Electronic supplementary information

Near-infrared luminescence and SMM behaviors of a family of dinuclear lanthanide 8-quinolinolate complexes

Hai−Yun Shen, Wen−Min Wang, Hong−Ling Gao, Jian−Zhong Cui*

Department of Chemistry, Tianjin University, Tianjin 300072, P. R. China.

*Corresponding author. E−mail address: cuijianzhong@tju.edu.cn

List of Contents

Supplementary Experimental Section.

Preparations of $Ln(dbm)_3 \cdot 2H_2O$ (Ln = Nd, Tb, Dy, Ho, Er). $Ln(dbm)_3 \cdot 2H_2O$ has been synthesized by the method reported [1] with some modifications. A solution of dibenzoylmethane (4 mmol) in ethanol (20 mL) was warmed (60 °C). The lanthanide acetate (12 mmol) was dissolved in distilled water (10 mL) and added drop-wise to the above solution. The mixture was heated for 4 h at approximately 60 °C and then cooled to room temperature. The precipitate was filtered, washed with water and dried under vacuum to afford the product.

[1] A. Lennartson, M. Vestergren and M. Håkansson, *Chem.–Eur. J.*, 2005, **11**, 1757.

Table S1 Selected bond lengths (Å) and angles (°) for $[Nd_2(dbm)_4(OQ)_2(CH_3OH)_2]$ (**1**)

Nd(1)−O(4)	2.387(2)	Nd(2)−O(7)	2.382(2)
Nd(1)−O(3)	2.388(2)	Nd(2)−O(8)	2.389(2)
Nd(1)−O(5)	2.421(2)	Nd(2)−O(10)	2.419(2)
Nd(1)−O(6)	2.437(2)	Nd(2)−O(1)	2.430(2)
Nd(1)−O(1)	2.449(2)	Nd(2)−O(2)	2.449(2)
Nd(1)−O(2)	2.461(2)	Nd(2)−O(9)	2.471(2)
Nd(1)−O(11)	2.533(3)	Nd(2)−O(12)	2.537(3)
Nd(1)−N(1)	2.593(3)	Nd(2)−N(2)	2.580(3)
Nd(1)−Nd(2)	4.0192(16)		
O(4)−Nd(1)−O(3)	71.29(9)	O(7)−Nd(2)−O(10)	76.07(8)
O(4)−Nd(1)−O(5)	76.48(8)	O(8)−Nd(2)−O(10)	73.23(9)
O(3)−Nd(1)−O(5)	73.53(9)	O(7)−Nd(2)−O(1)	85.11(8)
