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In search for tuneable intramolecular intermetallic interactions in polynuclear lanthanide complexes.

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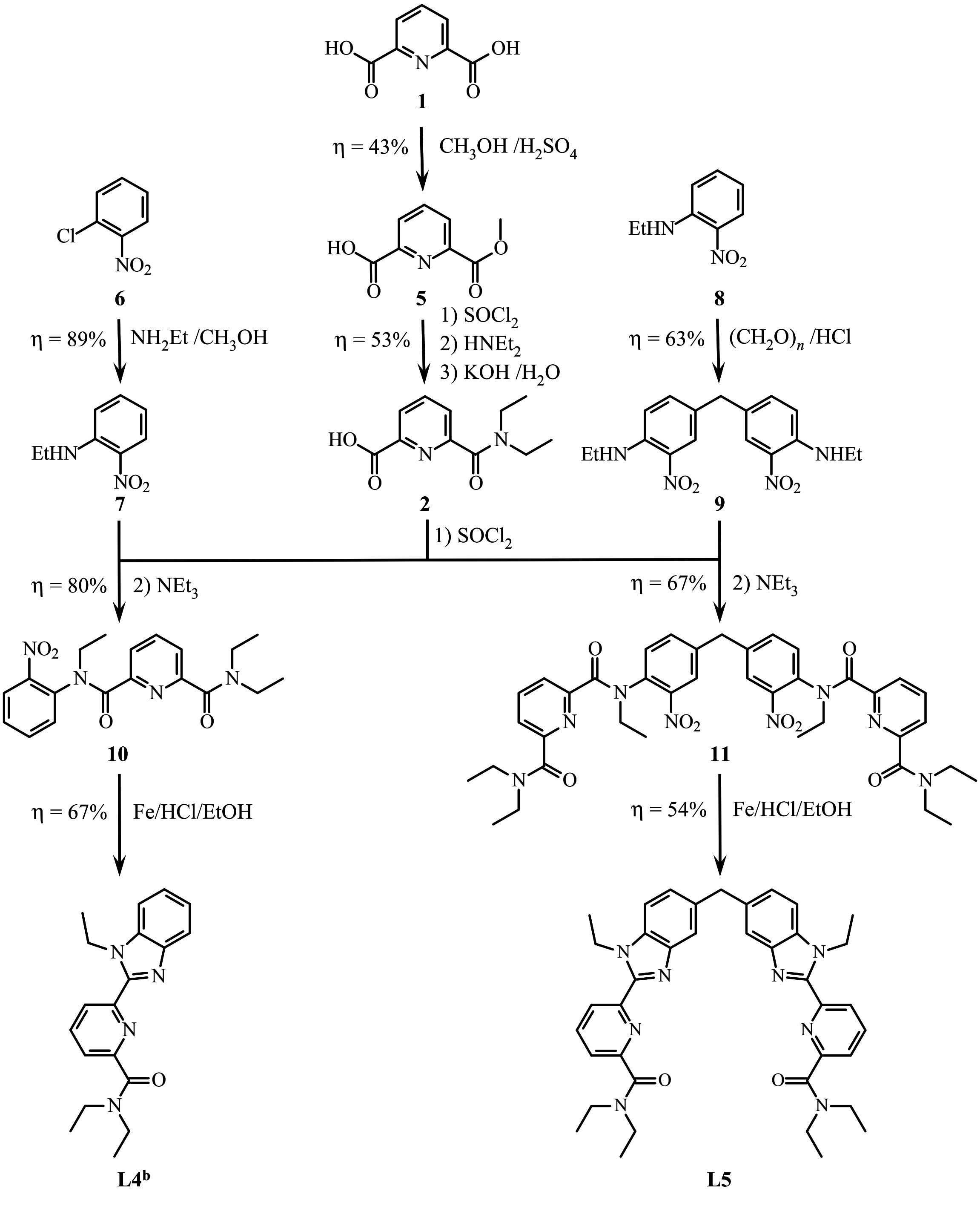
Supporting Information

(31 pages)

Preparation of the ligands L4b and L5.



Scheme S1 Multistep syntheses of **L4b** and **L5**.

Preparation of 2-ethoxycarbonyl-carboxypyridine (5). Dipicolinic acid (1, 10 g, 60 mmol) was refluxed for 20 min in a methanol:water mixture (50 cm^3:50 cm^3) containing concentrated H_2SO_4 (5 cm^3). The cooled solution was poured onto saturated $NaHCO_3$ (500 cm^3) and the aq. phase was extracted with dichloromethane (4x100 cm^3). Acidification of the resulting aq. phase (pH = 2) with concentrated hydrochloric acid (pH = 2) followed by extraction with dichloromethane (4x100 cm^3)

provided a second organic phase, which was dried (anhydrous Na_2SO_4) and evaporated to dryness to yield 43% of 2-ethoxycarbonyl-carboxypyridine (**3**, 4.69 g, 25.9 mmol) as a white powder.

TLC (CH_2Cl_2/MeOH: 9:1): Rf = 0.15. ^{1}H RMN (CD_3OD), δ (ppm): 8.35 (d, 1H, ^3J=7.9 Hz), 8.32 (d, 1H, ^3J=7.9 Hz), 8.18 (t, 1H, ^3J=7.9 Hz), 4.02 (s, 3H). IR**:** 1723, 1703 cm^{-1} (νC=O ester and νC=O acid). Mp: 146°C.

Preparation of 6-(*N,N*-diethylcarbamoyl)pyridine-2-carboxylic acid (**2**). Thionyl chloride (30 cm^3, 15 eq.), 2-ethoxycarbonyl-carboxypyridine (**3**, 5 g, 27.6 mmol) and freshly distilled *N,N*-dimethylformamide (0.2 cm^3) were refluxed in dry dichloromethane (100 cm^3) undert an inert atmosphere for 2h. The resulting brownish mixture was evaporated to dryness and then dissolved in dry dichloromethane (50 cm^3). *N,N*-diethylamine (28.7 cm^3, 0.276 mol, 10 eq.) were added dropwise at room temperature and the solution was refluxed for 2 h, and finally evaporated to dryness. The red brown residue was partitioned between dichloromethane (100 cm^3) and half-saturated NH_4Cl (200 cm^3). The aq. phase was extracted with dichloromethane (4x50 cm^3) and the combined org. phases were washed with saturated $NaHCO_3$ (2x100 cm^3), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The red powder was redissolved into 1.0 mol·dm^3 aq. KOH and stirred for 1 h at room temperature. After washing with dichloromethane (2x50 cm^3), the aq. phase was neutralized (pH = 2) with concentrated hydrochloric acid and kept at 4°C for 12 h. The whicte microcrystalline precipitate was filtered and crystallized from acetonitrile to yield 54% of 6-(*N,N*-diethylcarbamoyl)pyridine-2-carboxylic acid (**2**, 3.31 g, 14.9 mmol).

TLC (CH_2Cl_2 /MeOH: 9:1): Rf =0.2. ^{1}H NMR (CD_3OD), δ (ppm): 8.22 (d, 1H, ^3J=7.9 Hz), 8.11 (t, 1H, ^3J=7.9 Hz), 7.76 (d, 1H, ^3J=7.9 Hz), 3.58 (q, 2H, ^3J=7.3 Hz), 3.34 (q, 2H, ^3J=7.3 Hz), 1.28 (t, 3H, ^3J=7.3 Hz), 1.20 (t, 3H, ^3J=7.3 Hz). IR: 1710 cm^{-1} (νC=O acide), 1602 cm^{-1} (νC=O amide). Mp: 164-165°C.

Preparation of *N*-ethyl-2-nitroaniline (**7**). Ortho-nitrochlorobenzene (**4**, 10 g, 63 mmol) and ethyl amine (60 cm^3 of a 70% solution in water, 756 mmol) were heated at 120°C in an autoclave ($P \leq 5$ bar) for 24 h. After cooling, the mixture was concentrated and poured onto dichloromethane (200 cm^3) and half-saturated aq. NH_4Cl. The organic layer was separated and the aq. phase further extracted with dichloromethane (3x50 cm^3). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness to yield 89% of *N*-ethyl-2-nitroaniline (**7**, 9.46 g, 57 mmol) as an orange oil. ^{1}H NMR ($CDCl_3$), δ (ppm) : 8.17 (d, 1H, ^3J=7.9 Hz), 7.97 (s, 1H), 7.43 (t, 1H, ^3J=7.9 Hz), 6.85 (d, 1H, ^3J=7.9 Hz), 6.63 (t, 1H, ^3J=7.9 Hz), 3.37 (q, 2H, ^3J=7.3 Hz), 1.38 (t, 3H, ^3J=7.3 Hz).

Preparation of 3,3'-dinitro-4,4'-bis(*N*-ethylamino)diphenylmethane (**9**). *N*-ethyl-2-nitroaniline (**7**, 9.46 g, 57 mmol) and para-formaldehyde (0.855 g, 28.35 mmol, 0.5 eq) were stepwise heated in concentrated hydrochloric acid for 1 h. at 40°C, 1 h. at 60°C and 12 h. at 120°C. The cooled solution was poured onto water (350 cm^3) and the resulting viscous mixture was neutralized (pH=9) with concentrated NH_4OH. The amorphous solid was separated by filtration, grinded in a mortar, suspended in the mother liquor and treated in an ultrasonic bath for 15 minutes. The solution was filtered and the solid residue washed with water (3x50 cm^3) and dried under vacuum. The solid was purifed by column chromatography (Silica gel, CH_2Cl_2) to yield 63% of 3,3'-dinitro-4,4'-bis(*N*-ethylamino)diphenylmethane (**9**, 6.34 g , 18 mmol) as an orange powder. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.99 (s, 2H), 7.95 (s, 1H), 7.24 (d, 2H, ^3J=8.9 Hz), 6.80 (d, 2H, ^3J=8.9 Hz), 3.79 (s, 2H), 3.33 (q, 4H, ^3J=7.1 Hz), 1.36 (t, 6H, ^3J=7.3 Hz).

