

## Supporting Information

### **A supramolecular polypseudorotaxane material based on novel pillar[5]arene for ultrasensitive Fe<sup>3+</sup> reaction**

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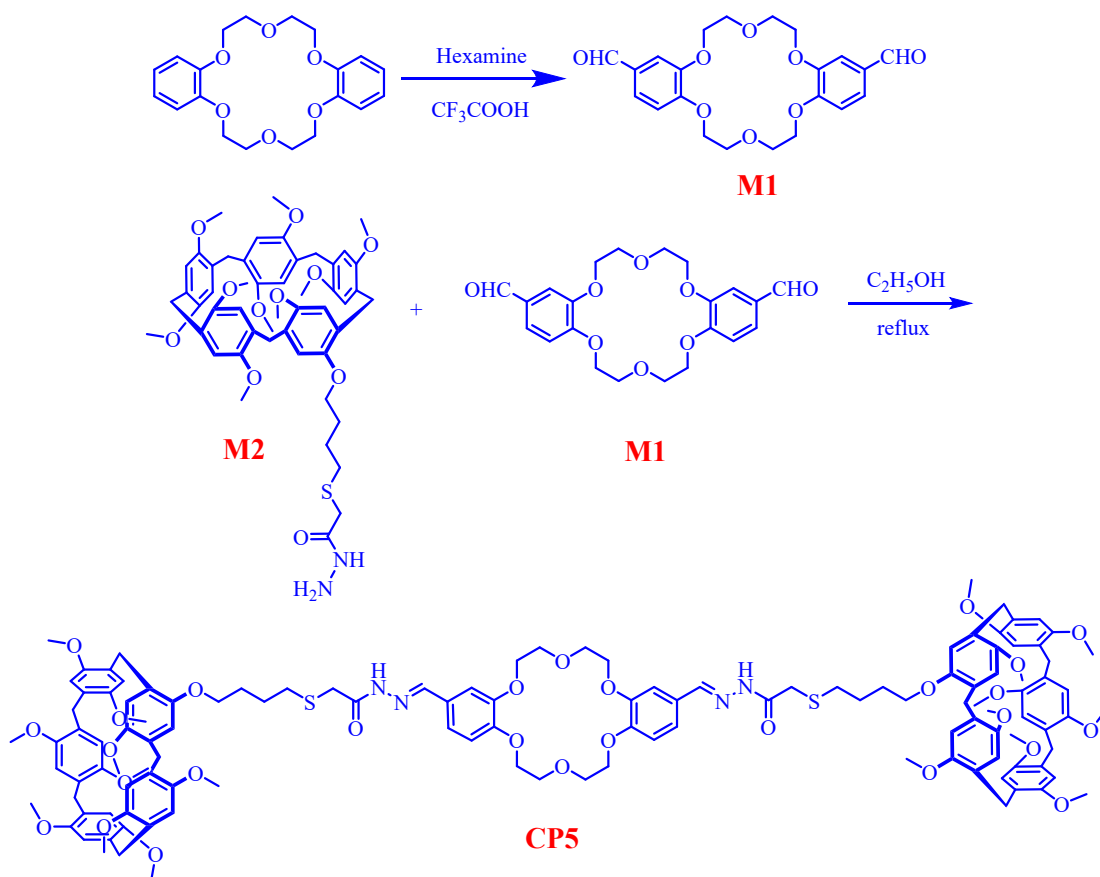
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## 1. Materials and methods

