

Supporting Information

Pillar[5]arene-based supramolecular pseudorotaxane polymer material for ultra-sensitive detection of Fe³⁺ and F⁻

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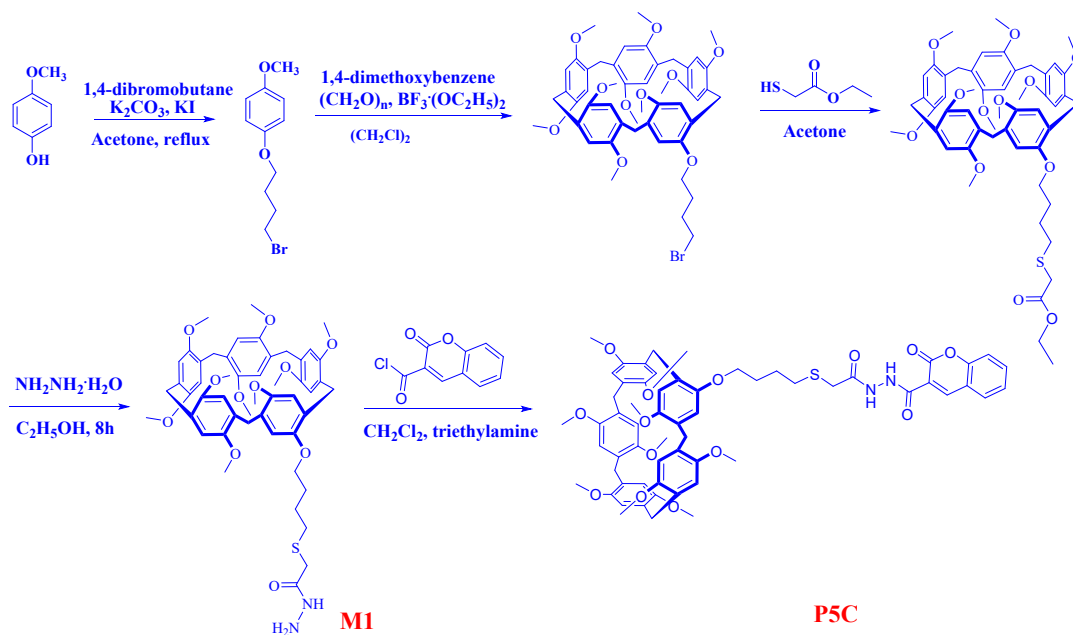
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1. Materials and methods

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. ^1H NMR (600 MHz) and ^{13}C NMR spectra (151 MHz) were carried out with a Mercury-600 BB spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ 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 P5C



Scheme S1 Synthesis of functionalized pillar[5]arene P5C.

Synthesis of compound M1

Compound **M1** was synthesized as previously reported^[S1]. The ethyl 2-mercaptoacetate functionalized pillar[5]arene (0.62 g, 0.68 mmol), hydrazine hydrate (3 mL, 93.6 mmol) and ethanol (30.0 mL) were mixed in a 100 mL round-bottom flask and stirred at 72 °C for 8h. After the solution cooled to room temperature, the crude product was filtered and then recrystallized with ethanol to get the solid compound **M1** as a white solid (0.46 g, yield 76%). Mp: 107-109 °C. 1H NMR ($CDCl_3$, 600 MHz), δ /ppm: 6.78 - 6.72 (m, 10H), 4.02 - 3.98 (q, $J = 7.1$ Hz, 2H), 3.84 - 3.83 (t, $J = 6.0$ Hz, 2H), 3.77 - 3.75 (dd, $J = 8.8, 5.8$ Hz, 10H), 3.65 - 3.61 (m, 27H), 3.2 (s, 2H), 2.72 - 2.69 (t, $J = 7.0$ Hz, 2H), 1.84 - 1.83 (d, $J = 5.3$ Hz, 2H), 1.08 - 1.05 (t, $J = 7.1$ Hz, 2H).

