Monitoring helical twists and effective molarities in dinuclear triple-stranded lanthanide helicates.

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Supporting Information (15 pages)

Appendix 1: Geometrical analysis of the helicity in $[La_2(\mathbf{L10})_3(CF_3SO_3)_2]^{4+}$ and $[Lu_2(\mathbf{L10})_3]^{6+}$.

The triple-stranded molecular structures found in $[La_2(\mathbf{L10})_3(CF_3SO_3)_2]^{4+}$ and $[Lu_2(\mathbf{L10})_3]^{6+}$ are considered as made of six helical sections packed along a pseudo-threefold axis defined by the axis passing through the two metals (Figure A1-1). Each helical portion is defined by two almost parallel facial planes (average interplanar angles: 2.45(8)° for $[La_2(\mathbf{L10})_3(CF_3SO_3)_2]^{4+}$ and 1.5(1)° for $[Lu_2(\mathbf{L10})_3]^{6+}$), each plane containing a set of three nitrogen atoms related by the pseudo-threefold symmetry. The distance between the facial planes gives the linear progression $d(F_i\text{-}F_j)$ of the helix, while its rotation is measured by the average twist angle α_{ij} defined by the angular rotation between the projections of N*i* and N*j* belonging to the same ligand strand onto a plane perpendicular to the pseudo-threefold axis. The pitch P_{ij} is finally calculated as the ratio of axial over angular progressions along the helical axis $P_{ij} = d(F_i\text{-}F_j)/(\alpha_{ij}/360)$ (Tables A1-1-A1-2).[S1]

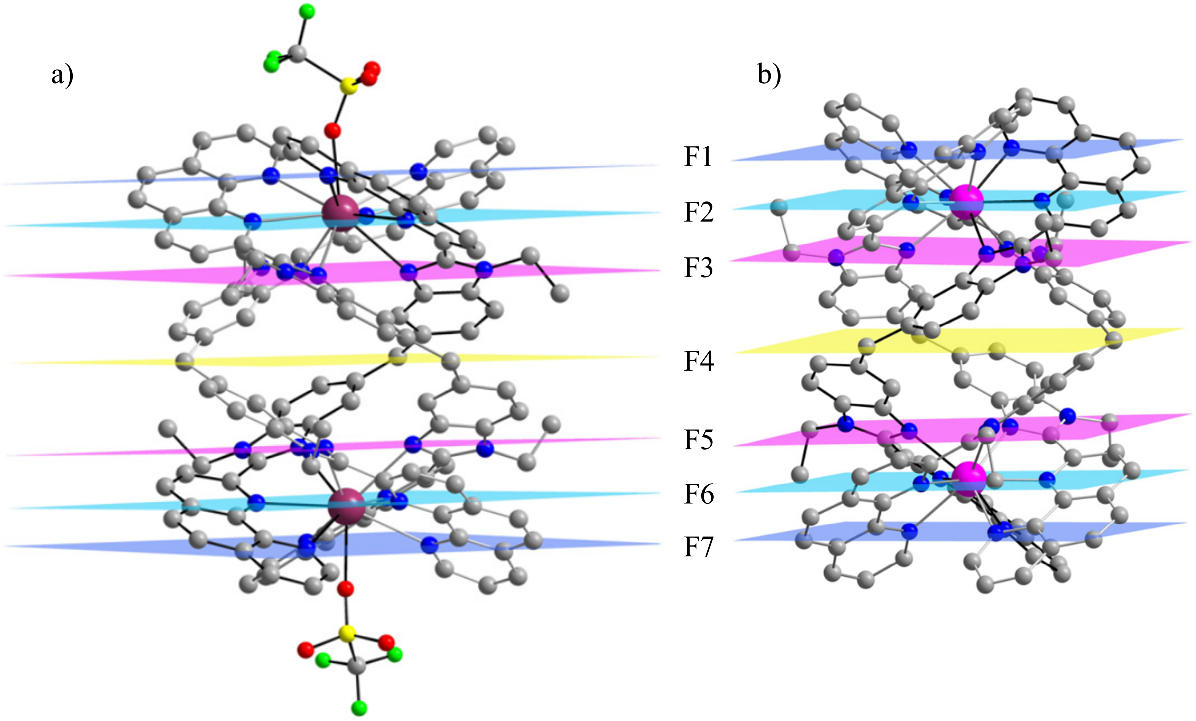


Figure A1-1 Representation of the facial planes in the molecular structures of (a) $[La_2(\mathbf{L10})_3(CF_3SO_3)_2]^{4+}$ and (b) $[Lu_2(\mathbf{L10})_3]^{6+}$.

