Supplementary Information

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1. The solvent sensing experiment was performed as follows: Complex **1** (2.5 mg) was immersed in different organic solvents (5 mL), treated by ultrasonication for 30 minutes, and then aged for three days.

The metal ion sensing experiment was performed as follows: Complex **1** (2.5 mg) was immersed in different solution, (including aqueous solution, isopropanol, acetone, ethyl acetate) (10^{-2} mol/L, 5 mL) of $M(NO_3)_n$ (M^{n+} = K^+, Cr^{3+}, Ag^+, Ba^{2+}, Pb^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}), treated by ultrasonication for 30 min, and then aged for three days.

2. The PXRD and temperature-dependent PXRD patterns of complexes **1** (a, c) and **5** (b, d). (Fig. S1).

3. The structure of complex **1**: (a) 3D porous structure with the free water molecules, (b) helical chains, (c) $\{3^6.4^8.5^6.6\}$ topology. (Fig. S2)

4. N_2 adsorption–desorption curves of complex 1. (Fig. S3)

5. 3D supramolecular structure of complex **4**. (Fig. S4)

6. 3D supramolecular architecture of complex **5** by the C−H···O hydrogen bonds. (Fig .S5)

7. The solid state emission spectra of complexes **2**, **4**, **6** and the free ligands. (Fig. S6)

8. Decay profile of solid state complexes **3** (a), **7** (b), **1** (c), **5** (d), activated complex **1** (e), complex **1** dispersed in Fe^{3+} aqueous solution (f), the solid state complex **1** after Fe^{3+} adsorption (g). (Fig. S7)

9. Solid state emission spectrum of complex **5**. Insert: excitation spectrum. (Fig. S8)

10. The luminescence intensity ($^5D_0 \rightarrow {}^7F_2$) of three recyclable experiments of sensing for benzaldehyde. (Fig. S9)

11. The plot of I_0/I versus Fe^{3+} concentration. (Fig. S10)

12. Emission spectra of **1** in aqueous solutions of Ba^{2+}, mixed Ba^{2+} and Fe^{3+} (a); Pb^{2+}, mixed Pb^{2+} and Fe^{3+} (b); Cr^{3+}, mixed Cr^{3+} and Fe^{3+} (c); Cd^{2+}, mixed Cd^{2+} and Fe^{3+} (d). (Fig. S11)

13. UV-Vis absorption spectra of metal cations in aqueous solutions. (Fig. S12)

14. Emission spectra of **1** dispersed in acetone containing different metal ions. Insert: the $^5D_0 \rightarrow {}^7F_2$ (618 nm) transition intensities (λ_{ex} = 358 nm). (Fig. S13)

15. Emission spectra of **1** dispersed in ethyl acetate containing different cations. Insert: the $^5D_0 \rightarrow {}^7F_2$ (618 nm) transition intensities (λ_{ex} = 358 nm). (Fig. S14)

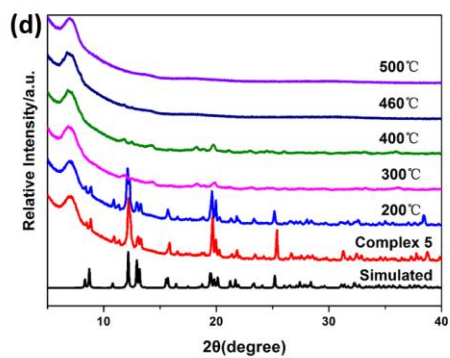16. Selected bond lengths [Å] and angles [º] for complexes **1-7**. (Table S1)
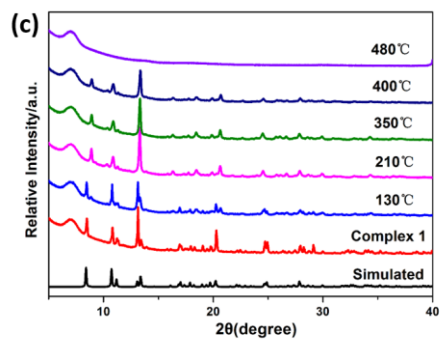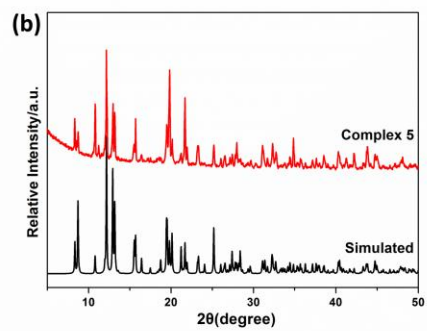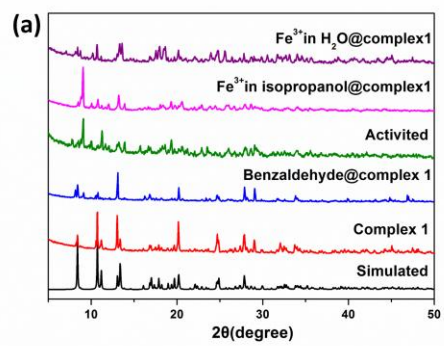
Fig. S1 The PXRD and temperature-dependent PXRD patterns of complexes **1** (a, c) and **5** (b, d).
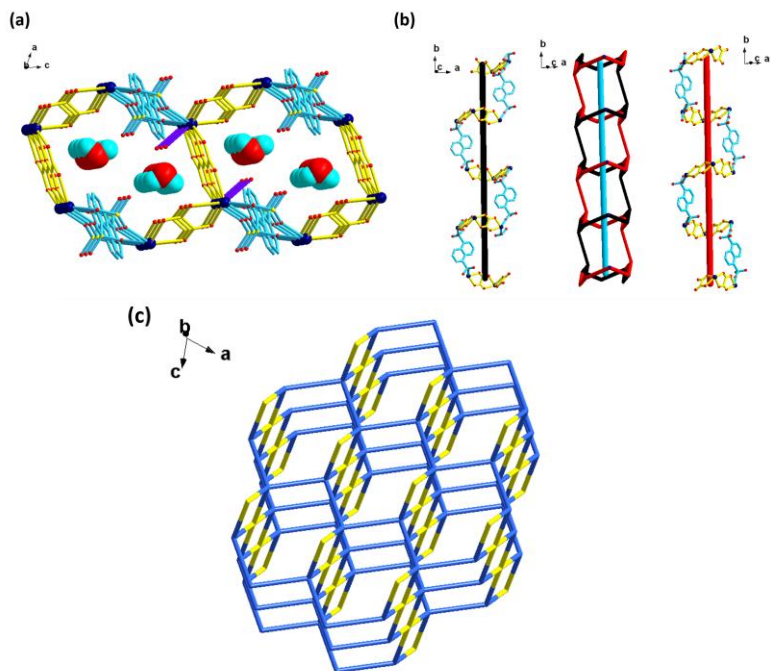
Fig. S2 Structure of complex **1**: (a) 3D porous structure with the free water molecules, (b) helical chains, (c) $\{3^6.4^8.5^6.6\}$ topology.

