

Supporting Information

A tubular porous coordination polymer exhibiting selective sensing Cu²⁺ ions upon mixed metal ions and small solvent molecules cyclohexane

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Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin-Elmer Thermal Analysis Pyris Diamond heated from room temperature to 900 °C under a N₂ atmosphere at a rate of 10 °C min⁻¹.

Table S1 The catalogue numbers and suppliers of the substrates

Name	CAS	Suppliers
Cd(NO ₃)·4H ₂ O	10325-94-7	Energy Chemical
2-H ₂ aip	10312-55-7	Alfa Aesar
2,2'-bipyridine	366-18-7	Energy Chemical

Synthesis of complex 1: A solution of Cd(NO₃)·4H₂O (0.105g), 2-H₂aip (0.054g), 2,2'-bipyridine (0.09 g) in DMF (5 mL) was heated at 130 °C for 3 days. The resulting brown crystals were collected, washed with ethanol, and dried at room temperature. Elemental analysis for C₂₄H₂₇CdN₅O₆ (593.91) (%): calcd. C 48.54 H 4.58 N 11.79; found C 48.56 H 4.56 N 11.75.

Luminescent measurements

The PL properties of **1** in various solvent were investigated at room temperature. The strongest emission wavelengths were located at 426 nm when excited at 350 nm. The **1**-solvent were prepared by introducing 3 mg of **1** powder into 5 mL of

acetonitrile, dichloromethane, acetic ether, DMF, isopropanol, acetone, 1, 3-propanediol, cyclohexane, tetrahydrofuran, methanol and ethanol. After sonication treatment 90 min, aging for 6 h, the fluorescence spectra were measured. For the experiment of sensing metal ions, the **1**-M^{x+} emulsions were prepared by introducing 3 mg of **1** powder into 5 mL of M(NO₃)_x (M = K⁺, Zn²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Co²⁺ or Ag⁺) DMF solution. After sonication treatment 90 min, aging for 1 h, the luminescent spectra were measured. The width of the excitation slit was 2.5 nm and the emission slit was 2.5 nm.

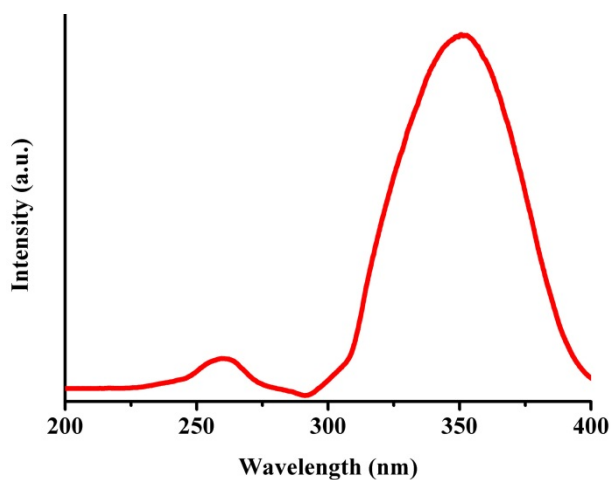


Fig. S1 Excitation spectrum ($\lambda_{em} = 426$ nm) of **1** in DMF.

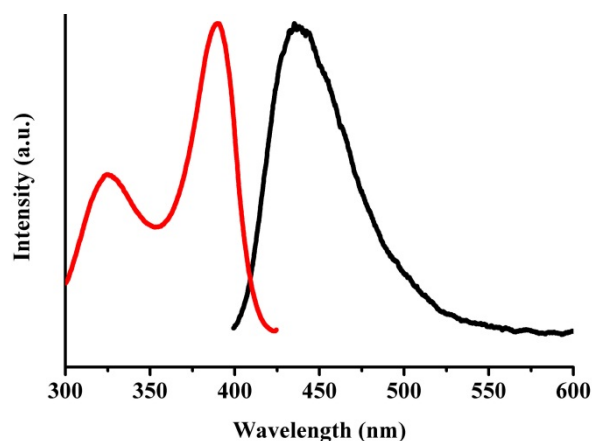


Fig. S2 Normalized excitation (red line) and emission spectra (black line) of 2-aip in CH₃OH.

