Electronic Supplementary Information

Salen–type Dy_4 Single–molecule magnet with enhanced energy barrier and its analogues

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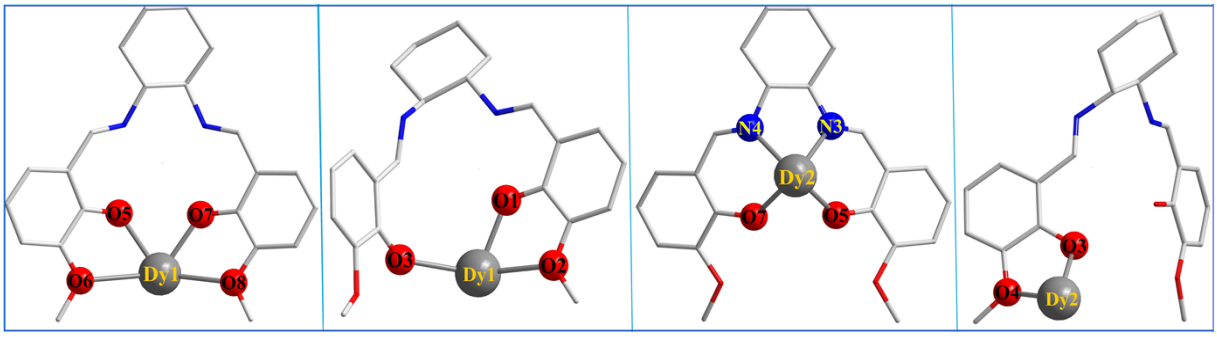
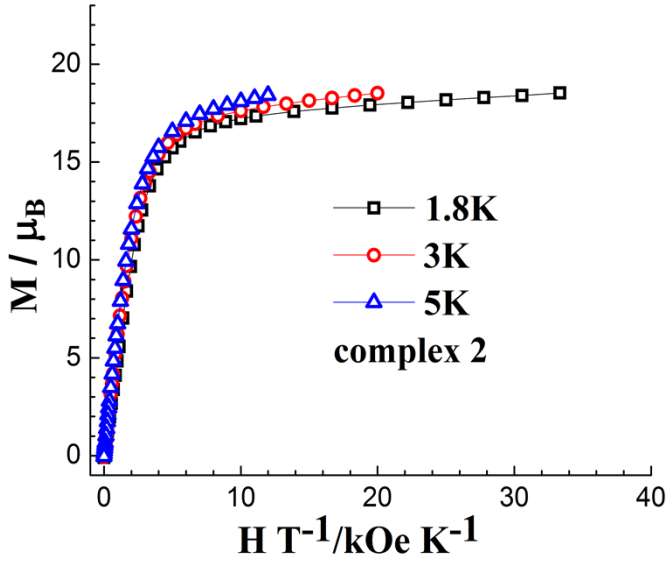
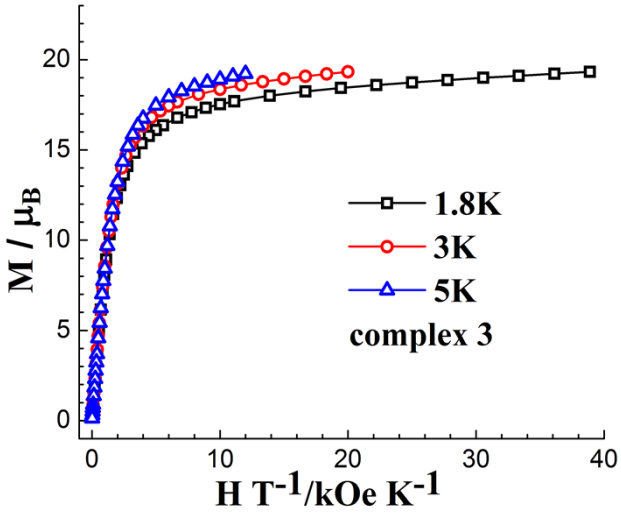