O(4)−Nd(1)−O(6)	84.34(9)	O(8)−Nd(2)−O(1)	124.33(8)
O(3)−Nd(1)−O(6)	139.78(8)	O(10)−Nd(2)−O(1)	149.00(8)
O(5)−Nd(1)−O(6)	69.87(8)	O(7)−Nd(2)−O(2)	147.27(8)
O(4)−Nd(1)−O(1)	152.91(8)	O(8)−Nd(2)−O(2)	139.14(8)
O(3)−Nd(1)−O(1)	134.27(8)	O(10)−Nd(2)−O(2)	115.52(8)
O(5)−Nd(1)−O(1)	115.47(8)	O(1)−Nd(2)−O(2)	69.85(8)
O(6)−Nd(1)−O(1)	78.08(8)	O(7)−Nd(2)−O(9)	79.72(9)
O(4)−Nd(1)−O(2)	87.34(8)	O(8)−Nd(2)−O(9)	137.79(8)
O(3)−Nd(1)−O(2)	129.11(8)	O(10)−Nd(2)−O(9)	69.58(8)
O(5)−Nd(1)−O(2)	146.17(8)	O(1)−Nd(2)−O(9)	83.11(8)
O(6)−Nd(1)−O(2)	79.22(8)	O(2)−Nd(2)−O(9)	76.74(8)
O(1)−Nd(1)−O(2)	69.34(8)	O(7)−Nd(2)−O(12)	113.38(9)
O(4)−Nd(1)−O(11)	106.09(9)	O(8)−Nd(2)−O(12)	71.54(8)
O(3)−Nd(1)−O(11)	70.57(8)	O(10)−Nd(2)−O(12)	138.02(8)
O(5)−Nd(1)−O(11)	140.65(8)	O(1)−Nd(2)−O(12)	72.16(8)
O(6)−Nd(1)−O(11)	148.86(8)	O(2)−Nd(2)−O(12)	79.39(8)
O(1)−Nd(1)−O(11)	80.43(8)	O(9)−Nd(2)−O(12)	150.29(8)
O(2)−Nd(1)−O(11)	72.22(8)	O(7)−Nd(2)−N(2)	144.68(9)
O(4)−Nd(1)−N(1)	140.88(9)	O(8)−Nd(2)−N(2)	81.42(9)
O(3)−Nd(1)−N(1)	78.23(9)	O(10)−Nd(2)−N(2)	73.80(9)
O(5)−Nd(1)−N(1)	71.71(8)	O(1)−Nd(2)−N(2)	129.87(8)
O(6)−Nd(1)−N(1)	104.96(9)	O(2)−Nd(2)−N(2)	65.06(9)
O(1)−Nd(1)−N(1)	64.68(8)	O(9)−Nd(2)−N(2)	106.10(9)
O(2)−Nd(1)−N(1)	131.49(8)	O(12)−Nd(2)−N(2)	79.04(9)
O(11)−Nd(1)−N(1)	85.57(9)	O(7)−Nd(2)−Nd(1)	116.98(6)
O(4)−Nd(1)−Nd(2)	121.32(6)	O(8)−Nd(2)−Nd(1)	144.16(6)
O(3)−Nd(1)−Nd(2)	143.30(6)	O(10)−Nd(2)−Nd(1)	141.39(6)
O(5)−Nd(1)−Nd(2)	140.40(6)	O(1)−Nd(2)−Nd(1)	34.70(5)
O(6)−Nd(1)−Nd(2)	76.78(6)	O(2)−Nd(2)−Nd(1)	35.16(5)
O(1)−Nd(1)−Nd(2)	34.39(5)	O(9)−Nd(2)−Nd(1)	77.09(6)
O(2)−Nd(1)−Nd(2)	34.96(6)	O(12)−Nd(2)−Nd(1)	73.20(6)