Table A1-1 Helical pitches P_{ij}, linear distances $d(F_i\text{-}F_j)$ and average twist angle α_{ij} along the pseudo-C_3 axis[a] in the crystal structures of $[La_2(\mathbf{L10})_3(CF_3SO_3)_2](CF_3SO_3)_4(CH_3CN)_4(C_6H_6)$ (**5**) and $[Lu_2(\mathbf{L10})_3](CF_3SO_3)_6(CH_3CN)_3$ (**6**).

5 (La)	$d(F_i\text{-}F_j)$ /Å	α_{ij} /° [b]	P_{ij} /Å	**6** (Lu)	$d(F_i\text{-}F_j)$ /Å	α_{ij} /° [b]	P_{ij} /Å
F1-F2	1.36	53.7	9.12	F_1-F_2	1.606	56.6	10.21
F2-F3	1.65	53.2	11.17	F_2-F_3	1.622	54.9	10.64
F3-F4	2.64	61.9	15.35	F_3-F_4	2.846	61.06	16.78
F4-F5	2.64	61.9	15.35	F_4-F_5	2.846	61.06	16.78
F5-F6	1.65	52.2	11.37	F_5-F_6	1.622	54.90	10.64
F6-F7	1.36	54.7	8.95	F_6-F_7	1.606	56.62	10.21
F1-F7	11.30	338.4	12.02	F_1-F_7	12.148	345.14	12.67
Ln···Ln	8.9402(3)			8.8252(3)			

[a] Each helical portion F_1-F_2, F_2-F_3, F_3-F_4 and F_4-F_5 is characterised by (i) a linear extension $d(F_i\text{-}F_j)$ defined by the separation between the facial planes, (ii) an average twist angle α_{ij} defined by the angular rotation between the projections of N*i* and N*j* belonging to the same ligand strand and (iii) its pitch P_{ij} defined as $P_{ij} = d(F_i\text{-}F_j)/(\alpha_{ij}/360)$ (P_{ij} corresponds to the length of a cylinder containing a single turn of the helix defined by geometrical characteristics $d(F_i\text{-}F_j)$ and α_{ij}).[S1] [b] α_{ij} are given as C_3-average values.

Table A1-2 Helical pitches P_{ij}, linear distances $d(F_i-F_j)$ and average twist angle α_{ij} along the pseudo-C_3 axis[a] in the crystal structures of $[Eu_2(\mathbf{L1})_3](ClO_6)_6(CH_3CN)_6$.[3a]

Ln = Eu	$d(F_i-F_j)$ /Å	α_{ij} /° [b]	P_{ij} /Å
F1-F2	1.603	52.81	10.93
F2-F3	1.615	55.47	10.48
F3-F4	2.83	61.05	16.69
F4-F5	2.83	61.29	16.62
F5-F6	1.62	54.07	10.79
F6-F7	1.63	54.12	10.84
F1-F7	12.00	338.81	12.75
Ln···Ln	8.876(3)	-	-

[a] Each helical portion F_1-F_2, F_2-F_3, F_3-F_4 and F_4-F_5 is characterised by (i) a linear extension $d(F_i-F_j)$ defined by the separation between the facial planes, (ii) an average twist angle α_{ij} defined by the angular rotation between the projections of N*i* and N*j* belonging to the same ligand strand and (iii) its pitch P_{ij} defined as $P_{ij} = d(F_i-F_j)/(\alpha_{ij}/360)$ (P_{ij} corresponds to the length of a cylinder containing a single turn of the helix defined by geometrical characteristics $d(F_i-F_j)$ and α_{ij}).[S1] [b] α_{ij} are given as C_3-average values.

Reference

[S1] M. Cantuel, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner and C. Piguet, *J. Chem. Soc.*, *Dalton Trans.*, **2002**, 1929 and references therein.

Table S1 Summary of crystal data, intensity measurements and structure refinements for $[La_2(\mathbf{L10})_3(CF_3SO_3)_2](CF_3SO_3)_4(CH_3CN)_6(C_6H_6)_6$ (**5**) and $[Lu_2(\mathbf{L10})_3](CF_3SO_3)_6(CH_3CN)_3$ (**6**).

