Supporting Information

for

Influence of N-heterocyclic Core on the Binding Capability of N,O-Hybrid Diamide Ligands towards Trivalent Lanthanides and Actinides

Ruixue Meng[†,‡,§], Lei Xu[†,§], Xiao Yang[†], Mingze Sun[†], Chao Xu[ǁ], Nataliya E. Borisova[Ω], Xingwang Zhang[†,‡], Lecheng Lei[†,‡], Chengliang Xiao[†,‡,*]

[†] College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

[‡] Institute of Zhejiang University - Quzhou, 78 Jiuhua Boulevard North, Quzhou 324000, China

[ǁ] Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

[Ω] Department of Chemistry, Lomonosov Moscow State University, 1/3 Leninskie Gory, GSP-1, 119991 Moscow, Russian Federation

*Email: xiaoc@zju.edu.cn (Chengliang Xiao)

Contents

1. ^{1}H NMR spectrum of Pyr-PyDA ligand in CD_3OD Page S3

2. ^{1}H NMR spectrum of Pyr-BPyDA ligand in CD_3OD Page S3

3. ^{1}H NMR spectrum of Pyr-DAPhen ligand in CD_3OD Page S4

4. ^{1}H NMR spectra of Pyr-PyDA titrated with $Lu(NO_3)_3$ in CD_3OD. Page S5

5. Spectrophotometric titration spectra of Pyr-PyDA, Pyr-BPyDA and Pyr-DAPhen with Eu(III) Page S6

6. The bond distances and bond angles for the crystal of Pyr-PyDA and $Nd(NO_3)_3$ Page S7-S10

7. The bond distances and bond angles for the crystal of Pyr-BPyDA and $Nd(NO_3)_3$ Page S10-S14

8. The bond distances and bond angles for the crystal of Pyr-DAPhen and $Er(NO_3)_3$ Page S14-S18

9. The bond distances and bond angles for the crystal of Pyr-DAPhen and $La(NO_3)_3$ Page S18-S22

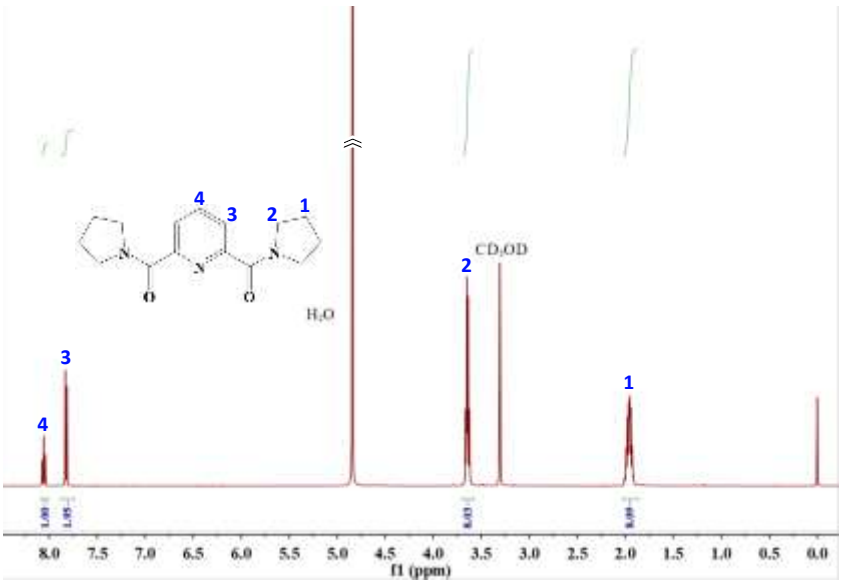

Figure S1. ^{1}H NMR spectrum of Pyr-PyDA ligand in CD_3OD

^{1}H NMR (500 MHz, CD_3OD) : δ=8.06 ppm (t, *J* = 7.9 Hz, 1H), 7.82 ppm (d, *J* = 7.8 Hz, 2H), 3.64 ppm (q, *J* = 6.8 Hz, 8H), 2.02 – 1.87 ppm (m, 8H).

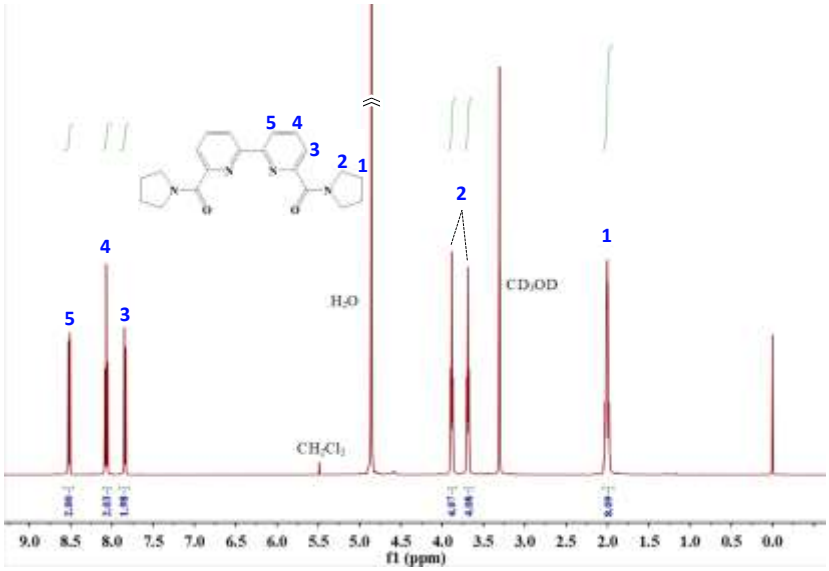

Figure S2. ^{1}H NMR spectrum of Pyr-BPyDA ligand in CD_3OD

^{1}H NMR (500 MHz, CD_3OD) : δ=8.52 ppm (dd, *J* = 8.0, 0.8 Hz, 2H), 8.07 ppm (t, *J* = 7.8 Hz, 2H), 7.84 ppm (dd, *J* = 7.7, 0.8 Hz, 2H), 3.88 ppm (t, *J* = 6.3 Hz, 4H), 3.69 ppm (t, *J* = 6.6 Hz, 4H), 2.05 – 1.92 ppm (m, 8H).