O(11)−Nd(1)−Nd(2)	72.75(6)	N(2)−Nd(2)−Nd(1)	98.13(7)
N(1)−Nd(1)−Nd(2)	97.78(7)	Nd(2)−O(1)−Nd(1)	110.91(9)
O(7)−Nd(2)−O(8)	72.54(8)	Nd(2)−O(2)−Nd(1)	109.88(9)

Table S2 Selected bond lengths (Å) and angles (°) for $[Tb_2(dbm)_4(OQ)_2(CH_3OH)_2]$ (**2**)

Tb(1)−O(5)	2.314(2)	Tb(1)−O(2)	2.389(2)
Tb(1)−O(4)	2.324(3)	Tb(1)−O(6)	2.443(2)
Tb(1)−O(3)	2.361(2)	Tb(1)−N(1)#1	2.526(3)
Tb(1)−O(1)#1	2.377(2)	Tb(1)−Tb(1)#1	3.940(2)
Tb(1)−O(1)	2.384(2)		
O(5)−Tb(1)−O(4)	73.73(9)	O(1)−Tb(1)−O(6)	72.67(9)
O(5)−Tb(1)−O(3)	77.81(9)	O(2)−Tb(1)−O(6)	149.38(8)
O(4)−Tb(1)−O(3)	72.63(9)	O(5)−Tb(1)−N(1)#1	144.82(9)
O(5)−Tb(1)−O(1)#1	146.45(8)	O(4)−Tb(1)−N(1)#1	79.37(10)
O(4)−Tb(1)−O(1)#1	138.58(8)	O(3)−Tb(1)−N(1)#1	72.76(9)
O(3)−Tb(1)−O(1)#1	115.47(8)	O(1)#1−Tb(1)−N(1)#1	66.36(9)
O(5)−Tb(1)−O(1)	84.31(9)	O(1)−Tb(1)−N(1)#1	130.61(8)
O(4)−Tb(1)−O(1)	127.74(9)	O(2)−Tb(1)−N(1)#1	107.55(10)
O(3)−Tb(1)−O(1)	147.51(8)	O(6)−Tb(1)−N(1)#1	82.22(10)
O(1)#1−Tb(1)−O(1)	68.31(10)	O(5)−Tb(1)−Tb(1)#1	116.29(7)
O(5)−Tb(1)−O(2)	79.79(9)	O(4)−Tb(1)−Tb(1)#1	145.37(6)
O(4)−Tb(1)−O(2)	138.44(8)	O(3)−Tb(1)−Tb(1)#1	140.33(6)
O(3)−Tb(1)−O(2)	70.85(9)	O(1)#1−Tb(1)−Tb(1)#1	34.21(6)
O(1)#1−Tb(1)−O(2)	76.55(8)	O(1)−Tb(1)−Tb(1)#1	34.10(6)
O(1)−Tb(1)−O(2)	79.48(9)	O(2)−Tb(1)−Tb(1)#1	75.48(6)
O(5)−Tb(1)−O(6)	109.26(9)	O(6)−Tb(1)−Tb(1)#1	74.36(6)
O(4)−Tb(1)−O(6)	71.11(9)	N(1)#1−Tb(1)−Tb(1)#1	98.74(7)
O(3)−Tb(1)−O(6)	138.95(9)	Tb(1)#1−O(1)−Tb(1)	111.69(10)
O(1)#1−Tb(1)−O(6)	81.48(8)		

The symmetry code: #1 -x+1,-y+1,-z+1

Table S3 Selected bond lengths (Å) and angles (°) for $[Dy_2(dbm)_4(OQ)_2(CH_3OH)_2]$ (**3**)

Dy(1)−O(5)	2.298(3)	Dy(1)−O(2)	2.376(3)
Dy(1)−O(4)	2.307(3)	Dy(1)−O(6)	2.430(3)
Dy(1)−O(1)	2.361(2)	Dy(1)−N(1)	2.510(3)
Dy(1)−O(3)	2.362(3)	Dy(1)−Dy(1)#1	3.908(2)
Dy(1)−O(1)#1	2.368(3)		
O(5)−Dy(1)−O(4)	73.78(10)	O(1)#1−Dy(1)−O(6)	72.55(10)
O(5)−Dy(1)−O(1)	145.91(10)	O(2)−Dy(1)−O(6)	149.60(9)
O(4)−Dy(1)−O(1)	139.00(10)	O(5)−Dy(1)−N(1)	145.13(10)
O(5)−Dy(1)−O(3)	78.31(10)	O(4)−Dy(1)−N(1)	79.58(11)
O(4)−Dy(1)−O(3)	72.79(10)	O(1)−Dy(1)−N(1)	66.62(10)
O(1)−Dy(1)−O(3)	115.32(9)	O(3)−Dy(1)−N(1)	72.53(10)
O(5)−Dy(1)−O(1)#1	83.62(9)	O(1)#1−Dy(1)−N(1)	130.97(9)

