Electronic Supplementary Information (ESI)

Direct Dizinc Displacement Approach for Efficient Detection of Cu^{2+} in Aqueous Media: Acetate versus Phenolate Bridging Platforms

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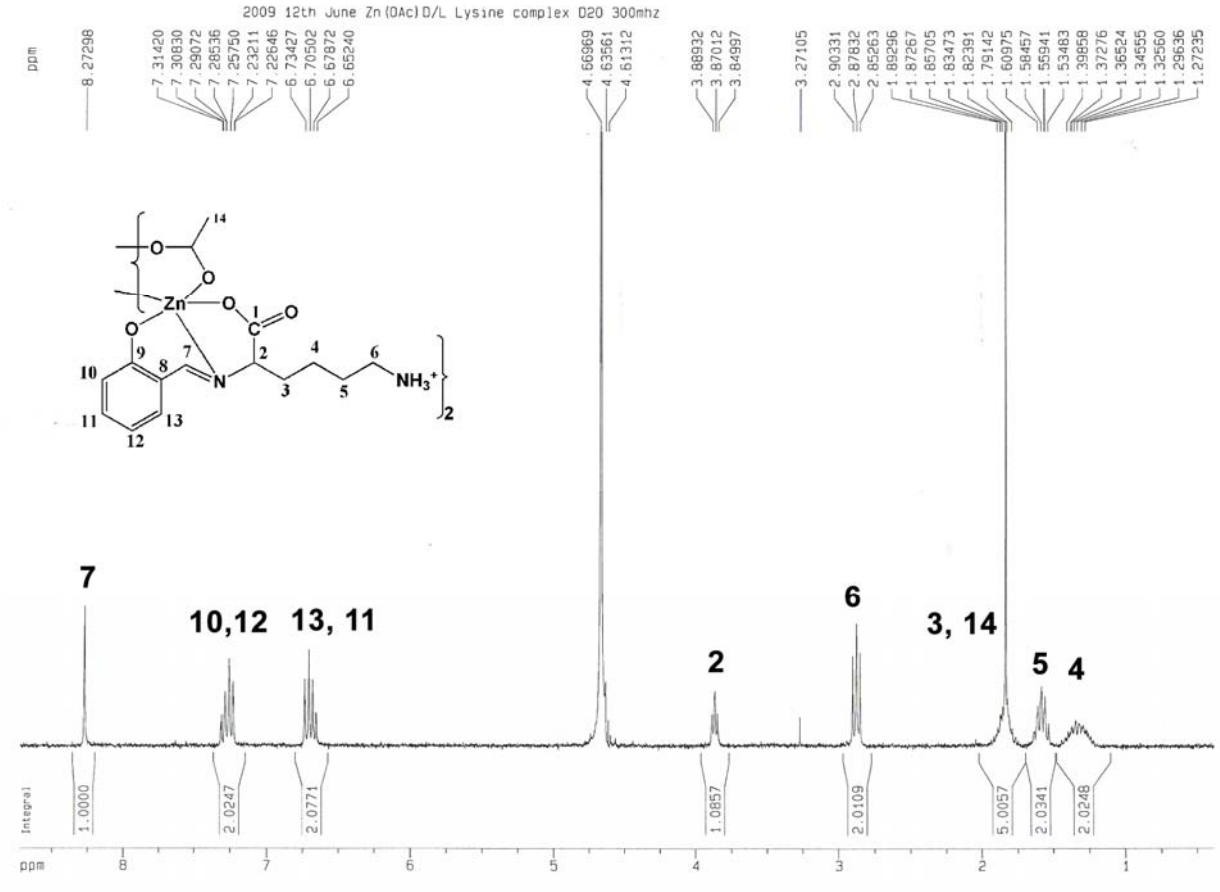


Figure S1. ^{1}H NMR spectrum of compound **3** in D_2O.

