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Tetranuclear lanthanide complexes showing magnetic refrigeration and single molecule magnet behavior

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Electronic supplementary information

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

Bond lengths			
Gd(2)-O(1)	2.365(10)	Gd(2)-O(2)	2.463(11)
Gd(2)-O(3)	2.370(10)	Gd(2)-O(8)#1	2.369(10)
Gd(2)-O(8)	2.416(10)	Gd(2)-O(7)	2.338(10)
Gd(2)-N(5)	2.563(12)	Gd(2)-O(6)	2.341(12)
Gd(3)-O(1)	2.372(10)	Gd(3)-O(2)	2.395(11)
Gd(3)-O(3)#1	2.424(10)	Gd(3)-O(8)	2.325(11)
Gd(3)-O(5)	2.320(11)	Gd(3)-N(3)	2.559(14)
Gd(3)-O(4)	2.283(11)	Gd(3)-N(1)	2.558(12)
Bond angles			
O(1)-Gd(2)-O(2)	66.7(4)	O(1)-Gd(2)-O(3)	147.1(4)
O(1)-Gd(2)-O(8)	71.1(4)	O(1)-Gd(2)-O(8)#1	77.1(4)
O(1)-Gd(2)-N(5)	137.3(4)	O(2)-Gd(2)-N(5)	75.3(4)
O(3)-Gd(2)-O(2)	141.9(4)	O(3)-Gd(2)-O(8)	101.1(4)
O(3)-Gd(2)-N(5)	66.7(4)	O(8)-Gd(2)-N(5)	78.0(4)
O(8)-Gd(2)-O(2)	69.3(4)	O(8)#1-Gd(2)-O(2)	132.4(4)
O(8)#1-Gd(2)-O(3)	70.3(4)	O(8)#1-Gd(2)-O(8)	70.4(4)
O(7)-Gd(2)-O(1)	81.5(4)	O(7)-Gd(2)-O(2)	123.3(4)
O(7)-Gd(2)-O(3)	87.6(4)	O(7)-Gd(2)-O(8)	141.8(3)
O(7)-Gd(2)-O(8)#1	78.0(3)	O(7)-Gd(2)-O(6)	71.8(4)
O(8)#1-Gd(2)-N(5)	119.2(4)	O(7)-Gd(2)-N(5)	138.0(4)
O(6)-Gd(2)-O(1)	114.7(4)	O(6)-Gd(2)-O(2)	80.5(4)
O(6)-Gd(2)-O(3)	90.7(4)	O(6)-Gd(2)-O(8)	144.1(4)

O(6)-Gd(2)-O(8)#1	144.9(4)	O(1)-Gd(3)-O(2)	67.7(3)
O(1)-Gd(3)-O(3)#1	79.0(4)	O(2)-Gd(3)-O(3)#1	135.3(3)
O(6)-Gd(2)-N(5)	75.8(4)	O(1)-Gd(3)-N(3)	109.2(4)
O(1)-Gd(3)-N(1)	65.7(4)	O(2)-Gd(3)-N(3)	66.8(4)
O(2)-Gd(3)-N(1)	108.2(4)	O(8)-Gd(3)-N(3)	133.4(4)
O(8)-Gd(3)-O(1)	72.6(3)	O(8)-Gd(3)-O(2)	72.0(4)
O(8)-Gd(3)-N(1)	133.5(4)	O(5)-Gd(3)-N(3)	78.9(4)
O(8)-Gd(3)-O(3)#1	70.1(3)	O(5)-Gd(3)-O(1)	140.7(3)
O(5)-Gd(3)-O(2)	82.0(4)	O(5)-Gd(3)-O(3)#1	109.5(4)
O(5)-Gd(3)-O(8)	74.7(3)	O(4)-Gd(3)-O(1)	144.0(4)
O(4)-Gd(3)-O(2)	141.3(4)	O(4)-Gd(3)-O(3)#1	82.3(4)
O(4)-Gd(3)-O(8)	128.3(4)	O(4)-Gd(3)-O(5)	74.7(4)
O(5)-Gd(3)-N(1)	151.5(4)	O(4)-Gd(3)-N(3)	78.5(5)
O(4)-Gd(3)-N(1)	81.7(4)	N(1)-Gd(3)-N(3)	81.0(4)

