Supporting Information: *Inorganic Chemistry*

An Isostructural Series of Chiral Nine-Coordinate Lanthanide Complexes Based on Triazacyclononane

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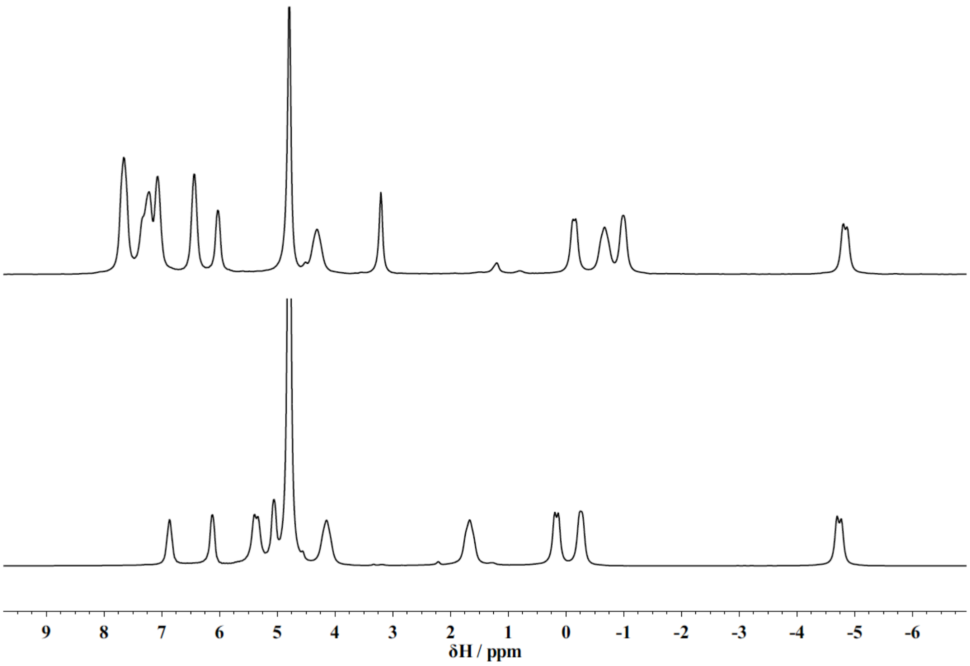


Figure S1 ^{1}H NMR spectra for [EuL^3] (upper, D_2O, 4.7T) and [EuL^1] (lower, CD_3OD). See main text for assignments

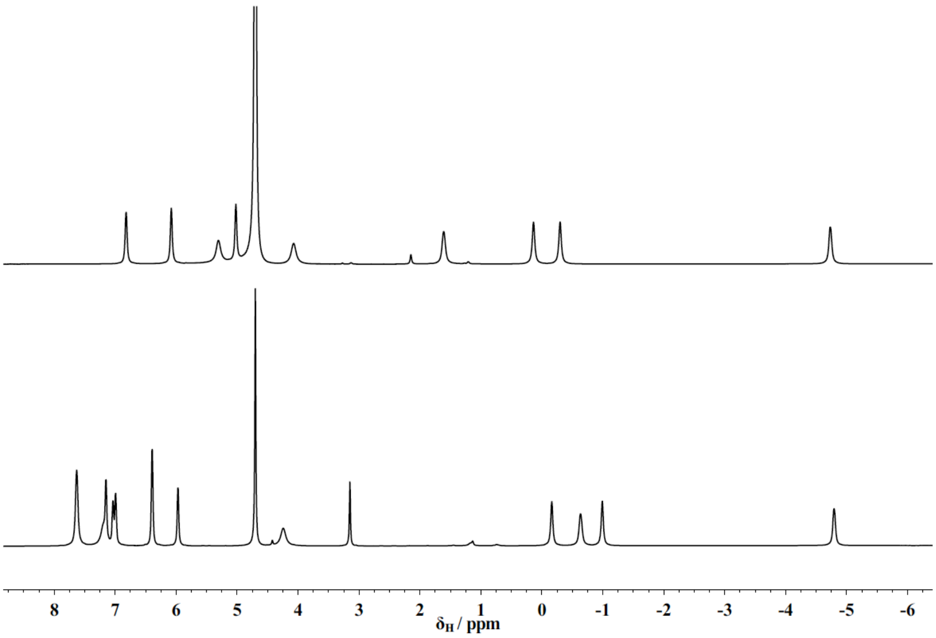
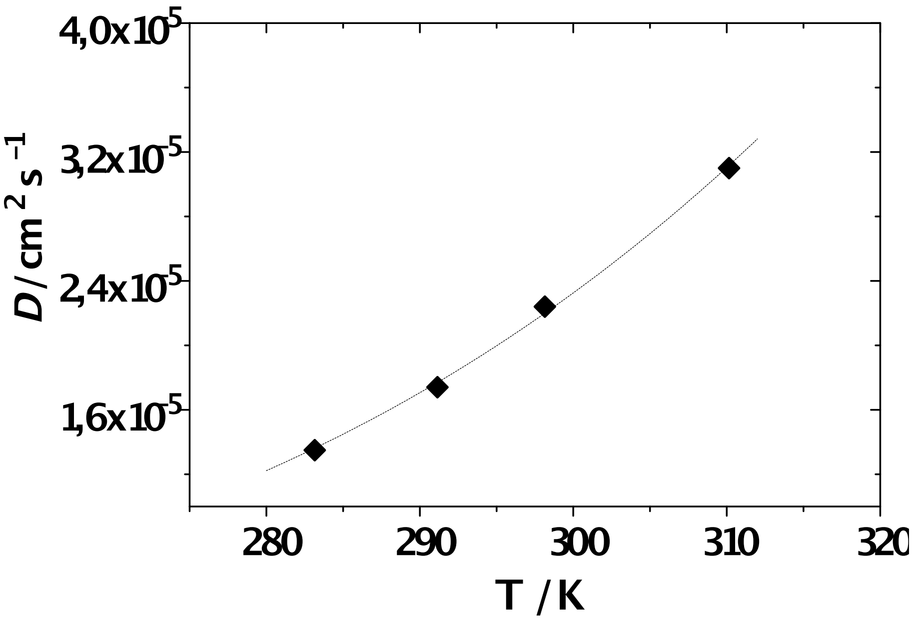


