

Supporting Information

Assembly of a rod indium-organic framework with fluorescence property for selective sensing of Cu²⁺, Fe³⁺ and nitroaromatics in water

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Materials and Measurements

All reagents and solvents were purchased from commercial sources and used without purification. TCA was prepared according to the literature¹. Powder X-ray diffraction (PXRD) patterns was collected on a PANalytical X'Pert Powder X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm), 2θ ranging from 5 to 50 ° with an increment of 0.02 °, and a scanning rate of 10 °/min. The FT-IR spectra was measured by using KBr pellets in the range 4000 - 500 cm^{-1} on a Thermo Scientific spectrometer. The UV-Vis absorption was measured with a PERSEE UV-Vis-NIR spectrophotometer. The fluorescent spectroscopy was measured on a FL-7000 HITACHI luminescence spectrometer at room temperature with a light source of Xenon lamp.

X-ray crystallography

Crystallographic diffraction data for **JOU-25** was recorded on a Bruker Apex CCD diffractometer with graphite monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. **JOU-25** was solved by Direct Method of SHELXS-2018 and refined by full-matrix least-squares technique by using the SHELXL-2018 program². All nonhydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms were placed in geometrically idealized position as a riding mode. The solvent molecules in the crystal are highly disordered and are removed by using the SQUEEZE routine of PLATON³. For **JOU-25-R**, SADI, DFIX, SIMU, ISOR and FLAT commands were used to restrict some of the atoms and bond length, whereas AFIX 66 was used to restrict the geometry of benzene ring of the ligand. For **JOU-25-S**, DFIX, SIMU and ISOR commands were used to restrict some of the atoms and bond length, whereas AFIX 66 was used to restrict the geometry of benzene ring of the ligand. For both **JOU-25-R** and **JOU-25-S**, PLAT420_ALERT_2_B may be due to the following reasons. The solvent molecules may be the acceptors of this O-H bonds, but the solvent molecules are highly disordered and removed using the SQUEEZE routine of PLATON. For **JOU-25-S**, although the crystallographic data have been recorded twice and Twin/BASF commands have been added, a relative high flack value was obtained, resulting in PLAT987_ALERT_1_B. PLAT342_ALERT_3_B may be due to the bad quality of the crystal. The crystallographic data for **JOU-25** was summarized in Table S1, and the selected bond lengths and angles are listed in Table S2 and S3. CCDC numbers for **JOU-25-R** and **JOU-25-S** are 2103362 and 2103363, respectively.

Table S1. Crystallographic data and structure refinements of **JOU-25**.

Compounds	JOU-25-R	JOU-25-S
Formula	C ₈₇ H ₆₄ In ₅ N ₅ O ₃₁	C ₈₇ H ₆₄ In ₅ N ₅ O ₃₁
Formula weight	2249.53	2249.53
Crystal system	hexagonal	hexagonal
Space group	$P6_1$	$P6_5$
a (Å)	37.5060(8)	37.662(5)
b (Å)	37.5060(8)	37.662(5)
c (Å)	16.9308(7)	17.189(2)

α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å ³)	20625.7(12)	21115(6)
Z	6	6
Density (g cm ⁻³)	1.087	1.061
μ / mm ⁻¹	0.881	0.861
$F(000)$	6384	6684
2θ (°)	4.466 - 50.485	4.901 - 50.565
Reflections	273224	115846
Data/restraints/parameters	31574/1305/1076	24522/2797/1052
GOF on F ²	1.040	1.049
R_1, wR_2 [I > 2 σ (I)]	0.0322, 0.0831	0.0891, 0.2265
R_1, wR_2 (all data)	0.0397, 0.0914	0.1159, 0.2602

$$^a R_1 = \sum ||F_o| - |Fc|| / \sum |F_o|; wR_2 = \sum [w(F_o^2 - Fc^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

Table S2. Selected bond lengths (Å) and angels (°) for **JOU-25-R**.

