

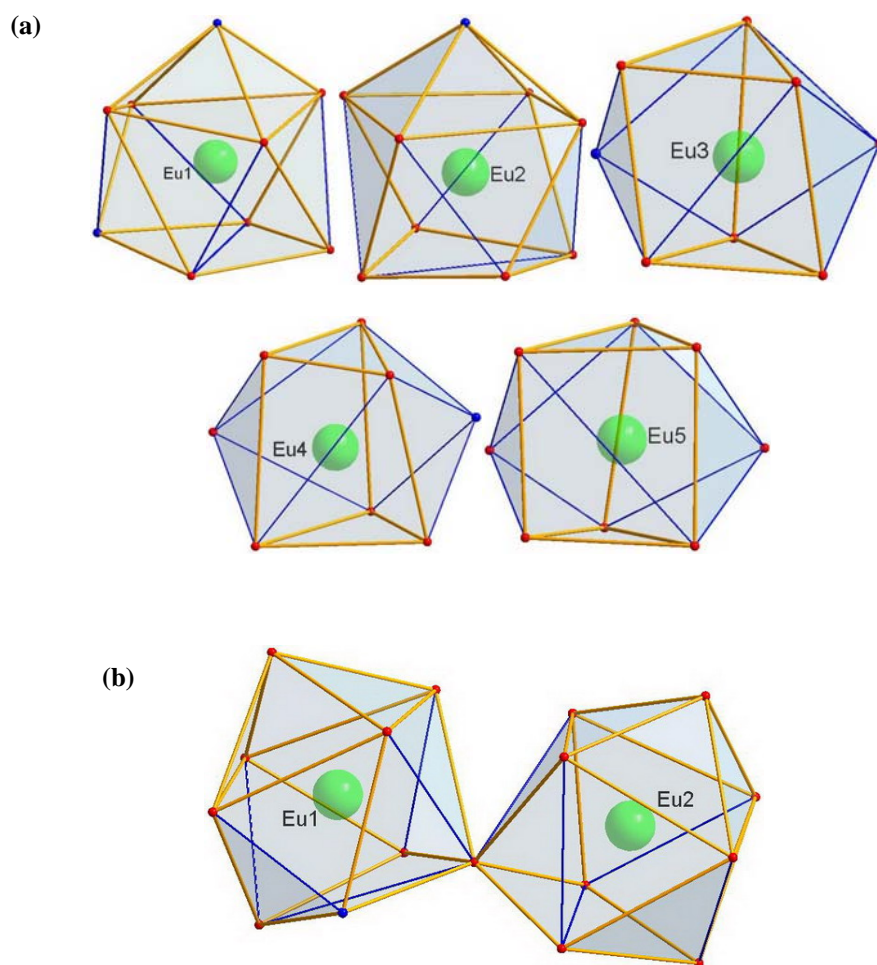
Supporting Information

Fig. S1. The coordination polyhedron of Eu atoms in **1** (a) and **2** (b), respectively.

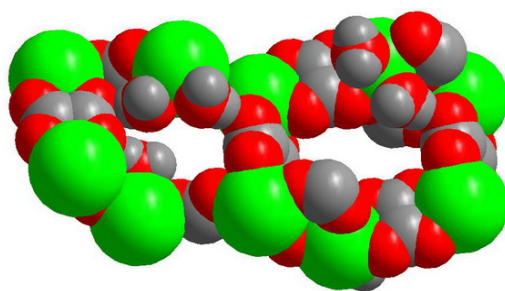


Fig. S2. The space-filling mode of two channels with aqua ligands in 2.

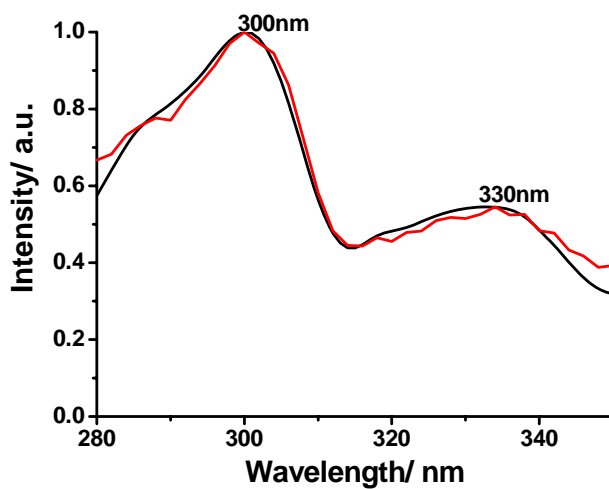


Fig. S3. Excitation spectra of complex 1 (red line) and 2 (black line) when excited at 616 nm.