The calculated results by Topological analysis[12]:   Eu1 Point (Schlafli) symbol:$\{3^6.4^8.5^6.6\}$
Extended point symbol: [3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.5.5.5.5.5.5(2).5(2).6(5)]
Point (Schlafli) symbol for net: $\{3^6.4^8.5^6.6\}$.
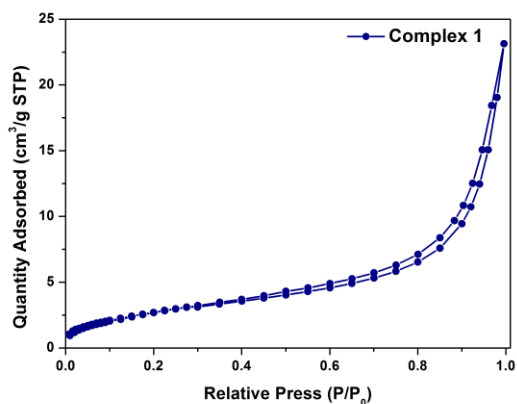
Fig S3 N_2 adsorption–desorption curves of complex 1.
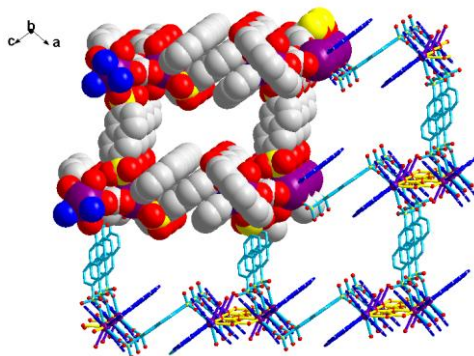
Fig. S4 3D supramolecular structure of complex **4.**
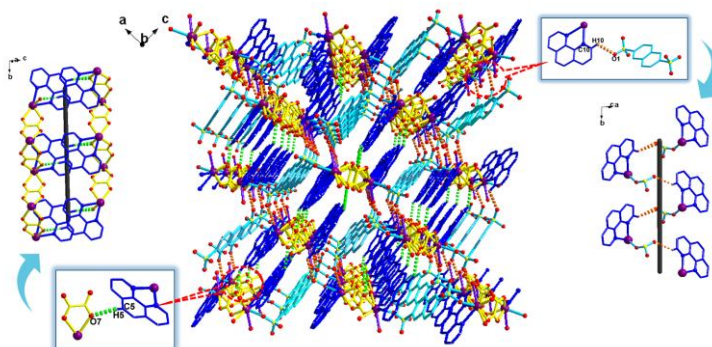
Fig. S5 3D supramolecular architecture of complex **5** by the C−H⋯O hydrogen bonds.
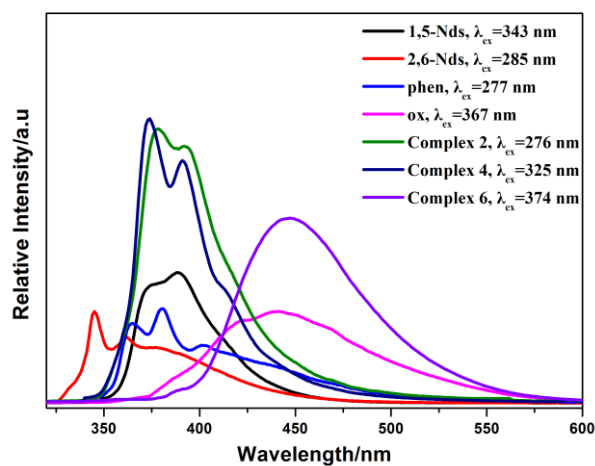
Fig. S6 The solid state emission spectra of complexes **2**, **4**, **6**, and the free ligands.
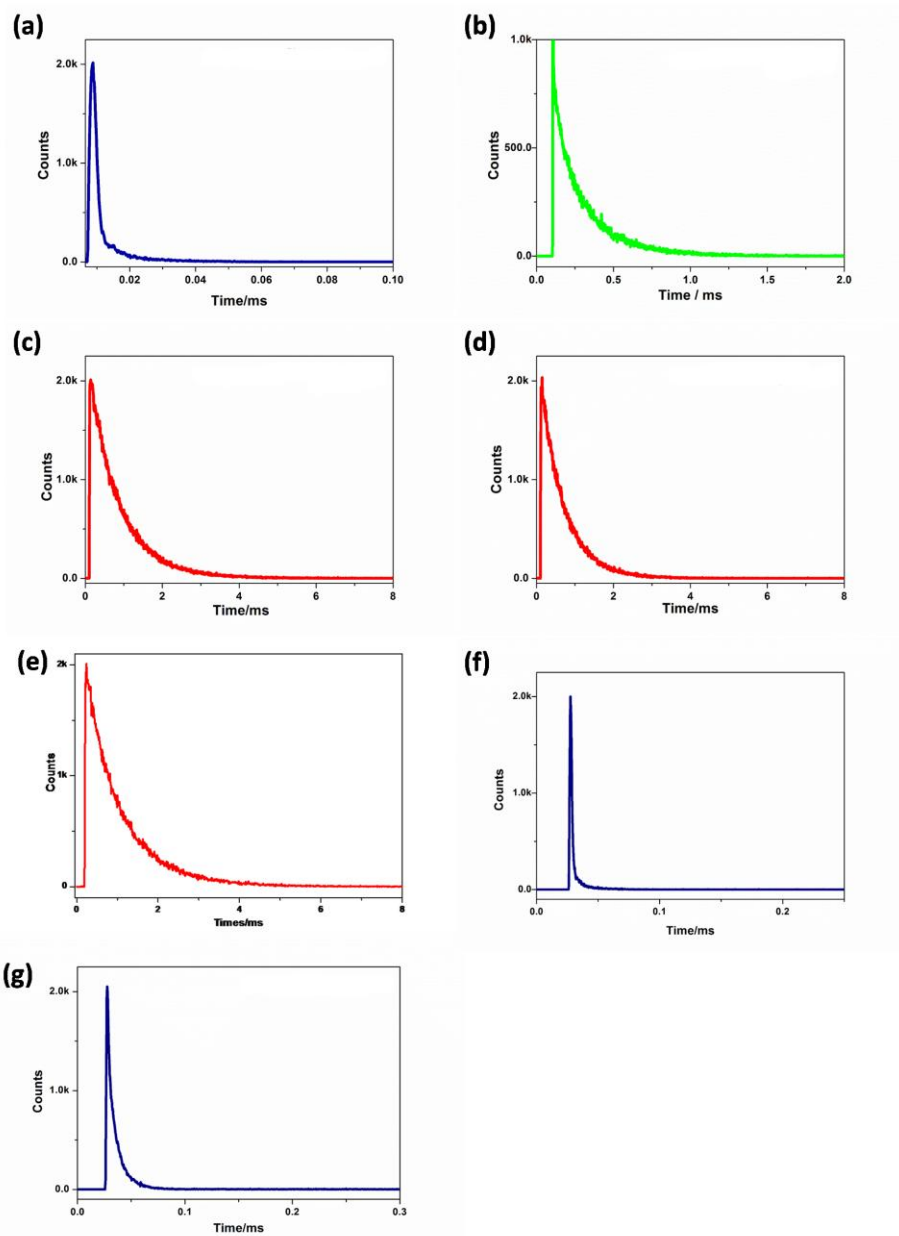
Fig. S7 Decay profile of solid state complexes **3** (a), **7** (b), **1** (c), **5** (d), activated complex **1** (e), complex **1** dispersed in Fe^{3+} aqueous solution (f), the solid state complex **1** after Fe^{3+} adsorption (g).

