Supporting Information

For

Ln(III) Complexes with Triptycene Based Tripodal Ligands: Speciation and Equilibria

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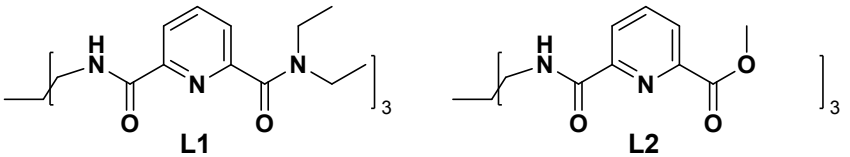
NMR characterization of Ln(III) complexes with L6

$[La_4\mathbf{L6}_4]^{12+}$: ^{1}H NMR ($CD_3CN/CDCl_3$) : δ = 1.11 (t, 3H, CH_3), 1.12 (t, 3H, CH_3), 3.38 (m, 1H, CH_2), 3.34 (m, 2H, CH_2), 3.69 (m, 1H, CH_2), 5.73 (s, H, CH), 5.91 (s, 1H, CH), 6.72 (s, 1H, CH), 6.80 (dd, 1H, CH), 7.46 (dd, 1H, CH), 7.66 to 7.75 (m, 3H, CH), 9.41 (s, 1H, NH) ppm.

$[La_3\mathbf{L6}_2]^{9+}$: ^{1}H NMR ($CD_3CN/CDCl_3$) : δ = 0.71 (t, 3H, CH_3), 1.26 (t, 3H, CH_3), 2.9 (m, 1H, CH_2), 3.1 (m, 1H, CH_2), 3.45 (m, 1H, CH_2), 3.65 (m, 1H, CH_2), 5.82 (s, H, CH), 6.25 (s, 1H, CH), 7.2 (d, 1H, CH), 7.63 (d, 1H, CH), 7.96 (d, 1H, CH), 8.37 (t, 1H, CH), 8.51 (d, 1H, CH), 8.64 (s, 1H, CH), 10.13 (s, 1H, NH) ppm.

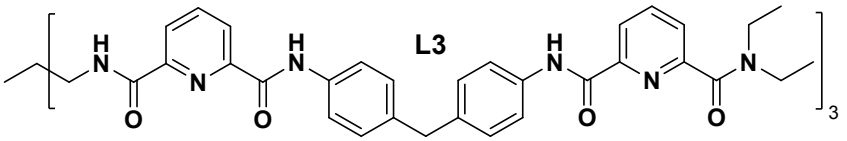
$[Lu_4\mathbf{L6}_4]^{12+}$: ^{1}H NMR ($CD_3CN/CDCl_3$) : δ = 0.96 (t, 3H, CH_3), 1.40 (t, 3H, CH_3), 3.28 (m, 1H, CH_2), 3.31 (m, 2H, CH_2), 3.38 (m, 1H, CH_2), 3.75 (m, 1H, CH_2), 5.83 (s, H, CH), 6.02 (d, 1H, CH), 6.70 (d, 1H, CH), 6.87 (s, 1H, CH), 7.52 (s, 1H, CH), 7.62 (s, 1H, CH), 7.82- 7.91 (m, 2H, CH), 9.37 (s, 1H, NH) ppm.

$[Lu_3\mathbf{L6}_2]^{9+}$: ^{1}H NMR ($CD_3CN/CDCl_3$) : δ = 0.68 (t, 3H, CH_3), 1.31 (t, 3H, CH_3), 3.02 to 3.78 (m, 4H, CH_2), 5.85 (s, 1H, CH), 6.60 (s, 1H, CH), 7.23 (dd, 1H, CH), 7.63 (s, 1H, CH), 8.08 (d, 1H, CH), 8.47 (t, 1H, CH), 8.61 (s, 1H, CH), 8.68 (d, 1H, CH), 10.33 (s, 1H, NH) ppm.

