Four Tetra-nuclear Lanthanide Complexes based on 8-hydroxyquinolin derivatives: Magnetic refrigeration and Single-Molecule Magnet behaviour

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Electronic supplementary information

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

Gd(1)-O(4)	2.333(3)	Gd(1)-O(8)	2.351(3)
Gd(1)-O(5)	2.356(3)	Gd(1)-O(3)	2.396(3)
Gd(1)-O(1)	2.412(3)	Gd(1)-O(2)#1	2.428(3)
Gd(1)-N(1)	2.553(3)	Gd(1)-N(7)	2.609(3)
Gd(2)-O(7)	2.317(3)	Gd(2)-O(6)	2.361(3)
Gd(2)-O(8)#1	2.364(3)	Gd(2)-O(2)	2.409(3)
Gd(2)-O(3)	2.424(3)	Gd(2)-O(1)	2.427(3)
Gd(2)-O(8)	2.448(3)	Gd(2)-N(4)	2.557(4)
Gd(1)-Gd(2)#1	3.9130(3)	Gd(1)-Gd(2)	3.6359(3)
Gd(2)-Gd(2)#1	3.8822(4)		
O(4)-Gd(1)-O(8)	133.49(10)	O(4)-Gd(1)-O(5)	74.09(10)
O(8)-Gd(1)-O(5)	81.40(10)	O(4)-Gd(1)-O(3)	139.62(10)
O(8)-Gd(1)-O(3	70.41(9)	O(5)-Gd(1)-O(3)	80.30(10)
O(4)-Gd(1)-O(1)	142.29(10)	O(8)-Gd(1)-O(1)	71.72(10)
O(5)-Gd(1)-O(1)	143.58(10)	O(3)-Gd(1)-O(1)	67.94(10)
O(4)-Gd(1)-O(2)#1	85.90(10)	O(8)-Gd(1)-O(2)#1	69.52(9)
O(5)-Gd(1)-O(2)#1	115.08(10)	O(3)-Gd(1)-O(2)#1	133.74(9)
O(1)-Gd(1)-O(2)#1	78.27(10)	O(4)-Gd(1)-N(1)	78.72(11)
O(8)-Gd(1)-N(1)	132.83(11)	O(5)-Gd(1)-N(1)	145.76(11)

O(3)-Gd(1)-N(1)	109.08(11)	O(1)-Gd(1)-N(1)	65.57(10)
O(2)#1-Gd(1)-N(1)	82.83(10)	O(4)-Gd(1)-N(7)	78.02(11)
O(8)-Gd(1)-N(7)	132.07(10)	O(5)-Gd(1)-N(7)	74.40(11)
O(3)-Gd(1)-N(7)	65.18(10)	O(1)-Gd(1)-N(7)	105.98(10)
O(2)#1-Gd(1)-N(7)	158.40(10)	N(1)-Gd(1)-N(7)	79.97(11)
O(7)-Gd(2)-O(6)	72.61(11)	O(7)-Gd(2)-O(8)#1	142.92(10)
O(6)-Gd(2)-O(8)#1	78.12(10)	O(7)-Gd(2)-O(2)	84.02(10)
O(6)-Gd(2)-O(2)	81.78(10)	O(8)#1-Gd(2)-O(2)	69.64(9)
O(7)-Gd(2)-O(3)	83.02(10)	O(6)-Gd(2)-O(3)	124.43(10)
O(8)#1-Gd(2)-O(3)	133.08(10)	O(2)-Gd(2)-O(3)	144.91(10)
O(7)-Gd(2)-O(1)	122.54(10)	O(6)-Gd(2)-O(1)	85.09(10)
O(8)#1-Gd(2)-O(1)	75.88(9)	O(2)-Gd(2)-O(1)	144.92(9)
O(3)-Gd(2)-O(1)	67.24(9)	O(7)-Gd(2)-O(8)	141.61(10)
O(6)-Gd(2)-O(8)	144.98(10)	O(8)#1-Gd(2)-O(8)	72.44(11)
O(2)-Gd(2)-O(8)	104.69(9)	O(3)-Gd(2)-O(8)	68.35(9)
O(1)-Gd(2)-O(8)	69.83(9)	O(7)-Gd(2)-N(4)	76.14(11)
O(6)-Gd(2)-N(4)	136.42(11)	O(8)#1-Gd(2)-N(4)	113.00(10)
O(2)-Gd(2)-N(4)	65.31(10)	O(3)-Gd(2)-N(4)	79.95(10)
O(1)-Gd(2)-N(4)	137.98(10)	O(8)-Gd(2)-N(4)	74.16(10)

