A supramolecular polymer network constructed by a pillararene-based multi-functional monomer and its application as rewritable fluorescence paper

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Electronic Supplementary Information (15 pages)

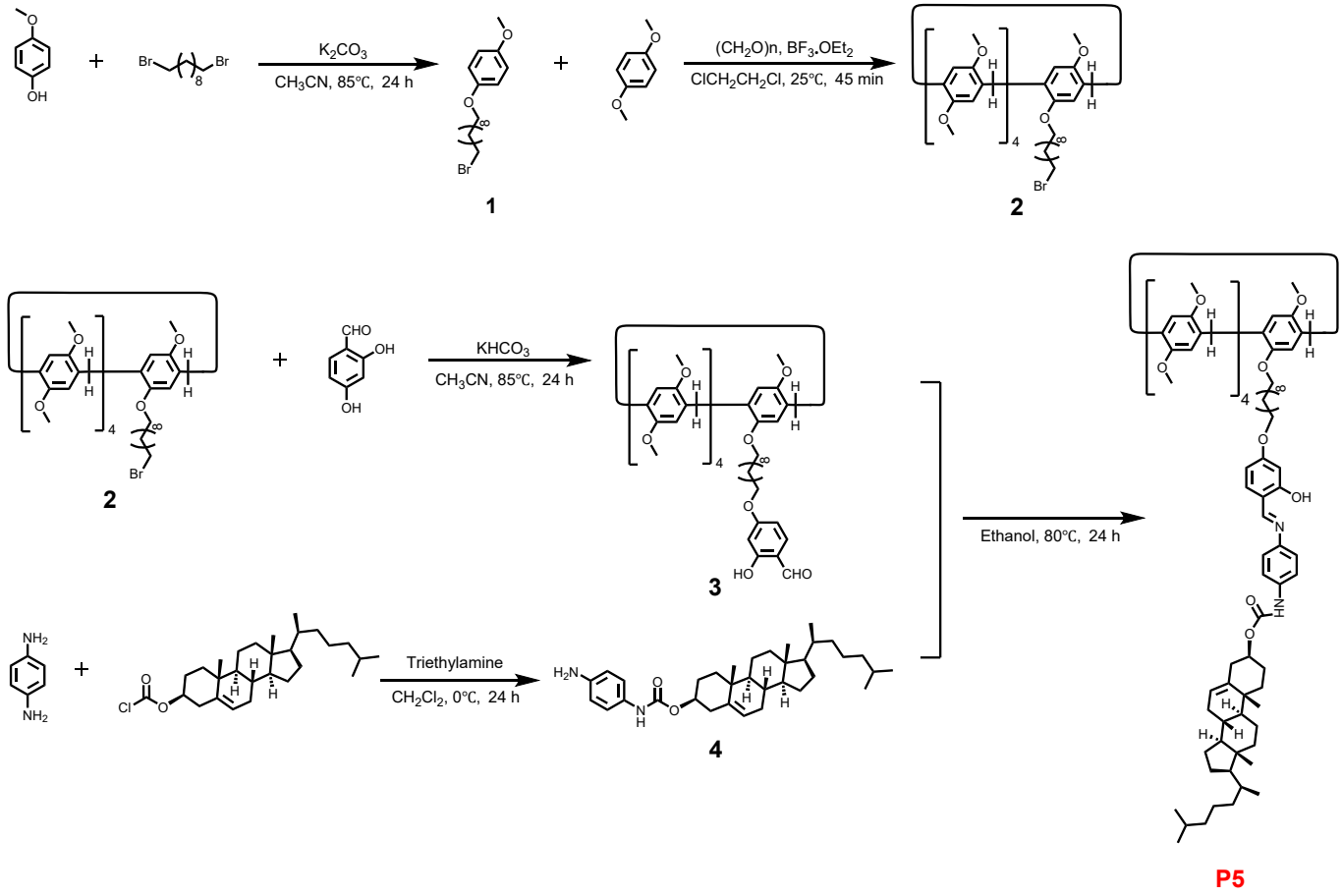
1. Materials and methods

All chemicals were obtained from commercial suppliers and were used as supplied without further purification. All reactions were conducted with oven-dried glassware under atmosphere or nitrogen. Solvents were dried and distilled following usual protocols. Column chromatography was carried out using silica gel (200-300 mesh). The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer spectrophotometer. Chemical shifts are reported in δ values in ppm using tetramethylsilane (TMS) (^{1}H: $CDCl_3$: δ 7.26 ppm; ^{13}C: $CDCl_3$: δ 77.23 ppm.), and are expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. High-resolution mass spectrometry experiments were performed with a Thermo Scientific Q Exactive instrument. The melting points were collected on a SGW X-4 automatic melting point apparatus. Scanning Electron Microscopy (SEM) investigations were carried out on a PerkinElmer Gemini SEM300 instrument. Fluorescent microscopy investigations were carried out on a HITACHI F-7100 fluorescence spectrometer.

The SPN-paper was prepared by a dip-coating method. The cellulosic paper (dimension: 5 cm × 5 cm) was immersed into the mixed solution of **P5** and **G** (10 mM **P5** + 5 mM **G**) for 1 min followed by volatilization at room temperature and one atmosphere for 24 h. Drawing with Cupric Acetate Anhydrous （$Cu(OAc)_2$） onto the SPN-paper was realized by coating a chloroform solution of $Cu(OAc)_2$ onto the paper followed by volatilization at room temperature and one atmosphere for 24 h. The pattern is erased by using chloroform solution of Tetrabutylammonium cyanide (TBACN) as an eraser to brush on SPN-paper. Subsequently, the rewritability of SPN-paper was tested by drawing and erasing onto the paper again with chloroform solutions of Cu $(OAc)_2$ and TBACN.

2. Synthesis and characterization (^{1}H, ^{13}C NMR, HRMS) of P5 and related intermediates.

The compounds **1**,[S1] **2**,[S1] **3**,[S2] and **4**[S3] were prepared according to published procedures. All compounds were thoroughly purified and analyzed by NMR. NMR data of the known compounds was consistent with literature. Full NMR and HRMS analyses for compounds are reported below.



Scheme S1 Synthetic route to **P5**

1,10-Dibromodecoxyl Monofunctionalized Benzene (1). Under a nitrogen atmosphere, 4-methoxyphenol (5.00 g, 40.0 mmol) and 1,10-dibromodecane (36.0 g, 120 mmol) were dissolved in acetonitrile (300 ml), followed by addition of K_2CO_3 (16.6 g, 120 mmol). The reaction mixture was stirred at reflux for 24 h. Then the cooled reaction mixture was filtered and washed with dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane = 5:1, *v*/*v*) to afford the desired product **1** as a white solid (12.4 g, 90.0%). The ^{1}H NMR spectrum of **1** is shown in Figure S1. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 6.83 (s, 4H),

3.90 (t, J = 6.6 Hz, 2H), 3.77 (s, 3H), 3.41 (t, J = 6.9 Hz, 2H), 1.88–1.83 (m, 2H), 1.77–1.73 (m, 2H), 1.45–1.30 (m, 12H).

