Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Multi-stimuli responsive metallosupramolecular polypseudorotaxane gel constructed by self-assembly of pillar[5]arene-based pseudo[3]rotaxane *via* zinc ion coordination and its application for highly sensitive fluorescent recognition mental ions

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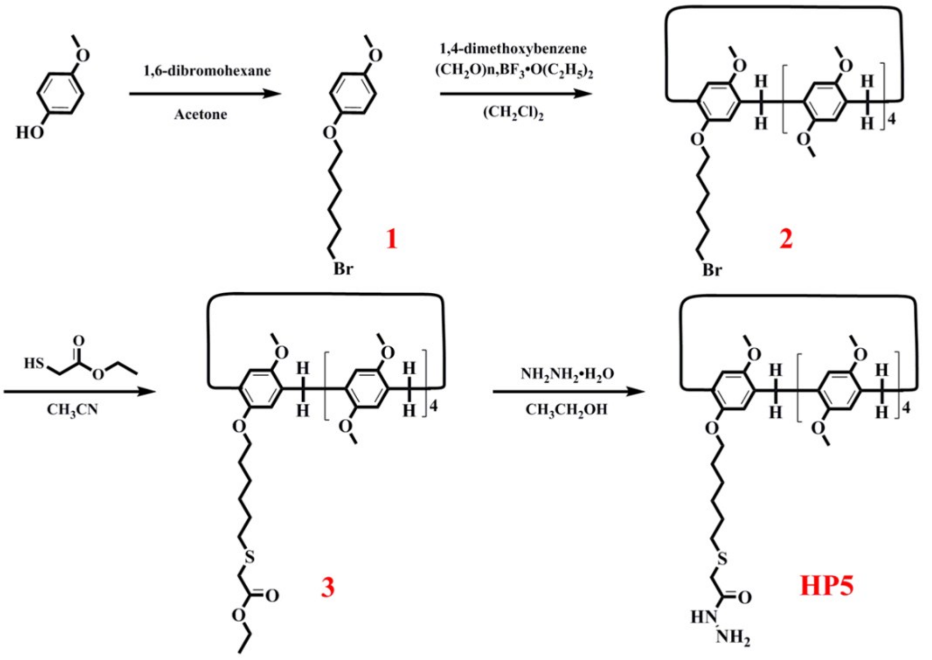
1. Materials and methods

Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. All cations were purchased from Alfa Aesar and used as received. ^{1}H 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). 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. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). 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. 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 infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Synthesis of functionalized pillar[5]arene HP5



Scheme S1 Synthesis of functionalized pillar[5]arene **HP5**.

Synthesis of compound 1: In a 500 mL round−bottom flask, 4−methoxyphenol (2.48 g, 20.0 mmol), K_2CO_3 (8.28 g, 60 mmol), KI (3.32 g, 20mmol), 1,6−dibromohexane (19.52 g, 80 mmol) and acetone (400 mL) were added. The reaction mixture was stirred at reflux for 3 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 : ethyl acetate=20:1) afforded a white solid (5.28 g, 92%). Mp 46-48 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.82 (s, 4H), 3.86 (s, 2H), 3.67 (s, 3H), 3.52 (s, 2H), 1.88–1.71 (m, 2H), 1.71–1.62 (m, 2H), 1.54–

1.30 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.66, 153.09, 115.73, 115.01, 68.17, 55.78, 35.56, 32.63, 29.06, 27.75, 25.14.

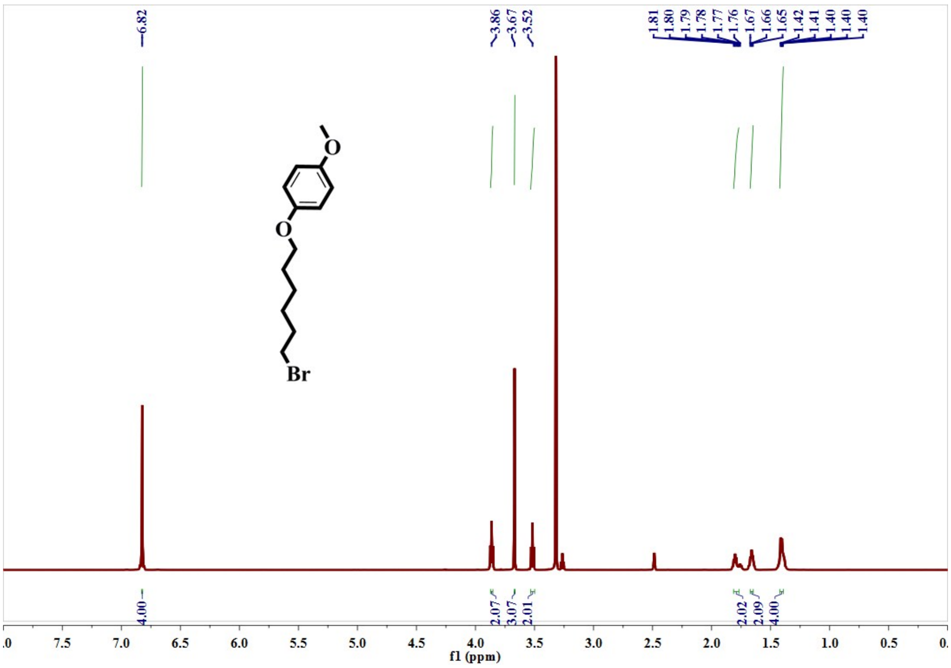


Fig. S1 ^{1}H NMR spectra (600 MHz, DMSO-d_6) of compound **1**.

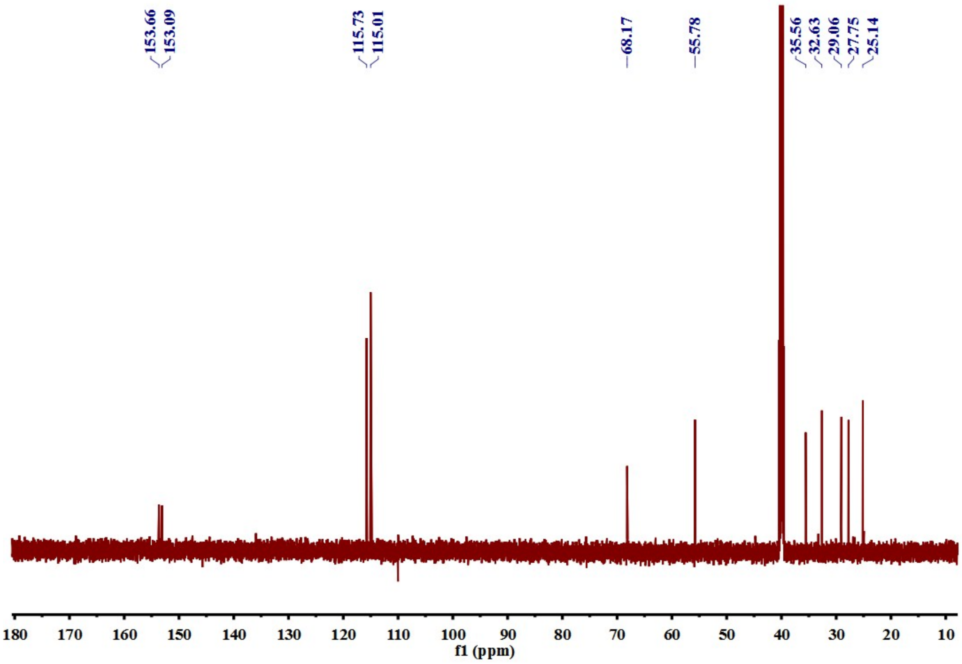


Fig. S2 ^{13}C NMR spectra (151 MHz, DMSO-d_6) of compound **1**.

Synthesis of a copillar[5]arene 2: To a solution of compound **1** (1.44 g, 5.0 mmol) and 1,4−dimethoxybenzene (2.76 g, 20.0 mmol) in 1,2−dichloroethane (80 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 1 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** (1.53 g, 34%) as a white solid. Mp 172-174 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96–6.79(m, 10H), 3.78(t, J=10.7Hz, 37H), 3.70(d, J=7.0Hz, 6H), 1.54–1.46(m, 2H), 1.26(s, 2H), 0.88(d, J=7.0Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.64, 128.07, 113.98, 55.62, 29.57. ESI−MS m/z: $(M+H)^+$ Calcd for $C_{50}H_{60}O_{10}Br$ 901.3349; Found 901.1102.

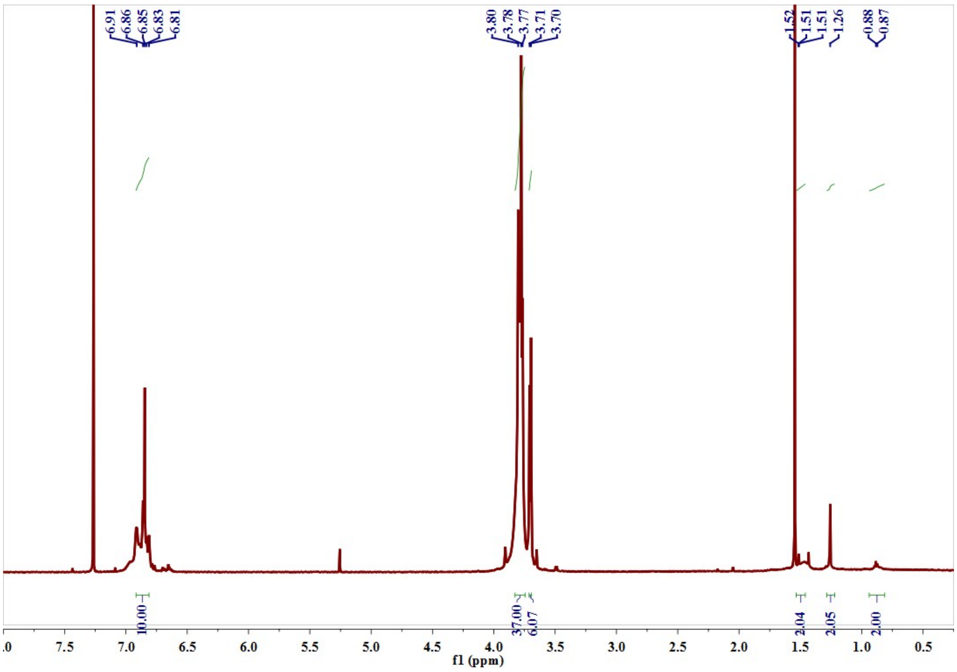


Fig. S3 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of a copillar[5]arene **2**.