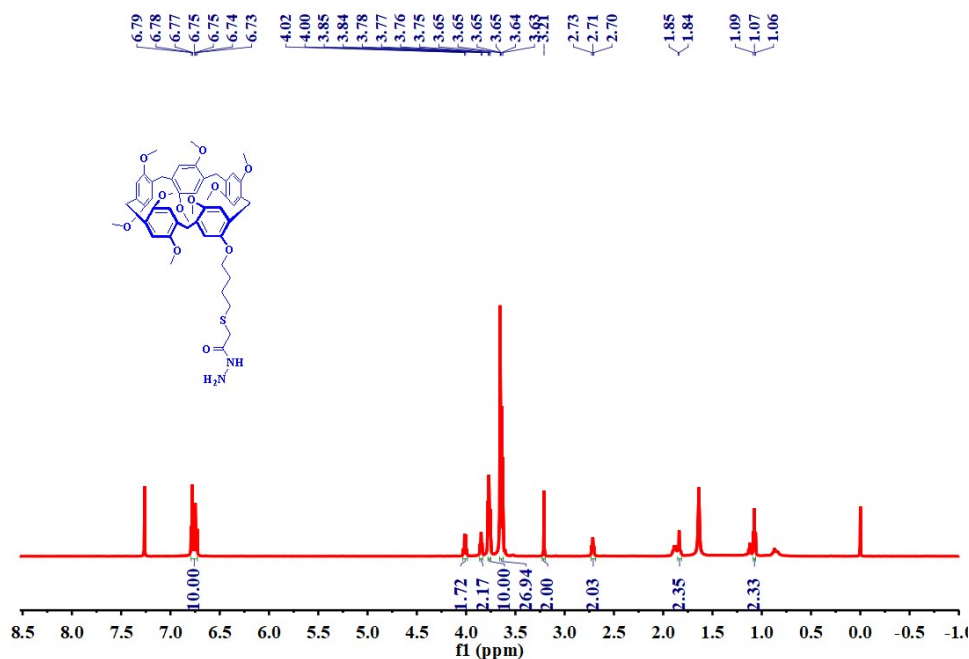


Fig. S1 ^1H NMR spectra (600 MHz, CDCl_3) of compound **M1**.

Synthesis of functionalized pillar[5]arene P5C.

The mixture of coumarin-3-carboxylic acid (0.5g, 2.5 mmol), sulfoxide chloride (20 mL) and DMF (20 uL) as catalyst was refluxed for 6 h. Then the solvent was evaporated under vacuum to give a white solid, and the product was put into the next reaction without purification. The product and compound M1 (0.4g, 0.45 mmol) were dissolved in CH_2Cl_2 , with triethylamine (60 uL) as a catalyst for 30 min at 0-10 °C and then returned to room temperature. After the reaction completed, the mixture solution was washed with water (100 mL), and the organic phase was dried with anhydrous sodium sulfate, evaporated, and recrystallized with EtOH/ H_2O to give a yellow solid. Mp: 107-109 °C. ^1H NMR (600 MHz, CDCl_3) δ /ppm: 10.93 (d, $J = 4.6$ Hz, 1H), 9.24 (s, 1H), 8.83 (s, 1H), 7.71 – 7.67 (m, 2H), 7.44 – 7.37 (m, 2H), 6.76 – 6.71 (m, 10H), 3.86 – 3.84 (t, $J = 5.9$ Hz, 2H), 3.77 – 3.72 (m, 10H), 3.65 – 3.59 (m, 27H), 3.33 (s, 2H), 2.70 – 2.68 (t, $J = 7.0$ Hz, 2H), 1.88 – 1.82 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ /ppm: 165.54, 160.61, 158.32, 154.54, 150.84, 150.81, 150.79, 150.76, 149.93, 148.99, 134.64, 129.95, 128.29, 128.22, 128.15, 125.46, 118.33, 116.84, 115.04, 114.22, 114.12, 114.00, 67.79, 55.88, 55.86, 55.82, 55.80, 55.76, 55.72, 40.94, 29.71, 29.62, 28.80, 25.92. ESI-MS m/z : ($\text{M}+\text{Na}$) $^+$ Calcd for $\text{C}_{60}\text{H}_{64}\text{N}_2\text{NaO}_{14}\text{S}$ 1091.3976;

Found:1091.3959.

