Electronic Supplementary Material (ESI) for CrystEngComm.

Enhancing Energy Barrier of Dysprosium(III) Single-Molecule Magnets by Tuning Magnetic Interactions through Different *N*-oxide Bridging Ligands

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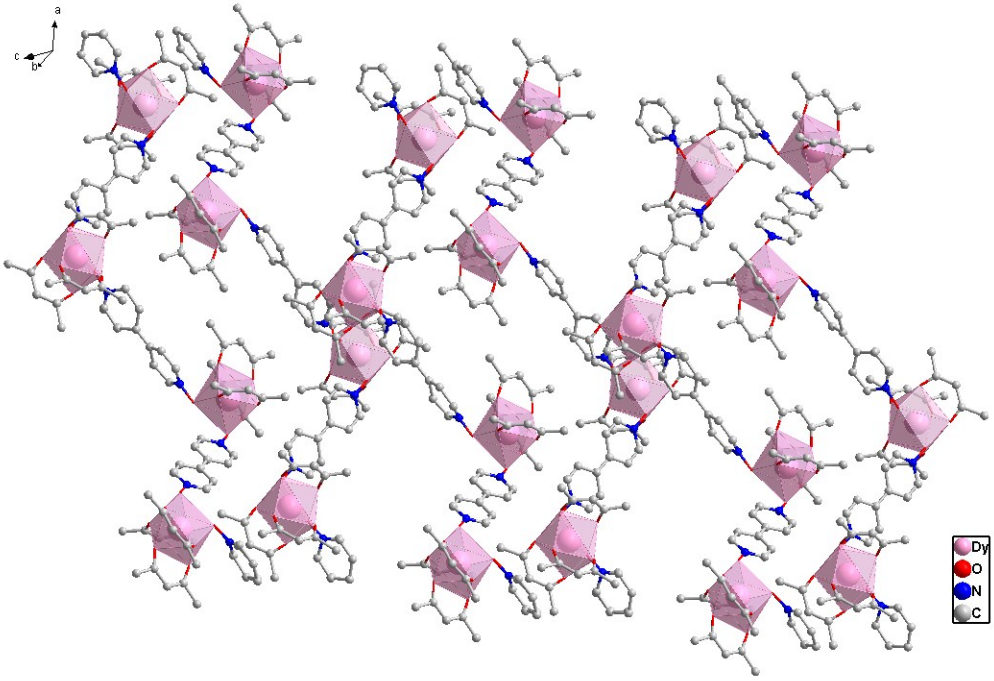

Figure S1. Packing diagram of complex **1**, all fluorine and hydrogen atoms are omitted for clarity.

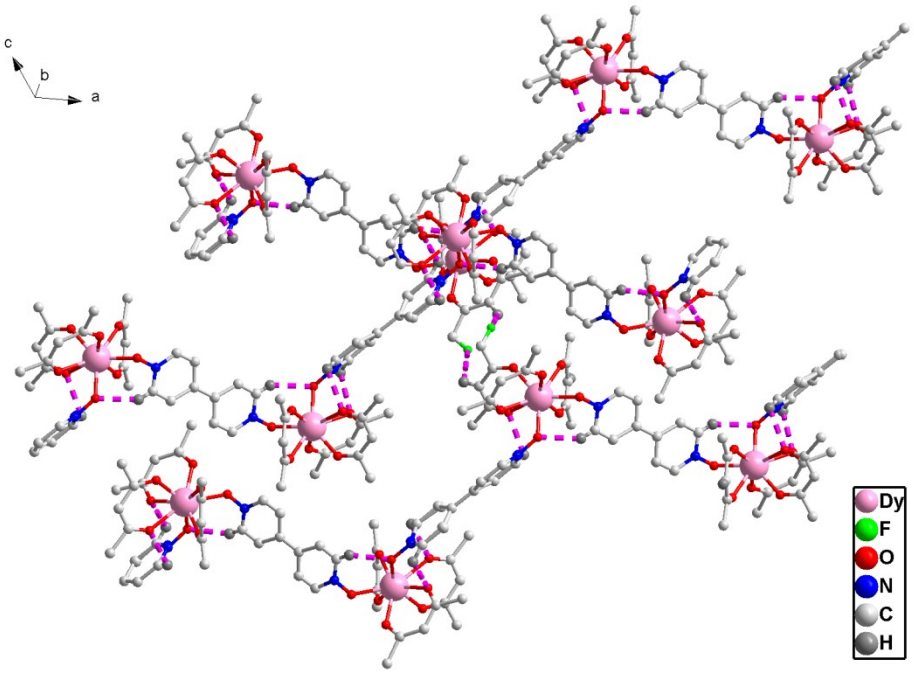

Figure S2. Hydrogen bonding interactions in complex **1** support the formation of three-dimensional networks arrangement, some hydrogen and fluorine atoms are omitted for clarity.

