Switching the recognition preference of thiourea derivative by replacing Cu^{2+}: Spectroscopic characteristic of aggregation-induced emission and the mechanism studies for recognition of Hg(II) in aqueous solution

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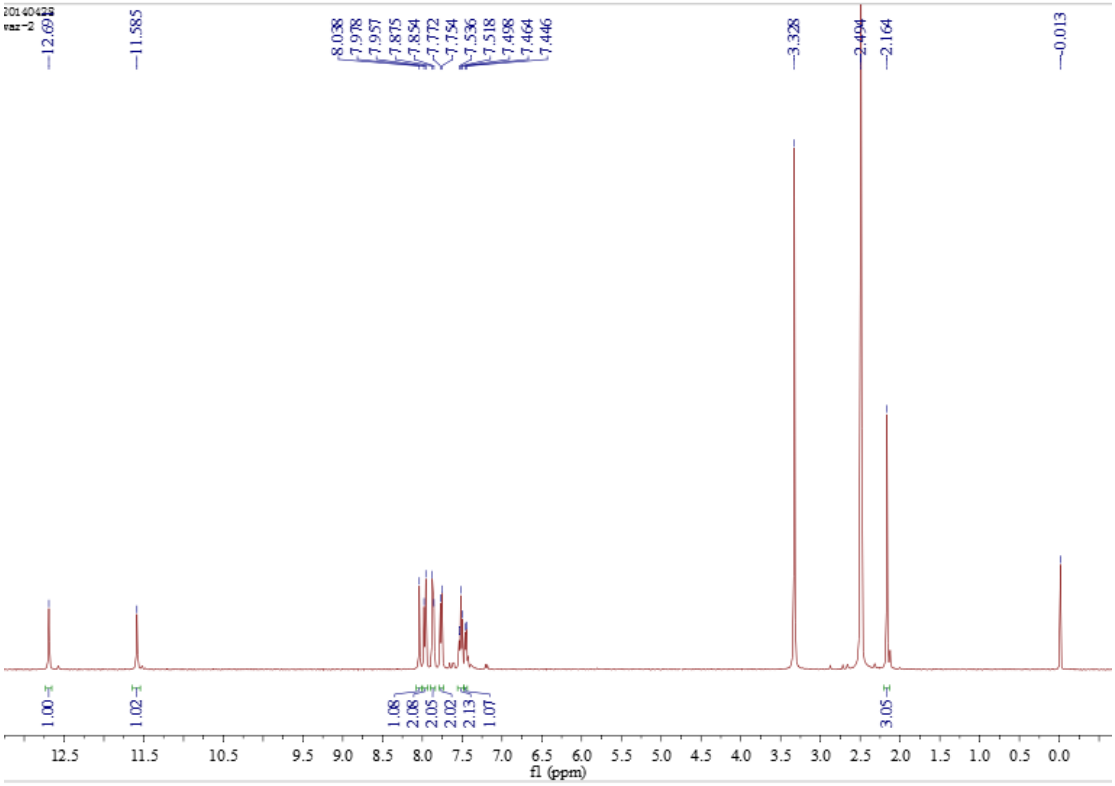


Figure. S1 The 1H NMR spectrum of **CN-S**.