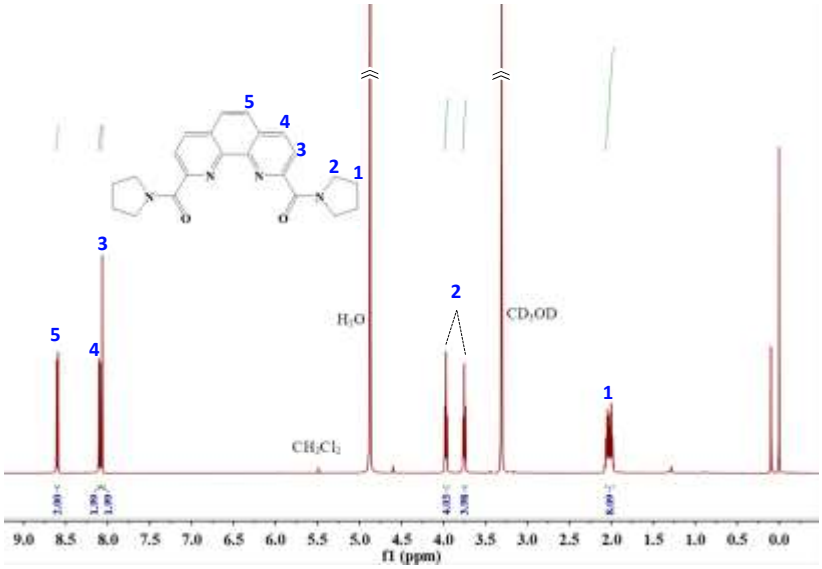

Figure S3. ^{1}H NMR spectrum of Pyr-DAPhen ligand in CD_3OD

^{1}H NMR (500 MHz, CD_3OD) : δ=8.60 ppm (d, *J* = 8.3 Hz, 2H), 8.10 ppm (d, *J* = 8.3 Hz, 2H), 8.07 ppm (s, 2H), 3.97 ppm (t, *J* = 6.6 Hz, 4H), 3.75 ppm (t, *J* = 6.8 Hz, 4H), 2.01 ppm (tt, *J* = 14.8, 4.1 Hz, 8H).

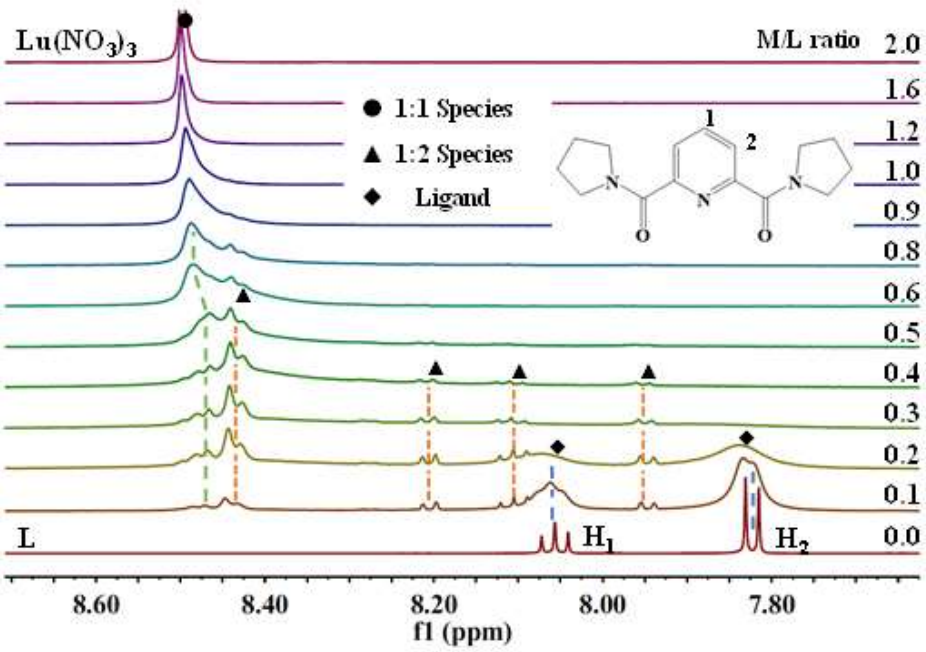

Figure S4. ^{1}H NMR spectra of Pyr-PyDA (15.0 mM) titrated with $Lu(NO_3)_3$ in CD_3OD. (M/L denotes the metal/ligand molar ratio.)

