

Supporting Information

for

Reduction of copper (II) complexes of tridentate ligand by nitric oxide and fluorescent detection of NO in methanol and water media

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Synthesis of **L**₁ and **L**₂

The ligands **L**₁ and **L**₂ were reported earlier¹⁻⁶ and have been prepared through a modified general procedure. The details are given for **L**₁.

Pyridine-2-ethylamine (1.22 g, 10 mmol) and 1-methyl-2-imidazolecarboxaldehyde (1.10 g, 10 mmol) were taken into a 50 ml round bottom flask equipped with a stirring bar. Methanol (20 ml) was added to this and heated to reflux for 4 hours (scheme 1). The resulting yellow solution was dried under reduced pressure and the dark yellow oil thus obtained was subjected to chromatographic purification using silica gel column to yield the pure Schiff base, **L**₁' as yellow oil (yield, 65%, 1.39 g). The Schiff base was then dissolved in methanol (10 ml) and subjected to reduction with 2.5 equivalents of NaBH₄. After complete addition of NaBH₄ the solvent was removed under reduced pressure using a rotavapor. The crude mass was then re-dissolved in 20 ml water and the organic part was extracted with dichloromethane (25 ml × 4 portions). Removal of the solvent resulted in a crude oil. The pure **L**₁ was obtained after chromatographic purification of the crude oil using silica gel column (yield, 60%, 0.834 g).

Synthesis of **L**₄

The synthesis of **L**₃ has been reported earlier. **L**₄ has been prepared following the same procedure and the details is given in the supporting information.

The procedure of synthesis of the fluorescent ligand **L**₄ is given bellow (scheme 2). **L**₂ (0.426 g, 0.2 mmol) was dissolved into distilled chloroform (15 ml) in a 50 ml round bottom flask equipped with a stirring bar. To this, triethyl amine (0.303 g, 0.3 mmol) and dansyl chloride

(0.540 g, 0.2 mmol) was added with constant stirring. The reaction mixture was then stirred at room temperature for 5 h. The volume of the resulting solution was then reduced in rotavapor and the greenish yellow fluorescent mass was subjected to column chromatographic purification using silica gel column to result in the pure greenish yellow fluorescent ligand **L₄** (yield: ~70%, 0.625 g)

References

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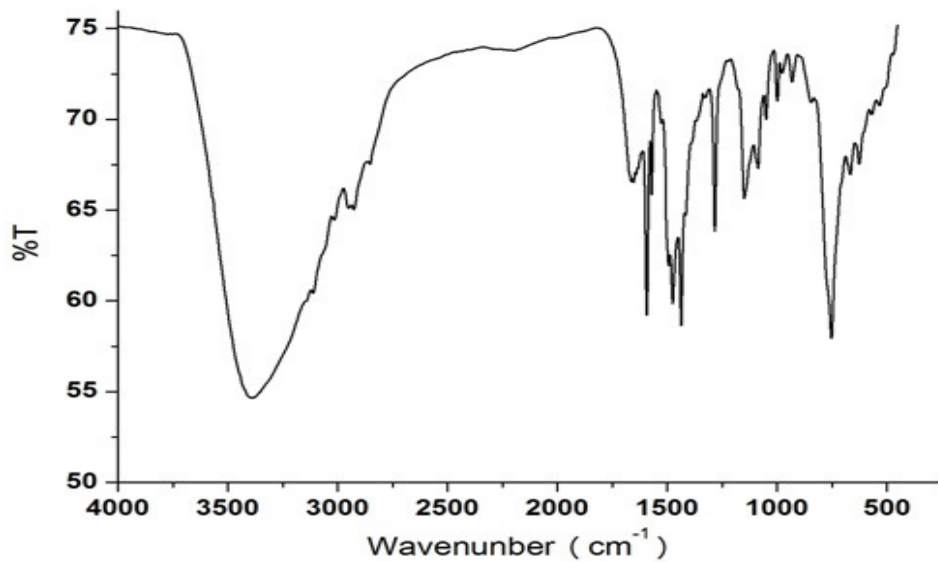


