

Supplementary information

Simple pillar[5]arene assembled multi-functional material with ultrasensitive sensing, self-healing, conductivity and host-guest stimuli-responsiveness properties

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1. Experiment

1.1 Materials

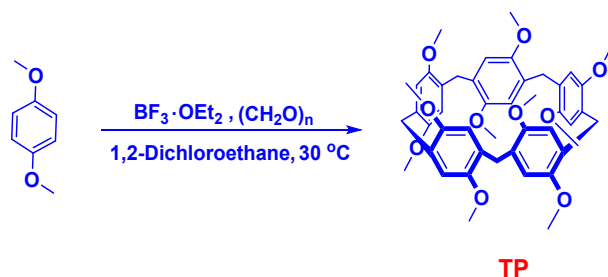
All reagents and starting materials were obtained from commercial suppliers and used as received unless otherwise noted. All cations were used as the perchlorate salts, which were purchased from Alfa Aesar and used as received. Fresh double distilled water was used throughout the experiment.

1.2 Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuK α radiation ($\lambda=1.54073\text{\AA}$). The morphologies of the **TP**, **Q** and **TP-QG** were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Synthesis of compound TP and Q.

2.1 Synthesis of compound TP.



Schemes S1 Synthesis route of the **TP**

According to previous report, the **TP** was synthesized.^{S1} In a 250 mL round-bottom flask, 1,4-dimethoxybenzene(1.38g, 10mmol), paraformaldehyde (0.64 g, 20 mmol) and 1,2-dichloroethane (200 mL) were added and the mixture was stirred at 30°C for 30 min. Then boron trifluoride diethyl etherate (2.5mL, 16.5 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 3~4 times 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/ dichloromethane (2 : 1,v/v) to give **TP** (0.78 g, 52%, yield) as a white solid. M.P.: 180-182°C. ^1H NMR (400 MHz, CDCl_3) δ /ppm: 6.90(s, 10H), 3.85(s, 10H), 3.77(s, 30H). ^{13}C NMR (150 MHz, CDCl_3) δ /ppm: 150.63, 128.26, 113.85-113.63, 55.76-55.58, 29.52; FT-IR (anhydrous KBr, cm^{-1}) ν : 2944 (Ar-H), 1208 (OCH_3); ESI-MS m/z : Calcd for $\text{C}_{45}\text{H}_{50}\text{O}_{10}$, [**TP** + Na] $^+$: 773.3296; Found 773.3116.

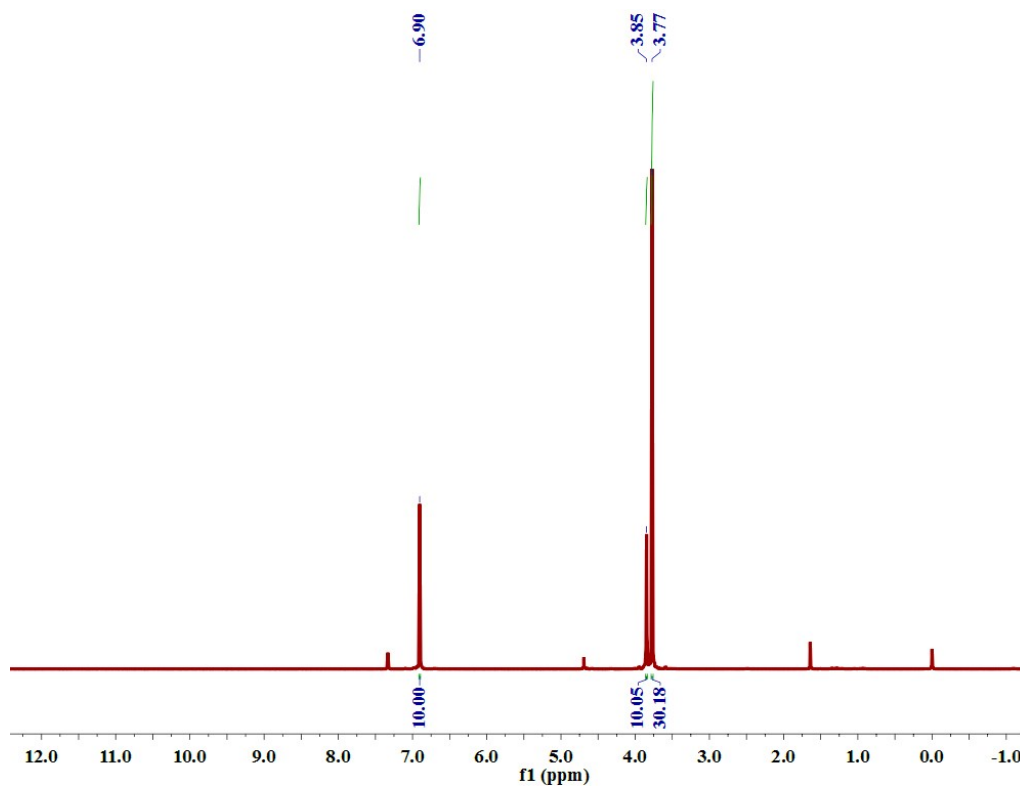


Fig. S1 ^1H NMR spectrum of the **TP** in CDCl_3 .