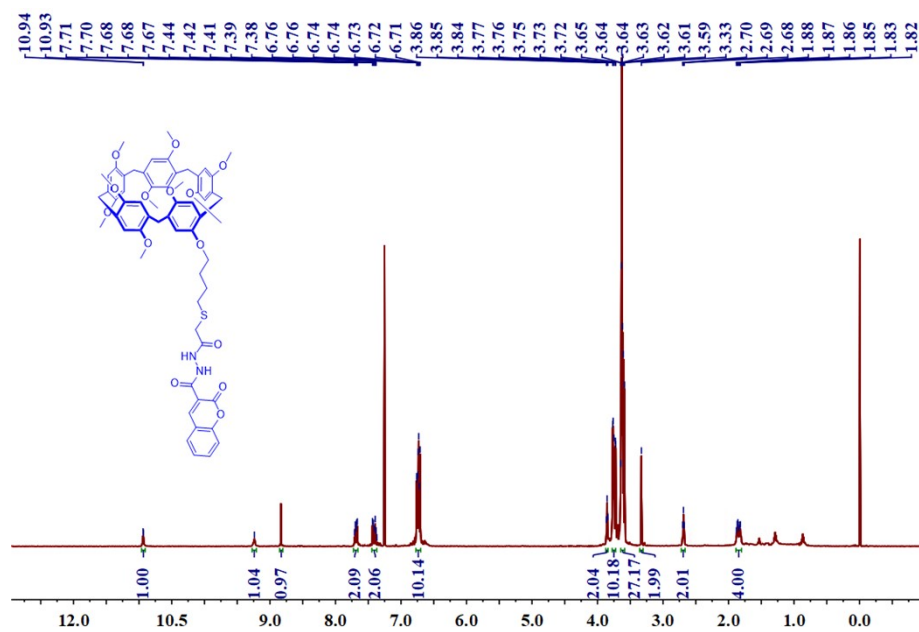


Fig. S2 ^1H NMR spectra (600 MHz, CDCl_3) of compound P5C.

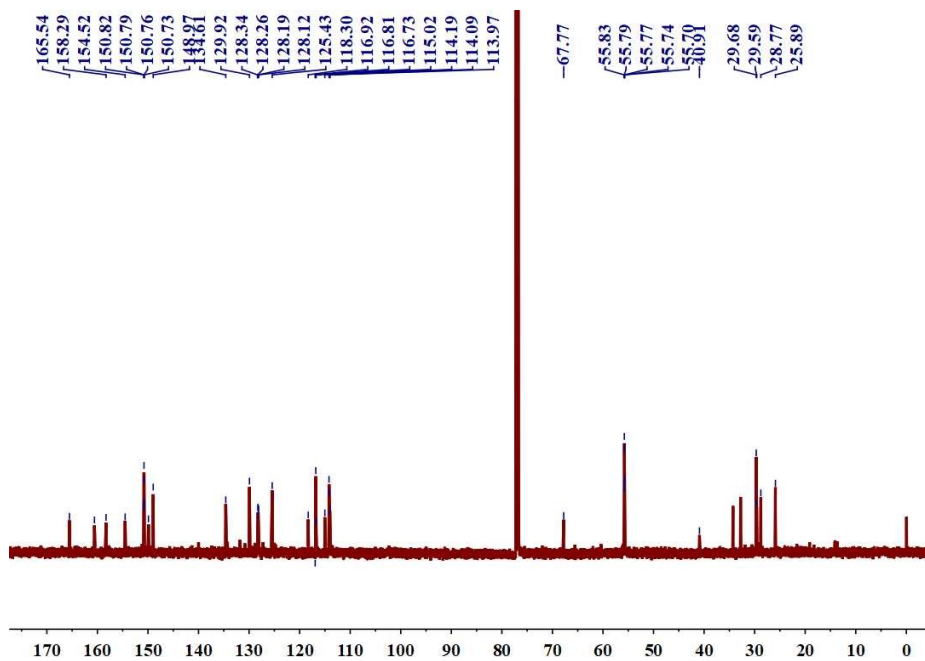
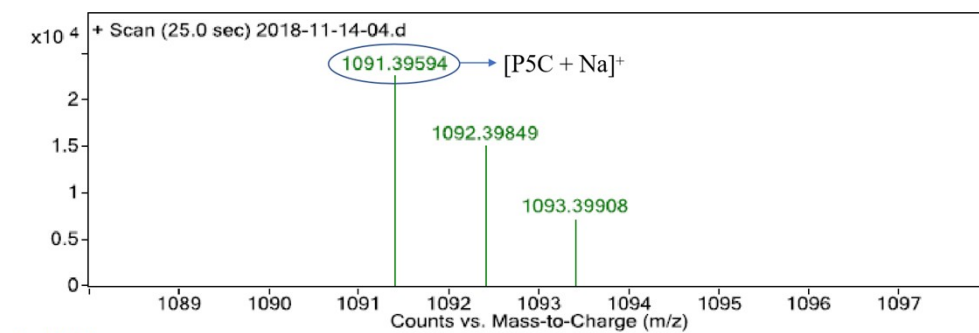


Fig. S3 ^{13}C NMR spectra (151 MHz, CDCl_3) of compound P5C.



