Lanthanide triple stranded helicates: controlling the yield of the heterobimetallic species

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Supporting Information

(8 pages)

Scheme S1

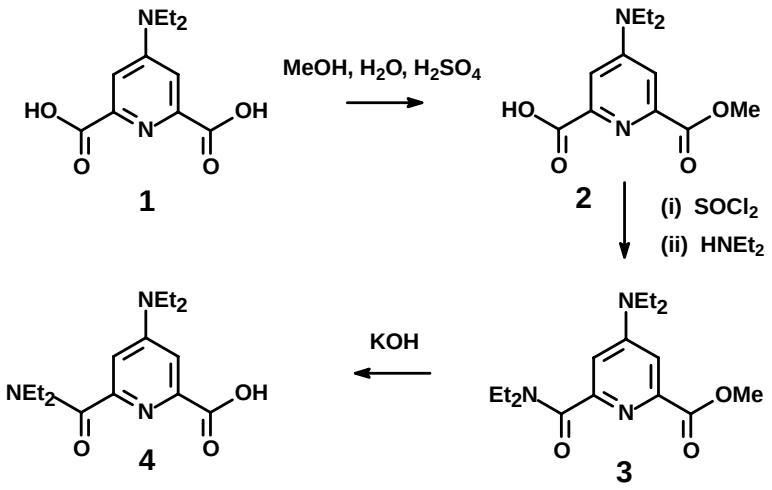

Table S1. **^{1}H NMR of L^{AB2} in $CDCl_3$**

	15 and 17		16	23	8 and 10		1 or 3	20	6, 12, 21, 22		7 and 11		3 or 1
δ / ppm	8.33		8.03	7.87	7.74	7.70	7.49	7.48	7.32 – 7.38		7.24	7.22	6.72
	2 x dd 2H		t 1H	dd 1H	s 1H	s 1H	d 1H	dd 1H	m 4H		dd 1H	dd 1H	d 1H
J / Hz	7.8; 2.2		7.9	6.6; 2.0			2.2	6.1; 2.7			8.3; 1.6	8.3; 1.6	2.6
	9	18	4 or 13	13 or 4	24 or 26	28	26 or 24	19	5 and 14		25 or 27	29	27 or 25
δ / ppm	4.29	4.80	4.76	4.72	3.58	3.47	3.39	1.36	1.42	1.34	1.26	1.21	1.08
	s 2H	q 2H	q 2H	q 2H	q 2H	q 4H	q 2H	t 3H	t 3H	t 3H	t 3H	t 6H	t 3H
J / Hz		7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.2	7.2	7.1	7.1	7.1

Table S2. **^{1}H NMR of L^{AB3} in $CDCl_3$.**

	3	15 and 17	16	23	8 and 10		1	20	6, 12, 21, 22		7 and 11
δ / ppm	8.45	8.37	8.06	7.89	7.77	7.70	7.53	7.49	7.33-7.42		7.28
	d 1H	d 2H	t 1H	dd 1H	s 1H	s 1H	d 1H	dd 1H	m 4H		d 2H
J / Hz	1.5	7.8	7.9	6.7; 1.7			2.0	6.1; 2.1			8.4
	18	13	4	9	24 and 26		5	19	14	25 and 27	
δ / ppm	4.80	4.78	4.75	4.31	3.61	3.36	1.45	1.38	1.36	1.28	1.10
	q 1H	q 1H	q 1H	s 2H	q 2H	q 2H	t 3H	t 3H	t 3H	t 3H	t 3H
J / Hz	7.2	7.3	7.1		7.1	7.1	7.1	7.2	7.0	7.2	7.1

Table S3. **Elemental analysis of $[LnLn'(L^{AB3})_3](ClO_4)_6 \cdot nH_2O$ complexes.**

LnLn'	n	Formula	*M* g/mol	C (calculated)	H (calculated)	N (calculated)
CeCe	9	$C_{129}Ce_2Cl_9H_{144}N_{27}O_{36}$	3133.41	47.65 (47.70)	4.27 (4.47)	11.41 (11.64)
PrPr	4	$C_{129}Cl_9H_{134}N_{27}O_{31}Pr_2$	3239.04	49.18 (49.04)	4.37 (4.27)	11.94 (11.97)
PrLu	4	$C_{129}Cl_9H_{134}LuN_{27}O_{31}Pr$	3184.60	48.49 (48.52)	4.72 (4.23)	10.96 (11.84)
NdLu	0	$C_{129}Cl_9H_{126}LuN_{27}NdO_{27}$	3115.87	50.31 (49.58)	4.37 (4.06)	11.94 (12.10)

