Supplementary Material (ESI) for Dalton Transactions

Tuning facial-meridional isomerisation in monometallic nine-co-ordinate lanthanide complexes with unsymmetrical tridentate ligands.

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Supporting Information

(5 Pages)

Table S1 Lifetimes (τ) of the ligand-centred $^3\pi\pi^*$, and Eu($^5D_0$) excited level in $[Eu(\mathbf{L2})_3]^{3+}$ and Tb($^5D_4$) in $[Tb(\mathbf{L2})_3]^{3+}$ in acetonitrile.

Compound	Conc / mol·dm^{-3}	T /K	$\tilde{\nu}_{ex}$ / cm^{-1}	τ/ms
L2	10^{-5}	77	31940	≥ 100
$[Lu(\mathbf{L2})_3]^{3+}$	$6\cdot10^{-4}$	77	39525	130(15)
$[Eu(\mathbf{L2})_3]^{3+}$	$8\cdot10^{-4}$	295	37040	2.25(2)
$[Eu(\mathbf{L2})_3]^{3+}$	$8\cdot10^{-4}$	77	39060	1.86(7)
$[Tb(\mathbf{L2})_3]^{3+}$	$8\cdot10^{-4}$	295	26109	0.029(1)
$[Tb(\mathbf{L2})_3]^{3+}$	$8\cdot10^{-4}$	77	39215	1.22(4)

Table S2 Elemental analyses for the $[Ln(\mathbf{L2})_3](ClO_4)_3\cdot xH_2O$ (Ln = Eu, x = 4: **1**; Ln = Tb, x = 5.5: **2;** Ln = Lu, x = 4: **3**) and $[Ln(\mathbf{L4})_3](CF_3SO_3)_3\cdot xC_7H_{15}$ (Ln = Eu, x = 0: **4**; Ln = Lu, x = 0.4: **5**). Calculated values are given in parentheses.

Compound	% C	% H	% N
$[Eu(\mathbf{L2})_3](ClO_4)_3\cdot4H_2O$ (**1**)	46.05 (45.96)	4.79 (5.01)	11.20 (11.28)
$[Tb(\mathbf{L2})_3](ClO_4)_3\cdot5.5H_2O$ (**2**)	44.82 (44.94)	4.59 (5.09)	10.69 (11.03)
$[Lu(\mathbf{L2})_3](ClO_4)_3\cdot4H_2O$ (**3**)	45.30 (45.26)	4.68 (4.93)	11.01 (11.11)
$[Eu(\mathbf{L4})_3](CF_3SO_3)_3$ (**4**)	46.55 (46.60)	5.05 (4.62)	9.79 (9.79)
$[Lu(\mathbf{L4})_3](CF_3SO_3)_3\cdot0.4C_7H_{15}$ (**5**)	46.93 (46.97)	4.83 (5.08)	9.53 (9.93)

Table S3 Selected structural data for the lanthanide coordination spheres in $[Eu(\mathbf{L1})_2(CF_3SO_3)_2(H_2O)](CF_3SO_3)(C_3H_5N)_2(H_2O)$ (**6**) and $[Eu(\mathbf{L4})_2(CF_3SO_3)_2(H_2O)](CF_3SO_3)(THF)_{1.5}$ (**7**) analysed as tricapped trigonal prims TTP).