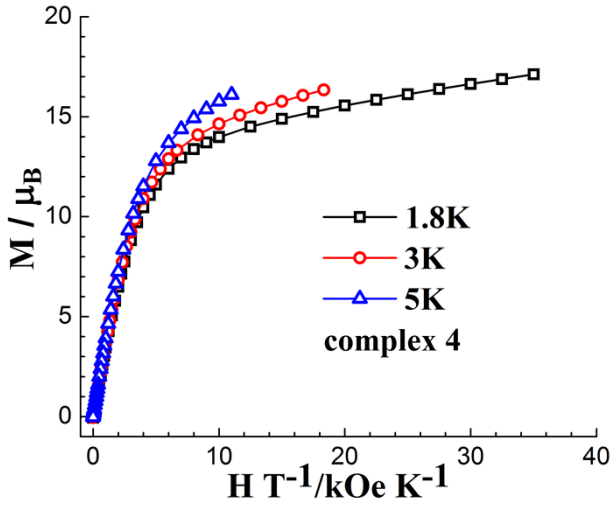
Fig. S1 The chelating modes of the ligand in complex **1**



(a)



(b)



(c)

Fig. S2 *M vs H/T* plots for **2**(a), **3**(b), **4(c)** at 1.8, 3 and 5 K

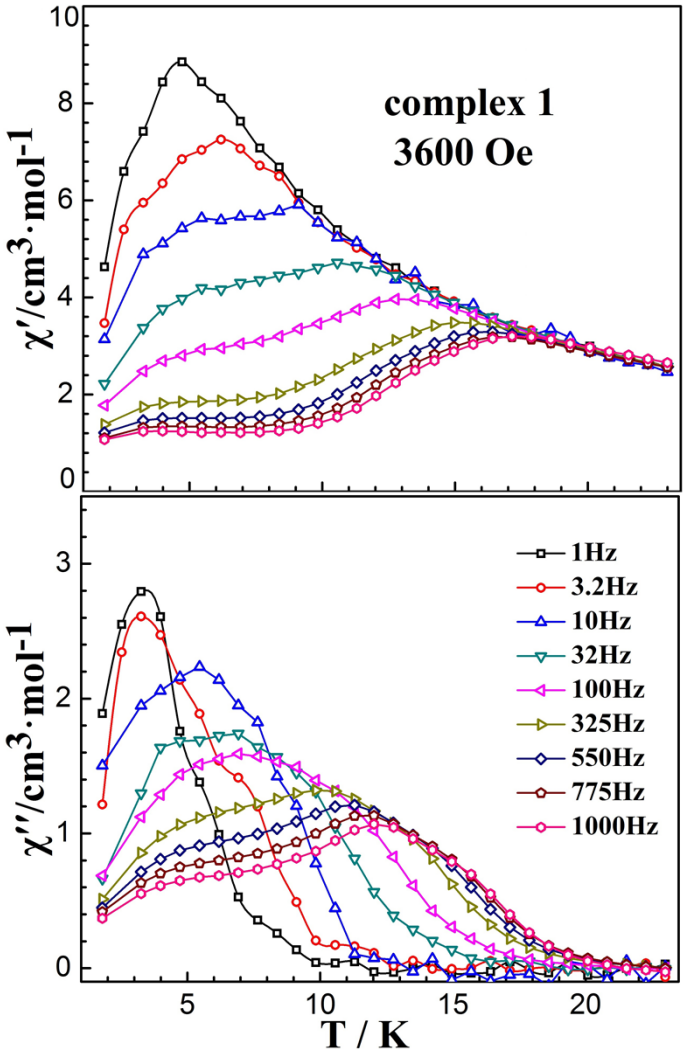


Fig. S3 Plots of χ′ versus T (top) and χ″ versus T (bottom) for **1** at H_{dc}=3600 Oe