5
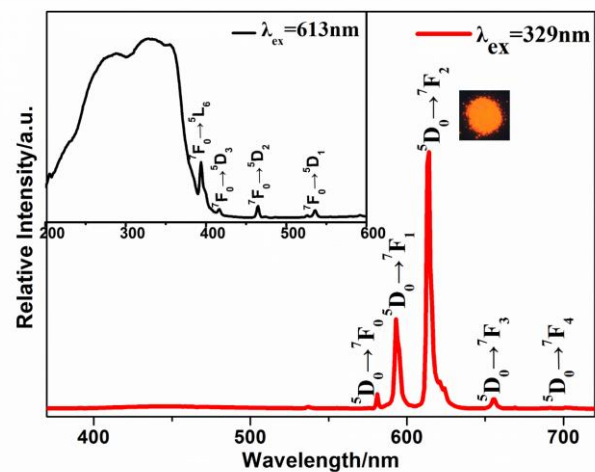
Fig. S8 Solid state emission spectrum of complex **5**. Insert: excitation spectrum.
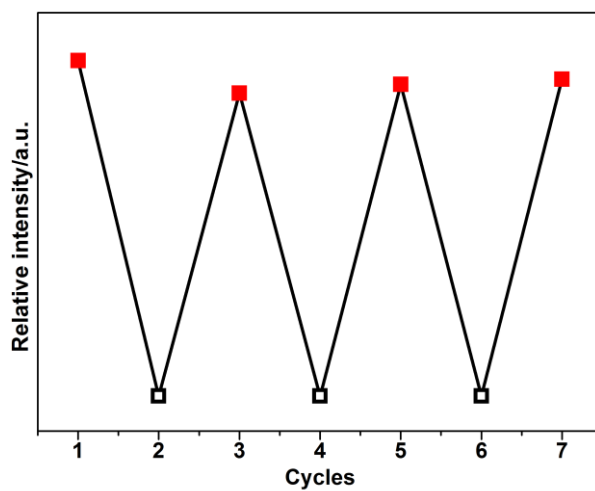
Fig. S9 The luminescence intensity ($^5D_0{\rightarrow}^7F_2$) of three recyclable experiments of sensing for benzaldehyde in isopropanol.
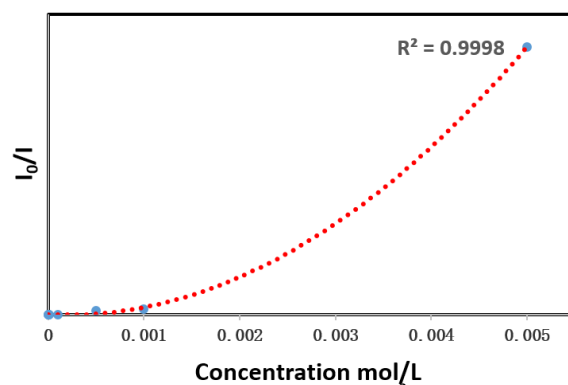
Fig. S10 The plot of I_0/I versus Fe^{3+} concentration.
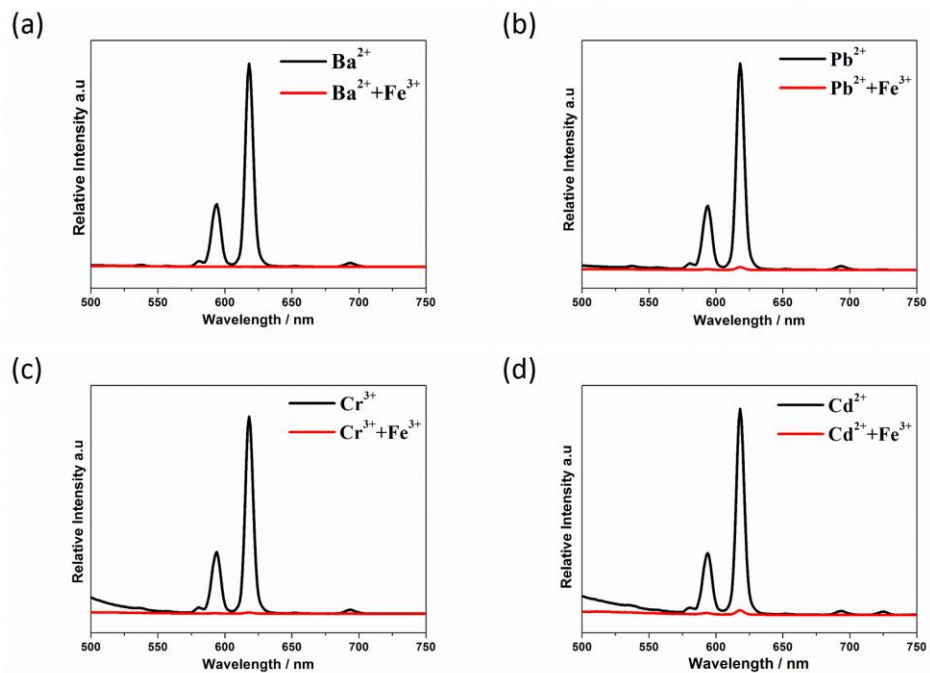
Fig. S11 Emission spectra of **1** in aqueous solutions of Ba^{2+}, mixed Ba^{2+} and Fe^{3+} (a); Pb^{2+}, mixed Pb^{2+} and Fe^{3+} (b); Cr^{3+}, mixed Cr^{3+} and Fe^{3+} (c); Cd^{2+}, mixed Cd^{2+} and Fe^{3+} (d).
