

Supporting Information

Fluorescein-based fluorescent porous aromatic framework for Fe³⁺ detection with high sensitivity

Table of Contents

S.1 Experimental Section	Page 2
Synthesis of PAF-1.....	Page 2
Synthesis of PAF-NO ₂	Page 2
Synthesis of PAF-NH ₂	Page 2
Synthesis of PAF-5CF.....	Page 2
Figure S1:Characterizations	Page 3
Table S1.....	Page 3
Figure S3.....	Page 4
S.2 Luminescent measurements.....	Page 4
Figure S3-Figure S4.....	Page 4
Figure S5.....	Page 5
S.3 Reference.....	Page 6

S.1 Experimental Section

Synthesis of PAF-1

PAF-1 was synthesized according to the previously reported synthesis method.¹ Tetrakis(4-bromo-phenyl)methane is used as the tetrahedral building block and its benzene rings are connected by the Ullmann cross-coupling reaction catalyzed by nickel (0). PAF-1 was obtained as an off-white powder.

Synthesis of PAF-NO₂

PAF-1 (100 mg) was suspended in acetic anhydride (50 mL), and put the reaction vessel in ice water, then the reaction was carried out at room temperature for 2 days after dropwisely adding concentrated nitric acid. The mixture was filtered and washed with plenty of water to give solid of PAF-1-NO₂. Dried to get light yellow solid at 70 °C.

Synthesis of PAF-NH₂

Dried 100 mg of PAF-1-NO₂ and 3.26 g of SnCl₂·2H₂O were suspended in 20 mL of ethanol and heated at 70 °C for 8 h. The solids were centrifuged and suspended in 20 ml concentrated hydrochloric acid for 30 minutes. And then the solids were filtered and washed with water and ethanol with three times respectively to give yellow PAF-1-NH₂.

Synthesis of PAF-5CF

The mixture of 50 mg PAF-1-NH₂, 80 mg 5-carboxyfluorescein, 0.23 g 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) and 0.16g Nhydroxybenzotrizole (HOBT) was dissolved in 24 mL of dry DMF. Then 0.9 mL of triethylamine was added to the flask and the mixture was reacted at room temperature for 48 h under nitrogen atmosphere. The product were filtered and washed with DMF, ethanol, CH₂Cl₂, respectively. PAF-5CF was obtained as a light orange solid powder after drying under vacuum.