O(4)−Dy(1)−O(1)#1	127.17(10)	O(2)−Dy(1)−N(1)	107.54(11)
O(1)−Dy(1)−O(1)#1	68.55(10)	O(6)−Dy(1)−N(1)	82.58(11)
O(3)−Dy(1)−O(1)#1	147.63(10)	O(5)−Dy(1)−Dy(1)#1	115.66(7)
O(5)−Dy(1)−O(2)	79.69(10)	O(4)−Dy(1)−Dy(1)#1	145.30(7)
O(4)−Dy(1)−O(2)	138.40(9)	O(1)−Dy(1)−Dy(1)#1	34.33(6)
O(1)−Dy(1)−O(2)	76.37(9)	O(3)−Dy(1)−Dy(1)#1	140.37(7)
O(3)−Dy(1)−O(2)	70.85(10)	O(1)#1−Dy(1)−Dy(1)#1	34.22(6)
O(1)#1−Dy(1)−O(2)	79.69(9)	O(2)−Dy(1)−Dy(1)#1	75.47(7)
O(5)−Dy(1)−O(6)	108.68(10)	O(6)−Dy(1)−Dy(1)#1	74.64(7)
O(4)−Dy(1)−O(6)	70.79(10)	N(1)−Dy(1)−Dy(1)#1	99.06(8)
O(1)−Dy(1)−O(6)	82.08(9)	Dy(1)−O(1)−Dy(1)#1	111.45(10)
O(3)−Dy(1)−O(6)	138.84(10)		

The symmetry code: #1 -x+1,-y+1,-z+1

Table S4 Selected bond lengths (Å) and angles (°) for $[Ho_2(dbm)_4(OQ)_2(CH_3OH)_2]$ (**4**)

Ho(1)−O(5)	2.294(3)	Ho(1)−O(2)	2.368(3)
Ho(1)−O(4)	2.304(3)	Ho(1)−O(6)	2.410(3)
Ho(1)−O(3)	2.350(3)	Ho(1)−N(1)	2.495(4)
Ho(1)−O(1)#1	2.356(3)	Ho(1)−Ho(1)#1	3.903(2)
Ho(1)−O(1)	2.358(3)		
O(5)−Ho(1)−O(4)	74.15(11)	O(1)−Ho(1)−O(6)	82.06(10)
O(5)−Ho(1)−O(3)	78.48(11)	O(2)−Ho(1)−O(6)	149.80(11)
O(4)−Ho(1)−O(3)	72.68(11)	O(5)−Ho(1)−N(1)	145.39(11)
O(5)−Ho(1)−O(1)#1	83.44(10)	O(4)−Ho(1)−N(1)	79.58(12)
O(4)−Ho(1)−O(1)#1	127.20(11)	O(3)−Ho(1)−N(1)	72.40(11)
O(3)−Ho(1)−O(1)#1	147.82(10)	O(1)#1−Ho(1)−N(1)	130.91(11)
O(5)−Ho(1)−O(1)	145.34(10)	O(1)−Ho(1)−N(1)	66.87(11)
O(4)−Ho(1)−O(1)	139.14(10)	O(2)−Ho(1)−N(1)	107.47(12)
O(3)−Ho(1)−O(1)	115.54(10)	O(6)−Ho(1)−N(1)	82.36(12)
O(1)#1−Ho(1)−O(1)	68.23(11)	O(5)−Ho(1)−Ho(1)#1	115.33(8)
O(5)−Ho(1)−O(2)	79.45(11)	O(4)−Ho(1)−Ho(1)#1	145.27(8)
O(4)−Ho(1)−O(2)	138.47(10)	O(3)−Ho(1)−Ho(1)#1	140.49(8)
O(3)−Ho(1)−O(2)	71.01(11)	O(1)#1−Ho(1)−Ho(1)#1	34.13(7)
O(1)#1−Ho(1)−O(2)	79.70(10)	O(1)−Ho(1)−Ho(1)#1	34.10(7)
O(1)−Ho(1)−O(2)	76.26(10)	O(2)−Ho(1)−Ho(1)#1	75.44(8)
O(5)−Ho(1)−O(6)	108.97(11)	O(6)−Ho(1)−Ho(1)#1	74.81(8)
O(4)−Ho(1)−O(6)	70.61(11)	N(1)−Ho(1)−Ho(1)#1	99.10(9)
O(3)−Ho(1)−O(6)	138.42(11)	Ho(1)#1−O(1)−Ho(1)	111.77(11)
O(1)#1−Ho(1)−O(6)	72.81(11)		

