum of compound **14** is shown in Figure S10. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 165.1, 158.3, 134.4, 131.5, 130.5, 129.0, 128.4, 114.4, 79.3, 68.0, 65.8, 49.7, 45.8, 30.1, 29.7, 29.5, 29.4, 29.3, 28.7, 28.5, 26.1, 26.0,

20.0, 13.9.

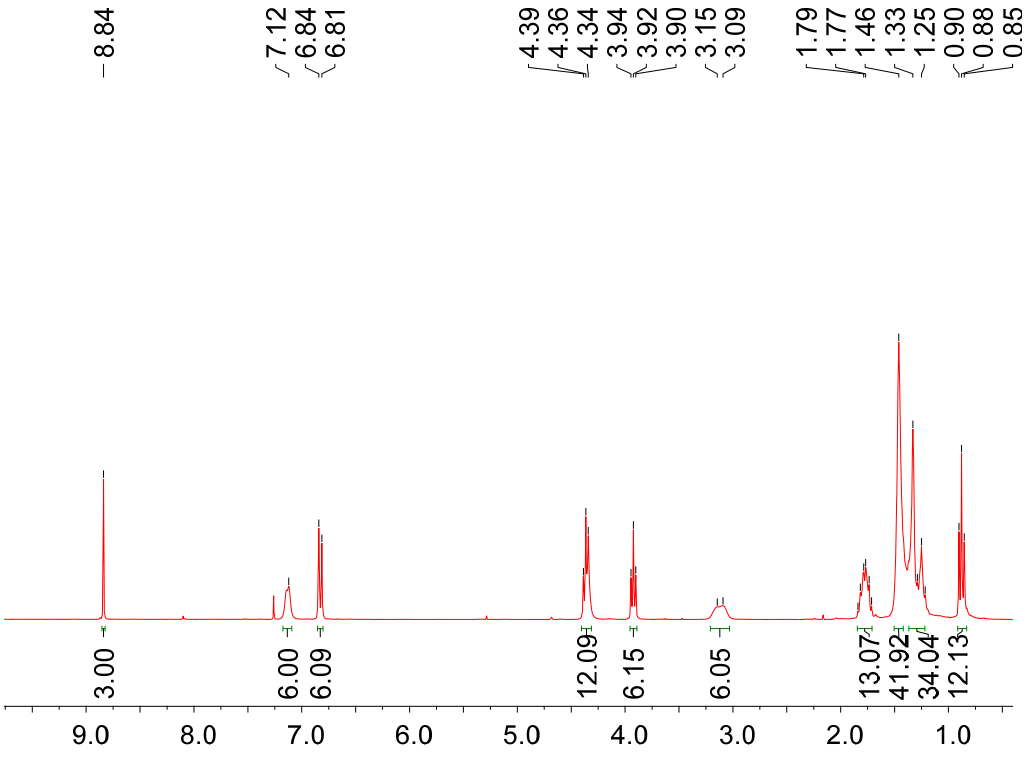


Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of **14**.