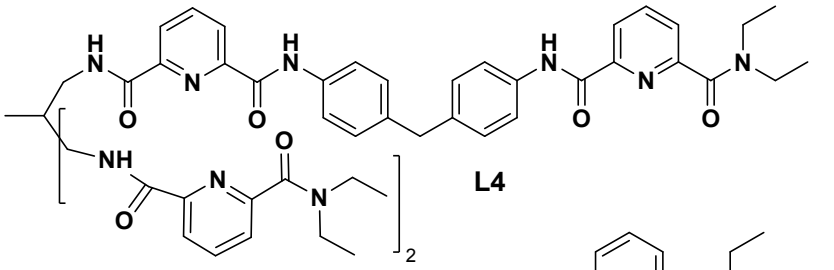


L1

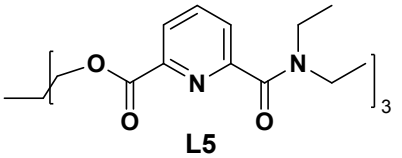
L2



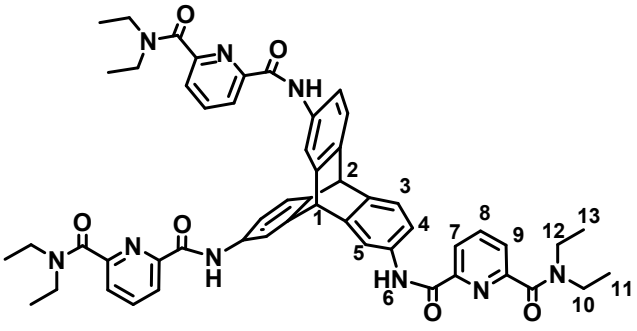
L3



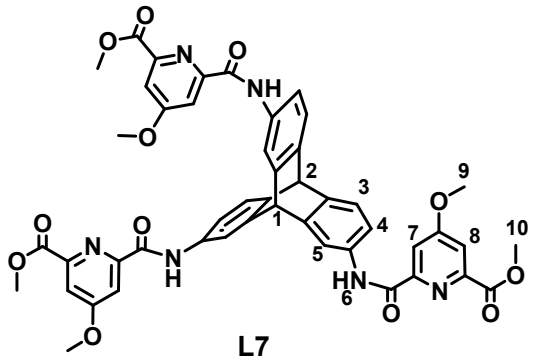
L4



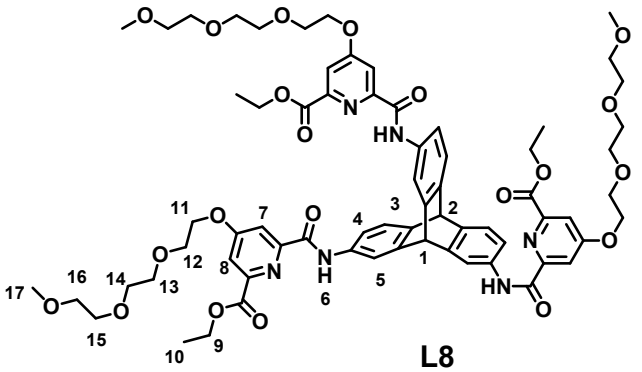
L5



L6

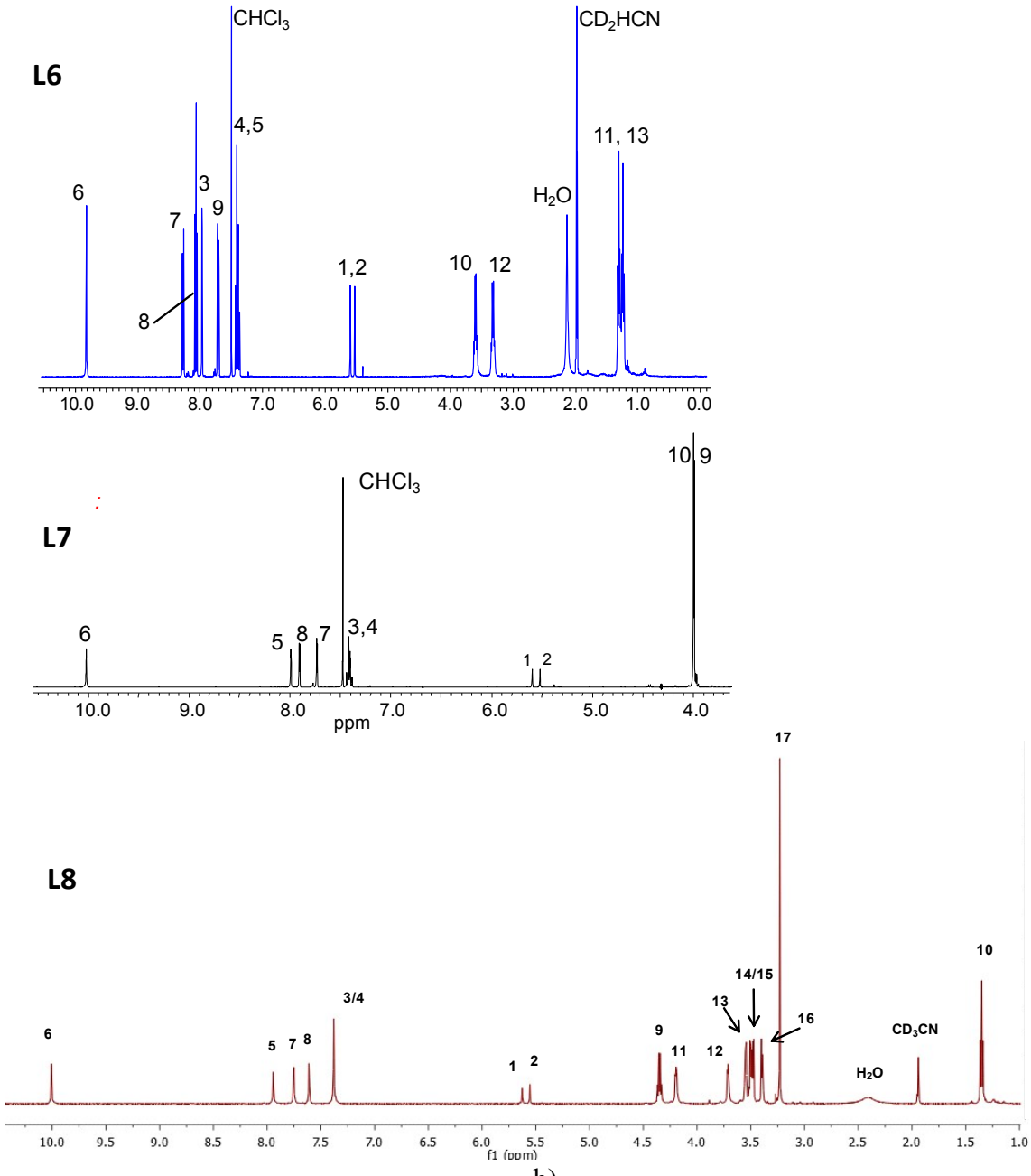


L7



L8

a)



b)

Scheme S1. a) Full chemical structure of ligands **L1**-**L8** with hydrogen atom numbering (only **L6**-**L8**) for NMR. b) NMR spectra of ligands **L6**-**L8**.

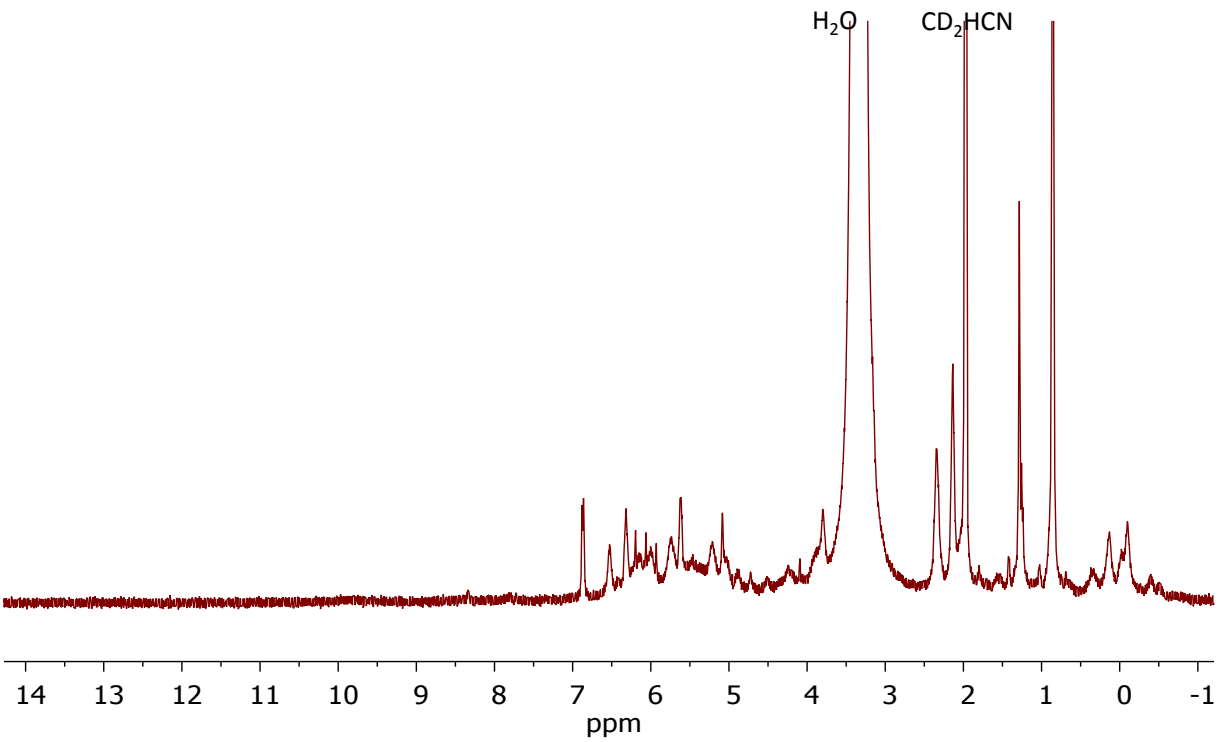


Figure S1. ^{1}H NMR spectrum in metal excess for [Eu]/[**L6**] ~5 (400 MHz, 294 K, $[\mathbf{L6}]_0$ = 9.1×10^{-3}M).