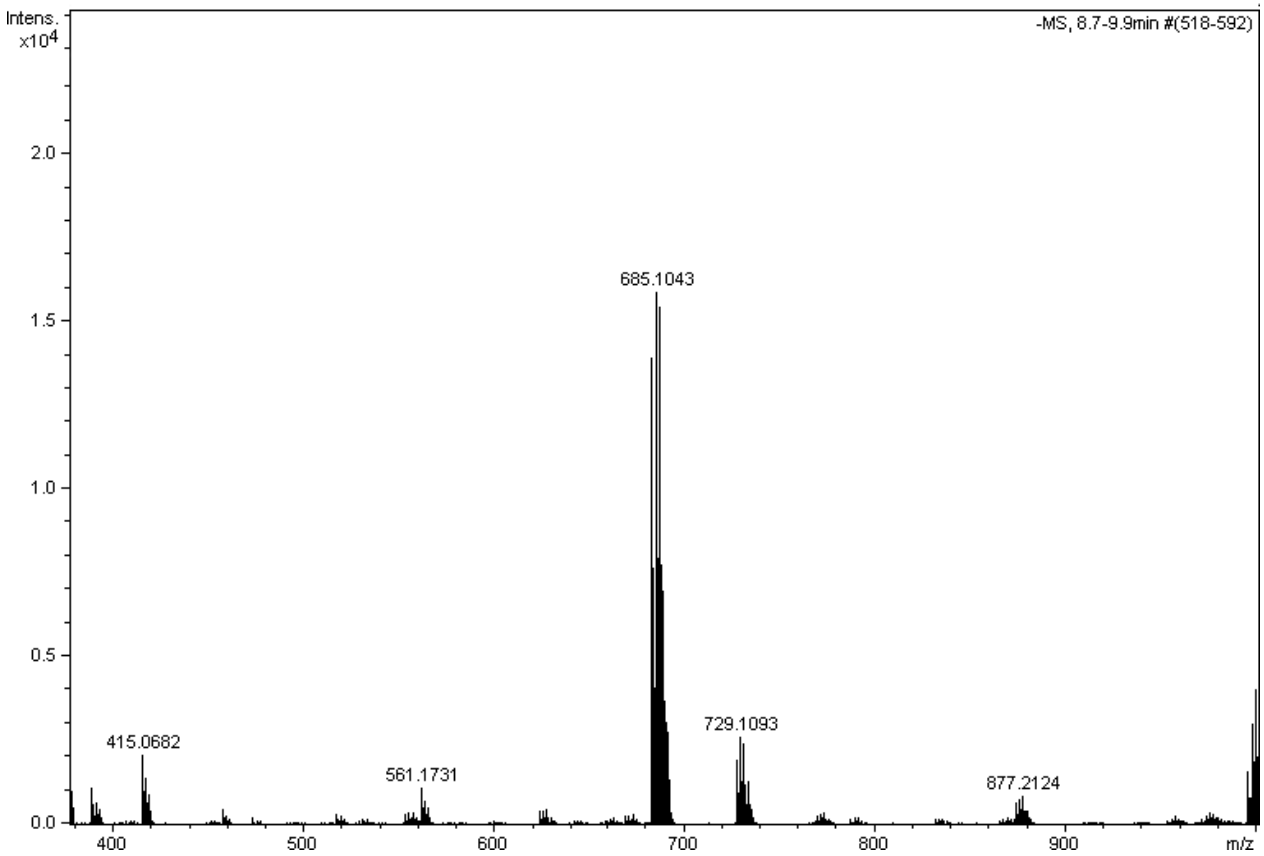


Figure S2. ESI mass spectrum of compound **3** in H_2O / MeOH (1:1) mixture.

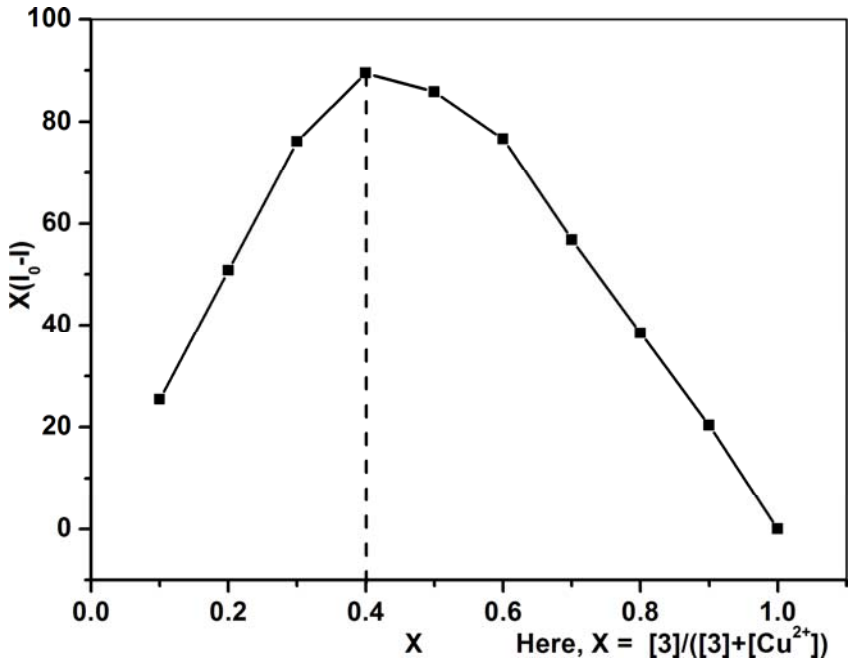


Figure S3. Job's plot for compound **3** and Cu^{2+} binding (λ_{ex} at 354 nm and λ_{em} at 452 nm) in an aqueous buffer solution (pH 7.4, 10 mM HEPES, H_2O : MeOH; 9 : 1) at 25 ^oC by emission spectroscopy. In the plot, the value 0.4 supports a nearly 1:2 compound, **3**:Cu^{2+} binding stoichiometry.