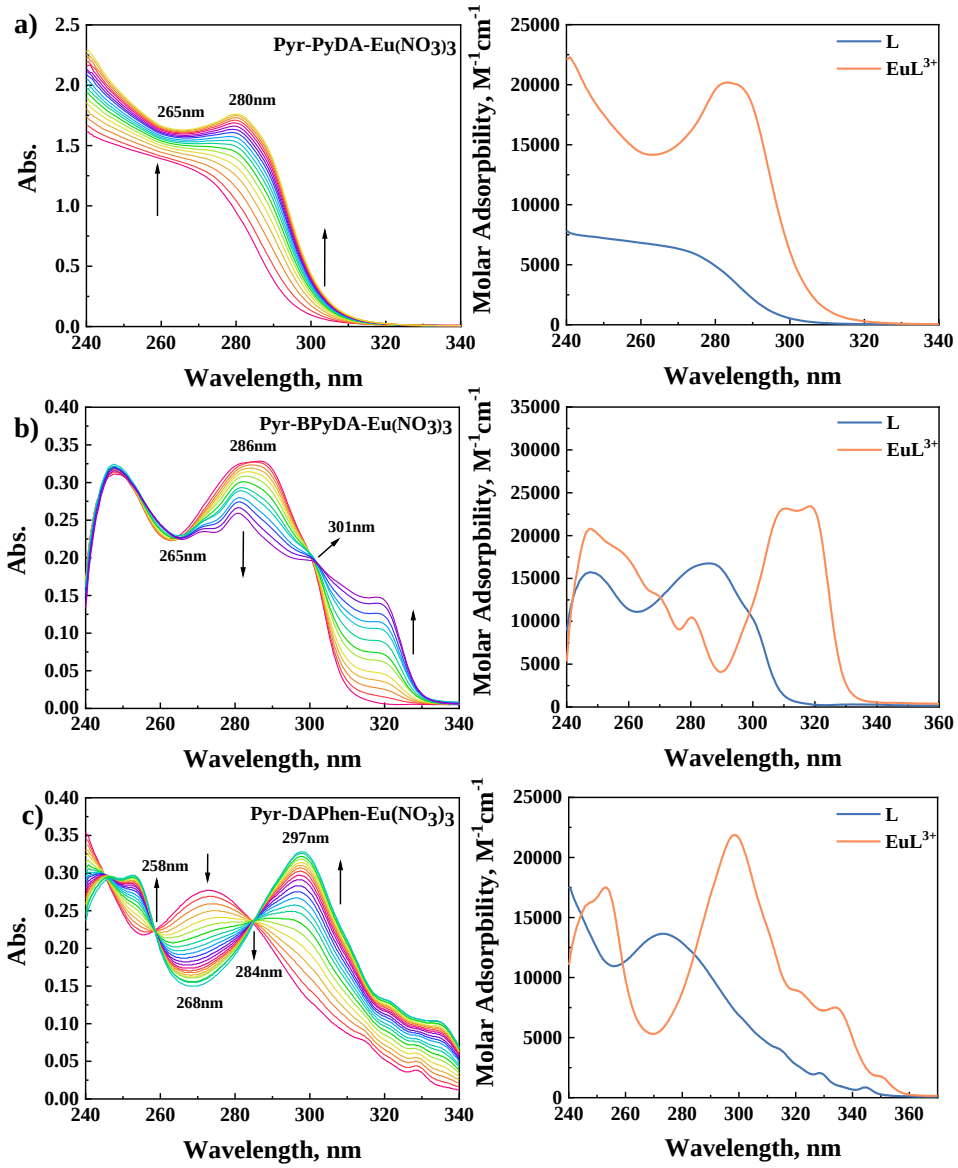

Figure S5. Spectrophotometric titrations of the three ligands a) Pyr-PyDA, b) Pyr-BPyDA and c) Pyr-DAPhen complexing with $Eu(NO_3)_3$ in methanol solution (T = 298 K, I = 0.01 M Et_4NNO_3, V_0 = 2.20 mL). Left row: the normalized titration spectra collected. Right row: the calculated molar absorptivities of Eu(III) complexes with three ligands. a) $C_L/C_{Eu(III)}$ = 0.20 mM/8.48 mM, a total of 0.40 mL titrant was added. b) $C_L/C_{Eu(III)}$ = 0.02 mM/0.51 mM, a total of 0.21 mL titrant was added. c) $C_L/C_{Eu(III)}$ = 0.02 mM/0.51 mM, a total of 0.13 mL titrant was added.

Table S1 The bond distances for the Nd(Pyr-PyDA)$(NO_3)_3CH_3OH$ (complex **1**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Nd1	O1	2.4656(13)	O11	N6	1.2223(19)
Nd1	O2	2.4556(13)	O12	C16	1.424(2)
Nd1	O3	2.5361(14)	N1	C1	1.486(2)
Nd1	O4	2.5952(14)	N1	C4	1.4884(19)
Nd1	O6	2.5855(14)	N1	C5	1.322(2)
Nd1	O7	2.6045(14)	N2	C6	1.3384(19)
Nd1	O9	2.5659(13)	N2	C10	1.3403(19)
Nd1	O10	2.5508(13)	N3	C11	1.317(2)
Nd1	O12	2.4739(12)	N3	C12	1.482(2)
Nd1	N2	2.6302(14)	N3	C15	1.474(2)
Nd1	N4	2.9895(17)	C1	C2	1.521(2)
Nd1	N6	2.9885(15)	C2	C3	1.527(3)
O1	C5	1.2644(18)	C3	C4	1.522(2)
O2	C11	1.2640(19)	C5	C6	1.511(2)
O3	N4	1.2778(18)	C6	C7	1.394(2)
O4	N4	1.2677(18)	C7	C8	1.392(2)
O5	N4	1.2250(19)	C8	C9	1.390(2)
O6	N5	1.2694(18)	C9	C10	1.399(2)
O7	N5	1.2799(19)	C10	C11	1.510(2)
O8	N5	1.2214(19)	C12	C13	1.506(3)
O9	N6	1.2670(18)	C13	C14	1.529(4)
O10	N6	1.2788(19)	C14	C15	1.530(3)

