

Electronic Supplementary Information

Synthesis, characterisation and ion-binding properties of oxathiacrown ethers appended to $[\text{Ru}(\text{bpy})_2]^{2+}$. Selectivity towards Hg^{2+} , Cd^{2+} and Pb^{2+}

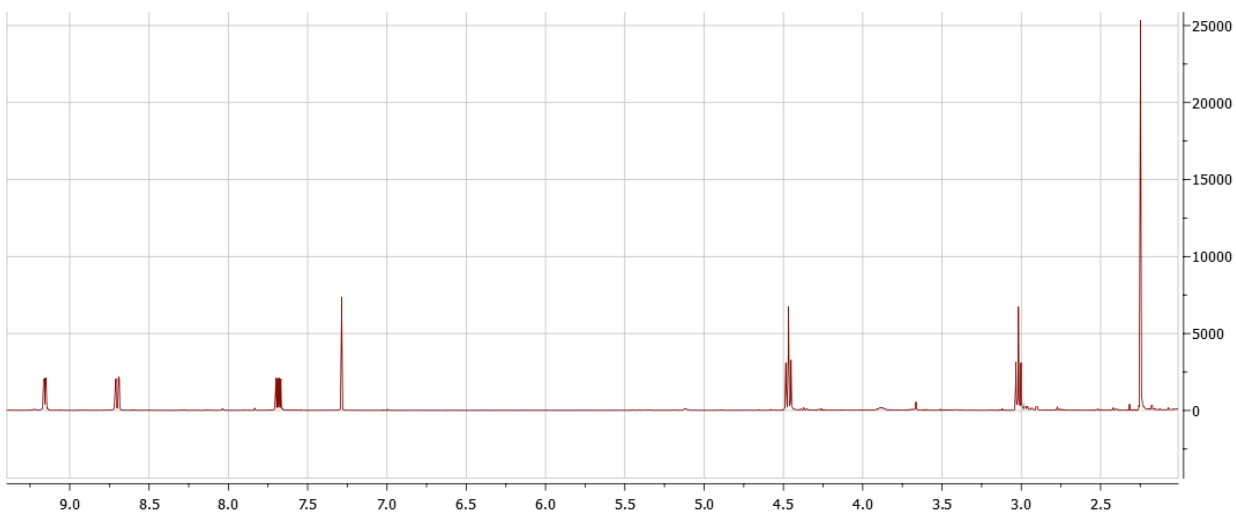
