Electronic Supplementary Material for CrystEngComm

Syntheses, structures, photoluminescence, and magnetic properties of nanoporous 3D lanthanide coordination polymers with 4,4′-biphenyldicarboxylate ligand

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Supplementary Information

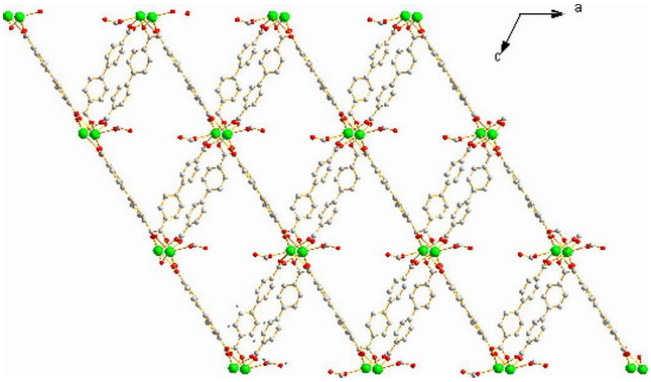


Fig. S1 The structure of **1**, 1-D inorganic columns are formed which are then cross-linked into a 3-D network.

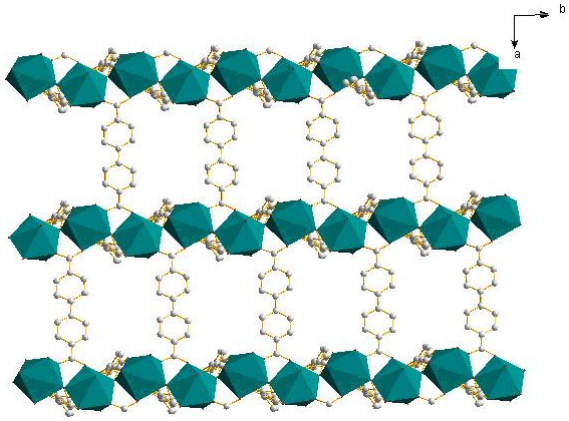


Fig. S2 Polyhedral representation of **1** with quadrate grids, {EuO_8} are depicted as dodecahedron

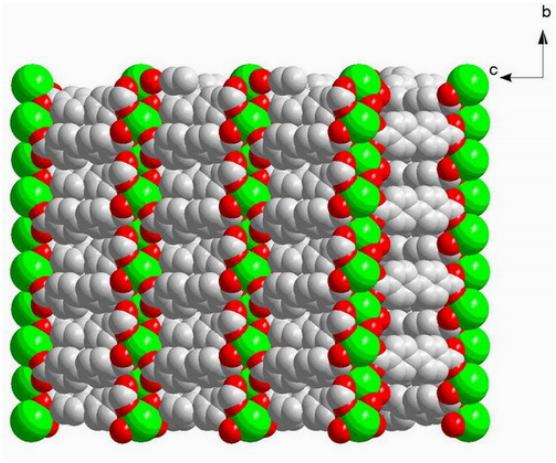
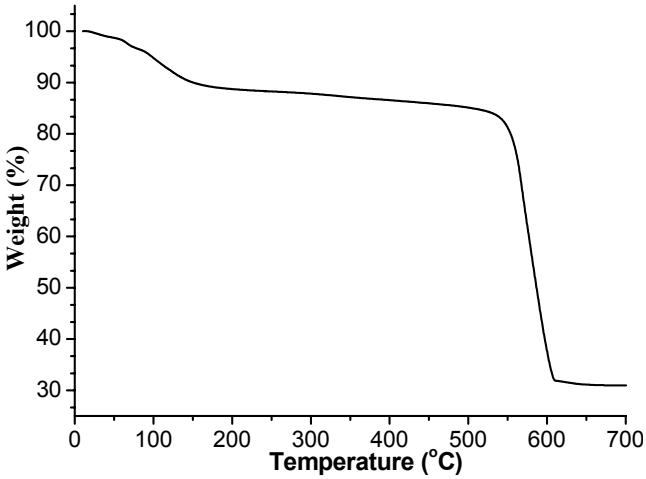
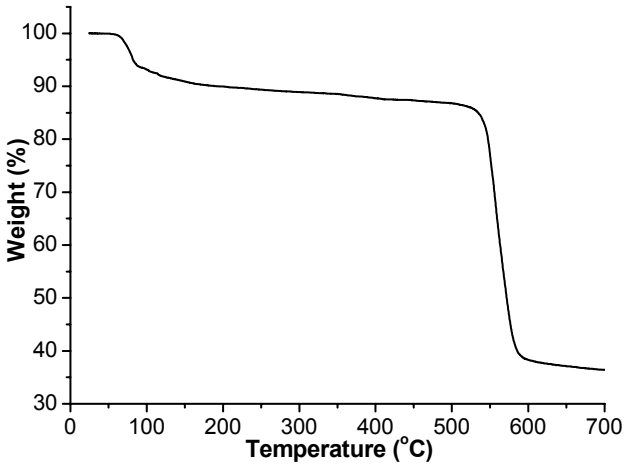