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

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

Bond lengths			
Tb(2)-O(6)	2.349(4)	Tb(2)-O(2)#1	2.359(3)
Tb(2)-O(5)	2.334(4)	Tb(2)-O(4)#1	2.371(4)
Tb(2)-O(4)	2.395(4)	Tb(2)-N(6)	2.552(4)
Tb(2)-O(1)	2.466(4)	Tb(2)-O(3)	2.370(4)
Tb(3)-O(2)	2.372(4)	Tb(3)-O(8)	2.335(4)
Tb(3)-O(4)#1	2.332(4)	Tb(3)-O(1)#1	2.380(4)
Tb(3)-O(7)	2.309(4)	Tb(3)-N(4)	2.539(5)
Tb(3)-O(3)	2.416(4)	Tb(3)-N(2)#1	2.542(5)
Bond angles			
O(6)-Tb(2)-O(2)#1	114.97(14)	O(6)-Tb(2)-O(4)	144.74(14)
O(6)-Tb(2)-O(4)#1	144.54(14)	O(6)-Tb(2)-N(6)	75.70(15)
O(6)-Tb(2)-O(1)	81.59(14)	O(6)-Tb(2)-O(3)	89.91(14)
O(2)#1-Tb(2)-N(6)	138.03(14)	O(2)#1-Tb(2)-O(4)	71.51(13)
O(2)#1-Tb(2)-O(4)#1	76.97(13)	O(2)#1-Tb(2)-O(1)	66.31(13)
O(2)#1-Tb(2)-O(3)	147.21(13)	O(5)-Tb(2)-O(6)	71.12(14)
O(5)-Tb(2)-O(2)#1	81.66(13)	O(5)-Tb(2)-O(4)#1	78.39(14)
O(5)-Tb(2)-O(4)	142.08(13)	O(5)-Tb(2)-O(1)	123.42(14)
O(5)-Tb(2)-O(3)	87.19(13)	O(5)-Tb(2)-N(6)	137.15(14)
O(4)#1-Tb(2)-O(4)	69.93(15)	O(4)#1-Tb(2)-O(4)	69.93(15)
O(4)-Tb(2)-N(6)	78.30(13)	O(4)#1-Tb(2)-O(1)	131.65(13)
O(4)#1-Tb(2)-N(6)	119.01(14)	O(1)-Tb(2)-N(6)	76.21(13)
O(4)-Tb(2)-O(1)	69.31(13)	O(3)-Tb(2)-O(4)	100.96(13)
O(3)-Tb(2)-N(6)	66.19(13)	O(3)-Tb(2)-O(4)#1	70.59(12)
O(3)-Tb(2)-O(1)	142.39(12)	O(2)-Tb(3)-N(4)	65.76(14)

