

Supporting Information

Highly selective luminescent sensing for Cu²⁺ ions and selective CO₂ capture in a doubly interpenetrated MOF with Lewis basic pyridyl sites

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Materials and Measurements. The chemicals of 4-(ethoxycarbonyl)phenylboronic acid, ethyl 4-carboxylphenylboronic acid, Pd(PPh₃)₄, and 4-(3,5-dibromophenyl)-2,4':6',4''-terpyridine(I) were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. Infrared spectra (IR) were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400–4000 cm⁻¹ region. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Synthesis of 4'-(3,5-di(4-ethoxycarbonylphenyl)phenyl)-2,4':6',4''-terpyridine (II).

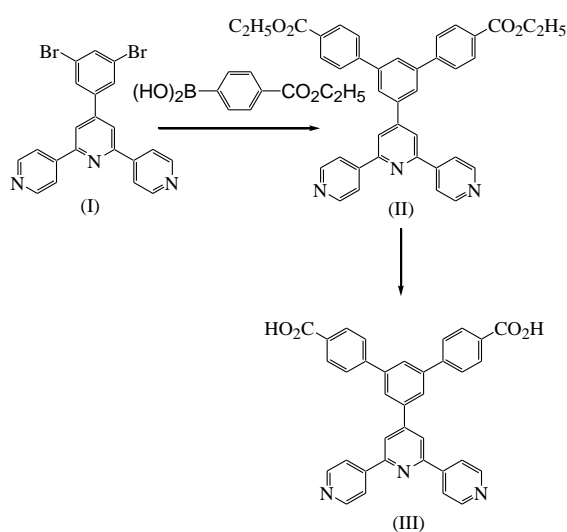
A mixture of 4-(ethoxycarbonyl)phenylboronic acid (5.79 g, 3 mmol), 4-(3,5-dibromophenyl)-2,4':6',4''-terpyridine (4.65 g, 1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.43 mmol), and potassium tribasic phosphate (3.30 g, 15.90 mmol) in dry dioxane (100 mL) was refluxed under argon for 72 h at 130 °C in an oil bath. The reaction mixture was evaporated to dryness and the solid residue was washed with water to remove inorganic salts. The insoluble

material was extracted with chloroform (three times by 50 mL), the extract was dried over magnesium sulfate, and the solvent volume was reduced under vacuum. The residue was boiled in tetrahydrofuran for 2h and filtered; the resulting filtrate contained mainly impurities. This procedure gave 1.20 g of 4'-(3,5-di(4-ethoxycarbonylphenyl)phenyl)-2,4':6',4''-terpyridine (66% yield). EI-MS: m/z $[M-H]^+$, 606.23 (calcd for $C_{39}H_{31}N_3O_4$, 605.23). Anal. (%) calcd. For $C_{39}H_{31}N_3O_4$: C, 77.34; H, 5.16; N, 6.94. Found: C, 77.22; H, 5.01; N, 6.85.

Synthesis of 4'-(3,5-di(4-carboxylphenyl)phenyl)-2,4':6',4''-terpyridine (III).

The mixture of **II** (2.00 mmol, 1.21 g), KOH (10.00 mmol, 5.90 g), and 100 mL $H_2O/MeOH$ was heated to reflux for 2 hours, and then cooled to room temperature. The solution was neutralized with concentrated HCl. White powder was obtained with the yield of 92%. EI-MS: m/z $[M-H]^+/[M-H]^-$, 550.17/548.17 (calcd for $C_{35}H_{23}N_3O_4$, 549.17). Anal. (%) calcd. for $C_{35}H_{23}N_3O_4$, C, 76.49; H, 4.22; N, 7.65. Found: C, 76.30; H, 4.06; N, 7.50.

Synthesis of $[Zn(L)] \cdot 4DMF$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.030g, 0.10 mmol) and H_2L (0.054g, 0.10 mmol) in DMF (6 mL) was placed in a screw-capped vial (10 mL) and heated at 100 °C for 24 h, and then cooled to room temperature at a rate of 5 °C min^{-1} . The resulting single crystals of **1** were isolated by washing with DMF and dried in air. The yield was 71.5 mg (79.1%, based on H_2L). Anal. (%) Calcd for $C_{47}H_{49}N_7O_8Zn$: C, 62.36; H, 5.46; N, 10.83. Found: C, 62.32; H, 5.51; N, 10.79.