	5	**6**
Empirical formula	$C_{183}H_{150}F_{18}La_2N_{30}O_{18}S_6$	$C_{143}H_{108}F_{18}Lu_2N_{28}O_{18}S_6$
Formula weight	3869.51	3390.86
Temperature	160(2) K	160(2) K
Wavelength	1.54184 Å	1.54184 Å
Crystal System, Space group	Monoclinic, *C*2/*c*	Monoclinic, *P*2/*c*
Unit cell dimensions	a = 32.4414(5) Å	a = 18.3243(3) Å
	b = 17.70112(17) Å	b = 23.0931(3) Å
	c = 33.7386(5) Å	c = 23.8096(4) Å
	α = 90°	α = 90°
	β = 117.1435(19)°	β = 130.3370(10)°
	γ = 90°	γ = 90°
Volume in $Å^3$	17240.6(4)	7680.0(2)
Z, Calculated density	4, 1.491 Mg/m^3	2, 1.466 Mg/m^3
Absorption coefficient	5.257 mm^{-1}	3.950 mm^{-1}
F(000)	7896	3412
Theta range for data collection	2.93 to 73.43°	3.10 to 73.62°
Limiting indices	$-40<=h<=39$,	$-17<=h<=22$,
	$-22<=k<=21$,	$-28<=k<=27$,
	$-41<=l<=34$	$-29<=l<=27$
Reflections collected / unique	50385 / 16936	33788 / 15190
	[R(int) = 0.0290]	[R(int) = 0.0294]
Completeness to theta	99.8 %	99.9 %
Data / restraints / parameters	16936 / 0 / 1054	15190 / 20 / 840
Goodness-of-fit on F^2	1.576	1.218
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0502,	R_1 = 0.0595,
	ωR_2 = 0.1544	ωR_2 = 0.1831
R indices (all data)	R_1 = 0.0540,	R_1 = 0.0723,
	ωR_2 = 0.1598	ωR_2 = 0.1993
Largest diff. peak and hole	1.763 and -1.379 e.$Å^{-3}$	2.037 and -1.761 e.$Å^{-3}$

Table S2 Selected bond distances (Å), bond angles (°) in $[La_2(\mathbf{L10})_3(CF_3SO_3)_2](CF_3SO_3)_4(CH_3CN)_6(C_6H_6)_6$ (**5**).

Bond distances (Å)

La(2A)-O(1)	2.520(3)	La(2A)-N(2B)	2.748(3)
La(2A)-N(3A)	2.694(3)	La(2A)-N(3B)	2.759(3)
La(2A)-N(2A)	2.719(3)	La(2A)-N(1A)	2.772(3)
La(2A)-N(7A)#1	2.734(3)	La(2A)-N(1B)	2.815(3)
La(2A)-N(5A)#1	2.743(3)	La(2A)···La(2A)#1	8.940(3)
La(2A)-N(8A)#1	2.744(3)		

Bond angles (°)

O(1)-La(2A)-N(3A)	127.20(8)	N(2A)-La(2A)-N(3B)	134.38(8)
O(1)-La(2A)-N(2A)	92.37(8)	N(7A)#1-La(2A)-N(3B)	69.23(7)
N(3A)-La(2A)-N(2A)	60.86(8)	N(5A)#1-La(2A)-N(3B)	79.14(8)
O(1)-La(2A)-N(7A)#1	98.83(8)	N(8A)#1-La(2A)-N(3B)	69.21(8)
N(3A)-La(2A)-N(7A)#1	133.54(8)	N(2B)-La(2A)-N(3B)	60.81(8)
N(2A)-La(2A)-N(7A)#1	117.93(8)	O(1)-La(2A)-N(1A)	67.81(8)
O(1)-La(2A)-N(5A)#1	136.24(8)	N(3A)-La(2A)-N(1A)	119.11(8)
N(3A)-La(2A)-N(5A)#1	79.24(8)	N(2A)-La(2A)-N(1A)	59.86(8)
N(2A)-La(2A)-N(5A)#1	69.54(8)	N(7A)#1-La(2A)-N(1A)	68.87(8)
N(7A)#1-La(2A)-N(5A)#1	60.65(8)	N(5A)#1-La(2A)-N(1A)	68.68(8)
O(1)-La(2A)-N(8A)#1	65.58(9)	N(8A)#1-La(2A)-N(1A)	100.66(8)
N(3A)-La(2A)-N(8A)#1	140.22(8)	N(2B)-La(2A)-N(1A)	158.23(8)
N(2A)-La(2A)-N(8A)#1	155.87(8)	N(3B)-La(2A)-N(1A)	135.82(8)
N(7A)#1-La(2A)-N(8A)#1	59.89(8)	O(1)-La(2A)-N(1B)	61.40(8)
N(5A)#1-La(2A)-N(8A)#1	119.13(8)	N(3A)-La(2A)-N(1B)	67.10(8)
O(1)-La(2A)-N(2B)	90.48(9)	N(2A)-La(2A)-N(1B)	72.48(8)
N(3A)-La(2A)-N(2B)	72.17(8)	N(7A)#1-La(2A)-N(1B)	159.07(8)
N(2A)-La(2A)-N(2B)	122.26(8)	N(5A)#1-La(2A)-N(1B)	138.08(8)
N(7A)#1-La(2A)-N(2B)	118.48(8)	N(8A)#1-La(2A)-N(1B)	102.78(8)
N(5A)#1-La(2A)-N(2B)	133.09(9)	N(2B)-La(2A)-N(1B)	59.01(8)
N(8A)#1-La(2A)-N(2B)	70.13(8)	N(3B)-La(2A)-N(1B)	117.90(8)
O(1)-La(2A)-N(3B)	132.59(8)	N(1A)-La(2A)-N(1B)	106.25(8)
N(3A)-La(2A)-N(3B)	81.73(8)		

Symmetry transformation used to generate equivalent atoms: #1: $-x+1$, y, $-z+\frac{1}{2}$.

