Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information 1

I_2 catalyzed access of spiro[indoline-3,4'-pyridine] appended amine dyad: New ON-OFF chemosensors for Cu^{2+} and imaging in living cells

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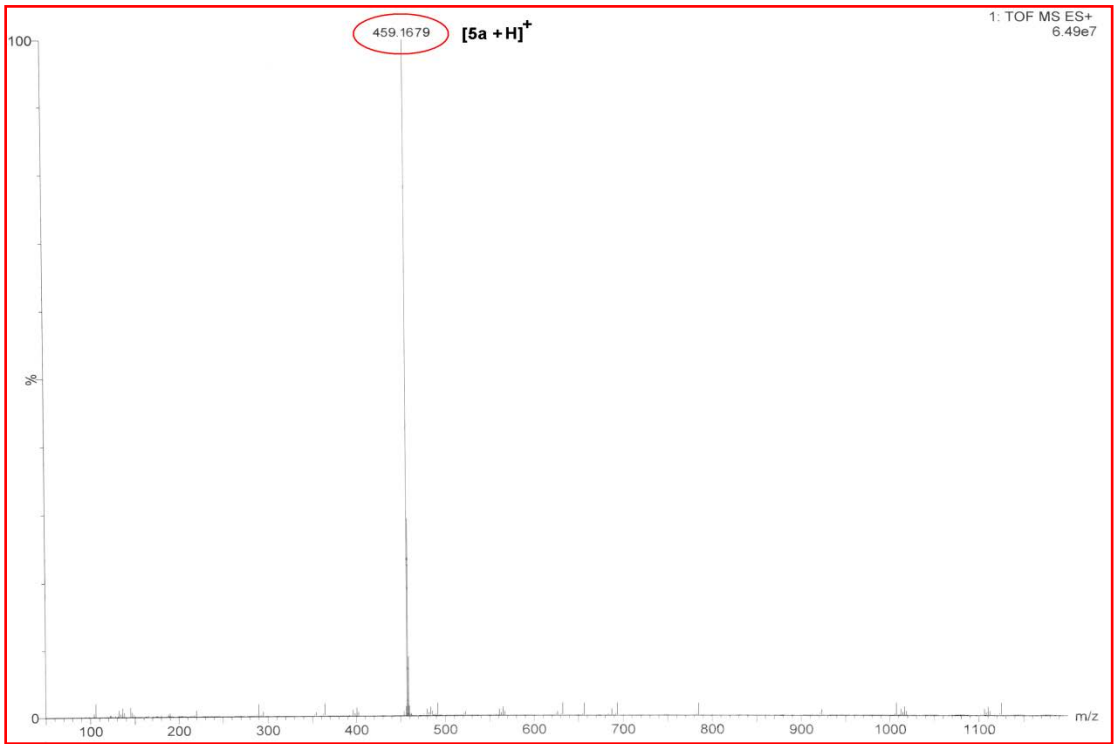
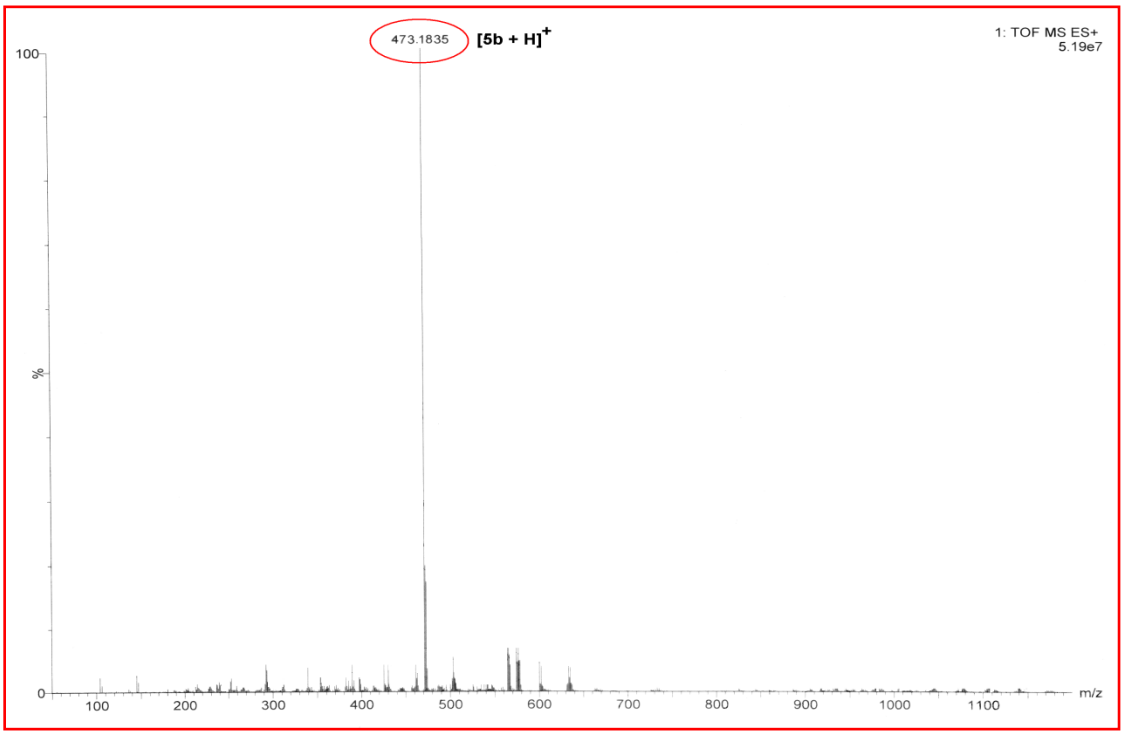
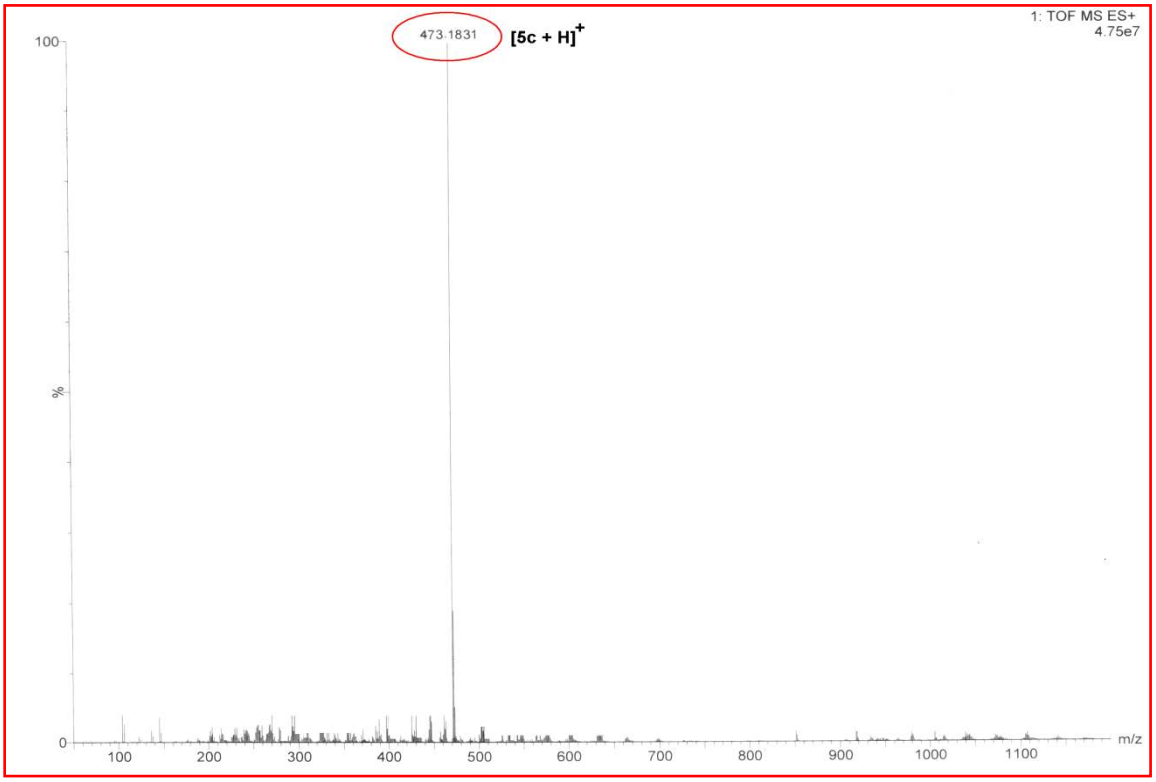
Figure S1. ESI-MS spectra of compound 5a−5f, 5h−5l and in copper complexes:



ESI-MS compound **5a**



ESI-MS **of compound 5b**



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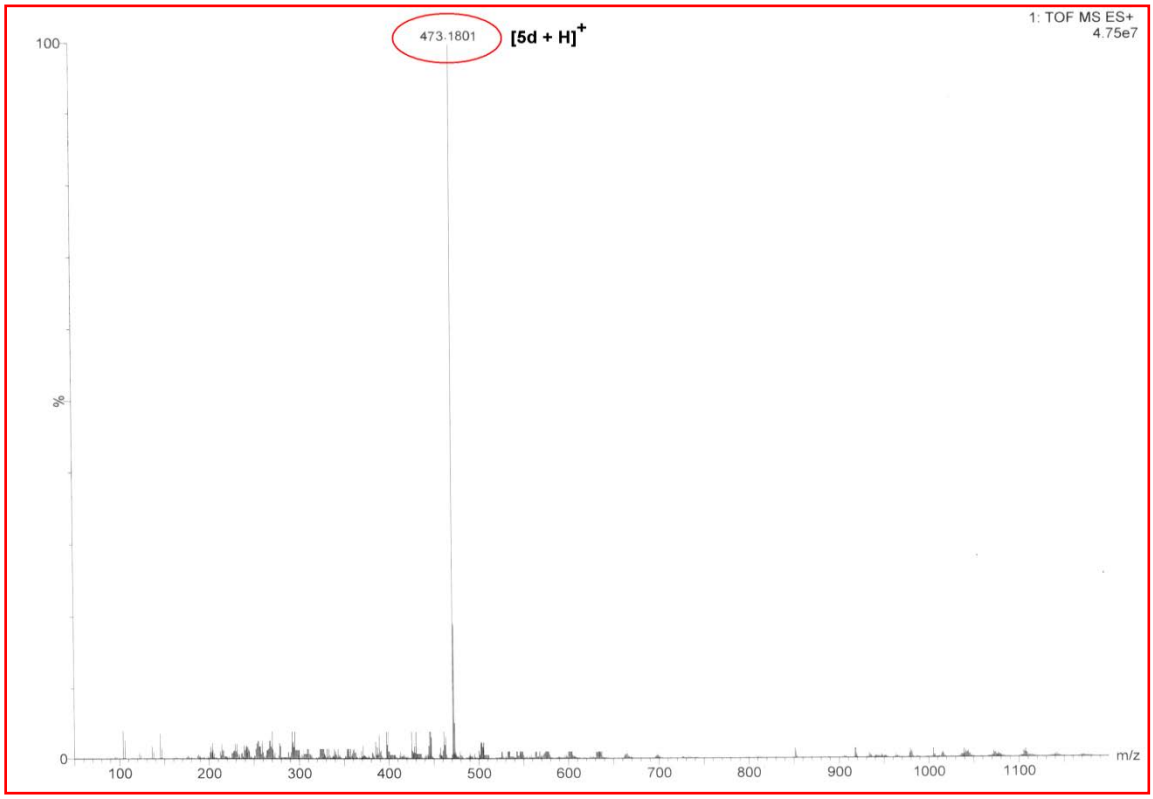

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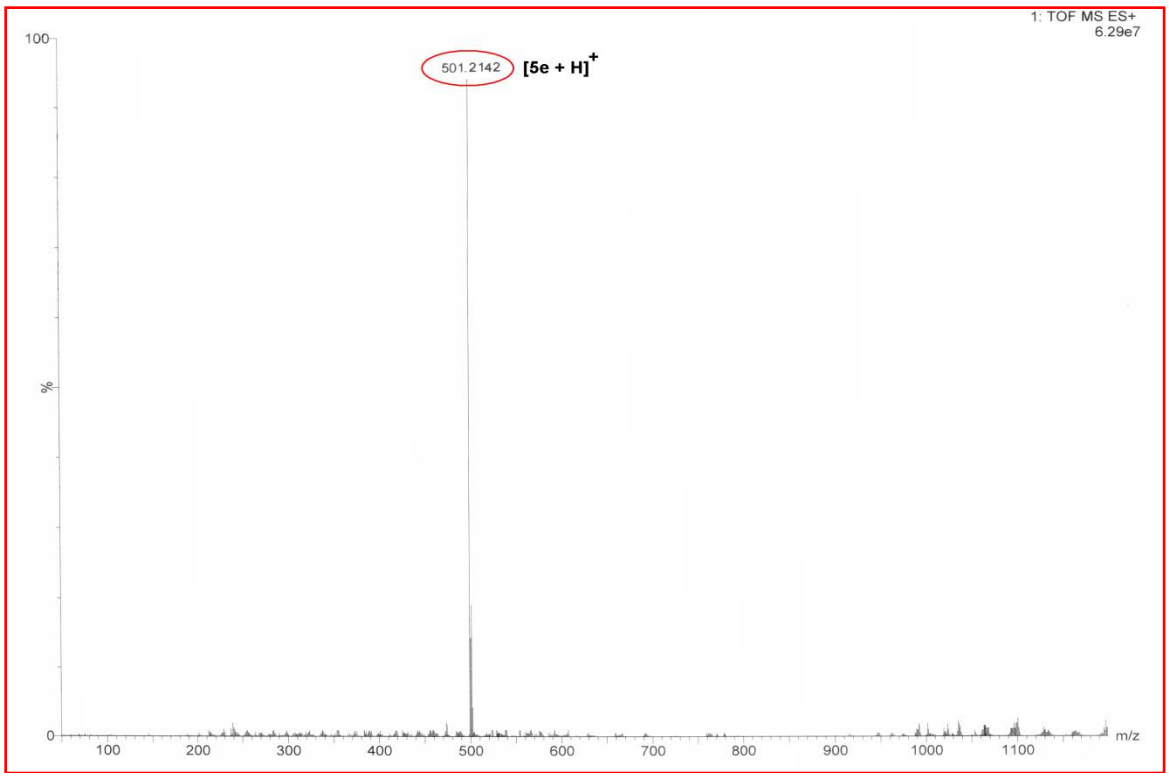

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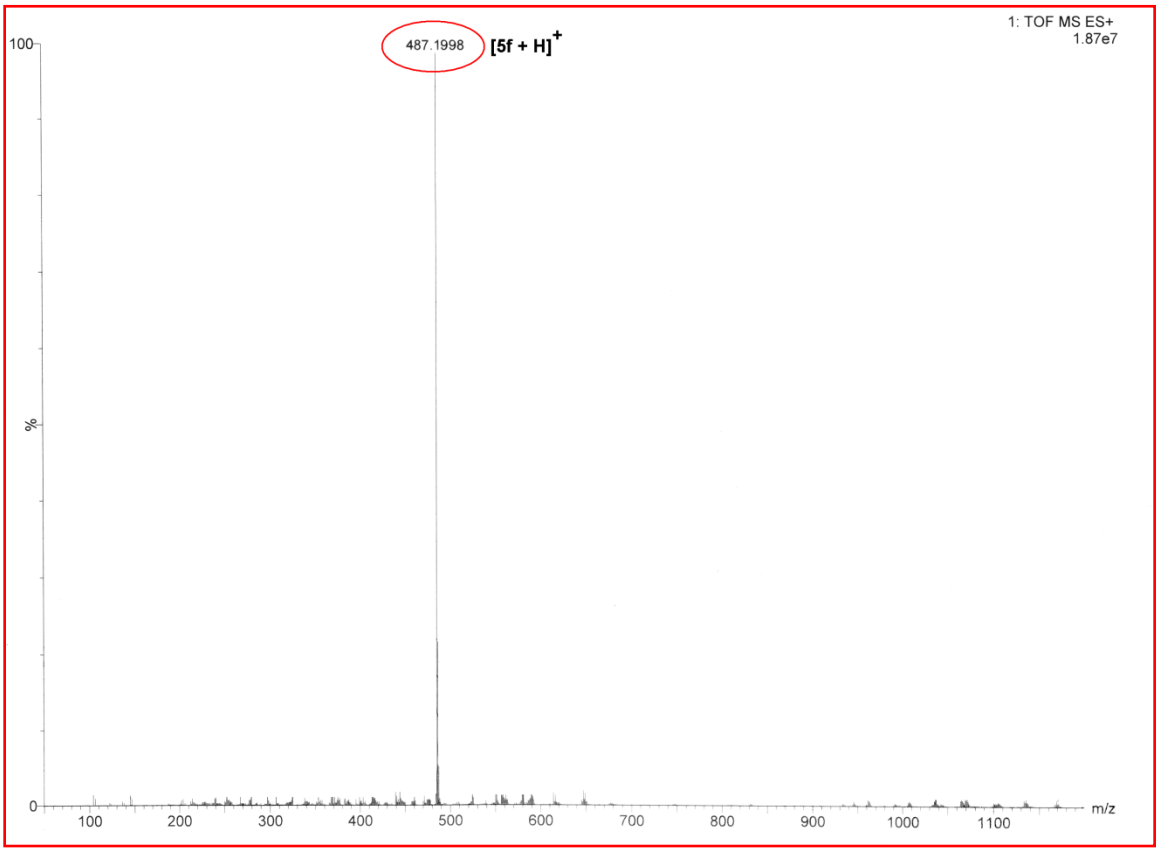

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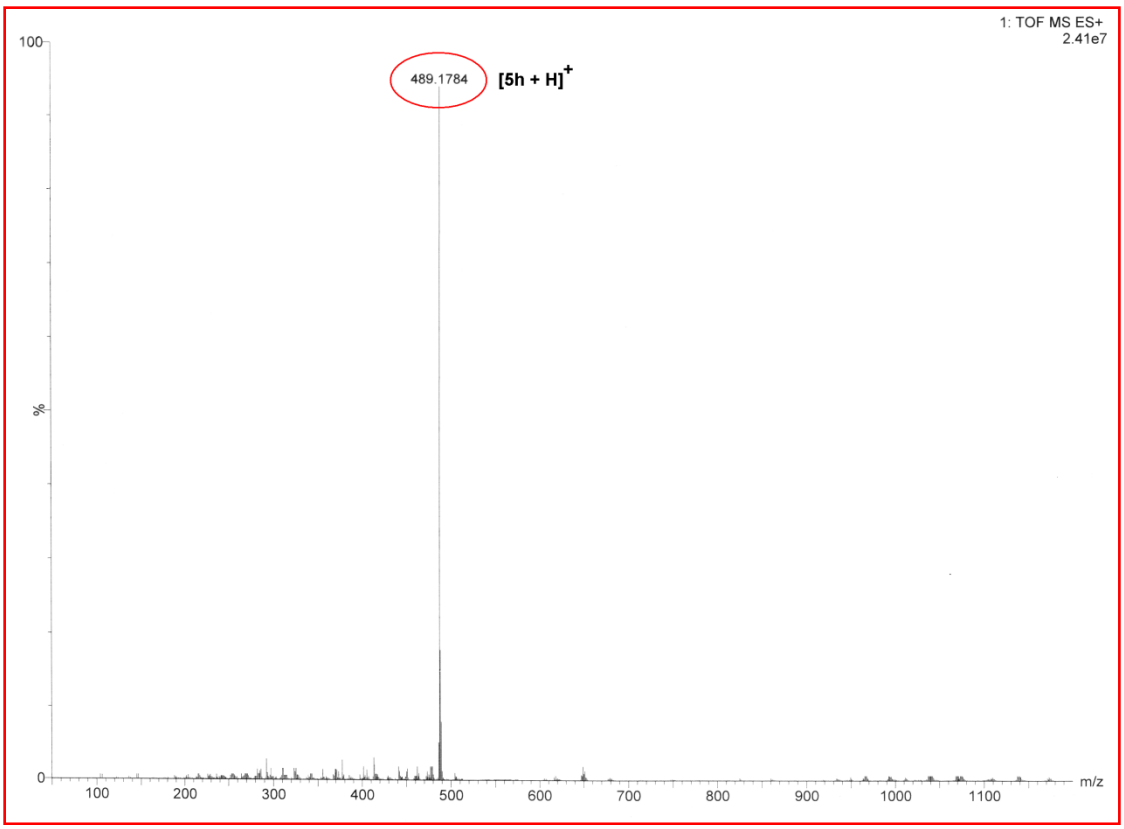

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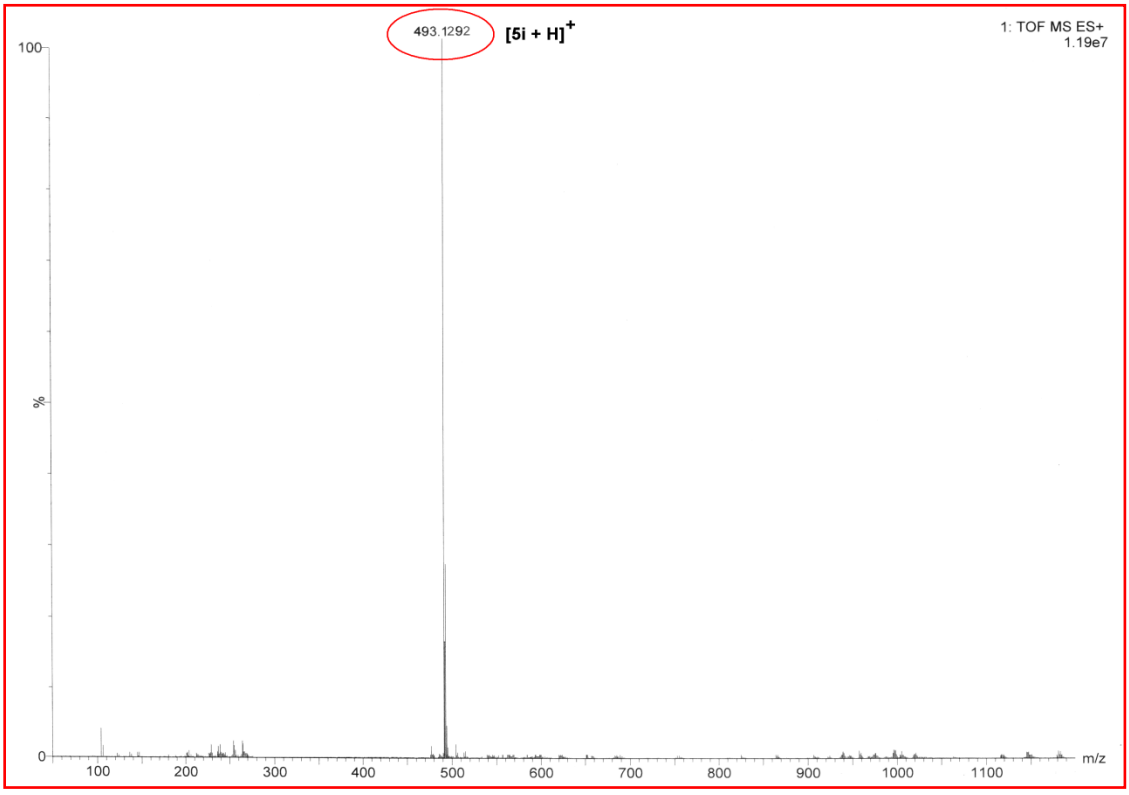

