Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Zn(II)-coordination and fluorescence studies of a new polyazamacrocycle incorporating 1*H*-pyrazole and naphthalene units

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1. ^{1}H and ^{13}C NMR spectra of **L1**·7HCl.

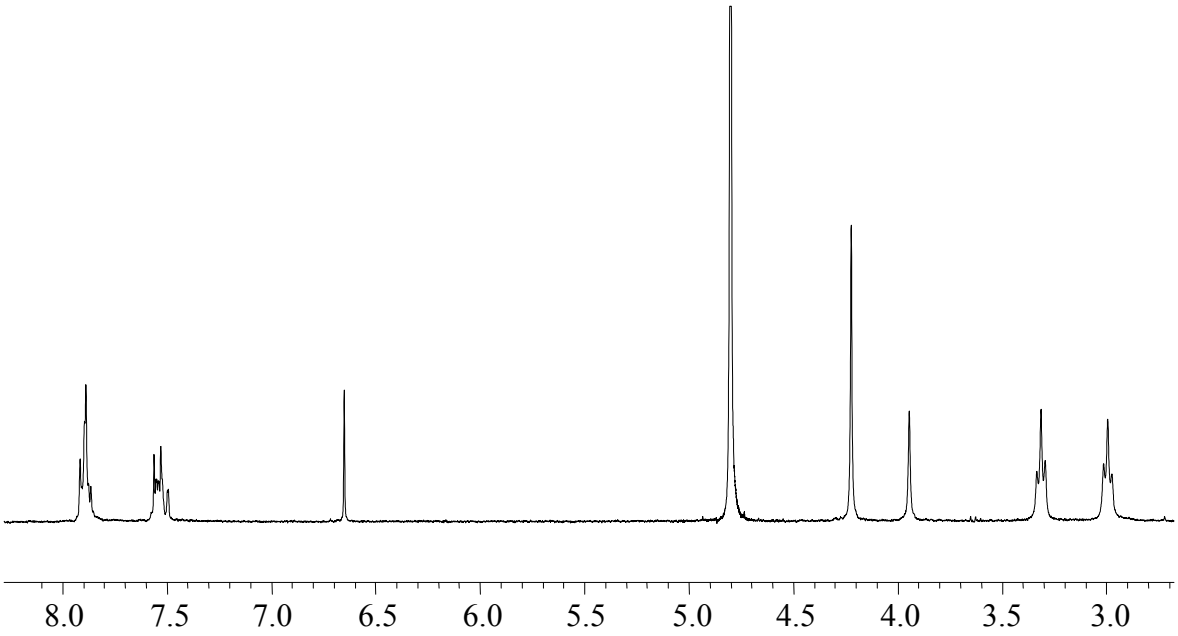
2. Details of the DFT calculations (Fig S1, Table S1, Fig S2).

3. Fig. S3.- Fluorescence emission intensity at 393 nm (pH = 10.0) as a function of the Zn^{2+}:**L1** molar ratio.

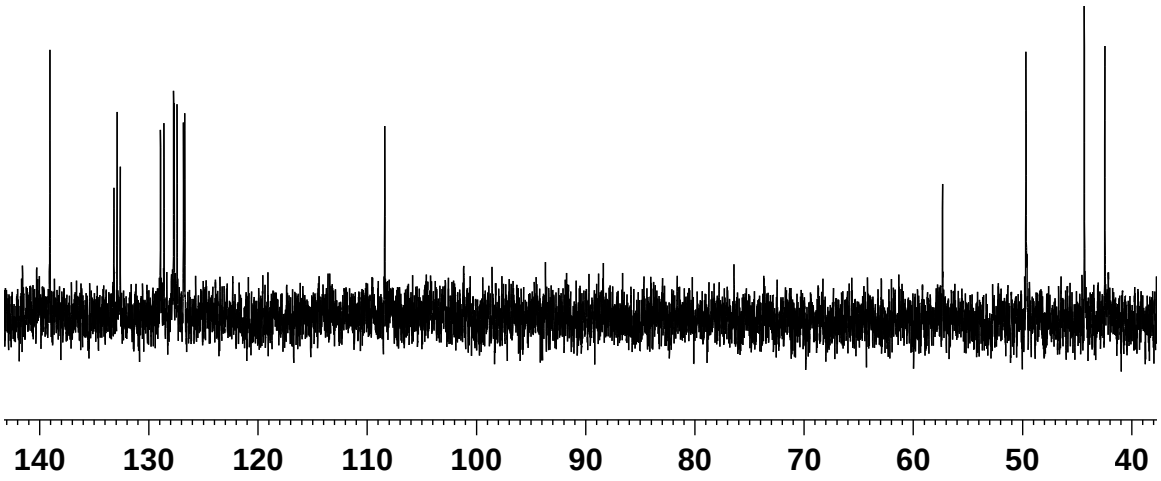
4. Fig. S4.- Fluorescence excitation spectra of the free ligand and of the ligand in the presence of one and two equivalents of Zn^{2+} collected at 335 and 393 nm at pH 7 and 10.