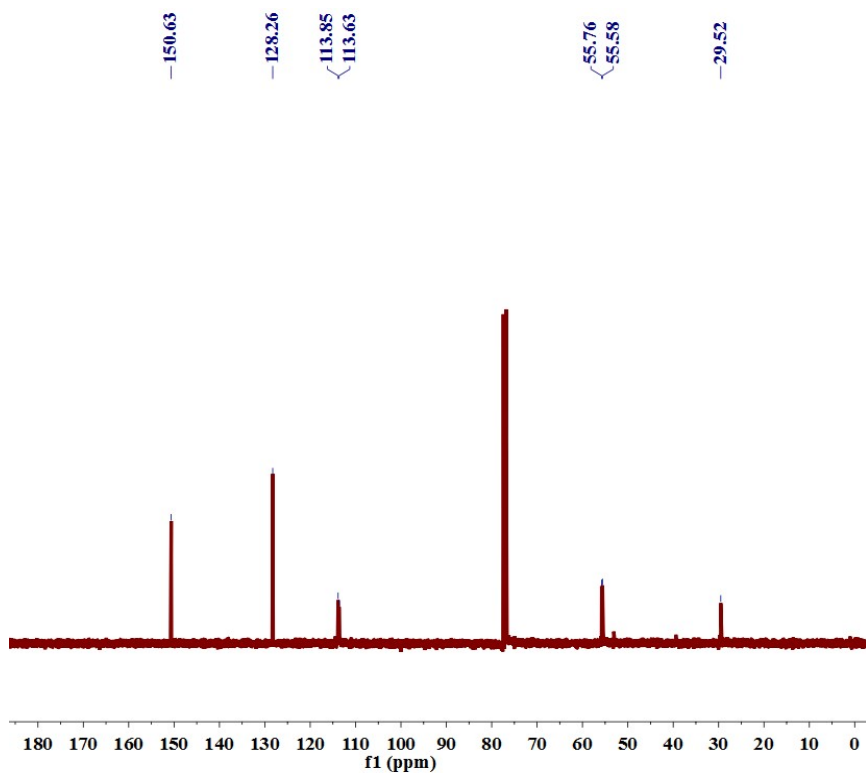


Fig. S2 ^{13}C NMR spectrum of the TP in CDCl_3 .

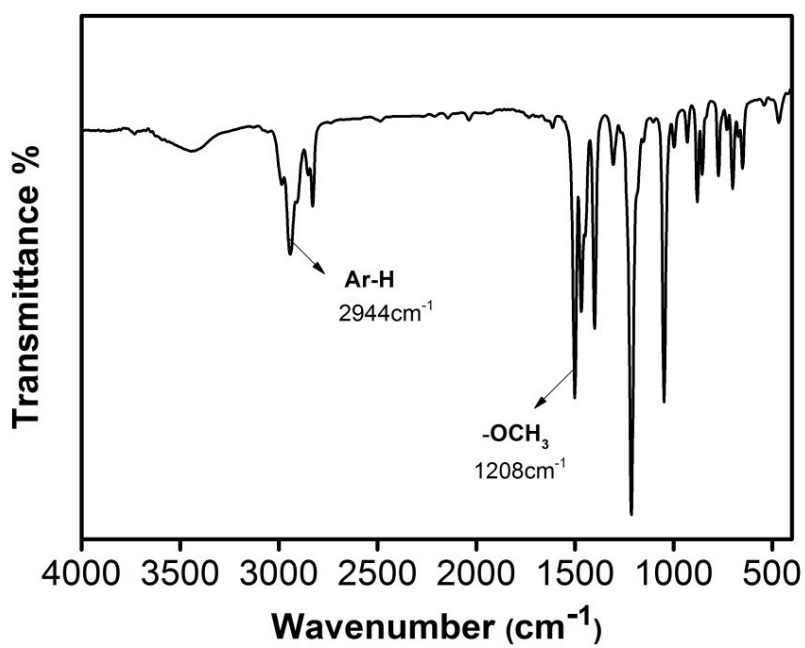


Fig. S3 FT-IR spectrum of the TP.