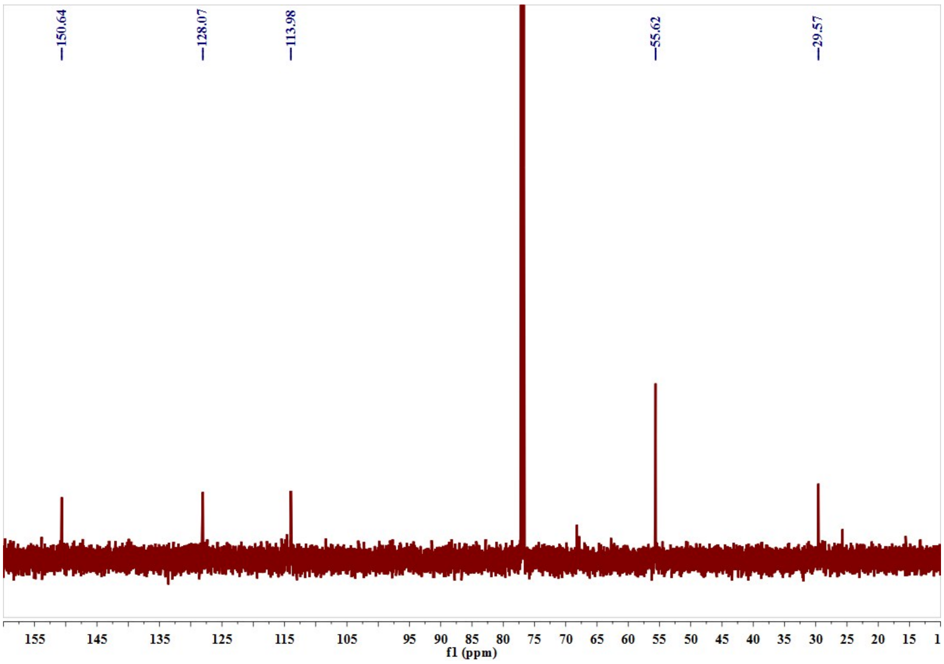
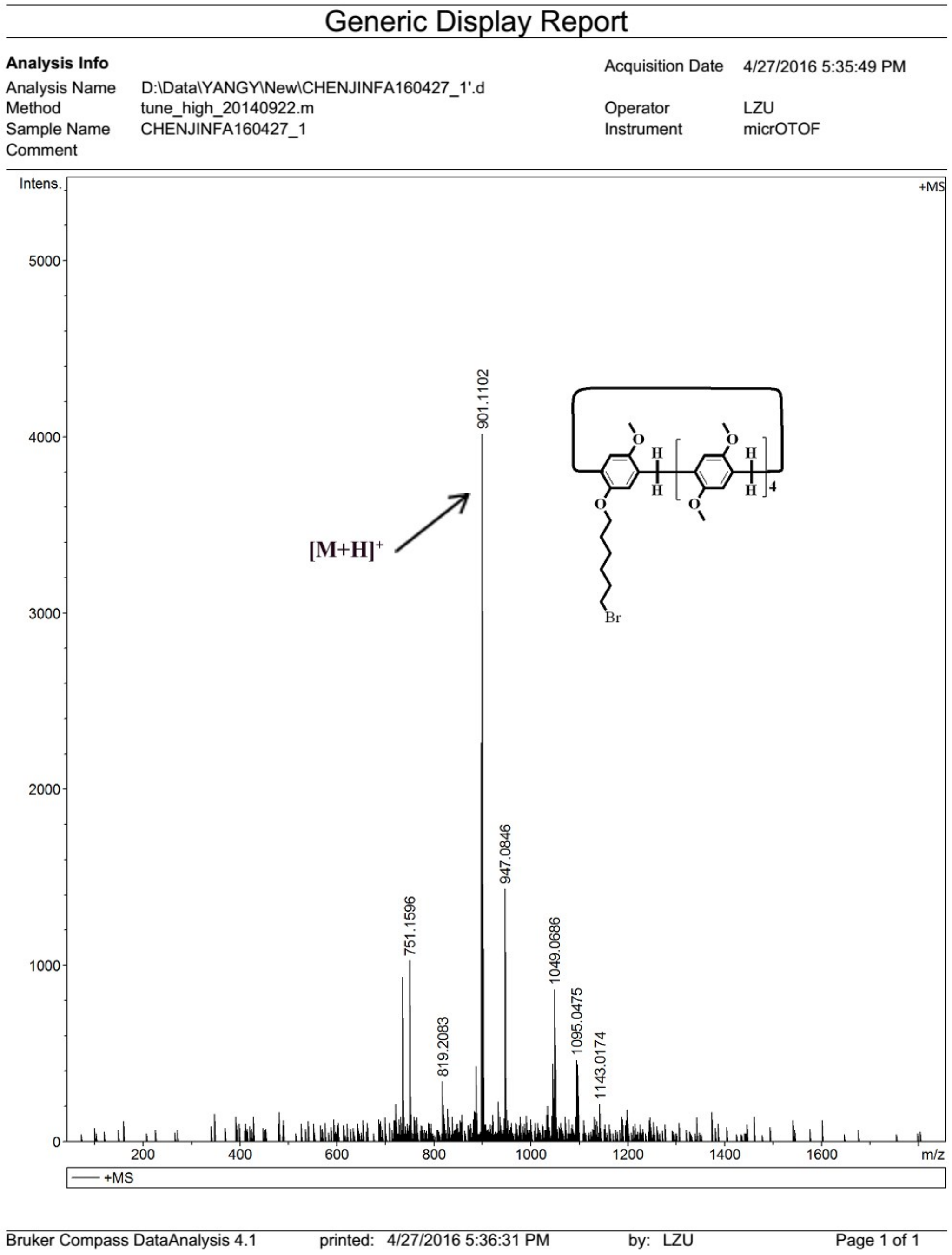


Fig. S4 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of a copillar[5]arene **2**.



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Acquisition Date 4/27/2016 5:35:49 PM
Operator LZU
Instrument micrOTOF

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Fig. S5 Mass data of a copillar[5]arene **2**.

Synthesis of functionalized pillar[5]arene 3: Copillar[5]arene **2** (0.45 g, 0.5 mmol), K_2CO_3 (0.14 g, 1.0 mmol) and ethyl mercaptoacetate (0.3 mL, 2.75 mmol) were added to acetonitrile (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 (0.38 g, 82%). Mp 168-170 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.80–6.75 (m, 10H), 3.79 (s, 2H), 3.65–3.62 (m, 37H), 1.71–1.69 (m, 2H), 1.45 (d, J = 37.0 Hz, 4H), 1.30 (s, 2H), 0.99 (s, 2H), 0.96–0.89 (m, 2H), 0.82 (dd, J = 13.2, 6.0 Hz, 3H), 0.76 (t, J = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.13, 150.32, 150.25, 127.93, 127.89, 113.65 113.61, 68.13, 55.80, 55.79, 55.73, 52.36, 33.16, 32.19, 29.54, 29.33, 28.83, 28.37, 26.80, 25.70, 14.38. ESI−MS m/z: $(M+H)^+$ Calcd for $C_{54}H_{67}O_{12}S$ 939.4348; Found 939.4003.

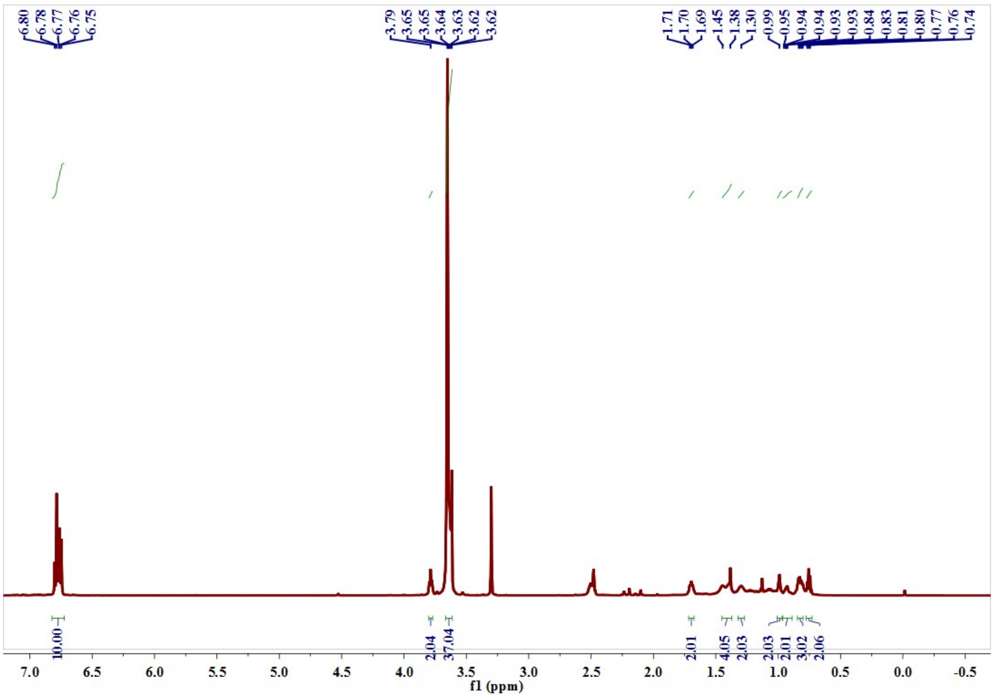


Fig. S6 ^{1}H NMR spectra (600 MHz, DMSO-d_6) of functionalized pillar[5]arene **3**.

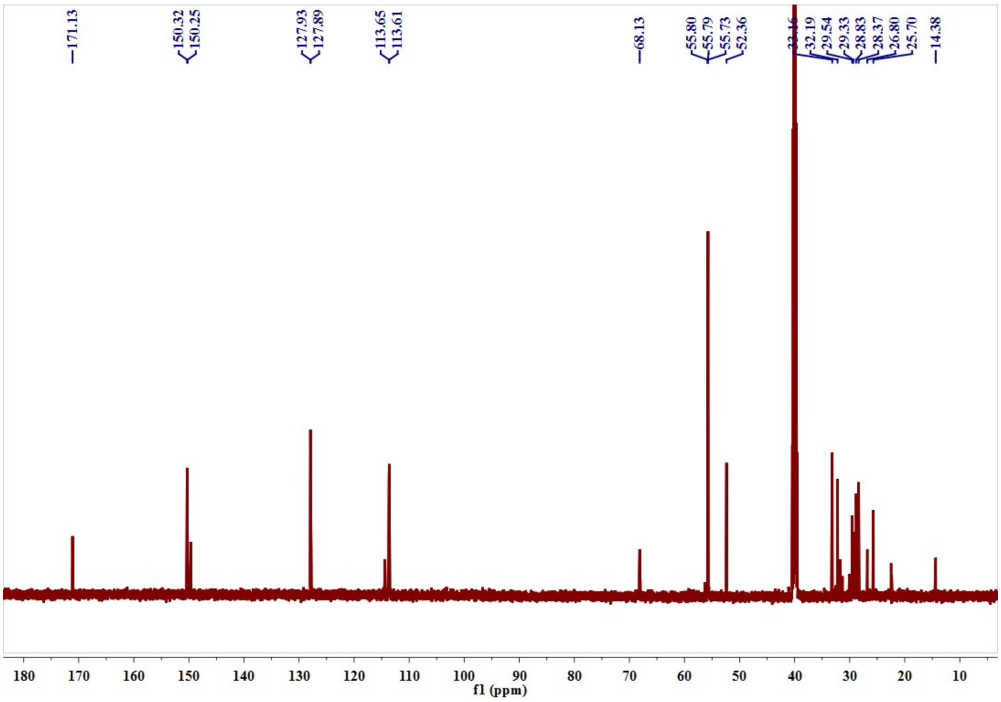
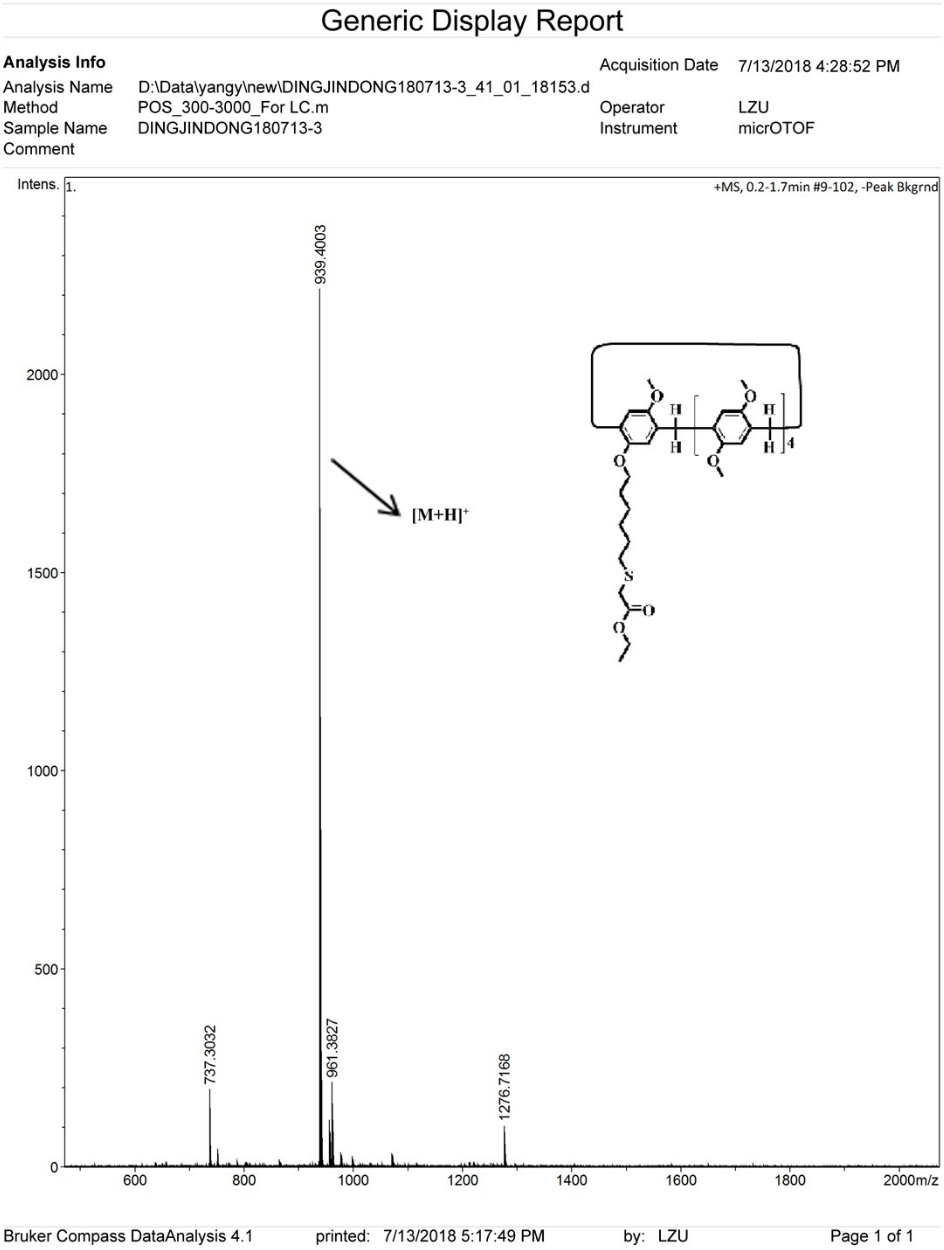


