Electronic Supporting Information

Lanthanide Mixed-Ligand Complexes of the $Ln(CAPh)_3Phen$ and $La_xEu_{1-x}(CAPh)_3Phen$ (CAPh = carbacylamidophosphate) type. Comparative Study of Their Spectral Properties

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Table S1 Element analyzes for the compounds synthesized

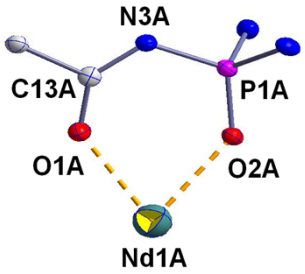
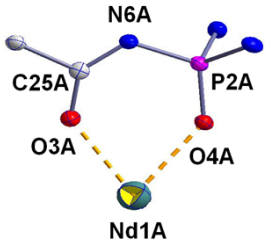
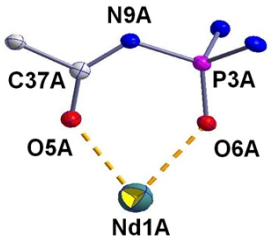
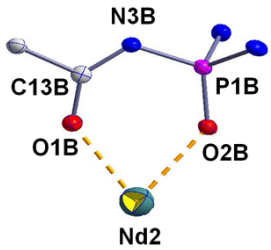
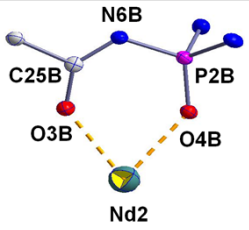
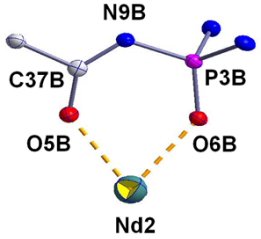
Compound	Color	M_w	% Found (Calcd.)			
			Ln	C	H	N
$[La(Pip)_3Phen]$	colorless	1445.82	9.57 (9.61)	39.02 (39.88)	4.54 (4.70)	10.12 (10.66)
$[Ce(Pip)_3Phen]$	orange	1447.04	9.53 (9.68)	38.90 (39.84)	4.61 (4.70)	10.32 (10.65)
$[Pr(Pip)_3Phen]$	light green	1447.82	9.54 (9.73)	39.23 (39.82)	4.56 (4.70)	10.48 (10.64)
$[Nd(Pip)_3Phen]$	pale blue	1451.16	9.87 (9.94)	38.80 (39.73)	4.60 (4.69)	10.04 (10.62)
$[Sm(Pip)_3Phen]$	colorless	1457.32	10.27 (10.32)	38.67 (39.56)	4.56 (4.67)	9.64 (10.57)
$[Eu(Pip)_3Phen]$	colorless	1458.88	10.38 (10.42)	38.49 (39.52)	4.58 (4.66)	9.77 (10.56)
$[Gd(Pip)_3Phen]$	colorless	1464.17	10.56 (10.74)	38.23 (39.38)	4.53 (4.64)	10.13 (10.52)
$[Tb(Pip)_3Phen]$	colorless	1465.84	10.60 (10.84)	38.30 (39.33)	4.48 (4.64)	10.03 (10.51)
$[Dy(Pip)_3Phen]$	colorless	1469.42	10.85 (11.06)	38.70 (39.24)	4.51 (4.63)	9.88 (10.49)
$[Ho(Pip)_3Phen]$	cream	1471.85	11.08 (11.21)	38.27 (39.17)	4.49 (4.62)	10.40 (10.47)
$[Er(Pip)_3Phen]$	light pink	1474.18	11.28 (11.35)	38.09 (39.11)	4.48 (4.61)	10.27 (10.45)
$[Tm(Pip)_3Phen]$	colorless	1475.85	11.26 (11.45)	38.10 (39.06)	4.55 (4.61)	10.33 (10.44)
$[Yb(Pip)_3Phen]$	colorless	1479.96	11.53 (11.69)	37.54 (38.96)	4.48 (4.59)	10.23 (10.41)
$[Lu(Pip)_3Phen]$	colorless	1481.89	11.77 (11.81)	38.17 (38.90)	4.46 (4.59)	9.97 (10.40)
$[La_{0.95}Eu_{0.05}(Pip)_3Phen]$	colorless	1446.47	9.58 (9.65)	38.98 (39.86)	4.61 (4.70)	10.47 (10.65)
$[La_{0.5}Eu_{0.5}(Pip)_3Phen]$	colorless	1452.35	9.95 (10.01)	38.90 (39.70)	4.54 (4.68)	10.20 (10.61)
$[La_{0.05}Eu_{0.95}(Pip)_3Phen]$	colorless	1458.23	10.32 (10.38)	38.48 (39.54)	4.56 (4.66)	10.20 (10.57)

