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New Journal of Chemistry

Supporting Information

A fluorescent porous covalent-organic polymer (COP-3) for highly selective and sensitive detection of Fe^{3+} in aqueous solution

*Han Zhang,[ab] Guan-yu Ding,[ab] Dong-Xu Cui,[b] Afifa Yousaf,[b] Li Chen,[a] Guo-Gang Shan,[b] Xin-Long Wang,[*ab] Chun-Yi Sun,[*ab] and Zhong-Min Su[*abc]*

[a] School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China.
[b] National & Local United Engineering Laboratory for Power Batteries, Key Laboratory of Polyoxometalate Science of Ministry of Education Department of Chemistry, Northeast Normal University, Changchun 130024, China.
[c] Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun University of Science and Technology, Changchun, 130022, China

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Figure S13 The fluorescence intensity change of **COP-3** after added Fe^{3+} ions (excitation intensity).

Table S1. Detailed contents of Fe^{3+} ion in the reported materials.

1. Materials and measurement

All reagents and solvents for the synthesis were purchased from commercial sources and used as received, unless otherwise indicated. Infrared spectra were obtained from KBr pellets in a wavelength ranging from 4000-400 cm^{-1} on a Nicolet 380 FT-IR spectrophotometer and UV-Vis absorption was performed on U-3010 spectrophotometer (Hitachi, Japan). Photoluminescence spectra were recorded on a FL-4600 FL spectrophotometer and RF-6000 spectrophotometer. PXRD pattern was recorded on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range of 1.5-15°. SEM images were recorded on XL-30 ESEM-FEG Scanning Electron Microscope. Elemental analysis were performed on a Perkin-Elmer 240CHN elemental analyzer. The N_2 sorption tests were measured on automatic volumetric adsorption equipment (Belsorp mini II).

2. Synthesis and Method

Synthesis route of COP-3. COP-3 was obtained by the Suzuki-coupling reaction. briefly, 1,1,2,2-Tetrakis(4-bromophenyl)ethene (TBTPE) and Pyrene-2,7-diboronic Acid Bis(pinacol) Ester (PDABE) (molar ratio 1:2) were dissolved in 16 mL DMF. Then 2 mL K_2CO_3 (3.2 mM) aqueous solution and tetrakis(triphenylphosphine) palladium (0.01 mM) was added. After that, the mixture was degassed by three freeze–pump–thaw cycles and purged with N_2. The well-sealed mixture was stirred at 150 °C for 72 h and then cooled to room temperature and poured into water. The precipitate was collected by filtration and repeatedly washed with hydrochloric acid (2 M), water, ethanol, dichloromethane, acetone. The obtained crude product was rigorously washed by Soxhlet extraction for 24 h with dichloromethane and acetone sequentially. Finally, after dried in vacuum, **COP-3** was collected as yellow green powder. Element analysis (%): calculated for **COP-3** ($C_{138}H_{102}$): C, 94.16, H, 5.84. Found: C, 93.07; H, 4.06.

Chemical sensing of metal ions. Titration experiments of metal ions were carried out

by adding different concentration of metal salt solutions (20 μL) into the dimethylacetamide (DMA) suspension (1 mL) containing **COP-3** (0.005 mg/mL) at intervals of 1 min. Fluorescence spectra were recorded after the addition of metal salt solutions. The excitation wavelength is 360 nm.

The fluorescence quenching was analyzed using the Stern-Volmer equations:

$$\mathbf{I_0/I = 1 + K_{sv}\,[Q]}$$

where I_0 and I are the fluorescence intensity, in the absence and presence of analyte, respectively, $\boldsymbol{K_{sv}}$ is the Stern-Volmer quenching constant and [Q] is the concentration of analyte. The quenching percentage was calculated using the equation as follows:

Fluorescence quenching % = $(1 - I/I_0) \times 100$ %

where I_0 is the initial fluorescence intensity in the absence of metal ions, I is the fluorescence intensity in the presence of corresponding analyte.

The limit of detection concentration (LOD) was calculated according to the formula:

$$\mathbf{LOD = 3\delta / K_{sv}.}$$

and $\boldsymbol{\delta}$ is the standard deviation of the detection method.

