Supplementary Information

Visual detection of Hg^{2+} without interference by alkali and alkaline earth metal ions using an iron(III) complex in a hetero-bimetallic environment

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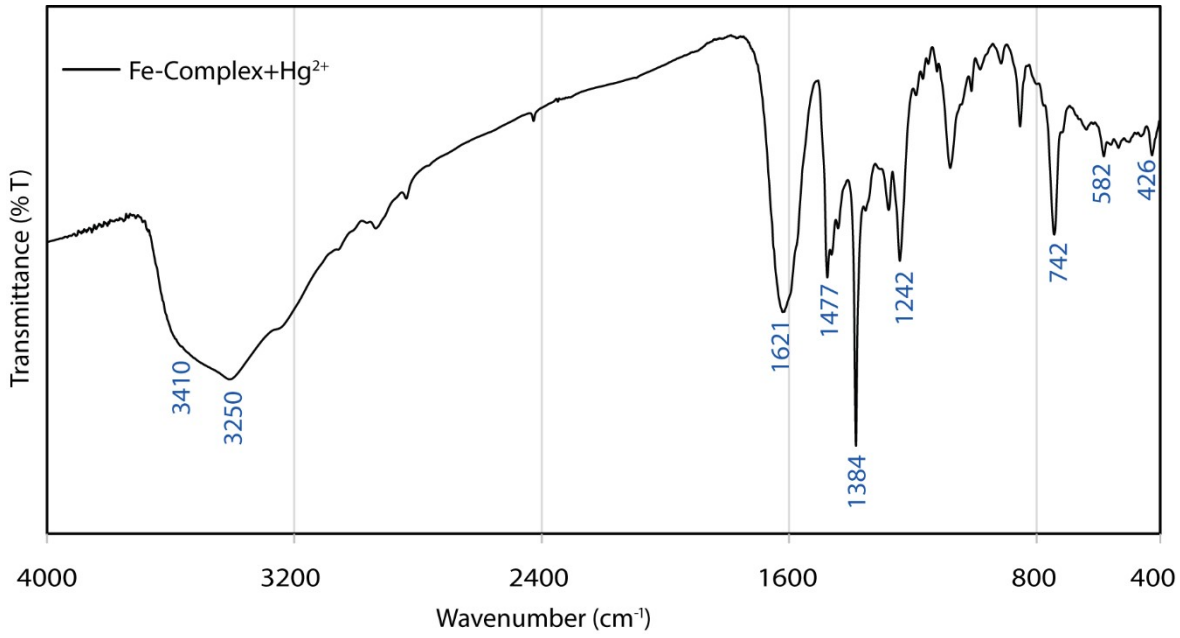


Figure S1. FTIR spectrum of Fe-complex+Hg^{2+} (**6**).

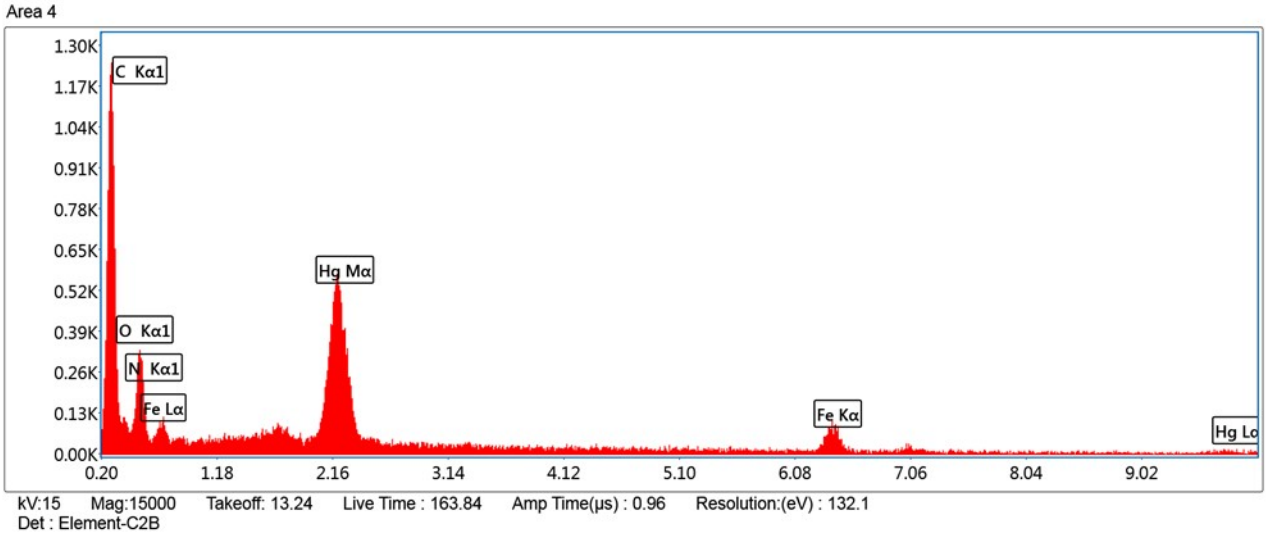


Figure S2. Energy dispersive X-ray analysis (EDAX) pattern of Fe-complex+Hg^{2+} (**6**).

