

A luminescent Cd(II) coordination polymer as a multi-responsive fluorescent sensor for Zn²⁺, Fe³⁺ and Cr₂O₇²⁻ in water with fluorescence enhancement or quenching

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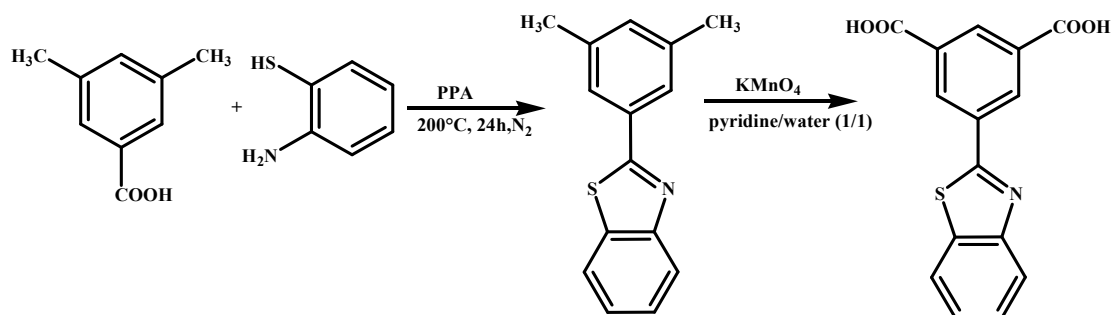
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Section 1. Synthesis of the ligand H₂btic.

3,5-dimethylbenzoic acid (7.50 g, 0.05 mol), 2-aminothiophenol (6.76 g, 0.05 mol) and polyphosphoric acid (PPA) (150 mL) was added to a 500mL round bottomed flask. Under the nitrogen atmosphere, the mixture was heated at 200°C for 24 h. The reaction solution was poured into water. The crude precipitate was filtered off and washed with water with 0.1 M Na₂CO₃, then washed with water, finally recrystallized from ethanol. The obtained product (11.96 g, 0.05 mol) and KMnO₄ (7.90 g, 0.05 mol) were dissolved in 350 mL of a mixed solvent of pyridine/water (1/1). The reaction was heated at 90°C for 24 h. The solution was filtered to eliminate the by-product MnO₂. The remaining clear solution was acidized to pH = 3 with 2 M HCl. The resulting precipitate was dissolved in 1 M NaOH and reprecipitated by acidification to pH = 3 with 1 M HCl. The precipitate was filtered off, washed with water and dried to afford H₂btic as white solid. The reaction route is shown in Scheme S1. ¹H NMR (400MHz, DMSO-*d*₆): δ 13.698 (s, 2H), 8.784 (s, 2H), 8.601 (s, 1H), 8.227 (d, 1H), 8.195 (d, 1H), 7.620(m, 2H).



Scheme S1. The synthesis of ligand H₂btic.

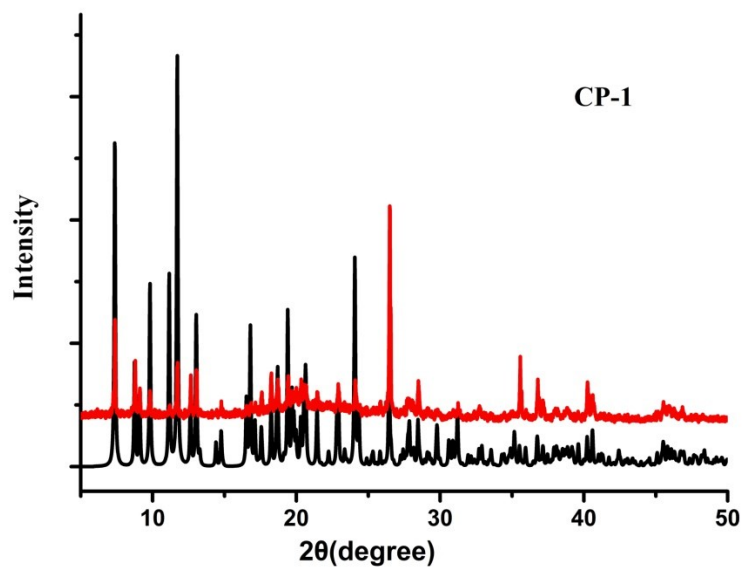


Figure S1. Experimental (red) and simulated (black) PXR D patterns of CP-1.