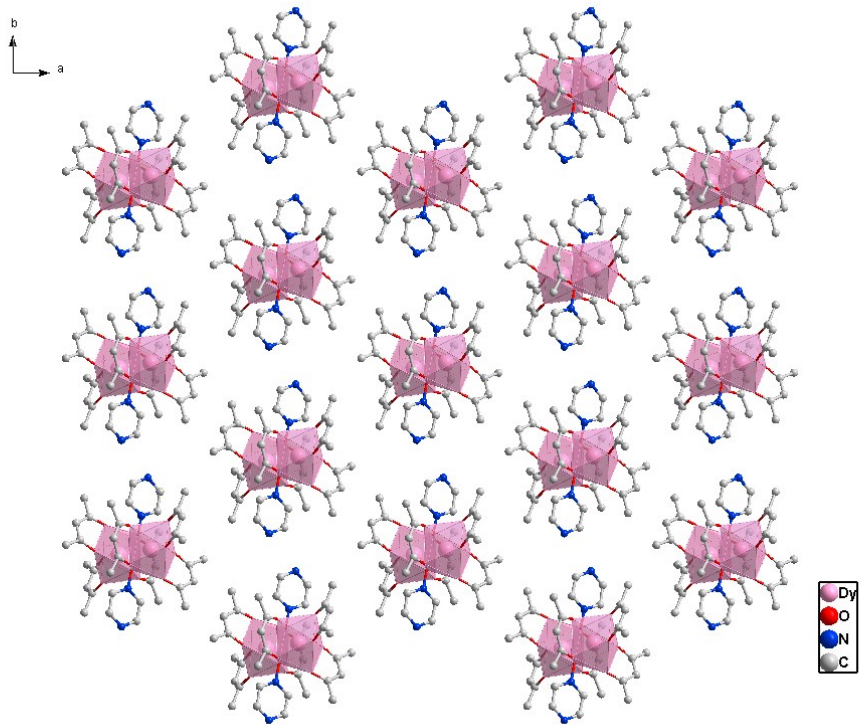

Figure S3. Packing diagram of complex **4** along **c** axis, all fluorine and hydrogen atoms are omitted for clarity.

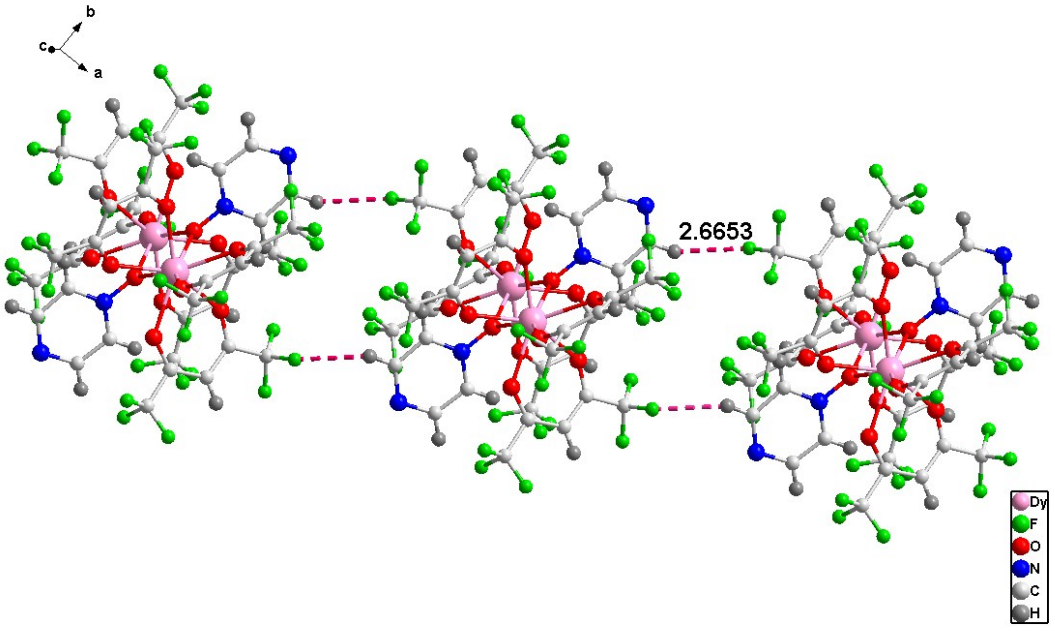

Figure S4. Hydrogen bonding interactions in complex **4** support the formation of one-dimensional chain arrangement.

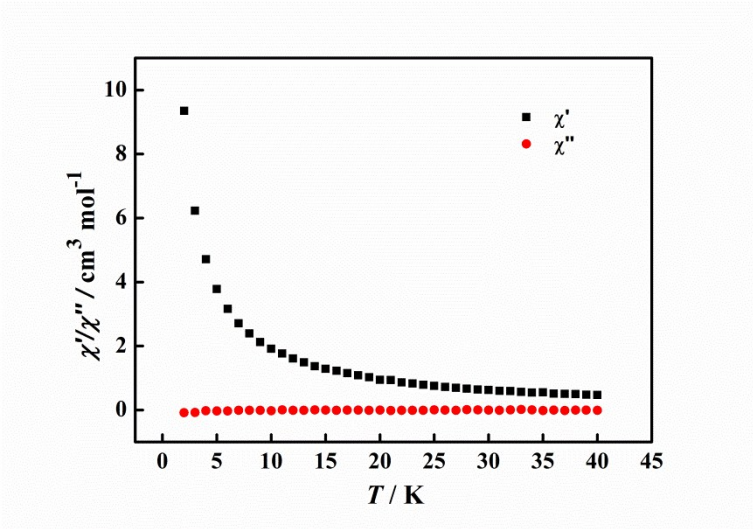

Figure S5. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility for **1** in 1000 Hz under zero dc field.