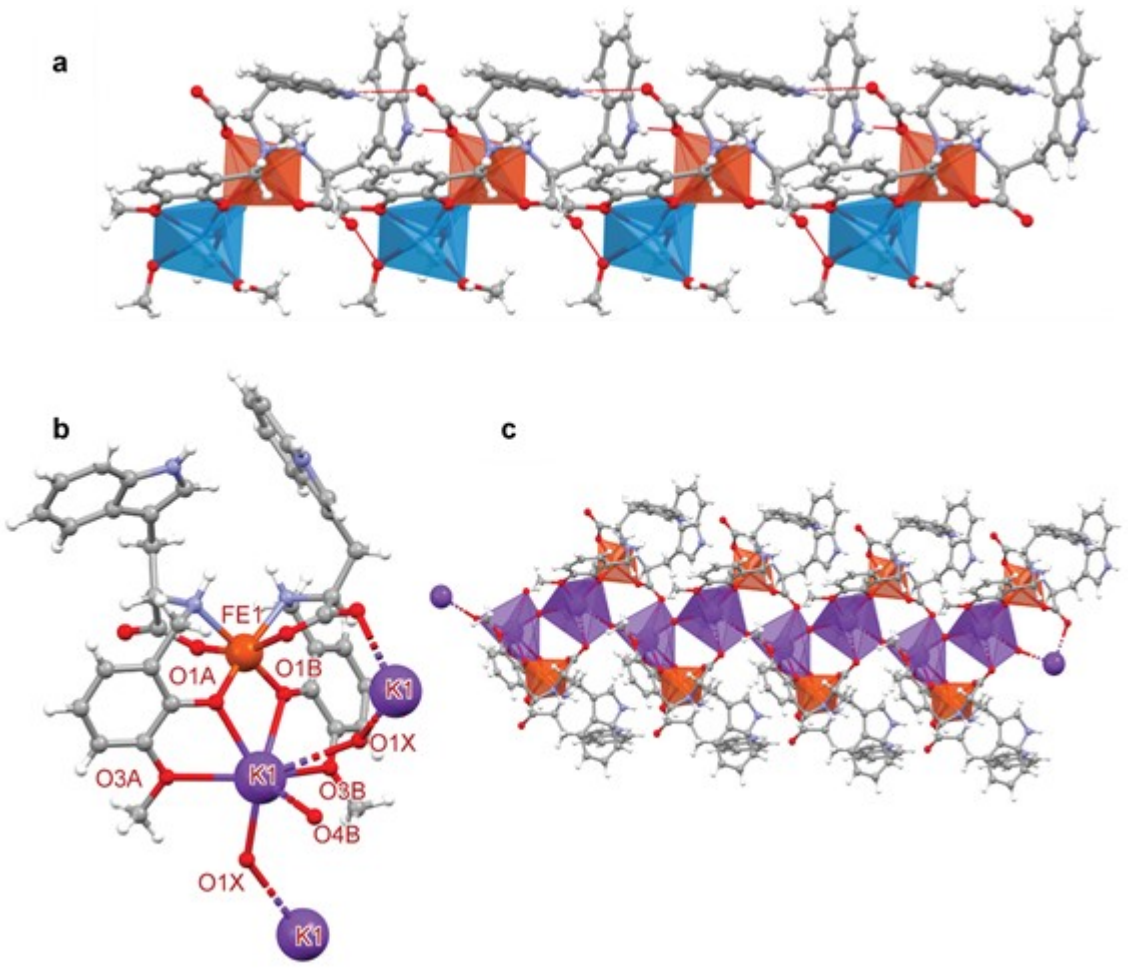


Figure S3. (a) H-bonded linear chain of complexes in **2**, (b) the coordination around the potassium ion in **3**, (c) 1D-polymeric chain of complexes connected through K^+ ion bridges along the *a*-axis in **3**.

Estimating Limits of Detection (LOD) of Mercury

Experimental details: A total of six solutions were prepared with fixed concentration of the Complex **1** (0.73 mM) with varying concentration of Hg^{2+} (0 – 0.523 mM) and absorption at 600 nm were determined. The standard deviation (**σ**) was determined by regression analysis and the Limits of detection (LOD) were calculated using the equation: LOD = 3.3**σ**/S where S = slope. (Ref. 1)

Ref: B. Magnusson and U. Ornemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics (2nd ed. 2014). Page 24.

Stock solutions. 10mL of Mercuric nitrate (5.23 mM) solution(**A**) in Methanol. 10mL of Complex 1 (7.3 mM)(**B**) solution in Methanol. Other solutions were prepared from this solutions (Table S1)

Table S1. Preparation of the solutions

	Hg^{2+} (Solution **A**) in mL	Complex1 Solution **B**) in mL	Total volume	Complex 1 conc. In mM	Hg^{2+} conc. In mM	Absorbance at 600 nm
Flask 0	0	1	10	0.73	0	0.623319
Flask 1	0.1	1	10	0.73	0.0523	0.711974
Flask 2	0.3	1	10	0.73	0.1569	0.776528
Flask 3	0.5	1	10	0.73	0.2615	0.850386
Flask 4	0.7	1	10	0.73	0.3661	0.943996
Flask 5	1	1	10	0.73	0.523	1.074766

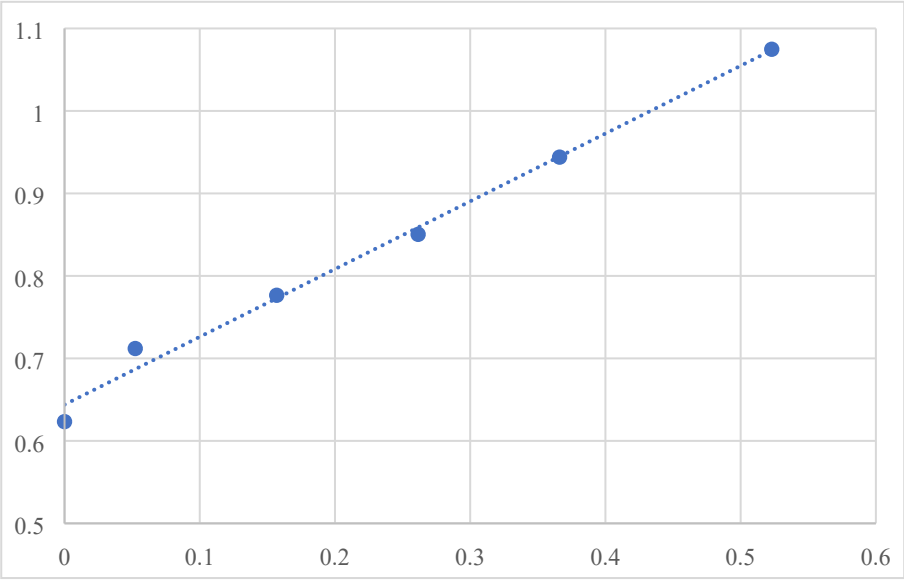


Figure S4. Concentration (x-axis) vs Absorbance (y axis) plot with absorbance measured at 600 nm of the solution

Regression analysis was performed in Excel Numeric tool box.