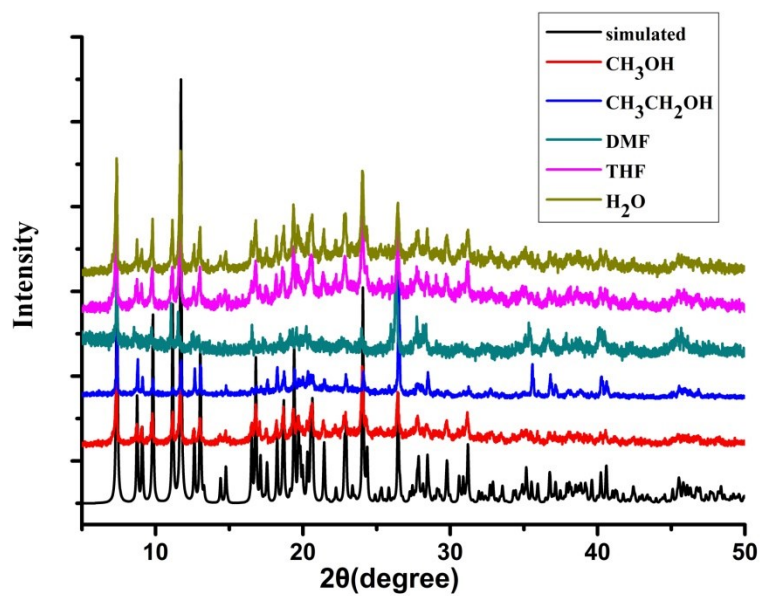


Figure S2. PXR D patterns of the as-synthesized CP-1, the simulated one and the samples after immersion in different solvents.

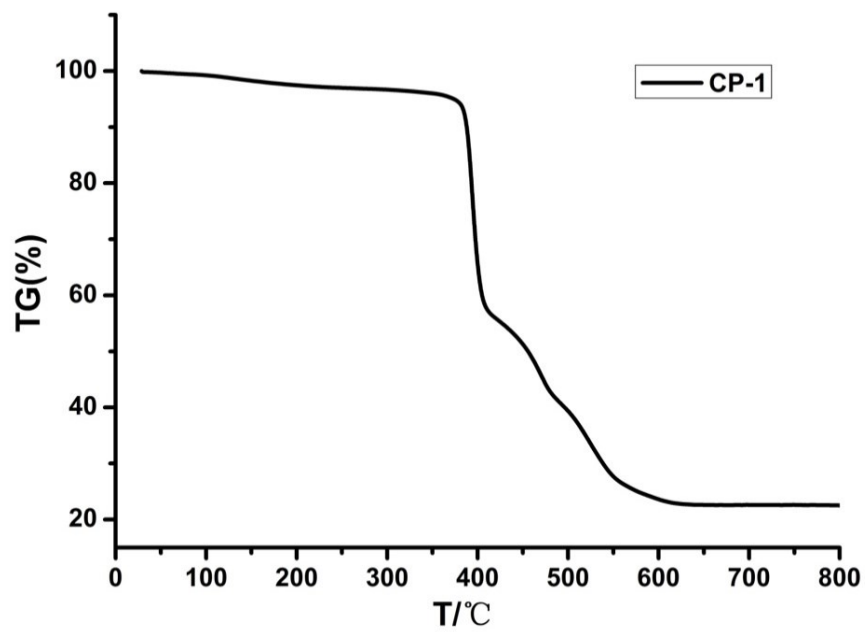


Figure S3. TGA curve of CP-1.