		Angles ϕ [a] / °	
Compd	**6**	**7**	Perfect TTP[b]
R^1-Eu-R^2	170.9	170.7	180
		Angles θ_t [a] / ° (distal tetrapodes)	
Compd	**6**	**7**	Perfect TTP[b]
R^1-Eu-N2b	45.0	44.7	α
R^1-Eu-O1c	50.3	52.4	α
R^1-Eu-O1a	45.3	43.6	α
R^2-Eu-N2a	48.6	46.5	α
R^2-Eu-O1d	44.0	42.8	α
R^2-Eu-O1b	43.9	44.0	α
		Angles ω_{ij} [a] / °	
Compd	**6**	**7**	Perfect TTP[b]
Proj[N2b]-Eu-Proj[O1c][c]	133.0	135.0	120
Proj[O1c]-Eu-Proj[O1a]	115.1	116.8	120
Proj[O1a]-Eu-Proj[N2b]	111.9	108.2	120
Proj[N1b]-Eu-Proj[O1w]	117.3	115.9	120
Proj[O1w]-Eu-Proj[N1a]	130.0	132.0	120
Proj[N1a]-Eu-Proj[N1b]	112.8	112.0	120
Proj[O1d]-Eu-Proj[N2a]	133.3	134.5	120
Proj[N2a]-Eu-Proj[O1b]	117.5	113,5	120
Proj[O1b]-Eu-Proj[O1d]	109.2	111.9	120
Proj[O1a]-Eu-Proj[O1b]	11.5	9.2	0
Proj[N2b]-Eu-Proj[O1d]	8.8	12.8	0
Proj[O1c]-Eu-Proj[N2a]	9.1	12.4	0
Proj[O1a]-Eu-Proj[O1w]	179.0	177.1	180
Proj[N2b]-Eu-Proj[N1a]	162.9	159.1	180
Proj[O1c]-Eu-Proj[N1b]	176.8	178.0	180
Proj[N1a]-Eu-Proj[O1d]	171.7	171.9	180

Proj[N1b]-Eu-Proj[N2a]	167.7	165.6	180
Proj[O1w]-Eu-Proj[O1b]	167.5	168.1	180

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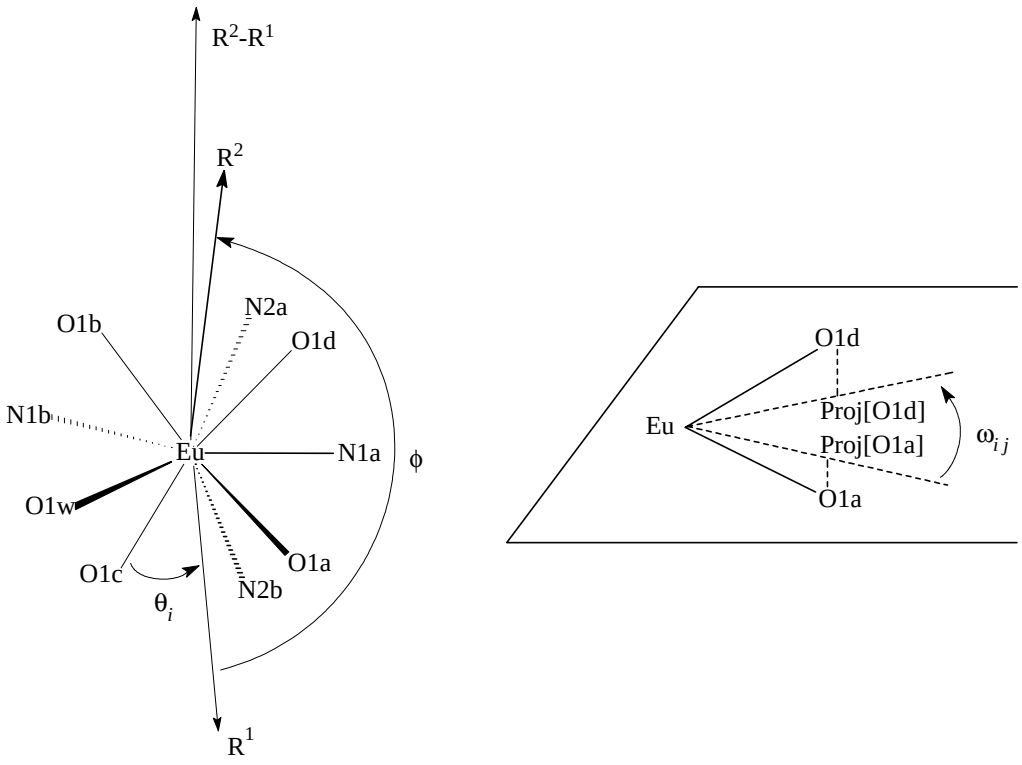
[a] For the definition of ϕ, θ_i and ω_{ij}, see the scheme below. The error in the angles is typically 0.5°. [b] TTP = tricapped trigonal prism. [c] Proj[O*i*] and Proj[N*i*] are the projections of O*i* and respectively N*i* along the R^2-R^1 direction onto a perpendicular plane passing through the lanthanide atom. R^1 = Eu-N2b + Eu-O1c + Eu-O1a and R^2 = Eu-N2a + Eu-O1b + Eu-O1d.