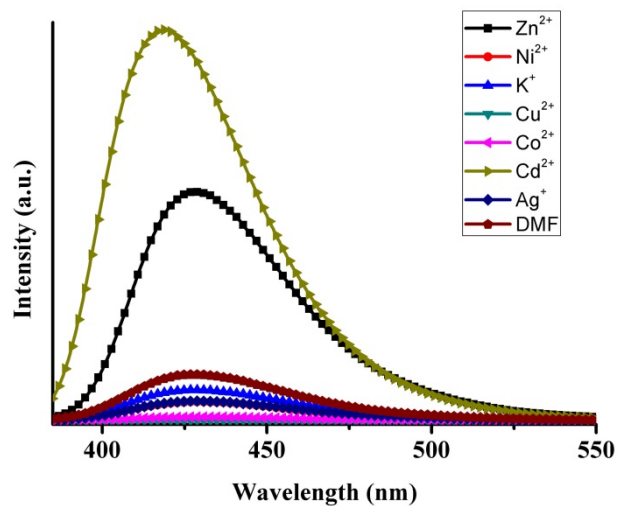


Fig. S3 The luminescent spectra of solid **1** in DMF emulsion containing 0.01 M $M(\text{NO}_3)_x$.

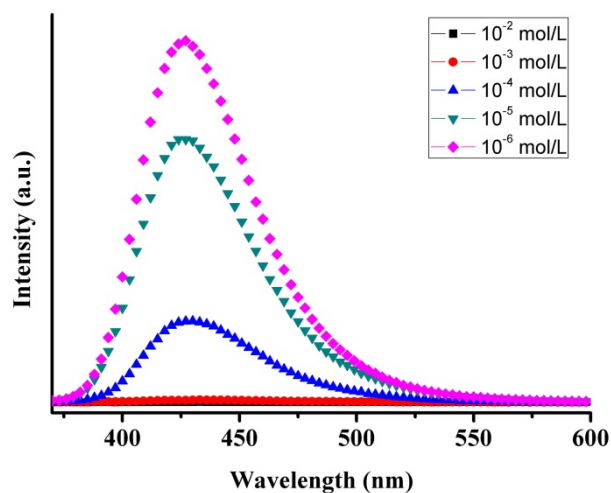


Fig. S4 The luminescent spectra of solid **1** in $\text{Cu}(\text{NO}_3)_2$ DMF solution at different concentrations.



Fig. S5 Optical images of the samples in $\text{Cu}(\text{NO}_3)_2$ DMF solutions at different concentrations (left to right: 10^{-6} mol/L, 10^{-5} mol/L, 10^{-4} mol/L, 10^{-3} mol/L, 10^{-2} mol/L) under 365 nm UV light irradiation.

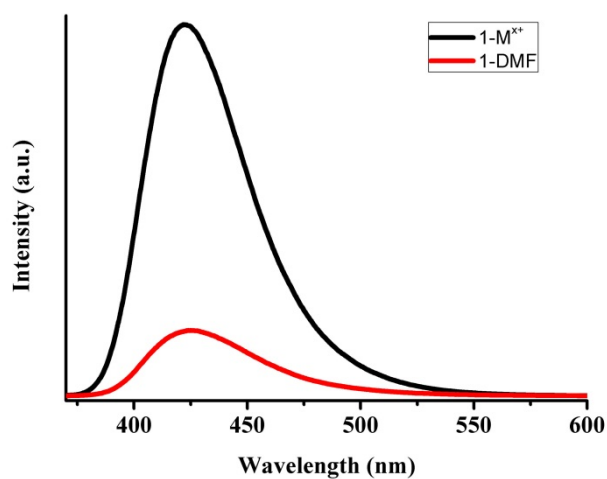


Fig. S5 The luminescent intensities of **1** in DMF solution before and after introducing M^{x+} ions ($M^{x+} = K^+, Cd^{2+}$ and Zn^{2+}).

