

Supplementary Information for:

Metal Induced Folding: Synthesis and Conformational Analysis of the Lanthanide Complexes of two 44-membered Hydrazone Macrocycles†

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1. X-ray Crystallography

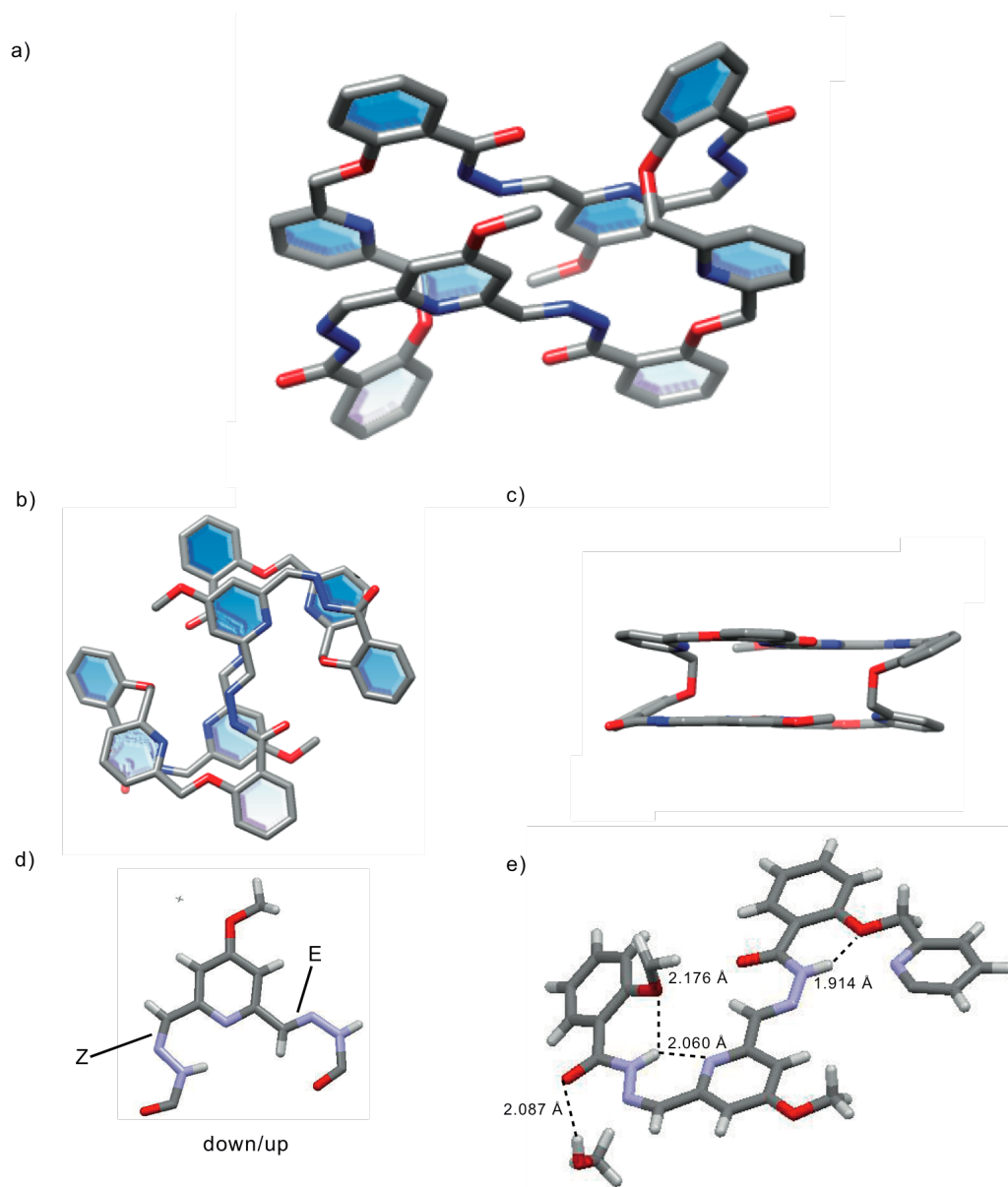


Fig. 1 Solid state structure of unbound ligand **1**. a) tilted view; b) top view; c) side view; d) orientation of hydrazone bonds; e) important hydrogen bonds.