Peak List

<i>m/z</i>	<i>z</i>	Abund	Formula	Ion
1036.47368	1	8268.4		
1037.48087	1	5735.5		
1069.41241	1	20310.9		
1070.41648	1	14740.5		
1071.41713	1	5643.7		
1086.4422		5388.9		
1091.39594	1	22621	C60 H64 N2 Na O14 S	(M+Na)+
1092.39849	1	15118.6	C60 H64 N2 Na O14 S	(M+Na)+
1093.39908	1	7292.1	C60 H64 N2 Na O14 S	(M+Na)+
1107.37011		5327.9		

Fig. S4 Mass data of compound P5C.

Table S1 Gelation Properties of Organogel **PCDP-G** in Organic Solvents.

Entry	Solvent	State ^a	CGC ^b (%)	T _{gel} ^c (°C,wt%)
1	Water	P	\	\
2	Acetone	S	\	\
3	Methanol	S	\	\
4	Ethanol	S	\	\
5	Isopropanol	P	\	\
6	Isoamylol	P	\	\
7	Acetonitrile	S	\	\
8	THF	S	\	\
9	DMF	S	\	\
10	DMSO	S	\	\
11	n-hexane	P	\	\
12	CH ₂ Cl ₂	S	\	\
13	CHCl ₃	S	\	\
14	Ethyl acetate	S	\	\
15	Cyclohexanol	G	10	58-60°C

State: $n_{P5C}/n_{DP5} = 2/1$

^aG, P and S denote gelation, precipitation and solution, respectively.

^bThe critical gelation concentration (wt%, 10mg/ml = 1.0%).

^cThe gelation temperature (°C)

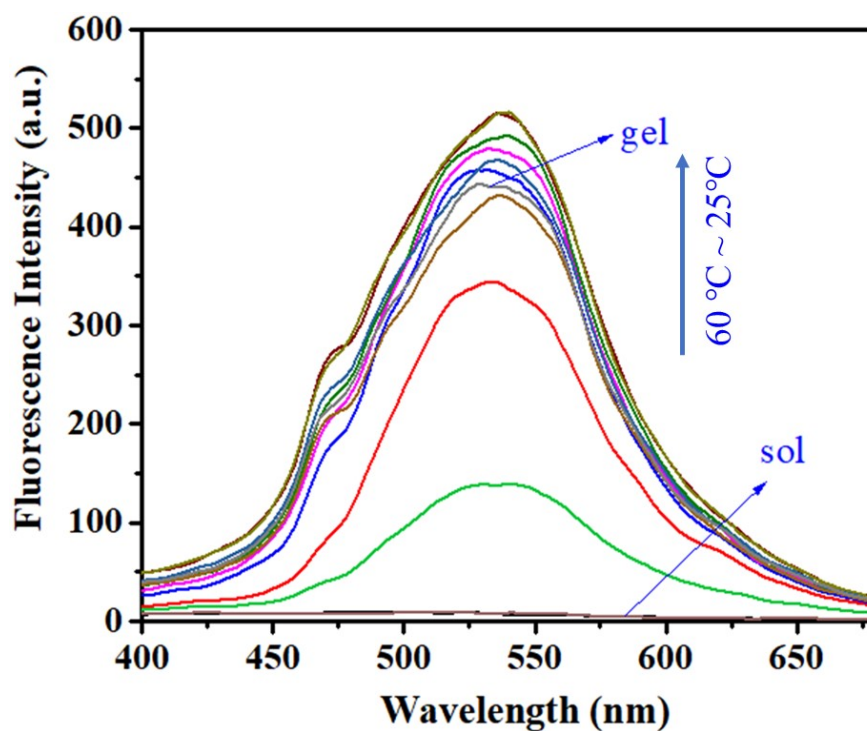


Fig. S5 Temperature-dependent fluorescence spectra of PCDP-G (in cyclohexanol, 10% (w/v)) during the gelation process ($\lambda_{\text{ex}} = 365 \text{ nm}$).

