Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Pillar[5]arene-based multi-stimuli responsive metal-organic gel was constructed for facile removal of mercury ions

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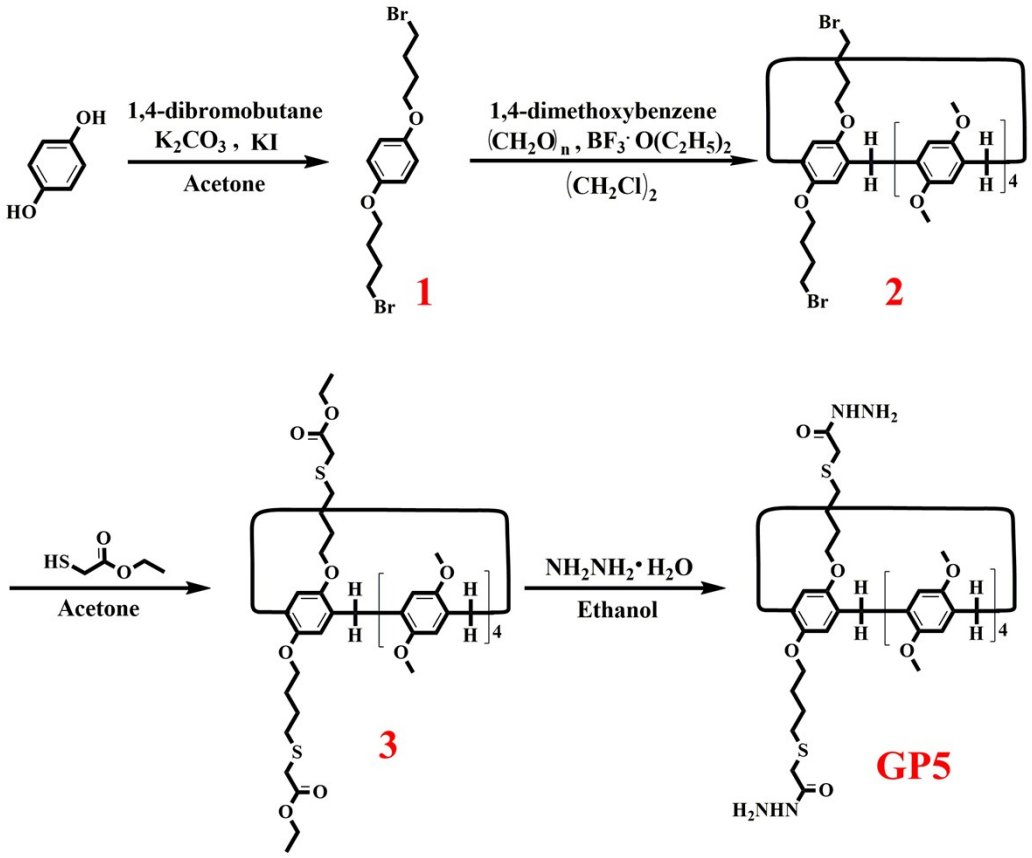
1. Materials and methods

1, 4−Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4−dibromobutane, and ethyl mercaptoacetate were reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^1H NMR spectra were recorded on a Mercury−600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury−600BB spectrometer at 151 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X−4 digital melting−point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker−FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKa radiation (λ = 1.54073 Å). The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV.

2. Synthesis of functionalized pillar[5]arene GP5



Scheme S1 Synthesis of functionalized pillar[5]arene **GP5**.

Synthesis of 1,4−bis(4−bromobutoxy)benzene 1: Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,4−dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round–bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 10 : 1) afforded a white solid(6.0 g, 80%). Mp 83−85°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, J = 0.8 Hz, 4H), 3.96 (t, J = 6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H).

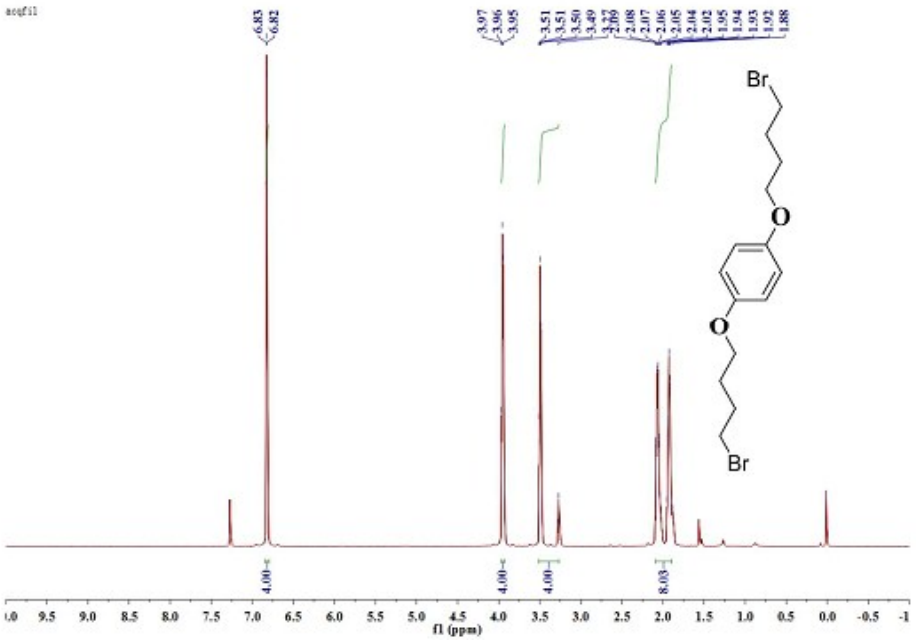


Fig. S1 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

Synthesis of a copillar[5]arene 2: To a solution of 1,4−bis(4−bromobutoxy) benzene (1.90 g, 5.0 mmol) and 1,4−dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2−dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1,*v*/*v*) to give **2**(1.69 g, 34%) as a white solid. Mp 187−189 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84–6.74 (m, 10H), 3.87 (t, J = 5.9 Hz, 4H), 3.83–3.78 (m, 10H), 3.72 (t, J = 19.9 Hz, 24H), 3.33 (s, 4H), 1.94 (s, 4H), 1.84 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.21–150.05 (m), 128.28 (s), 114.43–113.26 (m), 67.27–66.80 (m), 55.66 (s), 33.49 (s), 29.55 (s), 28.32 (s). ESI−MS m/z: $(M+NH_4)^+$ Calcd for $C_{51}H_{64}O_{10}Br_2N$ 1010.2871; Found 1010.2878.