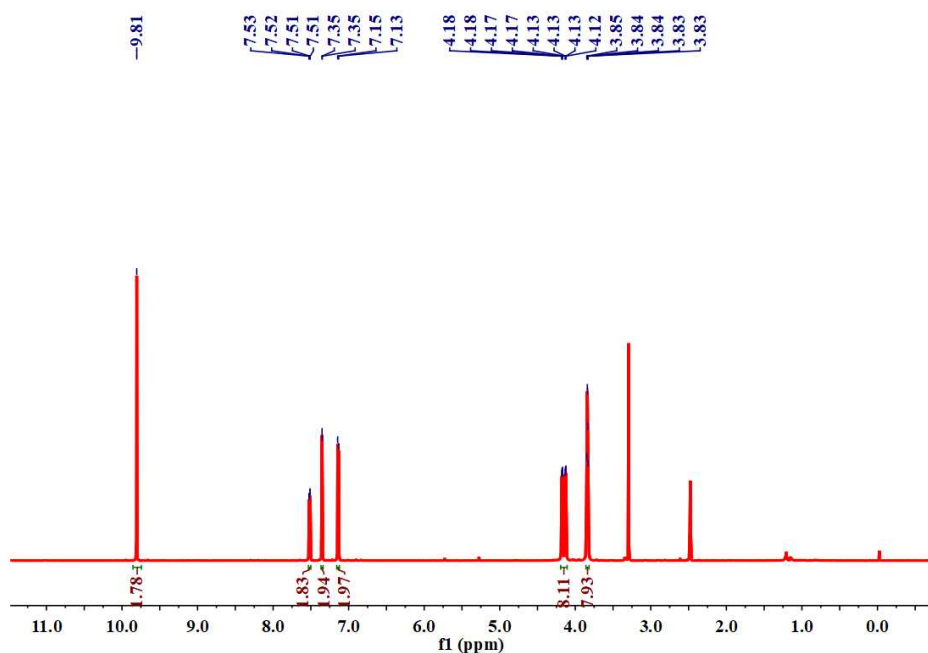
All reagents and solvents were commercially available at analytical grade and were used without further purification. All cations were purchased from Alfa Aesar and used as received. Fresh double distilled water was used throughout the experiment.  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR spectra (151 MHz) were carried out with a Mercury-600 BB spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS,  $\delta$  scale with solvent resonances as internal standards). High-resolution mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. The X-ray diffraction (XRD) pattern was generated using a Rigaku RINT2000 diffractometer equipped (copper target;  $\lambda = 0.154073$  nm). Scanning electron microscopy (SEM) images of the xerogels were investigated using JSM-6701F instrument. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected).

## 2. Synthesis of functionalized pillar[5]arene CP5



**Scheme S1** Synthesis of functionalized pillar[5]arene **CP5**.

**Synthesis of compound M1:** Compound **M1** was synthesized as previously reported<sup>[S1]</sup>. A mixture of dibenzo-18-crown-6 (2.016 g, 5.6 mmol), trifluoroacetic acid (8.3 mL), and hexamethylene tetramine (3.22 g, 22 mmol) was stirred at 90°C under nitrogen for 24 h. The mixture was extracted with 25 mL of benzene, and the extract was dried on magnesium sulfate. Concentration of the benzene extract under vacuum gave yellow oil, which, on cooling, solidified into brown crystals of compound **5**. Mp: 231-233 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600 MHz), δ/ppm: 9.81 (s, 2H), 7.52 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.35 (d, *J* = 1.8 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 4.15 (ddd, *J* = 27.1, 4.3, 2.0 Hz, 8H), 3.85 – 3.82 (m, 8H).