In ₁ -O ₁₂ ²	2.131(7)	In ₁ -O ₂₅	2.116(5)
In ₁ -O ₂₈ ¹	2.125(5)	In ₁ -O ₃ ³	2.145(7)
In ₁ -O ₁₀ ³	2.178(6)	In ₁ -O ₁	2.188(6)
In ₂ -O ₂₅	2.086(6)	In ₂ -O ₂₆	2.07(6)
In ₂ -O ₂	2.082(6)	In ₂ -O ₁₄	2.15(6)
In ₂ -O ₄ ³	2.152(7)	In ₂ -O ₇	2.2(6)
In ₃ -O ₂₆	2.125(6)	In ₃ -O ₂₇	2.115(6)
In ₃ -O ₈	2.115(7)	In ₃ -O ₅ ³	2.136(6)
In ₃ -O ₂₀	2.158(6)	In ₃ -O ₁₃	2.16 (6)
In ₄ -O ₂₇	2.068(5)	In ₄ -O ₂₈	2.101(5)
In ₄ -O ₉ ³	2.136(6)	In ₄ -O ₁₉	2.152(5)
In ₄ -O ₁₁ ¹	2.170(6)	In ₄ -O ₆ ³	2.17(6)
In ₅ -O ₂₉	2.096(6)	In ₅ -O ₂₁ ³	2.163(6)
In ₅ -O ₁₅	2.148(6)	In ₅ -O ₂₂	2.145(6)
In ₅ -O ₁₆ ³	2.173(6)	In ₅ -O ₂₉ ³	2.09(7)
O ₁₂ ¹ -In ₁ -O ₂₅	91.9(6)	O ₁₂ ¹ -In ₁ -O ₂₈ ²	93.1(6)
O ₂₅ -In ₁ -O ₂₈ ²	90.3(4)	O ₁₂ ¹ -In ₁ -O ₃ ³	172.3(6)
O ₂₅ -In ₁ -O ₃ ³	93.2(6)	O ₂₈ ² -In ₁ -O ₃ ³	92.7(5)
O ₁₂ ¹ -In ₁ -O ₁₀ ³	87.4(7)	O ₂₅ -In ₁ -O ₁₀ ³	175.9(5)
O ₂₈ -In ₁ -O ₁₀ ³	93.8(5)	O ₃ ³ -In ₁ -O ₁₀ ³	87.1(7)
O ₁₂ ¹ -In ₁ -O ₁	86.2(7)	O ₂₅ -In ₁ -O ₁	93.4(5)
O ₂₈ ² -In ₁ -O ₁	176.2(5)	O ₃₃ -In ₁ -O ₁	87. 7(7)
O ₁₀ ³ -In ₁ -O ₁	82.5(5)	O ₂₅ -In ₂ -O ₂₆	97.2(5)
O ₂₅ -In ₂ -O ₂	87.3(6)	O ₂₆ -In ₂ -O ₂	172.5(7)
O ₂₅ -In ₂ -O ₁₄	97.4(5)	O ₂₆ -In ₂ -O ₁₄	89.7(5)
O ₂ -In ₂ -O ₁₄	83.7(7)	O ₂₅ -In ₂ -O ₄ ³	93.4(6)
O ₂₆ -In ₂ -O ₄ ³	93.4(7)	O ₂ -In ₂ -O ₄ ³	92.3(8)

O ₁₄ -In ₂ -O ₄ ³	168.3(7)	O ₂₅ -In ₂ -O ₇	168.8(5)
O ₂₆ -In ₂ -O ₇	92.5(5)	O ₂ -In ₂ -O ₇	83.6(6)
O ₁₄ -In ₂ -O ₇	88.2(6)	O ₄ ³ -In ₂ -O ₇	80.4(6)
O ₂₆ -In ₃ -O ₂₇	88.4(5)	O ₂₆ -In ₃ -O ₈	91(6)
O ₂₇ -In ₃ -O ₈	91.9(6)	O ₂₆ -In ₃ -O ₅ ³	91(7)
O ₂₇ -In ₃ -O ₅ ⁵	90.2(6)	O ₈ -In ₃ -O ₅ ³	177.1(7)
O ₂₆ -In ₃ -O ₂₀	176(6)	O ₂₇ -In ₃ -O ₂₀	92(5)
O ₈ -In ₃ -O ₂₀	85(6)	O ₅ ³ -In ₃ -O ₂₀	93(7)
O ₂₆ -In ₃ -O ₁₃	93(5)	O ₂₇ -In ₃ -O ₁₃	174.5(5)
O ₈ -In ₃ -O ₁₃	93.3(7)	O ₅ ³ -In ₃ -O ₁₃	84.5(6)
O ₂₀ -In ₃ -O ₁₃	86.9(5)	O ₂₇ -In ₄ -O ₂₈	96.1(5)
O ₂₇ -In ₄ -O ₉ ³	174.2(6)	O ₂₈ -In ₄ -O ₉ ³	87.6(6)
O ₂₇ -In ₄ -O ₁₉	90.7(5)	O ₂₈ -In ₄ -O ₁₉	98.4(5)
O ₉ ³ -In ₄ -O ₁₉	84.4(6)	O ₂₇ -In ₄ -O ₁₁ ²	94.9(7)
O ₂₈ -In ₄ -O ₁₁ ²	93.5(6)	O ₉ ³ -In ₄ -O ₁₁ ²	89.3(8)
O ₁₉ -In ₄ -O ₁₁ ²	166.3(7)	O ₂₇ -In ₄ -O ₆ ³	92 (5)
O ₂₈ -In ₄ -O ₆ ³	170.1(5)	O ₉ ³ -In ₄ -O ₆ ³	84.8(6)
O ₁₉ -In ₄ -O ₆ ³	87.2(6)	O ₁₁ ² -In ₄ -O ₆ ³	80.1(6)
O ₂₉ -In ₅ -O ₂₉ ³	90.6(5)	O ₂₉ -In ₅ -O ₂₁ ³	96.8(7)
O ₂₉ ³ -In ₅ -O ₂₁ ³	92.8(7)	O ₂₉ -In ₅ -O ₁₅	171.3(8)
O ₂₉ ³ -In ₅ -O ₁₅	92.1(7)	O ₂₁ ³ -In ₅ -O ₁₅	91.3(8)
O ₂₉ -In ₅ -O ₂₂	90.9(7)	O ₂₉ ³ -In ₅ -O ₂₂	172.4(8)
O ₂₁ ³ -In ₅ -O ₂₂	79.6(9)	O ₁₅ -In ₅ -O ₂₂	87.5(8)
O ₂₉ -In ₅ -O ₁₆ ³	88.3(7)	O ₂₉ ² -In ₅ -O ₁₆ ³	94.2(7)
O ₂₁ ² -In ₅ -O ₁₆ ³	171.3(9)	O ₁₅ -In ₅ -O ₁₆ ³	83.2(9)

Symmetry transformations: ¹ 1 + x, + y, -1 + z; ² 2 - x, 1 - y, -1/2 + z; ³ 1 - y, + x - y, 1/3 + z.