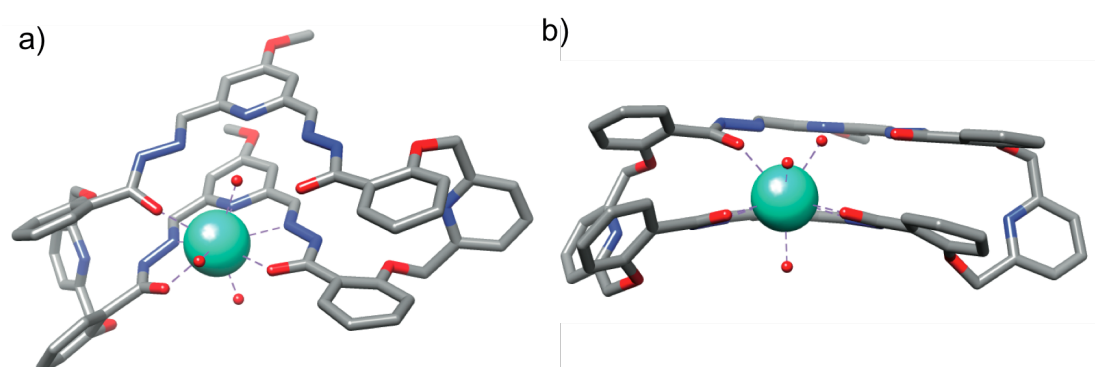


Fig. 2 Solid state structure of Eu^{3+} complex with CN nine. a) tilted view; b) side view.