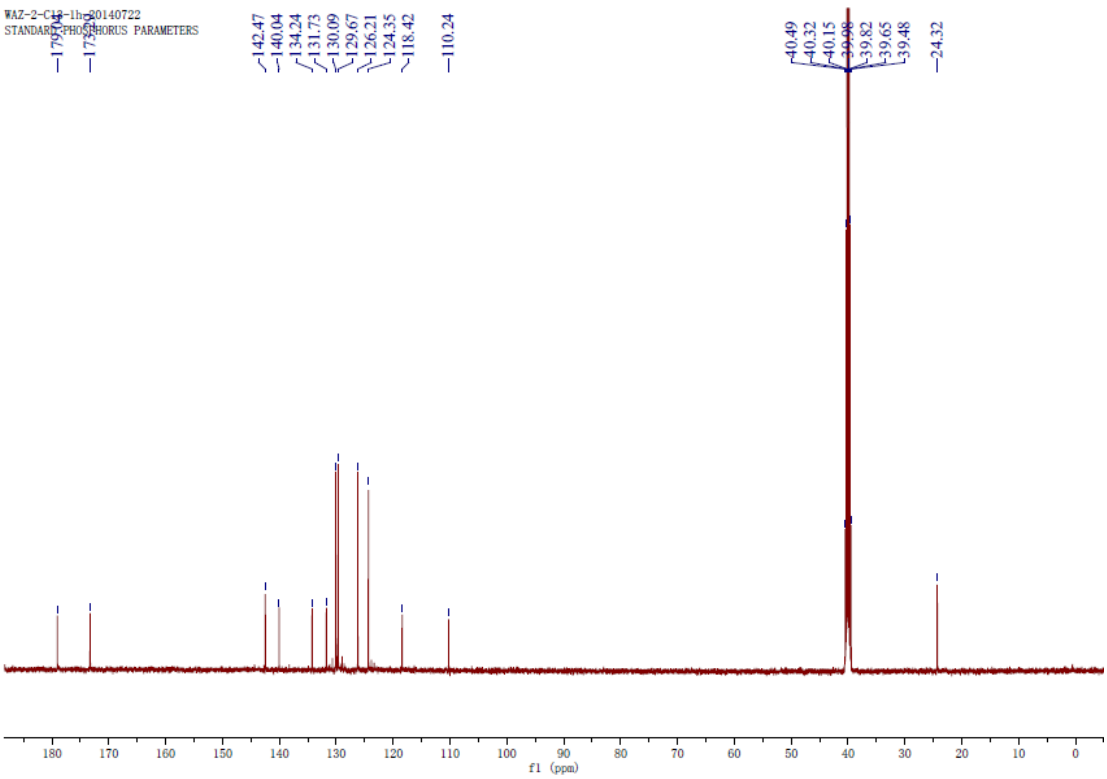


Figure. S2 The ^{13}C NMR spectrum of **CN-S**.

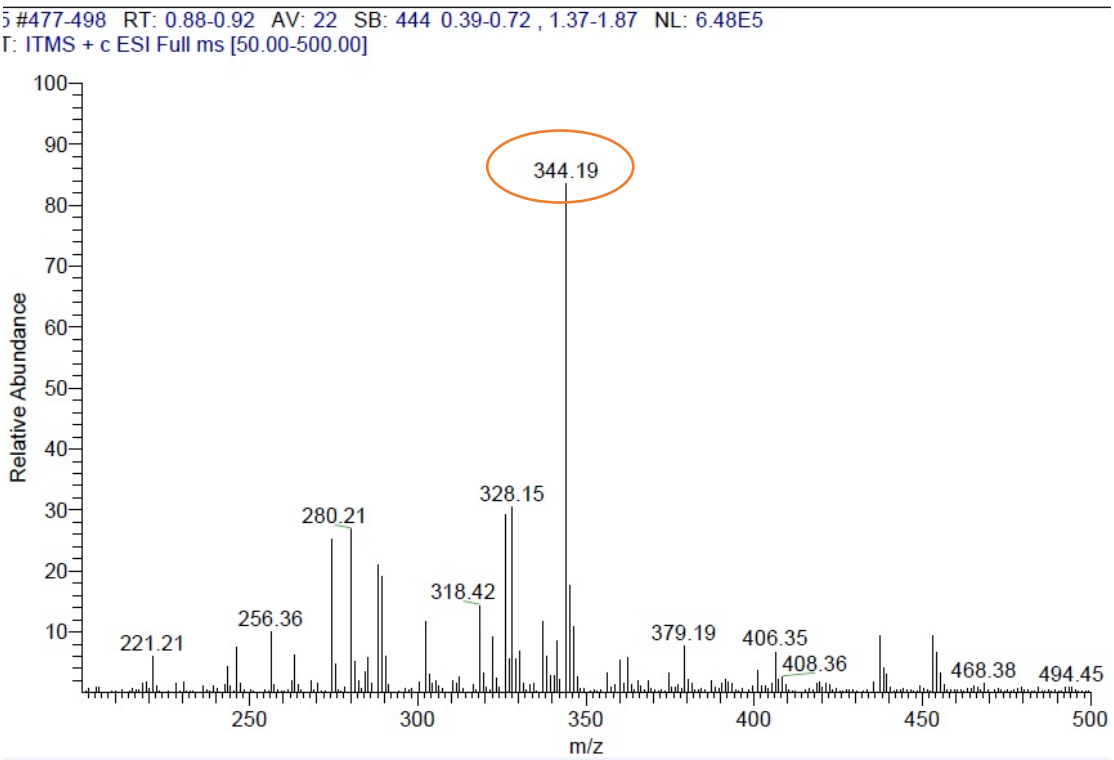


Figure. S3 The mass spectrum of **CN-S**.