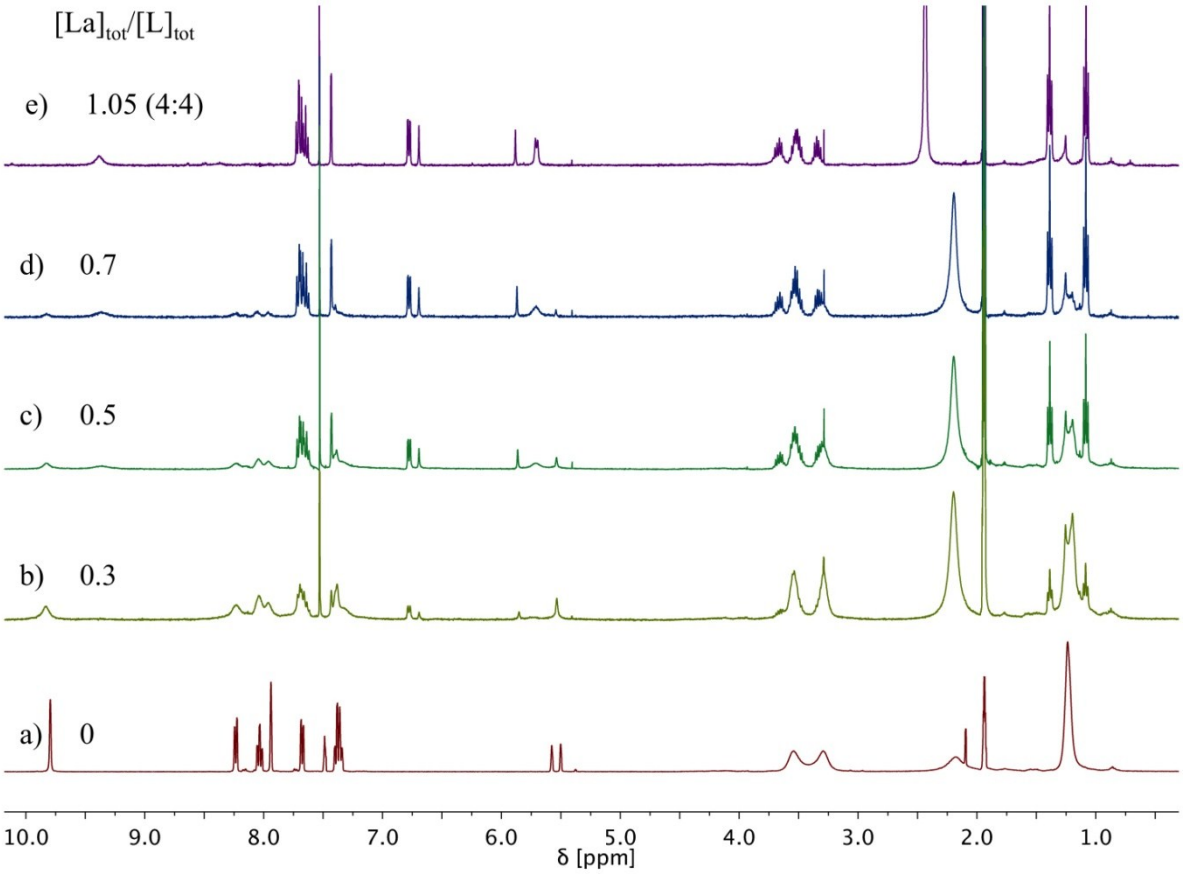


Figure S2. NMR spectra for the titration of **L6** with La(III) with the ratios [La]/[**L6**] (a), 0.3 (b), 0.5 (c), 0.7 (d) et 1.05 (e). (400 MHz, 294 K, $[\mathbf{L6}]_0 = 9.1\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

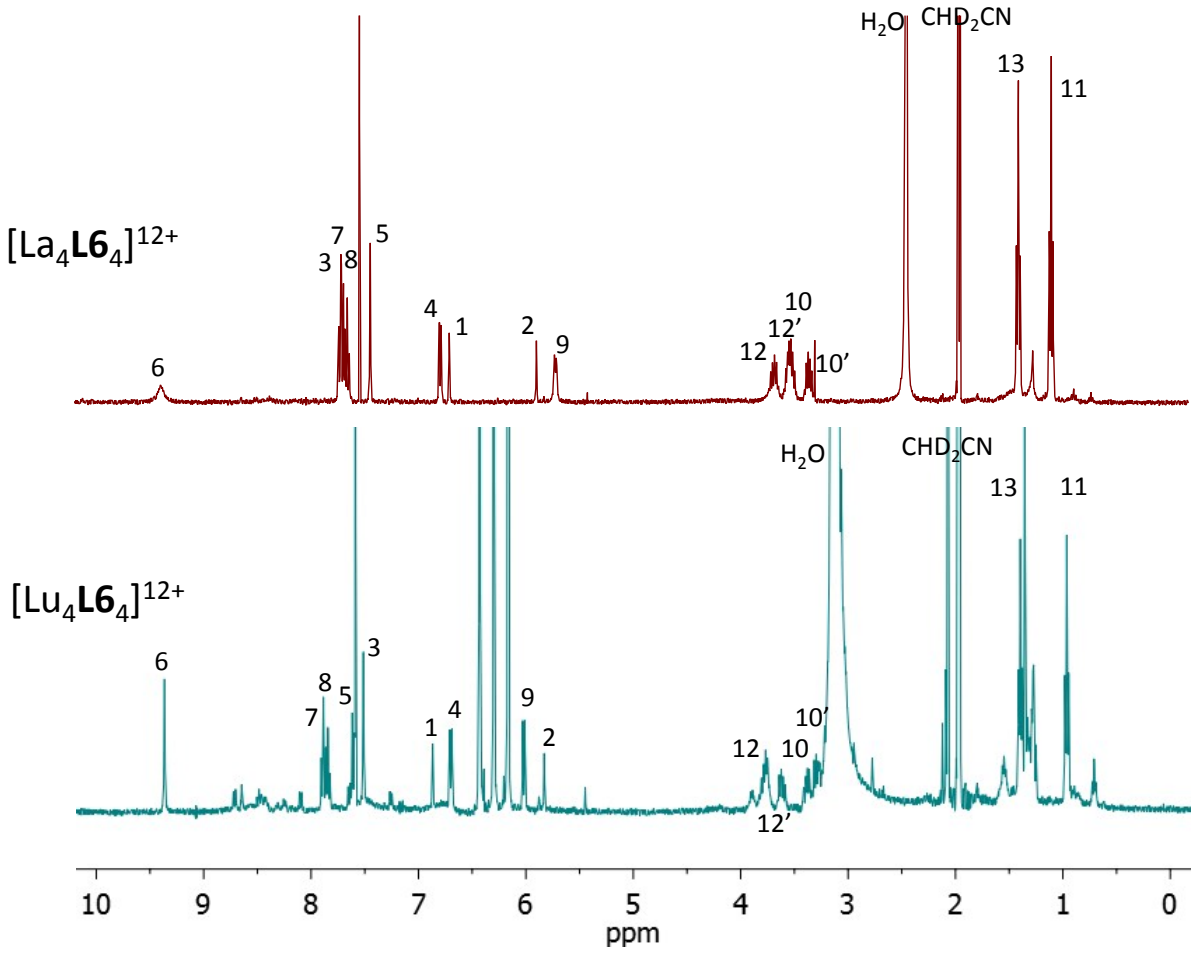


Figure S3. The NMR spectra of tetranuclear complexes $[La_4\mathbf{L6}_4]^{12+}$ and $[Lu_4\mathbf{L6}_4]^{12+}$ with the proton assignment. The spectra are extracted from related titrations in Figure 4 and Figure S6, respectively (400 MHz, 294 K).