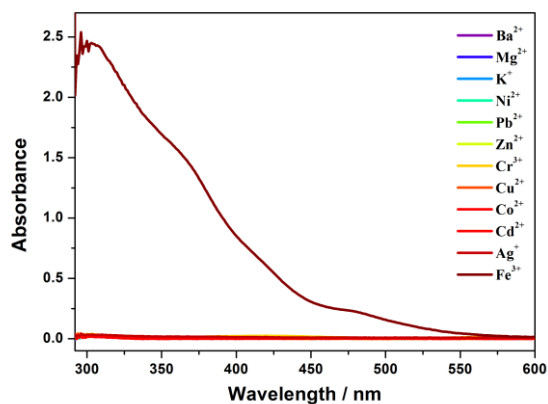
Fig. S12 UV-Vis absorption spectra of metal ions in aqueous solution.
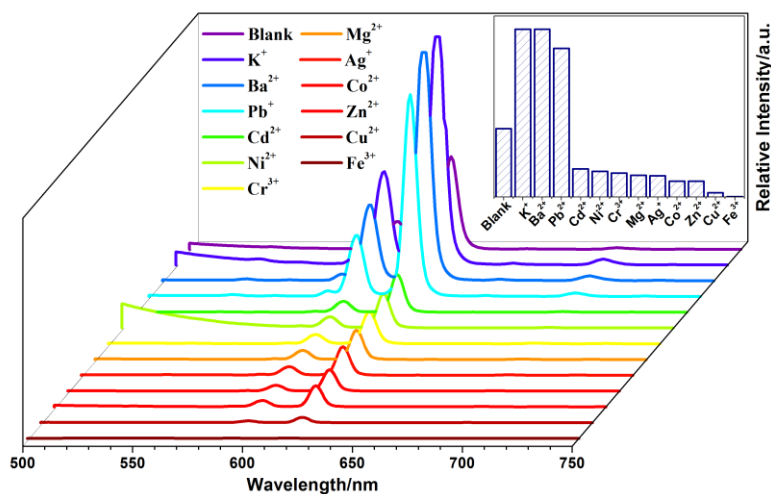
Fig. S13 Emission spectra of **1** dispersed in acetone containing different metal ions. Insert: the $^5D_0\rightarrow{}^7F_2$ (618 nm) transition intensities (λ_{ex} = 358 nm).
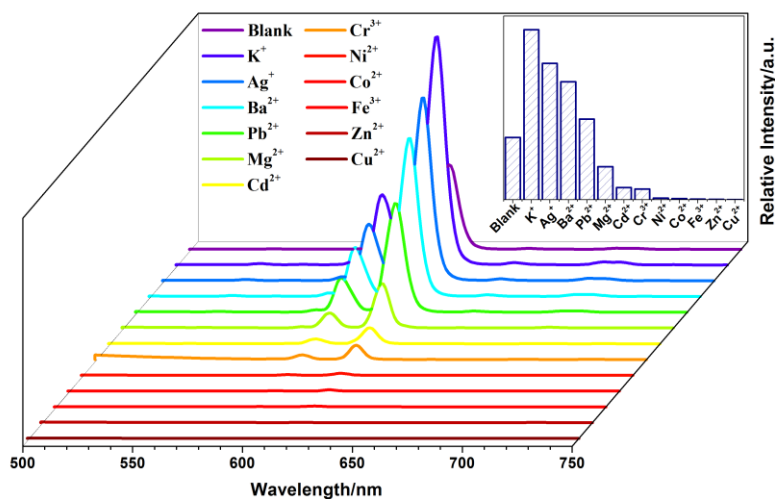
Fig. S14 Emission spectra of **1** dispersed in ethyl acetate containing different metal ions. Insert: the $^5D_0\rightarrow{}^7F_2$ (618 nm) transition intensities (λ_{ex} = 358 nm).