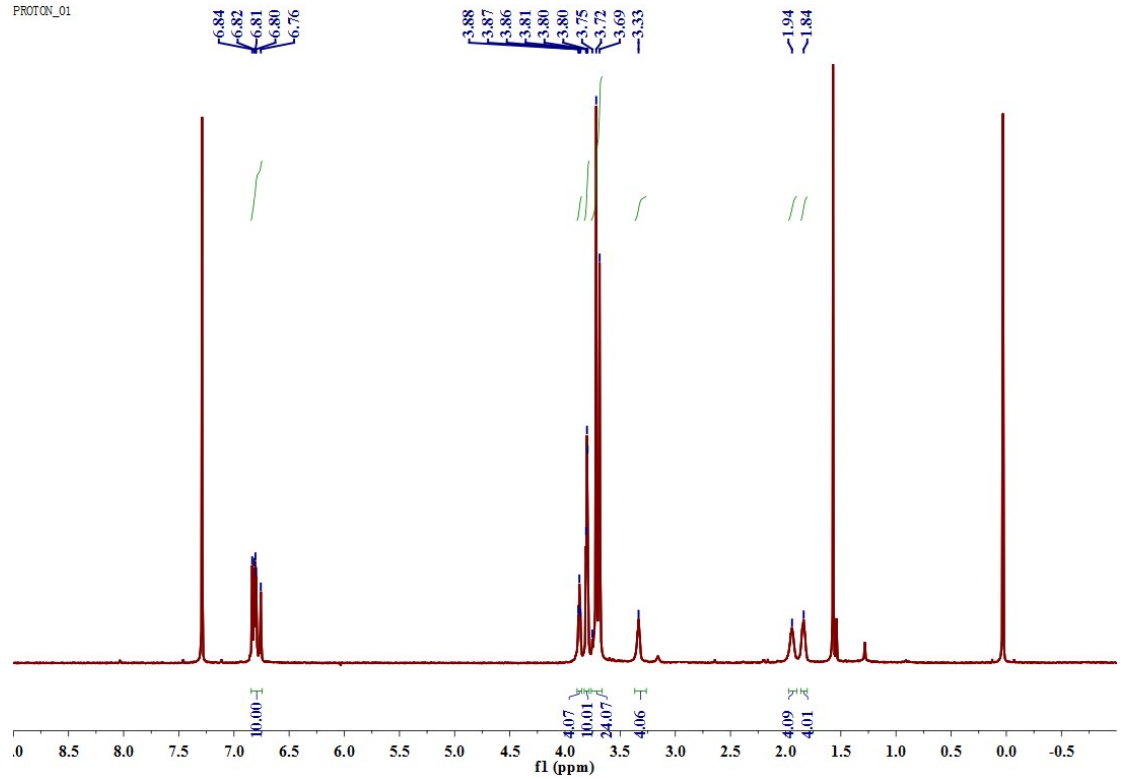


Fig. S2 ^{1}H NMR spectra(600 MHz, $CDCl_3$) of a copillar[5]arene **2**.

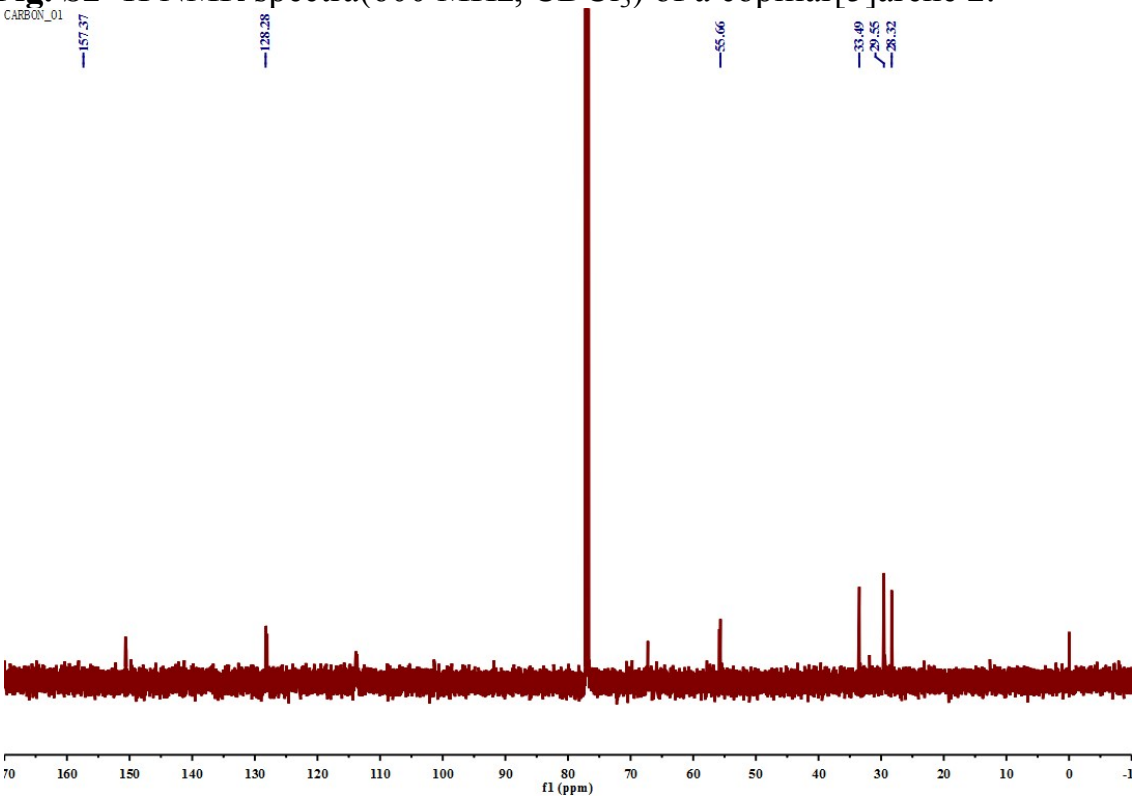


Fig. S3 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of a copillar[5]arene **2**.