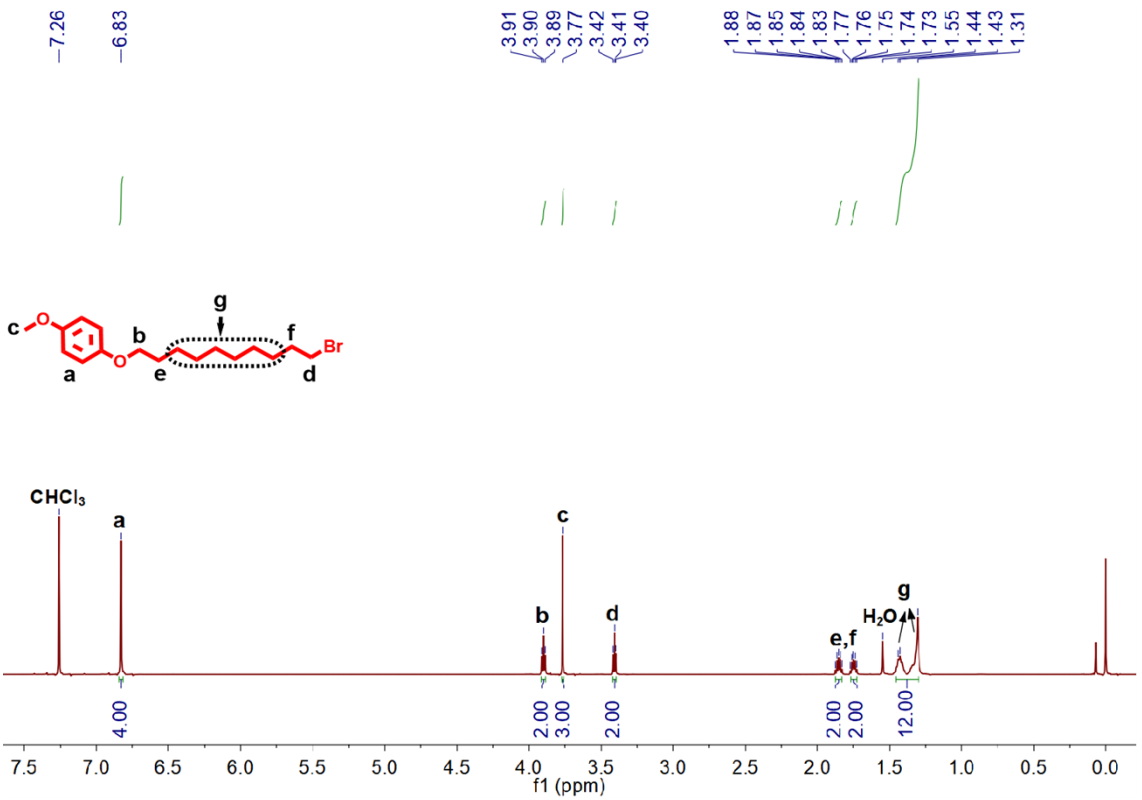


Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **1**.

1,10-Dibromodecane Monofunctionalized Pillar[5]arene (2). The compound **1** (3.43 g, 10.0 mmol), 1,4-dimethoxybenzene (5.52 g, 40.0 mmol) and paraformaldehyde (3.00 g, 100 mmol) was added in CH_2ClCH_2Cl (300 mL). Boron trifluoride etherate [(BF_3•OEt_2), 6.25 mL, 50.0 mmol] was then added to the solution and the mixture was stirred at room temperature for 45 min. The reaction mixture was then washed with water and dried with Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane = 1:1, *v*/*v*) to afford 1,10-dibromodecane monofunctionalized pillar[5]arene **2** (2.96 g, 31%). The ^{1}H NMR spectrum of **2** is shown in Figure S2. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 6.98–6.82 (m, 10H), 3.94 (s, 2H), 3.75 (dd, J = 22.9, 5.1 Hz, 37H), 1.84 (s, 2H), 1.54 (s, 2H), 1.43 (s, 2H), 1.35 (s, 2H), 1.29–0.78 (m, 10H).

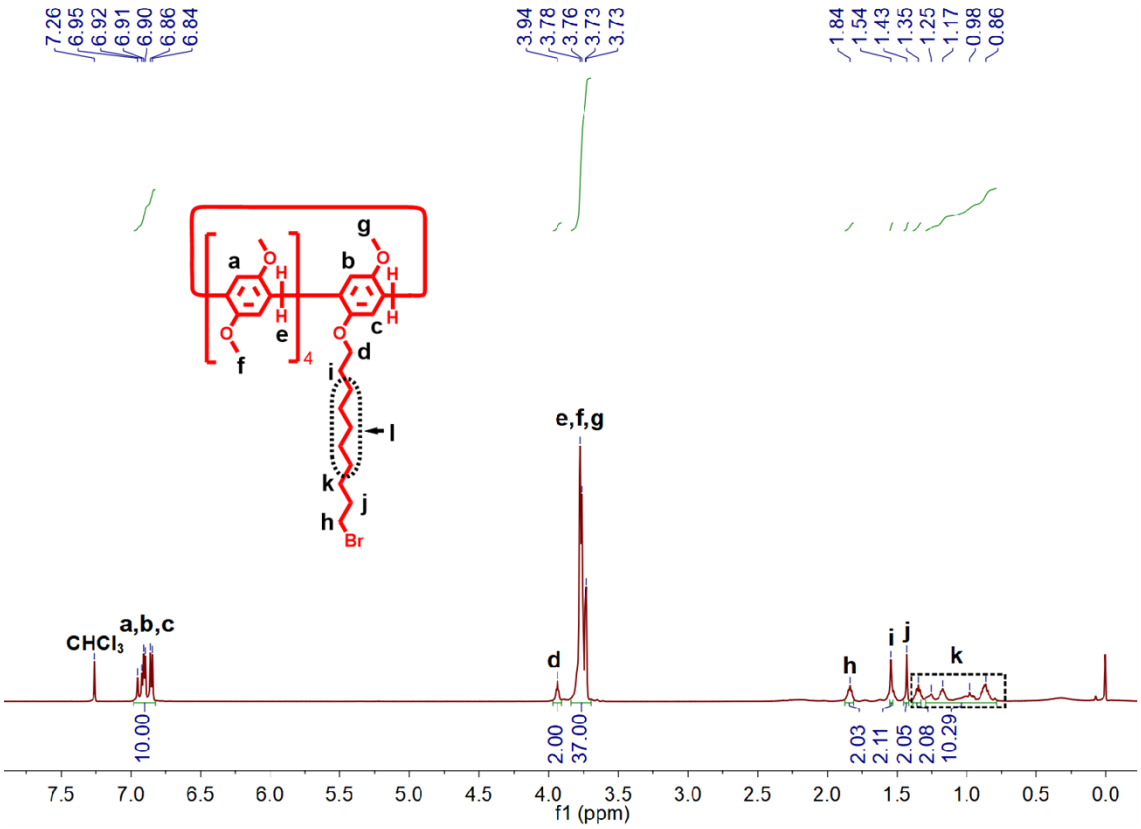


Figure S2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **2**.