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1

Table S2 Selected bond lengths (Å) and angles (°) for complex 2[a]

Tb(1)-O(1)	2.382(3)	Tb(1)-O(2)	2.389(3)
Tb(1)-O(3)	2.416(3)	Tb(1)-O(4)	2.339(3)
Tb(1)-O(5)	2.315(3)	Tb(1)-O(8)	2.336(3)
Tb(1)-N(1)	2.598(4)	Tb(1)-N(4)	2.546(4)
Tb(2)-O(1)#1	2.417(3)	Tb(2)-O(2)#1	2.417(3)
Tb(2)-O(3)	2.394(3)	Tb(2)-O(6)	2.351(3)
Tb(2)-O(7)	2.300(3)	Tb(2)-O(8)#1	2.427(3)
Tb(2)-O(8)	2.348(3)	Tb(2)-N(7)	2.549(4)
Tb(1)-Tb(2)#1	3.6258(4)	Tb(1)-Tb(2)	3.8932(6)
Tb(2)-Tb(2)#1	3.8487(5)		
O(1)-Tb(1)-O(2)	67.79(10)	O(1)-Tb(1)-O(3)	133.42(10)
O(1)-Tb(1)-N(1)	65.50(11)	O(1)-Tb(1)-N(4)	109.05(11)
O(2)-Tb(1)-O(3)	78.24(11)	O(2)-Tb(1)-N(1)	106.06(11)
O(2)-Tb(1)-N(4)	65.97(11)	O(3)-Tb(1)-N(1)	158.43(11)
O(3)-Tb(1)-N(4)	83.35(11)	O(4)-Tb(1)-O(1)	80.75(11)
O(4)-Tb(1)-O(2)	144.10(10)	O(4)-Tb(1)-O(3)	115.09(11)
O(4)-Tb(1)-N(1)	74.14(12)	O(4)-Tb(1)-N(4)	144.73(11)
O(5)-Tb(1)-O(1)	140.65(11)	O(5)-Tb(1)-O(2)	141.52(10)

O(5)-Tb(1)-O(3)	85.24(11)	O(5)-Tb(1)-O(4)	74.34(11)
O(5)-Tb(1)-O(8)	133.83(11)	O(5)-Tb(1)-N(1)	78.52(12)
O(5)-Tb(1)-N(4)	77.85(12)	O(8)-Tb(1)-O(1)	70.12(10)
O(8)-Tb(1)-O(2)	71.26(10)	O(8)-Tb(1)-O(3)	69.32(10)
O(8)-Tb(1)-O(4)	82.34(11)	O(8)-Tb(1)-N(1)	132.23(11)
O(8)-Tb(1)-N(4)	132.92(11)	O(1)#1-Tb(2)-O(8)#1	68.04(10)
O(1)#1-Tb(2)-N(7)	79.42(11)	O(2)#1-Tb(2)-O(1)#1	66.79(10)
O(2)#1-Tb(2)-O(8)#1	69.28(9)	O(2)#1-Tb(2)-N(7)	137.24(11)
O(3)-Tb(2)-O(1)#1	145.06(11)	O(3)-Tb(2)-O(2)#1	145.29(10)
O(3)-Tb(2)-O(8)#1	105.34(10)	O(3)-Tb(2)-N(7)	66.00(12)
O(6)-Tb(2)-O(1)#1	124.98(11)	O(6)-Tb(2)-O(2)#1	85.24(10)
O(6)-Tb(2)-O(3)	81.30(11)	O(6)-Tb(2)-O(8)#1	144.22(11)
O(6)-Tb(2)-N(7)	136.99(12)	O(7)-Tb(2)-O(1)#1	83.48(11)
O(7)-Tb(2)-O(2)#1	122.39(11)	O(7)-Tb(2)-O(3)	83.69(11)
O(7)-Tb(2)-O(6)	72.80(12)	O(7)-Tb(2)-O(8)#1	142.14(11)
O(7)-Tb(2)-O(8)	142.44(11)	O(7)-Tb(2)-N(7)	76.39(12)
O(8)-Tb(2)-O(1)#1	133.17(10)	O(8)-Tb(2)-O(2)#1	76.40(10)
O(8)-Tb(2)-O(3)	69.51(10)	O(8)-Tb(2)-O(6)	77.39(11)
O(8)-Tb(2)-O(8)#1	72.58(11)	O(8)-Tb(2)-N(7)	113.26(11)