Fig. S3 Impenetrable walls of **1**, [100] direction,





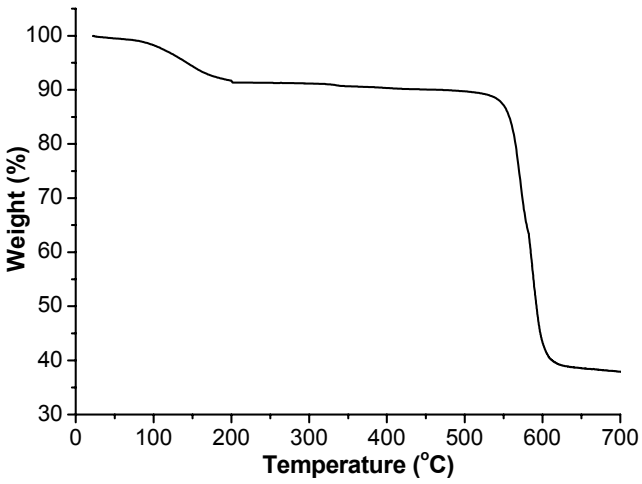


Fig. S4 TGA curves of **2**-**4**.

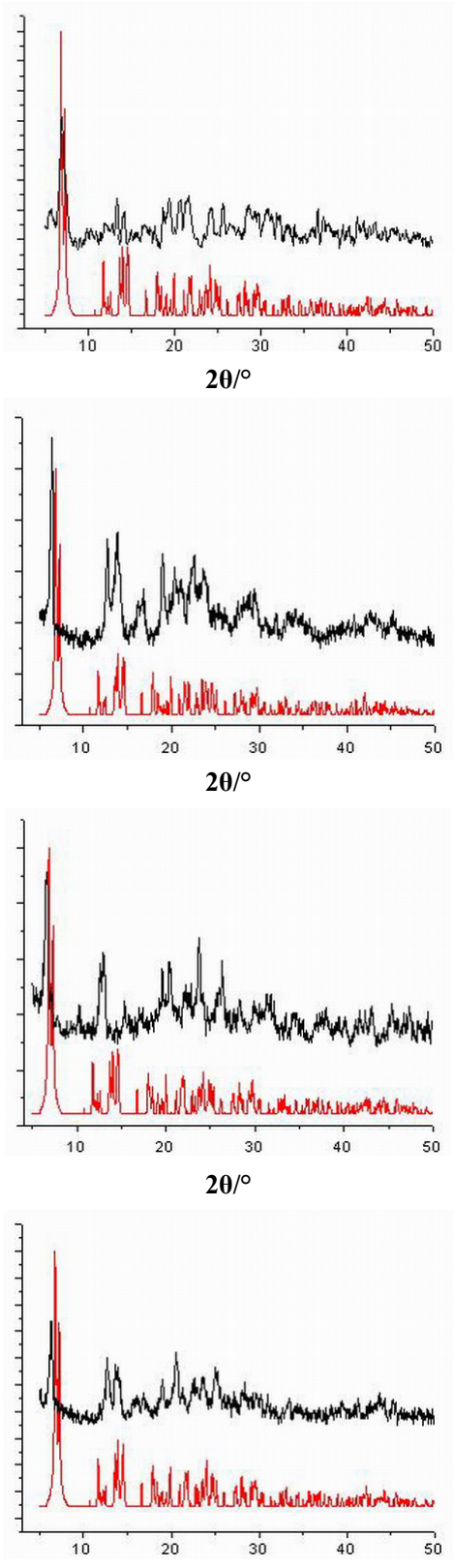


Fig. S5 Experimental (black) and simulated (red) X-ray powder diffraction patterns of **1**-**4**.

Selected bond lengths [Å] and angles [°] for compounds **1-6**

Table S1

Bond lengths [Å]		Bond angles [°]	
Eu(1)-O(1)	2.295(10)	Eu(1)#7-O(3)-Eu(1)#4	122.8(3)
Eu(1)-O(6)#1	2.319(11)	O(1)-Eu(1)-O(6)#1	135.7(4)
Eu(1)-O(5)	2.367(8)	O(1)-Eu(1)-O(5)	80.1(4)
Eu(1)-O(2)#1	2.373(10)	O(6)#1-Eu(1)-O(5)	140.9(4)
Eu(1)-O(7)	2.420(13)	O(1)-Eu(1)-O(2)#1	141.2(4)
Eu(1)-O(3)#2	2.431(9)	O(6)#1-Eu(1)-O(2)#1	76.8(4)
Eu(1)-O(4)#3	2.452(9)	O(5)-Eu(1)-O(2)#1	79.6(4)
Eu(1)-O(3)#3	2.699(9)	O(1)-Eu(1)-O(7)	71.2(4)
C(1)-O(1)	1.234(17)	O(6)#1-Eu(1)-O(7)	71.6(5)
C(1)-O(2)	1.274(16)	O(5)-Eu(1)-O(7)	120.9(4)
C(14)-O(3)	1.242(15)	O(2)#1-Eu(1)-O(7)	147.2(4)