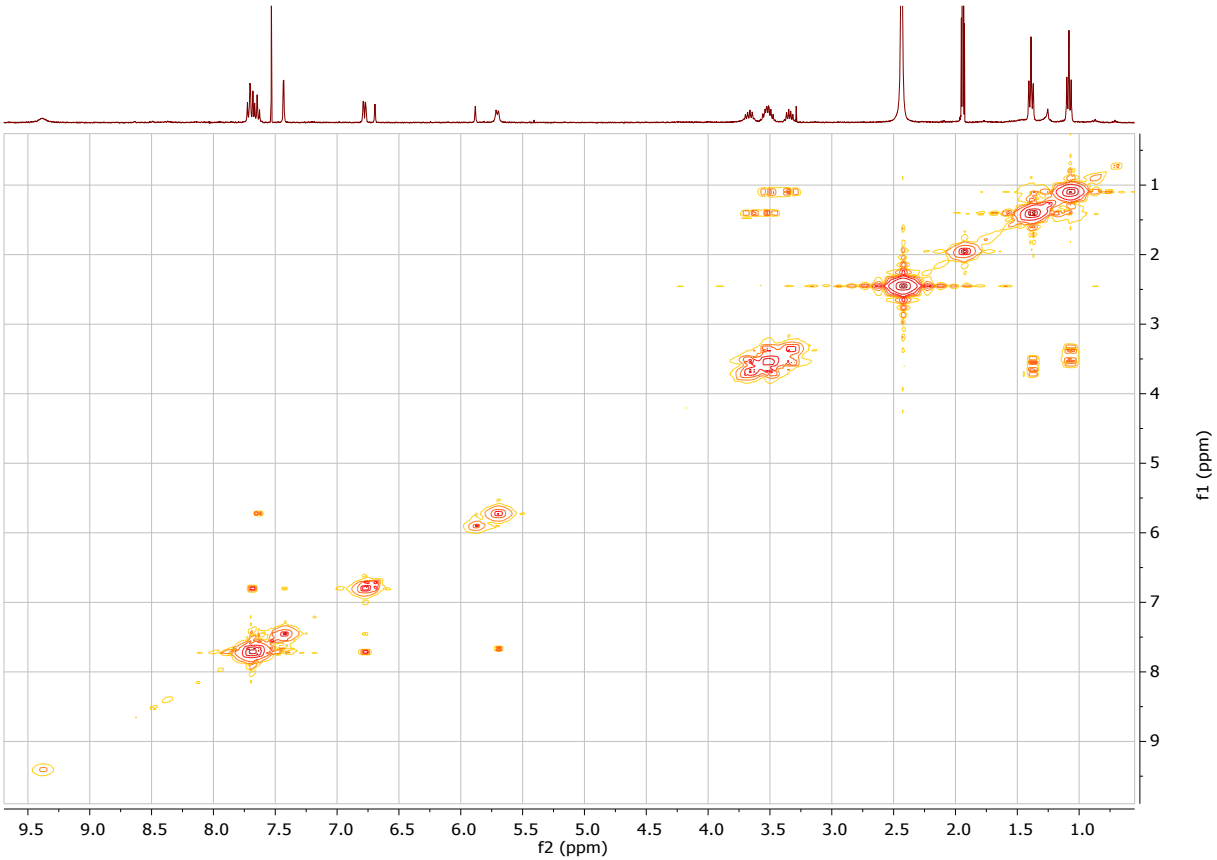


Figure S4. COSY NMR spectrum for the $[La_4\mathbf{L6}_4]^{12+}$ complex atthe ratios [La]/[**L6**] = 1.05. (400 MHz, 298 K, $[\mathbf{L6}]_0 = 9.1\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

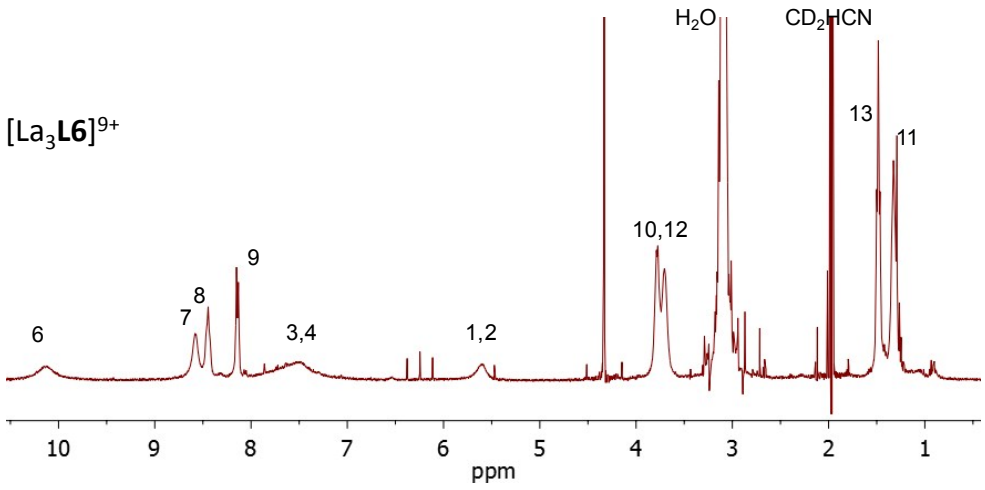


Figure S5. NMR spectrum of the complex with **L6** in excess of La(III). [La]/[**L6**] ~5, standing several months after mixing (400 MHz, 294 K).

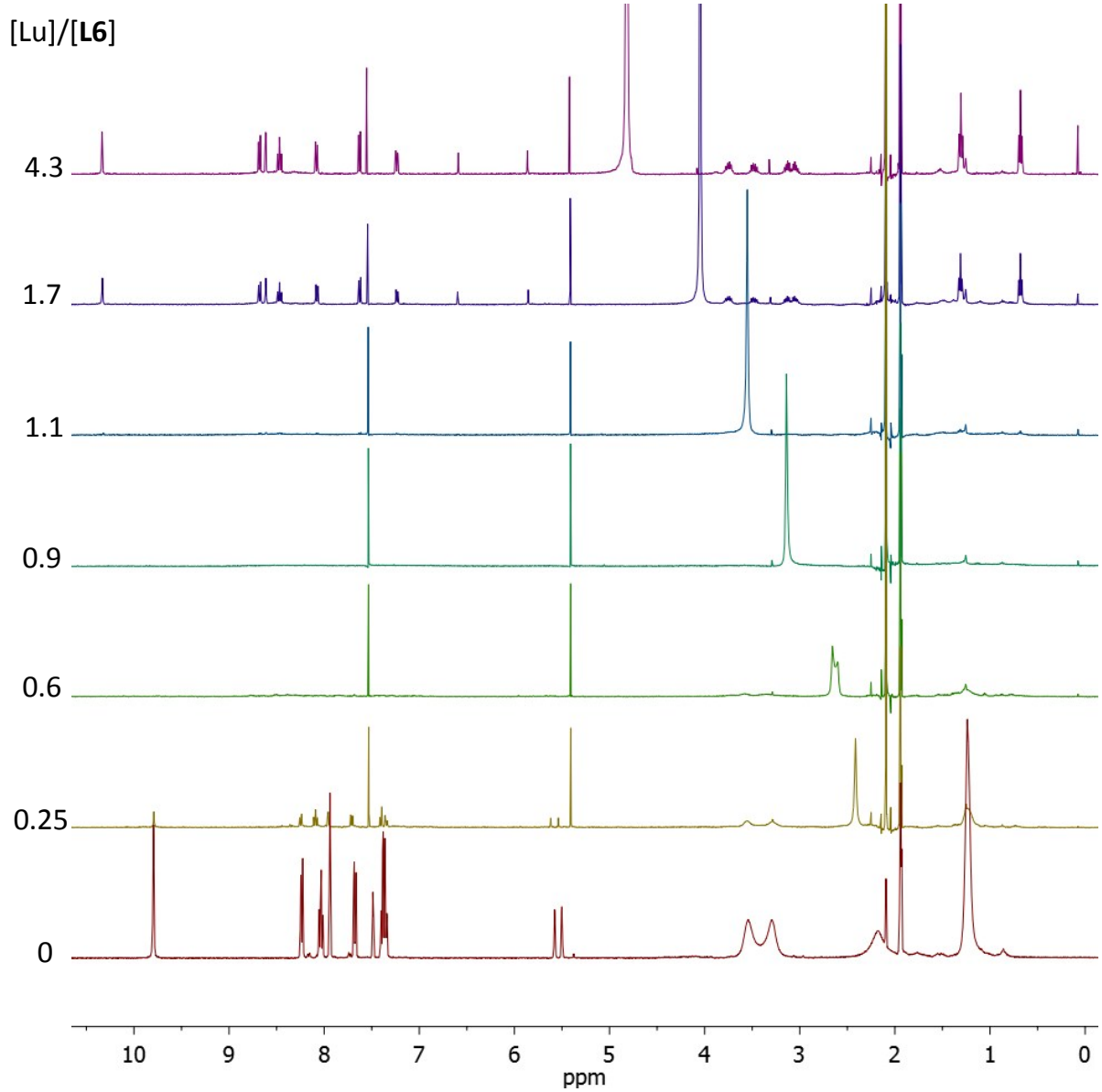


Figure S6. NMR spectra for the titration of **L6** with Lu(III) perchlorate. The [Lu]/[**L6**] ratio is given on the left (298 K). The spectrum for [Lu]/[**L6**] = 0 corresponds to **L6**. (400 MHz, 294 K, $[\mathbf{L6}]_0 = 9.1\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

