

Supporting Information

Figure S1. ORTEP drawing of $[\text{H}_2\text{L2}]\text{ZnCl}_4\cdot\text{H}_2\text{O}$

Figure S2. Crystal packing of $[\text{H}_2\text{L2}](\text{ClO}_4)_2$ (a) and $[\text{CuL2}](\text{ClO}_4)_2$ (b)

Figure S3. UV-vis. spectra recorded on solutions containing Cu(II) and increasing amounts of L1.

Figure S4. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (CD_3CN , 298 K) of L1 in the absence and in the presence of 1 eq. of Zn(II).

Figure S5. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (CD_3CN , 298 K) of L2 in the absence and in the presence of 1 eq. of Zn(II).

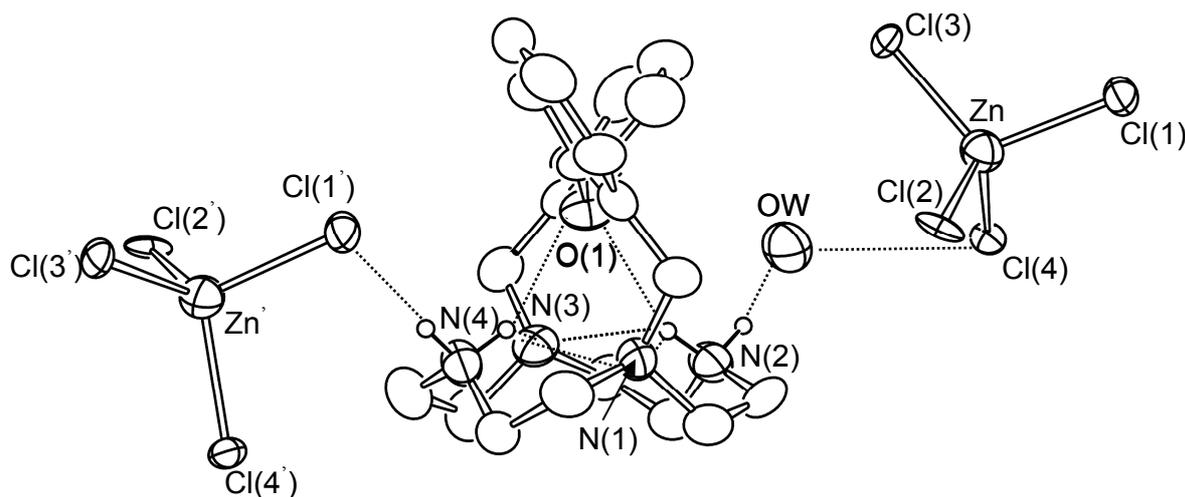


Figure S1. ORTEP drawing of $[\text{H}_2\text{L}_2]\text{ZnCl}_4\cdot\text{H}_2\text{O}$ (primed atoms related by $1+x, 0.5-y, 0.5+z$). The crystal structure consists of $[\text{H}_2\text{L}_2]^{2+}$ cations and ZnCl_4^{2-} anions. The phenyl rings are not coplanar (69.16°) and the O1 oxygen is $2.292(7)$ Å apart from the basal plane defined by the four nitrogen atoms. The overall conformation of the cyclen moiety can be described as [3333]. Both NH_2^+ groups give hydrogen bonds with the ethereal oxygen and the tertiary nitrogen atoms. A NH_2^+ group also interacts with the chlorine atom Cl(1') of a symmetry related ZnCl_4^{2-} anion ($1+x, 0.5-y, 0.5+z$), while a second one interacts with the ZnCl_4^{2-} group via a bridging water molecule (OW). Hydrogen bonding distances (Å): N(1)··N(2) 2.89(1), N(1)··N(4) 2.72(1), N(2)··N(3) 2.75(1), N(3)··N(4) 2.82(1), N2··O1 3.08(1), N4··O1 3.18(1), N2··OW 2.82(1), Cl4··OW 3.245(8), N4··Cl1' 3.153(9).