Table S1 Selected bond lengths [Å] and angles [°] for complex **1-7**

1			
Eu(1)-O(4)	2.405(5)	Eu(1)-O(6)	2.487(5)
Eu(1)-O(1)#1	2.418(5)	Eu(1)-O(5)	2.524(6)
Eu(1)-O(3)	2.432(5)	Eu(1)-N(2)	2.594(6)
Eu(1)-O(8)#2	2.441(5)	Eu(1)-N(1)	2.667(7)
Eu(1)-O(2)#3	2.451(5)		
O(4)-Eu(1)-O(1)#1	77.51(19)	O(8)#2-Eu(1)-O(5)	68.18(17)
O(4)-Eu(1)-O(3)	130.51(17)	O(2)#3-Eu(1)-O(5)	72.62(18)

O(1)#1-Eu(1)-O(3)	66.03(17)	O(6)-Eu(1)-O(5)	68.27(18)
O(4)-Eu(1)-O(8)#2	100.68(18)	O(4)-Eu(1)-N(2)	133.78(18)
O(1)#1-Eu(1)-O(8)#2	139.36(18)	O(1)#1-Eu(1)-N(2)	82.50(19)
O(3)-Eu(1)-O(8)#2	128.79(17)	O(3)-Eu(1)-N(2)	74.37(18)
O(4)-Eu(1)-O(2)#3	66.59(17)	O(8)#2-Eu(1)-N(2)	69.62(18)
O(1)#1-Eu(1)-O(2)#3	76.42(19)	O(2)#3-Eu(1)-N(2)	146.17(19)
O(3)-Eu(1)-O(2)#3	72.99(17)	O(6)-Eu(1)-N(2)	82.82(18)
O(8)#2-Eu(1)-O(2)#3	140.80(19)	O(5)-Eu(1)-N(2)	134.13(18)
O(4)-Eu(1)-O(6)	139.22(18)	O(4)-Eu(1)-N(1)	71.44(18)
O(1)#1-Eu(1)-O(6)	133.64(17)	O(1)#1-Eu(1)-N(1)	69.35(18)
O(3)-Eu(1)-O(6)	67.69(17)	O(3)-Eu(1)-N(1)	120.53(18)
O(8)#2-Eu(1)-O(6)	72.71(17)	O(8)#2-Eu(1)-N(1)	71.68(17)
O(2)#3-Eu(1)-O(6)	92.83(17)	O(2)#3-Eu(1)-N(1)	130.22(17)
O(4)-Eu(1)-O(5)	71.97(19)	O(6)-Eu(1)-N(1)	136.92(17)
O(1)#1-Eu(1)-O(5)	143.01(18)	O(5)-Eu(1)-N(1)	117.99(19)
O(3)-Eu(1)-O(5)	121.39(19)	N(2)-Eu(1)-N(1)	62.54(19)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z; #2 -x,-y+1,-z+1; #3 -x+1,-y+1,-z; #4 -x,-y,-z+1.