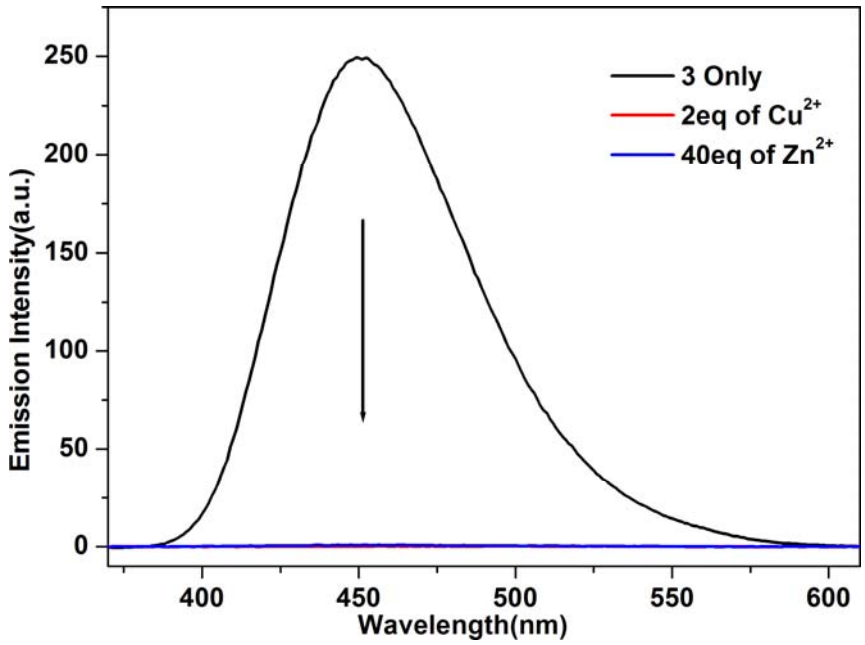
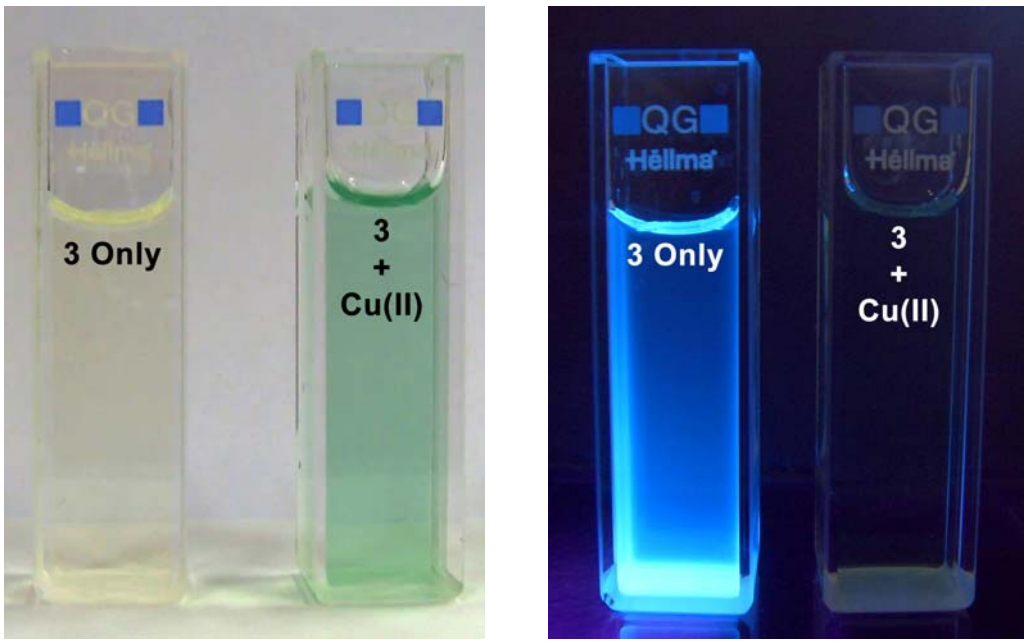


Figure S4. (a) Emission spectra of compound **3** (50 μM) in an aqueous buffer solution (pH 7.4, 0.01 M HEPES) with 2 equivalents of Cu^{2+} solution (100 μM) and 40 equivalents of Zn^{2+} solution to the mixture of **3** and Cu^{2+} ion.



(a) (b)

Figure S5. "Naked eye" colorimetric detection of Cu^{2+} ion: (a) Compound **3** (1000 μM) and **3** + Cu^{2+} (2000 μM) on visible light; (b) Compound **3** (100 μM) and **2** + Cu^{2+} (200 μM) under UV lamp light (365 nm).

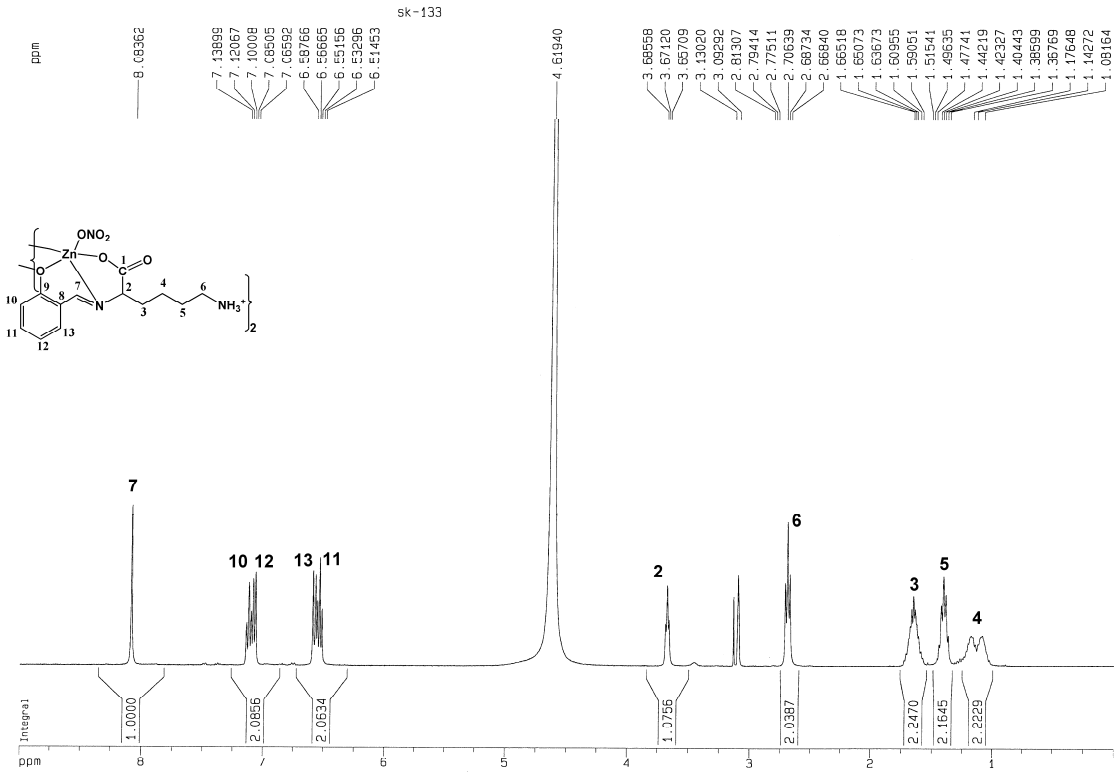


Figure S6. ^{1}H NMR spectrum of compound **2** in D_2O.[1]