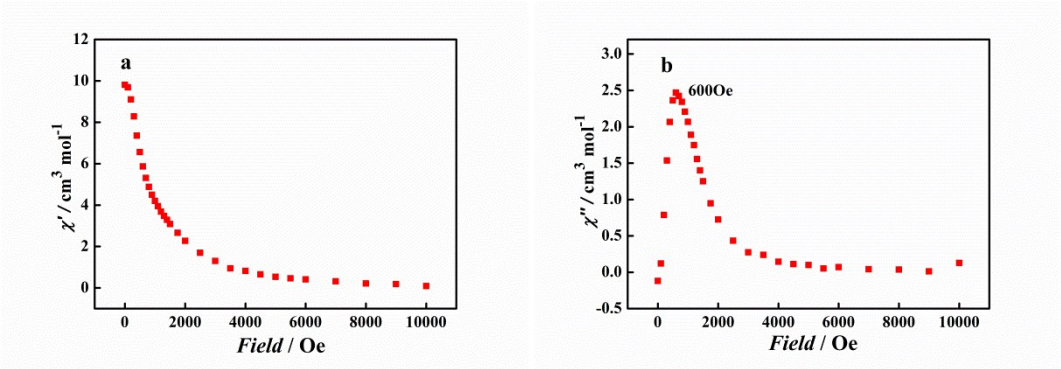

Figure S6. The field dependence of in-phase and out-of-phase ac magnetic susceptibilities of complex **1** at 1.9 K, 997 Hz.

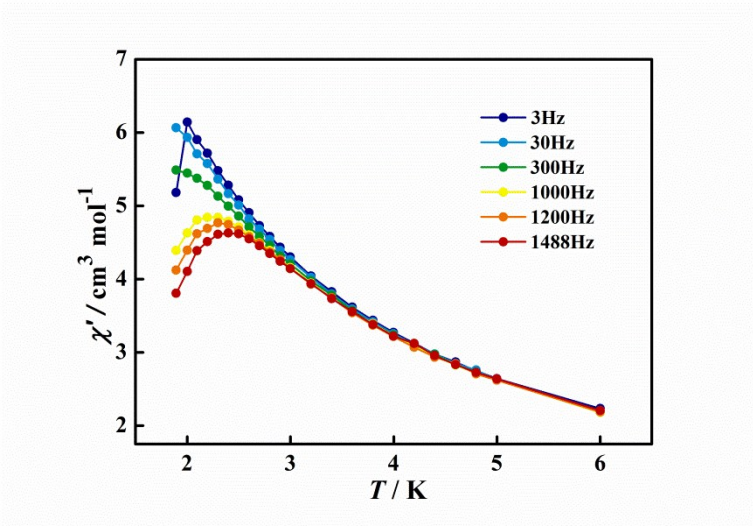

Figure S7.Temperature dependence of the in-phase (a) ac susceptibilities for **1** measured under 600 Oe dc field, the solid lines are a guide for the eyes.

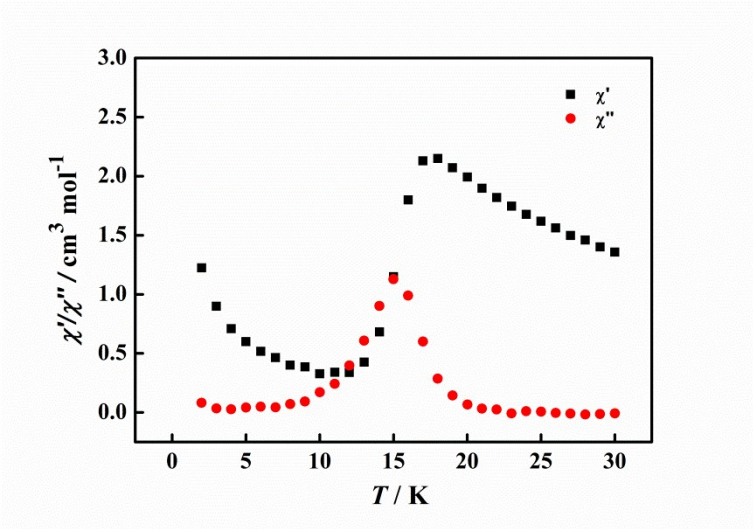

Figure S8. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibilities for complex **4** in 1000 Hz under zero dc field.