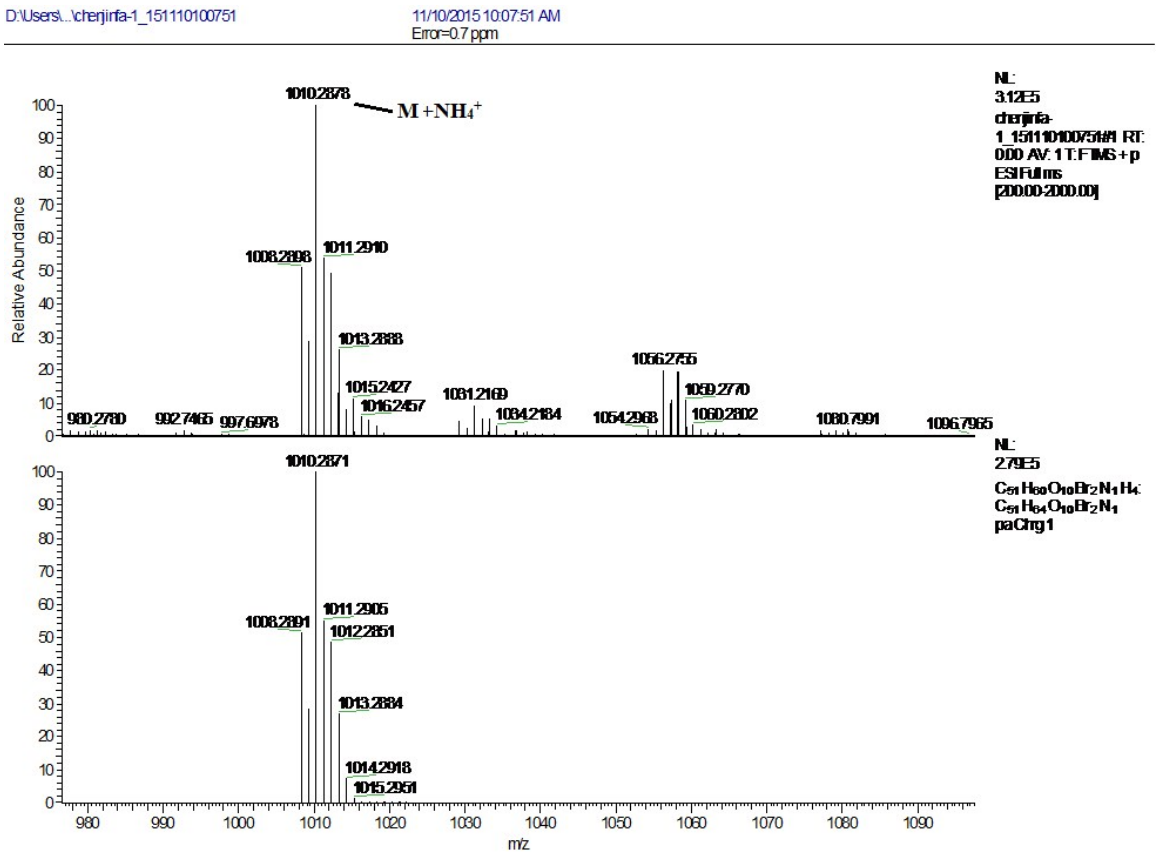


Fig. S4 High resolution mass data of a copillar[5]arene **2**.

Synthesis of functionalized pillar[5]arene 3: Copillar[5]arene **2** (0.5 g, 0.5 mmol) K_2CO_3 (0.28 g, 2 mmol) and ethyl mercaptoacetate (0.3 mL, 2.75 mmol) were added to acetone (80 mL). The solution was refluxed overnight. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 20 : 1) afforded a white solid (0.43 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, J = 14.3, 7.1 Hz, 10H), 3.85 (t, J = 5.8 Hz, 4H), 3.79–3.74 (m, 14H), 3.71 (s, 6H), 3.69 (s, 12H), 3.66 (s, 12H), 3.24 (s, 4H), 2.72 (t, J = 7.0 Hz, 4H), 1.87 (ddd, J = 26.5, 14.7, 7.9 Hz, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.88 (s), 151.71–148.89 (m), 129.38–126.85 (m), 116.55–112.46 (m), 67.71 (s), 55.73 (dd, J = 10.4, 5.9 Hz), 52.34 (s), 41.19 (s), 33.42 (s), 32.52 (s), 29.46 (s), 28.86 (s), 25.72 (s).

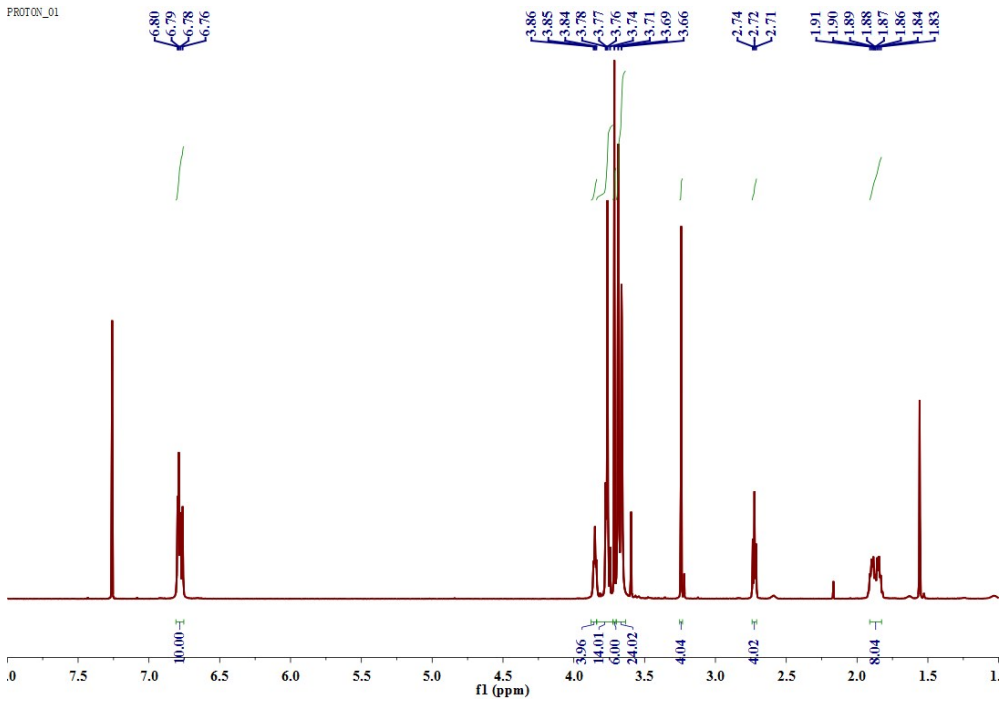


Fig. S5 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of functionalized pillar[5]arene **3**.