2,4-Dihydroxybenzaldehyde Monofunctionalized Pillar[5]arene (3). A solution of **2** (2.00 g, 2.09 mmol) and 2, 4-dihydroxybenzaldehyde (0.290 g, 2.09 mmol) in acetonitrile (100 mL) was stirred at room temperature. Then potassium carbonate (0.580 g, 4.18 mmol) was added. The reaction mixture was refluxed for 24 h, filtered, and concentrated to give a crude product, which was purified by flash column chromatography (dichloromethane) to afford **3** as a white solid (1.55 g, 73%). The ^{1}H NMR spectrum of **3** is shown in Figure S3. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 11.51 (s, 1H), 9.72 (s, 1H), 7.42 (d, J = 6 Hz, 1H), 6.89–6.78 (m, 10H), 6.49 (m, 1H), 6.42 (d, J = 6 Hz, 1H), 3.95 (t, J = 9 Hz, 2H), 3.79–3.64 (m, 39H), 3.43 (t, J = 9 Hz, 2H), 1.78 (m, 2H), 1.25 (m, 8H), 0.83 (m, 2H), 0.36 (m, 2H), 0.17–0.03 (m, 2H). The ^{13}C NMR spectrum of **3** is shown in Figure S4. ^{13}C NMR ($CDCl_3$, 150 MHz, 298 K) δ (ppm): δ 191.73, 164.15, 162.13, 148.26, 148.20, 148.12, 148.05, 147.87, 147.24, 132.62, 125.94, 125.91, 125.68, 125.65, 125.61, 125.57, 112.35, 111.90, 111.81, 111.64, 111.38, 111.15, 111.06, 106.18, 98.46, 66.38, 65.17, 53.56, 53.26, 53.21, 53.09, 52.93, 29.39, 28.92, 27.67, 27.20, 26.97, 26.86, 26.80, 26.22, 26.04, 25.76, 25.70, 22.62, 22.10, 20.16, 11.61.

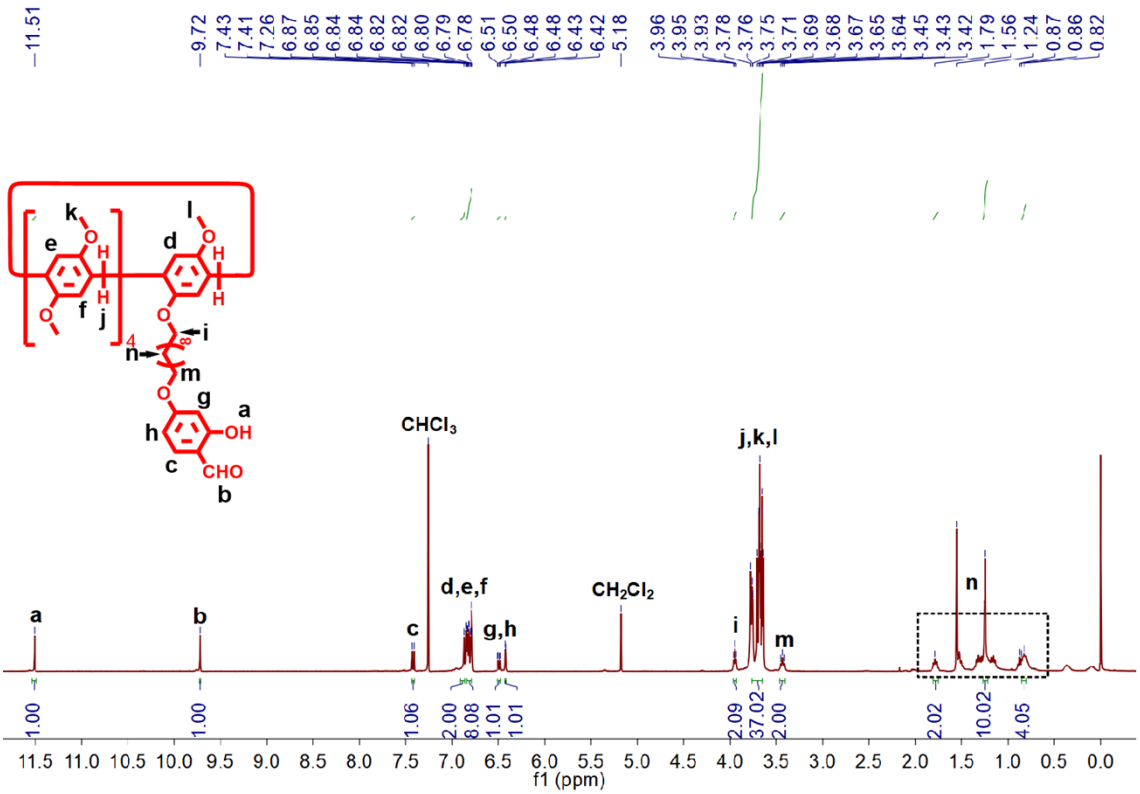


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **3**.

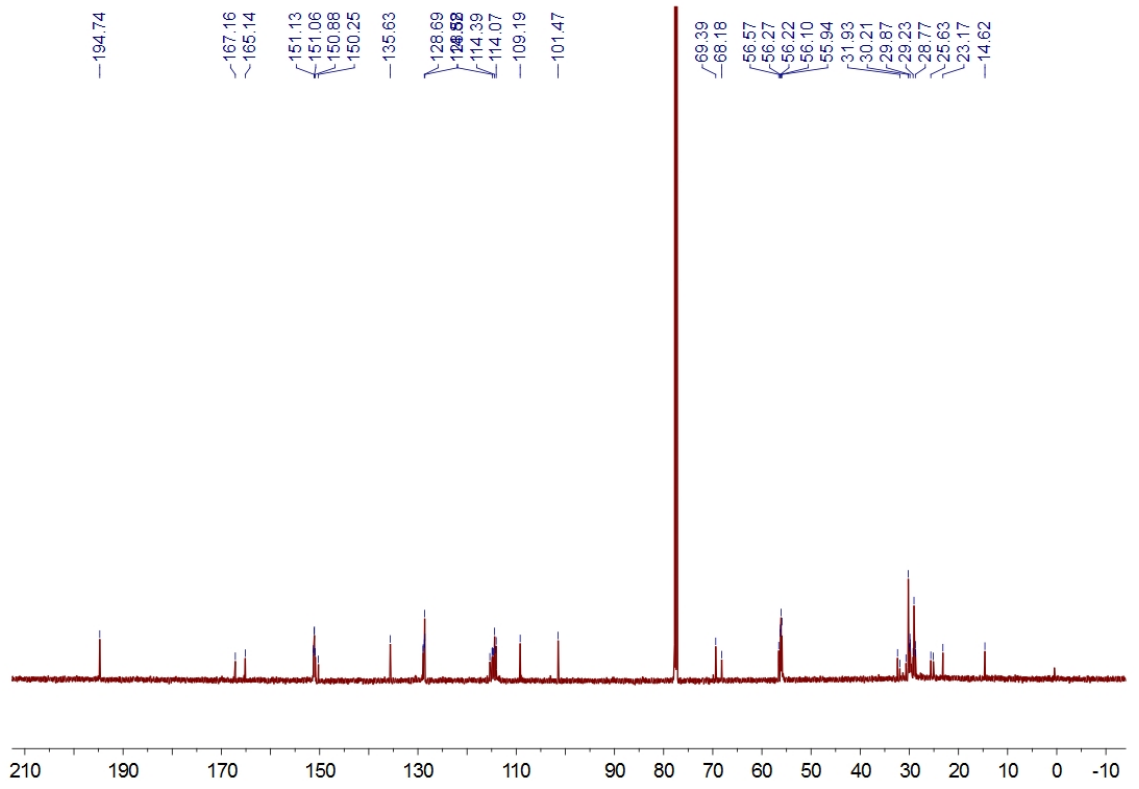


Figure S4. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of **3**.

