Supplementary Information (SI) for CrystEngComm.

Supporting Information

Surface Functionalized Chalcogenides for Highly Selective Removal of Hg^{2+}

Haochen Jie[a b], Zhiqing Lan[a b], Kefeng Li[b c], Xiaoliang Ye[*b], Shuilin Duan[a b], Zhihua Fu[*b], Guane Wang[*b] and Gang Xu[b]

[a]*College of Chemistry, Fuzhou UniversityFuzhou City, Fujian Province 350108, PR China*

[b]*State Key Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China*

[c]*College of Chemistry and Materials Science, Fujian Normal University, 32 Shangsan Road, Fuzhou 350007, P. R. China*

1. Experimental Procedures

1.1 Materials and General Methods

Chemicals: CuI was purchased from Sigma-Aldrich with a purity of 99%. The ligand pyrinine-2,4,6 (1H, 3H, 5H)-trithione (PMTT) was purchased from Jilin Chinese Academy of Sciences - Yanshen Technology Co., Ltd. with a purity of 95%. The organic solvents used are all from Shanghai Hushi, AR. All reagents were purchased directly and used without further purification.

Characterizations: Scanning electron microscopy (SEM) images were recorded on a Zeiss Sigma 300 field emission scanning electron microscope with the accelerating voltage of 3 kV. The powder X-ray diffraction (PXRD) was performed on a Rigaku SmartLab X-ray thin-film diffractometer with Cu Kα radiation (λ = 1.54 Å). The model of the detector is Dtex250 with a power of 10 KW. The PXRD of CuPMTT powder were performed. The 2θ scan range was 5 to 50° at a scan speed of 10° min^{-1} and with a scan step of 0.02°. The data of X-ray photoelectron spectroscopy (XPS) was collected from a Thermo Scientific ESCALAB 250 Xi XPS system (monochromatic Al K_α X-rays (1486.6 eV) operating at 15 kV; the base pressure: 5.0×10^{-8} Pa). Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 analyzer under a stream of synthetic air of 20 mL min^{-1}. The samples were heated from 30 to 700 °C at a heating rate of 10 °C min^{-1}. UV–VIS absorption spectra were recorded by a UV–VIS spectrophotometer (Lambda 365). Infrared spectroscopy (IR) spectra were recorded on a Bruker VERTEX70 FT-IR spectrometer (Germany) in 4000–400 cm^{-1} region using KBr pellets. The model of Ocean Optics electrochemical workstation is DH-2000-BAL, and the selected wavelength is 370.24 nm.

1.2 Synthesis of CuPMTT

CuPMTT was obtained by solvothermal method. Firstly, add 2 mL of acetonitrile solution (AN) to 0.019 g of CuI (0.1 mmol). Meanwhile, add 2 mL of N, N-dimethylformamide (DMF) solution to 0.0353 g of ligand PMTT (0.02 mmol). Then place two sets of solutions in glass bottles of the same capacity on an ultrasonic machine for 5 minutes until completely dissolved. Then pour the AN solution of CuI into the ligand DMF solution and let it react in an 85 °C oven for one day. After the reaction is complete, take it out and wash it three times with AN and DMF centrifugation, finally send it to a vacuum oven for 10 hours for drying.

1.3 CuPMTT adsorption selectivity

This article uses static adsorption experiments to measure the adsorption capacity of CuPMTT for metal salt M^{n+} ions (M = K, Na, Cu, Hg, Zn, Mg, Fe, Ca, Sr, Mn, Co, Ni, Cd, n = 1, 2, 3）。Firstly, weigh 30 mg of different metal salts and dissolve them in 100 mL of deionized water (DI). After complete dissolution, stir evenly to prepare a 300 mg/L salt solution. Subsequently, 3 mg of adsorbent was added to a glass bottle containing 10 mL of the above solution. They were placed in a magnetic stirrer at 25-30 °C and stirred at 200 r/min for 20 minutes. Then centrifuge the adsorbed solution. The supernatant was filtered using a syringe and filter membrane to obtain the adsorption solution, and the ion concentration after adsorption was measured by a plasma emission spectrometer (ICP). Continue to centrifuge and clean the precipitate with deionized water, and then send it to an oven for drying and later use.