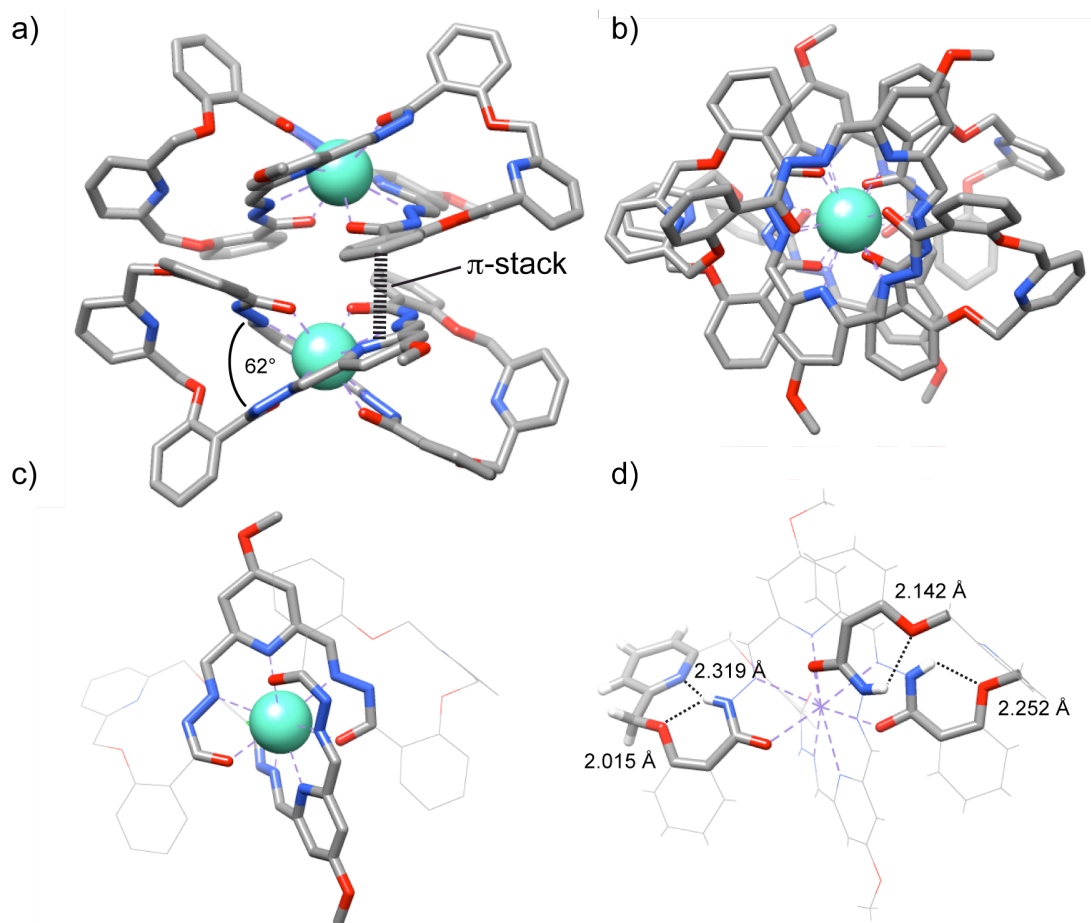


Fig. 3 Solid state structure of Europium complex with CN ten. a) side view; b) top view; c) arrangement of N_3O_2 binding motif; d) important hydrogen bonds.

