

Figure S1-S2 - Species distribution for solutions 2.21×10^{-4} M of **L**, as a function of Cu^+ concentration. Each curve represent the % of **L** employed in the relative species with respect to the total concentration of **L**. Accordingly, the % of $[\text{L}_2\text{Cu}]^+$ and $[\text{L}_2\text{Cu}_2]^{2+}$ species is obtained by multiplying their molar concentration by 2, dividing by the total concentration of **L**, and multiplying by 100. Cu^+/L molar ratio = 1 is reached at $[\text{Cu}^+] = 2.21 \times 10^{-4}$ M.

Figure S1. **L** = **L1**. At a 1:1 $\text{Cu}^+/\text{L1}$ molar ratio, the helicate $[\text{L1}_2\text{Cu}_2]^{2+}$ species represent the 96.3% of the ligand.

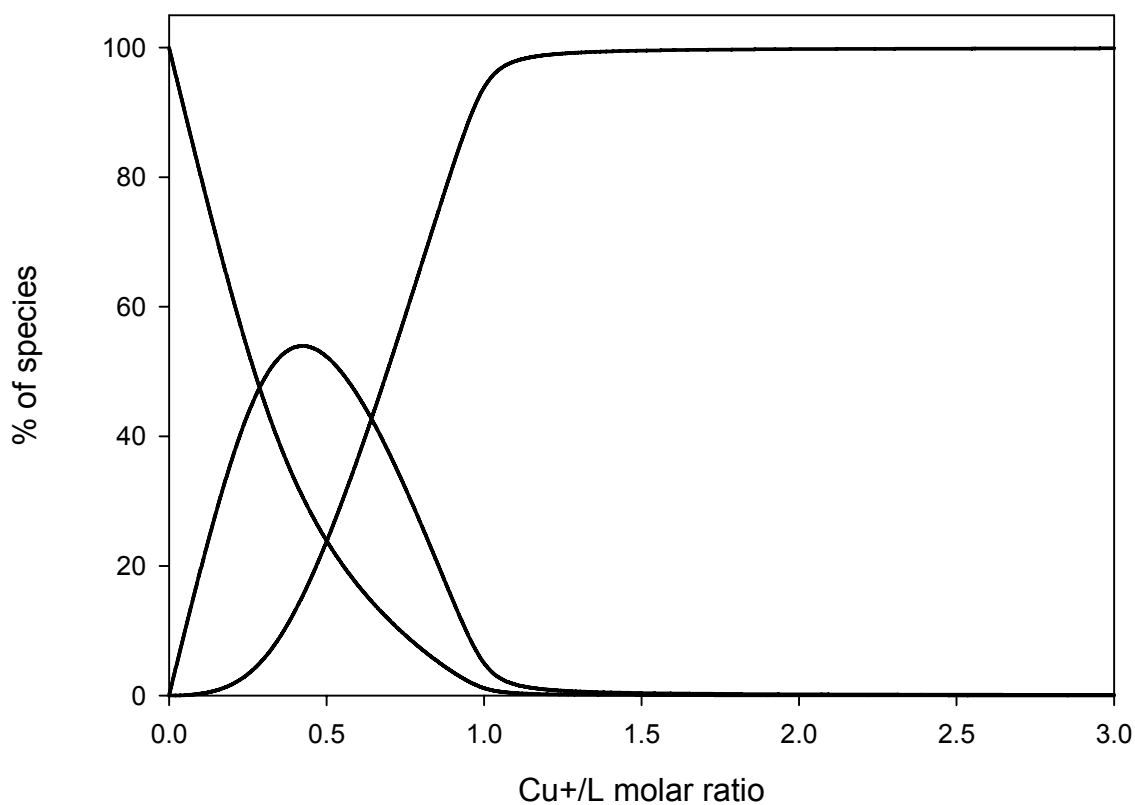


Figure S2. **L = L2.** At a 1:1 Cu⁺/L2 molar ratio, the helicate [L2₂Cu₂]²⁺ species represent the 94.2% of the ligand.