***p*-Phenylenediamine Functionalized Cholesterol (4).** The *p*-phenylenediamine (4.00 g, 47.0 mmol), triethylamine (1.50 g, 14.8 mmol) was added in CH_2Cl_2 (300 mL). Cholesteryl chloroformate (2.00 g, 4.70 mmol) was then added to the solution at 0 ℃. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue was purified by column chromatography (eluent: methanol/dichloromethane = 1:500, *v*/*v*) to afford **4** as a tawny solid (3.00 g, 86.2%). The ^{1}H NMR spectrum of **4** is shown in Figure S5. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 7.15 (s, 2H), 6.64 (d, J = 8.6 Hz, 2H), 6.33 (s, 1H), 5.39 (d, J = 5.0 Hz, 1H), 4.57 (tt, J = 11.0, 4.5 Hz, 1H), 3.54 (s, 2H), 2.42 (dd, J = 13.0, 2.9 Hz, 1H), 2.35–2.30 (m, 1H), 2.04–1.91 (m, 4H), 1.90–1.76 (m, 3H), 1.64–1.04 (m, 28H), 1.04–0.94 (m, 8H), 0.91 (d, J = 6.5 Hz, 4H), 0.86 (dd, J = 6.6, 2.7 Hz, 8H), 0.68 (s, 4H).

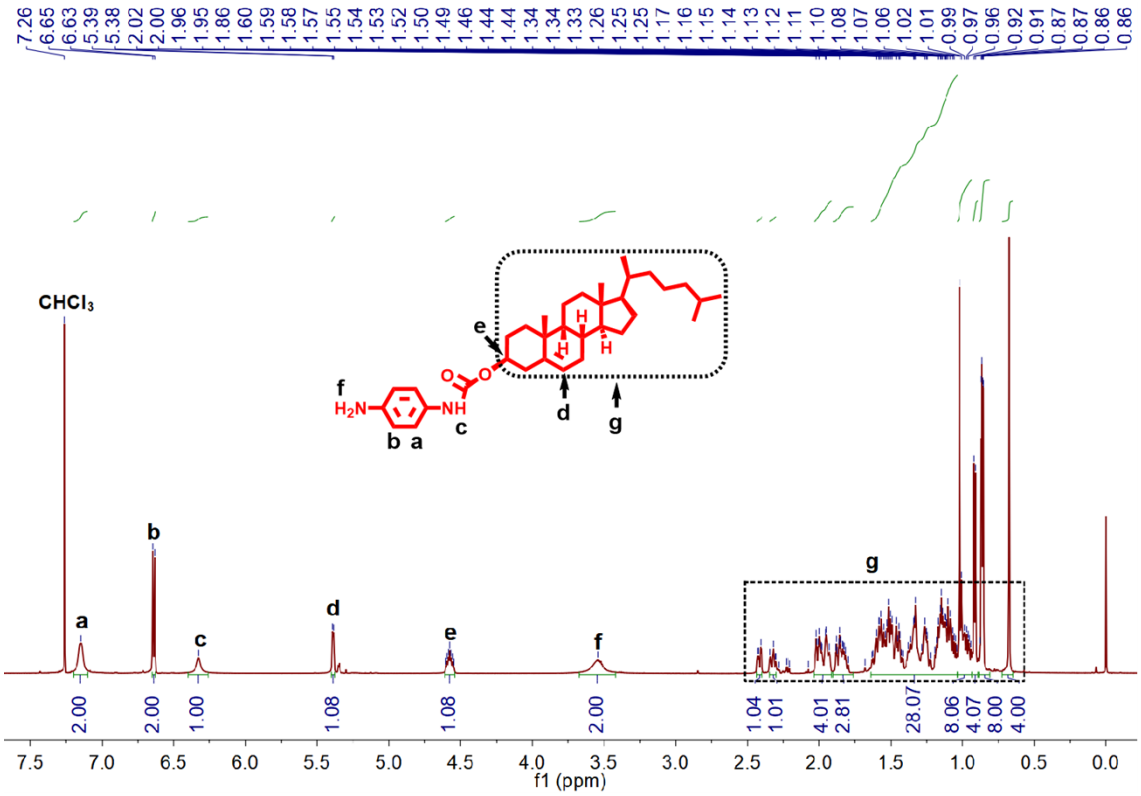


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **4**.

Cholesterol Monofunctionalized Pillar[5]arene (P5). A solution of compound **3** (1.01 g, 1.00 mmol) and compound **4** (1.56 g, 3.00 mmol) in ethanol (50. 0 mL) was refluxed for 24 h, the solid was filtrated and washed with ethanol and concentrated to afford **P5** as a yellow solid (1.35 g, 89.0%). Mp: 125–127 °C. The ^{1}H NMR spectrum of **P5** is shown in Figure S6. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 13.82 (s, 1H), 8.53 (s, 1H), 7.45–7.41 (m, 2H), 7.24 (s, 2H), 6.88 (s, 1H), 6.85 (d, J = 12.0 Hz, 6H), 6.81 (d, J = 6.0 Hz, 4H), 6.63 (s, 1H), 6.50 (s, 1H), 6.46 (d, J = 8.4 Hz, 1H), 5.42 (s, 1H), 4.63 (s, 1H), 3.95

(s, 2H), 3.78 (d, J = 10.1 Hz, 10H), 3.69 (t, J = 11.7 Hz, 27H), 3.57–3.55 (m, 2H), 2.46–2.35 (m, 2H), 2.04–1.77 (m, 8H), 1.59 (s, 6H), 1.21–0.79 (m, 39H), 0.69 (s, 4H), 0.46 (s, 2H), 0.30 (s, 2H). The ^{13}C NMR spectrum of **P5** is shown in Figure S7. ^{13}C NMR ($CDCl_3$, 150 MHz, 298 K) δ (ppm): δ 160.78, 151.28, 151.26, 151.22, 133.66, 128.98, 128.92, 128.89, 128.81, 128.77, 128.70, 123.18, 121.96, 119.90, 115.23, 114.77, 114.76, 114.60, 114.57, 114.47, 114.41, 114.39, 107.83, 102.04, 68.81, 68.63, 57.14, 56.64, 56.39, 56.24, 56.20, 56.16, 56.12, 56.05, 50.51, 42.77, 40.19, 39.94, 38.88, 37.42, 37.02, 36.62, 36.18, 32.33, 30.23, 30.08, 30.05, 29.98, 29.91, 29.58, 29.33, 29.29, 29.16, 28.60, 28.53, 28.39, 26.03, 25.63, 24.68, 24.26, 23.15, 22.92, 21.48, 19.70, 19.12, 12.26. HRESIMS of **P5** is shown in Figure S8: m/z calcd. for [M + H]$^+$ $C_{95}H_{122}N_2O_{14}$, 1515.88961; found 1515.89624 ; error 4 ppm.