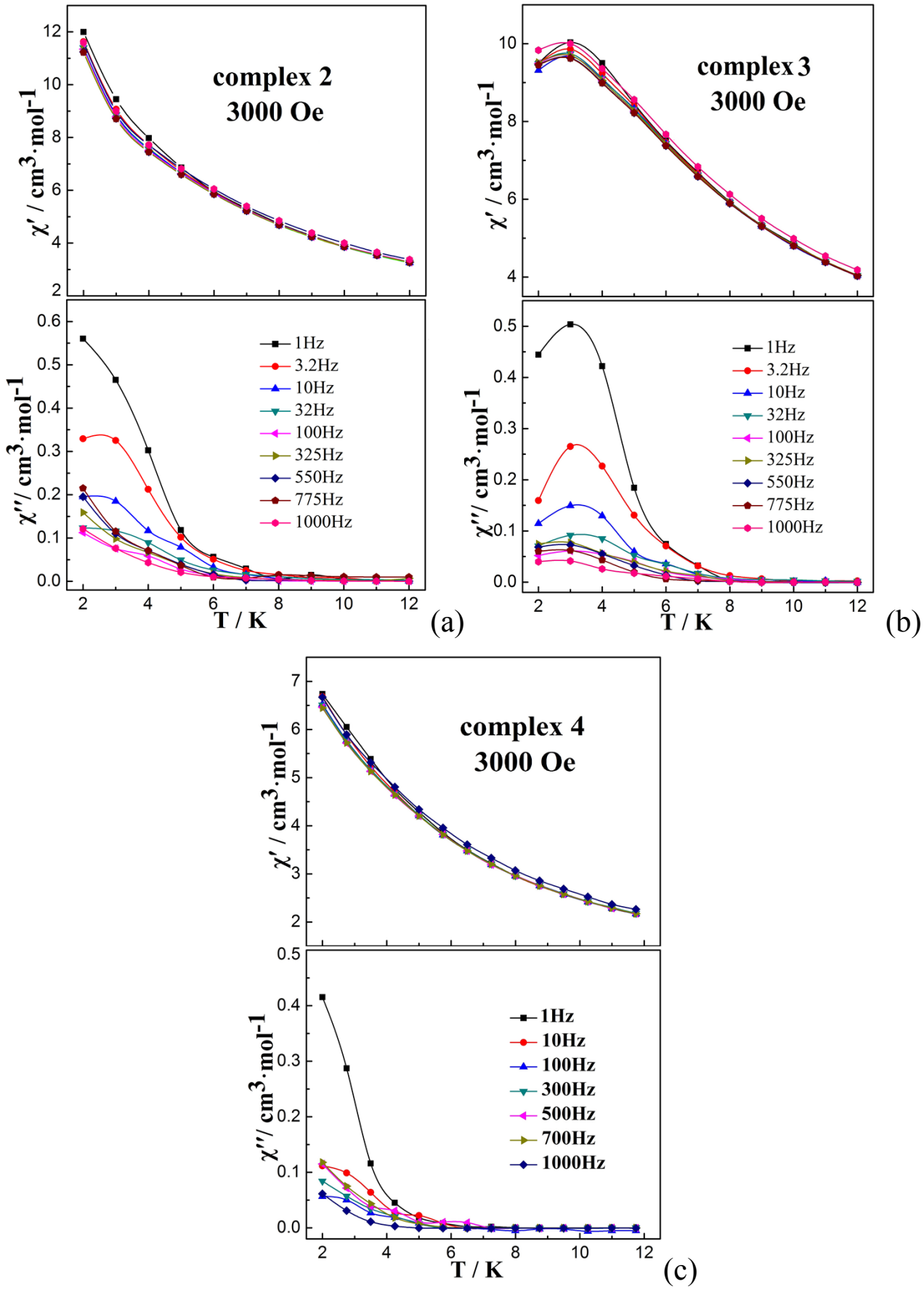


Fig. S4 Plots of χ′ versus T and χ″ versus T for complexes **2**(a), **3**(b) and **4**(c) under 3000 Oe.

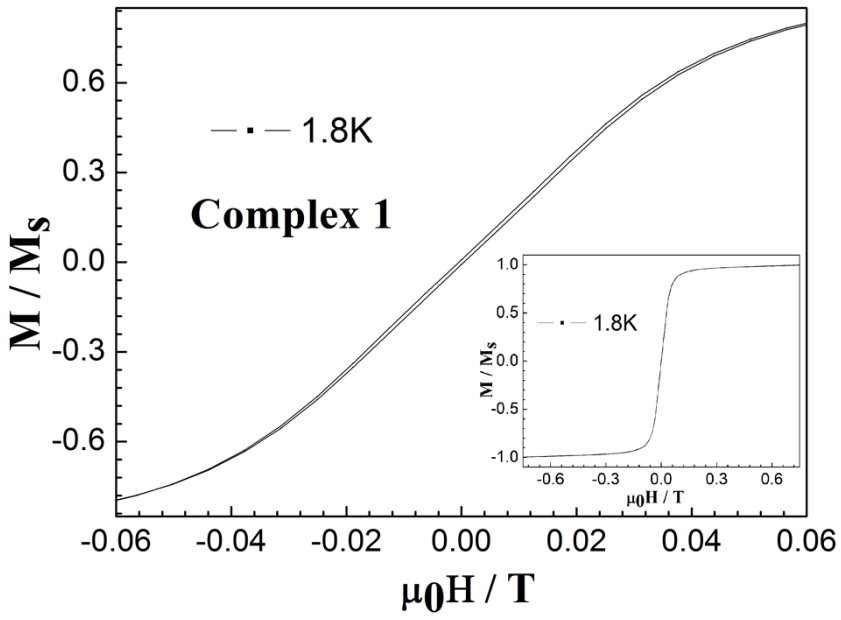


Fig. S5 Field dependence of the normalized magnetization of **1** at 1.8 K for dc applied field ranging from –7.0 T to 7.0 T.

