Electronic Supplementary Information

Structures, fluorescence properties and magnetic properties of a series of rhombus-shaped Ln^{III}_4 clusters: magnetocaloric effect and single-molecule-magnet behavior

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Experimental Section

Materials and methods

The chemicals used in this paper were reagent grade without further purification. The seven β-diketone salts ($Sm(acac)_3·2H_2O$, $Eu(acac)_3·2H_2O$, $Gd(acac)_3·2H_2O$, $Tb(acac)_3·2H_2O$, $Dy(acac)_3·2H_2O$, $Ho(acac)_3·2H_2O$ and $Er(acac)_3·2H_2O$) and the Schiff base ligand HL were synthesized according to the method in the literature.[1]

Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra for **1-7** were recorded in the range of 4000–650 cm^{-1} with a Bruker TENOR 27 spectrophotometer using KBr pellet. PXRD data were examined on a Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.54056 Å), with a scan speed of 10° min^{-1} in the range of 2θ = 5−50°. Luminescence properties were recorded on an *F*-4500 *FL* spectrophotometer with a xenon arc lamp as the light source. The magnetic measurements were carried out with a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Polycrystalline samples of clusters **1-7** were collected by solvent evaporation and dried in the air, which using for magnetic measurements were frozen in eicosane to avoid torquing of the crystallites. Dc susceptibility was measured in the temperature domain 2.0−300 K under an applied

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field of 1000 Oe. Ac susceptibility was measured with an oscillating ac field of 3.0 Oe using frequencies between 111 to 2311 Hz. The diamagnetic corrections for the complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.[2]

Tables S1 Selected bond lengths (Å) and angles (°) for cluster **1**[a]

Bond lengths			
Sm(1)-O(4)	2.348(3)	Sm(2)-O(7)	2.343(3)
Sm(1)-O(8)	2.355(3)	Sm(2)-O(8)#1	2.361(3)
Sm(1)-O(5)	2.398(3)	Sm(2)-O(6)	2.366(3)
Sm(1)-O(8)#1	2.429(3)	Sm(2)-O(3)	2.411(3)
Sm(1)-O(1)	2.454(3)	Sm(2)-O(2)	2.423(3)
Sm(1)-O(2)	2.458(3)	Sm(2)-O(1)#1	2.507(3)
Sm(1)-O(3)	2.468(3)	Sm(1)-N(1)	2.582(3)
Sm(2)-N(5)	2.548(3)	Sm(2)-N(3)	2.613(4)
Bond angles			
O(4)-Sm(1)-O(8)	141.25(10)	O(8)#1-Sm(1)-O(3)	70.07(9)
O(4)-Sm(1)-O(5)	70.44(10)	O(1)-Sm(1)-O(3)	149.13(9)
O(8)-Sm(1)-O(5)	73.14(10)	O(2)-Sm(1)-O(3)	66.38(9)
O(4)-Sm(1)-O(8)#1	148.24(9)	O(7)-Sm(2)-O(8)#1	129.05(10)
O(8)-Sm(1)-O(8)#1	70.51(10)	O(7)-Sm(2)-O(6)	73.39(10)
O(5)-Sm(1)-O(8)#1	138.73(9)	O(8)#1-Sm(2)-O(6)	73.54(10)
O(4)-Sm(1)-O(1)	91.29(10)	O(7)-Sm(2)-O(3)	145.55(10)
O(8)-Sm(1)-O(1)	71.82(9)	O(8)#1-Sm(2)-O(3)	72.20(9)
O(5)-Sm(1)-O(1)	83.67(10)	O(6)-Sm(2)-O(3)	140.40(10)
O(8)#1-Sm(1)-O(1)	102.65(9)	O(7)-Sm(2)-O(2)	139.63(10)
O(4)-Sm(1)-O(2)	81.89(10)	O(8)#1-Sm(2)-O(2)	70.91(9)
O(8)-Sm(1)-O(2)	132.81(9)	O(6)-Sm(2)-O(2)	82.68(10)
O(5)-Sm(1)-O(2)	128.54(10)	O(3)-Sm(2)-O(2)	67.81(9)
O(8)#1-Sm(1)-O(2)	69.22(9)	O(7)-Sm(2)-O(1)#1	85.19(9)
O(1)-Sm(1)-O(2)	140.82(9)	O(8)#1-Sm(2)-O(1)#1	70.76(9)
O(4)-Sm(1)-O(3)	110.67(11)	O(6)-Sm(2)-O(1)#1	109.38(10)
O(8)-Sm(1)-O(3)	77.58(9)	O(3)-Sm(2)-O(1)#1	77.10(9)
O(5)-Sm(1)-O(3)	83.71(10)	O(2)-Sm(2)-O(1)#1	134.06(9)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S2 Selected bond lengths (Å) and angles (°) for cluster **2**[a]