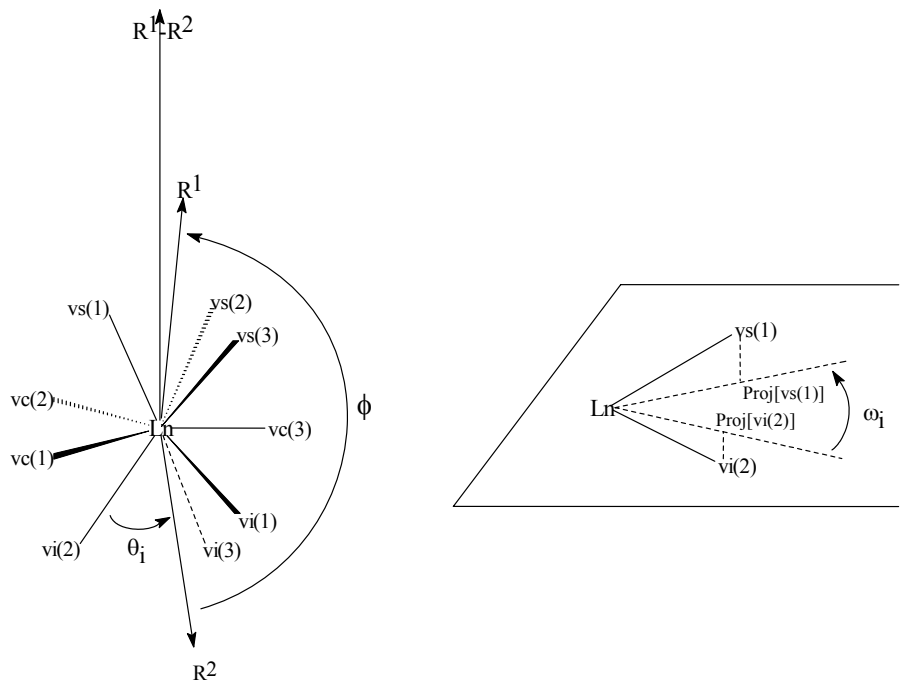

Figure S1. **Definition of angles in the coordination polyhedron.**

Table S4. **Angles (º) and distances (Å) in the benzimidazole-pyridine-carboxamide coordination polyhedron of L^{AB3} and L^{AB1} complexes.**

	Φ	θ(P1) θ(P3)	ω (P1-P3) interstrand ω(P1-P2) intrastrand	α P1-P2 P1-P3 P2-P3	β P1 P2 P3	Distances P1 - P2 P2 - P3	Distances Ln – P1 Ln – P2 Ln – P3
L^{AB3} complexes							
Ce Ce_2	178.4	47(1) 54(1)	15(1) 56(2)	1.0 2.6 2.0	6.8 7.3 6.7	1.491 1.768	1.679 0.189 1.578
Pr Pr_2	177.3	49.1(3) 54(3)	14(2) 57(2)	1.2 2.7 3.7	2.4 3.4 0.4	1.419 1.740	1.605 0.186 1.549
Lu PrLu	178.2	47.3(7) 53(2)	10.1(7) 59(1)	0.8 3.6 3.3	2.9 2.9 1.1	1.380 1.741	1.594 0.215 1.523
Lu NdLu	178.4	46.6(6) 53(1)	11.0(6) 58(2)	1.3 2.1 0.9	7.1 6.9 6.2	1.445 1.737	1.630 0.185 1.552
L^{AB1} complexes							
Eu LaEu	179.6	46.6(1) 54(1)	11.0(8) 56.7(4)	1.1 1.2 2.1	4.2 3.6 4.3	1.471 1.683	1.646 0.175 1.507
Eu Eu_2	178.2	46.5(4) 53.8(4)	11.3(8) 57.4(6)	1.1 1.5 2.4	4.3 3.5 4.5	1.508 1.671	1.653 0.145 1.526
Tb LaTb	179.2	46.9(4) 54(2)	11(1) 57(2)	0.6 4.0 3.8	3.4 3.9 5.3	1.432 1.673	1.607 0.175 1.494
Er PrEr	177.1	45.8(9) 52.6(5)	8.2(6) 59(2)	1.2 2.2 1.0	2.5 2.2 2.8	1.379 1.735	1.596 0.219 1.513
Lu PrLu	179.8	46(2) 53(2)	10(1) 57(2)	2.8 3.3 3.2	2.9 1.1 4.2	1.417 1.652	1.594 0.179 1.471
Regular trigonal tricapped prism	180	θ(P1) = θ(P3)	0 60	0 0 0	0 0 0	d(P1-P2)= d(P2-P3)	0