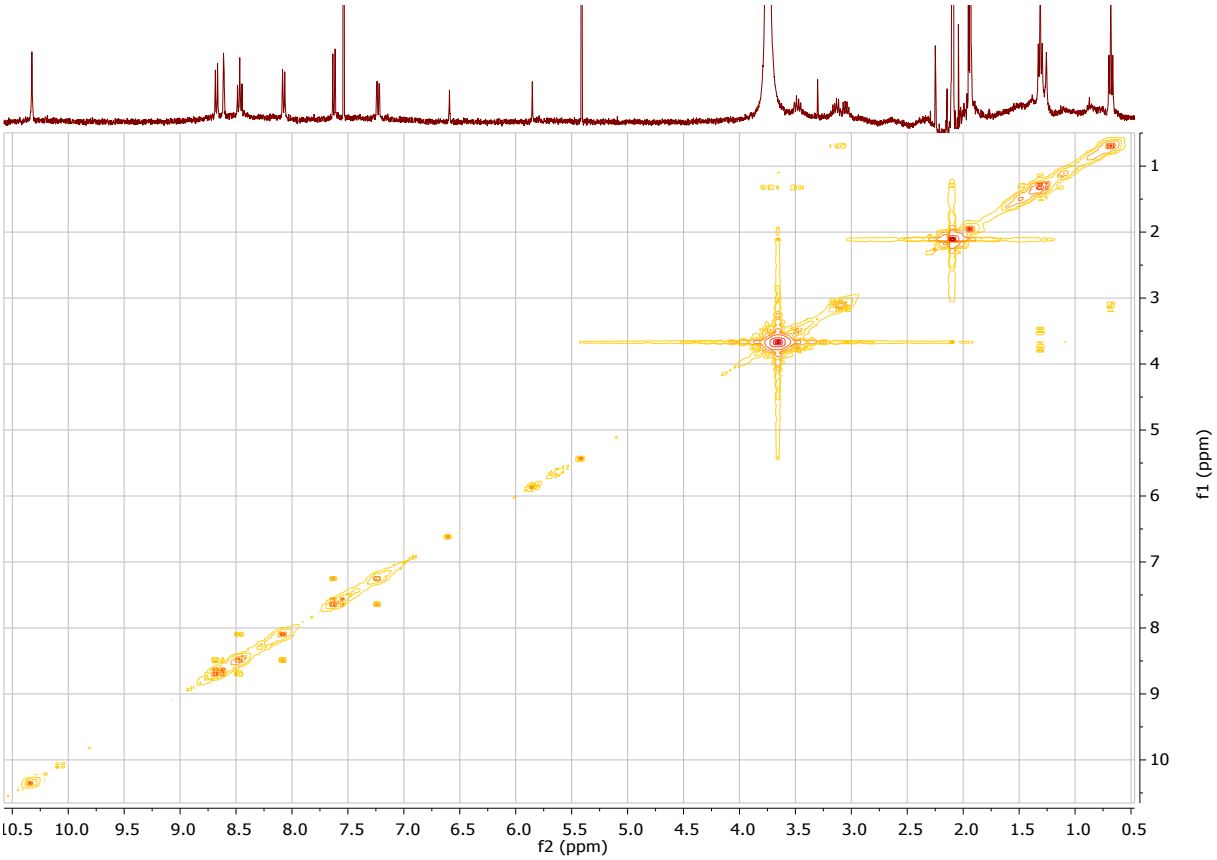


Figure S7. COSY NMR spectrum for the $[Lu_3\mathbf{L6}_2]^{9+}$ complex atthe ratios [Lu]/[**L6**] = 1.7. ($[\mathbf{L6}]_0 = 9.1\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

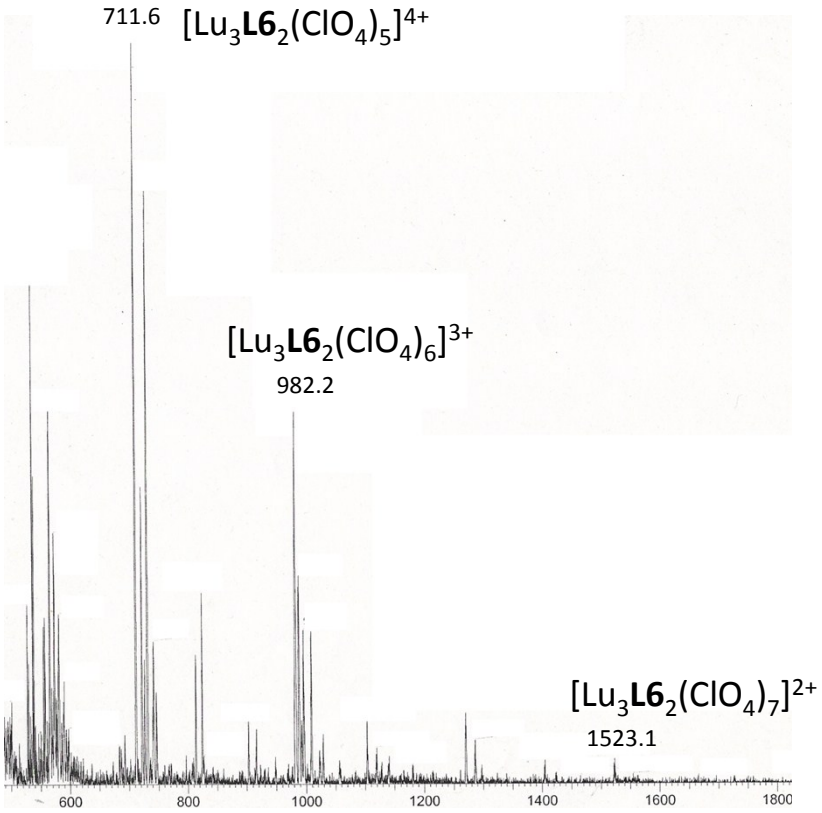


Figure S8. ESI-MS of the solution with [Lu]/[**L6**] ~ 5.