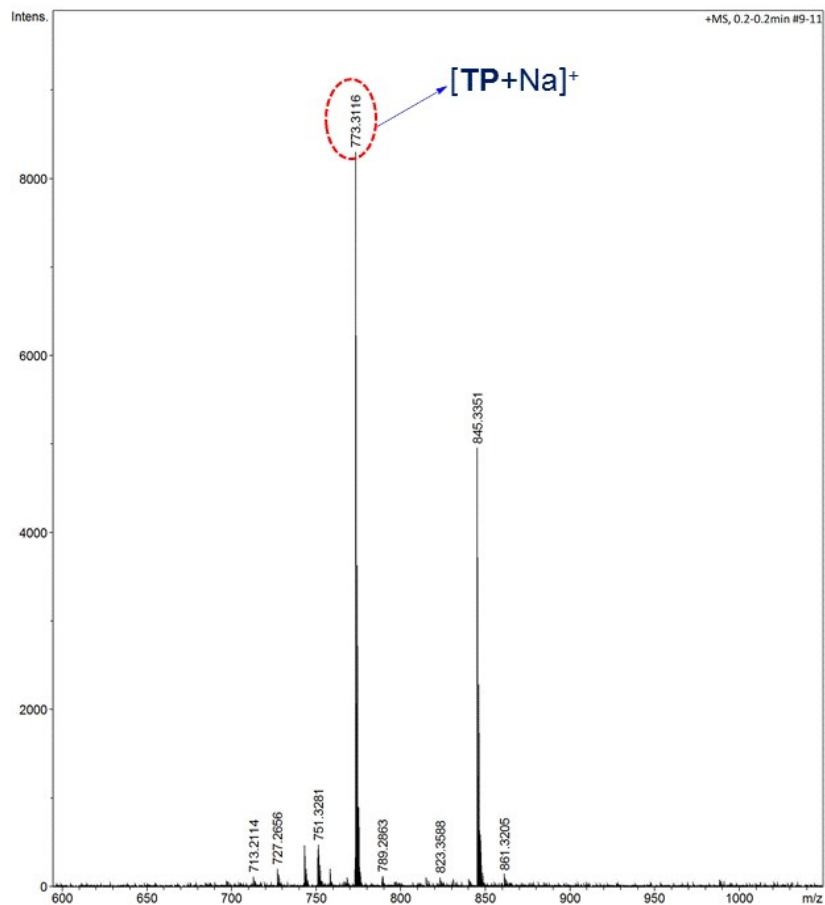
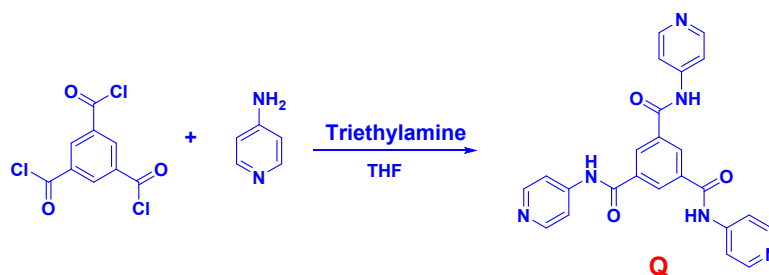


Fig. S4 ESI-MS spectrum of the **TP**.

2.2 Synthesis of compound **Q**.



Schemes S2 Synthesis route of the **Q**

According to our previous report, the **Q** was synthesized.^{S2} A 20 mL THF containing 10 mmol (2.64 g) of 1,3,5-benzene-tricarbonyl trichloride was added drop by drop to a 40 mL THF solution containing 30.5 mmol (2.86 g) of 4-aminopyridine and 35mmol (4.8 mL) of distilled triethylamine at 0°C with continuous stirring. After stirred for 12 h, the reaction temperature was allowed to rise to room temperature. The resulted product was recrystallized from a mixed solvent of DMF (100 mL) and H₂O

(200 mL) and dried at 80°C under vacuum (3.50 g, 80%, yield); M.P.: 167-170°C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.98 (s, 3H), 8.77 (s, 3H), 8.55-8.52 (t, $J = 5.0\text{Hz}$, 6H), 7.85-7.82 (t, $J = 4.4\text{Hz}$, 6H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ/ppm : 165.68, 156.37, 149.58, 135.07, 131.36, 114.75; FT-IR (anhydrous KBr, cm^{-1}) ν : 3432 (N-H), 3080 (Ar-H), 1682 (C=O); ESI-MS m/z : Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_3$, [$\text{Q} + \text{H}$] $^+$:439.1513; Found 439.1507.

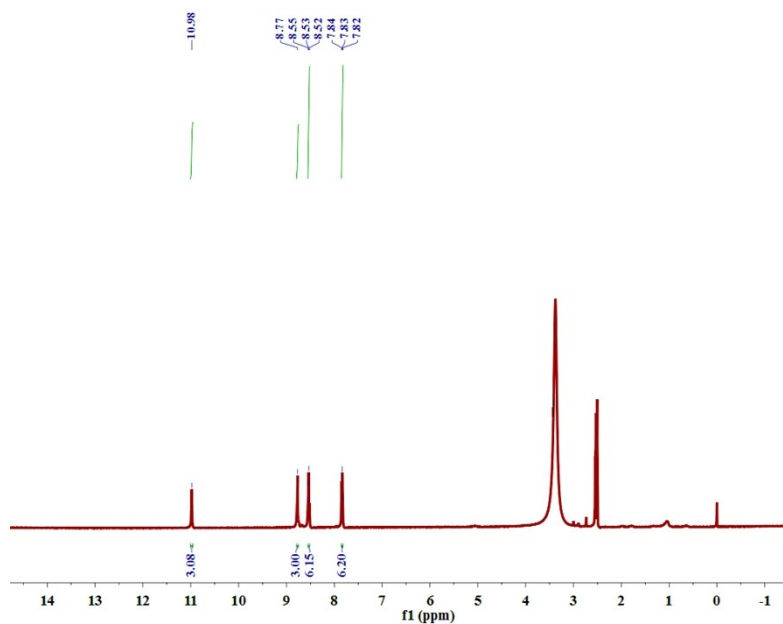


Fig. S5 ^1H NMR spectrum of the **Q** in $\text{DMSO-}d_6$.