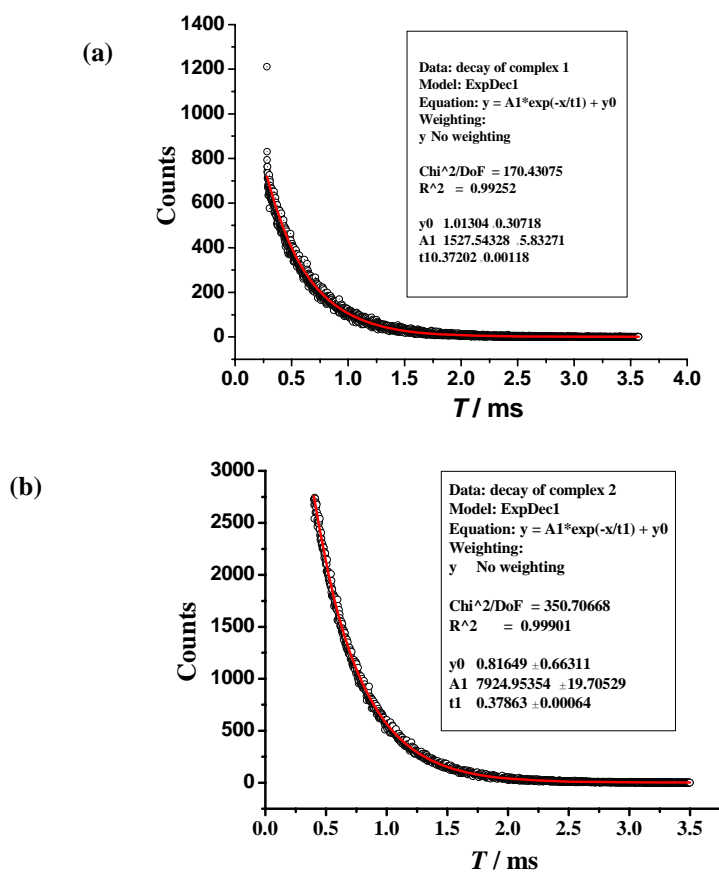


Fig. S4. Luminescent decay of 1 (a) and 2 (b).