Figure S1. FT-IR spectrum of the **L₁** in KBr pellet

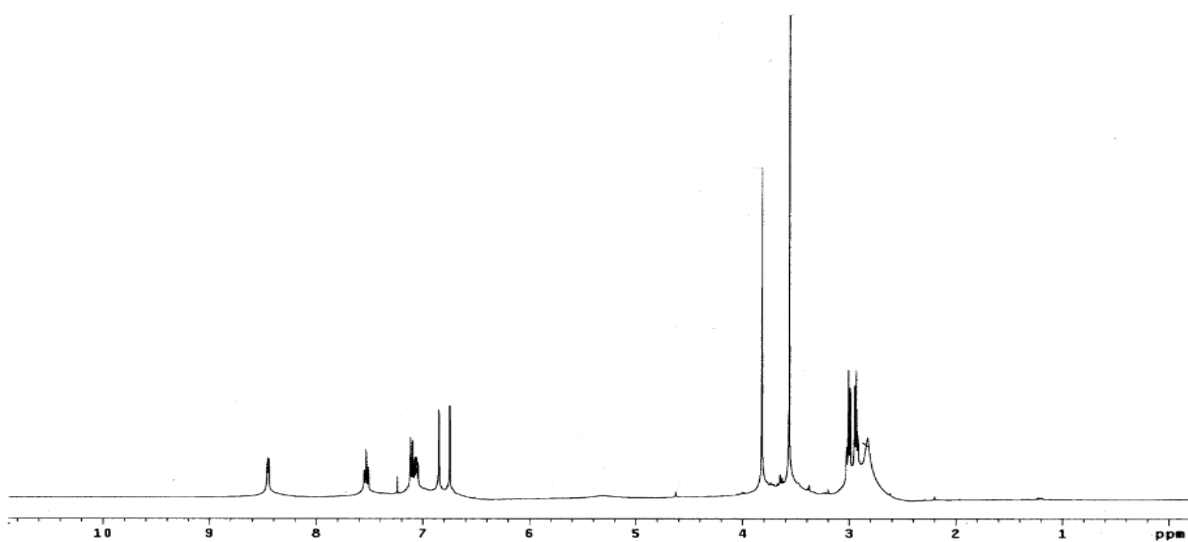


Figure S2. ¹H-NMR spectrum of **L₁** in CDCl₃

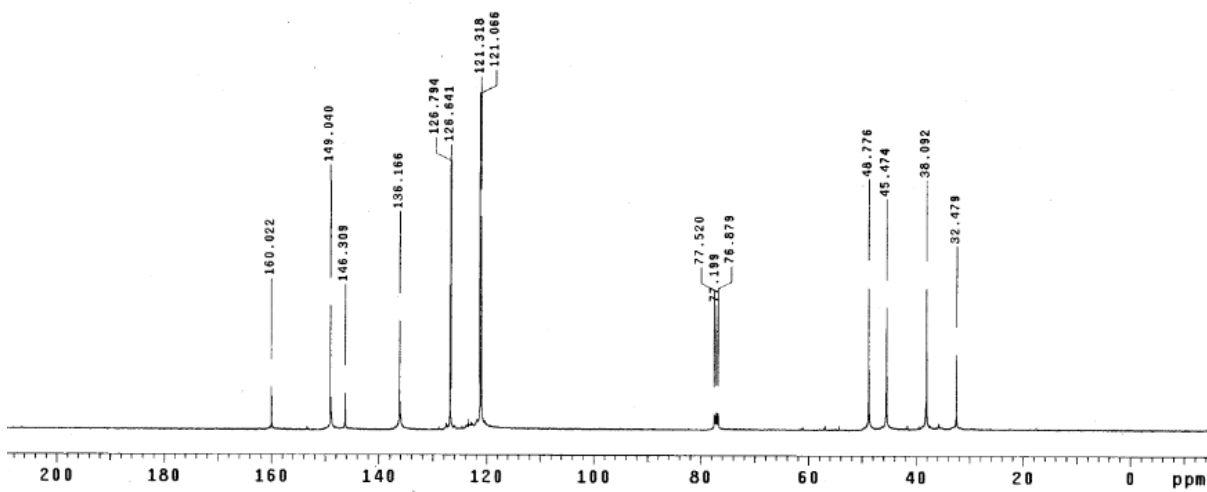


Figure S3. ^{13}C -NMR spectrum of L_1 in CDCl_3

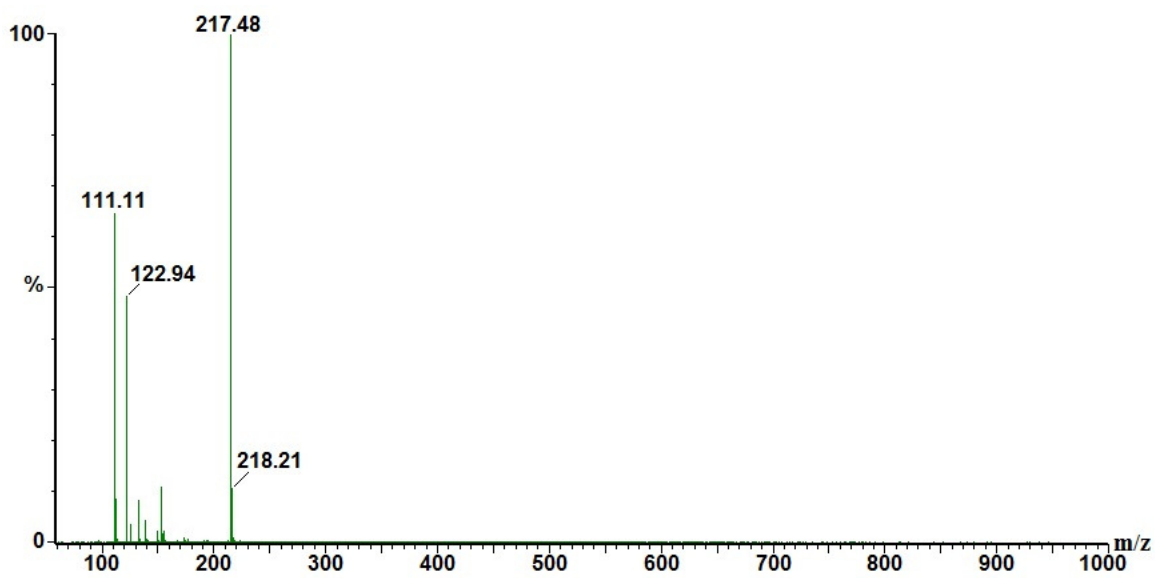


Figure S4. ESI-mass spectrum for L_1 in methanol

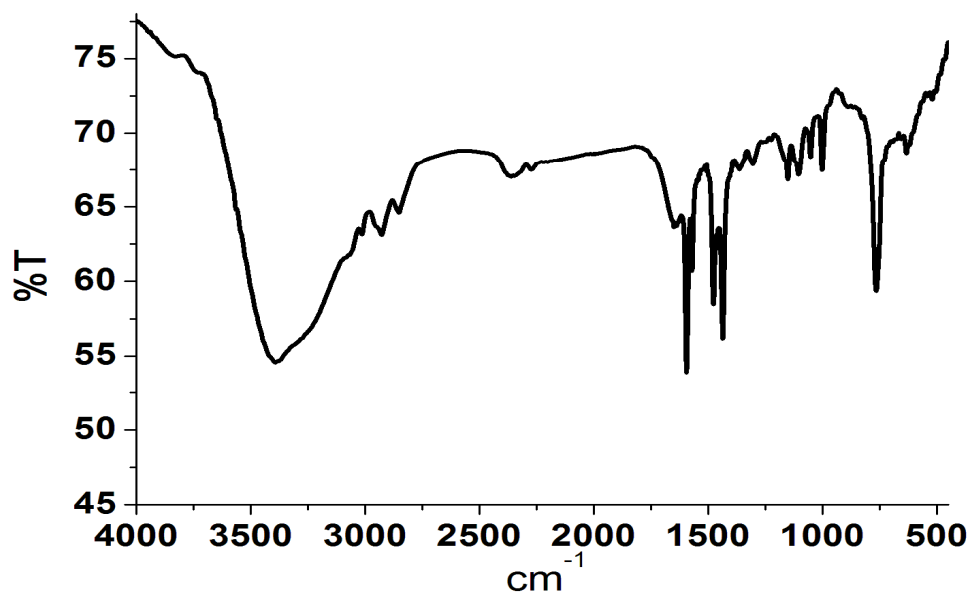


Figure S5. FT-IR spectrum of the L₂ in KBr pellet

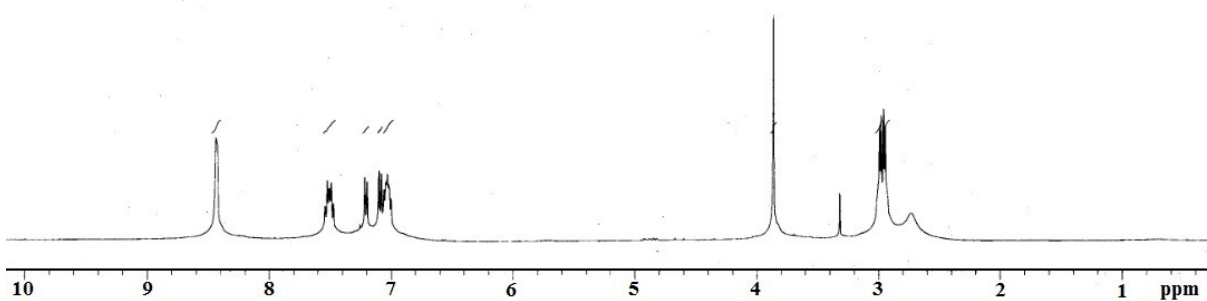


Figure S6. ¹H-NMR spectrum of L₂ in CDCl₃

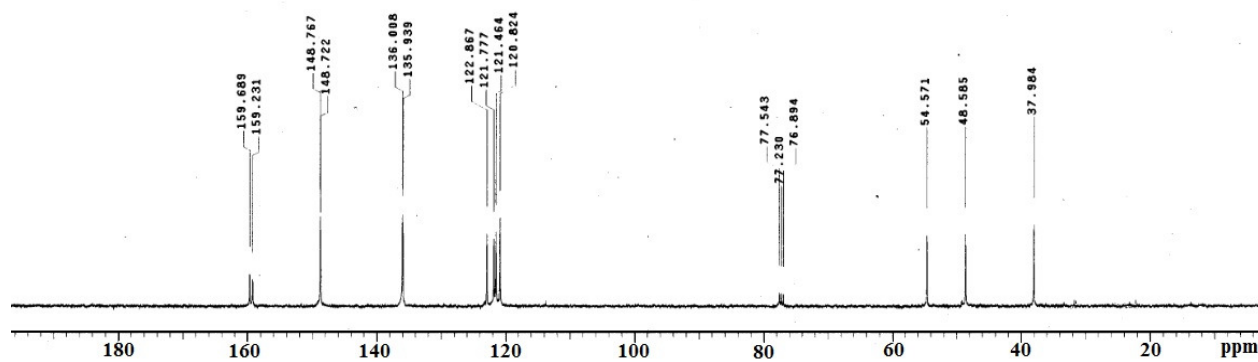


Figure S7. ^{13}C -NMR spectrum of L_2 in CDCl_3

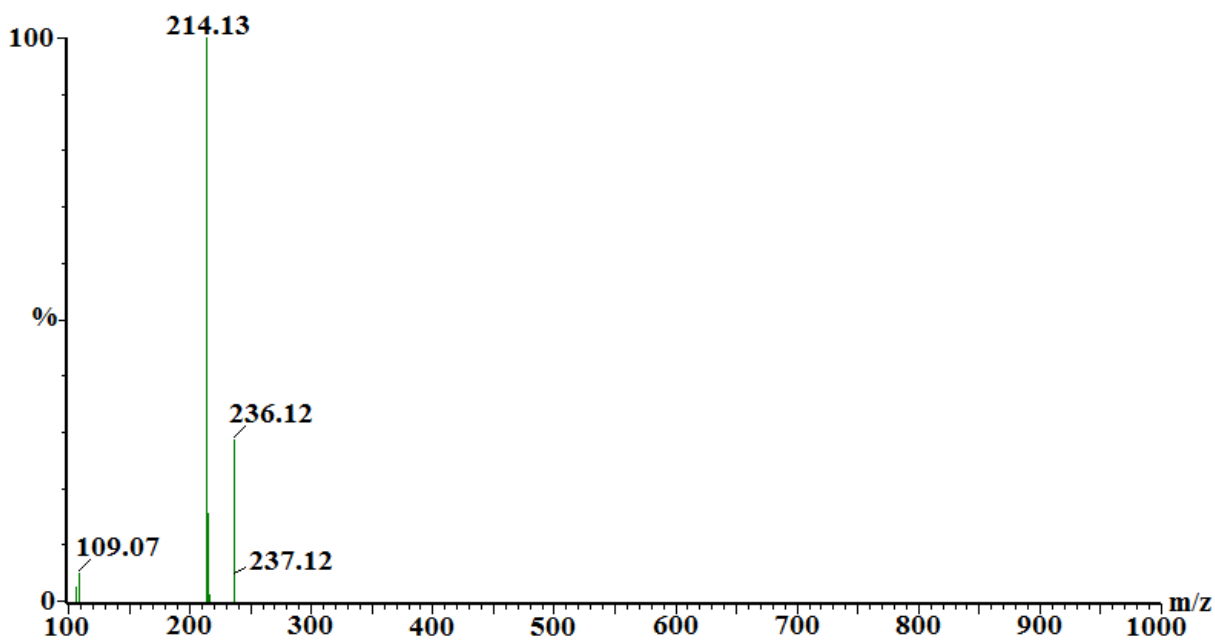


Figure S8. ESI-mass spectrum for L_2 in methanol

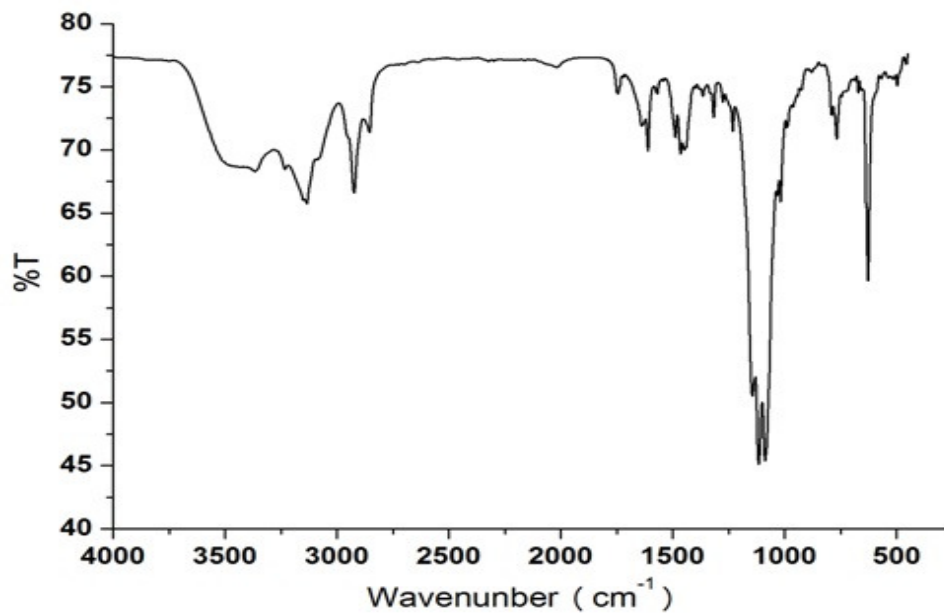


Figure S9. FT-IR spectrum of complex **1** in KBr pellet

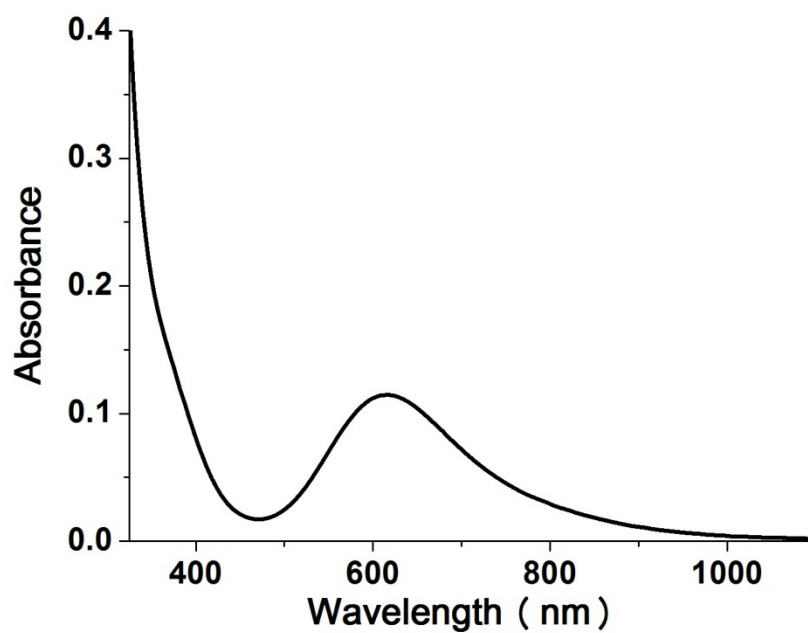


Figure S10. UV-visible spectrum of complex **1** in acetonitrile

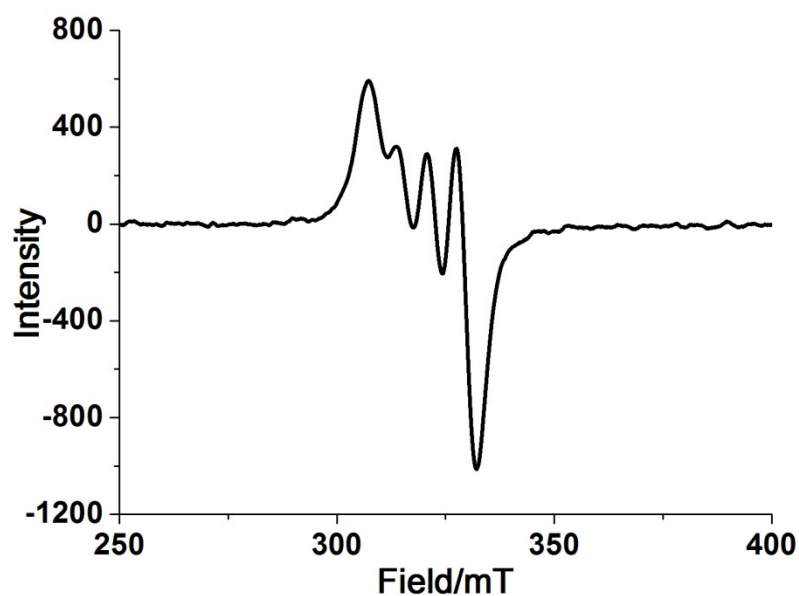


Figure S11. X-Band EPR spectrum of complex **1** in acetonitrile at 298K

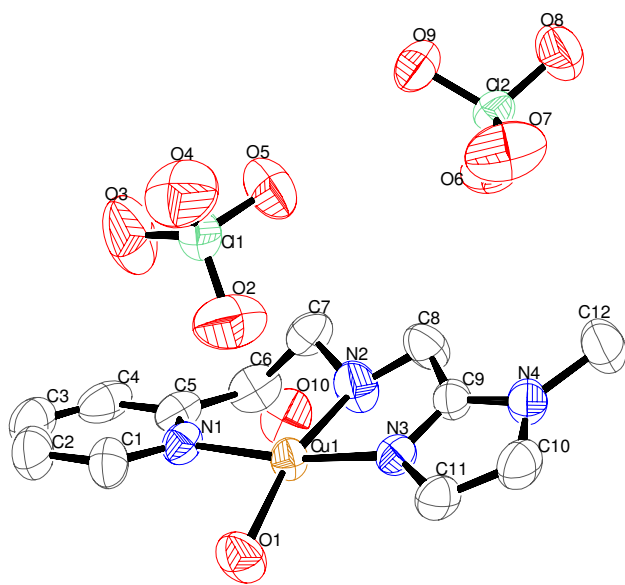


Figure S12. ORTEP diagram of complex **1** (50% thermal ellipsoid plot)