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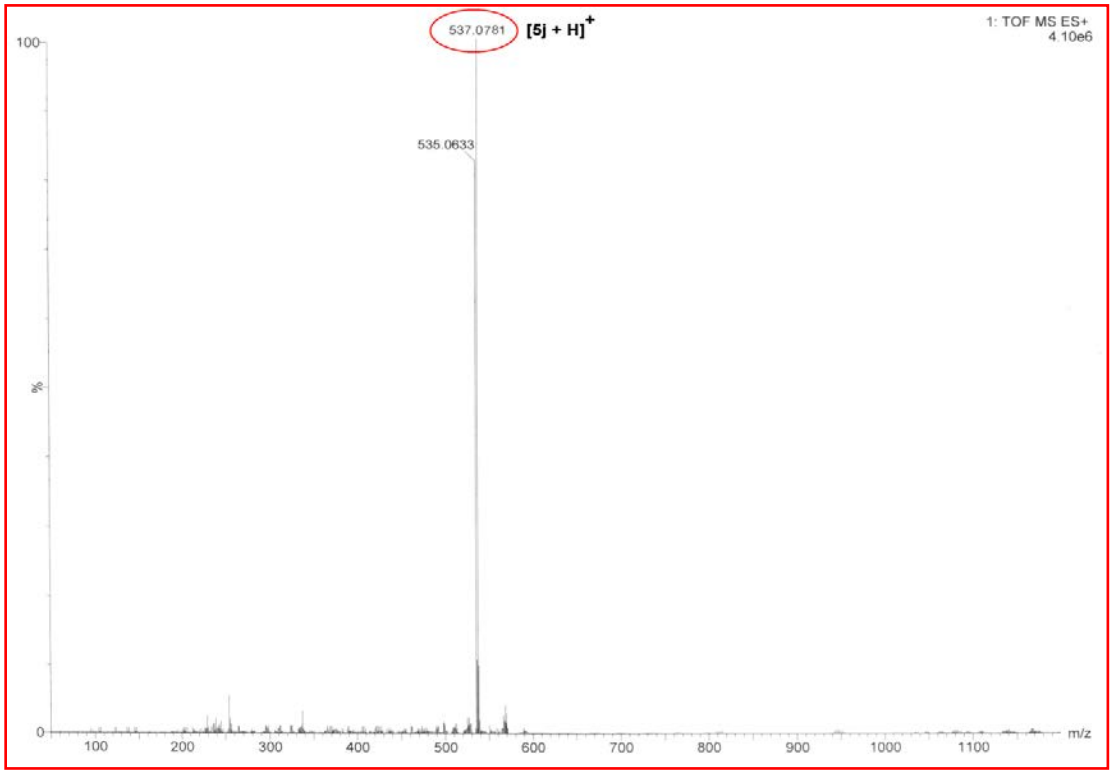

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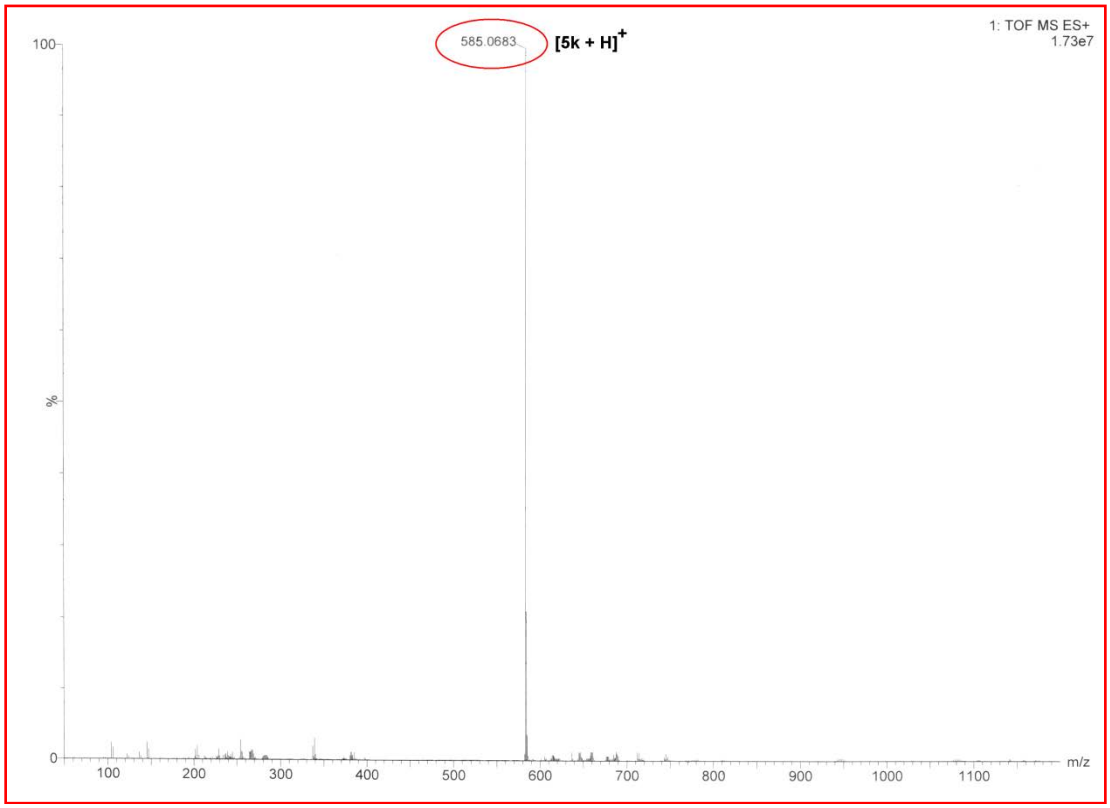

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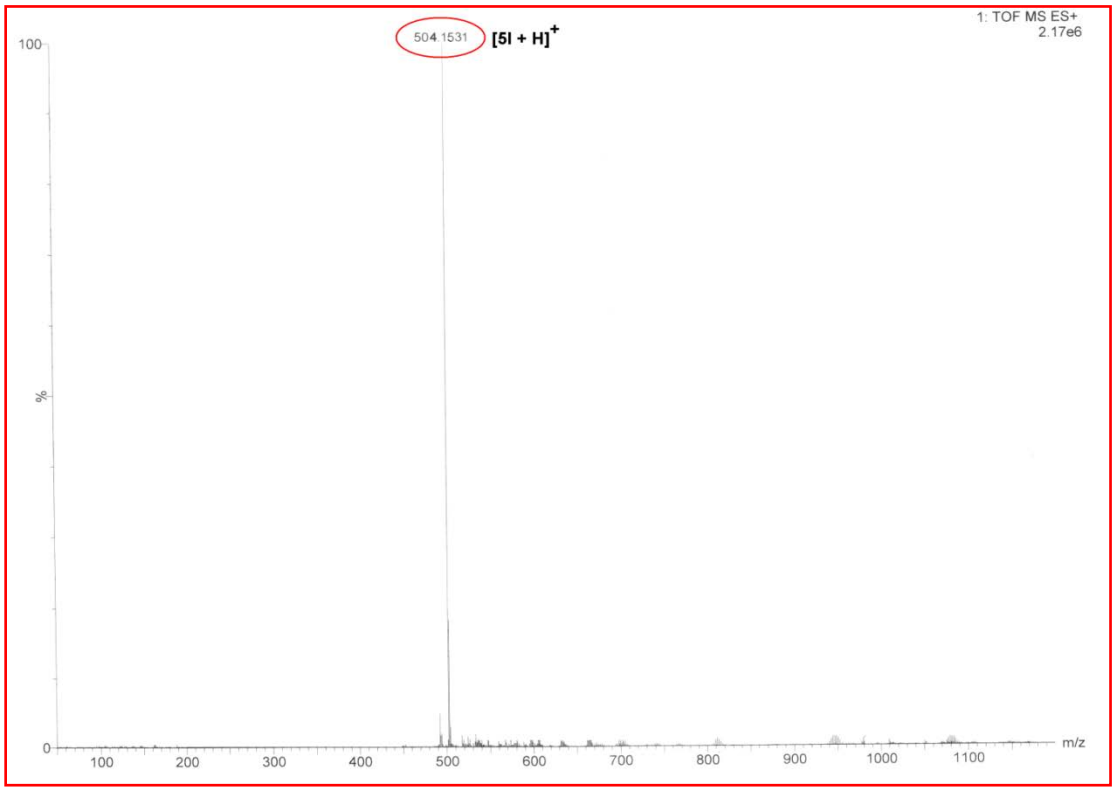

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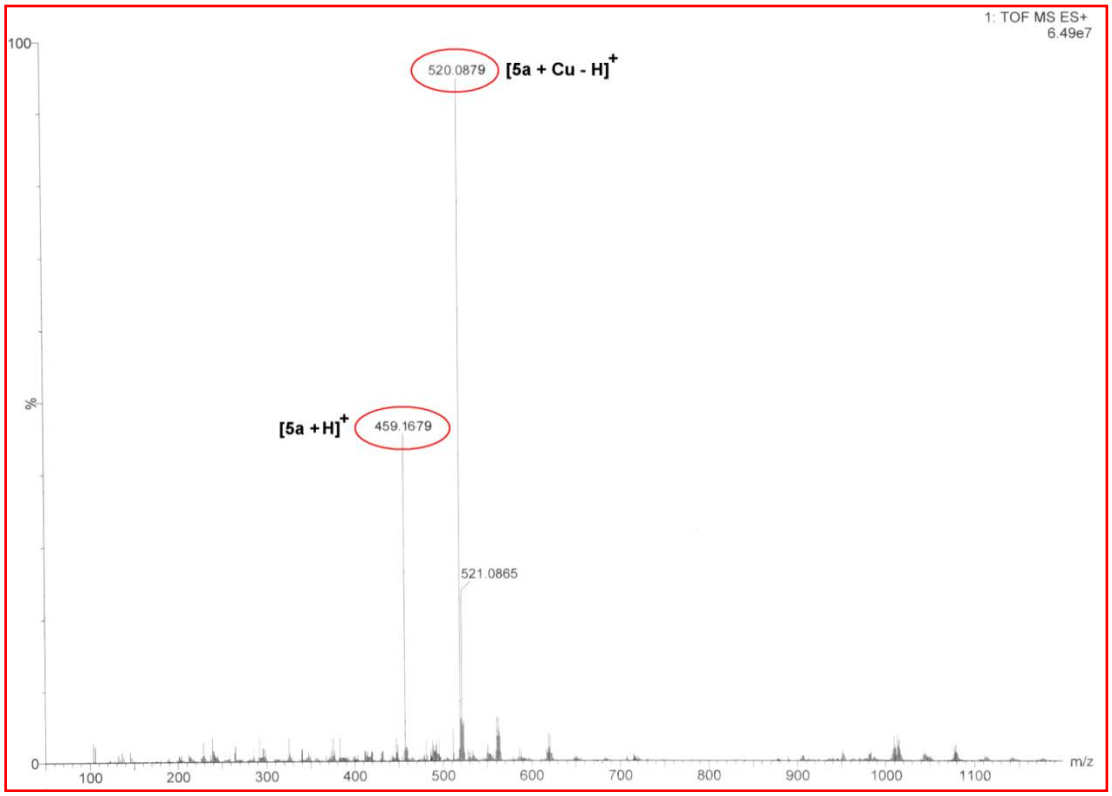
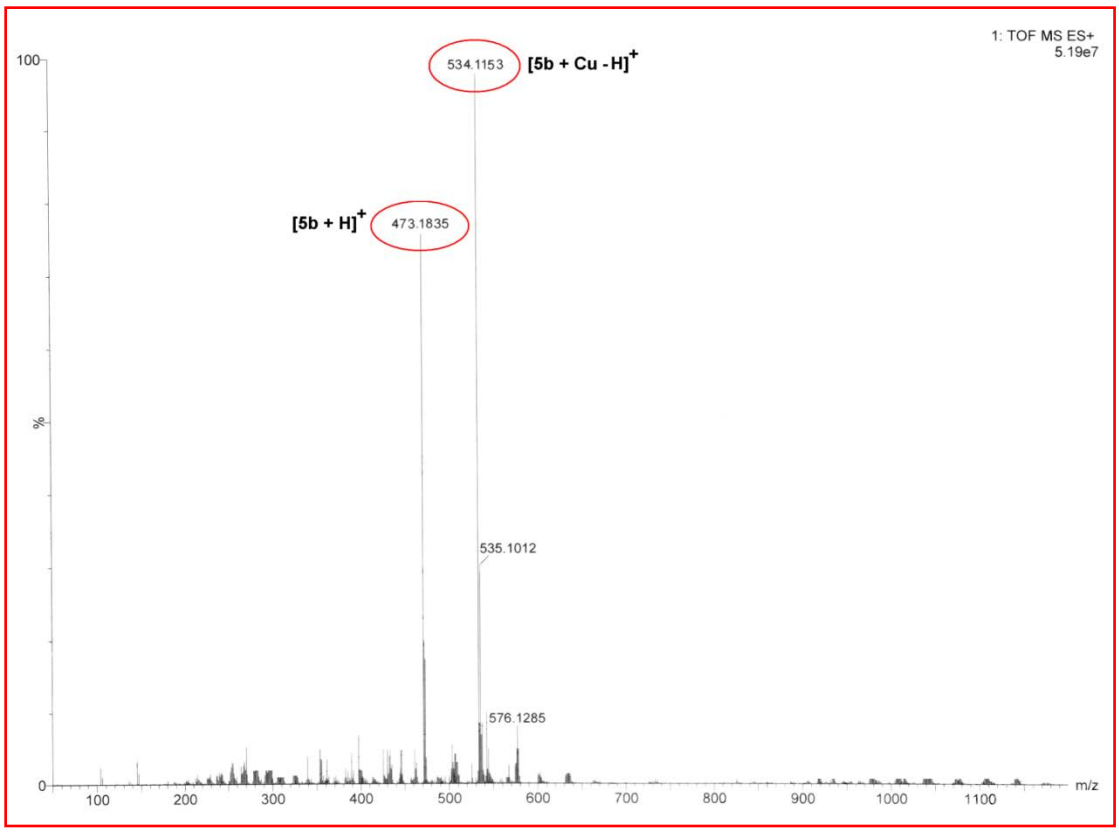


ESI-MS of compound **5a+Cu**



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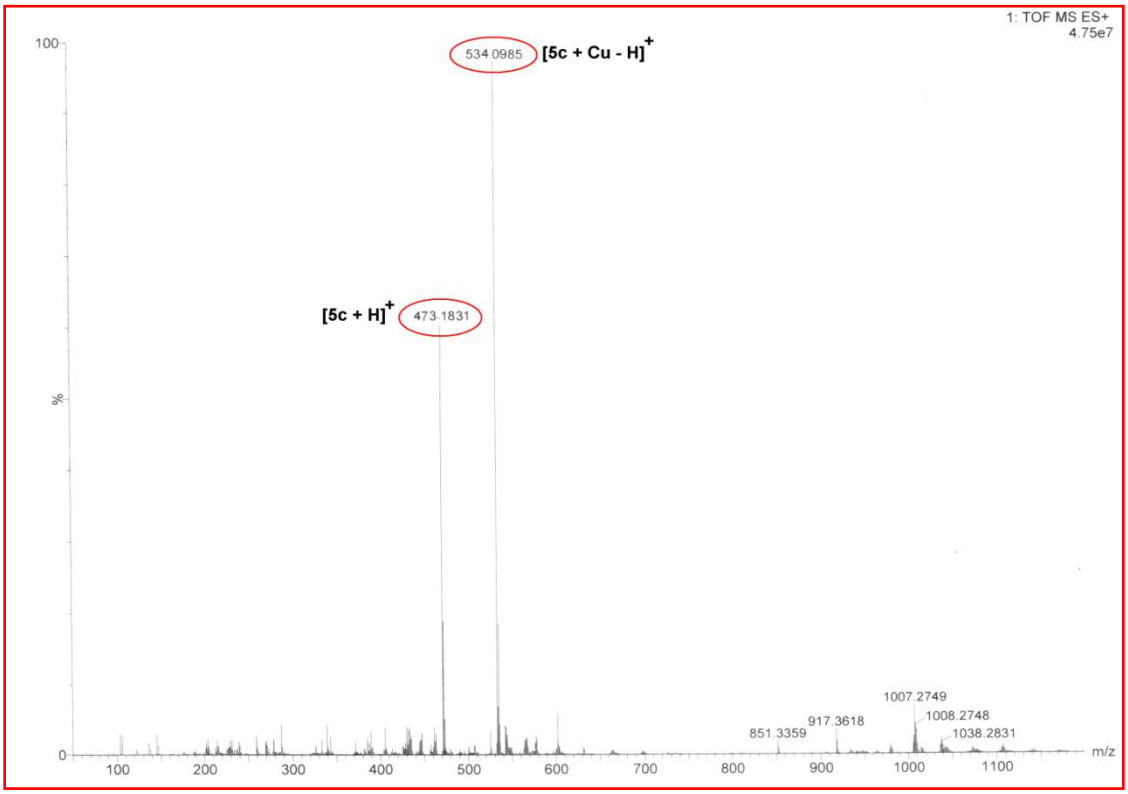

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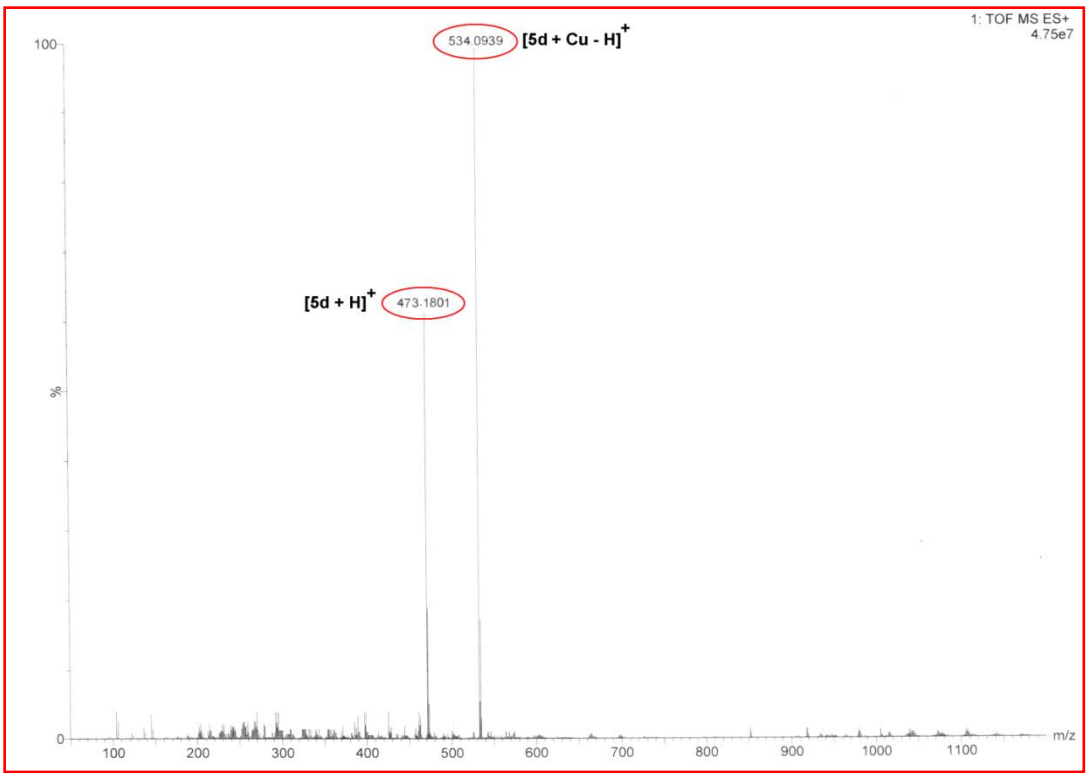

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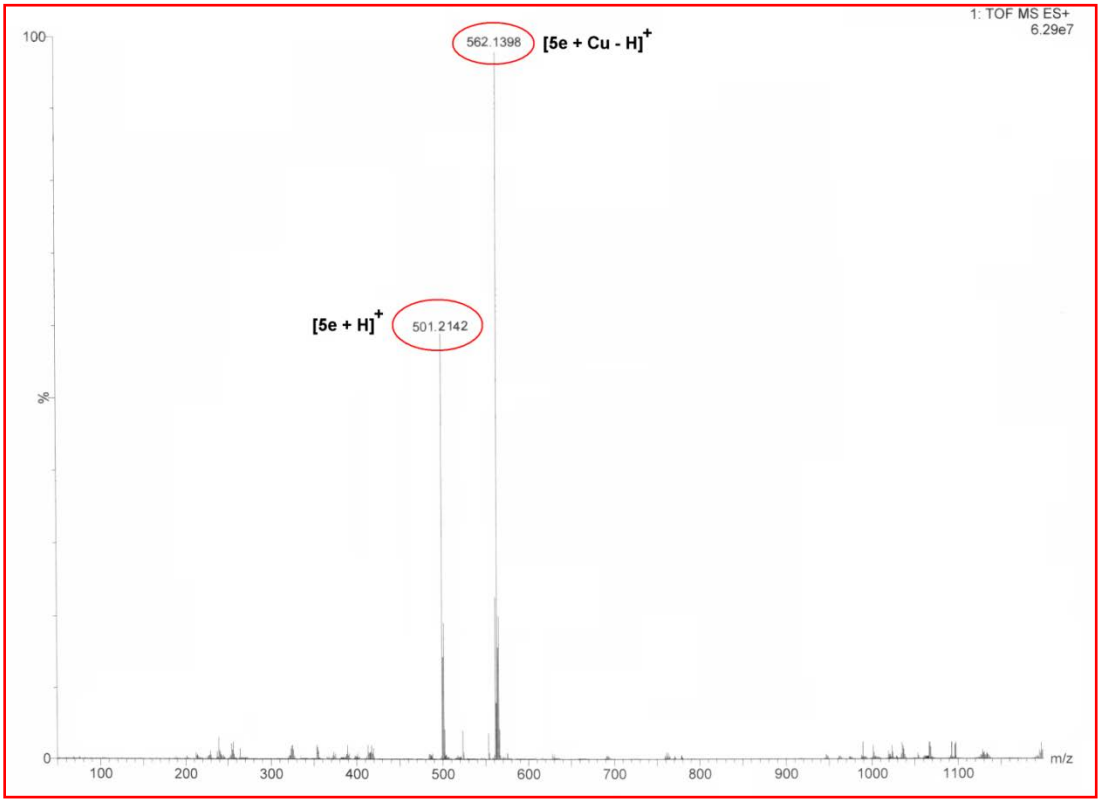