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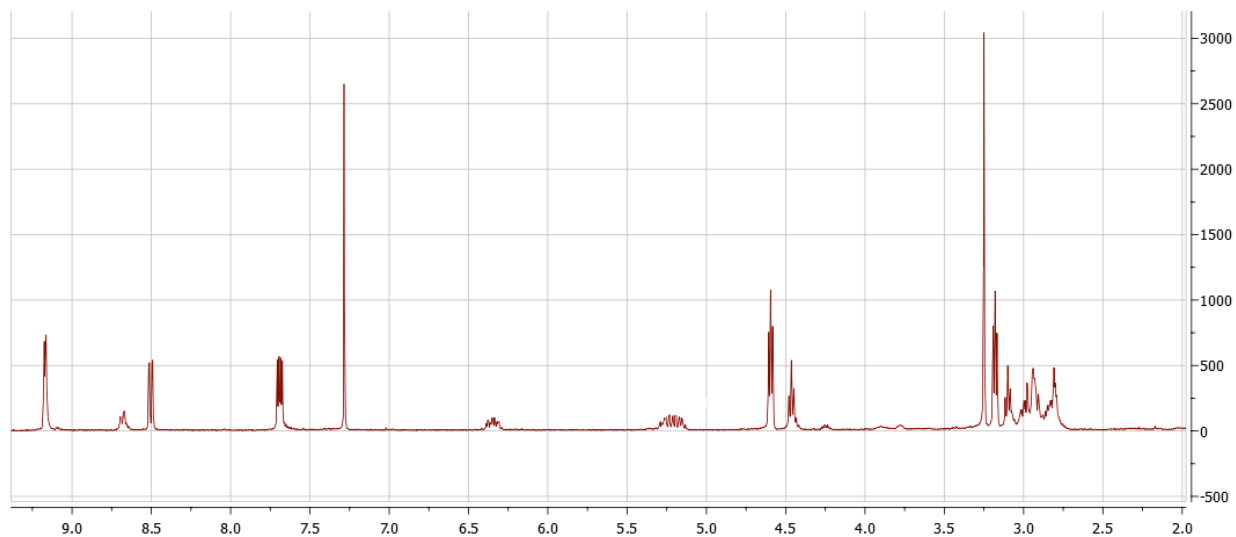
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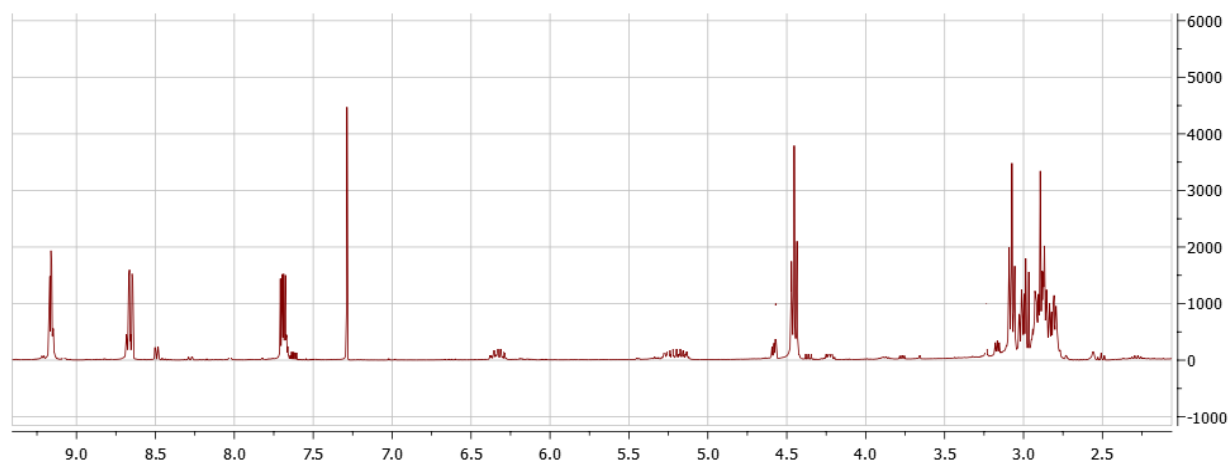
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(a) L1

