

## *Supplementary Information for*

### **Highly Selective Fluorescent Recognition of Zn<sup>2+</sup> in Water by Terpyridine-CuCl<sub>2</sub>**

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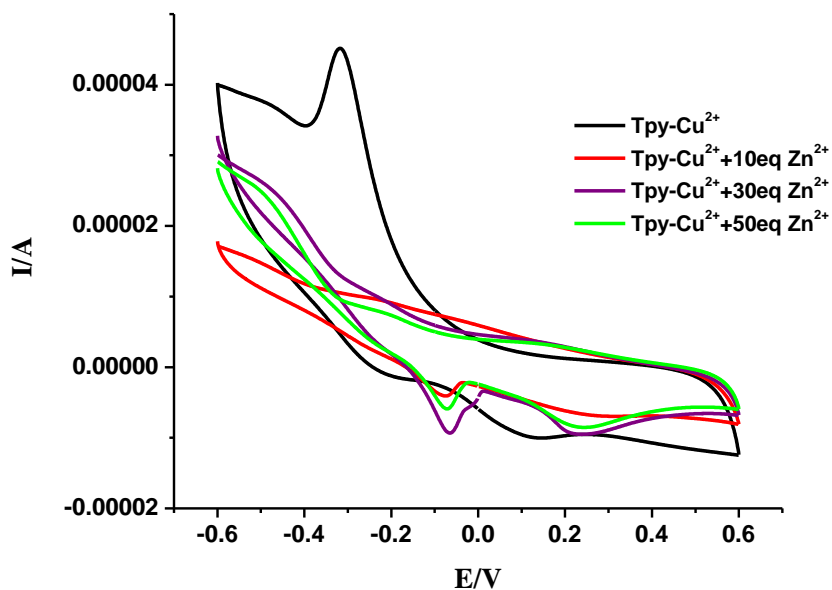
**Materials and Equipment.** Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies. Following are the metal salts used in the experiments: CuCl<sub>2</sub>·2H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Mg(ClO<sub>4</sub>)<sub>2</sub>, LiClO<sub>4</sub>·3H<sub>2</sub>O, NaNO<sub>3</sub>, BaCl<sub>2</sub>·2H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, KNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, HgCl<sub>2</sub>, LiClO<sub>4</sub>·3H<sub>2</sub>O and SnCl<sub>2</sub>·2H<sub>2</sub>O. Fluorescence spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon) at 298 K.

**Electrochemistry.** Electrochemical measurements were performed with a CHI660C instruments. All the measurements were carried out in a one-compartment cell at room temperature equipped with Pt working electrode, a platinum counter electrode, and a Hg(l)/Hg<sub>2</sub>Cl<sub>2</sub>(s) reference electrode. The supported electrolyte was a 0.1 M NaCl solution. The host solution was mixed with various equivalents of Zn<sup>2+</sup> at room temperature in a volumetric flask and diluted to the desired concentration. The resulting solutions were allowed to stand at room temperature for 2 h before measurement. The electrodes were soaked in 2N HNO<sub>3</sub> for 15 min and then washed with distilled water before each measurement.