Table S3 Selected least-squares planes data for $[La_2(\mathbf{L10})_3(CF_3SO_3)_2](CF_3SO_3)_4(CH_3CN)_6(C_6H_6)_6$ (**5**).

Least-squares planes description	Abbreviation	Max. deviation/Å	Atom
Phenanthroline 1a	Phen1a		
N1 C1 C2 C3 C4 C5 C6 N2 C7 C8 C9 C10 N2 C11 C12		0.066(1)	N2a
Benzimidazole 1a	Bz1a		
N3 C13 N4 C16 C17 C18 C19 C20 C21		0.038(1)	N3a
Benzimidazole 2a	Bz2a		
C23 C24 C25 C26 N6 C27 N5 C28 C29		0.029(1)	N5a
Phenanthroline 2a	Phen2a		
C32 C33 C34 C35 C36 C37 C38 C39 C40 C41 N8 C42 C43 N7		0.082(1)	C40a
Phenanthroline 1b	Phen1b		
N1 C1 C2 C3 C4 C5 C6 N2 C7 C8 C9 C10 N2 C11 C12		0.062(1)	N1b
Benzimidazole 1b	Bz1b		
N3 C13 N4 C16 C17 C18 C19 C20 C21		0.045(1)	N3b

Interplanar angles (°)[a]

	Bz1a	Phen1b	Bz1b	Phen2a’	Bz2a’	Phen2a	Bz2a
Phen1a	40.2	55.5	57.0	49.6	19.0	34.5	58.2
Bz1a		25.3	54.5	61.8	54.7	61.5	55.2
Phen1b			37.0	50.8	62.8	60.5	37.2
Bz1b				18.3	50.6	36.8	1.2
Phen2a							37.7

The error is typically ±0.1°.

Table S4 Selected bond distances (Å), bond angles (°) in [Lu_2(**L10**)$_3$](CF_3SO_3)$_6$(CH_3CN)$_4$ (**6**).

Bond distances (Å)			
Lu(1)-N(3A)	2.475(3)	Lu(1)-N(5A)#1	2.513(4)
Lu(1)-N(2A)	2.486(4)	Lu(1)-N(8A)#1	2.522(5)
Lu(1)-N(2B)	2.489(4)	Lu(1)-N(1A)	2.524(4)
Lu(1)-N(7A)#1	2.499(4)	Lu(1)-N(1B)	2.535(4)
Lu(1)-N(3B)	2.499(4)	Lu(1) ···Lu(2)#1	8.8253(3)

Bond angles (°)			
N(3A)-Lu(1)-N(2A)	64.41(12)	N(7A)#1-Lu(1)-N(8A)#1	64.91(14)
N(3A)-Lu(1)-N(2B)	72.02(12)	N(3B)-Lu(1)-N(8A)#1	80.45(14)
N(2A)-Lu(1)-N(2B)	120.72(13)	N(5A)#1-Lu(1)-N(8A)#1	128.97(15)
N(3A)-Lu(1)-N(7A)#1	142.22(12)	N(3A)-Lu(1)-N(1A)	128.87(15)
N(2A)-Lu(1)-N(7A)#1	118.76(15)	N(2A)-Lu(1)-N(1A)	64.49(15)
N(2B)-Lu(1)-N(7A)#1	120.37(15)	N(2B)-Lu(1)-N(1A)	137.12(14)
N(3A)-Lu(1)-N(3B)	85.62(11)	N(7A)#1-Lu(1)-N(1A)	68.92(15)
N(2A)-Lu(1)-N(3B)	142.50(13)	N(3B)-Lu(1)-N(1A)	140.46(14)
N(2B)-Lu(1)-N(3B)	64.48(12)	N(5A)#1-Lu(1)-N(1A)	81.23(14)
N(7A)#1-Lu(1)-N(3B)	71.65(13)	N(8A)#1-Lu(1)-N(1A)	80.58(16)
N(3A)-Lu(1)-N(5A)#1	84.45(12)	N(3A)-Lu(1)-N(1B)	79.40(13)
N(2A)-Lu(1)-N(5A)#1	71.46(14)	N(2A)-Lu(1)-N(1B)	69.60(14)
N(2B)-Lu(1)-N(5A)#1	141.61(12)	N(2B)-Lu(1)-N(1B)	64.41(13)
N(7A)#1-Lu(1)-N(5A)#1	64.06(14)	N(7A)#1-Lu(1)-N(1B)	138.32(12)
N(3B)-Lu(1)-N(5A)#1	84.30(13)	N(3B)-Lu(1)-N(1B)	128.89(13)
N(3A)-Lu(1)-N(8A)#1	141.55(13)	N(5A)#1-Lu(1)-N(1B)	141.05(14)
N(2A)-Lu(1)-N(8A)#1	137.05(14)	N(8A)#1-Lu(1)-N(1B)	81.93(14)
N(2B)-Lu(1)-N(8A)#1	69.63(13)	N(1A)-Lu(1)-N(1B)	81.86(13)