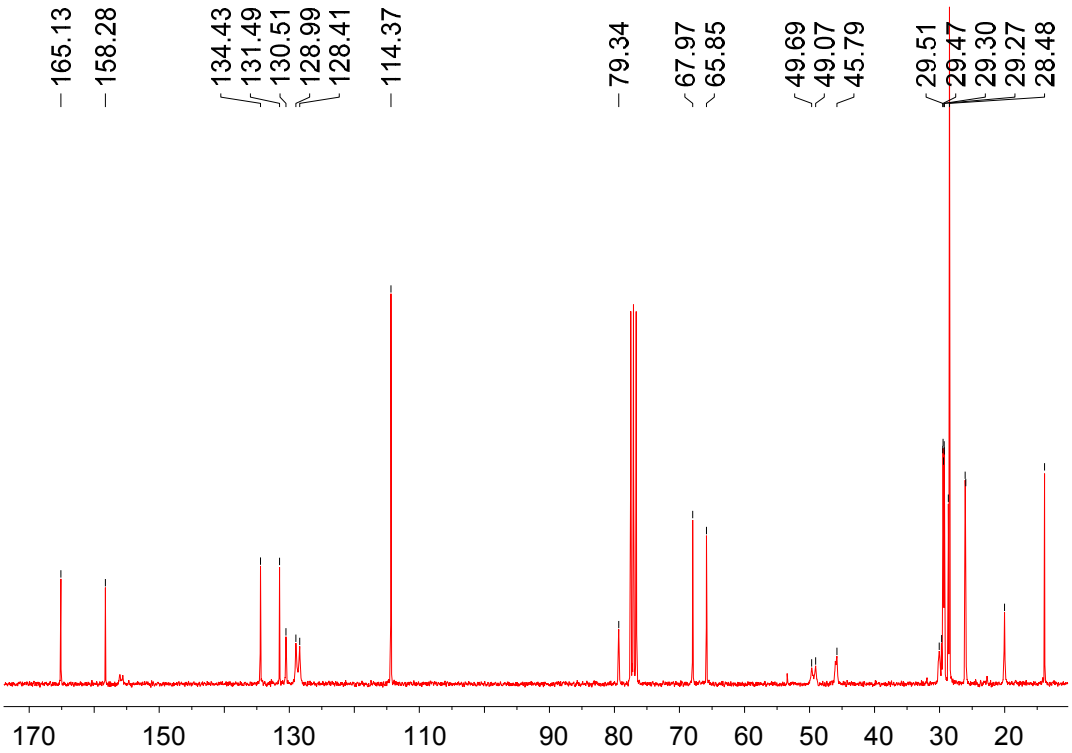
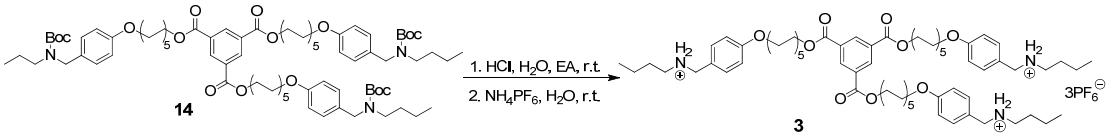


Figure S10. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of **14**.

*2.5. Synthesis of monomer **3***



Compound **14** (1.51 g, 1.03 mmol) was dissolved in 10% HCl/ethyl acetate (80 mL) and stirred overnight. After the reaction was complete, the white solid was filtered, washed with ethyl acetate and dissolved in water/acetone (120 mL). The saturated aqueous solution of NH_4PF_6 was added and stirred at room temperature for 3 hours. Then acetone was evaporated with a rotary evaporator to afford a white precipitate, which was filtered off and washed with deionized water to afford monomer **3** as a white solid (1.21 g, 92%).[S3] The ^{1}H NMR spectrum of monomer **3** is shown in Figure S11. ^{1}H NMR (300 MHz, CD_3CN, room temperature) δ (ppm): 8.72 (s, 3H), 7.33 (d, J = 8.6 Hz, 6H), 6.93 (d, J = 8.2 Hz, 6H), 4.34 (t, J = 6.8 Hz, 6H), 4.05 (s, 6H), 3.96 (t, J = 6.6 Hz, 6H), 2.99–2.93 (m, 6H), 1.69 (m, 12H), 1.53 (m, 6H), 1.44–1.17 (m, 42H), 0.92 (t, J = 7.3 Hz, 9H). The ^{13}C NMR spectrum of monomer **3** is shown in Figure S12.^{13}C NMR (75 MHz, CD_3CN, room temperature) δ (ppm): 164.3, 159.8, 133.3, 131.4, 131.3, 122.0, 114.4, 67.6, 65.4, 50.7, 47.0, 28.9, 28.7, 28.6, 28.0, 27.2, 25.4, 19.0, 12.4.