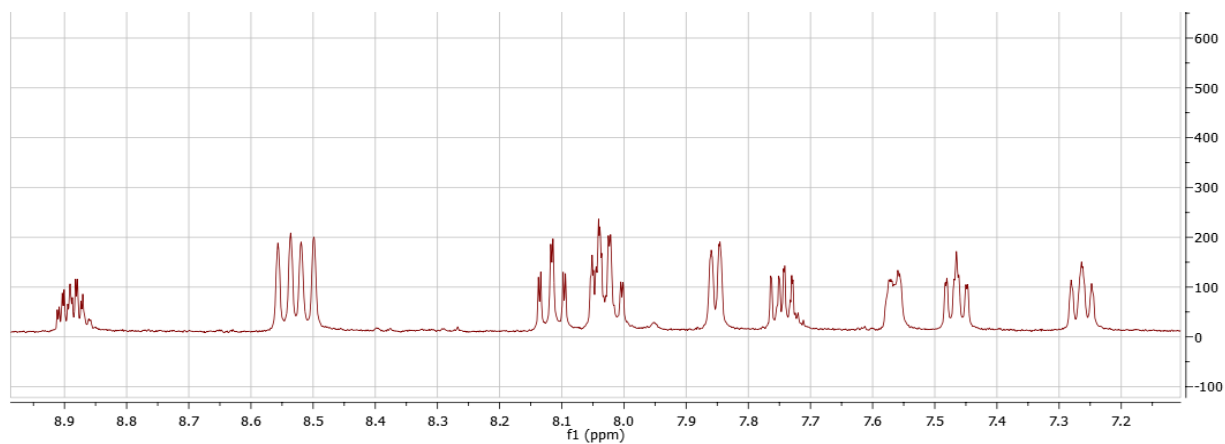


(b) L2

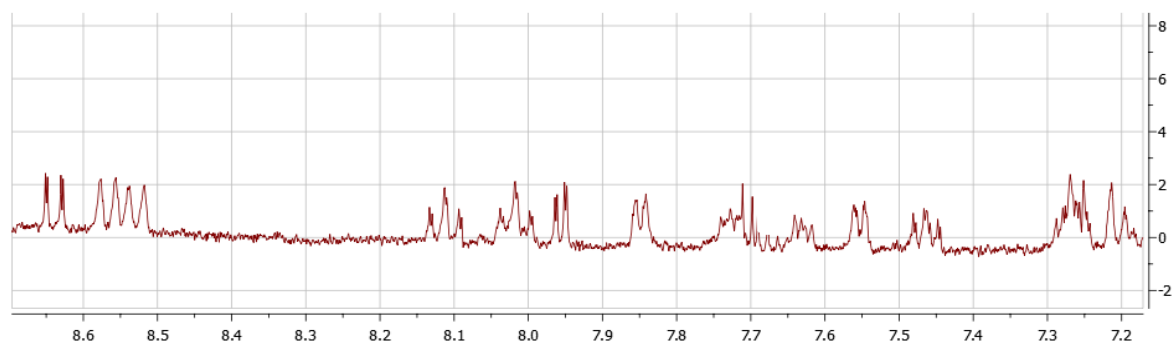


(c) L3

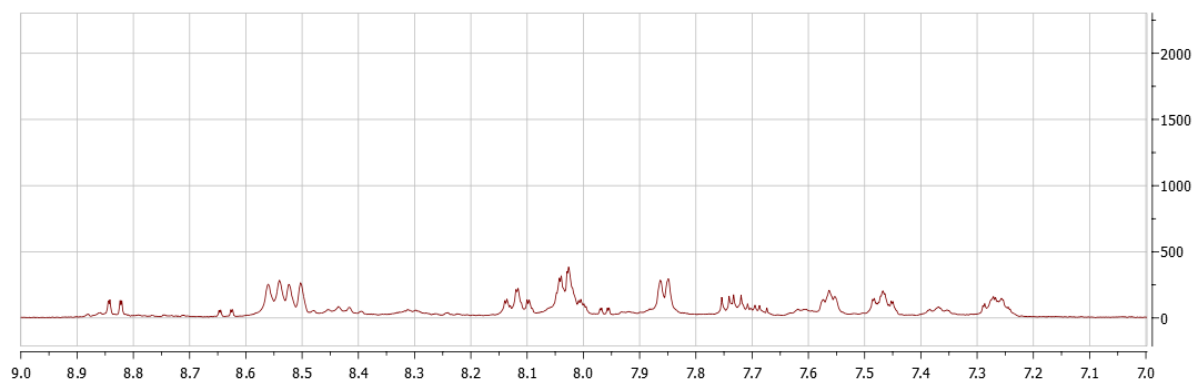
Fig S1 (a) - (c): ^1H NMR spectra of ligands L1 – L3 in CDCl_3



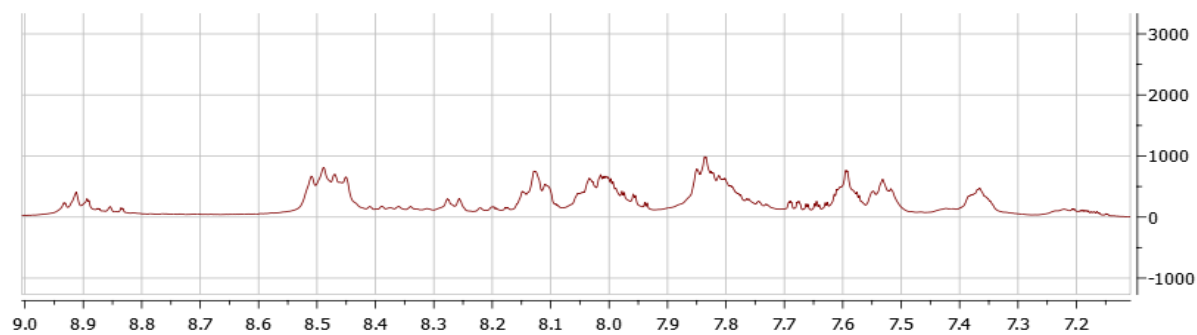
(a) Complex 1



(b) Complex 2



(c) Complex 3



(d) Complex 4

Fig S2 (a) – (d): Aromatic region of the ^1H NMR spectra of complexes **1-4** in CD_3CN

