Electronic Supplementary Information for Dalton Transactions

Gadolinium(III) Complexes of 1,4,7-triazacyclononane Based Picolinate Ligands: Simultaneous Optimization of Water Exchange Kinetics and Electronic Relaxation

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Table S1: Influence of the synthesis conditions on the yield of bisubstituted tacn.

N°	Base	Base eq	Tacn eq	Solvent	C (M)	Yield in TRI (%)	Yield in BI (%)	Yield in MON	Global Yield (%)
				Influence of the solvent					
1	iPr_2EtN	7.5	1.5	CH_3CN	0.05	36	39	10	85
2	iPr_2EtN	7.5	1.5	EtOH	0.05	10	55	22	87
3	iPr_2EtN	7.5	1.5	$CHCl_3$	0.05	21	41	20	81
4	iPr_2EtN	7.5	1.5	DMF	0.05	18	48	14	80
				Influence of the base					
5	iPr_2EtN	7.5	1.5	EtOH	0.05	10	55	22	87
6	Et_3N	7.5	1.5	EtOH	0.05	6	54	20	80
7	Me_5NC	7.5	1.5	EtOH	0.05	-			
8	iPr_2EtN	4.5	1.5	EtOH	0.05	3	36	13	52
9	K_2CO_3	4.5	1.5	EtOH	0.05	17	19	9	45
10	$CsCO_3$	4.5	1.5	EtOH	0.05	21	27	11	59
				Influence of the base stoechiometry					
11	iPr_2EtN	4.5	1.5	EtOH	0.05	3	36	13	52
12	iPr_2EtN	6	1.5	EtOH	0.05	8	53	9	70
13	iPr_2EtN	7.5	1.5	EtOH	0.05	10	55	22	87
14	iPr_2EtN	8	1.5	EtOH	0.05	12	52	11	75
				Influence of the 1,4,7-triazacyclononane (tacn) stoechiometry					
15	iPr_2EtN	7.5	3	EtOH	0.05	0	49	27	76
16	iPr_2EtN	7.5	2.5	EtOH	0.05	2	53	24	79
17	iPr_2EtN	7.5	2	EtOH	0.05	3	59	19	81
18	iPr_2EtN	7.5	1.5	EtOH	0.05	10	55	22	87
19	iPr_2EtN	7.5	1	EtOH	0.05	29	44	7	20
				Influence of the concentration					
20	iPr_2EtN	7.5	1.5	EtOH	0.01	0	32	25	57
21	iPr_2EtN	7.5	1.5	EtOH	0.05	10	55	22	87
22	iPr_2EtN	7.5	1.5	EtOH	0.1	10	56	17	83
23	iPr_2EtN	7.5	1.5	EtOH	0.5	16	58	13	87
				Optimal conditions					
24	iPr_2EtN	7.5	2	EtOH	0.5	5	62	18	85

2. NMR spectra of ligands and Ln complexes at different temperatures

Figure S1: ^{1}H NMR spectrum of H_3ebpatcn, D_2O, 298 K, pD=2.4.

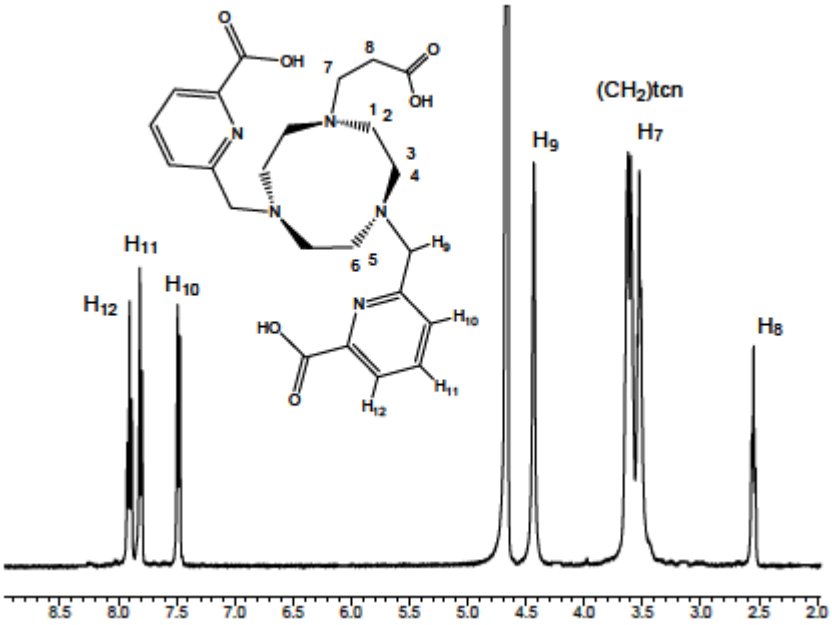


Figure S2: ^{1}H NMR spectrum of H_4pbpatcn, D_2O, 298 K, pD=2.2.