C(14)-O(4)	1.266(17)	O(1)-Eu(1)-O(3)#2	115.7(4)
C(15)-O(5)	1.241(16)	O(6)#1-Eu(1)-O(3)#2	75.9(4)
C(15)-O(6)	1.260(18)	O(5)-Eu(1)-O(3)#2	73.1(3)
C(22)-O(7)	1.253(9)	O(2)#1-Eu(1)-O(3)#2	89.3(3)
C(22)-O(8)	1.305(5)	O(7)-Eu(1)-O(3)#2	74.7(4)
O(2)-Eu(1)#6	2.373(10)	O(1)-Eu(1)-O(4)#3	86.4(4)
O(3)-Eu(1)#7	2.431(9)	O(6)#1-Eu(1)-O(4)#3	73.4(4)
O(3)-Eu(1)#4	2.699(9)	O(5)-Eu(1)-O(4)#3	134.6(3)
O(4)-Eu(1)#4	2.452(9)	O(2)#1-Eu(1)-O(4)#3	84.8(3)
O(6)-Eu(1)#6	2.319(11)	O(7)-Eu(1)-O(4)#3	94.5(4)
		O(3)#2-Eu(1)-O(4)#3	149.3(3)
		O(1)-Eu(1)-O(3)#3	75.2(3)
		O(6)#1-Eu(1)-O(3)#3	115.6(4)
		O(5)-Eu(1)-O(3)#3	84.2(3)
		O(2)#1-Eu(1)-O(3)#3	70.0(3)
		O(7)-Eu(1)-O(3)#3	132.6(4)
		O(3)#2-Eu(1)-O(3)#3	151.83(6)
		O(4)#3-Eu(1)-O(3)#3	50.4(3)
		O(1)-C(1)-O(2)	125.4(12)
		O(3)-C(14)-O(4)	123.2(12)
		O(5)-C(15)-O(6)	124.1(12)
		O(5)-C(15)-C(16)	119.7(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z #2 -x+1/2,y+1/2,-z+1 #3 x,y,z-1 #4 x,y,z+1 #5 -x+1,y,-z+1