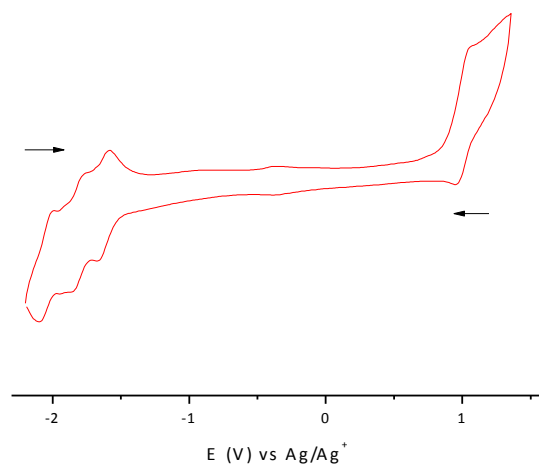


Fig S3: Cyclic voltammogram showing the redox potential of 2×10^{-4} M solution of complex **2** in 0.1 M $[\text{Bu}_4\text{N}]\text{P}[\text{F}_6]$ / CH_3CN vs Ag/Ag^+ , WE = Pt, CE = Pt; Scan rate = 100 mV/s

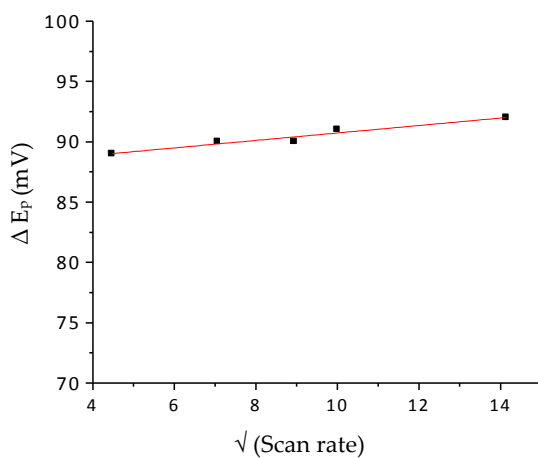


Fig S4: A plot of $\sqrt{\text{scan rate}}$ vs. ΔE_p for Complex **2** showing a y-intercept of 88 mV

Procedure to Determine the Stoichiometry of the Reactions. Job's plot experimental procedure was followed: 2×10^{-5} M solutions of the ruthenium complexes and Hg^{2+} / Cd^{2+} / Pb^{2+} stock solutions in acetonitrile were prepared. A series of solutions containing the host complex and the metal ion in varying mole ratios while keeping their total sum

constant were prepared, allowed to equilibrate for 30 min and both absorbance and fluorescence spectra obtained.

Procedure for Electronic Absorption and Luminescence Titrations. Stock solutions of the ruthenium chromophores, **1** - **4** (5×10^{-5} M) and triflate salts (5×10^{-4} M) of Hg^{2+} , Cd^{2+} and Pb^{2+} were prepared in freshly purified acetonitrile. Then 2 ml stock solution of the host complex and 2 ml acetonitrile were shaken together in a 5 ml volumetric flask and allowed to stand for 30 minutes to equilibrate before recording its absorption spectrum. To ascertain the interactions of the metal ions with the chromophore, the same procedure was followed, replacing acetonitrile with 2 ml of the metal triflate solutions of desired concentration (0.2 – 10 equivalents); prepared by appropriate dilution of the stock solution. The same solutions were used for emission titration studies.

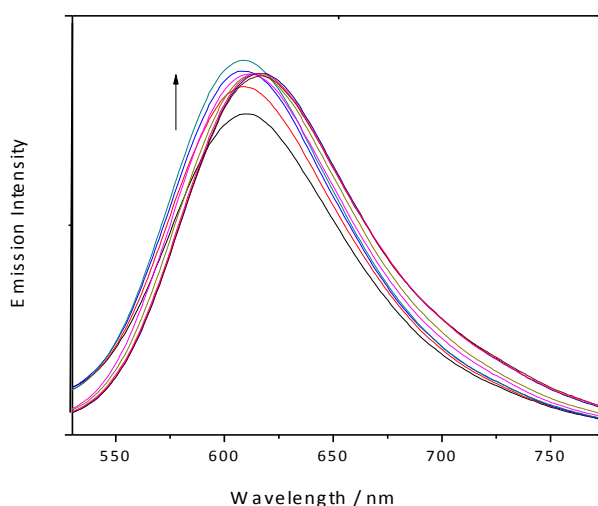


Fig S5: Emission titration spectra of complex **2** (5×10^{-5} M) with added Hg^{2+} ($0 - 2 \times 10^{-4}$ M) in CH_3CN at room temperature