From the regression analysis

σ	Standard Error	0.016877413
Slope		0.821533121

LOD =	**0.0678 mmolar**	**67.8 micromolar**
	13.6 ppm	**13.6 mg per L**

Additionally, we tested with the Hg^{2+} concentration between 0.08 to 0.004 mM range with Complex 1 concentration fixed at 0.1 mM. The LOD is found to be 0.028 mM but the plot loses it's linearity below 0.02 mM (Figure S4).

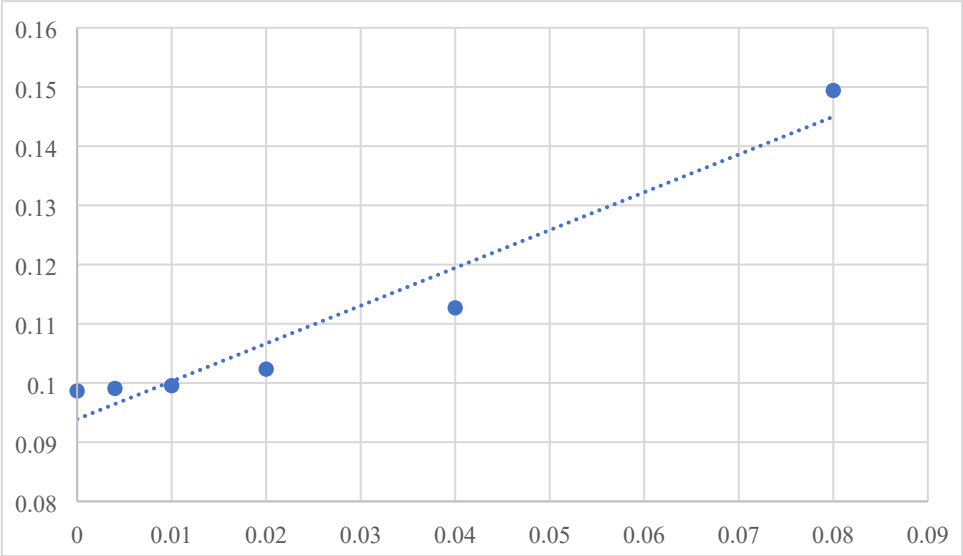
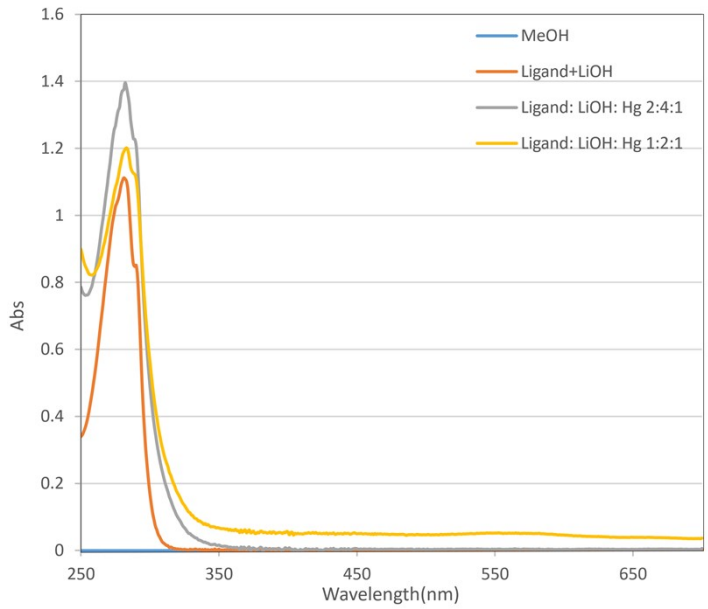


Figure S5. Concentration (x-axis) vs Absorbance (y axis) plot with absorbance measured at 600 nm of the solution.

Ruling out possibility of the 600nm band generated by Hg(II) replacing Fe(III) in the complex

Solution generation of Hg(II) complex and visible spectra. A solution of deprotonated ligand was prepared using $LiOH.H_2O$ as a base. A different amount of solid $Hg(NO_3)_2.H_2O$ was added to this, and the UV visible spectra were measured (Figure S6). The ligand : metal ratio used are 1:1 and 2:1. The spectra are shown below. All the solutions were colorless,



indicating no charge transfer bands occurred in the visible region.

Figure S6. UV-vis spectra of the solution generated Hg^{2+} species.

A charge transfer band is observed at 280 nm. In 1:1 reaction, the residual absorbance is higher most likely due to the formation of particulates.

NMR Experiment. Similar to the visible spectra experiment, A solution of deprotonated ligand in d_3-methanol was prepared. Same NMR condition: 3ml d_3-methanol, 30mg Ligand, Hg salt Three spectra recorded for the (i) deprotonated ligand, (ii) ligand: LiOH: Hg in 1:2:1, and (iii) ligand: LiOH: Hg in 2:4:1. The spectra shown below