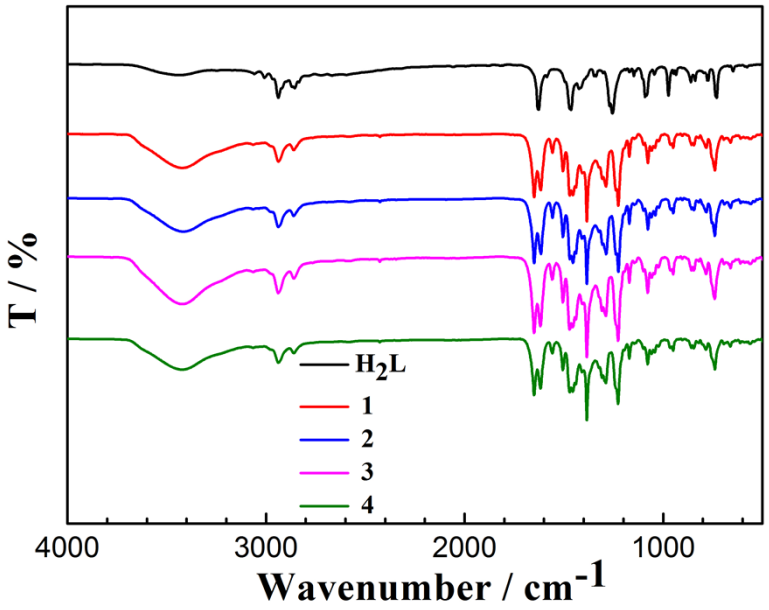


Fig. S6 *IR* spectra of the ligand and complexes **1**–**4**

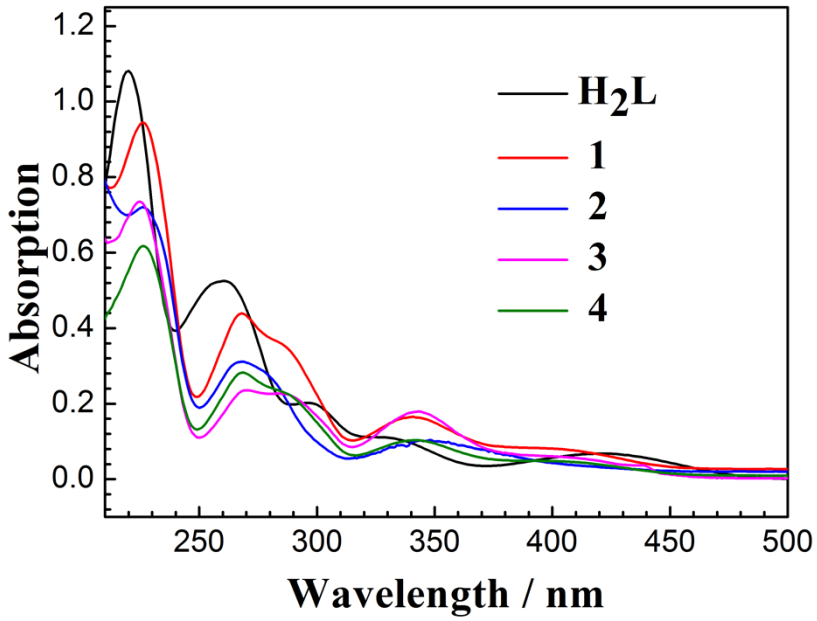
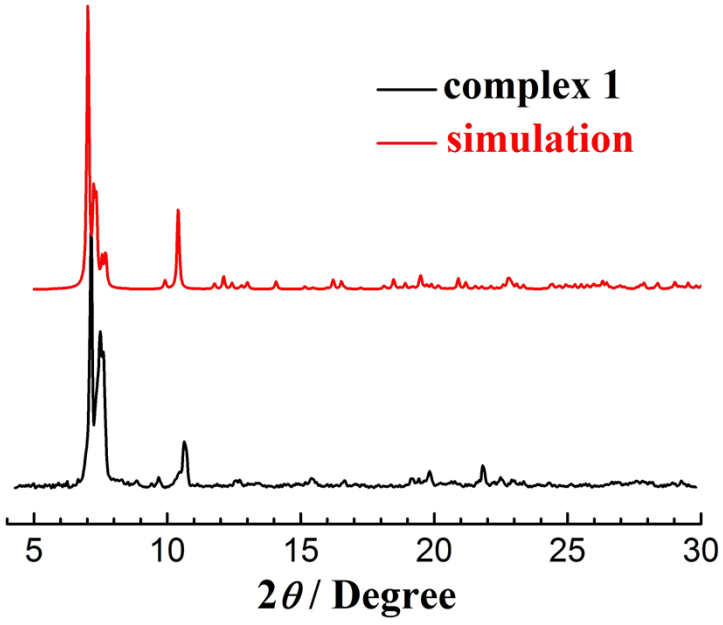