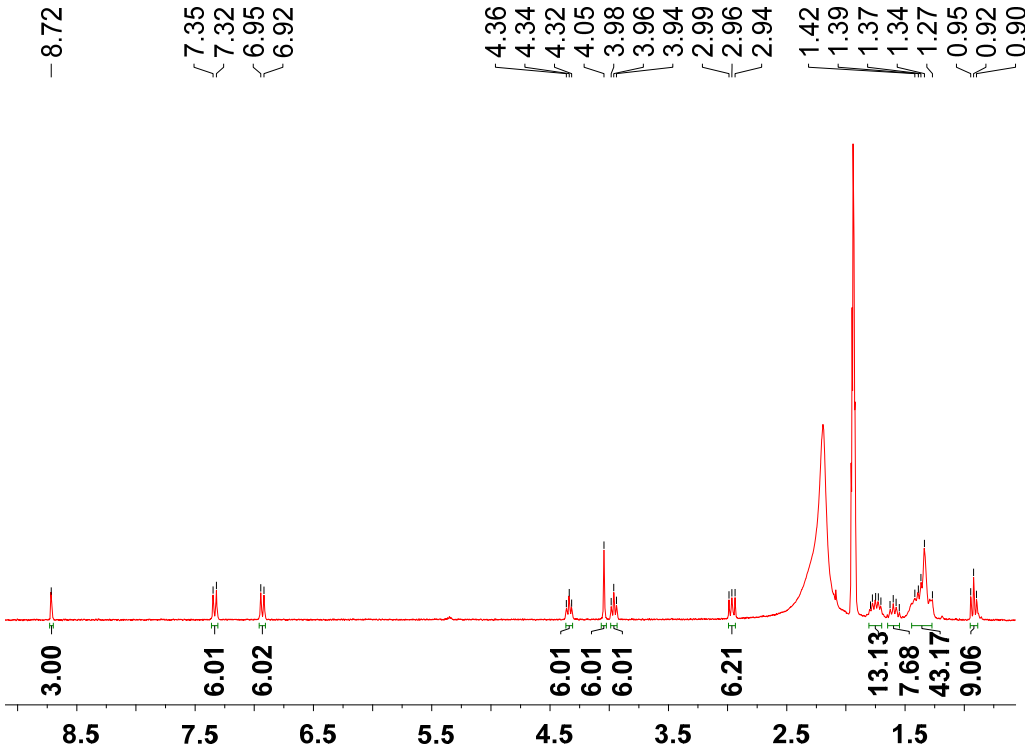


Figure S11. ^{1}H NMR spectrum (300 MHz, CD_3CN, room temperature) of **3.**

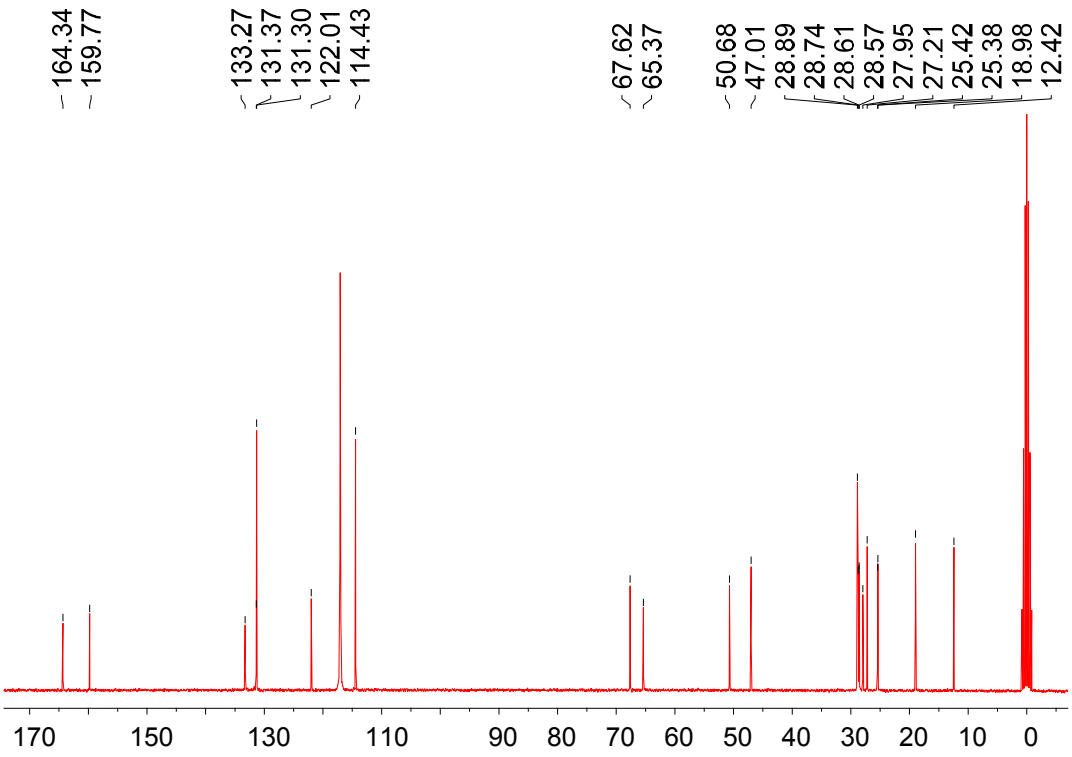


Figure S12. ^{13}C NMR spectrum (75 MHz, CD_3CN, room temperature) of **3**.

