Electronic Supplementary Material (ESI) for Dalton Transactions.
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Electronic supplementary information for

Symmetric CEST-active lanthanide complexes for redox monitoring

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Content :

m/z calculated for C48 H77 O8 N10 $[M]^+$ 921.59204

m/z found 921.59137

Error ppm -0.722

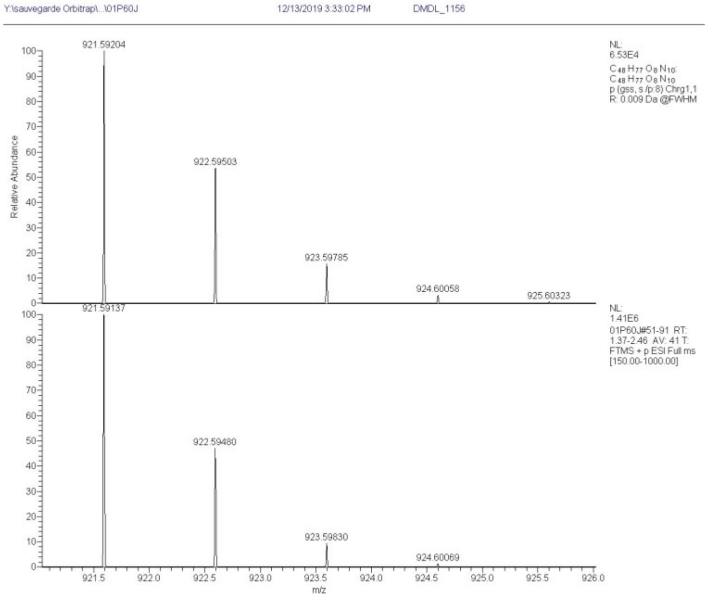

Fig. S1 HR-MS of ligand **L₁** : Top, experimental spectrum ; bottom, simulated spectrum.

m/z calculated for : C48 H71 O6 N10 F6 $[M]^+$: 997.54568

m/z found 997.54512

Error ppm -0.557

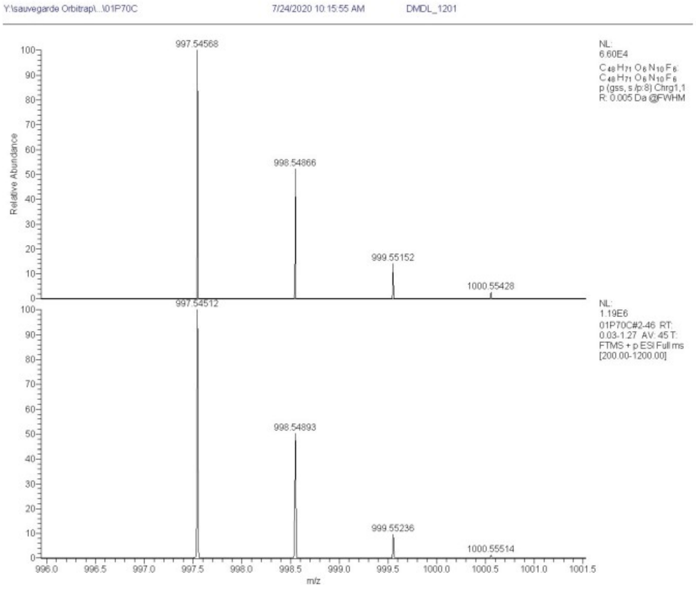

Fig. S2 HR-MS of ligand **L₂** : Top, experimental spectrum ; bottom, simulated spectrum.

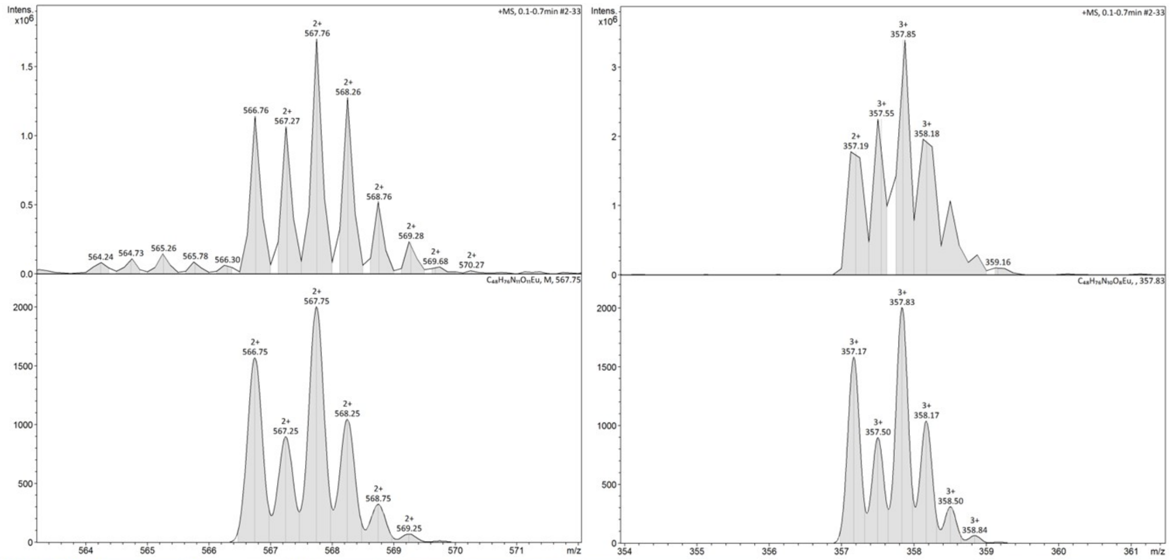

Fig. S3 HR-MS of complex **$[Eu(L_1)]^{3+}$** : Top, experimental spectrum ; bottom, simulated spectrum.

Fig. S4 HR-MS of complex **$[Eu(L_2)]^{3+}$** : Top, experimental spectrum ; bottom, simulated spectrum.