Figure S2 ^{1}H NMR spectra for [EuL^3] (upper, D_2O, 16.5T) and [EuL^1] (lower, CD_3OD)

Table S1 Best Fit parameters for the T dependence of NMRD profiles of [GdL^2]

"*outer sphere*" parameters				
	10°C	**18°C**	**25°C**	**37°C**
r_{1p}^{20} (mM^{-1} s^{-1})	2.90	2.33	1.93	1.57
Δ^2(s^{-2}; ×10^{19})	2.75*	2.75*	2.75±0.07	2.75*
τ_V (ps)	13±1	12±1	10±1	7.5±0.7
*q**	0	0	0	0
a (Å)	4.3*	4.3*	4.3±0.1	4.3*
D (cm^2s^{-1};×10^5)	1.35±0.02	1.74±0.01	2.24*	3.10±0.02

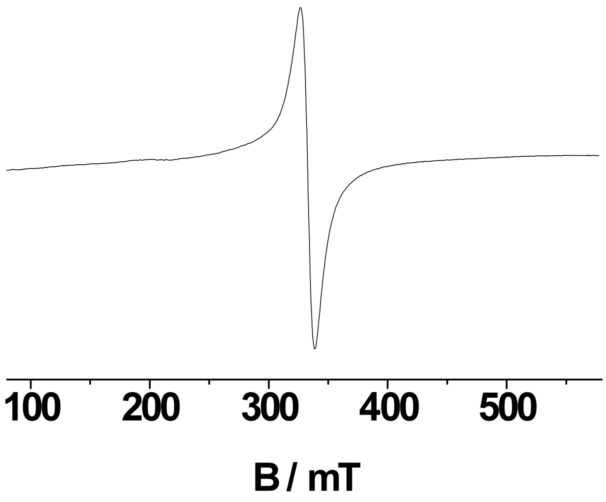
* fixed during the fit



From the fit of the data a $\Delta H_D°$ value of -24.8 kJ/mol is calculated.

$$(D)^{-1} = \frac{\left(D_0^{-1}\right)^{298,15} T}{298.15} \exp\left[\frac{\Delta H_D}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right]$$

Figure S3 ESR spectrum of [GdL^2] recorded at 25 °C (0.9 mM solution)



Center field = 0.33 T (14 MHz for ^1H). The experiment was repeated at 4 temperatures and estimated the T_{2e} values from the bandwidth according to a simplified equation:[a]

$$1/T_{2e} = (g\beta\pi 3^{1/2}/h)\Delta H$$

[a] J. Reuben *The Journal of Physical Chemistry,* **1972**, *Vol. 76,*N° *20,* 3164; D. H. Powell, A. Merbach, *Helvetica Chimica Acta*, (76) 2139 – 2146, **1993** (n.b: in this paper there is an error in the equation)

