

A H₂S and I⁻ dual-responsive supramolecular polymer constructed by pillar[5]arene-based host-guest interaction and metal coordination

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Electronic Supplementary Information (11 pages)

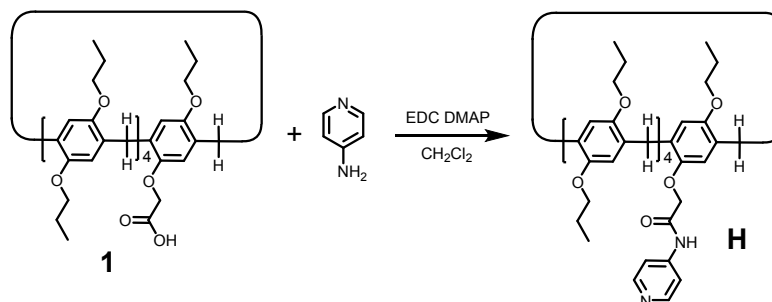
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **1**,^{S1} **2**^{S2} and **4**^{S3} were prepared according to published procedures. H₂S gas was prepared by a simple chemistry reactor and was permitted to pass an airtight conical flask containing a test tube in which the supramolecular polymer was placed previously.^{S4} NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in chloroform. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument or an Ultra-55 instrument. Dynamic light scattering was carried out on a Malvern Nanosizer S instrument at room temperature.

2. Syntheses of **H** and **G**

2.1. Synthesis of **H**



Scheme S1 Synthetic route to **H**

A solution of **1** (2.00 g, 1.91 mmol), 4-aminopyridine (0.360 g, 3.82 mmol) and catalytic amounts 4-dimethylaminopyridine (DMAP) in dichloromethane (50 mL) was stirred for 10 minutes at 0 °C. Then EDC (1.10 g, 5.73 mmol) was added. The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a crude product, which was purified by flash column chromatography (methanol/dichloromethane, 1:20 v/v) to afford **H** as a white solid (0.990 g, 44%). Mp: 74.0–75.4 °C. The ^1H NMR spectrum of **H** is shown in Fig. S1. ^1H NMR (400 MHz, CDCl_3) δ 8.69 (s, 1H), 8.53 (d, $J = 6.0$ Hz, 2H), 7.52 (d, $J = 6.4$ Hz, 2H), 6.82 (m, 10H), 6.72 (s, 1H), 6.63 (s, 1H), 5.18 (s, 2H), 4.50 (s, 2H), 3.87–3.67 (m, 28H), 3.60 (t, $J = 6.6$ Hz, 2H), 1.85–1.67 (m, 15H), 1.54 (m, 4H), 1.09–0.93 (m, 23H), 0.81 (m, 7H). The ^{13}C NMR spectrum of **H** is shown in Fig. S2. ^{13}C NMR (CDCl_3 , 293 K, 100 MHz) δ (ppm): 167.01, 150.55, 149.81, 149.21, 148.94, 148.85, 148.81, 148.70, 146.68, 143.00, 128.35, 127.63, 127.56, 127.35, 127.01, 126.57, 126.49, 115.28, 114.99, 114.01, 113.85, 113.74, 113.33, 112.66, 69.28, 69.20, 68.99, 68.89, 68.02, 29.16, 28.60, 28.35, 22.04, 21.96, 21.82, 21.77, 21.58, 9.78, 9.76, 9.74, 9.71, 9.68, 9.58, 9.52. LRESIMS is shown in Fig. S3: m/z 1123.5 $[\text{M} + \text{H}]^+$ (100%). HRESIMS: m/z calcd. for $[\text{M} + \text{H}]^+$ $\text{C}_{69}\text{H}_{91}\text{N}_2\text{O}_{11}$, 1123.6623; found 1123.6628; error 0.4 ppm.