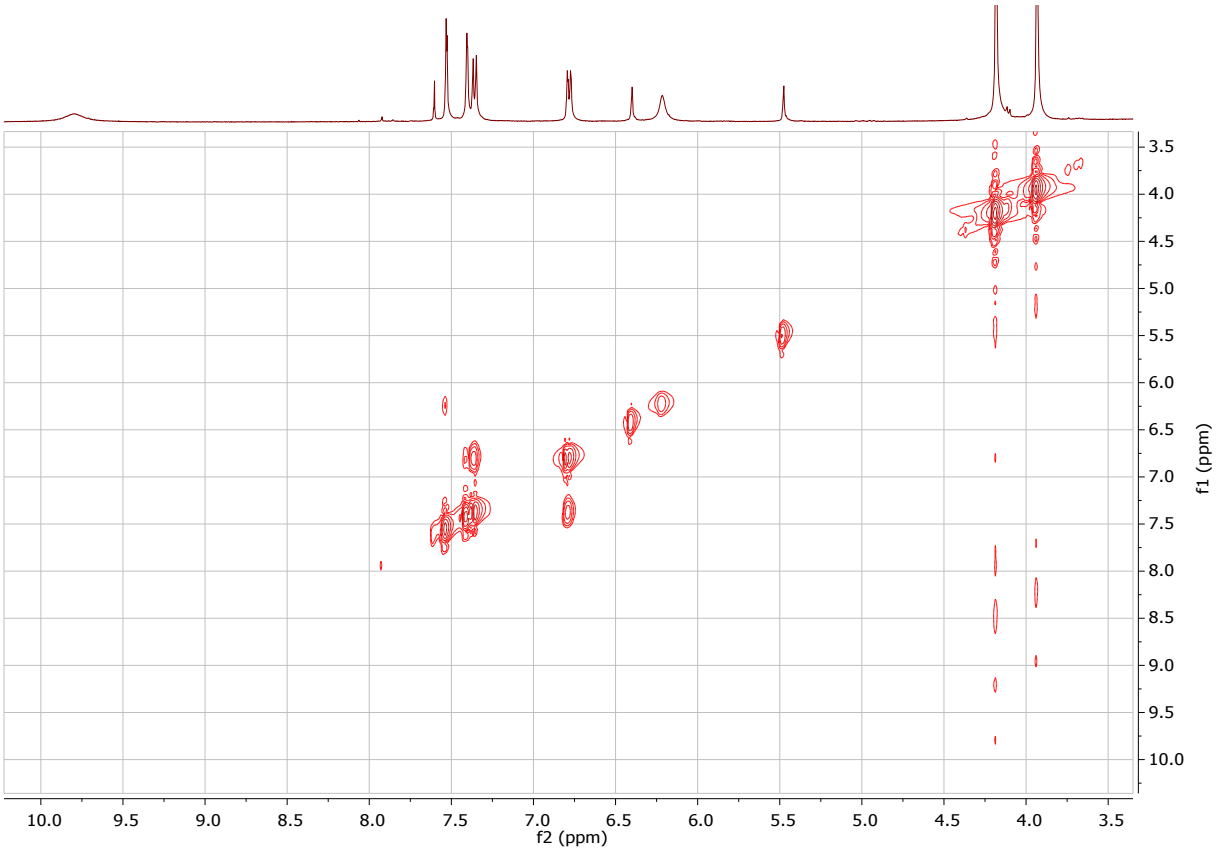


Figure S9. COSY NMR spectrum for the $[La_3\mathbf{L7}_2]^{9+}$ complex a tthe ratios [La]/[**L7**] = 4. (400 MHz, 298 K, $[\mathbf{L7}]_0 = 3\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

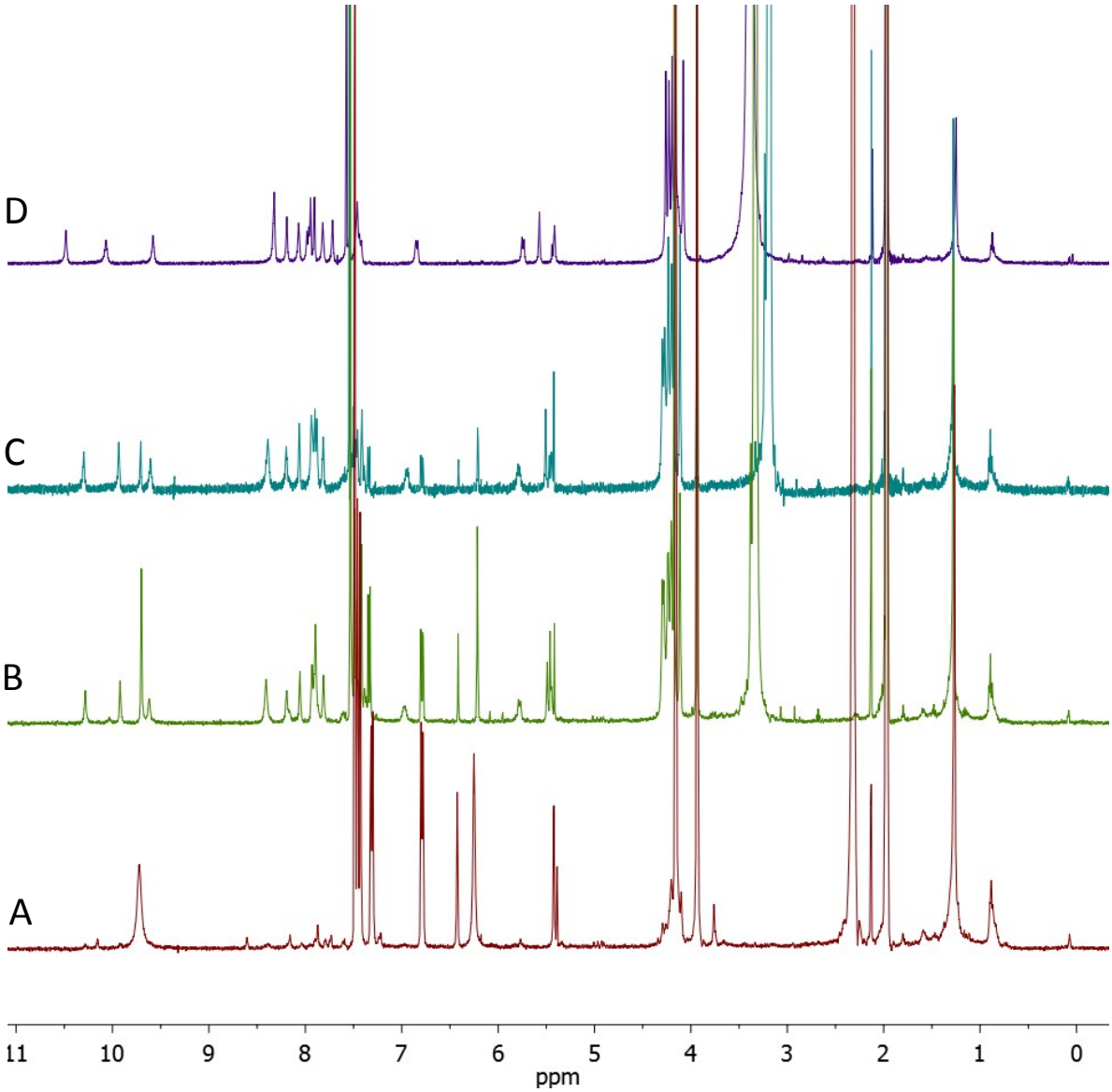


Figure S10. Evolution of the ^{1}H NMR spectra for the mixture of **L7** and La(III) with [La]/[**L7**] ~ 5. (A) The spectrum at the end of the NMR titration ; (B) after 2 weeks; (C) after additional 4 weeks; (D) after additional 2 months. (400 MHz, 298 K, $[\mathbf{L7}]_0 = 3\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