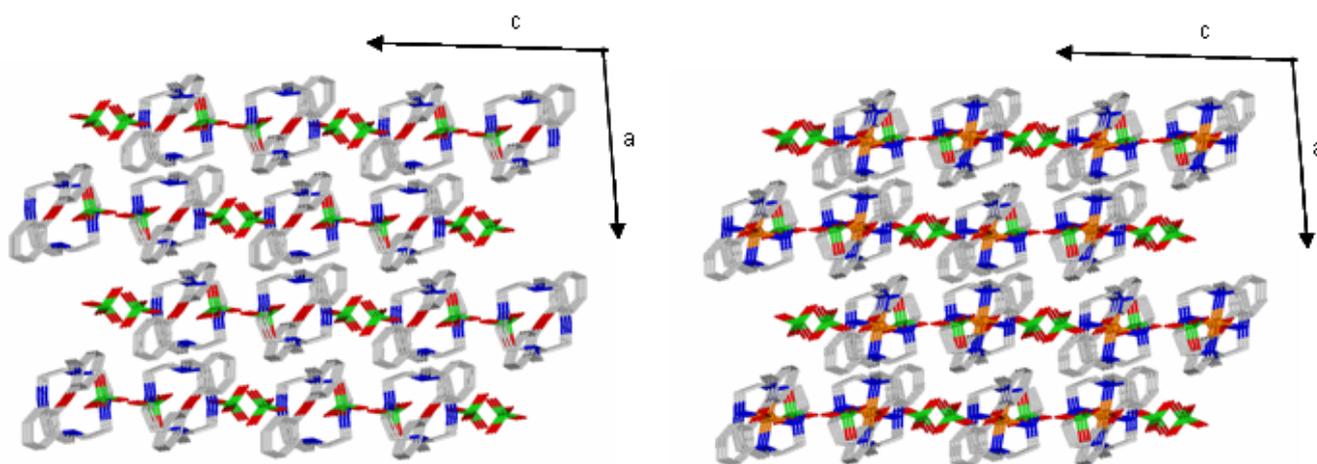


Figure S2. Crystal packing of $[\text{H}_2\text{L}_2](\text{ClO}_4)_2$ (a) and $[\text{CuL}_2](\text{ClO}_4)_2$ (b)

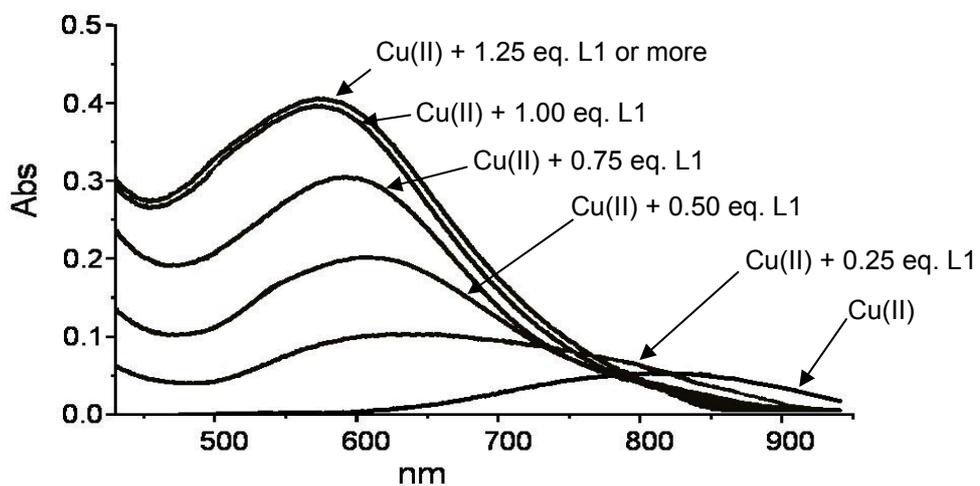


Figure S3. UV-vis. spectra recorded on solutions containing Cu(II) and increasing amounts of L1. The samples were heated at 45 °C for 5' min after each addition of Cu(II) to the solution of L1, to ensure complete formation of the complexes. The spectra were then recorded at room temperature.