O(2)-Tb(3)-O(1)#1	67.52(13)	O(2)-Tb(3)-O(3)	79.40(13)
O(2)-Tb(3)-N(4)	65.76(14)	O(2)-Tb(3)-N(2)#1	108.50(16)
O(8)-Tb(3)-N(4)	151.29(15)	O(8)-Tb(3)-N(2)#1	78.79(16)
O(8)-Tb(3)-O(2)	140.84(13)	O(8)-Tb(3)-O(1)#1	82.16(14)
O(8)-Tb(3)-O(3)	109.37(14)	O(4)#1-Tb(3)-O(2)	72.39(13)
O(4)#1-Tb(3)-O(8)	75.05(14)	O(4)#1-Tb(3)-O(1)#1	71.86(14)
O(4)#1-Tb(3)-N(4)	133.38(14)	O(4)#1-Tb(3)-N(2)#1	132.62(15)
O(4)#1-Tb(3)-O(3)	70.43(12)	O(1)#1-Tb(3)-O(3)	135.62(13)
O(1)#1-Tb(3)-N(4)	108.24(14)	O(1)#1-Tb(3)-N(2)#1	65.93(15)
O(7)-Tb(3)-O(2)	144.48(13)	O(7)-Tb(3)-O(8)	74.27(14)
O(7)-Tb(3)-O(4)#1	129.03(15)	O(7)-Tb(3)-O(1)#1	140.48(14)
O(7)-Tb(3)-O(3)	82.79(14)	O(7)-Tb(3)-N(4)	81.63(15)
O(7)-Tb(3)-N(2)#1	78.51(17)	N(4)-Tb(3)-N(2)#1	81.35(16)
O(3)-Tb(3)-N(4)	82.31(14)	O(3)-Tb(3)-N(2)#1	156.71(14)

[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]

Bond lengths			
Dy(1)-O(3)	2.421(4)	Dy(1)-O(2)	2.359(4)
Dy(1)-O(7)	2.294(4)	Dy(1)-O(8)	2.352(4)
Dy(1)-O(8)#1	2.347(4)	Dy(1)-O(1)	2.420(4)
Dy(1)-O(6)	2.320(4)	Dy(1)-N(4)	2.558(5)
Dy(2)-O(3)	2.375(4)	Dy(2)-O(2)#1	2.385(4)
Dy(2)-O(8)	2.340(4)	Dy(2)-O(1)	2.358(4)
Dy(2)-O(5)	2.323(4)	Dy(2)-O(4)	2.290(4)
Dy(2)-N(6)	2.533(5)	Dy(2)-N(2)	2.525(5)
Bond angles			
O(3)-Dy(1)-N(4)	77.47(15)	O(2)-Dy(1)-N(4)	66.33(15)
O(2)-Dy(1)-O(3)	143.79(14)	O(2)-Dy(1)-O(1)	147.62(14)
O(7)-Dy(1)-O(3)	84.82(13)	O(7)-Dy(1)-O(2)	83.26(14)
O(7)-Dy(1)-O(8)	144.22(14)	O(7)-Dy(1)-O(8)#1	142.42(14)
O(7)-Dy(1)-O(1)	120.08(14)	O(7)-Dy(1)-O(6)	73.17(14)
O(7)-Dy(1)-N(4)	72.10(15)	O(8)-Dy(1)-O(3)	70.18(14)
O(8)#1-Dy(1)-O(3)	132.00(14)	O(8)#1-Dy(1)-O(2)	70.22(14)
O(8)-Dy(1)-O(2)	101.79(14)	O(8)#1-Dy(1)-O(8)	69.55(16)
O(8)#1-Dy(1)-O(1)	78.25(14)	O(8)-Dy(1)-O(1)	73.01(14)
O(8)#1-Dy(1)-N(4)	117.35(15)	O(8)-Dy(1)-N(4)	77.63(15)
O(1)-Dy(1)-O(3)	65.84(14)	O(1)-Dy(1)-N(4)	138.83(15)
O(6)-Dy(1)-O(3)	125.42(14)	O(6)-Dy(1)-O(2)	83.11(15)
O(6)-Dy(1)-O(8)#1	77.52(14)	O(6)-Dy(1)-O(8)	142.36(14)