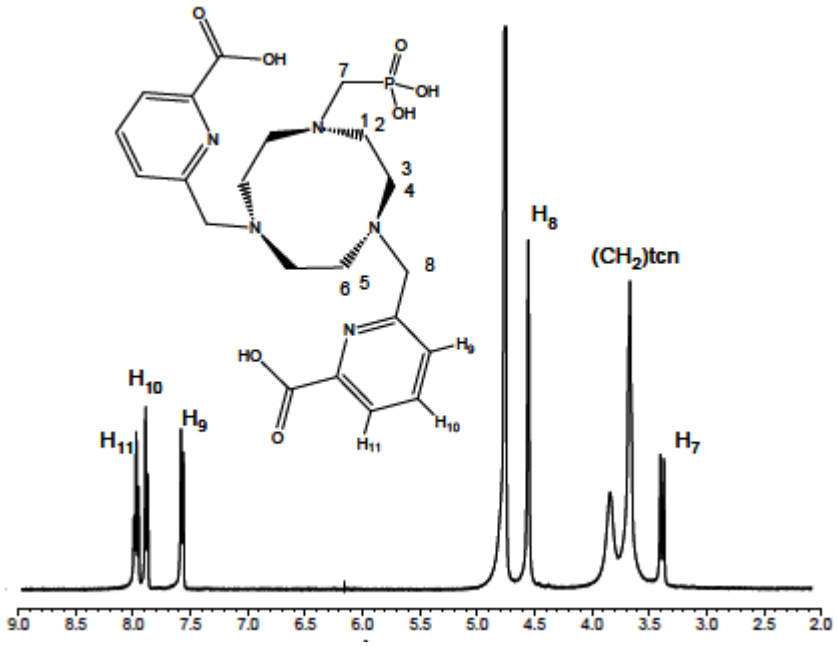


Figure S3: ^{1}H NMR spectrum of [Eu(ebpatcn)], D_2O, 278 K, 500 MHz, pD=7.4.

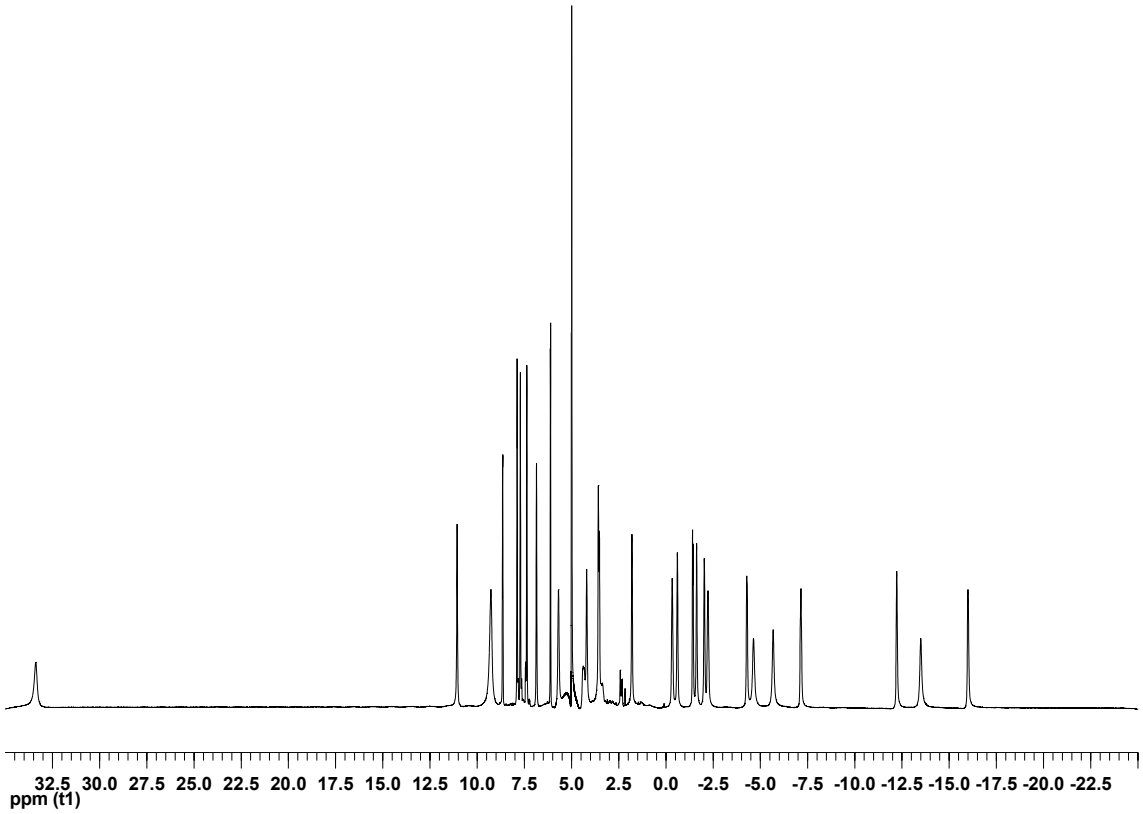


Figure S4: ^{1}H NMR spectrum of [La(pbpatcn)], D_2O, 278 K, 500 MHz, pD=7.2.