Table S1 The detailed information of the certified reference material of standard solution of Hg^{2+}

standard sample number	Unique Identification	Ingredients	Mass Concentration ρ/(μg/ml)	Medium	Medium concentration c/(mol/L)	relative expanded uncertainty U/%(k=2)
GSB 04-1729-2004	148029-1	Hg	1000	HNO_3	1.0	0.7

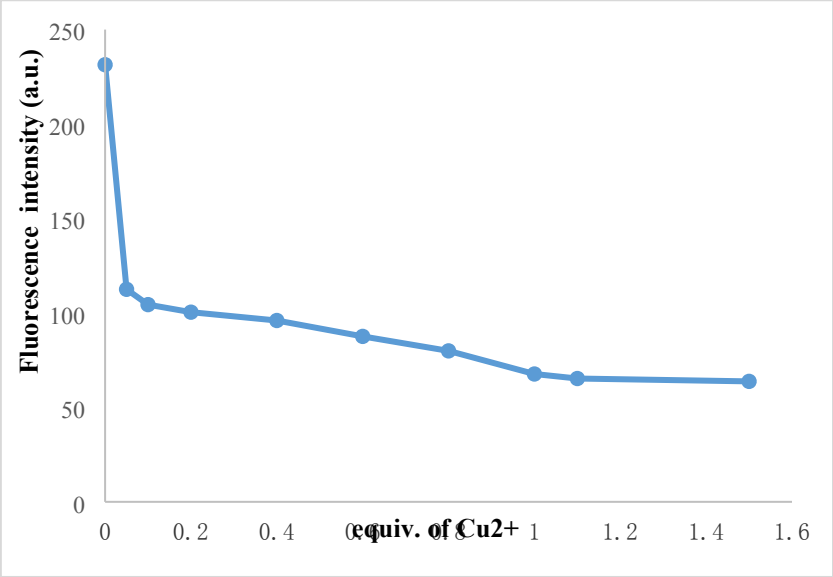


Figure S4. A plot of the fluorescence intensity obtained from the reaction of **CN-S** (10 μM) with Cu^{2+} (1.5 equiv.). All measurements were taken in 50 mM PBS buffer at pH 7.0 (containing 0.1% DMSO) at 25℃. Excitation and emission were at 380 nm/470 nm.

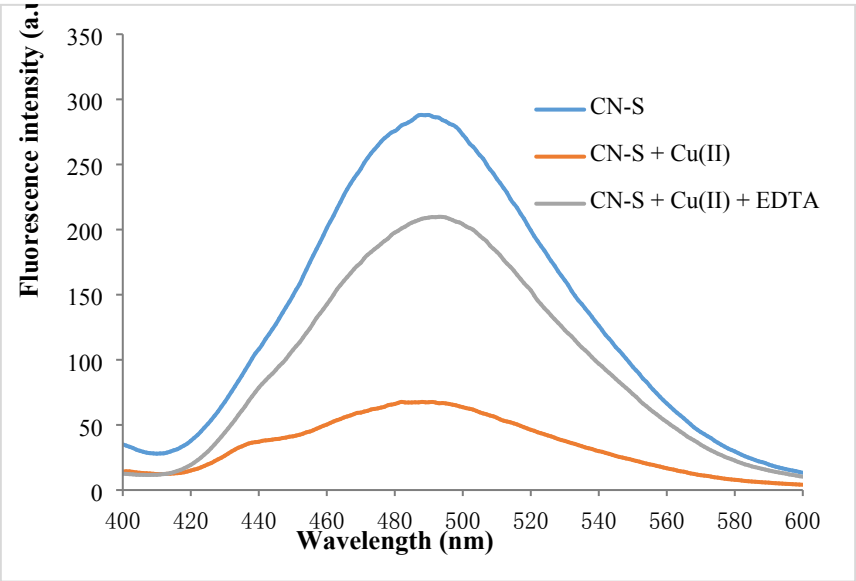


Figure. S5 Fluorescence spectra of **CN-S** (10 μM), **CN-S** (10 μM) + Cu^{2+} (1.0 equiv.) and **CN-S** (10 μM)+Cu^{2+} (1.0equiv.)+EDTA (5.0 equiv.) All measurements were taken in 50 mM PBS buffer at pH 7.0 (containing 0.1% DMSO) at 25℃. Excitation wavelength was 380 nm.