O(6)-Dy(1)-O(1)	83.08(14)	O(6)-Dy(1)-N(4)	135.70(15)
O(3)-Dy(2)-O(2)#1	135.23(14)	O(3)-Dy(2)-N(6)	66.33(15)
O(3)-Dy(2)-N(2)	114.14(15)	O(2)#1-Dy(2)-N(6)	155.77(16)
O(2)#1-Dy(2)-N(2)	78.47(15)	O(8)-Dy(2)-N(6)	134.35(16)
O(8)-Dy(2)-O(3)	71.19(14)	O(8)-Dy(2)-O(2)#1	69.88(13)
O(8)-Dy(2)-O(1)	74.35(14)	O(8)-Dy(2)-N(2)	132.35(16)
O(1)-Dy(2)-N(6)	103.19(16)	O(1)-Dy(2)-O(3)	67.53(14)
O(1)-Dy(2)-O(2)#1	81.34(13)	O(1)-Dy(2)-N(2)	66.26(16)
O(5)-Dy(2)-N(6)	84.68(16)	O(5)-Dy(2)-O(3)	83.09(14)
O(5)-Dy(2)-O(2)#1	106.43(14)	O(5)-Dy(2)-O(8)	74.23(15)
O(5)-Dy(2)-O(1)	142.38(15)	O(5)-Dy(2)-N(2)	150.88(17)
O(4)-Dy(2)-N(6)	78.31(17)	O(4)-Dy(2)-O(3)	139.32(15)
O(4)-Dy(2)-O(2)#1	84.12(15)	O(4)-Dy(2)-O(8)	130.47(15)
O(4)-Dy(2)-O(1)	143.55(15)	O(4)-Dy(2)-O(5)	73.92(16)
O(4)-Dy(2)-N(2)	78.17(17)	N(2)-Dy(2)-N(6)	81.68(17)

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

Table S4 The Dy^{III} geometry analysis by SHAPE 2.0 for **3**.

	D_{4d}SAPR	D_{2d}TDD	C_{2v}JBTPR	C_{2v}BTPR	D_{2d}JSD
$Dy1^{III}$	0.965	3.138	3.377	2.760	5.524
$Dy2^{III}$	1.360	1.643	2.902	2.120	2.120

SAPR = Square antiprism, TDD = Triangular dodecahedron, JBTPR = Biaugmented trigonal prism J50, BTPR = Biaugmented trigonal prism, JSD = Snub diphenoid J84.

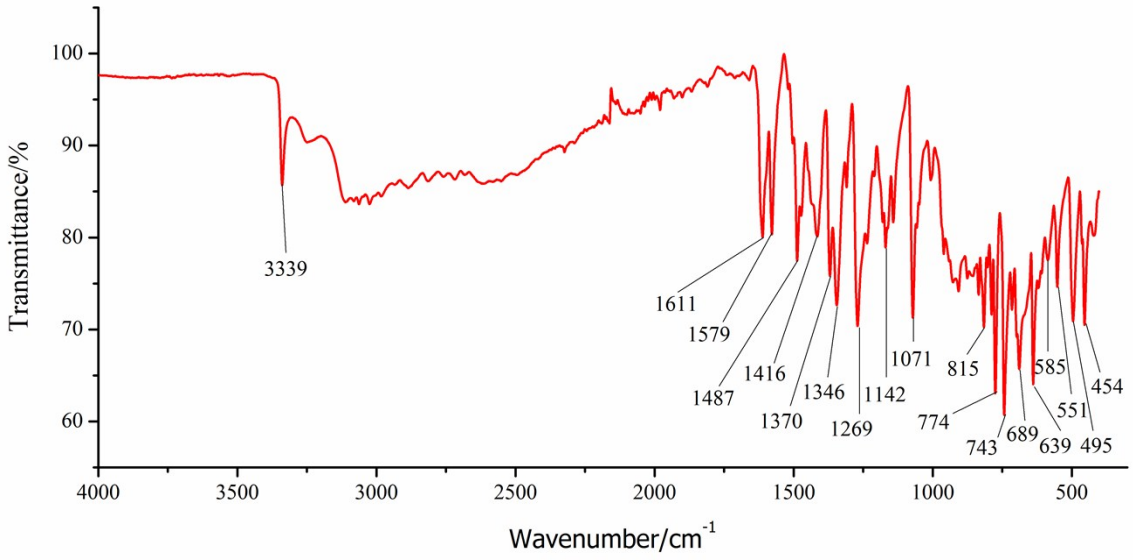

Figure S1. The IR spectra for 5-(benzylideneamino)quinolin-8-ol (HL).