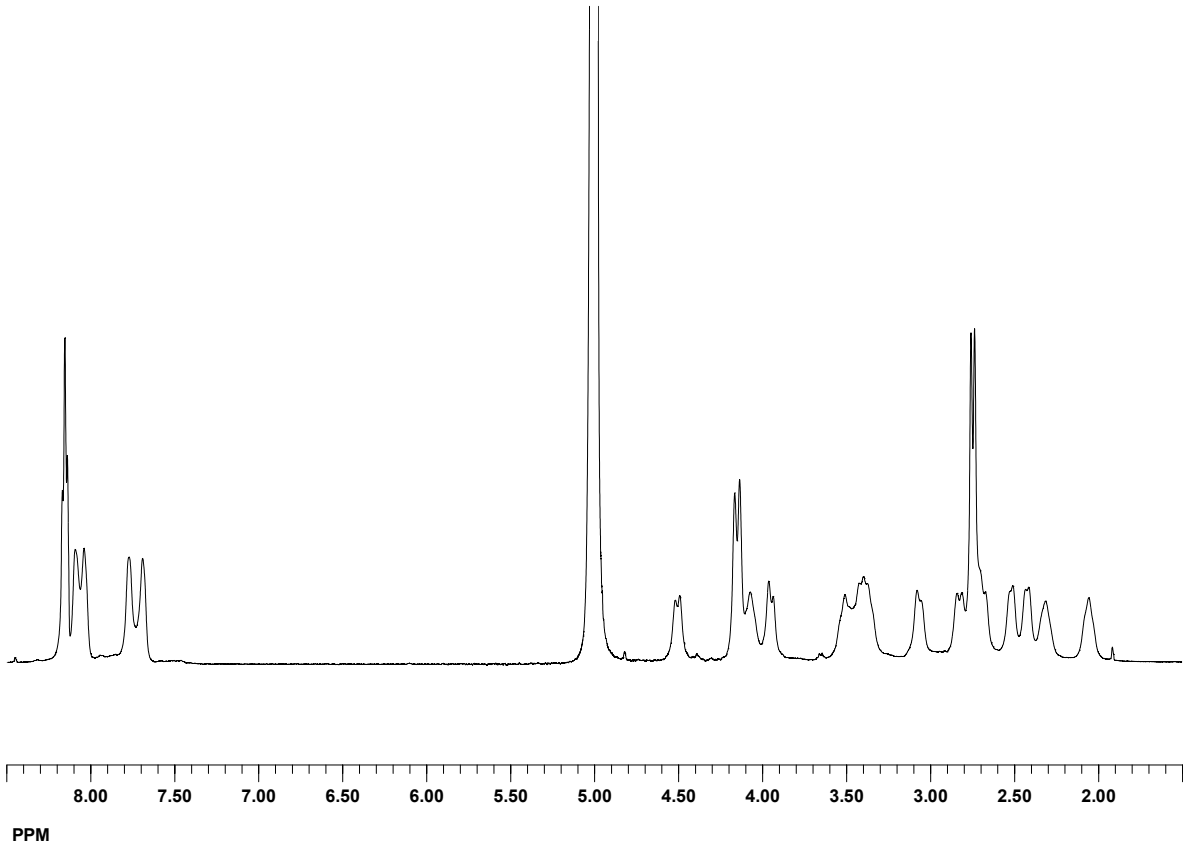


Figure S5: ^{1}H NMR spectrum of [La(pbpatcn)], D_2O, 298 K, 500 MHz, pD=7.2.