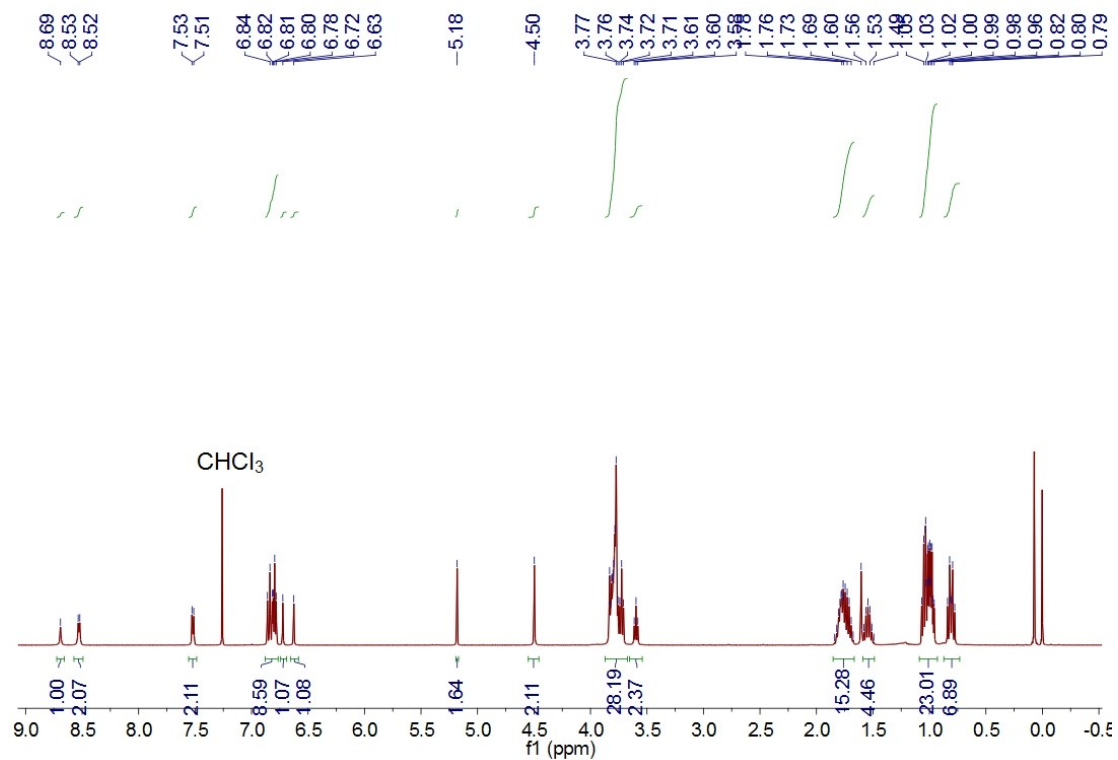


Figure S1. ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of **H**.

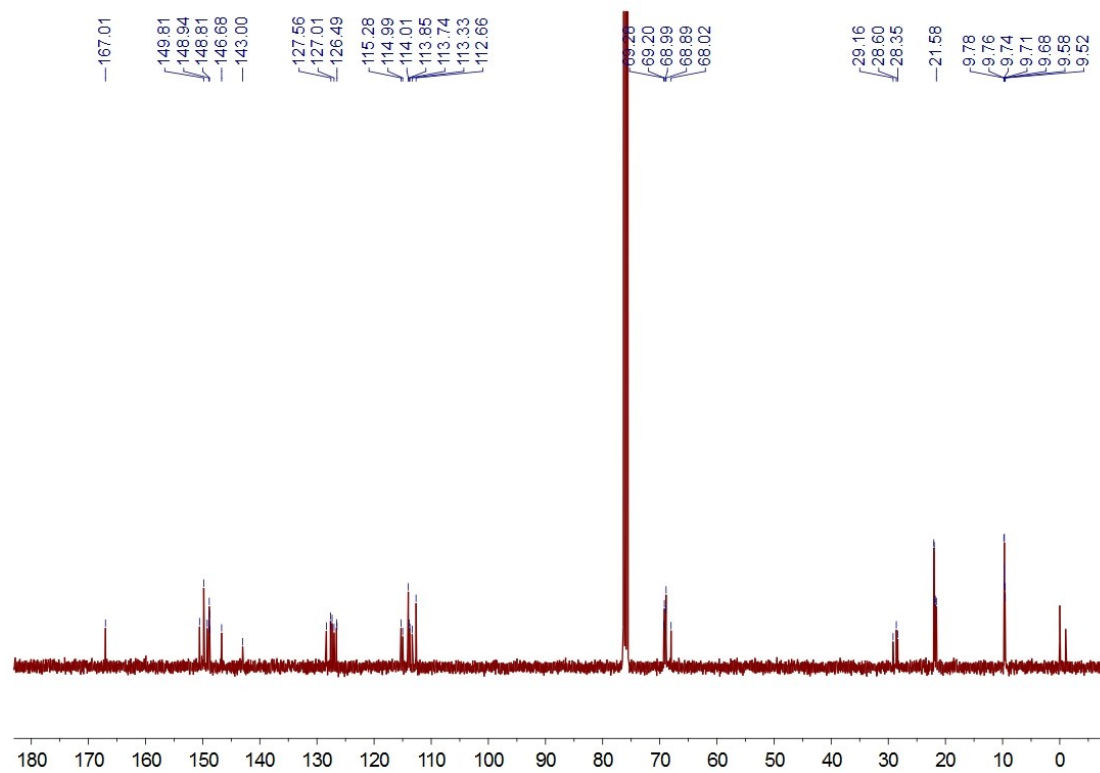


Figure S2. ¹³C NMR spectrum (CDCl₃, 293 K, 100 MHz) of **H**.