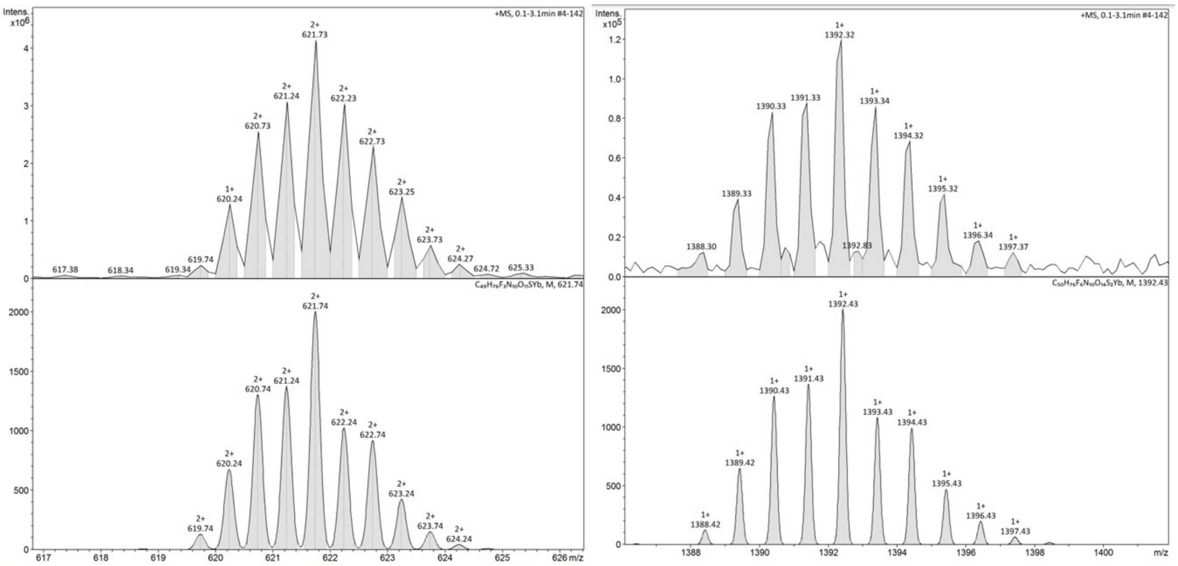

Fig. S5 HR-MS of complex **$[Yb(L_1)]^{3+}$** : Top, experimental spectrum ; bottom, simulated spectrum.

Fig. S6 HR-MS of complex **[Yb(L$_2$)]$^{3+}$** : Top, experimental spectrum ; bottom, simulated spectrum.

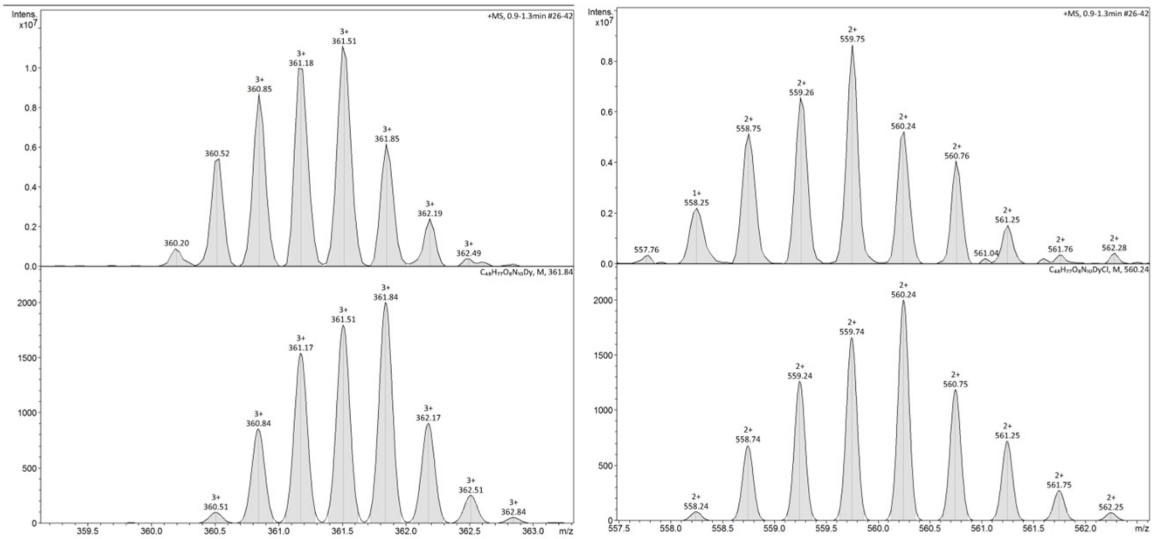

Fig. S7 HR-MS of complex **[Dy(L$_1$)]$^{3+}$** : Top, experimental spectrum ; bottom, simulated spectrum.

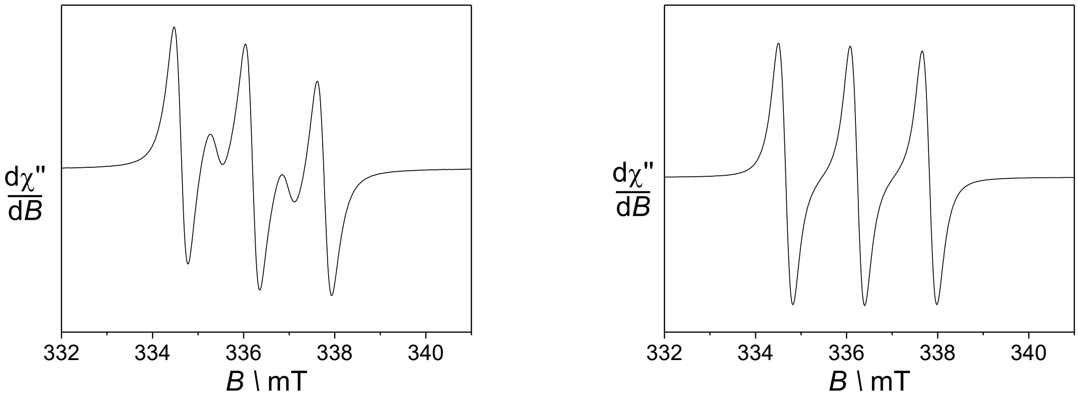

Fig. S8 X-band EPR spectra of 0.45 mM aqueous (+10% glycerol) solutions of the ytterbium complexes; (left) **[Yb(L$_1$)]$^{3+}$** and (right) **[Yb(L$_2$)]$^{3+}$**. Microwave Freq. 9.42 GHz; power, 3.5 mW; Mod. Amp. 0.2 mT, Freq. 100 KHz. *T* = 298 K.