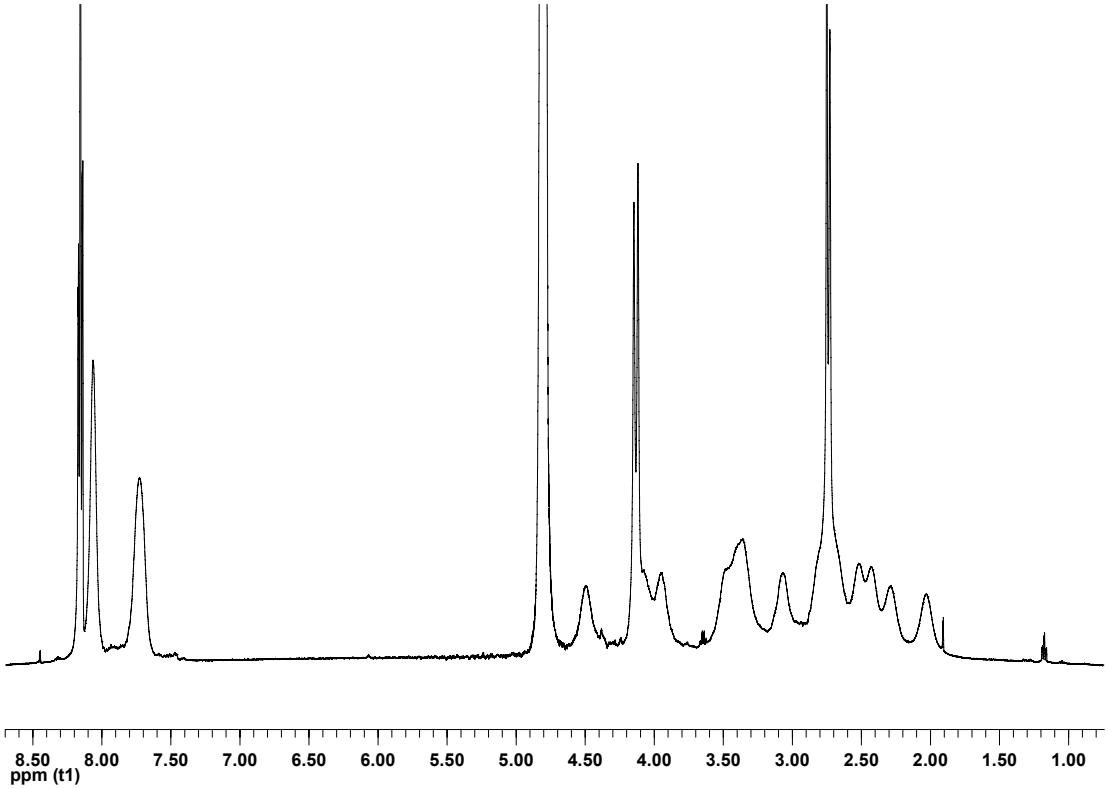


Figure S6: ^{1}H NMR spectrum of [La(pbpatcn)], D_2O, 343 K, 500 MHz, pD=7.2.