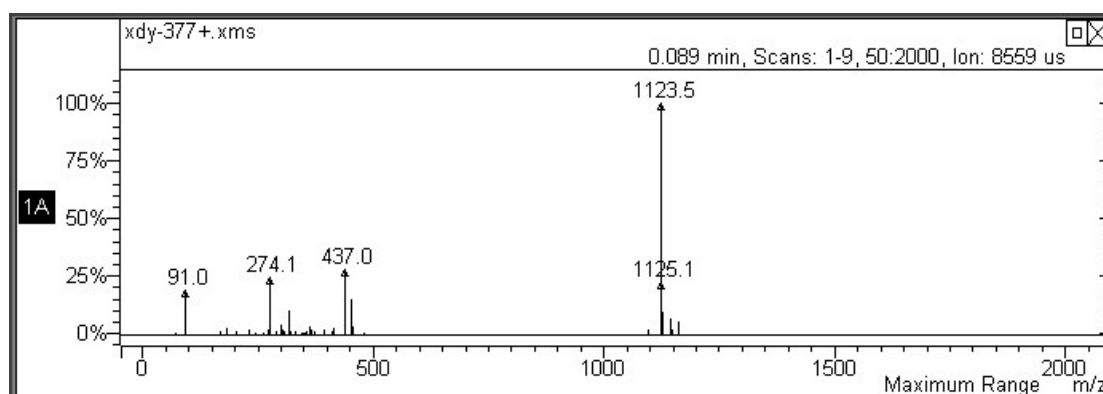
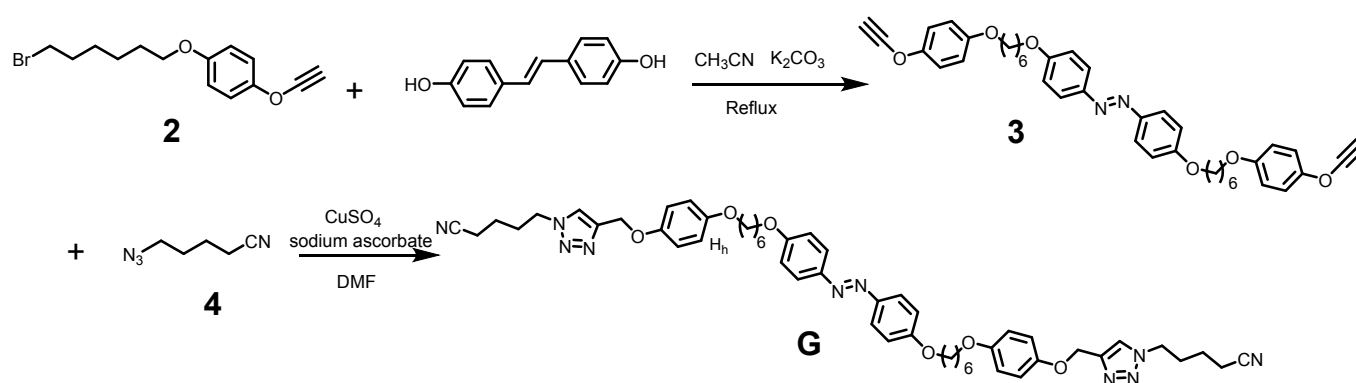


Figure S3. Electrospray ionization mass spectrum of **H**. Main peak: m/z 1123.5 $[M + H]^+$ (100%).

2.2. Synthesis of **G**



Scheme S2 Synthetic route to **G**.

Synthesis of **3**. A solution of **3** (10.0 g, 33.6 mmol), 4,4'-azobis(phenol) (2.38 g, 11.2 mmol) and potassium carbonate (4.64 g, 33.6 mmol) in acetonitrile (100 mL) was refluxed for 24 h. Then the solution was filtered and the filtrate was concentrated to give a crude product, which was purified by flash column chromatography (petroleum ether/dichloromethane, 3:1 v/v) to afford **3** as a pale yellow solid (6.72 g, 89%). Mp: 97.9–98.2°C. The ^1H NMR spectrum of **3** is shown in Fig. S4. ^1H NMR (400 MHz, CDCl_3) δ 8.31–8.09 (m, 4H), 7.03–6.87 (m, 8H), 6.90–6.77 (m, 4H), 4.64 (d, $J = 2.4$ Hz, 4H), 4.06 (t, $J = 6.4$ Hz, 4H), 3.93 (t, $J = 6.4$ Hz, 4H), 2.50 (t, $J = 2.4$ Hz, 2H), 1.91–1.75 (m, 8H), 1.56–1.52 (m, 8H). The ^{13}C NMR spectrum of **3** is shown in Fig. S5. ^{13}C NMR (CDCl_3 , 293 K, 100 MHz) δ (ppm): 125.94, 116.13, 115.30, 114.40, 75.29, 68.71, 68.27, 56.61, 29.26, 28.93, 25.84, 25.75. LRESIMS is shown in Fig. S6: m/z 437.1 $[M + 2H + 11\text{H}_2\text{O}]^{2+}$ (100%). HRESIMS: m/z calcd. for $[M + H]^+$ $\text{C}_{42}\text{H}_{49}\text{N}_2\text{O}_6$, 676.3512; found 676.3518; error 0.9 ppm.