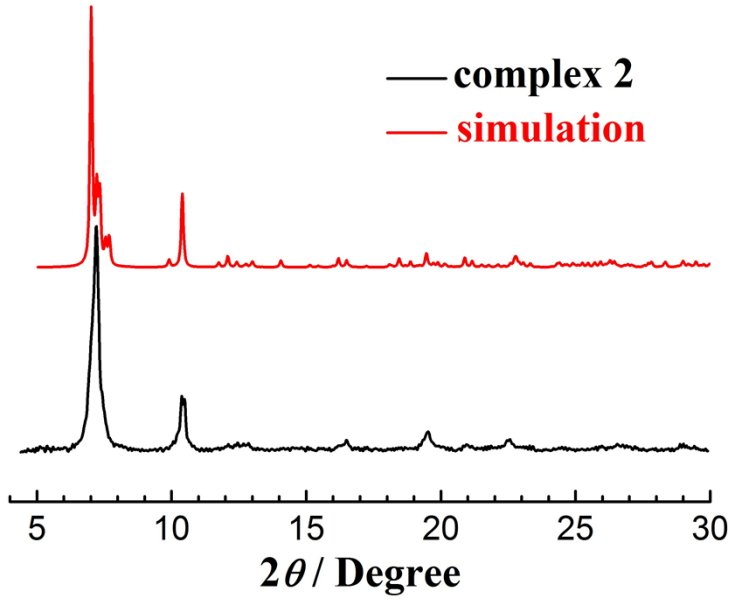


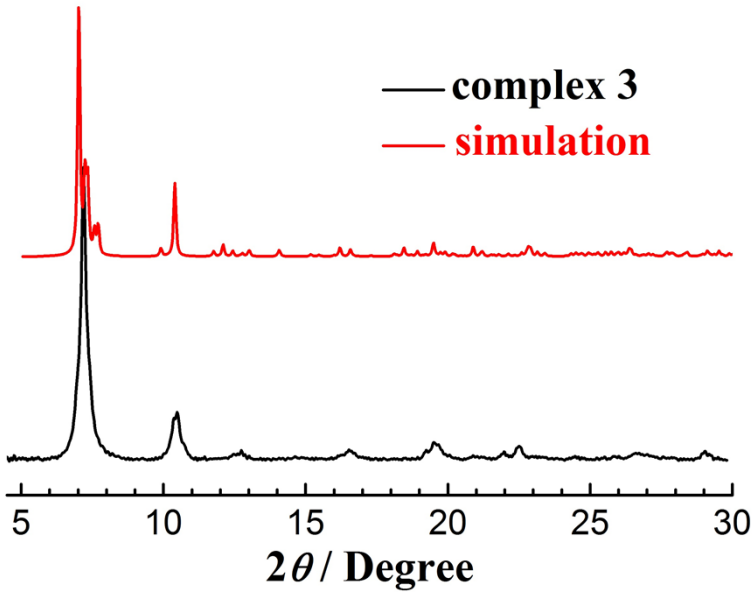
Fig. S7 *UV-vis* spectra of the ligand and complexes **1**–**4**.