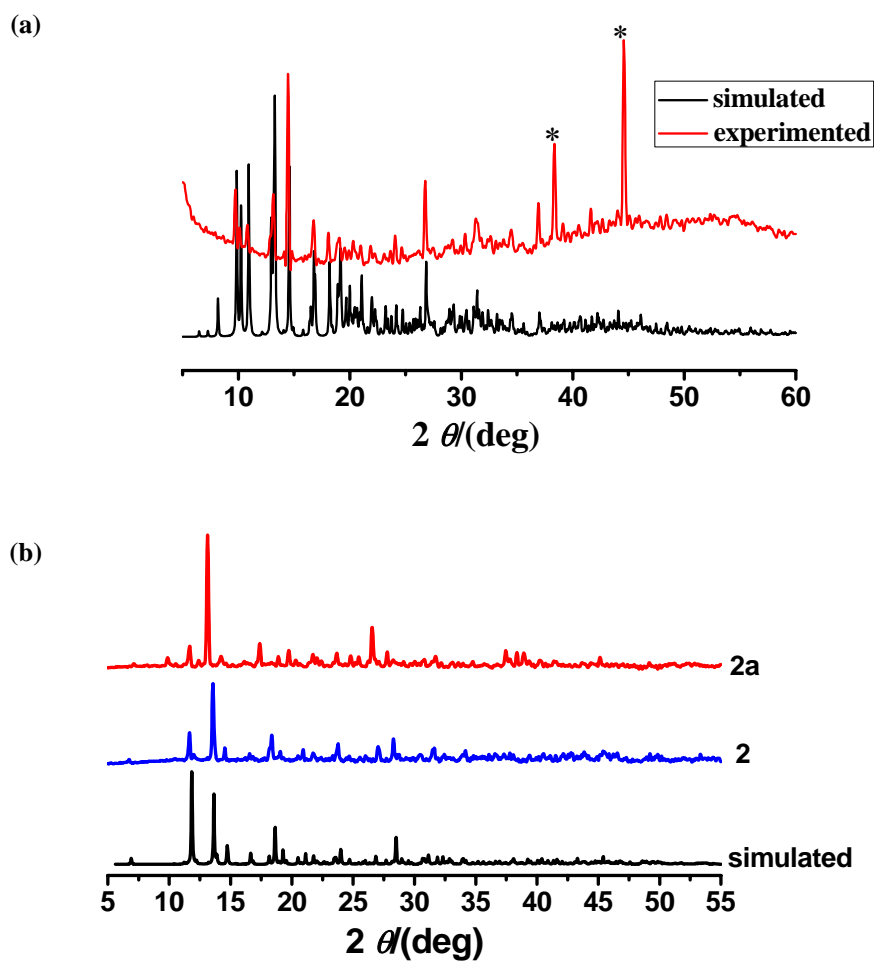


Fig. S5. Simulated and experimented XRD pattern of complex **1** (a), **2** and **2a** (b) (* indicates the peaks of background)

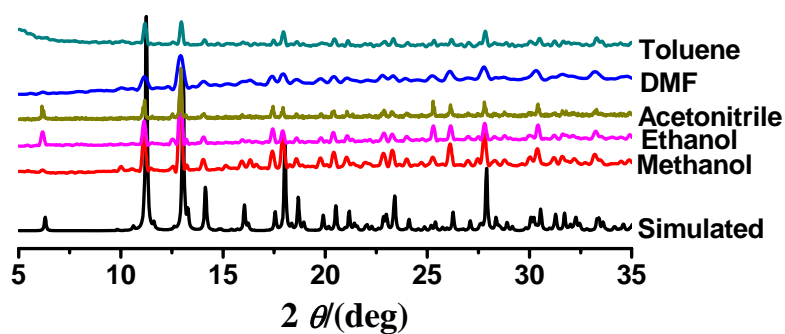


Fig. S6. XRD pattern of **2a** after immersed in different organic solvents for 24h.