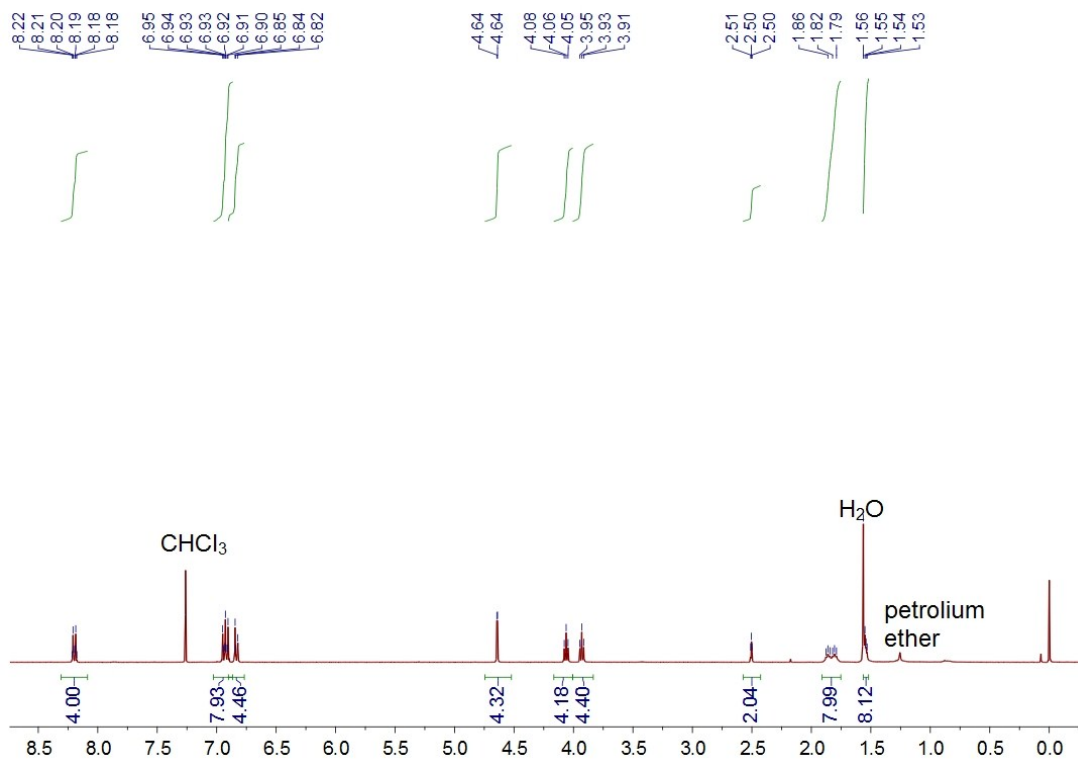


Figure S4. ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of **3**.

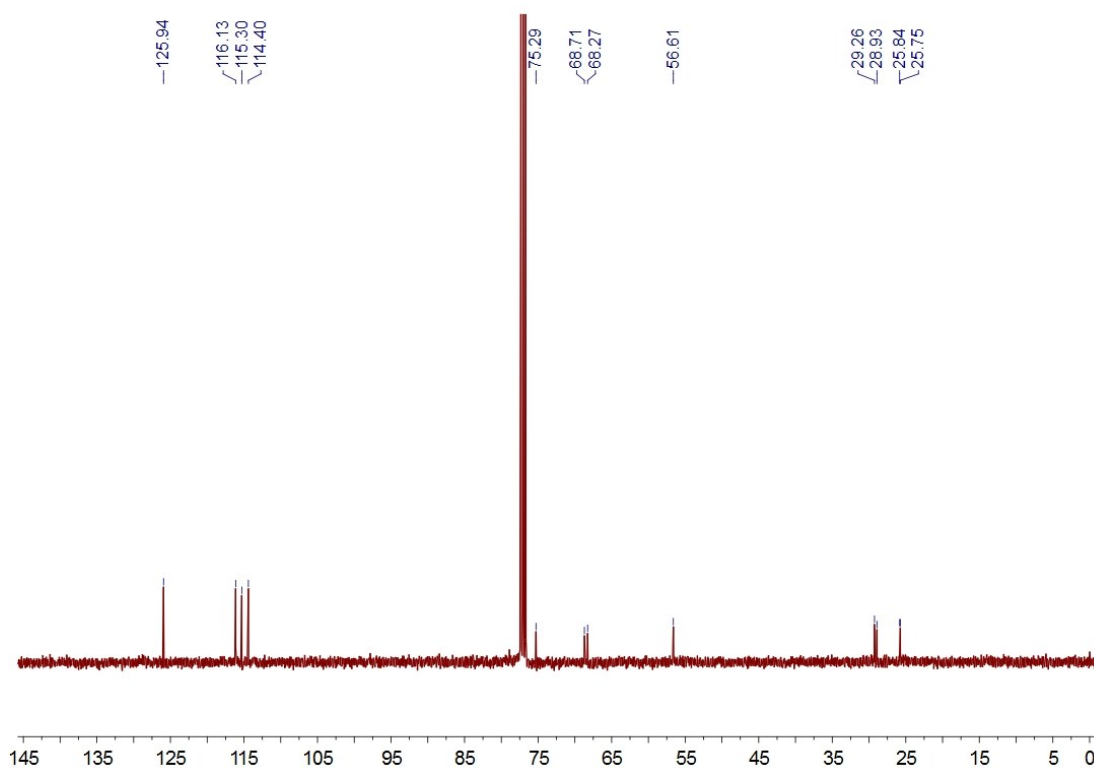


Figure S5. ¹³C NMR spectrum (CDCl₃, 293 K, 100 MHz) of **3**.