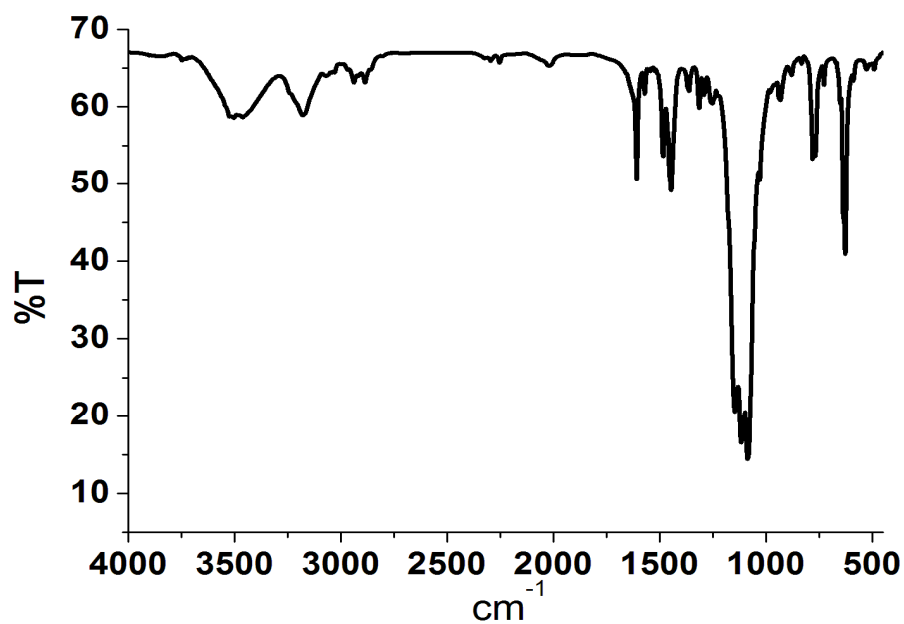


Figure S13. FT-IR spectrum of the complex **2** in KBr pallet

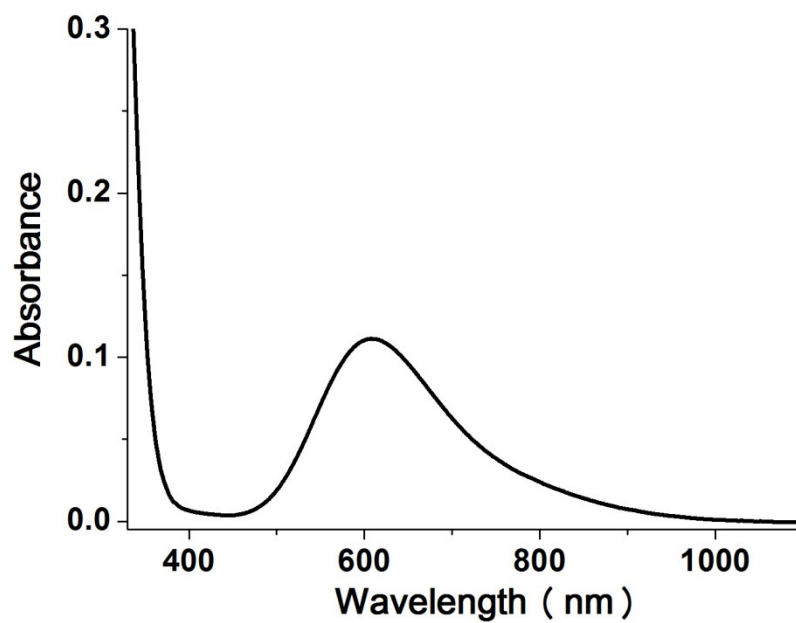


Figure S14. UV –visible spectrum of complex **2** in acetonitrile

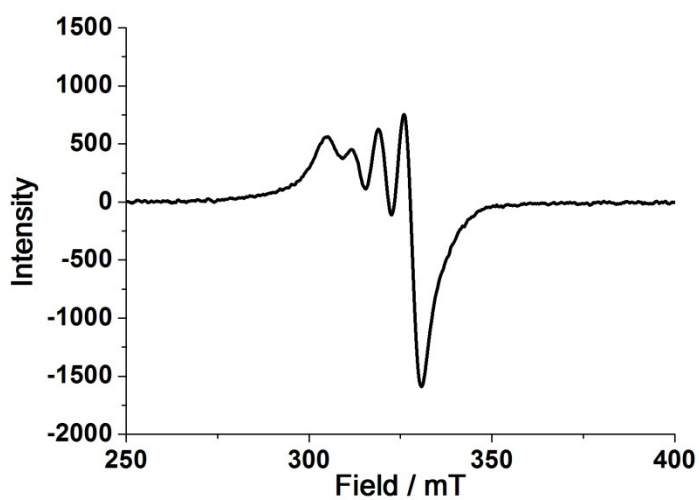


Figure S15. X-Band EPR spectrum of complex **2** in acetonitrile at 298K

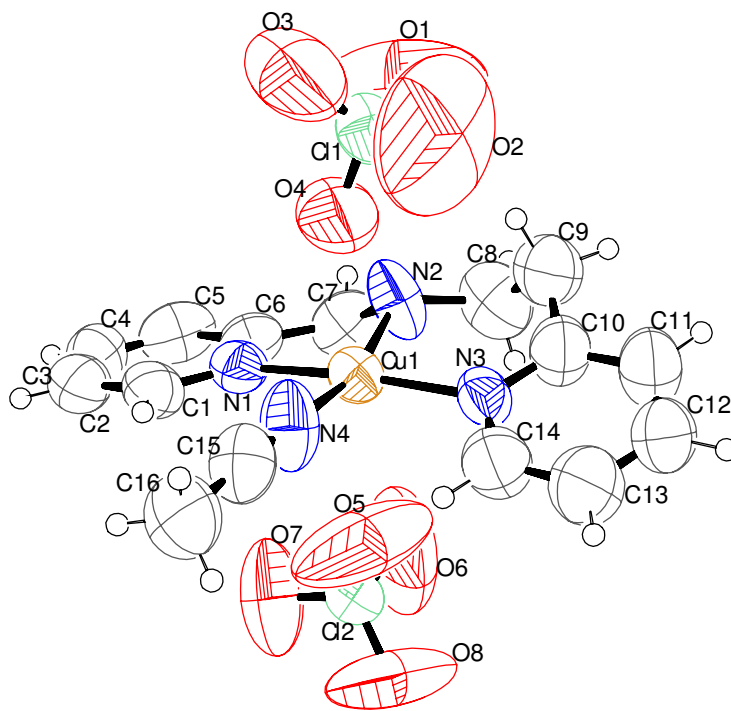


Figure S16. ORTEP diagram of complex **2** (50% thermal ellipsoid plot)

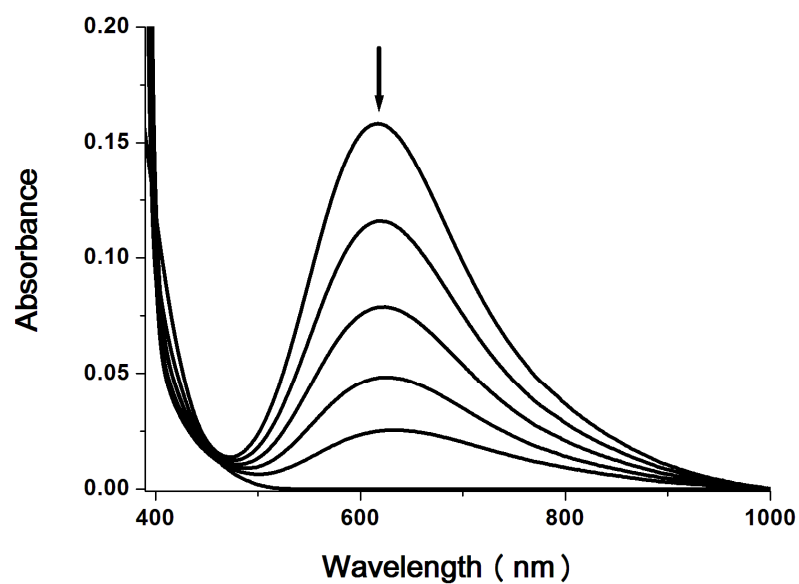


Figure S17. UV-visible spectrum of complex **1** in acetonitrile

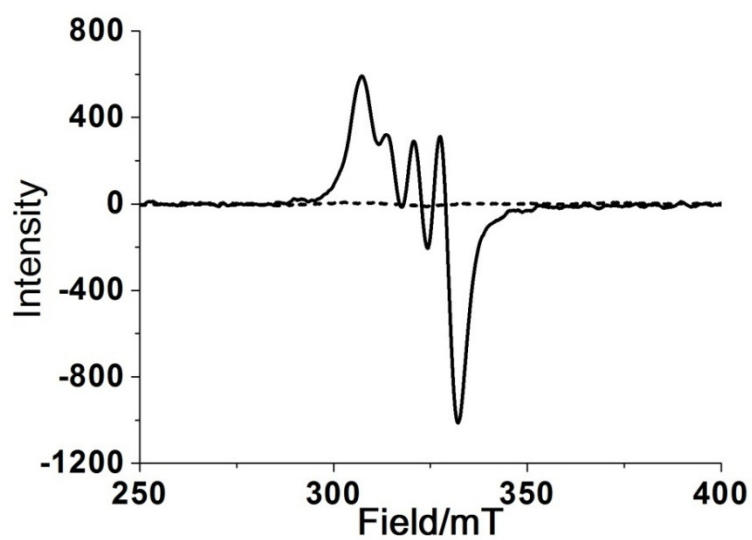


Figure S18. X-Band EPR spectra of complex **1** in acetonitrile before (**solid line**) and after (**dashed line**) purging nitric oxide