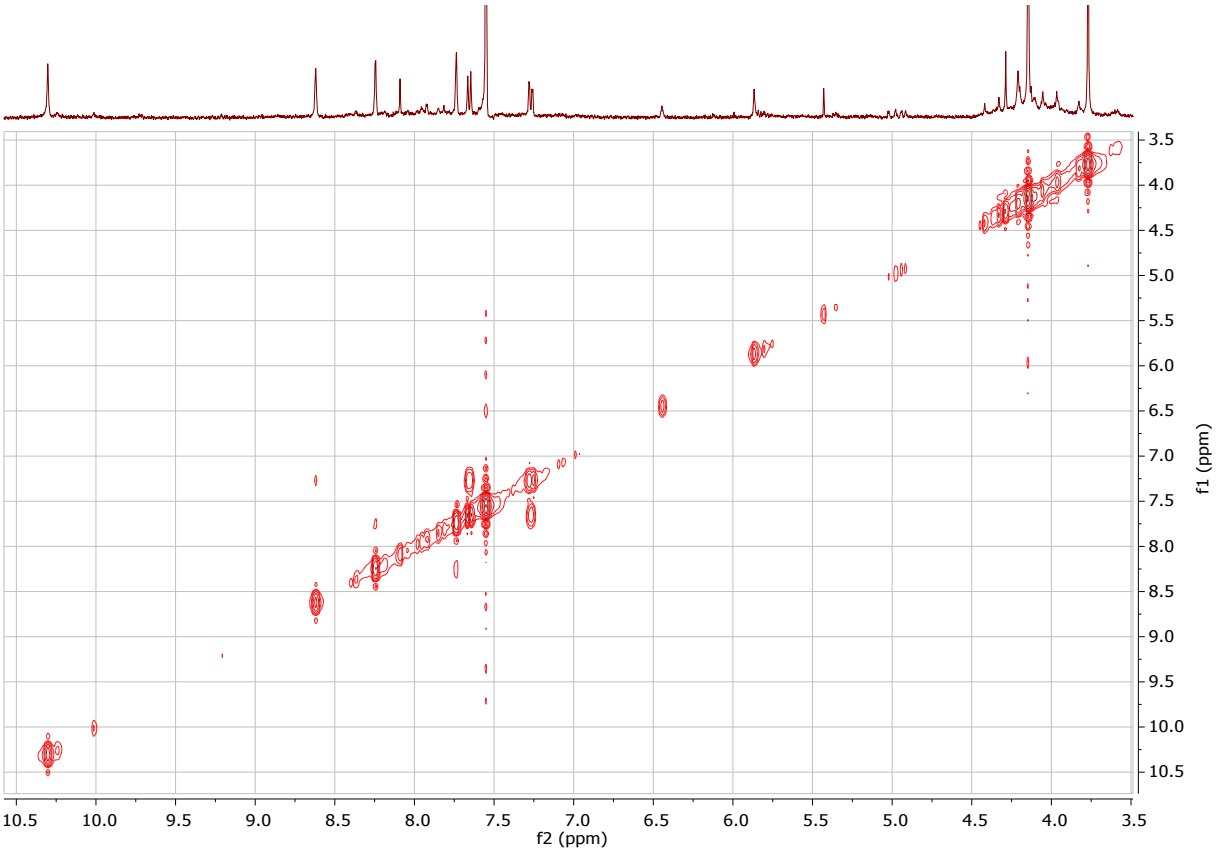


Figure S11. COSY NMR spectrum for the $[Lu_4\mathbf{L7}_4]^{12+}$ complex a tthe ratios [Lu]/[**L7**] = 1. (400 MHz, 296 K, $[\mathbf{L7}]_0 = 4\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

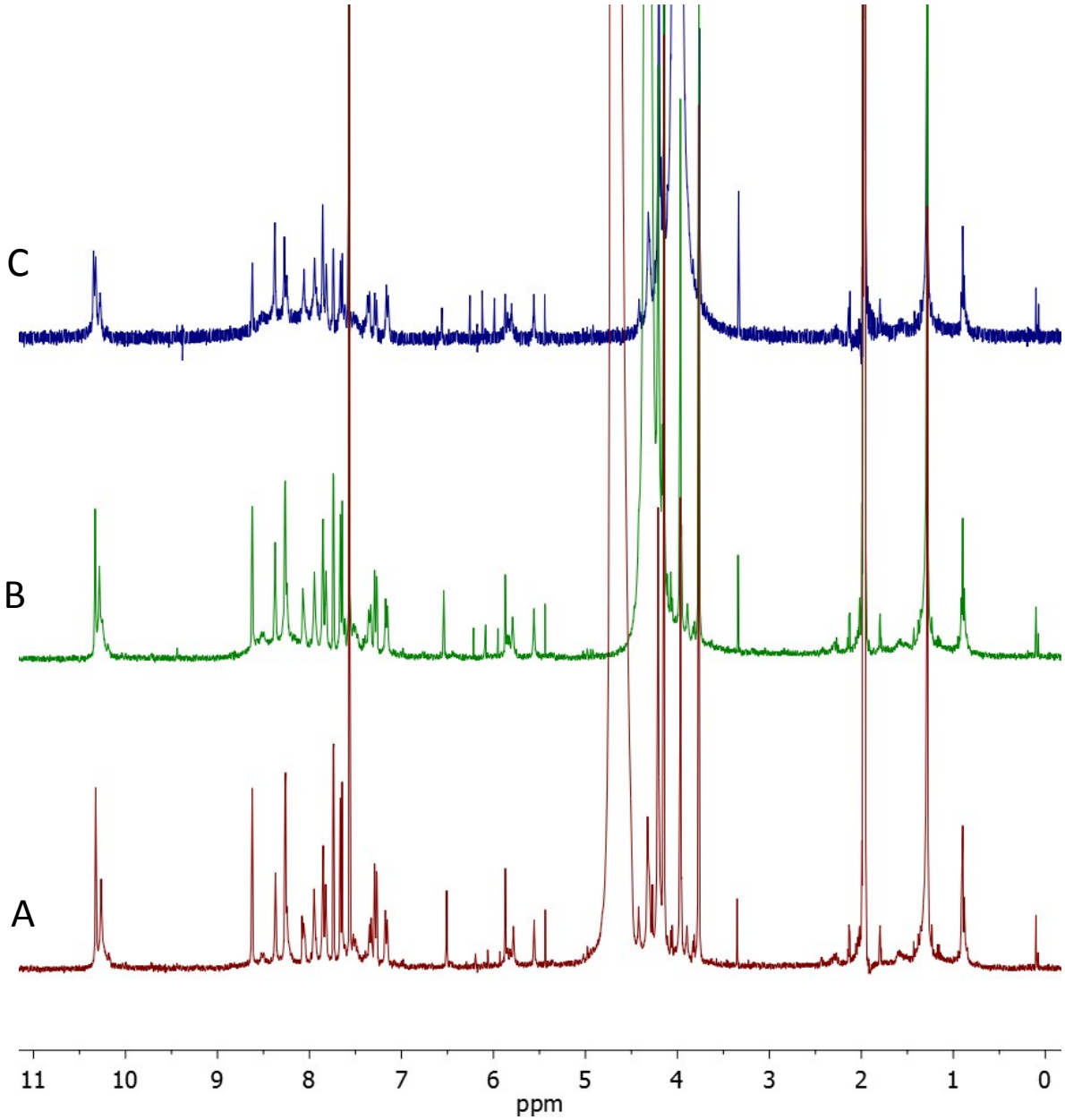


Figure S12. ^{1}H NMR spectra for the mixture of **L7** and Lu(III) with [Lu]/[**L7**] ~ 4.3. (A) The spectrum at the end of the titration ; (B) after 2 weeks; (C) after additional 3 weeks. (400 MHz, 296 K, $[\mathbf{L7}]_0 = 4\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