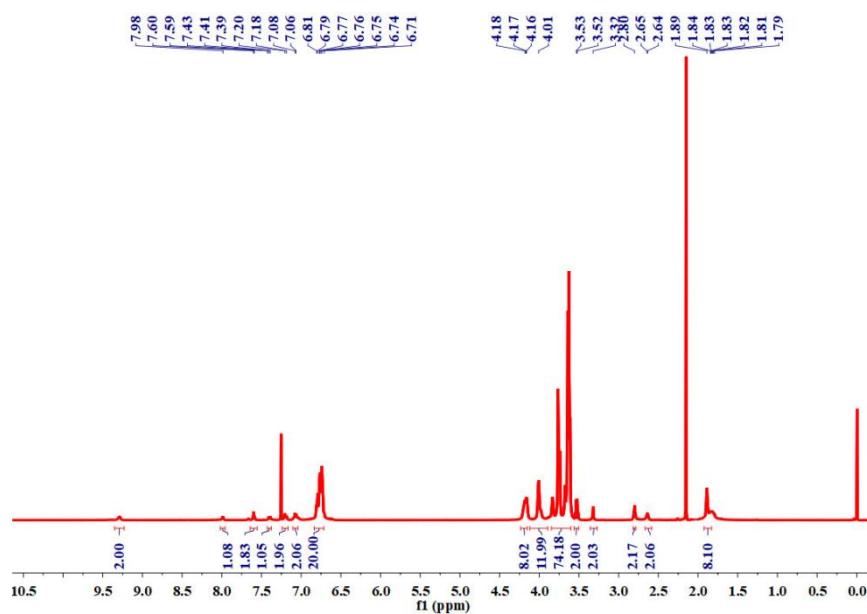


**Fig. S1**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{DMSO-}d_6$ ) of compound **M1**.

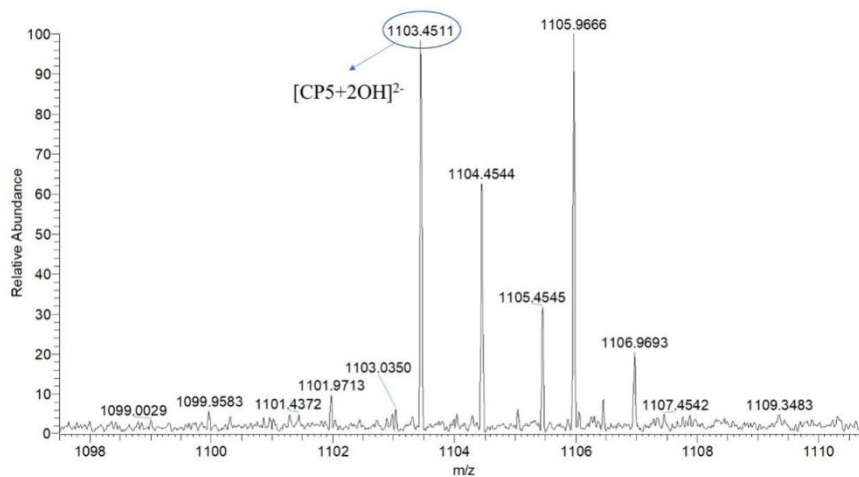
#### Synthesis of functionalized pillar[5]arene CP5:

Compound **M2** were synthesized according to our previously published procedures<sup>[S2]</sup>.

Compounds **M1** (0.08 g, 0.2 mmol) and **M2** (0.4 g, 0.45 mmol) as well as two drops of acetic acid (as a catalyst), were added to ethanol (30 mL). The solution was refluxed overnight. After the reaction completed, cooling occurred and the precipitate became a pink solid. The solid was washed by ethanol to obtain **CP5** as a pink solid (0.43 g, 82 %). Mp: 122-125 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 9.29 (s, 2H), 7.98 (s, 1H), 7.60 (d,  $J = 6.8$  Hz, 2H), 7.40 (d,  $J = 11.0$  Hz, 1H), 7.19 (d,  $J = 12.9$  Hz, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 6.85 – 6.69 (m, 20H), 4.22 – 4.12 (m, 8H), 4.01 (s, 12H), 3.87 – 3.58 (m, 74H), 3.53 (dd,  $J = 14.0, 7.0$  Hz, 2H), 3.32 (s, 2H), 2.80 (s, 2H), 2.64 (d,  $J = 7.0$  Hz, 2H), 1.92 – 1.81 (m, 8H). ESI-MS  $m/z=2$ :  $(\text{M}+2\text{OH})^{2-}$  Calcd for  $\text{C}_{122}\text{H}_{142}\text{N}_4\text{O}_{30}\text{S}_2$  1103.4580; Found 1103.4511.



**Fig. S2**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{CDCl}_3$ ) of compound **CP5**.



**Fig. S3** Mass data of compound **CP5**.

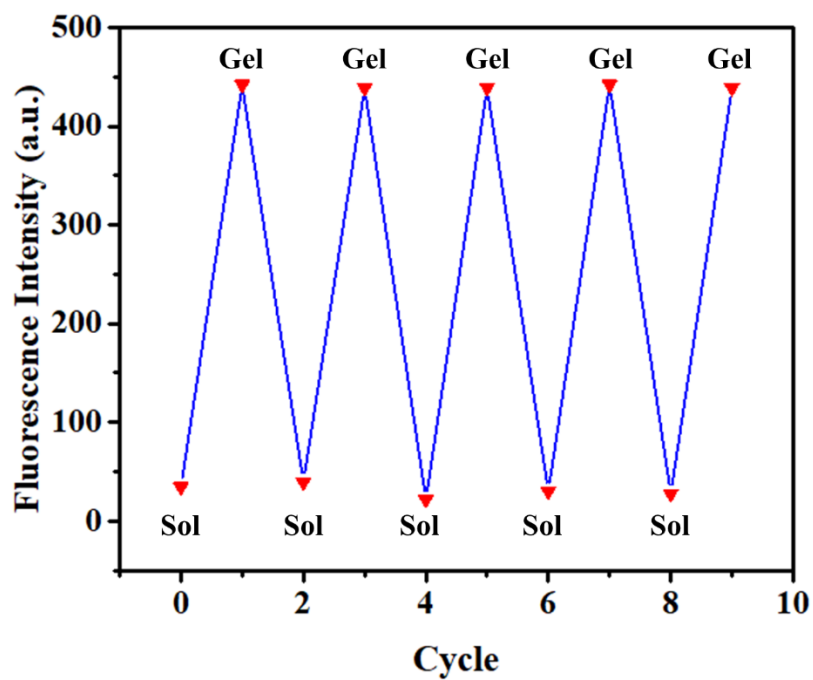
**Table S1.** Gelation Properties of supramolecular Organogel **CPDP** in various