*3. ^{1}H NMR complexation experiment between **1** and **2***

Upon mixing equimolar amounts of monomers **1** and **2** in $CDCl_3$, the NH protons $H_{29,33}$ on **1** and H_{13} on **2** move downfield significantly, suggesting the formation of hydrogen bonding complex **6**. Meanwhile no obvious chemical shift change occurs for the B21C7 protons such as $H_{7\text{-}9}$ and $H_{20\text{-}22}$ (Figure S13). Such phenomena support the preferential association for the Hamilton receptor/cyanuric acid recognition motif without the participation of B21C7 unit.

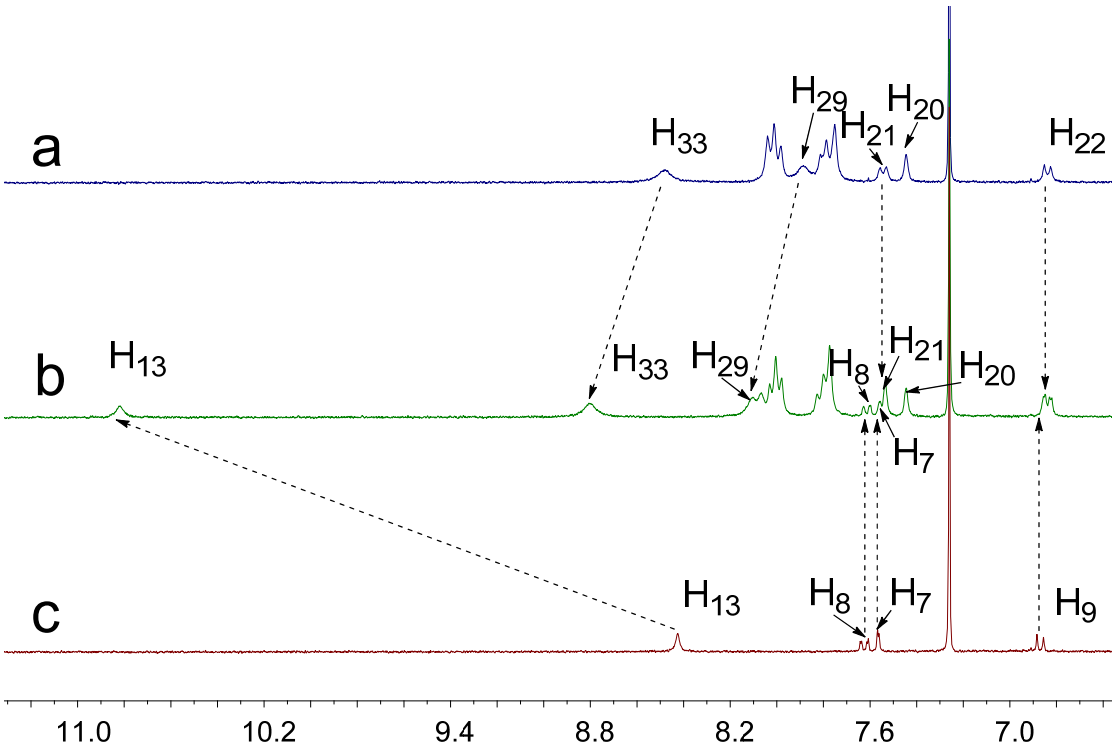


Figure S13. ^{1}H NMR spectra (300 MHz, $CDCl_3$, room temperature) of (a) 5.00 mM **1**, (b) mixture of 5.00 mM **1** and 5.00 mM **2**, (c) 5.00 mM **2**.

*4. ^{1}H NMR titration experiment between **1** and **2***

^{1}H NMR titration experiment was performed between monomers **1** and **2**, for which the initial concentration of **1** was kept constant at 3.00 mM, while concentration of **2** was systematically varied (Figure S14). Non-linear curve-fitting for the chemical shift changes of $H_{29,33}$ provides the corresponding association constants for **1•2** (Figure 1b and S14b).