Table S3. Selected bond lengths (Å) and angels (°) for **JOU-25-S**.

In ₁ -O ₂₆	2.07(2)	In ₁ -O ₁₃	2.09(3)
In ₁ -O ₁₇ ¹	2.11(3)	In ₁ -O ₂	2.13(3)
In ₁ -O ₂₀	2.13(3)	In ₁ -O ₂₅	2.17(3)
In ₂ -O ₁₉	2.08(3)	In ₂ -O ₂₇	2.13(3)
In ₂ -O ₂₆	2.15(3)	In ₂ -O ₁	2.15(3)
In ₂ -O ₈	2.18(3)	In ₂ -O ₁₆ ²	2.18(3)
In ₃ -O ₂₈ ³	2.04(3)	In ₃ -O ₂₄ ²	2.08(3)
In ₃ -O ₂₇	2.08(3)	In ₃ -O ₇	2.12(3)
In ₃ -O ₂₁ ³	2.16(3)	In ₃ -O ₁₅ ²	2.21(3)
In ₄ -O ₁₈ ¹	2.1(3)	In ₄ -O ₂₃ ²	2.1(3)
In ₄ -O ₂₅	2.14(3)	In ₄ -O ₂₈	2.14(3)
In ₄ -O ₁₄	2.15(3)	In ₄ -O ₂₂ ³	2.15(3)
In ₅ -O ₂₉ ²	2.06(3)	In ₅ -O ₁₀ ²	2.11(2)
In ₅ -O ₂₉	2.14(3)	In ₅ -O ₆ ³	2.16(3)
In ₅ -O ₉	2.17(3)	In ₅ -O ₅	2.19(3)

O ₂₆ -In ₁ -O ₁₃	177.1(12)	O ₂₆ -In ₁ -O ₁₇ ¹	92.4(12)
O ₁₃ -In ₁ -O ₁₇ ¹	90.3(12)	O ₂₆ -In ₁ -O ₂	91.6(11)
O ₁₃ -In ₁ -O ₂	85.9(11)	O ₁₇ ¹ -In ₁ -O ₂	169.4(13)
O ₂₆ -In ₁ -O ₂₀	94.6(11)	O ₁₃ -In ₁ -O ₂₀	86.6(11)
O ₁₇ ¹ -In ₁ -O ₂₀	83(12)	O ₂ -In ₁ -O ₂₀	86.9(12)
O ₂₆ -In ₁ -O ₂₅	94.3(11)	O ₁₃ -In ₁ -O ₂₅	84.7(11)
O ₁₇ ¹ -In ₁ -O ₂₅	92(12)	O ₂ -In ₁ -O ₂₅	97.5(12)
O ₂₀ -In ₁ -O ₂₅	170(11)	O ₁₉ -In ₂ -O ₂₇	91(11)
O ₁₉ -In ₂ -O ₂₆	91(11)	O ₂₇ -In ₂ -O ₂₆	91.8(9)
O ₁₉ -In ₂ -O ₁	91.2(12)	O ₂₇ -In ₂ -O ₁	176.2(12)
O ₂₆ -In ₂ -O ₁₄	83.7(7)	O ₂₅ -In ₂ -O ₄ ³	93.4(6)
O ₂₆ -In ₂ -O ₁	91.2(11)	O ₁₉ -In ₂ -O ₈	85.7(12)
O ₂₇ -In ₂ -O ₈	92.5(11)	O ₂₆ -In ₂ -O ₈	174.6(10)
O ₁ -In ₂ -O ₈	84.6(10)	O ₁₉ -In ₂ -O ₁₆ ²	178.2(13)
O ₂₇ -In ₂ -O ₁₆ ²	90.8(12)	O ₂₆ -In ₂ -O ₁₆ ²	88.7(11)
O ₁ -In ₂ -O ₁₆ ²	87(12)	O ₈ -In ₂ -O ₁₆ ²	94.5(12)
O ₂₈ ³ -In ₃ -O ₂₄ ²	89.4(11)	O ₂₈ ³ -In ₃ -O ₂₇	98.9(12)
O ₂₄ ² -In ₃ -O ₂₇	171.2(12)	O ₂₈ ³ -In ₃ -O ₇	97.8(11)
O ₂₄ ² -In ₃ -O ₇	88.3(12)	O ₂₇ -In ₃ -O ₇	87.8(11)
O ₂₈ ³ -In ₃ -O ₂₁ ³	91.5(11)	O ₂₄ ² -In ₃ -O ₂₁ ³	89.4(12)
O ₂₇ -In ₃ -O ₂₁ ³	93.2(12)	O ₇ -In ₃ -O ₂₁ ³	170.4(13)
O ₂₈ ³ -In ₃ -O ₁₅ ²	167.5(11)	O ₂₄ ² -In ₃ -O ₁₅ ²	80.5(11)
O ₂₇ -In ₃ -O ₁₅ ²	91.6(11)	O ₇ -In ₃ -O ₁₅ ²	89.4(12)
O ₂₁ ³ -In ₃ -O ₁₅ ²	81(12)	O ₁₈ ¹ -In ₄ -O ₂₃ ²	83.1(13)
O ₁₈ ¹ -In ₄ -O ₂₅	97.3(12)	O ₂₃ ² -In ₄ -O ₂₅	175.6(12)
O ₁₈ ¹ -In ₄ -O ₂₈	94.9(12)	O ₂₃ ² -In ₄ -O ₂₈	94.9(11)
O ₂₅ -In ₄ -O ₂₈	89.5(10)	O ₁₈ ¹ -In ₄ -O ₁₄	86(13)
O ₂₃ ³ -In ₄ -O ₁₄	84.2(11)	O ₂₅ -In ₄ -O ₁₄	91.5(11)
O ₂₈ -In ₄ -O ₁₄	178.6(12)	O ₁₈ ¹ -In ₄ -O ₂₂ ³	170.2(11)
O ₂₃ ² -In ₄ -O ₂₂ ³	88.6(12)	O ₂₅ -In ₄ -O ₂₂ ³	90.6(12)
O ₂₈ -In ₄ -O ₂₂ ³	91(10)	O ₁₄ -In ₄ -O ₂₂ ³	88(11)
O ₂₉ ² -In ₅ -O ₁₀ ²	90.2(12)	O ₂₉ ² -In ₅ -O ₂₉	90.8(11)
O ₁₀ ² -In ₅ -O ₂₉	95.3(12)	O ₂₉ ² -In ₅ -O ₆ ³	95.8(11)
O ₁₀ ² -In ₅ -O ₆ ³	171.2(12)	O ₂₉ -In ₅ -O ₆ ³	91 (13)
O ₂₉ ² -In ₅ -O ₉	170.5(12)	O ₁₀ ² -In ₅ -O ₉	80.6(13)
O ₂₉ -In ₅ -O ₉	92.7(11)	O ₆ ³ -In ₅ -O ₉	93(12)
O ₂₉ ² -In ₅ -O ₅	94(12)	O ₁₀ ² -In ₅ -O ₅	90.4(12)
O ₂₉ -In ₅ -O ₅	172.5(12)	O ₆ ³ -In ₅ -O ₅	82.8(12)