Symmetry transformation used to generate equivalent atoms: #1: $-x+1, y, -z+3/2$.

Table S5 Selected least-squares planes data for [Lu_2(**L10**)$_3$](CF_3SO_3)$_6$(CH_3CN)$_4$ (**6**).

Least-squares planes description	Abbreviation	Max. deviation/Å	Atom
Phenanthroline 1a	Phen1a		
N1 C1 C2 C3 C4 C5 C6 N2 C7 C8 C9 C10 N2 C11 C12		0.130(1)	N2
Benzimidazole 1a	Bz1a		
N3 C13 N4 C16 C17 C18 C19 C20 C21		0.044(1)	N3
Benzimidazole 2a	Bz2a		
C23 C24 C25 C26 N6 C27 N5 C28 C29		0.034(1)	C29
Phenanthroline 2a	Phen2a		
C32 C33 C34 C35 C36 C37 C38 C39 C40 C41 N8 C42 C43 N7		0.146(1)	C40
Phenanthroline 1b	Phen1b		
N1 C1 C2 C3 C4 C5 C6 N2 C7 C8 C9 C10 N2 C11 C12		0.141(1)	C9
Benzimidazole 1b	Bz1b		
N3 C13 N4 C16 C17 C18 C19 C20 C21		0.045(1)	N3

Interplanar angles (°)^{a}

	Bz1a	Phen1b	Bz1b	Phen2a’	Bz2a’	Phen2a	Bz2a
Phen1a	35.8	63.2	70.5	60.4	32.6	44.2	65.3
Bz1a		34.1	58.7	71.8	59.8	67.5	68.4
Phen1b			33.4	62.9	71.9	72.3	53.0
Bz1b				63.1	59.0	52.9	22.6
Phen2a							33.5

The error is typically ±0.1°.

Table S6 Bond Distances ($\delta_{i,j}$), bond Valences ($v_{\mathrm{Ln,j}}$)[a] and total atom valence (V_{Ln})[b] in the crystal structure of [La_2(**L10**)$_3$(CF_3SO_3)$_2$](CF_3SO_3)$_4$(CH_3CN)$_6$(C_6H_6)$_6$ (**5**).

Atom[c]	Donor type	$\delta_{\mathrm{La},j}$ / Å	$V_{\mathrm{La},j}$	
O(1)	Triflate	2.520	0.364	
N(3A)	Bzim	2.694	0.309	
N(2A)	Phen	2.719	0.289	
N(7A)#	Phen	2.734	0.278	
N(5A)#	Bzim	2.743	0.271	
N(8A)#	Phen	2.744	0.270	
N(2B)	Phen	2.748	0.267	
N(3B)	Bzim	2.759	0.260	
N(1A)	Phen	2.772	0.251	Average N-heterocyclic
N(1B)	Phen	2.815	0.223	0.27(2)
		V_{La}	2.783	

[a] $v_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln},j}-d_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,N}}$ and $R_{\mathrm{Ln,O}}$ are taken from ref 25 and b = 0.37 Å. [b] $V_{\mathrm{Ln}} = \sum_j v_{\mathrm{Ln},j}$. [c] Numbering taken from Fig S1a.

Table S7 Bond Distances ($\delta_{i,j}$), bond Valences ($v_{\mathrm{Ln,j}}$)[a] and total atom valence (V_{Ln})[b] in the crystal structure of [Lu_2(**L10**)$_3$](CF_3SO_3)$_6$(CH_3CN)$_4$ (**6**).