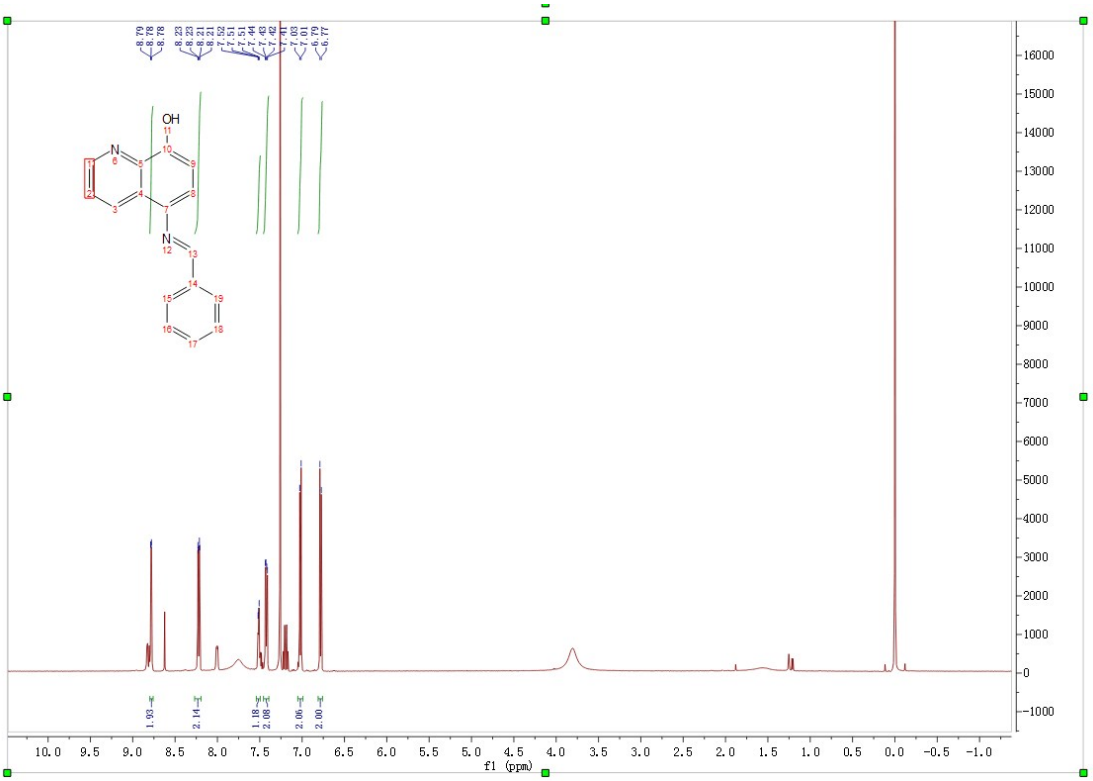

Figure S2. 1H NMR spectrum (500 MHz, $CDCl_3$) of HL.