Fig. S7 ^{13}C NMR spectra (151 MHz, DMSO-*d*$_6$) of functionalized pillar[5]arene **3**.



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Operator LZU

Instrument micrOTOF

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Fig. S8 Mass data of functionalized pillar[5]arene **3**.

Synthesis of functionalized pillar[5]arene HP5: Functionalized pillar[5]arene **3** (0.47 g, 0.5 mmol) and hydrazine hydrate (0.3 mL, 6.0 mmol) were added to ethanol (30 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 **HP5** as a white solid (0.43 g, 92 %). Mp 163-165 °C ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 6.77 (d, J = 9.7 Hz, 10H), 4.03 (d, J = 182.3 Hz, 4H), 3.66 (s, 37H), 3.03 (s, 2H), 2.58 (s, 2H), 1.73 (s, 2H), 1.62 – 1.28 (m, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 168.91, 150.42, 150.37, 150.30, 149.73, 127.98, 127.93, 114.56, 113.75, 68.22, 55.90, 55.87, 55.83, 33.08, 32.16, 29.38, 29.08, 28.51, 25.79. ESI−MS m/z: (M+Na)$^+$ Calcd for $C_{52}H_{64}N_2NaO_{11}S_1$ 947.4123; Found 947.4117.

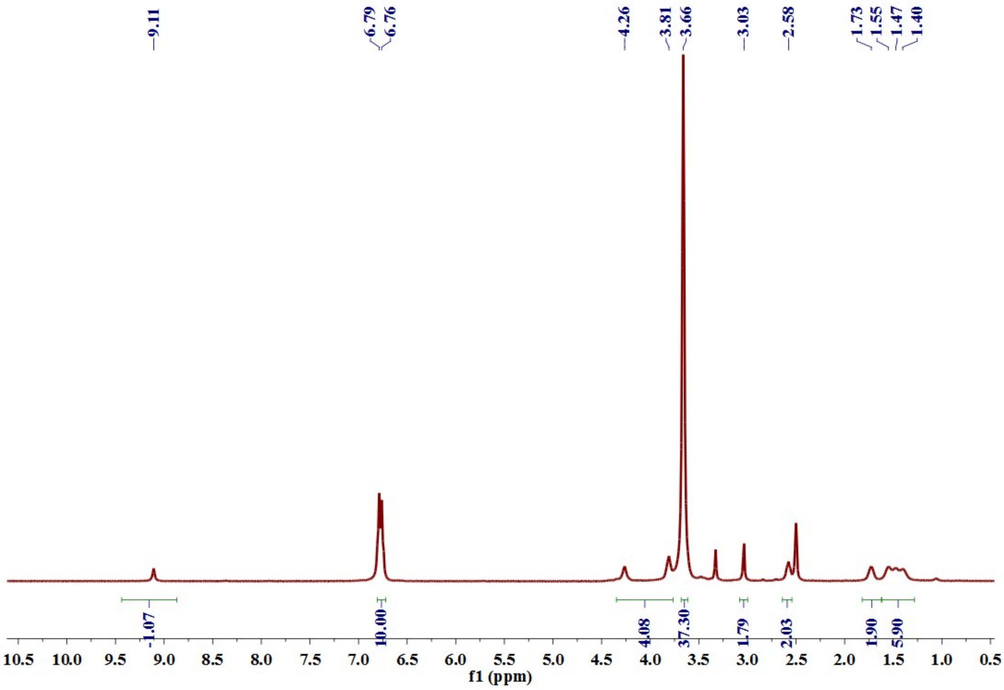

Fig. S9 ^{1}H NMR spectra (600 MHz, DMSO-d_6) of functionalized pillar[5]arene **HP5**.

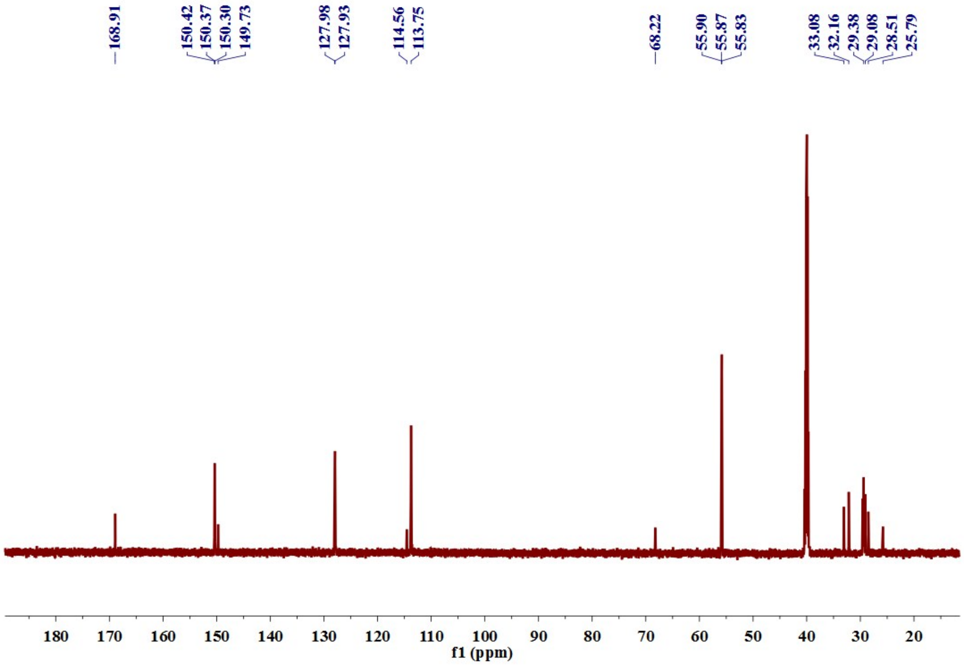

Fig. S10 ^{13}C NMR spectra (151 MHz, DMSO-d_6) of functionalized pillar[5]arene **HP5**.