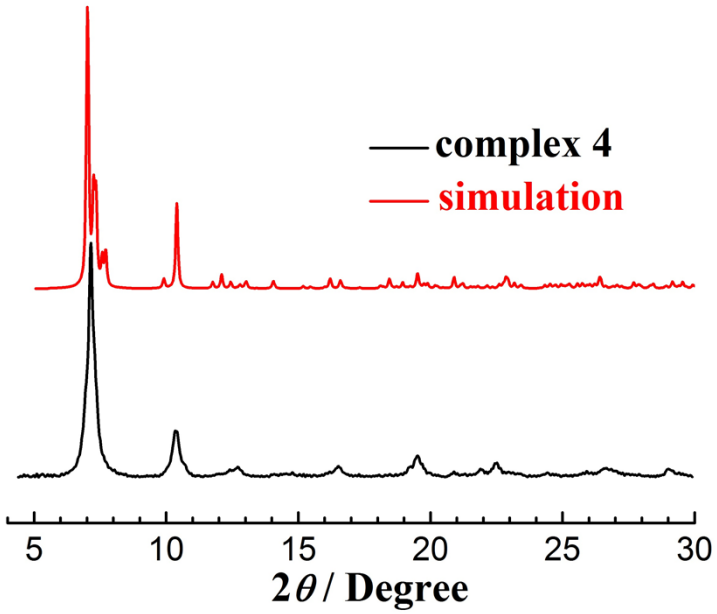
(a)


complex 2
simulation
5
10
15
20
25
30
2θ / Degree

(b)


complex 3
simulation
5
10
15
20
25
30
2θ / Degree

(c)



(d)

Fig. S8 The powder X-ray diffraction patterns and the simulated patterns of complexes **1**(a), **2**(b), **3**(c) and **4**(d)**.** (The experimental results of powder X-Ray was most probably caused by the loss of crystallization solvent during the experiment)