2. HRMS (High Resolution Mass Spectrometry)

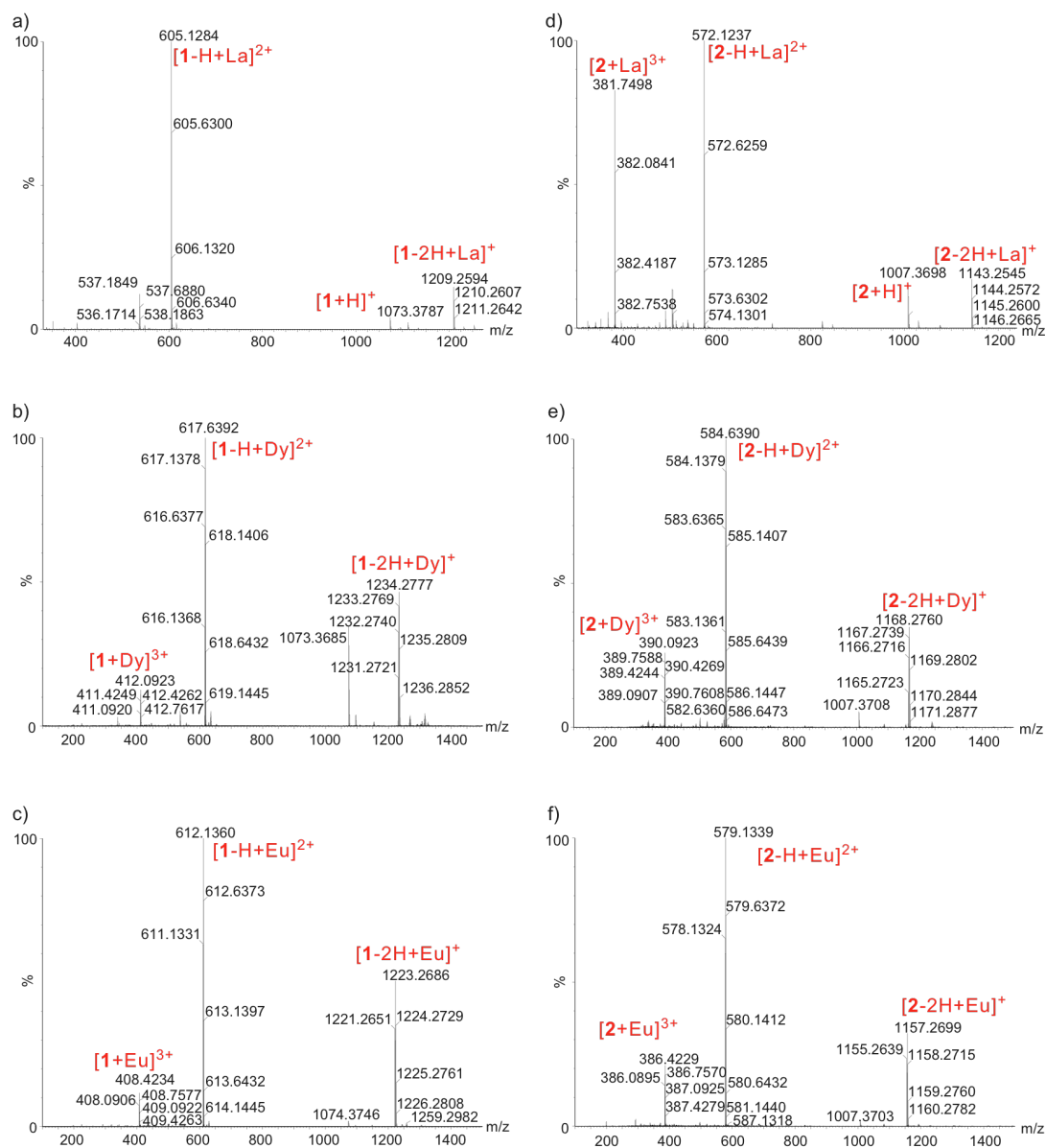


Fig. 4 (-)ESI-HRMS of a) [1][La³⁺]; b) [1][Dy³⁺]; c) [1][Eu³⁺]; d) [2][La³⁺]; e) [2][Dy³⁺]; f) [2][Eu³⁺]. All spectra were recorded in CDCl₃/MeOD (1:1).