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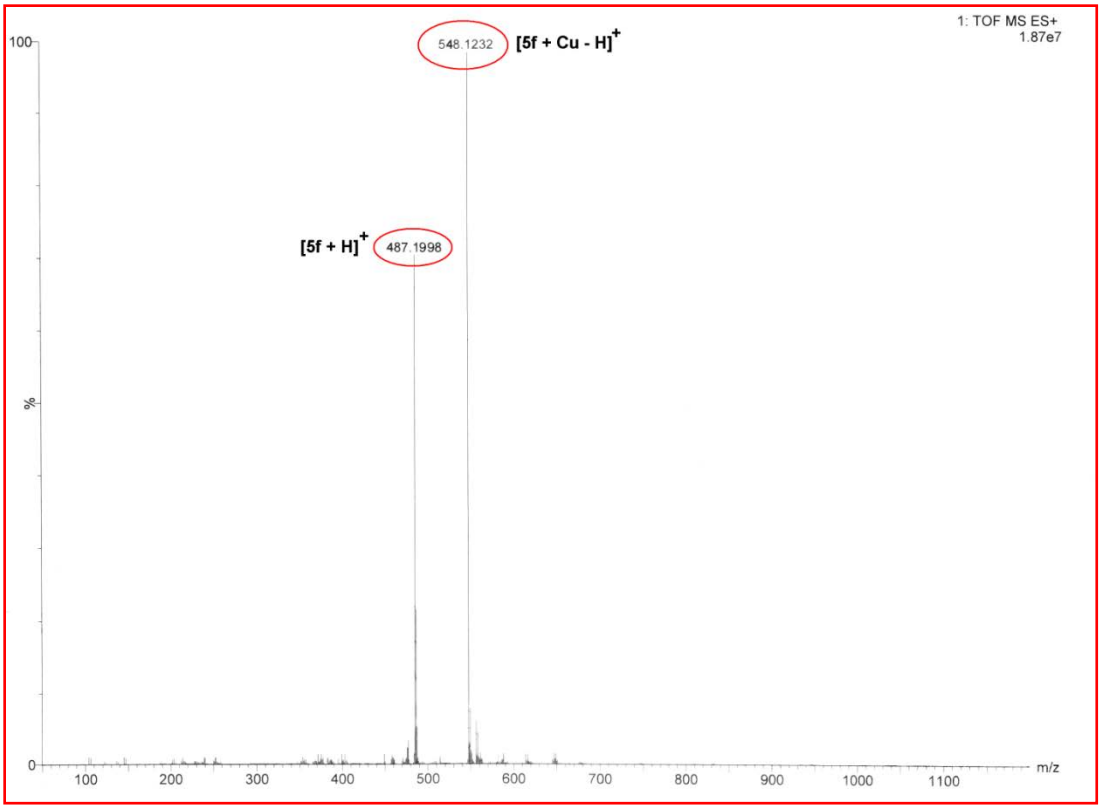

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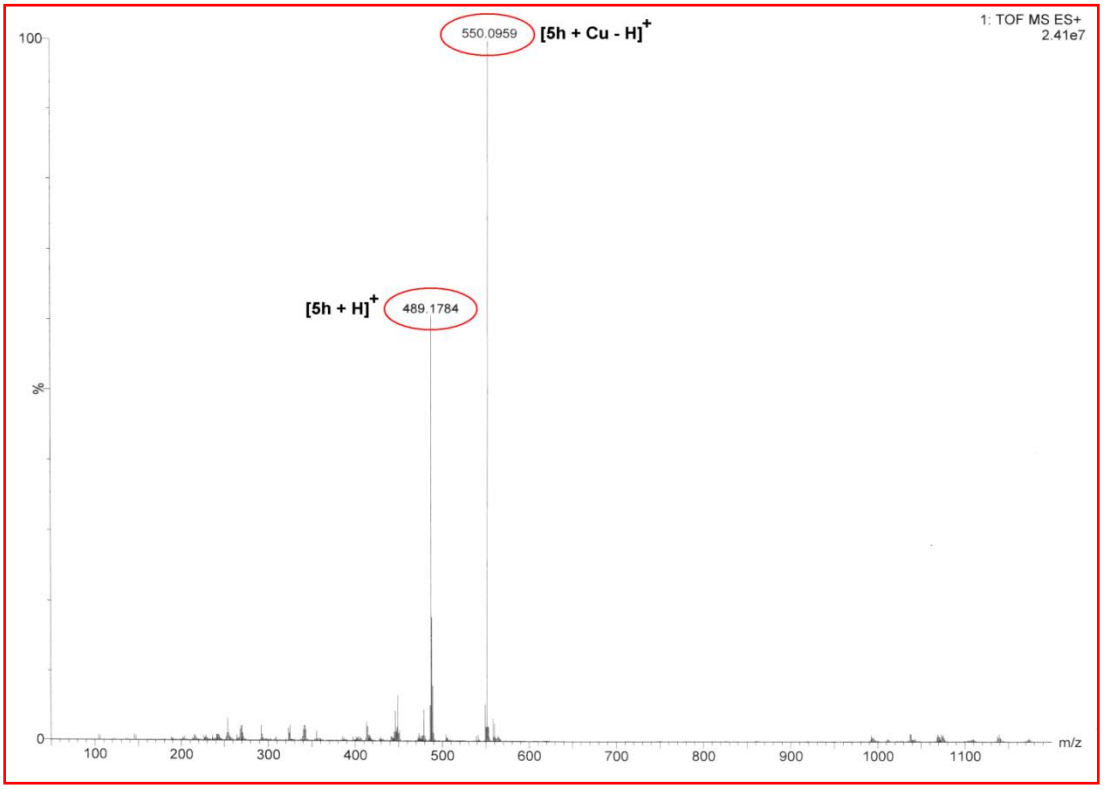

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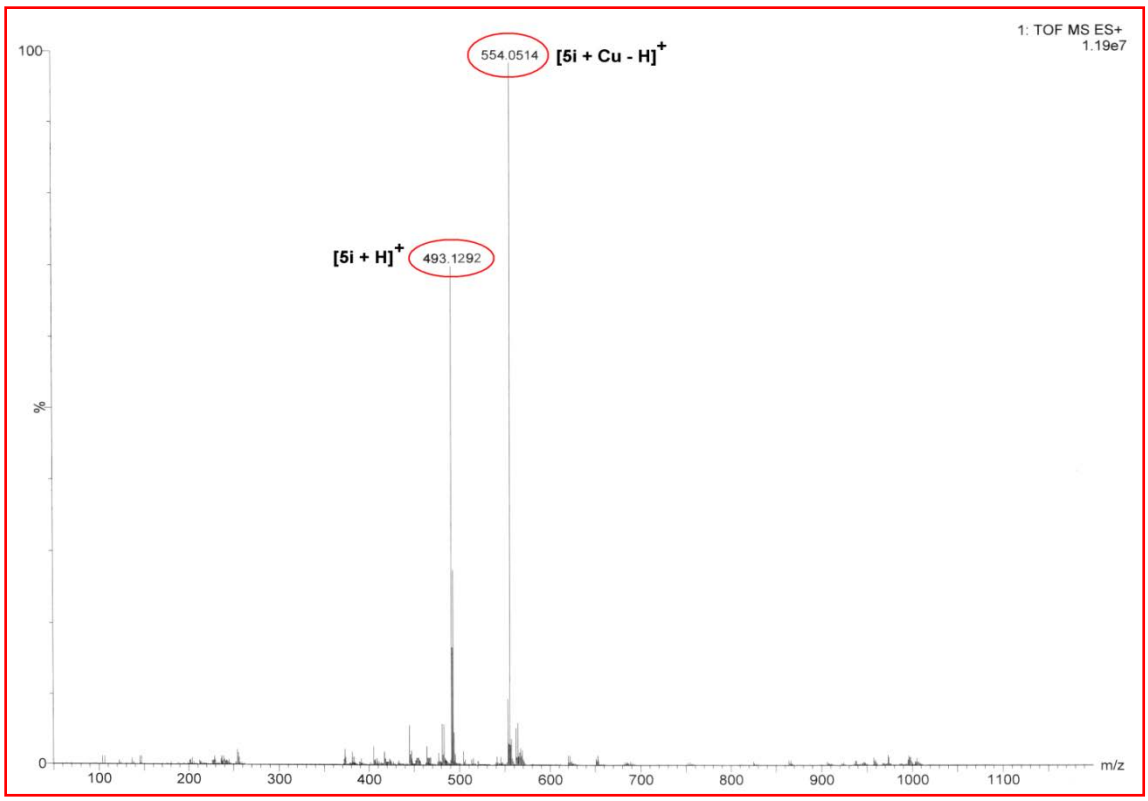

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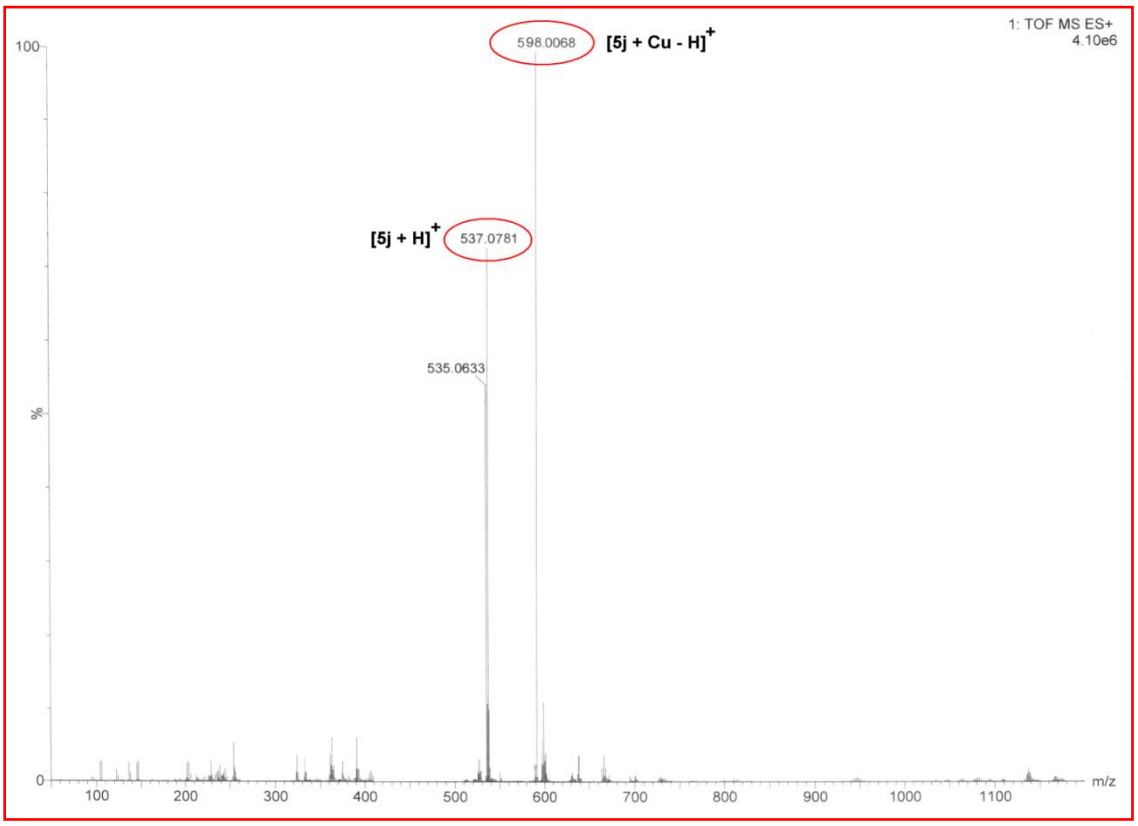

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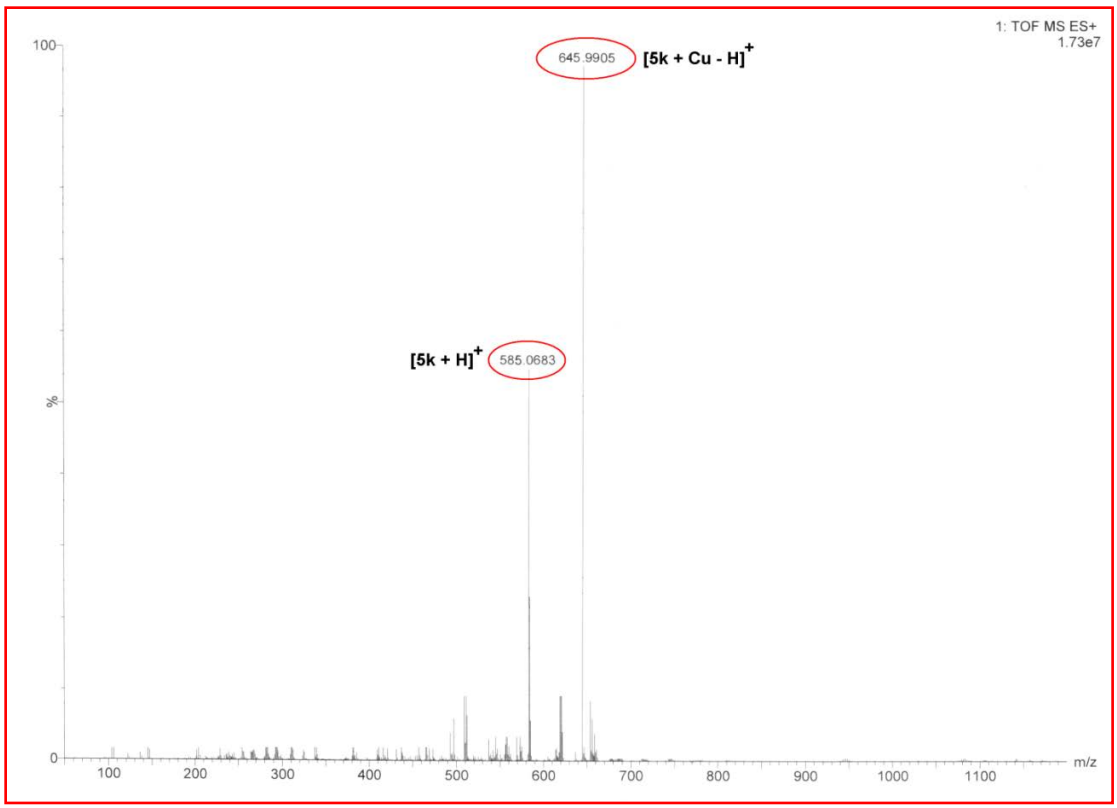

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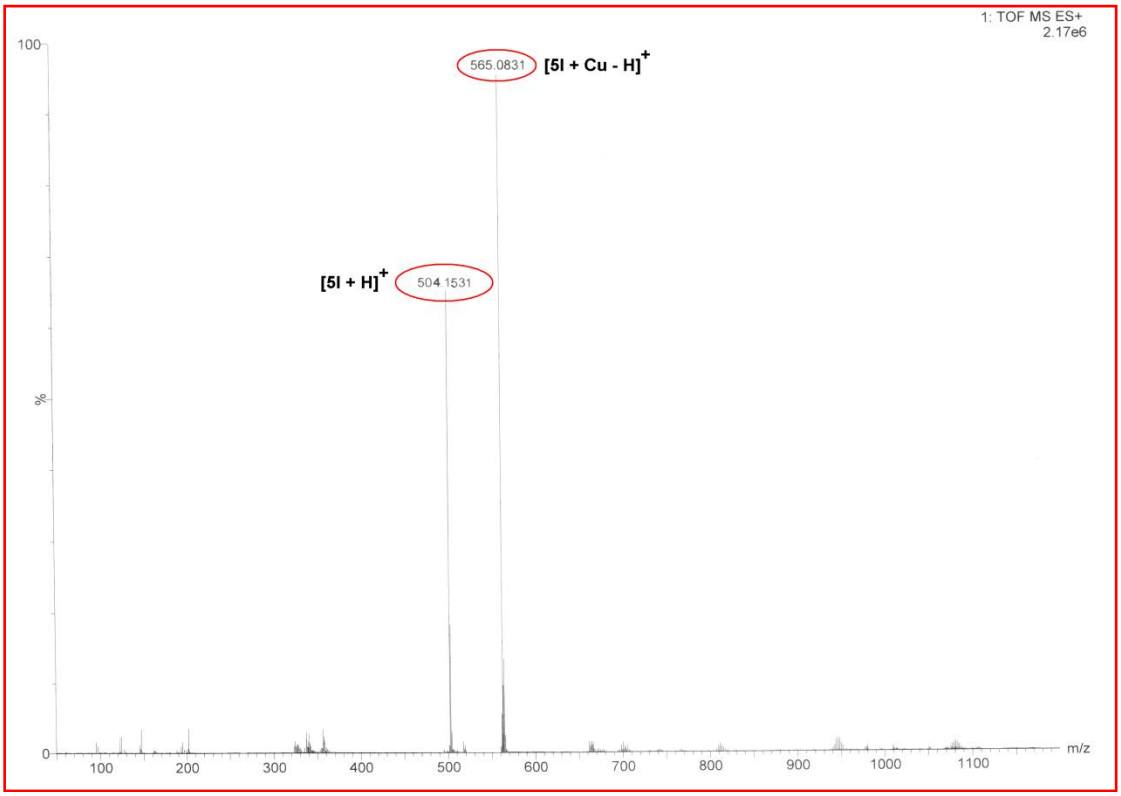

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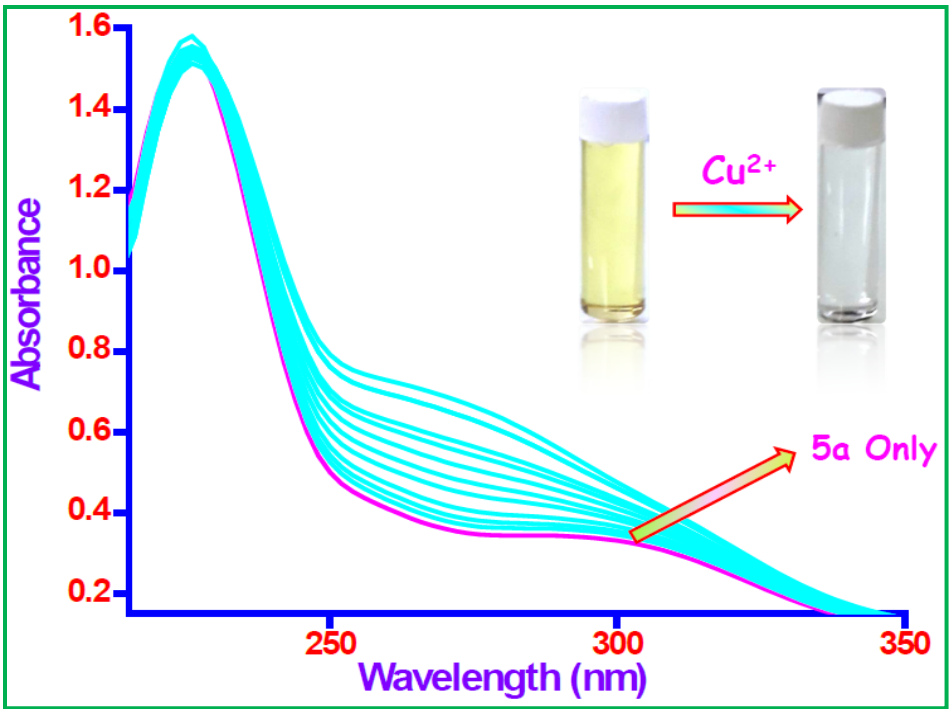

Figure S2. UV-vis spectra of **5a** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5a** solution.

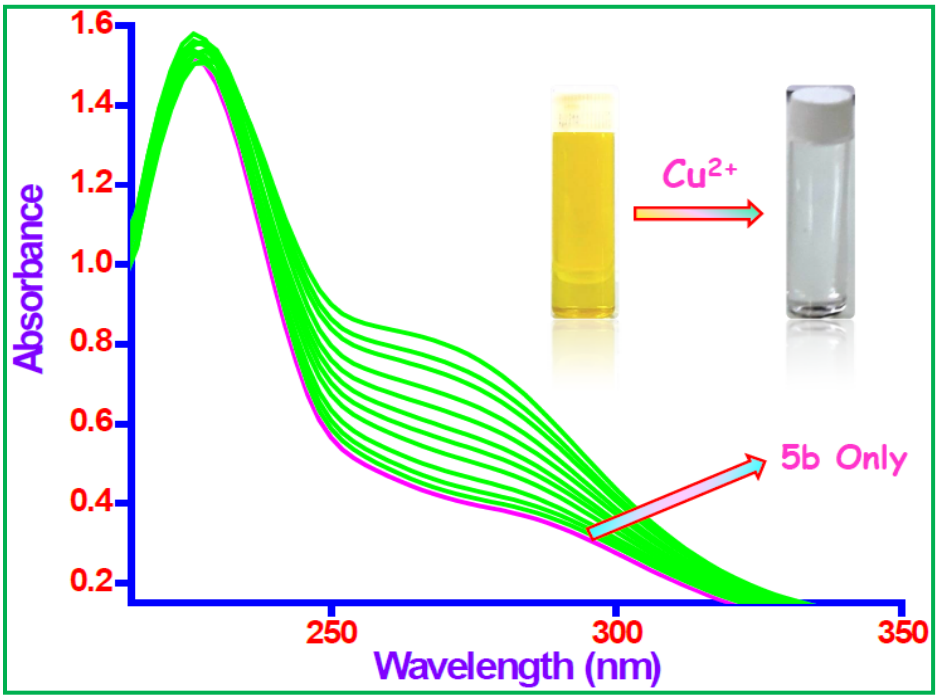

Figure S3. UV-vis spectra of **5b** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5b** solution.