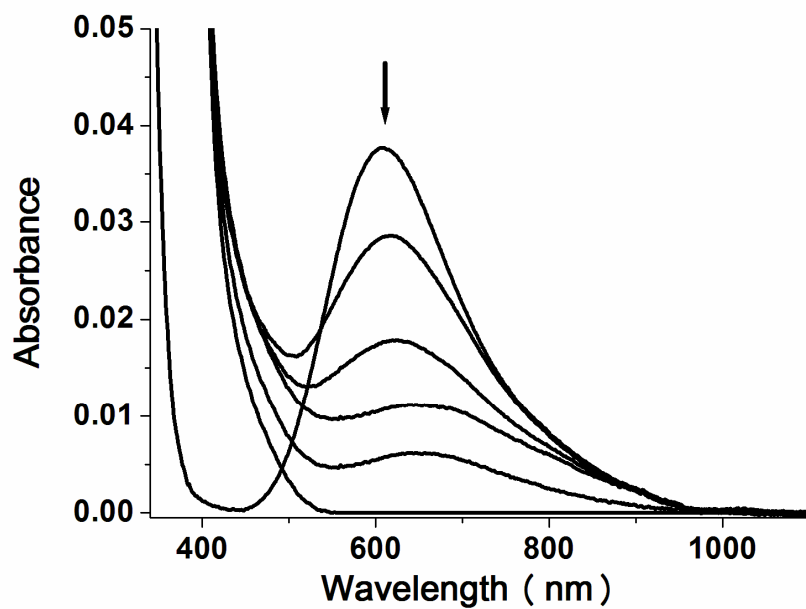


Figure S19. UV-visible spectra of complex **2** in acetonitrile

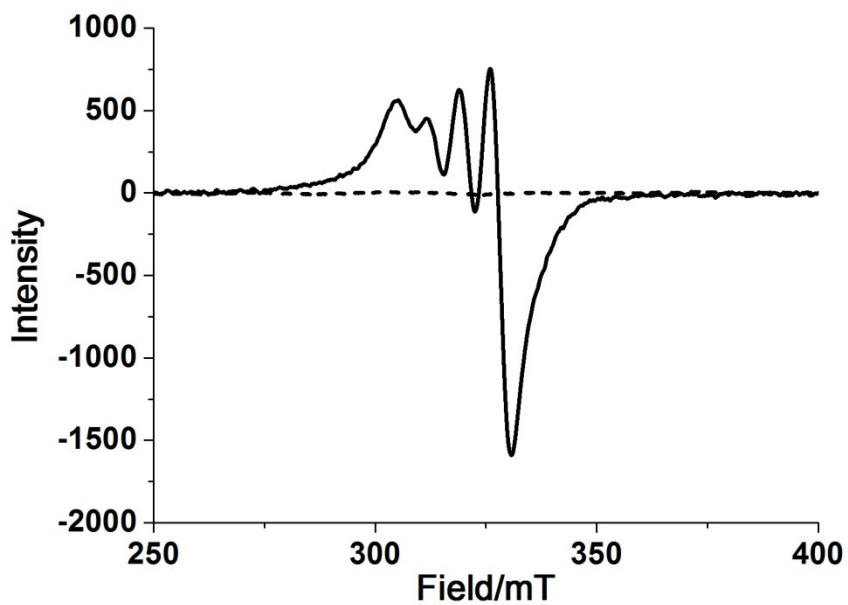


Figure S20. X-Band EPR spectra of complex **2** in acetonitrile before (**solid line**) and after (**dashed line**) purging nitric oxide