#6 -x+1/2,y-1/2,-z #7 -x+1/2,y-1/2,-z+1

Table S2

Bond lengths [Å]		Bond angles [°]	
Sm(1)-O(2)#1	2.331(8)	Sm(1)#7-O(3)-Sm(1)#5	123.7(3)
Sm(1)-O(6)#2	2.353(8)	O(2)#1-Sm(1)-O(6)#2	136.2(3)
Sm(1)-O(1)	2.379(7)	O(2)#1-Sm(1)-O(1)	142.4(3)
Sm(1)-O(5)	2.388(7)	O(6)#2-Sm(1)-O(1)	75.2(3)
Sm(1)-O(3)#3	2.431(8)	O(2)#1-Sm(1)-O(5)	80.7(3)
Sm(1)-O(7)	2.450(11)	O(6)#2-Sm(1)-O(5)	139.9(3)
Sm(1)-O(4)#4	2.464(7)	O(1)-Sm(1)-O(5)	80.1(3)
Sm(1)-O(3)#4	2.699(8)	O(2)#1-Sm(1)-O(3)#3	116.0(3)
C(1)-O(2)	1.227(14)	O(6)#2-Sm(1)-O(3)#3	75.6(3)
C(1)-O(1)	1.246(13)	O(1)-Sm(1)-O(3)#3	88.2(3)
C(14)-O(4)	1.234(13)	O(5)-Sm(1)-O(3)#3	72.4(3)
C(14)-O(3)	1.281(12)	O(2)#1-Sm(1)-O(7)	71.4(3)
C(15)-O(6)	1.235(14)	O(6)#2-Sm(1)-O(7)	72.1(4)
C(15)-O(5)	1.248(13)	O(1)-Sm(1)-O(7)	145.8(3)
C(22)-O(7)	1.248(9)	O(5)-Sm(1)-O(7)	120.1(3)
C(22)-O(8)	1.303(5)	O(3)#3-Sm(1)-O(7)	74.3(3)
O(2)-Sm(1)#2	2.331(8)	O(2)#1-Sm(1)-O(4)#4	86.6(3)
O(3)-Sm(1)#7	2.431(8)	O(6)#2-Sm(1)-O(4)#4	73.5(3)
O(3)-Sm(1)#5	2.699(8)	O(1)-Sm(1)-O(4)#4	84.6(3)
O(4)-Sm(1)#5	2.464(7)	O(5)-Sm(1)-O(4)#4	135.0(3)
O(6)-Sm(1)#1	2.353(8)	O(3)#3-Sm(1)-O(4)#4	149.1(3)
		O(7)-Sm(1)-O(4)#4	95.5(3)
		O(2)#1-Sm(1)-O(3)#4	75.1(3)
		O(6)#2-Sm(1)-O(3)#4	115.7(3)
		O(1)-Sm(1)-O(3)#4	71.2(3)
		O(5)-Sm(1)-O(3)#4	84.7(2)
		O(3)#3-Sm(1)-O(3)#4	151.65(5)
		O(7)-Sm(1)-O(3)#4	133.1(3)
		O(4)#4-Sm(1)-O(3)#4	50.4(2)
		O(2)-C(1)-O(1)	124.8(10)
		O(4)-C(14)-O(3)	122.7(9)
		O(6)-C(15)-O(5)	126.6(9)
		O(7)-C(22)-O(8)	121.9(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z #2 -x+1/2,y+1/2,-z #3 x,y,z-1 #4 -x+1/2,y-1/2,-z+1 #5 -x+1/2,y+1/2,-z+1