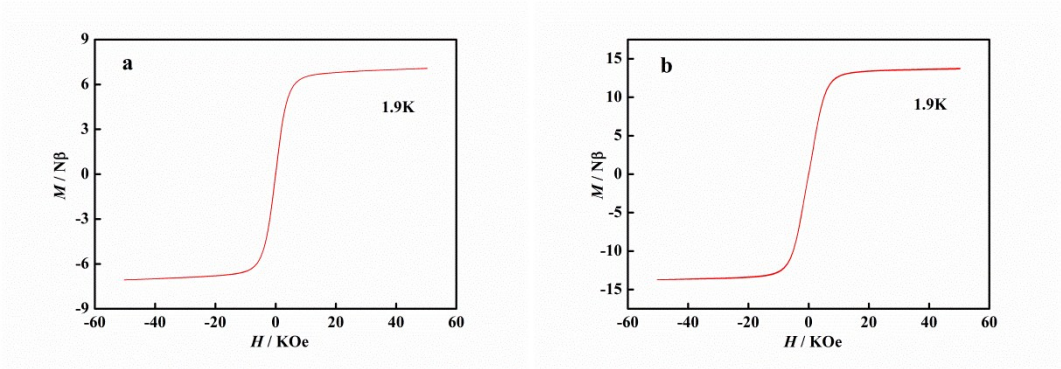

Figure S9. Magnetization curve versus applied field measured at 1.9 K for complex **1** (a) and **4** (b). It did not exhibit a hysteresis effect under our experimental conditions.

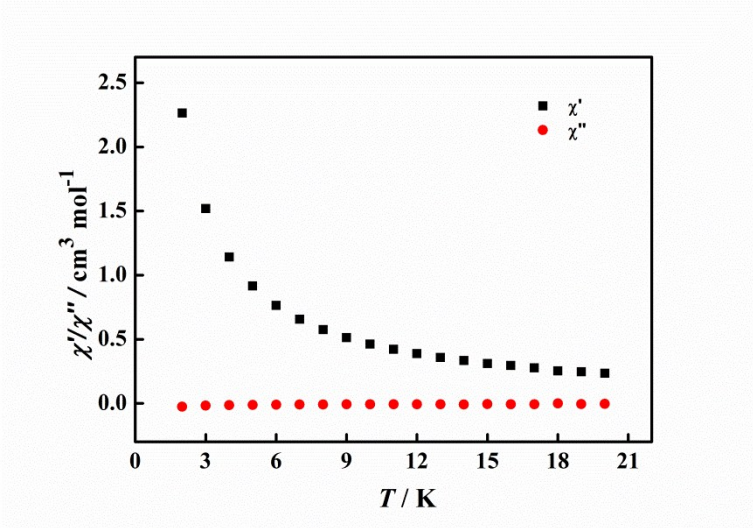

Figure S10. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility for complex **2** in 800 Hz under zero dc field.

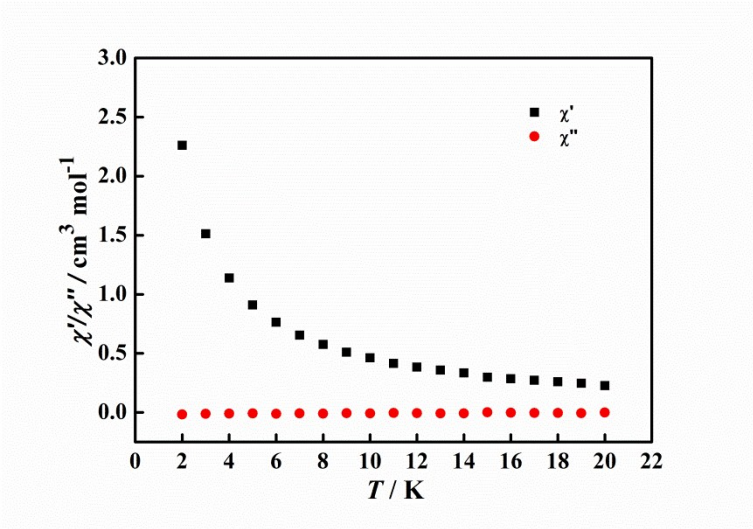

Figure S11. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility for complex **3** in 800 Hz under zero dc field.

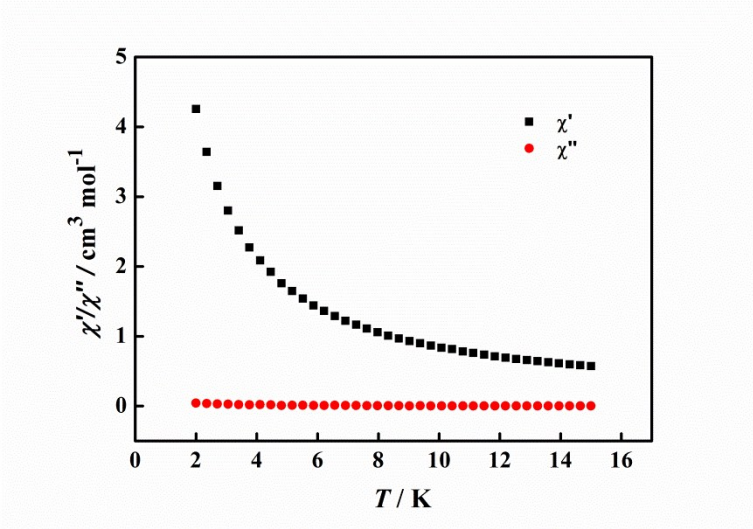

Figure S12. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility for complex **5** in 1000 Hz under zero dc field.