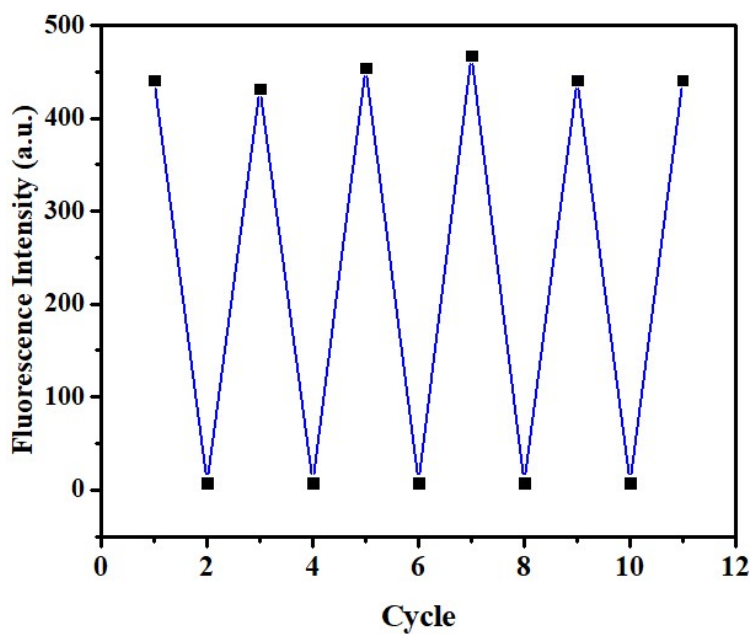


Fig. S6 Cycle index of the sol-gel transition process.

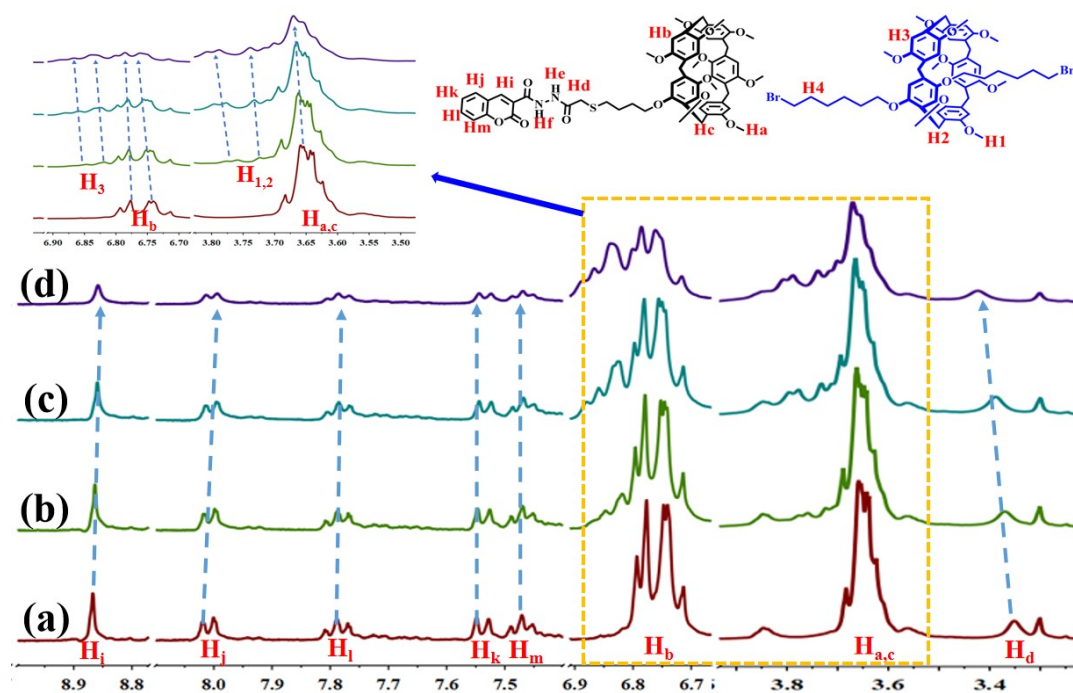


Fig. S7 Partial concentrations-dependent ^1H NMR spectra of (a) free **P5C** with different concentrations of **DP5** in $\text{DMSO-}d_6$, from bottom to top: 3.7×10^{-3} M, 9.3×10^{-3} M, 1.9×10^{-2} M, 2.8×10^{-2} M, 3.7×10^{-2} M.