Preparation of pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[*N*-ethyl-*N*-(2-nitrophenyl)-amide] (10). 6-(*N,N*-diethylcarbamoyl)pyridine-2-carboxylic acid (**2**, 1.5 g, 6.8 mmol), thionyl chloride (7.6 cm^3, 104 mmol) and *N,N*-dimethylformamide (0.1 cm^3) dissolved in dry dichloromethane (60 cm^3) were refluxed for 1.5 h. under an inert atmosphere. After evaporation to dryness, the white residue was dissolved in dry dichloromethane (60 cm^3) and *N*-ethyl-2-nitroaniline (1.13g, 6.8 mmol) in dichloromethane (40 cm^3) containing Et_3N (4 cm^3) were added dropwise at room temperature. The brown mixture was refluxed for 2 h. and then evaporated to dryness. The viscous oil was partitioned between dichloromethane (50 cm^3) and aq. half-saturated NH_4Cl (50 cm^3). The organic phase was separated and the aq. phase extracted with dichloromethane (4x25 cm^3). The combined organic phases were dried (Na_2SO_4) and evaporated to dryness. The brown oil was purifed by column chromatography (Silica gel, CH_2Cl_2/MeOH 100:0→97:3) to yield 80% of pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[N-ethyl-N-(2-nitrophenyl)-amide] (**10**, 2 g, 5.4 mmol) as a yellowish oil. ESI-MS (CH_2Cl_2/MeOH): m/z 371.3[M+H]$^+$.

Preparation of ligand L4^b. Pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[N-ethyl-N-(2-nitrophenyl)-amide] (**10**, 2 g, 5.4 mmol), iron powder (3 g, 54 mmol) and concentrated hydrochloric acid (7 cm^3, 84 mmol) were refluxed in ethanol:water (100 cm^3:30 cm^3) for 8 h under an inert atmosphere. The excess iron was filtered and ethanol was evaporated. Dichloromethane (50 cm^3) was added into the aq. phase followed by a solution of Na_2H_2EDTA (45g, 15eq) in water (100 cm^3). The mixture was neutralized (pH = 8.5) under vigourous stirring and hydrogen peroxyde (30%, 5 cm^3) was slowly added. After 25 min strirring, the organic phase was separated and the aq. phase extracted with dichloromethane (4x80 cm^3). The combined organic phases were washed with water (3x50 cm^3), dried (Na_2SO_4) and evaporated to dryness. The residual solid was purifed by column chromatography (Silica gel, CH_2Cl_2/MeOH 97:3→95:5) to yield 67 % of **L4^b** (1.2g, 3.6 mmol) as a white solid. ESI-MS (CH_2Cl_2/MeOH): m/z 323.3[M+H]$^+$. ^{1}H NMR (CD_3CN), δ (ppm): 8.38 (d, 1H, ^3J=7.4 Hz), 8.04 (t, 1H, ^3J=7.8 Hz), 7.76 (d, 1H), 7.54 (d, 1H, ^3J=7.8 Hz), 7.38 (t, 1H ,^3J=8.4 Hz), 7.32 (t, H, ^3J=8.6 Hz), 4.75 (q, 2H, ^3J=7.1 Hz), 3.88 (q, 2H), 3.78 (q, 2H, ^3J=7.1 Hz), 1.45 (t, 3H, ^3J=7.3 Hz), 1.26 (t, 3H, ^3J=7.3 Hz), 1.08 (t, 3H, ^3J=7.3 Hz). Elemental analyses ($C_{19}H_{22}N_4O{\cdot}0.3H_2O$): Calcd: C, 69.63%; H, 6.59%; N, 17.09%. Found: C, 69.64%; H, 6.82%; N, 17.04%.

Preparation of 3,3’-dinitro-4,4’-bis(pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[*N*-ethyl-*N*-(2-nitrophenyl)-amide]*N*-ethylamino)diphenylmethane (11). 6-(*N,N*-diethylcarbamoyl)pyridine-2-carboxylic acid (**2**, 3.0 g, 13.6 mmol), thionyl chloride (15 cm^3) and *N,N*-dimethylformamide (0.1 cm^3) dissolved in dry dichloromethane (60 cm^3) were refluxed for 2 h. under an inert atmosphere. After evaporation to dryness, the white residue was dissolved in dichloromethane (60 cm^3) and a solution of 3,3'-dinitro-4,4'-bis(*N*-ethylamino)diphenylmethane (**9**, 2.13g, 6.18 mmol) in dichloromethane (100 cm^3) containing Et_3N (9.5 cm^3) were added dropwise at room temperature. The brown mixture was refluxed for 2 h. and then evaporated to dryness. The residue was partitioned between dichloromethane (100 cm^3) and aq. half-saturated NH_4Cl (100 cm^3). The organic phase was separated and the aq. phase extracted with dichloromethane (4x50 cm^3). The combined organic phases were dried (Na_2SO_4) and evaporated to dryness. The solid was purifed by column chromatography (Silica gel, CH_2Cl_2/MeOH 98:2→97:3) to yield 67% of 3,3'-dinitro-4,4'-bis(pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[N-ethyl-N-(2-nitrophenyl)-amide]N-ethylamino)diphenylmethane (**11**, 3.09 g, 4.09 mmol). ESI-MS (CH_2Cl_2/MeOH): m/z 753.5 $[M+H]^+$.

Preparation of ligand L5. 3,3'-dinitro-4,4'-bis(pyridine–2,6-dicarboxylic acid-2-diethylamide-6-[N-ethyl-N-(2-nitrophenyl)-amide]N-ethylamino)diphenylmethane (**11**, 3.09 g, 4.09 mmol), iron powder (3.6 g, 65.5 mmol) and concentrated hydrochloric acid (10.2 cm^3, 123 mmol) were refluxed in ethanol:water (100 cm^3:30 cm^3) for 8 h under an inert atmosphere. The excess iron was filtered and ethanol was evaporated. Dichloromethane (100 cm^3) was added into the aq. phase followed by a solution of Na_2H_2EDTA (45g, 15eq) in water (100 cm^3). The mixture was neutralized (pH = 8.5) under vigourous stirring and hydrogen peroxyde (30%, 5 cm^3) was slowly added. After 25 min strirring, the organic phase was separated and the aq. phase extracted with dichloromethane (4x80 cm^3). The combined organic phase was washed with water (3x50 cm^3), dried (Na_2SO_4) and evaporated to dryness. The residual solid was purifed by column chromatography (Silica gel, CH_2Cl_2/MeOH 97:3→95:5) to yield 56% of **L5** (1.52 g, 2.3 mmol) as a white solid. ^{1}H NMR ($CDCl_3$), δ (ppm): 8.38 (d, 2H, ^3J=7.4 Hz); 7.93 (t, 2H, ^3J=7.8 Hz), 7.71 (s, 2H), 7.55 (d, 2H, ^3J=7.8 Hz), 7.35 (d, 2H ,^3J=8.4 Hz); 7.23 (t, 2H, ^3J=8.6 Hz), 4.75 (q, 4H, ^3J=7.1 Hz), 4.29 (s, 2H), 3.61 (q, 4H, ^3J=7.1 Hz), 3.36 (q, 4H, ^3J=7.1 Hz), 1.45 (t, 6H, ^3J=7.3 Hz), 1.28 (t, 6H, ^3J=7.3 Hz), 1.04 (t, 6H, ^3J=7.3 Hz). Elemental analyses ($C_{39}H_{44}N_8O_2\cdot0.5H_2O$): Calcd: C, 70.36% ; H, 6.81% ; N, 16.83%. Found : C, 70.36%; H, 6.76%; N, 16.82%.

Table S1 Bond distances (Å) and bond angles (°) in the crystal structure of **L4**[b].

O1-C6	1.241(2)	N1-C1	1.352(2)
N1-C5	1.345(2)	N2-C6	1.351(2)
N2-C7	1.473(2)	N2-C9	1.474(2)
N3-C11	1.330(2)	N3-C12	1.395(2)
N4-C11	1.373(3)	N4-C17	1.385(2)
N4-C18	1.475(2)	C1-C2	1.393(3)
C1-C11	1.482(3)	C2-C3	1.386(3)
C3-C4	1.387(2)	C4-C5	1.392(3)
C5-C6	1.512(2)	C7-C8	1.514(3)
C9-C10	1.522(4)	C12-C13	1.407(2)
C12-C17	1.406(2)	C13-C14	1.381(3)
C14-C15	1.410(3)	C15-C16	1.386(2)
C16-C17	1.395(3)	C18-C19	1.514(3)

C1-N1-C5	117.6(1)	C6-N2-C7	124.8(1)
C6-N2-C9	117.7(1)	C7-N2-C9	116.2(1)
C11-N3-C12	104.3(1)	C11-N4-C17	106.2(1)
C11-N4-C18	129.9(1)	C17-N4-C18	122.6(2)
N1-C1-C2	122.9(2)	N1-C1-C11	116.6(2)
C2-C1-C11	120.4(1)	C1-C2-C3	118.6(2)
C2-C3-C4	119.2(2)	C3-C4-C5	118.7(2)
N1-C5-C4	123.0(1)	N1-C5-C6	118.0(2)
C4-C5-C6	119.0(2)	O1-C6-N2	122.3(1)
O1-C6-C5	118.1(1)	N2-C6-C5	119.6(1)
N2-C7-C8	113.7(2)	N2-C9-C10	112.0(2)
N3-C11-N4	113.6(2)	N3-C11-C1	121.8(2)
N4-C11-C1	124.4(1)	N3-C12-C13	130.3(2)
N3-C12-C17	110.0(1)	C13-C12-C17	119.6(2)
C12-C13-C14	117.6(2)	C13-C14-C15	122.2(2)
C14-C15-C16	121.0(2)	C15-C16-C17	116.8(2)
N4-C17-C12	105.9(2)	N4-C17-C16	131.3(2)
C12-C17-C16	122.9(1)	N4-C18-C19	111.5(2)

Table S2 Bond distances (Å) and bond angles (°) in the crystal structure of **L5**.