Atom[c]	Donor type	$\delta_{\mathrm{Lu},j}$ / Å	$V_{\mathrm{Lu},j}$	
N(3A)	Bzim	2.475	0.346	
N(2A)	Phen	2.486	0.336	
N(7A)#	Phen	2.489	0.333	
N(5A)#	Phen	2.499	0.324	
N(8A)#	Bzim	2.499	0.324	
N(2B)	Bzim	2.513	0.312	
N(3B)	Phen	2.522	0.304	
N(1A)	Phen	2.524	0.303	Average N-heterocyclic
N(1B)	Phen	2.535	0.294	0.32(2)
		V_{Lu}	2.875	

[a] $v_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln},j}-d_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameter $R_{\mathrm{Ln,N}}$ is taken from ref 25 and b = 0.37 Å. [b] $V_{\mathrm{Ln}} = \sum_j v_{\mathrm{Ln},j}$. [c] Numbering taken from Fig S1b.

Table S8 Bond Distances ($\delta_{i,j}$), bond Valences ($\nu_{\mathrm{Ln,j}}$)[a] and total atom valence (V_{Ln})[b] in the crystal structure of $[\mathrm{Eu_2}(\mathbf{L1})_3](\mathrm{ClO_4})_6(\mathrm{CH_3CN})_9$.[3a]

Atom[c]	Donor type	$\delta_{\mathrm{Eu1},j}$ / Å	$V_{\mathrm{Eu1},j}$	
N(1)A	Bzim	2.57	0.33	
N(3)A	Py	2.59	0.32	
N(4)A	Bzim	2.60	0.31	
N(1)B	Bzim	2.58	0.33	
N(3)B	Py	2.59	0.32	
N(4)B	Bzim	2.58	0.33	
N(1)C	Bzim	2.57	0.33	
N(3)C	Py	2.61	0.30	Average N-heterocyclic
N(4)C	Bzim	2.54	0.36	0.33(2)
		V_{Eu1}	2.927	
N(6)A	Bzim	2.57	0.33	
N(8)A	Py	2.58	0.33	
N(9)A	Bzim	2.67	0.26	
N(6)B	Bzim	2.61	0.30	
N(8)B	Py	2.64	0.28	
N(9)B	Bzim	2.60	0.31	
N(6)C	Bzim	2.61	0.30	
N(8)C	Py	2.58	0.33	Average N-heterocyclic
N(9)C	Bzim	2.59	0.32	0.31(3)
		V_{Eu2}	2.745	

[a] $\nu_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln},j} - d_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,N}}$ and $R_{\mathrm{Ln,O}}$ are taken from ref 25 and b = 0.37 Å. [b] $V_{\mathrm{Ln}} = \sum_j \nu_{\mathrm{Ln},j}$. [c] Numbering taken from ref. 3a.

Table S9 ESI-MS peaks observed for the titration of **L10** with $La(CF_3SO_3)_3$ in CH_3CN.

	m/z exp	*m/z* cald
$[La_2(\mathbf{L10})_3(Otf)_4]^{2+}$ [a]	1428.3	1428.2
$[La_2(\mathbf{L10})_2(Otf)_4]^{2+}$	1098.1	1097.9
$[La_2(\mathbf{L10})\ Otf)_4(CH_3OH)_4(CH_3CN)_4]^{2+}$	913.7	913.1
$[La_2(\mathbf{L10})_3(Otf)_3]^{3+}$	902.5	902.5
$[La_2(\mathbf{L10})(Otf)_4(CH_3OH)(CH_3CN)]^{2+}$	804.6	803.5
$[La_2(\mathbf{L10})_3(Otf)_2]^{4+}$	639.7	639.6
$[La_2(\mathbf{L10})(Otf)_3(CH_3OH)(CH_3CN)]^{3+}$	485.1	486.0
$[La_2(\mathbf{L10})_3(Otf)]^{5+}$	482.2	481.9
$[La_2(\mathbf{L10})\ (Otf)_2(CH_3OH)_5(CH_3CN)_4]^{4+}$	390.6	390.1
$[La_2(\mathbf{L10})_3(Otf)]^{6+}$	377.0	376.4
$[La_2(\mathbf{L10})(Otf)_2(CH_3OH)_3(CH_3CN)_4]^{4+}$	374.3	374.0

[a] $Otf^- = CF_3SO_3^-$

Table S10 ESI-MS peaks observed for the titration of **L10** with $Eu(CF_3SO_3)_3$ in CH_3CN.

	m/z exp	*m/z* cald
$[Eu_2(\mathbf{L10})_3(Otf)_4]^{2+}$ [a]	1441.4	1441.3
$[Eu_2(\mathbf{L10})_2(Otf)_4]^{2+}$	1111.0	1110.9
$[Eu_2(\mathbf{L10})_3(Otf)_3]^{3+}$	911.2	911.2
$[Eu_2(\mathbf{L10})_3(Otf)_2]^{4+}$	646.7	646.1
$[Eu_2(\mathbf{L10})(Otf)_3(CH_3OH)_3]^{3+}$	503.2	503.0
$[Eu_2(\mathbf{L10})_3(Otf)]^{5+}$	487.4	487.1
$[Eu_2(\mathbf{L10})(Otf)_2(CH_3OH)_5(CH_3CN)_{10}]^{4+}$	458.6	458.7
$[Eu_2(\mathbf{L10})(Otf)_2(CH_3OH)_7(CH_3CN)_3]^{4+}$	402.0	402.8
$[Eu_2(\mathbf{L10})_3]^{6+}$	381.2	381.1