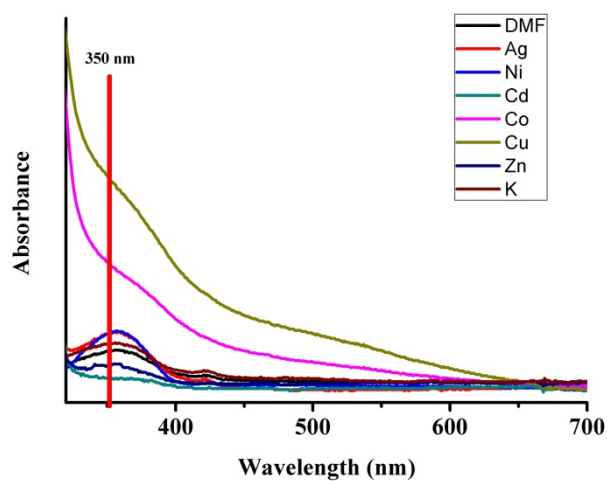


Fig. S6 The UV-vis spectra of the **1**- M^{x+} in DMF emulsions ($M^{x+} = K^+, Ag^+, Cd^+, Co^{2+}, Ni^{2+}, Cu^{2+}$ and Zn^{2+}).

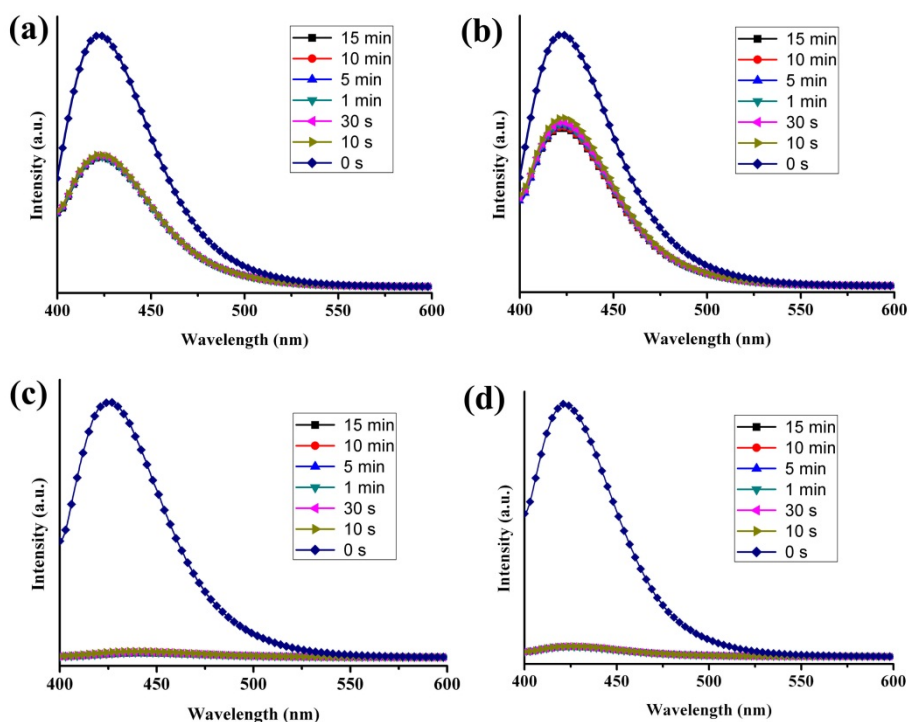


Fig. S7 Time-dependent photoluminescence intensities of 1- $M^{x+}Ni^{2+}$ (a), 1- $M^{x+}Co^{2+}$ (b), 1- $M^{x+}Ni^{2+}Cu^{2+}$ (c) and 1- $M^{x+}Co^{2+}Cu^{2+}$ (d) ($M^z = K^+, Cd^{2+}$ and Zn^{2+}).