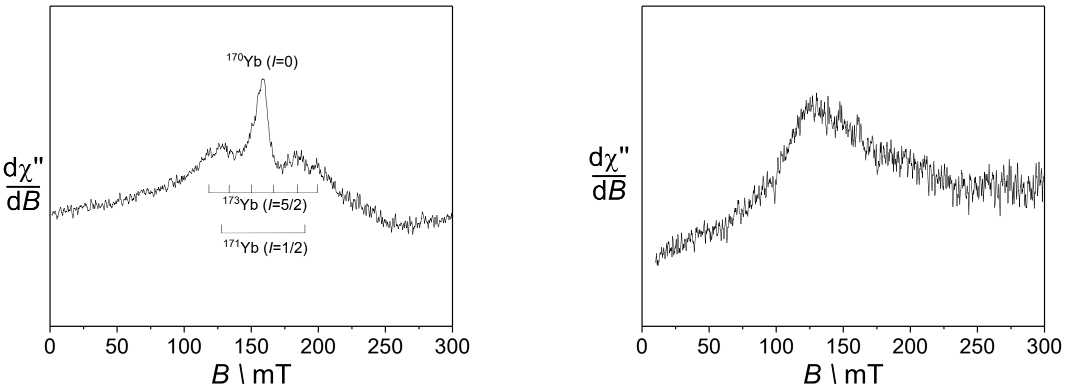

Fig. S9 X-band EPR spectra of 0.45 mM aqueous (+10% glycerol) solutions of the ytterbium complexes; (left) **[Yb(L$_1$)]$^{3+}$** and (right) **[Yb(L$_2$)]$^{3+}$**. Microwave Freq. 9.63 GHz; power, 20 mW or 2mW; Mod. Amp. 0.4 mT, Freq. 100 KHz. *T* = 6 K (left) or 8 K (right).

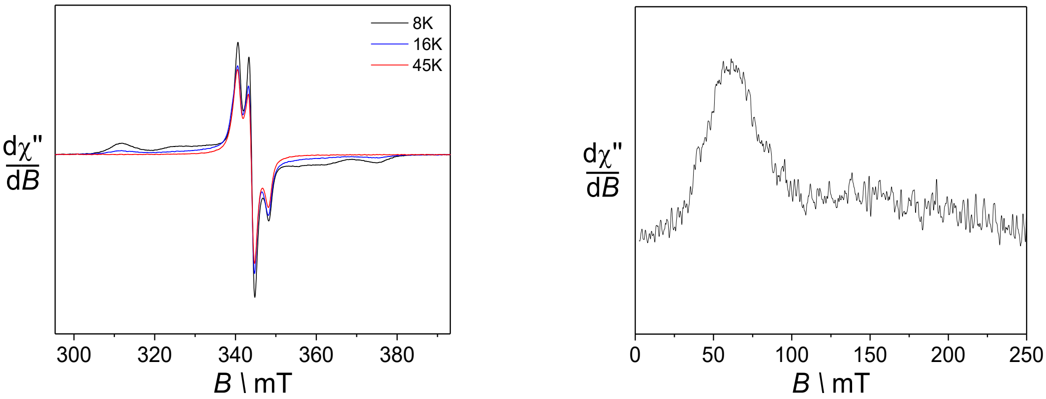

Fig. S10 X-band EPR spectra of a 0.45 mM aqueous (+10% glycerol) solution of **[Dy(L$_1$)]$^{3+}$**; (left) before addition of ascorbate, as a function of the temperature and (right) after addition of two molar eq. of ascorbate at 8 K (resonance of the isolated Dy^{3+}). Microwave Freq. 9.63 GHz; power, 0.2 mW (left) or 2mW (right); Mod. Amp. 0.4 mT, Freq. 100 KHz. *T* = 8 K (right).

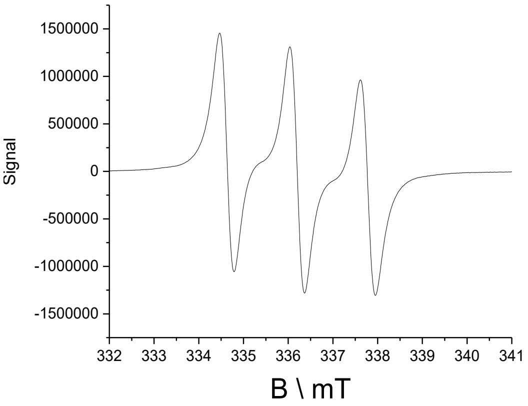

Fig. S11 X-band EPR spectrum of a 0.5 mM CH_3CN solution of the dysprosium complex **$[Dy(L_1)]^{3+}$**. Microwave Freq. 9.42 GHz; power, 3.5 mW; Mod. Amp. 0.2 mT, Freq. 100 KHz. *T* = 298 K.

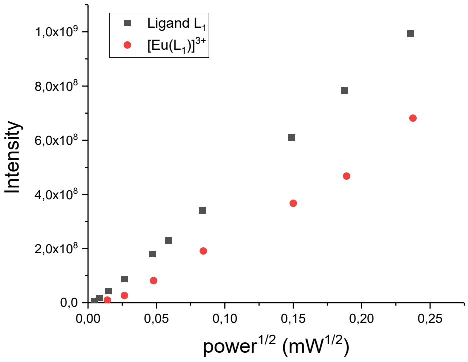

Fig. S12 Power saturation curves of **L_1** and its europium complex. Microwave Freq. 9.42 GHz; Mod. Amp. 0.2 mT, Freq. 100 KHz. *T* = 298 K.