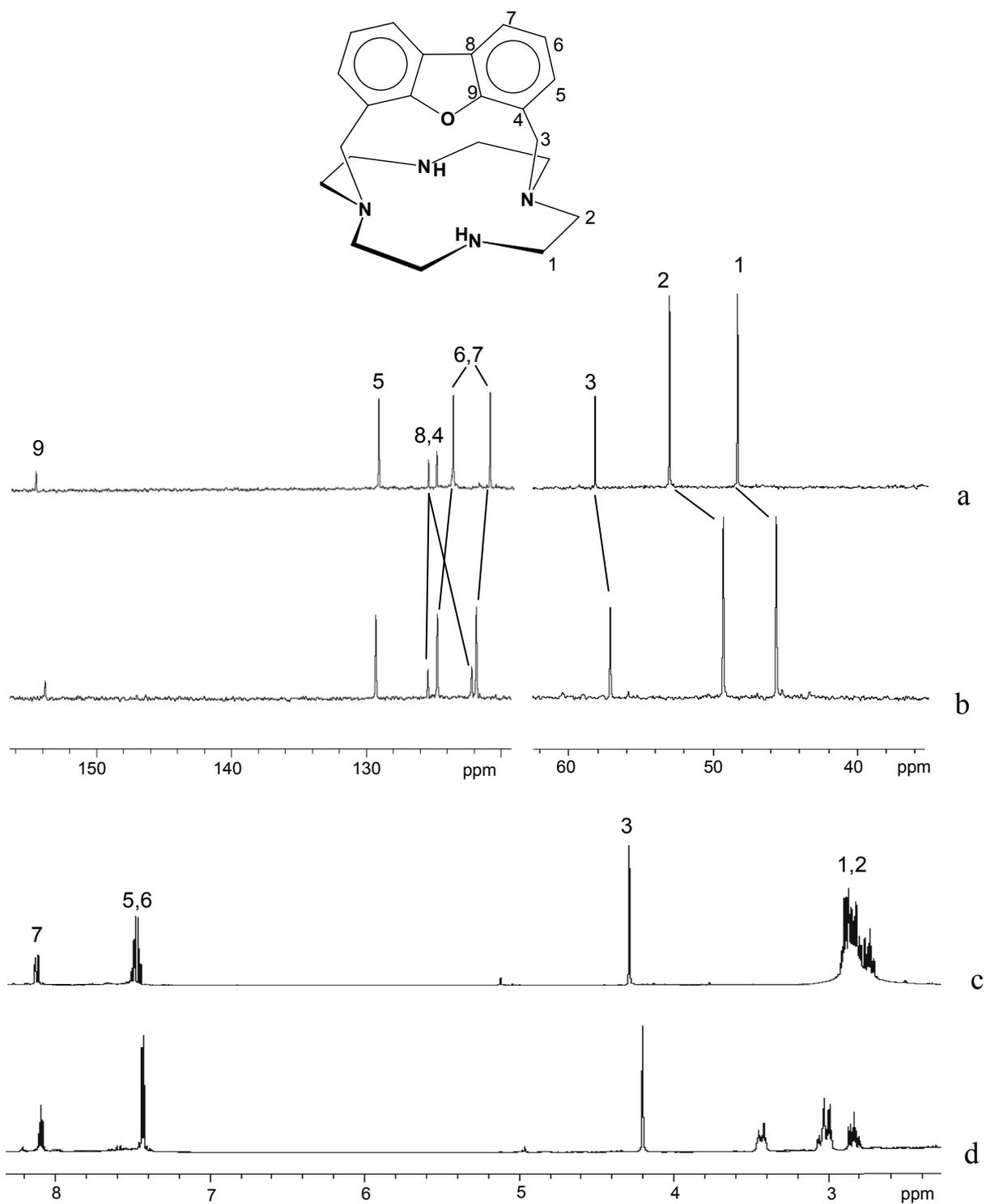


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (CD_3CN , 298 K) of L1 in the absence (a, c) and in the presence of 1 eq. of Zn(II) (b, d). The samples were heated at 45 °C for 5' min after the addition of Zn(II) to the solution of L2, in order to ensure complete formation of the complex. The spectra were then recorded at room temperature.