Symmetry transformations: ¹ 1 + y - x; 1 - x, 1/3 + z; ² 1 - y + x, +x, -1/6 + z; ³ 2 - x, 1 - y, 1/2 + z.

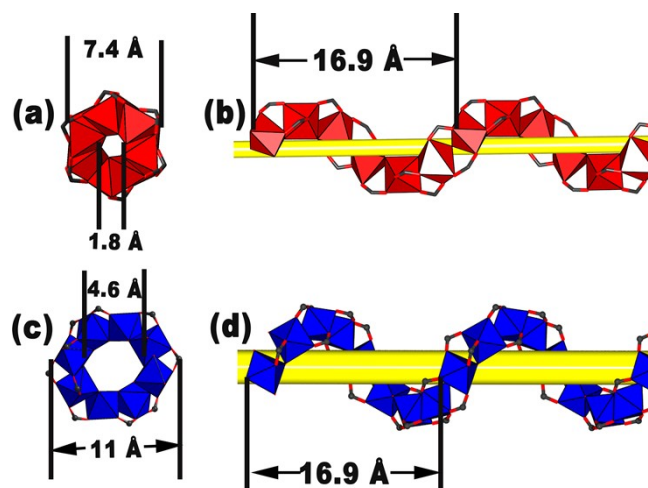


Fig. S1. (a) Outer diameter and inner diameter of **H2** along *c* axis. (b) The helical distance and angle of **H2** monomer. (c) Outer diameter and inner diameter of **H4** along *c* axis. (d) The helical distance and angle of **H4** monomer.

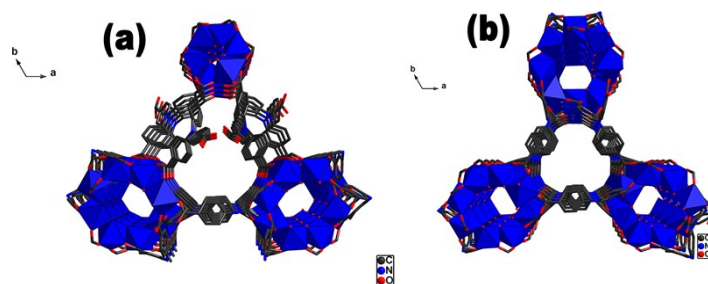


Fig. S2. (a) The structure of small pore along *c* axis. (b) The structure of large pore along *c* axis.