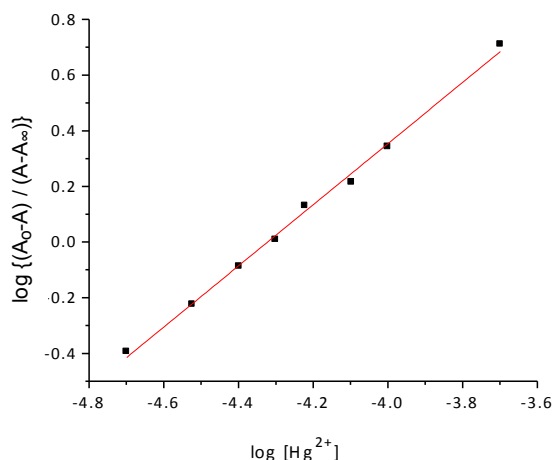


Fig S6: A plot of $\log \{(A_0-A) / (A-A_\infty)\}$ vs $\log [\text{Hg}^{2+}]$ for Complex **2** on adding Hg^{2+} . $R^2 = 0.996$

Procedure for Electrochemical Studies. A three-electrode electrochemical cell fitted with a platinum disk (WE), platinum gauze (CE) and Ag/0.01 M AgNO_3 (RE), was filled with a freshly prepared 20 ml acetonitrile solution of **1** (5×10^{-4} M) containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. It was saturated with N_2 gas for several minutes, scanned in the Ru(II) oxidation potential window (0.7 – 1.5 V) at a scan rate of 100 mV; and cyclic (CV) and differential pulse voltammograms (DPV) recorded. $4\mu\text{l}$ of Hg^{2+} ions (5×10^{-5} M) was sequentially added to the solution and the CV and DPV recorded. Addition was done until no more changes were observed in the oxidation peak potentials. The procedure was repeated for complexes **2** - **4** with all the metals (Hg^{2+} , Cd^{2+} and Pb^{2+}).

Procedure for Interference Studies. A similar procedure for both absorption and luminescence was followed to determine the effect of the presence of NO_3^- , I^- , Cl^- , Br^- , F^- , HSO_4^- , ClO_4^- , CH_3COO^- anions and Li^+ , Na^+ , K^+ , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ cations using 2 ml

of ruthenium stock solution and 2ml of the 5.0×10^{-4} M tetrabutylammonium salts of the anions and cation perchlorates/triflates.