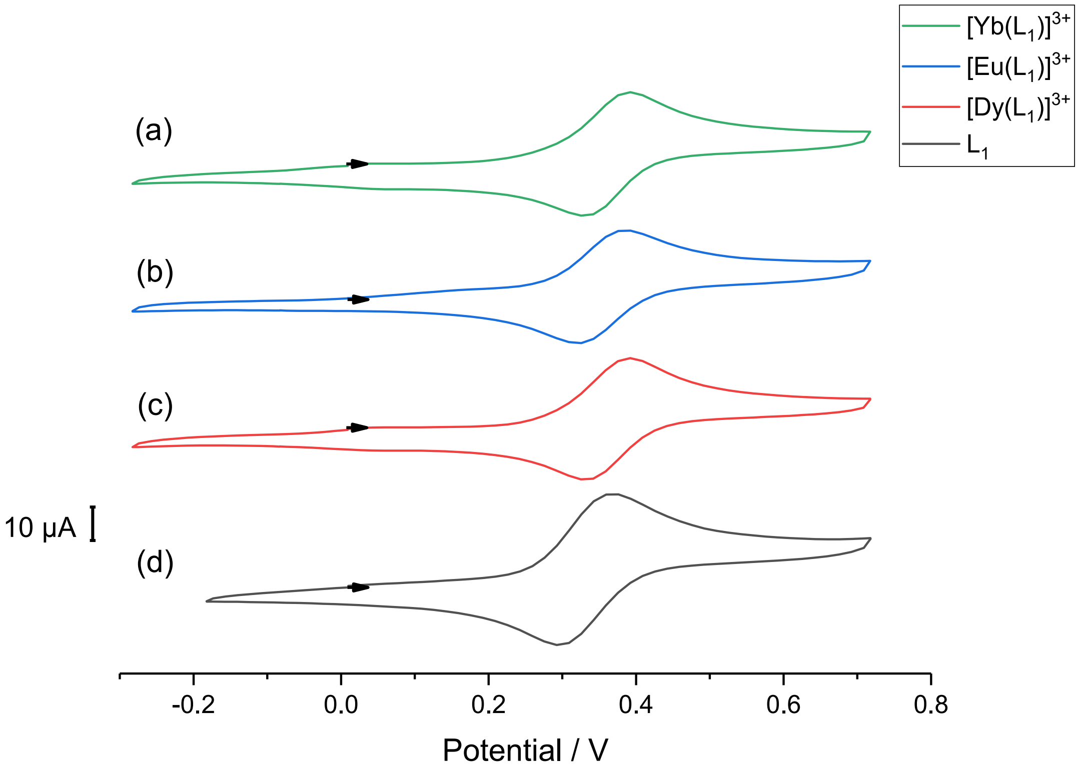

Fig. S13 Cyclic voltammetry curves of (a) $[Yb(L_1)]^{3+}$, (b) $[Eu(L_1)]^{3+}$, (c) $[Dy(L_1)]^{3+}$ and (d) ligand L_1, recorded in CH_3CN (+ 0.1 M TBAP) at a carbon electrode. Scan rate 0.1 V/s, T = 298 K.

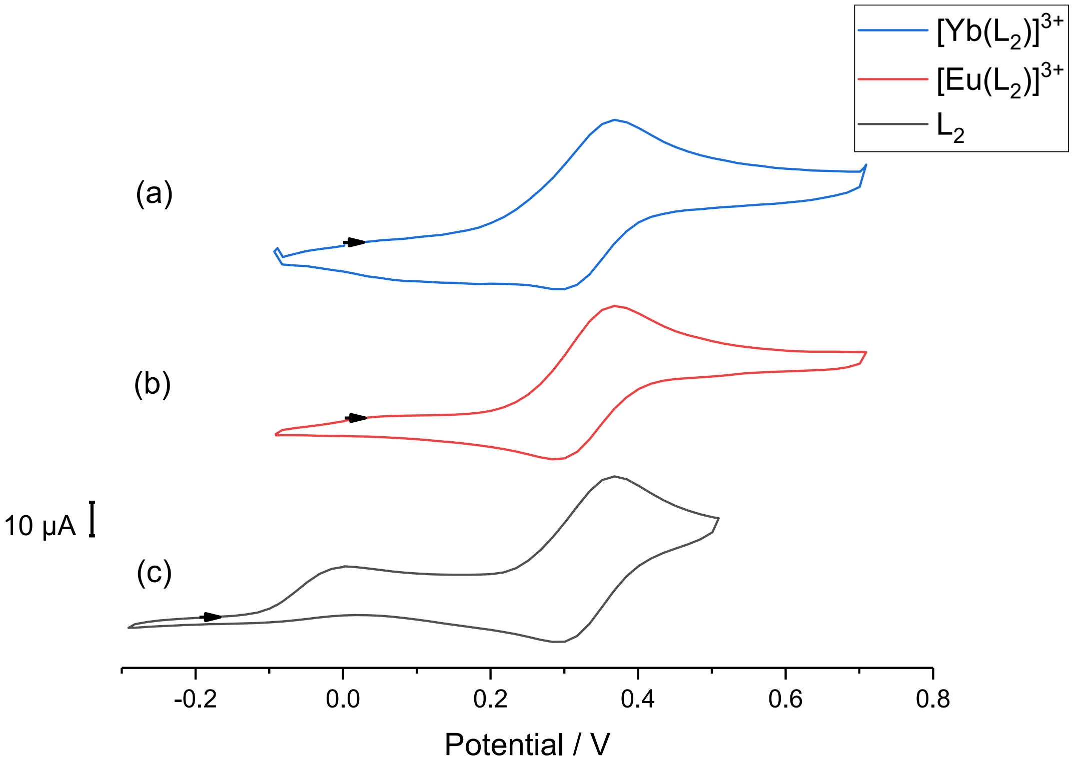

Fig. S14 Cyclic voltammetry curves of (a) $[Yb(L_2)]^{3+}$, (b) $[Eu(L_2)]^{3+}$, (c) ligand L_2, recorded in CH_3CN (+ 0.1 M TBAP) at a carbon electrode. Scan rate 0.1 V/s, T = 298 K.

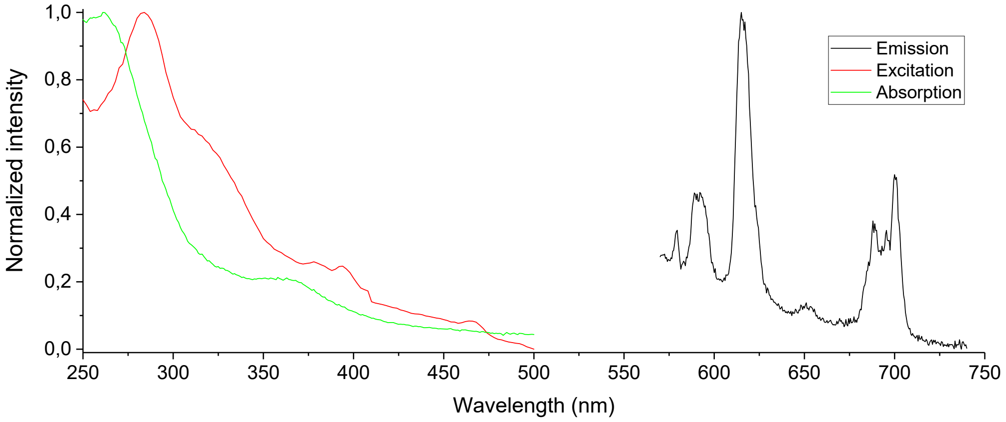

Fig S15. Spectra of $[Eu(L_1)]^{3+}$ in a 0.05 mM methanolic solution: (green) absorption spectrum; (red) excitation spectrum (with an emission at 614 nm); (black) luminescence spectra (with an excitation at 280 nm). *T* = 298 K.