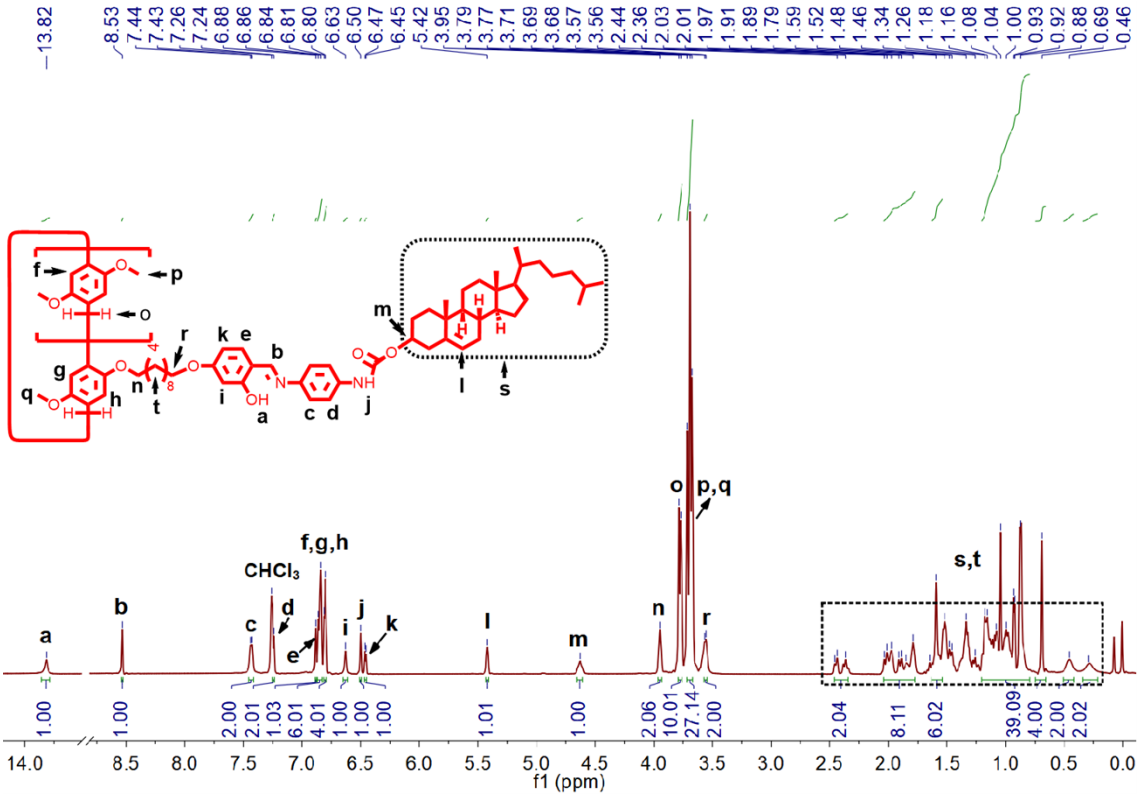


Figure S6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **P5**.

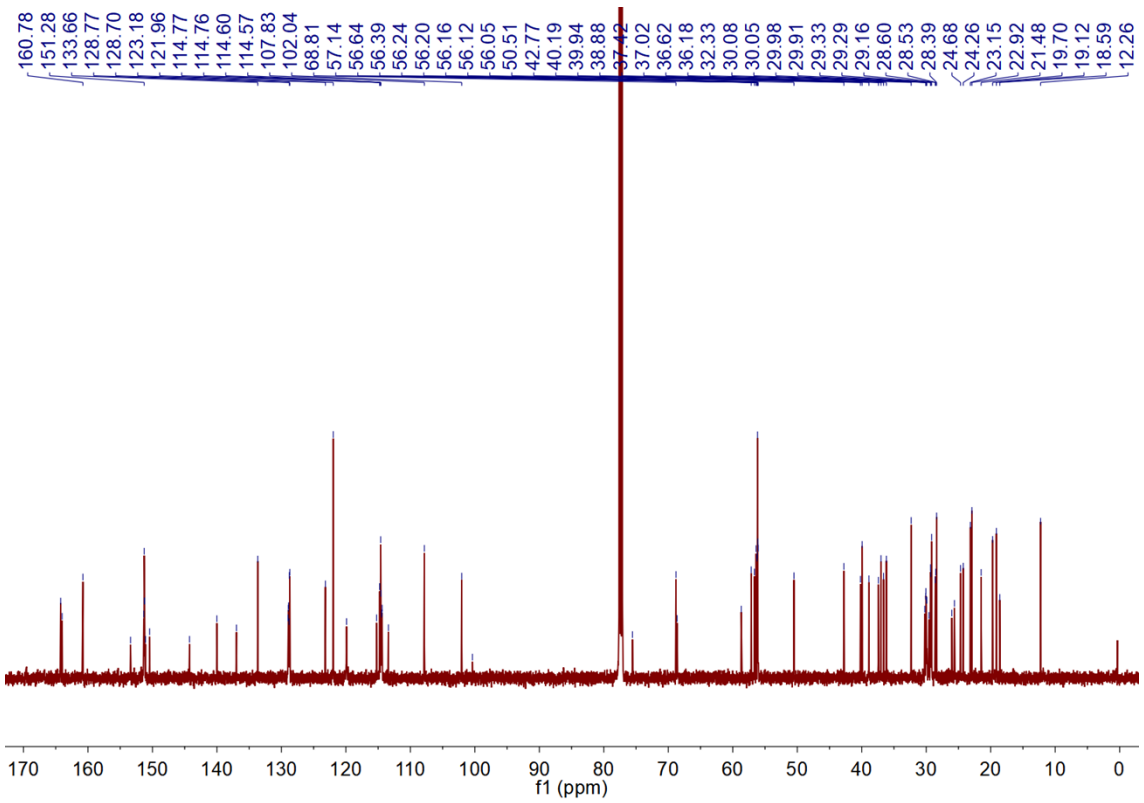


Figure S7. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of **P5**.