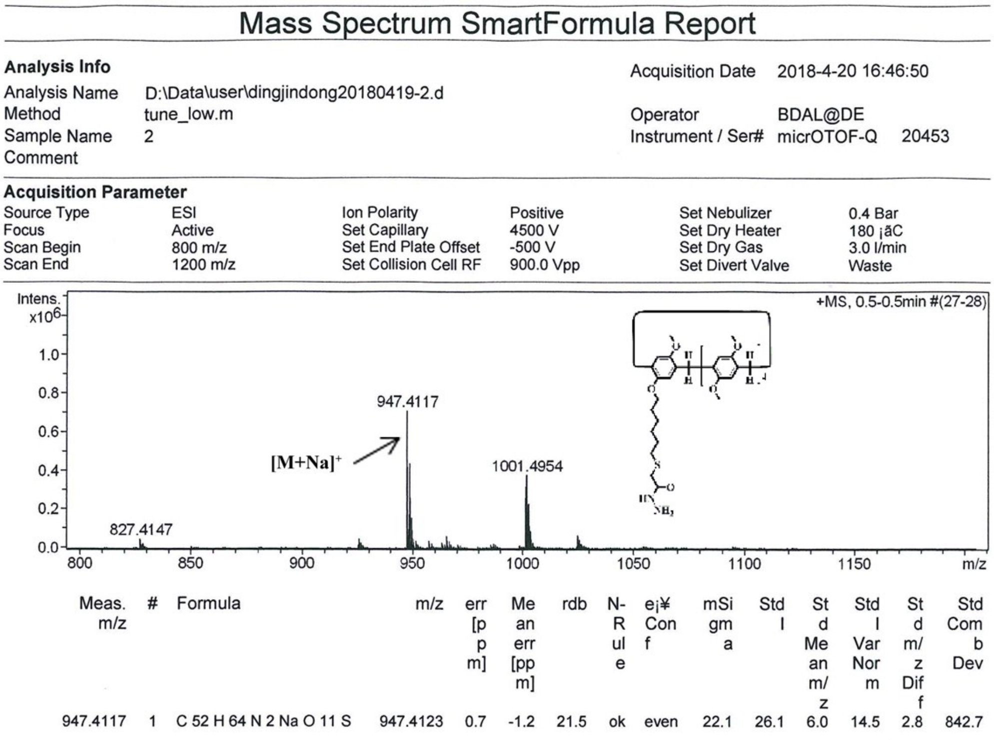

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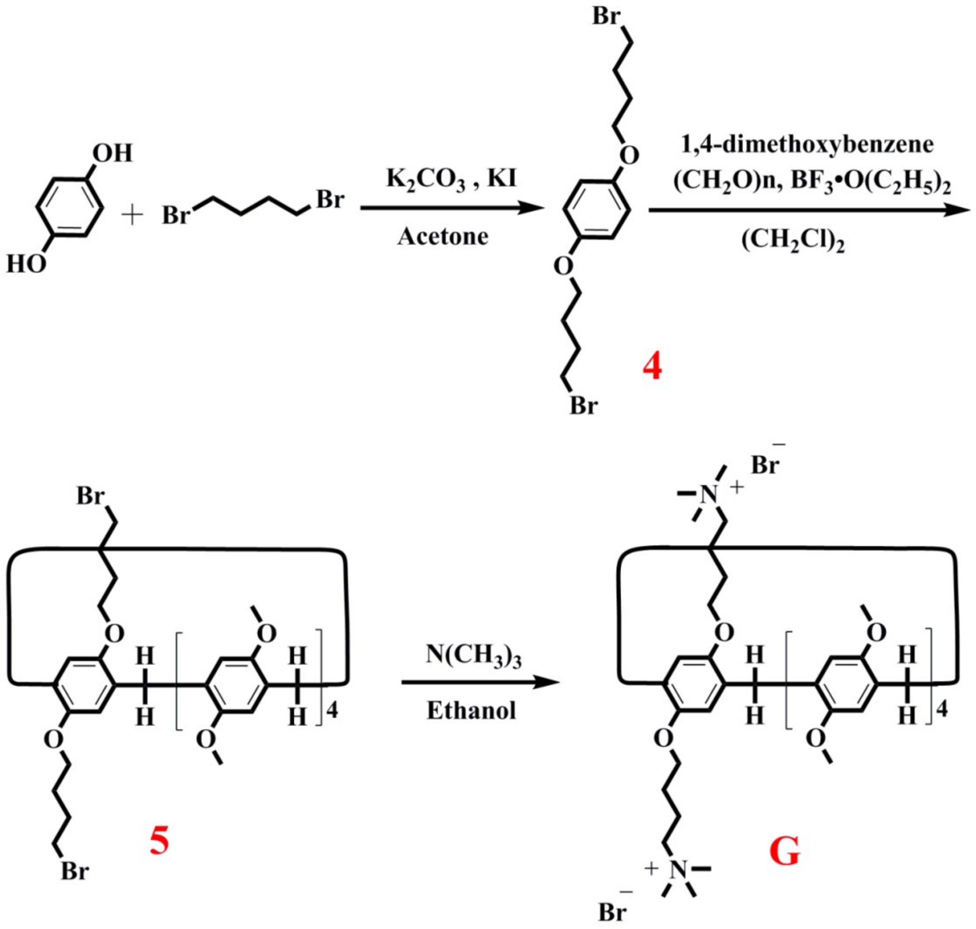
Fig. S11 High resolution mass data of functionalized pillar[5]arene **HP5**.

3. Synthesis of functionalized pillar[5]arene G



Scheme S2 Synthesis of functionalized pillar[5]arene **G**.

Synthesis of 1,4-bis(4-bromobutoxy)benzene 4: Hydroquinone (2.2 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 3 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 = 20 : 1) afforded a white solid (6.3 g, 83%). Mp 83-85°C. ^1H 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). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.07, 115.49, 67.35, 33.52, 29.50, 28.00. ESI−MS m/z: M^+ Calcd for $C_{14}H_{20}O_2Br_2$ 379.9804; Found 379.9799.

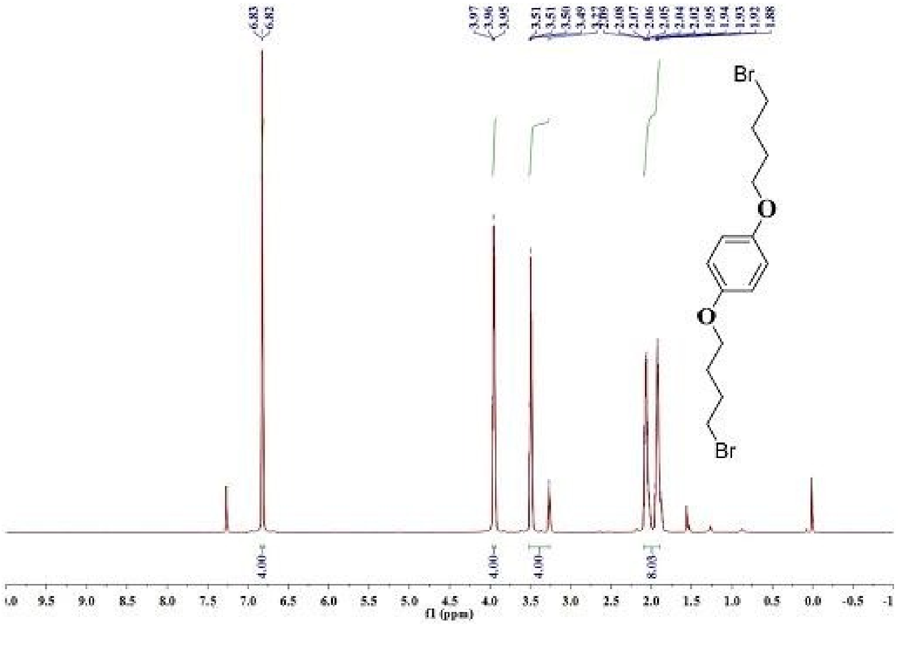


Fig. S12 ^1H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl)benzene **4**.

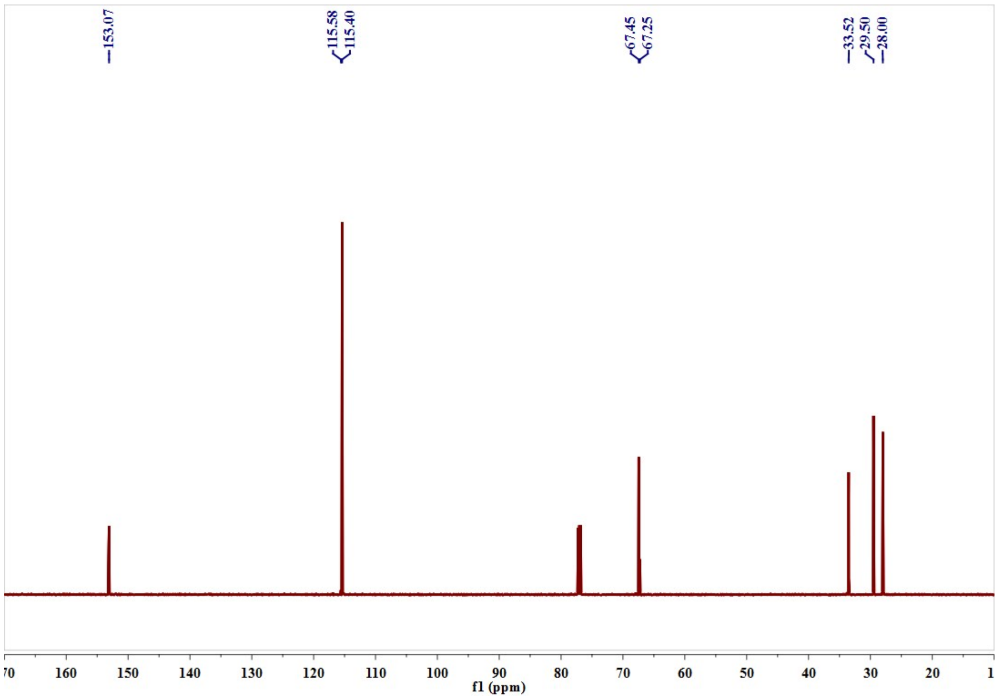


Fig. S13 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl)benzene **4**.

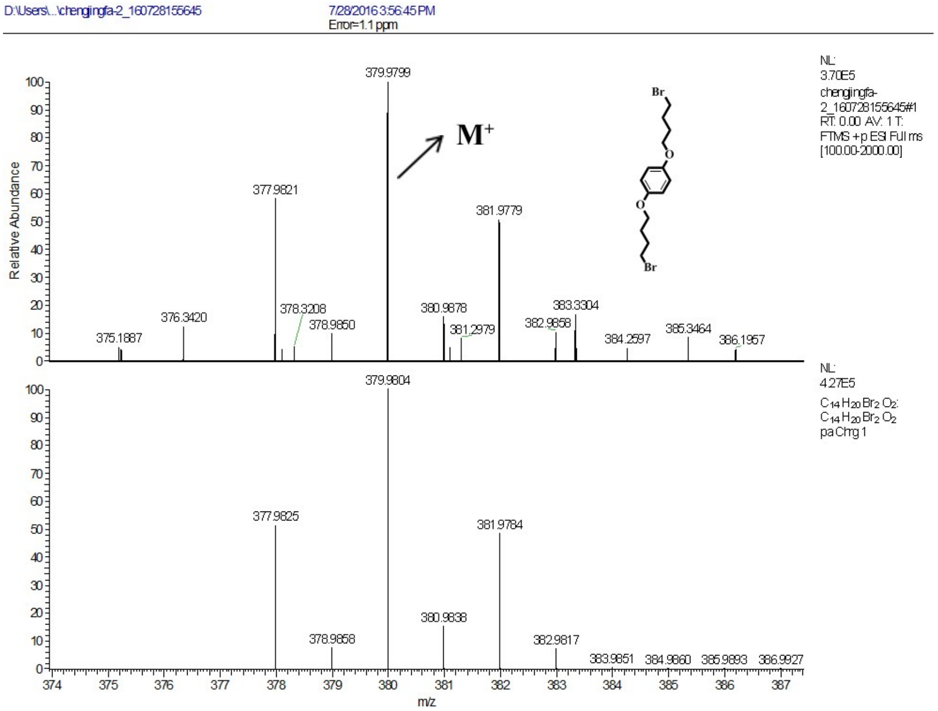


Fig. S14 High resolution mass data of 1,4–bis (4–bromobutoxyl) benzene **4**.

Synthesis of a copillar[5]arene 5: To a solution of 1,4-bis(4-bromobutoxy)benzene (1.9 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (160 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 1 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 **5** (1.58 g, 32%) 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 150.80, 150.75, 150.70, 150.58, 149.84, 128.44, 128.30, 128.08, 114.89, 114.15, 113.92, 113.71, 67.32, 55.95, 55.76, 55.70, 33.34, 30.55, 29.75, 29.48, 29.19, 28.32. ESI−MS m/z: $(M+NH_4)^+$ Calcd for $C_{51}H_{64}O_{10}Br_2N$ 1010.2871; Found 1010.2878.

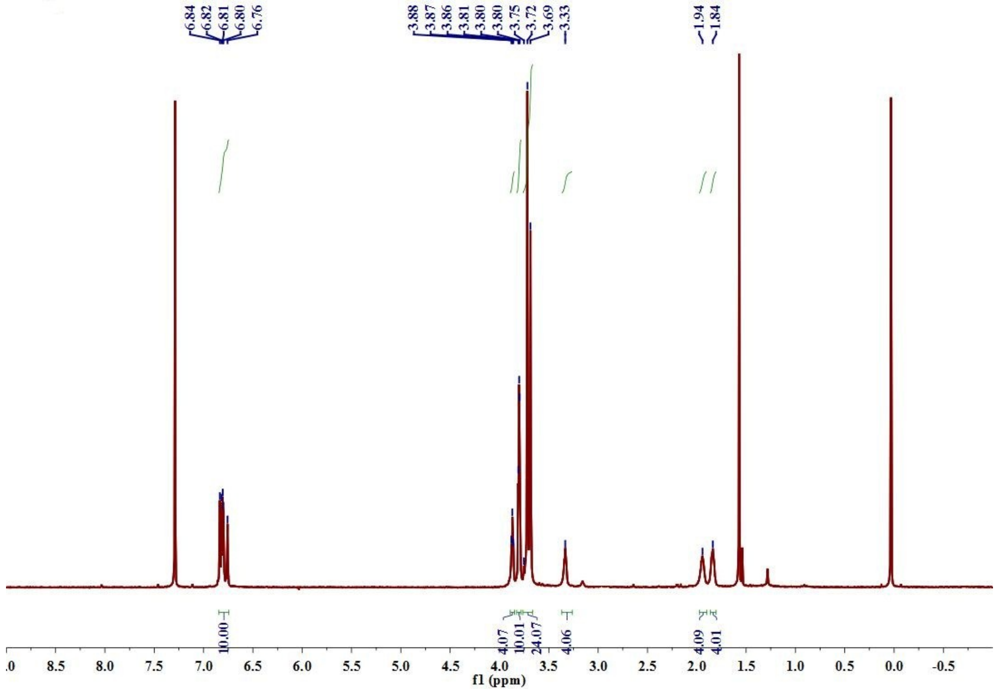


Fig. S15 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of copillar[5]arene **5**.