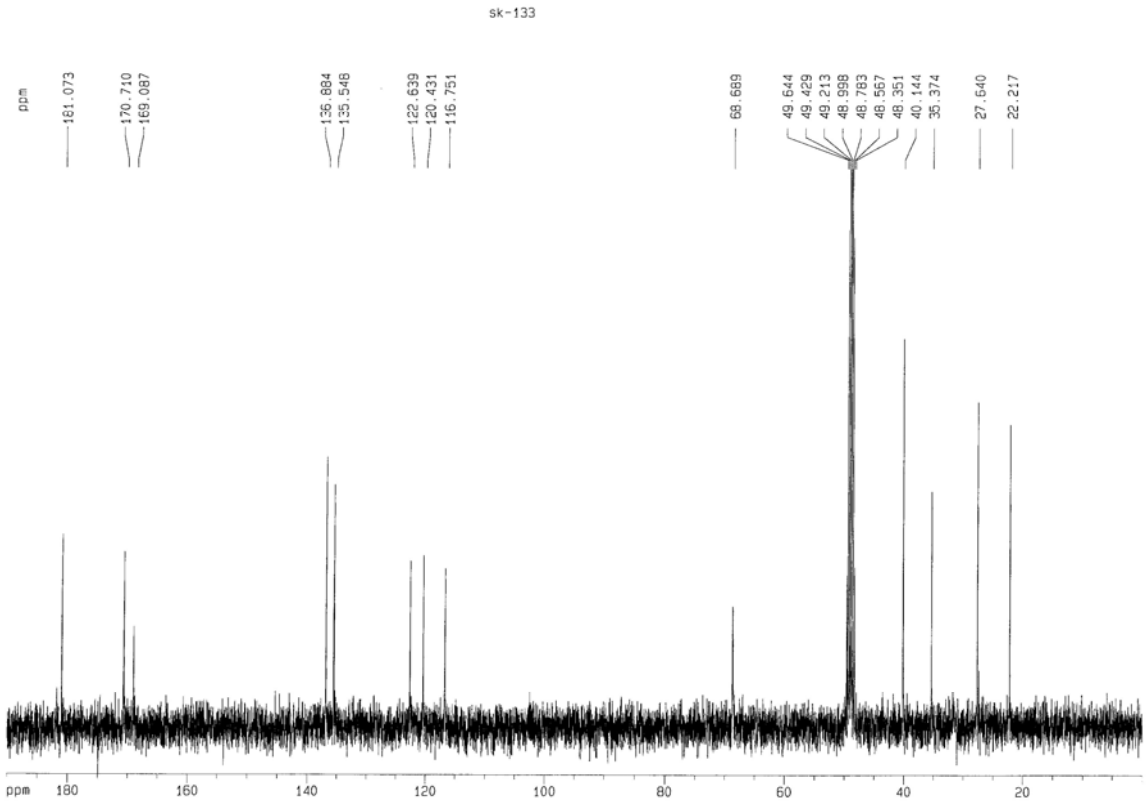


Figure S7. ^{13}C NMR spectrum of compound **2** in a D_2O/MeOD (4:1) mixture. (Though the compound is highly soluble in water, some MeOD is required for solubility purposes.[1])

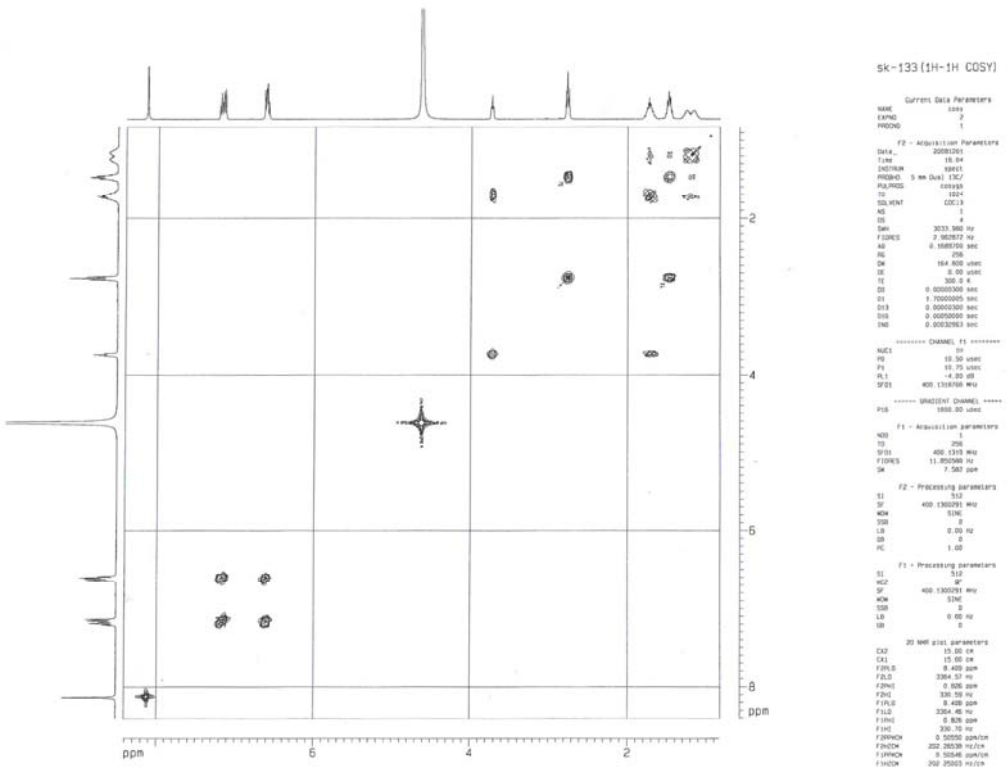


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of compound **2** in D_2O.[1]