In order to check the selectivity of **1** to Ni^{2+} or Co^{2+} ions upon other metal ions (K^+ , Zn^{2+} and Cd^{2+}), the experiments have been carried out under the same experimental conditions. When a solution (0.1 mL, containing 5×10^{-5} mole Ni^{2+}/Co^{2+} ions) is introduced into the solvent containing mixed metal ions, the time-dependent emission spectra of two mixed solvent were measured (Fig. 7a and 7b). Ni^{2+}/Co^{2+} ions show varying degrees of quenching. The luminescence intensities of 1- $M^{x+}Ni^{2+}$ and 1- $M^{x+}Co^{2+}$ are approximately a half and one third of that of 1- M^{x+} ten seconds later. Then, the luminescence of both solvent exhibit nearly no change.

In order to evaluate the interference of Ni^{2+}/Co^{2+} ions, new experiments are carried out. The sample is immersed in an DMF solution (5 mL) containing mixed metal ions (5×10^{-5} mole K^+ , Zn^{2+} , Cd^{2+} and Ni^{2+}/Co^{2+} respectively). When a solution (0.1 mL, containing 5×10^{-5} mole Cu^{2+} ions) is introduced into the solvent containing mixed metal ions respectively, the solvent shows a dark colour ten seconds later under UV light, which is easy to distinguish the colour difference to the naked eye. The measurement of the emission spectrum shows the luminescence is quenched fast,

indicating the selectivity for Cu^{2+} ions is not interfered by the existence of other metal ions. Summarily, the experimental results confirm that this material features such highly selective and fast sensing of Cu^{2+} ions in dilute solution through fluorescence quenching upon mixed metal ions again.

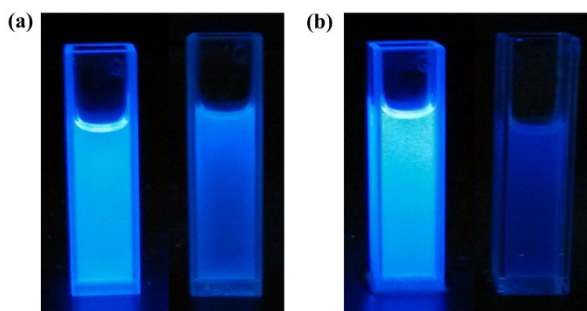


Fig. S8 Optical images of the samples (a) (left to right: $1\text{-M}^{x+}\text{Ni}^{2+}$ and $1\text{-M}^{x+}\text{Ni}^{2+}\text{Cu}^{2+}$) and (b) (left to right: $1\text{-M}^{x+}\text{Co}^{2+}$ and $1\text{-M}^{x+}\text{Co}^{2+}\text{Cu}^{2+}$) under the irradiation of UV light of 365 nm.

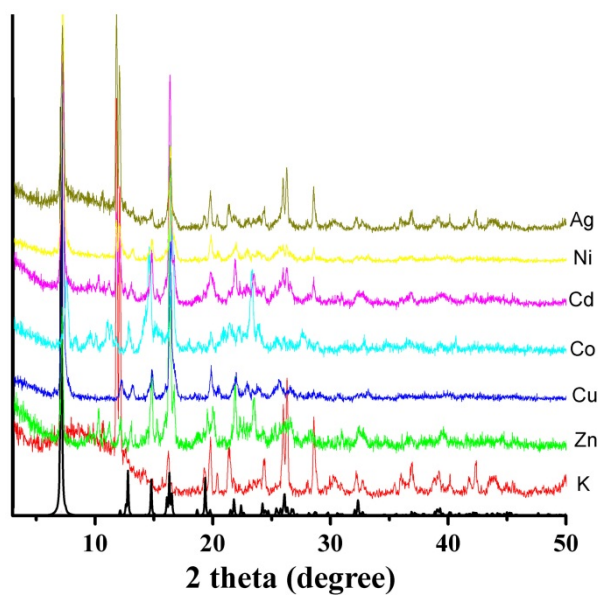


Fig. S9 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1** and diffraction patterns obtained after the introduction of various metal ions.