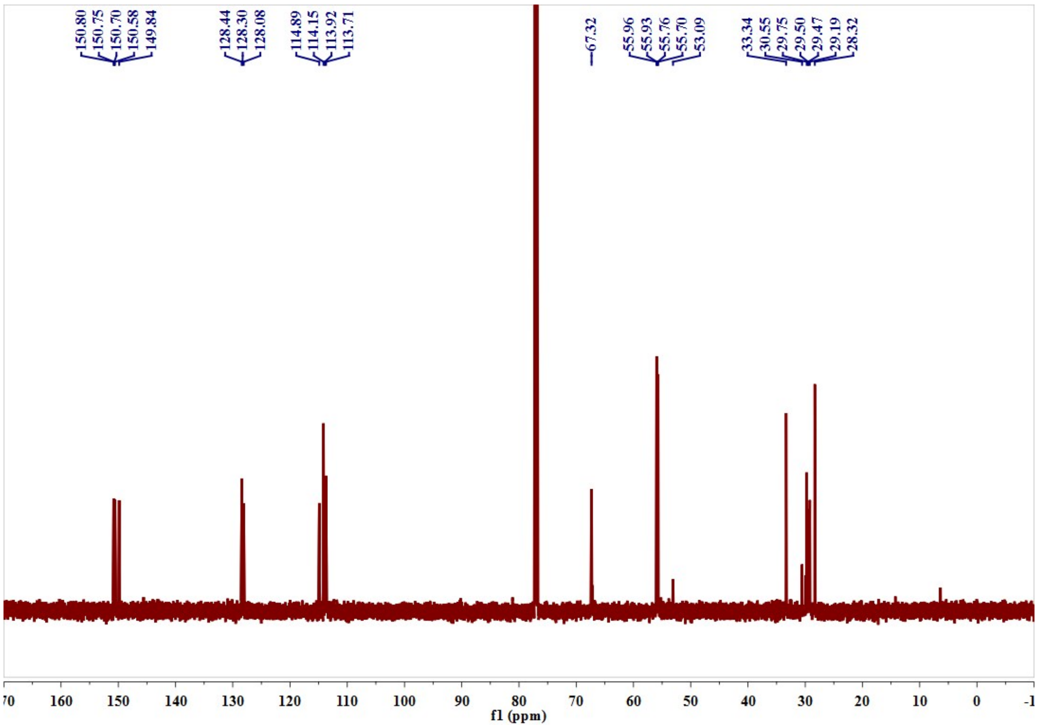


Fig. S16 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of copillar[5]arene **5**.

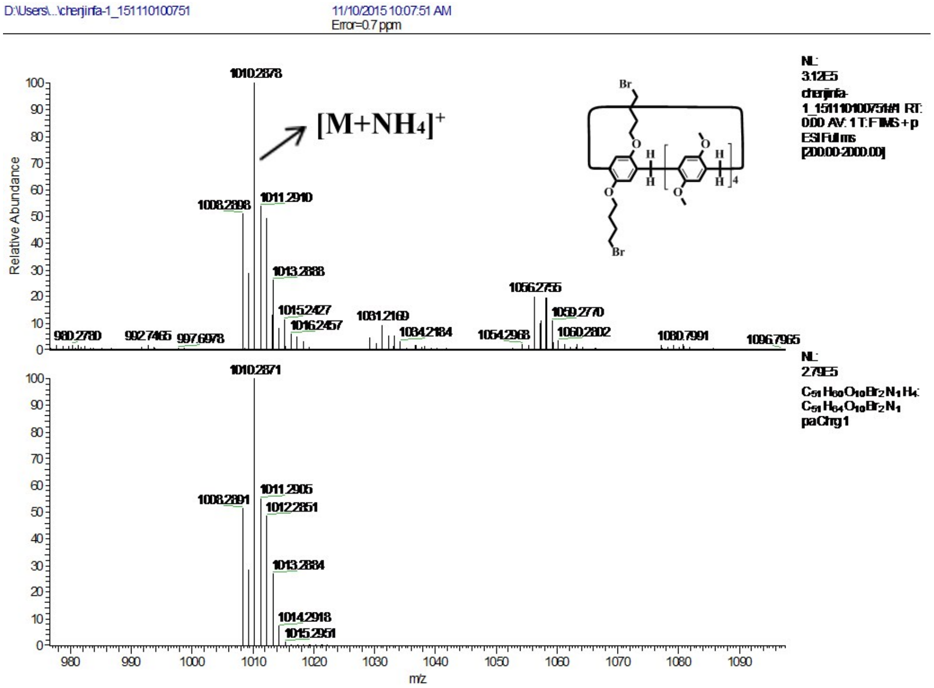


Fig. S17 High resolution mass data of copillar[5]arene **5**.

Synthesis of functionalized pillar[5]arene G: Copillar[5]arene **5** (0.5 g, 0.5 mmol) and trimethylamine (33 % in ethanol, 1.0 mL, 3.7 mmol) were added to ethanol (80 mL). The solution was refluxed overnight. The solvent was removed by rotary evaporation to afford the crude product, which was washed by diethyl ether to obtain **G** (0.52 g, 93 %) as a white solid. Mp 176-178 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.78 – 6.74 (m, 10H), 3.86 (d, J = 64.4 Hz, 4H), 3.65 (dd, J = 15.0, 5.4 Hz, 34H), 3.43 – 3.36 (m,4H), 3.08 (s, 18H), 1.92 – 1.73 (m, 8H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 150.41, 150.35, 149.62, 128.23, 128.06, 128.01, 127.91, 113.95, 113.84, 67.58, 65.46, 56.09, 56.03, 55.98, 55.96, 52.59, 29.45, 29.40, 26.71, 19.70. ESI-MS m/z: $(M\text{-}2Br)^{2+}/2$ Calcd for $C_{57}H_{78}N_2O_{10}$ 475.2823; Found 475.2837.

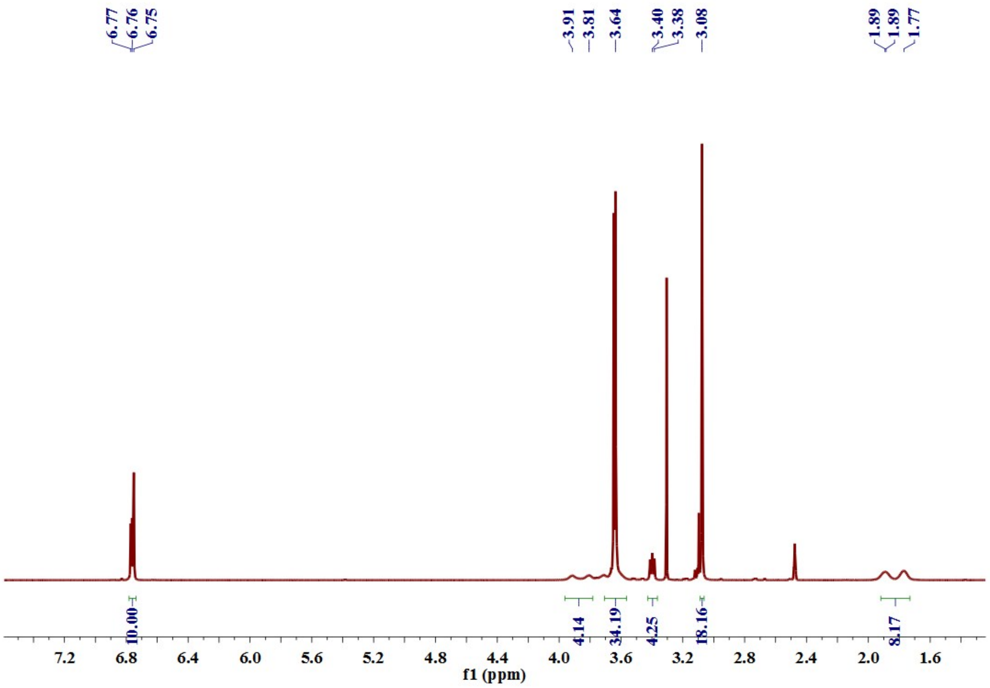


Fig. S18 ^{1}H NMR spectra(600 MHz, DMSO-d_6) of functionalized pillar[5]arene **G**.

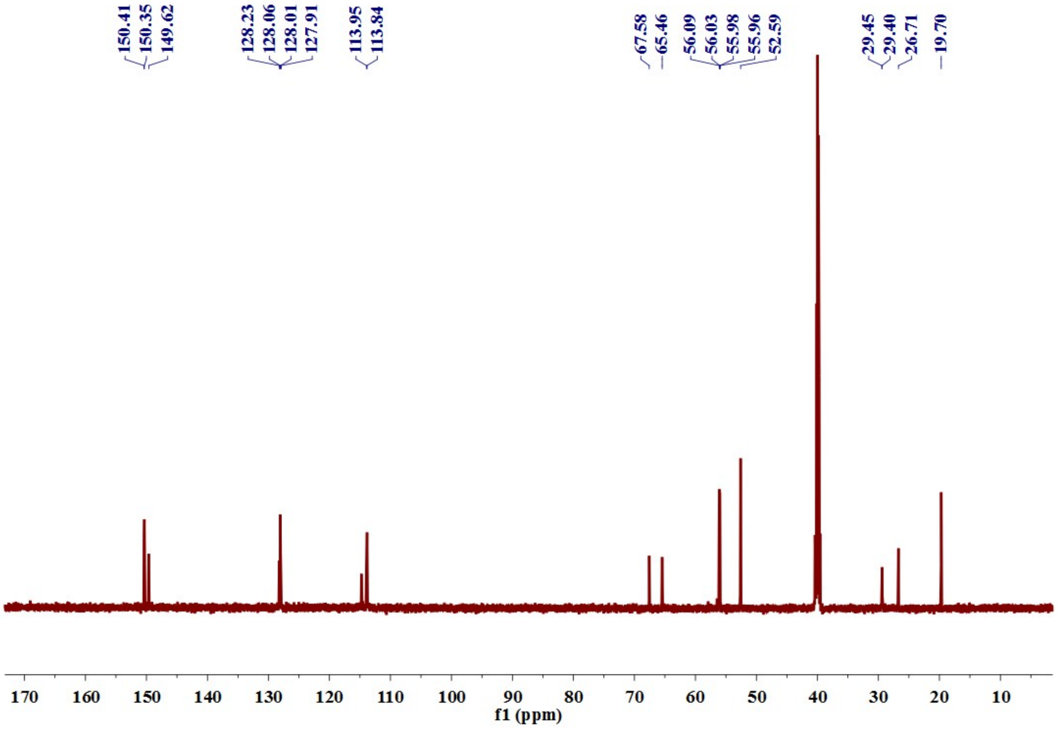
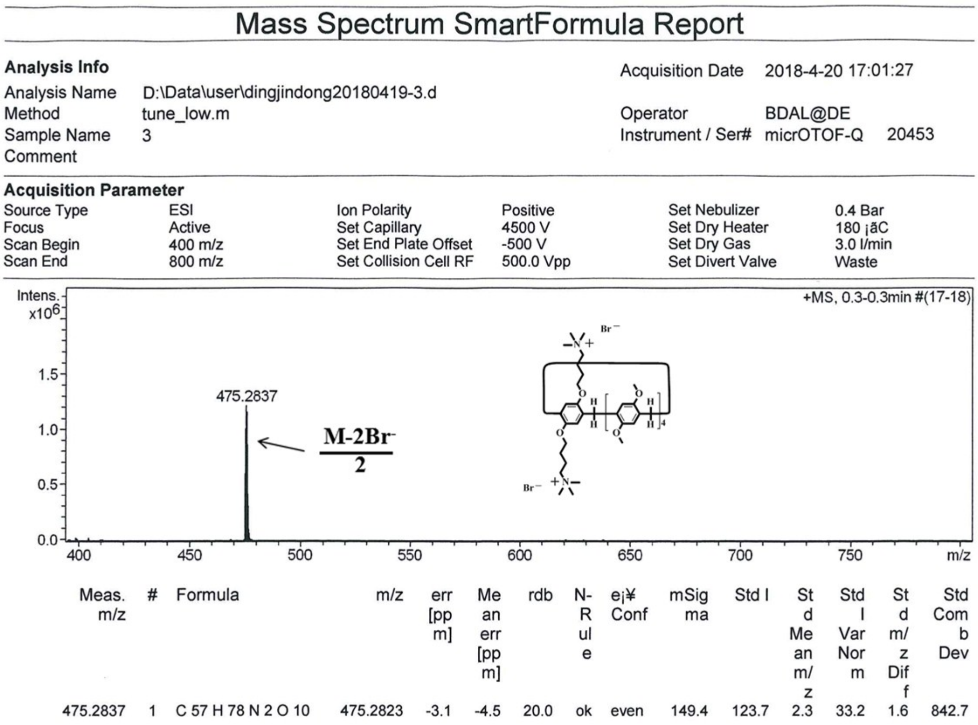


Fig. S19 ^{13}C NMR spectra(151 MHz, DMSO-d_6) of functionalized pillar[5]arene **G**.