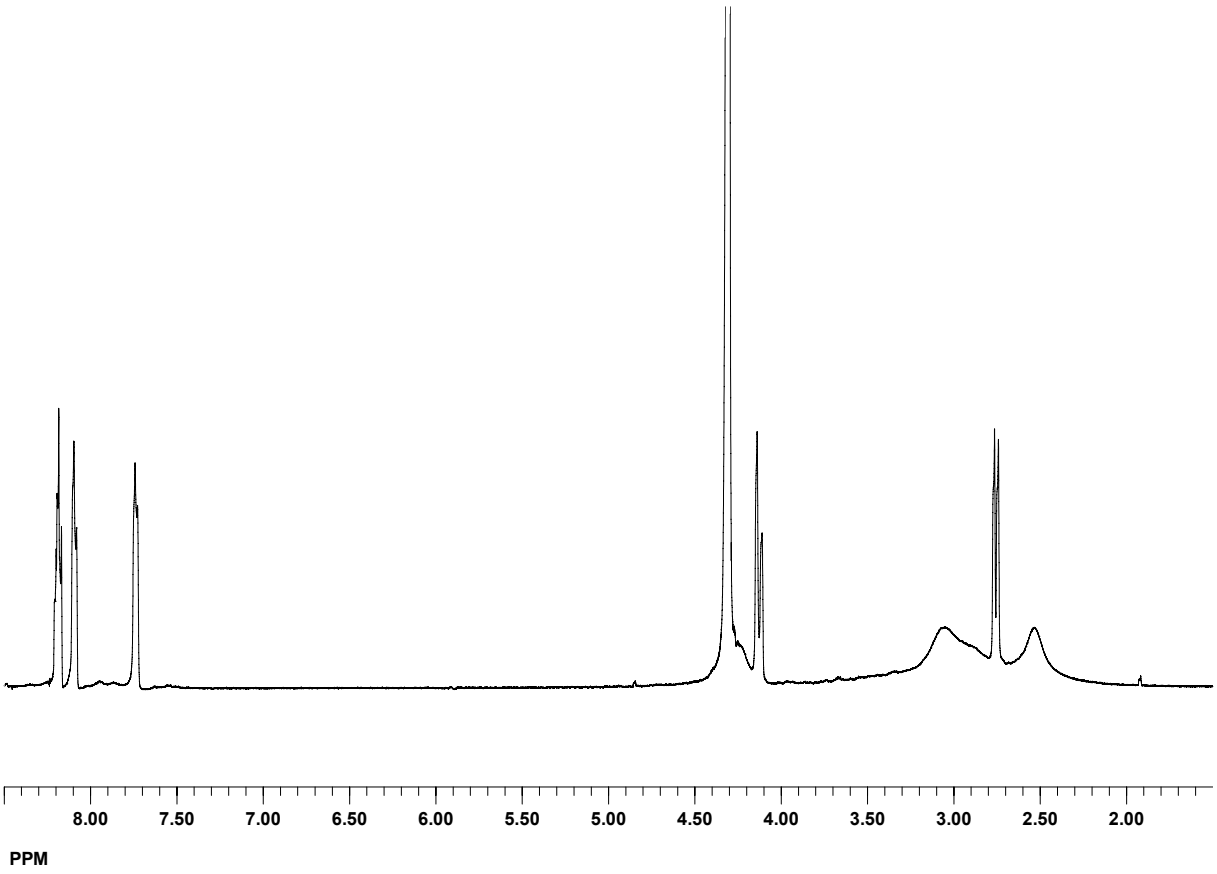


Figure S7: ^{1}H NMR spectrum of [Eu(pbpatcn)], D_2O, 278 K, 500 MHz, pD=5.5.

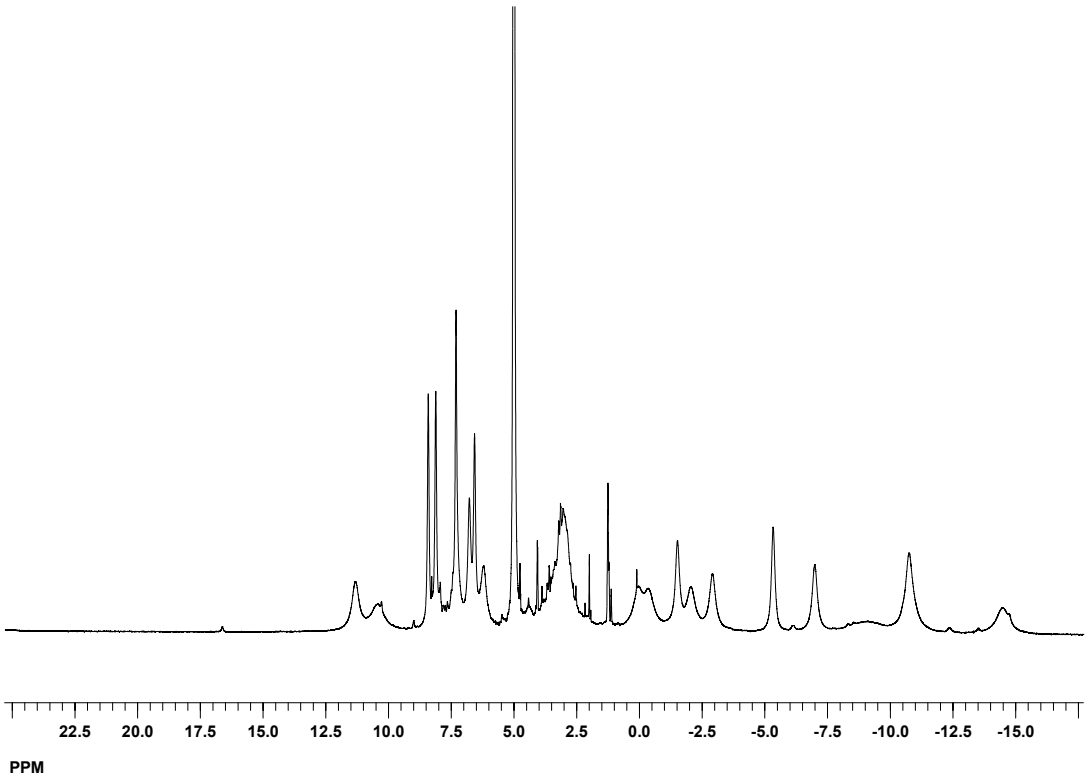


Figure S8: ^{1}H NMR spectrum of [Lu(pbpatcn)], D_2O, 298 K, 500 MHz, pD=6.8.