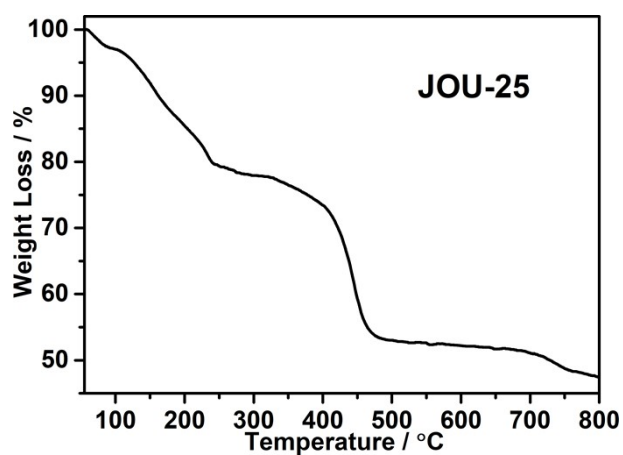


Fig. S3. TG curve of JOU-25.

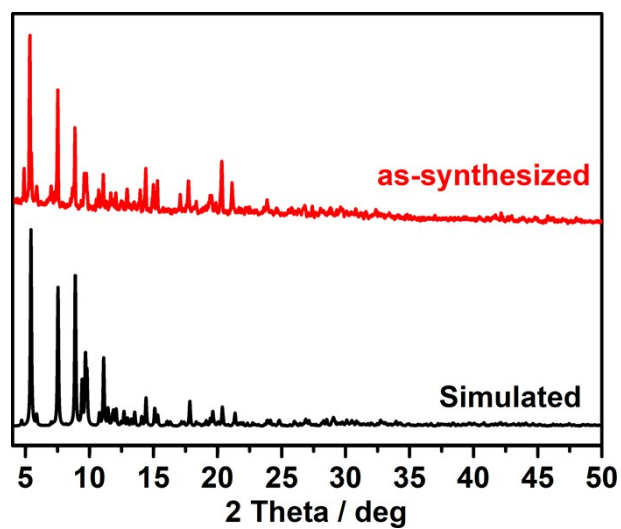


Fig. S4. As-synthesized PXRD pattern and simulated spectrum of JOU-25.

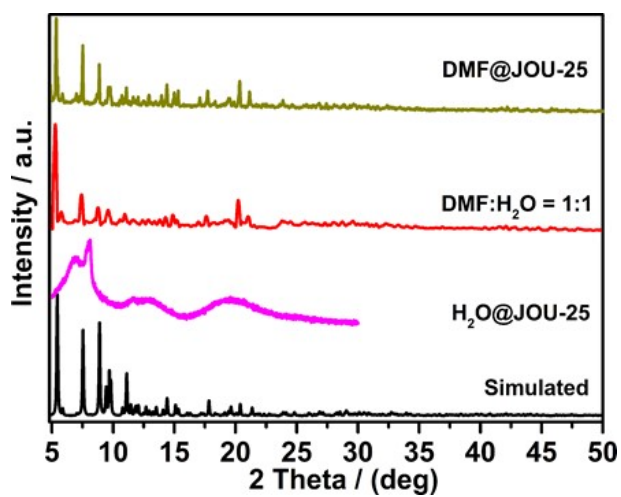


Fig. S5 The stability of JOU-25 in different solutions.

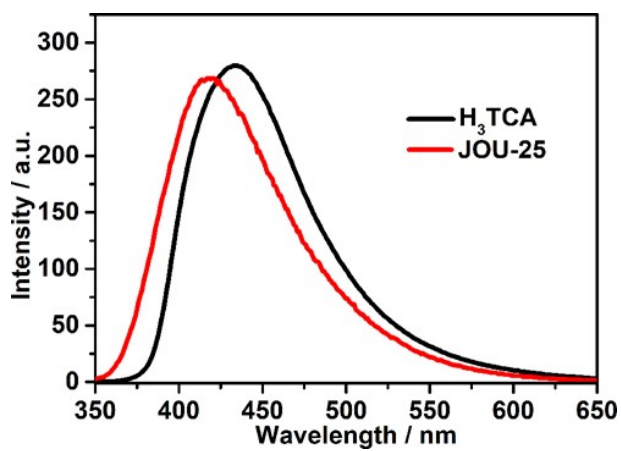


Fig. S6. The fluorescence spectra of JOU-25 and H₃TCA in mixed solution of DMF/H₂O (V/V = 1:1).

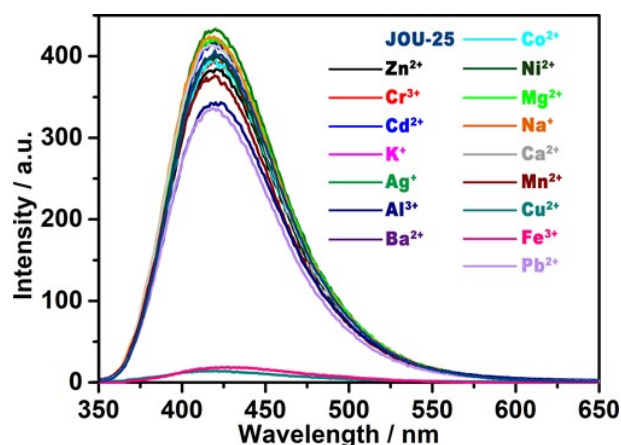


Fig. S7. Emission spectra of **JOU-25** in DMF solution in the presence of different metal ions.