Bond Distances (Å)

C1-N1	1.348(2)	C13-C14	1.388(2)	C27-N22	1.474(2)
C1-C2	1.391(2)	C14-C15	1.406(2)	C27-C28	1.518(3)
C1-C11	1.477(2)	C14-C20	1.516(2)	C29-N22	1.471(2)
C2-C3	1.384(2)	C15-C16	1.387(2)	C29-C30	1.520(2)
C3-C4	1.381(2)	C16-C17	1.393(2)	C31-N23	1.321(2)
C4-C5	1.389(2)	C17-N4	1.384(2)	C31-N24	1.378(2)
C5-N1	1.342(2)	C18-N4	1.468(2)	C32-N23	1.385(2)
C5-C6	1.512(2)	C18-C19	1.515(2)	C32-C33	1.399(2)
C6-O1	1.230(2)	C20-C34	1.515(2)	C32-C37	1.401(2)
C6-N2	1.348(2)	C21-N21	1.341(2)	C33-C34	1.390(2)
C7-N2	1.466(2)	C21-C22	1.396(2)	C34-C35	1.409(2)
C7-C8	1.513(2)	C21-C31	1.474(2)	C35-C36	1.383(2)
C9-N2	1.472(2)	C22-C23	1.384(2)	C36-C37	1.396(2)
C9-C10	1.503(3)	C23-C24	1.384(2)	C37-N24	1.384(2)
C11-N3	1.327(2)	C24-C25	1.389(2)	C38-N24	1.470(2)
C11-N4	1.372(2)	C25-N21	1.342(2)	C38-C39	1.513(2)
C12-N3	1.385(2)	C25-C26	1.509(2)		
C12-C13	1.402(2)	C26-O2	1.233(2)		
C12-C17	1.403(2)	C26-N22	1.342(2)		

Bond angles (°)

N1-C1-C2	123.5(1)	C22-C21-C31	119.0(1)	C15-C14-C20	118.9(1)
N1-C1-C11	117.8(1)	C23-C22-C21	118.5(1)	C16-C15-C14	122.5(1)

C2-C1-C11	118.7(1)	C24-C23-C22	119.2(1)	C15-C16-C17	116.4(1)
C3-C2-C1	118.3(1)	C23-C24-C25	118.5(1)	N4-C17-C16	131.5(1)
C4-C3-C2	119.1(1)	N21-C25-C24	123.3(1)	N4-C17-C12	105.9(1)
C3-C4-C5	118.8(2)	N21-C25-C26	114.2(1)	C16-C17-C12	122.5(1)
N1-C5-C4	123.3(2)	C24-C25-C26	122.1(1)	N4-C18-C19	112.0(1)
N1-C5-C6	119.2(1)	O2-C26-N22	123.4(1)	C34-C20-C14	114.8(1)
C4-C5-C6	117.3(1)	O2-C26-C25	117.8(1)	N21-C21-C22	123.0(1)
O1-C6-N2	123.3(2)	N22-C26-C25	118.8(1)	N21-C21-C31	118.0(1)
O1-C6-C5	117.0(1)	N22-C27-C28	113.3(1)	C35-C36-C37	116.4(1)
N2-C6-C5	119.7(1)	N22-C29-C30	113.3(1)	N24-C37-C36	131.7(1)
N2-C7-C8	113.3(1)	N23-C31-N24	113.2(1)	N24-C37-C32	106.1(1)
N2-C9-C10	112.6(1)	N23-C31-C21	121.5(1)	C36-C37-C32	122.2(1)
N3-C11-N4	113.2(1)	N24-C31-C21	125.3(1)	N24-C38-C39	112.5(1)
N3-C11-C1	121.7(1)	N23-C32-C33	129.9(1)	C5-N1-C1	116.9(1)
N4-C11-C1	125.1(1)	N23-C32-C37	109.8(1)	C6-N2-C7	124.9(1)
N3-C12-C13	130.4(1)	C33-C32-C37	120.2(1)	C6-N2-C9	117.0(1)
N3-C12-C17	109.9(1)	C34-C33-C32	118.5(1)	C7-N2-C9	116.6(1)
C13-C12-C17	119.7(1)	C33-C34-C35	119.9(1)	C11-N3-C12	104.8(1)
C14-C13-C12	118.7(1)	C33-C34-C20	119.9(1)	C11-N4-C17	106.1(1)
C13-C14-C15	120.1(1)	C35-C34-C20	120.2(1)	C11-N4-C18	130.9(1)
C13-C14-C20	121.0(1)	C36-C35-C34	122.8(1)	C17-N4-C18	123.0(1)
C21-N21-C25	117.5(1)	C26-N22-C29	118.6(1)	C26-N22-C27	124.1(1)
C29-N22-C27	117.3(1)	C31-N23-C32	105.1(1)	C31-N24-C37	105.8(1)
C31-N24-C38	130.8(1)	C37-N24-C38	122.9(1)		

Table S3 Elemental analyses for the complexes [Ln(**L4^b^**)$(NO_3)_3$]·xH_2O and [Ln_2(**L5**)$(NO_3)_6$]·xH_2O.

Complexes	%C [a]	%H [a]	%N [a]
[La(**L4^b^**)$(NO_3)_3$]·2.5H_2O	33.00(33.03)	3.92(3.78)	14.17(14.02)
[Eu(**L4^b^**)$(NO_3)_3$]·2H_2O	32.78(33.03)	3.76(3.78)	14.08(14.02)
[Gd(**L4^b^**)$(NO_3)_3$]·2.5H_2O	32.11(32.15)	3.83(3.74)	13.80(13.77)
[Tb(**L4^b^**)$(NO_3)_3$]·2.5H_2O	32.03(31.87)	3.82(3.72)	13.76(13.70)
[Lu(**L4^b^**)$(NO_3)_3$]·1.5H_2O	32.10(32.31)	3.55(3.83)	13.79(13.44)
[Y(**L4^b^**)$(NO_3)_3$]·1.5H_2O	36.55(36.22)	4.04(3.87)	15.70(15.80)
[La_2(**L5**)$(NO_3)_6$]·3H_2O	34.43(34.50)	3.70(3.68)	14.41(14.23)
[Eu_2(**L5**)$(NO_3)_6$]·3.5H_2O	33.56(33.47)	3.68(3.67)	14.05(13.98)
[Gd_2(**L5**)$(NO_3)_6$]·4H_2O	33.09(32.99)	3.70(3.60)	13.85(14.20)
[Tb_2(**L5**)$(NO_3)_6$]·3.5H_2O	33.23(33.04)	3.65(3.58)	13.91(14.18)
[Lu_2(**L5**)$(NO_3)_6$]·6H_2O	31.50(31.44)	3.80(3.78)	13.19(13.00)
[Y_2(**L5**)$(NO_3)_6$]·4H_2O	36.63(36.80)	4.09(3.90)	15.33(15.20)

[a] Calculated (found).

Table S4 Bond distances (Å) and bond angles (°) for [Eu(**L4**$^{\mathbf{b}}$)$(NO_3)_3CH_3CN$] in the crystal structure of **3**.

Eu-O1	2.370(2)	Eu-N1	2.630(2)
Eu-N3	2.543(2)	Eu-O1a	2.563(2)
Eu-O2a	2.533(2)	Eu-O1b	2.541(2)
Eu-O2b	2.493(2)	Eu-O1c	2.512(2)
Eu-O2c	2.496(2)	Eu-N1d	2.595(2)

O1-Eu-N1	62.37(7)	O1-Eu-N3	124.10(6)
O1-Eu-O1a	133.04(7)	O1-Eu-O2a	143.50(7)
O1-Eu-O1b	123.49(6)	O1-Eu-O2b	77.13(6)
O1-Eu-O1c	77.69(6)	O1-Eu-O2c	75.12(6)
O1-Eu-N1d	70.90(7)	N1-Eu-N3	61.95(7)
N1-Eu-O1a	164.11(7)	N1-Eu-O2a	116.17(6)
N1-Eu-O1b	109.30(7)	N1-Eu-O2b	69.90(6)
N1-Eu-O1c	68.63(6)	N1-Eu-O2c	111.85(7)
N1-Eu-N1d	126.08(6)	N3-Eu-O1a	102.86(7)
N3-Eu-O2a	70.08(6)	N3-Eu-O1b	72.22(7)
N3-Eu-O2b	80.06(7)	N3-Eu-O1c	86.90(7)
N3-Eu-O2c	131.57(7)	N3-Eu-N1d	146.90(8)
O1a-Eu-O2a	50.15(6)	O1a-Eu-O1b	67.22(6)
O1a-Eu-O2b	114.02(6)	O1a-Eu-O1c	107.87(6)
O1a-Eu-O2c	73.92(7)	O1a-Eu-N1d	68.99(6)
O2a-Eu-O1b	92.25(6)	O2a-Eu-O2b	138.79(7)
O2a-Eu-O1c	69.27(6)	O2a-Eu-O2c	72.35(6)
O2a-Eu-N1d	117.29(6)	O1b-Eu-O2b	50.87(6)
O1b-Eu-O1c	156.13(6)	O1b-Eu-O2c	138.74(6)
O1b-Eu-N1d	75.20(8)	O2b-Eu-O1c	137.89(6)
O2b-Eu-O2c	146.55(6)	O2b-Eu-N1d	75.01(7)
O1c-Eu-O2c	51.34(6)	O1c-Eu-N1d	126.19(8)
O2c-Eu-N1d	78.53(7)		

Table S5 Selected Least-Squares Plane Data for [Eu(**L4**^{b})(NO_3)$_3$$CH_3CN$] in the crystal structure of **3**.

Least-squares planes description	Abbreviation	Max. deviation /Å	Atom
Pyridine N1,C1,C2,C3,C4,C5	Py	0.0297	C5
Benzimidazole N3,N4,C11,C12,C13,C14,C15,C16,C17	Bz	0.0205	C11
Nitrate I N1a,O1a,O2a,O3a	NitI	-0.0033	N1a
Nitrate II N1b,O1b,O2b,O3b	NitII	0.0027	N1b
Nitrate III N1c,O1c,O2c,O3c	NitIII	-0.0028	N1c

Interplane Angles / ° [a]

	Bz	NitI	NitII	NitIII
Py	11.3	37.4	80.1	75.3
Bz		32.3	89.5	72.5
NitI			65.2	79.7
NitII				69.7

[a] Typical errors are within 0.1°.

Table S6 Bond distances ($\delta_{\mathrm{Eu},j}$), bond valences ($\nu_{\mathrm{Eu},j}$)[a] and bond valence sum (V_{Eu})[b] in the crystal structure of [Eu(**L3**$^{\mathbf{a}}$)(NO_3)$_3$(CH_3OH)].[18a]

Atom [c]	Donor type	$\delta_{\mathrm{Eu},j}$ / Å	$\nu_{\mathrm{Eu},j}$	
N1	bzim	2.477	0.426	
N3	py	2.611	0.296	Average N-heterocyclic
N4	bzim	2.537	0.362	0.36(6)
O101	nitrate	2.453	0.326	
O102	nitrate	2.535	0.261	
O201	nitrate	2.68	0.176	
O202	nitrate	2.478	0.304	
O301	nitrate	2.474	0.308	Average O-nitrate
O302	nitrate	2.498	0.288	0.28(5)
O001	methanol	2.494	0.292	
		V_{Eu}	3.039	

[a] $\nu_{\mathrm{Eu},j} = e^{\left[\left(R_{\mathrm{Eu},j} - d_{\mathrm{Eu},j}\right)/b\right]}$ with valence bond parameters $R_{\mathrm{Eu,N}}$ and $R_{\mathrm{Eu,O}}$ taken from ref 29 and b = 0.37 Å.[28] [b] $V_{\mathrm{Eu}} = \sum_j \nu_{\mathrm{Eu},j}$.[28] [c] Numbering taken from reference 18a.