Table S1. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Eu(1)-O(28 <i>a</i>)	2.332(5)	Eu(2)-O(20)	2.350(5)
Eu(1)-O(3 <i>b</i>)	2.390(5)	Eu(2)-O(18)	2.384(5)
Eu(1)-O(12)	2.412(5)	Eu(2)-O(26 <i>c</i>)	2.444(5)
Eu(1)-O(7)	2.449(5)	Eu(2)-O(2)	2.453(5)
Eu(1)-O(6)	2.455(5)	Eu(2)-O(13)	2.460(4)
Eu(1)-O(1)	2.484(5)	Eu(2)-O(3 <i>w</i>)	2.488(6)
Eu(1)-N(2)	2.530(6)	Eu(2)-O(16 <i>d</i>)	2.488(6)
Eu(1)-N(1)	2.537(6)	Eu(2)-N(3)	2.549(5)
Eu(1)-O(1 <i>w</i>)	2.595(5)	Eu(2)-O(2 <i>w</i>)	2.593(7)
Eu(3)-O(21 <i>d</i>)	2.298(5)	Eu(4)-O(10 <i>e</i>)	2.326(5)
Eu(3)-O(8 <i>d</i>)	2.340(5)	Eu(4)-O(22 <i>d</i>)	2.373(5)
Eu(3)-O(19)	2.396(5)	Eu(4)-O(5 <i>w</i>)	2.394(5)
Eu(3)-O(17 <i>d</i>)	2.400(5)	Eu(4)-O(30)	2.406(5)
Eu(3)-O(29 <i>e</i>)	2.407(5)	Eu(4)-O(25)	2.418(5)
Eu(3)-O(4 <i>w</i>)	2.419(6)	Eu(4)-N(5)	2.474(5)
Eu(3)-O(24)	2.472(4)	Eu(4)-O(24)	2.503(4)
Eu(3)-N(4)	2.526(6)	Eu(4)-O(23)	2.530(5)
Eu(5)-O(27)	2.290(5)	Eu(5)-O(4 <i>g</i>)	2.428(5)
Eu(5)-O(5 <i>f</i>)	2.336(5)	Eu(5)-O(13 <i>c</i>)	2.494(5)
Eu(5)-O(15 <i>g</i>)	2.375(5)	Eu(5)-O(14 <i>c</i>)	2.709(5)
Eu(5)-O(6 <i>w</i>)	2.415(5)	Eu(5)-O(7 <i>w</i>)	2.426(5)
O(28 <i>a</i>)-Eu(1)-O(3 <i>b</i>)	139.82(19)	O(20)-Eu(2)-O(18)	74.12(17)
O(28 <i>a</i>)-Eu(1)-O(12)	87.0(2)	O(20)-Eu(2)-O(26 <i>c</i>)	77.09(19)
O(3 <i>b</i>)-Eu(1)-O(12)	75.76(17)	O(18)-Eu(2)-O(26 <i>c</i>)	78.82(18)
O(28 <i>a</i>)-Eu(1)-O(7)	78.22(18)	O(20)-Eu(2)-O(2)	136.69(19)
O(3 <i>b</i>)-Eu(1)-O(7)	140.73(18)	O(18)-Eu(2)-O(2)	83.18(19)
O(12)-Eu(1)-O(7)	126.40(16)	O(26 <i>c</i>)-Eu(2)-O(2)	134.18(17)
O(28 <i>a</i>)-Eu(1)-O(6)	73.66(19)	O(20)-Eu(2)-O(13)	148.81(19)
O(3 <i>b</i>)-Eu(1)-O(6)	95.58(19)	O(18)-Eu(2)-O(13)	126.93(16)
O(12)-Eu(1)-O(6)	138.39(19)	O(26 <i>c</i>)-Eu(2)-O(13)	84.59(16)
O(7)-Eu(1)-O(6)	85.89(18)	O(2)-Eu(2)-O(13)	73.38(17)