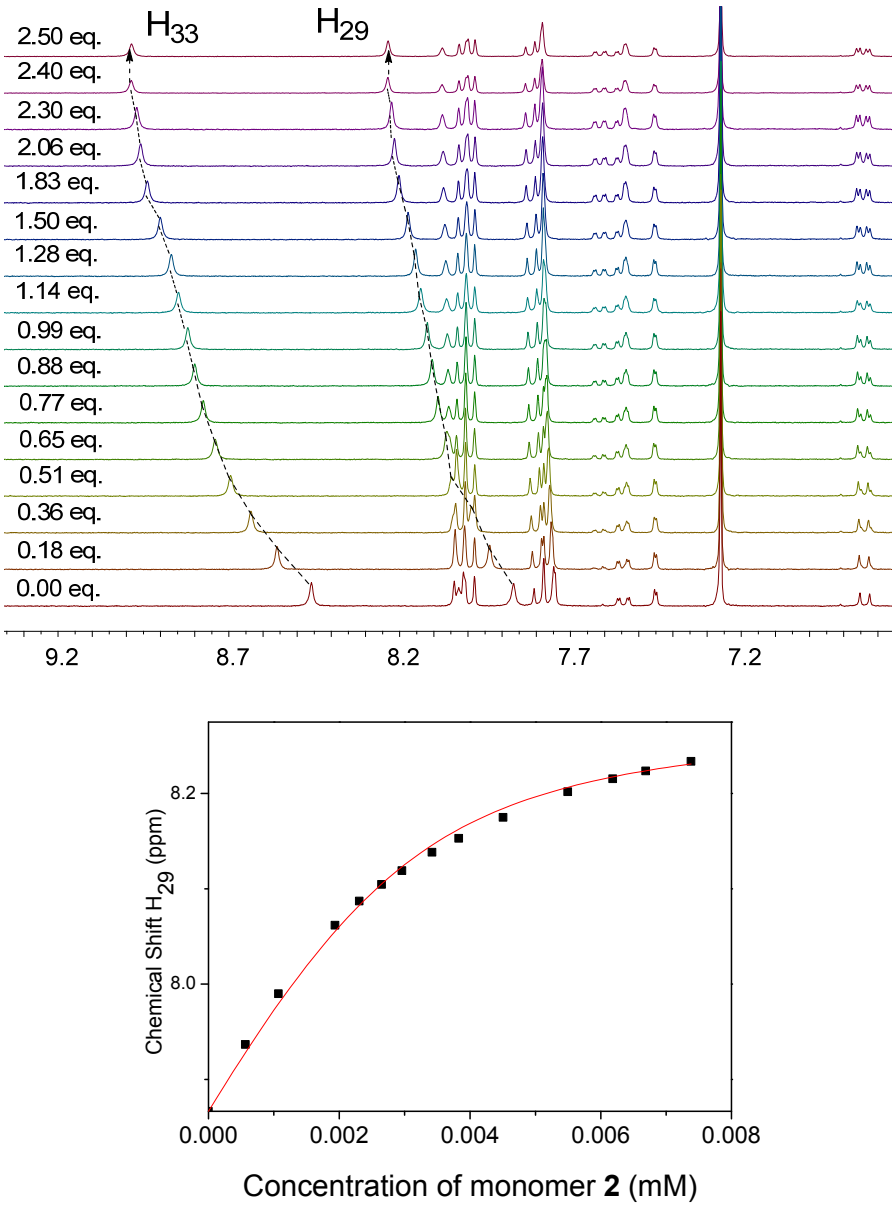


Figure S14. (a) ^{1}H NMR titration spectra (300 MHz, $CDCl_3$, room temperature) of monomer **1** at the concentration of 3.00 mM upon stepwise addition of monomer **2**. (b) Chemical shift changes of H_{29} on **1** upon gradual addition of **2**. The red line was obtained from the non-linear curve-fitting, which provides the $K_a = (1.40 \pm 0.16) \times 10^3$ M^{-1} for **1•2**.

*5. Supramolecualr polymers **8** via different self-assembling pathways*

The two stepwise procedures (one is first mixing **1** and **2** followed by adding **3**, another is first mixing **1** and **3** followed by adding **2)**, together with the "one-pot" mixing method (Figure S15a-e), were monitored *via* ^{1}H NMR measurements, which demonstrate the formation of the same supramolecular assemblies in the final stage. Hence, the pathway-independent behaviors validate the orthogonal recognition properties for the hydrogen–bonding and host–guest moieties.