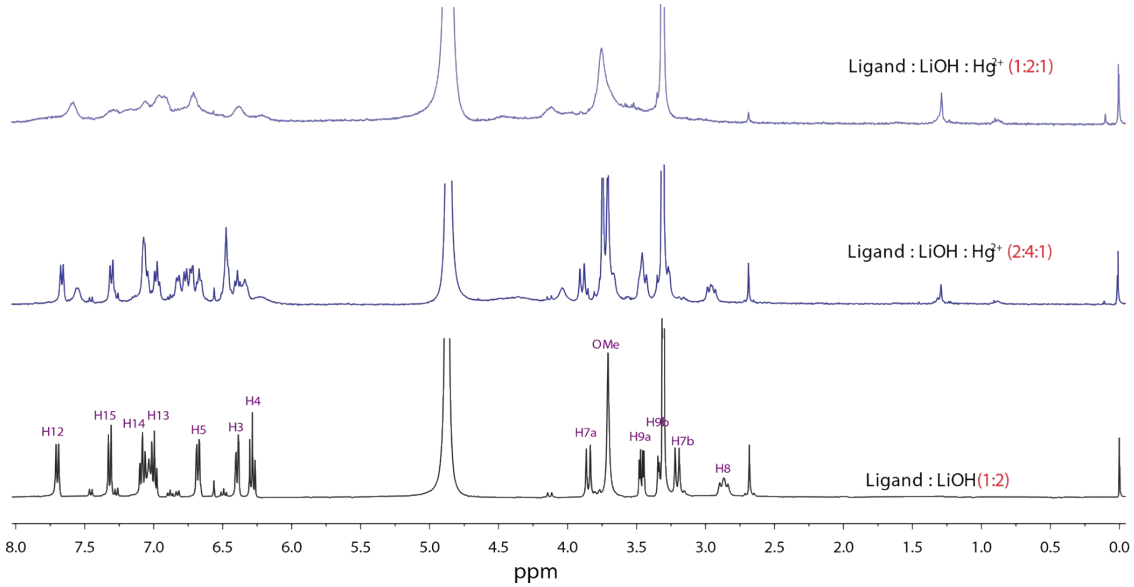


Figure S7. ^{1}H NMR spectra of solution generated Hg2+ species compared to the deprotonated ligand.

The spectra of the Hg(II) containing samples are broad and few peaks showed shift indicating coordination but spectra is too broad (usual for Hg/Zn ion due to lability). The 1:1 precipitated out as white powder during the experiment and the spectra is less sharp as a result of this.

Attempts to isolate the Hg-complex. Synthesis of both 1:1 and 1:2 complex were attempted in 200 mg scale. None are coloured. The 1:1 complex is a white powder and insoluble in the common organic solvent. Isolation of 1:2 (Hg: L) proved difficult due to higher solubility but the solution was colourless.

Conclusions from these experiments. None of the mercury complexes showed any visible colour. Hence, the 600 nm band cannot be from formation of mercury(II) complex by replacing the Iron(III). **Hg(II) form 1:1 complex as a white powder insoluble in common organic solvents.**

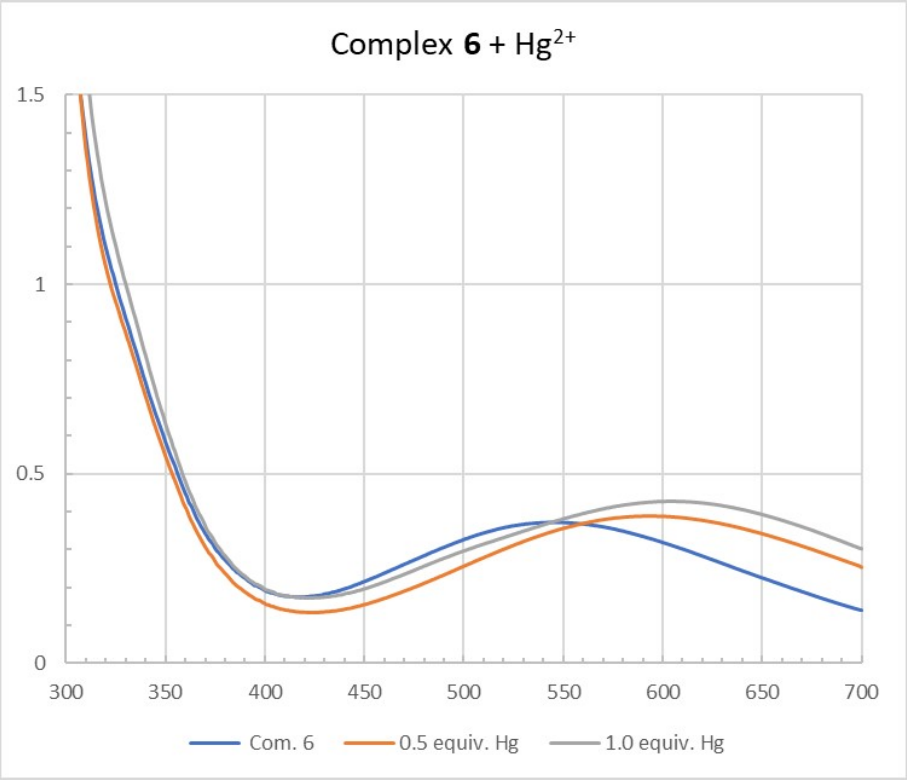


Figure S8. The titration of Complex 6 with Mercuric nitrate solution in methanol.