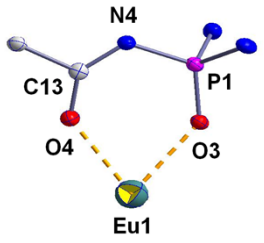
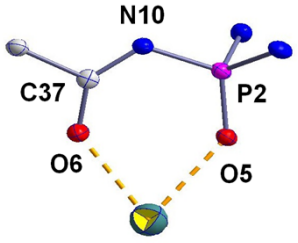
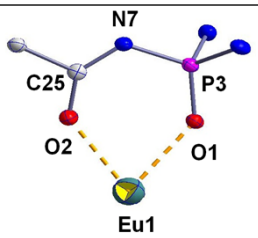
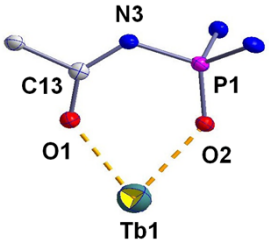
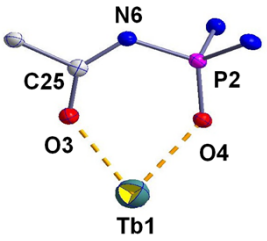
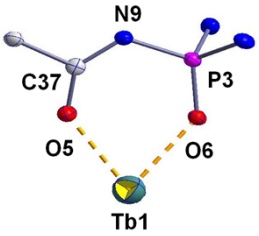
Table S2 Main IR absorption bands and their assignments to the carbacylamidophosphate compounds, cm^{-1}.

Compound	**Vibration Frequencies, cm^{-1}**			
	ν(NH)	**ν(C=O)**	**ν(P=O)**	**AmideII**
HPip	3027 m,b	1729 vs,sp	1194 s,sp	1430 m,sp
NaPip	-	1637 vs,sp	1136 s,sp	1358 m,sp
$[La(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1109 s,sp	1334 m,sp
$[Ce(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1108 s,sp	1335 m,sp
$[Pr(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1109 s,sp	1335 m,sp
$[Nd(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1112 s,sp	1337 m,sp
$[Sm(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1114 s,sp	1335 m,sp
$[Eu(Pip)_3Phen]$	-	1604 vs,sp, 1610 vs,sp	1115 s,sp	1337 m,sp
$[Gd(Pip)_3Phen]$	-	1604 vs,sp, 1610 vs,sp	1119 s,sp	1337 m,sp
$[Tb(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1121 s,sp	1337 m,sp
$[Dy(Pip)_3Phen]$	-	1604 vs,sp, 1610 vs,sp	1119 s,sp	1337 m,sp
$[Ho(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1121 s,sp	1337 m,sp
$[Er(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1119 s,sp	1338 m,sp
$[Tm(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1119 s,sp	1337 m,sp
$[Yb(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1122 s,sp	1337 m,sp
$[Lu(Pip)_3Phen]$	-	1603 vs,sp, 1610 vs,sp	1122 s,sp	1337 m,sp
$[La_{0.05}Eu_{0.95}(Pip)_3Phen]$	-	1604 vs,sp, 1610 vs,sp	1116 s,sp	1336 m,sp
$[La_{0.5}Eu_{0.5}(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1115 s,sp	1336 m,sp
$[La_{0.95}Eu_{0.05}(Pip)_3Phen]$	-	1603 vs,sp, 1609 vs,sp	1110 s,sp	1335 m,sp