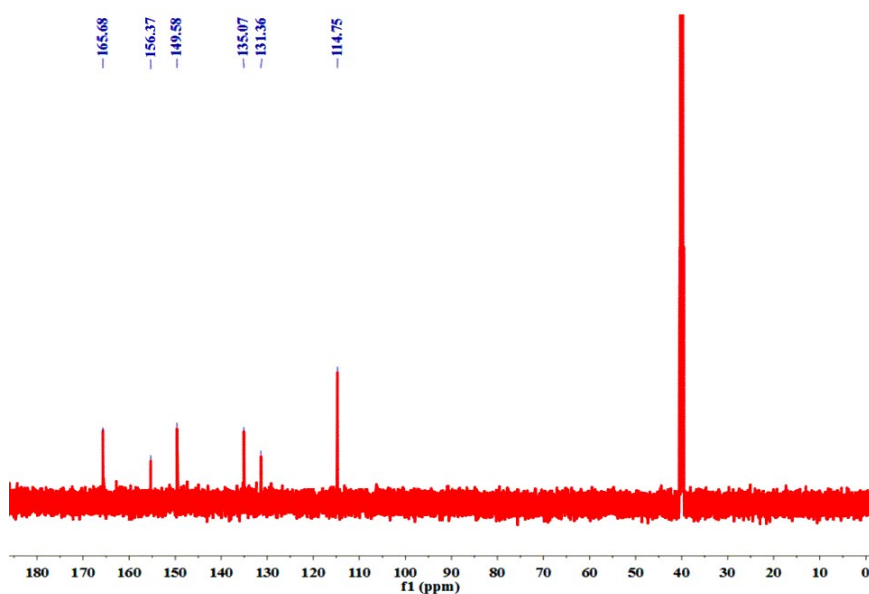


Fig. S6 ^{13}C NMR spectrum of the **Q**.

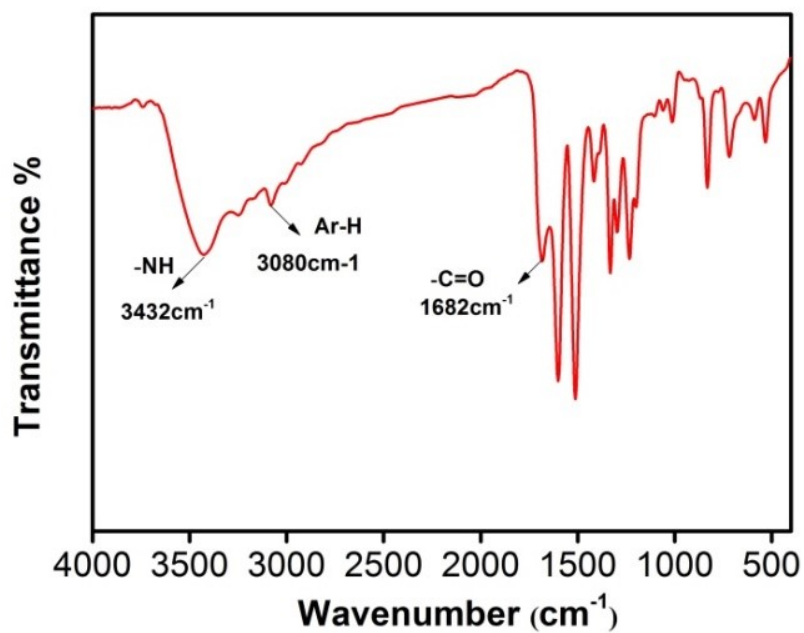


Fig. S7 FT-IR spectrum of the **Q**.

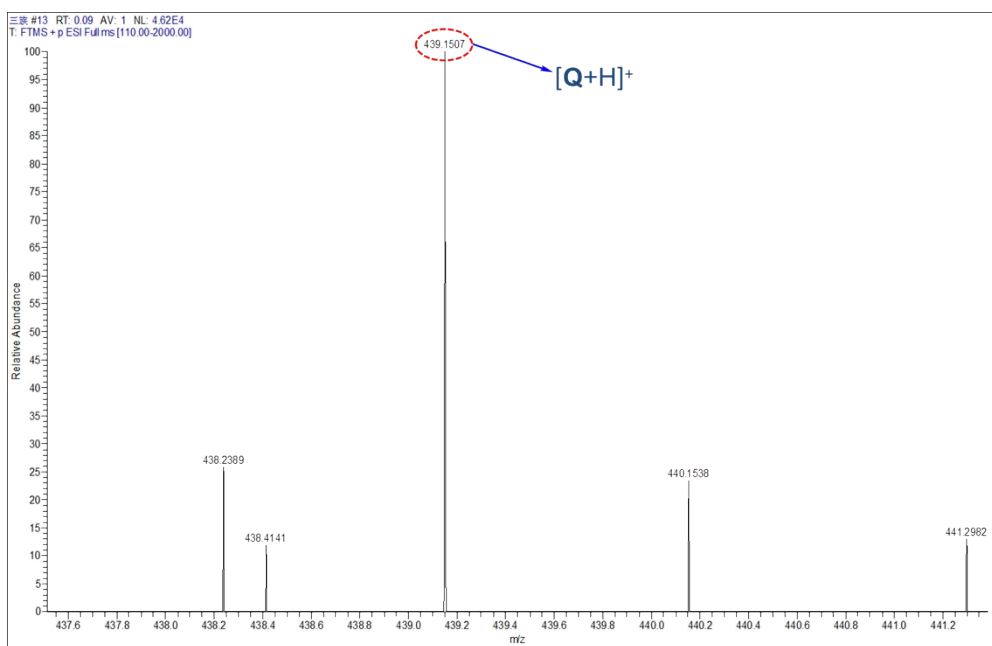


Fig. S8 ESI-MS spectrum of the **Q**.