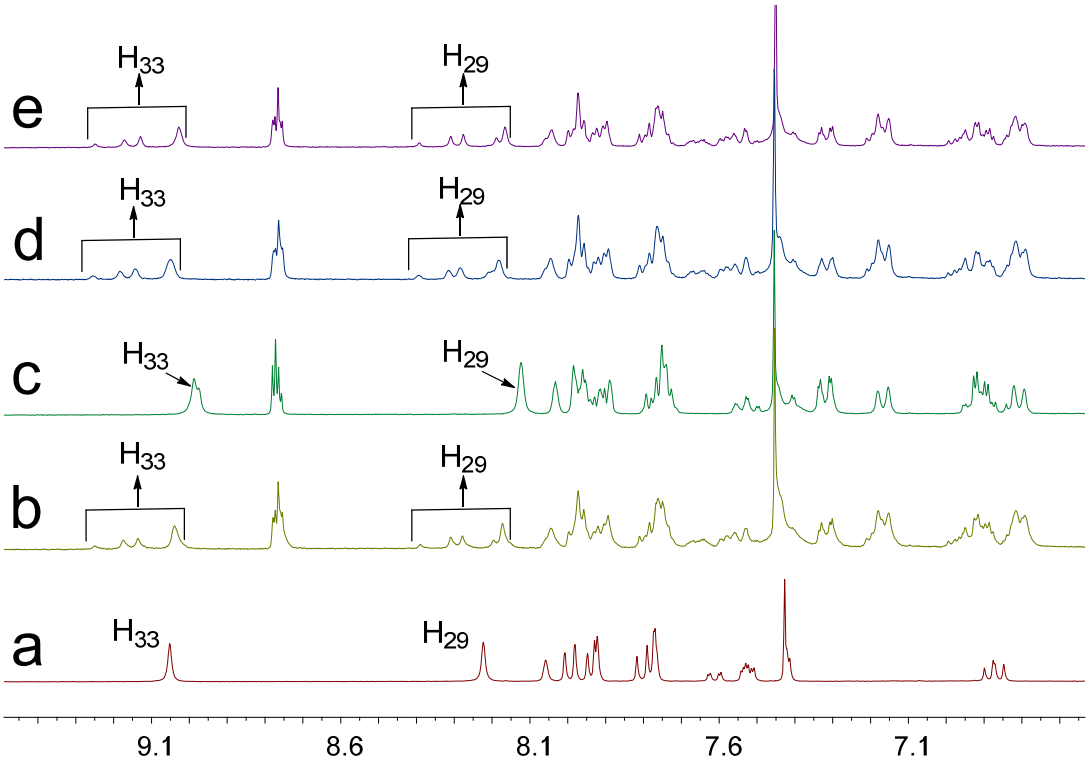


Figure S15. ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$, (2/1, *v*/*v*), room temperature) of (a) mixture of **1** and **2** with 1 : 1 molar ratio; (b) mixture of **1** and **2** was added **3** with 3 : 3 : 2 molar ratio; (c) mixture of **1** and **3** with 1 : 1 molar ratio; (d) mixture of **1** and **3** was added **2** with 3 : 3 : 2 molar ratio; (e) mixture of **1**, **2** and **3** with 3 : 3 : 2 molar ratio.

6. Concentration-dependent ^{1}H NMR measurements of 7

Concentration-dependent ^{1}H NMR measurements were performed to illustrate the formation of linear supramolecular polymers **7**. As the monomer concentration gradually increases, remarkable down-field shifts occur for both protons $H_{29l,33l}$, suggesting the expansion of linear species occur *via* ring-to-chain transition processes.