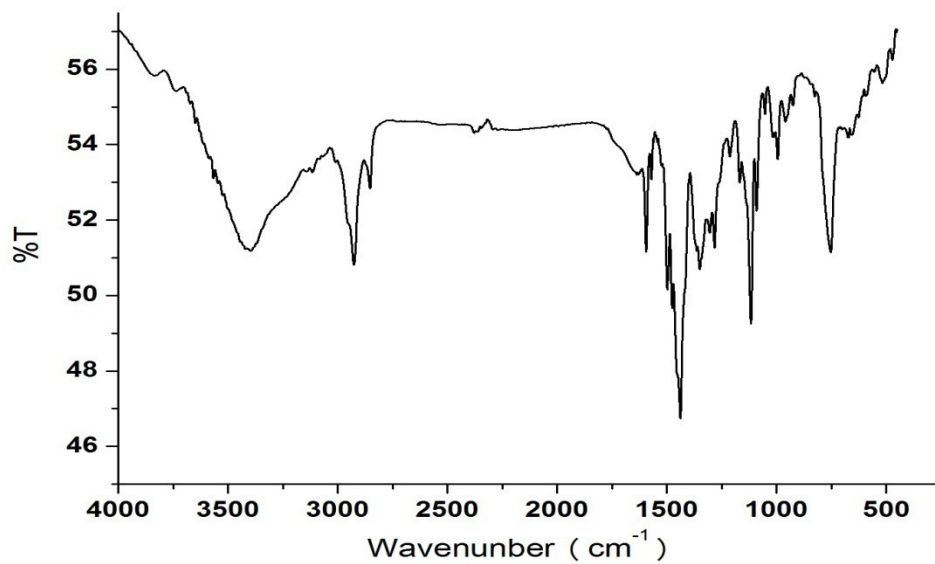


Figure S21. FT-IR spectrum of L_1'' in KBr pellet

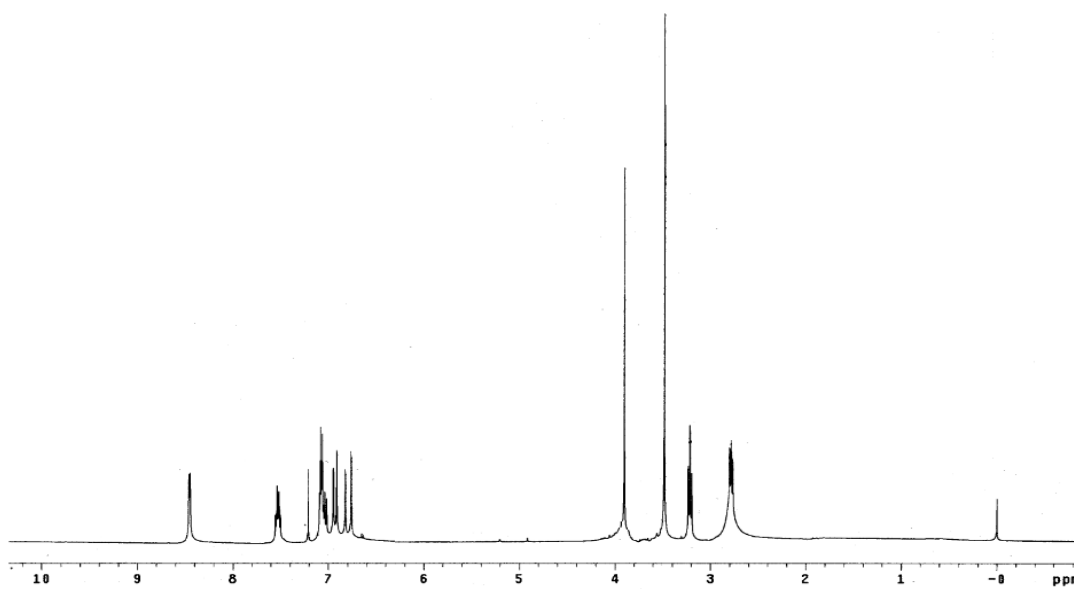


Figure S22. ¹H-NMR spectrum of L_1'' in CDCl₃

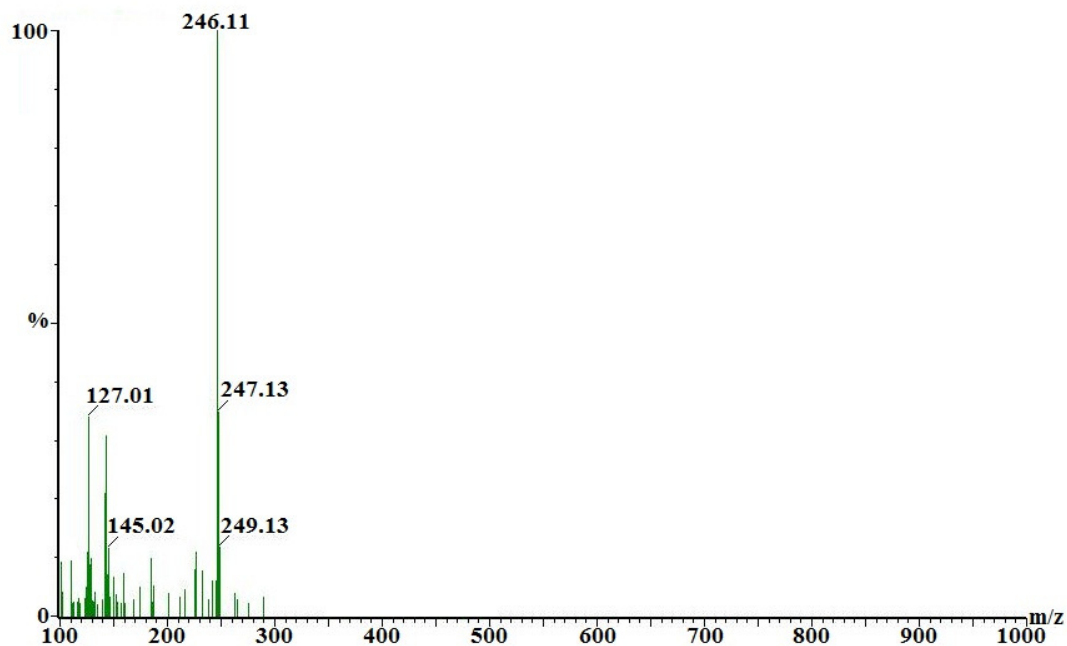


Figure S23. ESI-mass spectrum of L_1'' in methanol

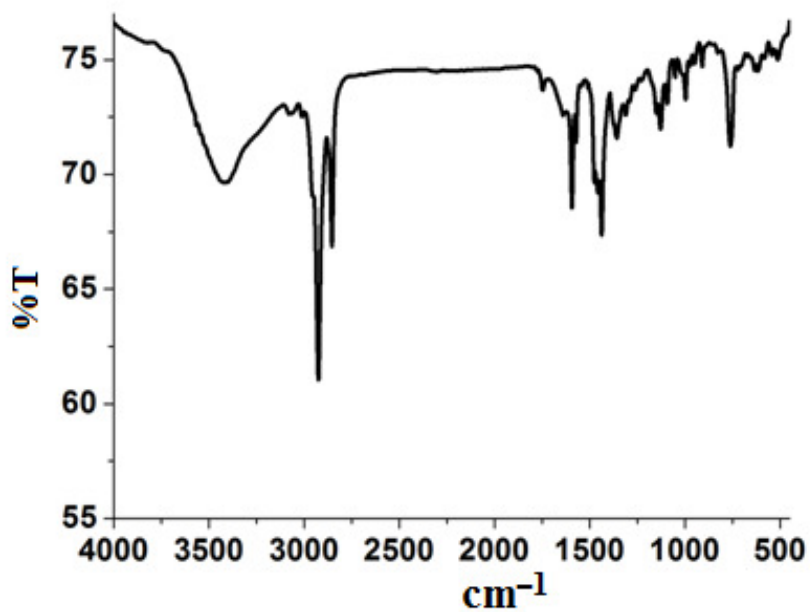


Figure S24. FT-IR spectrum of L_2'' in KBr pellet

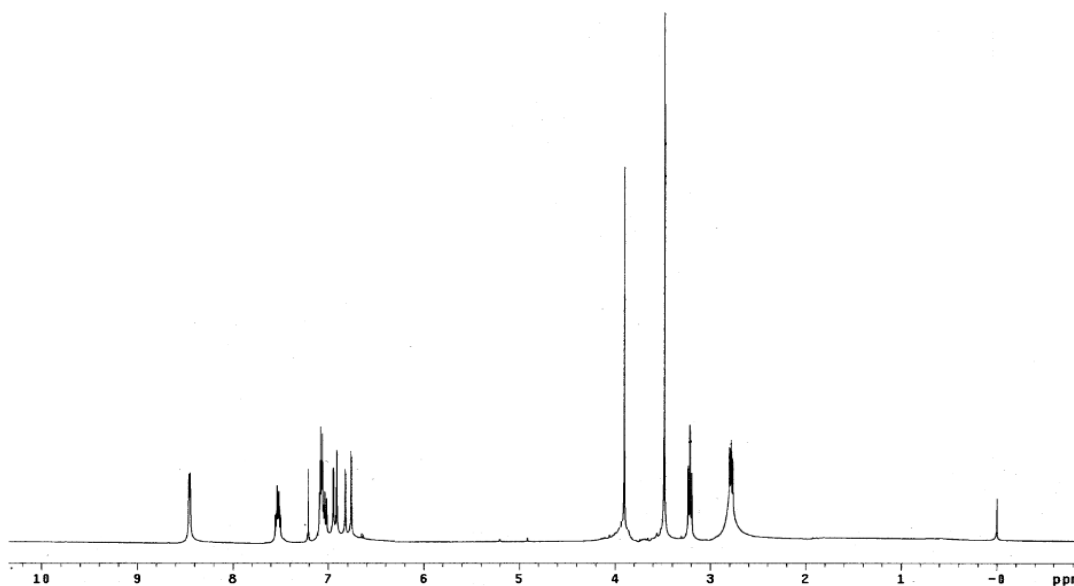


Figure S25. ¹H NMR spectrum of L₂'' in CDCl₃

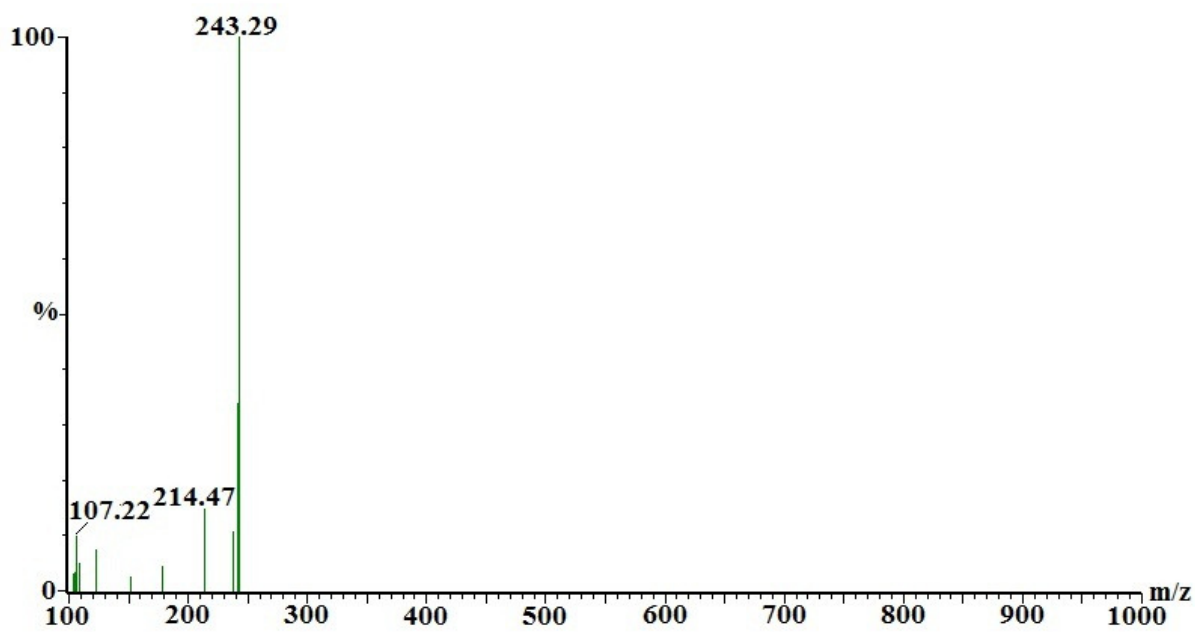


Figure S26. ESI-mass spectrum of L₂'' in methanol

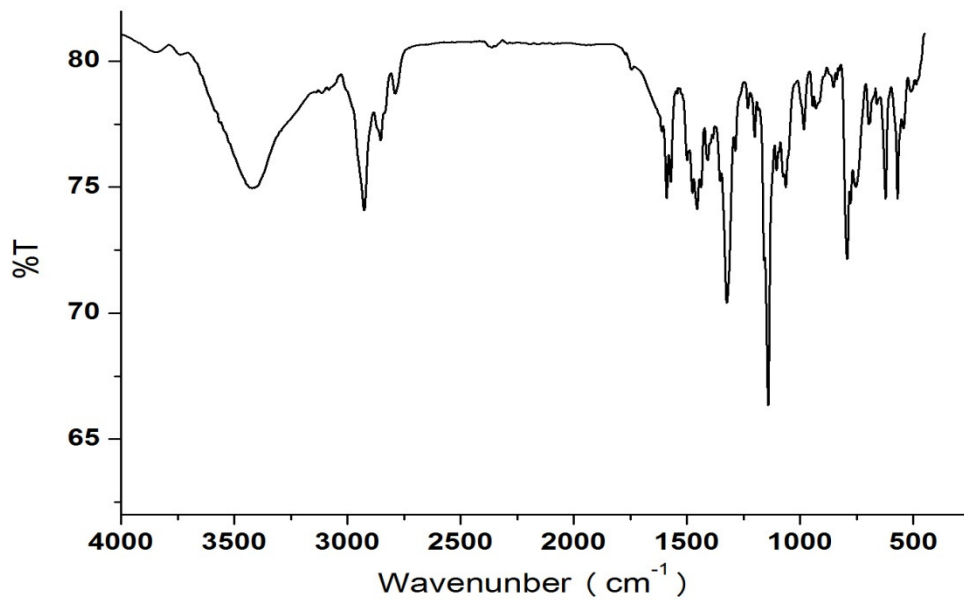


Figure S27. FT-IR spectrum of **L₃** in KBr pellet

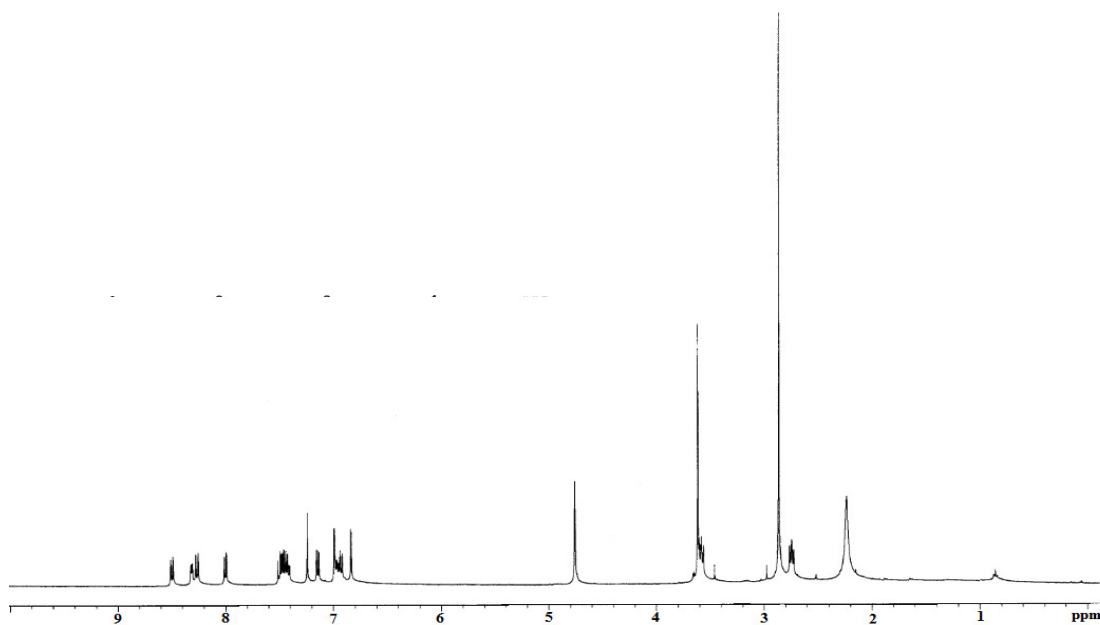


Figure S28. ¹H-NMR spectrum of **L₃** in CDCl₃

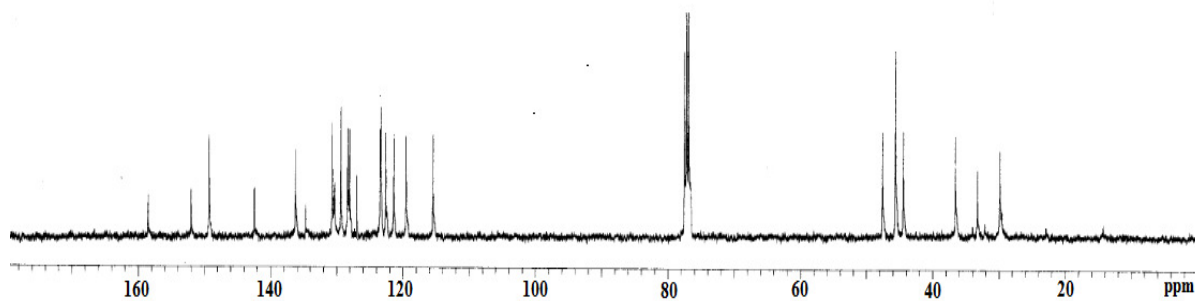


Figure S29. ^{13}C -NMR spectrum of L_3 in CDCl_3

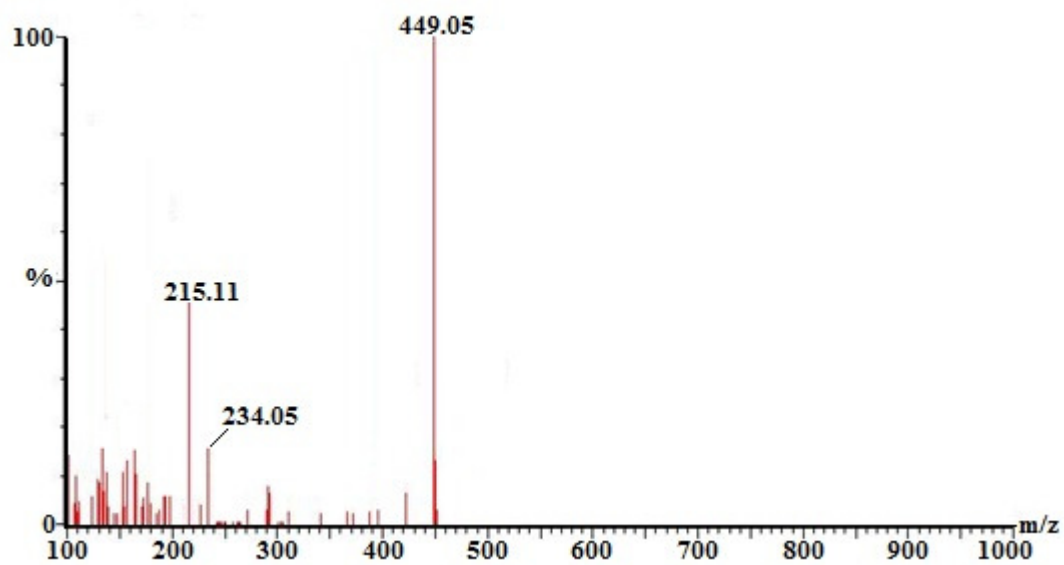


Figure S30. ESI-mass spectrum of L_3 in methanol