1.4 UV testing of Hg^{2+} adsorption

Firstly, weigh 10 mg of Hg^{2+} solid and then dissolve it in 100 mL of aqueous solution to obtain a 100 mg/L mercury ion aqueous solution. Prepare a series of concentration solutions using the 100 mg/L mercury ion solution as the original solution. The pH of the solution is controlled between 4 and 5. Weigh 10 groups of 4 mg CuPMTT powder and add them to different concentrations of mercury ion solutions. Stir for 30 minutes under a magnetic stirrer at a temperature of 25 °C and 200 r/min. After the reaction is complete, centrifuge 3 times and take the supernatant for testing.

1.5 The effect of anions on adsorption

Firstly, weigh 10 mg of Hg^{2+} solid and then dissolve it in 100 mL of aqueous solution to obtain a 100 mg/L mercury ion aqueous solution. Take six sets of the above-mentioned Hg^{2+} solutions and add equal amounts of sodium salt to each of them, including $NaNO_3$, Na_2SO_4, $NaHCO_3$, $NaNO_2$, CH_3COONa, and NaBr. Weigh 6 groups of 4 mg CuPMTT powder and add them to different anions of Hg^{2+} solutions. Stir for 30 minutes under a magnetic stirrer at a temperature of 25 °C and 200 r/min. After the reaction is complete, centrifuge 3 times and take the supernatant for testing.

1.6 The effect of pH on adsorption

Firstly, weigh 10 mg of Hg^{2+} solid and then dissolve it in 100 mL of aqueous solution to obtain a 100 mg/L mercury ion aqueous solution. Prepare nine aliquots of the aforementioned Hg^{2+} solution, and adjust the pH of each set to 2, 3, 4, 5, 6, 7, 8, 9, and 10 by titrating with HCl or NaOH, respectively. Additionally, set up a 10th group of Hg^{2+} solution without any pH control (the pH is between 4.5 and 5). Weigh 10 groups of 4 mg CuPMTT powder and add them to different pH of Hg^{2+} solutions. Stir for 30 minutes under a magnetic stirrer at a temperature of 25 °C and 200 r/min. After the reaction is complete, centrifuge 3 times and take the supernatant for testing.

1.7 Dynamics testing of Hg^{2+} adsorption

Take 4 mg of CuPMTT powder and add 20 mL of deionized water for ultrasonication to form an adsorbent suspension. After standing for a period of time, take the supernatant for testing. During each testing process, add the same volume of supernatant to the colorimetric dish. Subsequently, insert the colorimetric dish into the testing platform and wait for the baseline to stabilize. Slowly add 100 μL of mercury ion aqueous solutions of different concentrations to the adsorbent solution and observe the intensity changes of the UV absorption spectrum.

1.8 Calculation of the adsorption capacity Qt and adsorption rate η of CuPMTT for Hg^{2+}

The amount of mercury adsorption was considered the difference between the initial and final mercury concentrations of the solution. The adsorption capacity (Q_t, in mg g^{-1}) of mercury ions adsorbed onto CuPMTT was calculated according to the following equation:

$$Q_t = \frac{(C_0 - C_e)V}{m} \tag{1}$$

The removal efficiency of mercury was calculated based on the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

where the C_0 and C_e are the initial and the equilibrium concentrations of the mercury ions in the testing solution (mg L^{-1}), V is the volume of the testing solution (L), and m (g) is the mass of the adsorbent.