Scheme S1. The scheme for the synthesis of H_2L

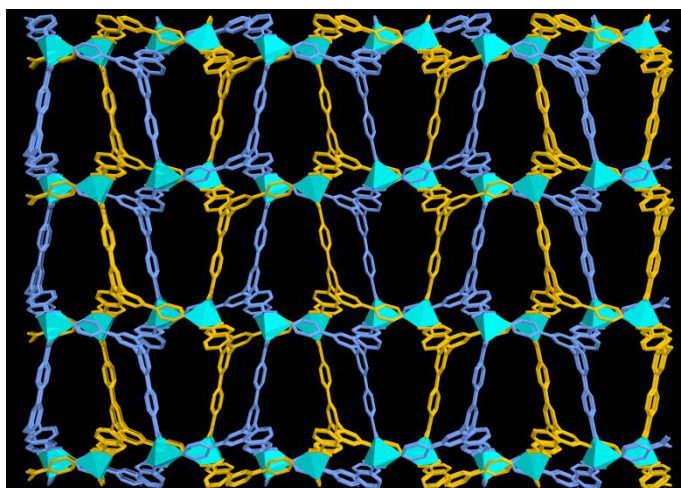
X-ray Single-Crystal Diffraction Analysis. The diffraction data were collected at 296(2) with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were carried out utilizing SADABS routine.¹ The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2 with the SHELXTL program.² All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. Since the heavily disordered solvent molecules were trapped in the channels of **1** and could not be modeled properly. Thereby the SQUEEZE routine of PLATON³ was applied to remove the contributions to the scattering from the solvents. Crystal data of **1**: C₃₅H₂₁N₃O₄Zn, $M = 612.92$, $T = 296(2) \text{ K}$, Monoclinic C2/c, $a = 18.020(5) \text{ \AA}$, $b = 27.937(7) \text{ \AA}$, $c = 23.201(6) \text{ \AA}$, $V = 11088(5) \text{ \AA}^3$, $Z = 8$, $D_c = 0.734 \text{ g cm}^{-3}$, $\mu = 0.466 \text{ mm}^{-1}$, collected reflections 33269, $R_{\text{int}} = 0.0602$, final $R_1 = 0.0668$, $wR_2 = 0.1563$ for 13564 unique reflections ($I \geq 2\sigma$), $S = 1.185$. CCDC-1016408 contains the crystallographic data for this paper. The final formula was determined by combining single-crystal structure, elemental microanalysis and TGA.

References

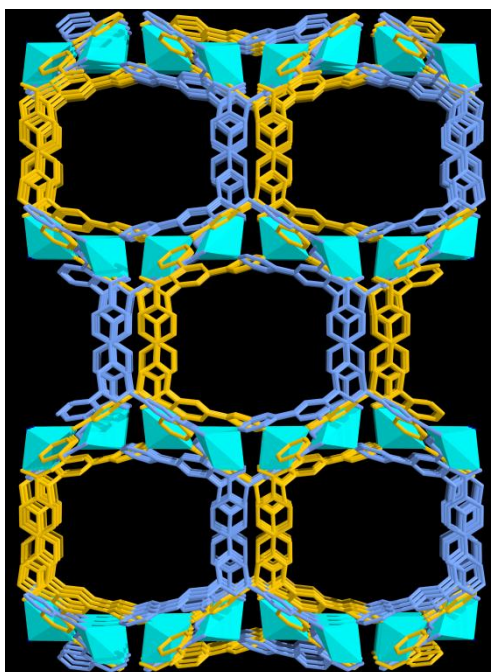
- 1) Bruker. *SADABS, SMART and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
- 2) G. M. Sheldrick, *SHELXL-97, program for the refinement of the crystal structures*. University of Göttingen, Germany, 1997.
- 3) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

Photoluminescence Measurements. The photoluminescence of **1** and **1a** were investigated in the solid state at room temperature. For the experiments of sensing metal ions, **1** powder (3 mg) was immersed in DMF solutions (3 mL) containing 10^{-2} M of $M(\text{NO}_3)_x$ ($M = \text{Na}^+$, K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} , and Ni^{2+}) as well as the same way used for the sensing in mixed metal ions. Before photoluminescence measurements, the suspensions were oscillated for 30 min using ultrasonic waves to ensure uniform dispersion.