[a] s: strong, vs: very strong, m: medium, b: broad, sp: sharp

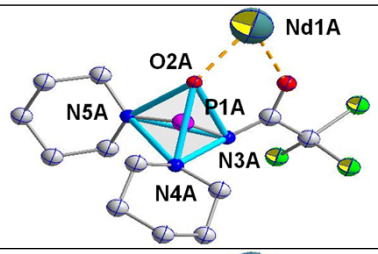
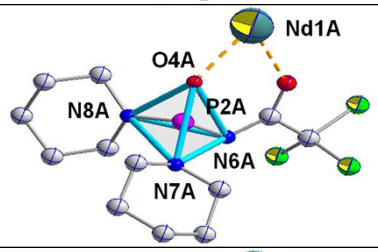
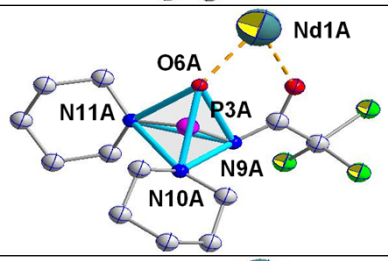
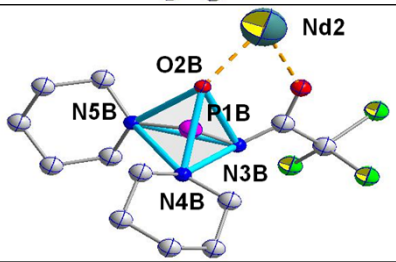
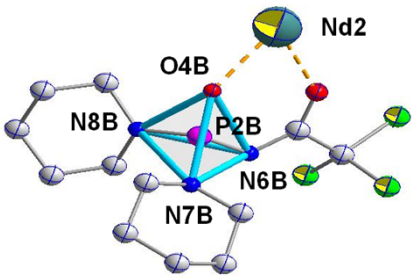
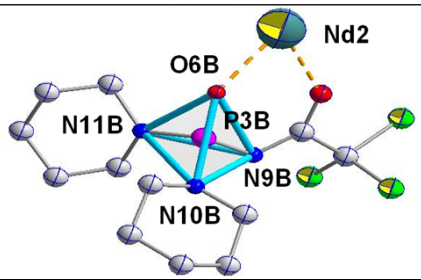
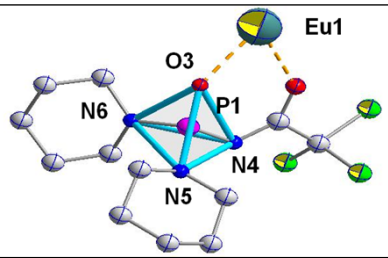
Table S3. The distances of the chelate cycle atoms from coordination bond planes