Table S5. **Angles (º) and distances (Å) in the benzimidazole-pyridine-benzimidazole coordination polyhedron of L^{AB3} and L^{AB1} complexes.**

	Φ	θ(P4) θ(P6)	ω (P4-P6) interstrand ω(P4-P5) intrastrand	α P4-P5 P4-P6 P5-P6	β P4 P5 P6	Distances P4 – P5 P5 – P6	Distances Ln – P4 Ln – P5 Ln – P6
L^{AB3} complexes							
Ce Ce_2	178.9	50(1) 53.4(6)	15(1) 51.9(5)	1.6 2.6 1.0	4.9 6.1 6.8	1.712 1.577	1.698 0.013 1.578
Pr Pr_2	179.4	50(3) 52(2)	15(3) 52(1)	1.7 6.1 4.4	1.8 0.3 4.2	1.709 1.563	1.672 0.034 1.592
Pr PrLu	178.7	50(2) 52(2)	14(3) 53(2)	1.2 4.9 4.0	1.8 0.7 3.3	1.704 1.592	1.681 0.022 1.611
Nd NdLu	178.9	50(1) 53(1)	14(1) 52.0(3)	1.6 3.2 1.7	5.8 6.3 7.9	1.693 1.581	1.681 0.011 1.582
L^{AB1} complexes							
La LaEu	177.4	49(1) 52(3)	16(3) 52(2)	1.4 6.2 5.6	3.5 4.8 9.4	1.729 1.611	1.716 0.011 1.606
La LaTb	177.4	50(1) 53(4)	16(2) 52(2)	1.6 6.2 5.4	2.8 4.3 8.9	1.719 1.597	1.706 0.012 1.598
Pr PrEr	178.4	50(1) 53(2)	15(2) 53.1(7)	2.1 3.9 3.2	2.2 4.3 5.3	1.689 1.583	1.678 0.010 1.588
Pr PrLu	178.0	50.7(9) 53(1)	15.8(3) 52.1(8)	1.2 2.1 1.8	3.5 2.8 4.6	1.701 1.537	1.668 0.031 1.563
Eu Eu_2	177.3	49(2) 51(4)	13(3) 53(3)	2.7 8.9 6.8	2.4 5.2 11.2	1.722 1.609	1.692 0.025 1.612
Regular trigonal tricapped prism	180	θ(P4) = θ(P6)	0 60	0 0 0	0 0 0	d(P4-P5)= d(P5-P6)	0

Table S6. Pitch and LnLn' distances in L^{AB3} and L^{AB1} complexes.

			L^{AB3}		
LnLn'	Ce_2	Pr_2	PrLu	NdLu	
Pitch (Å)	13.3(1)	13.4(1)	13.2(2)	13.2(1)	
d(Ln-Ln') Å)	9.10(15)	9.23(3)	9.18(2)	9.14(4)	
			L^{AB1}		
LnLn'	LaEu	LaTb	PrEr	PrLu	Eu_2
Pitch (Å)	13.4(2)	13.4(2)	13.2(1)	13.21(2)	13.5(2)
d(Ln-Ln') Å)	9.207(4)	9.199(5)	9.219(4)	9.215(5)	9.352(8)

Table S7. **Definition of Least Squares Planes.**

	$LaEu(L^{AB1})_3$			$Ce_2(L^{AB3})_3$ and $Pr_2(L^{AB3})_3$		
	L^1	L^2	L^3	L^1	L^2	L^3
bpb moiety						
terminal benzimidazole	*1*: C27-33; N8-9	*2*: C70-76; N17-18	*3*: C113-119; N26-27	*1*: C1-7; N1-2	*2*: C44-50; N10-11	*3*: C87-93; N19-20
imidazole only	*1i*: C27-29; N8-9	*2i*: C70-72; N17-18	*3i*: C113-115; N26-27	*1i*: C1,6-7; N1-2	*2i*: C44,49-50; N10-11	*3i*: C87,92-93; N19-20
pyridine	*4*: C22-26; N7	*5*: C65-69; N16	*6*: C108-112; N25	*4*: C8-12; N3	*5*: C51-55; N12	*6*: C94-98; N21
bridging benzimidazole	*7*: C15-21; N5-6	*8*: C58-64; N14-15	*9*: C101-107; N23-24	*7*: C13-19; N4-5	*8*: C56-62; N13-14	*9*: C99-105; N22-23
imidazole only	*7i*: C17-18, 21; N5-6	*8i*: C60-61, 64; N14-15	*9i*: C103-104, 107; N23-24	*7i*: C13-14, 19; N4-5	*8i:* C56-57, 62; N13-14	*9i*: C99-100, 105; N22-23
bpa moiety						
bridging benzimidazole	*10*: C7-13; N3-4	*11*: C50-56; N12-13	*12*: C93-99; N21-22	*10*: C21-27; N6-7	*11*: C64-70; N15-16	*12*: C107-113; N24-25
pyridine	*13*: C2-6; N2	*14*: C45-49; N11	*15*: C88-92; N20	*13*: C28-32; N8	*14*: C71-75; N17	*15*: C114-118; N26