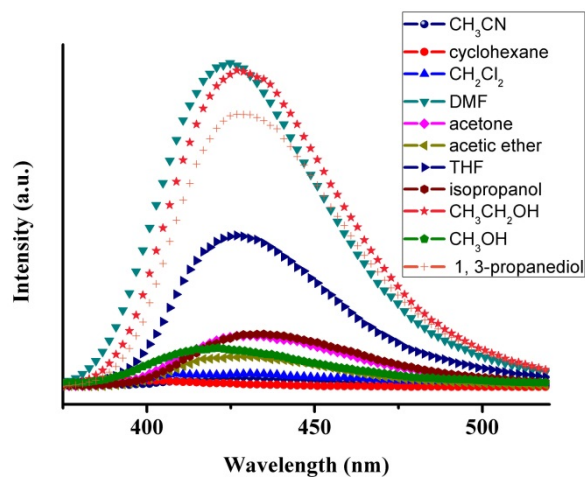


Fig. S10 The luminescent spectra of the dispersed **1** in various solvent.

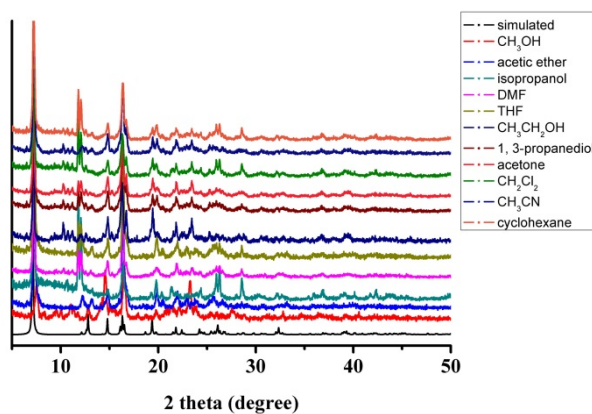


Fig. S11 The PXRD patterns of compound **1** in various solvent.