#6 -x,y,-z-1 #7 x,y,z+1

Table S3

Bond lengths [Å]		Bond angles [°]	
La(1)-O(3)#1	2.422(8)	La(1)#2-O(1)-La(1)	122.3(3)
La(1)-O(5)	2.420(9)	O(3)#1-La(1)-O(5)	137.4(3)
La(1)-O(6)#2	2.461(7)	O(3)#1-La(1)-O(6)#2	80.1(3)
La(1)-O(4)#3	2.476(7)	O(5)-La(1)-O(6)#2	138.7(3)
La(1)-O(1)#4	2.514(8)	O(3)#1-La(1)-O(4)#3	142.2(3)
La(1)-O(7)	2.522(10)	O(5)-La(1)-O(4)#3	73.5(3)
La(1)-O(1)	2.748(8)	O(6)#2-La(1)-O(4)#3	82.8(3)
C(1)-O(2)	1.256(14)	O(3)#1-La(1)-O(1)#4	115.6(3)
C(1)-O(1)	1.264(13)	O(5)-La(1)-O(1)#4	75.2(3)
C(14)-O(4)	1.239(14)	O(6)#2-La(1)-O(1)#4	71.3(3)
C(14)-O(3)	1.274(14)	O(4)#3-La(1)-O(1)#4	90.0(3)
C(15)-O(5)	1.230(14)	O(3)#1-La(1)-O(7)	72.7(3)
C(15)-O(6)	1.269(14)	O(5)-La(1)-O(7)	71.8(4)
C(22)-O(7)	1.247(9)	O(6)#2-La(1)-O(7)	119.4(3)
C(22)-O(8)	1.301(5)	O(4)#3-La(1)-O(7)	144.3(3)
O(1)-La(1)#2	2.514(8)	O(1)#4-La(1)-O(7)	73.6(3)
O(3)-La(1)#6	2.422(8)	O(3)#1-La(1)-O(1)	75.8(3)
O(4)-La(1)#7	2.476(7)	O(5)-La(1)-O(1)	115.3(3)
O(6)-La(1)#4	2.461(7)	O(6)#2-La(1)-O(1)	86.0(2)
		O(4)#3-La(1)-O(1)	69.6(3)
		O(1)#4-La(1)-O(1)	151.45(5)
		O(7)-La(1)-O(1)	134.3(3)
		O(2)-C(1)-O(1)	123.1(9)
		O(4)-C(14)-O(3)	126.0(9)
		O(5)-C(15)-O(6)	123.6(9)
		O(7)-C(22)-O(8)	131.7(17)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 -x+1/2,y-1/2,-z #3 -x+1/2,y+1/2,-z+1 #4 -x+1/2,y+1/2,-z #5 -x+1,y,-z+1 #6 x,y,z+1 #7 -x+1/2,y-1/2,-z+1

Table S4

Bond lengths [Å]		Bond angles [°]	
Ce(1)-O(5)	2.393(9)	O(5)-Ce(1)-O(3)#1	136.8(3)
Ce(1)-O(3)#1	2.394(8)	O(5)-Ce(1)-O(6)#2	139.3(3)
Ce(1)-O(6)#2	2.444(7)	O(3)#1-Ce(1)-O(6)#2	80.4(3)
Ce(1)-O(4)#3	2.445(7)	O(5)-Ce(1)-O(4)#3	75.1(3)
Ce(1)-O(2)#4	2.495(7)	O(3)#1-Ce(1)-O(4)#3	141.7(3)