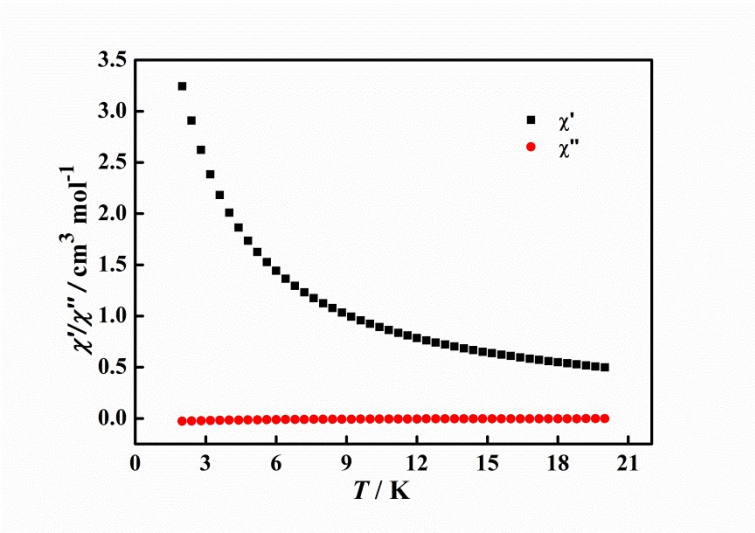

Figure S13. Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility for complex **6** in 800 Hz under zero dc field.

Table S1. Six complexes of Ln^{III} ion geometry analysis by SHAPE software.

Ln^{III} complexes	D_{2d}- TDD	D_{4d} - SAPR	C_{2v} - BTPR
1	1.245	1.972	2.815
2	0.531	1.364	1.821
3	0.480	1.587	1.754
4	0.904	1.014	1.987
5	0.928	1.005	2.074
6	1.158	0.795	2.109

Table S2. Selected bond lengths [Å] and angles [°] for complex **1**

Bond lengths			
Dy(1)-O(4)	2.179(3)	Dy(1)-O(7)	2.250(3)
Dy(1)-O(8)	2.296(3)	Dy(1)-O(2)	2.343(3)
Dy(1)-O(1)	2.410(3)	Dy(1)-O(3)	2.458(3)
Dy(1)-O(6)	2.458(3)	Dy(1)-O(5)	2.544(3)
Bond angles			
O(4)-Dy(1)-O(7)	116.32(13)	O(4)-Dy(1)-O(8)	137.59(11)
O(7)-Dy(1)-O(8)	83.75(11)	O(4)-Dy(1)-O(2)	80.39(12)
O(7)-Dy(1)-O(2)	146.85(11)	O(8)-Dy(1)-O(2)	103.18(11)
O(4)-Dy(1)-O(1)	131.80(9)	O(7)-Dy(1)-O(1)	83.67(11)
O(8)-Dy(1)-O(1)	84.71(9)	O(2)-Dy(1)-O(1)	65.11(11)
O(4)-Dy(1)-O(3)	75.28(12)	O(7)-Dy(1)-O(3)	129.96(10)
O(8)-Dy(1)-O(3)	64.03(11)	O(2)-Dy(1)-O(3)	80.50(10)
O(1)-Dy(1)-O(3)	126.56(11)	O(4)-Dy(1)-O(6)	72.05(13)
O(7)-Dy(1)-O(6)	69.35(11)	O(8)-Dy(1)-O(6)	148.27(12)
O(2)-Dy(1)-O(6)	91.51(10)	O(1)-Dy(1)-O(6)	76.13(12)
O(3)-Dy(1)-O(6)	147.22(12)	O(4)-Dy(1)-O(5)	71.31(10)
O(7)-Dy(1)-O(5)	70.11(12)	O(8)-Dy(1)-O(5)	82.97(10)
O(2)-Dy(1)-O(5)	142.39(11)	O(1)-Dy(1)-O(5)	152.03(10)
O(3)-Dy(1)-O(5)	68.87(11)	O(6)-Dy(1)-O(5)	102.41(11)
N(1)-O(1)-Dy(1)	123.7(2)	C(7)-O(2)-Dy(1)	126.4(3)
C(9)-O(3)-Dy(1)	126.9(3)	C(12)-O(4)-Dy(1)	129.9(3)
C(14)-O(5)-Dy(1)	139.1(3)	C(17)-O(6)-Dy(1)	130.6(3)
C(19)-O(7)-Dy(1)	135.3(3)	N(2)-O(8)-Dy(1)	121.0(3)