Bond lengths			
Eu(1)-O(5)	2.341(2)	Eu(2)-O(8)	2.350(2)
Eu(1)-O(8)	2.350(2)	Eu(2)-O(6)	2.361(3)
Eu(1)-O(4)	2.353(2)	Eu(2)-O(8)#1	2.366(3)
Eu(1)-O(2)	2.400(2)	Eu(2)-O(3)	2.411(3)
Eu(1)-O(1)	2.406(2)	Eu(2)-O(1)#1	2.423(3)
Eu(1)-O(3)	2.497(2)	Eu(2)-O(2)#1	2.507(3)
Eu(2)-O(7)	2.335(2)	Eu(1)-N(3)	2.537(3)
Eu(1)-N(1)	2.604(3)	Eu(2)-N(5)	2.572(3)
Bond angles			
O(5)-Eu(1)-O(8)	129.06(8)	O(7)-Eu(2)-O(8)#1	147.80(8)
O(5)-Eu(1)-O(4)	73.55(8)	O(8)-Eu(2)-O(8)#1	70.53(8)
O(8)-Eu(1)-O(4)	73.58(8)	O(6)-Eu(2)-O(8)#1	138.71(7)
O(5)-Eu(1)-O(2)	145.20(7)	O(7)-Eu(2)-O(3)	91.34(8)
O(8)-Eu(1)-O(2)	72.29(7)	O(8)-Eu(2)-O(3)	71.65(7)
O(4)-Eu(1)-O(2)	140.57(7)	O(6)-Eu(2)-O(3)	83.59(7)
O(5)-Eu(1)-O(1)	139.97(8)	O(8)#1-Eu(2)-O(3)	102.77(7)
O(8)-Eu(1)-O(1)	70.89(7)	O(7)-Eu(2)-O(1)#1	81.51(8)
O(4)-Eu(1)-O(1)	82.82(8)	O(8)-Eu(2)-O(1)#1	132.87(7)
O(2)-Eu(1)-O(1)	67.81(7)	O(6)-Eu(2)-O(1)#1	128.30(8)
O(5)-Eu(1)-O(3)	84.80(7)	O(8)#1-Eu(2)-O(1)#1	69.28(7)
O(8)-Eu(1)-O(3)	70.67(7)	O(3)-Eu(2)-O(1)#1	141.13(7)
O(4)-Eu(1)-O(3)	109.03(8)	O(7)-Eu(2)-O(2)#1	110.55(8)
O(2)-Eu(1)-O(3)	77.34(7)	O(8)-Eu(2)-O(2)#1	77.73(7)
O(1)-Eu(1)-O(3)	134.10(7)	O(6)-Eu(2)-O(2)#1	83.37(7)
O(7)-Eu(2)-O(8)	141.66(8)	O(8)#1-Eu(2)-O(2)#1	70.34(7)
O(7)-Eu(2)-O(6)	70.87(8)	O(3)-Eu(2)-O(2)#1	149.04(7)
O(8)-Eu(2)-O(6)	73.19(8)	O(1)#1-Eu(2)-O(2)#1	66.37(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S3 Selected bond lengths (Å) and angles (°) for cluster **3**[a]

Bond lengths			
Gd(1)-O(8)	2.335(7)	Gd(2)-O(8)	2.339(7)
Gd(1)-O(5)	2.339(7)	Gd(2)-O(6)	2.368(7)
Gd(1)-O(4)	2.340(7)	Gd(2)-O(8)#1	2.402(7)
Gd(1)-O(1)	2.393(7)	Gd(2)-O(3)	2.435(7)
Gd(1)-O(2)	2.396(7)	Gd(2)-O(1)#1	2.437(7)
Gd(1)-O(3)	2.478(7)	Gd(2)-O(2)#1	2.442(7)
Gd(2)-O(7)	2.330(7)	Gd(1)-N(3)	2.517(9)
Gd(1)-N(1)	2.602(8)	Gd(2)-N(5)	2.558(9)
Bond angles			
O(8)-Gd(1)-O(5)	129.1(2)	O(7)-Gd(2)-O(8)#1	147.5(2)
O(8)-Gd(1)-O(4)	73.6(2)	O(8)-Gd(2)-O(8)#1	70.7(3)