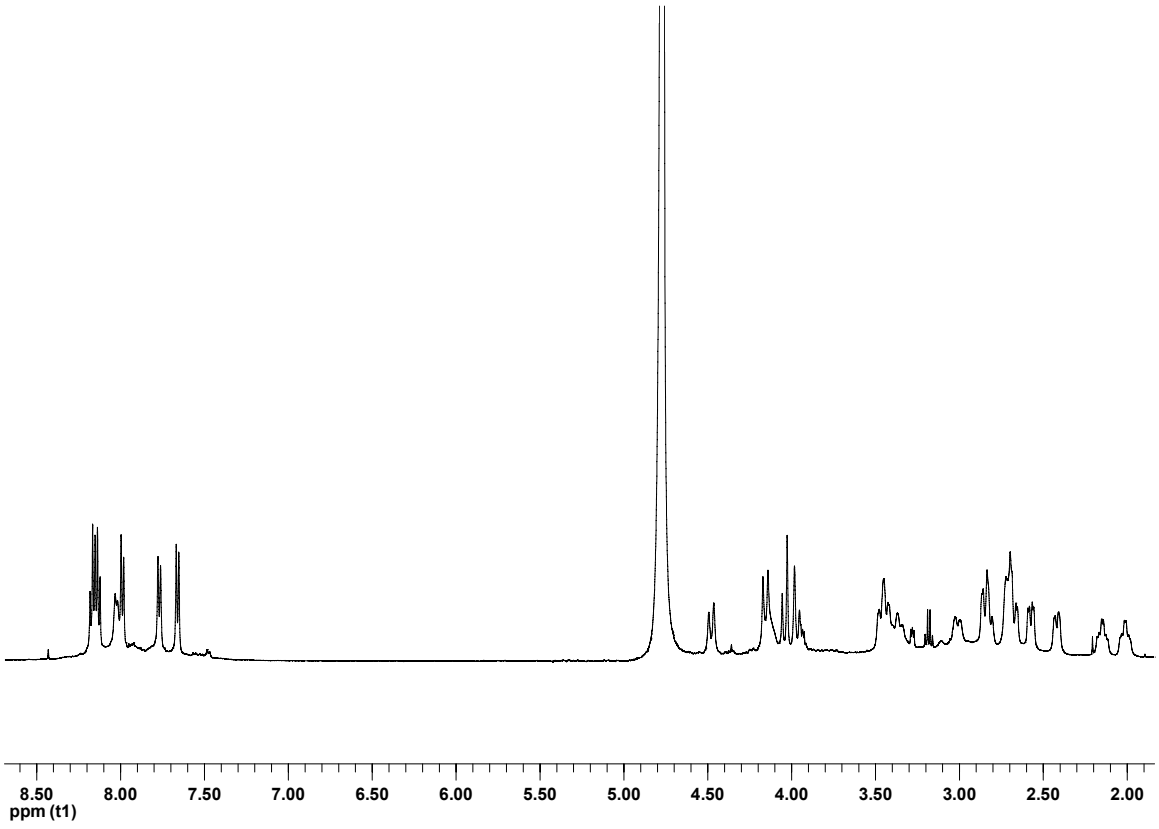
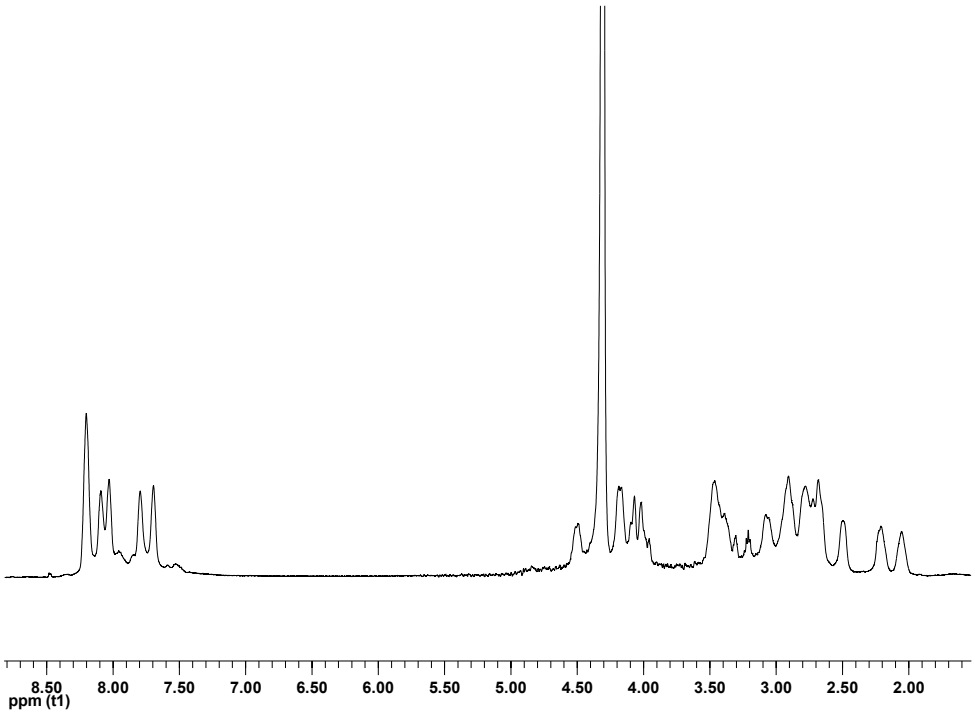


Figure S9: ^{1}H NMR spectrum of [Lu(pbpatcn)], D_2O, 343 K, 500 MHz, pD=6.8.