Temperature (K)	*Δ*Hpp (mT)	T_{2e} (ps)
283,75	14,18	462,34
290,85	13,20	497,36
296,55	11,73	561,13
306,85	9,78	669,92

In comparison, these are correlated data for GdDOTA and GdDTPA, under the same conditions

GdDOTA		
Temperatura (K)	*Δ*Hpp (mT)	T_{2e} (ps)
283,75	8,30	790,99
296,55	8,79	746,05
306,85	9,28	705,94

GdDTPA		
Temperatura (K)	*Δ*Hpp (mT)	T_{2e} (ps)
283,75	64,02	102,55
296,55	63,54	103,34
306,85	63,54	103,34

The ESR bandwidths of [GdDOTA] and[GdL2] are similar, confirming their similar electronic relaxation times (in the former this has in the past often been interpreted as a result of high symmetry and rigidity)

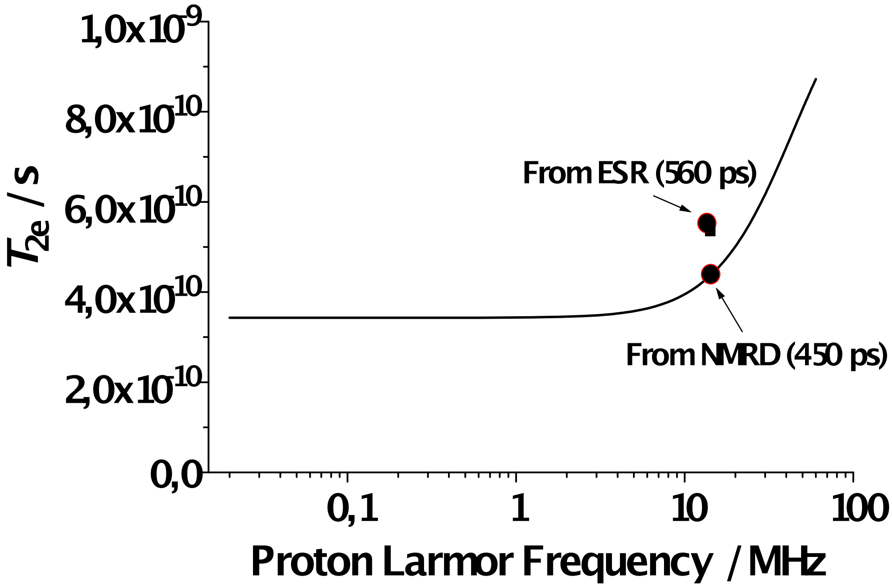


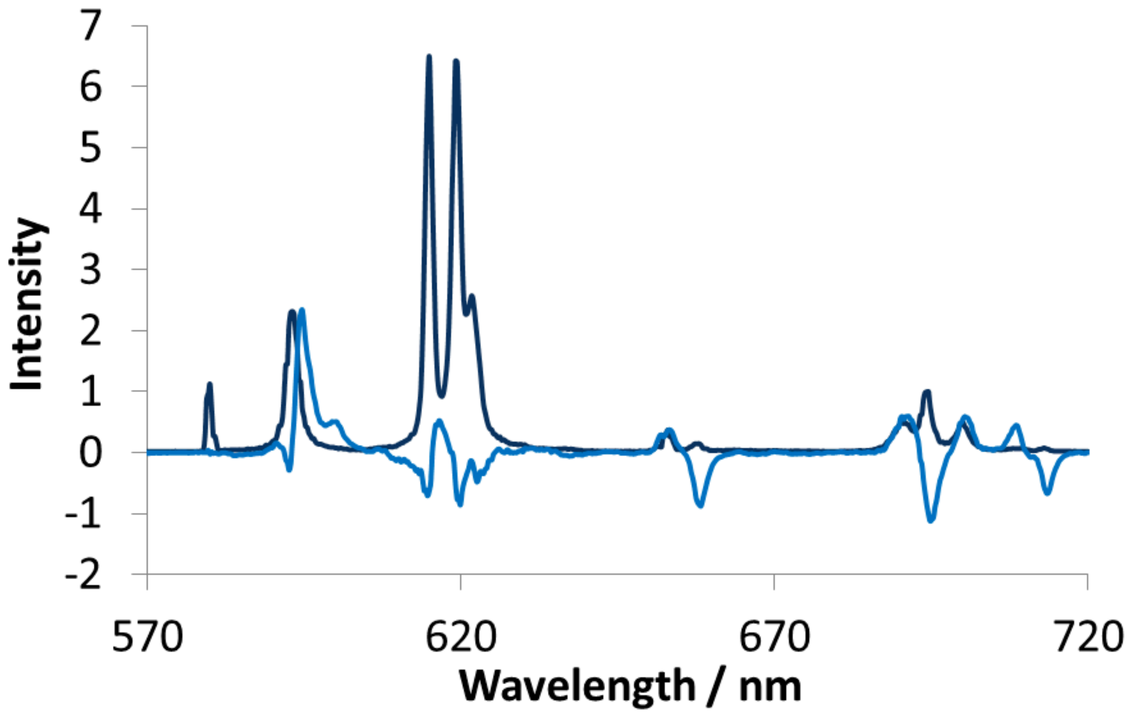
Figure S4 A simulation of the field dependence of T_{2e} according to SBM theory, (Morgan equation) using the best-fit parameters from the reported NMRD data. The agreement is good considering the approximations of the equations for each technique.