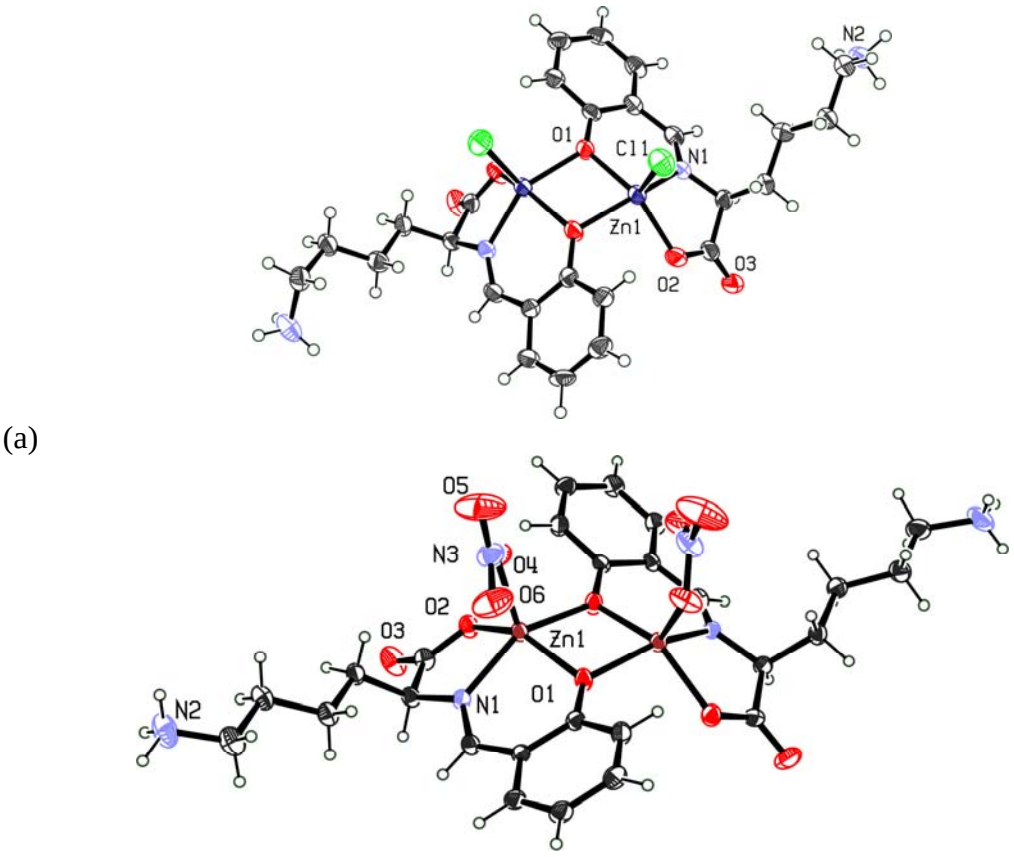


Figure S9. Crystal structure of (a) Compound **1**[2] and (b) **2**.[1] Thermal ellipsoids at 30 % probability. Solvent waters are omitted for clarity from the drawing.