Solvents				
Entry	Solvent	State <sup>a</sup>	CGC <sup>b</sup> (%)	T <sub>gel</sub> <sup>c</sup> (°C, wt%)
1	water	P	\	\
2	acetone	S	\	\
3	methanol	S	\	\
4	ethanol	S	\	\
5	isopropanol	S	\	\
6	isopentanol	S	\	\
7	acetonitrile	S	\	\
8	THF	S	\	\
9	DMF	S	\	\
10	DMF-H <sub>2</sub> O (90:10)	S	\	\
11	DMSO	S	\	\
12	DMSO- H <sub>2</sub> O (90:10)	S	\	\
13	DMSO-H <sub>2</sub> O (95:5)	P	\	\
14	n-hexane	P	\	\
15	CH <sub>2</sub> Cl <sub>2</sub>	S	\	\
16	CHCl <sub>3</sub>	S	\	\
17	ethyl acetate	S	\	\
18	cyclohexanol	G	10	60-62°C

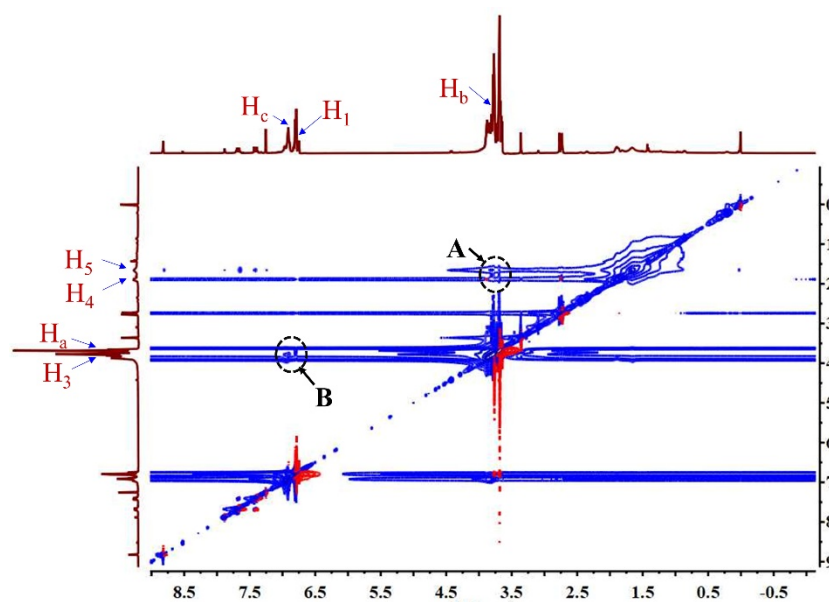
<sup>a</sup>G, P and S denote gelation, precipitation and solution, respectively, c = 0.8%.

<sup>b</sup>The critical gelation concentration (wt%, 10mg/ml = 1.0%).