Table S8. **Angles and Distances between Least Squares Planes.**

	$LaEu(L^{AB1})_3$		$Ce_2(L^{AB3})_3$		$Pr_2(L^{AB3})_3$	
Planes	Angle	*d*	Angle	*d*	Angle	*d*
1 - 6	47.3 º	4.185 Å	42.5 º	4.220 Å	48.4 º	4.250 Å
2 - 4	39.6 º	4.011 Å	62.7 º	4.472 Å	51.6 º	4.391 Å
3 - 5	42.8 º	4.028 Å	48.0 º	4.279 Å	57.7 º	4.436 Å
1i - 9i	11.5 º	3.997 Å	9.1 º	3.496 Å	28.4 º	3.831 Å
2i - 7i	23.1 º	3.746 Å	36.0 º	4.158 Å	15.8 º	3.695 Å
3i - 8i	33.9 º	4.029 Å	16.6 º	3.837 Å	10.4 º	3.924 Å
4 - 9	26.6 º	3.688 Å	22.8 º	3.842 Å	46.6 º	4.367 Å
5 - 7	28.3 º	3.931 Å	20.9 º	3.653 Å	29.8 º	3.904 Å
6 - 8	28.8 º	3.980 Å	39.0 º	4.119 Å	22.4 º	3.597 Å
7 - 12	25.3 º	4.151 Å	26.1 º	4.025 Å	27.1 º	4.288 Å
8 - 10	27.7 º	4.278 Å	19.9 º	4.556 Å	24.0 º	4.250 Å
9 - 11	26.3 º	4.437 Å	22.9 º	4.121 Å	33.1 º	4.148 Å
10 - 15	76.2 º	4.808 Å	53.2 º	4.364 Å	81.5 º	4.896 Å
11 - 13	86.4 º	5.063 Å	84.8 º	5.381 Å	84.7 º	5.190 Å
12 - 14	88.3 º	5.309 Å	81.4 º	5.035 Å	88.0 º	5.060 Å

Table S9. **Composition in % of L^{AB2} complexes in CD_3CN solution.**

			LnLn'		Ln'Ln			Ln_2		Ln'_2	
Ln	Ln'	$\Delta r_{Ln\text{-}Ln'}$ (pm)	*HHH*	*HHT*	*HHT*	*HHH*	Total hetero	*HHH*	*HHT*	*HHH*	*HHT*
Eu	Lu	8.8	4	17			21	10	47	3	19
Nd	Lu	13.1	7	18	2		27	5	32	3	31
Pr	Lu	14.7	18	33			51	2	21	3	24
Ce	Lu	16.4	21	39			60	3	18	2	17
La	Lu	18.4	27	34	4		65	3	13	1	17

Table S10. **Composition in % of L^{AB3} complexes in CD_3CN solution.**

			LnLn'		Ln'Ln			Ln_2		Ln'_2	
Ln	Ln'	$\Delta r_{Ln\text{-}Ln'}$ (pm)	*HHH*	*HHT*	*HHT*	*HHH*	Total hetero	*HHH*	*HHT*	*HHH*	*HHT*
La	Ce	2	30			19	49	28		23	
La	Pr	3.7	33			15	48	26		25	
La	Nd	5.3	45			12	57	16		28	
Eu	Lu	8.8	75				75	18		8	
La	Eu	9.6	63				63	18		19	
Sm	Lu	10	65				65	24		11	
Nd	Lu	13.1	70				70	14		15	
Pr	Lu	14.7	88				88	8		4	
Ce	Lu	16.4	80				80	10		10	
La	Lu	18.4	87				87	9		4	