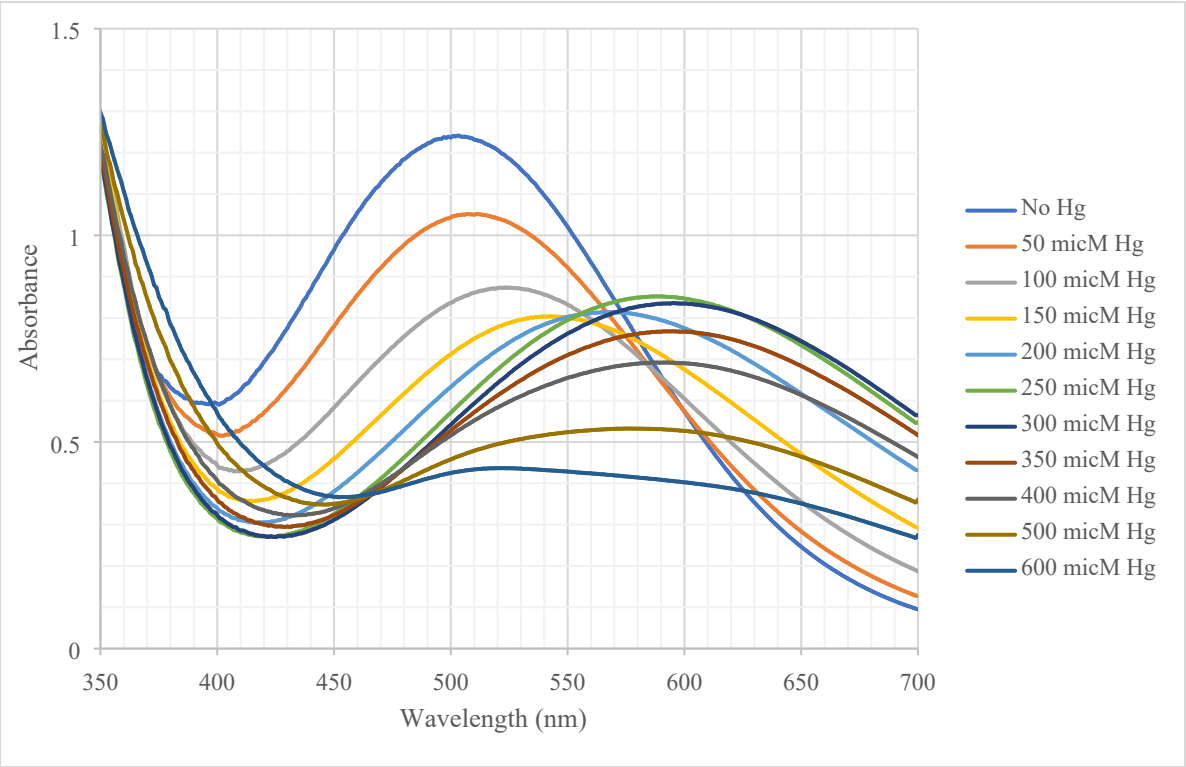


Figure S9. Titration plot: Addition of microlitre of 5mM Hg^{2+} solution to **Complex 2** (MeOH, 2mL, 0.5 mM). 50 µL Hg^{2+} ≅ 0.25 mol equivalent.

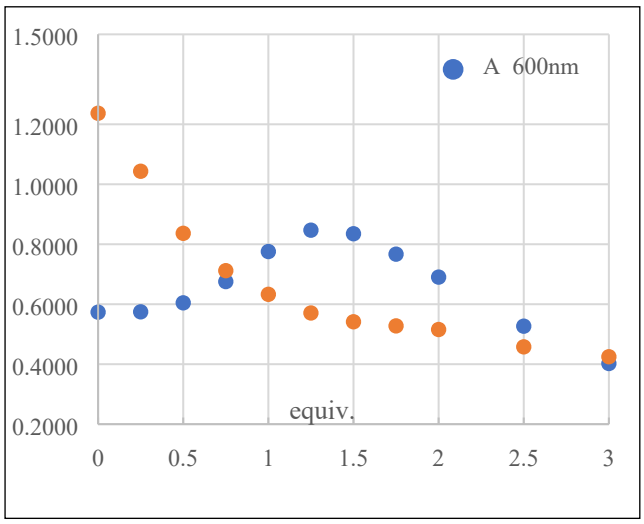


Figure S9b. Absorbance vs. equivalent of mercury(II) plot monitored at 500nm and at 600 nm, from the data of Figure S9a.

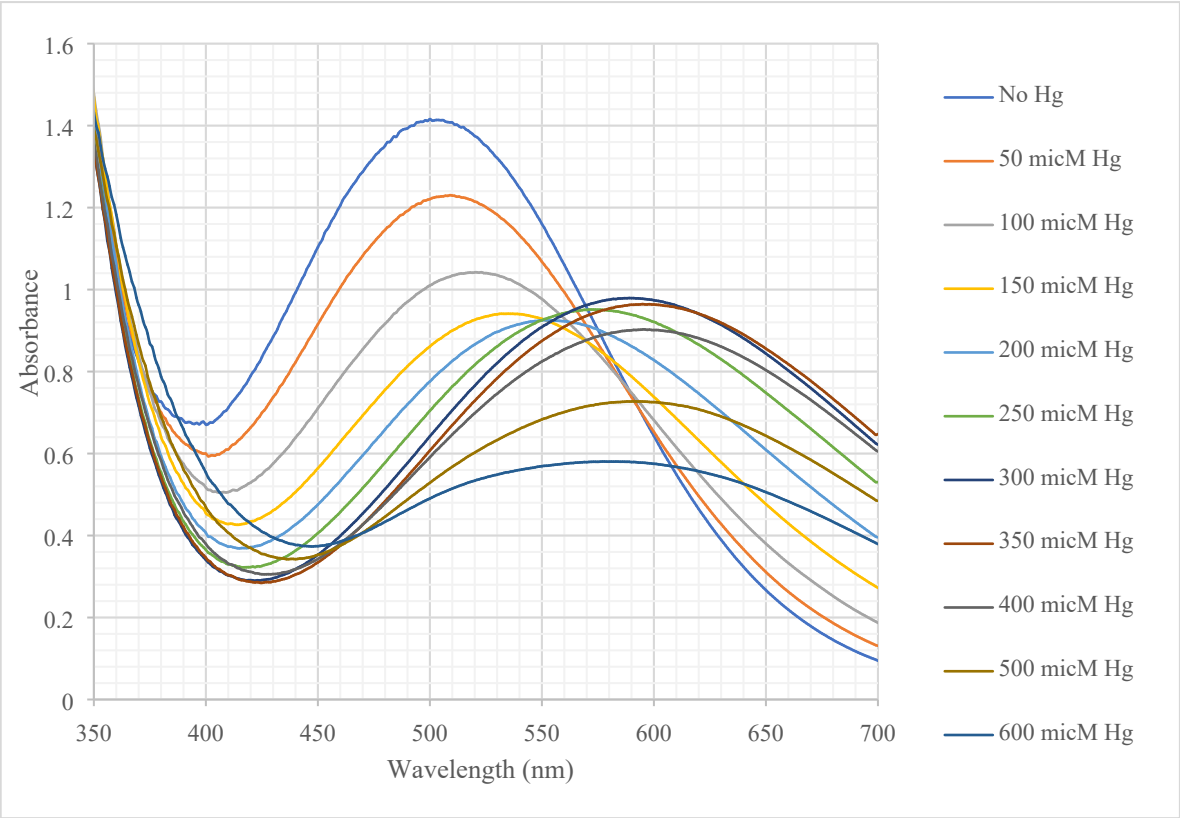


Figure S10. Titration plot: Addition of microlitre of 5mM Hg^{2+} solution to **Complex 3** (MeOH, 2mL, 0.5 mM). 50 µL Hg^{2+} ≅ 0.25 mol equivalent.