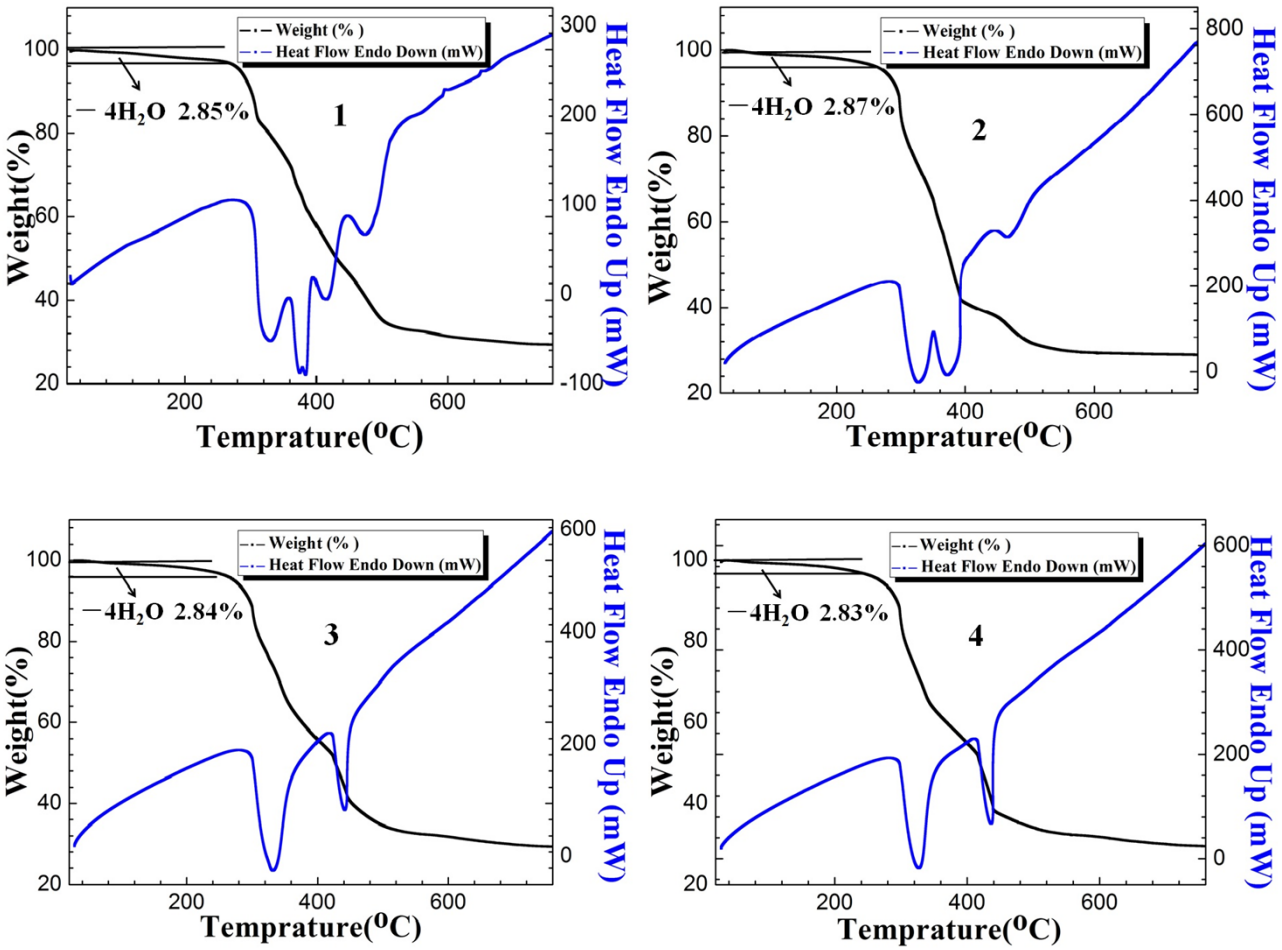


Fig. S9 Thermo-gravimetric curve for complexes **1-4**

Table S1 Selected bond lengths (Å) and angles (deg) for complex **1**

Bonds	Length/Angle	Bonds	Length/Angle
Dy(1)–O(1)	2.266(4)	Dy(1)–Dy(2a)	3.8524(5)
Dy(1)–O(7)	2.334(4)	Dy(2)–O(5)	2.312(4)
Dy(1)–O(12)	2.369(4)	Dy(2)–O(12a)	2.322(4)
Dy(1)–O(5)	2.374(4)	Dy(2)–O(12)	2.330(4)
Dy(1)–O(9)	2.384(4)	Dy(2)–O(3a)	2.346(4)
Dy(1)–O(3)	2.431(4)	Dy(2)–O(7)	2.345(4)
Dy(1)–O(2)	2.572(4)	Dy(2)–O(4a)	2.494(4)
Dy(1)–O(8)	2.651(4)	Dy(2)–N(4)	2.419(5)
Dy(1)–O(6)	2.695(4)	Dy(2)–N(3)	2.505(5)
Dy(1)–Dy(2)	3.5043(4)	Dy(2)–Dy(2a)	3.7609(6)
O(7)–Dy(1)–O(5)	68.52(13)	O(5)–Dy(2)–O(12)	69.40(14)
O(12)–Dy(1)–O(5)	67.72(14)	N(4)–Dy(2)–N(3)	65.04(17)
O(7)–Dy(1)–O(12)	72.74(13)	Dy(2)–O(5)–Dy(1)	96.81(14)
O(5)–Dy(2)–O(7)	69.37(13)	Dy(1)–O(7)–Dy(2)	97.00(14)
O(12)–Dy(2)–O(7)	73.23(14)	Dy(2)–O(12)–Dy(1)	96.47(15)
Dy(2)′–O(12)–Dy(1)	110.44(14)	Dy(2) ′–O(12)–Dy(2)	107.91(14)

Table S2 Selected bond lengths (Å) and angles (deg) for complex **2**

Bonds	Length/Angle	Bonds	Length/Angle
Tb(1)–O(1)	2.286(4)	Tb(1)–Tb(2a)	3.8689(4)
Tb(1)–O(7)	2.357(4)	Tb(2)–O(5)	2.325(3)
Tb(1)–O(12)	2.378(3)	Tb(2)–O(12a)	2.330(4)
Tb(1)–O(5)	2.377(4)	Tb(2)–O(12)	2.343(4)
Tb(1)–O(9)	2.408(4)	Tb(2)–O(3a)	2.363(3)
Tb(1)–O(3)	2.430(4)	Tb(2)–O(7)	2.361(3)
Tb(1)–O(2)	2.579(4)	Tb(2)–O(4a)	2.502(4)
Tb(1)–O(8)	2.658(4)	Tb(2)–N(4)	2.435(5)
Tb(1)–O(6)	2.693(4)	Tb(2)–N(3)	2.516(5)
Tb(1)–Tb(2)	3.5236(4)	Tb(2)–Tb(2a)	3.7748(5)
O(7)–Tb(1)–O(5)	68.37(13)	O(5)–Tb(2)–O(12)	69.33(13)
O(12)–Tb(1)–O(5)	67.88(12)	N(4)–Tb(2)–N(3)	64.70(16)
O(7)–Tb(1)–O(12)	72.85(12)	Tb(2)–O(5)–Tb(1)	97.07(12)
O(5)–Tb(2)–O(7)	69.18(13)	Tb(1)–O(7)–Tb(2)	96.64(13)
O(12)–Tb(2)–O(7)	73.40(12)	Tb(2)–O(12)–Tb(1)	96.55(13)
Tb(2)′–O(12)–Tb(1)	110.44(14)	Tb(2) ′–O(12)–Tb(2)	107.75(14)