3. UV-Vis Spectroscopy

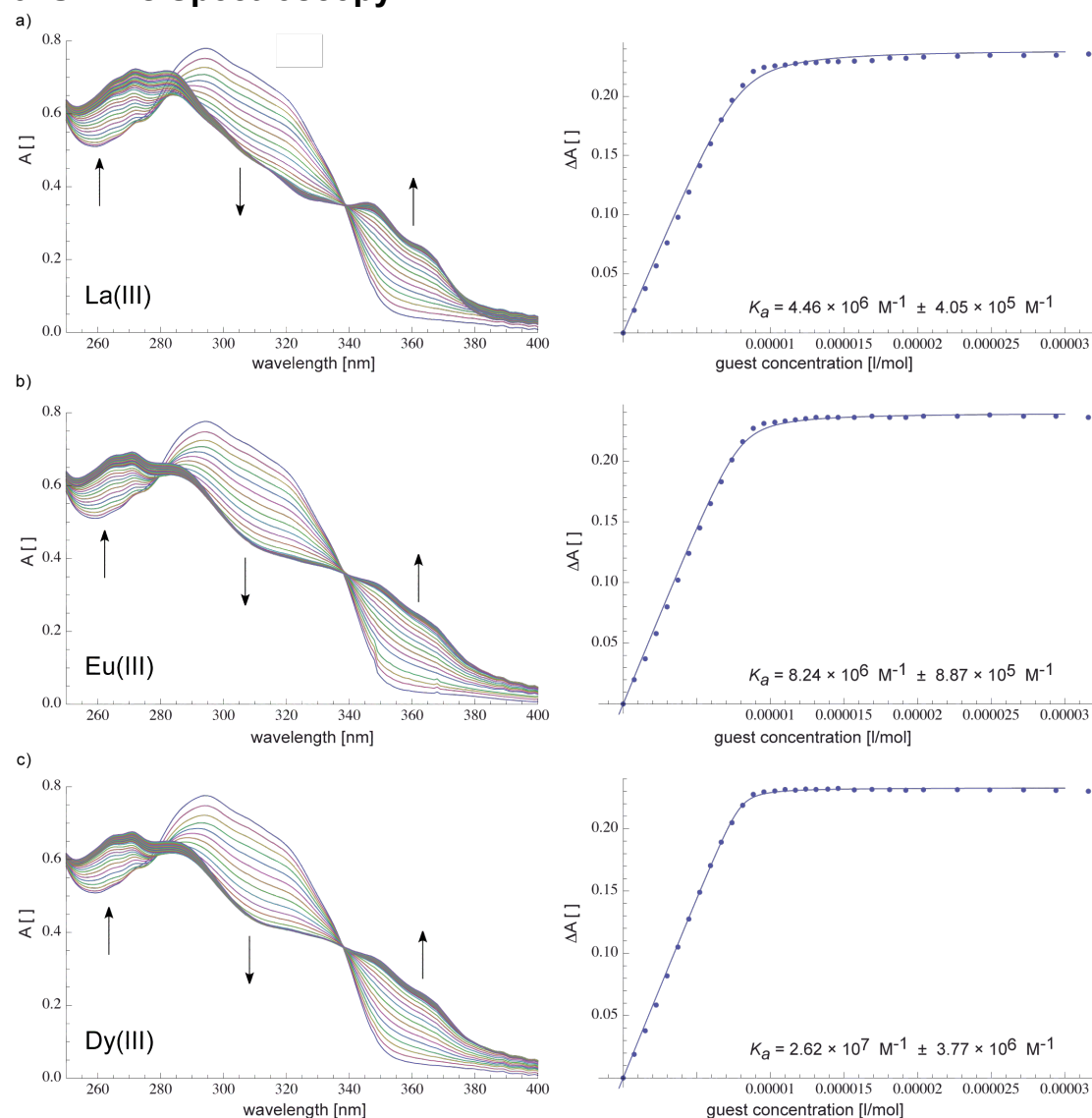


Fig. 5 UV-Vis spectra (left) and binding isotherms (right, $\Delta A_{320\text{nm}}$) of titrations of **1** with a) La³⁺, b) Eu³⁺, c) Dy³⁺. Increasing and decreasing bands are indicated by arrows. Binding isotherms are obtained by plotting the change in absorbance at 320 nm against the guest concentration (dots) and fitting it with a model (line).