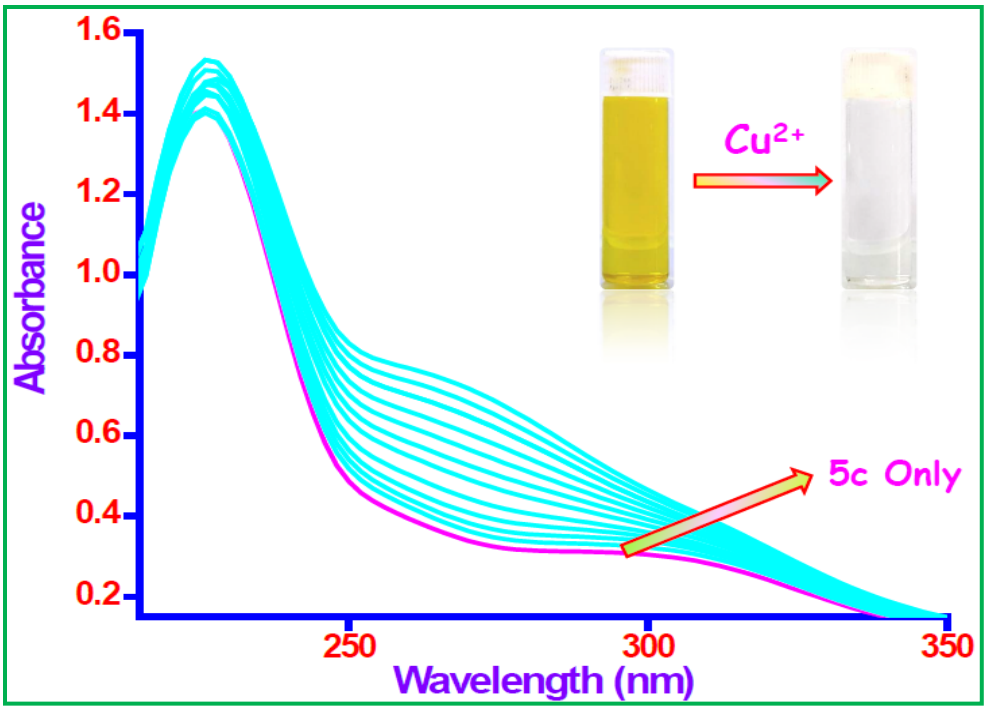

Figure S4. UV-vis spectra of **5c** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5c** solution.

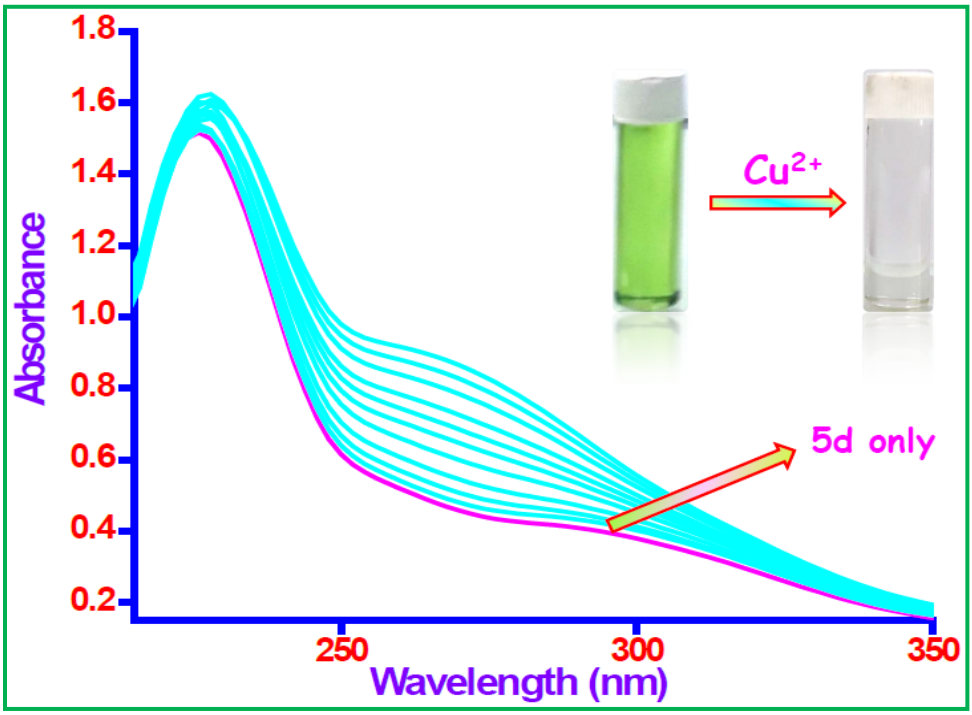

Figure S5. UV-vis spectra of **5d** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (green to colorless) observed with addition of Cu^{2+} ion to **5d** solution.

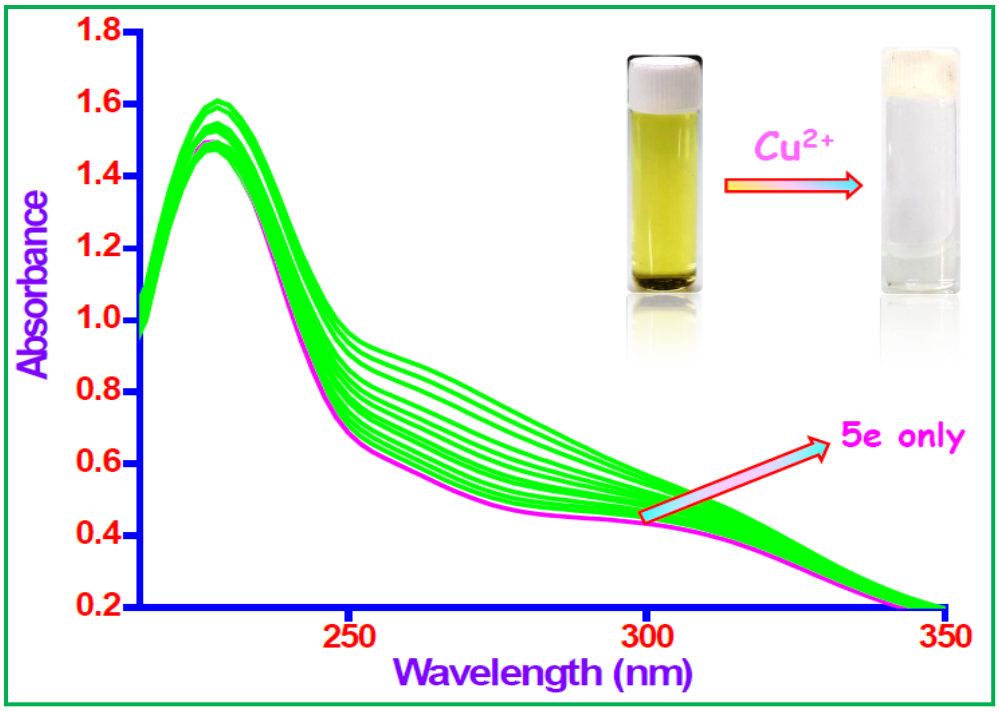

Figure S6. UV-vis spectra of **5e** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5e** solution.

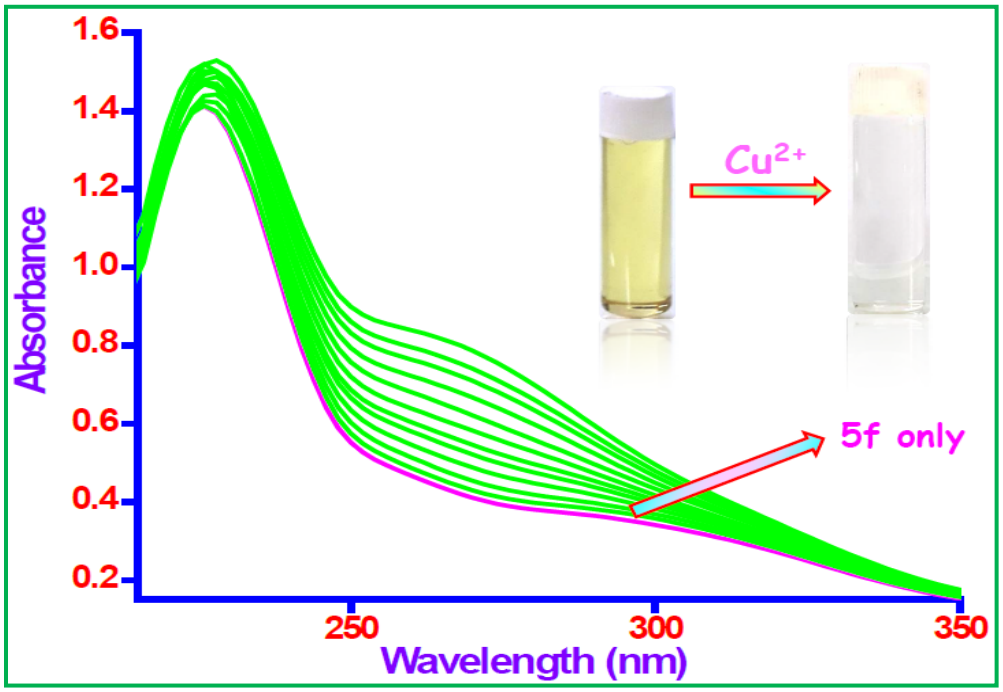

Figure S7. UV-vis spectra of **5f** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5f** solution.

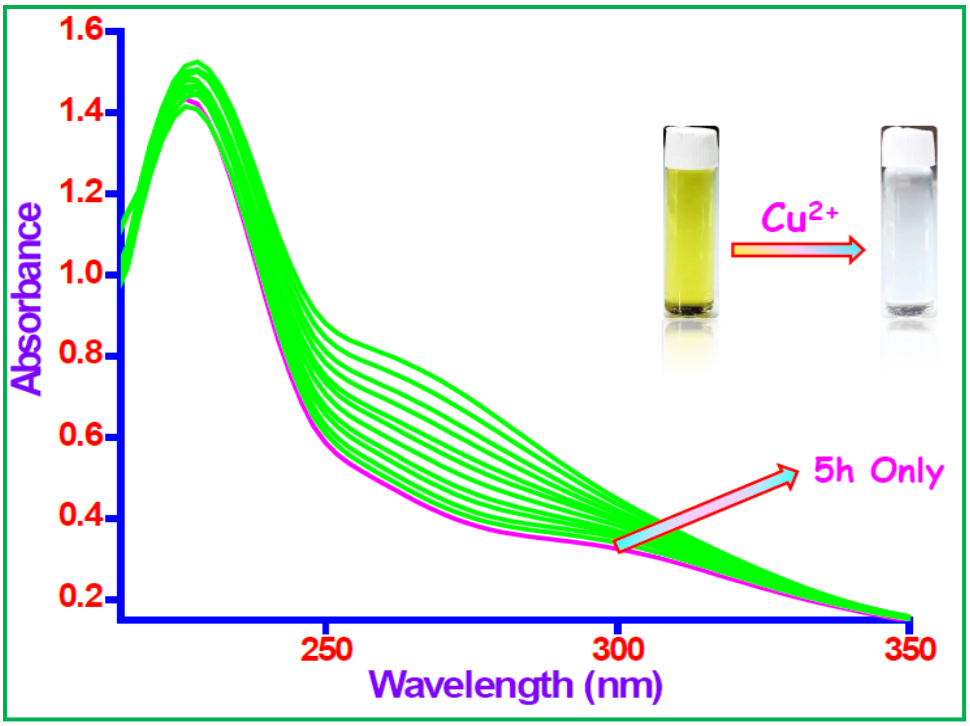

Figure S8. UV-vis spectra of **5h** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5h** solution.

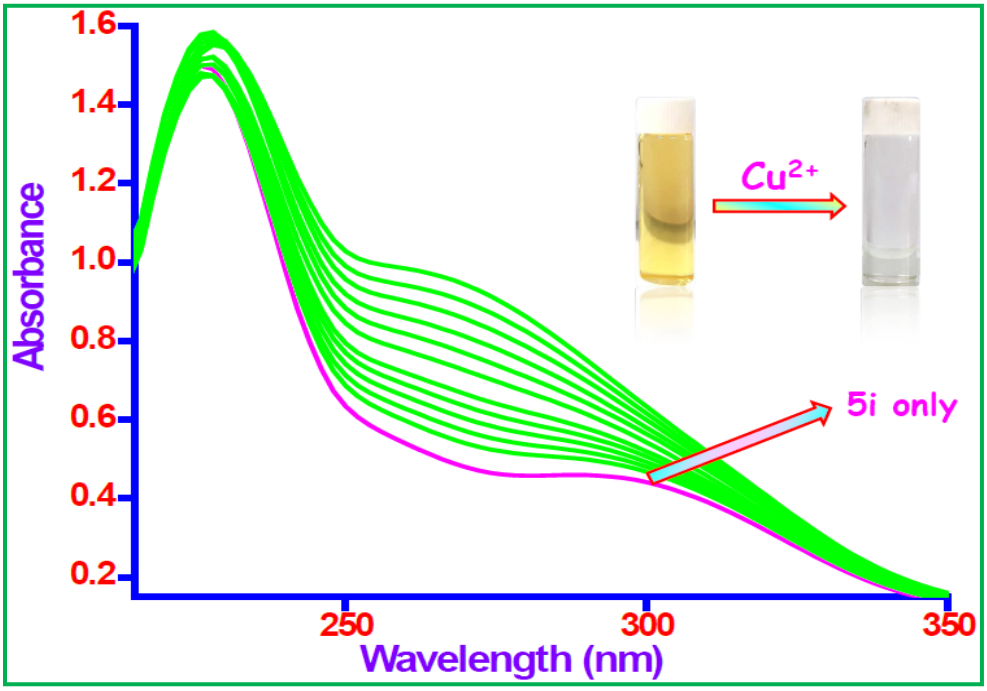

Figure S9. UV-vis spectra of **5i** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5i** solution.

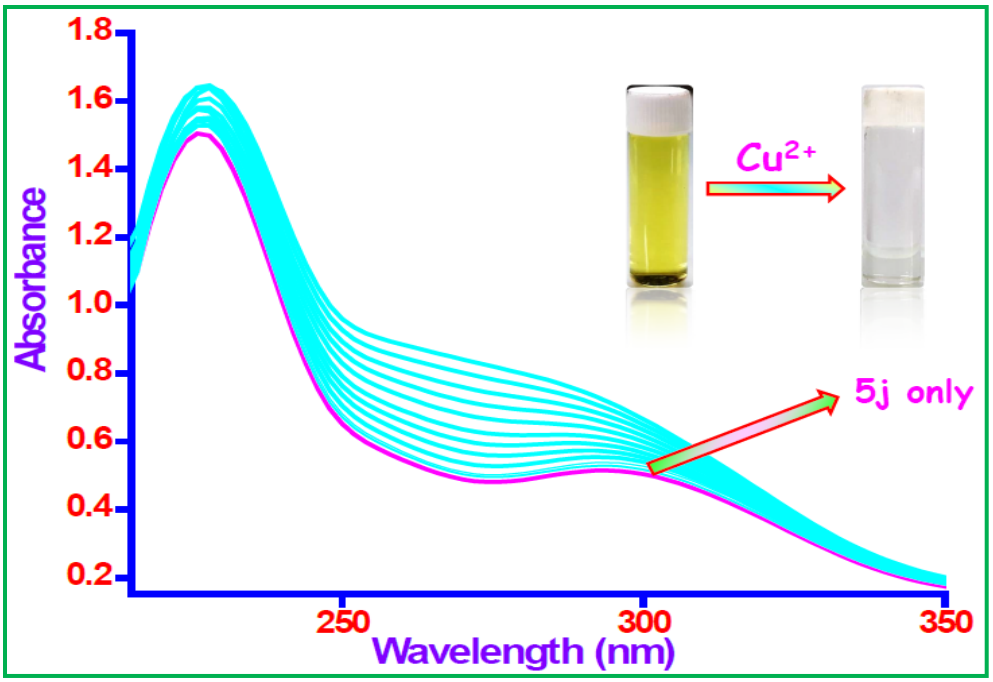

Figure S10. UV-vis spectra of **5j** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution solution in the presence of various concentrations of Cu^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5j** solution.

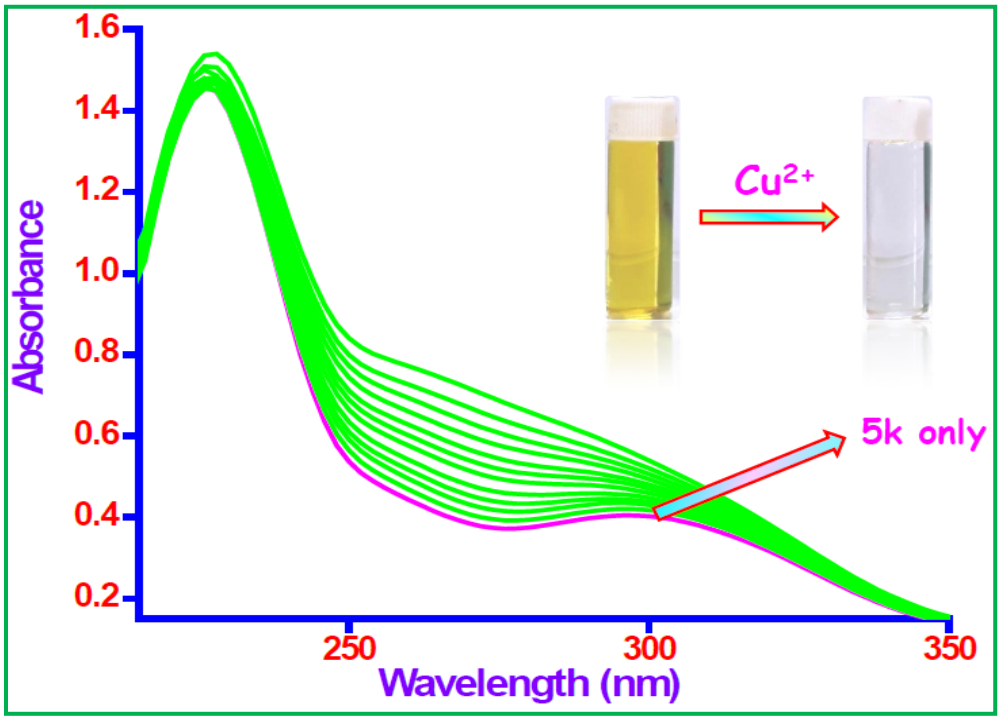

Figure S11. UV-vis spectra of **5k** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5k** solution.

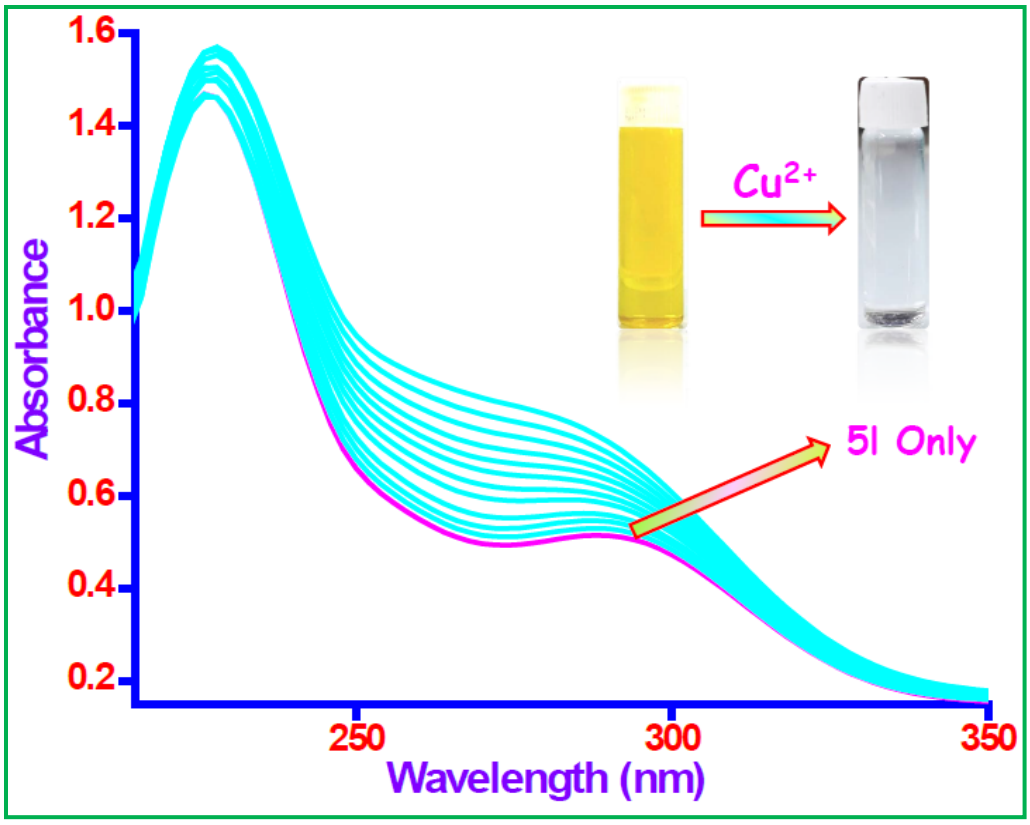

Figure S12. UV-vis spectra of **5l** (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) $\times10^{-6}$ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to **5l** solution.

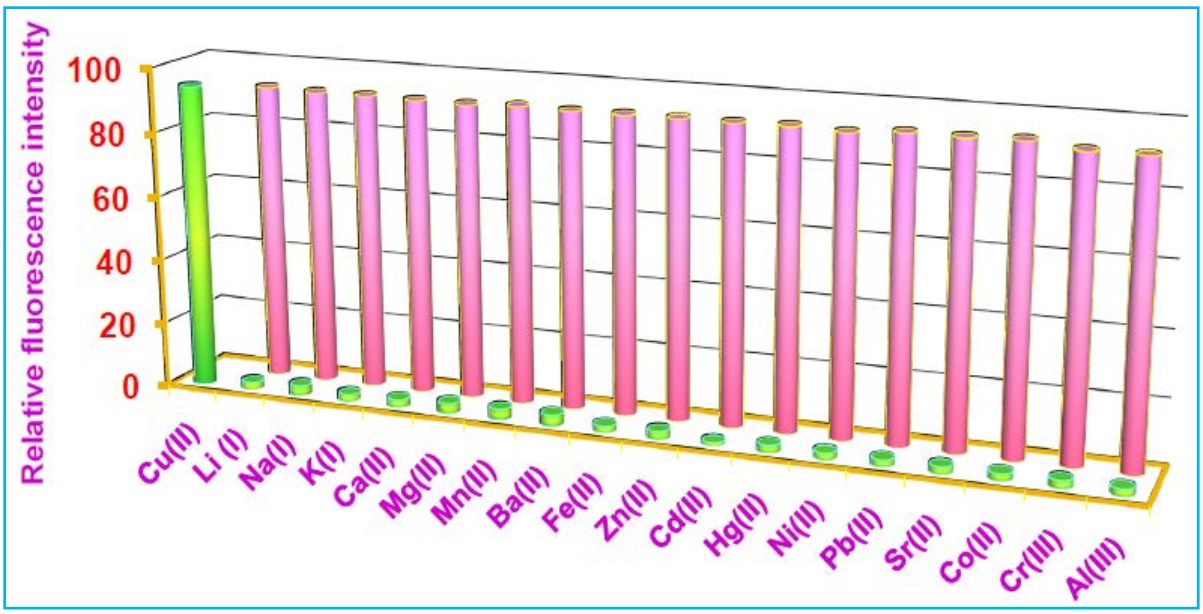

Figure S13. Fluorescence Quenching Efficiency (FQE), [{(F_0 − F)/F_0} × 100] of **5d** (5×10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of **5d** (5×10^{-6} M) with other metal ions (20×10^{-6} M) followed by the addition of Cu^{2+} (10×10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the red bar portion] (λ_{ex} = 375.7 nm, λ_{em} = 493.5 nm).