Table S3 Selected bond lengths (Å) and angles (deg) for complex **3**

Bonds	Length/Angle	Bonds	Length/Angle
Ho(1)–O(1)	2.262(4)	Ho(1)–Ho(2a)	3.8341(4)
Ho(1)–O(7)	2.329(4)	Ho(2)–O(5)	2.303(4)
Ho(1)–O(12)	2.356(4)	Ho(2)–O(12a)	2.315(4)
Ho(1)–O(5)	2.352(4)	Ho(2)–O(12)	2.318(4)
Ho(1)–O(9)	2.381(5)	Ho(2)–O(3a)	2.343(4)
Ho(1)–O(3)	2.412(4)	Ho(2)–O(7)	2.334(4)
Ho(1)–O(2)	2.555(4)	Ho(2)–O(4a)	2.494(4)
Ho(1)–O(8)	2.646(4)	Ho(2)–N(4)	2.415(6)
Ho(1)–O(6)	2.678(5)	Ho(2)–N(3)	2.491(5)
Ho(1)–Ho(2)	3.4851(4)	Ho(2)–Ho(2a)	3.7415(6)
O(7)–Ho(1)–O(5)	68.53(14)	O(5)–Ho(2)–O(12)	69.06(14)
O(12)–Ho(1)–O(5)	67.60(14)	N(4)–Ho(2)–N(3)	65.31(18)
O(7)–Ho(1)–O(12)	73.06(14)	Ho(2)–O(5)–Ho(1)	96.96(14)
O(5)–Ho(2)–O(7)	69.27(14)	Ho(1)–O(7)–Ho(2)	96.71(15)
O(12)–Ho(2)–O(7)	73.67(15)	Ho(2)–O(12)–Ho(1)	96.44(14)
Ho(2)′–O(12)–Ho(1)	110.32(16)	Ho(2) ′–O(12)–Ho(2)	107.72(16)

Table S4 Selected bond lengths (Å) and angles (deg) for complex **4**

Bonds	Length/Angle	Bonds	Length/Angle
Er(1)–O(1)	2.259(4)	Er(1)–Er(2a)	3.8219(4)
Er(1)–O(7)	2.310(4)	Er(2)–O(5)	2.291(4)
Er(1)–O(12)	2.352(4)	Er(2)–O(12a)	2.301(4)
Er(1)–O(5)	2.346(4)	Er(2)–O(12)	2.307(4)
Er(1)–O(9)	2.369(5)	Er(2)–O(3a)	2.333(4)
Er(1)–O(3)	2.400(4)	Er(2)–O(7)	2.327(4)
Er(1)–O(2)	2.560(4)	Er(2)–O(4a)	2.482(4)
Er(1)–O(8)	2.637(4)	Er(2)–N(4)	2.406(5)
Er(1)–O(6)	2.683(5)	Er(2)–N(3)	2.479(5)
Er(1)–Er(2)	3.4666(4)	Er(2)–Er(2a)	3.7236(6)
O(7)–Er(1)–O(5)	68.52(14)	O(5)–Er(2)–O(12)	69.45(14)
O(12)–Er(1)–O(5)	67.77(13)	N(4)–Er(2)–N(3)	65.32(18)
O(7)–Er(1)–O(12)	73.20(13)	Er(2)–O(5)–Er(1)	96.75(14)
O(5)–Er(2)–O(7)	69.16(14)	Er(1)–O(7)–Er(2)	96.78(15)
O(12)–Er(2)–O(7)	73.72(14)	Er(2)–O(12)–Er(1)	96.16(14)
Er(2)′–O(12)–Er(1)	110.44(16)	Er(2) ′–O(12)–Er(2)	107.83(15)