Morgan equation for T_{2e} in a form suitable for Gd(III):

$$\left(\frac{1}{T_{2e}}\right) = \Delta^2 \tau_v \left[\frac{5.26}{1 + 0.372\omega_S^2\tau_v^2} + \frac{7.18}{1 + 1.24\omega_S\tau_v}\right]$$

Figure S5 CPL and total emission spectra for Δ (blue) and Λ (red)-[EuL^1].

(The scale used in each CPL figure refers to (I_L- I_R) and is on a scale of x42 with respect to (I_L + I_R).)



= E1 = Λ

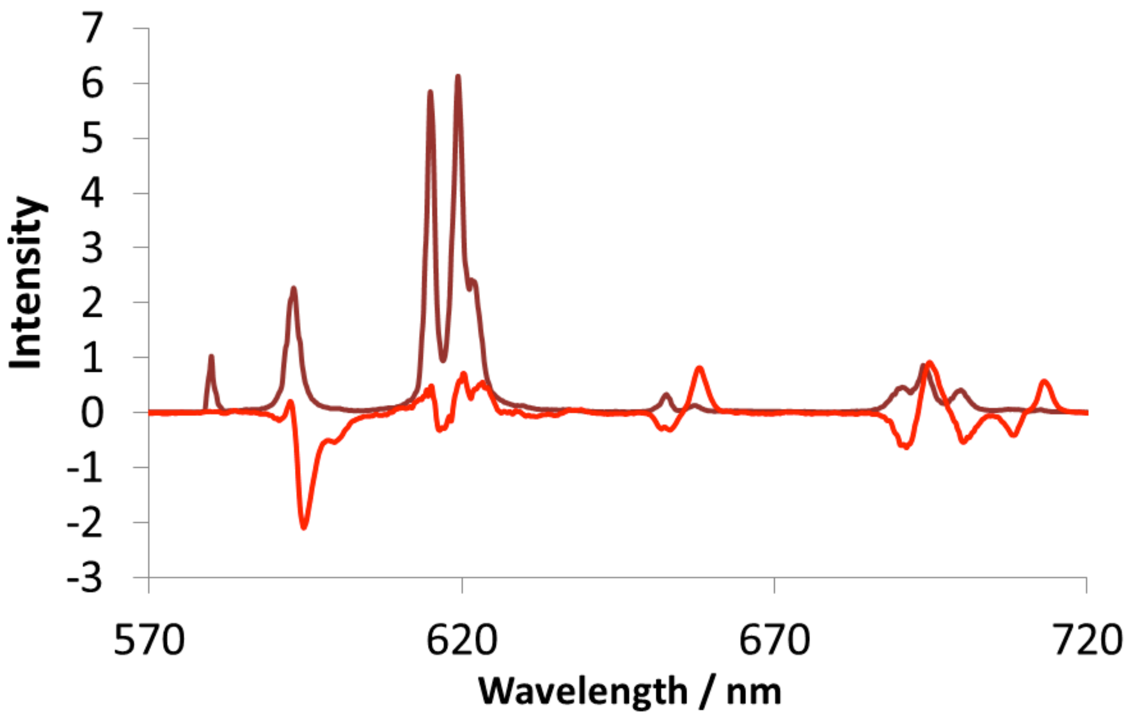


Figure S6 Emission spectra for $[EuL^1]$ at 298 and 77K in MeOH (λ_{exc} 365 nm)