Regeneration tests of COP-3. Regeneration tests of **COP-3** were carried out by adding 0.01 M Fe^{3+} ion (120 μL) into the dimethylacetamide (DMA) suspension (1 mL) containing **COP-1** (0.005 mg/mL) at intervals of 2 min. Fluorescence spectra were recorded after the addition of solution contains Fe^{3+} ion. After the fluorescence test, the Fe^{3+} ion was removed by centrifuging 5 min, washing with DMA three times. The re-generate **COP-3** suspension was obtained after 2 mL DMA was added to precipitant. Fluorescence spectra were recorded the performance of the re-generate **COP-3**.

3. Characterizations and results

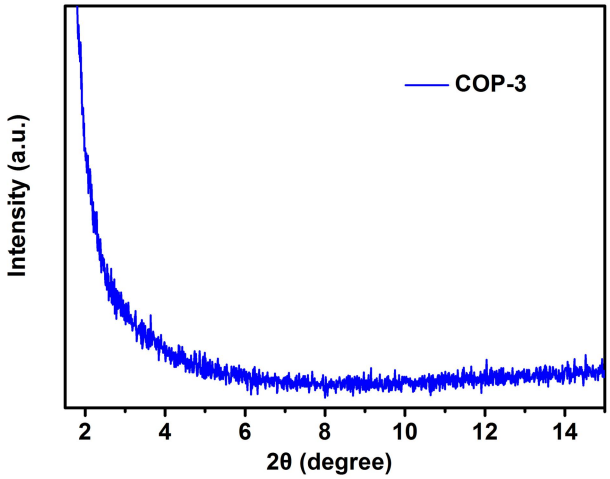


Figure S1 PXRD pattern of **COP-3**.

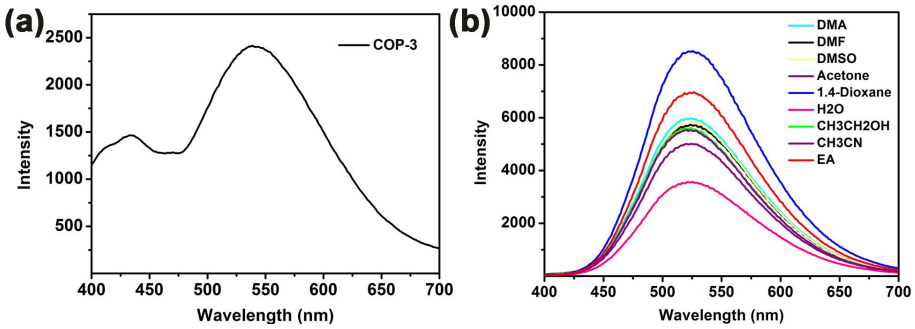


Figure S2 (a) Solid-state fluorescence spectrum of **COP-3**; (b) Fluorescence spectra in different solvents.

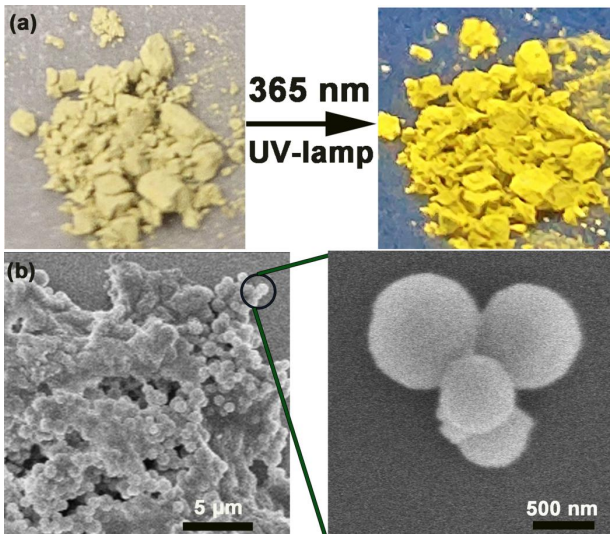


Figure S3 (a) Fluorescence photographs of COP-3 under 365 nm UV-Lamp; (b) SEM image of **COP-3**.