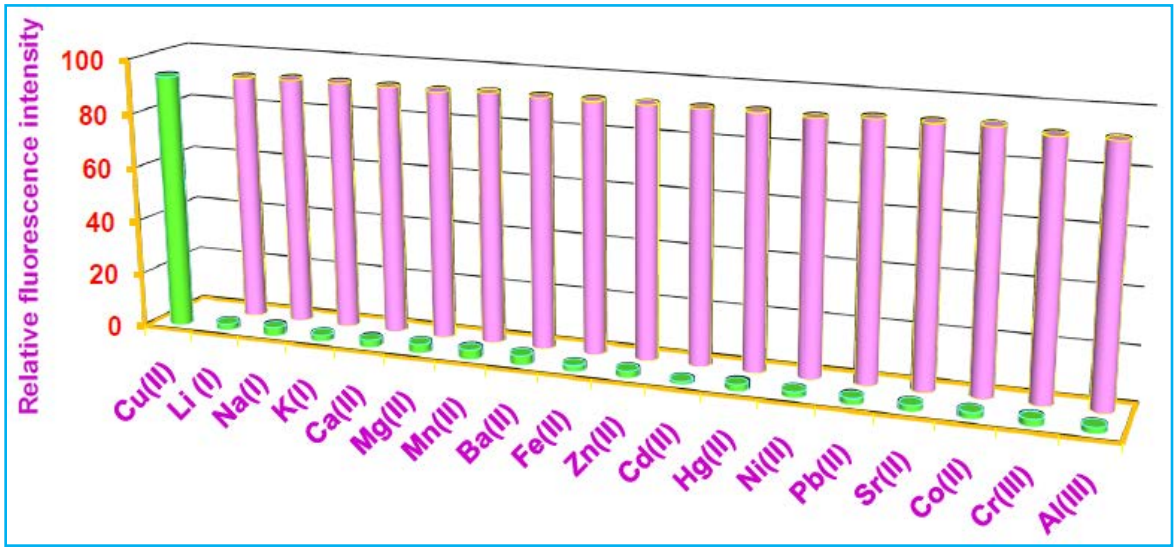

Figure S14. Fluorescence Quenching Efficiency (FQE), [{(F_0 − F)/F_0} × 100] of **5f** (5×10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of **5f** (5×10^{-6} M) with other metal ions (20×10^{-6} M) followed by the addition of Cu^{2+} (10×10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the pink bar portion] (λ_{ex} = 310.9 nm, λ_{em} = 491.7 nm).

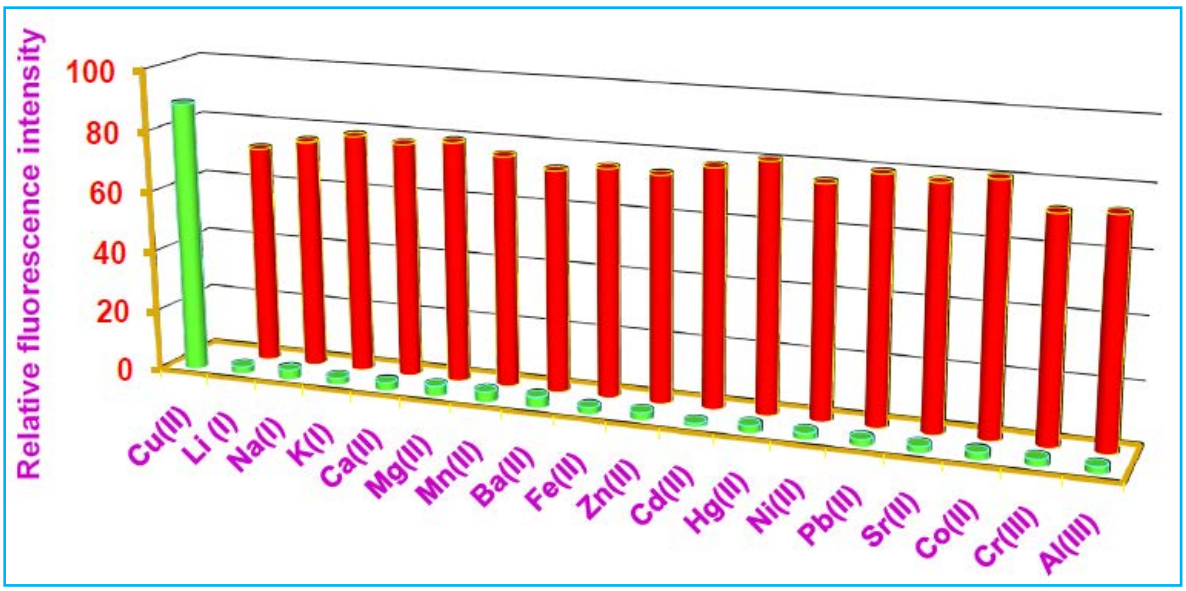

Figure S15. Fluorescence Quenching Efficiency (FQE), [{(F_0 − F)/F_0} × 100] of **5h** (5×10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of **5h** (5×10^{-6} M) with other metal ions (20×10^{-6} M) followed by the addition of Cu^{2+} (10×10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the red bar portion] (λ_{ex} = 308.5 nm, λ_{em} = 498.7 nm).

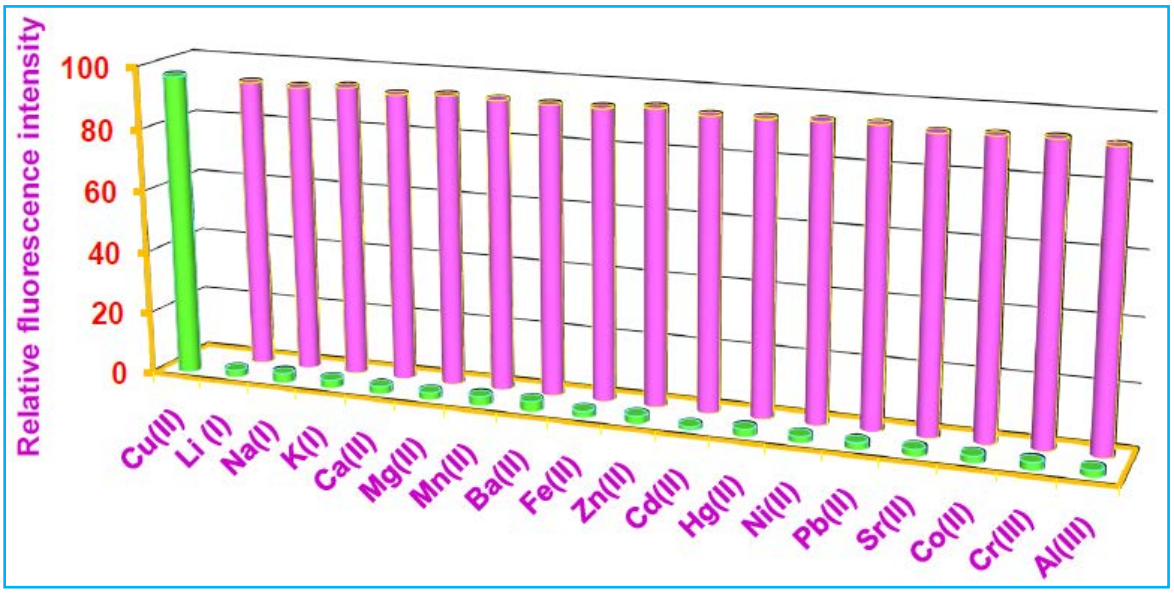

Figure S16. Fluorescence Quenching Efficiency (FQE), [{(F_0 − F)/F_0} × 100] of **5j** (5×10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of **5j** (5×10^{-6} M) with other metal ions (20×10^{-6} M) followed by the addition of Cu^{2+} (10×10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the pink bar portion] (λ_{ex} = 302.4 nm, λ_{em} = 497.8 nm).

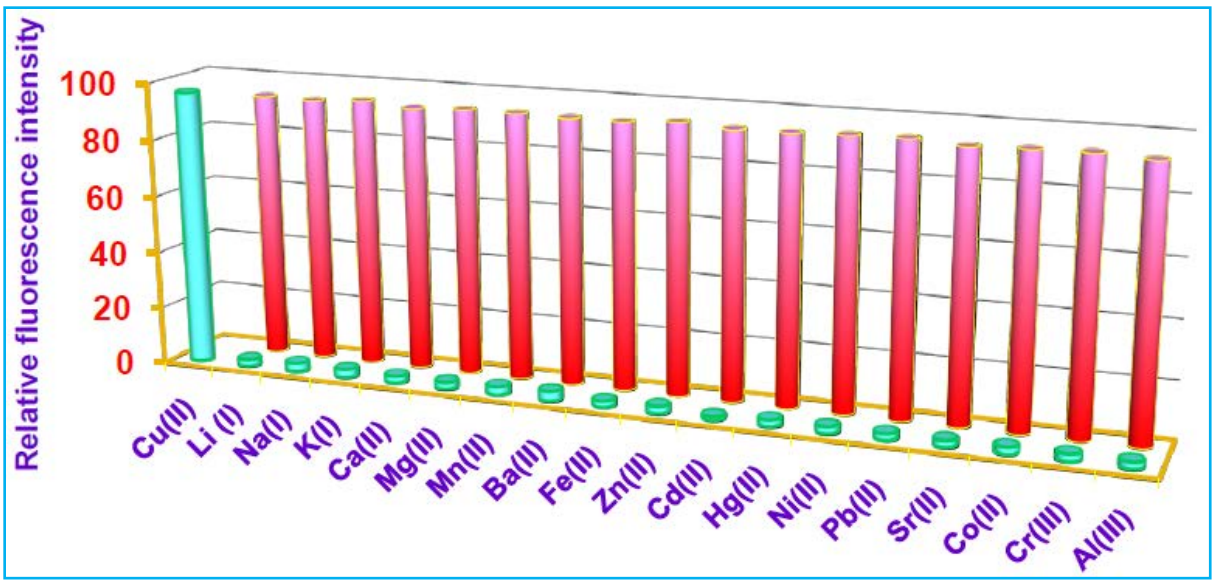

Figure S17. Fluorescence Quenching Efficiency (FQE), $[\{(F_0 - F)/F_0\} \times 100]$ of **5k** (5×10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the cyan bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of **5k** (5×10^{-6} M) with other metal ions (20×10^{-6} M) followed by the addition of Cu^{2+} (10×10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the red bar portion] (λ_{ex} = 312.5 nm, λ_{em} = 503.5 nm).

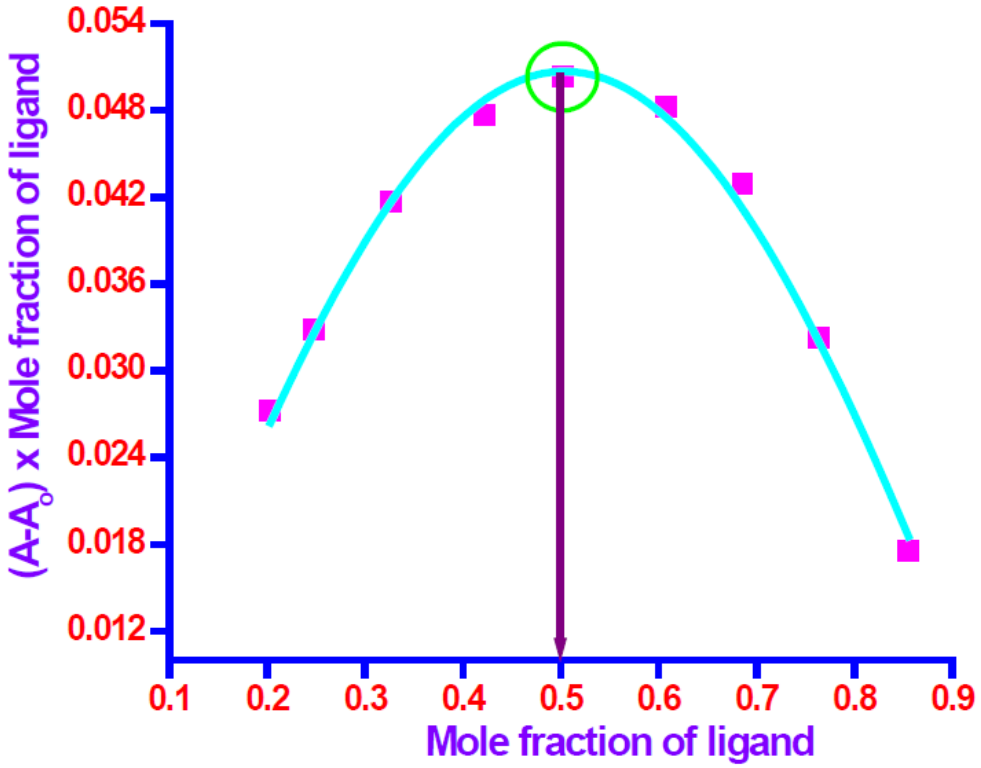

Figure S18. Job's plot for determination of stoichiometry of Cu^{2+}: **5a** complex in solution.

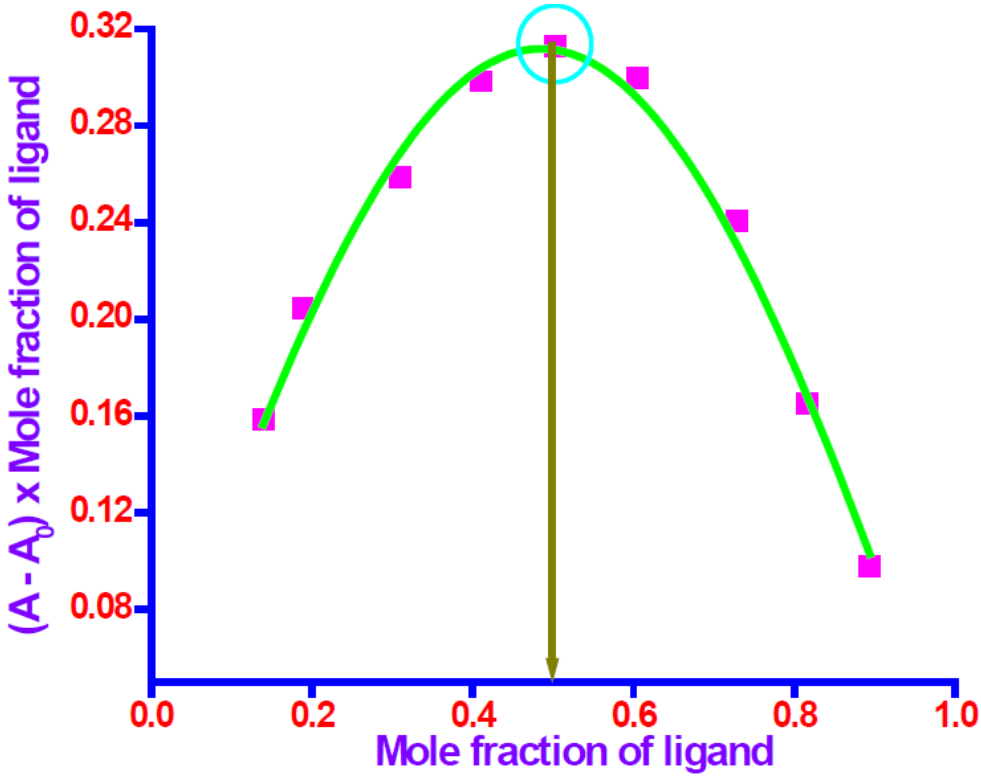

Figure S19. Job's plot for determination of stoichiometry of Cu^{2+} : **5b** complex in solution.

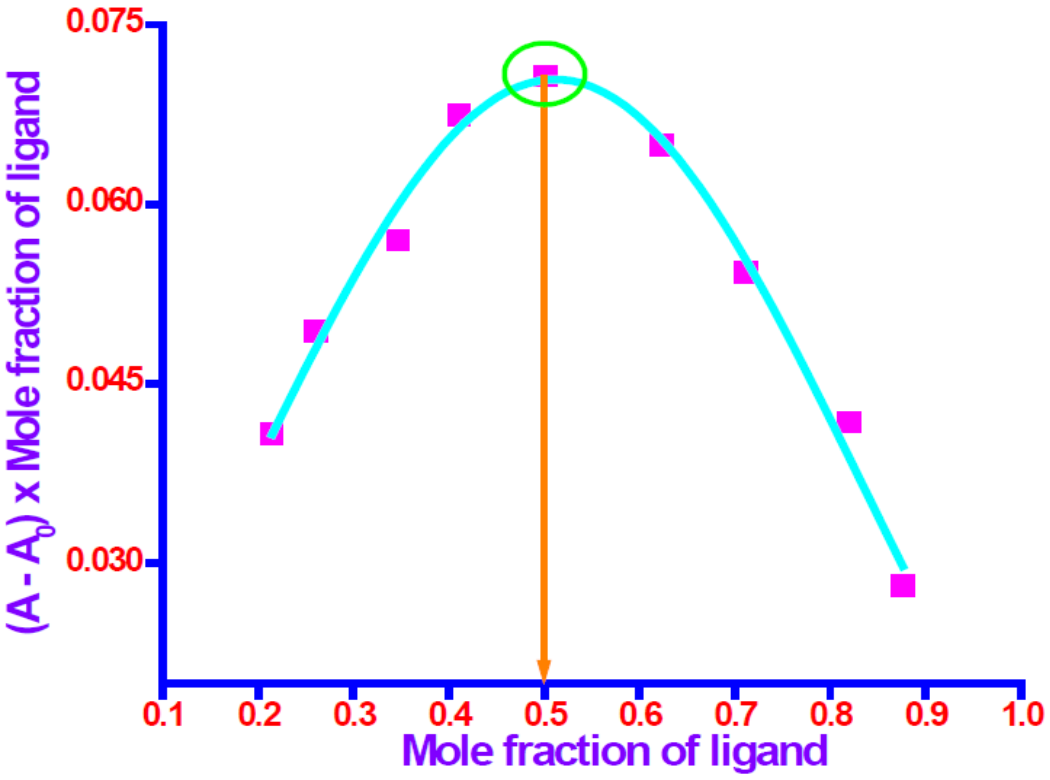

Figure S20. Job's plot for determination of stoichiometry of Cu^{2+} : **5c** complex in solution.

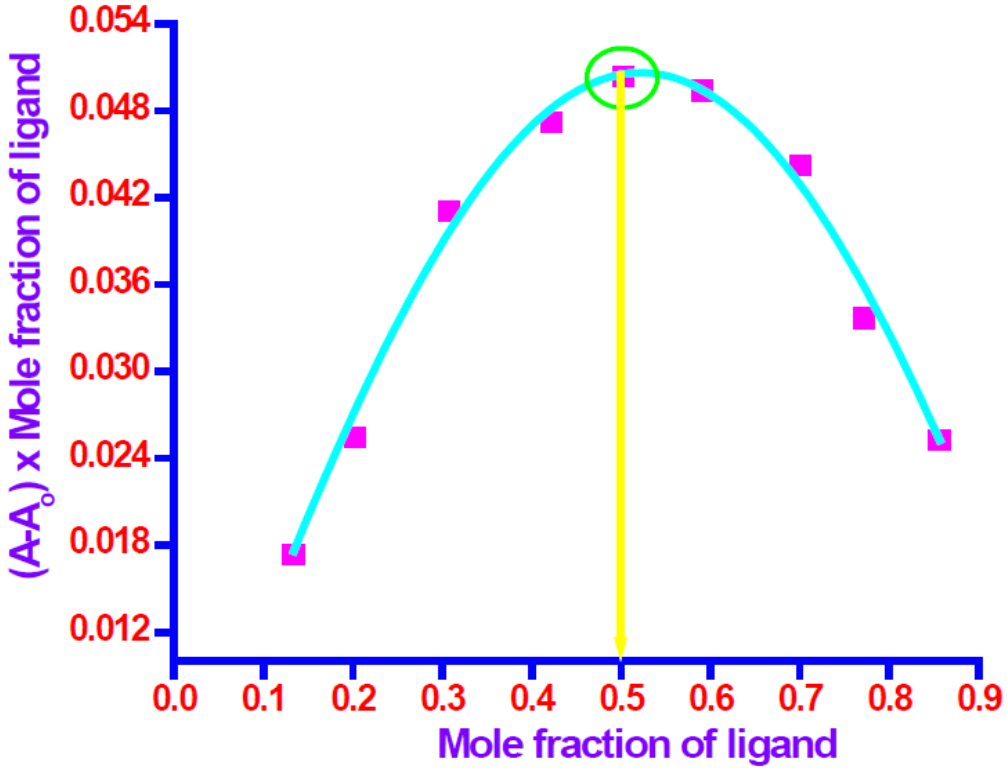

Figure S21. Job's plot for determination of stoichiometry of Cu^{2+} : **5d** complex in solution.