Table S2 The bond angles for the Nd(Pyr-PyDA)$(NO_3)_3CH_3OH$ (complex **1**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Nd1	O3	74.22(4)	O12	Nd1	N4	77.16(4)
O1	Nd1	O4	72.33(4)	O12	Nd1	N6	93.29(4)
O1	Nd1	O6	88.10(4)	N2	Nd1	N4	90.53(4)
O1	Nd1	O7	131.72(4)	N2	Nd1	N6	142.23(4)
O1	Nd1	O9	109.71(4)	N6	Nd1	N4	105.94(4)
O1	Nd1	O10	72.54(4)	C5	O1	Nd1	119.76(9)
O1	Nd1	O12	147.11(4)	C11	O2	Nd1	120.62(10)
O1	Nd1	N2	61.42(4)	N4	O3	Nd1	97.74(9)
O1	Nd1	N4	70.17(4)	N4	O4	Nd1	95.19(9)
O1	Nd1	N6	92.04(4)	N5	O6	Nd1	97.61(9)
O2	Nd1	O1	121.64(4)	N5	O7	Nd1	96.40(9)
O2	Nd1	O3	83.63(4)	N6	O9	Nd1	96.55(9)
O2	Nd1	O4	128.03(4)	N6	O10	Nd1	96.95(9)
O2	Nd1	O6	73.07(4)	C16	O12	Nd1	126.20(12)
O2	Nd1	O7	72.46(4)	C1	N1	C4	111.55(12)
O2	Nd1	O9	128.30(4)	C5	N1	C1	119.09(13)
O2	Nd1	O10	140.98(4)	C5	N1	C4	127.61(13)
O2	Nd1	O12	71.26(4)	C6	N2	Nd1	119.89(10)
O2	Nd1	N2	60.33(4)	C6	N2	C10	120.14(13)
O2	Nd1	N4	106.79(4)	C10	N2	Nd1	119.89(10)
O2	Nd1	N6	139.25(4)	C11	N3	C12	118.90(13)
O3	Nd1	O4	49.97(4)	C11	N3	C15	129.15(14)
O3	Nd1	O6	137.33(4)	C15	N3	C12	111.77(13)
O3	Nd1	O7	151.49(4)	O3	N4	Nd1	57.20(7)

O3	Nd1	O9	117.65(4)	O4	N4	Nd1	59.83(7)
O3	Nd1	O10	134.40(4)	O4	N4	O3	116.81(13)
O3	Nd1	N2	70.44(4)	O5	N4	Nd1	174.41(12)
O3	Nd1	N4	25.06(4)	O5	N4	O3	121.17(14)
O3	Nd1	N6	130.99(4)	O5	N4	O4	122.02(15)
O4	Nd1	O7	139.28(4)	O6	N5	O7	116.58(13)
O4	Nd1	N2	111.92(4)	O8	N5	O6	122.00(15)
O4	Nd1	N4	24.98(4)	O8	N5	O7	121.41(15)
O4	Nd1	N6	81.02(4)	O9	N6	Nd1	58.54(7)
O6	Nd1	O4	156.61(4)	O9	N6	O10	116.27(13)
O6	Nd1	O7	49.40(4)	O10	N6	Nd1	57.91(7)
O6	Nd1	N2	67.00(4)	O11	N6	Nd1	176.99(13)
O6	Nd1	N4	154.65(4)	O11	N6	O9	122.18(15)
O6	Nd1	N6	87.15(4)	O11	N6	O10	121.53(15)
O7	Nd1	N2	108.77(4)	N1	C1	C2	103.62(14)
O7	Nd1	N4	155.76(4)	C1	C2	C3	103.94(14)
O7	Nd1	N6	67.70(4)	C4	C3	C2	103.52(15)
O9	Nd1	O4	71.38(4)	N1	C4	C3	102.01(13)
O9	Nd1	O6	104.78(4)	O1	C5	N1	121.50(14)
O9	Nd1	O7	69.32(4)	O1	C5	C6	116.85(13)
O9	Nd1	N2	167.13(4)	N1	C5	C6	121.63(13)
O9	Nd1	N4	95.03(4)	N2	C6	C5	110.04(12)
O9	Nd1	N6	24.91(4)	N2	C6	C7	122.05(14)
O10	Nd1	O4	90.24(5)	C7	C6	C5	127.83(14)
O10	Nd1	O6	71.30(5)	C8	C7	C6	117.78(14)
O10	Nd1	O7	72.53(5)	C9	C8	C7	120.38(14)

O10	Nd1	O9	49.99(4)	C8	C9	C10	118.02(15)
O10	Nd1	N2	117.14(4)	N2	C10	C9	121.60(14)
O10	Nd1	N4	112.21(5)	N2	C10	C11	109.75(12)
O10	Nd1	N6	25.13(4)	C9	C10	C11	128.58(14)
O12	Nd1	O3	77.87(4)	O2	C11	N3	120.49(14)
O12	Nd1	O4	76.51(4)	O2	C11	C10	116.20(13)
O12	Nd1	O6	124.56(4)	N3	C11	C10	123.29(13)
O12	Nd1	O7	79.85(4)	N3	C12	C13	103.34(14)
O12	Nd1	O9	68.86(4)	C12	C13	C14	103.33(17)
O12	Nd1	O10	118.27(4)	C13	C14	C15	102.6(2)
O12	Nd1	N2	123.82(4)	N3	C15	C14	101.77(15)

Table S3 The bond distances for the Nd(Pyr-BPyDA)$(NO_3)_3$ (complex **2**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Nd1	O1	2.4011(10)	N1	C5	1.3259(17)
Nd1	O2	2.4492(9)	N2	C6	1.3491(17)
Nd1	O3	2.5790(11)	N2	C10	1.3434(17)
Nd1	O4	2.5527(12)	N3	C11	1.3466(17)
Nd1	O6	2.5584(11)	N3	C15	1.3428(17)
Nd1	O7	2.5714(11)	N4	C16	1.3139(17)
Nd1	O9	2.5259(11)	N4	C17	1.4751(18)
Nd1	O10	2.5350(11)	N4	C20	1.4813(19)
Nd1	N2	2.6671(12)	C1	C2	1.518(2)
Nd1	N3	2.5899(11)	C2	C3	1.516(3)
Nd1	N5	2.9837(13)	C3	C4	1.531(2)
Nd1	N7	2.9444(13)	C5	C6	1.5112(19)