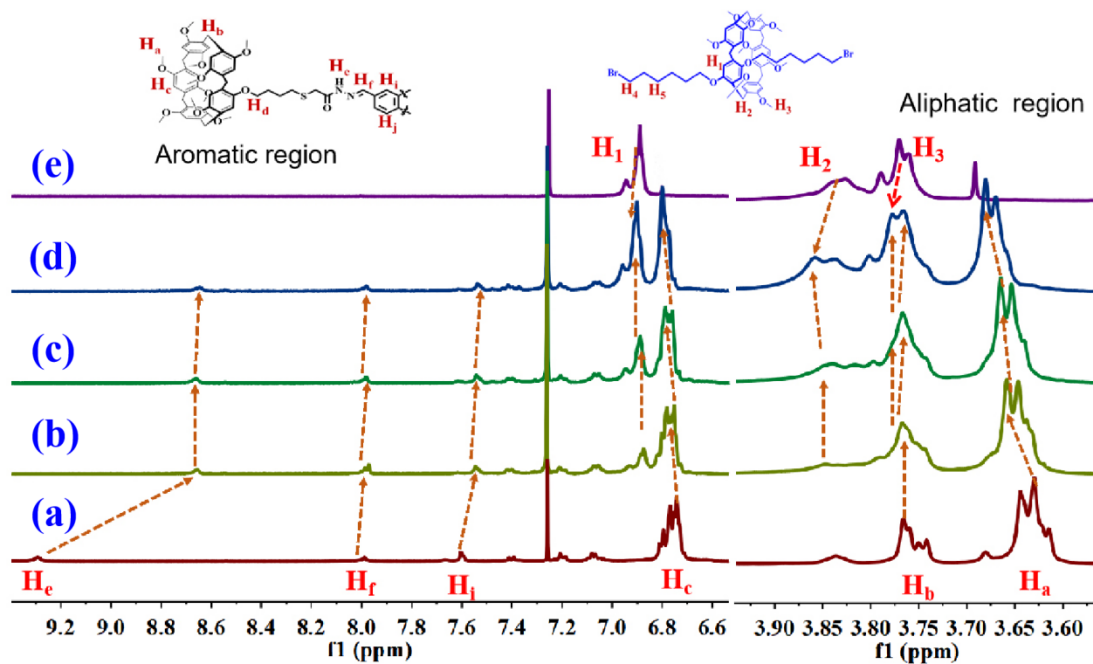
<sup>c</sup>The gelation temperature (°C).



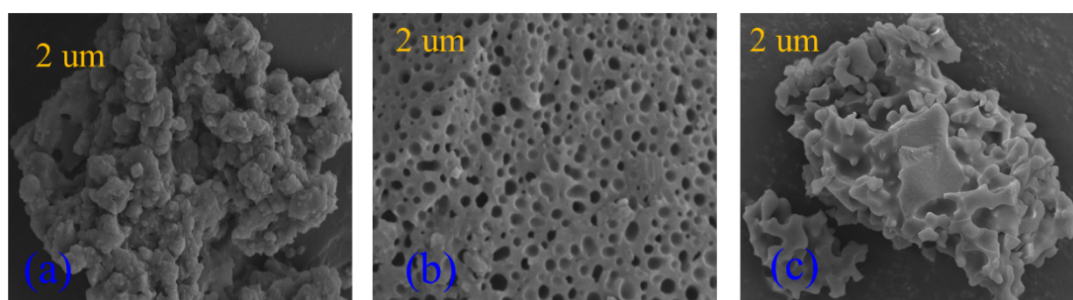
**Fig. S4** Temperature-dependent fluorescent spectra of **CPDP-G** (10% w/v in cyclohexanol solution) during gelation process was recorded under 365 nm ( $\lambda_{\text{ex}} = 330$  nm).



**Fig. S5** 2D NOESY NMR spectrum (600 MHz, 298 K) of 30.0 mM **CP5** and **DP5** in DMSO-*d*<sub>6</sub> solution.

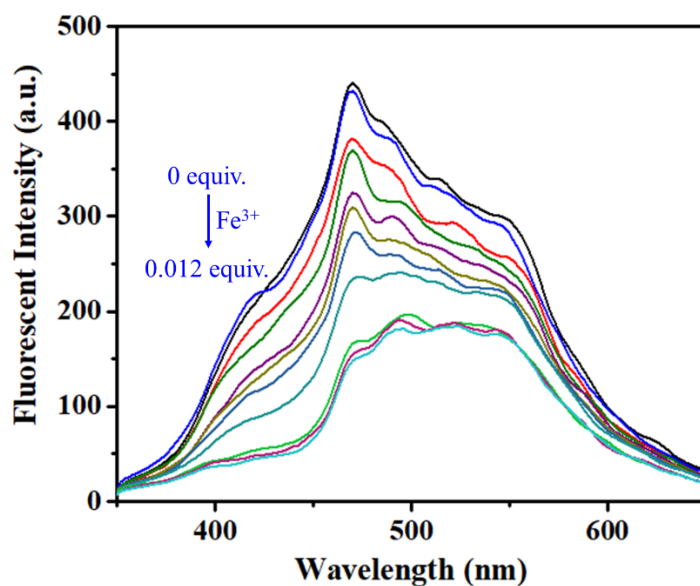


**Fig. S6** Partial  $^1\text{H}$  NMR spectra (600 MHz, 298 K) of **CP5** (0.01 mol/L) in  $\text{CDCl}_3-d_6$  with increasing amounts of **DP5**, (a) Free **CP5**; (b) 0.2 equiv. **DP5** and (a); (c) 0.5 equiv. **DP5** and (a); (d) 1.0 equiv. **DP5** and (a); (e) Free **DP5** (0.01 mol/L).