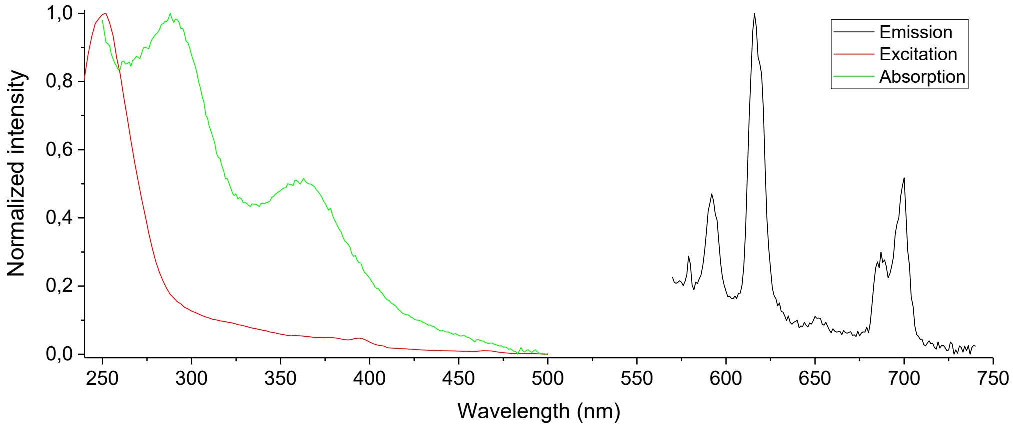

Fig S16. Spectra of $[Eu(L_2)]^{3+}$ in a 0.05 mM methanolic solution: (green) absorption spectrum; (red) excitation spectrum (with an emission at 614 nm); (black) luminescence spectra (with an excitation at 280 nm). *T* = 298 K.

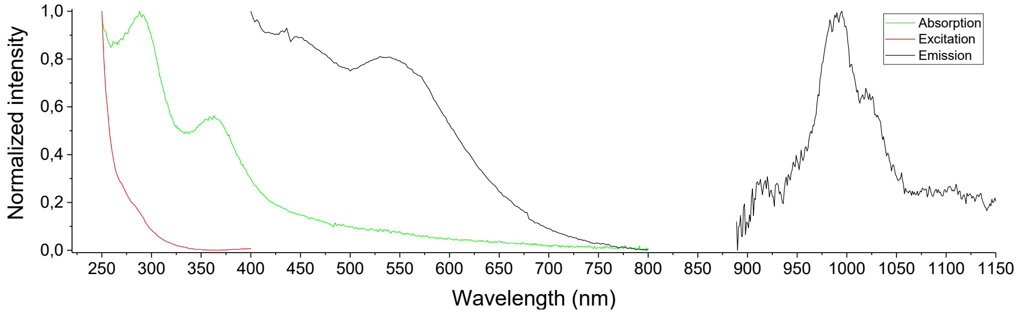

Fig S17. Spectra of $[Yb(L_1)]^{3+}$ in a methanolic solution: (green) absorption spectrum; (red) excitation spectrum (with an emission at 980 nm); (black) luminescence spectra (with an excitation at 280 nm).

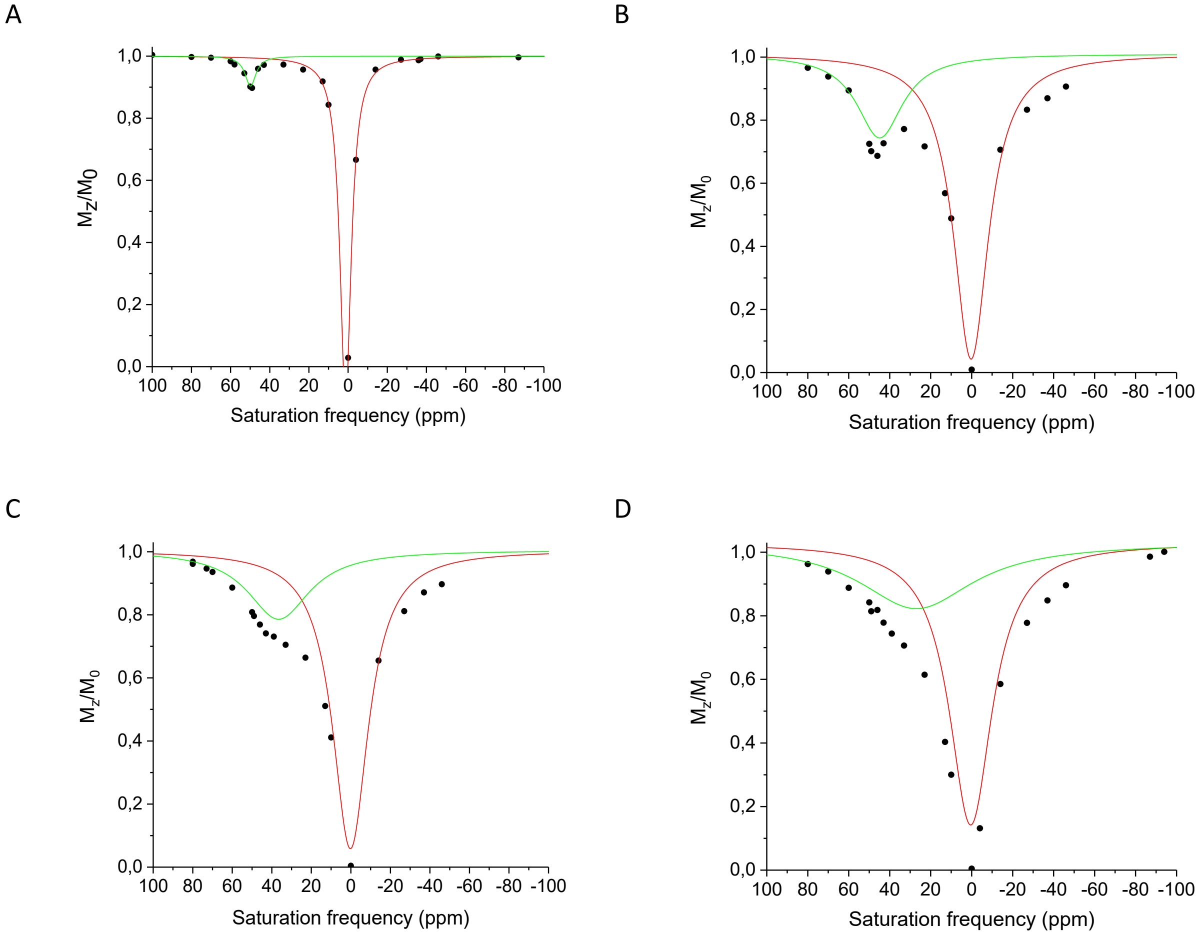

Fig. S18 Z spectra of $\mathbf{[Eu(L_1)]^{3+}}$ in a 20 mM H_2O:CD_3CN (2:1) mixture at pH = 7.4 ([HEPES] = 0,07 mol/L). Spectra recorded in the presence of 2 molar eq. of ascorbate. B_0 = 11.7 T; B_1 = 19 μT; Irradiation time = 4 s. A = 288 K, B = 298 K, B = 310 K, C = 318 K.