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Scan End	800 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
475.2837	1	C 57 H 78 N 2 O 10	475.2823	-3.1	-4.5	20.0	ok	even	149.4	123.7	2.3	33.2	1.6	842.7

Fig. S20 High resolution mass data of copillar[5]arene **G**.

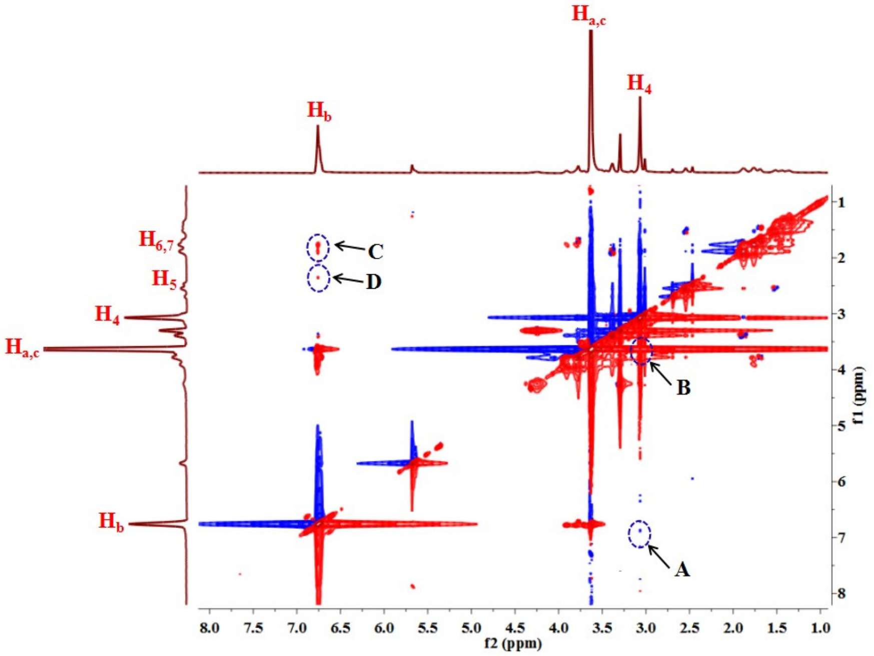


Fig. S21 2D NOESY NMR spectrum (600 MHz, 298 K) of 20.0 mM

HP5 and 10.0 mM **G** in DMSO-d_6 solution.

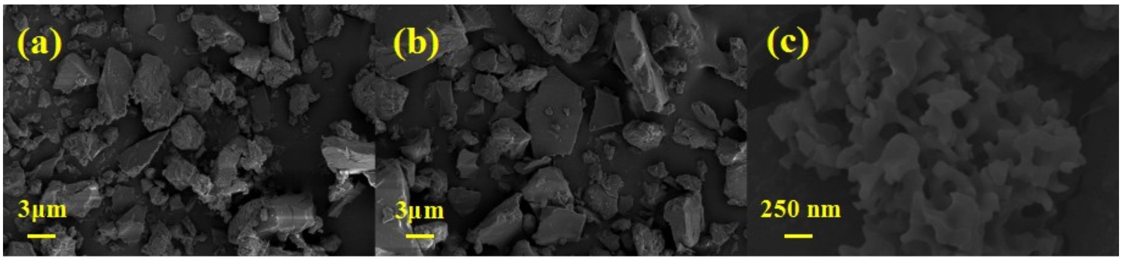


Fig. S22 Representative SEM images showing the morphology of (a) powder **HP5**; (b) powder **G**; (c) xerogel **HP5$_2$·Zn·G**.

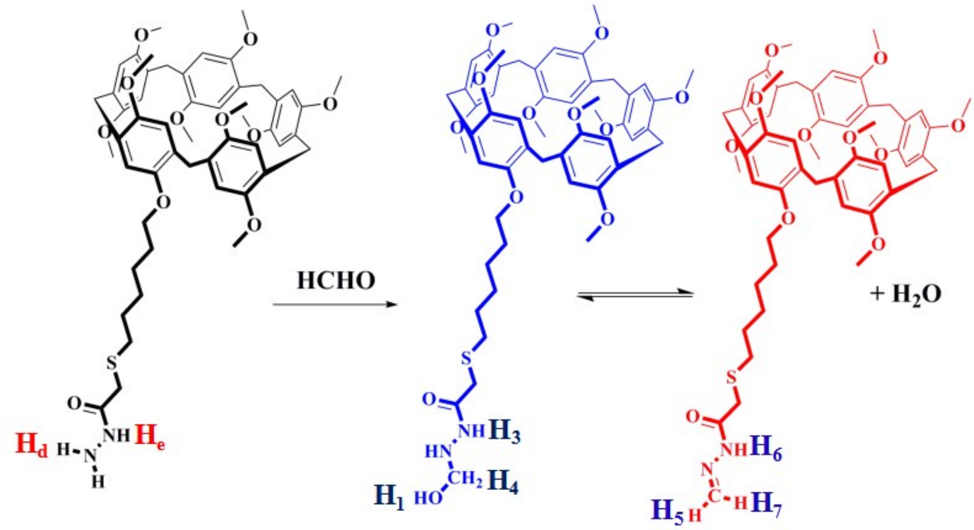


Fig.S23 The proposed stimuli responsive mechanism of **HP5$_2$·Zn·G** for HCHO.

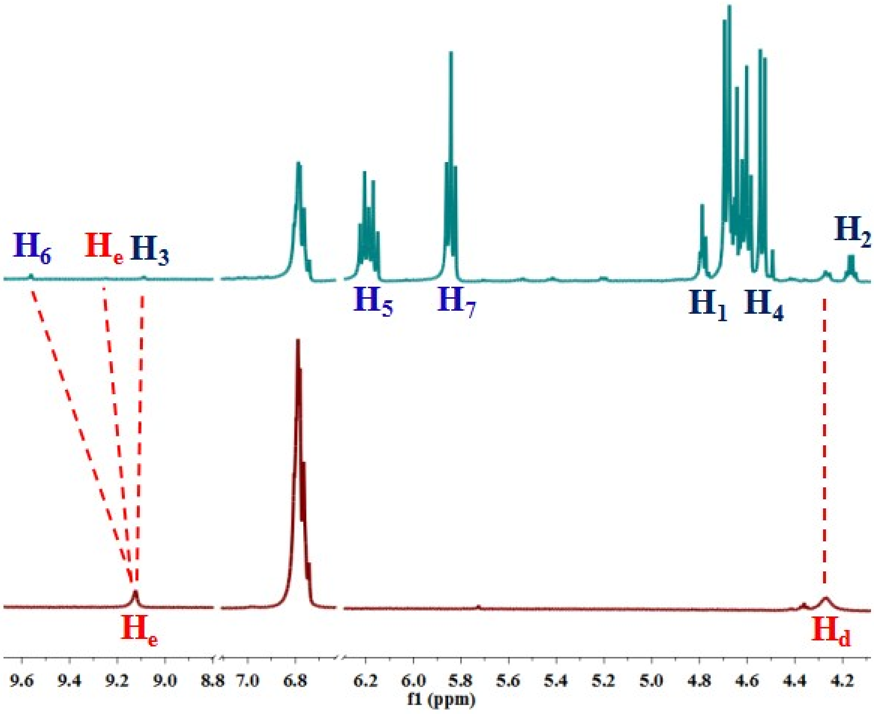


Fig. S24 Partial ^{1}H NMR spectra (600 MHz, 298 K) of (a) 20 mM **HP5$_2$·Zn·G**; (b) 20 mM **HP5$_2$·Zn·G** and HCHO.

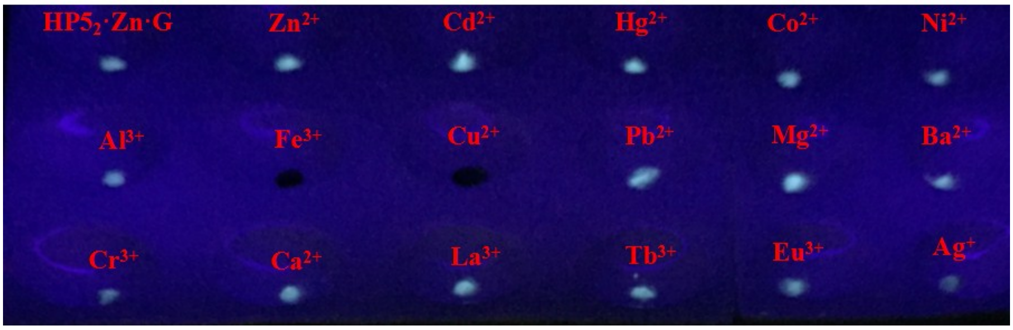


Fig. S25 Fluorescence responses of the metallosupramolecular polypseudorotaxane gel to the presence of various cations.

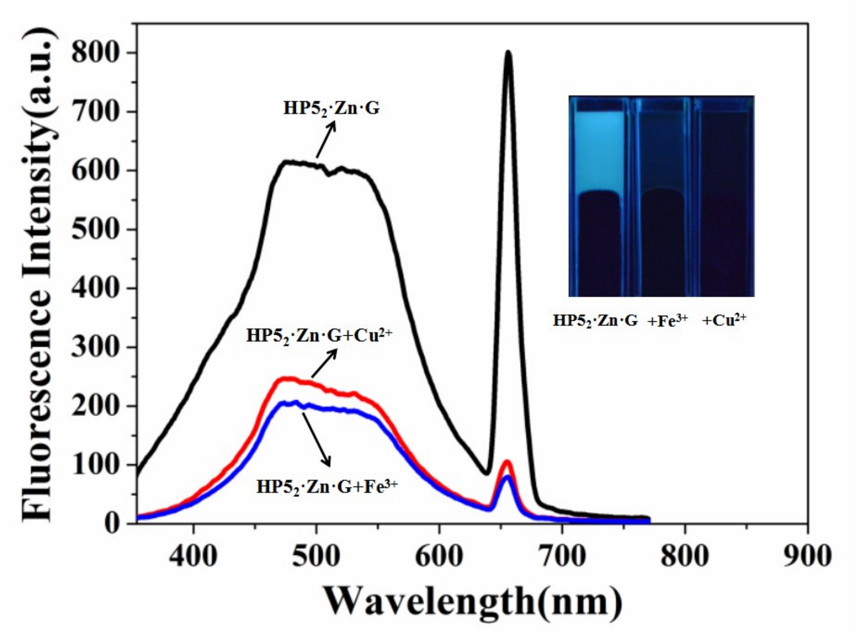


Fig. S26 Fluorescence spectra response of **HP5$_2$·Zn·G** (in the gelated state) upon addition of 1 equiv. of Fe^{3+} and Cu^{2+} (λ_{ex} = 330 nm).