2			
La(1)-O(4)	2.492(2)	La(1)-O(6)	2.552(2)
La(1)-O(2)#1	2.522(2)	La(1)-O(5)	2.619(3)
La(1)-O(3)	2.523(2)	La(1)-N(2)	2.706(3)
La(1)-O(8)#2	2.524(2)	La(1)-N(1)	2.751(3)
La(1)-O(1)#3	2.527(2)		
O(4)-La(1)-O(2)#1	64.80(7)	O(8)#2-La(1)-O(5)	68.61(8)
O(4)-La(1)-O(3)	128.31(8)	O(1)#3-La(1)-O(5)	141.65(8)
O(2)#1-La(1)-O(3)	74.27(8)	O(6)-La(1)-O(5)	68.93(8)
O(4)-La(1)-O(8)#2	102.86(8)	O(4)-La(1)-N(2)	133.48(8)
O(2)#1-La(1)-O(8)#2	140.68(8)	O(2)#1-La(1)-N(2)	147.11(9)
O(3)-La(1)-O(8)#2	128.81(7)	O(3)-La(1)-N(2)	73.95(8)
O(4)-La(1)-O(1)#3	75.62(8)	O(8)#2-La(1)-N(2)	69.12(9)
O(2)#1-La(1)-O(1)#3	75.09(8)	O(1)#3-La(1)-N(2)	83.62(8)
O(3)-La(1)-O(1)#3	64.06(7)	O(6)-La(1)-N(2)	83.50(8)
O(8)#2-La(1)-O(1)#3	140.81(8)	O(5)-La(1)-N(2)	134.42(8)
O(4)-La(1)-O(6)	140.11(8)	O(4)-La(1)-N(1)	73.60(8)
O(2)#1-La(1)-O(6)	92.40(7)	O(2)#1-La(1)-N(1)	130.99(8)
O(3)-La(1)-O(6)	68.08(7)	O(3)-La(1)-N(1)	117.40(8)
O(8)#2-La(1)-O(6)	73.59(7)	O(8)#2-La(1)-N(1)	71.76(8)
O(1)#3-La(1)-O(6)	132.14(7)	O(1)#3-La(1)-N(1)	70.34(8)
O(4)-La(1)-O(5)	72.87(8)	O(6)-La(1)-N(1)	136.61(7)
O(2)#1-La(1)-O(5)	72.06(8)	O(5)-La(1)-N(1)	119.43(9)
O(3)-La(1)-O(5)	123.05(8)	N(2)-La(1)-N(1)	60.22(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z; #2 -x,-y+1,-z+1; #3 -x,-y+1,-z; #4 -x,-y,-z+1.

3			
Sm(1)-O(6)#1	2.408(2)	Sm(1)-O(1)	2.497(2)
Sm(1)-O(4)#2	2.439(2)	Sm(1)-O(8)	2.538(3)
Sm(1)-O(3)#3	2.442(2)	Sm(1)-N(1)	2.610(3)
Sm(1)-O(5)	2.451(2)	Sm(1)-N(2)	2.676(3)
Sm(1)-O(7)	2.455(2)		

O(6)#1-Sm(1)-O(4)#2	77.49(9)	O(5)-Sm(1)-O(8)	121.18(9)
O(6)#1-Sm(1)-O(3)#3	100.68(9)	O(7)-Sm(1)-O(8)	72.17(9)
O(4)#2-Sm(1)-O(3)#3	139.40(8)	O(1)-Sm(1)-O(8)	68.32(8)
O(6)#1-Sm(1)-O(5)	130.67(8)	O(6)#1-Sm(1)-N(1)	133.60(8)
O(4)#2-Sm(1)-O(5)	66.01(7)	O(4)#2-Sm(1)-N(1)	82.60(9)
O(3)#3-Sm(1)-O(5)	128.64(8)	O(3)#3-Sm(1)-N(1)	69.45(9)
O(6)#1-Sm(1)-O(7)	66.63(8)	O(5)-Sm(1)-N(1)	74.38(9)
O(4)#2-Sm(1)-O(7)	76.36(9)	O(7)-Sm(1)-N(1)	146.34(9)
O(3)#3-Sm(1)-O(7)	140.83(8)	O(1)-Sm(1)-N(1)	83.00(8)
O(5)-Sm(1)-O(7)	73.15(8)	O(8)-Sm(1)-N(1)	134.42(9)
O(6)#1-Sm(1)-O(1)	139.25(8)	O(6)#1-Sm(1)-N(2)	71.80(8)
O(4)#2-Sm(1)-O(1)	133.43(8)	O(4)#2-Sm(1)-N(2)	69.35(8)
O(3)#3-Sm(1)-O(1)	72.94(7)	O(3)#3-Sm(1)-N(2)	71.64(8)
O(5)-Sm(1)-O(1)	67.48(7)	O(5)-Sm(1)-N(2)	120.08(8)
O(7)-Sm(1)-O(1)	92.63(7)	O(7)-Sm(1)-N(2)	130.50(8)
O(6)#1-Sm(1)-O(8)	71.92(9)	O(1)-Sm(1)-N(2)	136.86(8)
O(4)#2-Sm(1)-O(8)	142.64(8)	O(8)-Sm(1)-N(2)	118.64(9)
O(3)#3-Sm(1)-O(8)	68.66(9)	N(1)-Sm(1)-N(2)	61.99(9)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z; #2 -x,-y,-z; #3 -x,-y,-z+1; #4 -x,-y-1,-z+1.