O1	C5	1.2607(17)	C6	C7	1.391(2)
O2	C16	1.2668(15)	C7	C8	1.389(2)
O3	N5	1.2708(18)	C8	C9	1.380(2)
O4	N5	1.2702(18)	C9	C10	1.393(2)
O5	N5	1.2228(18)	C10	C11	1.4866(18)
O6	N6	1.2647(16)	C11	C12	1.3982(18)
O7	N6	1.2729(16)	C12	C13	1.388(2)
O8	N6	1.2180(16)	C13	C14	1.386(2)
O9	N7	1.2748(17)	C14	C15	1.3884(18)
O10	N7	1.2792(17)	C15	C16	1.4998(19)
O11	N7	1.2146(17)	C17	C18	1.522(2)
N1	C1	1.482(2)	C18	C19	1.527(3)
N1	C4	1.480(2)	C19	C20	1.526(2)

Table S4 The bond angles for the Nd(Pyr-BPyDA)$(NO_3)_3$ (complex **2**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Nd1	O2	154.73(4)	N5	O3	Nd1	95.57(8)
O1	Nd1	O3	80.84(4)	N5	O4	Nd1	96.84(9)
O1	Nd1	O4	82.30(4)	N6	O6	Nd1	97.56(8)
O1	Nd1	O6	106.48(4)	N6	O7	Nd1	96.70(8)
O1	Nd1	O7	71.86(4)	N7	O9	Nd1	95.92(8)
O1	Nd1	O9	132.06(4)	N7	O10	Nd1	95.37(8)
O1	Nd1	O10	87.38(4)	C4	N1	C1	110.95(11)
O1	Nd1	N2	61.22(3)	C5	N1	C1	118.32(12)
O1	Nd1	N3	121.74(4)	C5	N1	C4	130.71(13)

O1	Nd1	N5	83.66(4)	C6	N2	Nd1	118.77(9)
O1	Nd1	N7	108.59(4)	C10	N2	Nd1	121.61(9)
O2	Nd1	O3	77.39(4)	C10	N2	C6	119.19(12)
O2	Nd1	O4	73.89(4)	C11	N3	Nd1	124.55(8)
O2	Nd1	O6	71.81(4)	C15	N3	Nd1	116.35(8)
O2	Nd1	O7	118.28(3)	C15	N3	C11	118.98(11)
O2	Nd1	O9	72.38(3)	C16	N4	C17	128.18(12)
O2	Nd1	O10	117.52(3)	C16	N4	C20	119.66(11)
O2	Nd1	N2	121.74(3)	C17	N4	C20	111.42(11)
O2	Nd1	N3	63.63(3)	O3	N5	Nd1	59.35(7)
O2	Nd1	N5	71.19(4)	O4	N5	Nd1	58.15(7)
O2	Nd1	N7	96.58(4)	O4	N5	O3	116.36(13)
O3	Nd1	N2	70.99(4)	O5	N5	Nd1	168.85(12)
O3	Nd1	N3	73.68(4)	O5	N5	O3	121.95(15)
O3	Nd1	N5	25.08(4)	O5	N5	O4	121.68(15)
O3	Nd1	N7	153.56(4)	O6	N6	Nd1	57.74(7)
O4	Nd1	O3	49.76(4)	O6	N6	O7	116.01(12)
O4	Nd1	O6	66.48(4)	O7	N6	Nd1	58.37(7)
O4	Nd1	O7	95.79(4)	O8	N6	Nd1	177.30(10)
O4	Nd1	N2	114.58(4)	O8	N6	O6	121.86(13)
O4	Nd1	N3	114.89(4)	O8	N6	O7	122.13(13)
O4	Nd1	N5	25.00(4)	O9	N7	Nd1	58.57(7)
O4	Nd1	N7	153.53(4)	O9	N7	O10	115.96(12)
O6	Nd1	O3	114.46(4)	O10	N7	Nd1	59.00(7)
O6	Nd1	O7	49.61(3)	O11	N7	Nd1	166.37(12)
O6	Nd1	N2	166.43(4)	O11	N7	O9	121.95(14)

O6	Nd1	N3	131.71(4)	O11	N7	O10	122.07(14)
O6	Nd1	N5	89.67(4)	N1	C1	C2	102.85(13)
O6	Nd1	N7	87.14(4)	C3	C2	C1	102.83(13)
O7	Nd1	O3	139.01(4)	C2	C3	C4	103.70(13)
O7	Nd1	N2	117.78(3)	N1	C4	C3	103.37(13)
O7	Nd1	N3	147.09(4)	O1	C5	N1	119.07(13)
O7	Nd1	N5	119.47(4)	O1	C5	C6	117.16(11)
O7	Nd1	N7	66.53(4)	N1	C5	C6	123.70(13)
O9	Nd1	O3	144.96(4)	N2	C6	C5	111.75(11)
O9	Nd1	O4	132.89(4)	N2	C6	C7	121.71(12)
O9	Nd1	O6	72.31(4)	C7	C6	C5	126.49(12)
O9	Nd1	O7	72.97(4)	C8	C7	C6	118.68(13)
O9	Nd1	O10	50.66(4)	C9	C8	C7	119.76(14)
O9	Nd1	N2	110.89(4)	C8	C9	C10	118.55(13)
O9	Nd1	N3	77.24(4)	N2	C10	C9	122.09(12)
O9	Nd1	N5	142.87(4)	N2	C10	C11	116.09(12)
O9	Nd1	N7	25.51(4)	C9	C10	C11	121.82(12)
O10	Nd1	O3	138.33(4)	N3	C11	C10	116.04(11)
O10	Nd1	O4	165.50(4)	N3	C11	C12	121.24(12)
O10	Nd1	O6	107.21(4)	C12	C11	C10	122.70(12)
O10	Nd1	O7	71.21(4)	C13	C12	C11	119.21(13)
O10	Nd1	N2	68.32(4)	C14	C13	C12	119.42(12)
O10	Nd1	N3	79.25(4)	C13	C14	C15	118.14(12)
O10	Nd1	N5	162.59(4)	N3	C15	C14	122.98(13)
O10	Nd1	N7	25.63(4)	N3	C15	C16	111.98(11)
N2	Nd1	N5	94.28(4)	C14	C15	C16	124.86(12)