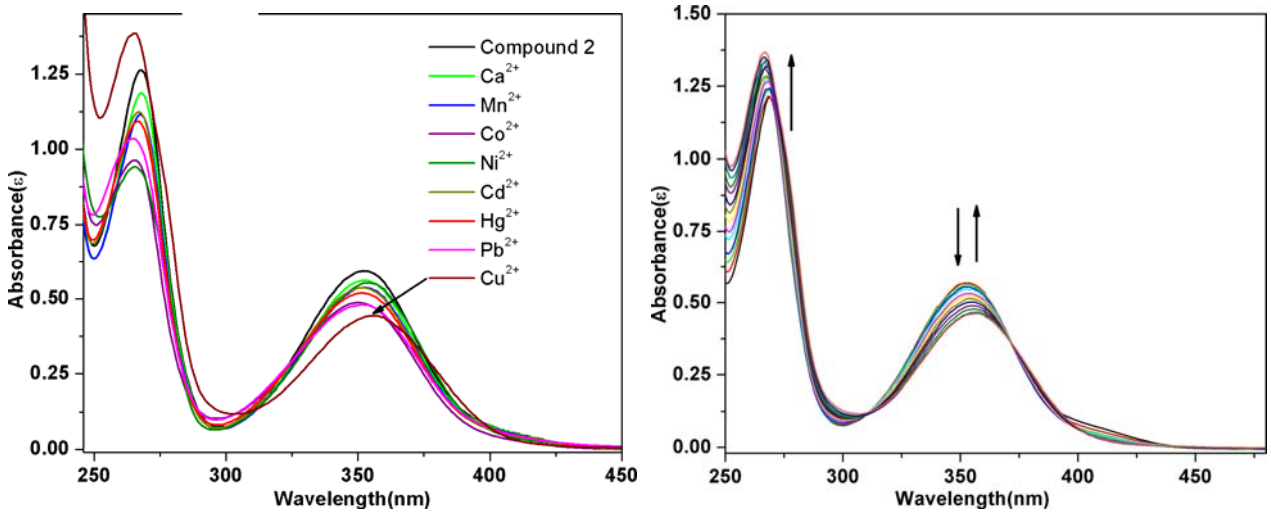
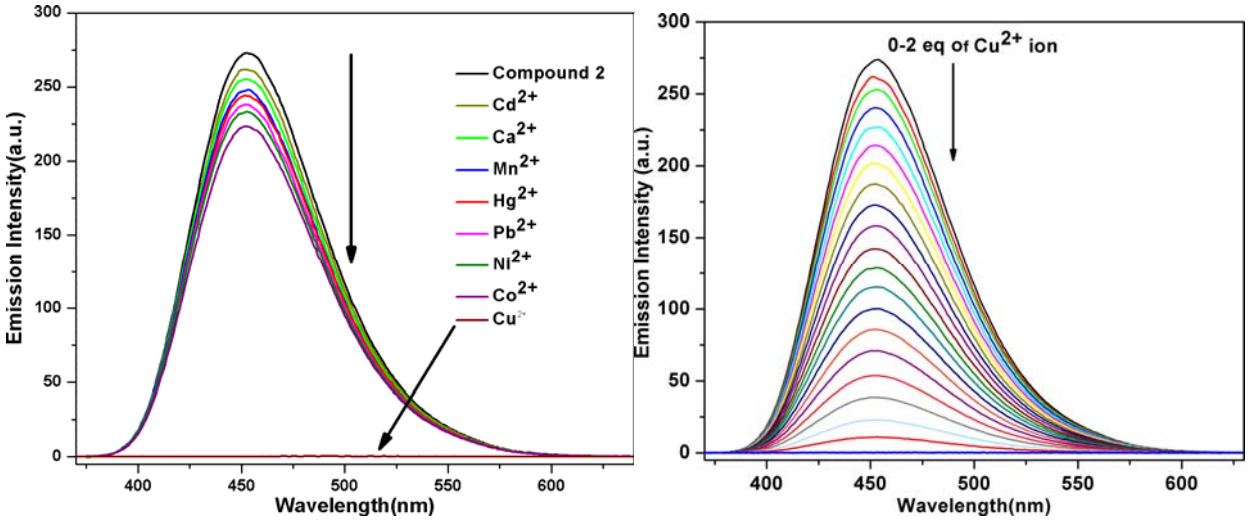
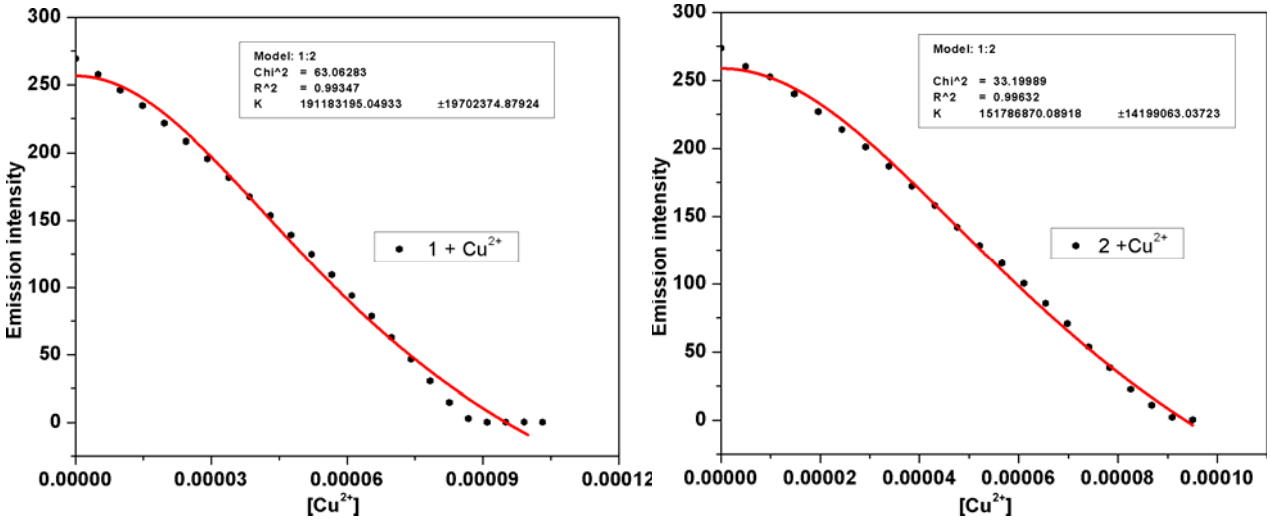


Figure S10. (a) UV-Vis spectra of **2** (50 μM) with different cations (100 μM) in aqueous buffer solution (pH 7.4, 0.01 M HEPES). (b) Absorbance titration of compound **2** (50 μM) in aqueous buffer solution (pH 7.4, 0.01 M HEPES) with an increasing amount of Cu^{2+} titrant (100 μM).[1]