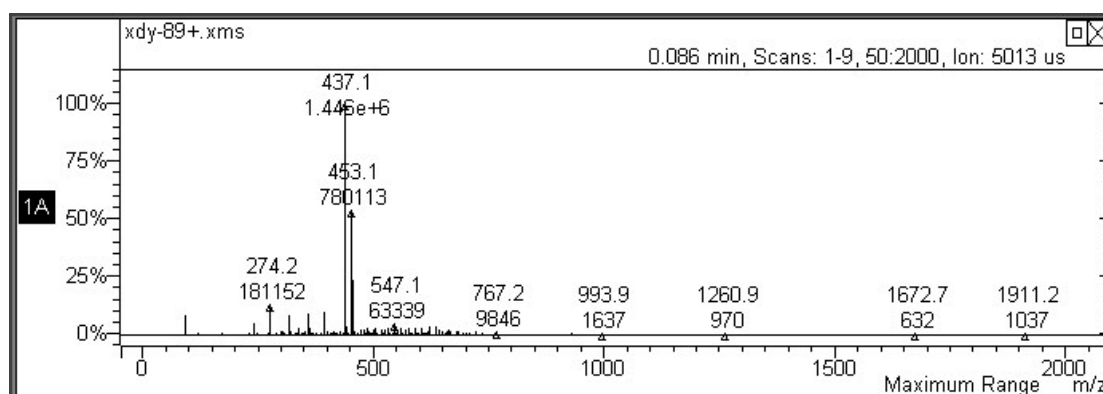


Figure S6. Electrospray ionization mass spectrum of **3**.

Main peak: m/z 437.1 $[M + 2H + 11H_2O]^{2+}$ (100%).

Synthesis of **G**. A solution of **3** (3.00 g, 4.45 mmol) and **4** (1.10 g, 9.50 mmol) in DMF (80 mL) in the presence of $CuSO_4 \cdot 5H_2O$ (0.250 g, 1.00 mmol) with sodium ascorbate (0.500 g, 2.50 mmol) was stirred at 50 °C for 24 h. The reaction mixture was concentrated and recrystallized to afford compound **G** as a pale yellow solid (2.67 g, 65%). Mp: 84.0–85.2°C. The 1H NMR spectrum of **G** is shown in Fig. S7. 1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 8.8$ Hz, 4H), 7.61 (s, 2H), 6.92 (t, $J = 9.0$ Hz, 8H), 6.82 (d, $J = 4.6$ Hz, 4H), 5.16 (s, 4H), 4.43 (t, $J = 6.8$ Hz, 4H), 4.06 (t, $J = 6.4$ Hz, 4H), 3.92 (t, $J = 6.4$ Hz, 4H), 2.41 (t, $J = 6.8$ Hz, 2H), 2.17–2.02 (m, 4H), 1.91–1.75 (m, 8H), 1.69 (m, 4H), 1.55 (m, 8H). The ^{13}C NMR spectrum of **G** is shown in Fig. S8. ^{13}C NMR ($CDCl_3$, 293 K, 100 MHz) δ (ppm): 164.19, 153.68, 152.26, 125.93, 115.84, 115.39, 114.40, 68.69, 68.28, 62.73, 49.25, 29.25, 29.05, 28.91, 25.81, 25.72, 22.33, 16.71. LRESIMS is shown in Fig. S9: m/z 516.1 $[M + 2H + 6H_2O]^{2+}$ (100%). HRESIMS: m/z calcd. for $[M + H]^+ C_{52}H_{63}N_{10}O_6$, 923.4932; found 923.4918; error -2 ppm.