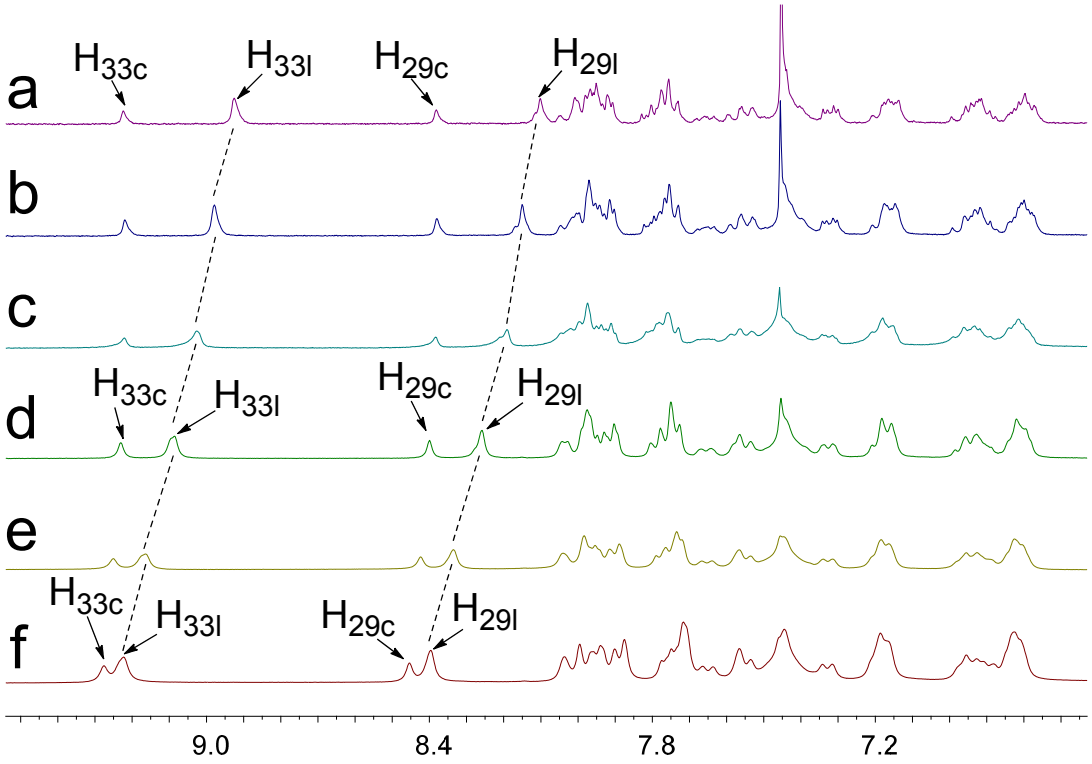


Figure S16. ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (2/1, *v*/*v*), room temperature) of the linear supramolecular polymers **7** at different monomer concentrations of **1**: (a) 2.80; (b) 4.20; (c) 8.30; (d) 20.0; (e) 37.5; and (f) 60.0 mM. Here ‘‘l’’ and ‘‘c’’ denote supramolecular linear and cyclic species, respectively.