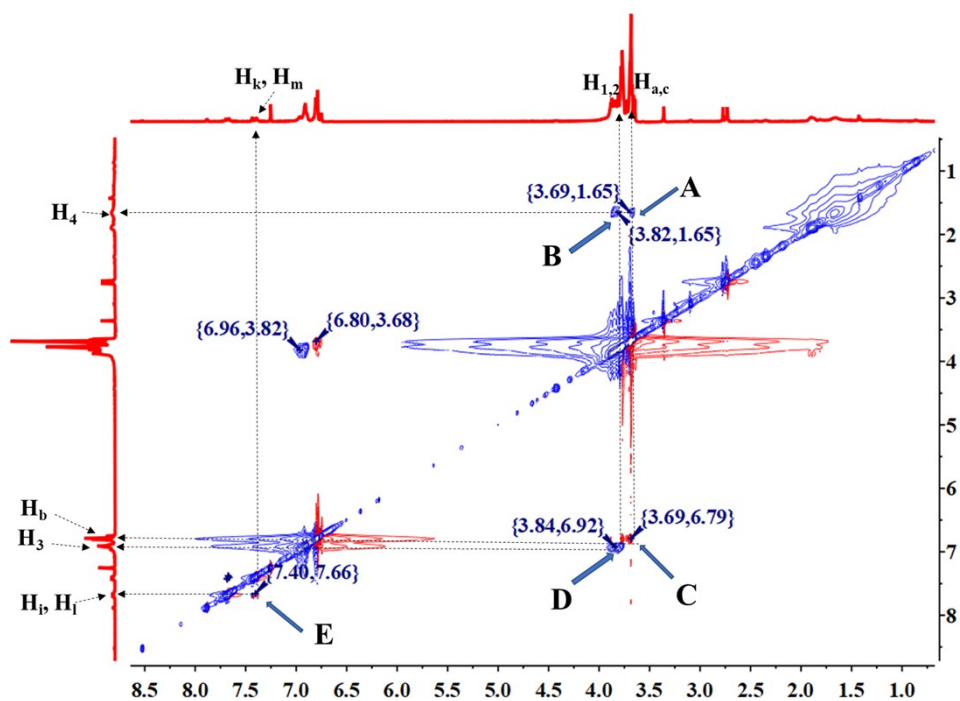


Fig. S8 2D NOESY NMR spectra (600 MHz, 298 K) of 50.0 mM **CP5** and 50.0 mM **DP5** in $\text{DMSO-}d_6$ solution.

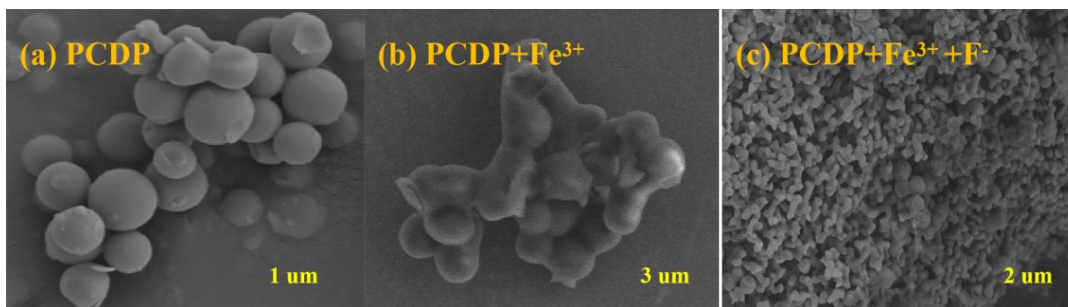


Fig. S9 SEM images of (a) xerogel PCDP-G; (b) PCDP-GFe and (c) PCDP-GFe + F⁻.

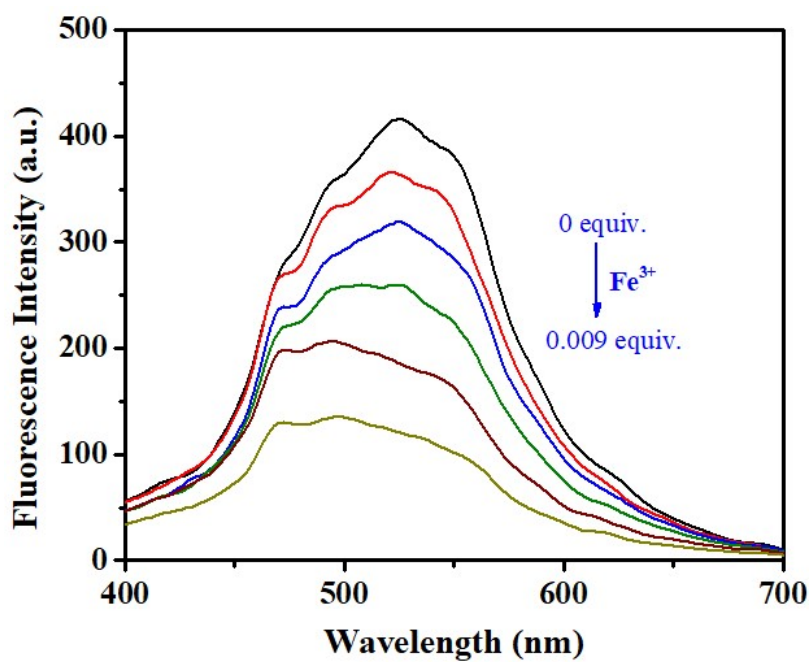


Fig. S10 The fluorescence spectra of PCDP-G in cyclohexanol solution with increasing concentrations of Fe³⁺ (0.1 M, water solution), $\lambda_{\text{ex}} = 365$ nm.