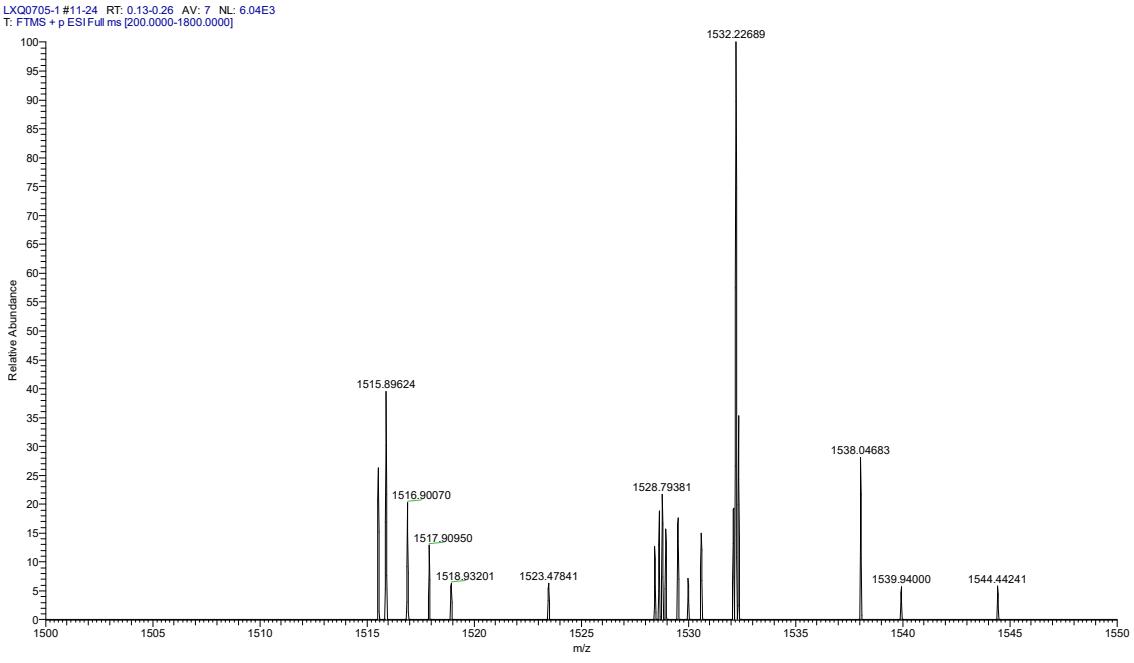
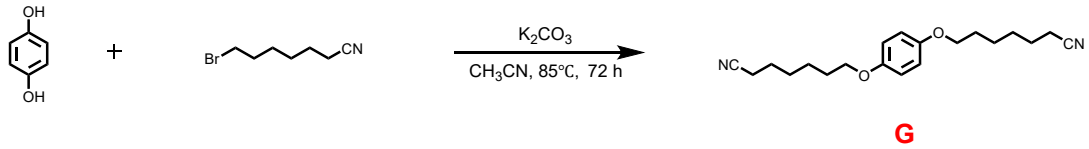


Figure S8. High-resolution mass electrospray ionization mass spectrum of **P5**. Main peak: m/z 1515.89624 $[M + H]^+$ (100 %).

3. Synthesis and characterization (^{1}H NMR) of G and related intermediates.

The compound **G**[S4] was synthesized according to published procedures.. All compounds were thoroughly purified and analyzed by NMR. NMR data of the known compounds was consistent with literature.



G

Scheme S2 Synthetic route to **G**

7-Bromoheptanenitrile Bifunctionalized Benzene (G). Under a nitrogen atmosphere, hydroquinone (4.40 g, 40.0 mmol) and 7-Bromoheptanenitrile (22.8 g, 120 mmol) were dissolved in acetonitrile (300 ml), followed by addition of K_2CO_3 (16.6 g, 120 mmol). The reaction mixture was stirred at reflux for 72 h. Then the cooled reaction mixture was filtered and washed with dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane = 1:5, *v*/*v*) to afford the desired product **G** as a white solid (10.7 g, 82.0%). The ^{1}H NMR spectrum of **G** is shown in Figure S9. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ (ppm): 6.81 (s, 4H), 3.91 (t, J = 6.1 Hz, 4H), 2.36 (t, J = 7.0 Hz, 4H), 1.81–1.75 (m, 4H), 1.72–1.67 (m, 4H), 1.56 (s, 4H), 1.52 (s, 4H).