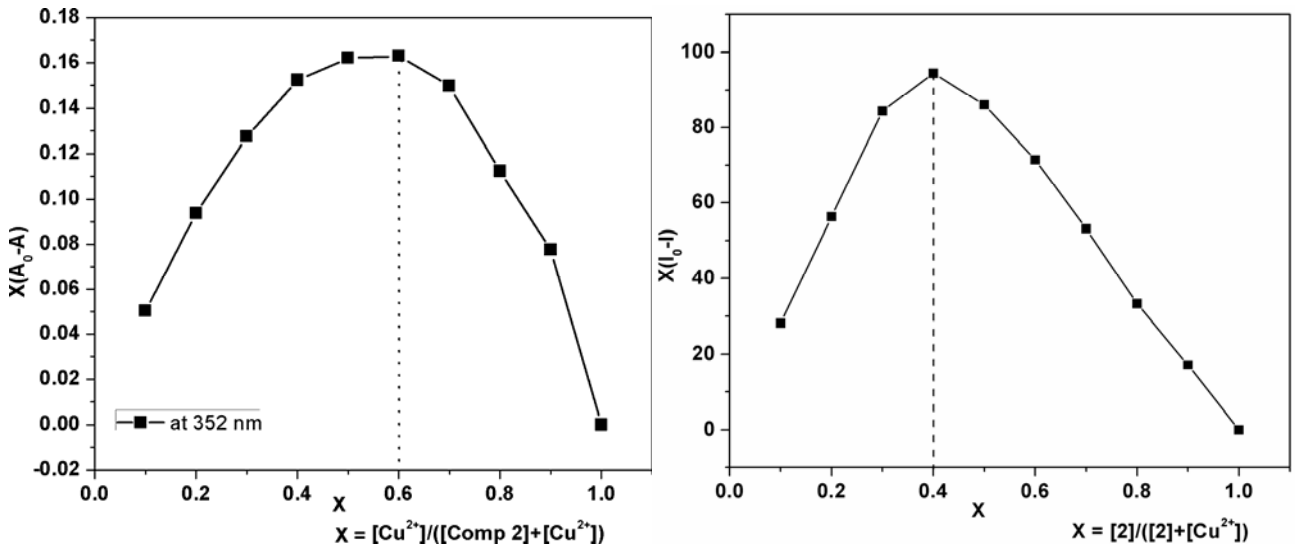
(a) (b)

Figure S11. (a) Emission spectra of **2** (50 μM, λ_{ex} = 352 nm, λ_{em} = 452 nm) with different cations (each with a concentration of 100 μM). (b) Emission titration of **2** (50 μM) in aqueous buffer solution (pH 7.4, 0.01 M HEPES) with increasing amounts of Cu^{2+} solution (100 μM).[1]



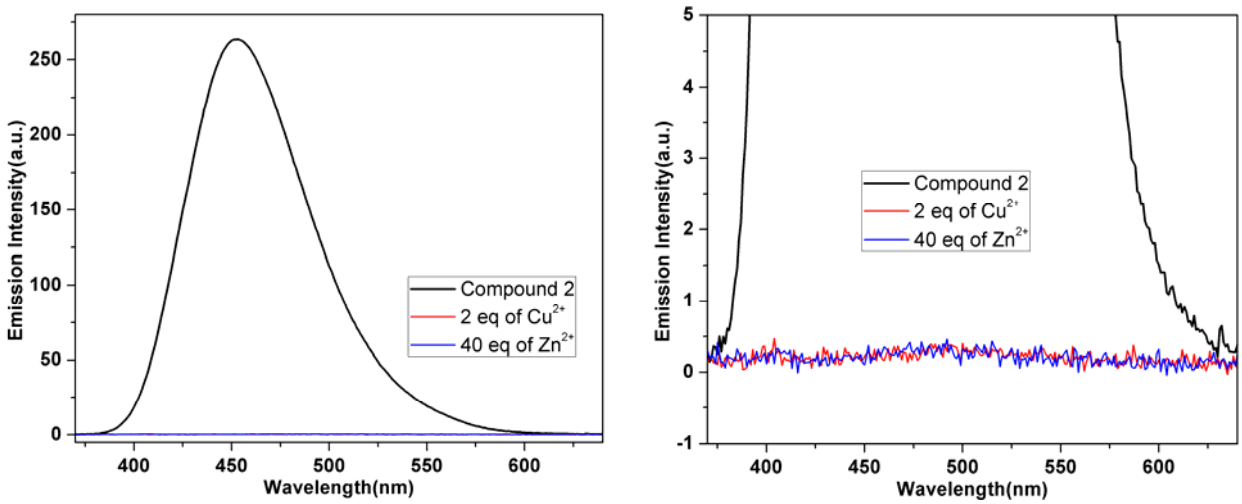
(a) (b)

Figure S12. Non-linear curve fitting of copper binding from emission titration data. (a) Compound **1** and increasing amounts of Cu^{2+}; (b) Compound **2** and increasing amounts of Cu^{2+}.[1]



(a) (b)

Figure S13. Job's plot for compound **2** and Cu^{2+} binding (λ_{max} at 352 nm) in an aqueous buffer solution (pH 7.4, 10 mM HEPES) at 25 ^{o}C by (a) by UV-vis spectroscopy (against a Cu^{2+} concentration; value of 0.6 suggests nearly 1 : 2 compound 2 : Cu^{2+} binding stoichiometry), and (b) by emission spectroscopy (plot against compound **2** concentration; value of 0.4 shows nearly a 1 : 2 compound **2** : Cu^{2+} binding stoichiometry).[1]



(a) (b)

Figure S14. (a) Emission spectra of Compound **2** (50 μM) in an aqueous buffer solution (pH 7.4, 0.01 M HEPES) with 2 equivalents of Cu^{2+} (100 μM solution) and 40 equivalents of Zn^{2+} (solution) to the mixture of **2** and Cu^{2+} ion. (b) Expanded spectra.[1]