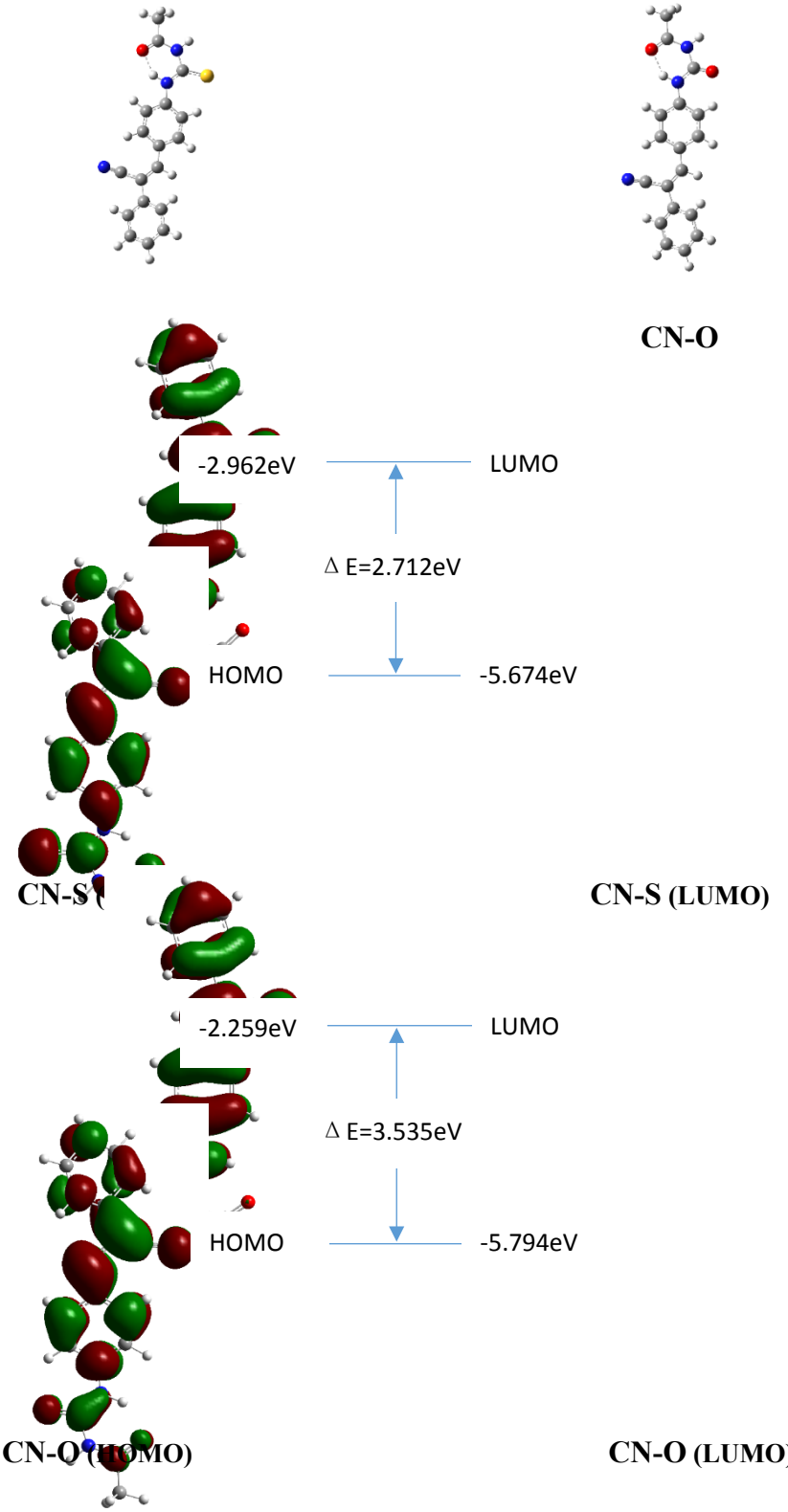


Figure. S6 Optimized structure and molecular amplitude plots HOMO and LUMO of **CN-S** and **CN-O.**