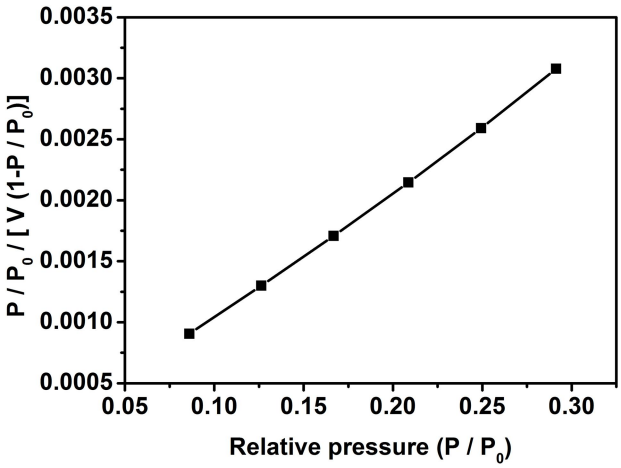


Figure S4 BET of **COP-3**.

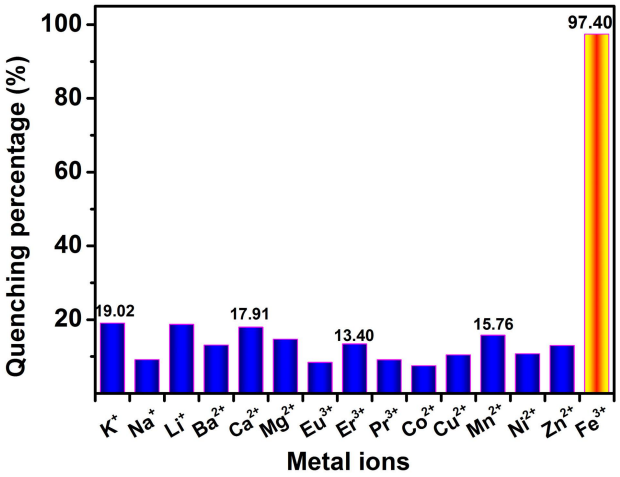


Figure S5 Quenching percentage of **COP-3** after added metal ions (120 μM).

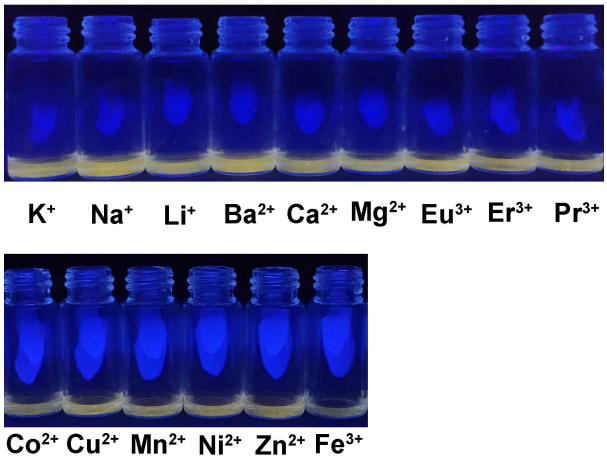


Figure S6 Fluorescence photographs of **COP-3** after added different metal ions (120 μM).