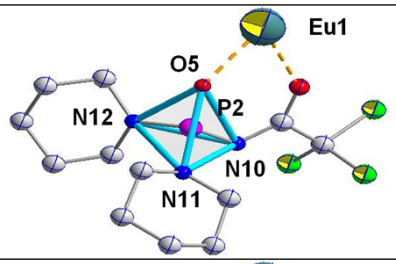
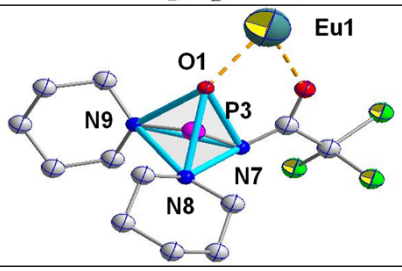
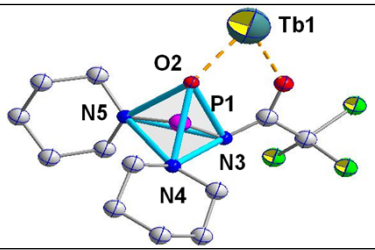
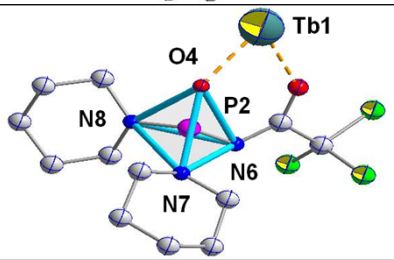
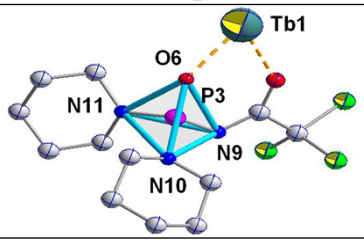
Nd(Pip)$_3$Phen		
Atom	Distances from plane, d[Å]	
Plane Nd1A O2A P1A N3A C13A O1A		
Nd1A	0.0009	
O2A	-0.1449	
P1A	0.0071	
N3A	0.1263	
C13A	0.0254	
O1A	-0.1172	
Plane Nd1A O4A P2A N6A C25A O3A		
Nd1A	0.0005	
O4A	-0.0888	
P2A	-0.0351	
N6A	0.3018	
C25A	0.1604	
O3A	-0.2271	
Plane Nd1A O6A P3A N9A C37A O5A		
Nd1A	0.0009	
O6A	-0.0434	
P3A	-0.0122	
N9A	0.2075	
C37A	0.0932	
O5A	-0.1984	
Plane Nd2 O2B P1B N3B C13B O1B		
Nd2	0.0008	
O2B	-0.0280	
P1B	-0.0157	
N3B	0.2669	
C13B	0.0990	
O1B	-0.1879	
Plane Nd2 O4B P2B N6B C25B O3B		
Nd2	0.0005	
O4B	0.0967	
P2B	-0.0380	
N6B	0.3142	
C25B	0.1725	
O3B	-0.2378	
Plane Nd2 O6B P3B N9B C37B O5B		
Nd2	0.0002	
O6B	0.0528	
P3B	-0.0184	
N9B	0.1369	
C37B	0.0871	
O5B	-0.1187	

Eu(Pip)$_3$Phen		
	Plane Eu1 O3 P1 N4 C13 O4	
Eu1	0.0005	
O3	-0.0741	
P1	-0.0362	
N4	0.3058	
C13	0.1460	
O4	-0.2314	
	Plane Eu1 O5 P2 N10 C37 O6	
Eu1	0.0006	
O5	-0.0300	
P2	-0.0122	
N10	0.1695	
C37	0.0826	
O6	-0.1662	
	Plane Eu1 O1 P3 N7 C25 O2	
Eu1	0.0010	
O1	-0.1610	
P3	0.0037	
N7	0.2207	
C25	-0.0102	
O2	-0.1613	
Tb(Pip)$_3$Phen		
	Plane Tb1 O2 P1 N3 C13 O1	
Tb1	-0.0008	
O2	0.2147	
P1	-0,0199	
N3	-0,1398	
C13	0.0070	
O1	0.1934	
	Plane Tb1 O4 P2 N6 C25 O3	
Tb1	0.0006	
O4	-0.1802	
P2	0.0071	
N6	0.2537	
C25	0.0228	
O3	-0.2447	
	Plane Tb1 O6 P3 N9 C37 O5	
Tb1	-0.0007	
O6	0.1001	
P3	-0,0072	
N9	-0,2982	
C37	-0.1371	
O5	0.2101	

* shadded gray the atoms with the maximum deviations

Table S4 The angles around the phosphorus atom, (°)

Nd(Pip)$_3$Phen	
O2A P1A N3A 114.65(17) O2A P1A N4A 114.84(18) O2A P1A N5A 107.72(17) N3A P1A N5A 111.97(19)	
O4A P2A N6A 116.68(15) O4A P2A N7A 114.34(19) O4A P2A N8A 108.08(16) N8A P2A N6A 110.83(19)	
O6A P3A N9A 114.84(17) O6A P3A N10A 107.61(15) O6A P3A N11A 115.91(17) N11A P3A N9A 104.59(16)	
O2B P1B N3B 116.05(18) O2B P1B N4B 108.05(18) O2B P1B N5B 115.04(19) N3B P1B N5B 103.3(2)	
O4B P2B N6B 116.51(15) O4B P2B N7B 114.20(18) O4B P2B N8B 108.97(16) N6B P2B N8B 109.91(19)	
O6B P3B N9B 114.68(17) O6B P3B N10B 107.57(15) O6B P3B N11B 115.77(17) N11B P3B N9B 105.23(16)	
Eu(Pip)$_3$Phen	
O3 P1 N4 116.22(15) O3 P1 N5 114.54(17) O3 P1 N6 108.30(14) N6 P1 N4 110.75(18)	