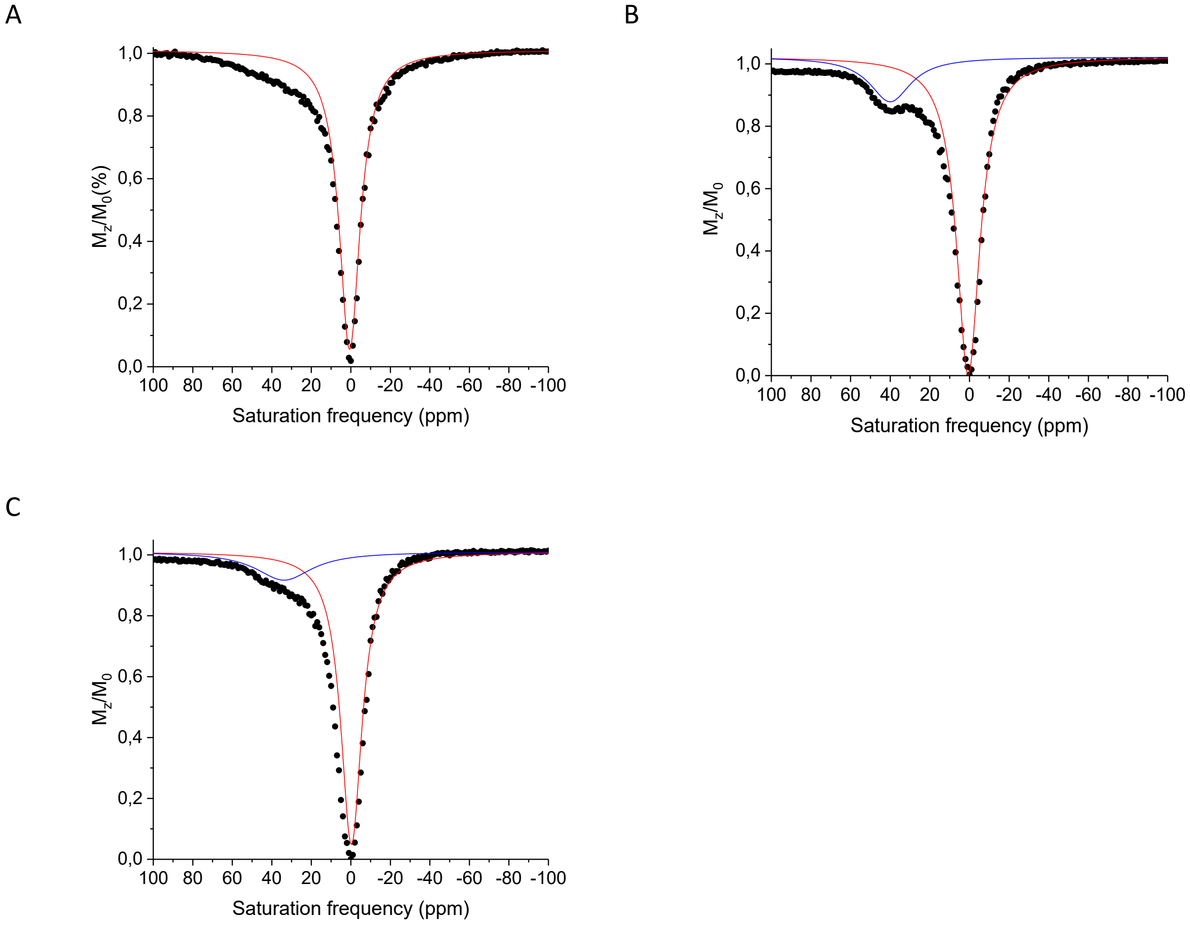

Fig. S19 Z spectra of **$[Eu(L_2)]^{3+}$** in a 20 mM H_2O:CD_3CN (2:1) mixture at pH = 7.4 ([HEPES] = 0,07 mol/L). Spectra recorded in the presence of 2 molar eq. of ascorbate. B_0 = 11.7 T; B_1 = 19 µT; Irradiation time = 4 s. A = 298 K, B = 310 K, C = 318 K.

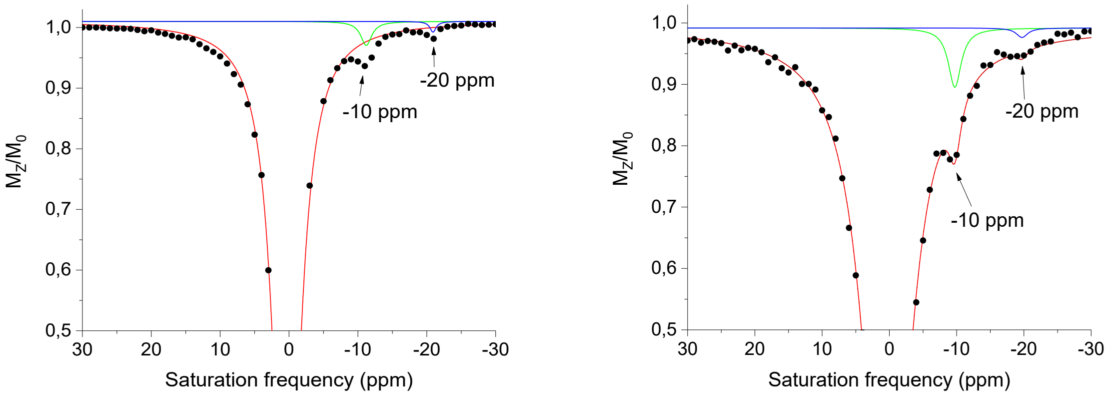

Fig. S20 Z spectra of **$[Yb(L_1)]^{3+}$** in a 20 mM H_2O:CD_3CN (2:1) mixture at pH = 7.4 ([HEPES] = 0,07 mol/L). Spectra recorded in the presence of 2 molar eq. of ascorbate. B_0 = 11.7 T; B_1 = 5 µT (left), 19 µT (right); Irradiation time = 4 s; *T* = 298 K.

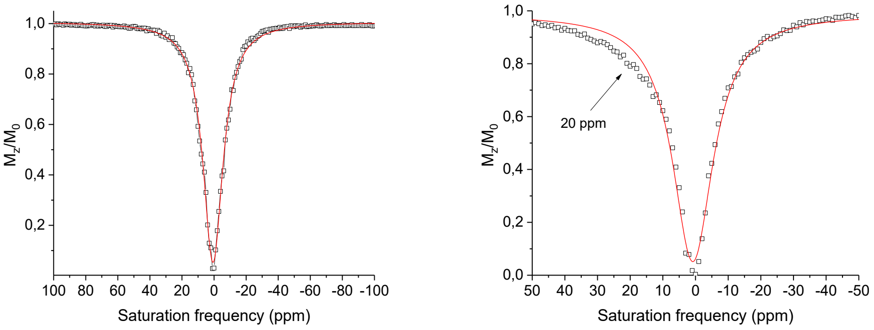

Fig. S21 Z spectra of **$[Yb(L_2)]^{3+}$** in a 20 mM H_2O:CD_3CN (2:1) mixture at pH = 7.4 ([HEPES] = 0,07 mol/L). Spectra recorded in the presence of 2 molar eq. of ascorbate. B_0 = 11.7 T; B_1 = 25 µT (left), 19 µT (right); Irradiation time = 4 s; *T* = 298 K.