Sorption Measurements. The activated samples (**1a**) were prepared by direct heat of **1** at $130 \text{ }^\circ\text{C}$ for 3 h and subsequent $160 \text{ }^\circ\text{C}$ for 1 h under vacuum.



(a)



(b)

Fig. S1 Views of the 3D framework of **1**: (a) along the [100] and (b) along the [001] directions, the polyhedrons represent Zn^{2+} atoms, One of the interpenetrating networks is shown in blue and the other in yellow.

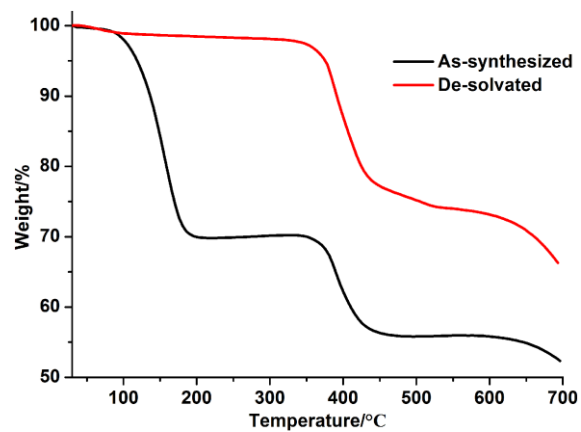


Fig. S2 TGA plots for **1** and **1a**.

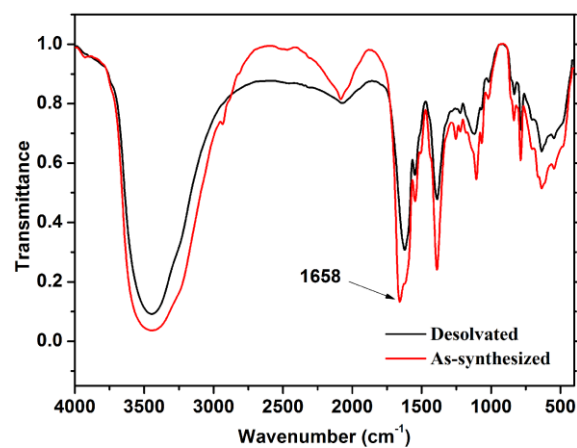


Fig. S3 IR spectra of the as-synthesized and desolvated **1** (**1a**). The characteristic C=O vibration at 1658 cm^{-1} of DMF in **1** is absent in **1a**, indicating the complete removal of DMF.

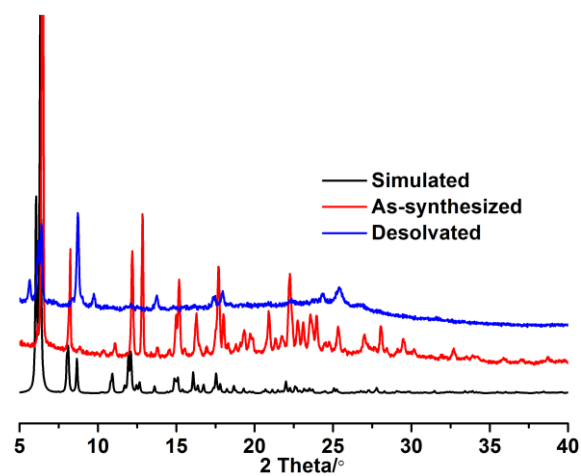


Fig. S4 PXRD of **1** from simulated by single-crystal structure, as-synthesized, desolvated samples.

