

Electronic Supplementary Information

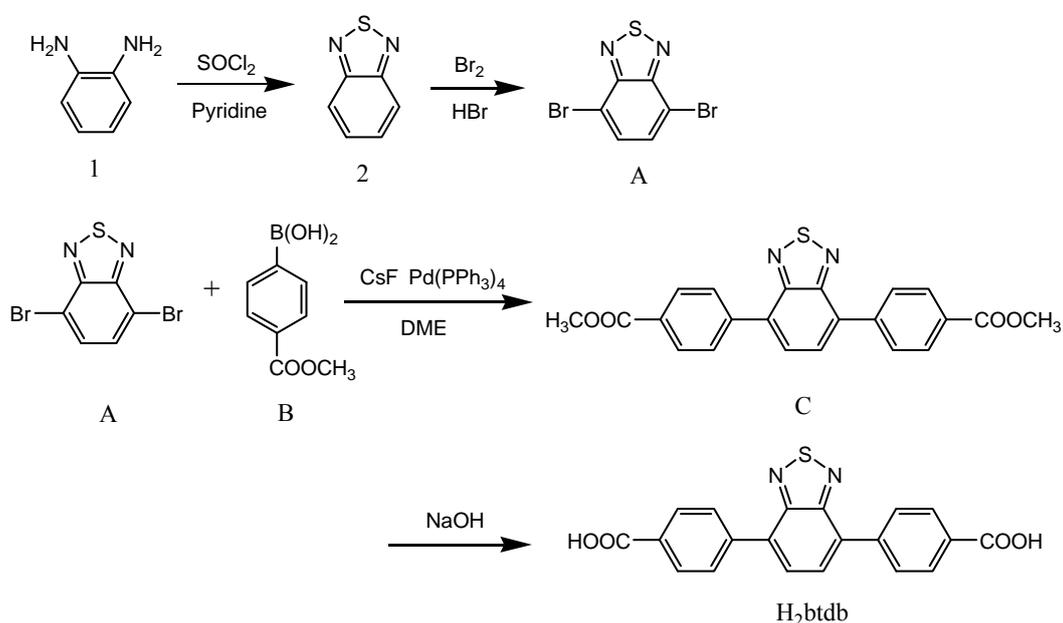
Thiadiazole-functional porous metal-organic framework as the luminescent probe for Cd²⁺

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Experimental Section

Synthesis of H₂btdb ligand



Synthesis of compound A

1. Synthesis of compound 2 (benzo-2,1,3-thiadiazole)

Compound 2 was synthesized through the reaction of compound 1 (o-phenylenediamine) and thionyl chloride in the presence of pyridine. Compound 1 (10.8 g, 0.1 mol) and thionyl chloride (53 mL) were added to a three-necked round-bottom flask. Then pyridine (1 mL) was added dropwise to the vigorously stirred solution at 0 °C and the mixture was refluxed for 24 hr. The excessive thionyl chloride was removed under reduced pressure and cooled down to room temperature. The remanent mixture was poured into distilled water (250 mL). The crude product was purified by steam distillation, extracted thrice with CH₂Cl₂ (100 mL), dried over anhydrous MgSO₄ overnight, and finally filtered. The extracted liquid was concentrated to obtain yellow compound 2 in 82% yield. Mp = 45-46 °C. ¹H-NMR (CDCl₃, TMS, d): 7.52 (s, 2H), 7.94 (s, 2H).

2.Synthesis of compound A (4,7-dibromobenzo-2,1,3-thiadiazole)

Compound A was synthesized through the reaction of compound 2 and bromine in hydrobromic acid (40%). Compound 2 (13.6 g, 0.1 mol) and hydrobromic acid (40%, 30 mL) were added in a two-necked round-bottom flask and heated to refluxing with stirring. Then, bromine (48.0 g, 0.3 mol) was added dropwise slowly. After bromine was completely added, the reaction mixture became a suspension solution. The additional hydrobromic acid (40%, 15 mL) was added again and the reaction mixture was kept refluxing for another 2.5 hr. Finally, the reaction mixture was filtrated, washed with distilled water, and recrystallized from CHCl₃. Finally, compound A was obtained as yellow needle crystal in 80% yield. Mp = 193-194 °C. ¹H-NMR (CDCl₃, TMS, d): 7.73 (s, 2H).