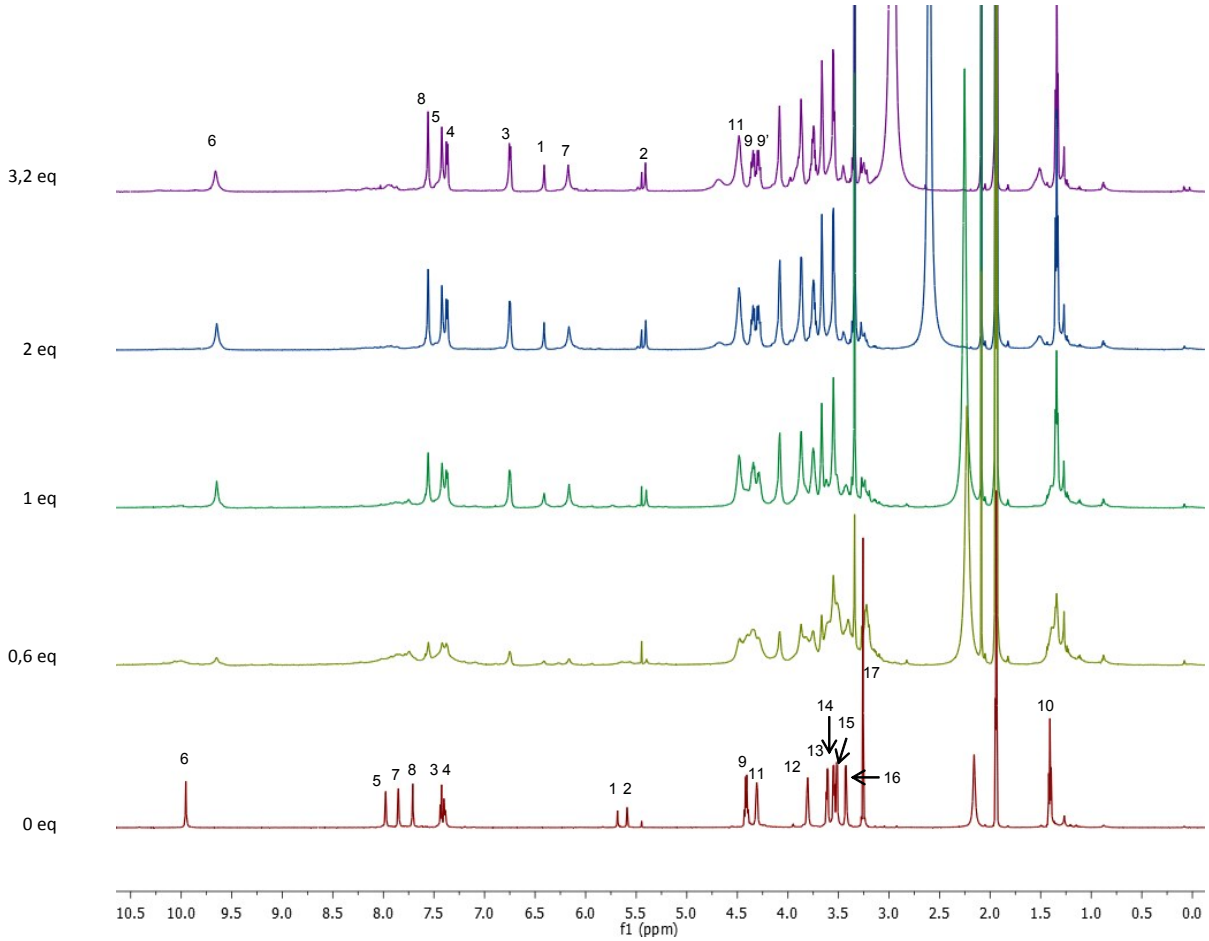


Figure S13. ^{1}H NMR spectra for the titration of **L8** with $La(ClO_4)_3$ in CD_3CN (600 MHz, 298 K, $[\mathbf{L8}]_0 = 6\times10^{-3}$M, $CD_3CN/CDCl_3$ (1:1, v/v).

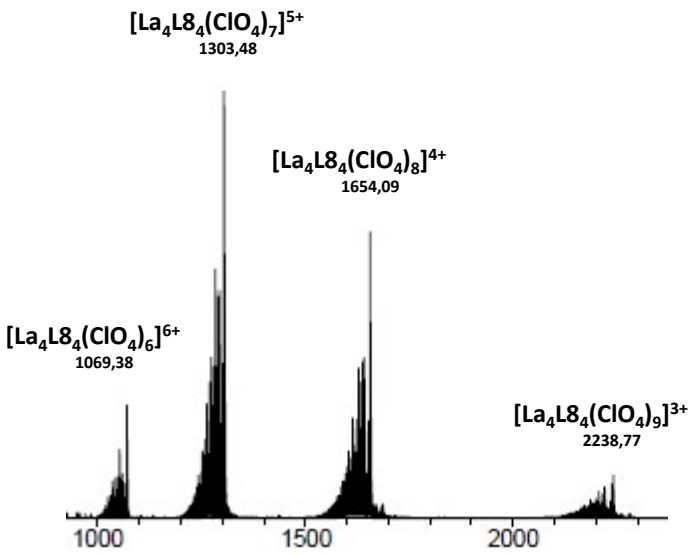


Figure S14. High resolution ESI-MS spectrum for the solution with [La]/[**L8**] ~ 1.

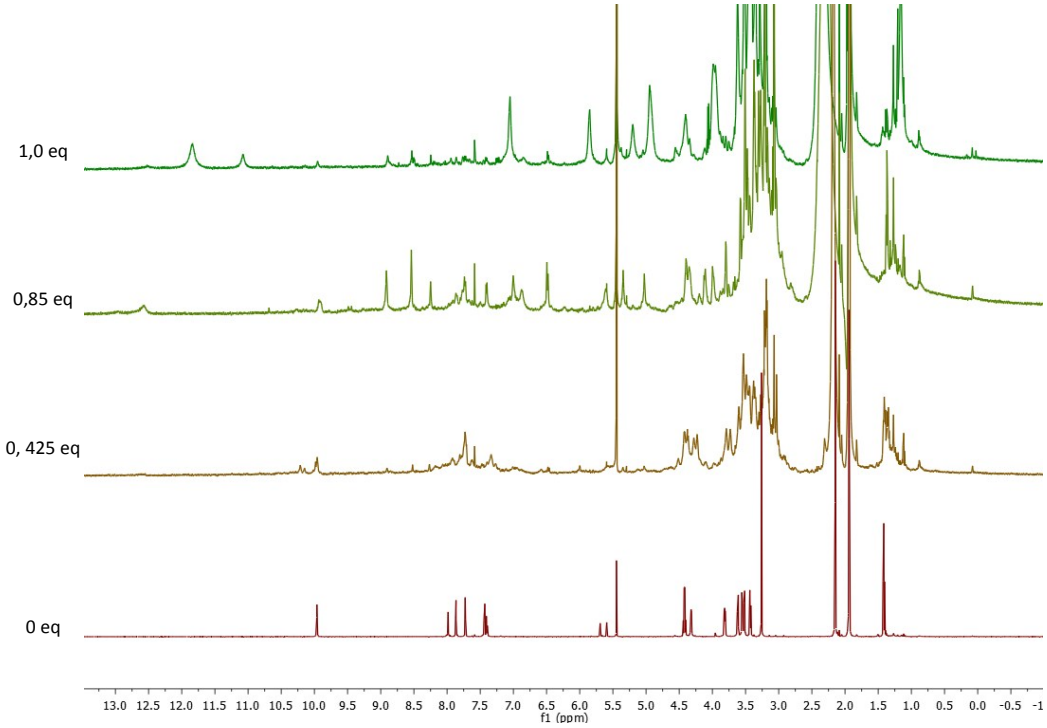


Figure S15. ^{1}H NMR spectra for the titration of **L8** with $Eu(ClO_4)_3$ in CD_3CN (600 MHz, 298 K, $[\mathbf{L8}]_0 = 6 \times 10^{-3}$M, [Eu]/[**L8**] = 0-1)