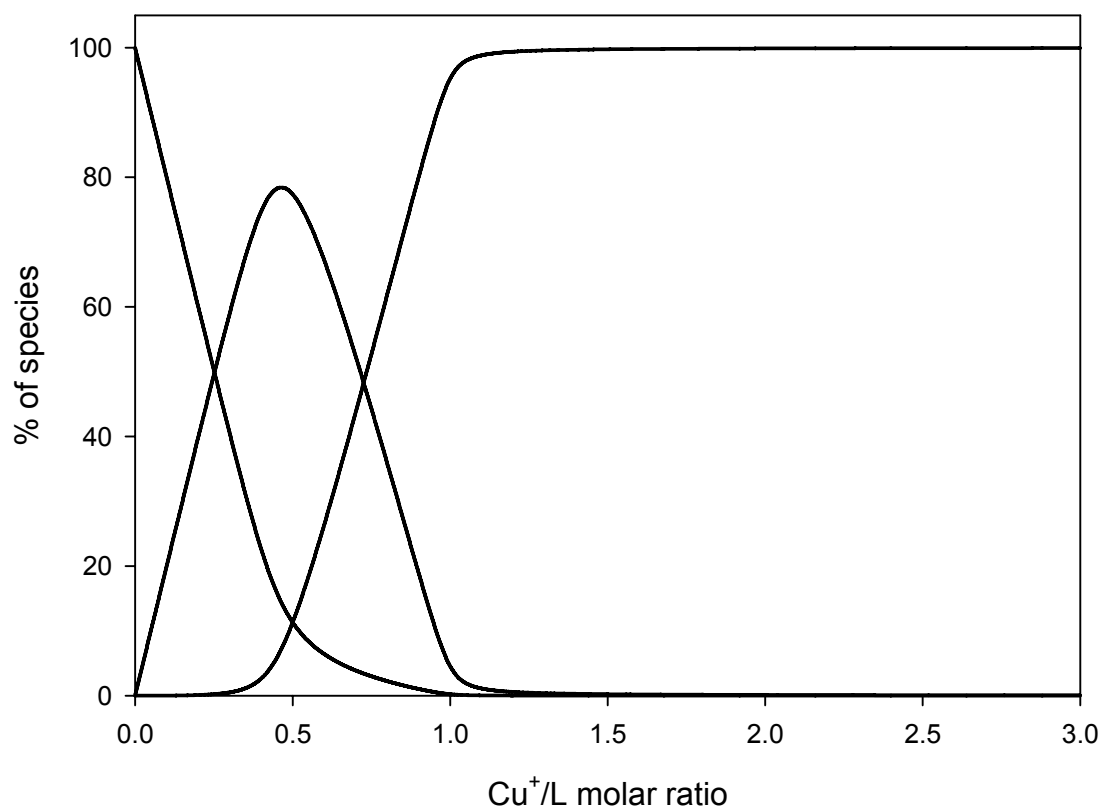


Figure S3: NMR spectrum (aromatic zone) of $[\mathbf{L1}_2\text{Cu}_2]^{2+}$ in CD_3CN . $[\mathbf{L1}_2\text{Cu}_2](\text{ClO}_4)_2$: δ 8.68 (d, 4H, $J=8.3$ Hz), 8.18 (4H, $\text{HC}=\text{N}$), 8.13 (d, 4H, $J=8.3$ Hz), 7.54 (m, 8H), 6.90 (d, 4H, $J=6.4$)