Ce(1)-O(7)	2.504(10)	O(6)#2-Ce(1)-O(4)#3	80.8(3)
Ce(1)-O(1)	2.546(7)	O(5)-Ce(1)-O(2)#4	75.4(3)
Ce(1)-O(2)	2.746(7)	O(3)#1-Ce(1)-O(2)#4	115.7(3)
C(1)-O(1)	1.247(13)	O(6)#2-Ce(1)-O(2)#4	72.0(3)
C(1)-O(2)	1.263(12)	O(4)#3-Ce(1)-O(2)#4	89.4(3)
C(14)-O(3)	1.237(14)	O(5)-Ce(1)-O(7)	72.0(4)
C(14)-O(4)	1.252(13)	O(3)#1-Ce(1)-O(7)	71.6(3)
C(15)-O(5)	1.223(14)	O(6)#2-Ce(1)-O(7)	120.3(4)
C(15)-O(6)	1.243(14)	O(4)#3-Ce(1)-O(7)	146.0(3)
C(22)-O(7)	1.239(9)	O(2)#4-Ce(1)-O(7)	74.6(3)
C(22)-O(8)	1.299(5)	O(5)-Ce(1)-O(1)	75.3(3)
O(2)-Ce(1)#2	2.495(7)	O(3)#1-Ce(1)-O(1)	85.9(3)
O(3)-Ce(1)#6	2.394(8)	O(6)#2-Ce(1)-O(1)	134.1(3)
O(4)-Ce(1)#7	2.445(7)	O(4)#3-Ce(1)-O(1)	83.7(3)
O(6)-Ce(1)#4	2.444(7)	O(2)#4-Ce(1)-O(1)	150.7(3)
		O(7)-Ce(1)-O(1)	95.7(3)
		O(5)-Ce(1)-O(2)	115.6(3)
		O(3)#1-Ce(1)-O(2)	75.4(2)
		O(6)#2-Ce(1)-O(2)	85.3(3)
		O(4)#3-Ce(1)-O(2)	70.0(3)
		O(2)#4-Ce(1)-O(2)	151.66(4)
		O(7)-Ce(1)-O(2)	133.0(3)
		O(1)-Ce(1)-O(2)	48.9(2)
		Ce(1)#2-O(2)-Ce(1)	121.7(3)
		O(1)-C(1)-O(2)	122.2(9)
		O(3)-C(14)-O(4)	124.8(9)
		O(5)-C(15)-O(6)	123.8(10)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 -x+1/2,y+1/2,-z+1 #3 -x+1/2,y-1/2,-z #4 -x+1/2,y-1/2,-z+1 #5 -x,y,-z

#6 x,y,z-1 #7 -x+1/2,y+1/2,-z

Table S5

Bond lengths [Å]		Bond angles [°]	
Gd(1)-O(6)#1	2.299(14)	O(6)#1-Gd(1)-O(1)	136.3(5)
Gd(1)-O(1)	2.323(12)	O(6)#1-Gd(1)-O(2)#1	75.5(5)
Gd(1)-O(2)#1	2.328(12)	O(1)-Gd(1)-O(2)#1	141.4(4)
Gd(1)-O(5)	2.336(12)	O(6)#1-Gd(1)-O(5)	141.0(5)
Gd(1)-O(3)#2	2.377(12)	O(1)-Gd(1)-O(5)	80.0(5)
Gd(1)-O(7)	2.380(15)	O(2)#1-Gd(1)-O(5)	80.0(5)