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

Table S3 Selected bond lengths (Å) and angles (°) for complex 3[a]

Dy(1)-O(4)	2.301(3)	Dy(1)-O(5)	2.329(3)
Dy(1)-O(2)#1	2.328(3)	Dy(1)-O(1)#1	2.370(3)
Dy(1)-O(3)	2.374(3)	Dy(1)-O(8)	2.408(3)
Dy(1)-N(4)	2.533(3)	Dy(1)-N(1)#1	2.587(4)
Dy(2)-O(6)	2.285(3)	Dy(2)-O(2)#1	2.338(3)
Dy(2)-O(7)	2.344(3)	Dy(2)-O(8)	2.382(3)
Dy(2)-O(1)	2.406(3)	Dy(2)-O(3)#1	2.408(3)
Dy(2)-O(2)	2.408(3)	Dy(2)-N(7)	2.536(4)
Dy(1)-Dy(2)	3.8764(3)	Dy(1)-Dy(2)#1	3.6033(3)
Dy(2)-Dy(2)#1	3.8285(4)		
O(4)-Dy(1)-O(5)	74.57(10)	O(4)-Dy(1)-O(2)#1	132.98(11)
O(5)-Dy(1)-O(2)#1	81.85(10)	O(4)-Dy(1)-O(1)#1	141.14(10)
O(5)-Dy(1)-O(1)#1	80.57(10)	O(2)#1-Dy(1)-O(1)#1	70.25(10)
O(4)-Dy(1)-O(3)	141.64(10)	O(5)-Dy(1)-O(3)	143.78(10)
O(2)#1-Dy(1)-O(3)	71.35(10)	O(1)#1-Dy(1)-O(3)	67.86(10)
O(4)-Dy(1)-O(8)	84.52(10)	O(5)-Dy(1)-O(8)	114.85(10)
O(2)#1-Dy(1)-O(8)	69.33(9)	O(1)#1-Dy(1)-O(8)	133.56(9)
O(3)-Dy(1)-O(8)	78.30(10)	O(4)-Dy(1)-N(4)	77.94(11)
O(5)-Dy(1)-N(4)	145.04(11)	O(2)#1-Dy(1)-N(4)	133.09(11)

