A luminescent Cd(II) coordination polymer as a multi-responsive fluorescent sensor for Zn$^{2+}$, Fe$^{3+}$ and Cr$_2$O$_7^{2-}$ in water with fluorescence enhancement or quenching

Liangjuan Liu,$^a$ Yungen Ran,$^b$ Jianlong Du,$^c$ Zhichao Wang,$^a$ Mei Liu,$^a$ Yajuan Mu,$^a$*

$^a$ College of Traditional Chinese Medicine, Hebei University, Baoding, 071000, P. R. China
$^b$ College of Life Science, Hebei University, Baoding, 071000, P. R. China
$^c$ College of Chemistry & Environmental Science, Hebei University, Baoding, 071000, P. R. China

* Corresponding author. E-mail: muyjhbu@hbu.edu.cn
Section 1. Synthesis of the ligand H₂btic.  Page 3

Figure S1. Experimental (red) and simulated (black) PXRD patterns of CP-1.  Page 4

Figure S2. PXRD patterns of the as-synthesized CP-1, the simulated one and the samples after immersion in different solvents.  Page 5

Figure S3. TGA curve of CP-1.  Page 6

Figure S4. Solid-state photoluminescent spectra of free ligands and CP-1 at room temperature.  Page 7

Figure S5. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Zn²⁺ test (Blue).  Page 8

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⁺.  Page 9

Figure S7. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Fe³⁺ test (Blue).  Page 10

Figure S8. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Cr₂O₇²⁻ test (Blue).  Page 11

Figure S9. UV-vis absorption spectra of varied metal ions and the emission spectra of CP-1 in water.  Page 12

Figure S10. UV-vis absorption spectra of varied anions and the emission spectra of CP-1 in water.  Page 13
Section 1. Synthesis of the ligand H$_2$btic.

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 Na$_2$CO$_3$, then washed with water, finally recrystallized from ethanol. The obtained product (11.96 g, 0.05 mol) and KMnO$_4$ (7.90 g, 0.5 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 MnO$_2$. 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 H$_2$btic as white solid. The reaction route is shown in Scheme S1. $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 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 H$_2$btic.
Figure S1. Experimental (red) and simulated (black) PXRD patterns of CP-1.
Figure S2. PXRD 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 Zn$^{2+}$ test (Blue).
Figure S6. N 1s and S 2p XPS spectra of CP-1 (black) and Zn$^{2+}$-incorporated CP-1 (red) activated by 0.001 mol/L aqueous solution of Zn$^{2+}$.
**Figure S7.** PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Fe$^{3+}$ test (Blue).
Figure S8. PXRD patterns of the simulated pattern (Black), experimental pattern (Red), and the sample of CP-1 after Cr$_2$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-I in water.