[a] $Otf^- = CF_3SO_3^-$

Table S11 ESI-MS peaks observed for the titration of **L10** with Lu(CF_3SO_3)$_3$ in CH_3CN.

	m/z exp	*m/z* cald
[Lu_2(**L10**)(Otf)$_5$(CH_3CN)]$^{+}$ [a]	1795.9	1795.3
[Lu_2(**L10**)$_3$(Otf)$_4$]$^{2+}$	1464.2	1464.3
[Lu_2(**L10**)$_2$(Otf)$_4$]$^{2+}$	1133.6	1133.9
[Lu_3(**L10**)$_2$(Otf)$_6$(CH_3OH)(CH_3CN)]$^{3+}$	937.4	938.0
[Lu_2(**L10**)$_3$(Otf)$_3$]$^{3+}$	926.7	926.5
[Lu_2(**L10**)(Otf)$_4$(CH_3CN)]$^{2+}$	822.6	823.5
[Lu_3(**L10**)$_2$(Otf)$_5$(CH_3OH)(CH_3CN)]$^{4+}$	665.5	665.8
[Lu_2(**L10**)$_3$(Otf)$_2$]$^{4+}$	657.7	657.6
[Lu_2(**L10**)(Otf)$_3$(CH_3CN)$_2$]$^{3+}$	513.0	513.0
[Lu_2(**L10**)(Otf)$_3$(CH_3OH)(CH_3CN)]$^{3+}$	509.9	510.0
[Lu_3(**L10**)$_2$(Otf)$_4$(CH_3OH)(CH_3CN)]$^{5+}$	502.8	502.9
[Lu_2(**L10**)(Otf)$_3$(CH_3CN)]$^{3+}$	500.2	499.3
[Lu_2(**L10**)$_3$(Otf)]$^{5+}$	496.6	496.3
[Lu_2(**L10**)(Otf)$_2$(CH_3OH)$_6$(CH_3CN)$_4$]$^{4+}$	416.2	416.1
[Lu_2(**L10**)(Otf)$_2$(CH_3OH)$_4$(CH_3CN)$_5$]$^{4+}$	409.6	410.3
[Lu_3(**L10**)$_2$(Otf)$_3$(CH_3CN)$_6$]$^{6+}$	395.7	395.7
[Lu_2(**L10**)$_3$]$^{6+}$	389.0	388.7

[a] $Otf^- = CF_3SO_3^-$

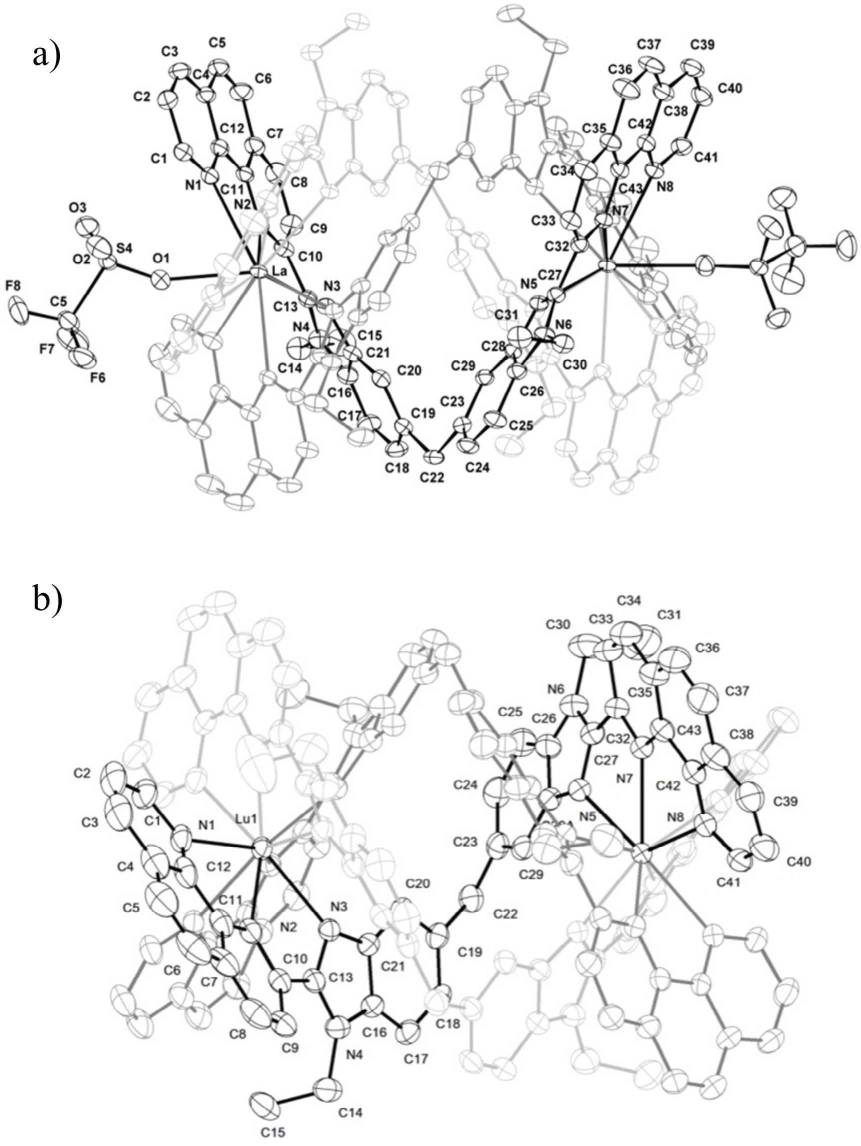
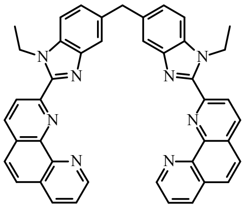