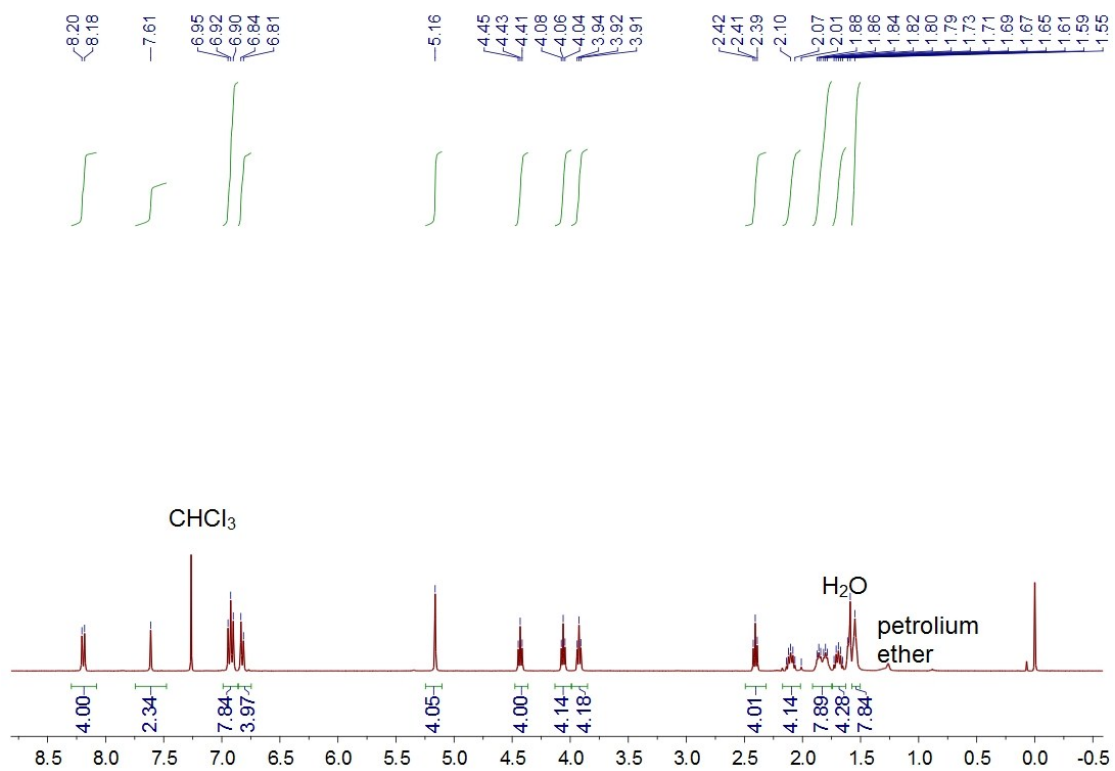


Figure S7. ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of **G**.

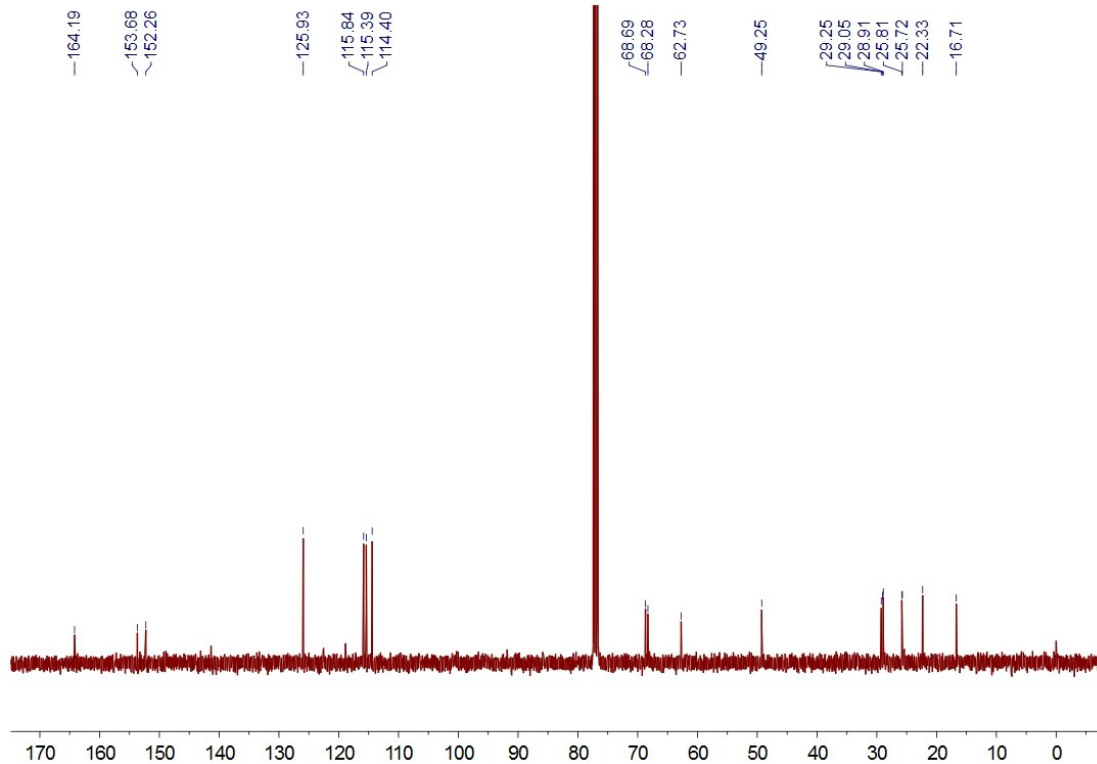


Figure S8. ¹³C NMR spectrum (CDCl₃, 293 K, 100 MHz) of **G**.