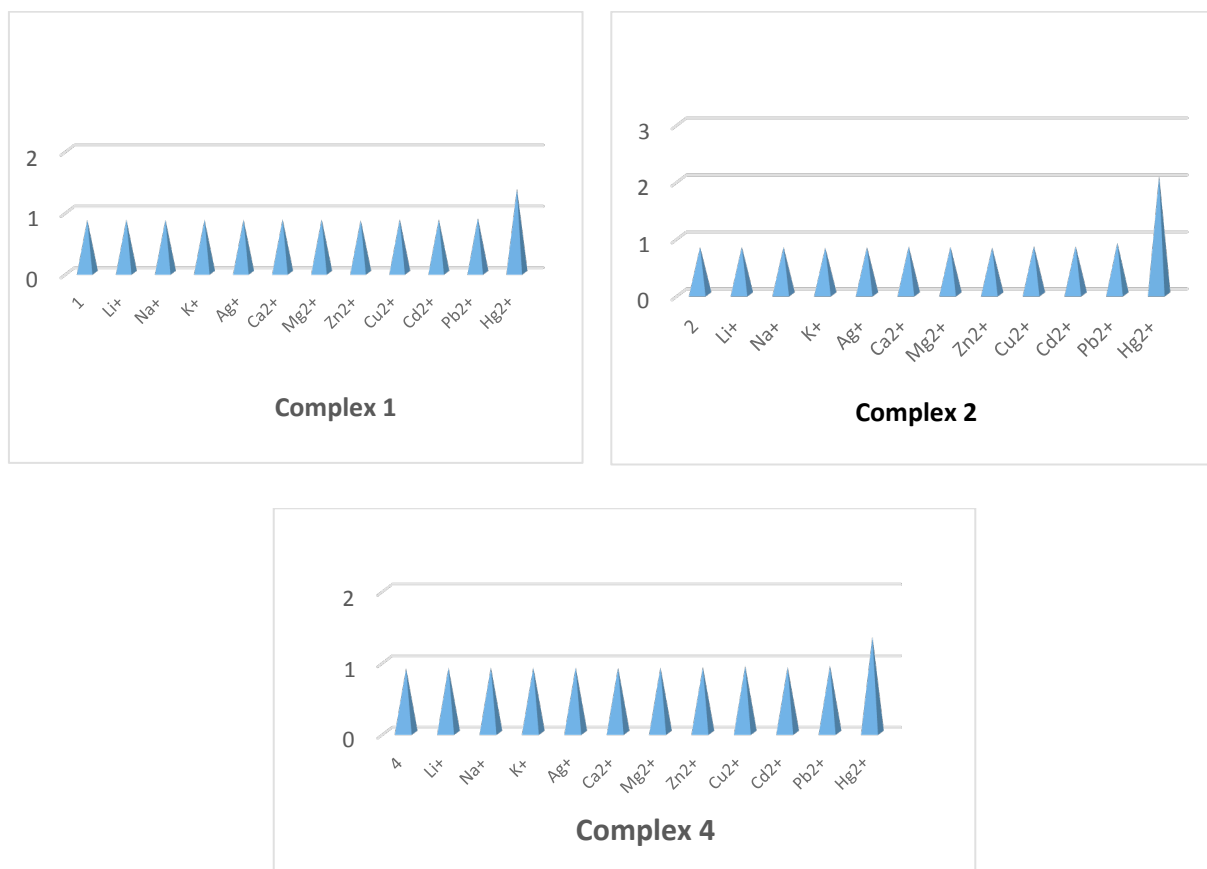


Fig S7: Ratiometric electronic responses of complexes **1**, **2** and **4** to 10 equiv of various guest cations at 427 nm : 457 nm

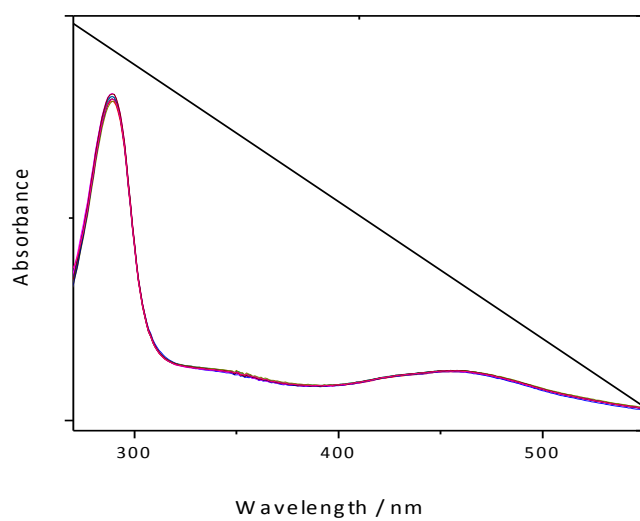


Fig S8: UV-Vis responses of complex **2** towards the addition of 10 equiv. of various anions

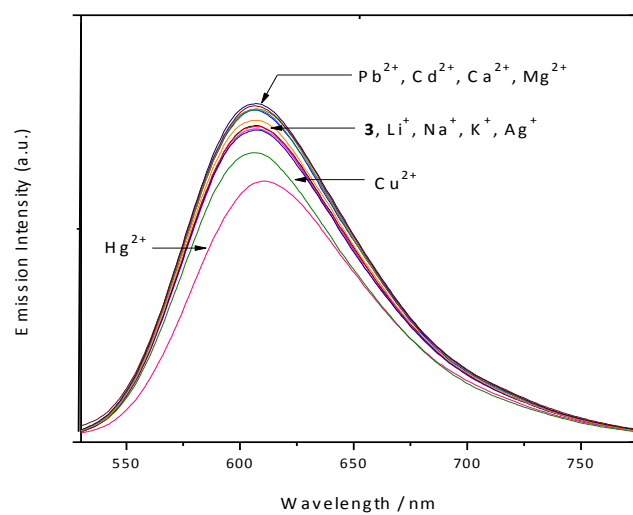


Fig S9: Luminescence spectra showing the effect of various guest cations on complex 3