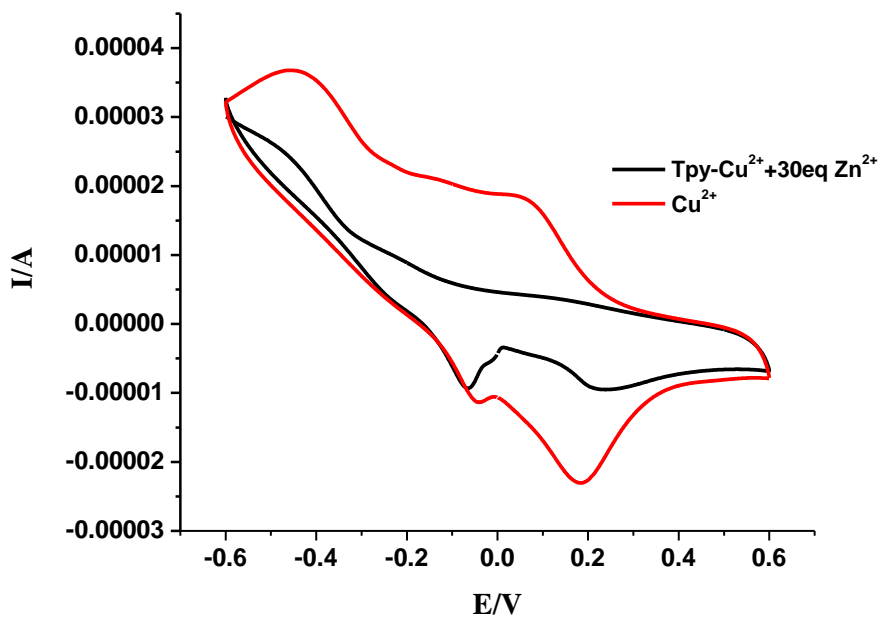
**Preparation of TpyCuCl<sub>2</sub>.** A mixture of Tpy (233 mg, 1.0 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (205 mg, 1.2 mmol) was stirred in H<sub>2</sub>O (30 mL) at room temperature for 30 min at which the solution became clear. Then the solution was concentrated to about 5 mL which produced green precipitate. The green solid was collected by filtration and washed with CH<sub>3</sub>OH (5 mL). After dried under vacuum, TpyCuCl<sub>2</sub> was obtained. (Reference: Morgan, G.; Burstall, F. H. *J. Chem. Soc.* **1937**, 1649-1655.)

**Reduction of the water solutions of CuCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O and HgCl<sub>2</sub> with Sn in the presence of Zn<sup>2+</sup>.** To a water solution (5 mL) of FeCl<sub>3</sub>·6H<sub>2</sub>O (129.8 mg, 0.48 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (178.5 mg, 0.6 mmol), excess Sn powder (356.1 mg, 3.0 mmol) was added. Distilled water was added to obtain a 10 mL solution. The solution was then heated gently until the color of Fe<sup>3+</sup> disappeared. After centrifugation to separate the precipitates, the upper clear solution (50 μL) was added to a 3 mL solution of TpyCuCl<sub>2</sub> (2.0 × 10<sup>-5</sup> M, H<sub>2</sub>O) and its fluorescence spectrum was measured. The reductions of CuCl<sub>2</sub>·2H<sub>2</sub>O and HgCl<sub>2</sub> with Sn in the presence of Zn<sup>2+</sup> were conducted similarly, and the dosages of CuCl<sub>2</sub>·2H<sub>2</sub>O and HgCl<sub>2</sub> respectively were 20.5 mg (0.12 mmol) and 97.7 mg (0.36 mmol) respectively.

**Figure S1.** (a) CV titration profile of TpyCuCl<sub>2</sub> (1 mM) with various amount of Zn<sup>2+</sup> in H<sub>2</sub>O. (b) Comparing the CV plot of TpyCuCl<sub>2</sub> (1 mM)+30 equiv Zn<sup>2+</sup> with that of CuCl<sub>2</sub> (1 mM) in H<sub>2</sub>O. Reference electrode = saturated Hg(l)/Hg<sub>2</sub>Cl<sub>2</sub>(s); supporting electrolyte : 0.1 M NaCl solution; scan rate = 50 mV S<sup>-1</sup>.



