Supporting Information


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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, $\delta$ 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 CuKα radiation ($\lambda = 1.54073$ 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.


**Synthesis of compound 1:** In a 500 mL round-bottom flask, 4-methoxyphenol (2.48 g, 20.0 mmol), K$_2$CO$_3$ (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$_2$Cl$_2$. 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-$d_6$) $\delta$ 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$_2$Cl$_2$ and washed twice with H$_2$O. The organic layer was dried over anhydrous Na$_2$SO$_4$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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.
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$_2$CO$_3$ (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 CH₂Cl₂. Column chromatography (silica gel; petroleum ether : CH₂Cl₂ = 20 : 1) afforded a white solid (0.38 g, 82%). Mp 168-170 °C. ¹H NMR (600 MHz, DMSO-d₆) 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). ¹³C NMR (151 MHz, DMSO-d₆) 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)+ Caled for C₅₄H₆₇O₁₂S 939.4348; Found 939.4003.

**Fig. S6** ¹H NMR spectra (600 MHz, DMSO-d₆) of functionalized pillar[5]arene 3.
**Fig. S7** $^{13}$C NMR spectra (151 MHz, DMSO-$d_6$) of functionalized pillar[5]arene 3.
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 ¹H NMR (400 MHz, DMSO-
²H) 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).
¹³C NMR (151 MHz, DMSO-²H) 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
C₅₂H₆₄N₂NaO₁₁S₁ 947.4123; Found 947.4117.

Fig. S9 ¹H NMR spectra (600 MHz, DMSO-²H) of functionalized
Fig. S10 $^{13}$C NMR spectra (151 MHz, DMSO-$d_6$) of functionalized pillar[5]arene HP5.

**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), \( \text{K}_2\text{CO}_3 \) (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 CH₂Cl₂. Column chromatography (silica gel; petroleum ether : CH₂Cl₂ = 20 : 1) afforded a white solid (6.3 g, 83%). Mp 83-85°C. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (151 MHz, CDCl₃) δ 153.07, 115.49, 67.35, 33.52, 29.50, 28.00. ESI–MS m/z: M⁺ Calcd for C₁₄H₂₀O₂Br₂ 379.9804; Found 379.9799.

![Fig. S12 ¹H NMR spectra (600 MHz, CDCl₃) of 1,4–bis (4–bromobutoxy)benzene 4.](image-url)
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 CH₂Cl₂ and washed twice with H₂O. The organic layer was dried over anhydrous Na₂SO₄ 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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (151 MHz, CDCl₃) 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+NH₄)⁺ Calcd for C₅₁H₆₄O₁₀Br₂N 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-$d_6$) $\delta$ 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-$d_6$) $\delta$ 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-2Br)$^{2+}$/2 Calcd for C$_{57}$H$_{78}$N$_2$O$_{10}$ 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.
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-\textit{d}_6 solution.

**Fig. S22** Representative SEM images showing the morphology of (a) powder **HP5**; (b) powder **G**; (c) xerogel **HP5\textsubscript{2}·Zn·G**.

**Fig. S23** The proposed stimuli responsive mechanism of **HP5\textsubscript{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 $\text{HP5}_2\cdot\text{Zn} \cdot \text{G}$ (in the gelated state) upon addition of 1 equiv. of Fe$^{3+}$ and Cu$^{2+}$ ($\lambda_{ex} = 330$ 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 $3\delta$ way to figure out the detection limit. The process of the analysis as follows.

**Fig. S28** The photograph of the linear range.

Linear Equation: $Y=-77144.231X+603.06295$ \hspace{1cm} $R^2=0.99481$

$$S=77144.231 \times 10^6 \quad \delta = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n-1}} = 22.97 (n=20) \quad K=3$$

$$LOD=K\times\delta/S=8.93 \times 10^{-10} \text{ M}$$
**Fig. S29** Fluorescence spectra of HP$_5$$_2$·Zn·G (in the gelated state) with increasing concentration of Cu$^{2+}$ ($\lambda_{ex} = 330$ 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: $Y = -1997.38855X + 413.15073 \quad R^2 = 0.99353$

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

$LOD = K \times \delta / S = 4.57 \times 10^{-8} \text{ M}$
Fig. S32 FT-IR spectra of xerogel $\text{HP5}_2 \cdot \text{Zn} \cdot \text{G}$, xerogel $\text{HP5}_2 \cdot \text{Zn} \cdot \text{G} + \text{Fe}^{3+}$ and xerogel $\text{HP5}_2 \cdot \text{Zn} \cdot \text{G} + \text{Cu}^{2+}$. 
**Fig. S33** Powder XRD patterns of xerogel $\text{HP5}_2\cdot\text{Zn}\cdot\text{G}$, xerogel $\text{HP5}_2\cdot\text{Zn}\cdot\text{G}+\text{Fe}^{3+}$ and xerogel $\text{HP5}_2\cdot\text{Zn}\cdot\text{G}+\text{Cu}^{2+}$.

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

**Fig. S35** A possible sensing mechanism of the $\text{HP5}_2\cdot\text{Zn}\cdot\text{G}$ gel to Fe$^{3+}$. 
Fig. S36 A possible sensing mechanism of the HP5₂·Zn·G gel to Cu²⁺.

Fig. S37 Photos of the thin film based on HP5₂·Zn·G gel utilized to sense Fe³⁺ and Cu²⁺ cations under irradiation at 365 nm using a UV lamp.