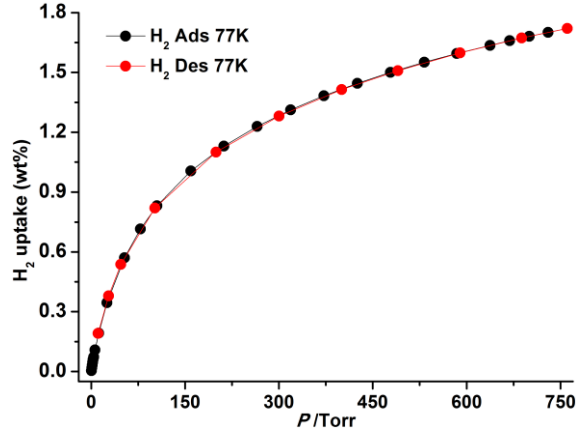


Fig. S5 H₂ sorption isotherm at 77 K and 1 bar for 1a.

IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO₂, CH₄ and N₂ (measured at 298) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * P^c}{1 + b * P^c}$$

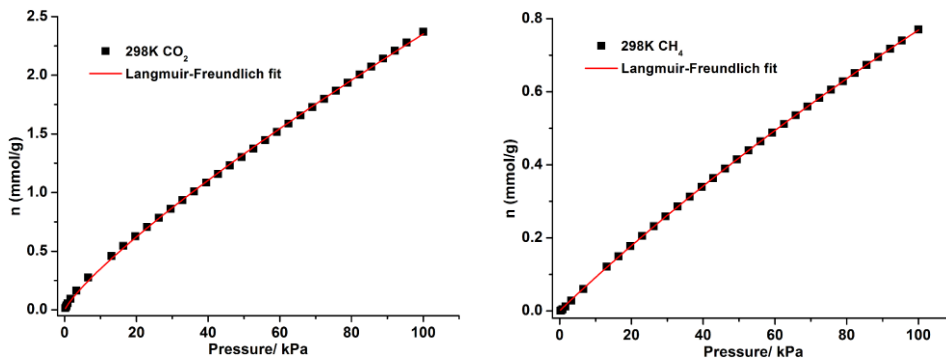
Where q and p are adsorbed amounts and pressures of component i , respectively.

The adsorption selectivities for binary mixtures of CO₂/CH₄ and CO₂/N₂, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz.

Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.



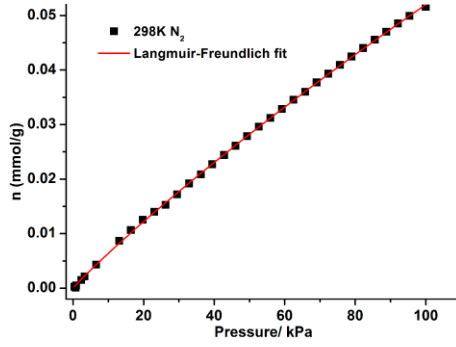


Fig. S6 CO₂ adsorption isotherms of **1a** with fitting by L-F model: $a = 190.41047$, $b = 0.00027$, $c = 0.83182$, $\text{Chi}^2 = 1.53 \times 10^{-4}$, $R^2 = 0.99973$; CH₄ adsorption isotherms of **1a** with fitting by L-F model: $a = 5.20258$, $b = 0.00186$, $c = 0.98498$, $\text{Chi}^2 = 2.35 \times 10^{-6}$, $R^2 = 0.99996$; N₂ adsorption isotherms of **1a** with fitting by L-F model: $a = 0.57582$, $b = 0.00127$, $c = 94679$, $\text{Chi}^2 = 2.17 \times 10^{-7}$, $R^2 = 0.99983$.