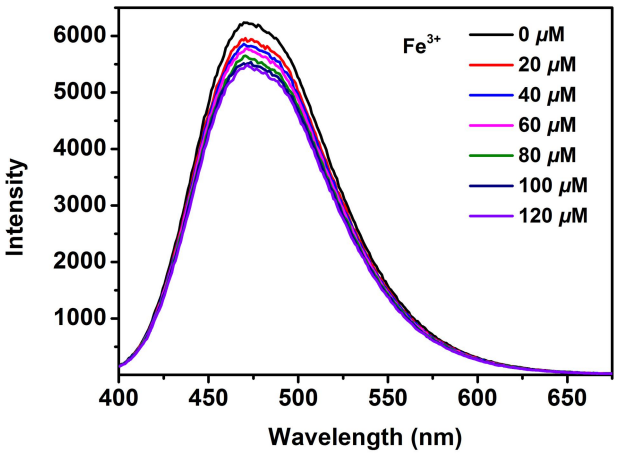
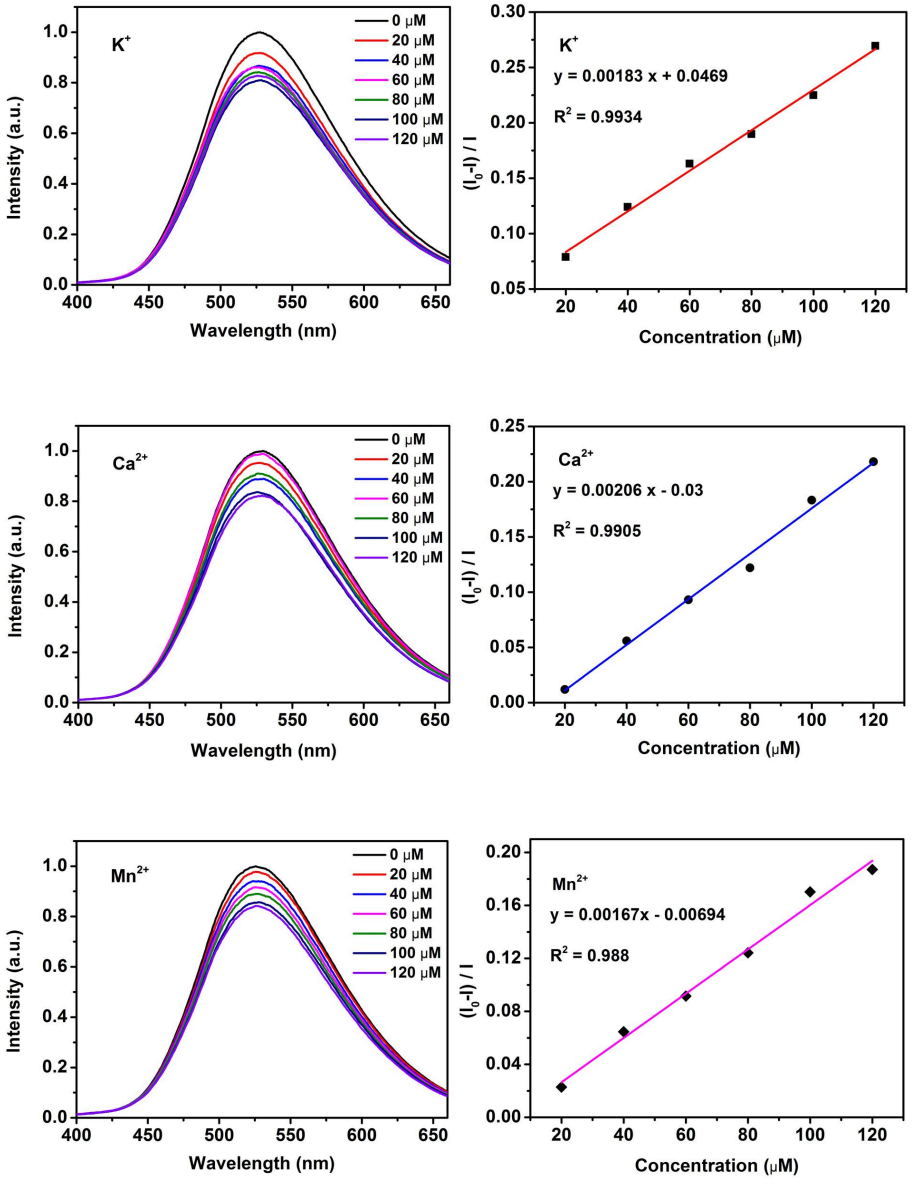


Figure S7 Fluorescence emission spectra of TBTPE (c = 0.2 mg / mL, V_{DMA}:V_{H2O} = 1:4). (λex = 365 nm).