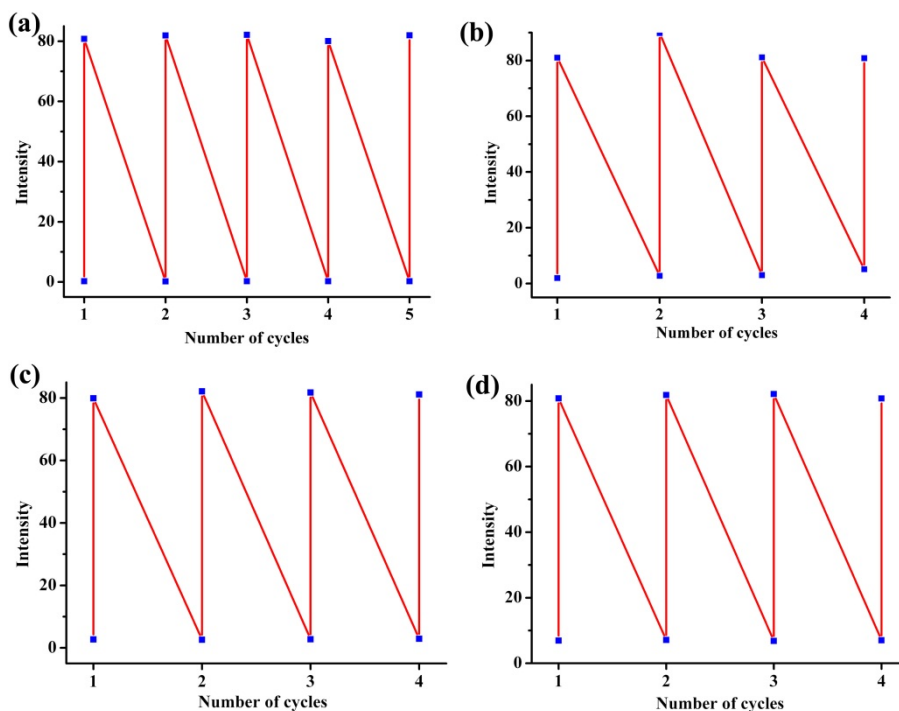


Fig. S12 Reproducibility of the quenching ability of **1** dispersed in DMF and various solvent (cyclohexane (a), CH_3CN (b), CH_2Cl_2 (c) and acetic ether (d)).

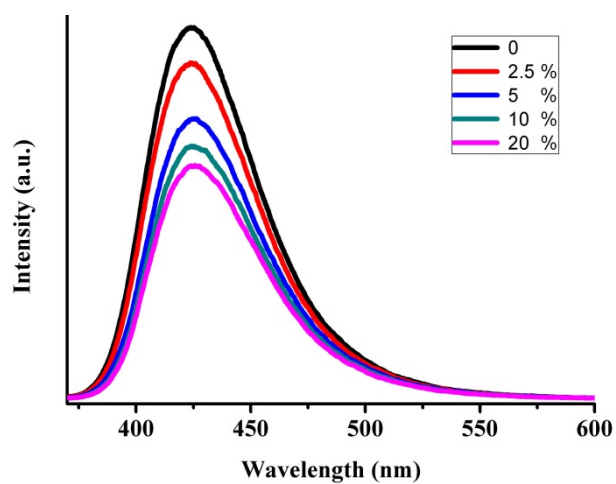


Fig. S13 The luminescent spectra of the dispersed **1** in DMF in the presence of various contents of cyclohexane solvent (vol. %) (excited at 350 nm).

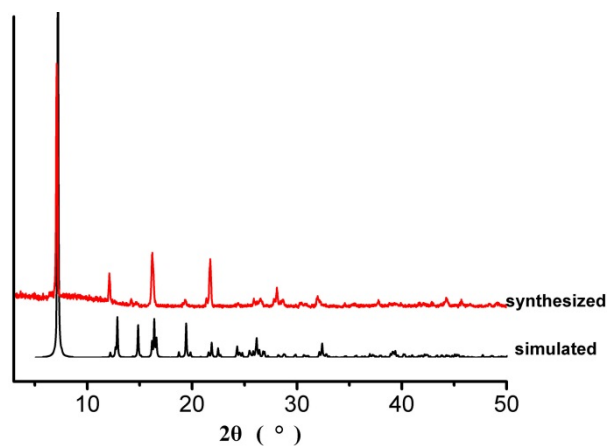


Fig. S14 Experimental and simulated powder X-Ray diffraction patterns for **1**.

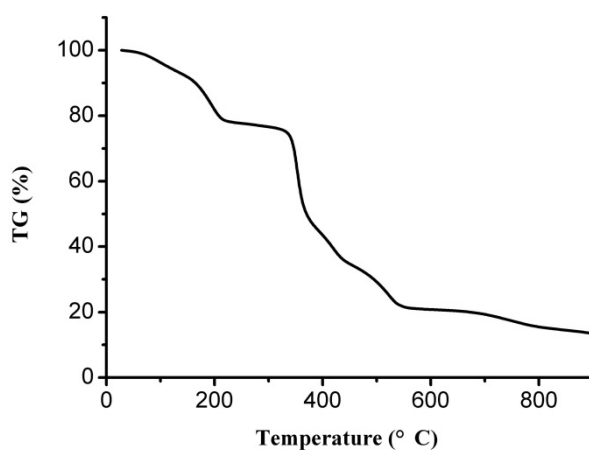


Fig. S15 The TG profile of **1**.