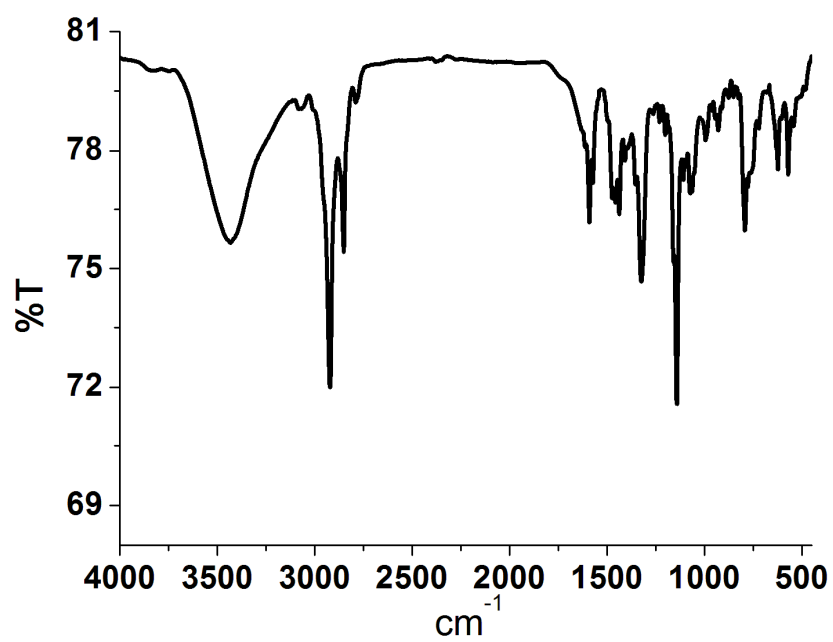


Figure S31. FT-IR spectrum of L₄ in KBr pellet

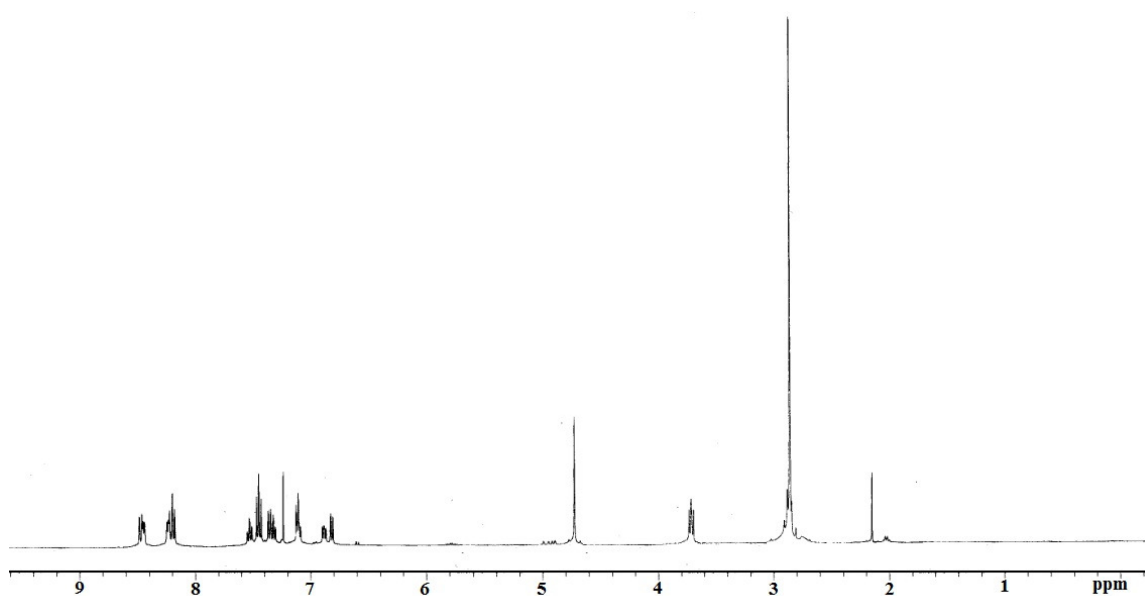


Figure S32. ¹H-NMR spectrum of L₄ in CDCl₃

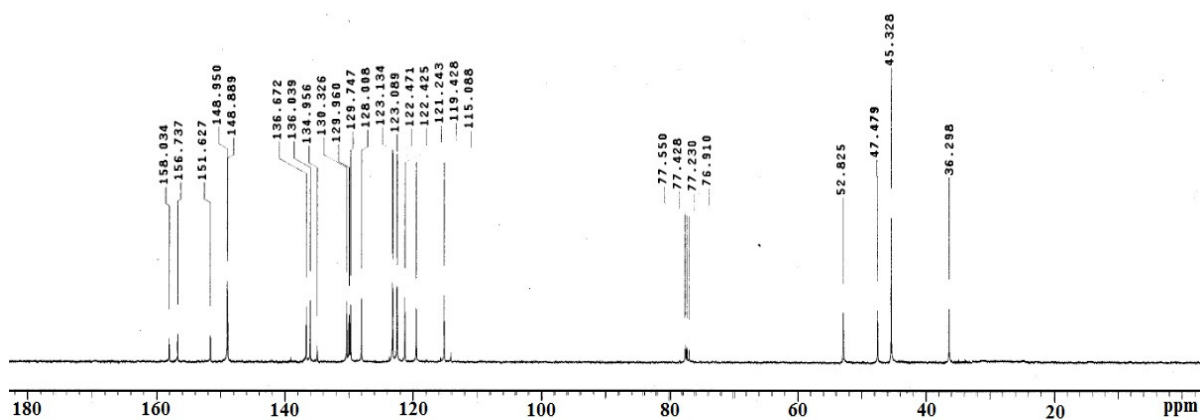


Figure S33. ^{13}C -NMR spectrum of L_4 in CDCl_3

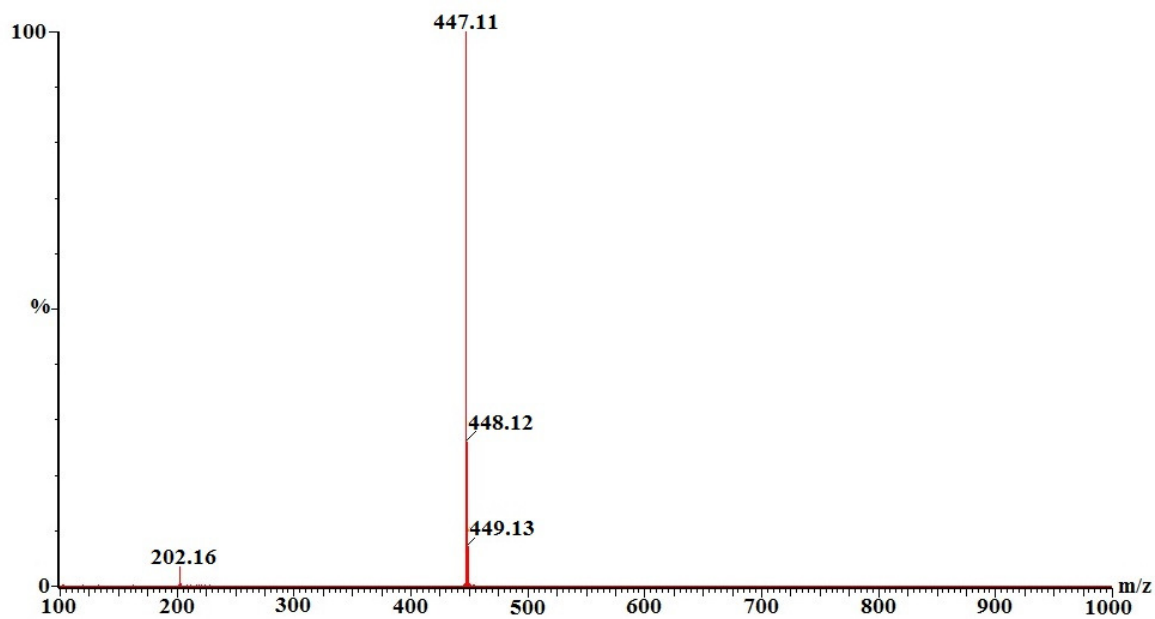


Figure S34. ESI-mass spectrum of L_4 in methanol

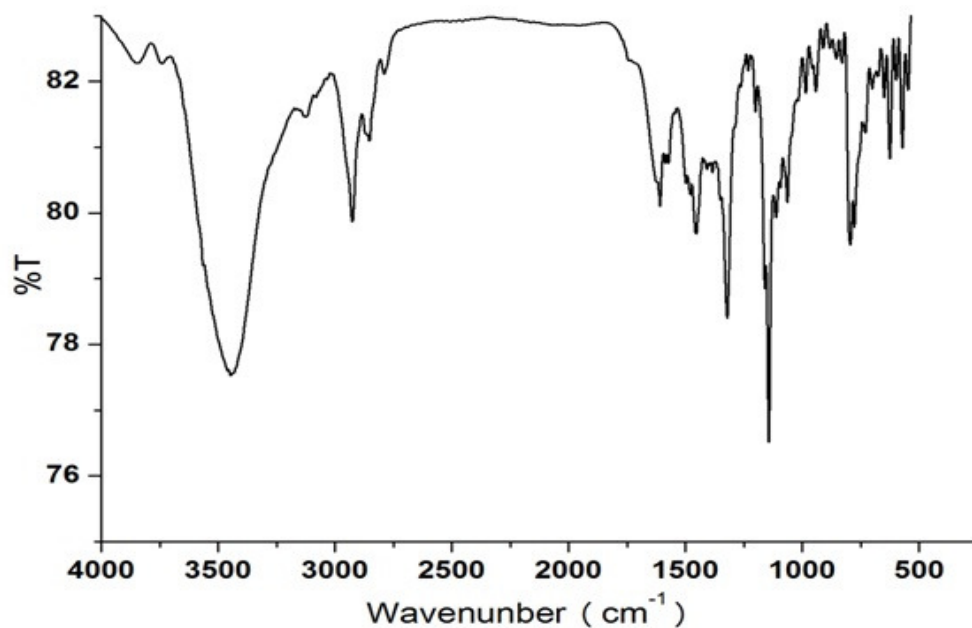


Figure S35. FT-IR spectrum of L₃ in KBr pellet

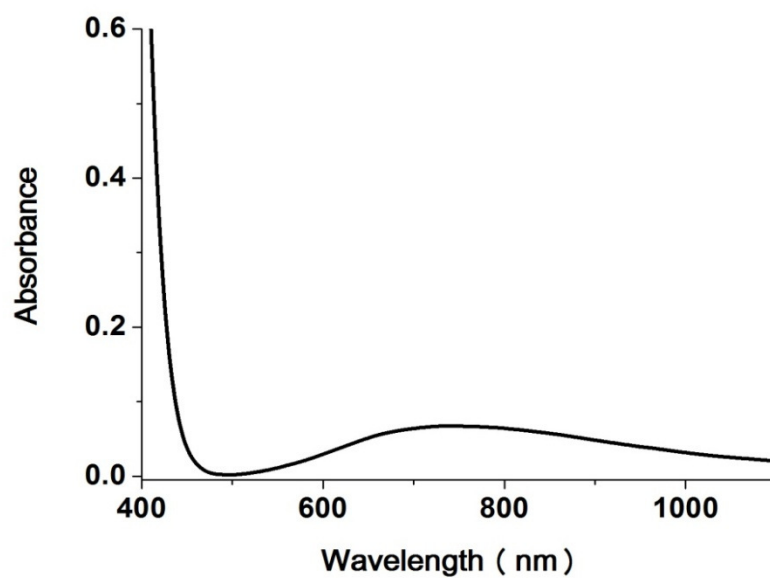


Figure S36. UV-visible spectrum of complex 3 in methanol

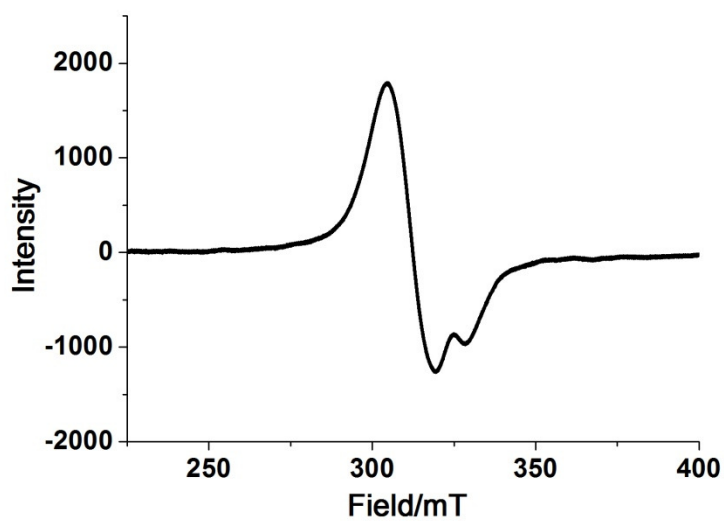


Figure S37. X-Band EPR spectrum of complex **3** in methanol at 298K

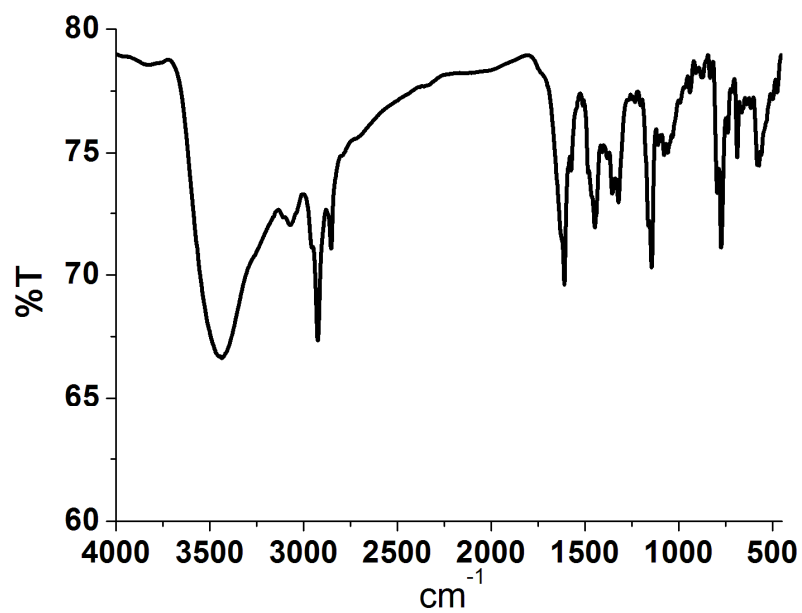


Figure S38. FT-IR spectrum of complex **4** in KBr pellet

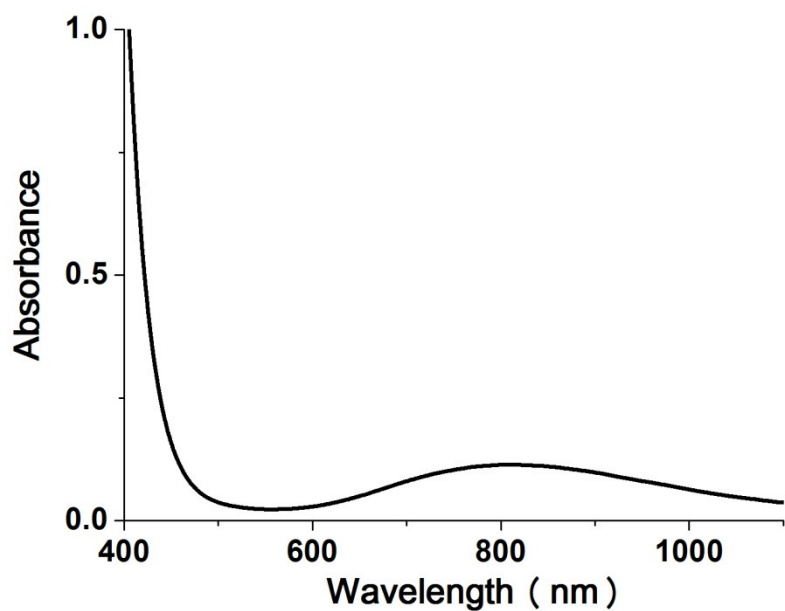


Figure S39. UV –visible spectrum of complex **4** in methanol

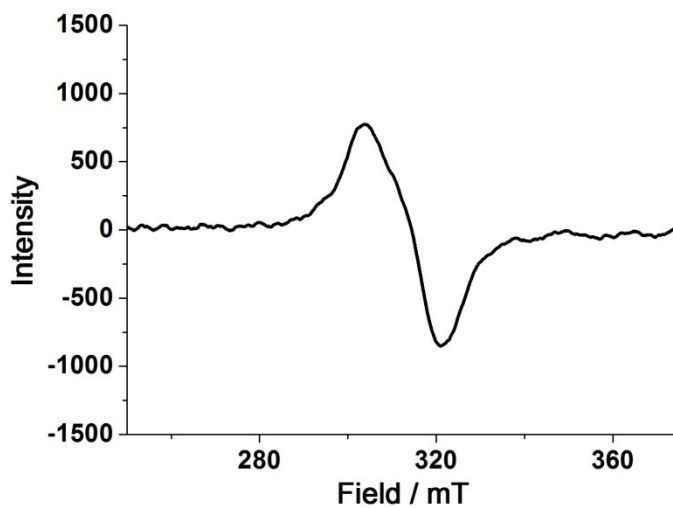


Figure S40. X-Band EPR spectrum of complex **3** in methanol at 298K