O(5)-Gd(1)-O(4)	74.0(3)	O(6)-Gd(2)-O(8)#1	138.9(2)
O(8)-Gd(1)-O(1)	71.2(2)	O(7)-Gd(2)-O(3)	91.2(2)
O(5)-Gd(1)-O(1)	140.4(2)	O(8)-Gd(2)-O(3)	71.3(2)
O(4)-Gd(1)-O(1)	82.9(3)	O(6)-Gd(2)-O(3)	83.1(2)
O(8)-Gd(1)-O(2)	72.3(2)	O(8)#1-Gd(2)-O(3)	103.1(2)
O(5)-Gd(1)-O(2)	144.5(2)	O(7)-Gd(2)-O(1)#1	81.3(2)
O(4)-Gd(1)-O(2)	140.7(2)	O(8)-Gd(2)-O(1)#1	133.1(2)
O(1)-Gd(1)-O(2)	68.1(2)	O(6)-Gd(2)-O(1)#1	128.2(3)
O(8)-Gd(1)-O(3)	70.6(2)	O(8)#1-Gd(2)-O(1)#1	69.3(2)
O(5)-Gd(1)-O(3)	84.0(2)	O(3)-Gd(2)-O(1)#1	141.6(2)
O(4)-Gd(1)-O(3)	108.7(2)	O(7)-Gd(2)-O(2)#1	110.8(3)
O(1)-Gd(1)-O(3)	134.5(2)	O(8)-Gd(2)-O(2)#1	77.6(2)
O(2)-Gd(1)-O(3)	77.5(2)	O(6)-Gd(2)-O(2)#1	83.3(2)
O(7)-Gd(2)-O(8)	141.8(2)	O(8)#1-Gd(2)-O(2)#1	70.3(2)
O(7)-Gd(2)-O(6)	71.0(3)	O(3)-Gd(2)-O(2)#1	148.5(2)
O(8)-Gd(2)-O(6)	73.3(3)	O(1)#1-Gd(2)-O(2)#1	66.6(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S4 Selected bond lengths (Å) and angles (°) for cluster **4**[a]

Bond lengths			
Tb(1)-O(4)	2.297(3)	Tb(2)-O(7)	2.311(3)
Tb(1)-O(5)	2.340(3)	Tb(2)-O(8	2.323(3)
Tb(1)-O(8)#1	2.342(3)	Tb(2)-O(6)	2.330(3)
Tb(1)-O(1)	2.378(3)	Tb(2)-O(3)	2.380(3)
Tb(1)-O(8)	2.381(3)	Tb(2)-O(2)	2.393(3)
Tb(1)-O(3)	2.411(3)	Tb(2)-O(1)#1	2.414(3)
Tb(1)-O(2)	2.431(3)	Tb(1)-N(1)	2.552(3)
Tb(2)-N(5)	2.516(3)	Tb(2)-N(3)	2.569(4)
Bond angles			
O(4)-Tb(1)-O(5	72.76(10)	O(1)-Tb(1)-O(2)	131.04(10)
O(4)-Tb(1)-O(8)#1	140.86(10)	O(8)-Tb(1)-O(2)	74.11(10)
O(5)-Tb(1)-O(8)#1	75.30(10)	O(3)-Tb(1)-O(2)	74.87(10)
O(4)-Tb(1)-O(1)	83.62(10)	O(7)-Tb(2)-O(8)	143.52(10)
O(5)-Tb(1)-O(1)	82.95(10)	O(7)-Tb(2)-O(6)	72.58(10)
O(8)#1-Tb(1)-O(1)	70.47(9)	O(8)-Tb(2)-O(6)	142.00(10)
O(4)-Tb(1)-O(8)	145.03(10)	O(7)-Tb(2)-O(3)	139.92(11)
O(5)-Tb(1)-O(8)	141.70(9)	O(8)-Tb(2)-O(3)	70.94(9)
O(8)#1-Tb(1)-O(8)	71.48(11)	O(6)-Tb(2)-O(3)	83.54(10)
O(1)-Tb(1)-O(8)	103.00(9)	O(7)-Tb(2)-O(2)	67.73(10)
O(4)-Tb(1)-O(3)	120.15(10)	O(8)-Tb(2)-O(2)	85.07(10)
O(5)-Tb(1)-O(3)	83.74(10)	O(6)-Tb(2)-O(2)	70.14(9)
O(8)#1-Tb(1)-O(3)	77.48(9)	O(3)-Tb(2)-O(2)	108.42(10)
O(1)-Tb(1)-O(3)	147.47(9)	O(7)-Tb(2)-O(1)#1	78.19(10)
O(8)-Tb(1)-O(3)	71.03(9)	O(8)-Tb(2)-O(1)#1	134.13(10)