5. Fig. S5.- Plot of the normalised fluorescence intensity *versus* Zn^{2+} concentration for calculating the detection limit of the system Zn^{2+}-**L1**.

1.- ^{1}H and ^{13}C NMR spectra of L1·7HCl



^{1}H NMR (δ, ppm): 2.99 (t, J = 6 Hz, 8H), 3.31 (t, J = 6 Hz, 8H), 3.94 (s, 4H), 4.22 (s, 8H), 6.65 (s, 2H), 7.49 - 7.56 (m, 6H), 7.86 – 7.91 (m, 8H).



^{13}C NMR (δ, ppm): 42.47, 44.35, 49.69, 57.33, 108.39, 126.71, 126.82, 127.41, 127.68, 127.72, 128.61, 128.93, 132.61, 132.90, 133.19, 139.05.

2.- Theoretical Calculations

Figure S1 shows the minimum-energy geometries optimized for the free macrocycle **L1** and the mononuclear $[Zn\mathbf{L1}]^{2+}$ and binuclear $[Zn_2H_{-2}\mathbf{L1}]^{2+}$ species. Table S1 summarizes the total energies calculated in water for boat-like and chair-like conformations of the three species. For **L1** the chair-like conformation results to be more stable than the boat-like conformation by 4.77 kcal mol^{-1}. The coordination of one Zn^{2+} ion is sufficient to reverse the stability of the two conformations and the boat-like structure is more stable by 3.11 kcal mol^{-1} for the mononuclear $[Zn\mathbf{L1}]^{2+}$ species. The boat-like structure is even more favoured for the binuclear $[Zn_2H_{-2}\mathbf{L1}]^{2+}$ species, for which the energy difference between both conformations increases to 8.88 kcal mol^{-1}. The HOMO and HOMO – 1 and the LUMO and LUMO + 1 are very close in energy for both the mononuclear $[Zn\mathbf{L1}]^{2+}$ and the binuclear $[Zn_2H_{-2}\mathbf{L1}]^{2+}$ species and are located over the naphthalene moieties (see Fig. S2 for $[Zn\mathbf{L1}]^{2+}$).

Table S1. Total energies calculated in water for the ground state of **L1**, $[Zn\mathbf{L1}]^{2+}$ and $[Zn_2H_{-2}\mathbf{L1}]^{2+}$.

Compounds	Total energy (a.u.)	
	Boat-like conformation	Chair-like conformation
L1	–2101.909657	–2101.917262
$[Zn\mathbf{L1}]^{2+}$	–2167.140191	–2167.135232
$[Zn_2H_{-2}\mathbf{L1}]^{2+}$	–2231.647901	–2231.633751

