Electronic Supplementary Material (ESI) for CrystEngComm

A New D_{2d}-symmetry Dy^{III} Mononuclear Single-Molecule Magnet Containing Monodentate N-Heterocyclic Donor Ligand

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

Dy(1)-O(4)	2.297(6)	Dy(1)-O(1)	2.344(6)
Dy(1)-O(5)	2.307(6)	Dy(1)-O(3)	2.357(6)
Dy(1)-O(6)	2.308(6)	Dy(1)-N(1)	2.452(8)
Dy(1)-O(2)	2.338(6)	Dy(1)-N(3)	2.459(8)
O(4)-Dy(1)-O(5)	143.3(2)	O(1)-Dy(1)-O(3)	132.7(2)
O(4)-Dy(1)-O(6)	144.2(2)	O(4)-Dy(1)-N(1)	96.1(3)
O(5)-Dy(1)-O(6)	71.1(2)	O(5)-Dy(1)-N(1)	79.3(2)
O(4)-Dy(1)-O(2)	83.2(2)	O(6)-Dy(1)-N(1)	102.0(2)
O(5)-Dy(1)-O(2)	128.0(2)	O(2)-Dy(1)-N(1)	72.1(2)
O(6)-Dy(1)-O(2)	73.56(19)	O(1)-Dy(1)-N(1)	143.8(2)
O(4)-Dy(1)-O(1)	75.1(2)	O(3)-Dy(1)-N(1)	72.8(2)
O(5)-Dy(1)-O(1)	128.2(2)	O(4)-Dy(1)-N(3)	86.3(2)
O(6)-Dy(1)-O(1)	72.1(2)	O(5)-Dy(1)-N(3)	77.8(2)
O(2)-Dy(1)-O(1)	71.9(2)	O(6)-Dy(1)-N(3)	96.2(2)
O(4)-Dy(1)-O(3)	71.1(2)	O(2)-Dy(1)-N(3)	143.2(2)
O(5)-Dy(1)-O(3)	72.8(2)	O(1)-Dy(1)-N(3)	71.3(2)
O(6)-Dy(1)-O(3)	143.8(2)	O(3)-Dy(1)-N(3)	74.3(2)
O(2)-Dy(1)-O(3)	133.5(2)	N(1)-Dy(1)-N(3)	144.2(3)

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

Tb(1)-O(3)	2.326(6)	Tb(1)-O(4)	2.378(6)
Tb(1)-O(5)	2.332(6)	Tb(1)-O(1)	2.384(5)
Tb(1)-O(6)	2.347(5)	Tb(1)-N(1)	2.492(7)
Tb(1)-O(2)	2.364(5)	Tb(1)-N(3)	2.495(7)
O(3)-Tb(1)-O(5)	143.1(2)	O(4)-Tb(1)-O(1)	132.7(2)
O(3)-Tb(1)-O(6)	144.35(19)	O(3)-Tb(1)-N(1)	96.5(3)
O(5)-Tb(1)-O(6)	70.9(2)	O(5)-Tb(1)-N(1)	79.8(2)
O(3)-Tb(1)-O(2)	83.60(19)	O(6)-Tb(1)-N(1)	102.0(2)
O(5)-Tb(1)-O(2)	128.1(2)	O(2)-Tb(1)-N(1)	71.8(2)
O(6)-Tb(1)-O(2)	73.76(19)	O(4)-Tb(1)-N(1)	73.1(2)
O(3)-Tb(1)-O(4)	70.7(2)	O(1)-Tb(1)-N(1)	143.4(2)
O(5)-Tb(1)-O(4)	73.1(2)	O(3)-Tb(1)-N(3)	85.7(2)
O(6)-Tb(1)-O(4)	144.0(2)	O(5)-Tb(1)-N(3)	78.1(2)
O(2)-Tb(1)-O(4)	133.3(2)	O(6)-Tb(1)-N(3)	95.7(2)
O(3)-Tb(1)-O(1)	75.1(2)	O(2)-Tb(1)-N(3)	142.6(2)
O(5)-Tb(1)-O(1)	127.8(2)	O(4)-Tb(1)-N(3)	74.9(2)
O(6)-Tb(1)-O(1)	71.89(19)	O(1)-Tb(1)-N(3)	70.7(2)
O(2)-Tb(1)-O(1)	71.91(19)	N(1)-Tb(1)-N(3)	145.2(2)