Calculation of sorption heat for CO₂ uptake using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^m aiN^i + \sum_{i=0}^n biN^i \quad Q_{st} = -R \sum_{i=0}^m aiN^i$$

The above equation was applied to fit the combined CO₂ isotherm data for desolvated **1a** at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

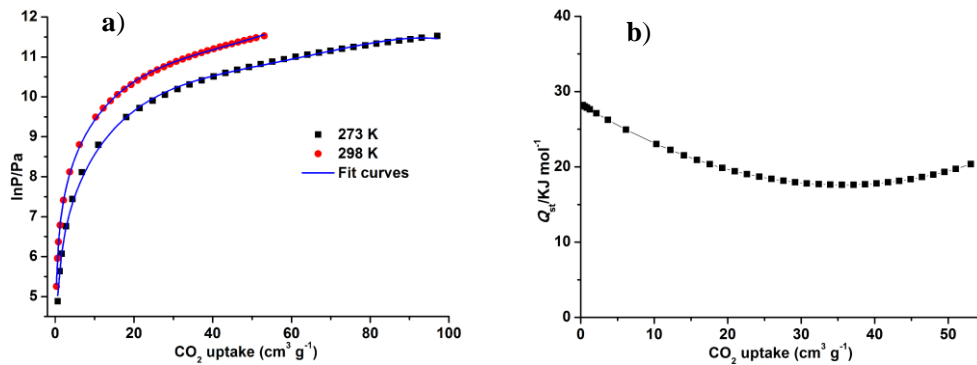


Fig. S7 a) CO₂ adsorption isotherms for **1a** with fitting by Virial 2 model. Fitting results: $a_0 = -3412.99694$, $a_1 = 74.10956$, $a_2 = -1.15512$, $a_3 = 0.00421$, $a_4 = -0.00004$, $b_0 = 17.93963$, $b_1 = -0.16268$, $b_2 = 0.00115$, $b_3 = 0.00002$, $\text{Chi}^2 = 0.00214$, $R^2 = 0.99931$. b) CO₂ adsorption heat calculated according to the virial equation.

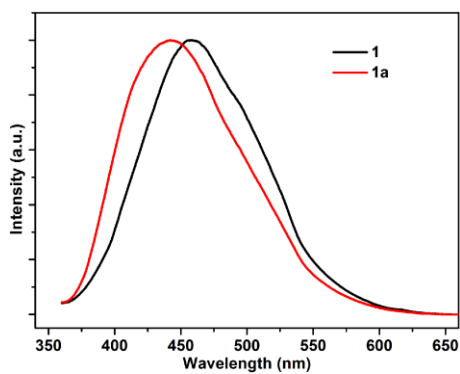


Fig. S8 Fluorescent emission spectra of **1** and **1a** in solid state at room temperature.



Fig. S9 Photographs of crystals of **1** soaked in DMF solution containing $M(\text{NO}_3)_2$ with 10^{-1} M, a) Mn^{2+} , b) Co^{2+} , c) Ni^{2+} , d) Cu^{2+} for 24 h, indicating selective color changes for Cu^{2+} .

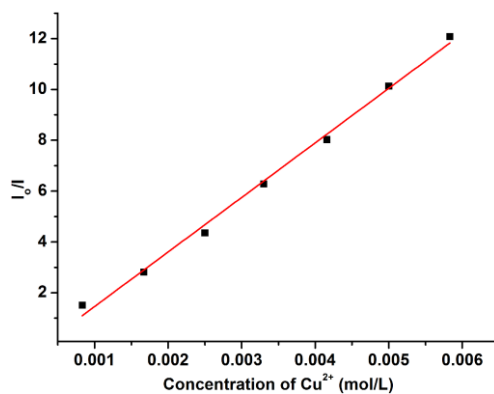


Fig. S10 The K_{sv} value is Stern-Volmer plots for the quenching of **1** by Cu^{2+} . Quenching effect coefficients (K_{sv}) of different metal ions on the luminescence intensity of metal-ion-incorporated **1b**, calculated by Stern–Volmer equation: $I_0/I = 1 + K_{\text{sv}}[\text{M}]$, in which the values I_0 and I are the luminescent intensity of metal-ion-free **1b** in DMF and metal-ion- incorporated **1b** in DMF, respectively, $[\text{M}]$ is the molar concentration of metal ion, and K_{sv} is the quenching effect coefficient of metal ion (see reference *Angew. Chem. Int. Ed.*, 2009, **48**, 500).