O(28a)-Eu(1)-O(1)	142.04(18)	O(20)-Eu(2)-O(3w)	99.3(2)
O(3b)-Eu(1)-O(1)	75.44(18)	O(18)-Eu(2)-O(3w)	137.0(2)
O(12)-Eu(1)-O(1)	91.45(19)	O(26c)-Eu(2)-O(3w)	142.3(2)
O(7)-Eu(1)-O(1)	72.37(18)	O(2)-Eu(2)-O(3w)	73.1(2)
O(6)-Eu(1)-O(1)	126.25(16)	O(13)-Eu(2)-O(3w)	80.07(19)
O(28a)-Eu(1)-N(2)	71.8(2)	O(20)-Eu(2)-O(16d)	77.22(18)
O(3b)-Eu(1)-N(2)	126.92(19)	O(18)-Eu(2)-O(16d)	143.91(19)
O(12)-Eu(1)-N(2)	62.98(18)	O(26c)-Eu(2)-O(16d)	73.74(19)
O(7)-Eu(1)-N(2)	63.44(17)	O(2)-Eu(2)-O(16d)	132.90(19)
O(6)-Eu(1)-N(2)	137.44(19)	O(13)-Eu(2)-O(16d)	73.49(17)
O(1)-Eu(1)-N(2)	73.85(19)	O(3w)-Eu(2)-O(16d)	69.0(2)
O(28a)-Eu(1)-N(1)	126.3(2)	O(20)-Eu(2)-N(3)	129.54(18)
O(3b)-Eu(1)-N(1)	76.87(17)	O(18)-Eu(2)-N(3)	64.06(16)
O(12)-Eu(1)-N(1)	146.73(19)	O(26c)-Eu(2)-N(3)	68.50(18)
O(7)-Eu(1)-N(1)	68.97(17)	O(2)-Eu(2)-N(3)	65.71(18)
O(6)-Eu(1)-N(1)	62.91(18)	O(13)-Eu(2)-N(3)	62.94(16)
O(1)-Eu(1)-N(1)	63.45(17)	O(3w)-Eu(2)-N(3)	130.4(2)
N(2)-Eu(1)-N(1)	123.21(19)	O(16d)-Eu(2)-N(3)	123.67(18)
O(28a)-Eu(1)-O(1w)	76.04(18)	O(20)-Eu(2)-O(2w)	68.0(2)
O(3b)-Eu(1)-O(1w)	64.33(18)	O(18)-Eu(2)-O(2w)	72.1(2)
O(12)-Eu(1)-O(1w)	73.07(18)	O(26c)-Eu(2)-O(2w)	139.30(19)
O(7)-Eu(1)-O(1w)	146.62(18)	O(2)-Eu(2)-O(2w)	70.09(19)
O(6)-Eu(1)-O(1w)	66.72(18)	O(13)-Eu(2)-O(2w)	135.83(19)
O(1)-Eu(1)-O(1w)	139.22(17)	O(3w)-Eu(2)-O(2w)	66.3(2)
N(2)-Eu(1)-O(1w)	125.82(18)	O(16d)-Eu(2)-O(2w)	116.2(2)
N(1)-Eu(1)-O(1w)	110.96(17)	N(3)-Eu(2)-O(2w)	119.8(2)
O(21d)-Eu(3)-O(8d)	85.04(19)	O(21d)-Eu(3)-O(24)	72.41(16)
O(21d)-Eu(3)-O(19)	159.14(18)	O(8d)-Eu(3)-O(24)	134.83(17)
O(8d)-Eu(3)-O(19)	84.51(17)	O(19)-Eu(3)-O(24)	126.89(15)
O(21d)-Eu(3)-O(17d)	86.81(19)	O(17d)-Eu(3)-O(24)	141.00(17)
O(8d)-Eu(3)-O(17d)	72.93(18)	O(29e)-Eu(3)-O(24)	76.19(17)
O(19)-Eu(3)-O(17d)	72.87(17)	O(4w)-Eu(3)-O(24)	76.37(19)
O(21d)-Eu(3)-O(29e)	101.5(2)	O(21d)-Eu(3)-N(4)	135.08(18)
O(8d)-Eu(3)-O(29e)	70.57(18)	O(8d)-Eu(3)-N(4)	131.09(19)