3. Data analysis of the variable temperature ^{17}O NMR

The reduced relaxation rates and chemical shift ($1/T_{1r}$, $1/T_{2r}$ and $\Delta\omega_r$) can be calculated from the measured ^{17}O NMR relaxation rates and angular frequencies of the Gd^{3+} containing solutions, $1/T_1$, $1/T_2$, and ω, and of the diamagnetic water reference, $1/T_{1d}$, $1/T_{2d}$, and ω_d with equations 1-3 where $1/T_{1m}$, $1/T_{2m}$ are the relaxations rates in the bound water, $\Delta\omega_m$ is the chemical shift difference between bound water and bulk water, P_m is the mole fraction of bound water, and τ_m is the mean residence time of water molecule in the inner-coordination sphere ($k_{ex} = 1/\tau_m$). It has been shown that the outer-sphere contributions to longitudinal and transversal relaxivities can be neglected.

$$\frac{1}{T_{1r}} = \frac{1}{P_m}\left[\frac{1}{T_1} - \frac{1}{T_{1d}}\right] = \frac{1}{T_{1m} + \tau_m} \qquad \textbf{(1)}$$

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left[\frac{1}{T_2} - \frac{1}{T_{2d}}\right] = \frac{1}{\tau_m}\frac{T_{2m}^{-2} + \tau_m^{-1}T_{2m}^{-1} + \Delta\omega_m^2}{\left(\tau_m^{-1} + T_{2m}^{-1}\right)^2 + \Delta\omega_m^2} \qquad \textbf{(2)}$$

$$\Delta\omega_r = \frac{1}{P_m}(\omega - \omega_d) = \frac{\Delta\omega_m}{\left(1 + \tau_m T_{2m}^{-1}\right)^2 + \tau_m^2\Delta\omega_m^2} \qquad \textbf{(3)}$$

At high temperatures, the inner-sphere contribution to $\Delta\omega_r$ is given by the chemical shift of the bound water molecules, which is determined by the hyperfine interaction between the Gd^{3+} electron spin and the ^{17}O nucleus via equation 4 where g_L is the isotropic Landé

factor, μ_B the Bohr magnetron, S the electron spin, A/ħ the scalar coupling constant and B_0 the magnetic field.

$$\Delta\omega_m = \frac{g_L \mu_B S(S+1) B_0}{3k_B T} \frac{A}{\hbar} \qquad \textbf{(4)}$$

When it is not negligible, the outer-sphere contribution has a similar temperature dependence to $\Delta\omega_m$ and is given by equation 5 where C_{OS} is an empirical constant ($0 < C_{OS} < 0.1$).

$$\Delta\omega_{os} = C_{os}\Delta\omega_m \qquad \textbf{(5)}$$

The ^{17}O longitudinal relaxation rates in Gd^{3+} solutions are dominated by the dipole-dipole and quadrupolar mechanisms and are given by equation 6 where γ_I is the ^{17}O nuclear magnetic ratio, r_{GdO} the mean Gd^{3+}-O distance, I the nuclear spin, χ the quadrupolar coupling constant, η an asymmetry parameter and τ_{d1} is defined by equation 7.

$$\frac{1}{T_{1m}} = \left[\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2 \gamma_I^2 \gamma_S^2}{r_{GdO}^6} S(S+1)\right] \times 6\tau_{d1} + \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \chi^2 \left(1+\frac{\eta^2}{3}\right)\tau_R \qquad \textbf{(6)}$$

$$\frac{1}{\tau_{d1}} = \frac{1}{T_{1e}} + \frac{1}{\tau_R} + \frac{1}{\tau_m} \qquad \textbf{(7)}$$

According to crystallographic studies an a series of Gd^{3+} complexes, the mean distance r_{GdO} can be considered as independent of the complex and fixed to 2.5 Å. χ and η have been fixed, considering that the quadrupolar coupling constant is the same as the one for acidified water (Equation 8).

$$\chi\left(1+\frac{\eta^2}{3}\right)^{1/2} = 7.58 \ MHz \qquad \textbf{(8)}$$

The ^{17}O transverse relaxation rate $1/T_{2m}$ in bound water in Gd^{3+} solutions are dominated by the scalar relaxation mechanism and are given to an excellent approximation by equations 9 and 10.