O(4)-Tb(1)-O(2	84.61(10)	O(6)-Tb(2)-O(1)#1	143.52(10)
O(5)-Tb(1)-O(2)	126.37(10	O(3)-Tb(2)-O(1)#1	72.58(10)
O(8)#1-Tb(1)-O(2)	133.33(9)	O(2)-Tb(2)-O(1)#1	142.00(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S5 Selected bond lengths (Å) and angles (°) for cluster **5** [a]

Bond lengths			
Dy(1)-O(4)	2.2786(17)	Dy(2)-O(6)	2.3000(18)
Dy(1)-O(5)	2.3288(19)	Dy(2)-O(7)	2.3150(19)
Dy(1)-O(8)	2.3285(16)	Dy(2)-O(8)	2.3214(17)
Dy(1)-O(8)#1	2.3567(16)	Dy(2)-O(1)#1	2.3561(18)
Dy(1)-O(3)	2.3710(17)	Dy(2)-O(2)#1	2.3741(17)
Dy(1)-O(1)	2.4078(17)	Dy(2)-O(3)	2.4012(16)
Dy(1)-O(2)	2.4197(19)	Dy(1)-N(5)	2.541(2)
Dy(2)-N(1)#1	2.507(2)	Dy(2)-N(3)#1	2.559(2)
Bond angles			
O(4)-Dy(1)-O(5)	72.88(7)	O(8)#1-Dy(1)-O(2)	69.68(6)
O(4)-Dy(1)-O(8)	141.28(6)	O(3)-Dy(1)-O(2)	143.17(6)
O(5)-Dy(1)-O(8)	75.47(6)	O(1)-Dy(1)-O(2)	66.31(6)
O(4)-Dy(1)-O(8)#1	145.09(6)	O(6)-Dy(2)-O(7)	74.38(7)
O(5)-Dy(1)-O(8)#1	141.41(6)	O(6)-Dy(2)-O(8)	130.65(6)
O(8)-Dy(1)-O(8)#1	71.20(7)	O(7)-Dy(2)-O(8)	74.53(6)
O(4)-Dy(1)-O(3)	83.99(6)	O(6)-Dy(2)-O(1)#1	143.36(6)
O(5)-Dy(1)-O(3)	83.33(6)	O(7)-Dy(2)-O(1)#1	141.90(6)
O(8)-Dy(1)-O(3)	70.64(6)	O(8)-Dy(2)-O(1)#1	73.02(6)
O(8)#1-Dy(1)-O(3)	102.99(6)	O(6)-Dy(2)-O(2)#1	140.03(6)
O(4)-Dy(1)-O(1)	119.28(6)	O(7)-Dy(2)-O(2)#1	83.15(6)
O(5)-Dy(1)-O(1)	83.01(6)	O(8)-Dy(2)-O(2)#1	71.06(6)
O(8)-Dy(1)-O(1)	77.65(6)	O(1)#1-Dy(2)-O(2)#1	67.86(6)
O(8)#1-Dy(1)-O(1)	71.48(6)	O(6)-Dy(2)-O(3)	84.40(6)
O(3)-Dy(1)-O(1)	147.71(6)	O(7)-Dy(2)-O(3)	108.12(6)
O(4)-Dy(1)-O(2)	84.20(6)	O(8)-Dy(2)-O(3)	70.22(6)
O(5)-Dy(1)-O(2)	125.63(6)	O(1)#1-Dy(2)-O(3)	78.85(6)
O(8)-Dy(1)-O(2)	133.17(6)	O(2)#1-Dy(2)-O(3)	134.59(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S6 Selected bond lengths (Å) and angles (°) for cluster **6** [a]

