Supporting Information

Pillar[5]arene-Based Multifunctional Supramolecular Hydrogel: Multistimuli Responsiveness, Self-Healing, Fluorescence Sensing, and Conductivity

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1. Materials and methods

1,4-dimethoxybenzene, boron trifluoride ethvl ether complex, 1,4-dibromobutane and trimethylamine were reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl₂. ¹H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ¹³C NMR spectra were recorded on a Mercury-600BB spectrometer at MHz. Chemical shifts are reported in ppm downfield from 151 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 morphologies and sizes of the polymer 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 ($\lambda = 1.54073$ Å). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The electrical conductivity of hybrid hydrogels was tested by the fourprobe method using a sourcemeter (SX1934(SZ-82), China).

2. Synthesis of functionalized pillar[5]arene BTAP5



Scheme S1 Synthesis of functionalized pillar[5]arene BTAP5.

Synthesis of 1,4–bis(4–bromobutoxy)benzene 1: Hydroquinone (2.3 g, 20.0 mmol), K₂CO₃ (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 2 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 = 10 : 1) afforded a white solid (6.0 g, 80%). 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 (s), 115.49 (d, *J* = 28.1 Hz), 67.35 (d, *J* = 30.2 Hz), 33.52 (s), 29.50 (s), 28.00 (s). ESI–MS m/z: M⁺ Calcd for C₁₄H₂₀O₂Br₂ 379.9804; Found 379.9799.



Fig. S1 ¹H NMR spectra (600 MHz, CDCl₃) of 1,4–bis (4–bromobutoxyl) benzene **1**.



Fig. S2 ¹³C NMR spectra(151 MHz, CDCl₃) of 1,4–bis (4–bromobutoxyl) benzene **1**.



Fig. S3 High resolution mass data 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 (1.9 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 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 2(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 (s), 150.75 (s), 150.70 (s), 150.58 (s), 149.84 (s), 128.44 (s), 128.30 (s), 128.08 (s), 114.89 (s), 114.15 (s), 113.92 (s), 113.71 (s), 67.32 (s), 55.95 (d, J = 3.6Hz), 55.76 (s), 55.70 (s), 33.34 (s), 30.55 (s), 29.75 (s), 29.48 (d, J = 5.2 Hz), 29.19 (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. S4 ¹H NMR spectra(600 MHz, CDCl₃) of a copillar[5]arene **2**.





Fig. S6 High resolution mass data of a copillar[5]arene 2.

Synthesis of functionalized pillar[5]arene BTAP5: Copillar[5]arene 2 (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 **BTAP5**(0.52 g, 93 %) as a white solid. Mp 176–178 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 6.76 (dd, *J* = 7.2, 2.2 Hz, 10H), 3.85 (s, 4H), 3.65 (t, *J* = 10.0 Hz, 34H), 3.40–3.36 (m, 4H), 3.06 (s, 18H), 1.83 (s, 8H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 150.42, 150.36, 149.64, 128.24, 128.07, 128.02, 127.92, 113.85, 67.59, 65.49, 56.10, 56.03, 56.00, 55.97, 52.62, 29.41, 26.72, 19.72. ESI–MS m/z: (M-2Br)²⁺ Calcd for C₅₇H₇₈O₁₀N₂ 475.2823; Found 475.2828.



Fig. S7 ¹H NMR spectra(600 MHz, DMSO-*d*₆) of gelator BTAP5.



Fig. S8 13 C NMR spectra(151 MHz, DMSO- d_6) of gelator BTAP5.



Fig. S9 High resolution mass data of gelator BTAP5.



Fig. S10 ¹H NMR spectra (600 MHz, DMSO- d_6 , 298 K) of **BTAP5** at various concentrations: (a) 5.0 mM; (b) 10.0 mM; (c) 20.0 mM; (d) 50.0 mM; (e) 100.0 mM.



Fig. S11 The 2D NOESY spectrum of (600 MHz, DMSO- d_6 , 298 K) of BTAP5 at 20.0 mM.



Fig. S12 Plots of T_{gel} at the different concentrations of hydrogel HG.



Fig. S13 Absorbance spectra of gelator BTAP5 (0.1 mM) at different temperatures in H_2O solution.



Fig. S14 XRD diagrams of HG xerogel. Inset: Peak list and corresponding information.



Fig. S15 Two possible assembly processes of the gelator BTAP5.





Fig. S16 ESI-MS spectrum of the host-guest complex formed between DMP5 and G'.



Fig. S17 (a) Calculated minimize energy sturcture of compound **H'** by ChemBio 3D 12.0, and (b) Possible length of the [c2]daisy chain dimer.



Fig. S18 Representative SEM images showing the morphology of (a) **HG** hydrogel treated with CH₃COOH, (b) **HG** hydrogel treated with KClO₄, (c) **HG** hydrogel treated with adiponitrile, and (d) **HG** hydrogel treated with Fe³⁺.



Fig. S19 Partial ¹H NMR spectra (600 MHz, 298 K) of (a) 20 mM **BTAP5**; (b) 20 mM **BTAP5** and CH_3COOH .



Fig. S20 Partial ¹H NMR spectra (600 MHz, 298 K) of (a) 20 mM **BTAP5**; (b) 20 mM **BTAP5** and KClO₄.



Fig. S21 Fluorescence spectral response of **HG** (in the gelated state) upon addition of 1 equiv. of Fe³⁺ ($\lambda_{ex} = 360$ nm; slit widths: ex 3 nm, em 5 nm). Inset: Photograph of the hydrogel under 365 nm using a UV lamp.

Determination of the detection limit

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



Fig. S22 The photograph of the linear range.

Linear Equation: Y=-25447.92523X+862.57043 R²=0.94689 S=25447.93×10⁶

 $\delta = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} = 6.67(n = 20)$ LOD = $3\delta/S = 7.86 \times 10^{-10}$ M

Analytical techniques	The detection limits	Ref.
Spectrophotometry	1.8×10 ⁻⁶ mol/L (0.1 mg/L)	[S1]
Atomic absorption spectroscopy	10 ⁻⁷ mol/L	[S2]
Voltammetry	7.7×10 ⁻⁹ mol/L	[S3]
Electrophoresis	8.9×10 ⁻⁶ mol/L (0.5 mg/L)	[S4]
Fluorescence	$7.86 \times 10^{-10} \text{ mol/L}$	This work

Table S1 The detection limits of various analytical techniques about Fe^{3+} .

Table S2 Comparison of the analytical performance of pillararene-based fluorescent sensors for Fe^{3+} determination.^a

$\lambda_{\rm ex}/\lambda_{\rm em}({\rm nm})$	The detection limits	Ref.
370/420	N. A.	[\$5]
360/430	9.00×10 ⁻⁷ mol/L	[S6]
330/380	$1.25 \times 10^{-8} \text{ mol/L}$	[S7]
295/330	1.65×10 ⁻⁸ mol/L	[S8]
376/510	8.24×10 ⁻⁷ mol/L	[S9]
380/470	5.01×10 ⁻⁷ mol/L	[S10]
490/550	2.13×10 ⁻⁷ mol/L	[S11]
400/544	1.56×10 ⁻⁷ mol/L	[S12]
360/499	$7.86 \times 10^{-10} \text{ mol/L}$	This work

^a N. A. indicates not available.



Fig. S23 Photos of the thin film utilized to sense Fe^{3+} under irradiation at 365 nm using a UV lamp.



Fig. S24 FT-IR spectra of xerogel of HG and xerogel of HG treated with Fe^{3+} .



Fig. S25 Powder XRD patterns of xerogel of HG and xerogel of HG treated with Fe^{3+} .

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