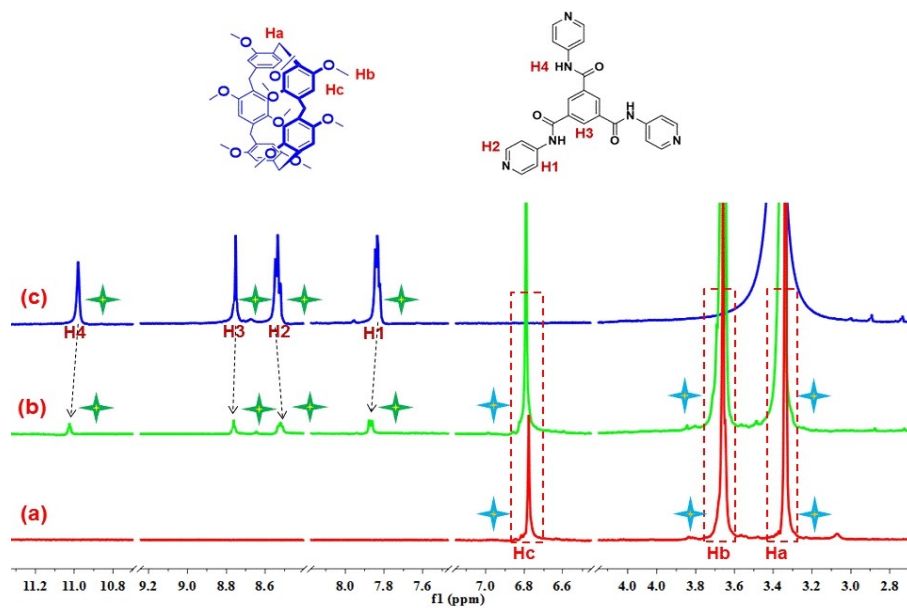


Fig. 9 The partial ^1H NMR spectra of the TP in $\text{DMSO-}d_6$ with Q [(a) Free TP; (b) TP + Q; (g) Free Q].

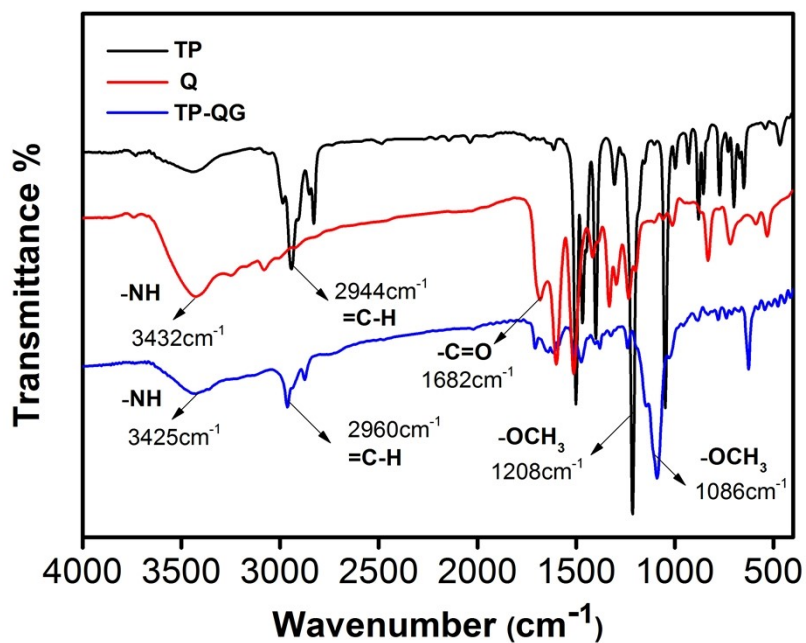


Fig. S10 IR spectra of the TP (black), Q (red) and TP-QG (blue) in KBr disks.

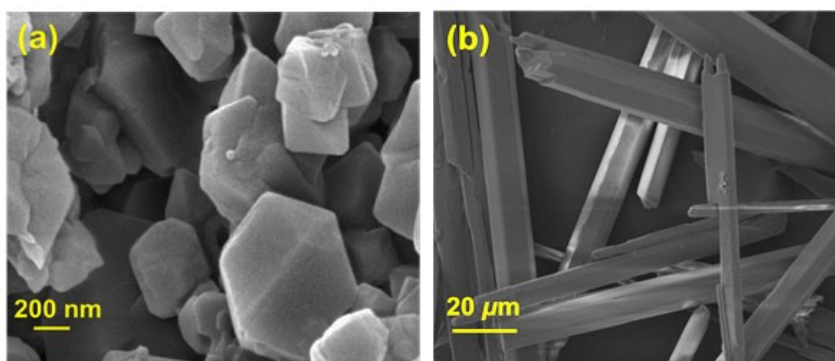


Fig. S11 SEM images of the (a) TP and (b) Q.