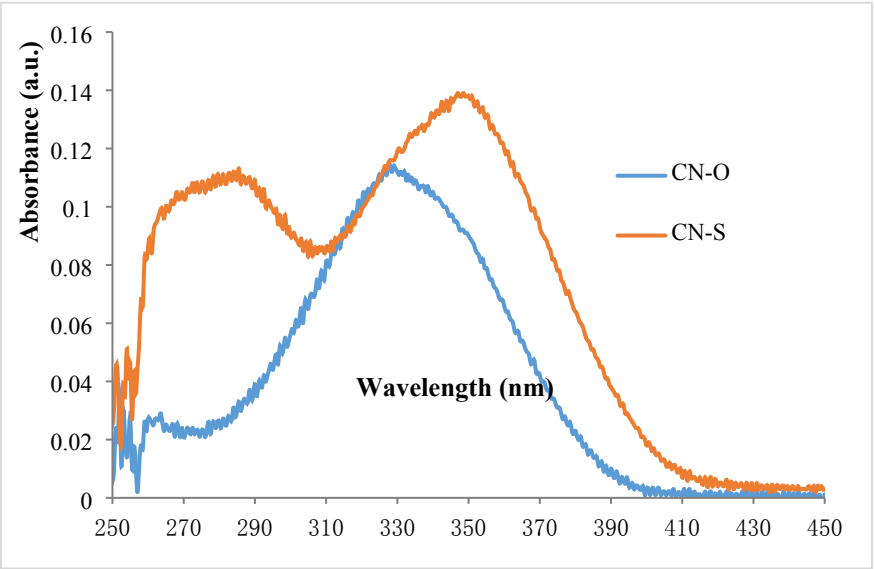
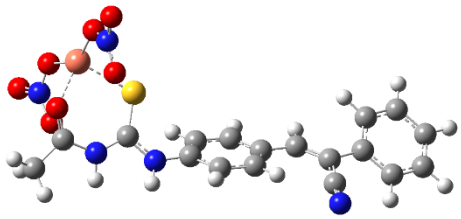


Figure. S7 Absorption spectra of **CN-S** (5 μM) and **CN-O** (5 μM) in DMSO.



HF=-2089.35354314
Enthalpy= 0.360190 a.u.= 9.80113009 eV;
Gibbs Free Energy= 0.254515 a.u.= 6.925607665 eV;
Zero-point correction= 0.327241 a.u.= 8.904554851 eV.
d(Cu-S)=2.431Å
d(Cu-O)=2.153Å

Figure. S8 Optimized structure and some useful data of **Cu-CN-S**

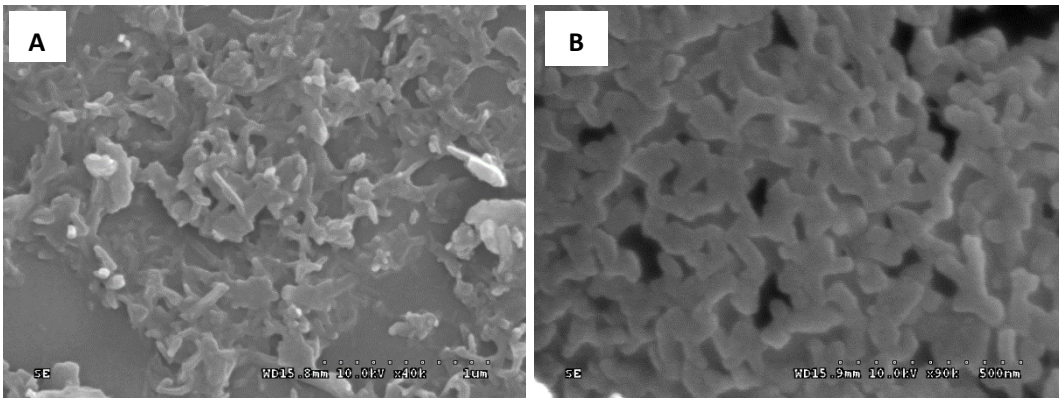


Figure S9 SEM images of **CN-S** in aqueous solution (containing 0.1% DMSO) in the absence (A) and presence (B) of 1.0 equiv. Cu^{2+} ions.