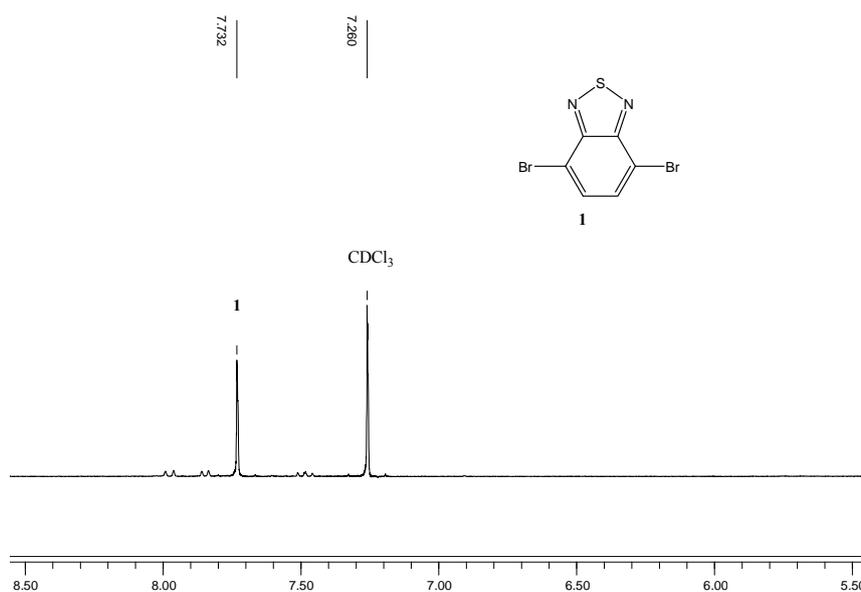


Fig S1. ¹H-NMR (300 MHz, CDCl₃, r.t.) of A.

Synthesis of compound C (Suzuki-coupling reaction)

A (2 g, 6.8 mmol) and B (2.8 g, 15.6 mmol) (mol/mol = 1 : 2.3), CsF (3 g, 19.7 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were mixed in a 250 mL two-necked flask and pumped for 30 minutes. 100 mL degassed CH₃OCH₂CH₂OCH₃ (DME) was added through a syringe. The mixture was heated to reflux under the protection of N₂ for 48 hours. Water was added after the mixture was cooled to room temperature. The water phase was extracted thrice with CH₂Cl₂. The mixed organic phases were dried with anhydrous MgSO₄ overnight, and filtered. After the solvent was removed, the crude product was purified by column chromatography (silica, CHCl₃) to give the pure product. ¹H-NMR (CDCl₃): 3.98 (s, 6H), 7.87 (s, 2H), 8.08 (d, 4H), 8.21 (d, 4H).

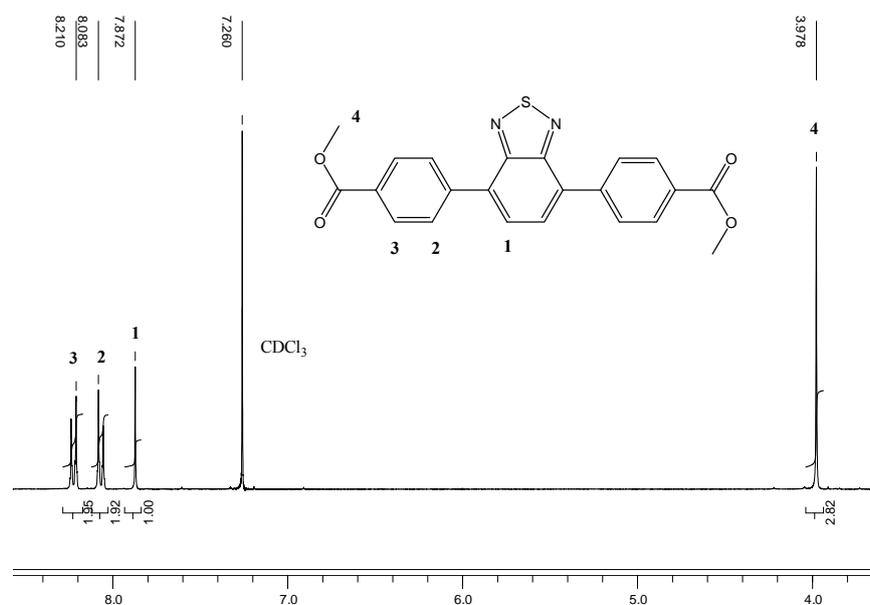


Fig S2. ¹H-NMR (300 MHz, CDCl₃, r.t.) of compound C.