Bond lengths			
Ho(1)-O(4)	2.292(4)	Ho(3)-O(12)	2.295(4)
Ho(1)-O(8)	2.296(4)	Ho(3)-O(16)#2	2.300(4)
Ho(1)-O(5)	2.301(4)	Ho(3)-O(13)	2.315(4)
Ho(1)-O(1)	2.346(4)	Ho(3)-O(9)	2.357(4)
Ho(1)-O(2)	2.352(4)	Ho(3)-O(11)	2.362(4)
Ho(1)-O(3)	2.402(4)	Ho(3)-O(10)	2.366(4)

Ho(2)-O(7)	2.285(4)	Ho(4)-O(14)	2.289(4)
Ho(2)-O(6)	2.306(4)	Ho(4)-O(15)	2.316(4)
Ho(2)-O(8)	2.309(3)	Ho(4)-O(9)#2	2.335(4)
Ho(2)-O(3)	2.345(4)	Ho(4)-O(16)	2.342(4)
Ho(2)-O(8)#1	2.359(3)	Ho(4)-O(16)#2	2.353(4)
Ho(2)-O(1)#1	2.392(4)	Ho(4)-O(11)	2.371(4)
Ho(2)-O(2)#1	2.399(4)	Ho(4)-O(10)	2.395(4)
Ho(1)-N(3)	2.489(5)	Ho(3)-N(11)	2.496(4)
Ho(1)-N(1)	2.535(5)	Ho(3)-N(9)	2.516(5)
Ho(2)-N(5)	2.521(5)	Ho(4)-N(7)#2	2.553(4)
Bond angles			
O(4)-Ho(1)-O(8)	126.97(13)	O(12)-Ho(3)-O(16)#2	126.88(13)
O(4)-Ho(1)-O(5)	74.92(14)	O(12)-Ho(3)-O(13)	75.04(14)
O(8)-Ho(1)-O(5)	72.81(13)	O(16)#2-Ho(3)-O(13)	73.83(14)
O(4)-Ho(1)-O(1)	142.05(13)	O(12)-Ho(3)-O(9)	82.80(13)
O(8)-Ho(1)-O(1)	72.06(12)	O(16)#2-Ho(3)-O(9)	69.76(12)
O(5)-Ho(1)-O(1)	82.54(13)	O(13)-Ho(3)-O(9)	110.79(14)
O(4)-Ho(1)-O(2)	143.89(14)	O(12)-Ho(3)-O(11)	145.63(13)
O(8)-Ho(1)-O(2)	72.56(13)	O(16)#2-Ho(3)-O(11)	73.79(12)
O(5)-Ho(1)-O(2)	139.96(14)	O(13)-Ho(3)-O(11)	139.11(13)
O(1)-Ho(1)-O(2)	68.14(12)	O(9)-Ho(3)-O(11)	80.15(12)
O(4)-Ho(1)-O(3)	81.99(13)	O(12)-Ho(3)-O(10)	140.48(13)
O(8)-Ho(1)-O(3)	69.60(13)	O(16)#2-Ho(3)-O(10)	72.50(13)
O(5)-Ho(1)-O(3)	107.83(13)	O(13)-Ho(3)-O(10)	80.02(14)
O(1)-Ho(1)-O(3)	134.62(12)	O(9)-Ho(3)-O(10)	135.29(12)
O(2)-Ho(1)-O(3)	77.89(12)	O(11)-Ho(3)-O(10)	66.88(13)
O(7)-Ho(2)-O(6)	72.99(13)	O(14)-Ho(4)-O(15)	73.44(15)
O(7)-Ho(2)-O(8)	142.18(13)	O(14)-Ho(4)-O(9)#2	81.32(13)
O(6)-Ho(2)-O(8)	79.36(13)	O(15)-Ho(4)-O(9)#2	83.34(14)
O(7)-Ho(2)-O(3)	82.93(13)	O(14)-Ho(4)-O(16)	141.97(13)
O(6)-Ho(2)-O(3)	87.47(13)	O(15)-Ho(4)-O(16)	79.35(14)
O(8)-Ho(2)-O(3)	70.39(13)	O(9)#2-Ho(4)-O(16)	69.44(12)
O(7)-Ho(2)-O(8)#1	143.46(13)	O(14)-Ho(4)-O(16)#2	141.33(13)
O(6)-Ho(2)-O(8)#1	142.26(13)	O(15)-Ho(4)-O(16)#2	145.07(14)
O(8)-Ho(2)-O(8)#1	70.96(14)	O(9)#2-Ho(4)-O(16)#2	102.13(12)
O(3)-Ho(2)-O(8)#1	103.41(12)	O(16)-Ho(4)-O(16)#2	70.81(14)
O(7)-Ho(2)-O(1)#1	83.78(13)	O(14)-Ho(4)-O(11)	124.39(13)
O(6)-Ho(2)-O(1)#1	119.61(13)	O(15)-Ho(4)-O(11)	83.46(14)
O(8)-Ho(2)-O(1)#1	133.06(12)	O(9)#2-Ho(4)-O(11)	145.69(12)
O(3)-Ho(2)-O(1)#1	144.41(13)	O(16)-Ho(4)-O(11)	77.06(13)
O(8)#1-Ho(2)-O(1)#1	70.15(12)	O(16)#2-Ho(4)-O(11)	72.69(12)
O(7)-Ho(2)-O(2)#1	122.28(13)	O(14)-Ho(4)-O(10)	84.44(13)
O(6)-Ho(2)-O(2)#1	80.29(13)	O(15)-Ho(4)-O(10)	122.09(14)
O(8)-Ho(2)-O(2)#1	76.42(12)	O(9)#2-Ho(4)-O(10)	145.57(12)