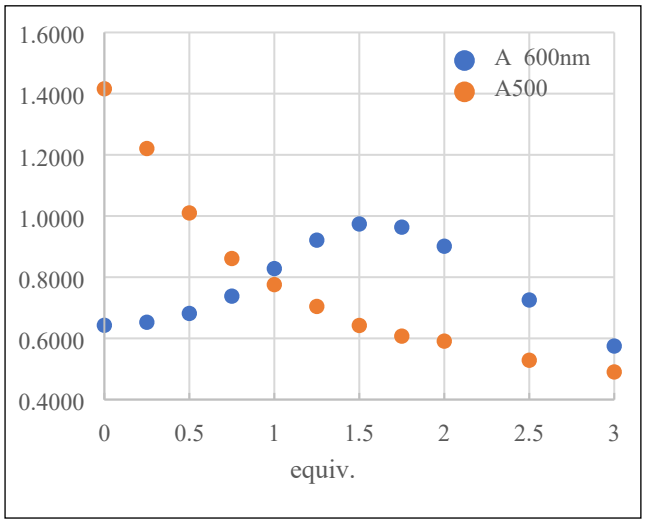


Figure S10b. Absorbance vs. equivalent of mercury(II) plot monitored at 500nm and at 600 nm, from the data of Figure S10a.

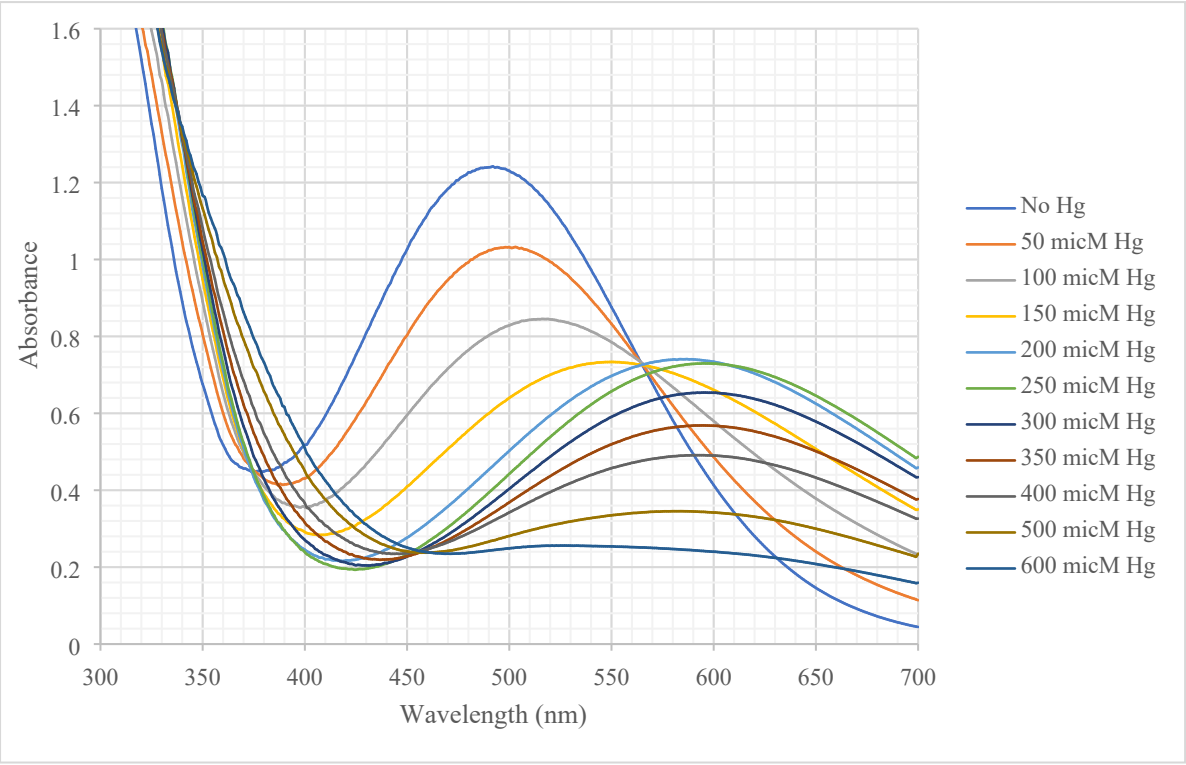


Figure S11. Titration plot: Addition of microlitre of 5mM Hg^{2+} solution to **Complex 4** (MeOH, 2mL, 0.2 mM). 50 µL Hg^{2+} ≅ 0.25 mol equivalent.