Detection limit

The detection limit for Hg^{2+} ions was calculated by the fluorescencetitration experiments according to the reported method. A good linear relationship between the fluorescence intensity and Hg^{2+} concentration could be obtained in the 0～10 μM (R^2=0.9966). The value obtained for the Hg^{2+} was found to be 45 nM by the equation of $L_{OD}=3\delta/m$ (δ was the standard deviation of the blank solution and m is the Absolute value of the slope between intensity versus Hg^{2+} concentration).

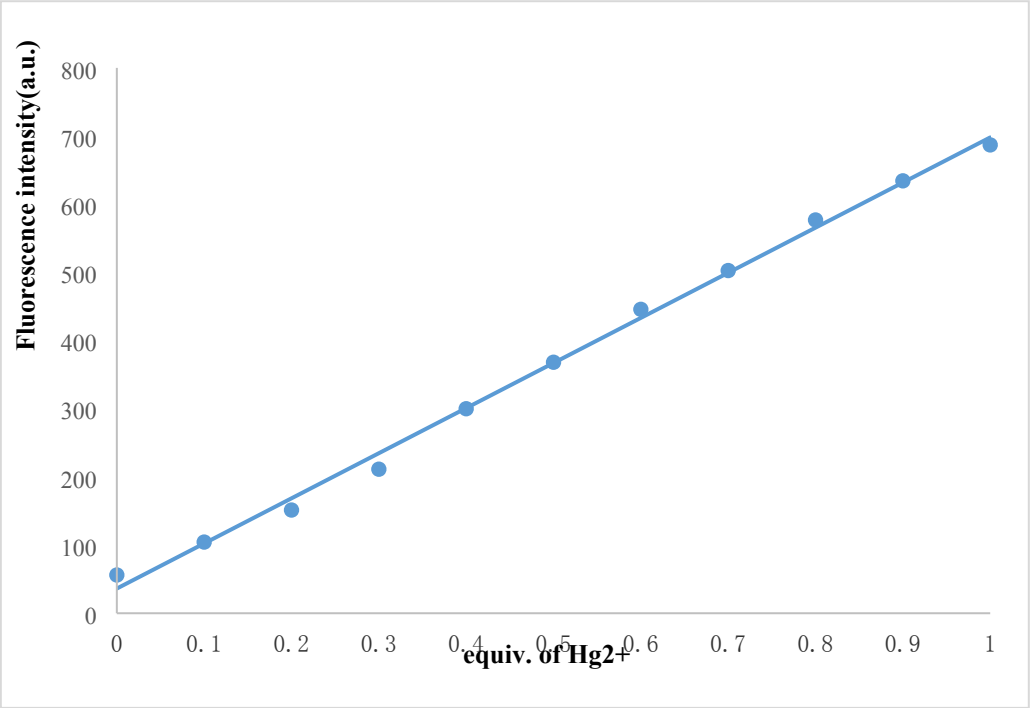


Figure. S10 The relationship between the fluorescence intensity and Hg^{2+}concentration. All measurements were taken in 50 mM PBS buffer at pH 7.0 (containing 0.1% DMSO) at 25℃. Excitation and emission were at 380 nm/470 nm.

Separate of CN-O

To a solution of **CN-S** (30 mg, 0.1mmol) and Copper nitrate trihydrate (24.1mg, 0.1 mmol) in dimethylsulfoxide (2.16 mL) was added a solution of mercury(II) chlorid (54.2mg, 0.2mmol) in water (27 mL) at rt. After stirring for 1 h, The mixture was then extracted with $CHCl_3$ and the organic layer was washed with water, dried over Na_2SO_4, and then filtered out. Excess solvent was evaporated under reduced pressure to afford **CN-O**.