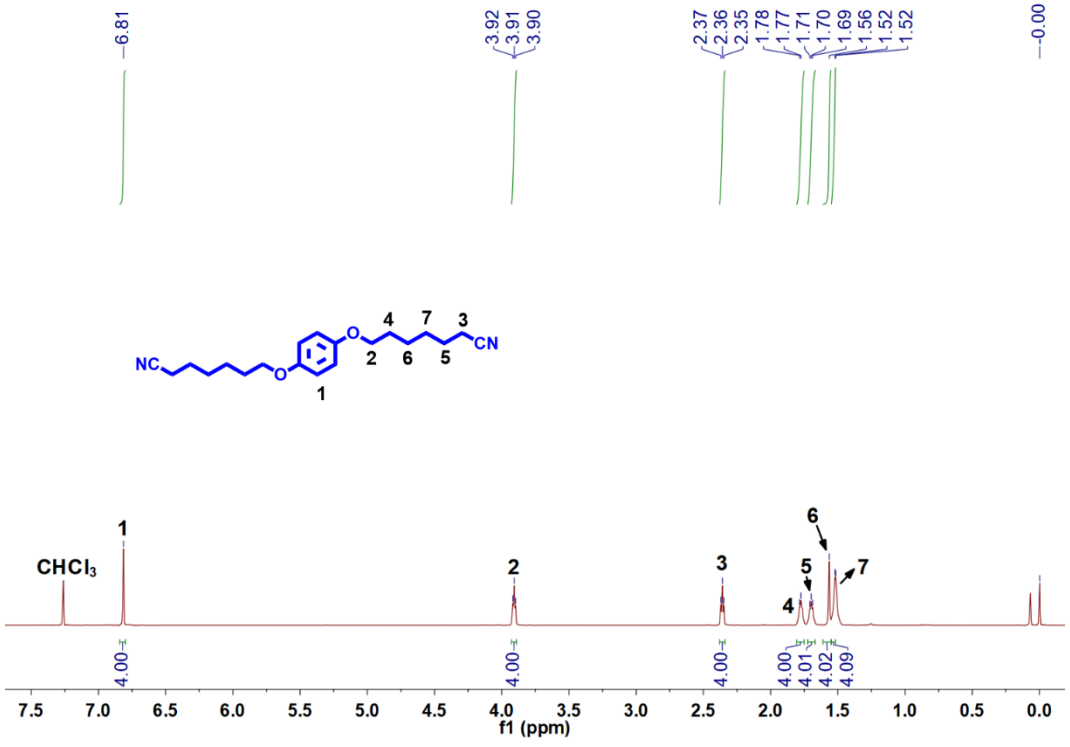


Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **G**

4. Partial ^{1}H NMR spectra of the host–guest interactions between the P5 and G

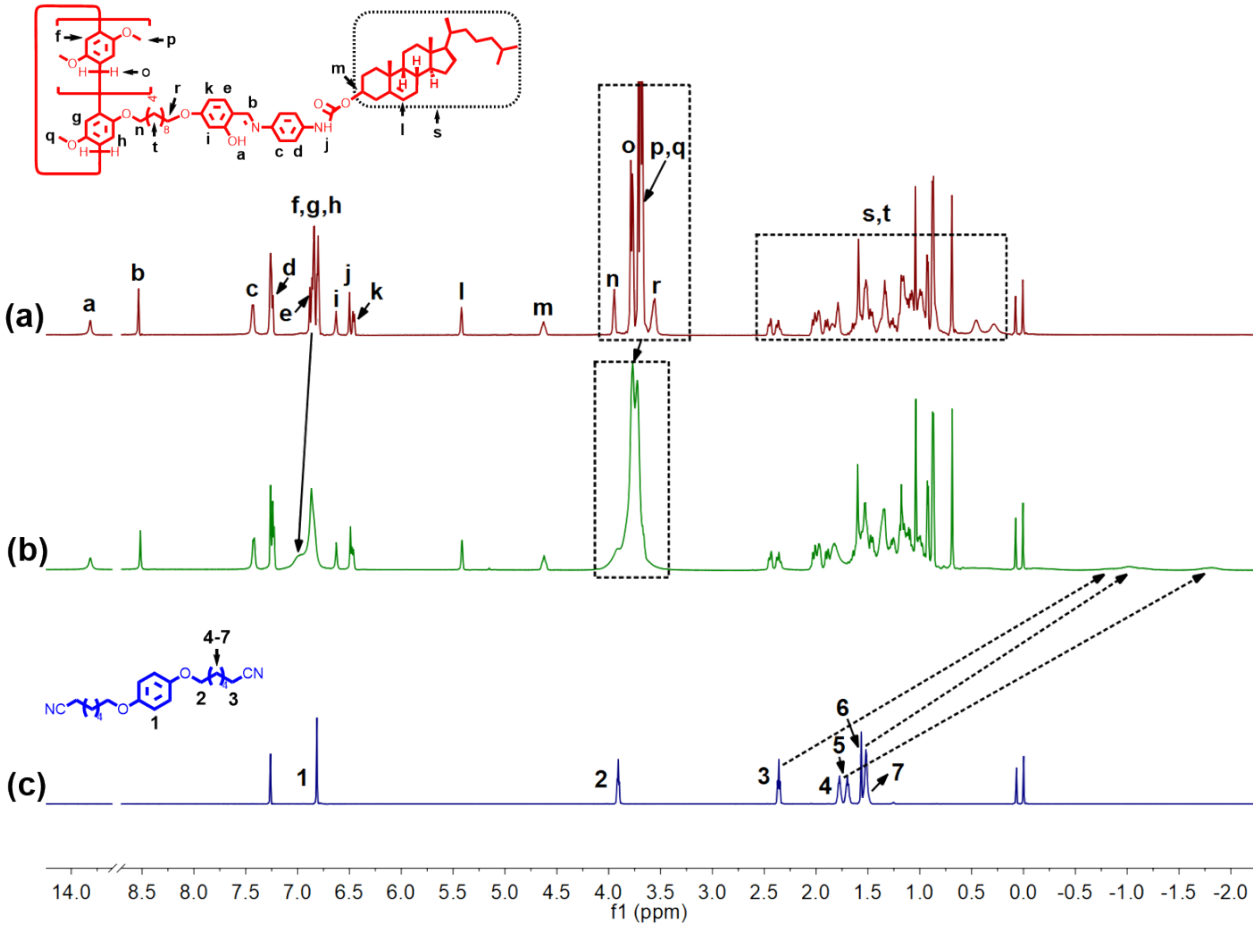


Figure S10. ^{1}H NMR spectra (600 MHz，$CDCl_3$，298 K): (a) **P5** (10.0 mM); (b) **P5** (10.0 mM) + **G** (5.00 mM); (c) **G** (5.00 mM).

5. 2D DOSY NMR spectroscopy experiments of the linear supramolecular polymer based on P5 and G

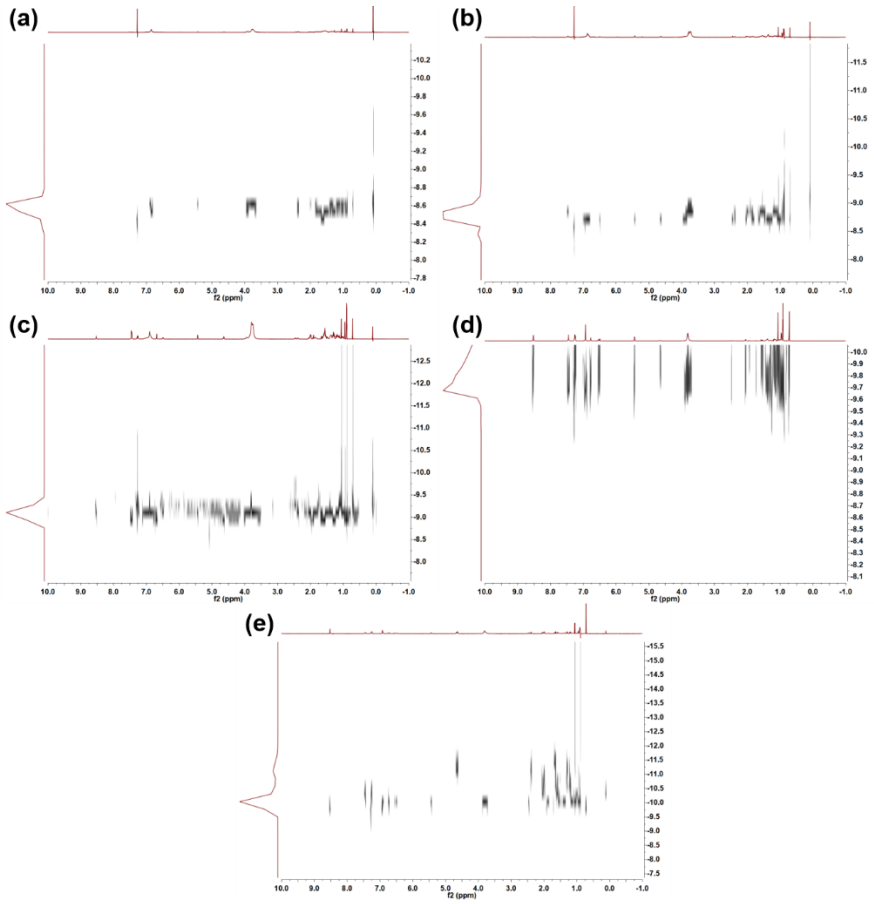


Figure S11. 2D DOSY NMR spectra of mixtures of **P5** and **G** in the molar ratio of 2:1 at different concentrations of **P5** (600 MHz, $CDCl_3$, room temperature): (a) 5.00 mM; (b) 10.0 mM; (c) 33.3 mM; (d) 71.4 mM; (e) 100 mM.

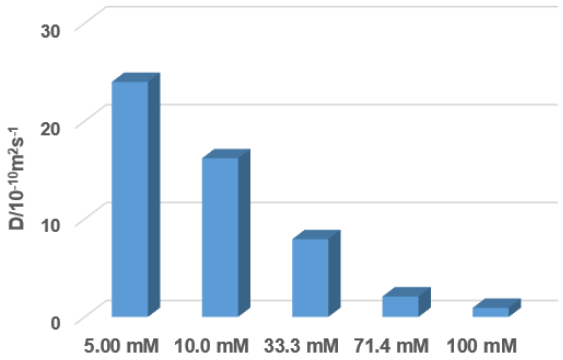


Figure S12. Schematic illustration of the concentration dependence of diffusion coefficient D (600 MHz, $CDCl_3$, room temperature) of equimolar **P5** and **G**.

