Supplementary Information

Effect of coordination geometry on the magnetic properties of a series of Ln_2 and Ln_4 clusters

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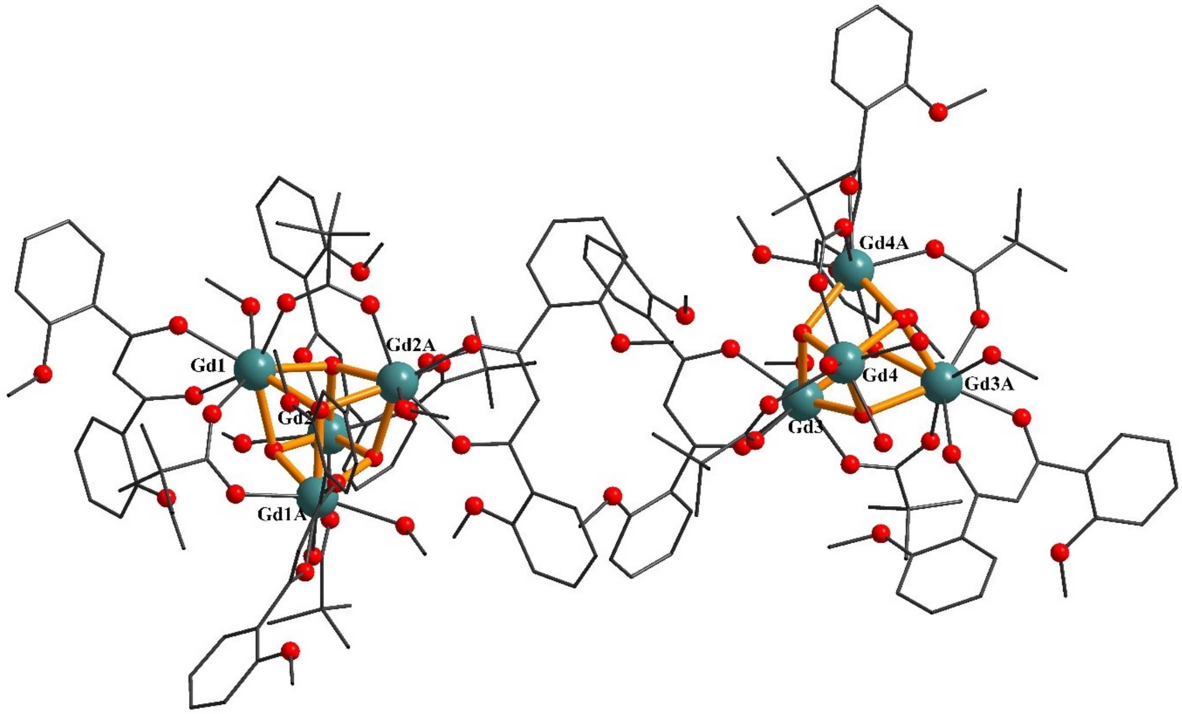

Figure S1. Molecular Structure of **1**, (hydrogen atoms on carbon atom are omitted for clarity).