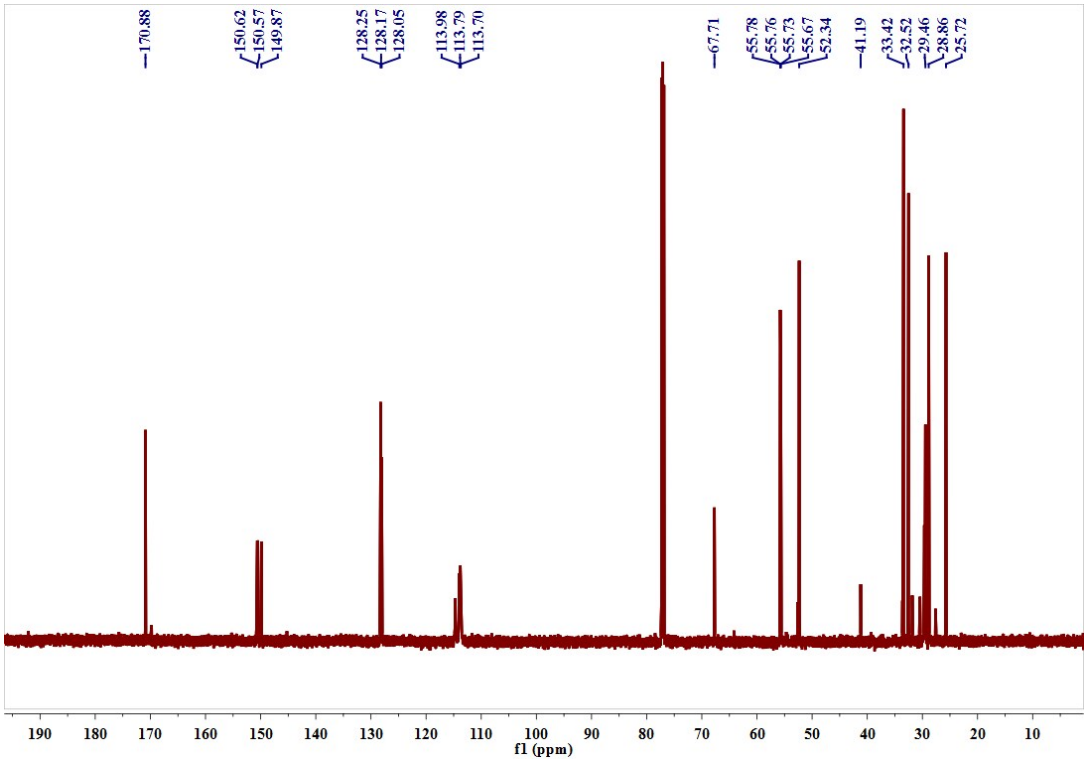


Fig. S6 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of functionalized pillar[5]arene **3**.

Synthesis of functionalized pillar[5]arene GP5: functionalized pillar[5]arene **3** (0.5 g, 0.5 mmol) and hydrazine hydrate (0.3 mL, 6 mmol) were added to ethanol (20 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, you can afford a white solid. After white solid was washed by ethanol to obtain **GP5** as a white solid (0.48 g, 93 %). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.11 (s, 2H), 6.78 (d, J = 3.4 Hz, 10H), 4.34 (s, 4H), 3.84 (s, 4H), 3.75-3.61 (m, 34H), 3.06 (s, 4H), 2.67 (s, 4H), 1.80 (dd, J = 29.0, 7.3 Hz, 8H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 168.92 (s), 150.32 (s), 127.90 (s), 113.69 (s), 67.84 (s), 55.89 (s), 32.99 (s), 32.09 (s), 29.42 (s), 28.80 (s), 25.96 (s). ESI−MS m/z: $(M+H)^+$ Calcd for $C_{55}H_{71}O_{12}N_4S_2$ 1043.44; Found 1043.2296.

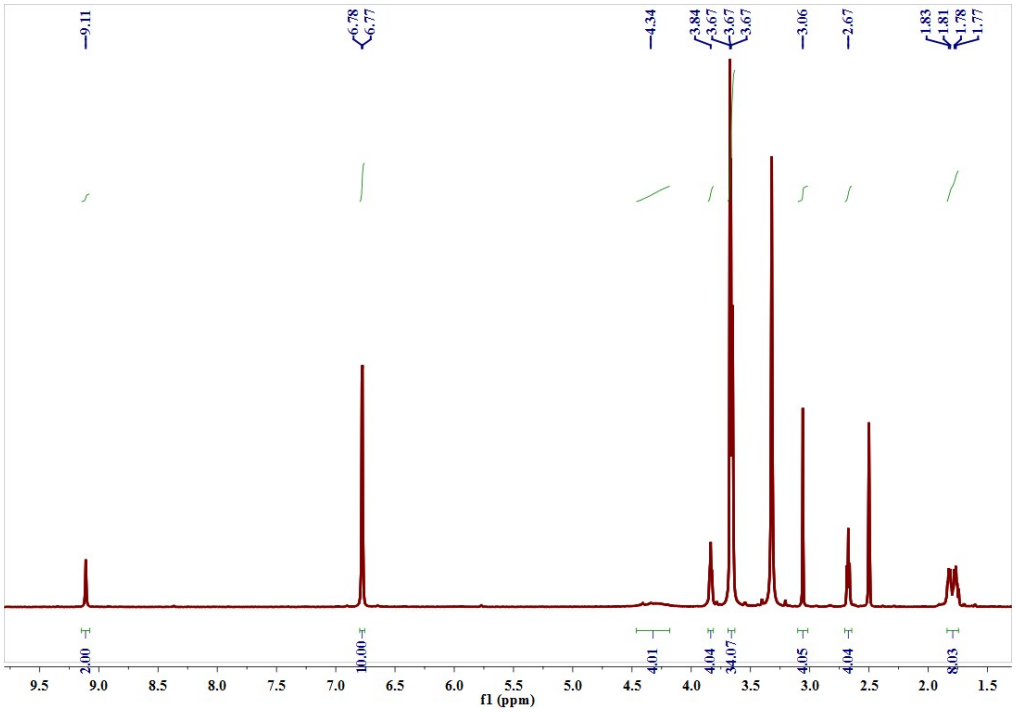


Fig. S7 ^{1}H NMR spectra (600 MHz, DMSO-d_6) of functionalized pillar[5]arene **GP5**.