6. Partial X-ray diffraction patterns of P5, P5 + G and P5 + G + Cu^{2+} at room temperature.

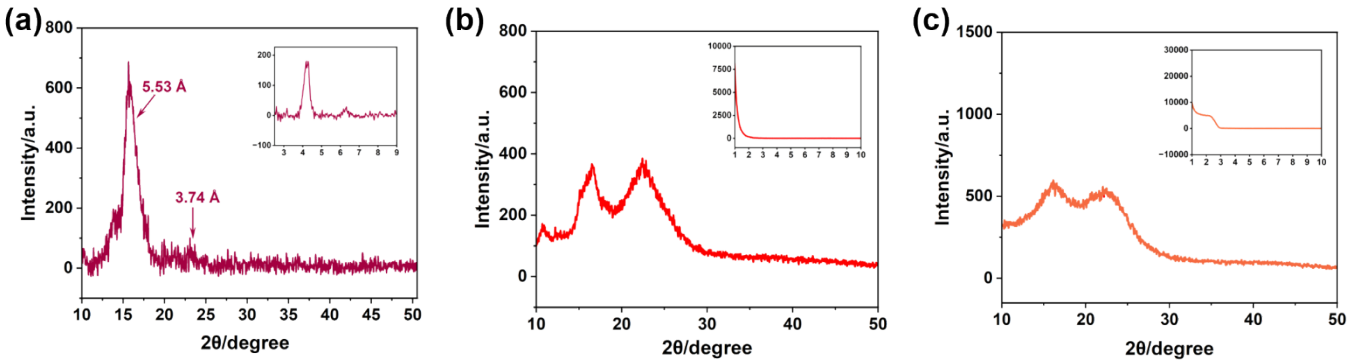


Figure S13. Partial X-ray diffraction patterns at room temperature: (a) **P5**; (b) **P5** + **G**; (c) **P5** + **G** + **Cu^{2+}**.

7. Fluorescence emission spectroscopy experiments of the P5 + G, P5 + G + Cu^{2+} and P5 + G + Cu^{2+} + TBACN.

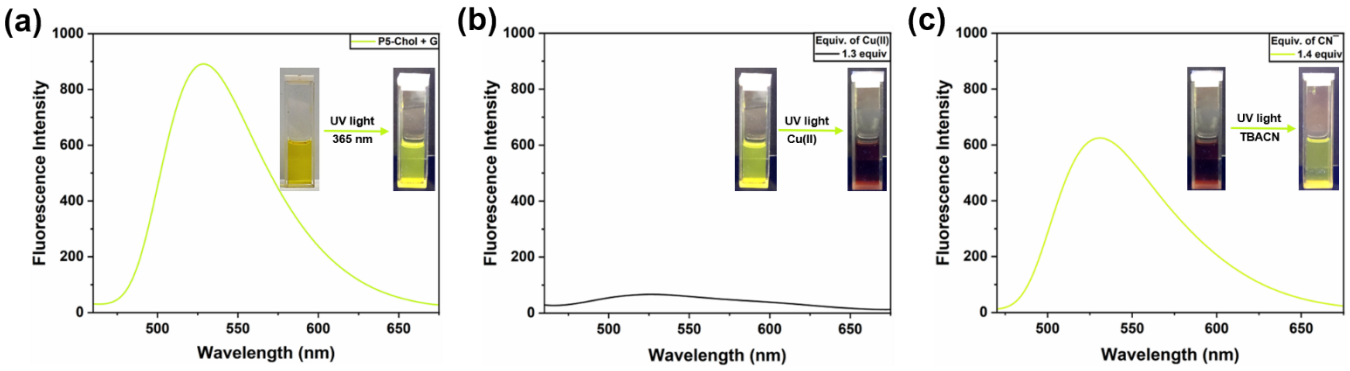


Figure S14. Fluorescence emission spectra : (a) **P5** (10.0 mM) + **G** (5.00 mM); (b) after addition of 1.3 molar equiv. cupric acetate anhydrous (13.0 mM) to a; (c) after addition of 1.4 molar equiv. tetrabutylammonium cyanide (14.0 mM) to b.

8. ^{1}H NMR spectroscopy titration experiments of [3]pseudorotaxane and Cu^{2+}

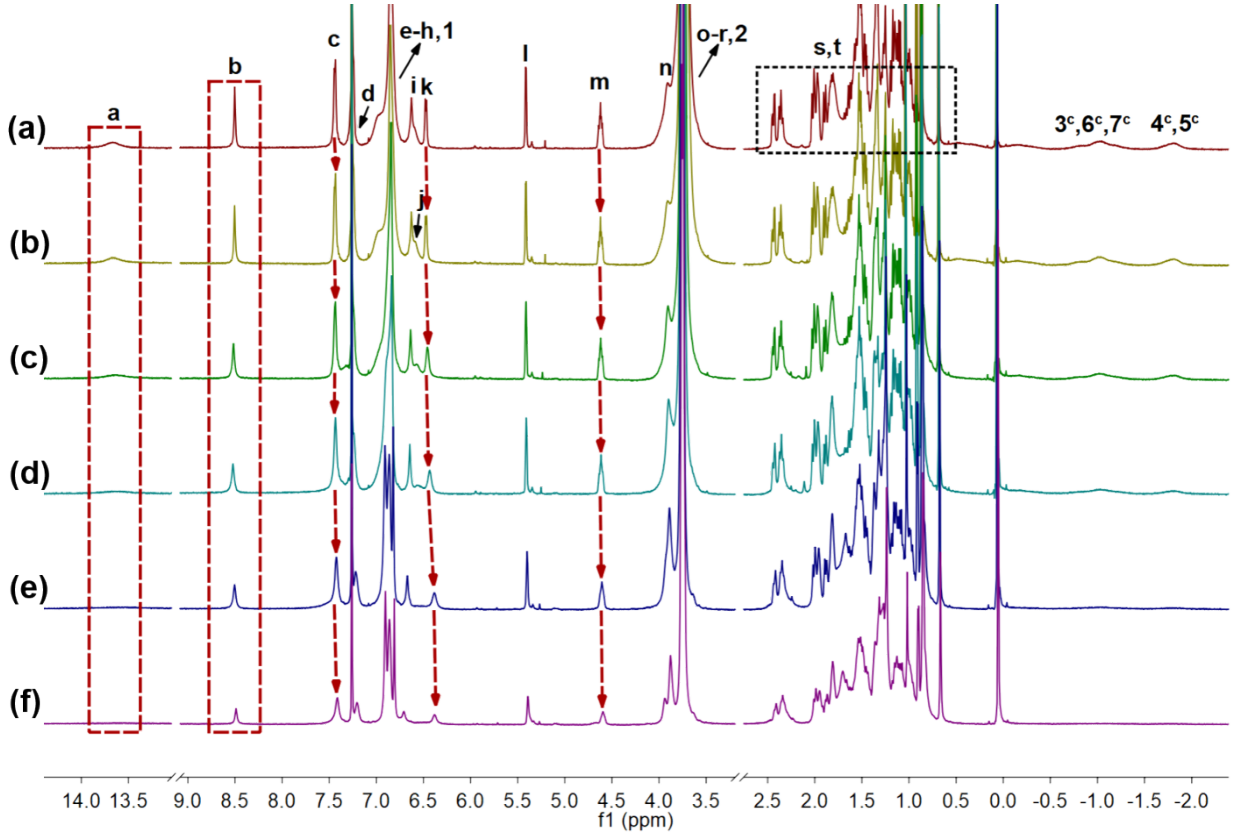


Figure S15. Partial ^{1}H NMR spectra (600 MH, $CDCl_3$, room temperature) of **P5** (10.0 mM) + **G** (5.00 mM) with successive addition of Cu^{2+}: (a) 0.00 eqv.; (b) 0.10 eqv.; (c) 0.20 eqv.; (d) 0.30 eqv.; (e) 0.40 eqv; (f) 0.50 eqv.

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