O5 P2 N10 113.78(15) O5 P2 N11 107.70(15) O5 P2 N12 116.32(16) N12 P2 N10 104.80(16)	
O1 P3 N7 116.34(16) O1 P3 N8 114.51(16) O1 P3 N9 107.35(16) N7 P3 N9 108.19(17)	
$Tb(Pip)_3Phen$	
O2 P1 N3 116.34(19) O2 P1 N4 113.9(2) O2 P1 N5 108.5(2) N5 P1 N3 110.0(2)	
O4 P2 N6 116.35(19) O4 P2 N7 112.5(2) O4 P2 N8 107.8(2) N6 P2 N8 109.4(2)	
O6 P3 N9 115.1(2) O6 P3 N10 108.0(3) O6 P3 N11 115.0(2) N11 P3 N9 103.8(2)	

* shadded gray the atoms with the maximum deviations

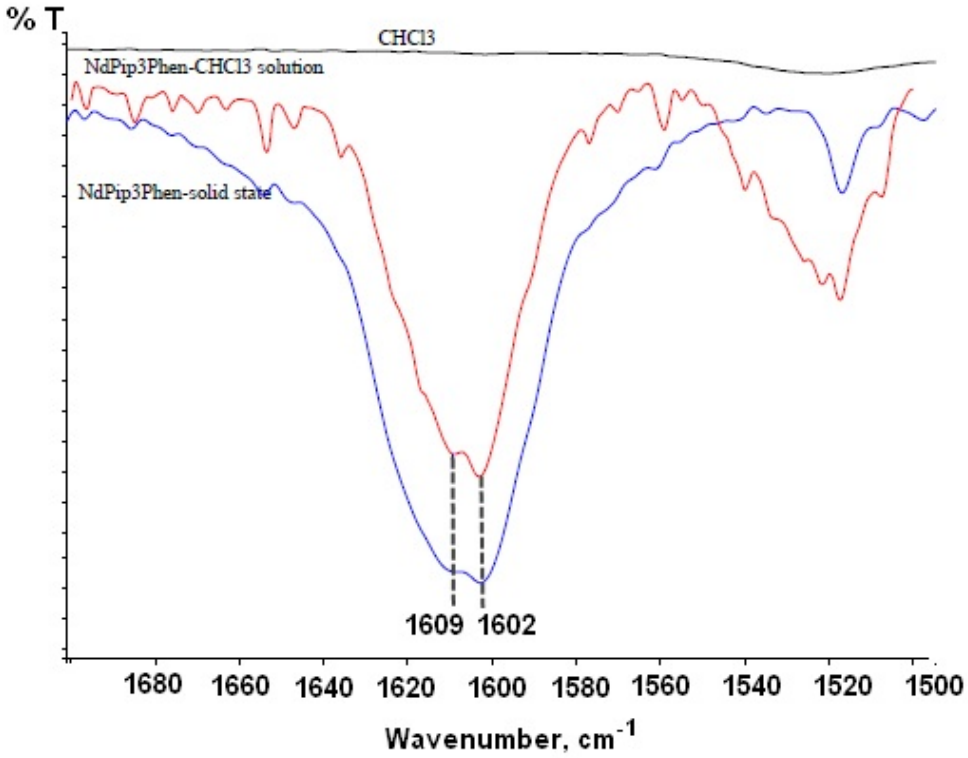


Fig. 1S FT-IR spectra of [Nd(Pip)$_3$Phen] in solid state and in the $CHCl_3$ solution