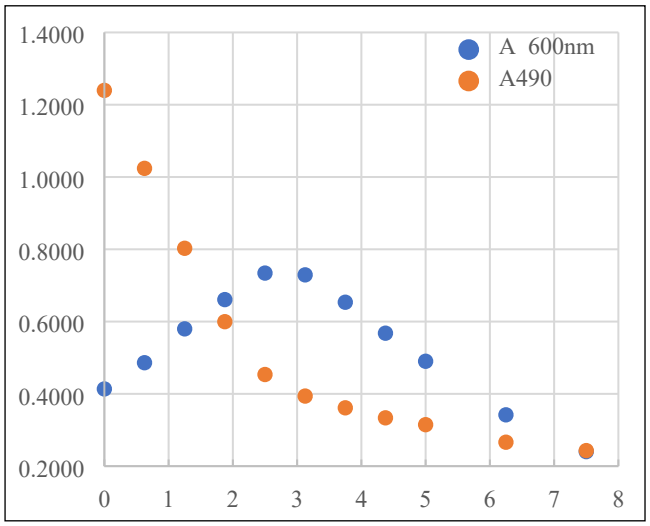


Figure S11a. Absorbance vs. equivalent of mercury(II) plot monitored at 500nm and at 600 nm, from the data of Figure S11a. No. of mol equivalent required for max absorbance at 600 nm, 2.5-3.0 (or 1.25 to 1.5 eq~ per Iron(III) complex).

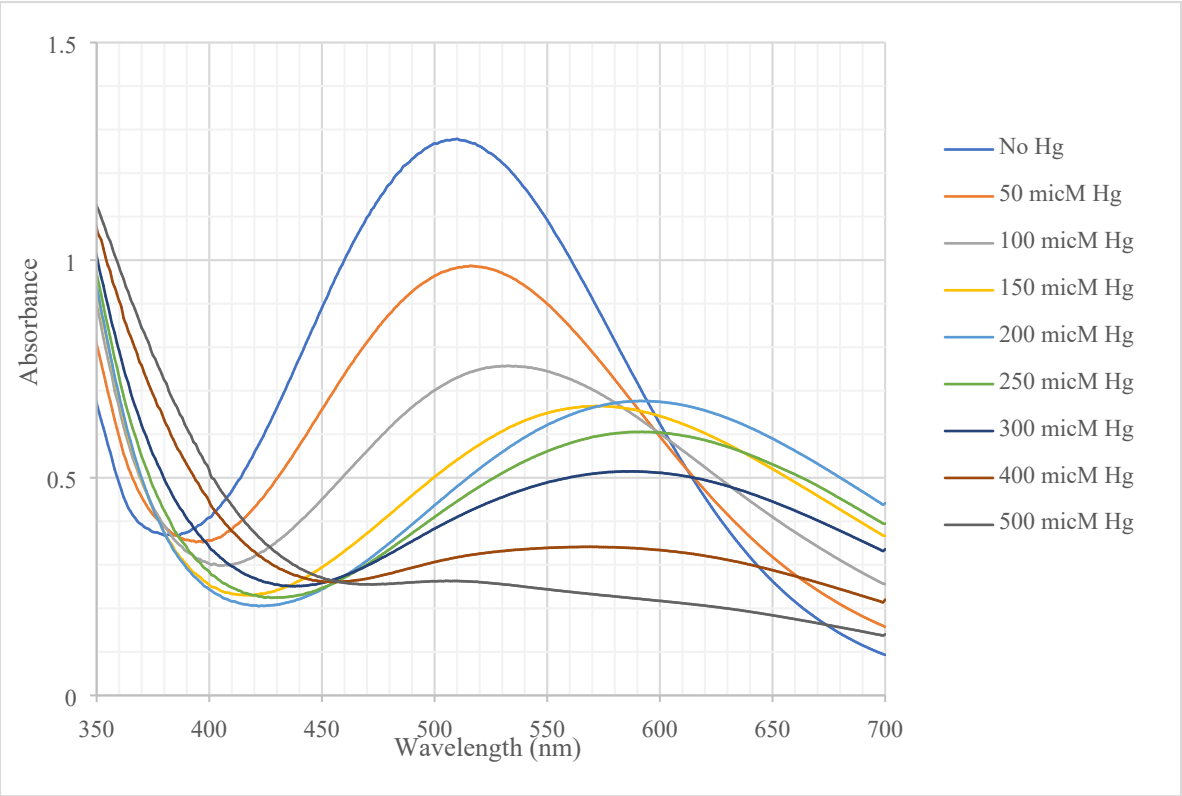


Figure S12. Titration plot: Addition of microlitre of 5mM Hg^{2+} solution to **Complex 5** (MeOH, 2mL, 0.2 mM). 50 µL Hg^{2+} ≅ 0.25 mol equivalent.

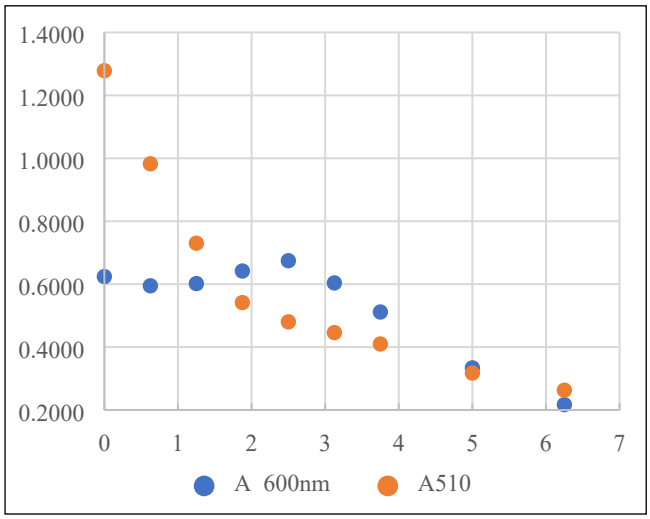


Figure S12b. Absorbance vs. equivalent of mercury(II) plot monitored at 500nm and at 600 nm, from the data of Figure S12a. No. of mol equivalent required for max absorbance at 600 nm, 2.5 (or 1.25 eq~ per Iron(III) complex).