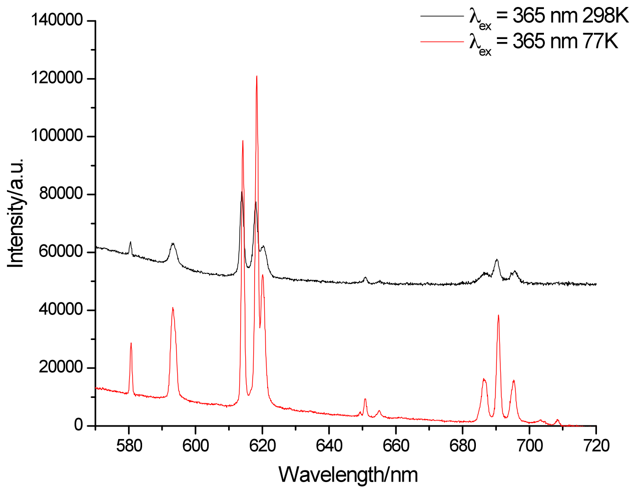


Figure S7 Variable temperature ^1H NMR spectra for $[YbL^1]$ (CD_3OD, 500MHz)

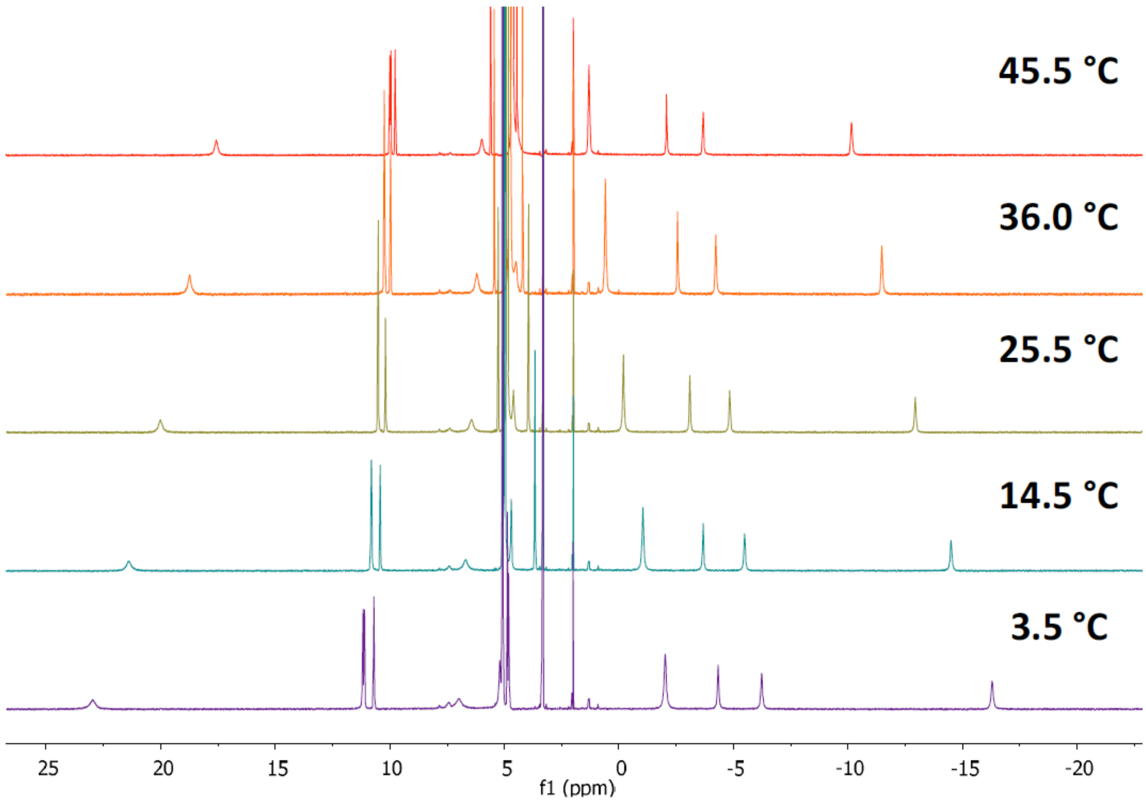


Figure S9 Eu emission spectra for (*upper*) [EuL[1]] and (lower) [EuL[3]] (λ_{exc} 272 nm, H_2O, A = 0.1, 295K) showing the increase in the $\Delta J = 2$ (ca 620 nm) : $\Delta J = 1$ (ca 593 nm) ratio for [EuL[3]], (6.4 vs 5.2). (Increment 0.1 nm, integration time 0.5 s, excitation slits 2.5 nm, emission slits 1 nm)
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