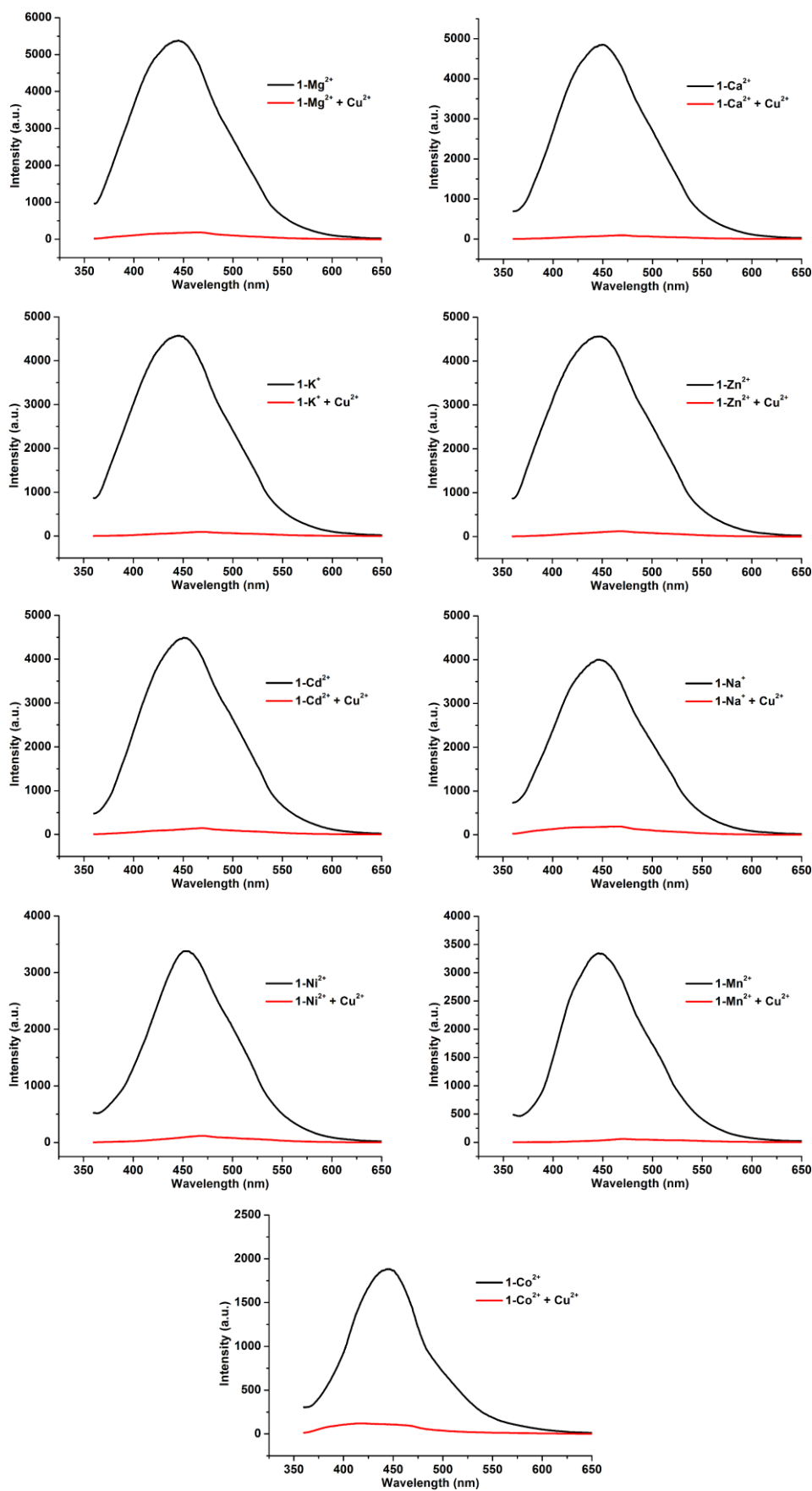


Fig. S11 The luminescence spectra of **1** in DMF with different metal ions (10^{-2} M) the absence (black) and presence (red) of Cu^{2+} ion (10^{-2} M).