Table S7 Bond distances ($\delta_{\mathrm{Eu},j}$), bond valences ($\nu_{\mathrm{Eu},j}$)[a] and bond valence sum (V_{Eu})[b] in the crystal structure of [Eu(**L3**$^{\mathbf{c}}$)(NO_3)$_3$(CH_3CN)].[18b]

Atom [c]	Donor type	$\delta_{\mathrm{Eu},j}$ / Å	$\nu_{\mathrm{Eu},j}$	
N2	Bzim	2.522	0.377	
N4	Bzim	2.492	0.409	Average N-heterocyclic
N1	Py	2.617	0.292	0.36(6)
O1a	Nitrate	2.526	0.267	
O2a	Nitrate	2.473	0.309	
O1b	Nitrate	2.546	0.253	
O2b	Nitrate	2.48	0.303	
O1c	Nitrate	2.61	0.213	Average O-nitrate
O2c	Nitrate	2.478	0.304	0.28(4)
N1d	Acetonitrile	2.57	0.331	
		V_{Eu}	3.058	

[a] $\nu_{\mathrm{Eu},j} = e^{\left[\left(R_{\mathrm{Eu},j} - d_{\mathrm{Eu},j}\right)/b\right]}$ with valence bond parameters $R_{\mathrm{Eu,N}}$ and $R_{\mathrm{Eu,O}}$ taken from ref 29 and b = 0.37 Å.[28] [b] $V_{\mathrm{Eu}} = \sum_j \nu_{\mathrm{Eu},j}$.[28] [c] Numbering taken from reference 18b.

Table S8 Bond distances ($\delta_{\mathrm{Eu},j}$), bond valences ($\nu_{\mathrm{Eu},j}$)[a] and bond valence sum (V_{Eu})[b] in the crystal structure of [Eu(**L4$^{\mathbf{b}}$**)(NO_3)$_3$(CH_3CN)] (**3**).

Atom [c]	Donor type	$\delta_{\mathrm{Eu},j}$ / Å	$\nu_{\mathrm{Eu},j}$	
N3	bzim	2.543	0.356	Average N-heterocyclic
N1	py	2.630	0.282	0.32(5)
O1	amide	2.370	0.408	
O1a	nitrate	2.563	0.242	
O2a	nitrate	2.533	0.262	
O1b	nitrate	2.541	0.257	
O2b	nitrate	2.493	0.292	
O1c	nitrate	2.512	0.278	Average O-nitrate
O2c	nitrate	2.496	0.290	0.27(2)
N1d	acetonitrile	2.595	0.309	
		V_{Eu}	2.976	

[a] $\nu_{\mathrm{Eu},j} = e^{\left[\left(R_{\mathrm{Eu},j} - d_{\mathrm{Eu},j}\right)/b\right]}$ with valence bond parameters $R_{\mathrm{Eu,N}}$ and $R_{\mathrm{Eu,O}}$ taken from ref 29 and $b = 0.37$ Å.[28] [b] $V_{\mathrm{Eu}} = \sum_j \nu_{\mathrm{Eu},j}$.[28] [c] Numbering taken from Figure 5a.

Table S9 Bond distances ($\delta_{\mathrm{Eu},j}$), bond valences ($\nu_{\mathrm{Eu},j}$)[a] and bond valence sum (V_{Eu})[b] in the crystal structure of [Eu$_2$(**L5**)(NO$_3$)$_6$(H$_2$O)$_2$] (**4**).

Atom [c]	Donor type	$\delta_{\mathrm{Eu},j}$ / Å	$\nu_{\mathrm{Eu},j}$	
N4	Bzim	2.510	0.389	Average N-heterocyclic
N2	Py	2.628	0.283	0.34(8)
O1	Amide	2.362	0.417	
O3	Nitrate	2.505	0.283	
O4	Nitrate	2.515	0.275	
O6	Nitrate	2.610	0.213	
O7	Nitrate	2.518	0.273	
O9	Nitrate	2.542	0.256	Average O-nitrate
O10	Nitrate	2.544	0.255	0.26(3)
O21	Water	2.440	0.337	
		V_{Eu}	2.982	

[a] $\nu_{\mathrm{Eu},j} = e^{\left[\left(R_{\mathrm{Eu},j} - d_{\mathrm{Eu},j}\right)/b\right]}$ with valence bond parameters $R_{\mathrm{Eu,N}}$ and $R_{\mathrm{Eu,O}}$ taken from ref 29 and b = 0.37 Å.[28] [b] $V_{\mathrm{Eu}} = \sum_j \nu_{\mathrm{Eu},j}$.[28] [c] Numbering taken from Figure 5b.

Table S10 Selected bond distances (Å) and bite angles (°) for $[Eu_2(\mathbf{L5})(NO_3)_6(H_2O)_2]$ in the crystal structure of **4**.

Bond Distances

Eu1- Eu1’	8.564(1)	Eu1 – Eu1’’	8.720(1)		
Eu1 – O1	2.362(2)	Eu1 – O3	2.505(2)	Eu1 – O9	2.542(2)
Eu1 – N2	2.628(3)	Eu1 – O4	2.515(2)	Eu1 – O10	2.544(2)
Eu1 – N4	2.510(2)	Eu1 – O6	2.610(2)	Eu1 – O21	2.440(2)
		Eu1 – O7	2.518(2)		

Eu1’ (1-*x*, *y*, 0.5-*z*), Eu1’’ (1.5-*x* 1.5-*y* 1-*z*)

Bond angles (°)

O1 -Eu-O21	73.40(6)	O21-Eu-N4	146.47(7)	O3 -Eu-O9	133.89(7)
O1 -Eu-O3	76.59(5)	O21-Eu-O4	79.77(7)	O3 -Eu-O10	161.47(6)
O1 -Eu-N4	124.18(7)	O21-Eu-O7	72.22(7)	O3 -Eu-O6	65.63(6)
O1 -Eu-O4	78.14(6)	O21-Eu-O9	76.03(7)	O3 -Eu-N2	66.09(7)
O1 -Eu-O7	140.16(7)	O21-Eu-O10	70.98(6)	N4 -Eu-O4	128.82(6)
O1 -Eu-O9	73.06(6)	O21-Eu-O6	116.74(7)	N4 -Eu-O7	95.66(7)
O1 -Eu-O10	118.18(5)	O21-Eu-N2	129.95(6)	N4 -Eu-O9	82.40(6)
O1 -Eu-O6	138.92(6)	O3 -Eu-N4	86.95(6)	N4 -Eu-O10	75.49(7)
O1 -Eu-N2	62.74(6)	O3 -Eu-O4	51.02(7)	N4 -Eu-O6	70.80(7)
O21-Eu-O3	126.43(7)	O3 -Eu-O7	109.07(7)	N4 -Eu-N2	61.81(6)
O4 -Eu-O7	76.53(7)	O4 -Eu-O6	66.00(6)	O7 -Eu-O10	67.66(7)
O4 -Eu-O9	146.55(5)	O4 -Eu-N2	111.62(7)	O7 -Eu-O6	49.64(7)
O4 -Eu-O10	138.99(7)	O7 -Eu-O9	116.54(7)	O7 -Eu-N2	156.59(6)
O9 -Eu-O10	50.37(6)	O9 -Eu-N2	69.37(6)	O10-Eu-N2	109.16(7)
O9 -Eu-O6	146.58(6)	O10-Eu-O6	102.26(6)	O6 -Eu-N2	112.07(6)

Table S11 Selected Least-Squares Plane Data for [Eu_2(**L5**)$(NO_3)_6(H_2O)_2$] in the crystal structure of **4**.

Least-squares planes description	Abbreviation	Max. deviation/Å	Atom
Pyridine N2	Py	0.022(3)	C10
Benzimidazole N3, N4	Bz	.013(3)	N4
Nitrate 1 N9 O3 O4 O5	NitI	0.0015	N9
Nitrate 2 N10 O6 O7 O8	NitII	-0.0028	N10
Nitrate 3 N11 O9 O10 O11	NitIII	0.0072	N11

Interplane Angles / °

	Bz	NitI	NitII	NitIII
Py	14.3	75.3	57.8	77.9
Bz		68.0	68.7	87.9
NitI			49.0	63.3
NitII				44.1

Bz'' (1-*x*, 1-*y*, 1-*z*)

Table S12. ^{1}H NMR shifts (in ppm with respect to TMS) for the ligand **L4^{b}**, **L5** and their complexes [Ln(**L4^{b}**)(NO_3)$_3$] and [Ln$_2$(**L5**)(NO_3)$_6$] in CD_3CN at 293 K (Ln = La, Eu, Lu, Y).[a]

Protons	**L4^{b}**	[La(**L4^{b}**)(NO_3)$_3$]	[Eu(**L4^{b}**)(NO_3)$_3$]	[Lu(**L4^{b}**)(NO_3)$_3$]	[Y(**L4^{b}**)(NO_3)$_3$]	**L5**	[La$_2$(**L5**)(NO_3)$_6$]	[Lu$_2$(**L5**)(NO_3)$_6$]
H1	7.60	7.7	6.5	7.78	7.77	4.25	4.3	4.33
H2	7.37	7.5	6.8	7.56	7.55	7.27	7.48	7.46
H3	7.32	7.5	5.0	7.51	7.50	7.49	7.75	7.69
H4	7.75	7.9	6.4	8.11	8.07	7.66	7.90	8.07
H5	8.39	8.27	7.4	8.40	8.37	7.49	8.27	8.36
H6	8.04	8.39	8.2	8.47	8.44	8.01	8.39	8.47
H7	7.53	8.01	7.6	8.07	8.07	8.37	8.01	8.07
H8	3.57	3.78	2.2	3.84	3.81	3.55	3.78	3.82
H9	3.36	3.68	4.0	3.7	3.7	3.34	3.68	3.69
H10	1.1	1.32	0.6	1.35	1.33	1.24	1.42	1.5
H11	1.26	1.44	1.9	1.52	1.49	1.06	1.29	1.33
H12	4.81	4.64	5.6	4.73	4.72	4.75	4.72	4.67
H13	1.45	1.66	2.2	1.68	1.67	1.4	1.69	1.62

[a] Numbering is shown in Scheme 2.