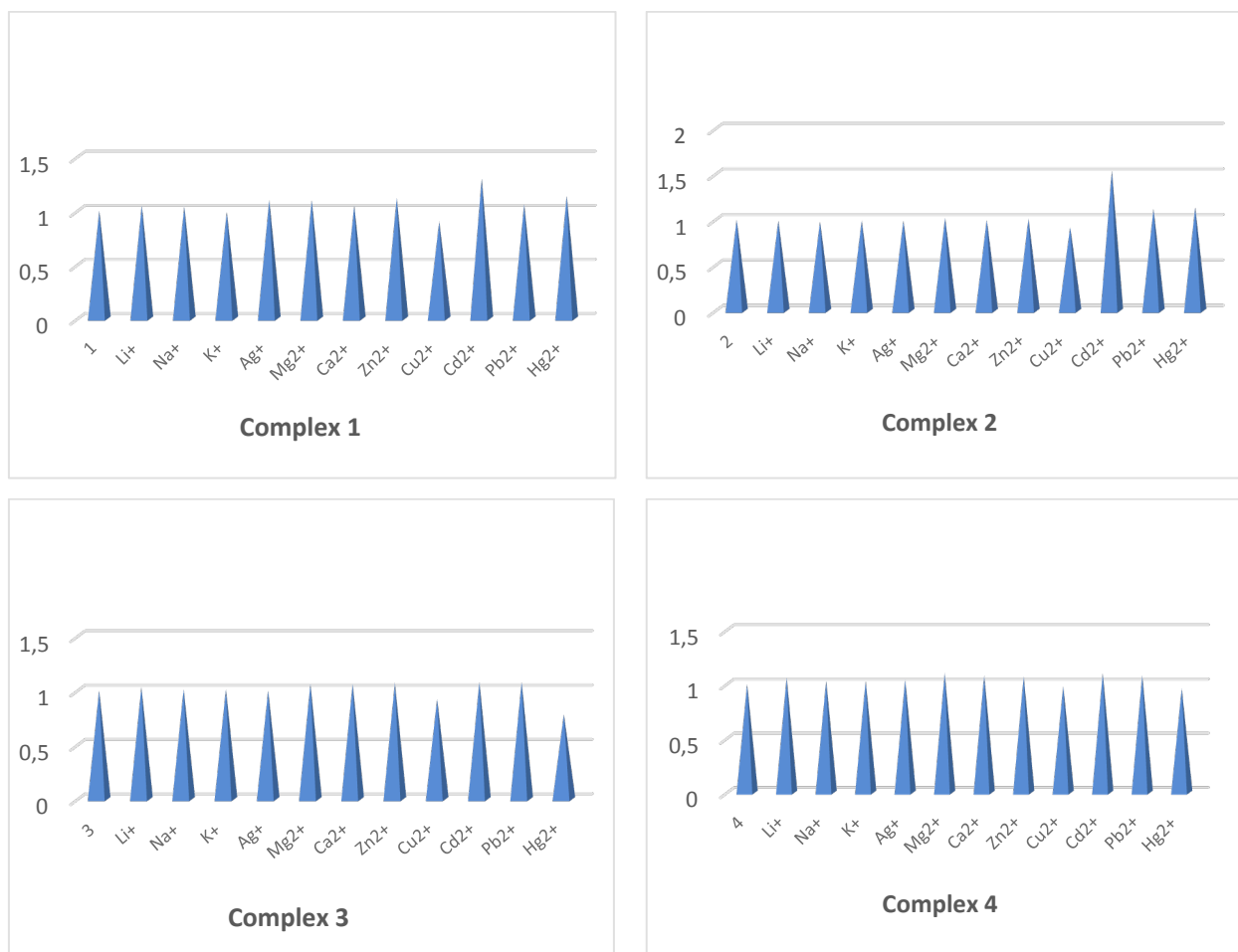


Fig S10: Graphical representation of the emission responses of various metal ions to complexes 1 - 4