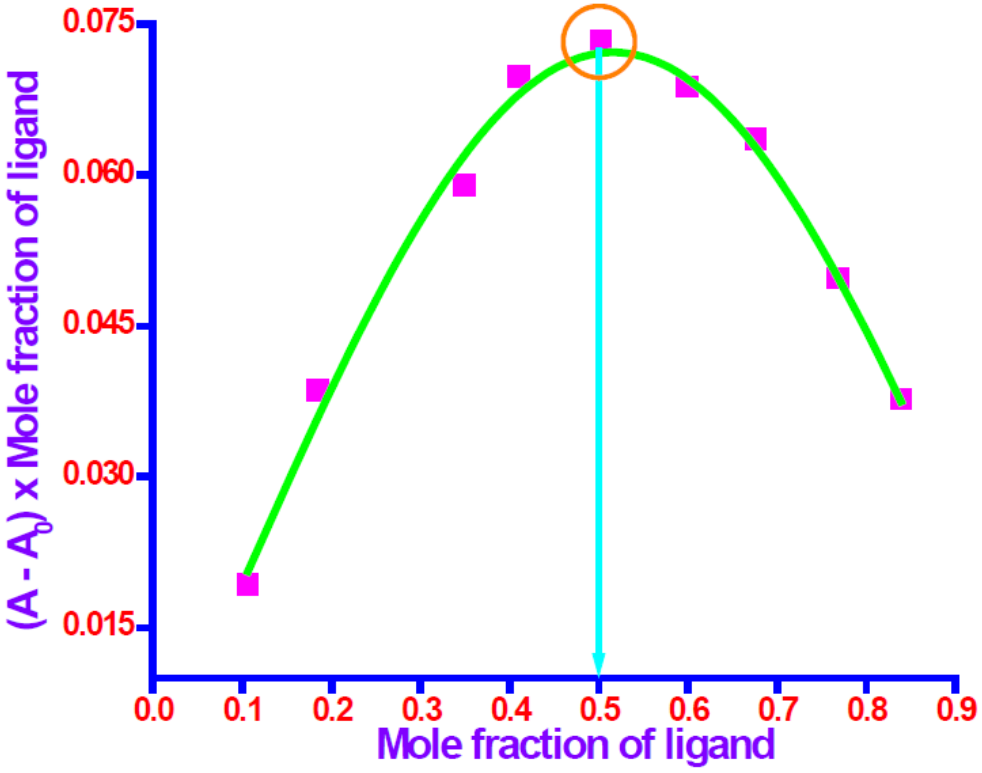

Figure S22. Job's plot for determination of stoichiometry of Cu^{2+} : **5e** complex in solution.

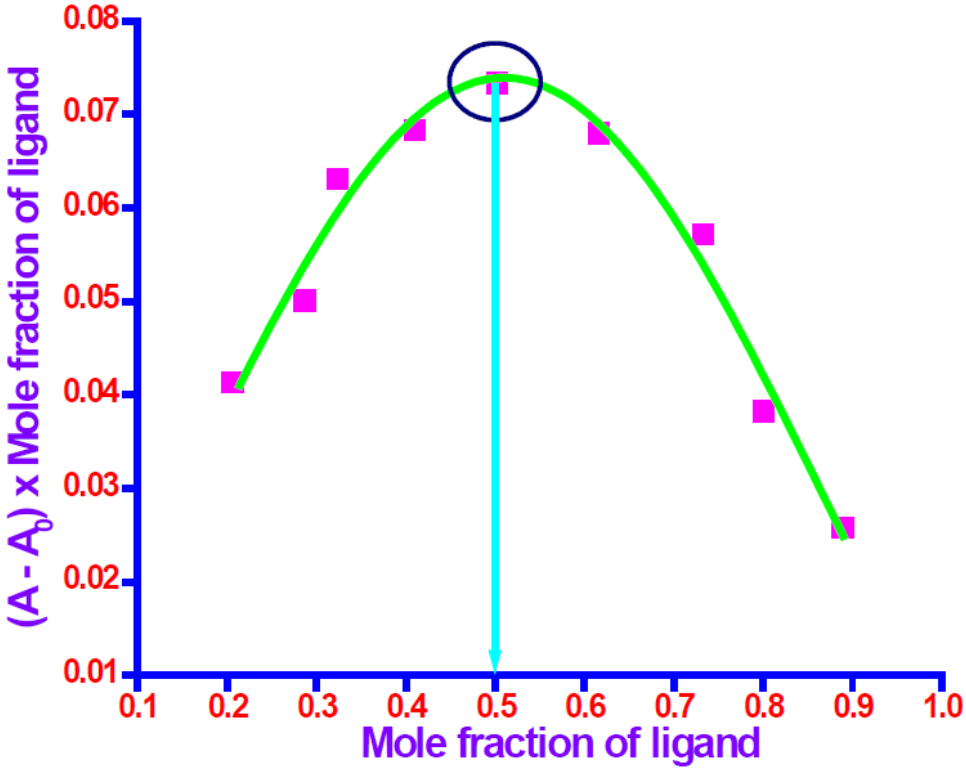

Figure S23. Job's plot for determination of stoichiometry of Cu^{2+} : **5f** complex in solution.

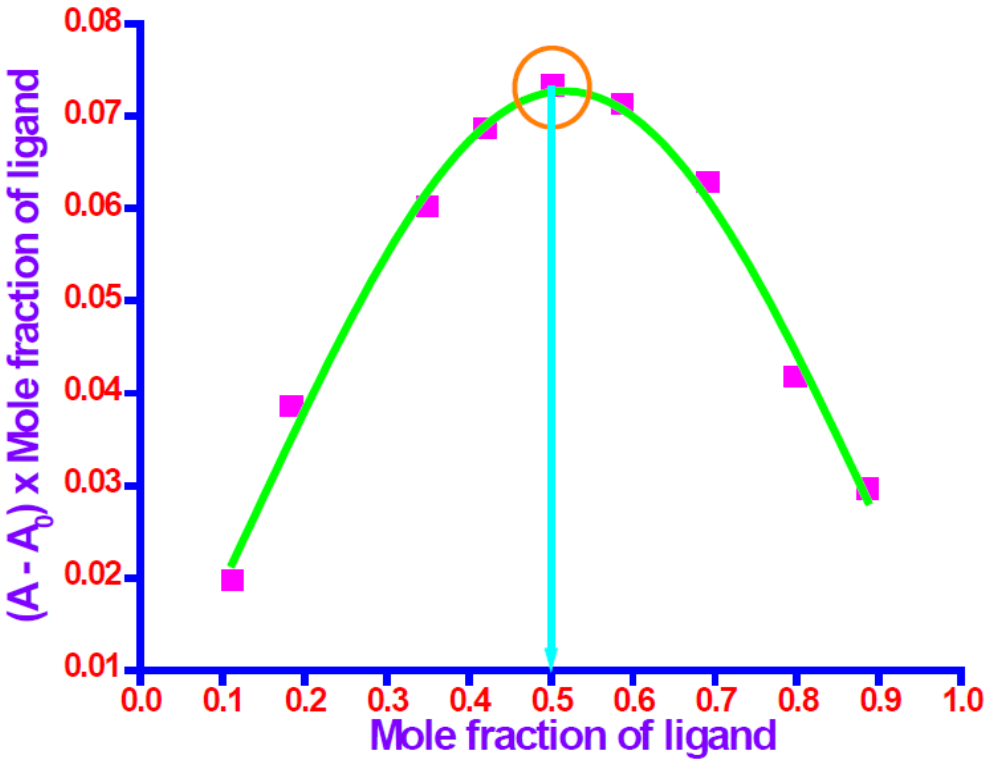

Figure S24. Job's plot for determination of stoichiometry of Cu^{2+} : **5h** complex in solution.

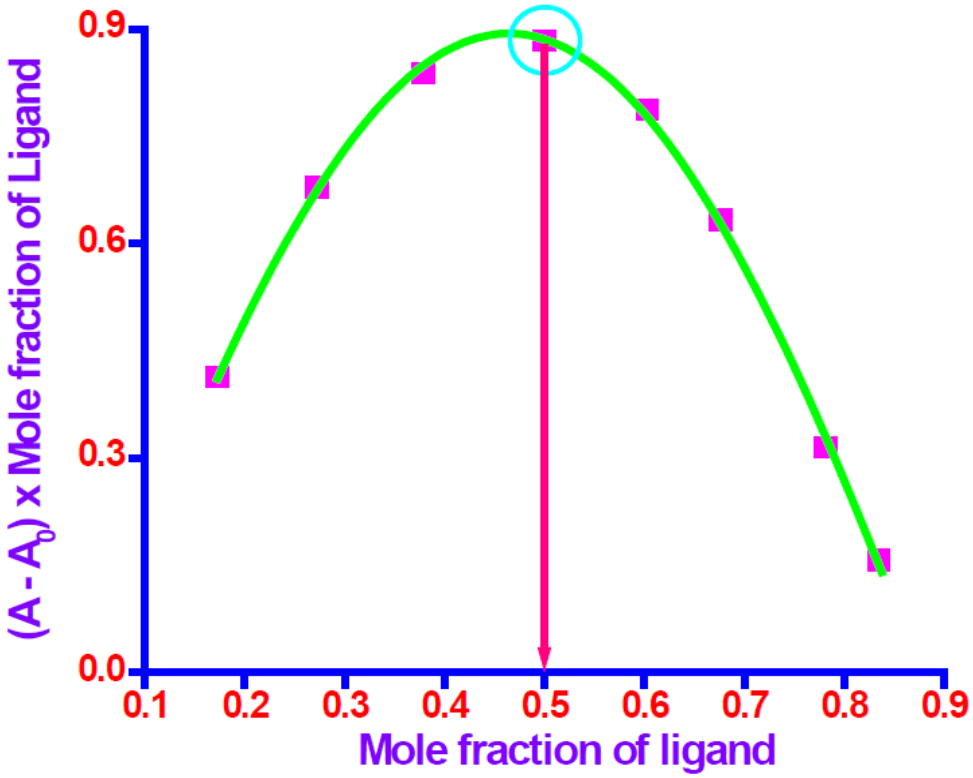

Figure S25. Job's plot for determination of stoichiometry of Cu^{2+} : **5i** complex in solution.

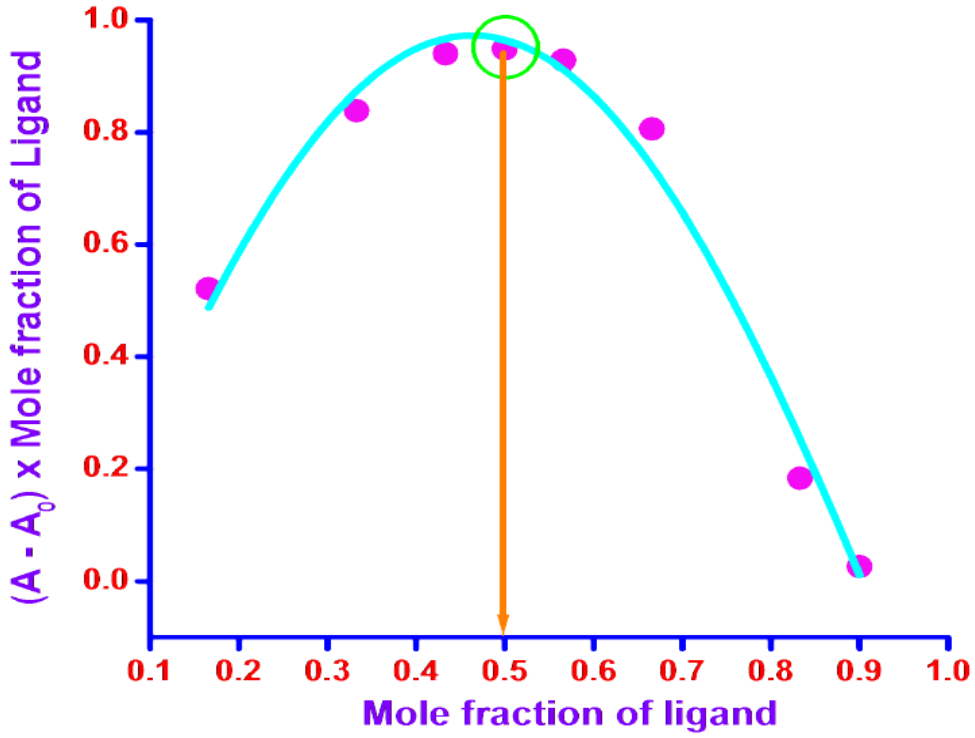

Figure S26. Job′s plot for determination of stoichiometry of Cu^{2+} : **5j** complex in solution.

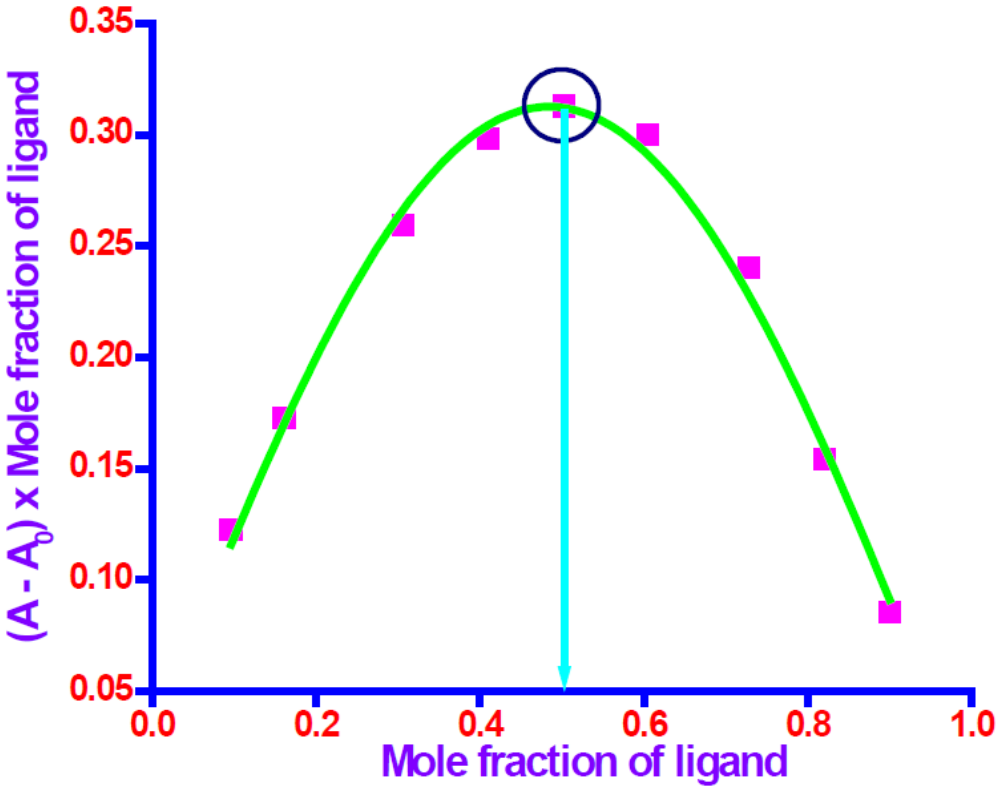

Figure S27. Job′s plot for determination of stoichiometry of Cu^{2+} : **5k** complex in solution.

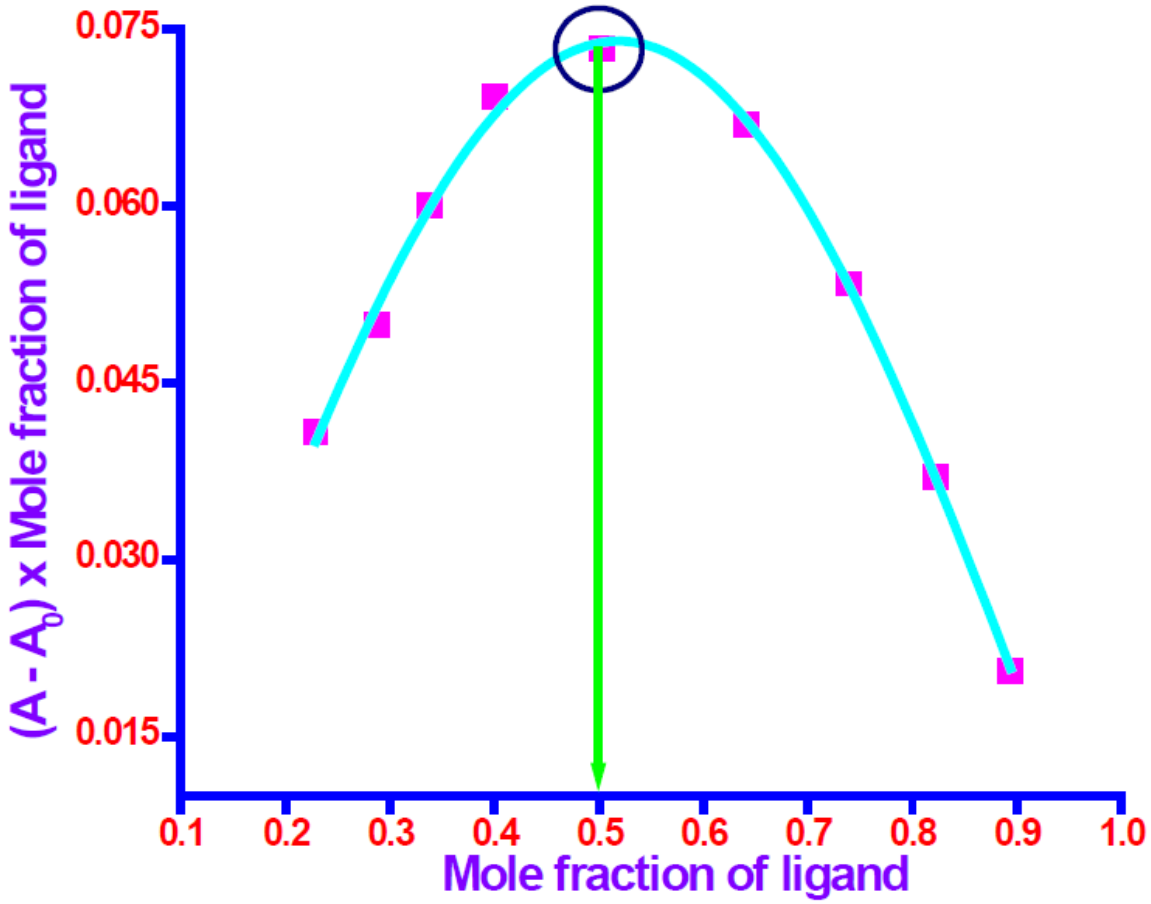

Figure S28. Job's plot for determination of stoichiometry of Cu^{2+} : **5l** complex in solution.

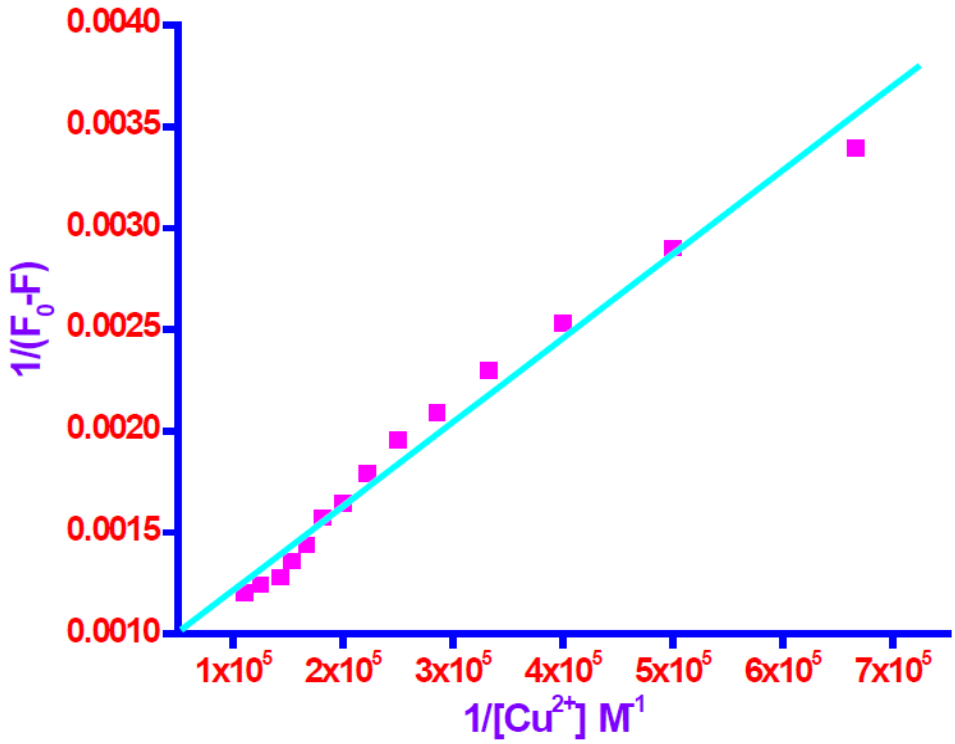

Figure S29. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/[Cu^{2+}]$ for complexation between **5d** and Cu^{2+} derived from emission titration curve.

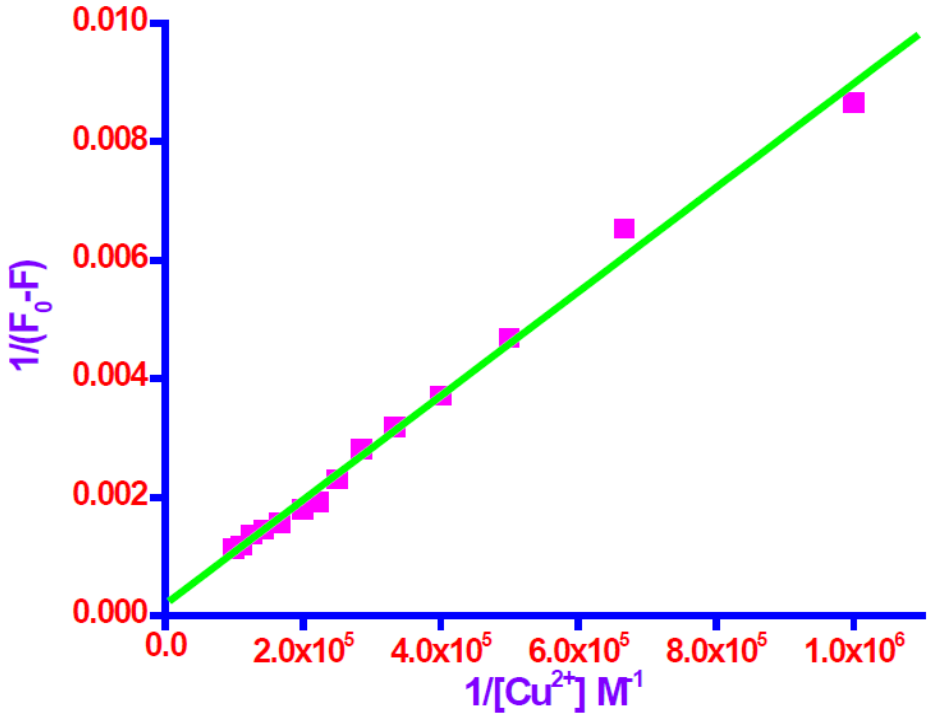

Figure S30. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/[Cu^{2+}]$ for complexation between **5f** and Cu^{2+} derived from emission titration curve.