O(19)-Eu(3)-O(29e)	91.97(19)	O(19)-Eu(3)-N(4)	63.91(17)
O(17d)-Eu(3)-O(29e)	141.58(17)	O(17d)-Eu(3)-N(4)	124.83(18)
O(21d)-Eu(3)-O(4w)	88.0(2)	O(29e)-Eu(3)-N(4)	74.09(19)
O(8d)-Eu(3)-O(4w)	142.7(2)	O(4w)-Eu(3)-N(4)	76.6(2)
O(19)-Eu(3)-O(4w)	89.4(2)	O(24)-Eu(3)-N(4)	63.05(16)
O(17d)-Eu(3)-O(4w)	70.1(2)	O(10e)-Eu(4)-O(22d)	83.09(19)
O(29e)-Eu(3)-O(4w)	146.6(2)	O(10e)-Eu(4)-O(5w)	100.9(2)
O(22d)-Eu(4)-O(24)	78.34(16)	O(22d)-Eu(4)-O(5w)	77.34(19)
O(5w)-Eu(4)-O(24)	83.73(18)	O(10e)-Eu(4)-O(30)	80.9(2)
O(30)-Eu(4)-O(24)	119.60(17)	O(22d)-Eu(4)-O(30)	144.62(18)
O(25)-Eu(4)-O(24)	80.15(16)	O(5w)-Eu(4)-O(30)	75.05(18)
N(5)-Eu(4)-O(24)	116.24(16)	O(10e)-Eu(4)-O(25)	88.4(2)
O(10e)-Eu(4)-O(23)	143.57(18)	O(22d)-Eu(4)-O(25)	81.44(18)
O(22d)-Eu(4)-O(23)	129.85(16)	O(5w)-Eu(4)-O(25)	155.53(18)
O(5w)-Eu(4)-O(23)	101.48(18)	O(30)-Eu(4)-O(25)	129.12(16)
O(30)-Eu(4)-O(23)	77.62(17)	O(10e)-Eu(4)-N(5)	72.90(19)
O(25)-Eu(4)-O(23)	82.91(17)	O(22d)-Eu(4)-N(5)	138.24(18)
N(5)-Eu(4)-O(23)	71.41(16)	O(5w)-Eu(4)-N(5)	139.75(19)
O(24)-Eu(4)-O(23)	52.10(14)	O(30)-Eu(4)-N(5)	64.71(17)
O(27)-Eu(5)-O(5f)	144.01(18)	O(25)-Eu(4)-N(5)	64.59(17)
O(27)-Eu(5)-O(15g)	77.21(19)	O(10e)-Eu(4)-O(24)	159.4(2)
O(5f)-Eu(5)-O(15g)	134.21(19)	O(5f)-Eu(5)-O(4g)	69.52(18)
O(27)-Eu(5)-O(6w)	80.47(18)	O(15g)-Eu(5)-O(4g)	71.40(19)
O(5f)-Eu(5)-O(6w)	118.99(19)	O(6w)-Eu(5)-O(4g)	80.86(17)
O(15g)-Eu(5)-O(6w)	76.38(17)	O(7w)-Eu(5)-O(4g)	117.0(2)
O(27)-Eu(5)-O(7w)	82.73(19)	O(27)-Eu(5)-O(13c)	88.89(17)
O(5f)-Eu(5)-O(7w)	76.5(2)	O(5f)-Eu(5)-O(13c)	82.27(19)
O(15g)-Eu(5)-O(7w)	144.5(2)	O(15g)-Eu(5)-O(13c)	79.51(17)
O(6w)-Eu(5)-O(7w)	71.57(18)	O(6w)-Eu(5)-O(13c)	155.26(16)
O(27)-Eu(5)-O(4g)	146.42(19)	O(7w)-Eu(5)-O(13c)	129.41(18)
O(7w)-Eu(5)-O(14c)	79.71(17)	O(4g)-Eu(5)-O(13c)	96.73(17)
O(4g)-Eu(5)-O(14c)	132.06(18)	O(27)-Eu(5)-O(14c)	75.44(18)
O(13c)-Eu(5)-O(14c)	50.02(14)	O(5f)-Eu(5)-O(14c)	72.18(18)
O(6w)-Eu(5)-O(14c)	144.46(16)	O(15g)-Eu(5)-O(14c)	121.95(16)