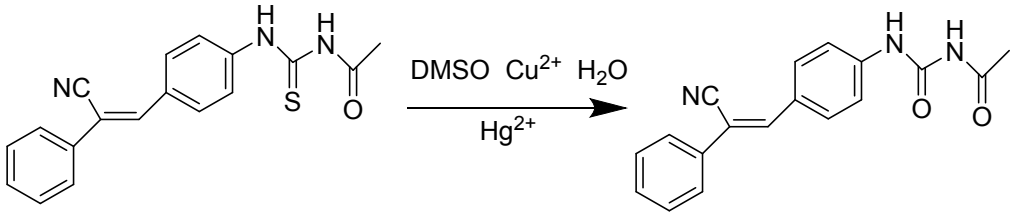


Figure S11.Separate of **CN-O**

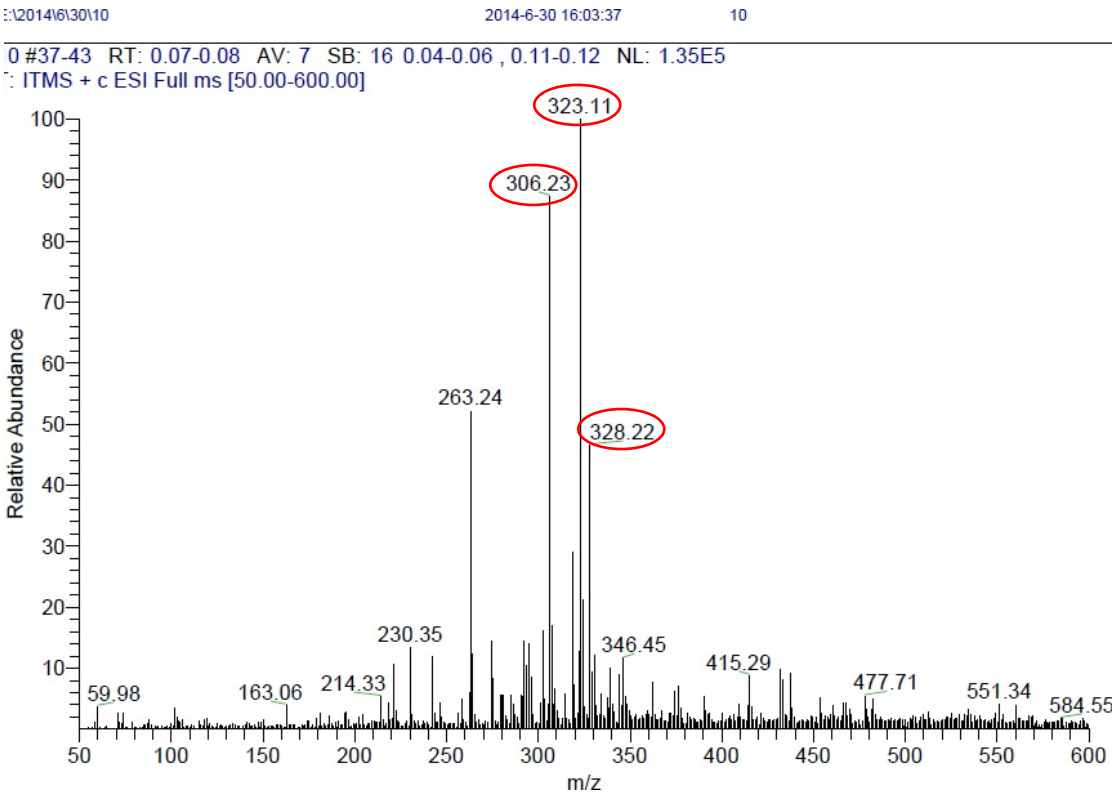


Figure. S12 The mass spectrum of the reacting syetem of **Cu-CN-S** with Hg^{2+}.

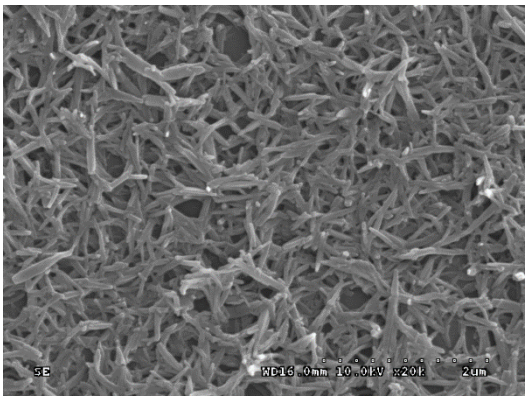


Figure S13 SEM images of **CN-O** in aqueous solution (containing 0.1% DMSO).