4			
La(1)-O(7)	2.461(3)	La(1)-N(4)	2.698(3)
La(1)-O(1)	2.512(3)	La(1)-N(2)	2.733(3)
La(1)-O(8)#3	2.521(3)	La(1)-N(1)	2.754(4)
La(1)-O(9)	2.567(3)	La(1)-N(3)	2.754(4)
La(1)-O(4)	2.579(3)		
O(7)-La(1)-O(1)	87.01(11)	O(9)-La(1)-N(2)	91.87(11)
O(7)-La(1)-O(8)#3	64.84(9)	O(4)-La(1)-N(2)	76.24(10)
O(1)-La(1)-O(8)#3	140.32(10)	N(4)-La(1)-N(2)	132.18(11)
O(7)-La(1)-O(9)	75.51(11)	O(7)-La(1)-N(1)	142.54(11)
O(1)-La(1)-O(9)	76.91(11)	O(1)-La(1)-N(1)	76.59(11)
O(8)#3-La(1)-O(9)	69.57(11)	O(8)#3-La(1)-N(1)	108.51(10)
O(7)-La(1)-O(4)	85.61(11)	O(9)-La(1)-N(1)	68.11(11)
O(1)-La(1)-O(4)	135.77(10)	O(4)-La(1)-N(1)	129.20(10)
O(8)#3-La(1)-O(4)	72.29(10)	N(4)-La(1)-N(1)	124.34(11)
O(9)-La(1)-O(4)	141.71(11)	N(2)-La(1)-N(1)	59.77(11)
O(7)-La(1)-N(4)	77.09(11)	O(7)-La(1)-N(3)	137.18(10)
O(1)-La(1)-N(4)	67.38(11)	O(1)-La(1)-N(3)	82.40(11)
O(8)#3-La(1)-N(4)	126.44(11)	O(8)#3-La(1)-N(3)	137.26(11)
O(9)-La(1)-N(4)	135.60(12)	O(9)-La(1)-N(3)	140.19(11)
O(4)-La(1)-N(4)	68.45(10)	O(4)-La(1)-N(3)	74.14(11)
O(7)-La(1)-N(2)	131.83(10)	N(4)-La(1)-N(3)	60.52(11)
O(1)-La(1)-N(2)	135.84(11)	N(2)-La(1)-N(3)	79.80(11)
O(8)#3-La(1)-N(2)	67.17(10)	N(1)-La(1)-N(3)	74.23(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+3,-y+2,-z+1; #3 -x+2,-y+1,-z.

5			
Eu(1)-O(3)	2.369(6)	Eu(1)-O(4)#3	2.411(6)
Eu(1)-O(6)	2.387(6)	Eu(1)-O(8)	2.464(6)

Eu(1)-O(7)#3	2.390(6)	Eu(1)-N(2)	2.561(7)
Eu(1)-O(5)	2.391(6)	Eu(1)-N(1)	2.581(7)
O(3)-Eu(1)-O(6)	90.3(2)	O(4)#3-Eu(1)-O(8)	69.6(2)
O(3)-Eu(1)-O(7)#3	148.9(2)	O(3)-Eu(1)-N(2)	95.4(2)
O(6)-Eu(1)-O(7)#3	109.4(2)	O(6)-Eu(1)-N(2)	158.0(2)
O(3)-Eu(1)-O(5)	92.3(2)	O(7)#3-Eu(1)-N(2)	75.4(2)
O(6)-Eu(1)-O(5)	67.5(2)	O(5)-Eu(1)-N(2)	133.2(2)
O(7)#3-Eu(1)-O(5)	74.5(2)	O(4)#3-Eu(1)-N(2)	84.1(2)
O(3)-Eu(1)-O(4)#3	142.5(2)	O(8)-Eu(1)-N(2)	80.1(2)
O(6)-Eu(1)-O(4)#3	78.6(2)	O(3)-Eu(1)-N(1)	73.8(2)
O(7)#3-Eu(1)-O(4)#3	67.1(2)	O(6)-Eu(1)-N(1)	137.5(2)
O(5)-Eu(1)-O(4)#3	115.2(2)	O(7)#3-Eu(1)-N(1)	75.6(2)
O(3)-Eu(1)-O(8)	73.4(2)	O(5)-Eu(1)-N(1)	74.0(2)
O(6)-Eu(1)-O(8)	81.3(2)	O(4)#3-Eu(1)-N(1)	136.1(2)
O(7)#3-Eu(1)-O(8)	131.8(2)	O(8)-Eu(1)-N(1)	128.0(2)
O(5)-Eu(1)-O(8)	145.7(2)	N(2)-Eu(1)-N(1)	64.3(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1; #2 -x+1,y+1/2,-z+3/2; #3 -x+1,y-1/2,-z+3/2