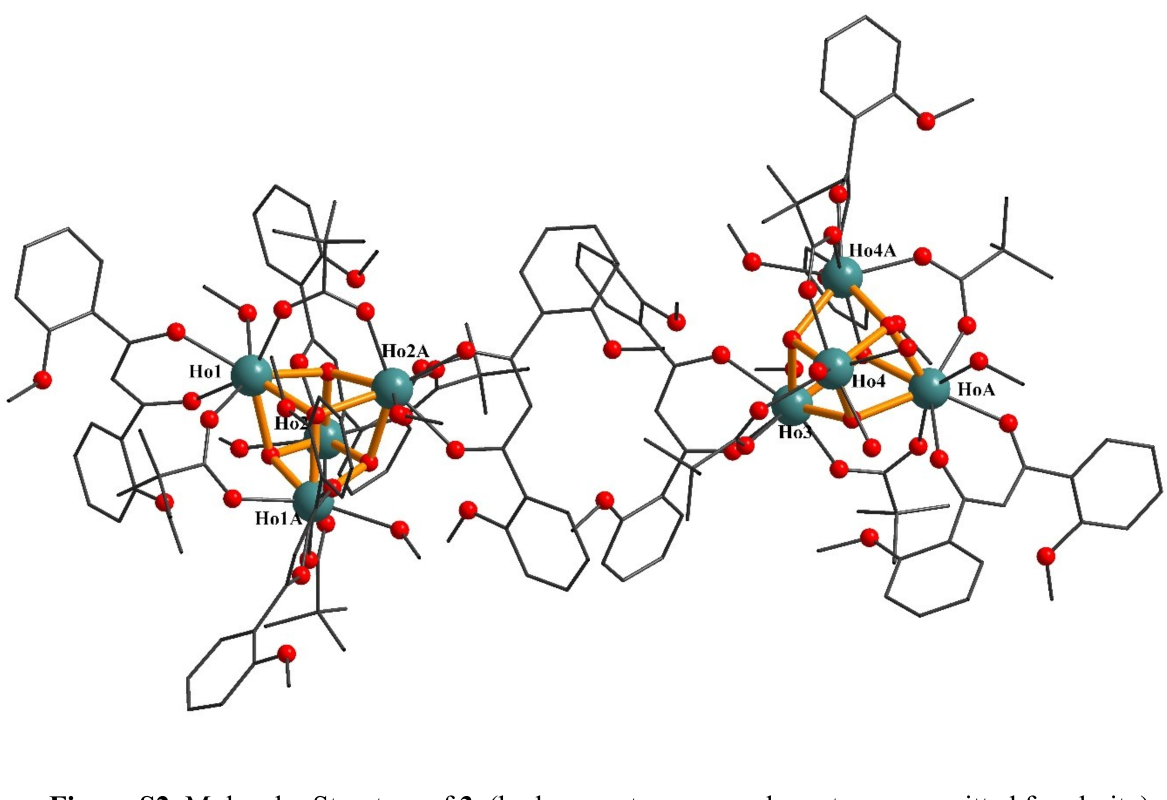

Figure S2. Molecular Structure of **3**, (hydrogen atoms on carbon atom are omitted for clarity).

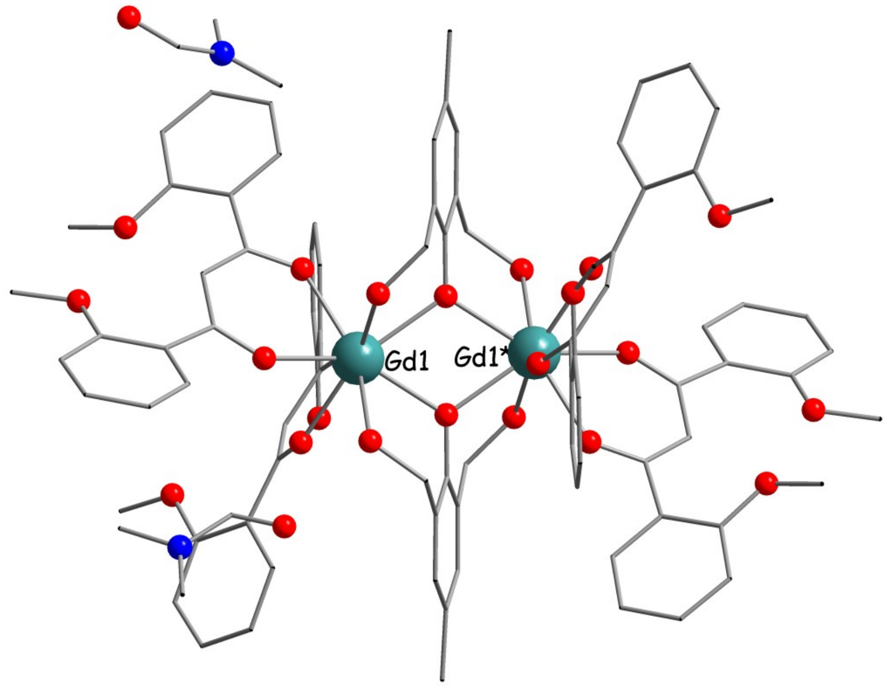

Figure S3. Molecular Structure of 4, (hydrogen atoms on carbon atom are omitted for clarity).