The symmetry code: #1 -x+1,-y+1,-z+1

Table S5 Selected bond lengths (Å) and angles (°) for $[Er_2(dbm)_4(OQ)_2(CH_3OH)]\cdot CH_3COCH_3$ (**5**)

Er(1)−O(3)	2.240(3)	Er(2)−O(8)	2.293(3)
Er(1)−O(6)	2.248(3)	Er(2)−O(7)	2.293(3)
Er(1)−O(5)	2.269(3)	Er(2)−O(9)	2.302(3)
Er(1)−O(4)	2.282(4)	Er(2)−O(1)	2.344(3)
Er(1)−O(2)	2.282(3)	Er(2)−O(2)	2.350(3)
Er(1)−O(1)	2.309(3)	Er(2)−O(10)	2.374(3)
Er(1)−O(11)	2.360(3)	Er(2)−N(2)	2.458(4)
Er(1)−Er(2)	3.7889(9)	Er(2)−N(1)	2.470(4)
O(3)−Er(1)−O(6)	112.11(13)	O(9)−Er(2)−O(1)	114.37(12)
O(3)−Er(1)−O(5)	72.70(13)	O(8)−Er(2)−O(2)	129.87(12)
O(6)−Er(1)−O(5)	73.59(12)	O(7)−Er(2)−O(2)	75.20(12)
O(3)−Er(1)−O(4)	73.55(13)	O(9)−Er(2)−O(2)	142.14(12)
O(6)−Er(1)−O(4)	80.84(13)	O(1)−Er(2)−O(2)	69.68(11)
O(5)−Er(1)−O(4)	125.15(12)	O(8)−Er(2)−O(10)	130.91(12)
O(3)−Er(1)−O(2)	107.21(13)	O(7)−Er(2)−O(10)	147.78(12)
O(6)−Er(1)−O(2)	123.46(13)	O(9)−Er(2)−O(10)	70.96(12)
O(5)−Er(1)−O(2)	81.46(12)	O(1)−Er(2)−O(10)	82.00(12)
O(4)−Er(1)−O(2)	150.27(12)	O(2)−Er(2)−O(10)	72.60(12)
O(3)−Er(1)−O(1)	161.52(13)	O(8)−Er(2)−N(2)	76.46(14)
O(6)−Er(1)−O(1)	82.13(12)	O(7)−Er(2)−N(2)	93.07(13)
O(5)−Er(1)−O(1)	124.23(12)	O(9)−Er(2)−N(2)	93.22(13)
O(4)−Er(1)−O(1)	98.32(12)	O(1)−Er(2)−N(2)	136.23(13)
O(2)−Er(1)−O(1)	71.48(11)	O(2)−Er(2)−N(2)	67.92(13)
O(3)−Er(1)−O(11)	80.19(13)	O(10)−Er(2)−N(2)	75.61(13)
O(6)−Er(1)−O(11)	150.90(12)	O(8)−Er(2)−N(1)	79.51(13)
O(5)−Er(1)−O(11)	135.27(13)	O(7)−Er(2)−N(1)	83.82(13)
O(4)−Er(1)−O(11)	77.63(13)	O(9)−Er(2)−N(1)	74.85(13)
O(2)−Er(1)−O(11)	73.36(12)	O(1)−Er(2)−N(1)	67.89(13)
O(1)−Er(1)−O(11)	81.86(12)	O(2)−Er(2)−N(1)	133.47(12)
O(3)−Er(1)−Er(2)	140.59(10)	O(10)−Er(2)−N(1)	118.50(13)
O(6)−Er(1)−Er(2)	103.86(10)	N(2)−Er(2)−N(1)	155.58(14)
O(5)−Er(1)−Er(2)	103.82(9)	O(8)−Er(2)−Er(1)	150.02(8)
O(4)−Er(1)−Er(2)	129.37(9)	O(7)−Er(2)−Er(1)	77.54(9)
O(2)−Er(1)−Er(2)	35.72(8)	O(9)−Er(2)−Er(1)	138.25(9)
O(1)−Er(1)−Er(2)	35.79(8)	O(1)−Er(2)−Er(1)	35.18(8)
O(11)−Er(1)−Er(2)	75.90(9)	O(2)−Er(2)−Er(1)	34.54(8)
O(8)−Er(2)−O(7)	72.68(12)	O(10)−Er(2)−Er(1)	75.62(8)
O(8)−Er(2)−O(9)	71.23(12)	N(2)−Er(2)−Er(1)	102.07(10)
O(7)−Er(2)−O(9)	140.69(12)	N(1)−Er(2)−Er(1)	100.88(10)
O(8)−Er(2)−O(1)	142.91(12)	Er(1)−O(1)−Er(2)	109.03(12)
O(7)−Er(2)−O(1)	86.27(12)	Er(1)−O(2)−Er(2)	109.74(13)