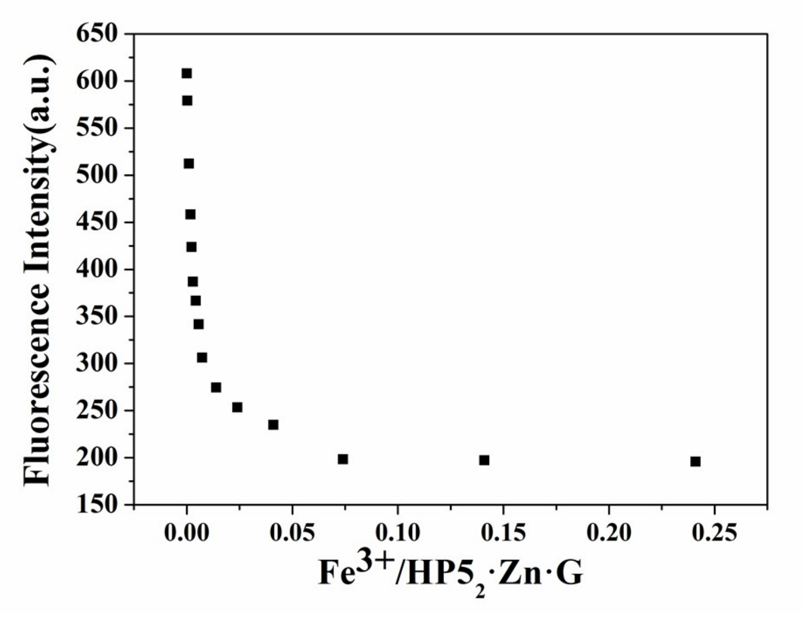
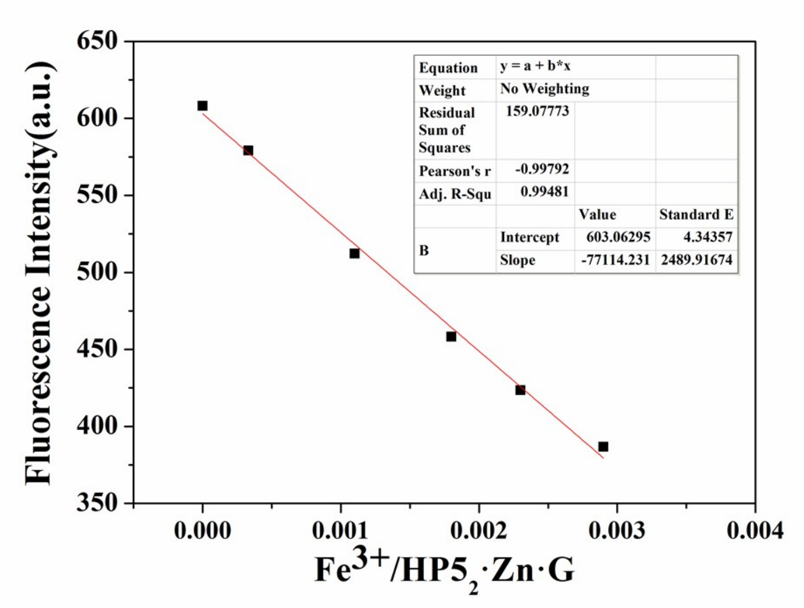


Fig. S27 A plot of emission at 503 nm versus number of equivalents of Fe^{3+}.

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	159.07773		
Pearson's r	-0.99792		
Adj. R-Squ	0.99481		
		Value	Standard E
B	Intercept	603.06295	4.34357
	Slope	-77114.231	2489.91674

Fig. S28 The photograph of the linear range.

Linear Equation: Y=-77144.231X+603.06295 $R^2=0.99481$

$S=77144.231\times10^6$ $\delta=\sqrt{\frac{\sum(X_i-\overline{X})^2}{n-1}}=22.97(n=20)$ K=3

LOD=K×δ/S=8.93×10^{-10} M

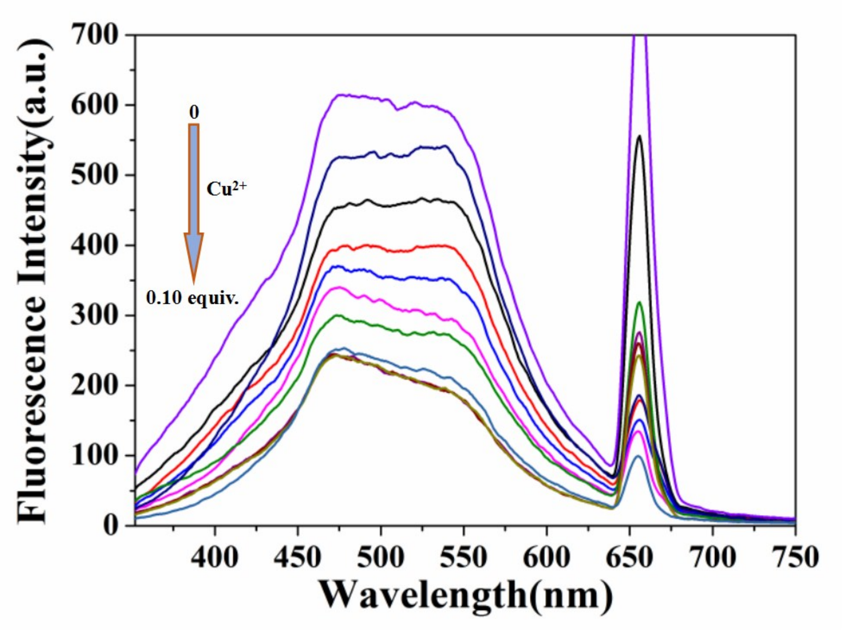


Fig. S29 Fluorescence spectra of **$HP5_2$·Zn·G** (in the gelated state) with increasing concentration of Cu^{2+} (λ_{ex} = 330 nm).

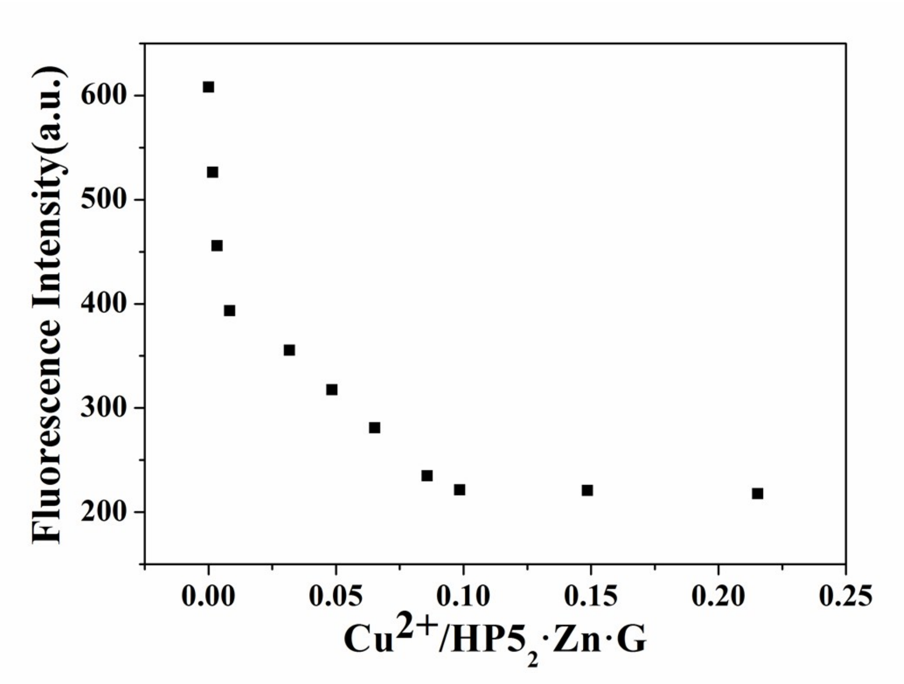


Fig. S30 A plot of emission at 503 nm versus number of equivalents of Cu^{2+}.

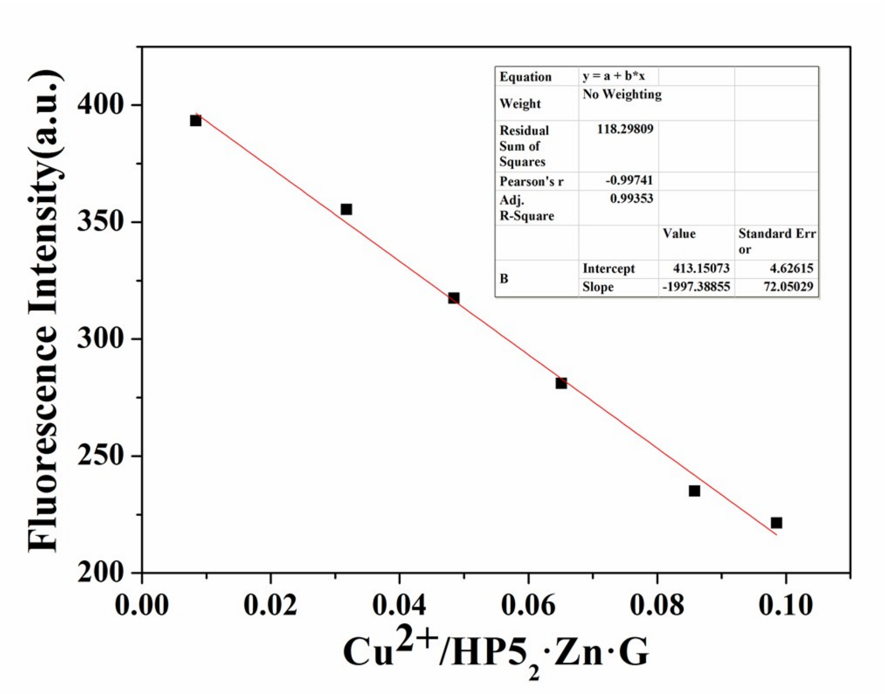


Fig. S31 The photograph of the linear range.