*7. DOSY experiments for supramolecuar polymers 7–**8***

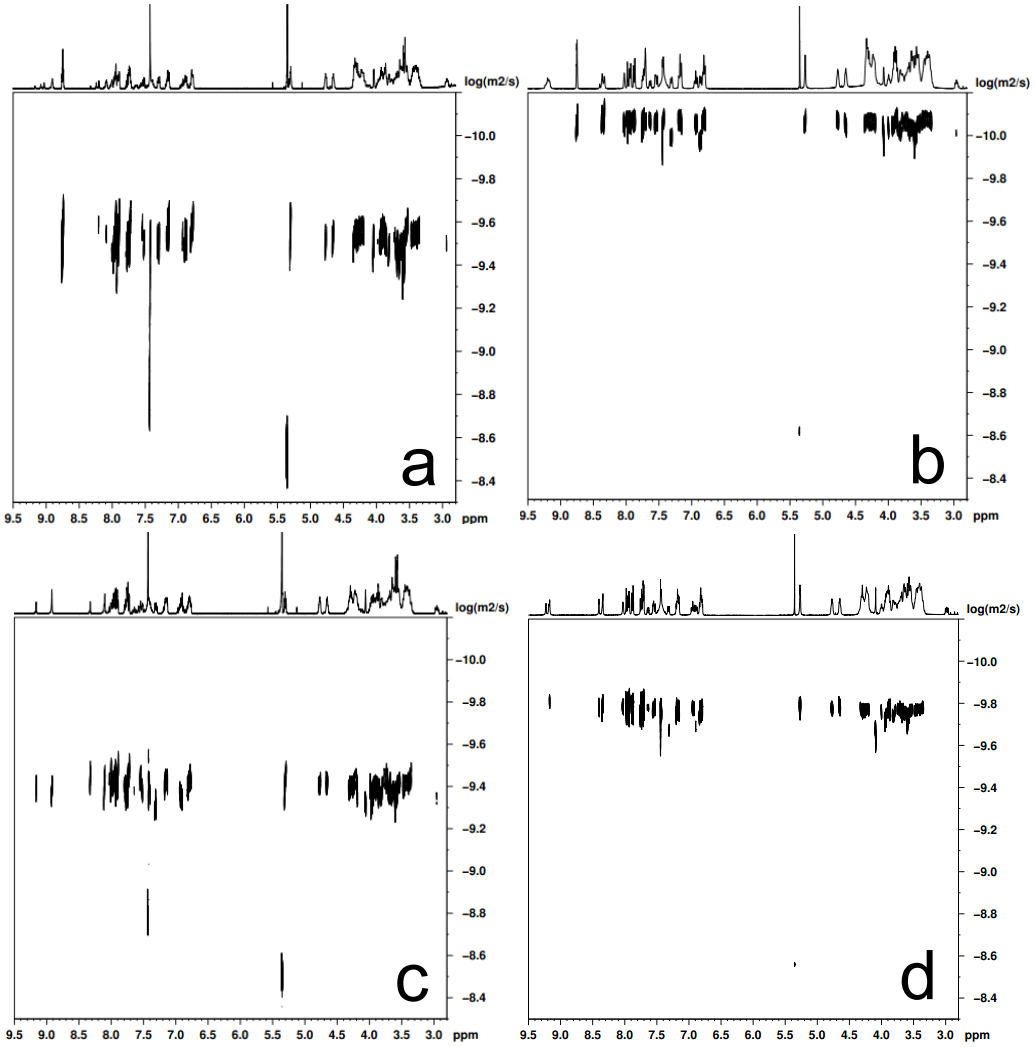


Figure S17. Two-dimensional diffusion-ordered NMR spectra of the supramolecular hyperbranched polymers **8** (a and b) and the linear polymers **7** (c and d) in $CDCl_3/CD_3CN$ (2/1, *v*/*v*) at different monomer concentrations: (a) and (c), 6.00 mM; (b) and (d), 60.0 mM for **1**. For the supramolecular hyperbranched polymers **8**, as the monomer concentration increases from 6.00 mM to 60.0 mM, the measured diffusion coefficients decrease dramatically from 2.75×10^{-10} to 8.79×10^{-11} m^2 s^{-1}. Under the same conditions, to the values decline from 3.92×10^{-10} to 1.69×10^{-10} m^2 s^{-1} for the linear supramolecular polymer **7**.

8. Viscosity measurements for supramolecular polymers 7–8

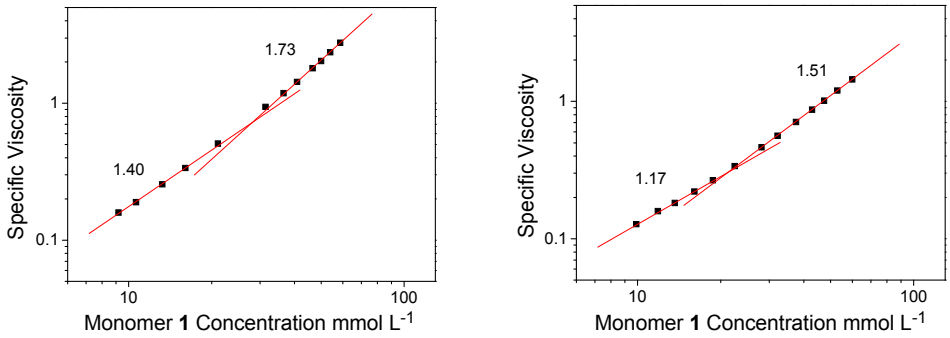


Figure S18. Specific viscosity of the supramolecular polymers **7**–**8** as a function of monomer concentration. The double logarithmic plot of specific viscosity versus concentration exhibits a clear slope change from 1.40 to 1.73 for hyperbranched polymers **8**. Meanwhile for linear species **7** the values vary from 1.17 to 1.51. The higher slope values for **8** above CPC demonstrate stronger concentration dependence of supramolecular polymerization.

*9. SEM image of supramolecualr polymers **8***

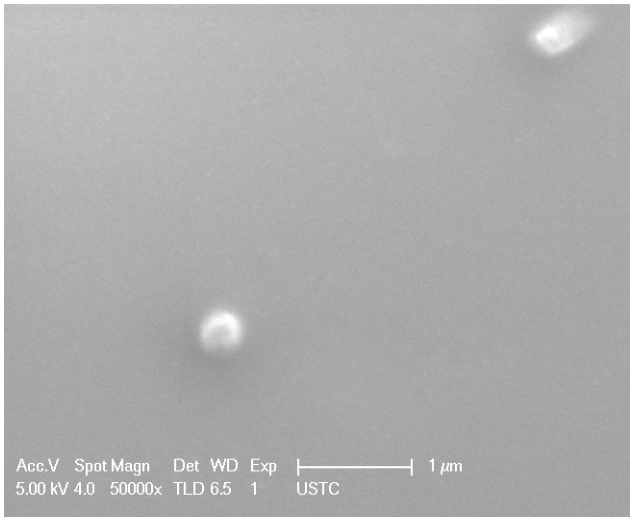


Figure S19. FE-SEM images of a 3 : 3 : 2 mixture of **1**, **2** and **3** (**1** = 1.00 mM) recorded by drop-casting of the $CHCl_3/CH_3CN$ (2/1, *v*/*v*) solution on silicon wafer at 298 K. **8** tends to form agglomerated spherical-like morphologies, probably resulting from the phase segregation due to the coexistence of rigid hydrogen–bonding and host–guest units and flexible alkyl chains in the structure.

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