N2	Nd1	N7	91.54(4)	O2	C16	N4	121.49(12)
N3	Nd1	N2	61.13(3)	O2	C16	C15	116.69(11)
N3	Nd1	N5	92.83(4)	N4	C16	C15	121.81(11)
N3	Nd1	N7	80.56(4)	N4	C17	C18	102.61(13)
N7	Nd1	N5	167.75(4)	C17	C18	C19	103.28(13)
C5	O1	Nd1	129.41(9)	C20	C19	C18	103.80(13)
C16	O2	Nd1	114.65(8)	N4	C20	C19	103.90(12)

Table S5 The bond distances for the Er(Pyr-DAPhen)$(NO_3)_3$ (complex **3**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Er1	O1	2.3541(14)	N3	C13	1.327(2)
Er1	O2	2.3766(13)	N3	C14	1.487(3)
Er1	O3	2.4264(15)	N3	C17	1.483(3)
Er1	O4	2.4193(15)	N4	C18	1.312(2)
Er1	O6	2.6555(17)	N4	C20	1.477(3)
Er1	O7	2.4343(15)	N4	C23	1.475(3)
Er1	O9	2.4324(15)	C1	C2	1.373(3)
Er1	O10	2.4214(15)	C1	C5	1.401(3)
Er1	N1	2.5683(16)	C2	C3	1.405(3)
Er1	N2	2.5100(15)	C3	C13	1.507(3)
Er1	N5	2.8439(18)	C4	C5	1.409(3)
Er1	N7	2.8542(19)	C4	C9	1.440(3)
O1	C13	1.257(2)	C5	C6	1.440(3)
O2	C18	1.257(2)	C6	C7	1.349(3)
O3	N5	1.280(2)	C7	C8	1.437(3)
O4	N5	1.269(2)	C8	C9	1.410(3)

O5	N5	1.218(2)	C8	C12	1.411(3)
O6	N6	1.250(2)	C10	C11	1.401(3)
O7	N6	1.275(2)	C10	C18	1.502(3)
O8	N6	1.230(2)	C11	C12	1.374(3)
O9	N7	1.271(2)	C14	C15	1.523(3)
O10	N7	1.281(2)	C15	C16	1.517(3)
O11	N7	1.215(2)	C16	C17	1.521(3)
N1	C3	1.335(2)	C20	C21	1.521(3)
N1	C4	1.352(2)	C21	C22	1.530(3)
N2	C9	1.347(2)	C22	C23	1.522(3)
N2	C10	1.337(2)			

Table S6 The bond angles for the Er(Pyr-DAPhen)$(NO_3)_3$ (complex **3**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Er1	O2	155.56(5)	N6	O6	Er1	91.89(12)
O1	Er1	O3	83.72(5)	N6	O7	Er1	101.90(11)
O1	Er1	O4	74.44(5)	N7	O9	Er1	95.71(12)
O1	Er1	O6	107.59(5)	N7	O10	Er1	95.93(11)
O1	Er1	O7	68.84(5)	C3	N1	Er1	121.29(12)
O1	Er1	O9	130.90(5)	C3	N1	C4	118.60(16)
O1	Er1	O10	85.46(5)	C4	N1	Er1	120.09(12)
O1	Er1	N1	62.04(5)	C9	N2	Er1	122.43(12)
O1	Er1	N2	124.91(5)	C10	N2	Er1	118.78(12)
O1	Er1	N5	79.18(5)	C10	N2	C9	118.51(16)
O1	Er1	N7	107.94(5)	C13	N3	C14	130.53(17)

O2	Er1	O3	77.78(5)	C13	N3	C17	118.98(17)
O2	Er1	O4	81.66(5)	C17	N3	C14	110.46(15)
O2	Er1	O6	65.80(5)	C18	N4	C20	119.01(16)
O2	Er1	O7	114.02(5)	C18	N4	C23	128.69(17)
O2	Er1	O9	70.75(5)	C23	N4	C20	111.43(16)
O2	Er1	O10	118.95(5)	O3	N5	Er1	58.18(10)
O2	Er1	N1	124.59(5)	O4	N5	Er1	57.81(10)
O2	Er1	N2	64.13(5)	O4	N5	O3	115.77(17)
O2	Er1	N5	77.12(5)	O5	N5	Er1	175.14(14)
O2	Er1	N7	95.55(5)	O5	N5	O3	122.08(19)
O3	Er1	O6	111.69(5)	O5	N5	O4	122.15(18)
O3	Er1	O7	134.12(5)	O6	N6	O7	116.52(17)
O3	Er1	O9	144.41(5)	O8	N6	O6	123.1(2)
O3	Er1	N1	71.06(5)	O8	N6	O7	120.41(18)
O3	Er1	N2	72.59(5)	O9	N7	Er1	57.99(10)
O3	Er1	N5	26.63(5)	O9	N7	O10	115.17(17)
O3	Er1	N7	153.69(5)	O10	N7	Er1	57.55(10)
O4	Er1	O3	52.92(5)	O11	N7	Er1	173.44(15)
O4	Er1	O6	65.73(5)	O11	N7	O9	122.4(2)
O4	Er1	O7	83.83(5)	O11	N7	O10	122.41(19)
O4	Er1	O9	134.40(5)	C2	C1	C5	119.94(19)
O4	Er1	O10	155.15(5)	C1	C2	C3	119.53(19)
O4	Er1	N1	111.29(5)	N1	C3	C2	121.77(18)
O4	Er1	N2	120.68(5)	N1	C3	C13	110.57(16)
O4	Er1	N5	26.36(5)	C2	C3	C13	127.55(18)
O4	Er1	N7	152.13(5)	N1	C4	C5	123.32(17)