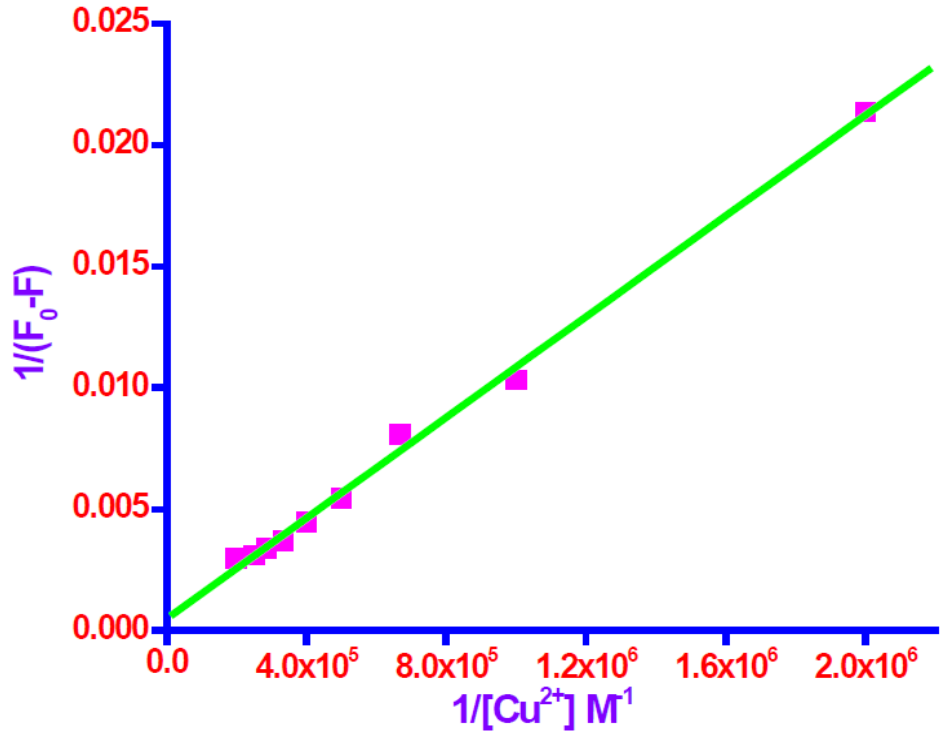

Figure S31. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/[Cu^{2+}]$ for complexation between **5h** and Cu^{2+} derived from emission titration curve.

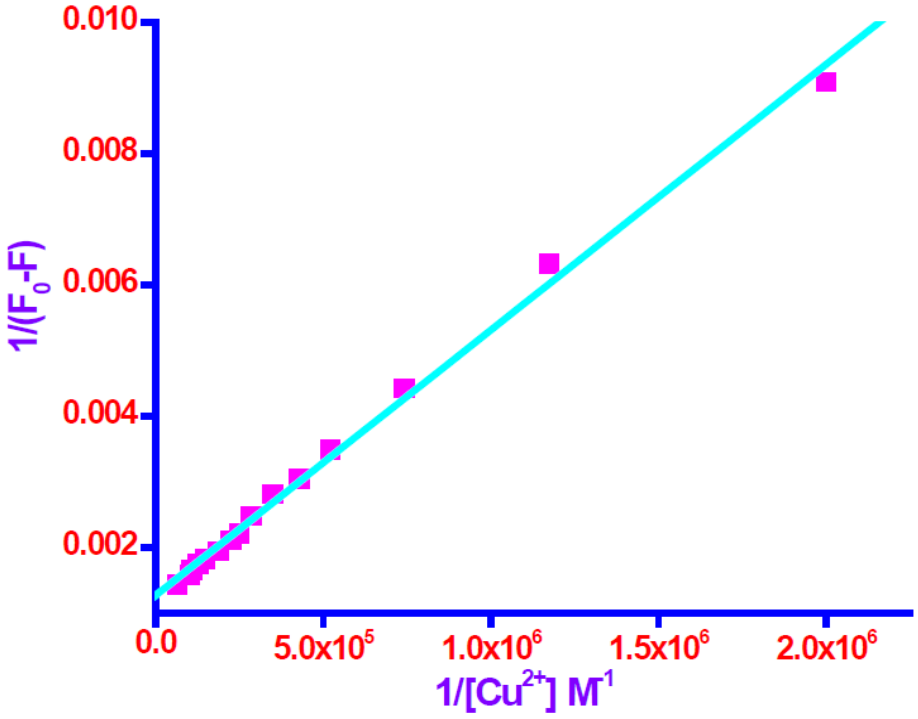

Figure S32. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/[Cu^{2+}]$ for complexation between **5j** and Cu^{2+} derived from emission titration curve.

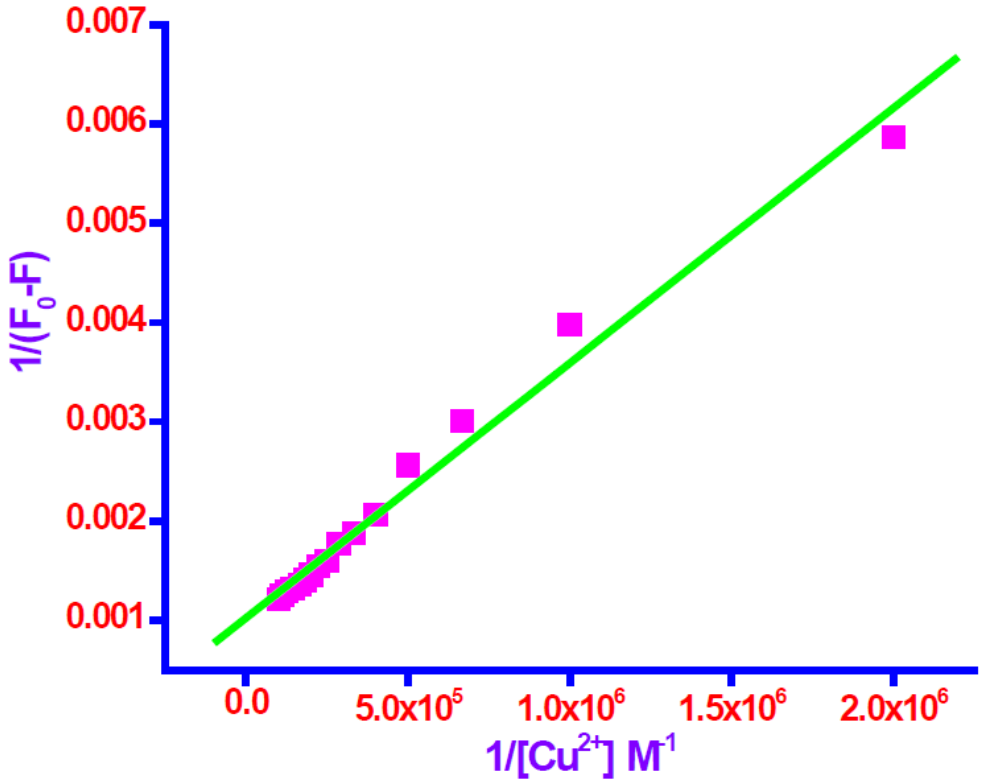

Figure S33. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/[Cu^{2+}]$ for complexation between **5k** and Cu^{2+} derived from emission titration curve.

Detection limit calculation in emission spectroscopy:

The limit of detection (LOD) of compounds (**5d**, **5f**, **5h**, **5j**, **5k**) with Cu^{2+} was measured on the basis of fluorescence titration measurement. The detection limit was calculated using the following equation:

$$DL = K \times \frac{\sigma}{S}$$

where K = 2 or 3 (we take 3 in this case), 'σ' is the standard deviation of the blank solution and 'S' is the slope between the ratio of emission intensity *versus* [Cu^{2+}].

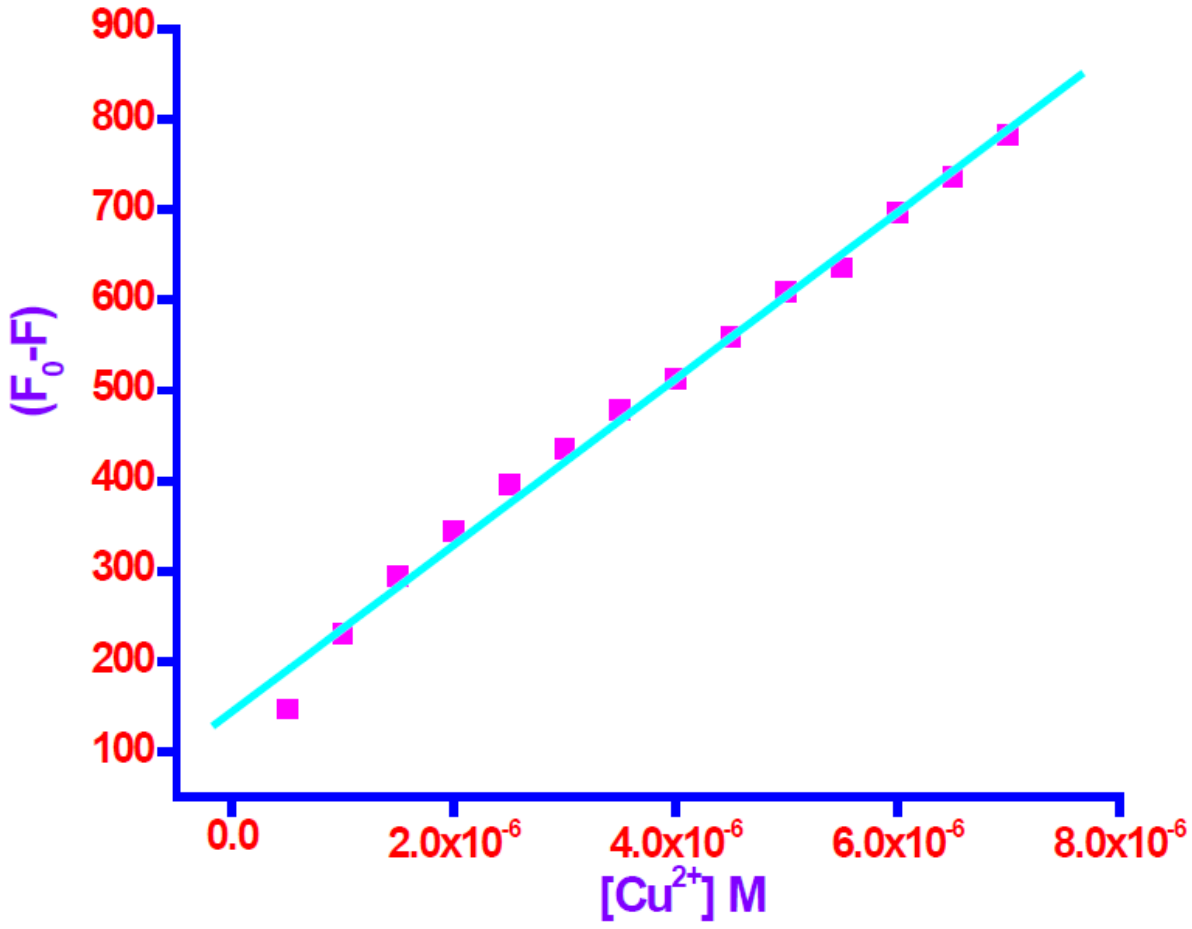

Figure S34. The limit of detection (LOD) of **5d** for Cu^{2+} as a function of [Cu^{2+}].

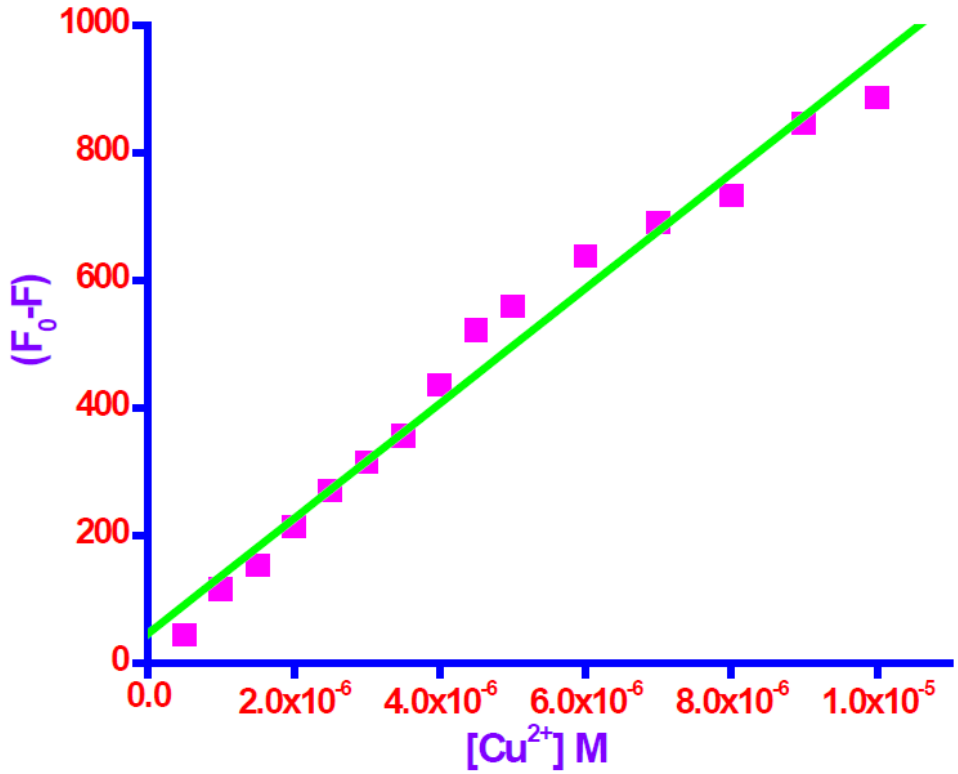

Figure S35. The limit of detection (LOD) of **5f** for Cu^{2+} as a function of [Cu^{2+}].

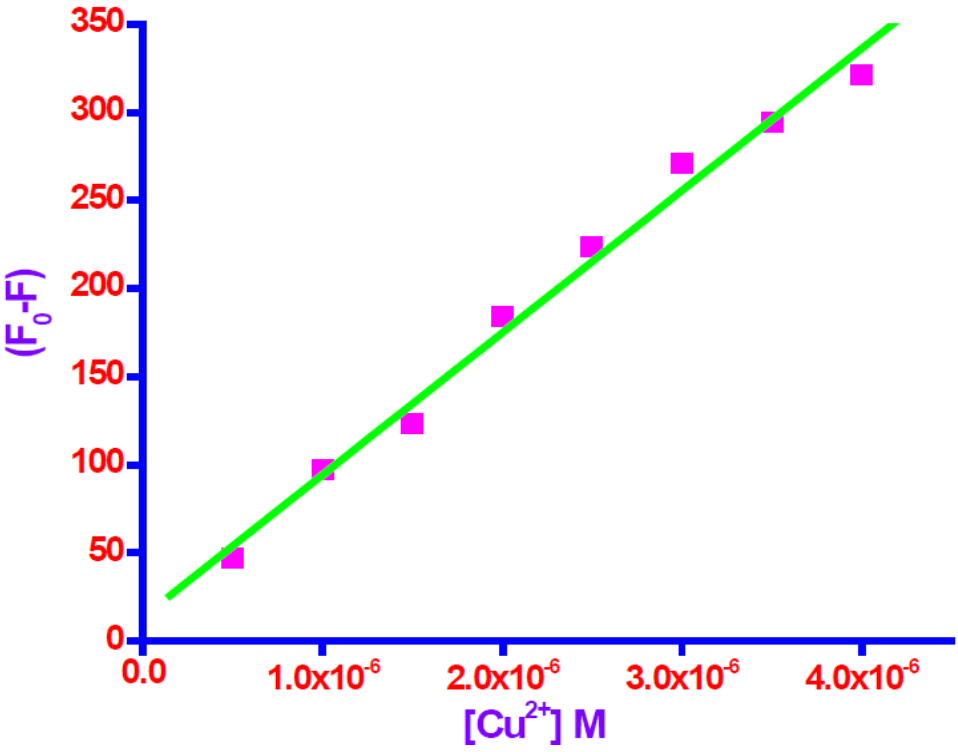

Figure S36. The limit of detection (LOD) of **5h** for Cu^{2+} as a function of [Cu^{2+}].

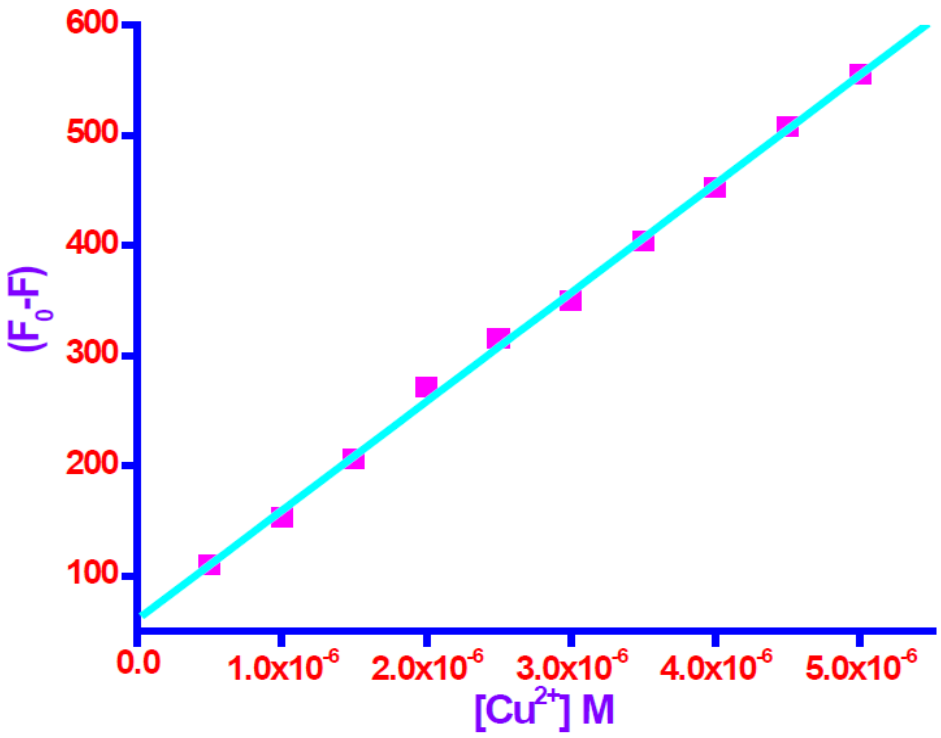

Figure S37. The limit of detection (LOD) of **5j** for Cu^{2+} as a function of $[Cu^{2+}]$.

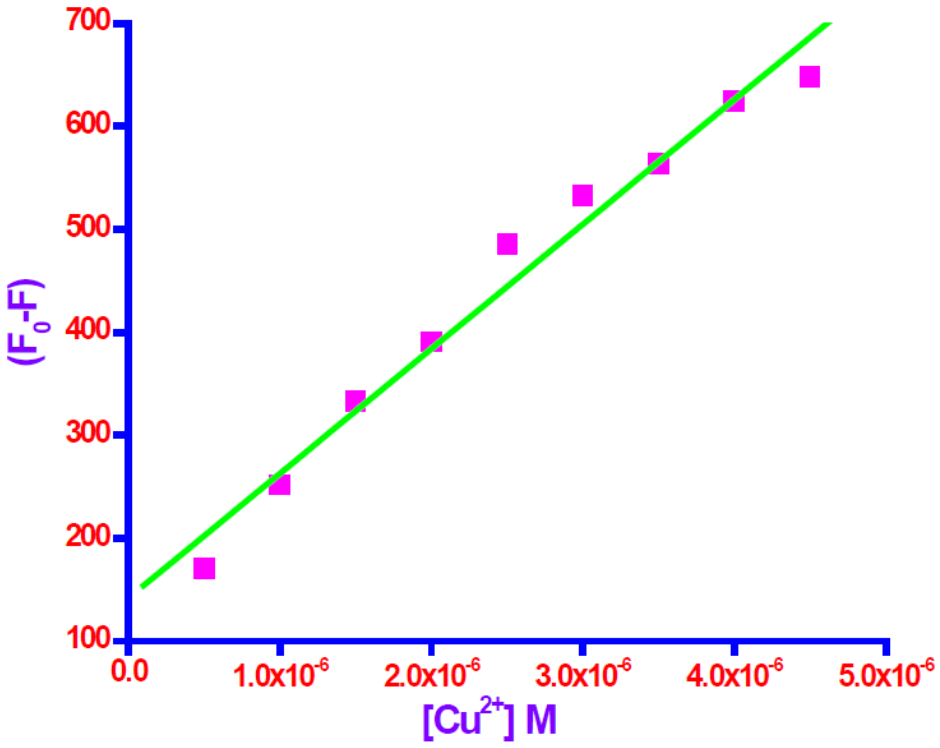

Figure S38. The limit of detection (LOD) of **5k** for Cu^{2+} as a function of $[Cu^{2+}]$.

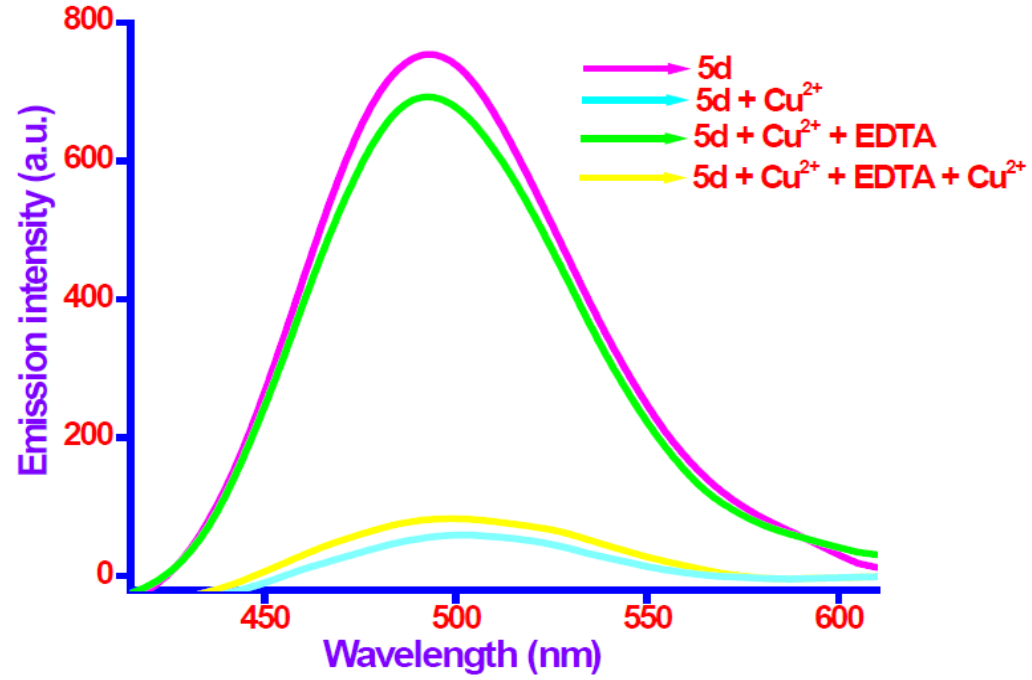

Figure S39. Fluorescence emission spectra of chemosensor (**5d**) in the presence of Cu^{2+} ion followed by addition of EDTA.