Comment [FT]: Bizarre que 25 ici et 5 uT au dessus, C'est sûr que c'est différent ????

Comment [u]: En effet le L2 a été fait à des fortes puissances seulement. Dans le cas du L1 les premières mesures été faites à faibles puis à fortes puissances.

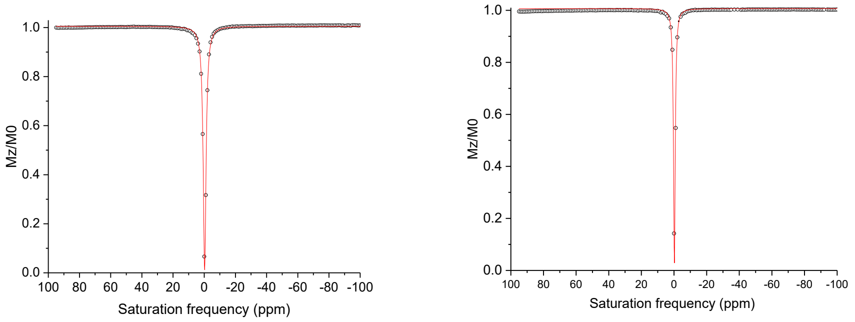

Fig. S22 Z spectra of **$[Dy(L_1)]^{3+}$** in a 20 mM H_2O:CD_3CN (2:1) mixture at pH = 7.4 ([HEPES] = 0,07 mol/L). Spectra recorded in the absence (left) and in presence (right) of 2 molar eq. of ascorbate. B_0 = 11.7 T; B_1 = 2.4 µT; Irradiation time = 4 s; *T* = 298 K.

Comment [FT]: Bizarre que 25 ici et 5 uT au dessus, C'est sûr que c'est différent ????

Comment [u]: En effet le L2 a été fait à des fortes puissances seulement. Dans le cas du L1 les premières mesures été faites à faibles puis à fortes puissances.

Calculation of the number of coordinated water molecules q in the europium complexes

The number of coordinated water molecules q was calculated by using two empirical formula developed by W. Horrocks *et al.*[123] (Eq. 1) and D. Parker et al. [124] (Eq. 2) :

$$q = 1{,}11\ [\Delta k_{obs} - 0{,}31 - 0{,}45q^{OH} - 0{,}99q^{NH} - 0{,}075q^{CONH}] \qquad \textbf{Eq. 1}$$

$$q = 1{,}2\ [\Delta k_{obs} - 0{,}25 - 0{,}075q^{CONHR}] \qquad \textbf{Eq. 2}$$

where $\Delta k_{obs} = k_{H2O} - k_{D2O} = 1/\tau_{H2O} - 1/\tau_{D2O}$

q^{OH} is the number of -OH oscillators in the first coordination sphere

q^{NH} is the number of -NH oscillators in the first coordination sphere

q^{CONH} is the number of CONH (amide) oscillators in the first coordination sphere.

Table S1. Calculation of the q values for the europium complexes

complex	$\tau_{H2O\ (msec)}$	$\tau_{H2O\ (msec)}$	Δk_{obs}	*q* (Eq. 1 / Eq. 2)
$[Eu(L_1)]^{3+}$	0.48	1.43	1.38	1.1/0.9
$[Eu(L_2)]^{3+}$	0.25	0.32	0.88	0.5/0.4

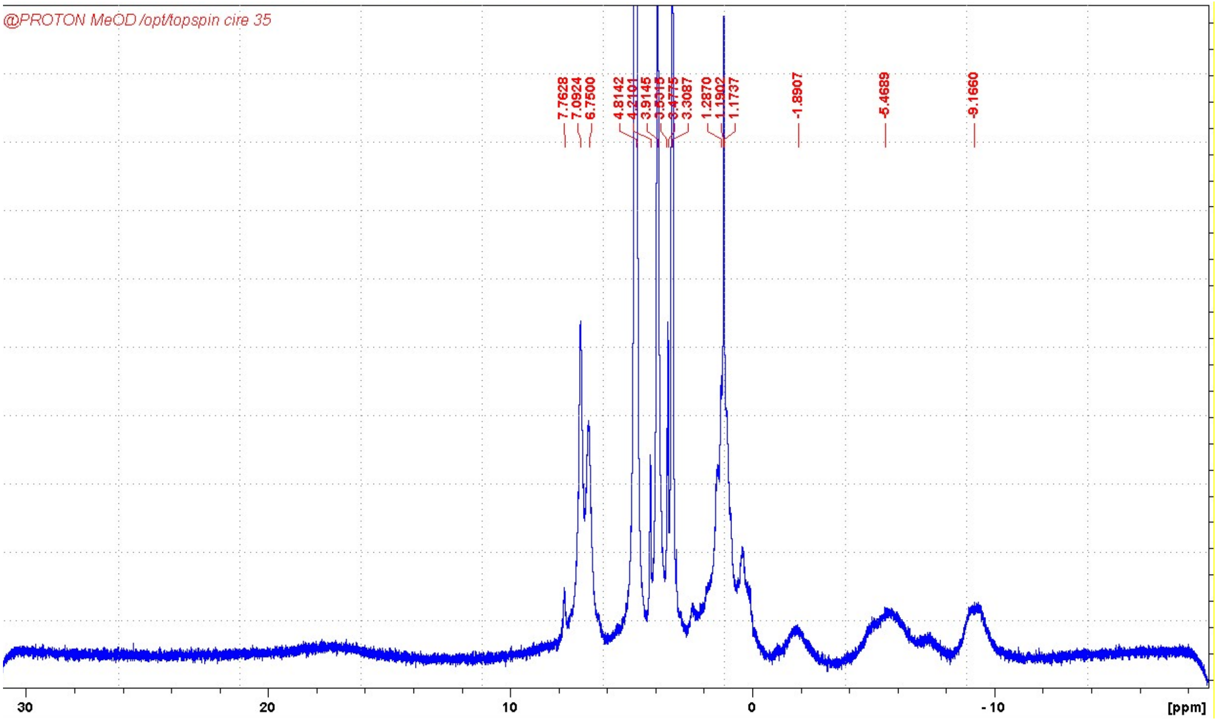

Fig. S23: ^1H NMR spectrum in CH_3CN of complex $L_1.Eu$.