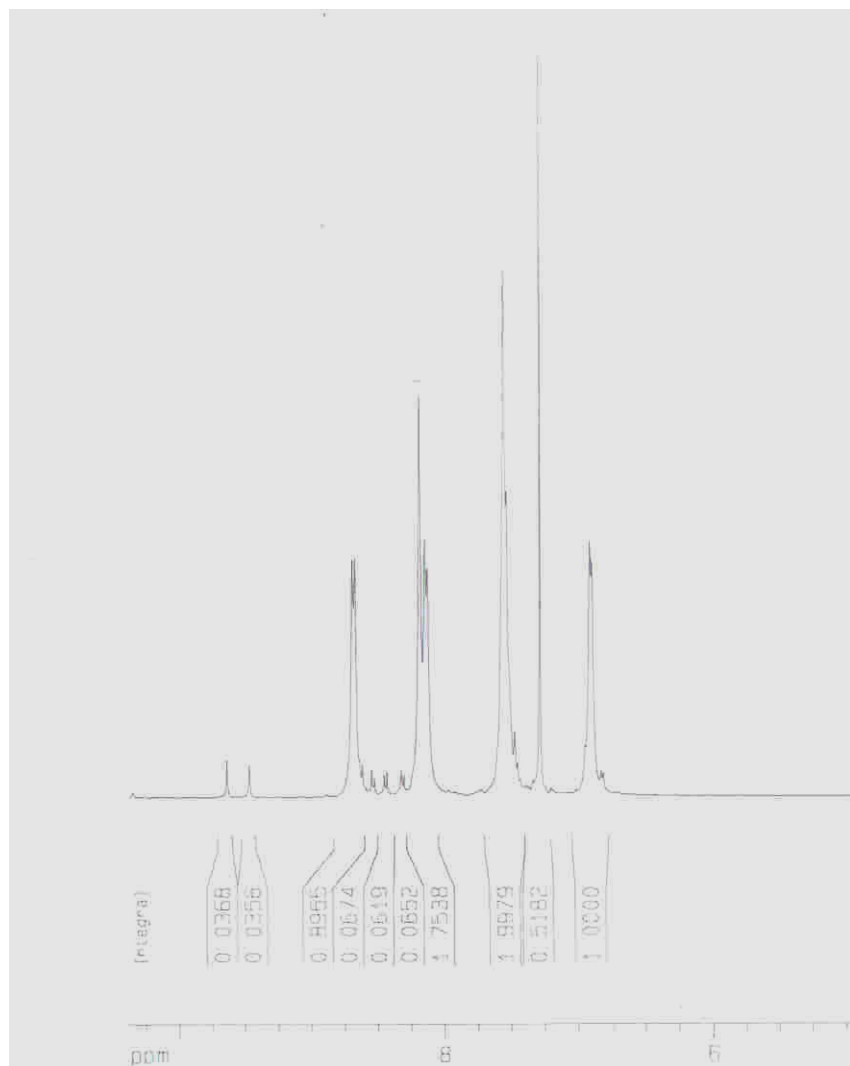


Figure S4: NMR spectrum (aromatic zone) of $[\mathbf{L2}_2\text{Cu}_2]^{2+}$ in CD_3CN . $[\mathbf{L2}_2\text{Cu}_2](\text{ClO}_4)_2$: δ 8.98 (d, 4H, $J=7.8$ Hz), 8.38 (4H, d, $J=7.8$ Hz), 7.72 (s, 4H, $\text{HC}=\text{N}$), 7.67 (d, 4H, $J=7.8$ Hz), 7.60 (t, 4H, $J=7.8$ Hz), 7.05 (d, 4H, $J=7.8$ Hz)

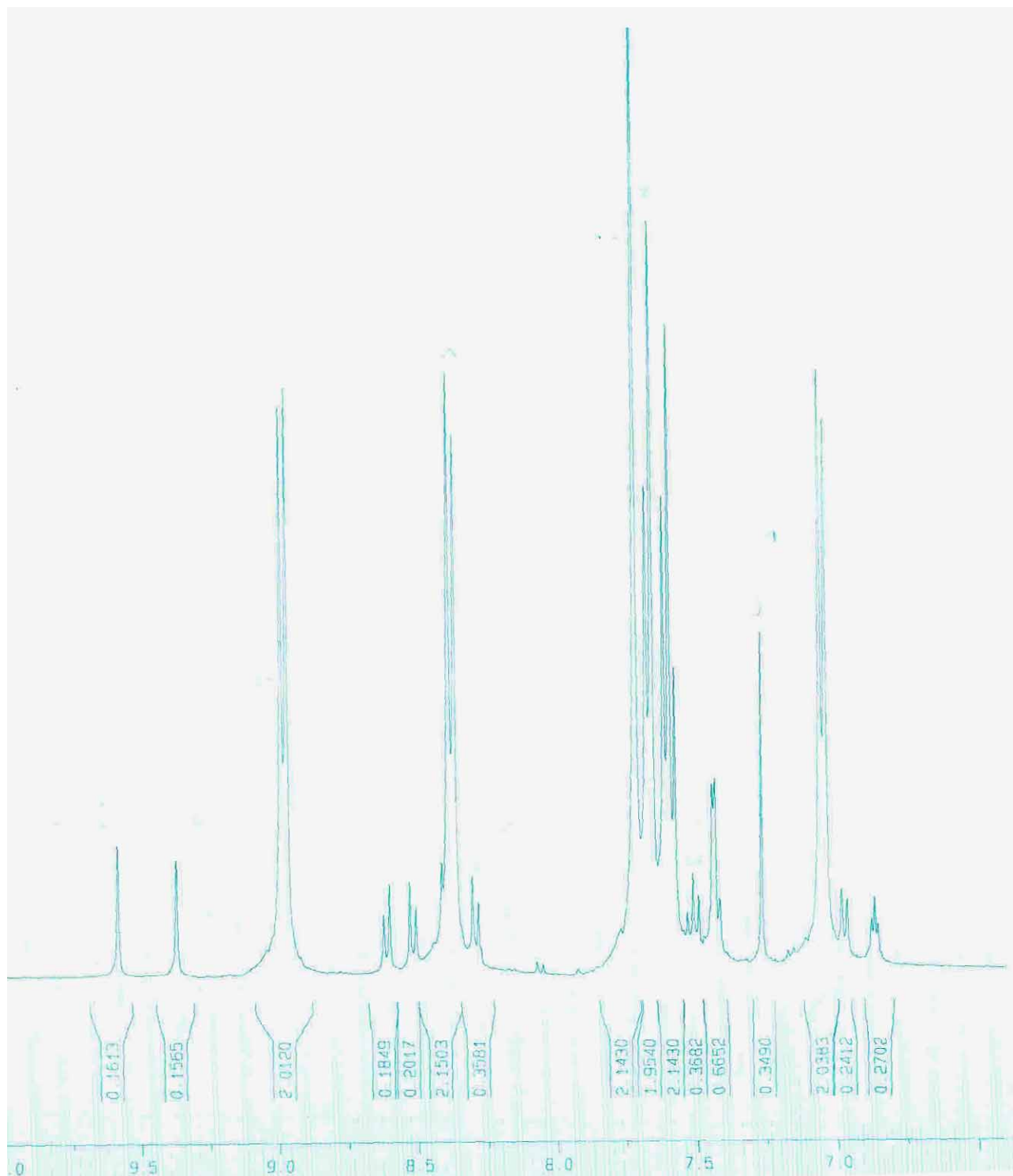


Figure S5. Series of spectra relative to the Controlled potential coulometry (oxidation) of $[\text{L1}_2\text{Cu}_2]^{2+}$. The band at ~ 400 nm and at 580 nm decreases in intensity, the band under 350 nm increases. In the inset, the quantity of charge passed through the electrode is plotted versus time. 1 Q.C. corresponds to the full oxidation of the complex (two moles of electrons per mol of complex)..