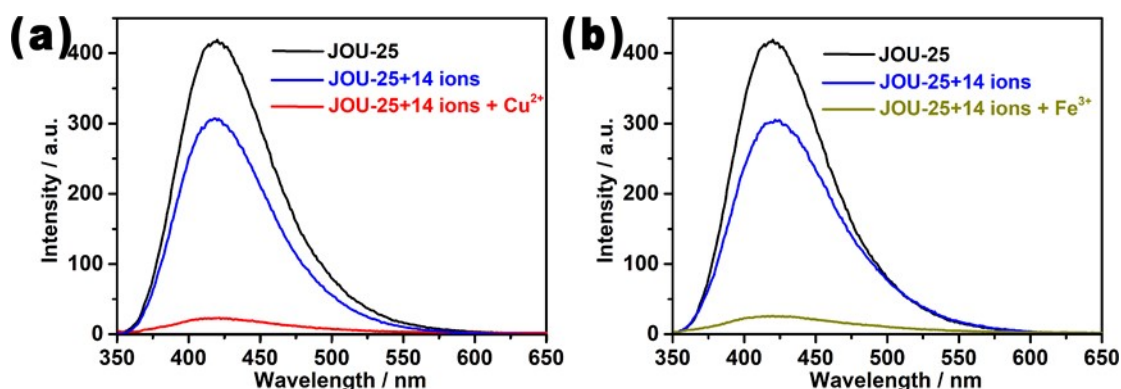


Fig. S8. (a) Emission spectra of **JOU-25** in DMF/H₂O solution with different concentration of Cu²⁺. (b) Emission spectra of **JOU-25** in DMF/H₂O solution with different concentration of Fe³⁺.

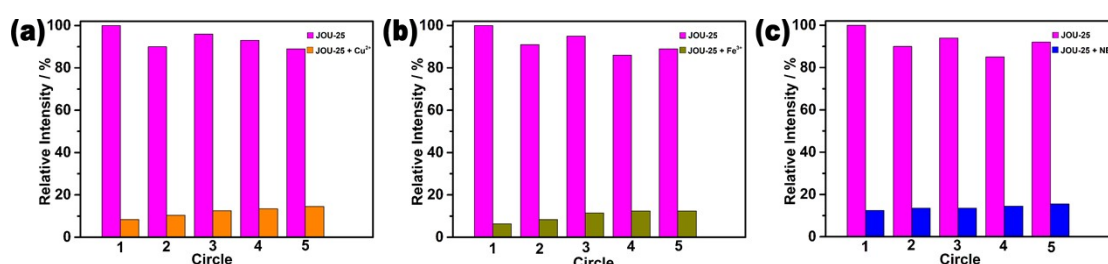


Fig. S9. (a) The recyclability test of **JOU-25** regarding Cu²⁺ detection. (b) The recyclability test of **JOU-25** regarding Fe³⁺ detection. (c) The recyclability test of **JOU-25** regarding NB detection. Magenta column: luminescent intensity of **JOU-25** dispersion before adding detected molecules; orange column: the relative luminescent intensity after adding Cu²⁺ solution; green column: the relative luminescent intensity after adding Fe³⁺ solution; blue volume: the relative luminescent intensity after adding NB solution.

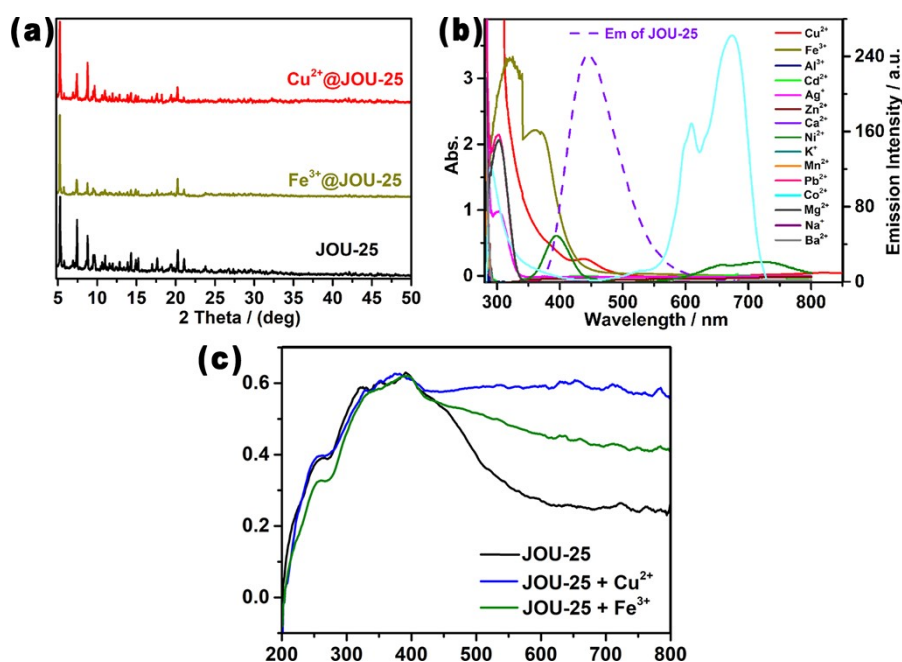


Fig. S10. (a) Stability of **JOU-25** after releasing Cu²⁺/Fe³⁺. (b) UV-Vis absorption spectra of metal ions and emission spectra of **JOU-25**. (c) The solid UV-Vis absorption spectra of **JOU-25**, Cu²⁺@**JOU-25** and Fe³⁺@**JOU-25**.