Figure S1 Molecular structures with partial numbering schemes of (a) $[La_2(\mathbf{L10})_3(CF_3SO_3)_2]^{4+}$ and (b) $[Lu_2(\mathbf{L10})_3]^{6+}$ observed in the crystal structures of $[La_2(\mathbf{L10})_3(CF_3SO_3)_2](CF_3SO_3)_4(CH_3CN)_6(C_6H_6)_6$ (**5**) and $[Lu_2(\mathbf{L10})_3](CF_3SO_3)_6(CH_3CN)_4$ (**6**) (thermal ellipsoids are represented at the 30% probability level). Hydrogen atoms are omitted for clarity.



$$2\,[\mathrm{Ln(CH_3CN)_9}]^{2+} + \quad 3\,\mathbf{L10} \underset{\beta_{1,2}^{\mathrm{Ln},\mathbf{L7}}}{\rightleftarrows} [\mathrm{Ln_2}(\mathbf{L10})_3]^{3+} \quad + \quad 18\ \mathrm{CH_3CN}$$

Point groups:	D_{3h}	$C_{2\mathrm{v}}$	D_3	$C_{3\mathrm{v}}$
σ^{ext}:	6	2	6	3
σ^{int}:	3^9	3^2	3^6	1
σ^{chiral}:	1	1	1/2	1

$$\omega_{2,3}^{\mathrm{Ln},\mathbf{L10}} = \frac{\left(\sigma_{\mathrm{Ln}}^{\mathrm{ext}}\sigma_{\mathrm{Ln}}^{\mathrm{int}}\sigma_{\mathrm{Ln}}^{\mathrm{chiral}}\right)^2 \cdot \left(\sigma_{\mathbf{L10}}^{\mathrm{ext}}\sigma_{\mathbf{L10}}^{\mathrm{int}}\sigma_{\mathbf{L10}}^{\mathrm{chiral}}\right)^3}{\left(\sigma_{\mathrm{complex}}^{\mathrm{ext}}\sigma_{\mathrm{complex}}^{\mathrm{int}}\sigma_{\mathrm{complex}}^{\mathrm{chiral}}\right) \cdot \left(\sigma_{\mathrm{CH_3CN}}^{\mathrm{ext}}\sigma_{\mathrm{CH_3CN}}^{\mathrm{int}}\sigma_{\mathrm{CH_3CN}}^{\mathrm{chiral}}\right)^{18}} = \frac{\left(6\cdot 3^9\right)^2\left(2\cdot 3^2\right)^3}{6\cdot {}^1\!/_2 \cdot 3^6 \cdot 3^{18}} = 96$$

$$\Rightarrow \beta_{2,3}^{\mathrm{Ln},\mathbf{L10}} = 96\left(f_{\mathrm{N_3}}^{\mathrm{Ln},\mathbf{L10}}\right)^6 \left(EM^{\mathrm{Ln},\mathbf{L10}}\right)^2 \left(u_{\mathrm{Ln}}^{\mathbf{L10},\mathbf{L10}}\right)^6 u_{\mathbf{L10}}^{\mathrm{Ln,Ln}} \qquad (5)$$

Figure S2 Symmetry numbers (σ) and statistical factors (ω) for the complexation of $[\mathrm{Ln(CH_3CN)_9}]^{3+}$ with **L10** in acetonitrile.[32]