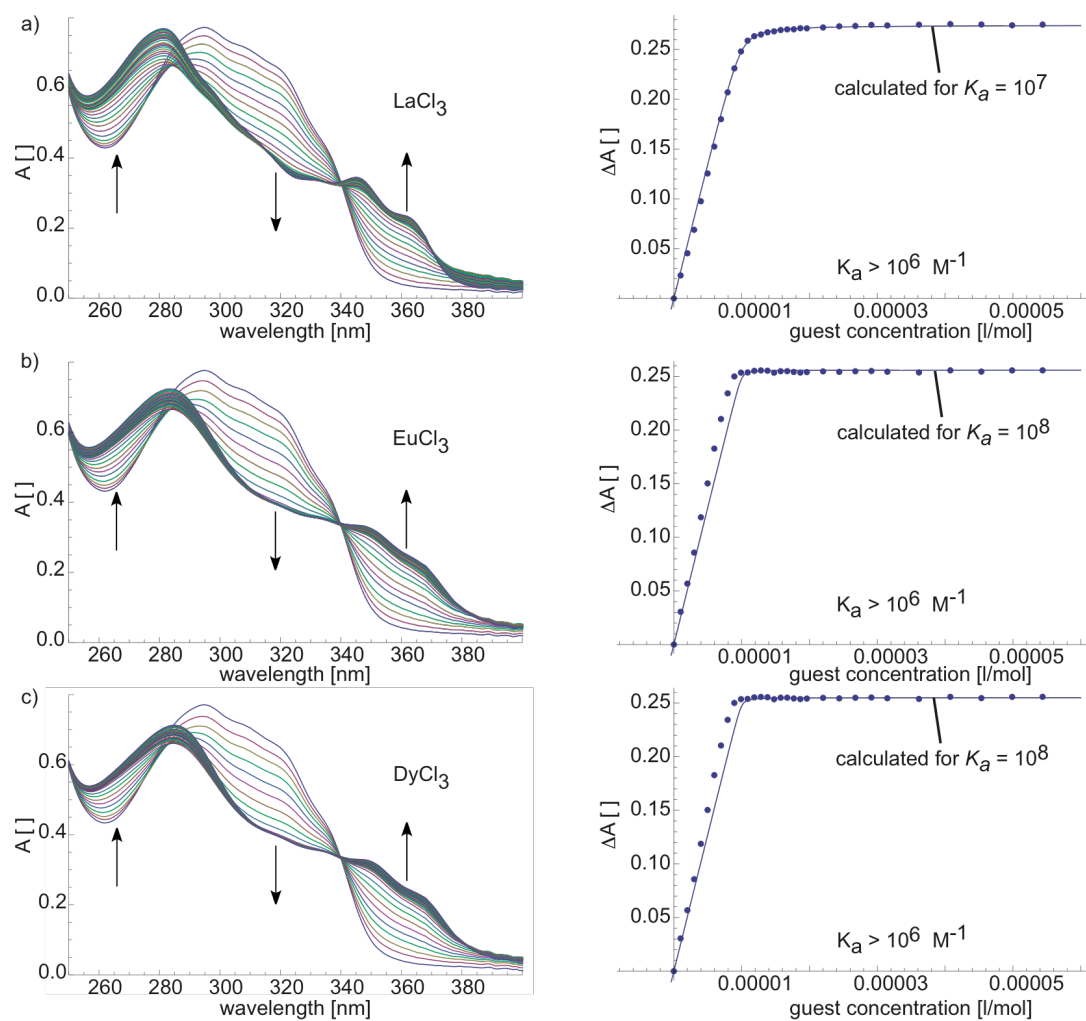


Fig. 6 UV-Vis spectra (left) and binding isotherms (right, $\Delta A_{320\text{nm}}$) of titrations of **2** with a) La^{3+} , b) Eu^{3+} , c) Dy^{3+} . Increasing and decreasing bands are indicated by arrows. Binding isotherms are obtained by plotting the change in absorbance at 320 nm against the guest concentration (dots) and fitting it with a model (line).

3. NMR

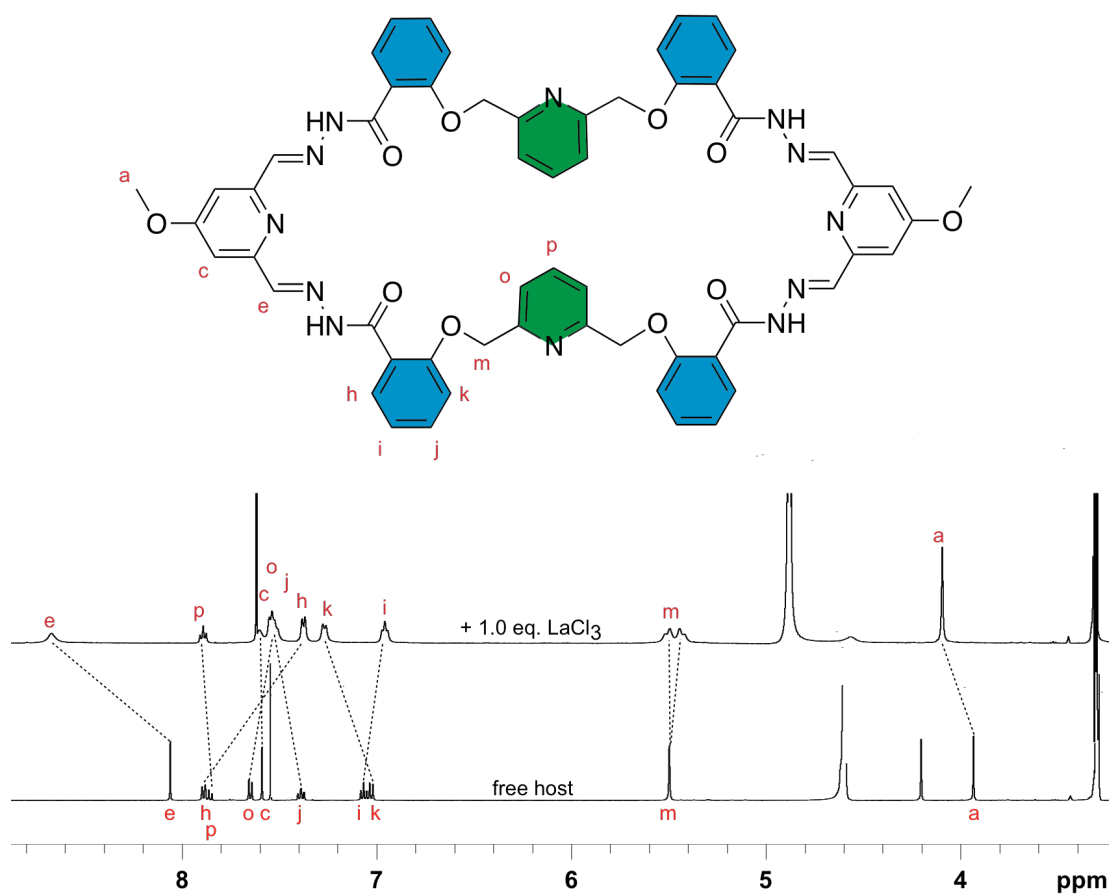


Fig. 7 NMR spectra (500 MHz, 295 K, $\text{CDCl}_3/\text{MeOD}$, 1:1) of **1** and its La^{3+} complex (1 mM).