O6	Er1	N5	87.88(5)	N1	C4	C9	117.05(16)
O6	Er1	N7	87.72(5)	C5	C4	C9	119.52(17)
O7	Er1	O6	49.68(5)	C1	C5	C4	116.79(17)
O7	Er1	N1	120.70(5)	C1	C5	C6	123.95(18)
O7	Er1	N2	153.25(5)	C4	C5	C6	119.25(18)
O7	Er1	N5	109.48(5)	C7	C6	C5	120.96(18)
O7	Er1	N7	71.94(5)	C6	C7	C8	121.21(18)
O9	Er1	O6	69.98(5)	C9	C8	C7	119.05(18)
O9	Er1	O7	75.70(5)	C9	C8	C12	116.96(18)
O9	Er1	N1	114.23(5)	C12	C8	C7	123.94(17)
O9	Er1	N2	78.92(5)	N2	C9	C4	117.03(16)
O9	Er1	N5	146.28(5)	N2	C9	C8	123.07(17)
O9	Er1	N7	26.30(5)	C8	C9	C4	119.76(17)
O10	Er1	O3	140.12(5)	N2	C10	C11	122.54(18)
O10	Er1	O6	108.18(5)	N2	C10	C18	110.70(15)
O10	Er1	O7	75.25(5)	C11	C10	C18	126.53(17)
O10	Er1	O9	52.71(5)	C12	C11	C10	119.03(18)
O10	Er1	N1	69.96(5)	C11	C12	C8	119.80(17)
O10	Er1	N2	82.76(5)	O1	C13	N3	119.76(17)
O10	Er1	N5	160.60(5)	O1	C13	C3	116.65(16)
O10	Er1	N7	26.52(5)	N3	C13	C3	123.48(17)
N1	Er1	O6	169.34(5)	N3	C14	C15	103.35(17)
N1	Er1	N5	92.22(5)	C16	C15	C14	103.44(18)
N1	Er1	N7	93.21(5)	C15	C16	C17	102.55(18)
N2	Er1	O6	127.24(5)	N3	C17	C16	103.20(17)
N2	Er1	N1	63.35(5)	O2	C18	N4	121.61(18)

N2	Er1	N5	96.32(5)	O2	C18	C10	116.41(17)
N2	Er1	N7	81.57(5)	N4	C18	C10	121.97(17)
N5	Er1	N7	172.52(5)	N4	C20	C21	104.22(17)
C13	O1	Er1	129.15(12)	C20	C21	C22	104.23(18)
C18	O2	Er1	118.73(12)	C23	C22	C21	103.23(18)
N5	O3	Er1	95.20(11)	N4	C23	C22	102.95(18)
N5	O4	Er1	95.82(11)				

Table S7 The bond distances for the La(Pyr-DAPhen)$(NO_3)_3CH_3OH$ (complex **4**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
La1	O1	2.4962(14)	N4	C19	1.481(3)
La1	O2	2.4954(15)	N4	C22	1.481(3)
La1	O6	2.6131(18)	C1	C2	1.367(3)
La1	O7	2.6647(16)	C1	C5	1.397(3)
La1	O9	2.6812(16)	C2	C3	1.405(3)
La1	O10	2.6966(16)	C3	C13	1.502(3)
La1	O12	2.5714(18)	C4	C5	1.415(3)
La1	N2	2.7583(17)	C4	C9	1.450(3)
La1	O3	2.606(3)	C5	C6	1.433(3)
La1	O4	2.701(3)	C6	C7	1.342(3)
La1	O3A	2.719(13)	C7	C8	1.440(3)
La1	O4A	2.737(14)	C8	C9	1.416(3)
O1	C13	1.246(2)	C8	C12	1.396(3)
O2	C18	1.250(2)	C10	C11	1.403(3)
O6	N6	1.264(2)	C10	C18	1.516(3)
O7	N6	1.266(3)	C11	C12	1.374(3)

O8	N6	1.223(3)	C14	C15	1.516(4)
O9	N7	1.262(2)	C15	C16	1.493(4)
O10	N7	1.278(2)	C16	C17	1.529(3)
O11	N7	1.225(2)	C19	C20	1.533(4)
O12	C23	1.392(3)	C20	C21	1.487(4)
N1	C3	1.336(3)	C21	C22	1.500(4)
N1	C4	1.349(3)	O3	N5	1.257(4)
N2	C9	1.351(2)	O4	N5	1.260(4)
N2	C10	1.340(3)	O5	N5	1.227(4)
N3	C13	1.328(3)	O3A	N5A	1.274(13)
N3	C14	1.484(3)	O4A	N5A	1.259(14)
N3	C17	1.476(3)	O5A	N5A	1.248(13)
N4	C18	1.325(3)			