Characterizations

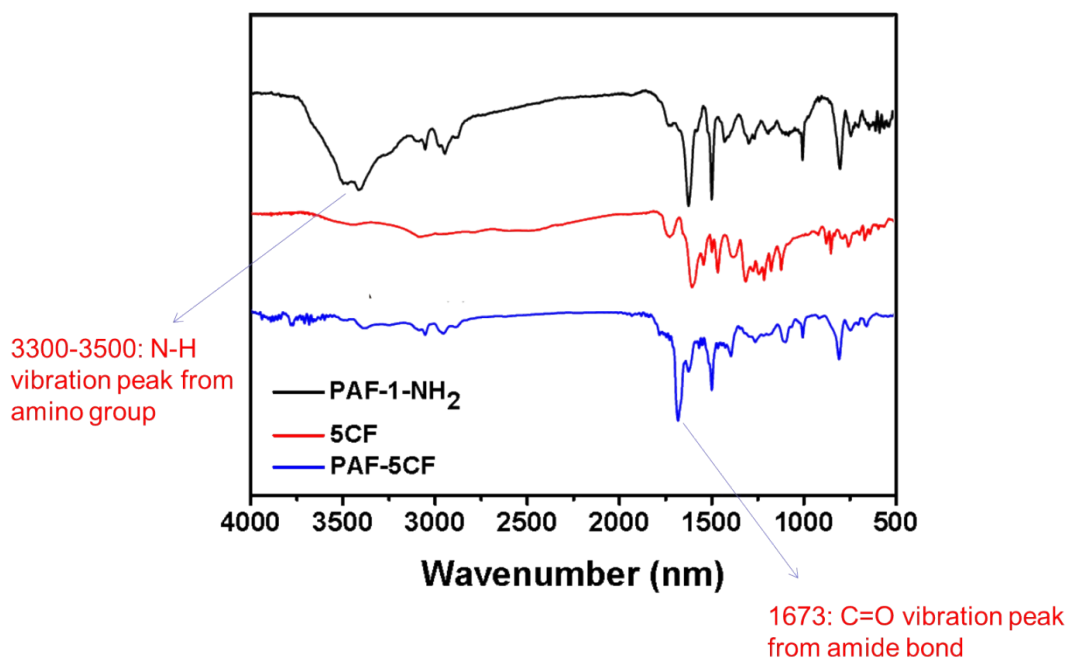


Fig. S1. FT-IR spectra of PAF-1-NH₂, 5-carboxyfluorescein and PAF-5CF.

Table S1. Peak assignment for the FT-IR spectra of PAF-1-NH₂.

Peak (cm ⁻¹)	Assignment and notes
3300-3500	N-H vibration peak from amino group
3410	O-H stretching from water
3037	Aromatic C-H stretching from phenyl rings.
2980, 2940	Aliphatic C-H stretching from CH ₃ and CH ₂ .
1673	C=O vibration peak from amide bond
1607	Aromatic ring C=C stretching

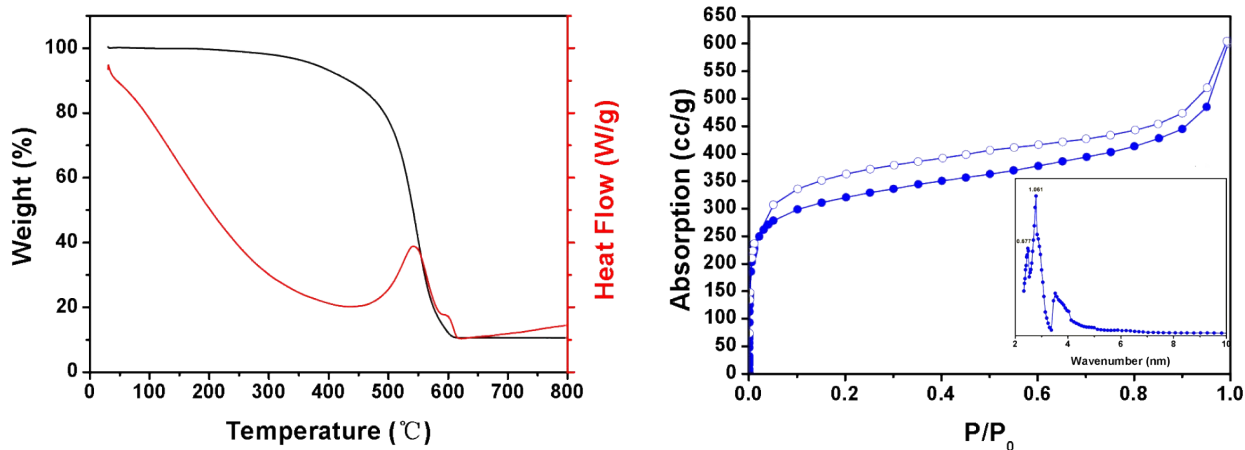


Fig. S2 (a) TGA and DSC curves of PAF-5CF. (b) N₂ adsorption isotherm of PAF-5CF at 77 K and its pore size distribution.