6			
Gd(1)-O(1)	2.357(4)	Gd(1)-O(7)#1	2.398(5)
Gd(1)-O(5)	2.379(5)	Gd(1)-O(1W)	2.421(5)
Gd(1)-O(4)	2.385(5)	Gd(1)-N(1)	2.543(6)
Gd(1)-O(6)	2.386(5)	Gd(1)-N(2)	2.566(6)
O(1)-Gd(1)-O(5)	89.80(16)	O(7)#1-Gd(1)-O(1W)	69.51(17)
O(1)-Gd(1)-O(4)	149.14(17)	O(1)-Gd(1)-N(1)	95.81(17)
O(5)-Gd(1)-O(4)	109.69(17)	O(5)-Gd(1)-N(1)	157.44(18)
O(1)-Gd(1)-O(6)	91.83(17)	O(4)-Gd(1)-N(1)	75.48(18)
O(5)-Gd(1)-O(6)	67.90(16)	O(6)-Gd(1)-N(1)	133.45(18)
O(4)-Gd(1)-O(6)	74.79(18)	O(7)#1-Gd(1)-N(1)	84.07(18)
O(1)-Gd(1)-O(7)#1	142.06(17)	O(1W)-Gd(1)-N(1)	79.95(19)
O(5)-Gd(1)-O(7)#1	78.20(18)	O(1)-Gd(1)-N(2)	74.07(17)
O(4)-Gd(1)-O(7)#1	67.52(17)	O(5)-Gd(1)-N(2)	137.98(18)
O(6)-Gd(1)-O(7)#1	115.64(17)	O(4)-Gd(1)-N(2)	75.52(17)
O(1)-Gd(1)-O(1W)	73.12(17)	O(6)-Gd(1)-N(2)	74.02(17)
O(5)-Gd(1)-O(1W)	80.83(18)	O(7)#1-Gd(1)-N(2)	136.33(17)
O(4)-Gd(1)-O(1W)	132.04(17)	O(1W)-Gd(1)-N(2)	127.81(18)
O(6)-Gd(1)-O(1W)	145.43(18)	N(1)-Gd(1)-N(2)	64.35(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y-1/2,-z-1/2; #2 -x+2,y+1/2,-z-1/2; #3 -x+1,-y,-z

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Tb(1)-O(1)	2.345(4)	Tb(1)-O(6)#1	2.383(4)
Tb(1)-O(8)	2.363(4)	Tb(1)-O(4)	2.428(4)
Tb(1)-O(7)	2.367(4)	Tb(1)-N(2)	2.523(4)
Tb(1)-O(5)#1	2.376(4)	Tb(1)-N(1)	2.549(4)
O(1)-Tb(1)-O(8)	89.67(13)	O(6)#1-Tb(1)-O(4)	69.43(14)
O(1)-Tb(1)-O(7)	91.81(13)	O(1)-Tb(1)-N(2)	96.20(14)
O(8)-Tb(1)-O(7)	68.18(13)	O(8)-Tb(1)-N(2)	156.73(14)
O(1)-Tb(1)-O(5)#1	148.86(13)	O(7)-Tb(1)-N(2)	133.79(13)
O(8)-Tb(1)-O(5)#1	110.14(14)	O(5)#1-Tb(1)-N(2)	75.22(15)

O(7)-Tb(1)-O(5)#1	74.76(14)	O(6)#1-Tb(1)-N(2)	83.63(14)
O(1)-Tb(1)-O(6)#1	142.36(13)	O(4)-Tb(1)-N(2)	80.16(15)
O(8)-Tb(1)-O(6)#1	78.11(13)	O(1)-Tb(1)-N(1)	73.81(13)
O(7)-Tb(1)-O(6)#1	115.37(14)	O(8)-Tb(1)-N(1)	137.75(13)
O(5)#1-Tb(1)-O(6)#1	67.51(13)	O(7)-Tb(1)-N(1)	73.68(13)
O(1)-Tb(1)-O(4)	73.45(13)	O(5)#1-Tb(1)-N(1)	75.45(14)
O(8)-Tb(1)-O(4)	79.99(14)	O(6)#1-Tb(1)-N(1)	136.60(13)
O(7)-Tb(1)-O(4)	145.06(15)	O(4)-Tb(1)-N(1)	128.56(14)
O(5)#1-Tb(1)-O(4)	132.09(14)	N(2)-Tb(1)-N(1)	65.27(14)

Symmetry transformations used to generate equivalent atoms: #1 -x,y+1/2,-z+1/2; #2 -x,y-1/2,-z+1/2; #3 -x+1,-y+2,-z