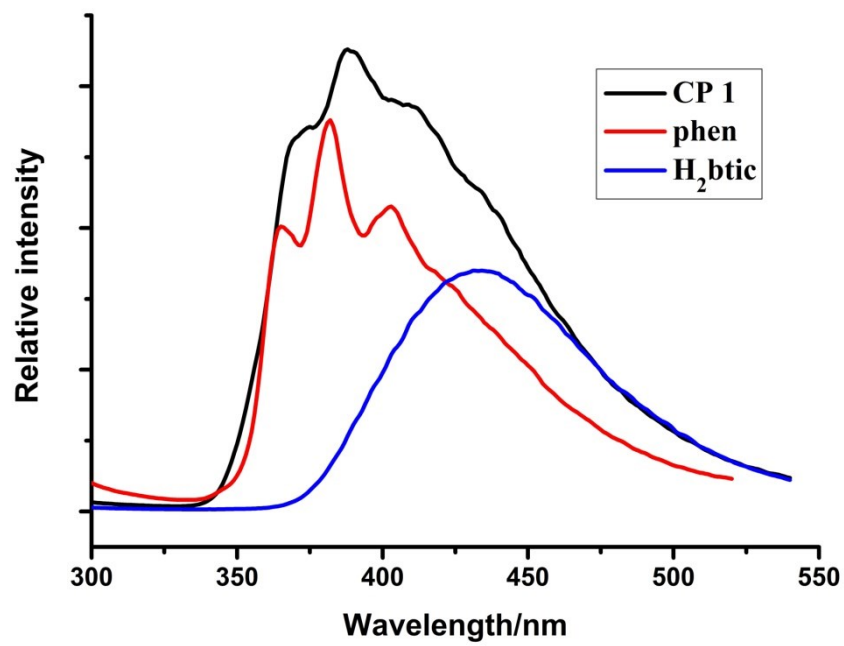


Figure S4. Solid-state photoluminescent spectra of free ligands and CP-1 at room temperature.

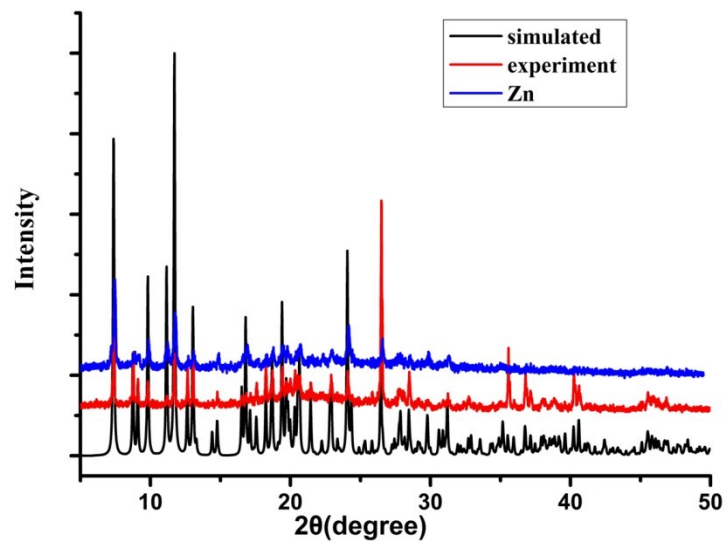


Figure S5. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Zn²⁺ test (Blue).