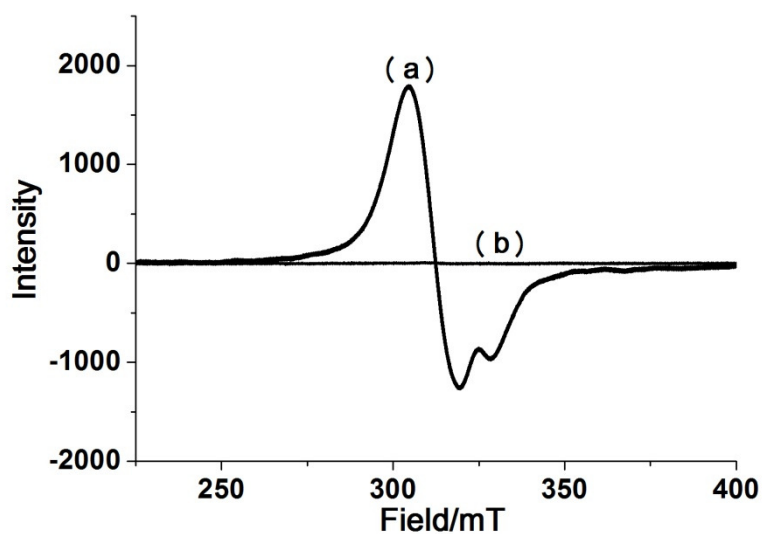


Figure S41. X-Band EPR spectra of complex **3** in methanol before (a) and after (b) purging nitric oxide

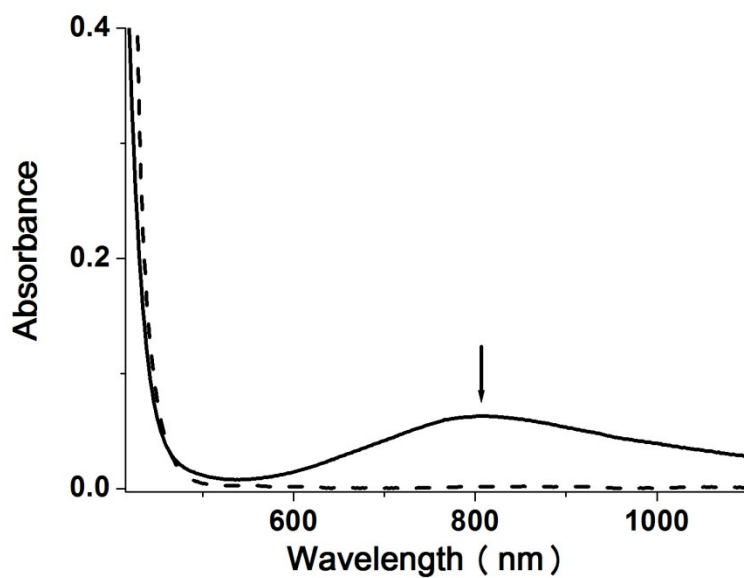


Figure S42. UV-visible spectra of complex **3** in methanol before (solid line) and after (dashed line) purging nitric oxide

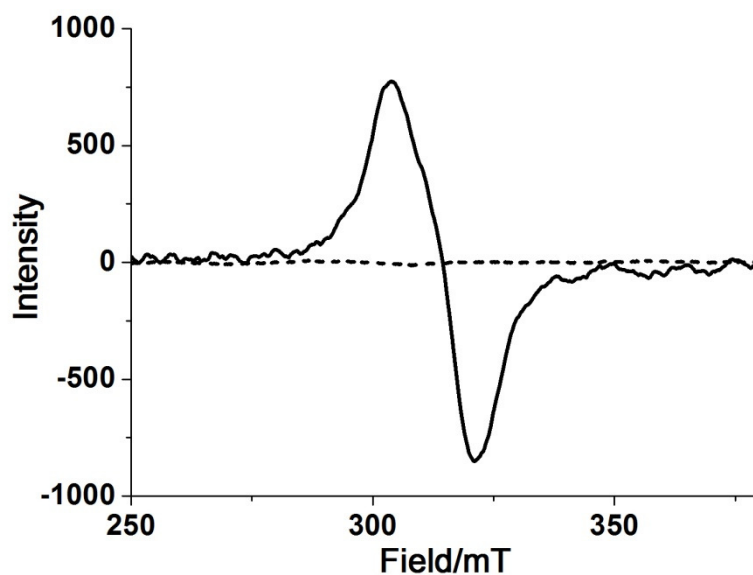


Figure S43. X-Band EPR spectra of complex **4** in methanol before (**solid line**) and after (**dashed line**) purging nitric Oxide

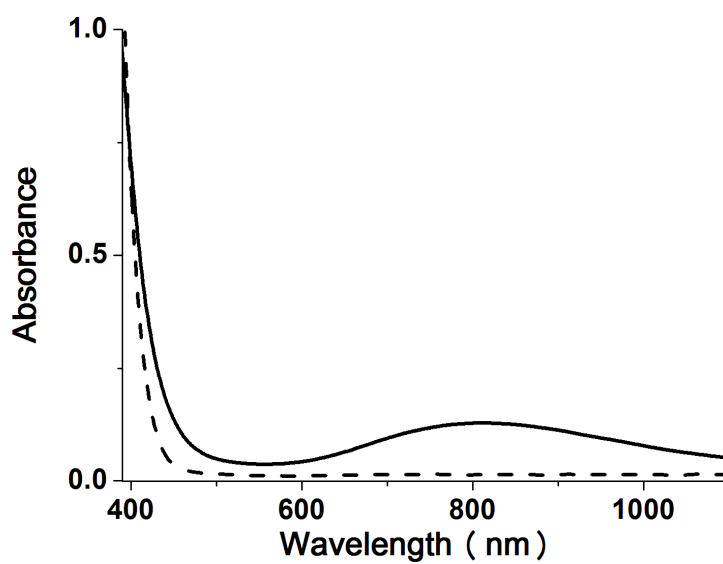


Figure S44. UV-visible spectra of complex **4** in methanol before (**solid line**) and after (**dashed line**) purging nitric oxide

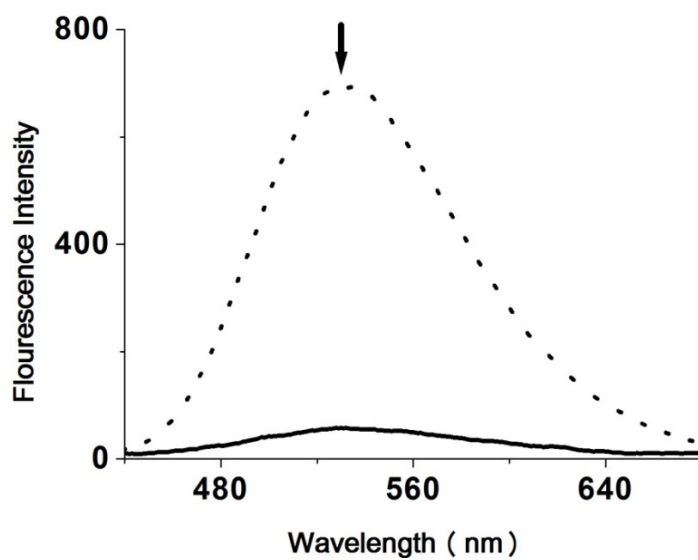


Figure S45. Fluorescence responses (λ_{ex} , 342 nm) for 25 μM solution of free ligand, **L₃** (**dotted line**) and after addition of one equivalent of [Cu(H₂O)₂]Cl₂(75 μM) in methanol (**solid line**).