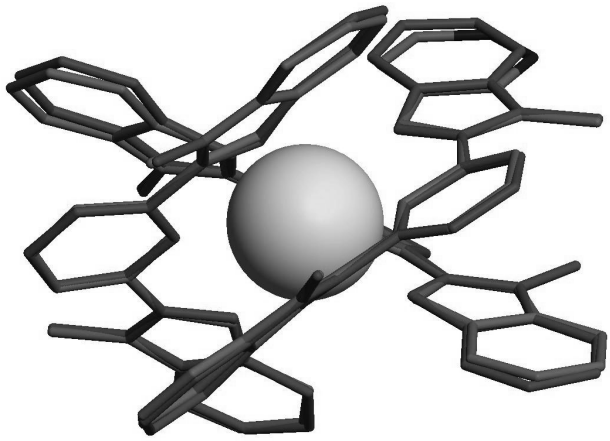
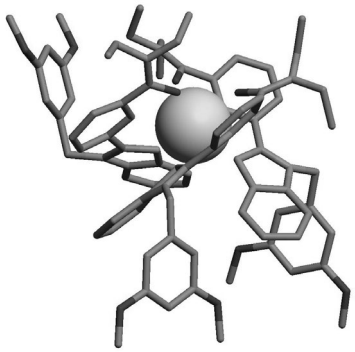


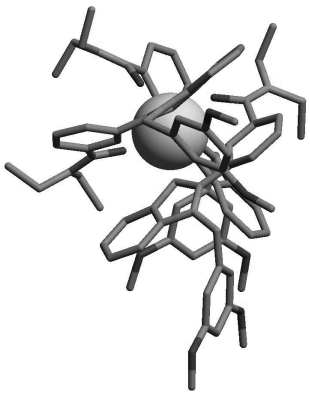
Figure S1 Perspective view of the optimized superimposition of the two molecular structures of $[Eu(\mathbf{L5})_3]^{3+}$ obtained by X-ray diffraction in the solid state (in blue) and by MM simulation in the gas-phase (in red) with the parameters reported by Van Veggel and Reinhoudt.[31]

a)



fac-$[Lu(\mathbf{L3})_3]^{3+}$

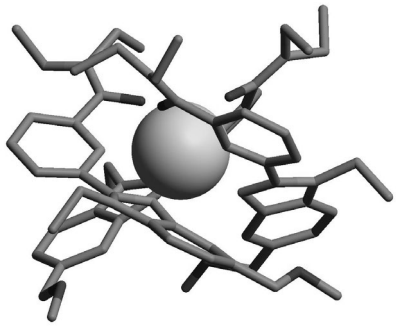
b)



mer-$[Lu(\mathbf{L3})_3]^{3+}$

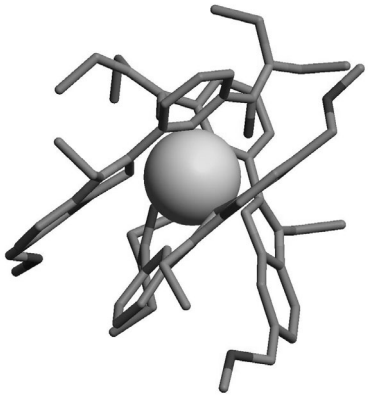
Figure S2 Perspective views of the molecular structures of the two cations a) *fac*-$[Lu(\mathbf{L3})_3]^{3+}$ and b) *mer*-$[Lu(\mathbf{L3})_3]^{3+}$ obtained by molecular mechanic in the gas-phase.

a)



fac-[Lu(**L4**)$_3$]$^{3+}$

b)



mer-[Lu(**L4**)$_3$]$^{3+}$

Figure S3 Perspective views of the molecular structures of the two cations a) *fac*-[Lu(**L4**)$_3$]$^{3+}$ and b) *mer*-[Lu(**L4**)$_3$]$^{3+}$ obtained by molecular mechanic in the gas-phase.