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

Ho(1)-O(5)	2.313(7)	Ho(1)-O(3)	2.365(6)
Ho(1)-O(2)	2.319(6)	Ho(1)-O(6)	2.368(6)
Ho(1)-O(1)	2.321(6)	Ho(1)-N(1)	2.469(9)
Ho(1)-O(4)	2.354(6)	Ho(1)-N(3)	2.478(9)
O(5)-Ho(1)-O(2)	144.0(2)	O(3)-Ho(1)-O(6)	132.7(2)
O(5)-Ho(1)-O(1)	143.5(2)	O(5)-Ho(1)-N(1)	96.5(3)
O(2)-Ho(1)-O(1)	71.2(2)	O(2)-Ho(1)-N(1)	101.4(3)
O(5)-Ho(1)-O(4)	82.9(2)	O(1)-Ho(1)-N(1)	79.3(3)
O(2)-Ho(1)-O(4)	73.8(2)	O(4)-Ho(1)-N(1)	71.3(2)
O(1)-Ho(1)-O(4)	128.0(2)	O(3)-Ho(1)-N(1)	143.4(2)
O(5)-Ho(1)-O(3)	74.7(2)	O(6)-Ho(1)-N(1)	73.3(3)
O(2)-Ho(1)-O(3)	72.3(2)	O(5)-Ho(1)-N(3)	86.4(3)
O(1)-Ho(1)-O(3)	128.3(2)	O(2)-Ho(1)-N(3)	96.2(3)
O(4)-Ho(1)-O(3)	72.4(2)	O(1)-Ho(1)-N(3)	77.9(3)
O(5)-Ho(1)-O(6)	71.6(2)	O(4)-Ho(1)-N(3)	143.5(2)
O(2)-Ho(1)-O(6)	143.7(2)	O(3)-Ho(1)-N(3)	71.1(3)
O(1)-Ho(1)-O(6)	72.5(2)	O(6)-Ho(1)-N(3)	74.5(3)
O(4)-Ho(1)-O(6)	133.1(2)	N(1)-Ho(1)-N(3)	144.9(3)

Table S4 δ(°) and φ(°) values for Complexes **2** and **3**.

	2		**3**		DD	TP	SAP
δ_1	O1-[O6-N3]-O5	30.94	O3-[O2-N3]-O1	30.71	29.5	0.0	0.0
δ_2	O2-[O3-N1]-O4	34.38	O4-[O5-N1]-O6	34.02	29.5	21.8	0.0
δ_3	O1-[O3-N3]-O4	40.72	O3-[O5-N3]-O6	40.34	29.5	48.2	52.4
δ_4	O2-[O6-N1]-O5	26.42	O4-[O2-N1]-O1	26.27	29.5	48.2	52.4
φ_1	N3-N1-O1-O2	1.67	N3-N1-O3-O4	1.55	0.0	14.1	24.5
φ_2	O6-O3-O5-O4	2.71	O2-O5-O1-O6	2.48	0.0	14.1	24.5

A[BC]D is the dihedral angle between the ABC plane and the BCD plane. A–B–C–D is the dihedral angle between the (AB)CD plane and the AB(CD) plane, where (AB) is the center of A and B.

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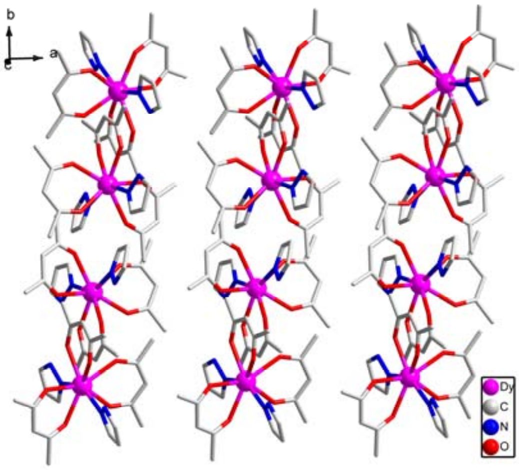

Fig. S1 Packing diagram of complex **1**. The hydrogen atoms and fluorine atoms are omitted for clarity.

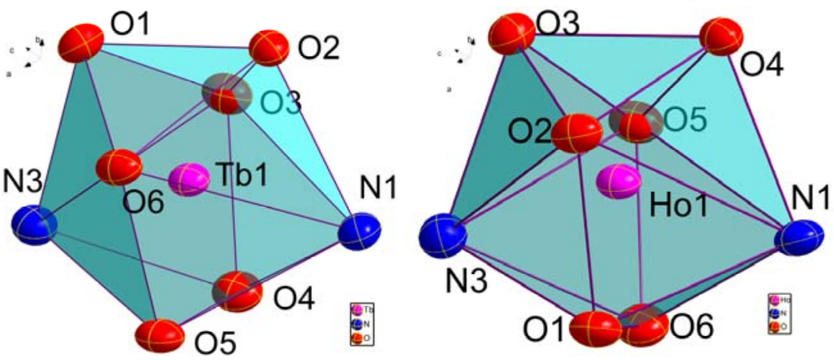

Fig. S2 D_{2d}-symmetry polyhedron of complexes **2** and **3**.

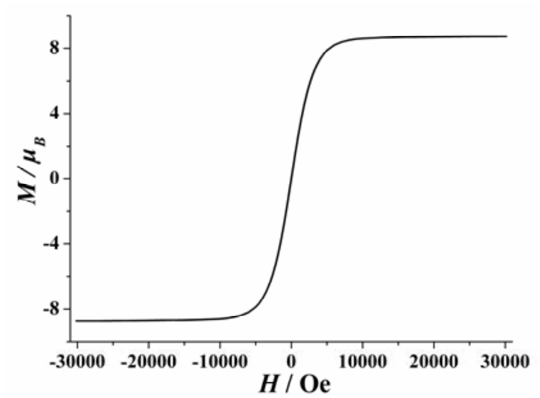

Fig. S3 Field dependence of the magnetization at 1.9 K showing the absence of hysteresis effect for **1**.