Linear Equation: Y=-1997.38855X+413.15073 R^2=0.99353

S=1997.38855×10^6 $\delta=\sqrt{\frac{\sum(X_i-\overline{X})^2}{n-1}}=30.40(n=20)$ K=3

LOD =K×δ/S=4.57×10^{-8} M

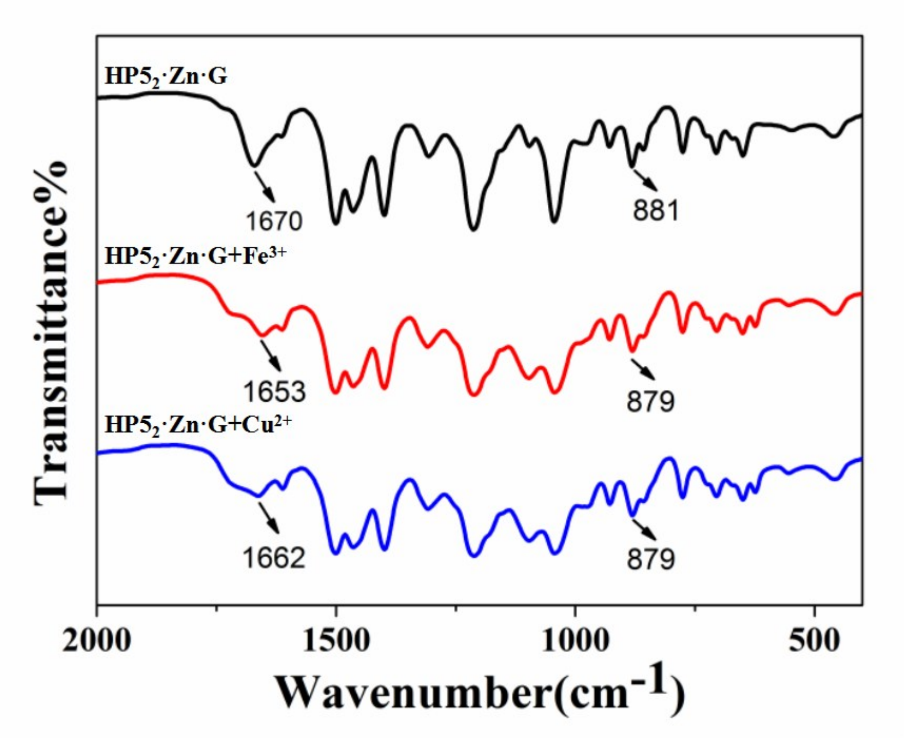


Fig. S32 FT-IR spectra of xerogel **$HP5_2$·Zn·G**, xerogel **$HP5_2$·Zn·G**+Fe^{3+} and xerogel **$HP5_2$·Zn·G**+Cu^{2+}.

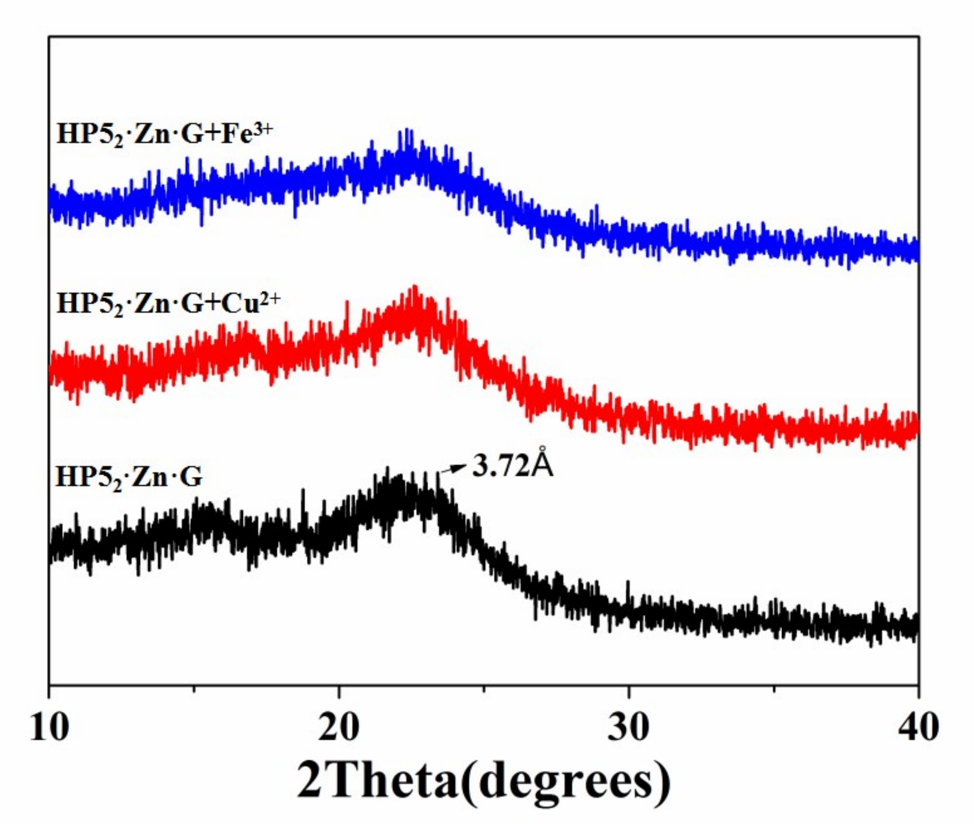


Fig. S33 Powder XRD patterns of xerogel **HP5$_2$·Zn·G**, xerogel **HP5$_2$·Zn·G**+Fe^{3+} and xerogel **HP5$_2$·Zn·G**+Cu^{2+}.

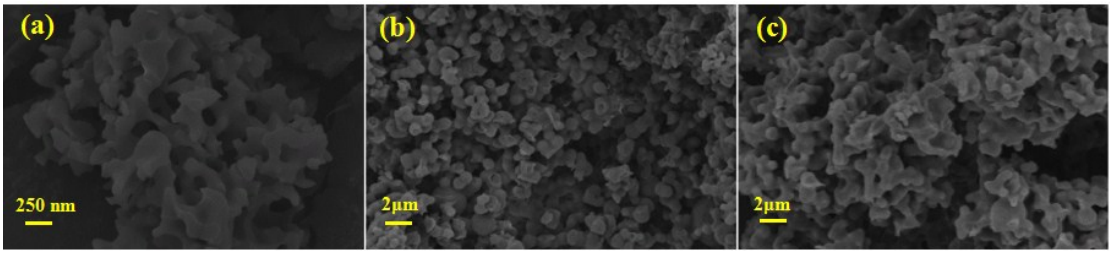


Fig. S34 Representative SEM images showing the morphology of (a) **HP5$_2$·Zn·G** gel, (b) **HP5$_2$·Zn·G** gel treated with Fe^{3+}, (c) **HP5$_2$·Zn·G** gel treated with Cu^{2+}.

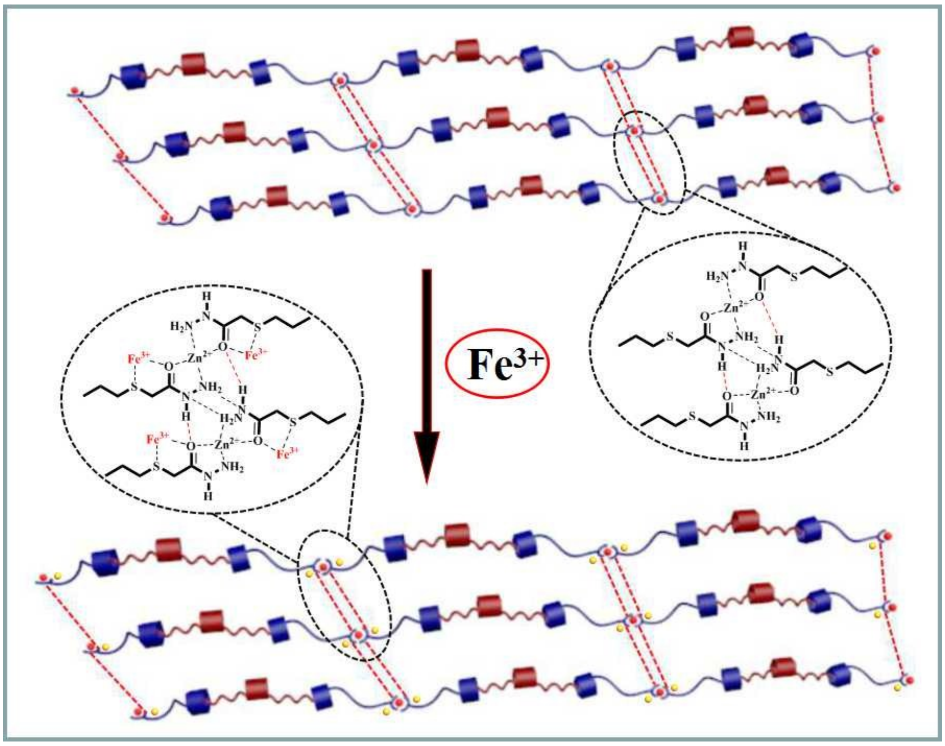


Fig. S35 A possible sensing mechanism of the **HP5$_2$·Zn·G** gel to Fe^{3+} .

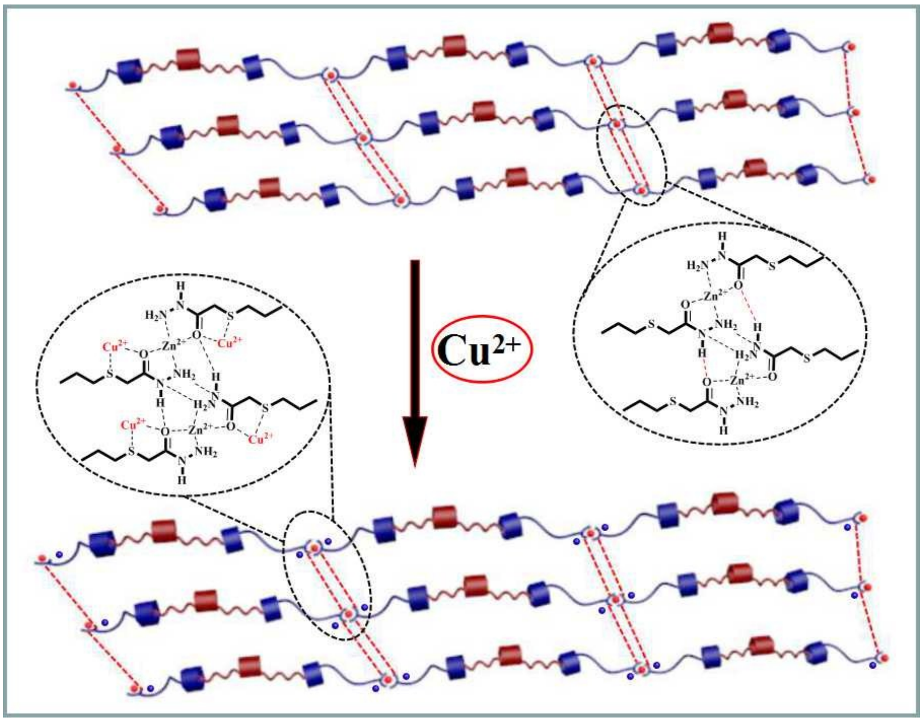


Fig. S36 A possible sensing mechanism of the $\mathbf{HP5_2 \cdot Zn \cdot G}$ gel to Cu^{2+}.

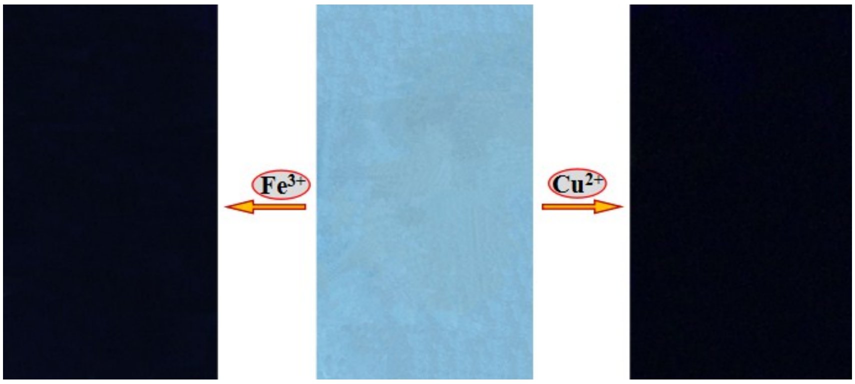


Fig. S37 Photos of the thin film based on $\mathbf{HP5_2 \cdot Zn \cdot G}$ gel utilized to sense Fe^{3+} and Cu^{2+} cations under irradiation at 365 nm using a UV lamp.