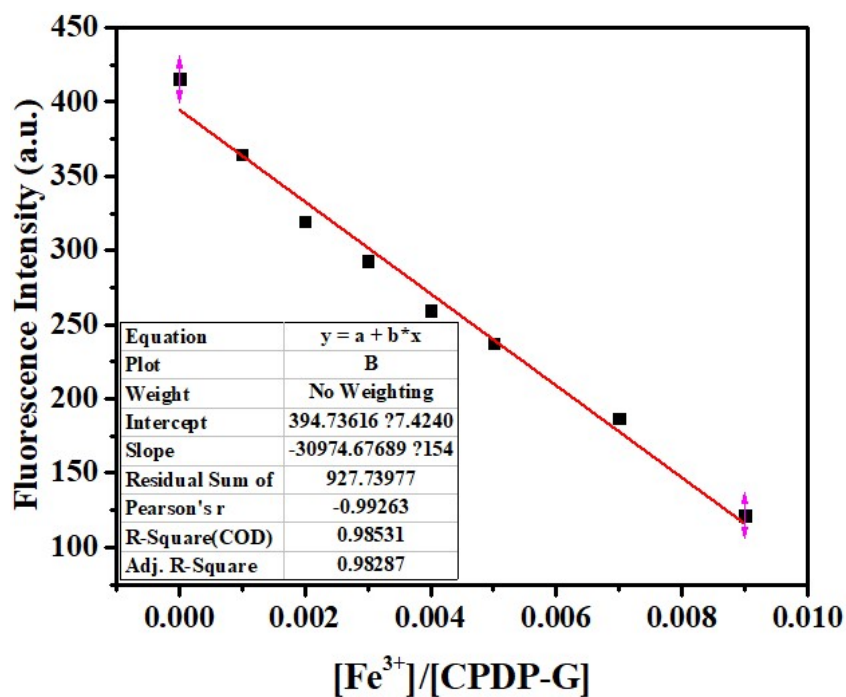


Fig. S11 The photograph of the linear range for Fe³⁺.

The result of the analysis as follows:

Linear Equation: $Y = -30947.67 \times X + 394.74$ $R^2 = 0.98287$

$S = 3.0947 \times 10^{10}$

$$\delta = \frac{\sqrt{\sum_{i=1}^N (F_i - \bar{F})^2}}{N-1} = 4.29$$

(N = 20) K = 3

$LOD = K \times \delta/S = 0.416 \text{ nM}$

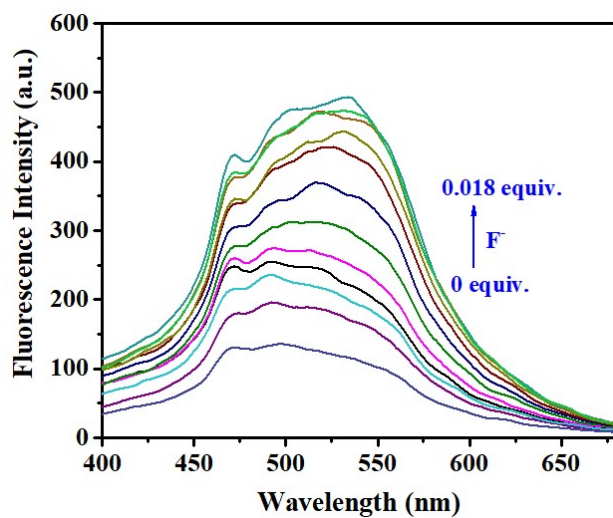


Fig. S12 The fluorescence spectra of PCDDP-GFe in cyclohexanol solution with

increasing concentration of F⁻ (0.1 M, water solution), $\lambda_{\text{ex}} = 365 \text{ nm}$.