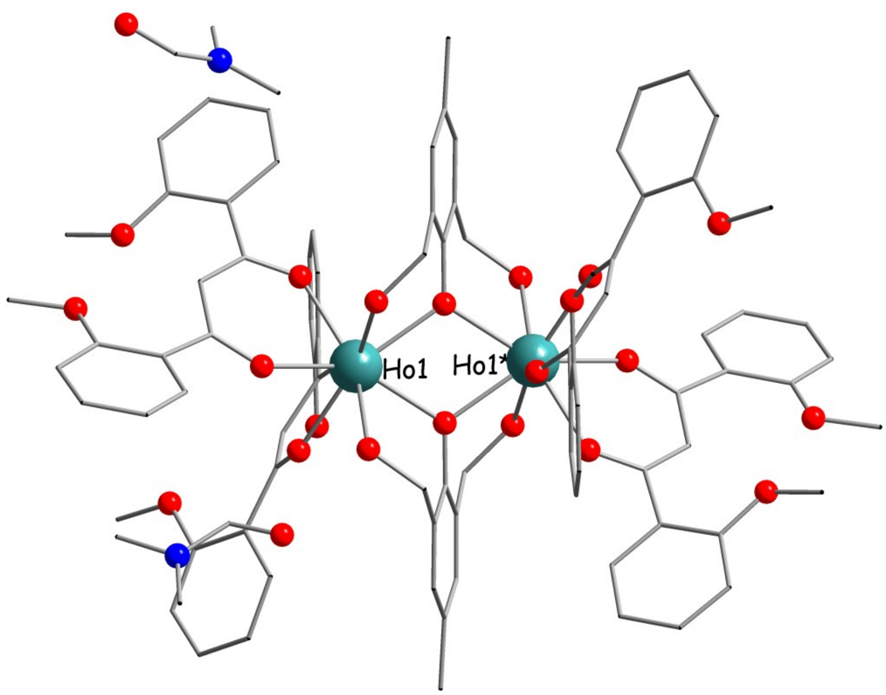

Figure S4. Molecular Structure of 6, (hydrogen atoms on carbon atom are omitted for clarity).

Table S1. Summary of **SHAPE** analysis for complex **2** and **5**.

Shape analysis:

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S H A P E   v2.1        Continuous Shape Measures calculation
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                    Contact:  llunell@ub.edu
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Complex 2

S. No.	Geometry	CShM value for Dy1	CShM value for Dy3
1	Octagon(D8h)	30.499	30.354
2	Heptagonal pyramid(C7v)	23.324	23.230
3	Hexagonal bipyrami(D6h)	16.074	15.755
4	Cube(Oh)	11.044	11.458
5	Square antiprism(D4d)	**1.474**	1.410
6	Triangular dodecahedron(D2d)	1.607	**1.281**
7	Johnson gyrobifastigium J26(D2d)	14.578	13.992
8	Johnson elongated triangular bipyramid J14(D3h)	29.407	29.560
9	Biaugmented trigonal prism J50(C2v)	2.055	2.202
10	Biaugmented trigonal prism(C2v)	1.540	1.670
11	Snub diphenoid J84(D2d)	3.868	3.807
12	Triakis tetrahedron(Td)	11.794	12.090
13	Elongated trigonal bipyramid(D3h)	24.511	24.452

Complex 5

S. No.	Geometry	CShM value for Dy1
1	Octagon(D8h)	30.595
2	Heptagonal pyramid(C7v)	22.709
3	Hexagonal bipyrami(D6h)	15.856
4	Cube(Oh)	10.0183
5	Square antiprism(D4d)	**0.745**
6	Triangular dodecahedron(D2d)	1.889
7	Johnson gyrobifastigium J26(D2d)	14.116
8	Johnson elongated triangular bipyramid J14(D3h)	27.296
9	Biaugmented trigonal prism J50(C2v)	2.507
10	Biaugmented trigonal prism(C2v)	1.828
11	Snub diphenoid J84(D2d)	4.552
12	Triakis tetrahedron(Td)	10.990
13	Elongated trigonal bipyramid(D3h)	22.665