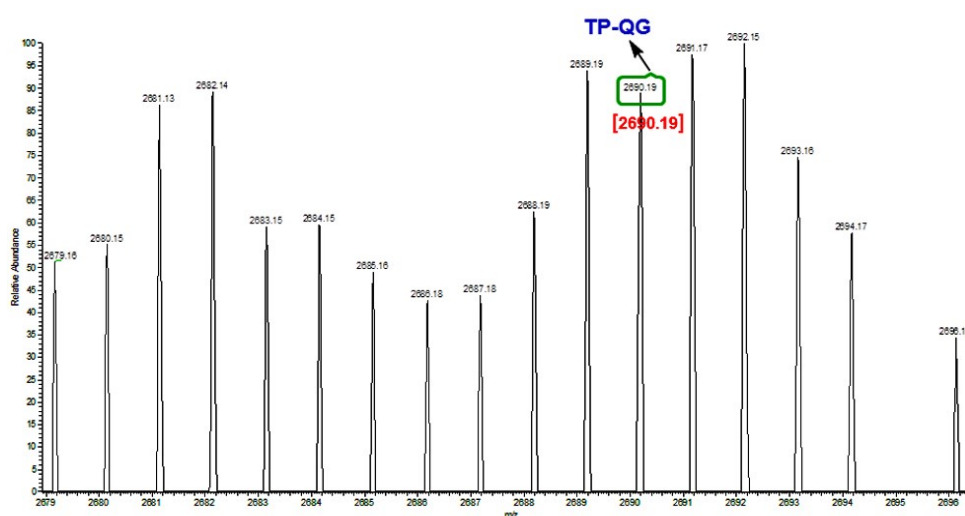
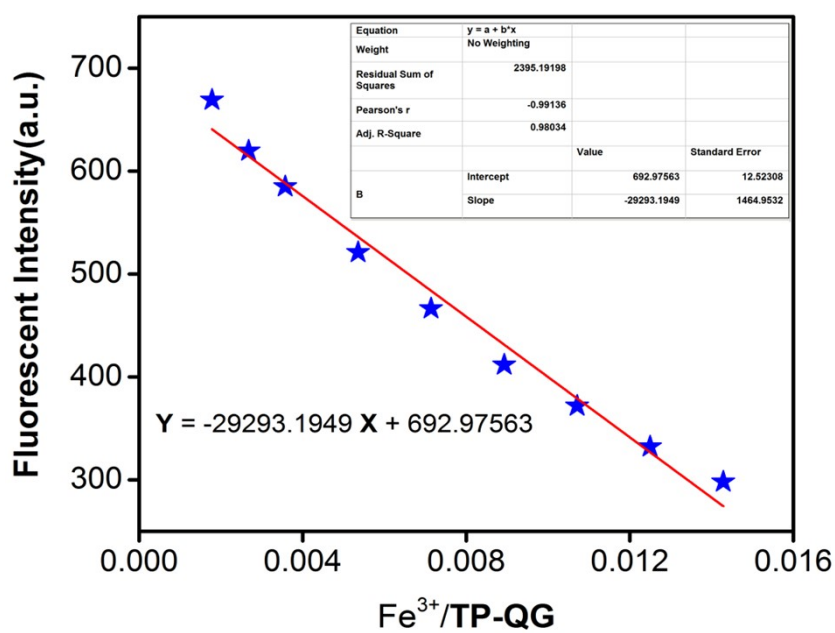


Fig. S12 ESI-MS spectrum of the TP-QG.

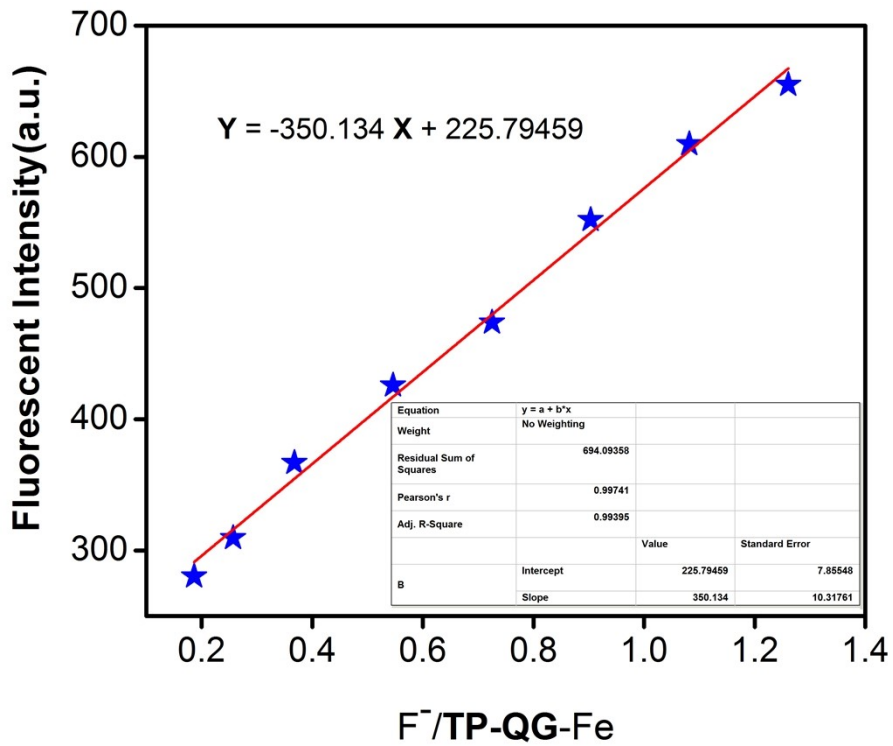


Linear Equation: Y= -29293.1949X + 692.97563

$$\delta = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}} = 2.2636 \quad K = 3$$