O(1)#1-Dy(1)-N(4)	109.39(11)	O(3)-Dy(1)-N(4)	66.21(10)
O(8)-Dy(1)-N(4)	83.15(11)	O(4)-Dy(1)-N(1)#1	78.95(11)
O(5)-Dy(1)-N(1)#1	74.35(11)	O(2)#1-Dy(1)-N(1)#1	132.48(10)
O(1)#1-Dy(1)-N(1)#1	65.72(10)	O(3)-Dy(1)-N(1)#1	106.33(11)
O(8)-Dy(1)-N(1)#1	158.19(10)	N(4)-Dy(1)-N(1)#1	79.57(11)
O(6)-Dy(2)-O(2)#1	142.89(11)	O(6)-Dy(2)-O(7)	73.03(11)
O(2)#1-Dy(2)-O(7)	77.60(11)	O(6)-Dy(2)-O(8)	84.01(10)
O(2)#1-Dy(2)-O(8)	69.62(10)	O(7)-Dy(2)-O(8)	81.76(10)
O(6)-Dy(2)-O(1)	82.95(10)	O(2)#1-Dy(2)-O(1)	133.17(10)
O(7)-Dy(2)-O(1)	124.26(10)	O(8)-Dy(2)-O(1)	145.23(10)
O(6)-Dy(2)-O(3)#1	122.04(10)	O(2)#1-Dy(2)-O(3)#1	76.34(10)
O(7)-Dy(2)-O(3)#1	84.72(10)	O(8)-Dy(2)-O(3)#1	145.32(10)
O(1)-Dy(2)-O(3)#1	66.73(9)	O(6)-Dy(2)-O(2)	141.93(10)
O(2)#1-Dy(2)-O(2)	72.46(11)	O(7)-Dy(2)-O(2)	144.07(10)
O(8)-Dy(2)-O(2)	105.33(10)	O(1)-Dy(2)-O(2)	68.33(10)
O(3)#1-Dy(2)-O(2)	69.42(10)	O(6)-Dy(2)-N(7)	76.10(12)
O(2)#1-Dy(2)-N(7)	113.56(10)	O(7)-Dy(2)-N(7)	137.21(11)
O(8)-Dy(2)-N(7)	66.08(11)	O(1)-Dy(2)-N(7)	79.53(11)
O(3)#1-Dy(2)-N(7)	137.43(11)	O(2)-Dy(2)-N(7)	74.56(11)

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

Table S4 Selected bond lengths (Å) and angles (°) for complex 4[a]

Ho(1)-O(1)	2.412(5)	Ho(1)-O(3)#1	2.432(5)
Ho(1)-O(8)	2.359(4)	Ho(1)-O(2)	2.390(5)
Ho(1)-O(5)	2.348(5)	Ho(1)-N(1)	2.558(6)
Ho(1)-O(4)	2.330(5)	Ho(1)-N(4)	2.602(6)
Ho(2)-O(1)	2.418(4)	Ho(2)-O(7)	2.314(5)
Ho(2)-O(3)	2.412(5)	Ho(2)-O(8)	2.445(5)
Ho(2)-O(8)#1	2.357(4)	Ho(2)-O(2)	2.425(5)
Ho(2)-N(7)	2.561(6)	Ho(2)-O(6)	2.362(5)
O(1)-Ho(1)-O(3)#1	78.66(16)	O(1)-Ho(1)-N(1)	65.75(17)
O(1)-Ho(1)-N(4)	105.99(17)	O(3)#1-Ho(1)-N(1)	83.04(17)
O(3)#1-Ho(1)-N(4)	158.30(17)	O(8)-Ho(1)-O(1)	71.57(16)
O(8)-Ho(1)-O(3)#1	69.38(15)	O(8)-Ho(1)-O(2)	70.41(15)
O(8)-Ho(1)-N(1)	132.77(17)	O(8)-Ho(1)-N(4)	132.32(17)
O(2)-Ho(1)-O(1)	67.81(16)	O(2)-Ho(1)-O(3)#1	133.82(16)
O(2)-Ho(1)-N(1)	109.20(17)	O(2)-Ho(1)-N(4)	65.39(17)
O(5)-Ho(1)-O(1)	143.40(16)	O(5)-Ho(1)-O(3)#1	114.79(17)
O(5)-Ho(1)-O(8)	81.48(16)	O(5)-Ho(1)-O(2)	80.23(17)
O(5)-Ho(1)-N(1)	145.74(18)	O(5)-Ho(1)-N(4)	74.43(18)
N(1)-Ho(1)-N(4)	79.88(18)	O(4)-Ho(1)-O(1)	142.55(16)