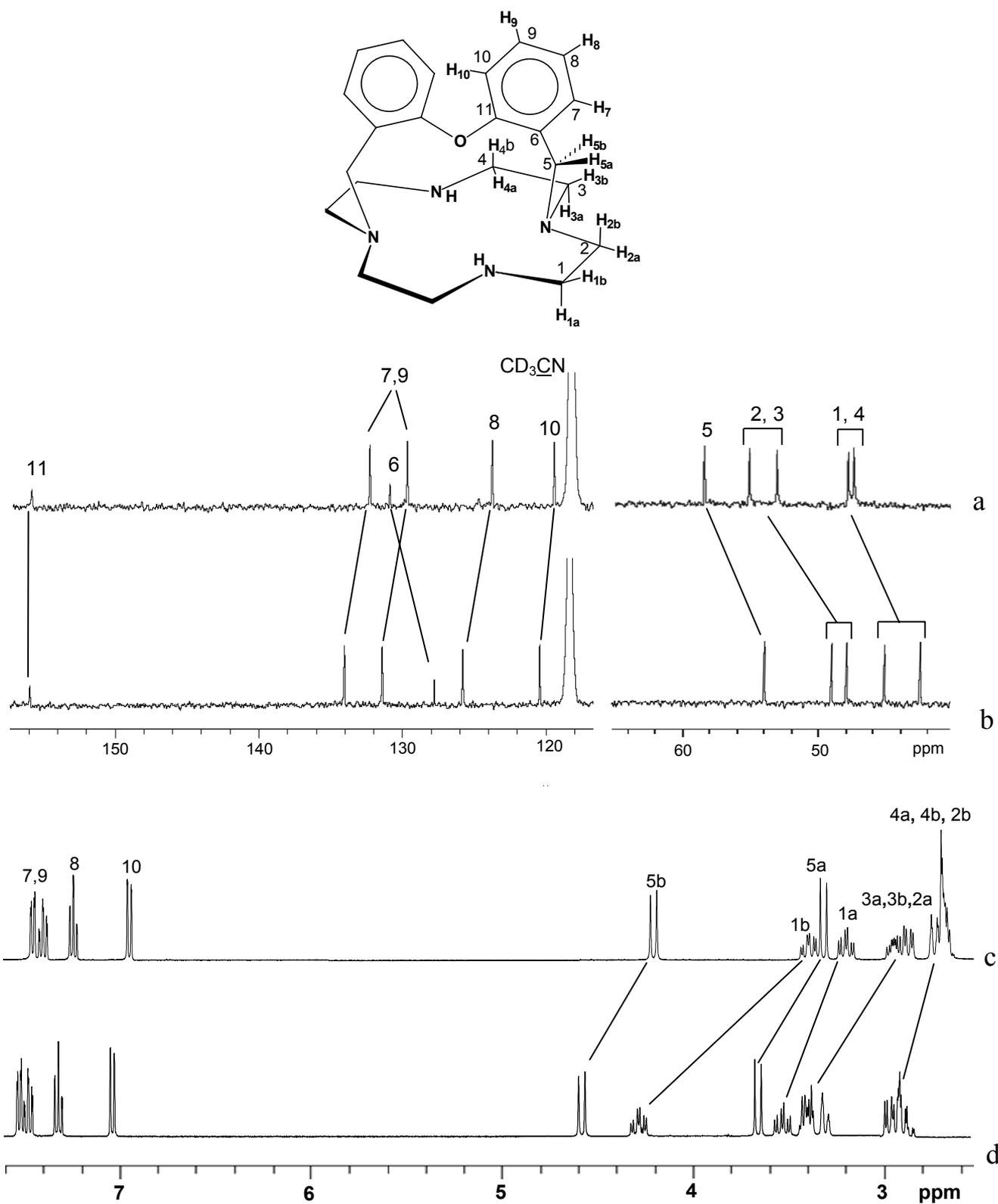


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (CD_3CN , 298 K) of L2 in the absence (a, c) and in the presence of 1 eq. of Zn(II) (b, d). The samples were heated at 45 °C for 5' min after the addition of Zn(II) to the solution of L2, in order to ensure complete formation of the complex. The spectra were then recorded at room temperature.