2. Figures

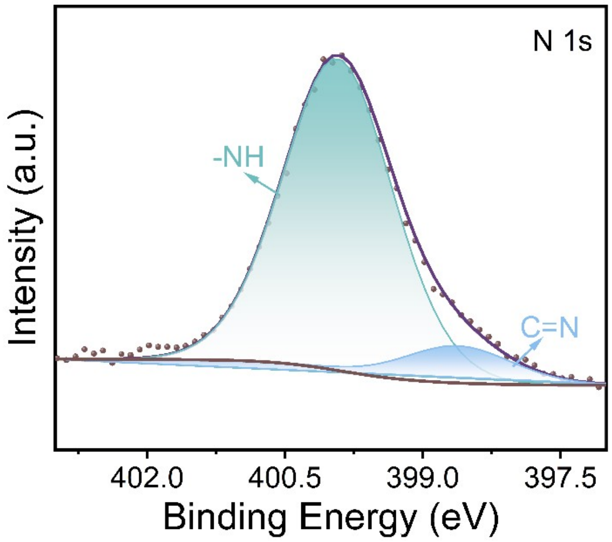

Fig. S1 XPS spectrum of N element in PMTT.

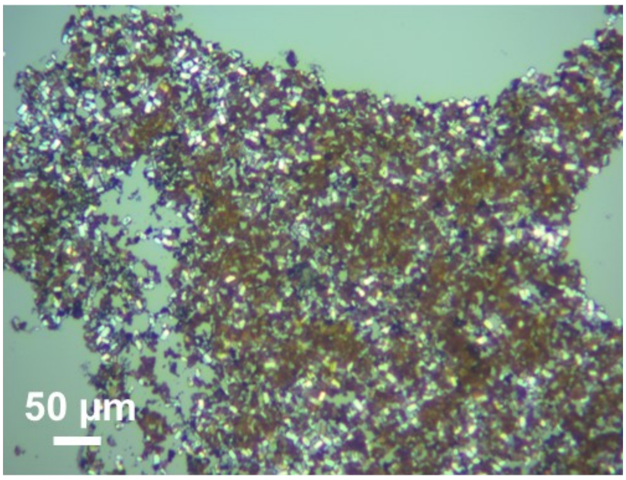

Fig. S2 Optical photograph of CuPMTT microcrystal.

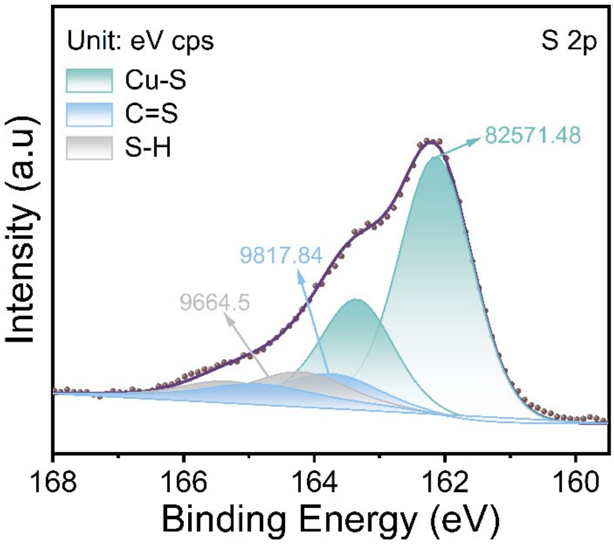

Fig. S3 XPS spectra of S elements before adsorption.

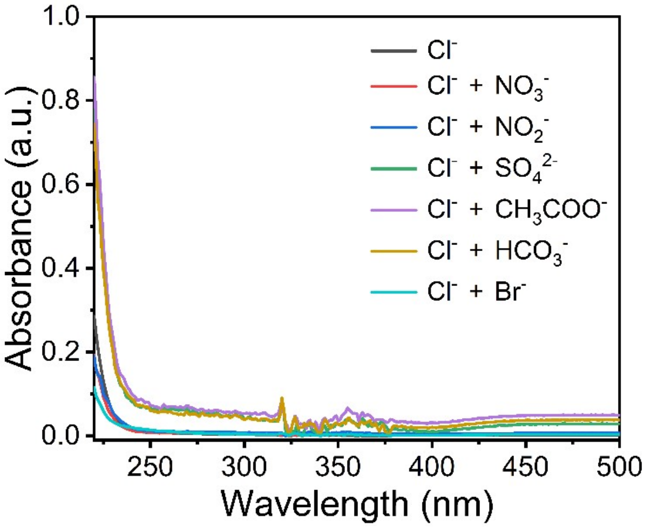

Fig. S4 The UV absorption spectra of CuPMTT after Hg^{2+} adsorption in different anionic environments.