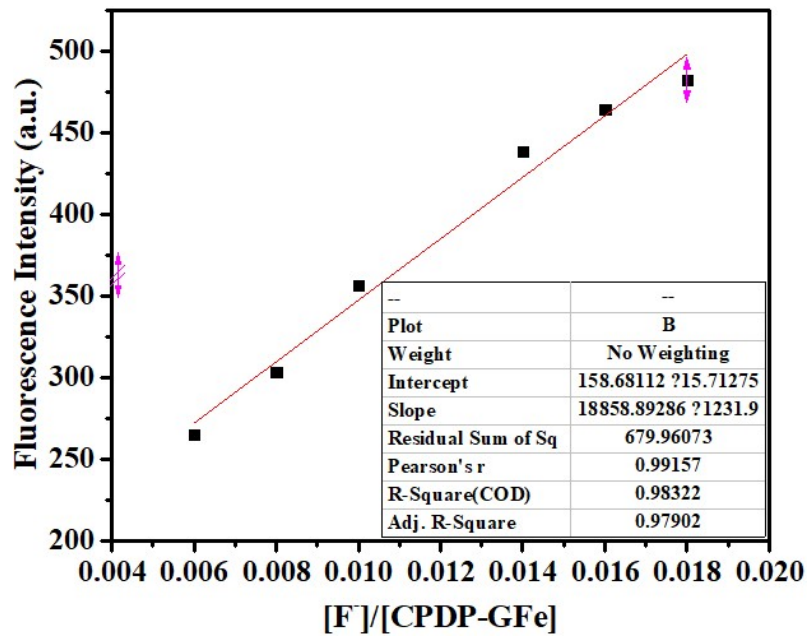


Fig. S13 The photograph of the linear range for F⁻.

The result of the analysis as follows:

$$\text{Linear Equation: } Y = 18858.89 \times X + 158.68 \quad R^2 = 0.97902$$

$$S = 1.8858 \times 10^{10}$$

$$\delta = 4.29 \quad (N = 20) \quad K = 3$$

$$\text{LOD} = K \times \delta / S = 0.682 \text{ nM}$$

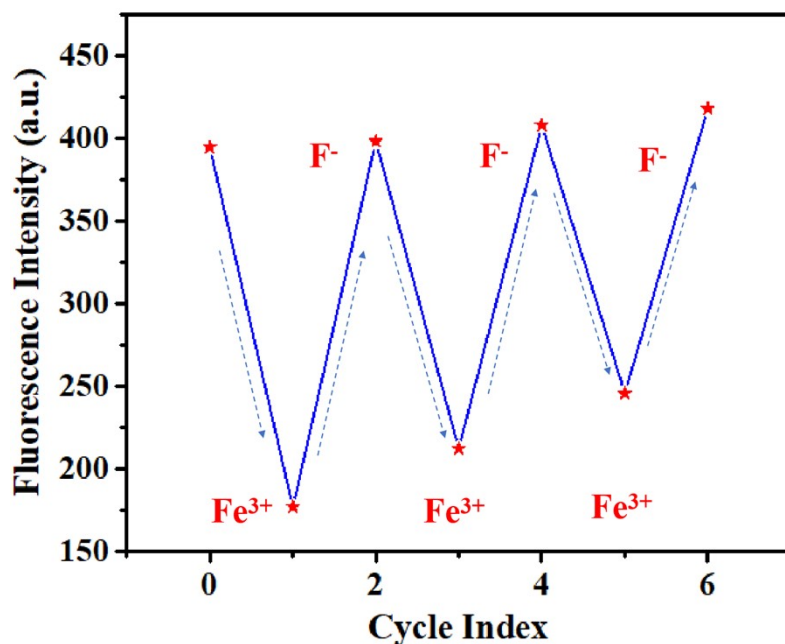


Fig. S13 Fluorescent “on-off-on” cycles of PCDP-G, controlled by the alternative addition of Fe^{3+} and F^- ($\lambda_{\text{ex}} = 365 \text{ nm}$).

Table S2. Comparison the LODs of Different Fluorescence Sensors for Fe^{3+}

Refs	Solvent	LOD
S2	aqueous solution	900 nM
S3	deionized water	450 nM
S4	$\text{CH}_3\text{CN-H}_2\text{O}$ (1:1, v/v)	261 nM
S5	drinking water	240 nM
This work	cyclohexanol solution	0.416 nM

Table S3. Comparison the LODs of Different Fluorescence Sensors for F^-

Refs	Solvent	LOD
S6	$\text{DMF/H}_2\text{O}$ (v:v=1:1)	9.24 nM
S7	DMSO	1.44 μM
S8	DMSO	289 ppm
S9	$\text{DMSO - H}_2\text{O}$ (1:1, v/v)	108 nM

Reference:

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