O(4)-Ho(1)-O(3)#1	85.85(17)	O(4)-Ho(1)-O(8)	133.50(17)
O(4)-Ho(1)-O(2)	139.52(16)	O(4)-Ho(1)-O(5)	74.00(17)
O(4)-Ho(1)-N(1)	78.74(17)	O(4)-Ho(1)-N(4)	77.79(18)
O(1)-Ho(2)-O(8)	70.01(15)	O(1)-Ho(2)-O(2)	67.16(15)
O(1)-Ho(2)-N(7)	138.11(18)	O(7)-Ho(2)-O(1)	122.27(17)
O(7)-Ho(2)-O(3)	83.98(17)	O(7)-Ho(2)-O(8)#1	143.14(17)
O(7)-Ho(2)-O(8)	141.63(17)	O(7)-Ho(2)-O(2)	82.94(17)
O(7)-Ho(2)-N(7)	75.91(19)	O(7)-Ho(2)-O(6)	72.62(19)
O(3)-Ho(2)-O(1)	145.06(15)	O(3)-Ho(2)-O(8)	104.82(16)
O(3)-Ho(2)-O(2)	145.00(16)	O(3)-Ho(2)-N(7)	65.49(17)
O(8)#1-Ho(2)-O(1)	76.00(15)	O(8)#1-Ho(2)-O(3)	69.74(15)
O(8)#1-Ho(2)-O(8)	72.29(17)	O(8)#1-Ho(2)-O(2)	133.01(15)
O(8)-Ho(2)-N(7)	74.36(17)	O(8)#1-Ho(2)-N(7)	113.22(17)
O(8)#1-Ho(2)-O(6)	78.18(17)	O(2)-Ho(2)-O(8)	68.43(15)
O(2)-Ho(2)-N(7)	79.86(17)	O(6)-Ho(2)-O(1)	85.02(16)
O(6)-Ho(2)-O(3)	81.58(17)	O(6)-Ho(2)-O(8)	144.96(16)
O(6)-Ho(2)-O(2)	124.46(17)	O(6)-Ho(2)-N(7)	136.28(19)

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

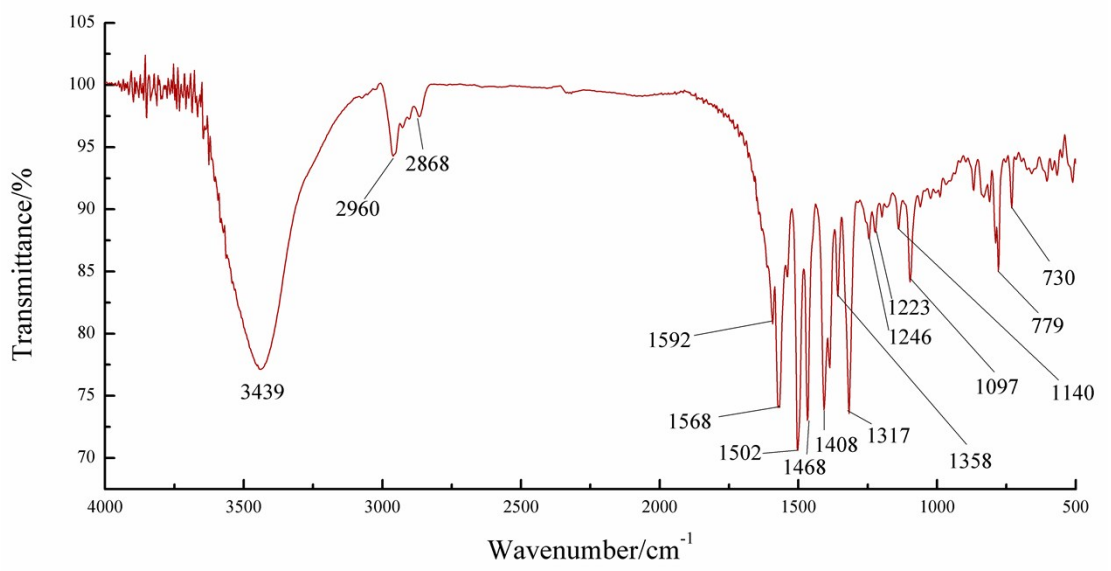

Figure S1. The IR spectra for compound **1**.