O(3)-Ho(2)-O(2)#1	146.21(12)	O(16)-Ho(4)-O(10)	133.11(12)
O(8)#1-Ho(2)-O(2)#1	70.63(12)	O(16)#2-Ho(4)-O(10)	71.07(12)
O(1)#1-Ho(2)-O(2)#1	66.64(13)	O(11)-Ho(4)-O(10)	66.29(12)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Tables S7 Selected bond lengths (Å) and angles (°) for cluster **7** [a]

Bond lengths			
Er(1)-O(4)	2.2664(19)	Er(2)-O(6)	2.284(2)
Er(1)-O(8)	2.2989(17)	Er(2)-O(7)	2.294(2)
Er(1)-O(5)	2.310(2)	Er(2)-O(8)	2.2936(17)
Er(1)-O(8)#1	2.3394(18)	Er(2)-O(1)#1	2.3484(19)
Er(1)-O(3)	2.3483(18)	Er(2)-O(2)#1	2.3500(19)
Er(1)-O(1)	2.3767(18)	Er(2)-O(3)	2.3750(18)
Er(1)-O(2)	2.390(2)	Er(2)-N(1)#1	2.481(2)
Er(1)-N(5)	2.515(2)	Er(2)-N(3)#1	2.536(2)
Bond angles			
O(4)-Er(1)-O(8)	141.37(7)	O(8)#1-Er(1)-O(2)	69.69(6)
O(4)-Er(1)-O(5)	73.38(7)	O(3)-Er(1)-O(2)	143.51(6)
O(8)-Er(1)-O(5)	75.48(7)	O(1)-Er(1)-O(2)	66.51(6)
O(4)-Er(1)-O(8)#1	144.59(7)	O(6)-Er(2)-O(7)	74.94(7)
O(8)-Er(1)-O(8)#1	71.40(7)	O(6)-Er(2)-O(8)	130.24(7)
O(5)-Er(1)-O(8)#1	141.40(6)	O(7)-Er(2)-O(8)	74.50(7)
O(4)-Er(1)-O(3)	83.61(7)	O(6)-Er(2)-O(1)#1	143.26(7)
O(8)-Er(1)-O(3)	70.50(6)	O(7)-Er(2)-O(1)#1	141.40(7)
O(5)-Er(1)-O(3)	83.27(7)	O(8)-Er(2)-O(1)#1	72.81(6)
O(8)#1-Er(1)-O(3)	103.37(6)	O(6)-Er(2)-O(2)#1	140.76(7)
O(4)-Er(1)-O(1)	119.79(7)	O(7)-Er(2)-O(2)#1	82.84(7)
O(8)-Er(1)-O(1)	77.54(6)	O(8)-Er(2)-O(2)#1	71.17(6)
O(5)-Er(1)-O(1)	82.60(7)	O(1)#1-Er(2)-O(2)#1	67.61(7)
O(8)#1-Er(1)-O(1)	71.50(6)	O(6)-Er(2)-O(3)	83.75(7)
O(3)-Er(1)-O(1)	147.38(6)	O(7)-Er(2)-O(3)	108.46(7)
O(4)-Er(1)-O(2)	84.03(7)	O(8)-Er(2)-O(3)	70.11(6)
O(8)-Er(1)-O(2)	133.35(6)	O(1)#1-Er(2)-O(3)	78.86(7)
O(5)-Er(1)-O(2)	125.25(7)	O(2)#1-Er(2)-O(3)	134.53(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

Table S8 The Gd^{III} geometry analysis by **SHAPE** 2.0 for cluster **3**.