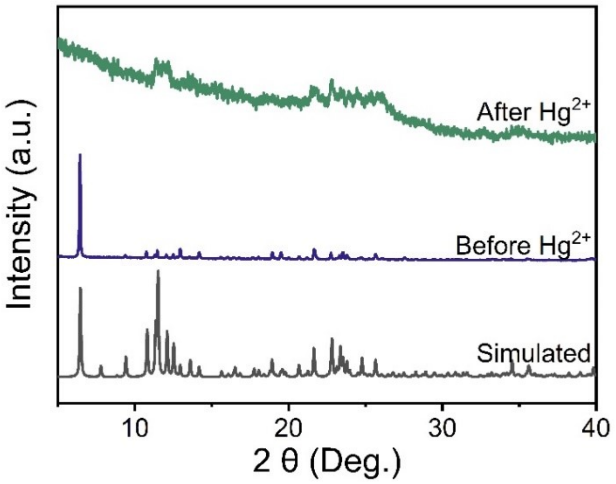

Fig. S5 PXRD of CuPMTT before and after adsorption of Hg^{2+}.

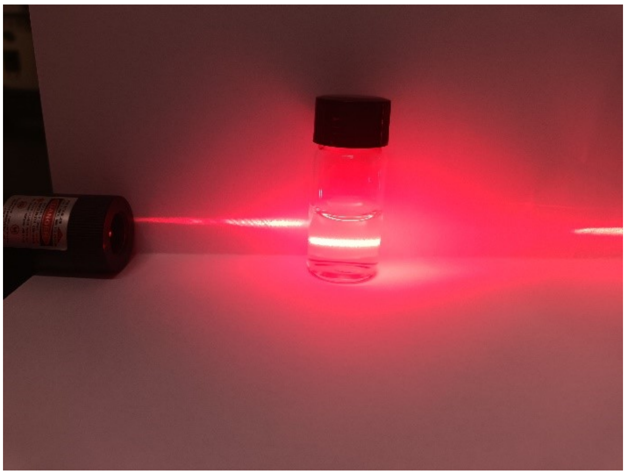

Fig. S6 The supernatant of the CuPMTT solution following Hg^{2+} adsorption.

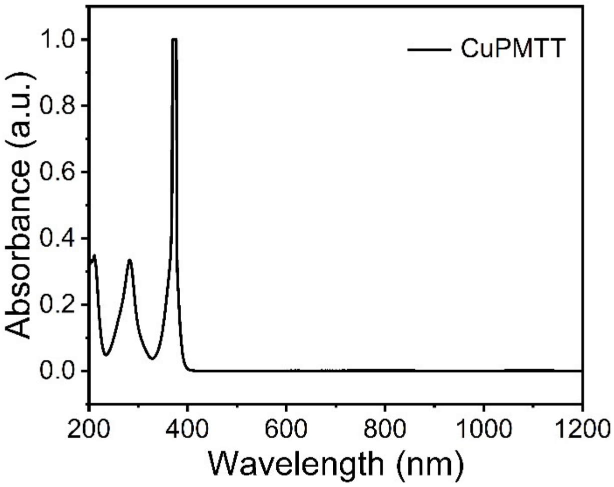

Fig. S7 UV absorption spectrum of CuPMTT.

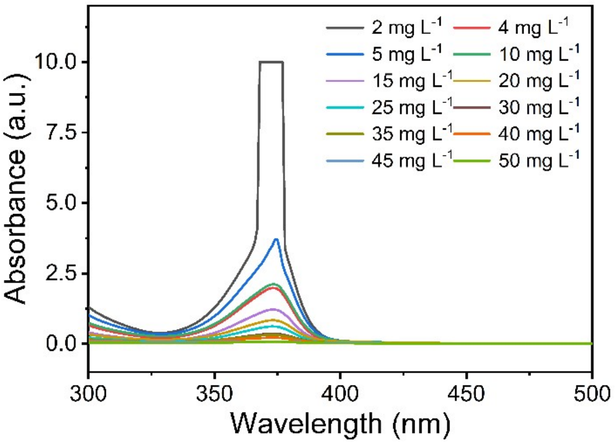

Fig. S8 UV absorption spectrum of CuPMTT under different concentrations of Hg^{2+}.