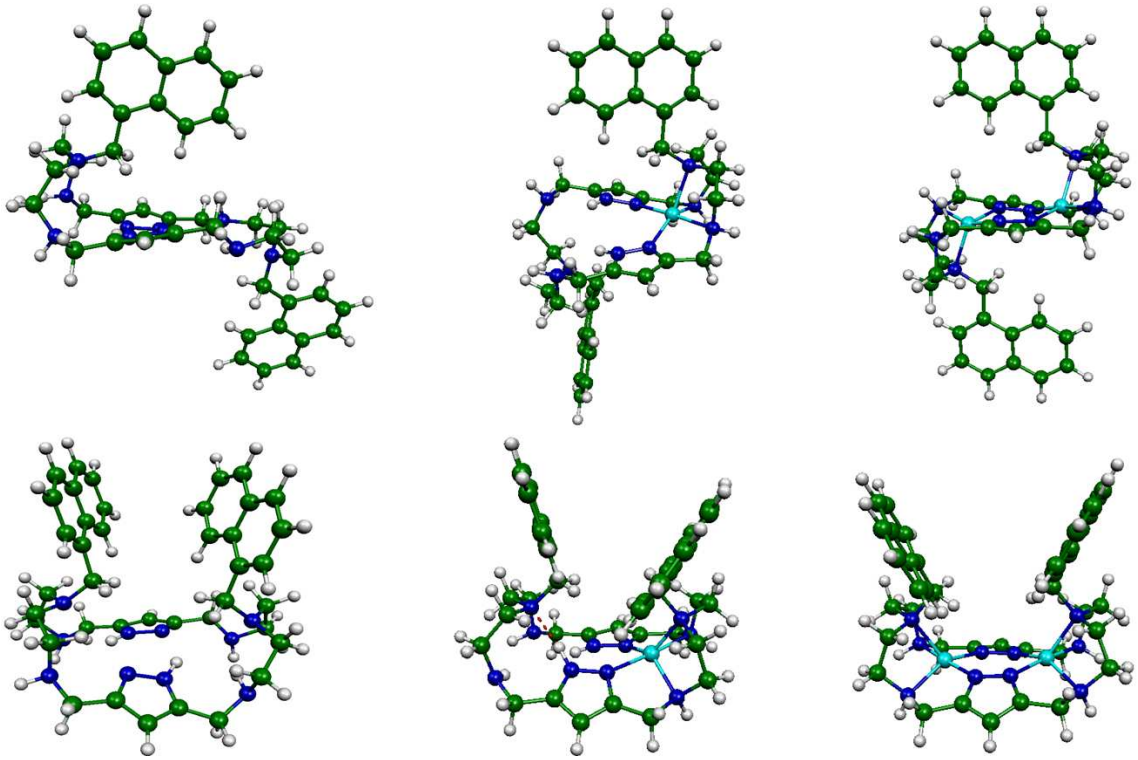


Figure S1. B3LYP/6-31G**-optimized molecular structures calculated for the free macrocycle **L1** (left), the mononuclear $[Zn\mathbf{L1}]^{2+}$ species (middle) and the binuclear $[Zn_2H_{-2}\mathbf{L1}]^{2+}$ species (right) in chair-like (top) and boat-like (bottom) conformations. The Zn^{2+} ions are represented in cyan and the hydrogen bond in the boat-like conformation of the $[Zn\mathbf{L1}]^{2+}$ species is in red.

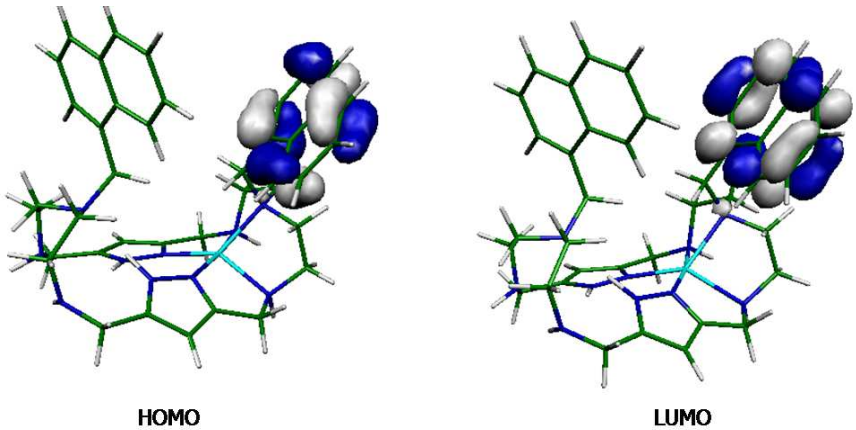


Figure S2. Frontier molecular orbitals for the mononuclear $[Zn\mathbf{L1}]^{2+}$ species. The Zn^{2+} ion is represented in cyan colour.