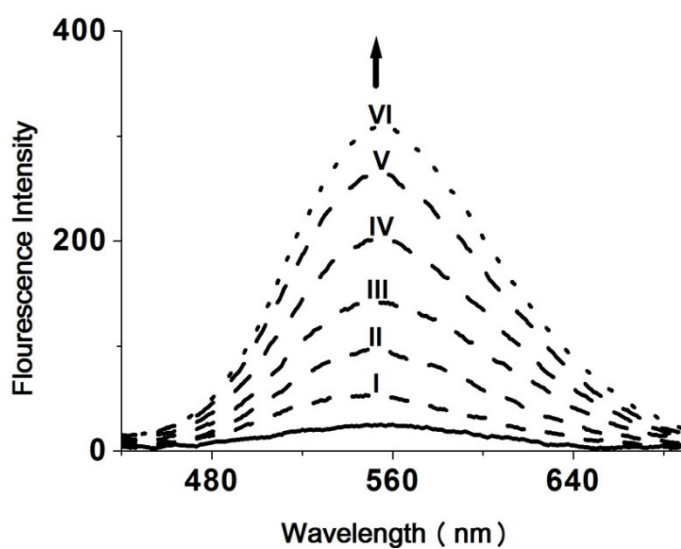


Figure S46. Fluorescence responses (λ_{ex} , 342 nm) of deoxygenated methanol solution(25 μM) of complex **3** before (**solid line**) and after (**dashed lines**) purging of 5 equivalent of NO at 2, 5, 10, 15, 20 and 30 minutes at 298 K (lines I – VI, respectively)

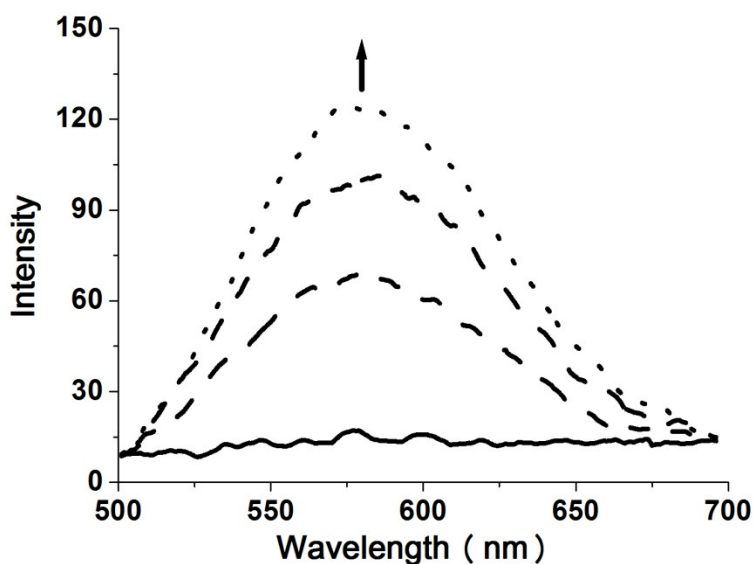


Figure S47. Fluorescence emission spectra of the complex **3** (25 μM) in water medium upon addition of excess NO

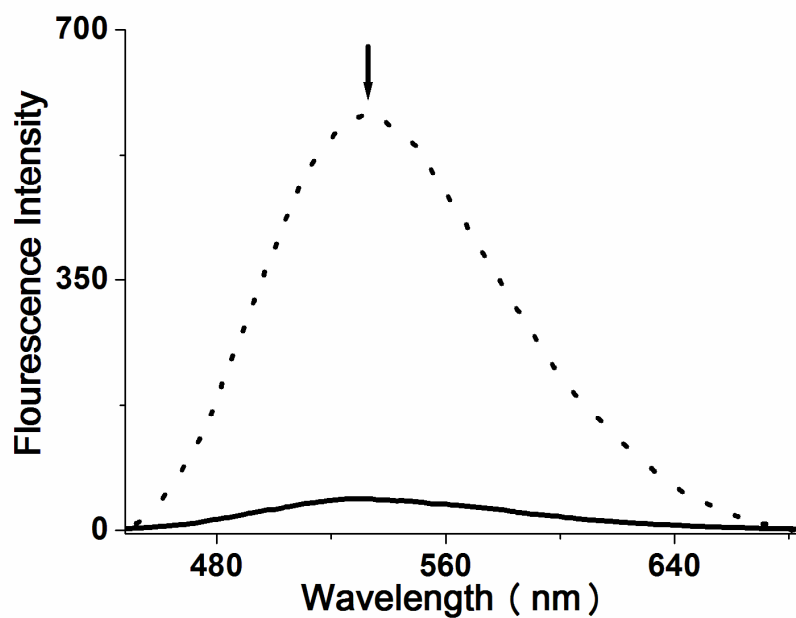


Figure S48. Fluorescence responses (λ_{ex} , 350 nm) for 25 μM solution of free ligand, **L₄** (dotted line) and after addition of one equivalent of $[\text{Cu}(\text{H}_2\text{O})_2]\text{Cl}_2$ (75 μM) in methanol (solid line)

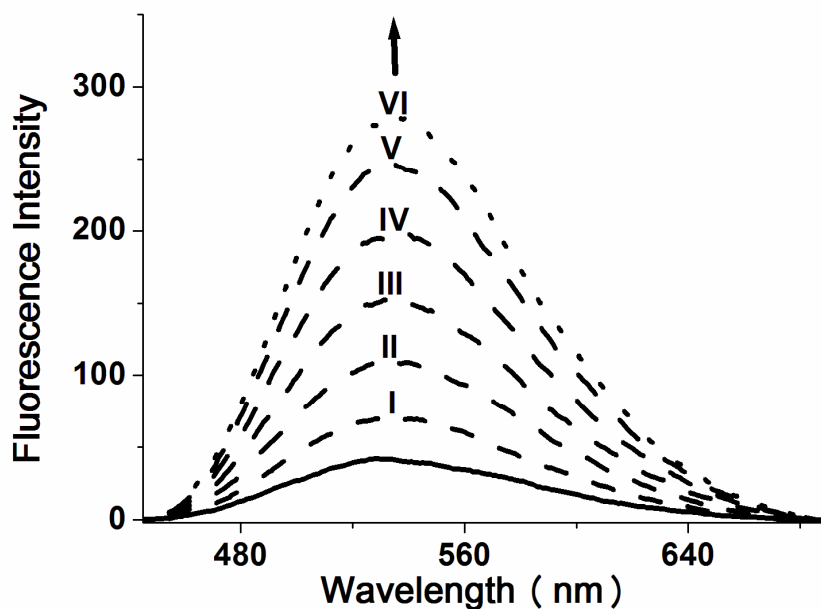


Figure S49. Fluorescence responses (λ_{ex} , 350 nm) of deoxygenated methanol solution of complex **4** before (**solid line**) and after (**dashed lines**) purging of 5 equivalent of NO at 10, 20, 30, 40, 50 and 60 minutes at 298 K (lines I – VI, respectively)

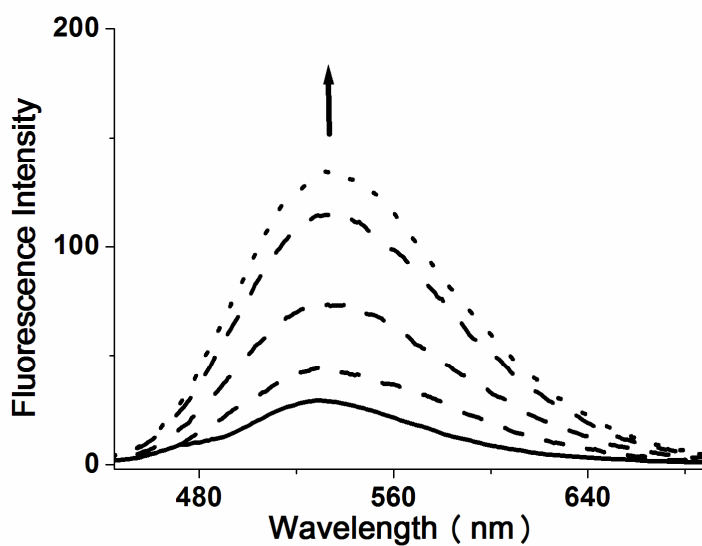


Figure S50. Fluorescence emission spectra of the Complex **4** (25 μM) in water medium upon addition of excess NO

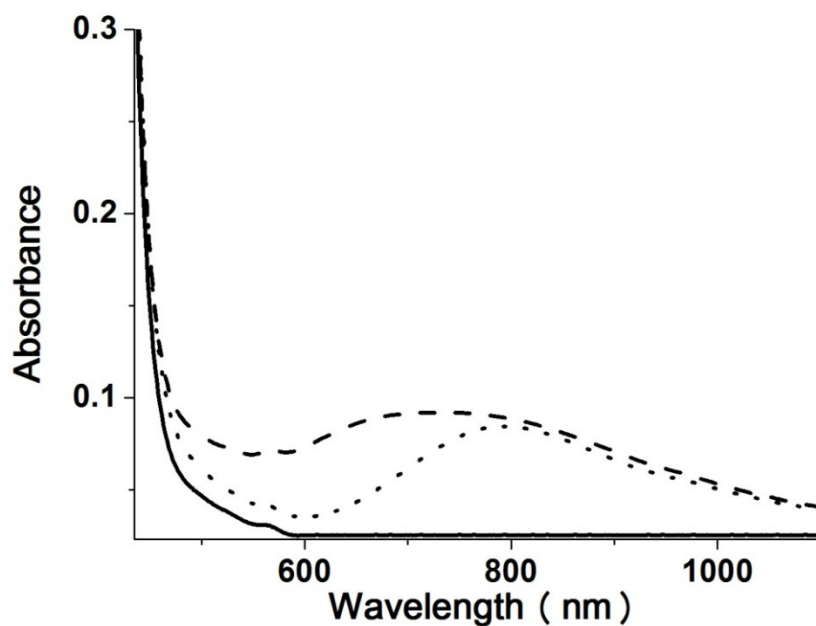


Figure S51. UV-visible spectra of complex **3** in methanol before (**dashed line**) and after (**solid line**) nitric oxide and upon expose to oxygen (**dotted line**)

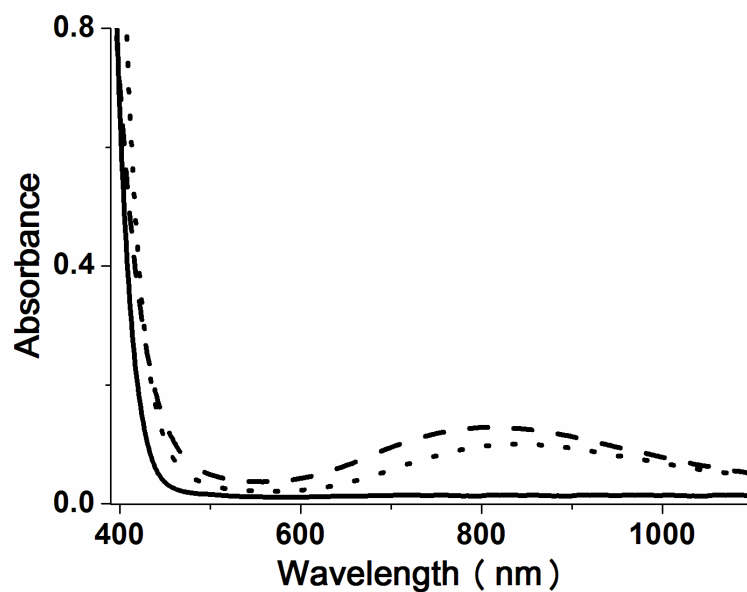


Figure S52. UV-visible spectra of complex **4** in methanol before (**dashed line**) and after (**solid line**) nitric oxide and upon expose to oxygen (**dotted line**)