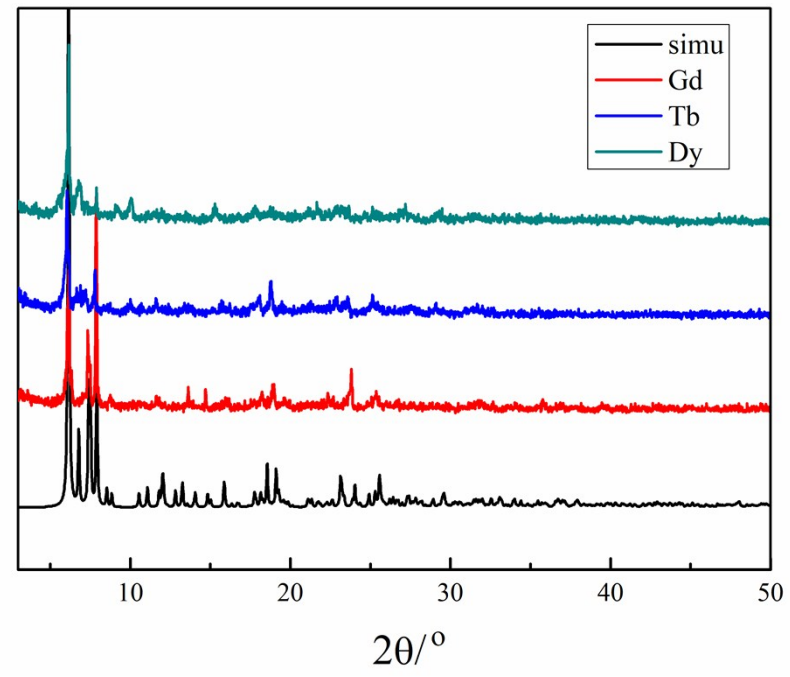

Figure S3. The simulated and experimental PXRD patterns for **1**-**3**.

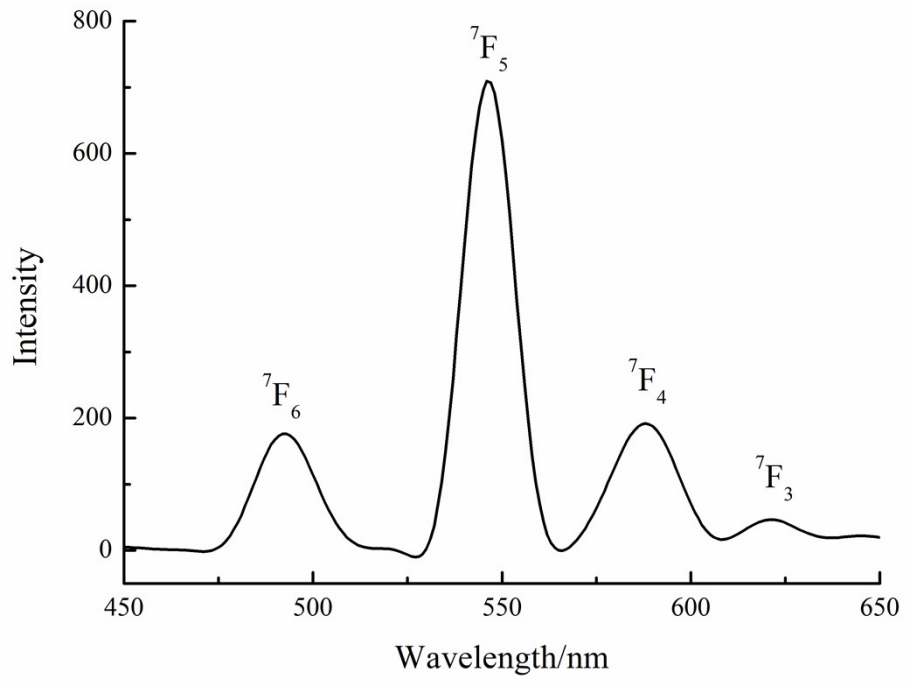

Figure S4. The emission spectra of **2** in solid state when excited at 300 nm.