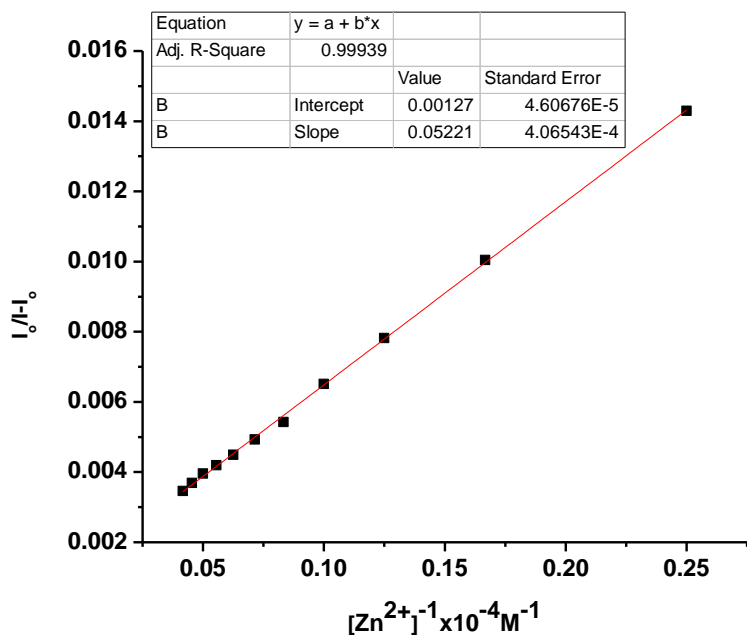
(a)



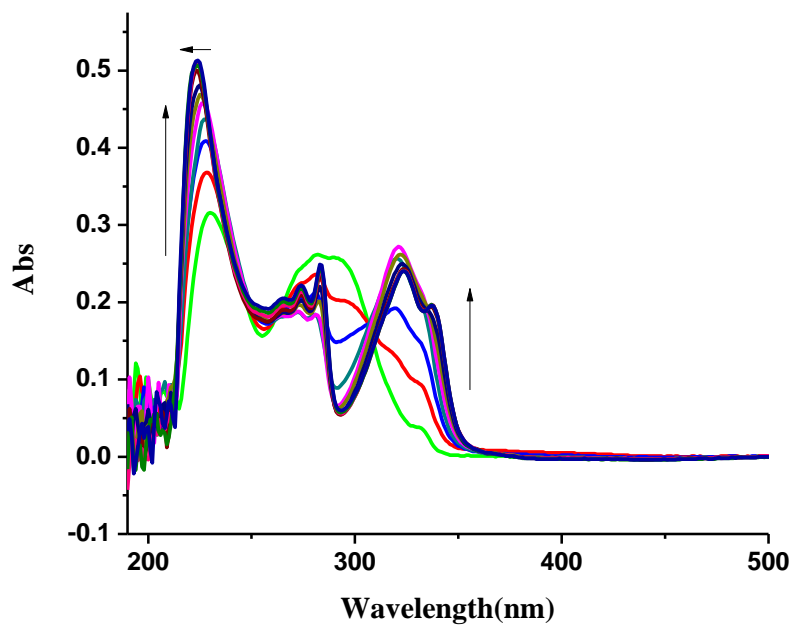
(b)

Figure S1a shows that when the water solution of TpyCuCl<sub>2</sub> was treated with excess Zn<sup>2+</sup>, two new peaks at 0.222V and -0.066V appeared in the CV. These two CV peaks were also observed in the CV plot of CuCl<sub>2</sub> in water solution (Figure S1b). Zn<sup>2+</sup> or Tpy-Zn<sup>2+</sup> complex was not redox active in the region. These results support that excess Zn<sup>2+</sup> can displace Cu<sup>2+</sup> in the coordination with Tpy. We also conducted the UV titration of TpyCuCl<sub>2</sub> with 10 – 50 equiv Zn<sup>2+</sup>, but the changes in the UV spectra were too small to allow the assessment of the reaction.

**Figure S2.** Plot the fluorescence enhancement of TpyCuCl<sub>2</sub> (2.0 x 10<sup>-5</sup> M, H<sub>2</sub>O) at λ<sub>emi</sub> = 351 nm in the presence of Zn<sup>2+</sup> (> 20 equiv) according to the Benesi-Hildebrand expression.



**Figure S3.** UV titration of Tpy ( $2.0 \times 10^{-5}$  M, 25 mM hepes buffer, pH = 7.35) with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.



**Figure S4.** Plot of the UV absorption of Tpy at  $\lambda = 224$  nm titrated with  $\text{CuCl}_2$  according to the Benesi-Hilderand equation.