Table S3. Selected bond lengths [Å] and angles [°] for complex **2**

Bond lengths			
Tb(1)-O(8)	2.336(8)	Tb(1)-O(3)	2.345(8)
Tb(1)-O(6)	2.362(8)	Tb(1)-O(7)	2.373(8)
Tb(1)-O(2)	2.374(9)	Tb(1)-O(5)	2.374(8)
Tb(1)-O(1)	2.380(8)	Tb(1)-O(4)	2.394(8)
Bond angles			
O(8)-Tb(1)-O(3)	149.5(3)	O(8)-Tb(1)-O(6)	72.1(3)
O(3)-Tb(1)-O(6)	137.6(3)	O(8)-Tb(1)-O(7)	76.1(3)
O(3)-Tb(1)-O(7)	86.6(3)	O(6)-Tb(1)-O(7)	104.8(3)
O(8)-Tb(1)-O(2)	81.9(3)	O(3)-Tb(1)-O(2)	99.9(3)
O(6)-Tb(1)-O(2)	93.2(3)	O(7)-Tb(1)-O(2)	145.3(3)
O(8)-Tb(1)-O(5)	123.0(3)	O(3)-Tb(1)-O(5)	72.6(3)
O(6)-Tb(1)-O(5)	73.0(3)	O(7)-Tb(1)-O(5)	71.2(3)
O(2)-Tb(1)-O(5)	143.3(3)	O(8)-Tb(1)-O(1)	78.6(3)
O(3)-Tb(1)-O(1)	73.2(3)	O(6)-Tb(1)-O(1)	148.8(3)
O(7)-Tb(1)-O(1)	77.6(3)	O(2)-Tb(1)-O(1)	71.9(3)
O(5)-Tb(1)-O(1)	134.4(3)	O(8)-Tb(1)-O(4)	134.9(3)
O(3)-Tb(1)-O(4)	72.5(3)	O(6)-Tb(1)-O(4)	74.2(3)
O(7)-Tb(1)-O(4)	142.2(3)	O(2)-Tb(1)-O(4)	71.0(3)
O(5)-Tb(1)-O(4)	72.6(3)	O(1)-Tb(1)-O(4)	123.0(3)
C(4)-O(2)-Tb(1)	133.4(9)	C(2)-O(1)-Tb(1)	133.4(9)
C(7)-O(3)-Tb(1)	134.4(8)	C(14)-O(6)-Tb(1)	133.2(9)
C(12)-O(5)-Tb(1)	131.8(9)	C(9)-O(4)-Tb(1)	132.3(8)
N(2)-O(8)-Tb(1)	130.8(6)	N(1)-O(7)-Tb(1)	120.4(6)

Table S4. Selected bond lengths [Å] and angles [°] for complex **3**

Bond lengths			
Ho(1)-O(8)	2.319(4)	Ho(1)-O(6)	2.338(4)
Ho(1)-O(3)	2.339(5)	Ho(1)-O(2)	2.341(4)
Ho(1)-O(7)	2.343(4)	Ho(1)-O(5)	2.365(4)
Ho(1)-O(4)	2.380(5)	Ho(1)-O(1)	2.389(4)
Bond angles			
O(8)-Ho(1)-O(6)	73.37(15)	O(8)-Ho(1)-O(3)	147.35(16)
O(6)-Ho(1)-O(3)	138.92(17)	O(8)-Ho(1)-O(2)	83.00(17)
O(6)-Ho(1)-O(2)	94.06(17)	O(3)-Ho(1)-O(2)	96.36(17)
O(8)-Ho(1)-O(7)	75.31(14)	O(6)-Ho(1)-O(7)	104.45(16)
O(3)-Ho(1)-O(7)	88.39(15)	O(2)-Ho(1)-O(7)	145.77(17)
O(8)-Ho(1)-O(5)	124.21(17)	O(6)-Ho(1)-O(5)	73.29(17)
O(3)-Ho(1)-O(5)	74.38(19)	O(2)-Ho(1)-O(5)	142.43(19)
O(7)-Ho(1)-O(5)	71.43(16)	O(8)-Ho(1)-O(4)	135.55(15)
O(6)-Ho(1)-O(4)	74.48(17)	O(3)-Ho(1)-O(4)	72.32(17)
O(2)-Ho(1)-O(4)	69.53(18)	O(7)-Ho(1)-O(4)	142.95(16)
O(5)-Ho(1)-O(4)	72.99(18)	O(8)-Ho(1)-O(1)	78.24(16)
O(6)-Ho(1)-O(1)	149.55(16)	O(3)-Ho(1)-O(1)	70.76(17)
O(2)-Ho(1)-O(1)	71.49(17)	O(7)-Ho(1)-O(1)	78.31(16)
O(5)-Ho(1)-O(1)	133.89(16)	O(4)-Ho(1)-O(1)	121.61(16)
C(4)-O(2)-Ho(1)	131.9(5)	C(2)-O(1)-Ho(1)	131.8(5)
C(7)-O(3)-Ho(1)	134.5(5)	C(14)-O(6)-Ho(1)	132.2(5)
C(12)-O(5)-Ho(1)	131.2(5)	C(9)-O(4)-Ho(1)	133.6(5)
N(2)-O(8)-Ho(1)	126.1(3)	N(1)-O(7)-Ho(1)	122.8(3)