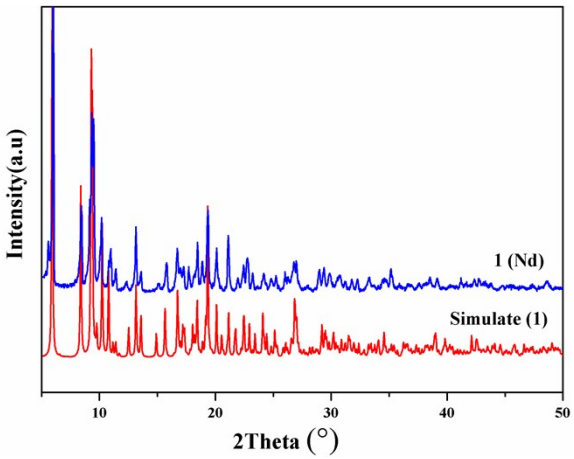

Fig. S1 PXRD patterns of complex **1**.

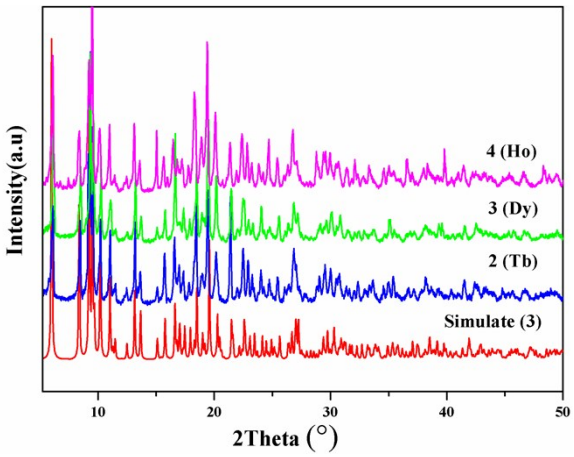

Fig. S2 PXRD patterns of complexes **2**−**4**.

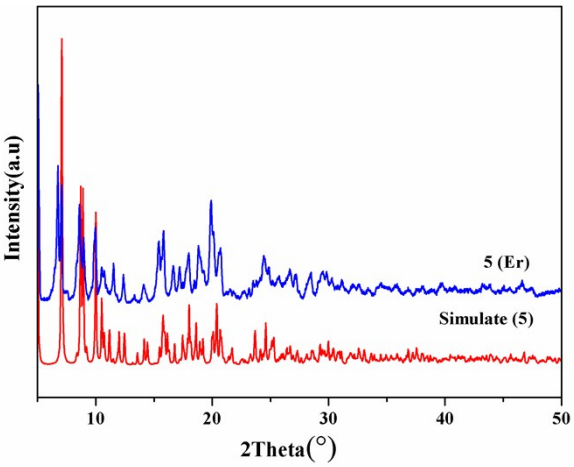

Fig. S3 PXRD patterns of complex **5**.