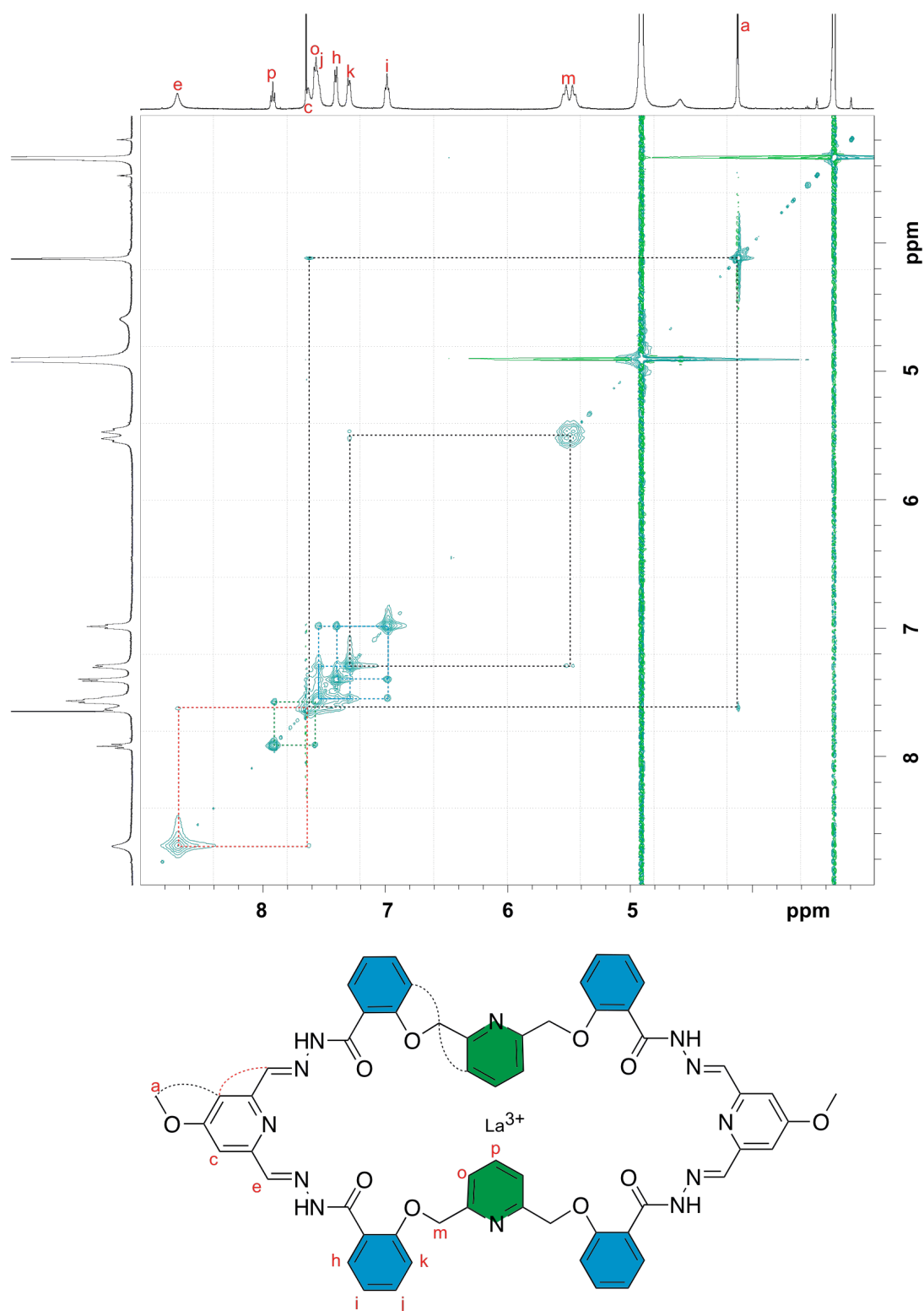


Fig.8: NOESY spectra of **1**[La³⁺] (1 mM in CDCl₃/MeOD, 1:1, 298 K, 500 MHz, mixing time = 800 ms). The cross-peaks are indicated by dotted lines with corresponding colours in the NOESY spectrum and the structure below.