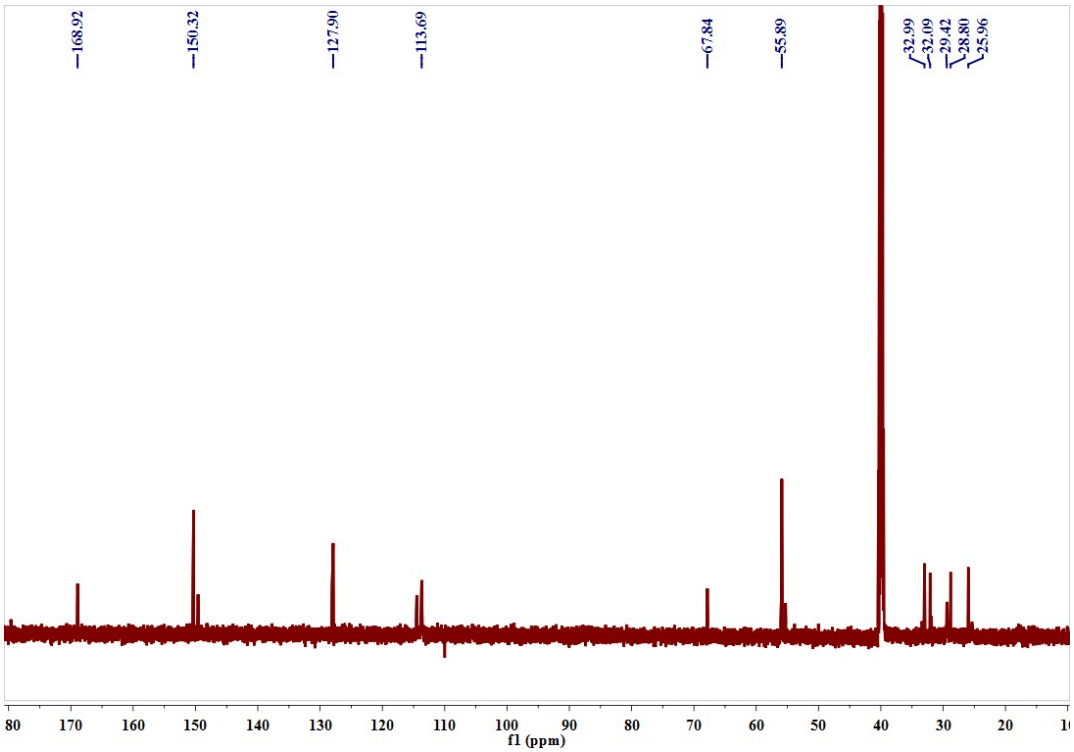


Fig. S8 ^{13}C NMR spectra (151 MHz, DMSO-d_6) of functionalized pillar[5]arene **GP5**.

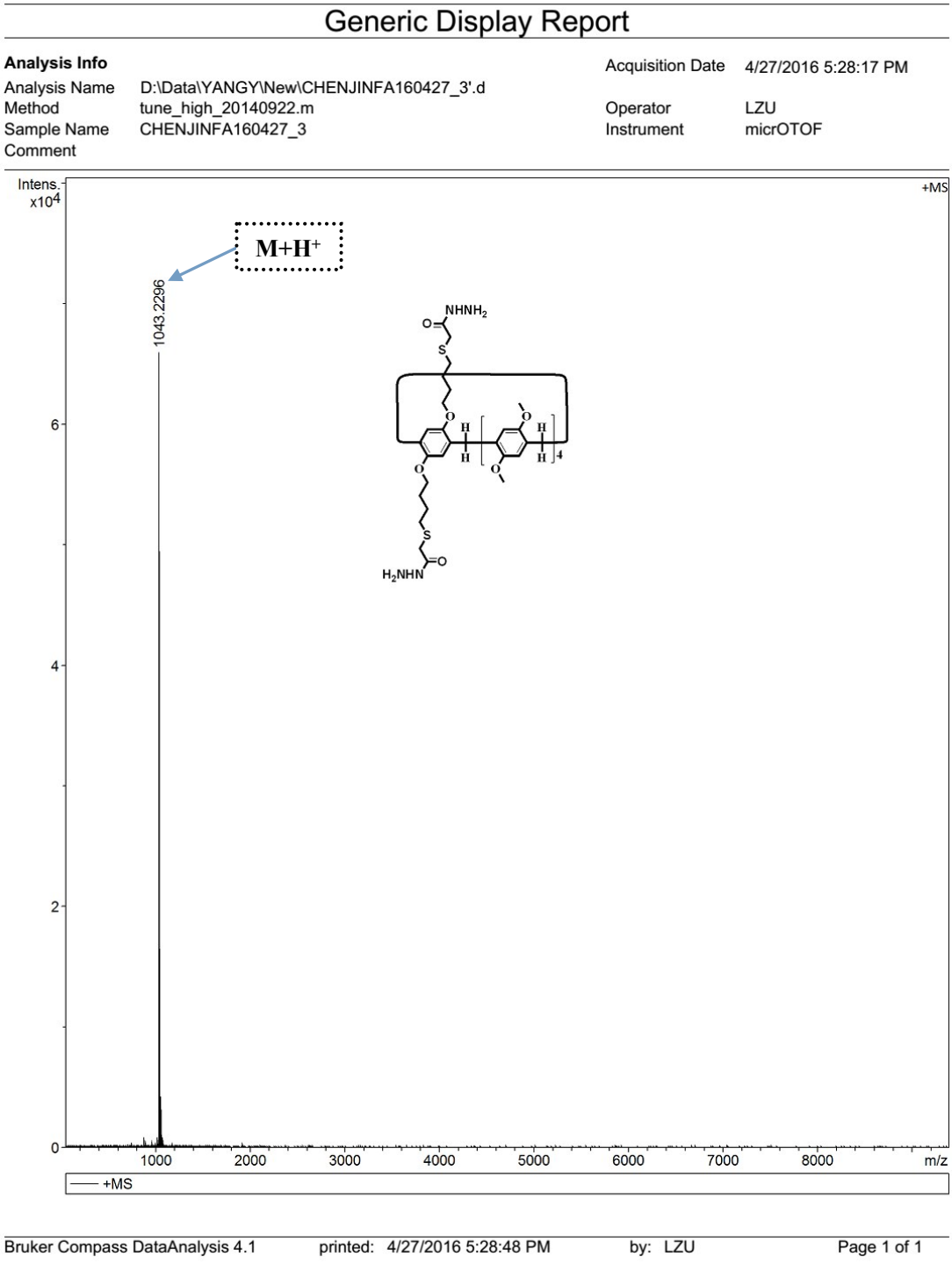


Fig. S9 High resolution mass data of functionalized pillar[5]arene **GP5**.