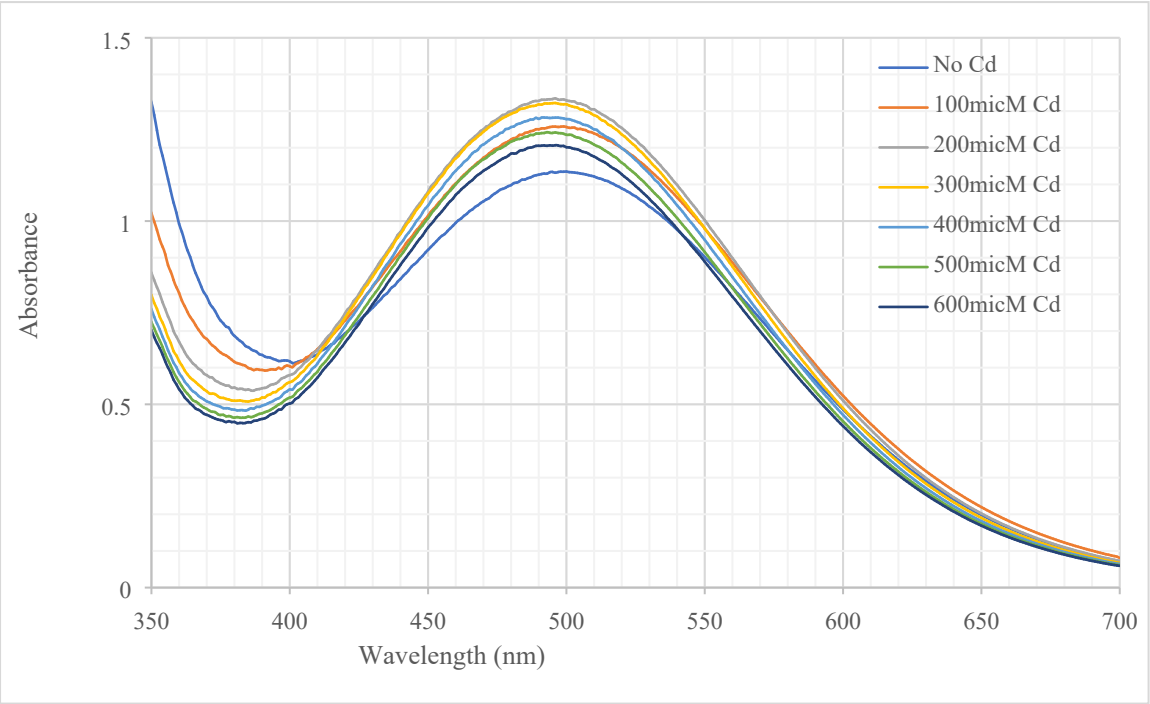


Figure S13. Titration plot of Addition of microlitre of 5mM Cd^{2+} solution to complex **1** (MeOH, 2mL, 0.5 mM). 100 µL Cd^{2+} ≅ 0.5 mol equivalent.

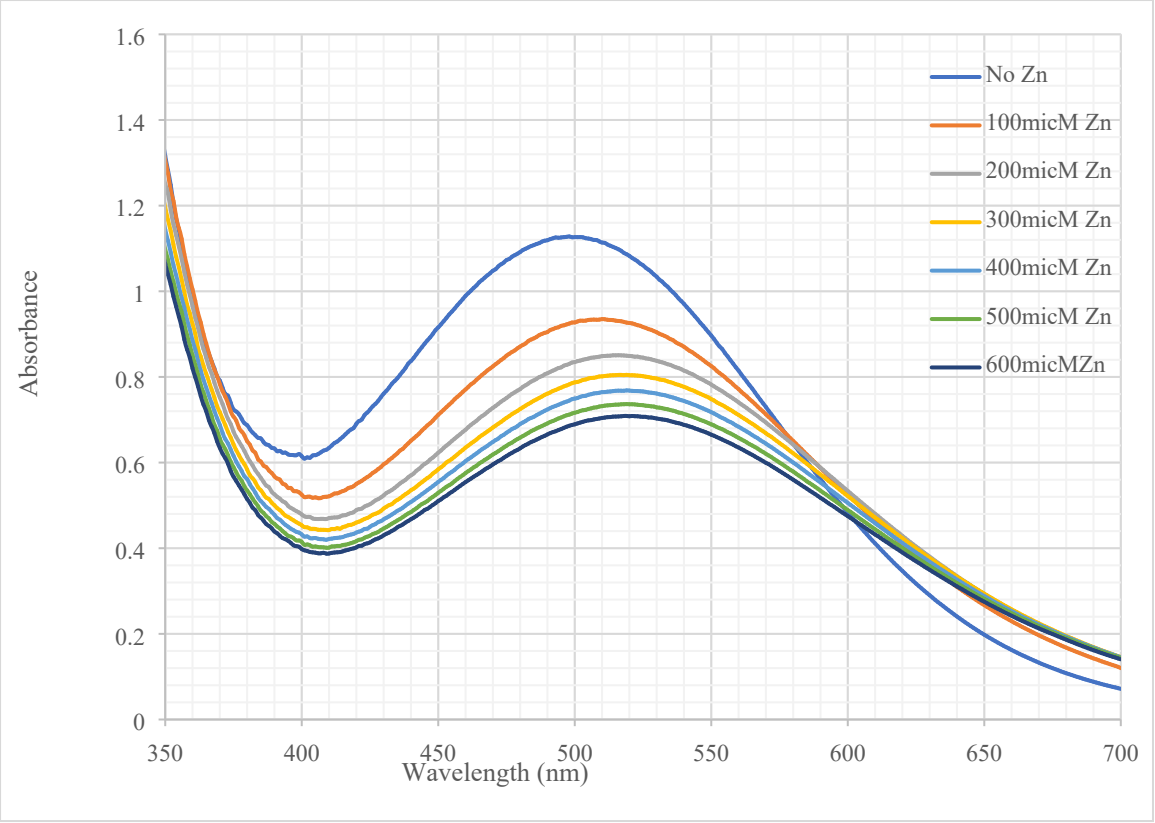


Figure S14. Titration plot of Addition of microlitre of 5mM Zn^{2+} solution to complex **1** (MeOH, 2mL, 0.5 mM). 100 µL Cd^{2+} ≅ 0.5 mol equivalent.