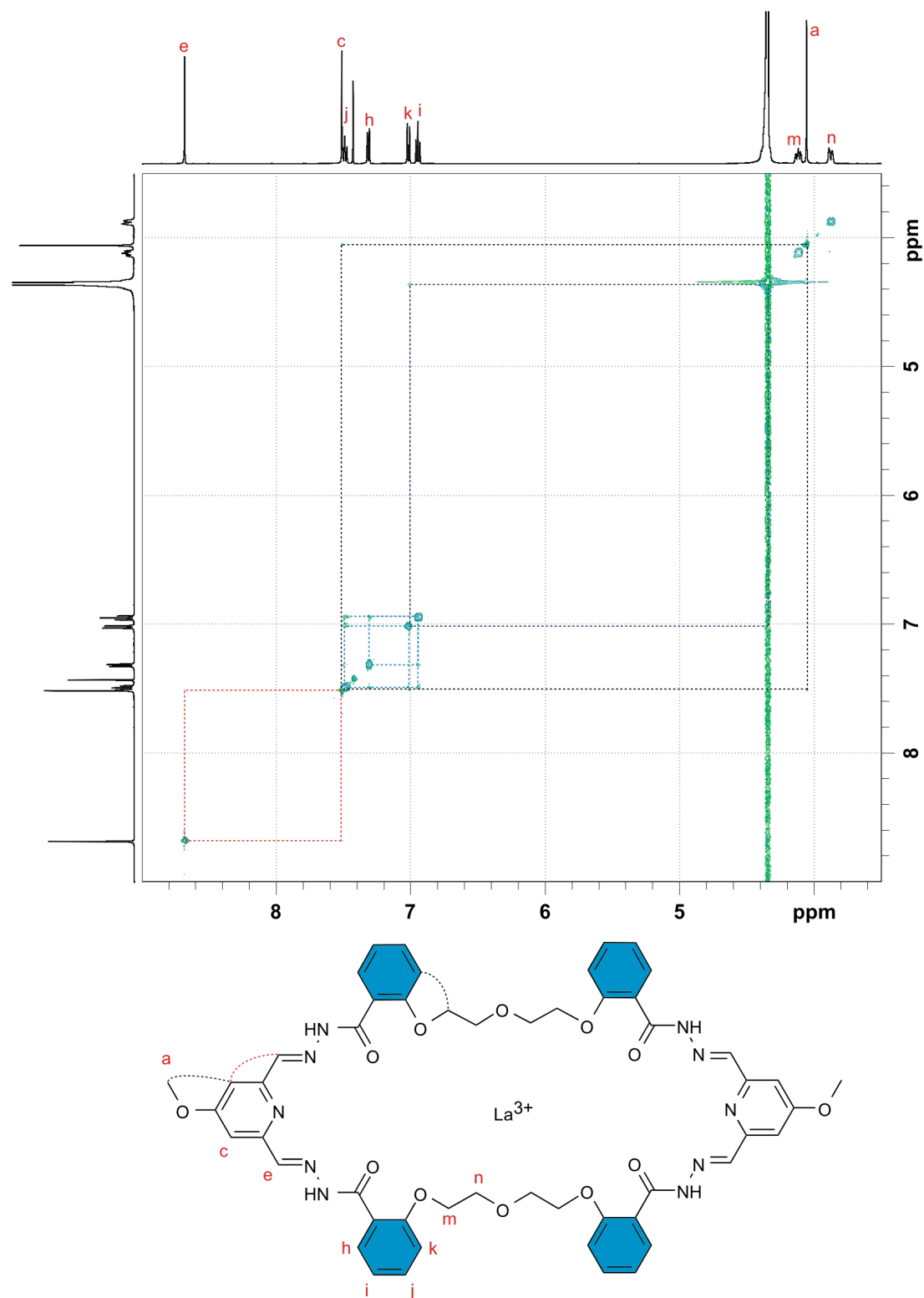


Fig. 9: NOESY spectra of $2[La^{3+}]$ (1 mM in $CDCl_3/MeOD$, 1:1, 298 K, 500 MHz, mixing time = 800 ms). The cross-peaks are indicated by dotted lines with corresponding colours in the NOESY spectrum and the structure below.