Gd(1)-O(4)#3	2.431(11)	O(6)#1-Gd(1)-O(3)#2	76.5(4)
Gd(1)-O(3)#3	2.716(12)	O(1)-Gd(1)-O(3)#2	115.5(5)
C(1)-O(1)	1.21(2)	O(2)#1-Gd(1)-O(3)#2	89.6(4)
C(1)-O(2)	1.29(2)	O(5)-Gd(1)-O(3)#2	73.4(4)
C(14)-O(4)	1.22(2)	O(6)#1-Gd(1)-O(7)	71.4(5)
C(14)-O(3)	1.28(2)	O(1)-Gd(1)-O(7)	72.0(5)
C(15)-O(5)	1.24(2)	O(2)#1-Gd(1)-O(7)	145.9(5)
C(15)-O(6)	1.28(2)	O(5)-Gd(1)-O(7)	122.2(5)
C(22)-O(7)	1.248(10)	O(3)#2-Gd(1)-O(7)	74.8(4)
C(22)-O(8)	1.301(5)	O(6)#1-Gd(1)-O(4)#3	73.6(5)
C(22)-H(22)	0.9300	O(1)-Gd(1)-O(4)#3	86.2(5)
O(2)-Gd(1)#6	2.328(12)	O(2)#1-Gd(1)-O(4)#3	84.1(4)
O(3)-Gd(1)#7	2.377(12)	O(5)-Gd(1)-O(4)#3	133.5(4)
O(3)-Gd(1)#4	2.716(12)	O(3)#2-Gd(1)-O(4)#3	150.1(4)
O(4)-Gd(1)#4	2.431(11)	O(7)-Gd(1)-O(4)#3	94.4(5)
O(6)-Gd(1)#6	2.299(14)	O(6)#1-Gd(1)-O(3)#3	115.5(4)
		O(1)-Gd(1)-O(3)#3	74.7(4)
		O(2)#1-Gd(1)-O(3)#3	70.5(4)
		O(5)-Gd(1)-O(3)#3	83.3(4)
		O(3)#2-Gd(1)-O(3)#3	151.77(7)
		O(7)-Gd(1)-O(3)#3	132.5(4)
		O(4)#3-Gd(1)-O(3)#3	50.2(4)
		O(1)-C(1)-O(2)	124.4(14)
		O(4)-C(14)-O(3)	123.1(15)
		O(5)-C(15)-O(6)	121.2(16)
		O(7)-C(22)-O(8)	125(2)

Table S6

Bond lengths [Å]		Bond angles [°]	
Nd(1)-O(6)#1	2.354(9)	Nd(1)#7-O(3)-Nd(1)#4	122.2(3)
Nd(1)-O(1)	2.368(9)	O(6)#1-Nd(1)-O(1)	136.4(3)
Nd(1)-O(2)#1	2.392(9)	O(6)#1-Nd(1)-O(2)#1	75.1(3)
Nd(1)-O(5)	2.403(9)	O(1)-Nd(1)-O(2)#1	141.5(3)
Nd(1)-O(3)#2	2.449(8)	O(6)#1-Nd(1)-O(5)	139.8(3)
Nd(1)-O(7)	2.451(12)	O(1)-Nd(1)-O(5)	80.7(3)
Nd(1)-O(4)#3	2.489(8)	O(2)#1-Nd(1)-O(5)	80.4(3)
Nd(1)-O(3)#3	2.737(8)	O(6)#1-Nd(1)-O(3)#2	76.4(3)
C(1)-O(1)	1.221(15)	O(1)-Nd(1)-O(3)#2	115.7(3)
C(1)-O(2)	1.293(15)	O(2)#1-Nd(1)-O(3)#2	89.6(3)