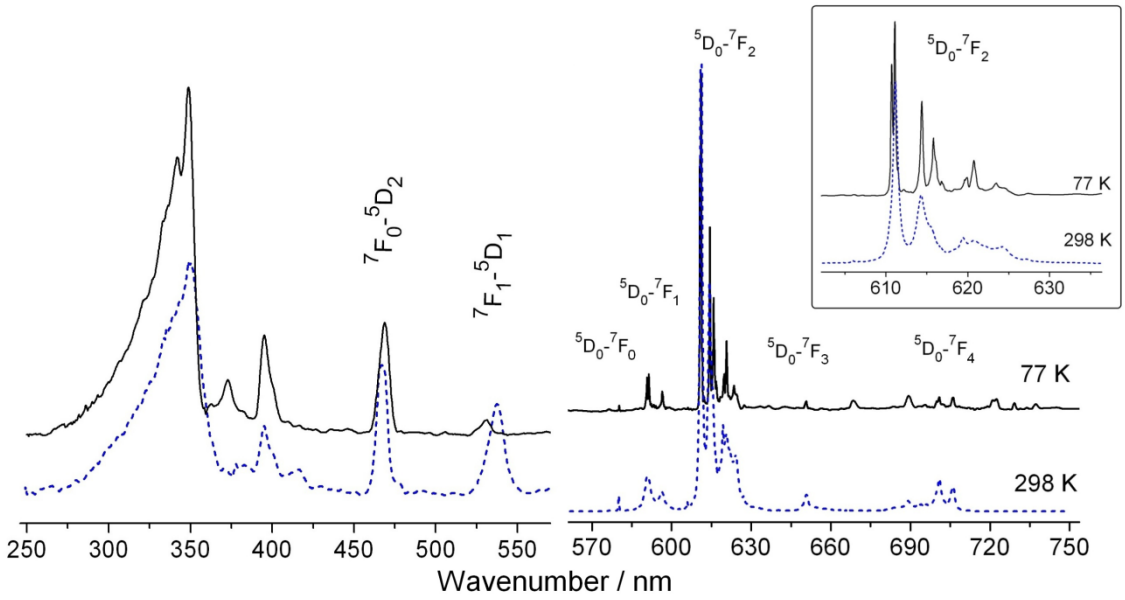


Fig. 2S Solid-state excitation and emission for [Eu(Pip)$_3$(Phen)] excited at 337 nm, emission monitored at 612 nm at 298 K compared to 77 K. The $^5D_0 \rightarrow {}^7F_2$ transition in the emission spectrum is shown in the inset