LOD = K ⚡ δ/s = 2.32 ⚡ 10⁻¹⁰ M

Fig. S13 The photograph of the linear range.



Linear Equation: Y= -350.134X + 225.79459

$$\delta = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}} = 5.0144 \quad K =$$

LOD = K ⚡ δ/s = 4.30 ⚡ 10⁻⁸ M

Fig. S14 The photograph of the linear range.

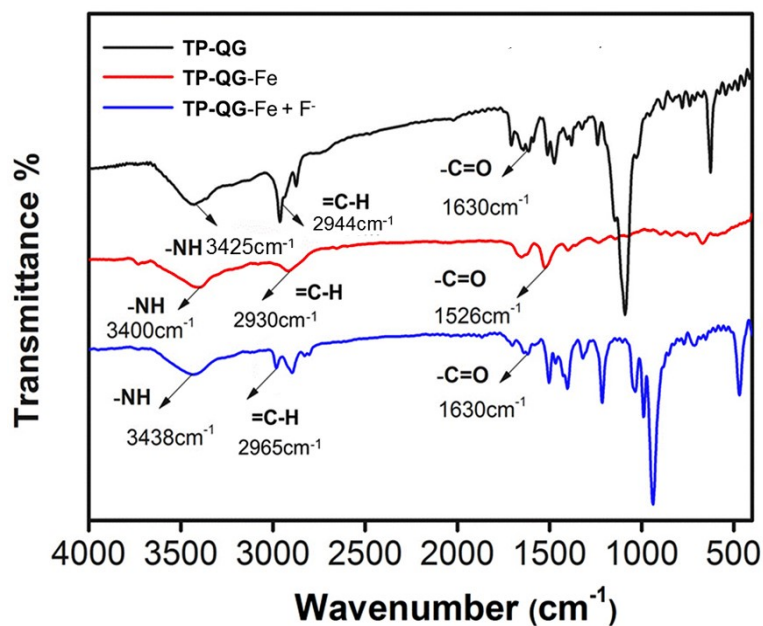


Fig. S15 IR spectra of the TP-QG (black), TP-QG-Fe (red) and TP-QG-Fe + F⁻ (blue) in KBr disks.

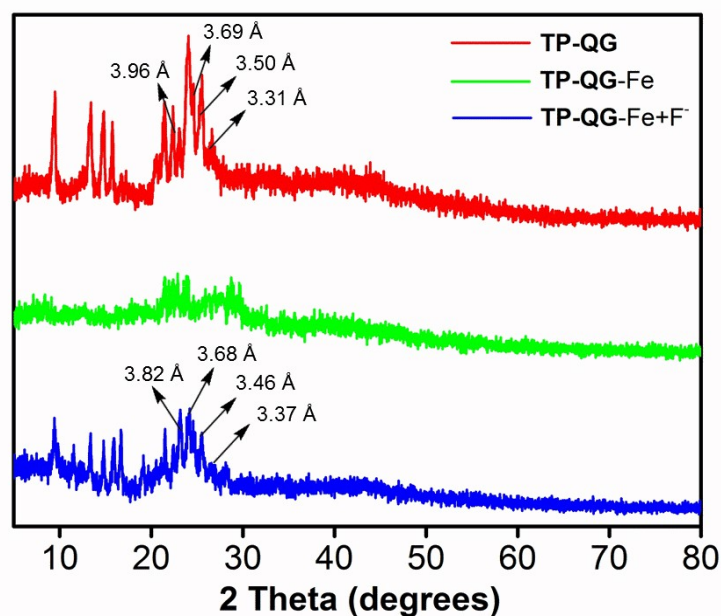


Fig. S16 Powder XRD patterns of xerogel TP-QG, TP-QG-Fe and TP-QG-Fe + F⁻.

Table S1 The ICP date of xerogel TP-QG with Fe³⁺.