Eu(1)-O(5a)	2.324(4)	Eu(2)-O(3b)	2.378(4)
Eu(1)-O(4b)	2.379(4)	Eu(2)-O(11)	2.410(4)
Eu(1)-O(1)	2.434(4)	Eu(2)-O(7)	2.429(4)
Eu(1)-O(10c)	2.445(4)	Eu(2)-O(3w)	2.431(5)
Eu(1)-O(6)	2.446(4)	Eu(2)-O(12d)	2.459(4)
Eu(1)-O(1w)	2.517(4)	Eu(2)-O(4w)	2.463(4)
Eu(1)-O(2w)	2.520(4)	Eu(2)-O(9)	2.489(4)
Eu(1)-O(8c)	2.527(4)	Eu(2)-O(1)	2.540(4)
Eu(1)-N(1)	2.559(5)	Eu(2)-O(2)	2.546(4)
O(5a)-Eu(1)-O(4b)	90.17(15)	O(6)-Eu(1)-O(8c)	69.06(15)
O(5a)-Eu(1)-O(1)	142.47(14)	O(1w)-Eu(1)-O(8c)	132.03(14)
O(4b)-Eu(1)-O(1)	77.44(14)	O(2w)-Eu(1)-O(8c)	125.79(14)
O(5a)-Eu(1)-O(10c)	136.91(15)	O(5a)-Eu(1)-N(1)	135.03(15)
O(4b)-Eu(1)-O(10c)	77.50(16)	O(4b)-Eu(1)-N(1)	134.31(15)
O(1)-Eu(1)-O(10c)	75.20(14)	O(1)-Eu(1)-N(1)	62.39(14)
O(5a)-Eu(1)-O(6)	87.16(14)	O(10c)-Eu(1)-N(1)	72.18(15)
O(4b)-Eu(1)-O(6)	141.62(15)	O(6)-Eu(1)-N(1)	62.85(14)
O(1)-Eu(1)-O(6)	124.11(13)	O(1w)-Eu(1)-N(1)	107.50(15)
O(10c)-Eu(1)-O(6)	78.61(15)	O(2w)-Eu(1)-N(1)	69.30(15)
O(5a)-Eu(1)-O(1w)	74.65(15)	O(8c)-Eu(1)-N(1)	120.46(15)
O(4b)-Eu(1)-O(1w)	73.52(16)	O(3b)-Eu(2)-O(11)	82.89(16)
O(1)-Eu(1)-O(1w)	67.89(14)	O(3b)-Eu(2)-O(7)	72.04(15)
O(10c)-Eu(1)-O(1w)	136.90(15)	O(11)-Eu(2)-O(7)	80.72(15)
O(6)-Eu(1)-O(1w)	141.28(15)	O(3b)-Eu(2)-O(3w)	143.24(17)
O(5a)-Eu(1)-O(2w)	70.07(15)	O(11)-Eu(2)-O(3w)	83.16(18)
O(4b)-Eu(1)-O(2w)	141.23(16)	O(7)-Eu(2)-O(3w)	138.14(17)
O(1)-Eu(1)-O(2w)	97.91(14)	O(3b)-Eu(2)-O(12d)	74.00(16)
O(10c)-Eu(1)-O(2w)	139.25(15)	O(11)-Eu(2)-O(12d)	66.48(14)
O(6)-Eu(1)-O(2w)	72.48(15)	O(7)-Eu(2)-O(12d)	134.99(15)
O(1w)-Eu(1)-O(2w)	69.26(15)	O(3w)-Eu(2)-O(12d)	69.25(17)
O(5a)-Eu(1)-O(8c)	71.29(14)	O(3b)-Eu(2)-O(4w)	86.99(17)
O(4b)-Eu(1)-O(8c)	73.84(15)	O(11)-Eu(2)-O(4w)	133.92(15)
O(1)-Eu(1)-O(8c)	135.25(13)	O(7)-Eu(2)-O(4w)	137.55(15)

O(10c)-Eu(1)-O(8c)	65.62(14)	O(3w)-Eu(2)-O(4w)	78.69(18)
O(12d)-Eu(2)-O(1)	129.13(14)	O(12d)-Eu(2)-O(4w)	67.51(16)
O(4w)-Eu(2)-O(1)	67.67(14)	O(3b)-Eu(2)-O(9)	132.67(15)
O(9)-Eu(2)-O(1)	104.29(14)	O(11)-Eu(2)-O(9)	71.16(15)
O(3b)-Eu(2)-O(2)	132.15(14)	O(7)-Eu(2)-O(9)	65.32(14)
O(11)-Eu(2)-O(2)	139.41(15)	O(3w)-Eu(2)-O(9)	72.94(17)
O(7)-Eu(2)-O(2)	90.94(15)	O(12d)-Eu(2)-O(9)	125.32(15)
O(3w)-Eu(2)-O(2)	76.97(16)	O(4w)-Eu(2)-O(9)	139.13(17)
O(12d)-Eu(2)-O(2)	134.01(16)	O(3b)-Eu(2)-O(1)	80.88(14)
O(4w)-Eu(2)-O(2)	76.14(17)	O(11)-Eu(2)-O(1)	152.07(14)
O(9)-Eu(2)-O(2)	69.30(15)	O(7)-Eu(2)-O(1)	72.72(14)
O(1)-Eu(2)-O(2)	51.27(13)	O(3w)-Eu(2)-O(1)	122.69(16)

Symmetry codes: *a*) $-x+3, -y+3, -z+1$; *b*) $-x+3, -y+2, -z$; *c*) $-x+2, -y+2, -z+1$; *d*) $x-1, y, z$; *e*) $-x+2, -y+3, -z+1$; *f*) $x-1, y, z+1$; *g*) $-x+3, -y+2, -z+1$ for **1**; *a*) $1-x, y-1/2, -z+1/2$; *b*) $x, y-1, z$; *c*) $x-1, y, z$; *d*) $-x+1, -y+1, -z$ for **2**.