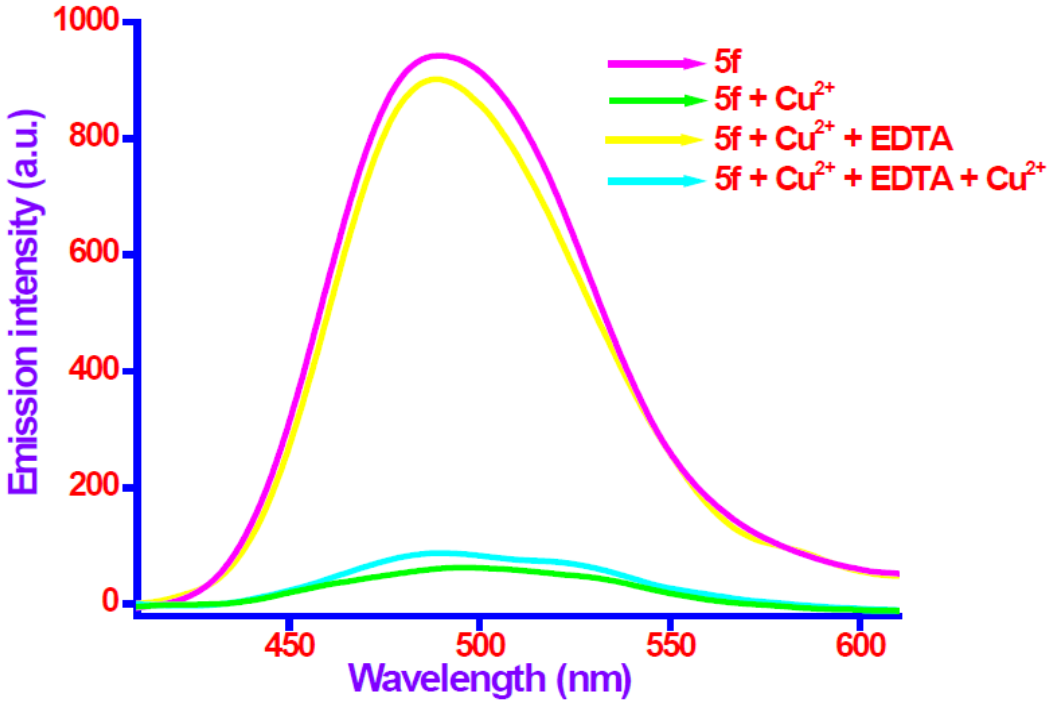

Figure S40. Fluorescence emission spectra of chemosensor (**5f**) in the presence of Cu^{2+} ion followed by addition of EDTA.

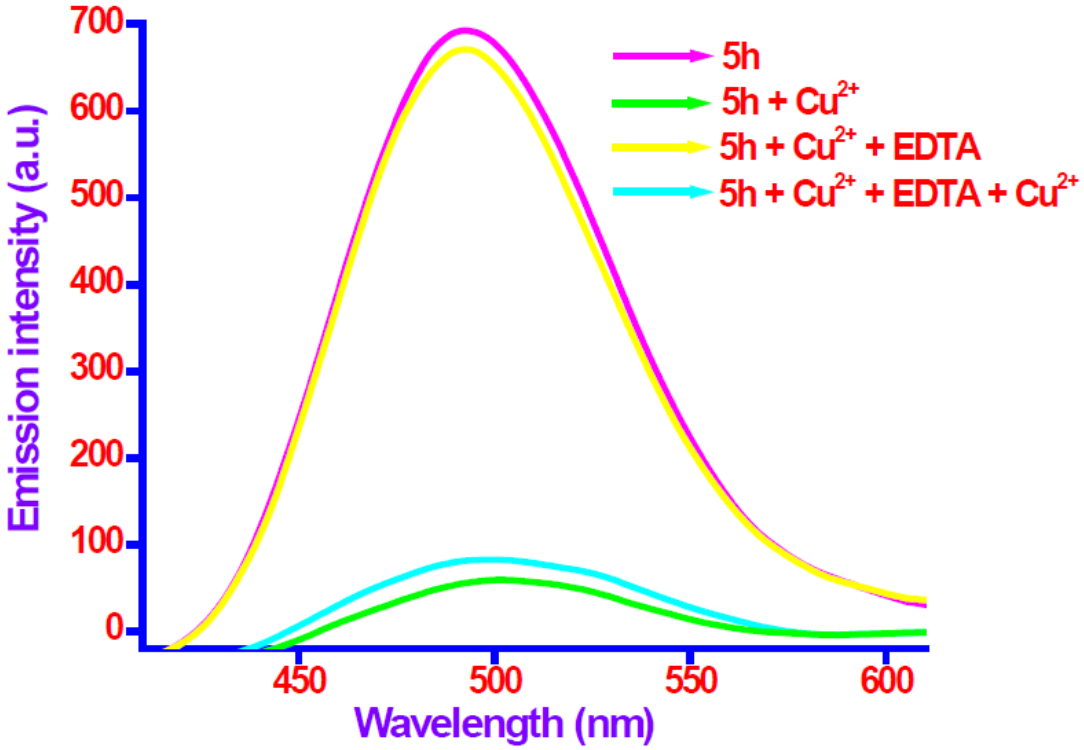

Figure S41. Fluorescence emission spectra of chemosensor (**5h**) in the presence of Cu^{2+} ion followed by addition of EDTA.

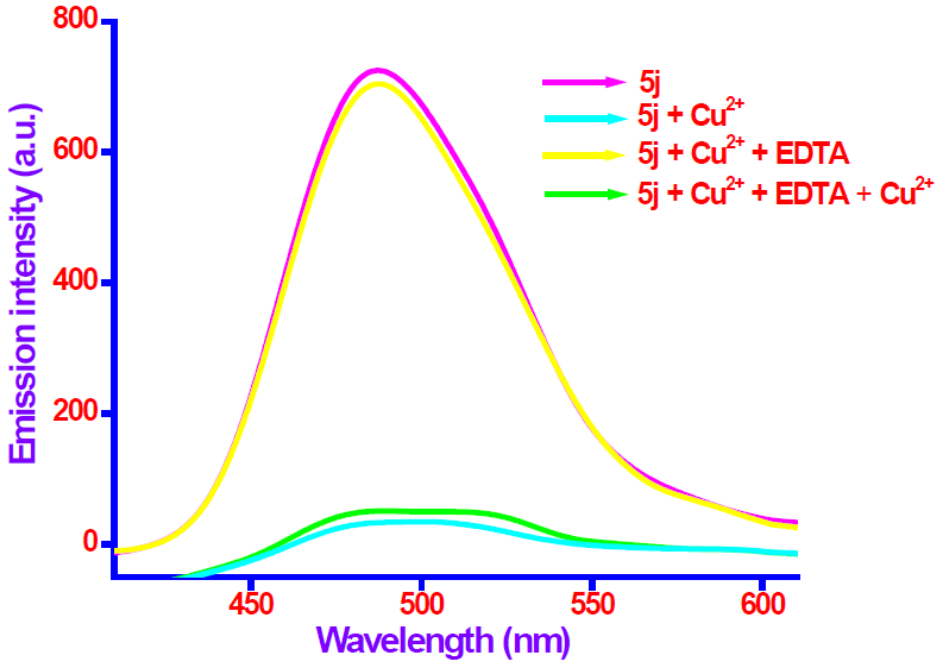

Figure S42. Fluorescence emission spectra of chemosensor (**5j**) in the presence of Cu^{2+} ion followed by addition of EDTA.

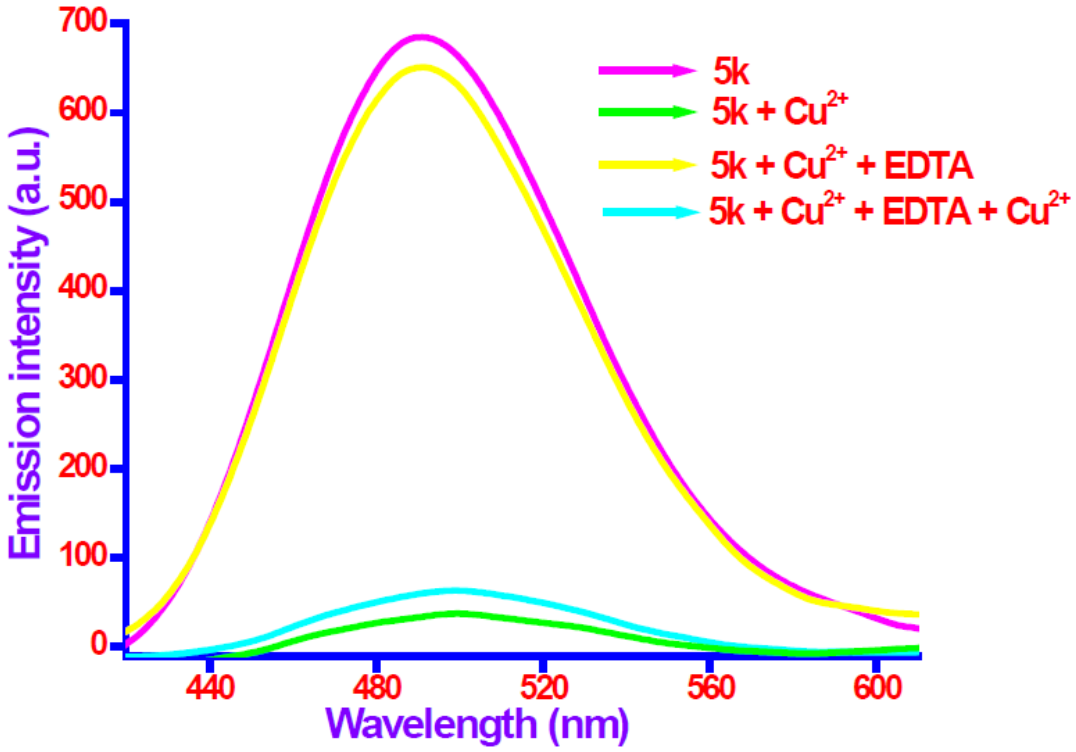

Figure S43. Fluorescence emission spectra of chemosensor (**5k**) in the presence of Cu^{2+} ion followed by addition of EDTA.

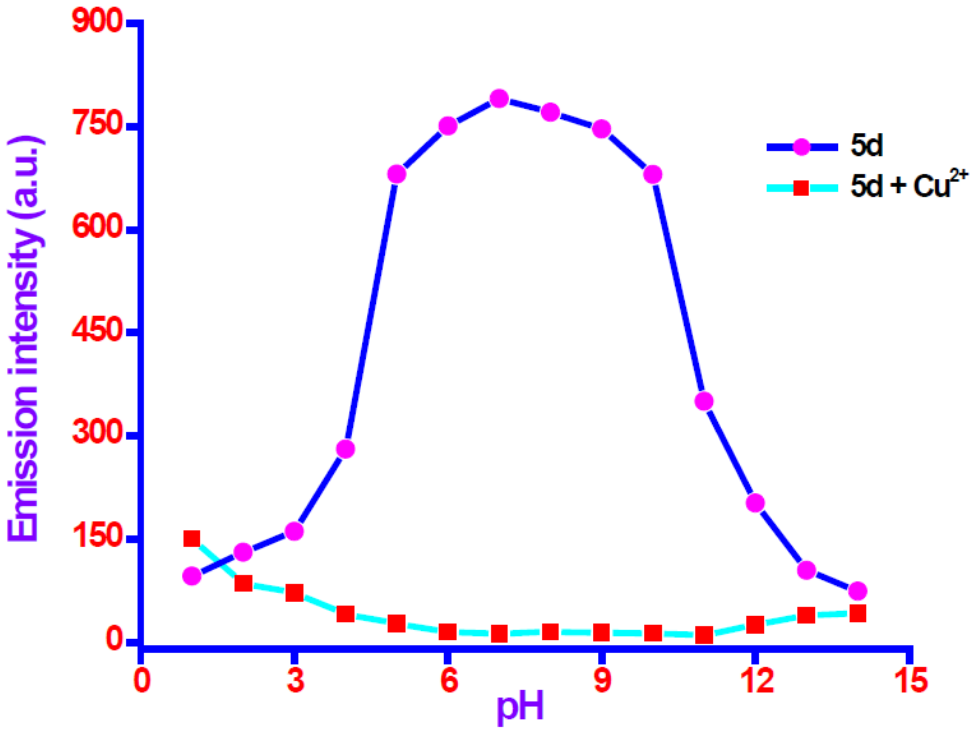

Figure S44. Emission intensity of **5d** (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 493.5 nm.

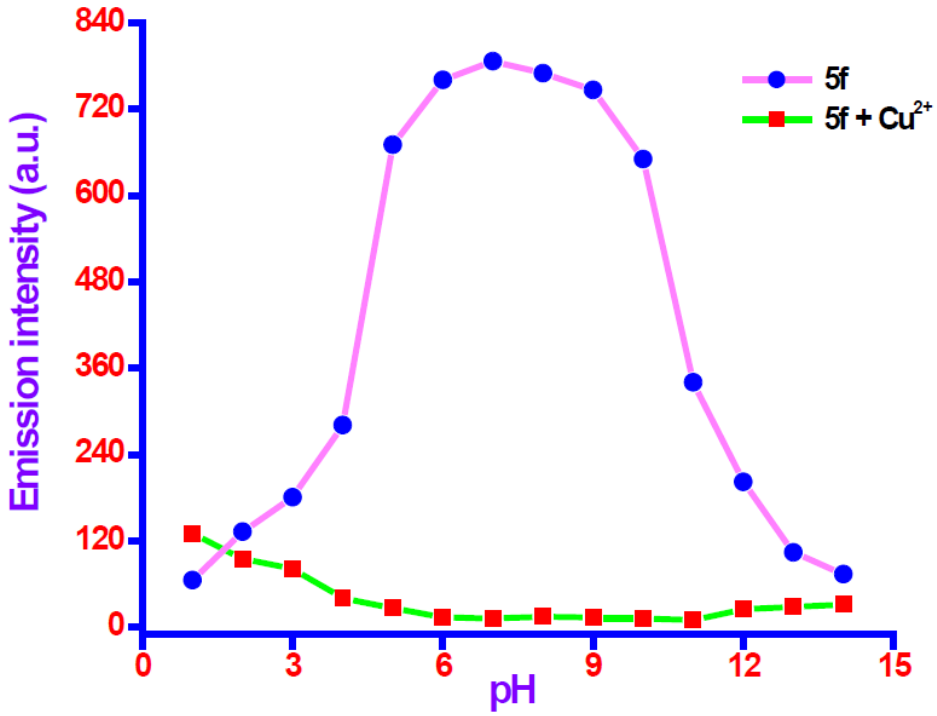

Figure S45. Emission intensity of **5f** (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 491.7 nm.

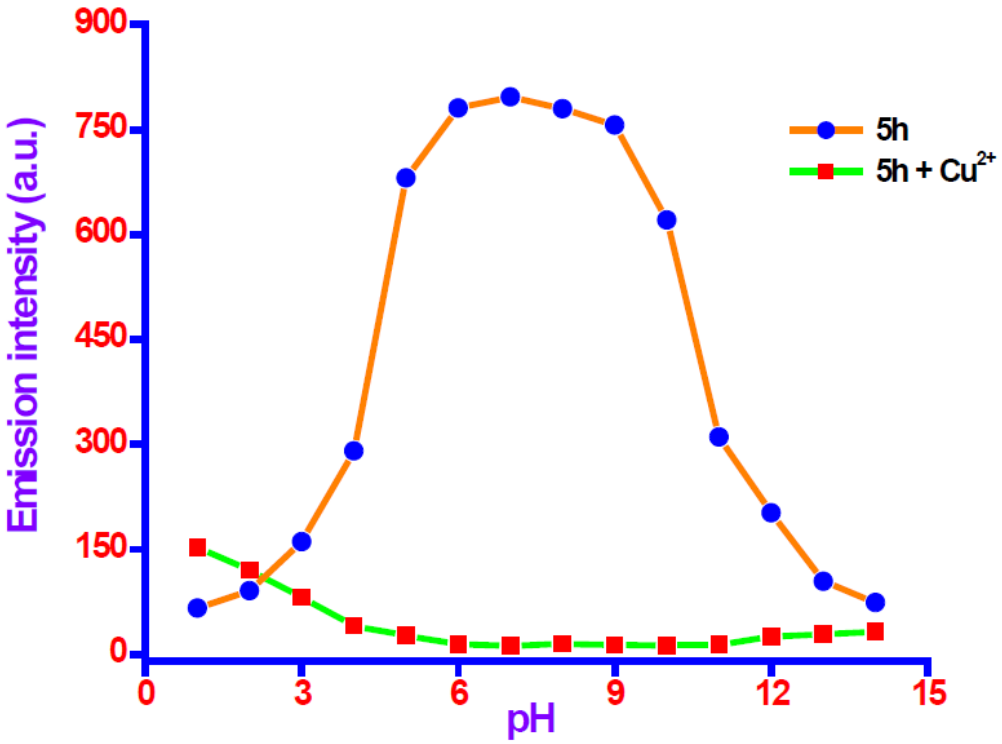

Figure S46. Emission intensity of **5h** (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 498.7 nm.

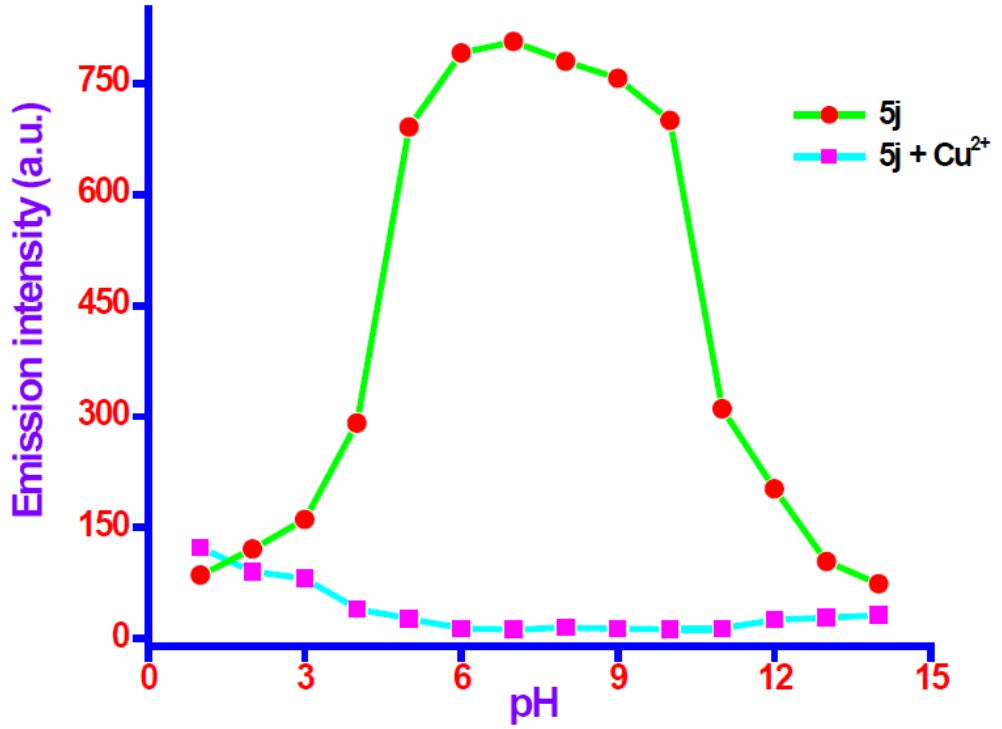

Figure S47. Emission intensity of **5j** (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 497.8 nm.

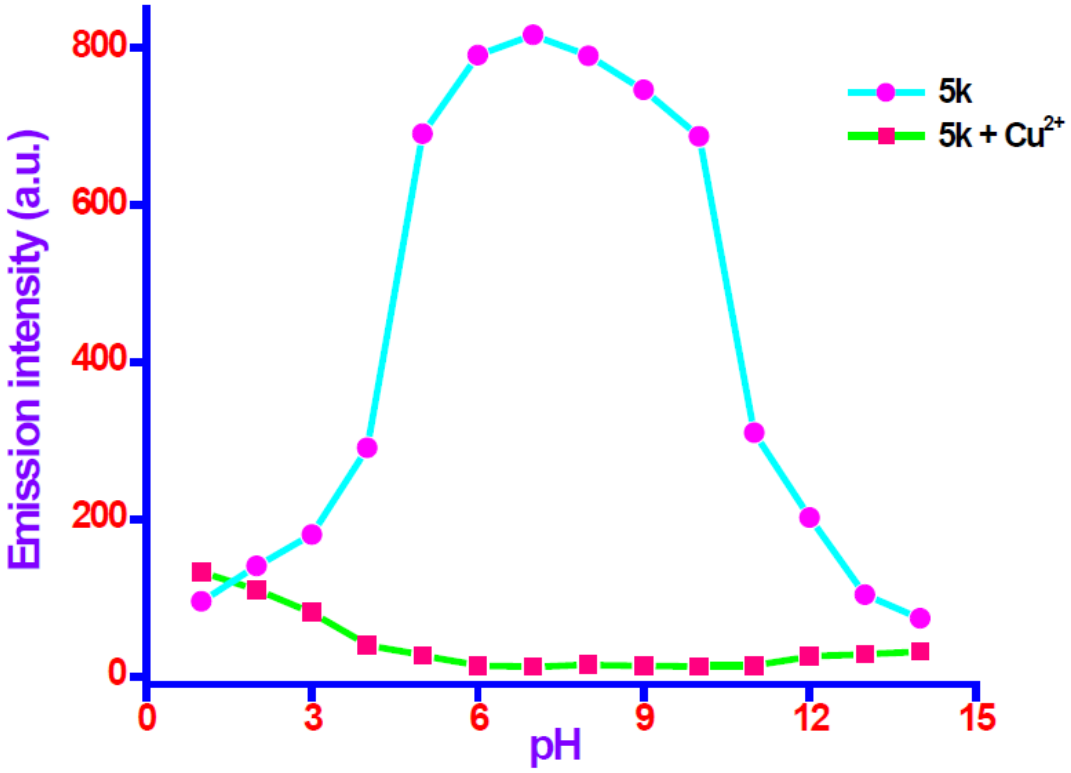

Figure S48. Emission intensity of **5k** (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 503.5 nm.