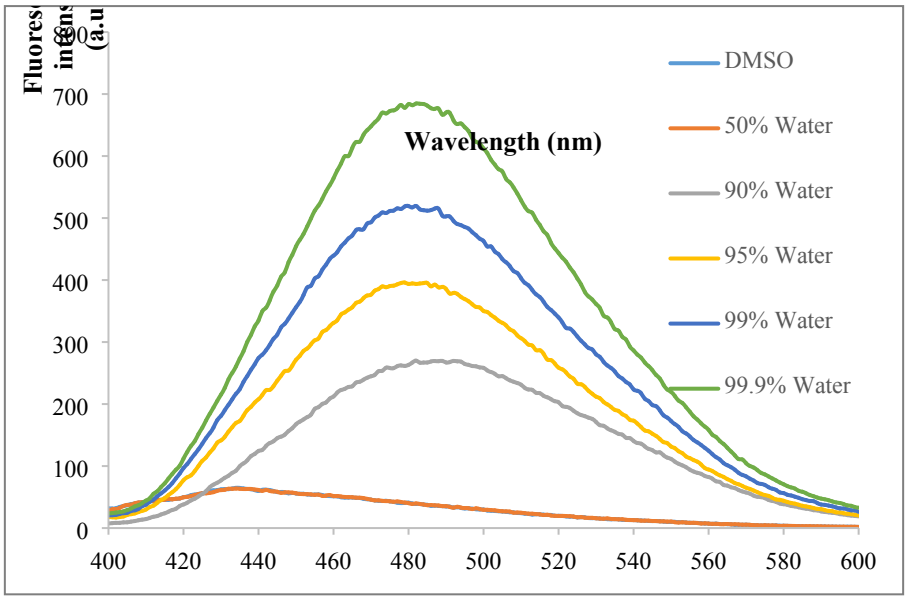


Figure. S14 Fluorescent spectra of **CN-O** (10 μM) in a DMSO/water mixture (excitation wavelength was 380 nm).

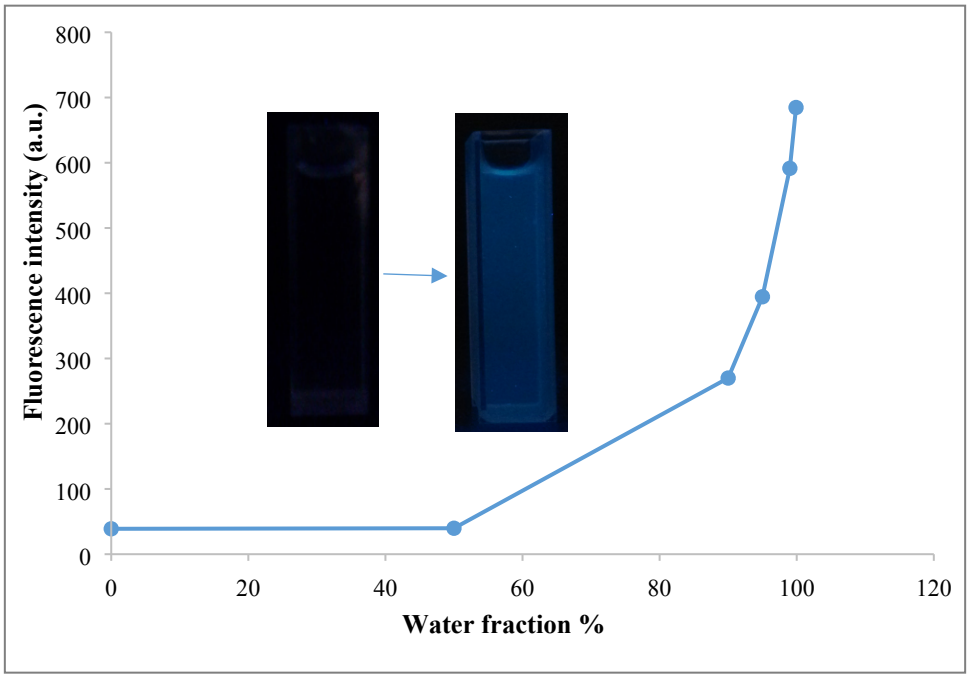


Figure. S15 Effect of water volume fraction on the emission intensity of **CN-O** (10 μM) in DMSO/water containing 50 mM PBS at pH 7.0. Inset show photographs of **CN-O** (10 μM) in dilute DMSO solution and a DMSO/water mixture with a high water fraction under a UV lamp (365 nm). Excitation and emission was at 380nm/470nm respectively.