3.- Fluorescence emission spectra

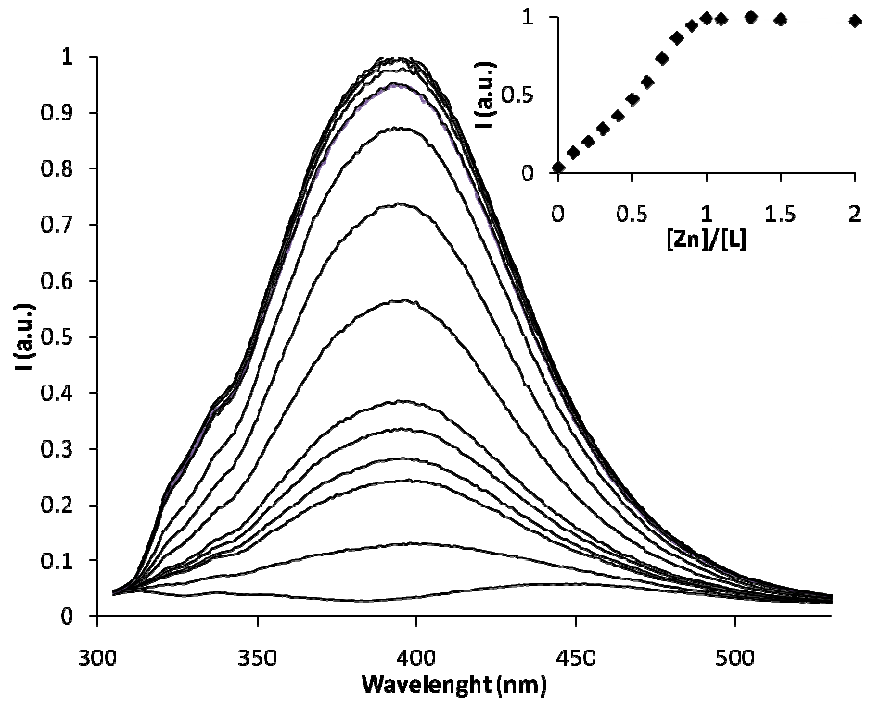


Figure S3. Variation of the fluorescence emission spectra of **L1** upon addition of increasing amounts of Zn^{2+}. The inset plots the emission intensity at 393 nm (pH = 10.0) as a function of the Zn^{2+}:**L1** molar ratio.

4.- Fluorescence excitation spectra

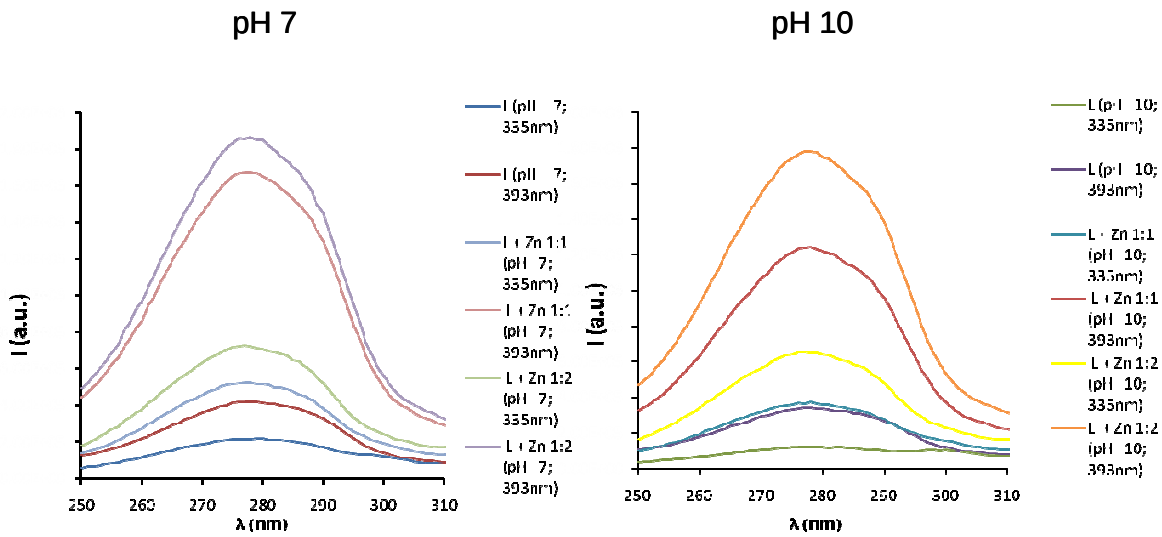


Figure S4. Fluorescence excitation spectra of the free ligand and of **L1** in the presence of one and two equivalents of Zn^{2+} collected at 335 and 393 nm at pH 7 and 10.

5.- Detection limit

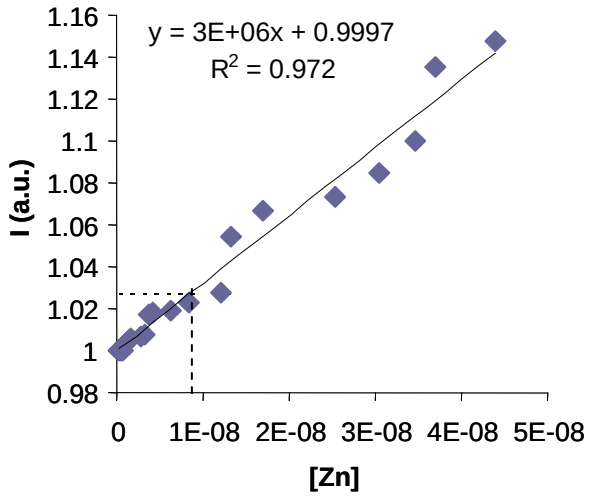


Figure S5. Plot of the normalised fluorescence intensity *versus* Zn^{2+} concentration for calculating the detection limit of the system Zn^{2+}-**L1**.