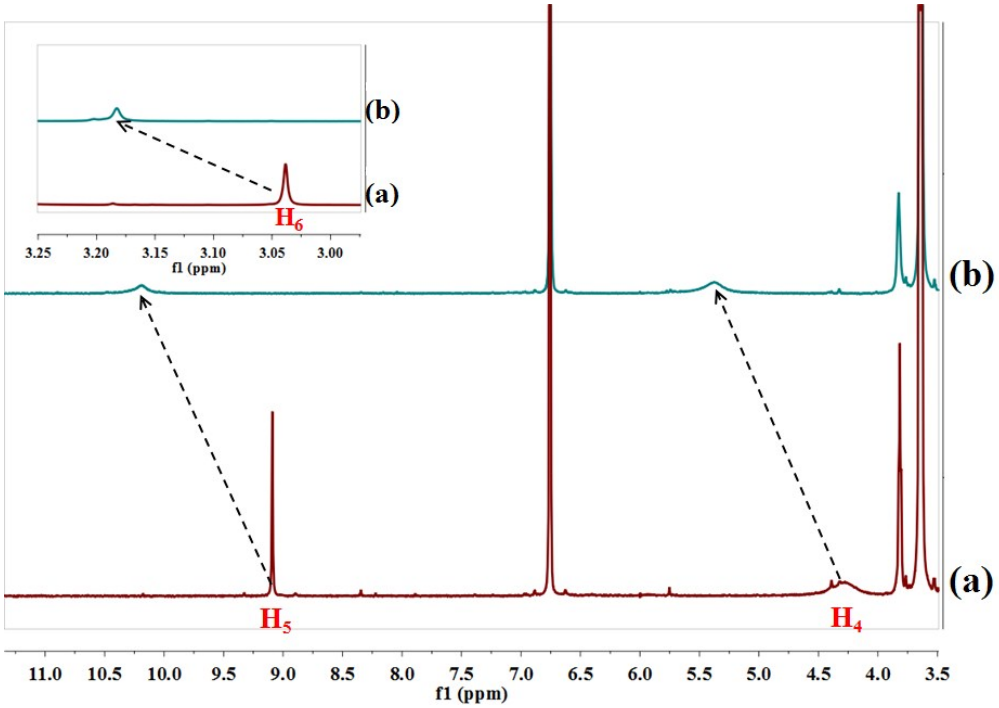


Fig. S10 Partial ^{1}H NMR spectra (600 MHz, DMSO-d_6) of (a) 10 mM **GP5**; (b) 10 mM **GP5** and 20 mM Zn^{2+}.

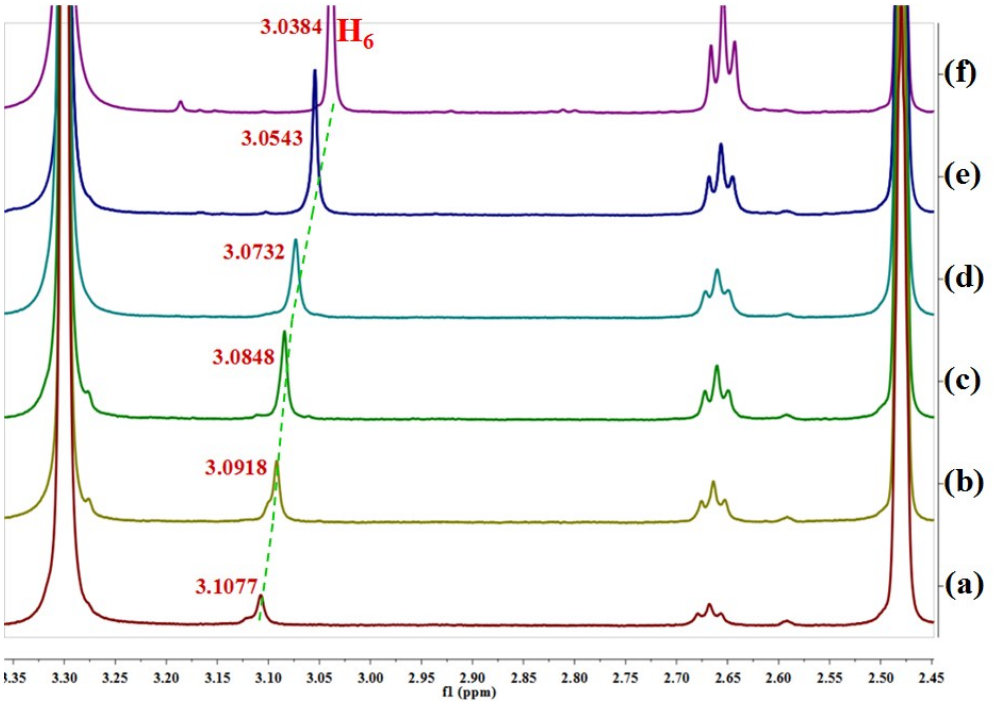


Fig. S11 Partial ^{1}H NMR spectra (600 MHz, DMSO-d_6) of **GP5** and Zn^{2+} at different molar ratios while [**GP5**] + [Zn^{2+}] = 5 mM. (a) [**GP5**]/[Zn^{2+}] = 2:8, (b) [**GP5**]/[Zn^{2+}] = 4:6, (c) [**GP5**]/[Zn^{2+}] = 5:5, (d) [**GP5**]/[Zn^{2+}] = 6:4, (e) [**GP5**]/[Zn^{2+}] = 8:2, (f) [**GP5**]/[Zn^{2+}] = 10:0.

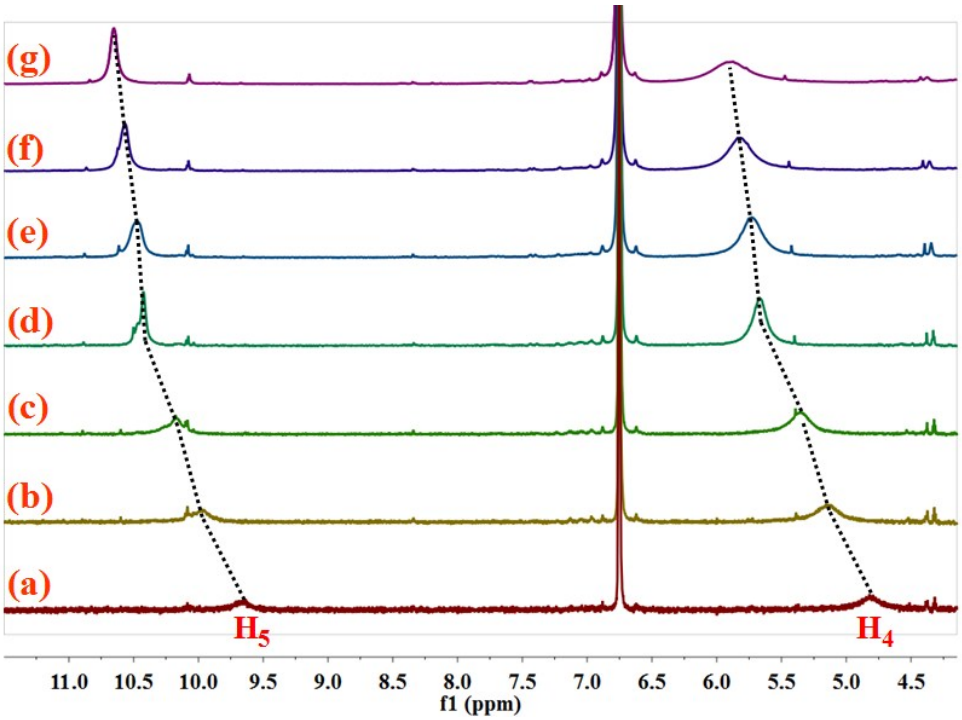


Fig. S12 ^{1}H NMR spectra (600 MHz, 298 K) of **GP5·Zn** in DMSO-d_6 at various concentrations: (a) 2.0 mM; (b) 5.0 mM; (c) 10.0 mM; (d) 20.0 mM; (e) 70.0 mM; (f) 110.0 mM; (g) 180.0 mM.