Table S13 Fitted microscopic thermodynamic parameters for [Ln(**L4$^{\mathbf{b}}$**)(NO_3)$_3$] and [Ln$_m$(**L5**)(NO_3)$_6$] (m = 1, 2) in acetonitrile (eqns 13-15 using a single affinity parameter $f_{\mathrm{N2O}}^{\mathrm{Ln}}$, Ln = La, Eu, Lu, Y, 293 K).[a]

$\mathrm{Ln}^{\mathrm{III}}$	$\log\left(f_{\mathrm{N2O}}^{\mathrm{Ln}}\right)$	$\Delta G_{\mathrm{N2O}}^{\mathrm{Ln}}$ /kJ·mol^{-1}	$\log\left(u^{\mathrm{Ln,Ln}}\right)$	$\Delta E^{\mathrm{Ln,Ln}}$ /kJ·mol^{-1}
La	4.8(5)	-27(3)	-1.4(1.2)	8(7)
Eu	4.75(4)	-27.1(5)	-1.0(1)	6(1)
Y	5.2(3)	-30(2)	-1.3(7)	7(4)
Lu	5.3(3)	-30(2)	-1.2(7)	7(4)

[a] The uncertainties correspond to those obtained during the multi-linear least-square fit of eqns (13)-(15).

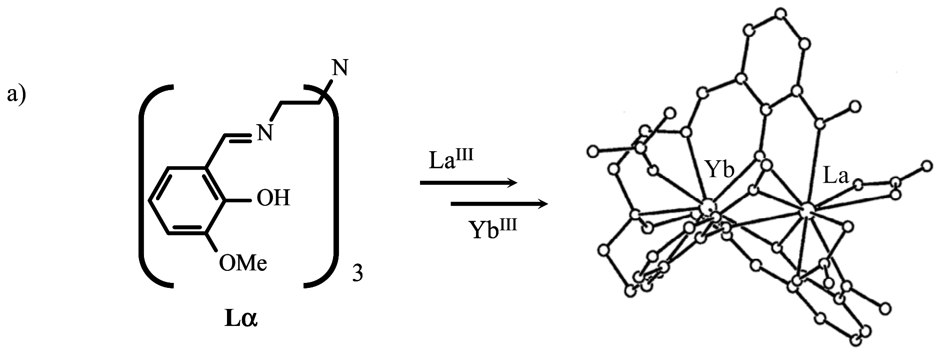
Table S14 Summary of Crystal Data , Intensity Measurement and Structure Refinement for **L4**^{b}, **L5**, $[Eu(\mathbf{L4}^b)(NO_3)_3(CH_3CN)](CH_3CN)_2$ (**3**) and $[Eu_2(\mathbf{L5})(NO_3)_6(H_2O)_2](H_2O)_4(CH_3CH_2CN)_2$ (**4**).

Compound	**L4**^{b}	**L5**	**3**	**4**
Formula	$C_{19}H_{22}N_4O$	$C_{39}H_{44}N_8O_2$	$C_{25}H_{31}EuN_{10}O_{10}$	$C_{45}H_{66}Eu_2N_{16}O_{26}$
fw	322.5	656.8	783.6	1551.2
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space Group	$P\,2_1/c$	$P\,2_1/c$	$P\bar{1}$	$C\,2/c$
a (Å)	12.5918(11)	22.2062(9)	9.7831(7)	33.2594(16)
b (Å)	11.5723(8)	12.4592(6)	9.9818(7)	11.3096(7)
c (Å)	12.3018(8)	12.6087(5)	16.8841(12)	18.1293(8)
α (deg)	90	90	94.322(8)	90
β (deg)	105.483(9)	101.188(3)	93.184(9)	116.890(5)
γ(deg)	90	90	105.660(8)	90
V (Å^3)	1727.5(2)	3422.2(3)	1578.1(2)	6082.0(6)
Z	4	4	2	4

Crystal Size (mm)	0.096 x 0.194 x 0.28	0.13 x 0.16 x 0.25	0.095 x 0.175 x 0.368	0.20 x 0.24 x 0.34
d_{calcd} (Mg m^{-3})	1.240	1.275	1.649	1.694
μ(MoKα) (mm^{-1})	0.079	0.082	2.06	2.14
Tmin, Tmax	0.9824 , 0.9924	0.9849 , 0.9916	0.6241 , 0.8314	0.5921 , 0.7357
2θmax (deg)	53.4	66.9	53.09	56.2
No. of reflns collected	20448	45534	20807	28970
No. of independent reflns	3590	13246	6349	7079
Criterion (q) for obsd reflns[a]	4	4	4	3
No. of obsd [a] (used[b]) reflns	1814 (1971)	7112 (8936)	5416 (5466)	5696 (5809)
No. of variables	305	574	415	501
Weighting scheme p [c]	0.0002	0.0004	0.0001	0.0003
Max and min Δρ (e Å^{-3})	0.35 , -0.37	0.56 , -0.66	1.08 , -0.63	0.76 , -0.66
GOF (F) [d] (all data)	1.07(2)	1.17(1)	1.36(1)	1.05(1)
R [e], ωR [f] (reflns used)	0.031, 0.028	0.047 , 0.044	0.022 , 0.024	0.022 , 0.026

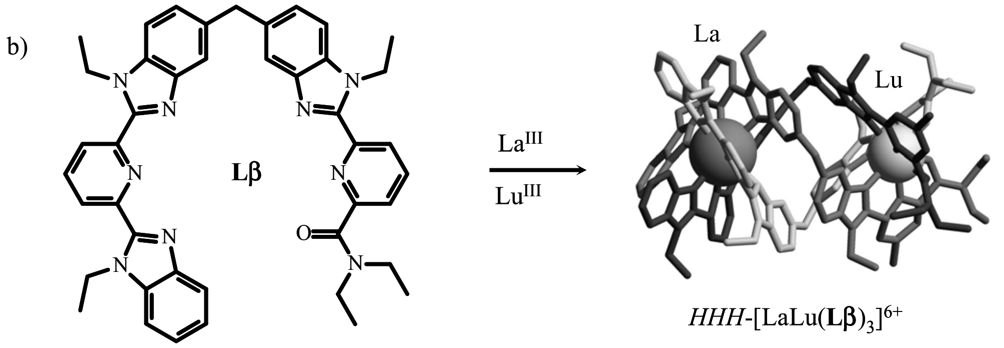
---

[a] $|Fo| > q\sigma(Fo)$; [b] Used in the refinements (including reflns with $|Fo| \leq q\sigma(Fo)$ if $|Fc| > |Fo|$) ; [c] $\omega = 1/[\sigma^2 (F_o) + p (F_o)^2]$; [d] $S = [\Sigma \{((F_o\text{-}F_c) / \sigma(F_o))^2 \} / (N_{ref} - N_{var})]^{1/2}$; [e] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [f] $\omega R = [\Sigma (\omega|Fo|\text{-}|Fc|)^2 / \Sigma \omega|Fo|^2]^{1/2}$;.



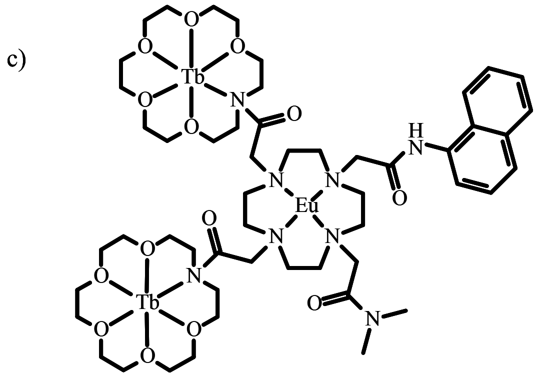
$[\mathrm{LaYb}(\mathbf{L\alpha}\text{-}3\mathrm{H})(\mathrm{NO_3})_2]^+$

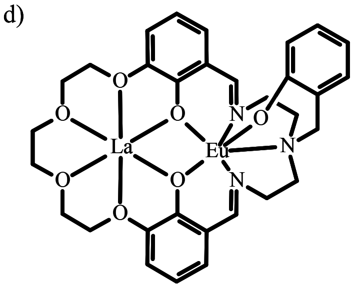
Costes and coworkers[7]



HHH-$[\mathrm{LaLu}(\mathbf{L\beta})_3]^{6+}$

Bünzli and coworkers[8]



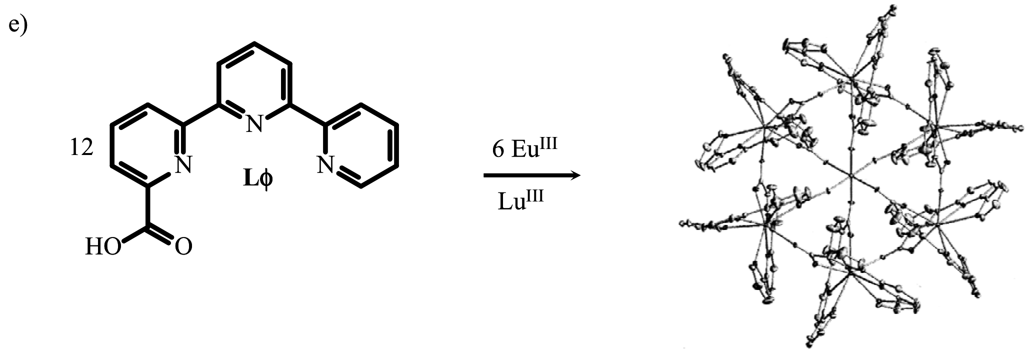


$[\mathrm{Tb_2Eu}(\mathbf{L\chi})]^{9+}$

Gunnlaugsson and coworkers[9]

$[\mathrm{LaEu}\,(\mathbf{L\delta}\text{-}3\mathrm{H})]^{3+}$

Tamburini and coworkers[10]



$[\mathrm{Lu}{\subset}(\mathrm{Eu}(\mathbf{L\phi}\text{-}\mathrm{H}))_2)_6]^{9+}$

Mazzanti and coworkers[11]

Figure S1 Selected successful syntheses of pure heterometallic 4f-4f' polynuclear complexes obtained under apparent thermodynamic control.[7-11]