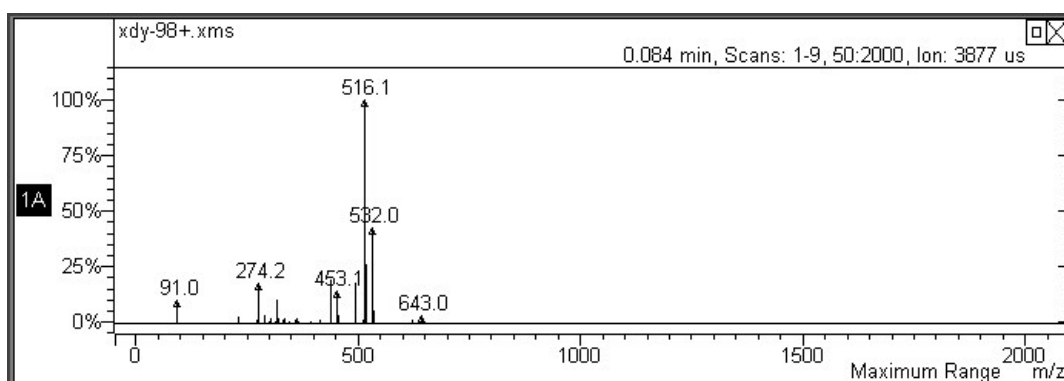


Figure S9. Electrospray ionization mass spectrum of **G**.

Main peak: m/z 516.1 $[M + 2H + 6H_2O]^{2+}$ (100%).

3. Partial 1H NMR spectra of the formation of the pillar[5]arene-based dimer and host-guest interaction between the dimer and **G**

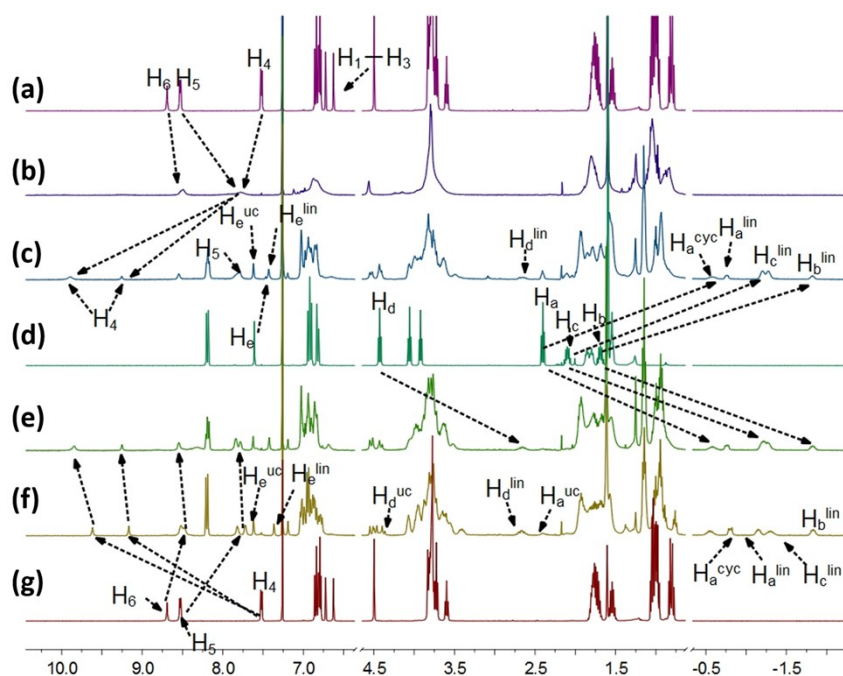


Figure S10 Partial 1H NMR spectra ($CDCl_3$, 293 K, 500 MHz): (a) **H** (20.0 mM); (b) **H** (20.0 mM) + Ag^+ (10.0 mM); (c) **H** (20.0 mM) + Ag^+ (10.0 mM) + **G** (10.0 mM); (d) **G** (10 mM); (e) **H** (20.0 mM) + **G** (10.0 mM) + Ag^+ (10.0 mM); (f) **H** (20.0 mM) + **G** (10.0 mM); (g) **H** (20.0 mM).