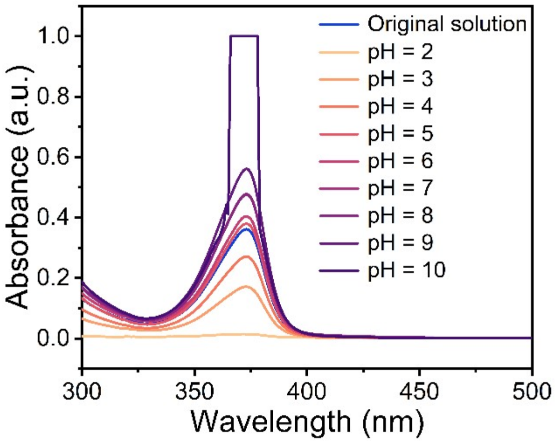

Fig. S9 The UV absorption spectra of CuPMTT after Hg^{2+} adsorption at different pH values.

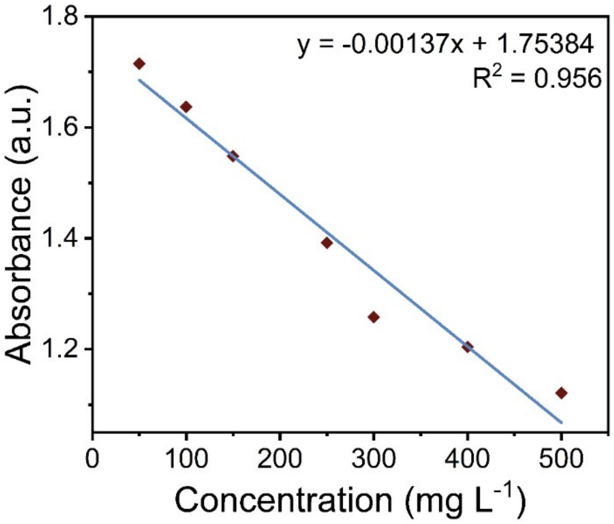

Fig. S10 Relationship between Hg^{2+} concentration and the intensity of ultraviolet absorption at 370 nm.

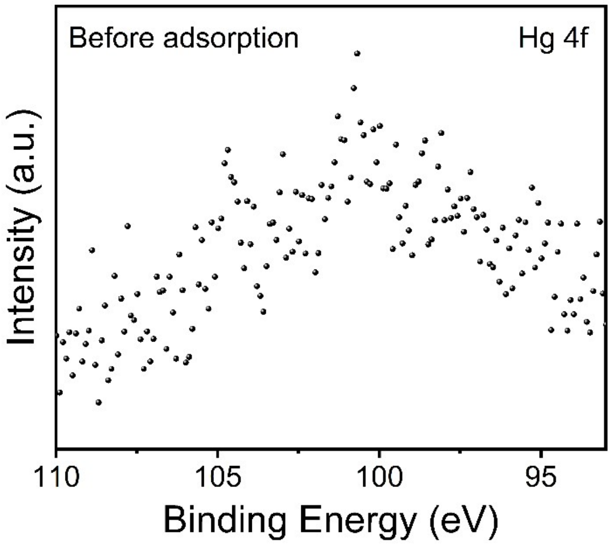

Fig. S11 XPS spectrum of Hg element in CuPMTT before adsorption.

3. Table

Table S1 Adsorption selectivity coefficient for Hg^{2+}.

Ions	**Adsorption Selectivity Coefficient for Hg(II)**
Cu^{2+}	4.51
Cd^{2+}	6.48
K^{+}	8.78
Na^{+}	11.17
Fe^{2+}	12.31
Ca^{2+}	14.14
Ni^{2+}	14.29
Sr^{2+}	14.29
Co^{2+}	20.20
Zn^{2+}	20.50
Mn^{2+}	25.15
Mg^{2+}	35.04
Fe^{3+}	44.09