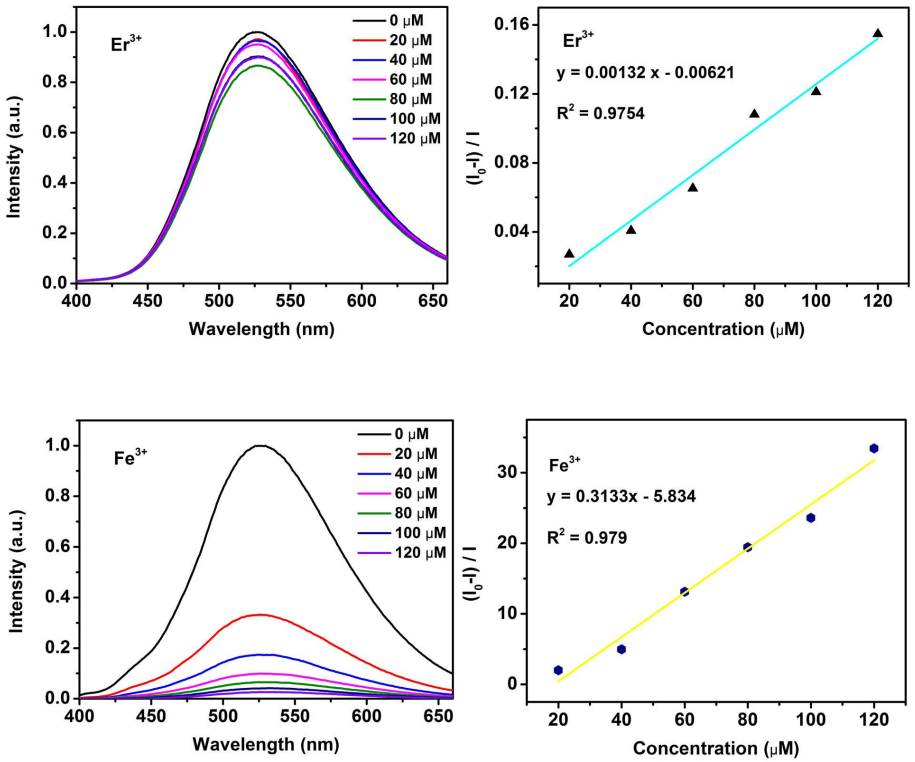


Figure S8 Fluorescence emission spectra of **COP-3** upon titration with different metal ions solution at room temperature (λex = 365 nm).

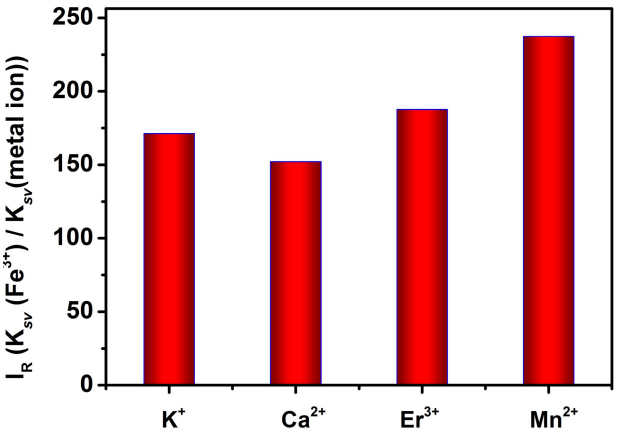


Figure S9 Relative intensity of K_{sv} (I_R = Ksv (Fe^{3+}) / Ksv (metal ion)).

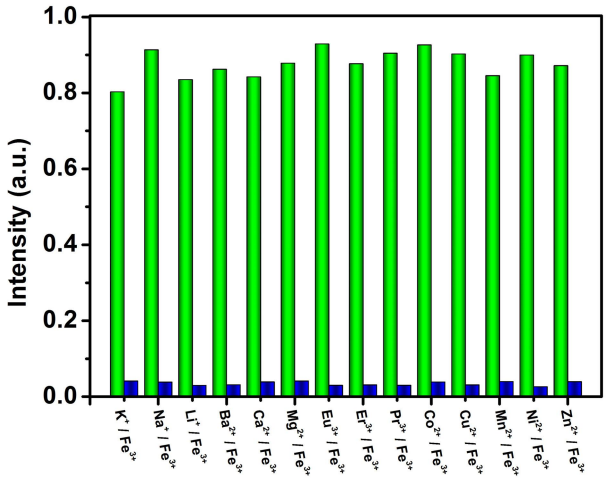


Figure S10 Competition tests in the absence or presence of Fe^{3+} (c = 120 μM).