4. DLS results

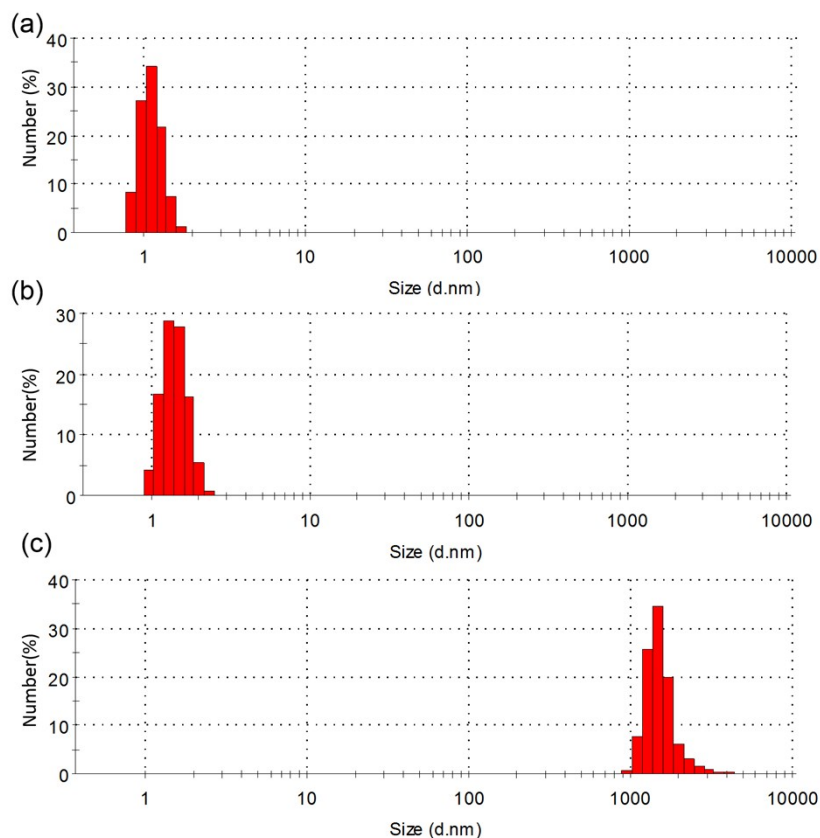


Figure S11 DLS results of (a) **G** (30.0 mM); (b) pillararene-based dimer (30.0 mM); (c) pillararene-based dimer and **G** (30.0 mM for both).

5. Reversible stimuli-responsive supramolecular polymer to monomers transformation investigated by viscosity measurements

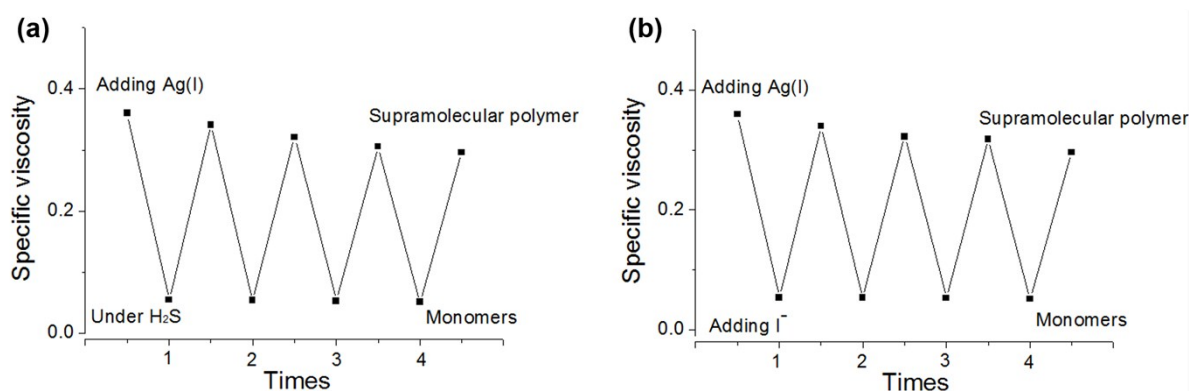


Figure S12 Reversible stimuli-responsive supramolecular polymer to monomers transformation: (a) H₂S-responsive transformation, (b) I⁻-responsive transformation.

6. AFM image of the fibers drawn from the supramolecular polymer

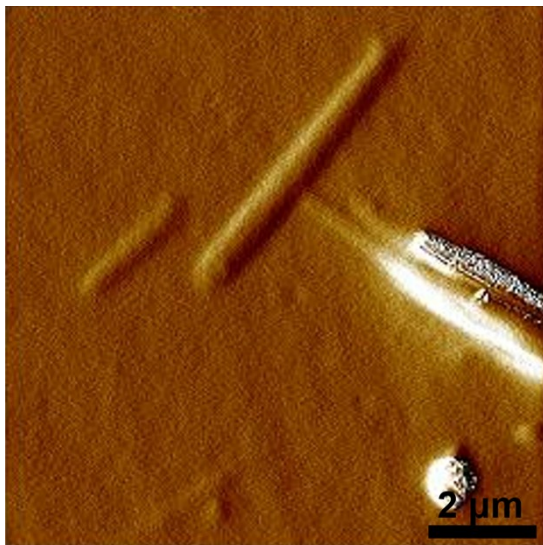


Figure S13 AFM image of fibers drawn from a high concentration solution of equimolar mixtures of pillararene-based dimer and **G**.

References:

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- S3. Wang, H. Deng, J. Li, K. Zheng, X. Jia and C. Li, *Macromol. Rapid. Commun.* 2013, **34**, 1856–1862.
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