S.2 Luminescent measurements

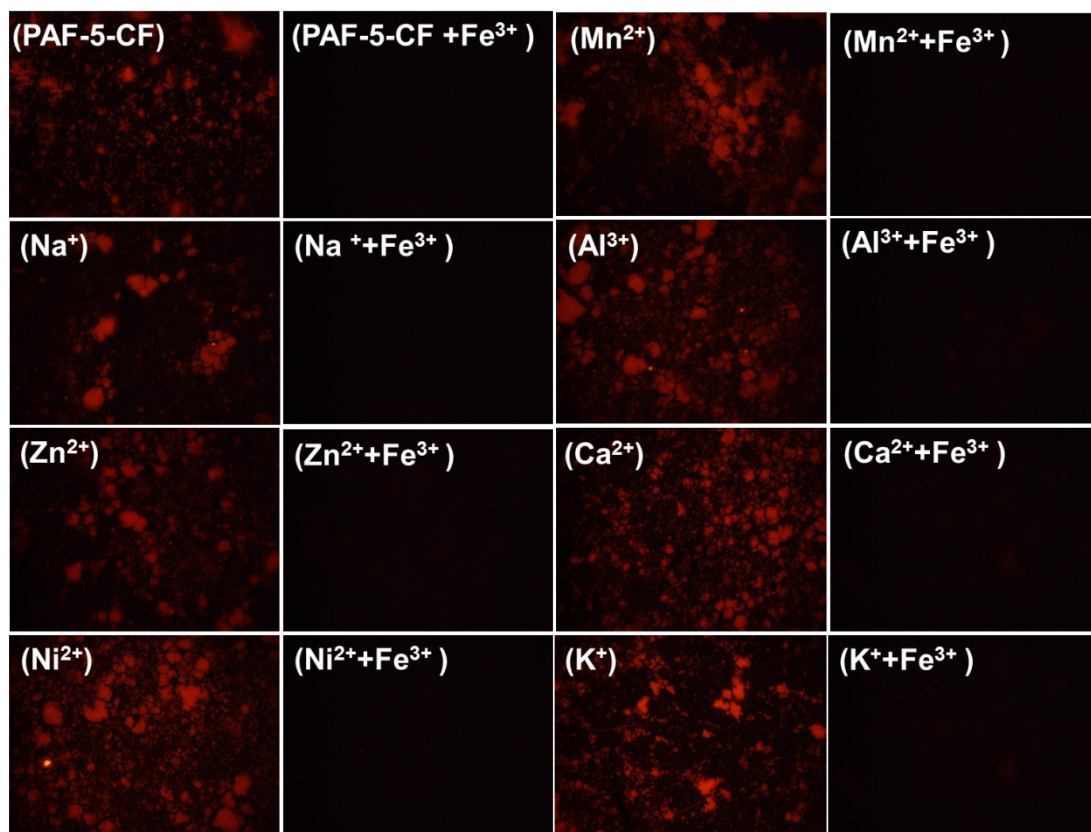


Fig. S3 Solid-state fluorescent photographs of PAF5-CF using a laser scanning confocal microscope.

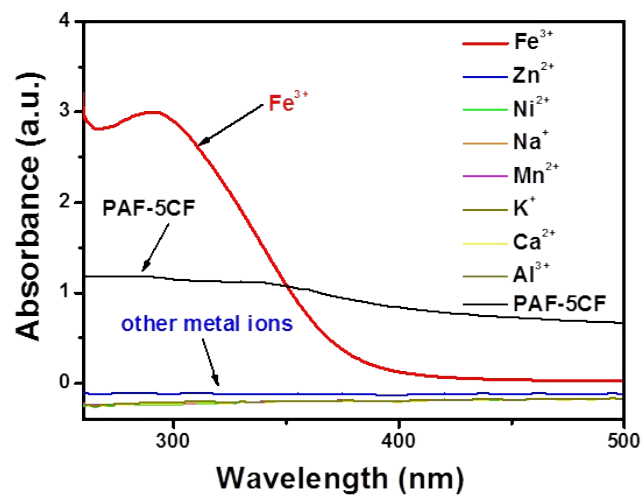


Fig. S4 Absorption spectra of metal ion solutions (1 mmol·L⁻¹) and PAF-5CF/ethanol suspension (0.5 mg/10 mL).