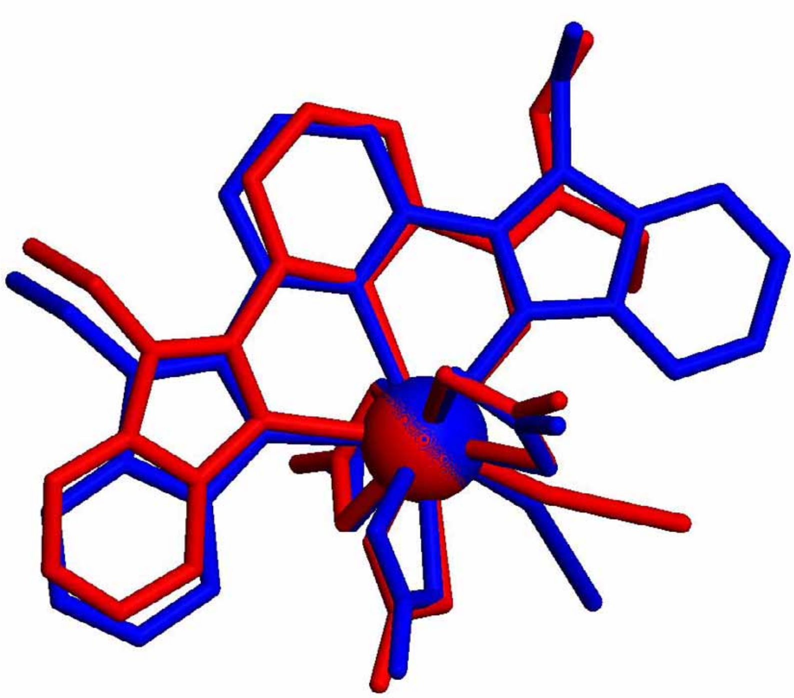


Figure S2 Optimized superimposition of the molecular structures of [Eu(**L3^e^**)$(NO_3)_3(CH_3CN)$] (blue) and [Eu(**L4^b^**)$(NO_3)_3(CH_3CN)$] (red).

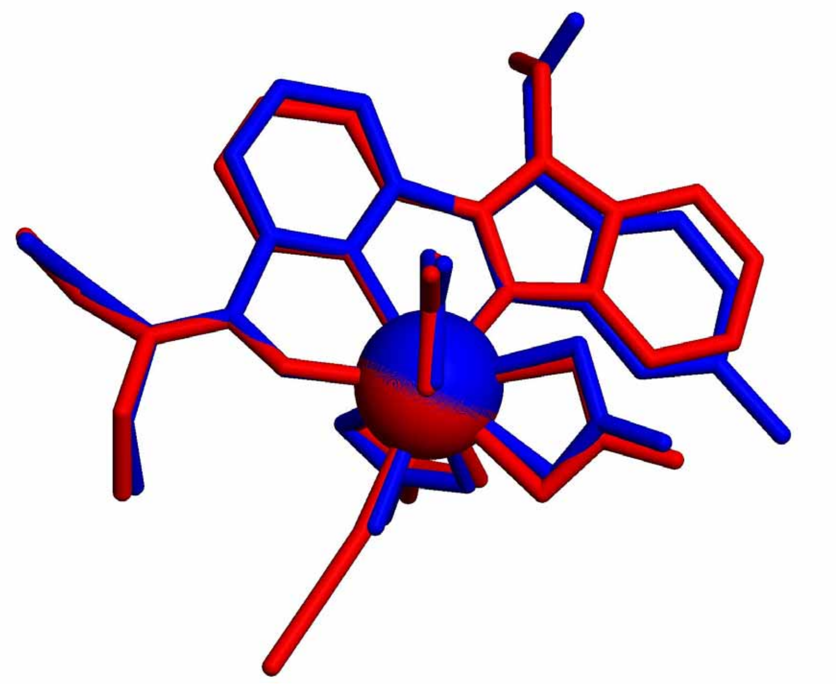


Figure S3 Optimized superimposition of the molecular structures of [Eu(**L4^b^**)$(NO_3)_3(CH_3CN)$] (red) and the asymmetrical unit of [Eu_2(**L5**)$(NO_3)_6(H_2O)_2$] (blue).

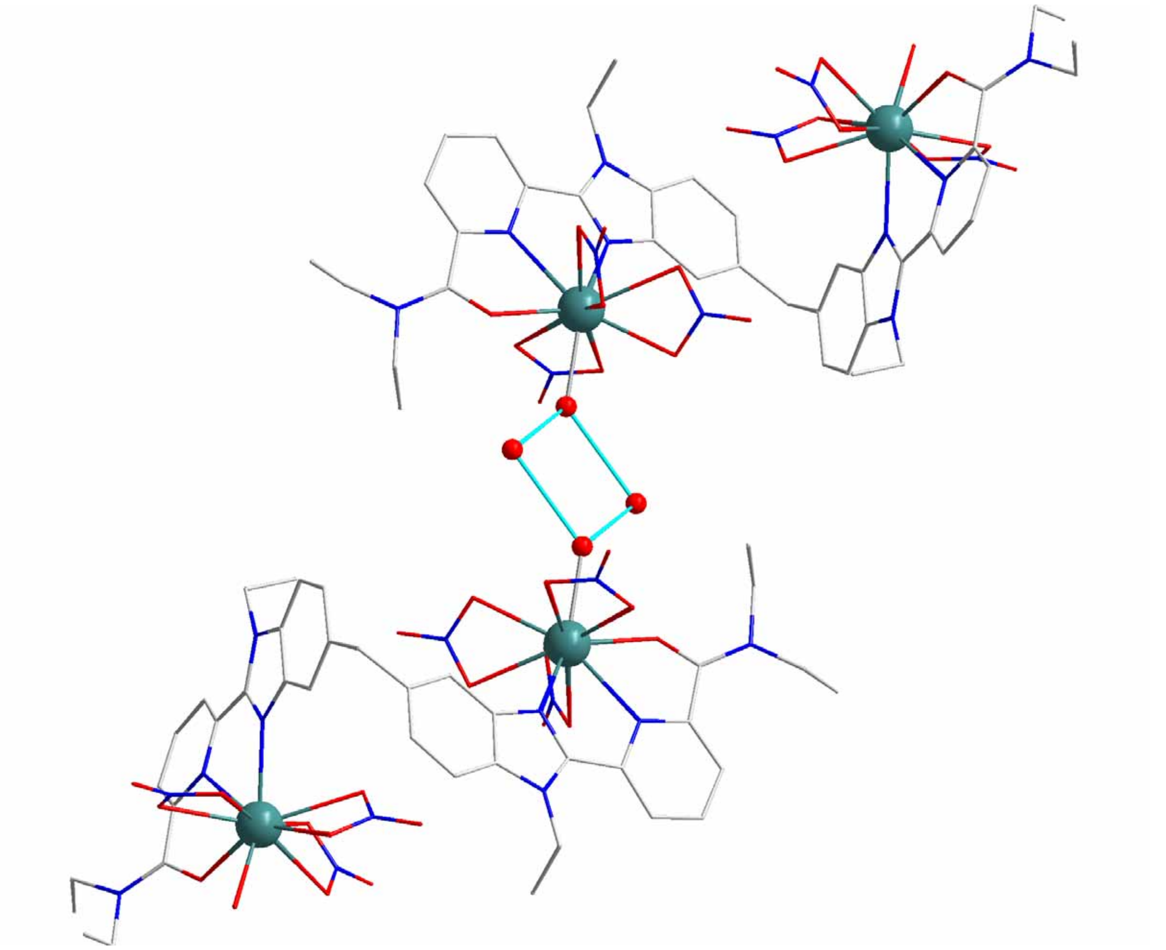


Figure S4 Network of hydrogen bonds involving coordinated and interstitial water molecules in the crystal structure of **4**. The chain of [Eu_2(**L5**)(NO_3)$_6$(H_2O)$_2$] complexes is roughly aligned with the [1 0 1] direction.

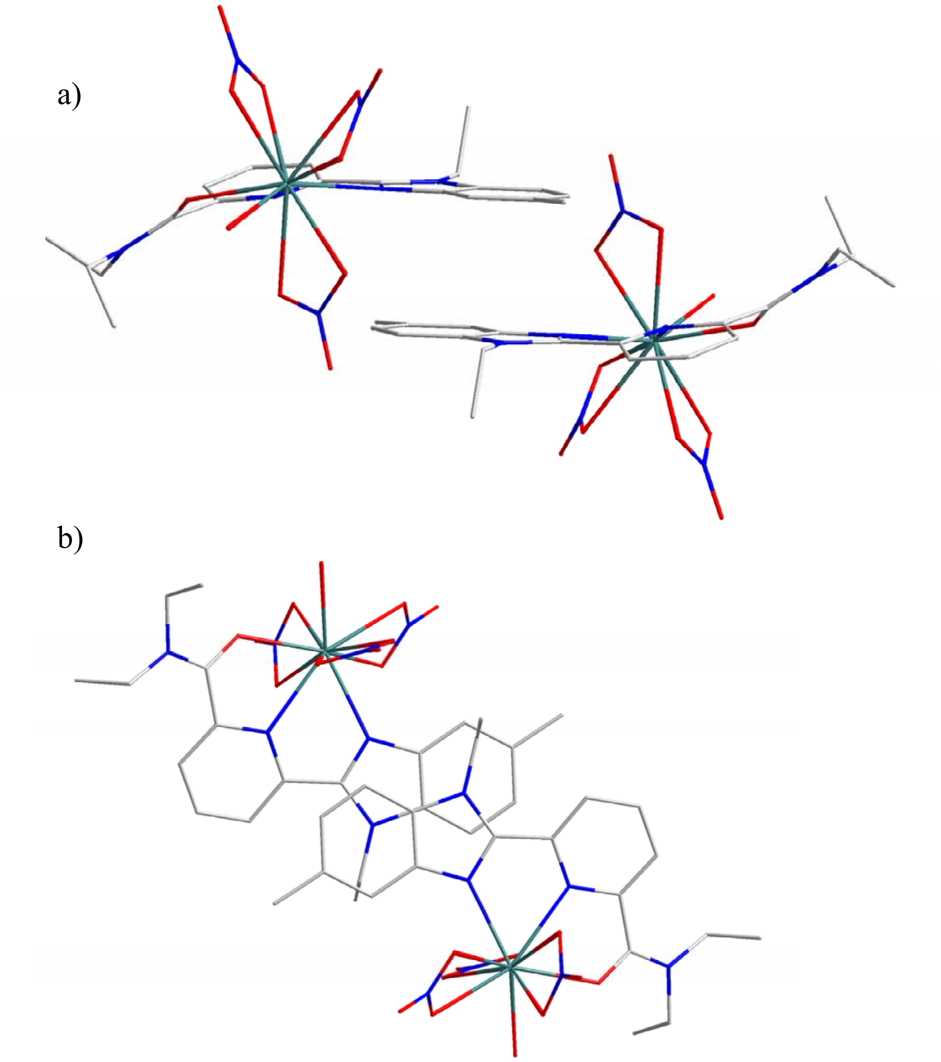


Figure S5 Perspective views of two $[\mathrm{Eu}_2(\mathbf{L5})(\mathrm{NO}_3)_6(\mathrm{H}_2\mathrm{O})_2]$ complexes related by a centre of inversion (1-x, 1-y, 1-z) and highligting the interchain π-stacking interactions operating between the benzimidazole rings.