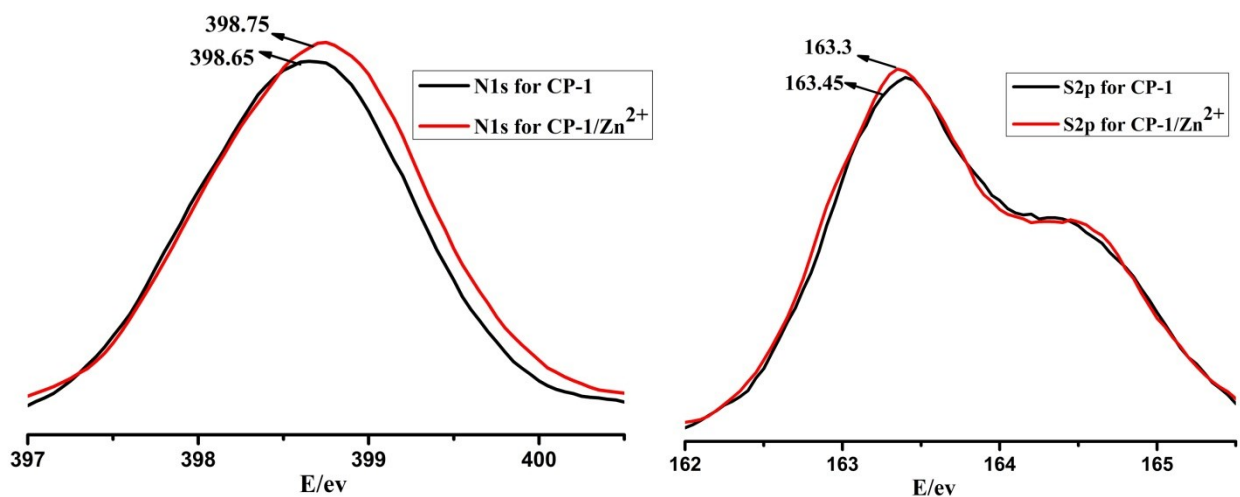


Figure S6. N 1s and S 2p XPS spectra of CP-1 (black) and Zn²⁺-incorporated CP-1 (red) activated by 0.001 mol/L aqueous solution of Zn²⁺.

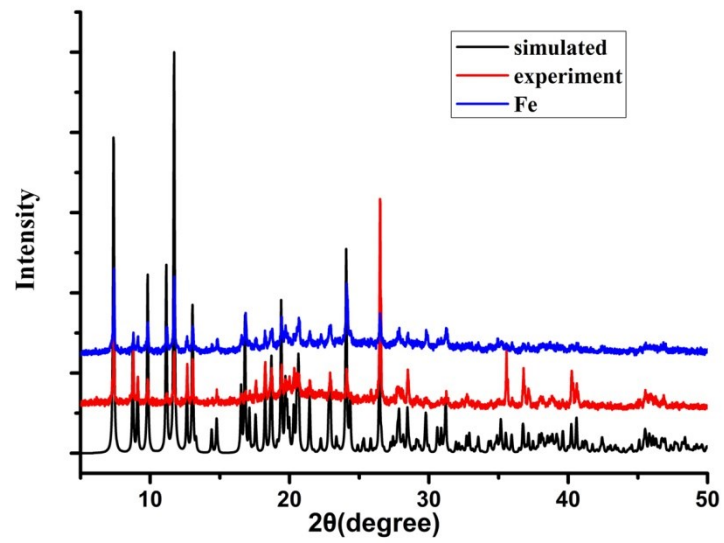


Figure S7. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Fe³⁺ test (Blue).

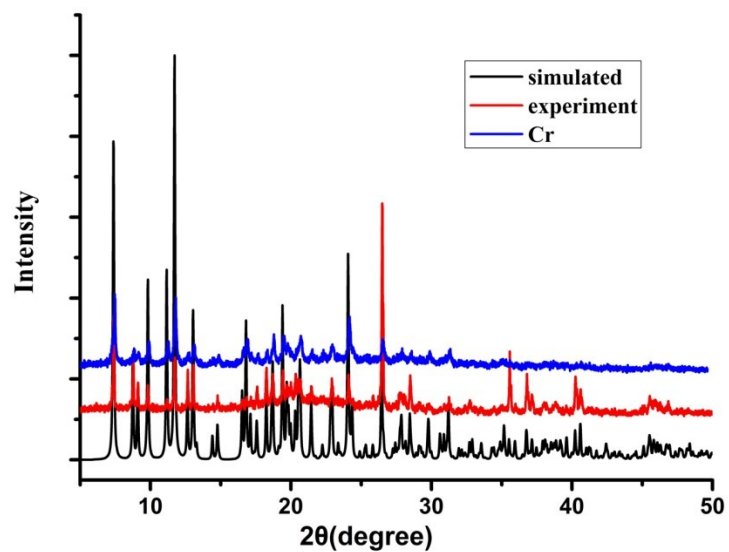


Figure S8. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after $\text{Cr}_2\text{O}_7^{2-}$ test (Blue).