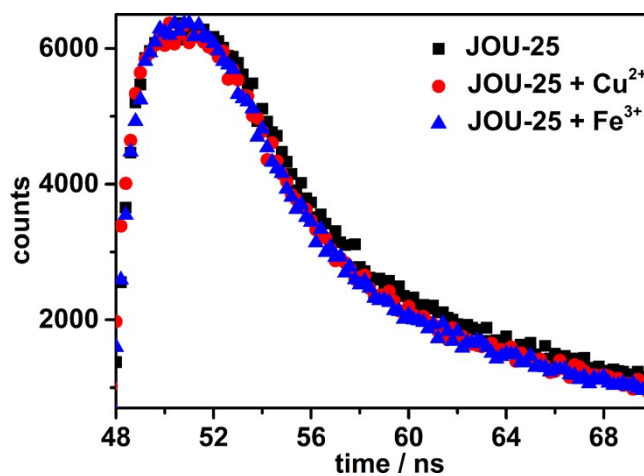


Fig. S11. Fluorescence decay curves of **JOU-25**, **JOU-25** + Fe³⁺ and **JOU-25** + Cu²⁺.

Table S4 Comparison of reported MOF sensors for Cu²⁺ ion detection.

MOFs	K_{SV} (M ⁻¹)	Detection limit (M ⁻¹)	Ref.
JOU-25	392867	3.82×10^{-7}	This work
Cd(INA)(pytpy)(OH)·2H ₂ O	130000	3.05×10^{-6}	4
UiO-66-(COOH) ₂	41200	2.3×10^{-7}	5
MIL-53-L	6150	-	6
[Cd(L) ₂](DMF) _{0.92}	4430	7×10^{-5}	7
[Tb ₃ (L) ₂ (HCOO)(H ₂ O) ₅](DMF)·4H ₂ O	2021.8	1×10^{-6}	8

Table S5 Comparison of reported MOF sensors for Fe³⁺ ion detection.

MOFs	K_{SV} (M ⁻¹)	Detection limit (M ⁻¹)	Ref.
Bi-TCBPE	578000	9.8×10^{-7}	9
JOU-25	313907	3.82×10^{-7}	This work
Eu-MOF	20280	4×10^{-5}	10
Tb-MOF	16590	-	11
UiO-66-NDC	16000	6.5×10^{-7}	12
[Tb ₁₀ (DBA) ₆ (OH) ₄ (H ₂ O) ₅](H ₃ O) ₄	9580	1×10^{-9}	13
[Zn(oba)(L) _{0.5}].dma	9300	-	14
Eu-MOF/ALD-PPS	4366	5.4×10^{-6}	15

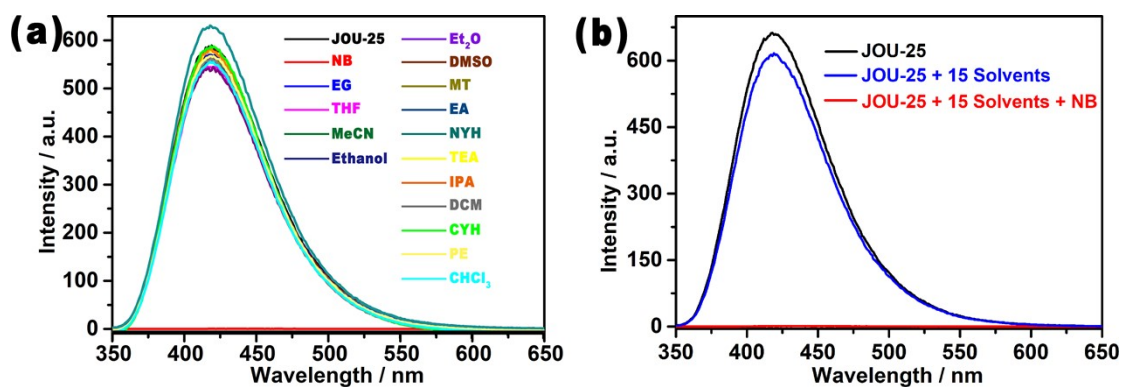


Fig. S12. (a) Emission spectra of **JOU-25** in DMF solution in the presence of different organic solvents. (b) Emission spectra of **JOU-25**, **JOU-25 + 15 organic solvents** and **JOU-25 + 15 solvents + NB** in DMF/H₂O solution.

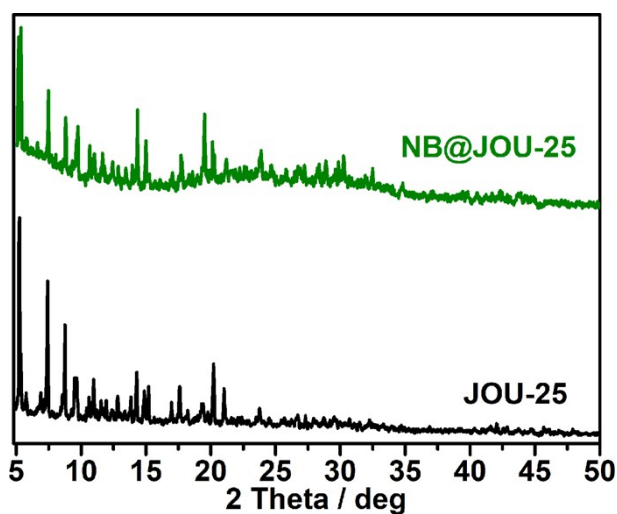


Fig. S13. Stability of **JOU-25** after releasing NB.