	D_{4d}**SAPR**	D_{2d}**TDD**	C_{2v}**JBTPR**	C_{2v}**BTPR**	D_{2d}**JSD**
$Gd1^{III}$	1.195	2.121	3.085	2.252	5.002
$Gd2^{III}$	1.285	2.104	2.907	2.251	4.254

SAPR-8 = Square antiprism; **TDD-8** = Triangular dodecahedron; **JBTPR-8** = Biaugmented trigonal prism J50; **BTPR-8** = Biaugmented trigonal prism; **JSD-8** = Snub diphenoid J84.

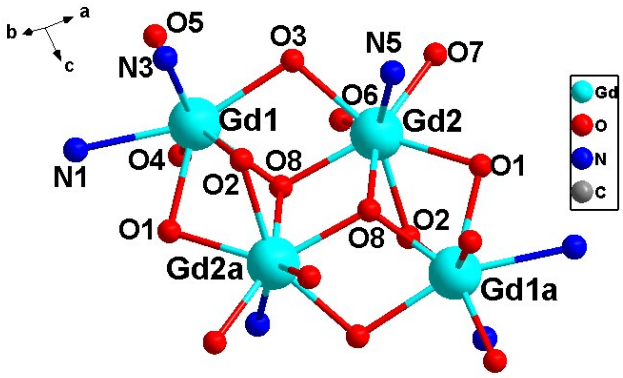

Fig. S1 The coordinate atom labels of central Gd(III) ions in cluster **3**.

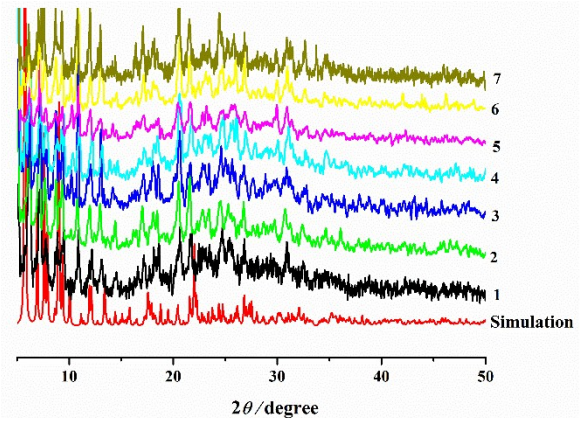

Fig. S2 The PXRD patterns for **1**-**7** and the corresponding simulated ones.