Table S5. Selected bond lengths [Å] and angles [°] for complex **4**

Bond lengths			
Dy(1)-O(1)	2.280(4)	Dy(1)-O(3)	2.307(4)
Dy(1)-O(4)	2.309(4)	Dy(1)-O(6)	2.311(4)
Dy(1)-O(5)	2.318(4)	Dy(1)-O(2)	2.329(3)
Dy(1)-O(7)	2.405(3)	Dy(1)-O(7)A	2.417(3)
Bond angles			
O(1)-Dy(1)-O(3)	87.04(16)	O(1)-Dy(1)-O(4)	77.58(15)
O(3)-Dy(1)-O(4)	71.85(15)	O(1)-Dy(1)-O(6)	105.42(16)
O(3)-Dy(1)-O(6)	139.51(15)	O(4)-Dy(1)-O(6)	147.92(15)
O(1)-Dy(1)-O(5)	74.49(14)	O(3)-Dy(1)-O(5)	147.30(16)
O(4)-Dy(1)-O(5)	77.87(15)	O(6)-Dy(1)-O(5)	72.49(14)
O(1)-Dy(1)-O(2)	73.11(14)	O(3)-Dy(1)-O(2)	73.98(14)
O(4)-Dy(1)-O(2)	135.57(15)	O(6)-Dy(1)-O(2)	73.31(13)
O(5)-Dy(1)-O(2)	123.54(14)	O(1)-Dy(1)-O(7)	146.27(13)
O(3)-Dy(1)-O(7)	105.22(13)	O(4)-Dy(1)-O(7)	76.78(14)
O(6)-Dy(1)-O(7)	85.67(13)	O(5)-Dy(1)-O(7)	79.00(13)
O(2)-Dy(1)-O(7)	140.22(13)	O(1)-Dy(1)-O(7)A	150.11(12)
O(3)-Dy(1)-O(7)A	74.99(15)	O(4)-Dy(1)-O(7)A	117.51(13)
O(6)-Dy(1)-O(7)A	75.92(14)	O(5)-Dy(1)-O(7)A	131.81(14)
O(2)-Dy(1)-O(7)A	78.99(12)	O(7)-Dy(1)-O(7)A	63.07(13)
C(2)-O(1)-Dy(1)	136.1(4)	C(4)-O(2)-Dy(1)	133.6(4)
C(7)-O(3)-Dy(1)	133.5(5)	C(9)-O(4)-Dy(1)	133.1(5)
C(12)-O(5)-Dy(1)	134.4(4)	C(14)-O(6)-Dy(1)	134.8(4)
N(1)-O(7)-Dy(1)	122.5(3)	Dy(1)-O(7)-Dy(1)A	116.93(13)

Table S6. Selected bond lengths [Å] and angles [°] for complex **5**

Bond lengths			
Tb(1)-O(1)	2.301(7)	Tb(1)-O(4)	2.335(6)
Tb(1)-O(3)	2.340(6)	Tb(1)-O(6)	2.355(7)
Tb(1)-O(5)	2.357(6)	Tb(1)-O(2)	2.376(6)
Tb(1)-O(7)	2.439(6)	Tb(1)-O(7)A	2.431(6)
Bond angles			
O(1)-Tb(1)-O(4)	77.8(2)	O(1)-Tb(1)-O(3)	86.5(2)
O(4)-Tb(1)-O(3)	71.5(2)	O(1)-Tb(1)-O(6)	106.0(2)
O(4)-Tb(1)-O(6)	148.2(2)	O(3)-Tb(1)-O(6)	139.4(2)
O(1)-Tb(1)-O(5)	75.6(2)	O(4)-Tb(1)-O(5)	79.1(2)
O(3)-Tb(1)-O(5)	148.3(2)	O(6)-Tb(1)-O(5)	71.7(2)
O(1)-Tb(1)-O(2)	72.5(2)	O(4)-Tb(1)-O(2)	135.1(2)
O(3)-Tb(1)-O(2)	73.8(2)	O(6)-Tb(1)-O(2)	73.7(2)
O(5)-Tb(1)-O(2)	123.2(2)	O(1)-Tb(1)-O(7)A	149.3(2)
O(4)-Tb(1)-O(7)A	117.2(2)	O(3)-Tb(1)-O(7)A	74.7(2)
O(6)-Tb(1)-O(7)A	75.9(2)	O(5)-Tb(1)-O(7)A	131.4(2)
O(2)-Tb(1)-O(7)A	79.0(2)	O(1)-Tb(1)-O(7)	147.0(2)
O(4)-Tb(1)-O(7)	77.0(2)	O(3)-Tb(1)-O(7)	105.1(2)
O(6)-Tb(1)-O(7)	85.3(2)	O(5)-Tb(1)-O(7)	78.9(2)
O(2)-Tb(1)-O(7)	140.2(2)	O(7)A-Tb(1)-O(7)	63.1(2)
C(2)-O(1)-Tb(1)	136.2(7)	C(4)-O(2)-Tb(1)	134.1(6)
C(7)-O(3)-Tb(1)	133.0(8)	C(9)-O(4)-Tb(1)	132.6(8)
C(12)-O(5)-Tb(1)	135.0(7)	C(14)-O(6)-Tb(1)	134.7(7)
N(1)-O(7)-Tb(1)	121.9(5)	Tb(1)A-O(7)-Tb(1)	116.9(2)