The magnetic data of **2** and **3** can be analyzed by the following approximate treatment of Eqs (1)-(3).

$$\chi_{\mathrm{Tb}} = \frac{2Ng^2\beta^2}{kT}\left[\frac{36\exp\left(\frac{-36\Delta}{kT}\right)+25\exp\left(\frac{-25\Delta}{kT}\right)+16\exp\left(\frac{-16\Delta}{kT}\right)+9\exp\left(\frac{-9\Delta}{kT}\right)+4\exp\left(\frac{-4\Delta}{kT}\right)+\exp\left(\frac{-\Delta}{kT}\right)}{2\exp\left(\frac{-36\Delta}{kT}\right)+2\exp\left(\frac{-25\Delta}{kT}\right)+2\exp\left(\frac{-16\Delta}{kT}\right)+2\exp\left(\frac{-9\Delta}{kT}\right)+2\exp\left(\frac{-4\Delta}{kT}\right)+2\exp\left(\frac{-\Delta}{kT}\right)+1}\right] \quad (1)$$

$$\chi_{\mathrm{Ho}} = \frac{2Ng^2\beta^2}{kT}\left[\frac{64\exp\left(\frac{-64\Delta}{kT}\right)+49\exp\left(\frac{-49\Delta}{kT}\right)+36\exp\left(\frac{-36\Delta}{kT}\right)+25\exp\left(\frac{-25\Delta}{kT}\right)+16\exp\left(\frac{-16\Delta}{kT}\right)+9\exp\left(\frac{-9\Delta}{kT}\right)+4\exp\left(\frac{-4\Delta}{kT}\right)+\exp\left(\frac{-\Delta}{kT}\right)}{2\exp\left(\frac{-64\Delta}{kT}\right)+2\exp\left(\frac{-49\Delta}{kT}\right)+2\exp\left(\frac{-36\Delta}{kT}\right)+2\exp\left(\frac{-25\Delta}{kT}\right)+2\exp\left(\frac{-16\Delta}{kT}\right)+2\exp\left(\frac{-9\Delta}{kT}\right)+2\exp\left(\frac{-4\Delta}{kT}\right)+2\exp\left(\frac{-\Delta}{kT}\right)+1}\right] \quad (2)$$

$$\chi_{\mathrm{M}} = \frac{\chi_{(\mathrm{Tb\ or\ Ho})}}{1-\left(2zJ'/Ng^2\beta^2\right)\chi_{(\mathrm{Tb\ or\ Ho})}} \quad (3)$$

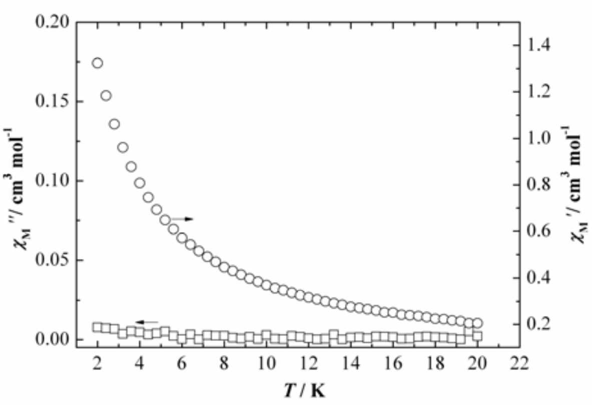

Fig. S4 Temperature dependence of the in-phase χ' (○) and out-of-phase χ'' (□) components of the alternating-current susceptibility for complex Tb(**2**) under zero *dc* field at the frequency of 944 Hz.

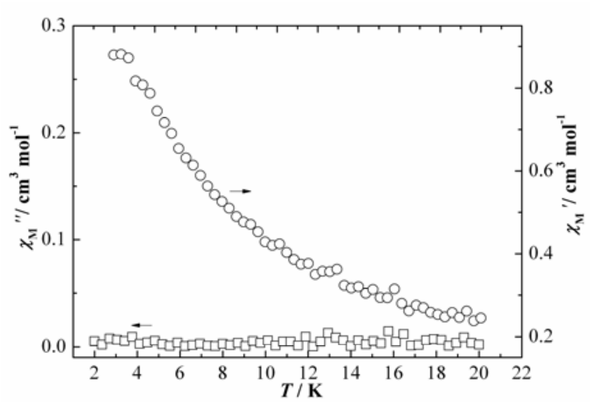

Fig. S5 Temperature dependence of the in-phase χ' (○) and out-of-phase χ'' (□) components of the alternating-current susceptibility for complex Ho(**3**) under zero *dc* field at the frequency of 944 Hz.