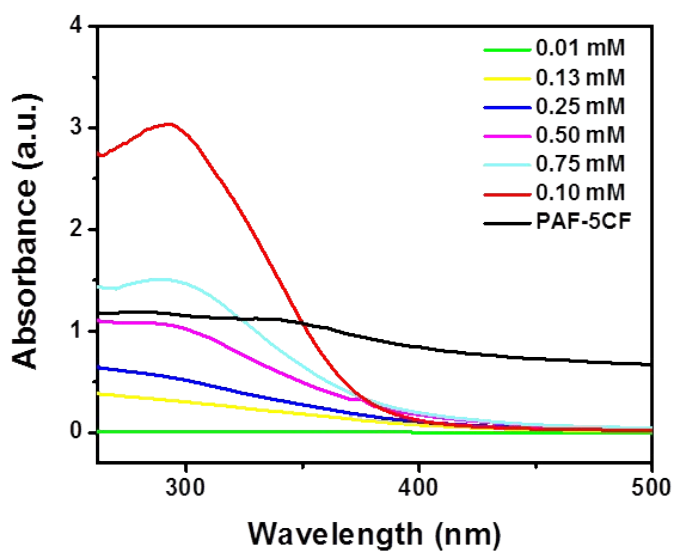


Fig. S5 Absorption spectra of PAF-5CF response to Fe³⁺ of different concentrations

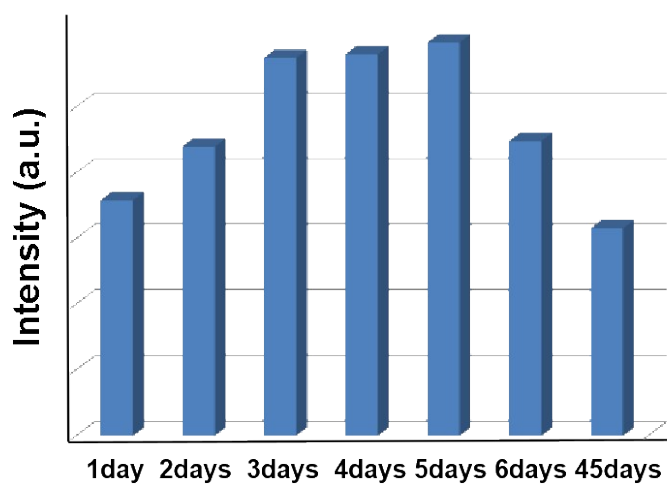


Fig. S6 The fluorescent intensity of PAF-5CF over different times.

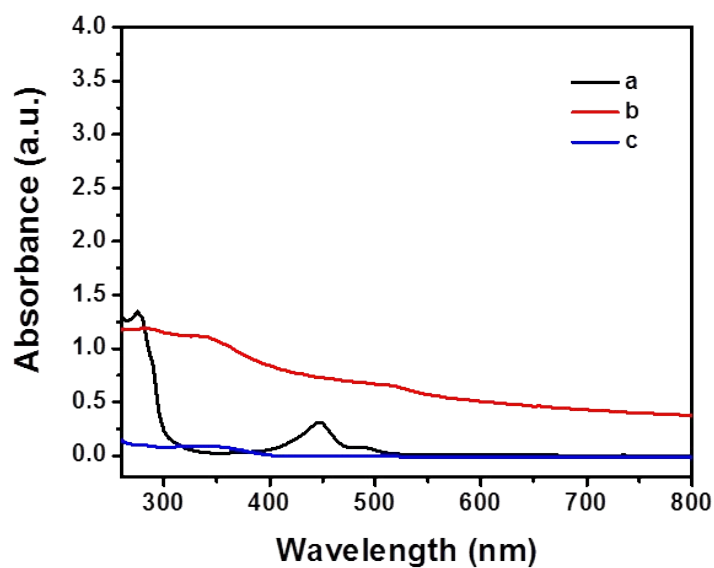


Fig. S7 Absorption spectra of the leaking test: (a) 5-CF solution; (b) PAF-5F suspension; (c) the filtrate of PAF-5F/ethanol suspension after stirring and washing for 24 h.

S.3 Reference

- 1 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9457.