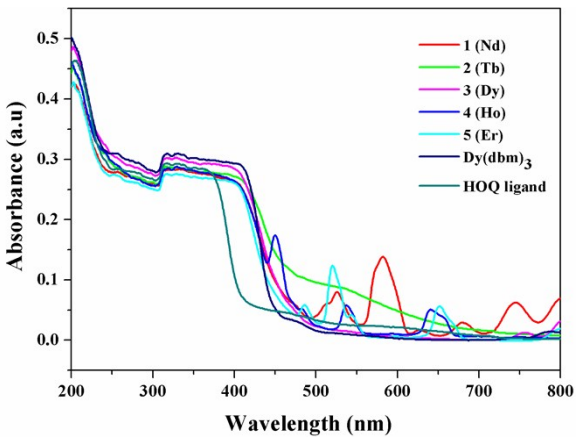

Fig. S4 UV-vis absorption spectra of complexes **1**–**5** in the solid state at room temperature.

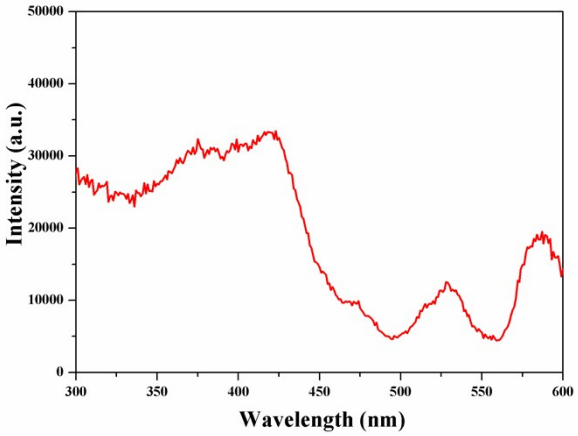

Fig. S5 Excitation spectra of complex **1** (λ_{em} = 1060 nm) in the solid-state.

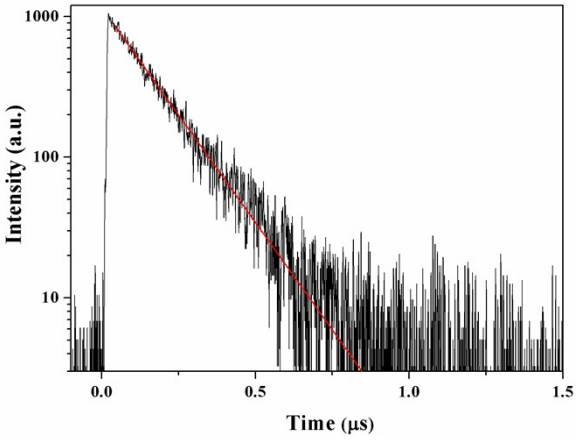

Fig. S6 Luminescence decay of complex **1** in solid state at room temperature. Red trace is a fit to a single exponential decay function.

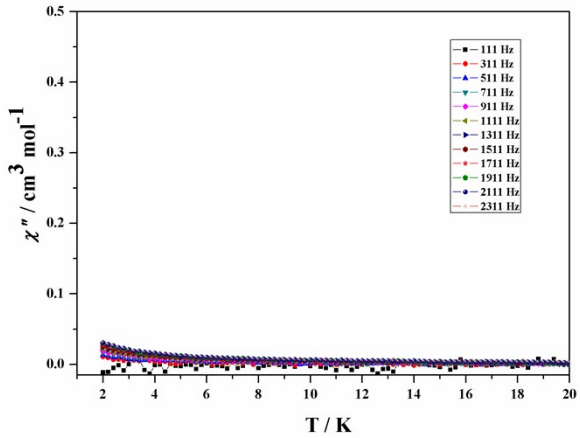

Fig. S7 Temperature dependence of the out-of-phase component of ac susceptibility for **2** in zero dc field with an oscillating of 3 Oe.