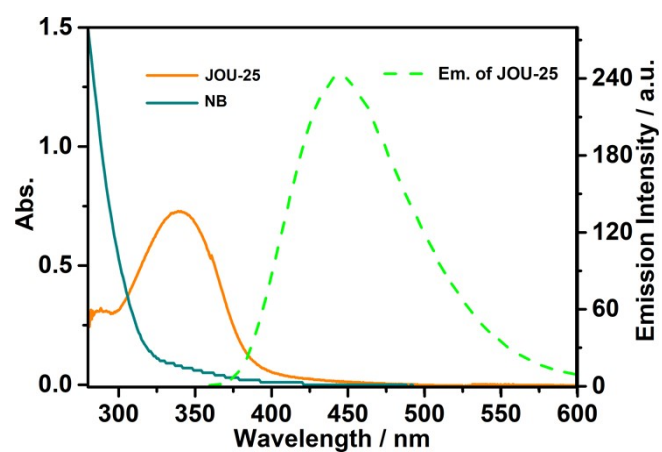


Fig. S14. UV-Vis absorption spectra of NB and **JOU-25**, and emission spectrum of **JOU-25**.

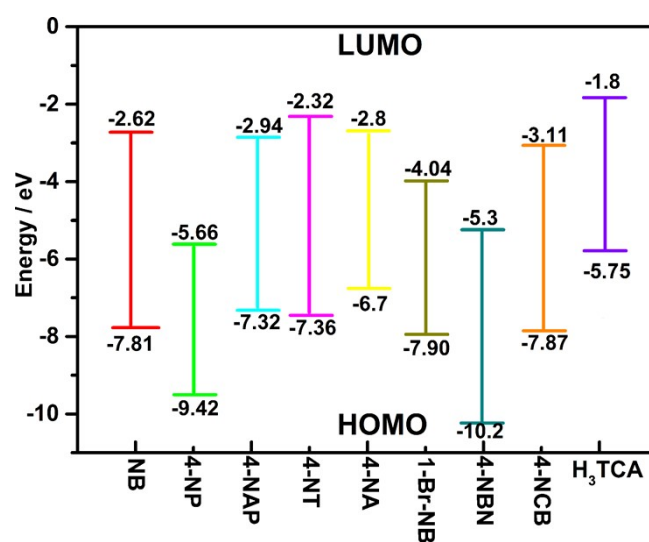


Fig. S15. The LUMO and HOMO energy levels of H₃TCA and NACs.

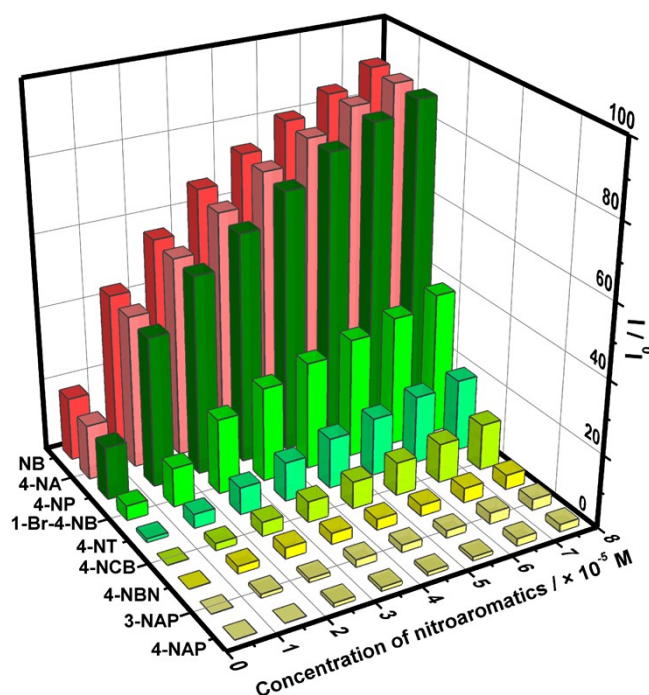


Fig. S16. Emission quenching percentage of **JOU-25** dispersion with different nitroaromatics.

Table S6. Comparison of reported MOF sensors for NB detection.

MOFs	K_{SV} (M^{-1})	Detection limit (M^{-1})	Quenching efficiency (%)	Ref.
FJU-35	1630000	-	43	16
FJU-36	913000	-	49	16
JOU-25	49803	2.41×10^{-6}	90	This work
In/Eu-CBDA	16900	8.88×10^{-6}	82	17
[Cu(L)(I)] ₂ ·2DMF·MeCN	9500	6.6×10^{-6}	40	18
[Cd(bipy)][HL] _n	9300	-	100	19
Ln-MOFs	3340	2.89×10^{-5}	100	20
Cd-MOF	2700	2.54×10^{-3}	100	21

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