Table S8 The bond angles for the La(Pyr-DAPhen)$(NO_3)_3CH_3OH$ (complex **4**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	La1	O6	68.30(6)	C3	N1	La1	119.07(13)
O1	La1	O7	109.73(5)	C3	N1	C4	118.67(17)
O1	La1	O9	66.69(5)	C4	N1	La1	121.04(12)
O1	La1	O10	110.49(5)	C9	N2	La1	121.52(13)
O1	La1	O12	85.14(6)	C10	N2	La1	119.24(13)
O1	La1	N2	118.17(5)	C10	N2	C9	118.61(17)
O1	La1	O3	120.52(10)	C13	N3	C14	129.46(19)
O1	La1	O4	77.08(9)	C13	N3	C17	118.62(18)
O1	La1	O3A	110.0(4)	C17	N3	C14	111.35(17)

O1	La1	O4A	69.4(4)	C18	N4	C19	129.61(19)
O2	La1	O1	172.27(6)	C18	N4	C22	118.79(18)
O2	La1	O6	118.42(6)	C22	N4	C19	109.93(17)
O2	La1	O7	74.92(5)	O6	N6	La1	57.43(11)
O2	La1	O9	110.93(5)	O6	N6	O7	116.90(18)
O2	La1	O10	65.23(5)	O7	N6	La1	59.79(11)
O2	La1	O12	87.13(6)	O8	N6	La1	173.56(17)
O2	La1	N2	59.42(5)	O8	N6	O6	121.5(2)
O2	La1	O3	66.63(10)	O8	N6	O7	121.6(2)
O2	La1	O4	108.41(10)	O9	N7	O10	116.54(18)
O2	La1	O3A	77.2(4)	O11	N7	O9	122.4(2)
O2	La1	O4A	116.2(4)	O11	N7	O10	121.1(2)
O6	La1	O7	48.21(5)	C2	C1	C5	119.9(2)
O6	La1	O9	70.77(6)	C1	C2	C3	119.0(2)
O6	La1	O10	102.82(5)	N1	C3	C2	122.36(19)
O6	La1	N2	142.50(6)	N1	C3	C13	112.17(16)
O6	La1	O4	69.57(11)	C2	C3	C13	125.35(19)
O6	La1	O3A	65.2(5)	N1	C4	C5	122.23(19)
O6	La1	O4A	65.9(5)	N1	C4	C9	118.21(17)
O7	La1	O9	66.80(5)	C5	C4	C9	119.55(18)
O7	La1	O10	65.98(5)	C1	C5	C4	117.7(2)
O7	La1	N2	129.75(5)	C1	C5	C6	122.6(2)
O7	La1	O4	101.83(11)	C4	C5	C6	119.6(2)
O7	La1	O3A	71.3(4)	C7	C6	C5	121.1(2)
O7	La1	O4A	102.7(5)	C6	C7	C8	121.2(2)
O9	La1	O10	47.36(5)	C9	C8	C7	119.8(2)

O9	La1	N2	146.73(6)	C12	C8	C7	123.1(2)
O9	La1	O4	133.68(10)	C12	C8	C9	117.1(2)
O9	La1	O3A	132.7(5)	N2	C9	C4	118.61(17)
O9	La1	O4A	126.7(5)	N2	C9	C8	122.67(19)
O10	La1	N2	107.85(5)	C8	C9	C4	118.71(18)
O10	La1	O4	167.03(11)	N2	C10	C11	122.17(19)
O10	La1	O3A	128.5(4)	N2	C10	C18	112.39(17)
O10	La1	O4A	168.3(5)	C11	C10	C18	125.42(19)
O12	La1	O6	143.05(6)	C12	C11	C10	118.9(2)
O12	La1	O7	127.81(5)	C11	C12	C8	120.3(2)
O12	La1	O9	75.38(5)	O1	C13	N3	119.92(19)
O12	La1	O10	62.00(5)	O1	C13	C3	117.77(18)
O12	La1	N2	72.49(6)	N3	C13	C3	122.28(18)
O12	La1	O3	144.74(11)	N3	C14	C15	102.7(2)
O12	La1	O4	130.35(11)	C16	C15	C14	103.5(2)
O12	La1	O3A	151.3(5)	C15	C16	C17	103.8(2)
O12	La1	O4A	128.9(5)	N3	C17	C16	102.25(19)
O3	La1	O6	72.19(11)	O2	C18	N4	120.44(19)
O3	La1	O7	69.39(11)	O2	C18	C10	116.99(18)
O3	La1	O9	134.79(11)	N4	C18	C10	122.55(19)
O3	La1	O10	120.43(9)	N4	C19	C20	103.2(2)
O3	La1	N2	73.89(11)	C21	C20	C19	105.6(2)
O3	La1	O4	47.91(9)	C20	C21	C22	103.1(2)
O4	La1	N2	76.02(11)	N4	C22	C21	103.7(2)
O3A	La1	N2	78.8(5)	N5	O3	La1	99.3(2)
O3A	La1	O4A	45.0(4)	N5	O4	La1	94.6(2)

O4A	La1	N2	81.5(5)	O3	N5	O4	117.9(3)
C13	O1	La1	130.11(14)	O5	N5	O3	121.3(3)
C18	O2	La1	130.33(14)	O5	N5	O4	120.9(3)
N6	O6	La1	98.51(13)	N5A	O3A	La1	102.0(9)
N6	O7	La1	95.97(12)	N5A	O4A	La1	101.5(10)
N7	O9	La1	98.60(12)	O4A	N5A	O3A	111.2(13)
N7	O10	La1	97.41(12)	O5A	N5A	O3A	125.5(15)
C23	O12	La1	136.08(16)	O5A	N5A	O4A	123.3(14)