C(14)-O(4)	1.225(15)	O(5)-Nd(1)-O(3)#2	72.0(3)
C(14)-O(3)	1.273(14)	O(6)#1-Nd(1)-O(7)	72.5(4)
C(15)-O(6)	1.228(16)	O(1)-Nd(1)-O(7)	71.5(4)
C(15)-O(5)	1.276(15)	O(2)#1-Nd(1)-O(7)	146.4(4)
C(22)-O(7)	1.242(9)	O(5)-Nd(1)-O(7)	120.2(4)
C(22)-O(8)	1.301(5)	O(3)#2-Nd(1)-O(7)	74.4(3)
O(2)-Nd(1)#6	2.392(9)	O(6)#1-Nd(1)-O(4)#3	73.8(4)
O(3)-Nd(1)#7	2.449(8)	O(1)-Nd(1)-O(4)#3	86.4(3)
O(3)-Nd(1)#4	2.737(8)	O(2)#1-Nd(1)-O(4)#3	83.4(3)
O(4)-Nd(1)#4	2.489(8)	O(5)-Nd(1)-O(4)#3	134.4(3)
O(6)-Nd(1)#6	2.354(9)	O(3)#2-Nd(1)-O(4)#3	150.2(3)
		O(7)-Nd(1)-O(4)#3	96.0(3)
		O(6)#1-Nd(1)-O(3)#3	115.0(3)
		O(1)-Nd(1)-O(3)#3	75.1(3)
		O(2)#1-Nd(1)-O(3)#3	70.1(3)
		O(5)-Nd(1)-O(3)#3	85.0(3)
		O(3)#2-Nd(1)-O(3)#3	151.74(5)
		O(7)-Nd(1)-O(3)#3	132.9(3)
		O(4)#3-Nd(1)-O(3)#3	49.4(3)
		O(1)-C(1)-O(2)	123.5(12)
		O(4)-C(14)-O(3)	123.0(12)
		O(6)-C(15)-O(5)	123.9(12)
		O(7)-C(22)-O(8)	122.8(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z #2 -x+1/2,y+1/2,-z+1 #3 x,y,z-1 #4 x,y,z+1 #5 -x+1,y,-z+1

#6 -x+1/2,y-1/2,-z #7 -x+1/2,y-1/2,-z+1

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y-1/2,-z+2 #2 -x+3/2,y-1/2,-z+1 #3 x,y,z+1 #4 x,y,z-1 #5 -x+1,y,-z+1

#6 -x+3/2,y+1/2,-z+2 #7 -x+3/2,y+1/2,-z+1

Table S7 Crystallographic data and structural refinements for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{22}H_{14}O_8Eu$	$C_{22}H_{14}O_8Sm$	$C_{22}H_{14}O_8La$	$C_{22}H_{14}O_8Ce$	$C_{22}H_{14}O_8Gd$	$C_{22}H_{14}O_8Nd$
Formula weight	558.29	556.58	545.24	546.45	563.58	550.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2	C2	C2	C2	C2	C2
a/Å	28.945(7)	29.007(6)	27.615(10)	28.912(8)	28.905(8)	28.769(1)
b/Å	8.655(2)	8.688(2)	8.842(3)	8.789(2)	8.622(3)	8.723(3)

c/Å	14.105(4)	14.166(3)	14.318(5)	14.257(4)	14.066(4)	14.179(6)
β/º	116.326(4)	116.276(3)	114.311(4)	116.141(7)	116.395(5)	116.028(1)
Volume/Å^3	3167(1)	3201(1)	3186(2)	3252 (1)	3140(2)	3197(2)
Z	4	4	4	4	4	4
Dcalc/mg.m^{-3}	1.171	1.155	1.137	1.116	1.192	1.144
μ/mm^{-1}	2.011	1.865	1.371	1.429	2.143	1.654
F(000)	1092	1088	1068	1072	1096	1080
Data/restraints/parameters	5415/32/282	5222/ 32/281	3926/44/281	4417/32/281	6544/32/282	5251/212/281
GOF on F^2	1.115	1.091	1.119	1.133	1.053	1.163
$R_1[I>2\sigma(I)]$[a]	0.0681	0.0684	0.0663	0.0629	0.0978	0.0676
$wR_2[I>2\sigma(I)]$[b]	0.1828	0.1976	0.1919	0.1838	0.2416	0.1903
R_1(all data)[a]	0.0755	0.0692	0.0696	0.0648	0.1077	0.0731
wR_2(all data)[b]	0.1875	0.1986	0.1981	0.1855	0.2495	0.1935
Flack χ	0.47(4)	0.56(4)	0.33(6)	0.50(5)	0.58(5)	0.36(4)

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma F_o|.$ $\quad wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$