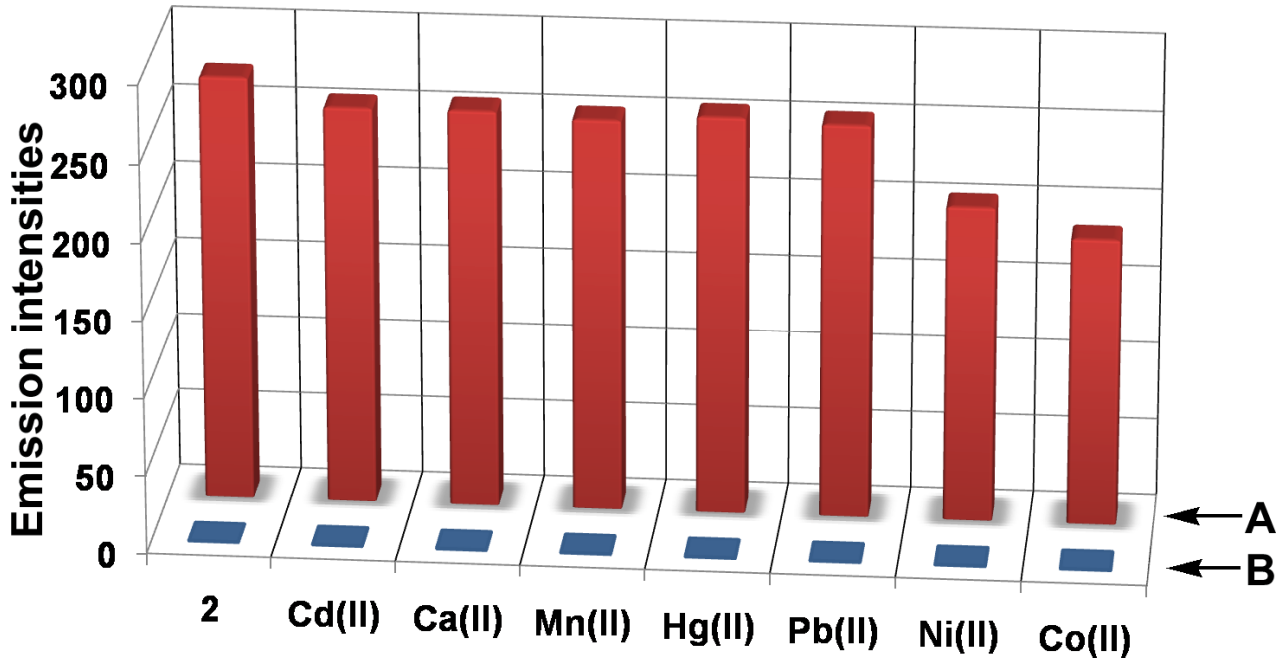
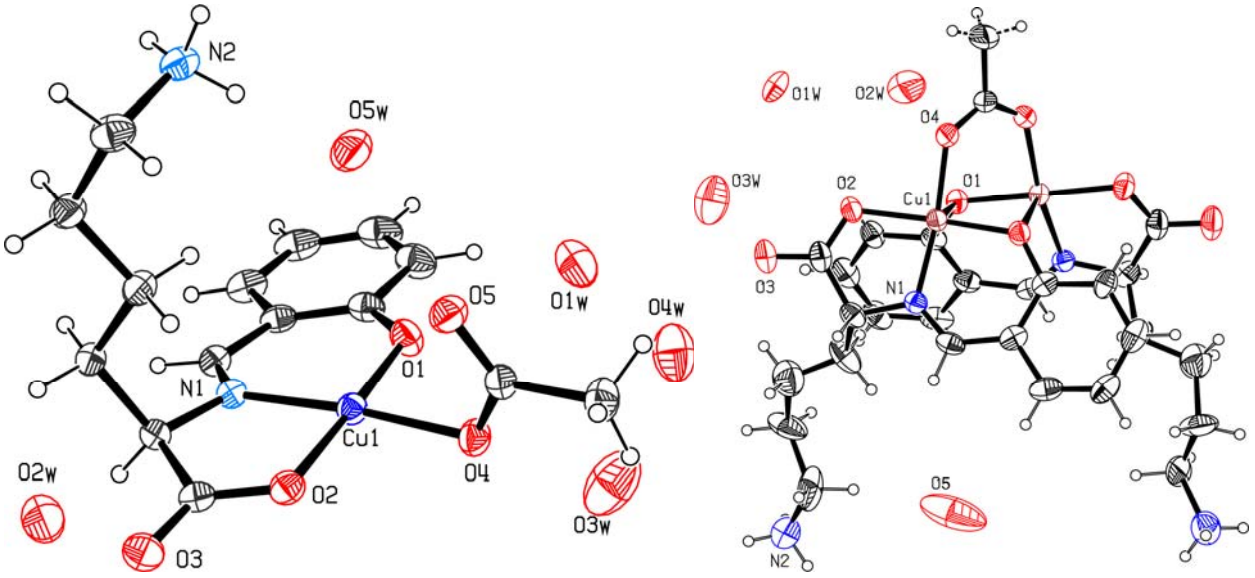


Figure S15. (*Row A*) Emission spectra of **2** (50 μM) in aqueous buffer solution (pH 7.4, 0.01 M HEPES) with different cations (500 μM), the bar on far left is only compound **2**. (*Row B*) Emission spectra of a mixture of **2** (50 μM) with other metal ions (500 μM) and with Cu^{2+} solution (100 μM) [1].



(a) (b)

Figure S16. Crystal structures of copper acetate and D/L lysine-based schiff base complex obtained from one pot reactions and one pot crystallization methods. (a) Mononuclear purple and (b) dinuclear blue complexes.[3]

References:

1. S. Khatua, S. H. Choi, J. Lee, J. O. Huh, Y. Do, D. G. Churchill, *Inorg. Chem.* 2009, **48**, 1799-1801.
2. S. Khatua, S. H. Choi, J. Lee, K. Kim, Y. Do, D. G. Churchill, *Inorg. Chem.* 2009, **48**, 2993-2999.
3. S. Khatua, J. Kang, J. O. Huh, C. S. Hong, D. G. Churchill, *Cryst. Growth Des.* 2010, **10**, 327-334.

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