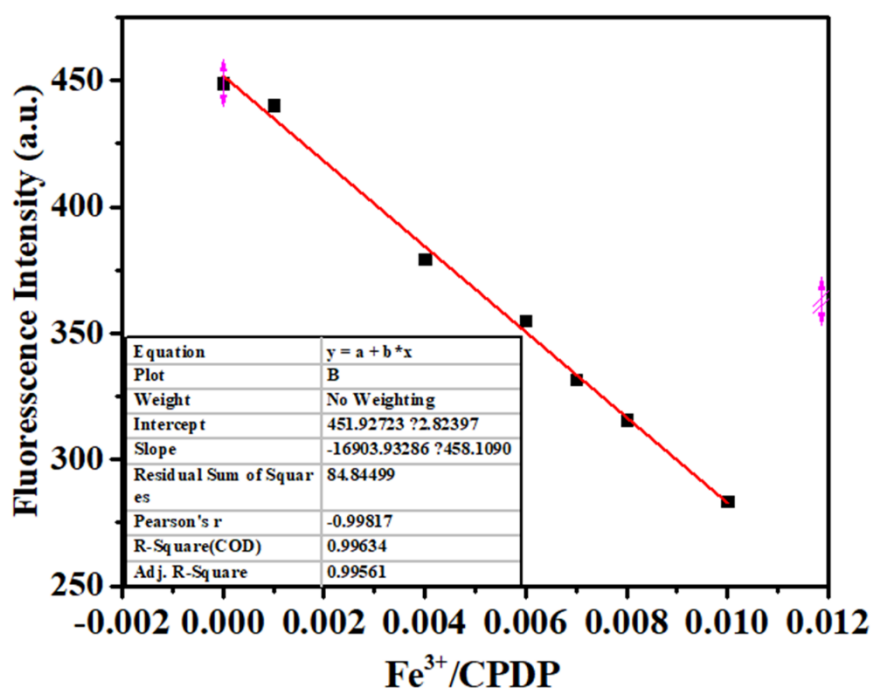


**Fig. S7** The SEM of powdered (a) **CP5** (b) the xerogel of **CPDP-G** (c) the xerogel of **CPDP-G** +  $\text{Fe}^{3+}$ . The relevant powder is obtained by treating with solvent  $\text{DMSO-H}_2\text{O}$ .





**Fig. S8** Fluorescence spectra of the CPDP-G upon addition of a 0.1 M Fe<sup>3+</sup> aqueous solution ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ) in cyclohexanol solution.



**Fig. S9** The photograph of the linear range of CPDP-G for Fe<sup>3+</sup>.

Linear Equation:  $Y = 1156.57228X + 120.85206$        $R^2 = 0.99817$

$S = 16903.93286 \times 10^6$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 3.06 \quad (N = 20)$$

$K = 3$

$\text{LOD} = K \times \delta / S = 5.43 \times 10^{-10} \text{ M}$

$F_i$  is the absorbance intensity of CPDP-G +  $Fe^{3+}$ ;  $F_0$  is the average of the  $F_i$ .

**Table S2. Comparison the LODs of Different Fluorescence**

**Sensors for  $Fe^{3+}$**

Refs	Solvent	LOD (nM)
S3	aqueous solution	900
S4	deionized water	450
S5	CH <sub>3</sub> CN-H <sub>2</sub> O (1:1, v/v)	261
S6	drinking water	240
This work	cyclohexanol solution	0.543

**Reference**

**S1** S. D. Jagadale, A.D. Sawant, M. B. Deshmukh, *J. Heterocyclic Chem.*, 2017, **54**, 2307.

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**S3** C.-X. Yang, H.-B. Ren and X.-P. Yan, *Anal. Chem.*, 2013, **85**, 7441.

**S4** X. Zhu, Z. Zhang, Z. Xue, C. Huang, Y. Shan, C. Liu, X. Qin, W. Yang, X. Chen and T. Wang, *Anal. Chem.*, 2017, **89**, 12054.

**S5** S. D. Padghan, A. L. Puyad, R. S. Bhosale, S. V. Bhosale and S. V. Bhosale, *Photochem. Photobiol. Sci.*, 2017, **16**, 1591.

**S6** M. Faraz, A. Abbasi, F. K. Naqvi, N. Khare, R. Prasad, I. Barman and R. Pandey, *Sens. Actuators B*, 2018, **269**, 195.