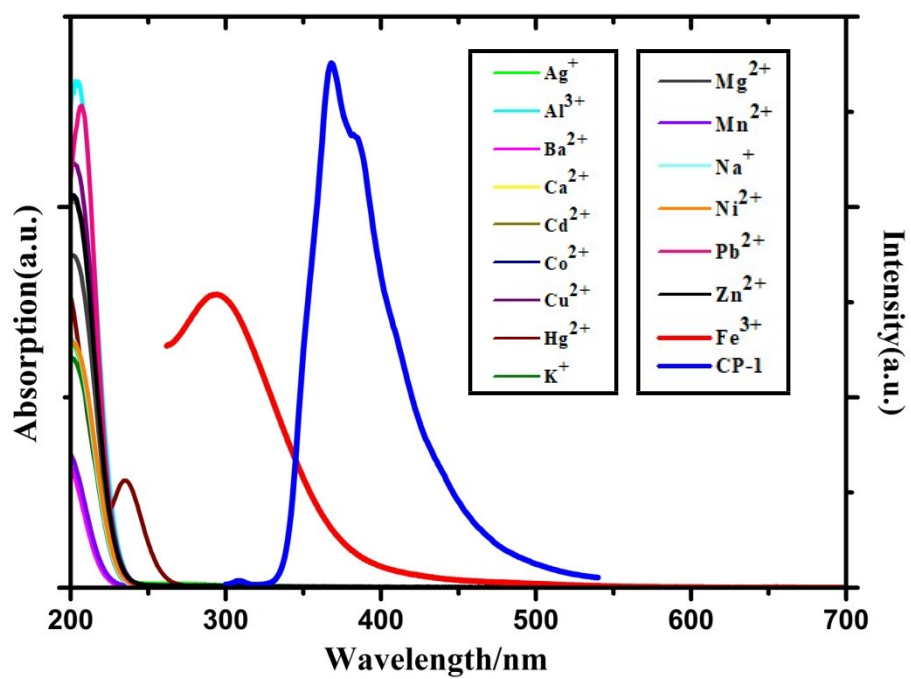


Figure
S9. UV-
vis

absorption spectra of varied metal ions and the emission spectra of CP-1 in water.

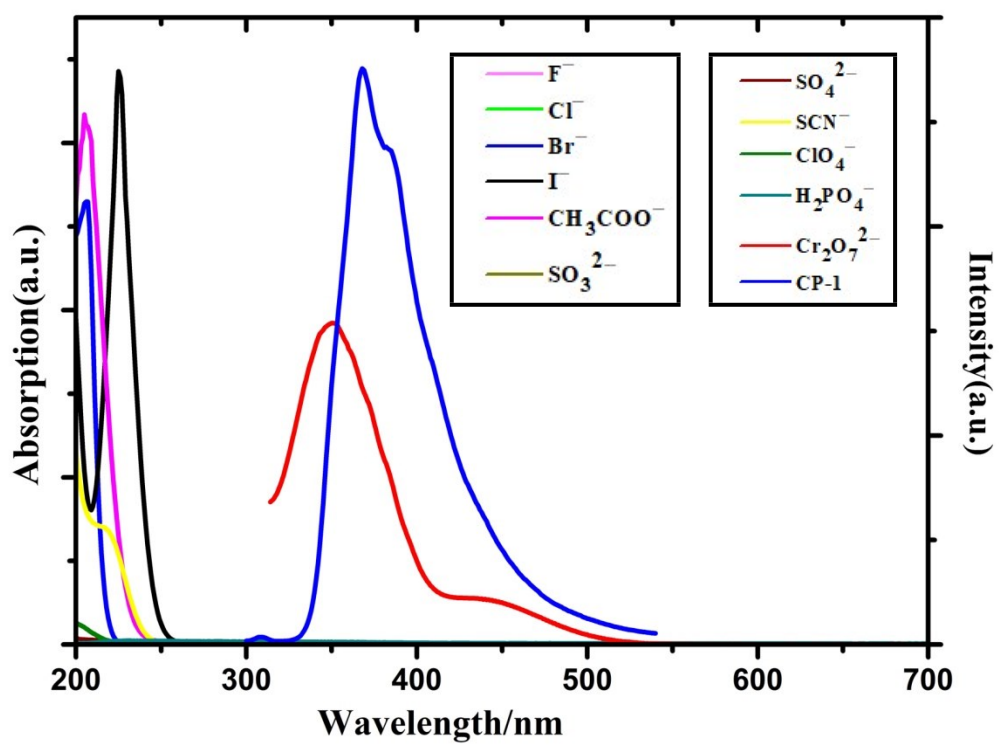


Figure
S10.
UV-vis

absorption spectra of varied anions and the emission spectra of CP-1 in water.