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2 \times \tau_{1s} \qquad \textbf{(9)}$$

$$\frac{1}{\tau_{1s}} = \frac{1}{T_{1e}} + \frac{1}{\tau_m} \qquad \textbf{(10)}$$

The longitudinal electronic relaxation rate $1/T_{1e}$ is accounted for by modulation of the zero field splitting (ZFS) either by rotation or by transient distortions of the complex. At the

experimental field, we assumed that $1/T_{1e}$ can be obtained by the approach of McLachlan (equations 11 and 12) within a good agreement.[1,2]

$$\frac{1}{T_{1e}} = 2C\left(\frac{1}{1+\omega_S^2\tau_v^2} + \frac{4}{1+4\omega_S^2\tau_v^2}\right) \qquad \textbf{(11)}$$

$$C = \frac{1}{50}\Delta^2\tau_v\left[4S(S+1)-3\right] \qquad \textbf{(12)}$$

Δ^2 is the mean-square zero field splitting energy and τ_v is the correlation time for modulation of the zero field splitting interaction. This modulation may result either from rotation or from transient distortions of the complex. We assume that τ_v has the simple exponential temperature dependence given by equation 13 were τ_v^{298} is the correlation time at 298.15 K and E_v is the activation energy. It should be noted that the electronic relaxation time τ_{s0} commonly used in the interpretation of the NMRD profiles corresponds to $(12\Delta^2\tau_v)^{-1}$.

$$\tau_v = \tau_v^{298}\exp\left[\frac{E_v}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right] \qquad \textbf{(13)}$$

The exchange rate of water molecules in the inner-sphere is assumed to obey the Eyring equation (equation 14) where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are respectively the entropy and the enthalpy of activation for the exchange process and k_{ex}^{298} is the exchange rate at 298.15 K.

$$k_{ex} = \frac{1}{\tau_m} = \frac{k_B T}{h}\exp\left[\frac{\Delta S^{\mp}}{R} - \frac{\Delta H^{\mp}}{RT}\right] = \frac{k_{ex}^{298}T}{298.15}\exp\left[\frac{\Delta H^{\mp}}{R}\left(\frac{1}{298.15}-\frac{1}{T}\right)\right] \qquad \textbf{(14)}$$

4. Potentiometric titrations

Figure S10: Normalized titration curves (pH= $f(n_{OH^-}/n_{Ligand})$ for solution of H_4pbpatcn (0.51 mM) and Gd-pbpatcn ([pbpatcn]=0.26 mM, [Gd]=0.24 mM).

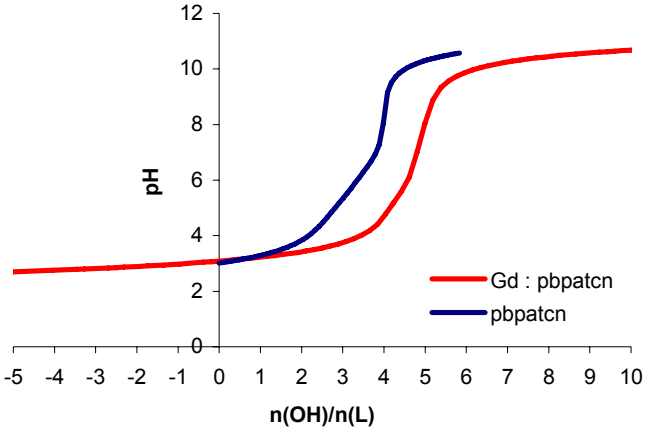
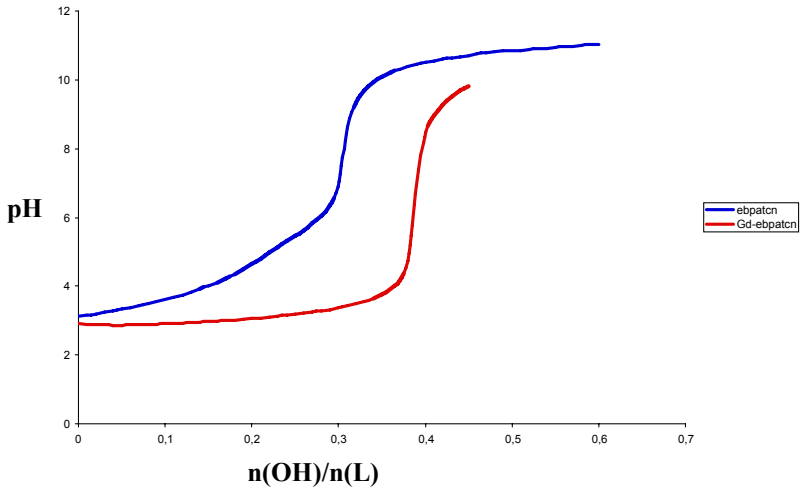


Figure S11: Normalized titration curves (pH= f(n_{OH^-} /n_{Ligand}) for solution of H_3ebpatcn (0.91 mM, blue line), Gd-ebpatcn ([ebpatcn]=0.91 mM, [Gd]=0.91 mM, red line).



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[2] P.H Fries, C. Gateau, M. Mazzanti, *J. Am. Chem. Soc*. **2005**, *127*, 15801.