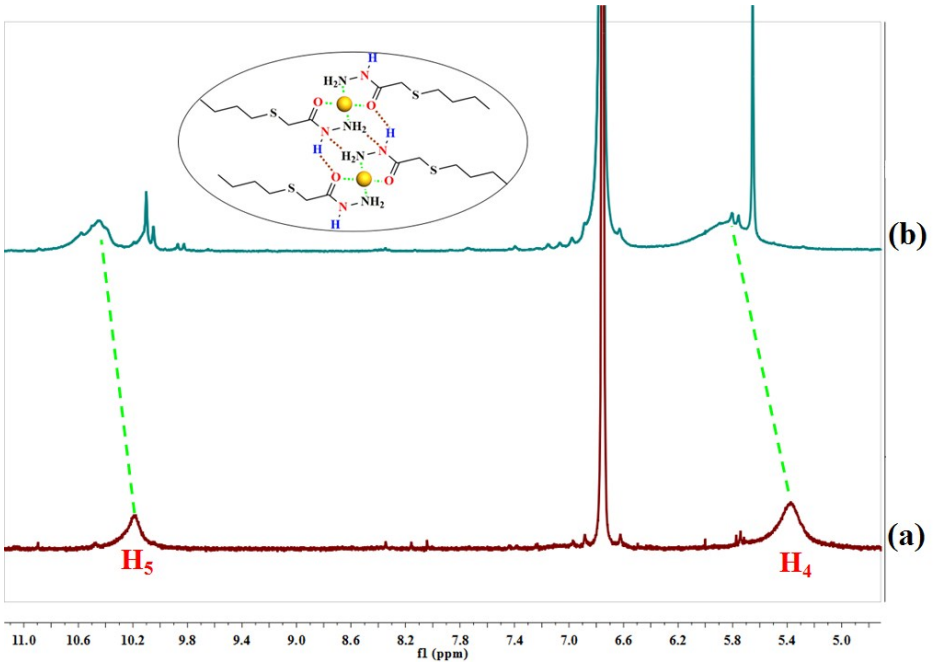


Fig. S13 ^{1}H NMR spectra (600 MHz, 298 K) of **GP5·Zn** in DMSO-d_6 at various concentrations: (a) 10 mM; (b) 50 mM.

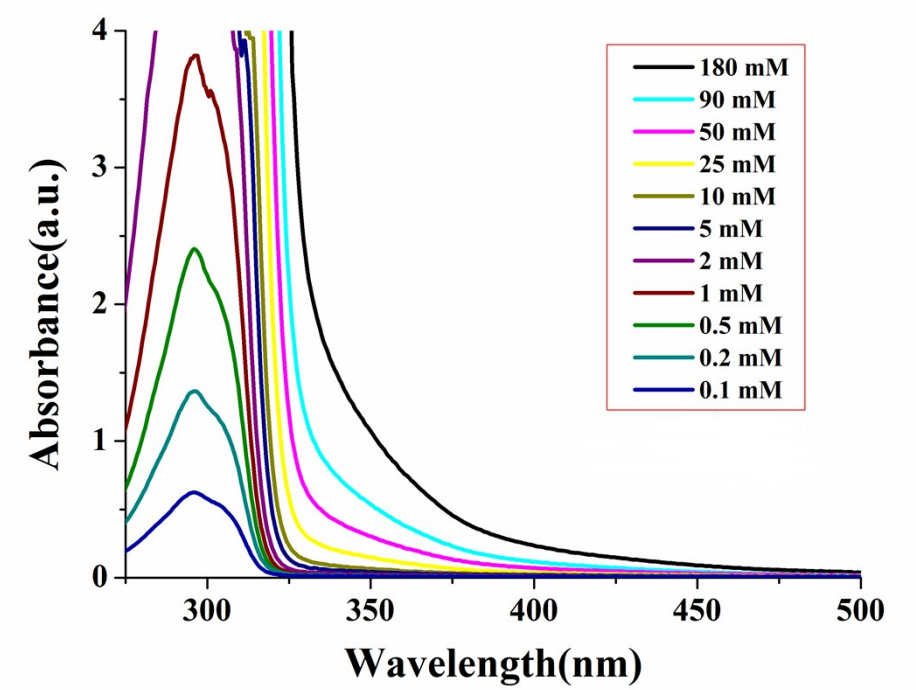


Fig. S14 Absorbance spectra of **GP5·Zn** at different concentrations in DMSO solution.

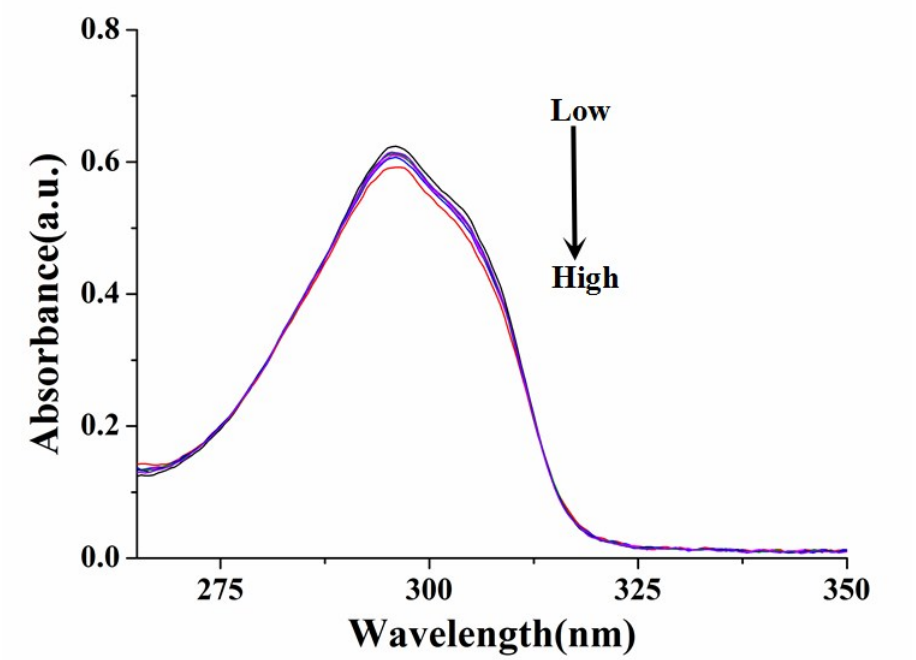


Fig. S15 Absorbance spectra of **GP5·Zn** (0.1 mM) at different temperatures in DMSO solution.