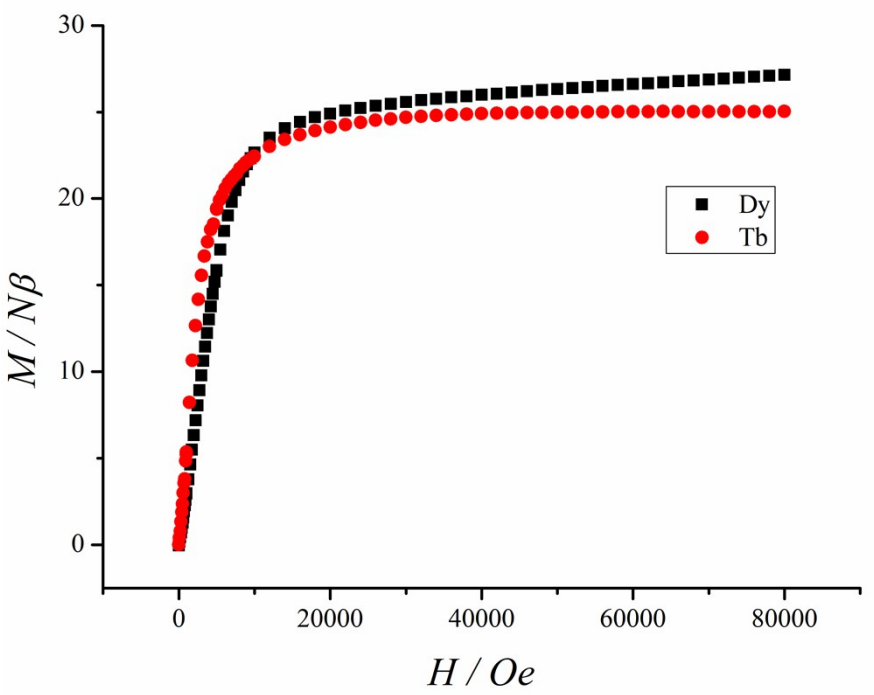

Figure S5. Field-dependent magnetizations of **2** and **3** at 2 K.

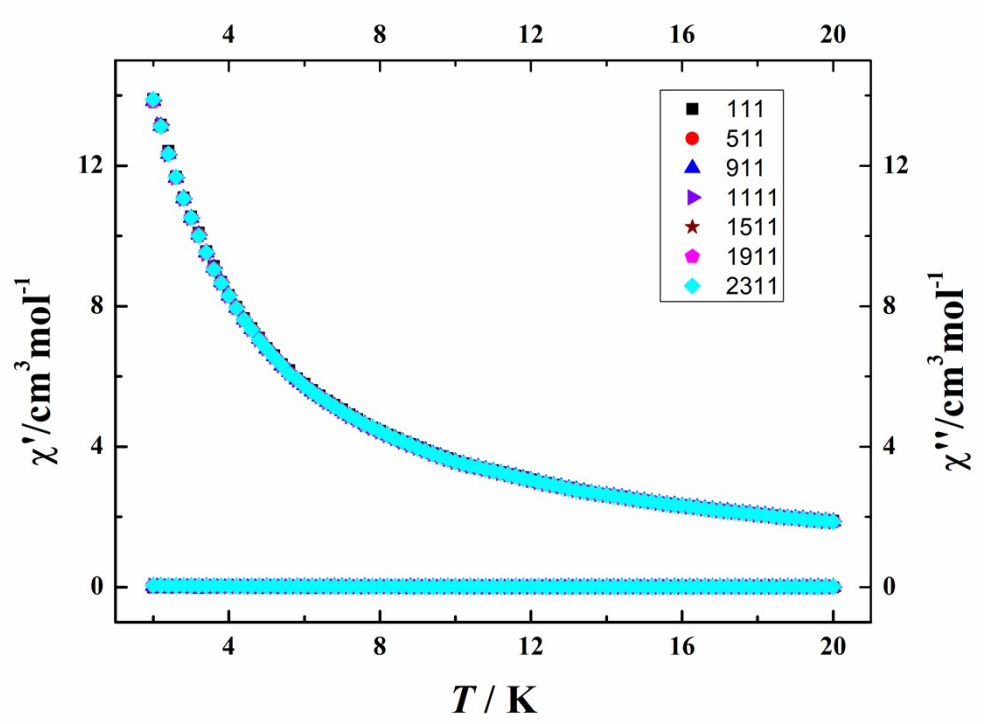

Figure S6. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities for **2** (Tb_4) in H_{dc}= 0 Oe with an oscillation of 3.0 Oe**.**