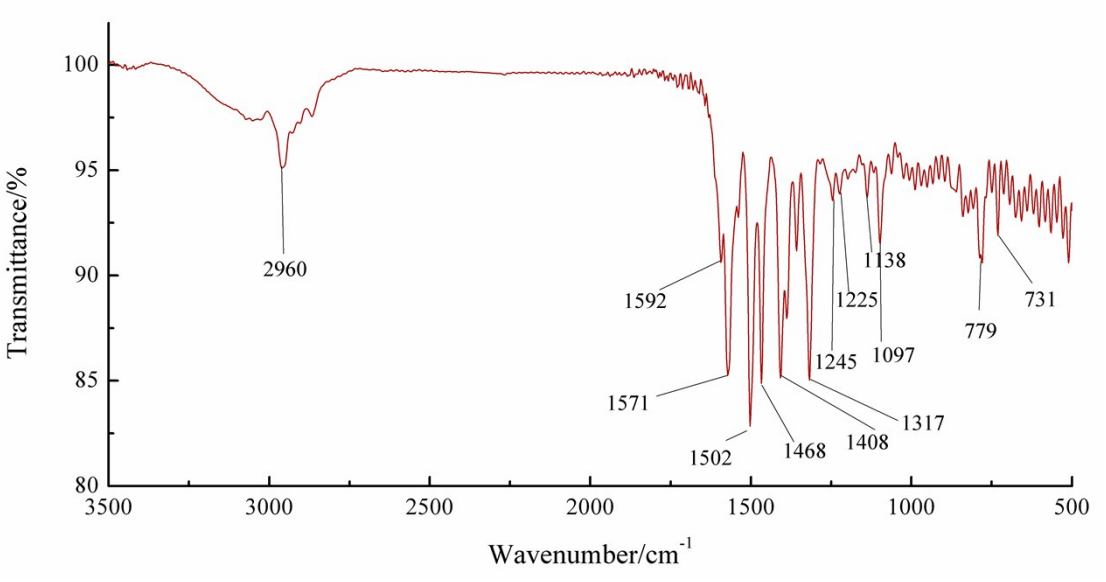

Figure S2. The IR spectra for compound **2**.

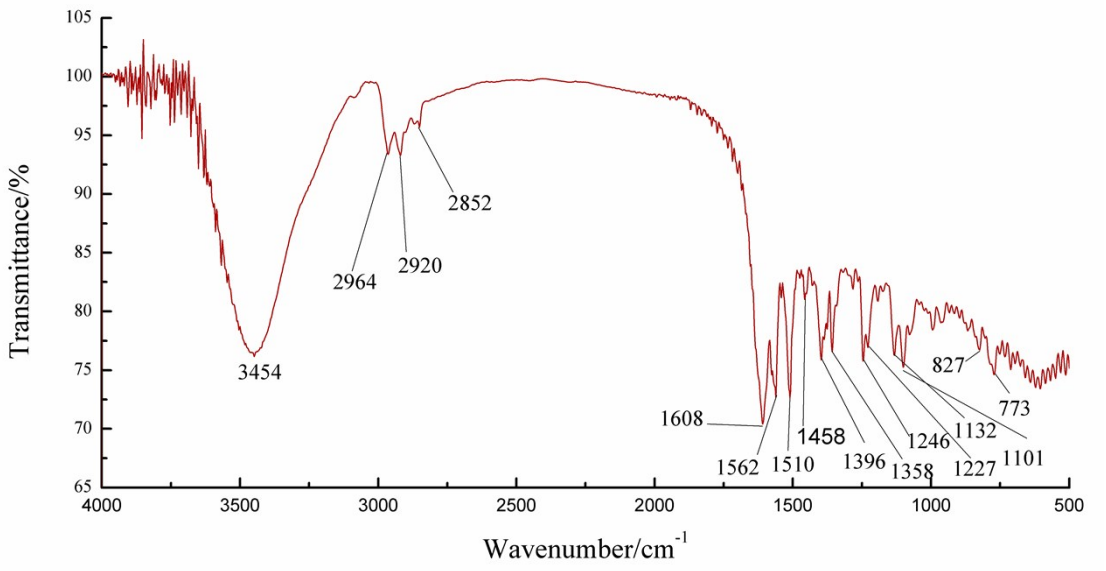

Figure S3. The IR spectra for compound **3**.