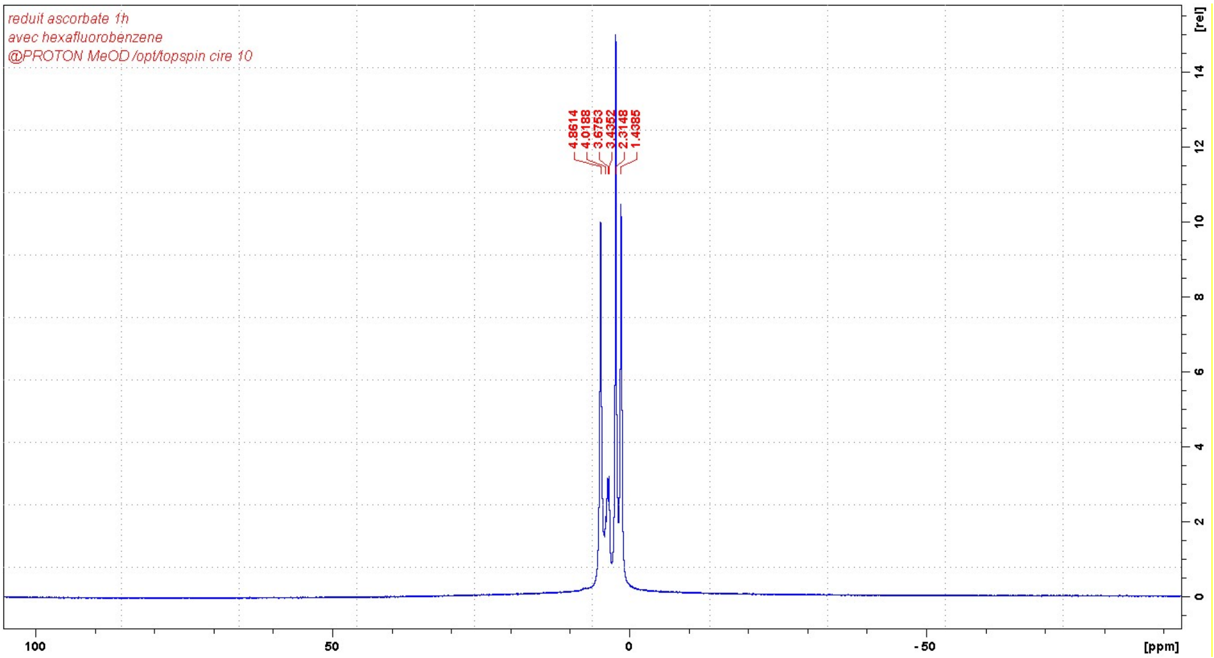

Fig. S24: ^{1}H NMR spectrum in CH_3CN of complex L_2.Eu

Exchange rate measurements $[Eu.D_5]^{3+}$

Experimentally the intenisty of the CEST signal is measured as a function of the strength of B1 applied. At 15°C, the intensity of the signal evolves from 0% to almost 40% When the power isaltered from 0 Hz to 3500 Hz. At 25°C and 37°C, The intensity is close for the weak power applied but reaches almost 19% and 22% at 3500 Hz, respectively.

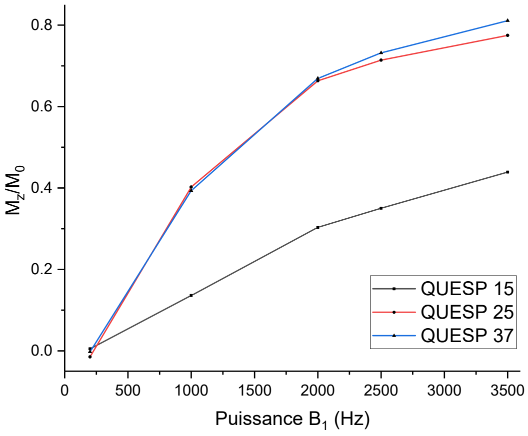

Figure **S25.**: Experimental measurement of the CEST signal obtained for the complex as a function of the saturation power applied.

Applying the 'Omega Plot' method the rate of exchange measured are 2450 s^{-1} at 15°C, 2640 s^{-1} at 25°C and 3270 s^{-1}at 37°C.

Exchange rate measurements $[Eu(L_1)(NO_3)_3]$

At 37°C, the exchange rate obtained is 4000 s^{-1} which is equivalent to a residence time of the water molecule of 250 µs (A et B). This value is higher than that obtained for the complex ***$[Eu(L_1)(NO_3)_3]$*** which was 3270 s^{-1}.

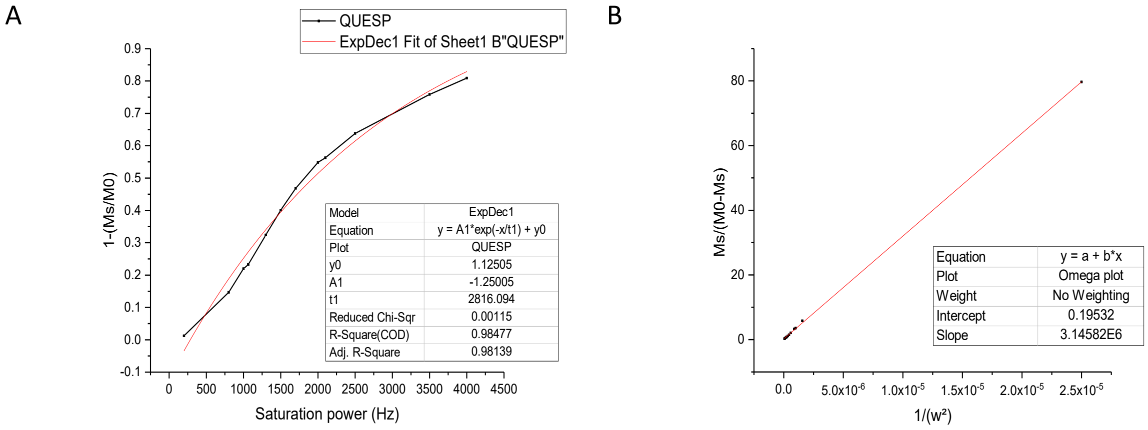

Fig.S26: Measure of the rate of exchange of the complex and fit A= Measure QUESP B= Omega Plot.

Table S2 : Values of exchange rates and residence times calculated via the Omega Plot method.

Omega plot	*$[Eu.L_1]^{3+}$*	*$[Eu.L_2]^{3+}$*
Exchange rate at 15°C τ : residence time	2450 s^{-1} 410 µs	
Exchange rate at 25°C τ : residence time	2650 s^{-1} 380 µs	
Exchange rate at 37°C τ : residence time	3300 s^{-1} 300 µs	4000 s^{-1} 250 µs