Synthesis of H₂btdb ligand

C was dissolved in mixture of THF (70mL) and MeOH (70ml, v/v = 1:1), 50 mL 4N NaOH aqueous solution was added. Heated to reflux and add moderate water until completely dissolved, then the mixture was stirred at this temperature overnight. After the mixture being cooled to room temperature, The mixture was acidified with add concentrated HCl with stirred to give yellow flocculent precipitate, which was filtered and washed with water several times. ¹H-NMR (DMSO): 8.08 (d, 4H), 8.13 (s, 2H), 8.15 (d, 4H).

¹H-NMR of H₂btdb ligand

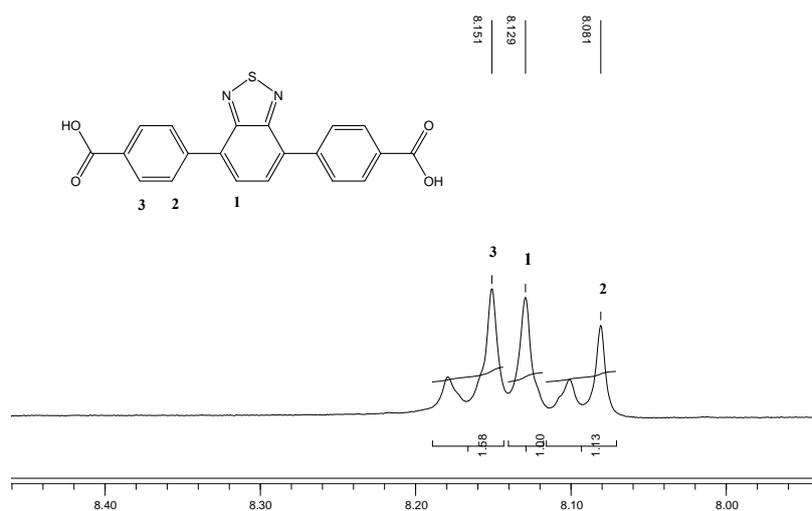


Fig S3. ¹H-NMR (300 MHz, DMSO, r.t.) spectra for the H₂btdb.

Synthesis and characterization of complex 1

Solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_2btbd in the presence of DMA leads to the generation of light yellow crystals with an overall formula of $[\text{Zn}(\text{btbd})(\text{DMA}) \cdot (\text{H}_2\text{O})]$, the framework stability under different conditions was evaluate based on an power X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA) patterns.

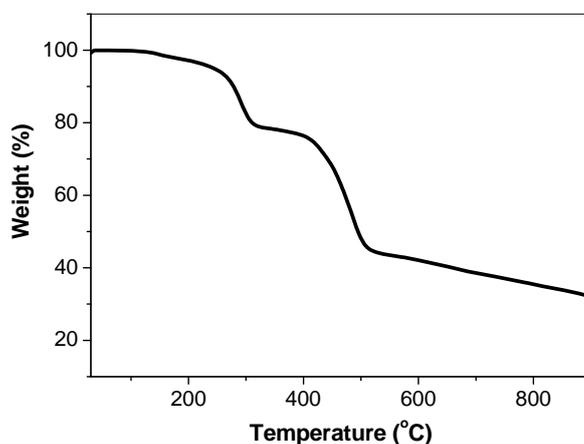


Fig S4. TGA curve of complex 1. Conditions: temperature ramp from 30 °C to 900 °C at 15 °C / min under flow of N_2 gas.

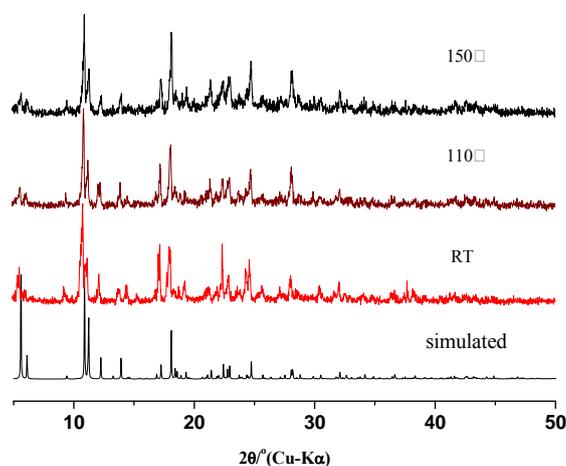


Fig S5. The PXRD patterns of simulated and complex 1 at varied temperature.