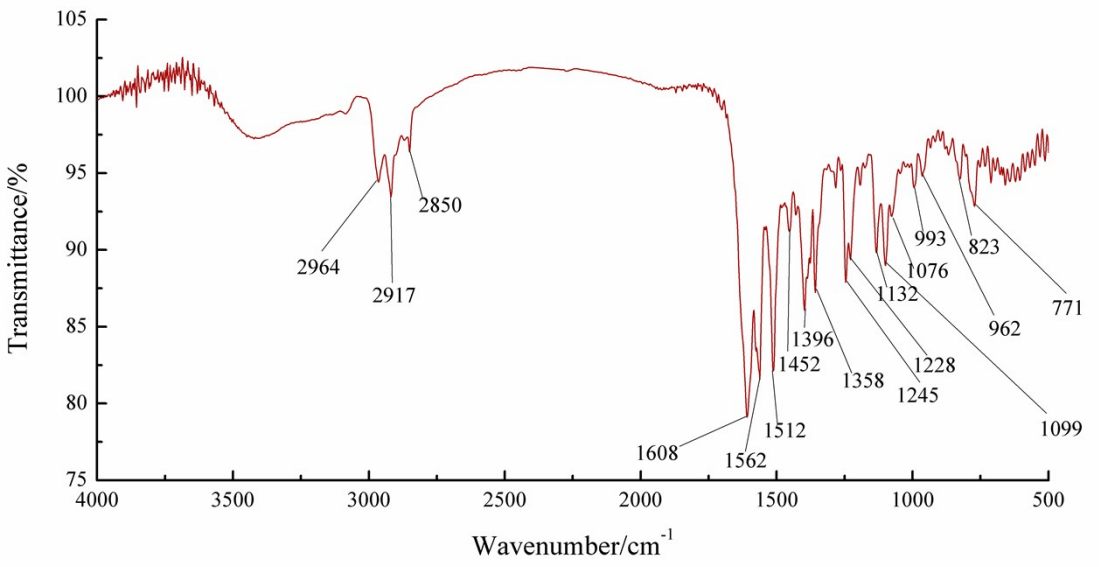

Figure S4. The IR spectra for compound **4**.

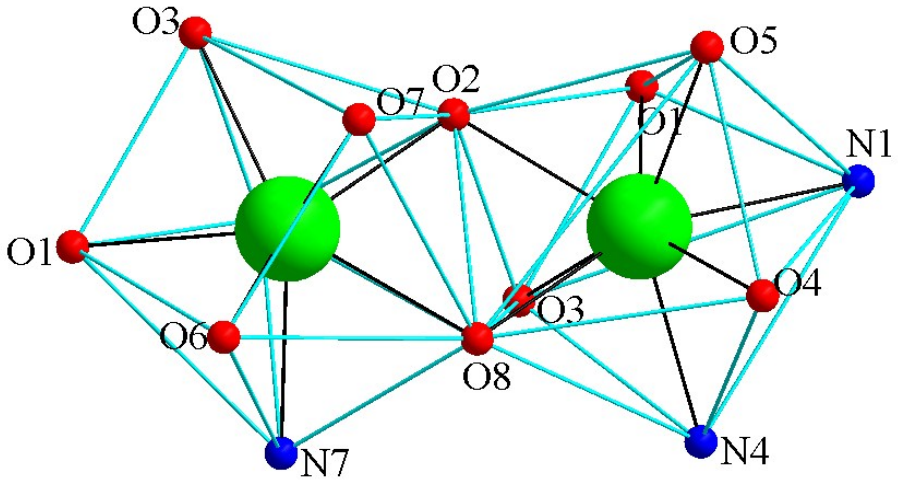

Figure S5. The distorted bicapped trigonal prism coordination geometry of Dy center.