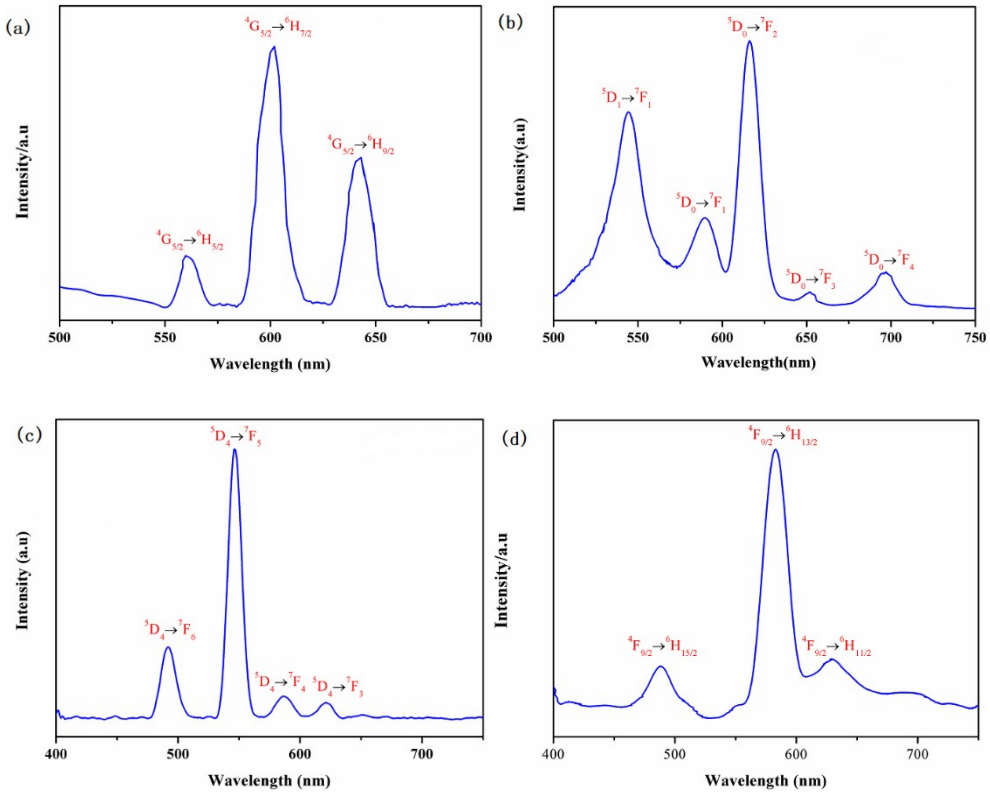

Fig. S3 The solid-state luminescence spectra of cluster **1** (a), **2** (b), **4** (c) and **5** (d) at room temperature.

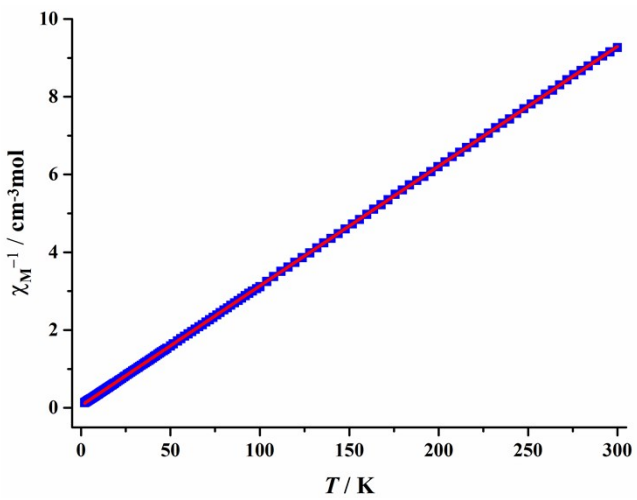

Fig. S4 χ_M^{-1} vs T plot for **3** at an applied field of 1000 Oe between 2.0 and 300 K. The red solid line was generated from the best fit by the Curie-Weiss expression.

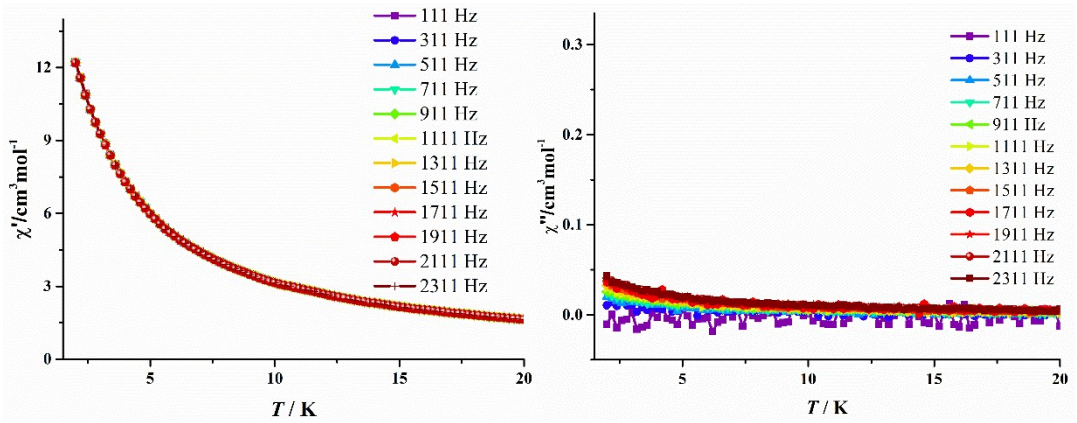

Fig. S5 Temperature dependence of in-phase (χ') and out-of-phase (χ'') components of the *ac* magnetic susceptibility under zero *dc* field for **4**.

Notes and references

1 (a) S. Katagiri, Y. Tsukahara, Y. Hasegawa and Y. Wada, *Bull. Chem. Soc. Jpn*., 2007, **80**, 1492; (b) C. Caris, P. Baret, J.L. Pierre, G. Serratrice, Tetrahedron 1996, 52, 4659.

2 O. Kahn, Molecular Magnetism, *VCH Publishers Inc*., 1991.