A small amount of dried complex 1 was heated at a constant rate of 5 °C /min from 25 °C to 110 °C and 150 °C respectively under protection of nitrogen, four hours later cooled at a constant rate of 10 °C /min to room temperature. The resulting sample was confirmed by Powder X-ray diffraction. Variable-temperature PXRD studies indicated that 1 is stable up to 150 °C under a nitrogen atmosphere. All of the peaks are complete to the simulated.

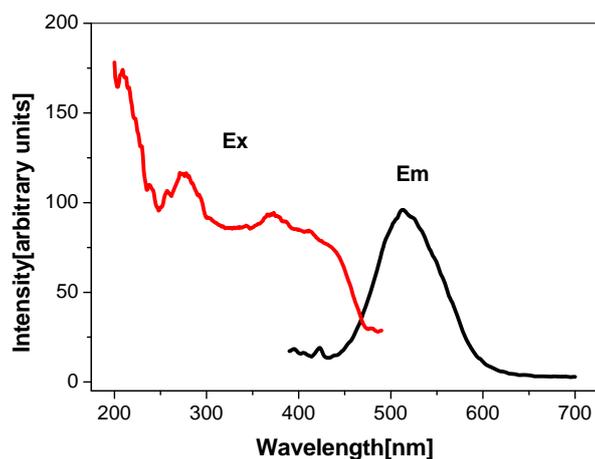


Fig S6. Luminescence excitation (at 512 nm) and emission (at 370 nm) spectra of H₂btbd ligand in the solid state at room temperature.

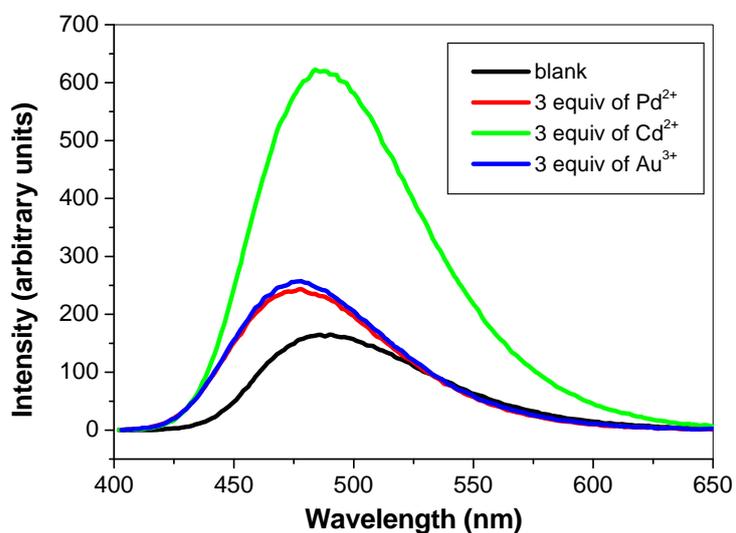


Fig S7. Luminescence emission (at 350 nm) spectra of **1** in methanol under different conditions.

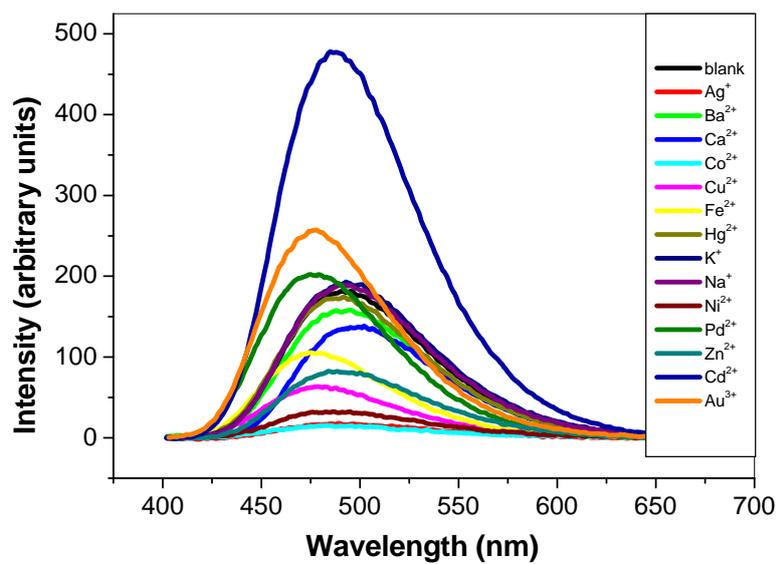


Fig S8. Room-temperature luminescent emission spectra of **1** after heating to 210°C in methanol upon addition of various metal ions (excited at 350 nm).