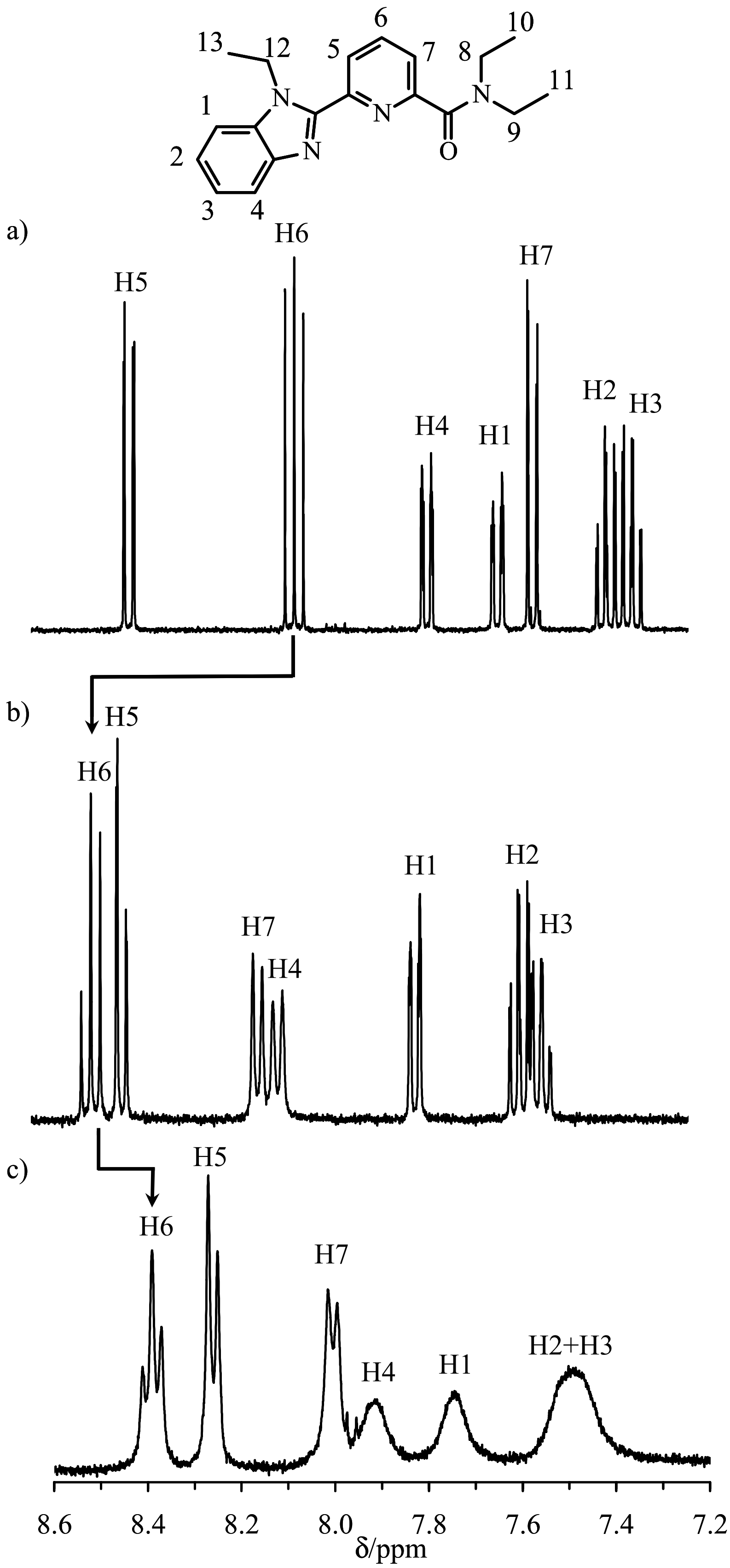


Figure S6 Aromatic part of the ^{1}H NMR spectra of a) **L4**$^{\mathbf{b}}$, b) [Lu(**L4**$^{\mathbf{b}}$)(NO_3)$_3$] and c) [La(**L4**$^{\mathbf{b}}$)(NO_3)$_3$] (total ligand concentration **L4**$^{\mathbf{b}}$: 10 mol·dm^{-3} in CD_3CN).

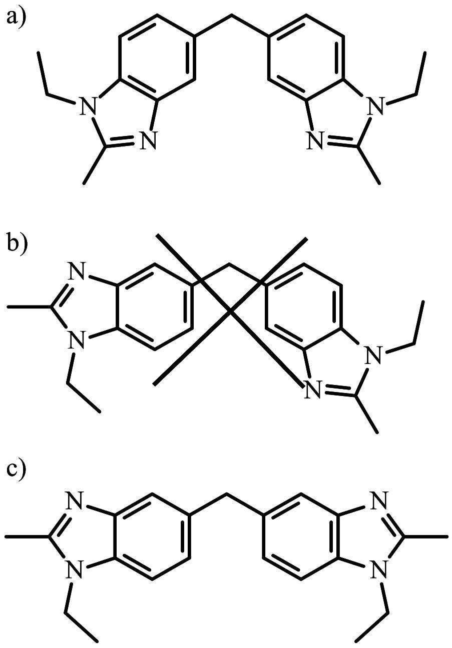


Figure S7 The three possible planar arrangements of the diphenylmethane spacer of ligand **L5**. a) proximal C_{2v}-symmetrical, b) alternated C_s-symmetrical (never observed on the NMR time scale) and c) distal C_{2v}-symmetrical.

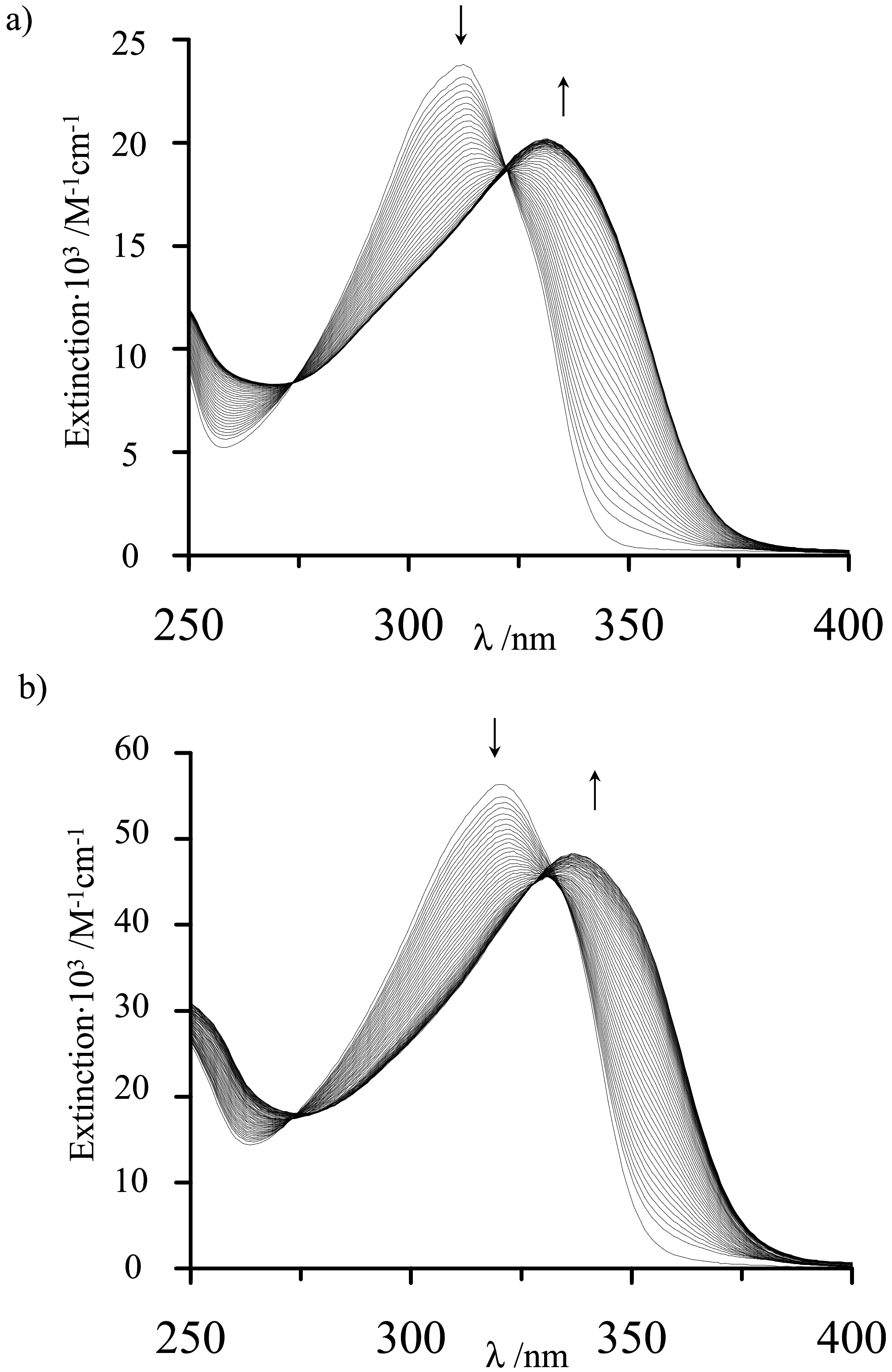
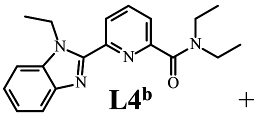


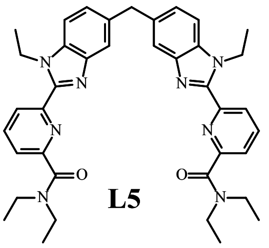
Figure S8 Variation of absorption spectra observed during the spectrophotometric titrations of a) **L4b** with $Lu(NO_3)_3 \cdot 2H_2O$ and b) **L5** with $Eu(NO_3)_3 \cdot 3H_2O$ (293 K, CH_3CN, total ligand concentration: 10^{-4} mol·dm^3).