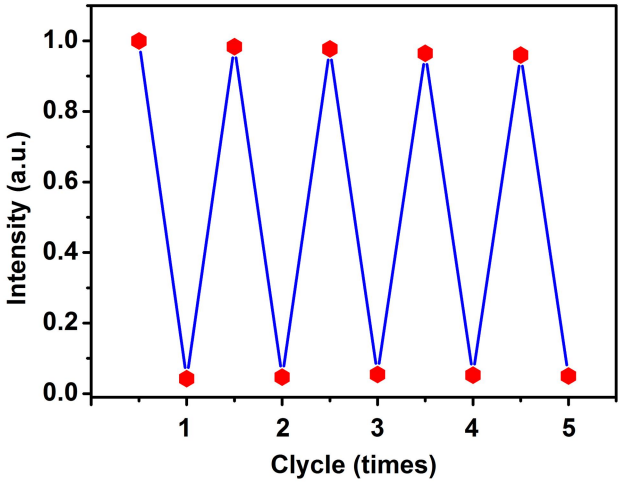


Figure S11 Recycle tests of **COP-3** after added Fe^{3+} ions.

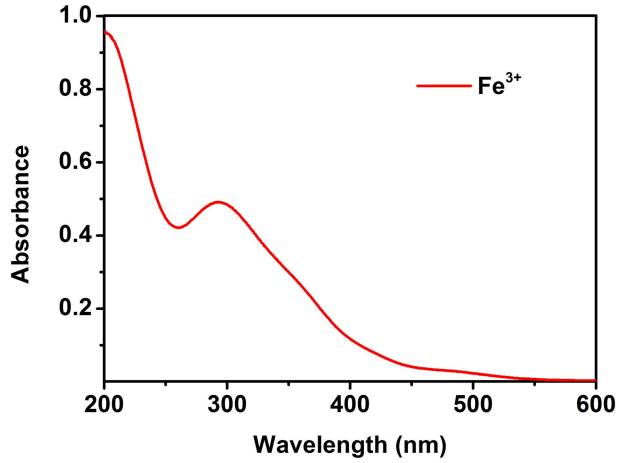


Figure S12 UV-Vis spectrum of Fe^{3+} solution.

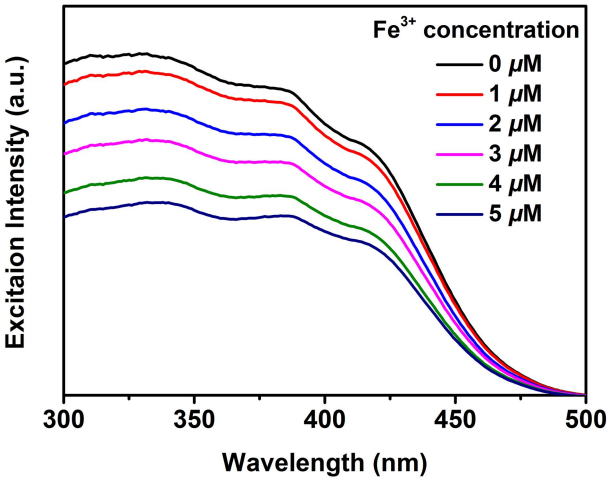


Figure S13 The fluorescence intensity change of **COP-3** after added Fe^{3+} (excitation intensity).

Table S1 Detailed contents of Fe^{3+} ion in the reported materials.

Materials	**Quenching percentage (%)**	**LOD (*μ*M)**	**DOI**
NUS-24 [1]	91.7	900	10.1038/s41467-017-01293-x
CNQD [2]	95	1	10.1021/acsnano.5b05924
NCQDs[3]		4.67	10.1039/C5NJ03252K
GQD [4]	68	7.22	10.1002/adfm.201303441
P2 [5]	-	100	j.dyepig.2019.04.010
PAF-5CF[6]	-	38	previous work
Salen-COP [7]	-	0.54	10.1007/s10853-018-2821-3
P1 [8]	-	0.699	10.1039/c7ra00540g
Compound 1[9]	-	70.8	10.1039/C9CE00542K
COP-1[10]	94.2	0.42	previous work
Compound [11]	-	18.8	10.1039/D0CE00457J
COP-3	**97.5**	**0.191**	**This work**

Notes and references

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