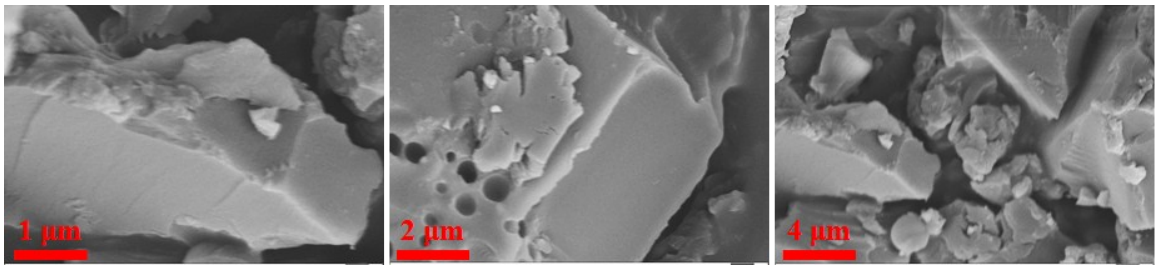


Fig. S16 SEM images of three-dimensional cubic structures of **GP5·Zn** metal-organic gel.

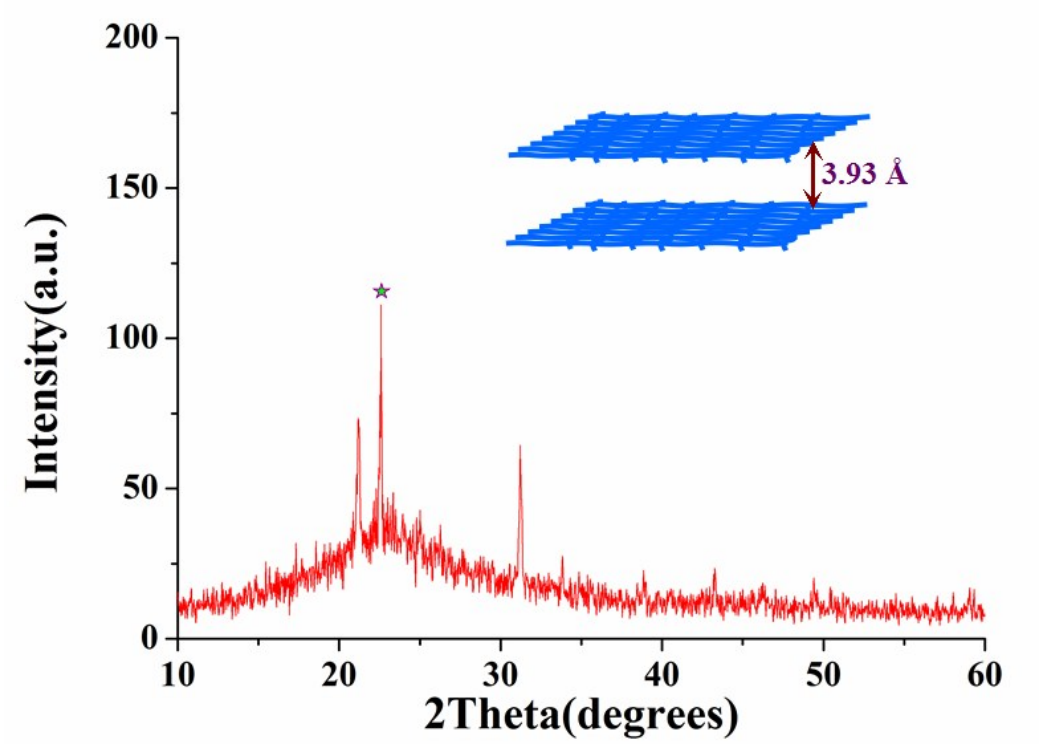


Fig. S17 XRD diagrams of xerogels powder formed by the gelator of **GP5·Zn** in cyclohexanol.

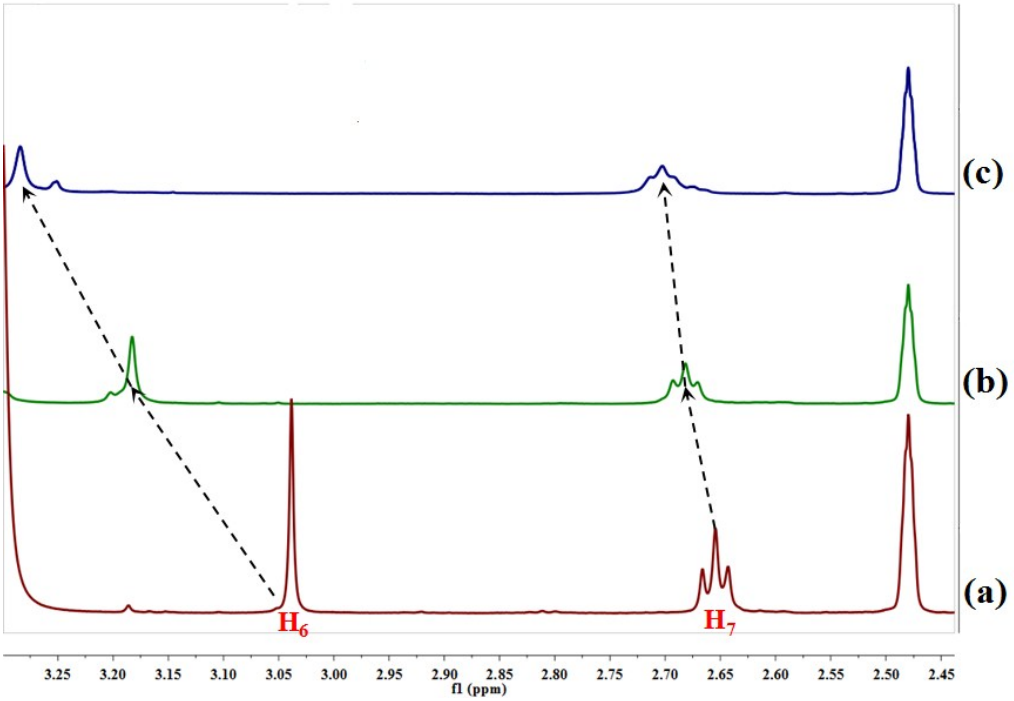


Fig. S18 Partial ^{1}H NMR spectra (600 MHz, DMSO-d_6) of (a) 10 mM **GP5**; (b) 10 mM **GP5** and 20 mM Zn^{2+}; (c) 10 mM **GP5**, 20 mM Zn^{2+} and 20 mM Hg^{2+}.

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