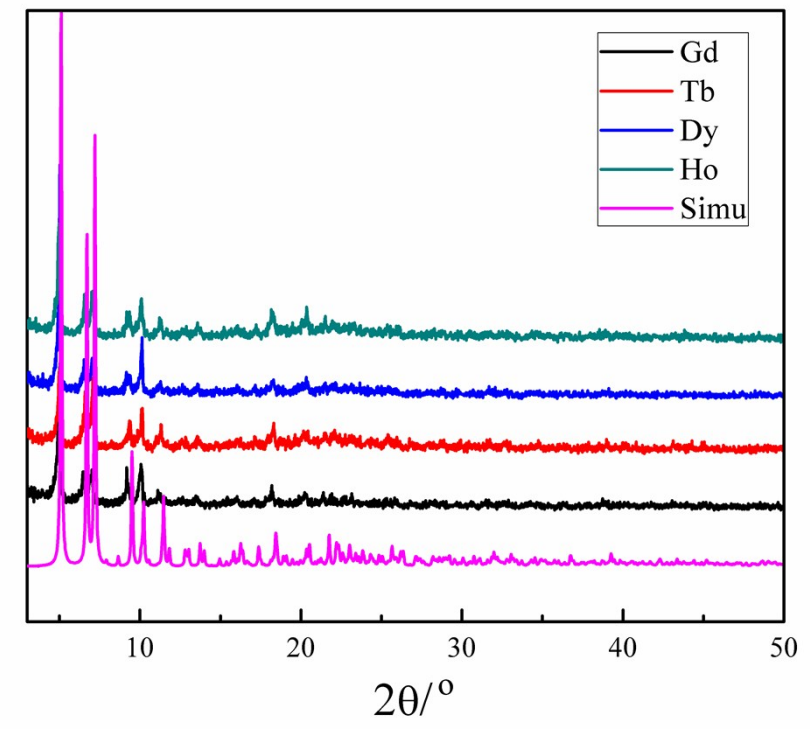

Figure S6. The simulated and experimental PXRD patterns for **1**-**4**.

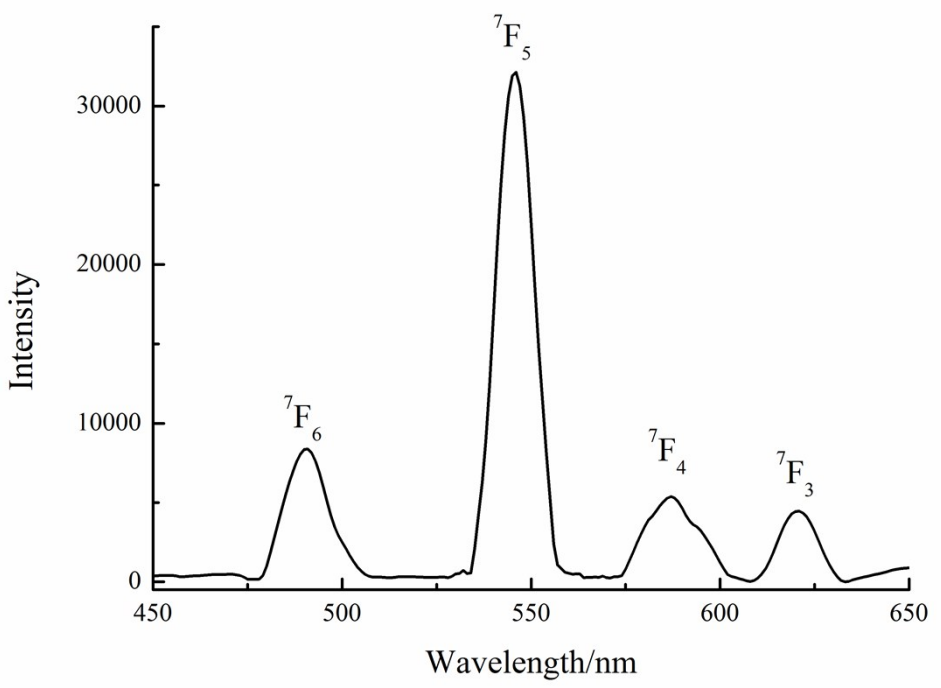

Figure S7. The emission spectra of **2** in solid state when excited at 305 nm.