Table S7. Selected bond lengths [Å] and angles [°] for complex **6**

Bond lengths			
Ho(1)-O(1)	2.286(2)	Ho(1)-O(4)	2.3090(19)
Ho(1)-O(2)	2.3236(18)	Ho(1)-O(3)	2.3241(18)
Ho(1)-O(5)	2.3260(19)	Ho(1)-O(6)	2.329(2)
Ho(1)-O(7)	2.3939(18)	Ho(1)-O(7)A	2.3921(18)
Bond angles			
O(1)-Ho(1)-O(4)	77.80(7)	O(1)-Ho(1)-O(2)	73.73(7)
O(4)-Ho(1)-O(2)	136.71(7)	O(1)-Ho(1)-O(3)	85.07(7)
O(4)-Ho(1)-O(3)	72.21(7)	O(2)-Ho(1)-O(3)	73.46(7)
O(1)-Ho(1)-O(5)	75.33(7)	O(4)-Ho(1)-O(5)	78.87(7)
O(2)-Ho(1)-O(5)	122.94(7)	O(3)-Ho(1)-O(5)	147.90(7)
O(1)-Ho(1)-O(4)	77.80(7)	O(1)-Ho(1)-O(2)	73.73(7)
O(4)-Ho(1)-O(2)	136.71(7)	O(1)-Ho(1)-O(3)	85.07(7)
O(4)-Ho(1)-O(3)	72.21(7)	O(2)-Ho(1)-O(3)	73.46(7)
O(1)-Ho(1)-O(5)	75.33(7)	O(4)-Ho(1)-O(5)	78.87(7)
O(2)-Ho(1)-O(5)	122.94(7)	O(3)-Ho(1)-O(5)	147.90(7)
O(1)-Ho(1)-O(4)	77.80(7)	O(1)-Ho(1)-O(2)	73.73(7)
O(4)-Ho(1)-O(7)	76.19(6)	O(2)-Ho(1)-O(7)	139.34(6)
O(3)-Ho(1)-O(7)	106.21(7)	O(5)-Ho(1)-O(7)	79.45(6)
O(6)-Ho(1)-O(7)	84.26(7)	O(7)A-Ho(1)-O(7)	62.85(7)
C(2)-O(1)-Ho(1)	134.97(18)	C(4)-O(2)-Ho(1)	133.41(17)
C(7)-O(3)-Ho(1)	133.44(18)	C(9)-O(4)-Ho(1)	133.21(19)
C(12)-O(5)-Ho(1)	134.42(18)	C(14)-O(6)-Ho(1)	134.33(19)
N(1)-O(7)-Ho(1)	121.56(14)	Ho(1)A-O(7)-Ho(1)	117.15(7)

Table S8. The structures and magnetic parameters for selected dinuclear Dy-SMMs with magnetic interactions.

Complex	$J_{Dy\text{-}Dy}$ (cm^{-1})	U_{eff} / K	Ref.
$[Dy(\mu\text{-}OH)(DBP)_2(THF)]_2$	-4.6	721	3c
$[Dy(Cy_2N)_2(\mu\text{-}Cl)(THF)]_2$	-0.83	624	8d
$[Ln(hfac)_3(PzNO)]_2$	-2.36	226.7	This work
$[Dy(hfac)_3(PyNO)]_2$	-2.46	167	17c
$Dy_2(HL_1)_2(NO_3)_2(DMF)_4$	9.69	155	8g
$Dy_2(L_2)_2(NO_3)_2(MeOH)_2$	5.09	90.9	21b
$[Dy_2(opch)_2(\mu\text{-}Cl)Cl(MeOH)_2]$	4.36	89	8d
$[DyL_4ClCH_3OH)]_2$	3.82	88.4	8e
$[\{Dy(tta)_3(L_3)\}_2] \cdot 0.5CH_2Cl_2$	-2.30	87	16a
$[Dy_2(L_5)_2(DBM)_2(DMA)_2] \cdot 2DMA$	-5.78	77	21c

DBP=2,6-di-*tert*-butylphenolate; PzNO=pyrazine-*N*-oxide; PyNO=pyridine-*N*-oxide; HL_1=3-hydroxy-*N'*-(2-hydroxy-3-methoxybenzylidene)picolinohydrazide; L_2=2-(((2-hydroxybenzylidene)amino)methyl)-6-methoxyphenol); opch=(*E*)-*N'*-(2-hydroxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide; tta=2-thenoyltrifluoroacetonate; L_3=tetrathiafulvalene-3-pyridine-*N*-oxide,L_4=*N'*-(2-hydroxybenzylidene)picolinohydrazide;HDBM=dibenzoyl-methane; H_2L_5=2-hydroxy-*N'*-(2-hydroxy-3-methoxybenzyl idene)benzohydrazide;