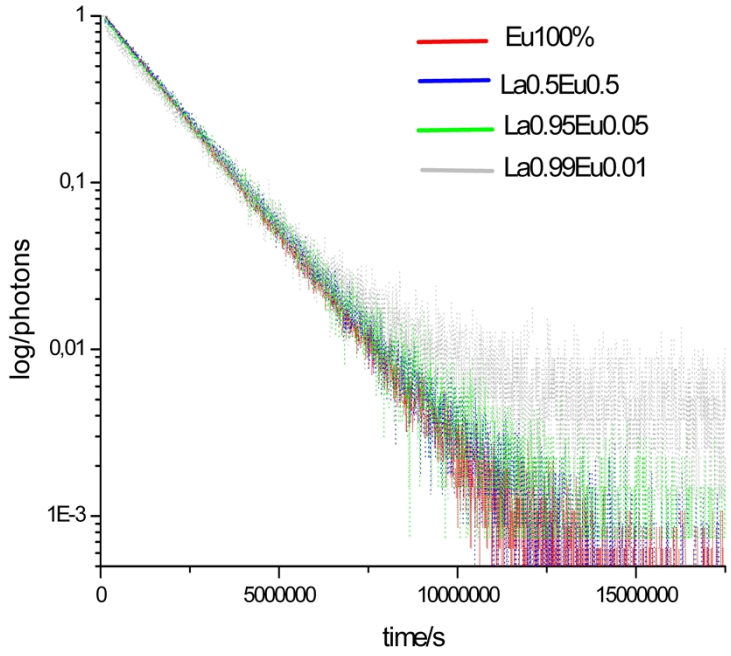


Fig. 3S The luminescence decay curves recorded at 77 K

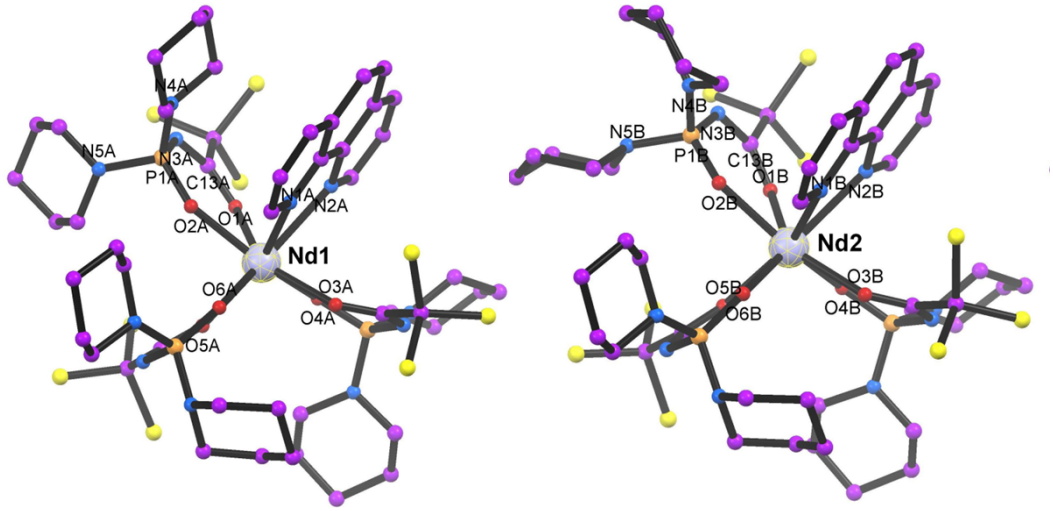


Fig. 4S The view of the [Nd(Pip)$_3$(Phen)] asymmetric unit with the atom numbering scheme. H atoms have been omitted

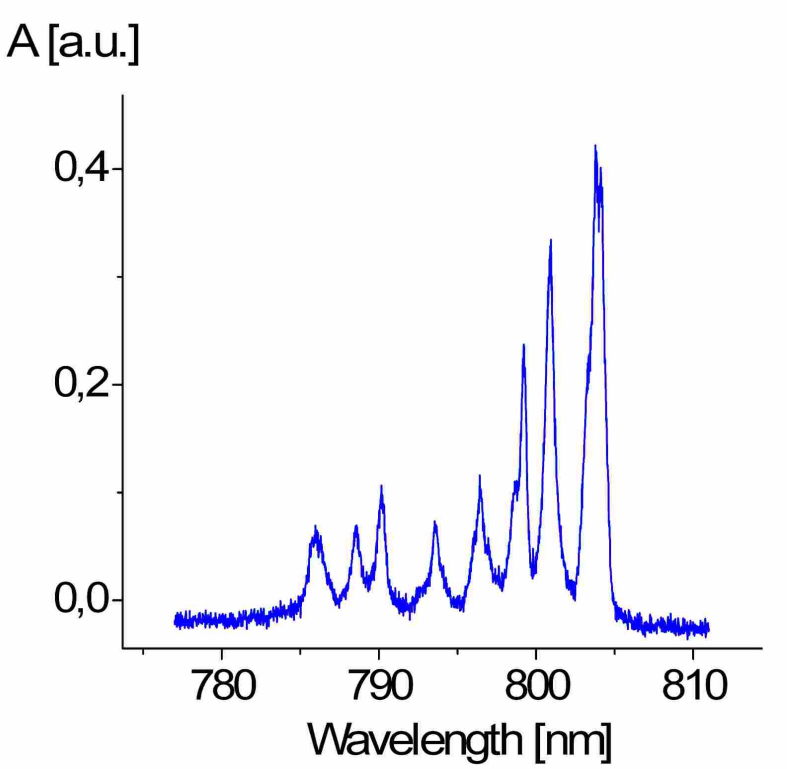


Fig. 5S Electronic diffuse reflection spectrum of [Nd(Pip)$_3$(Phen)] at 4 K in the 770-810 nm region