$$\mathbf{L4^b} + [\mathrm{Ln(NO_3)_3(CH_3CN)_3}] \xrightleftharpoons{\beta_{1,1}^{\mathrm{Ln,L4b}}} [\mathrm{Ln}(\mathbf{L4^b})(\mathrm{NO_3})_3] + 3\,\mathrm{CH_3CN} \quad (10)$$

Point groups:	C_s	C_{3v}	C_s	C_{3v}
σ^{ext}:	1	3	1	3
σ^{int}:	3^3	3^3	3^3	1
σ^{chiral}:	1	1	1	1

$$\Rightarrow \omega_{1,1}^{\mathrm{chiral}} = \frac{1\cdot 1}{1\cdot 1} = 1 \qquad \omega_{1,1}^{\mathrm{Ln,L4b}} = \frac{1\cdot 3^2\cdot 3\cdot 3^3}{1\cdot 3^3\cdot 3^3} = 3$$



$$\mathbf{L5} + [\mathrm{Ln(NO_3)_3(CH_3CN)_3}] \xrightleftharpoons{\beta_{1,1}^{\mathrm{Ln,L5}}} [\mathrm{Ln}(\mathbf{L5})(\mathrm{NO_3})_3] + 3\,\mathrm{CH_3CN} \quad (11)$$

Point groups:	C_{2v}	C_{3v}	C_s	C_{3v}
σ^{ext}:	2	3	1	3
σ^{int}:	3^6	3^3	3^6	1
σ^{chiral}:	1	1	1	1

$$\Rightarrow \omega_{1,1}^{\mathrm{chiral}} = \frac{1\cdot 1}{1\cdot 1} = 1 \qquad \omega_{1,1}^{\mathrm{Ln,L5}} = \frac{2\cdot 3^6\cdot 3\cdot 3^3}{1\cdot 3^6\cdot 3^3} = 6$$

$$\mathbf{L5} + 2\,[\mathrm{Ln(NO_3)_3(CH_3CN)_3}] \xrightleftharpoons{\beta_{2,1}^{\mathrm{Ln,L5}}} [\mathrm{Ln_2}(\mathbf{L5})(\mathrm{NO_3})_6] + 6\,\mathrm{CH_3CN} \quad (12)$$

Point groups:	C_{2v}	C_{3v}	C_{2v}	C_{3v}
σ^{ext}:	2	3	2	3
σ^{int}:	3^6	3^3	3^6	1
σ^{chiral}:	1	1	1	1

$$\Rightarrow \omega_{2,1}^{\mathrm{chiral}} = \frac{1\cdot 1}{1\cdot 1} = 1 \qquad \omega_{2,1}^{\mathrm{Ln,L5}} = \frac{2\cdot 3^6\cdot \left(3\cdot 3^3\right)^2}{2\cdot 3^6\cdot 3^6} = 9$$

Figure S9 Symmetry numbers (σ) and statistical factors (ω) for the complexation of nine-coordinate $[\mathrm{Ln(NO_3)_3(CH_3CN)_3}]$[17] to **L4$^{\mathbf{b}}$** and **L5** in acetonitrile. The somewhat arbitrary choice[17] of an ideal symmetry C_{3v} for the metallic unit $[\mathrm{Ln(NO_3)_3(CH_3CN)_3}]$ is not crucial since each equilibrium refers to the same starting metal-containing entity.

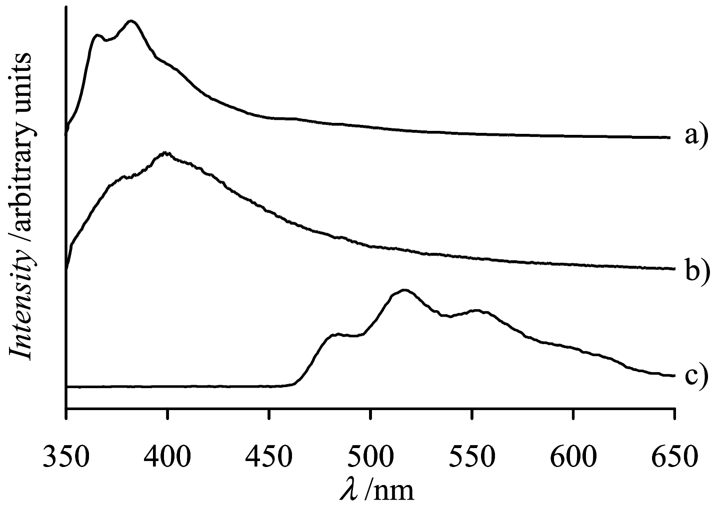


Figure S10 Emission spectra recorded in the solid state (λ_{exc} = 310 nm, 77K) for a) **L4**^{b}, b) [Gd(**L4b**)(NO$_3$)$_3$] (delay time: 0 ms, fluorescence) and c) [Gd(**L4b**)(NO$_3$)$_3$] (delay time 0.1 ms, phosphorescence).

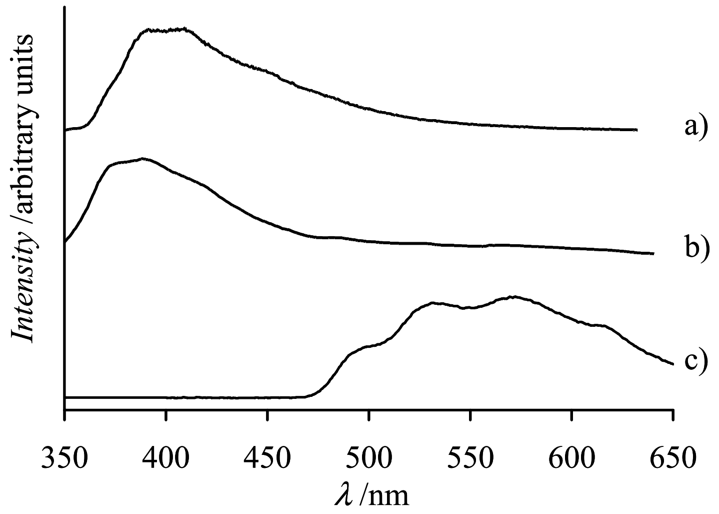


Figure S11 Emission spectra recorded in the solid state (λ_{exc} = 310 nm, 77K) for a) **L5**, b) [Gd$_2$(**L5**)(NO$_3$)$_6$] (delay time: 0 ms, fluorescence) and c) [Gd$_2$(**L5**)(NO$_3$)$_6$] (delay time 0.1 ms, phosphorescence).

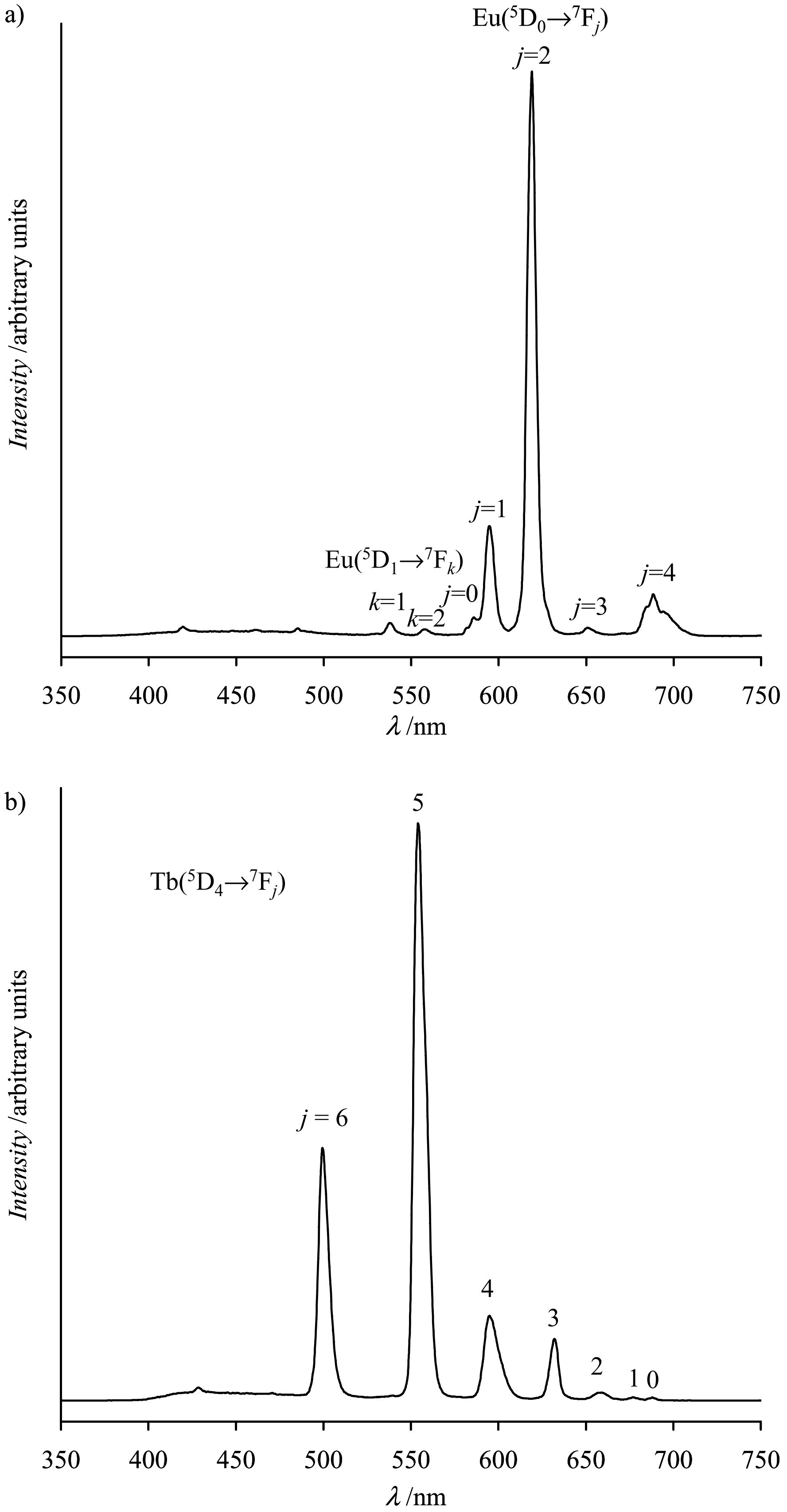


Figure S12 Fluorescence emission spectra recorded in the solid state (λ_{exc} = 310 nm, 295K) for a) [Eu(**L4**^{b})(NO_3)$_3$] and b) [Tb(**L4**^{b})(NO_3)$_3$].