Ion	Initial concentration (mg/L)	Residual concentration (mg/L)	Absorbing rate %
Fe ³⁺	4.62×10^{-5}	1.32×10^{-7}	98.68%

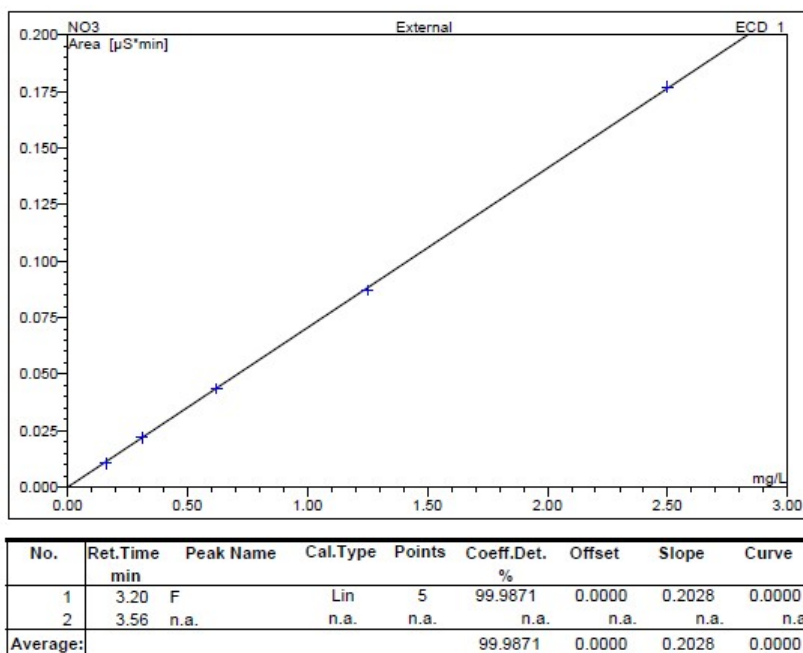


Fig. S17 The photograph of the IC linear range.

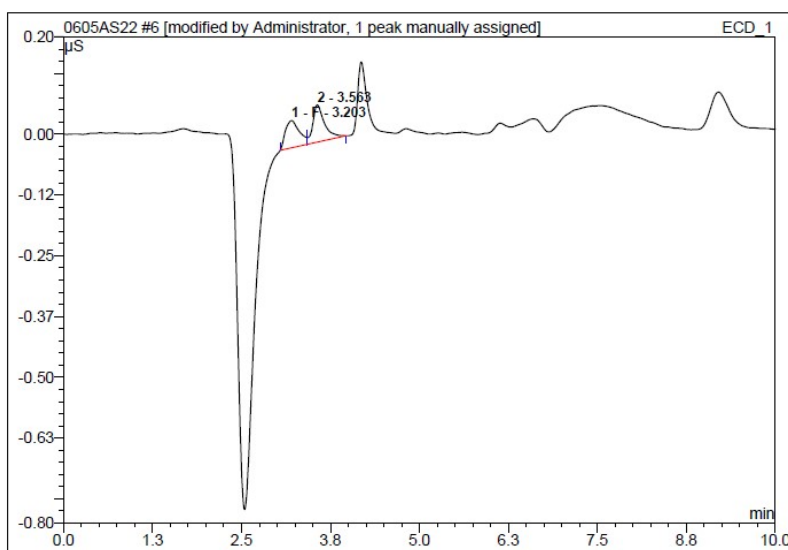


Fig. S18 Ion chromatogram of fluoride using an eluent containing Na_2CO_3 (4.5 mM) + NaHCO_3 (1.4 mM), a flow rate of 1.20 mL min^{-1} , injection volume of $25 \text{ }\mu\text{L}$ and suppress current of 31 mA. The peaks highlighted are due to 1-F^- . Detailed Data shown in **Table S2**.

Table S2 The detailed data of Fig. S18

No.	Ret.Time min	Peak Name	Height μS	Area $\mu\text{S}\cdot\text{min}$	Rel.Area %	Amount mg/L	Type
1	3.20	F	0.056	0.013	46.56	0.632	BM ^{^^}
2	3.56	n.a.	0.077	0.015	53.44	n.a.	MB [*]
Total:			0.133	0.028	100.00	0.632	

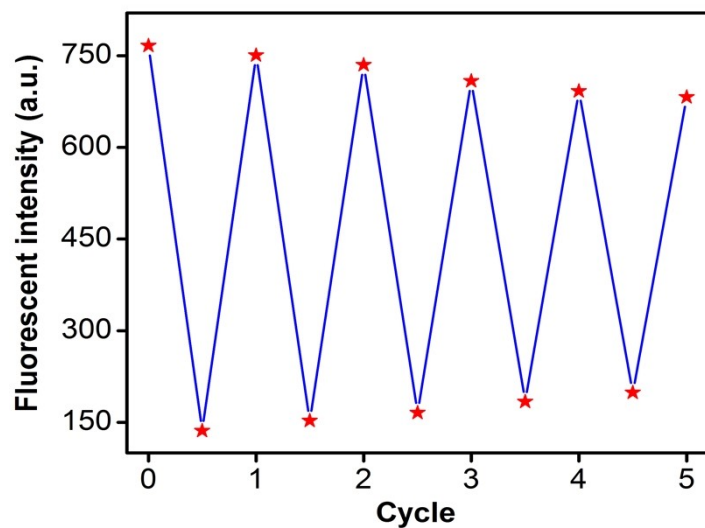


Fig. S19 The changes of fluorescent intensity "ON-OFF-ON" cycles of the TP-QG, controlled by the alternative addition of Fe^{3+} and F^- .

Notes and references

- [S1] T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022-5023.
- [S2] Y. Q. Fan, J. Liu, Y. Y. Chen, X. W. Guan, J. Wang, H. Yao, Y. M. Zhang, T. B. Wei and Q. Lin, *J. Mater. Chem. C*, 2018, **6**, 13331-13335.