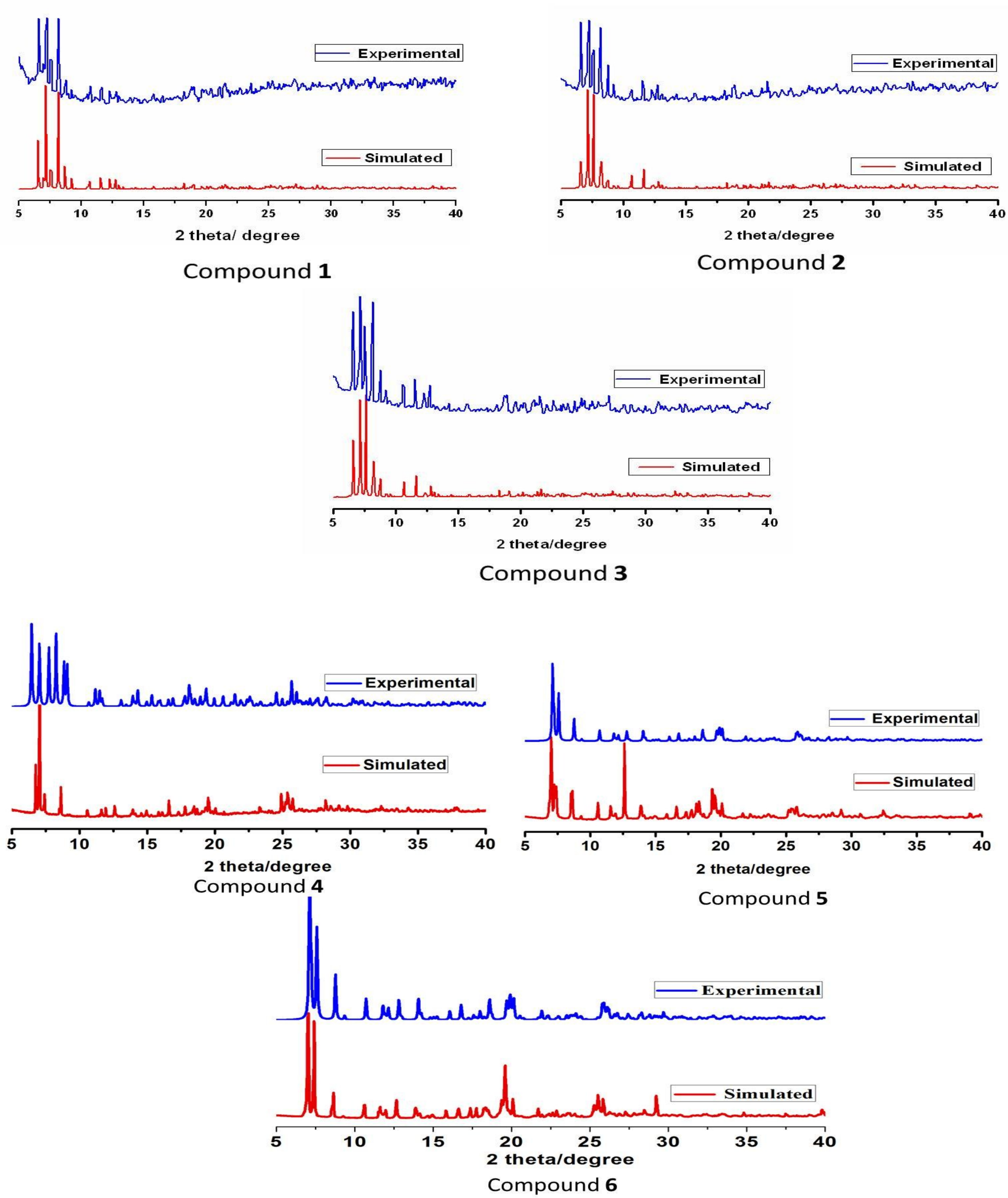

Figure S5. PXRD of compounds **1-6**

Table S2. Bond Distances (Å) and Bond angles (°) comparison table with literature reports

	Dy-$O_{hydroxy}$ Å	Dy-O_{alkoxy} Å	Dy-Dy Å	Dy-O-Dy °	U_{eff}
$[Dy_4(\mu_3\text{-}OH)_4(L)_4(\mu_2\text{-}piv)_4(MeOH)_4]$	2.353-2.382		3.74-3.83	104.54-108.51	SMM (maxima is observed below 2K level)
$[Dy_4(L)_4(\mu_2\text{-}\eta^1\eta^1Piv)_2]\cdot 4H_2O\cdot 6CH_3OH$		2.36-2.49	3.68-4.15	99.20-115.10	73 K[1]
$[Dy_4(\mu_3\text{-}OH)_4(isonicotinate)_6(py)(CH_3OH)_7](ClO_4)_2\cdot py\cdot 4CH_3OH$	2.33-2.40		3.72-3.85	103.63-110.1	40.2 K[2]
$Dy_8(HL)_{10}(C_6H_4NH_2COO)_2(\mu_3\text{-}OH)_8(OH)_2(NO_3)_2(H_2O)_4]$	2.31-2.40		3.67-3.85	102.5-109.50	SMM[3]
$[Dy_4(\mu_3\text{-}OH)_4(na)(pyzc)]n$	2.343-2.362		3.75-3.78	106.15-107.23	39.6 K[4]
$[Dy_4(\mu_3\text{-}OH)_2(\mu_3\text{-}O)_2(cpt)6(MeOH)6(H2O)]$	2.31-2.37		3.74-3.84	103.7-108.9	SMM [5]
$[Dy_4(OH)_4(TBSOC)_2(H_2O)_4(CH_3OH)_4]\cdot 4H_2O$	2.33-2.36		2.57-2.73	105.7-107.9	22.9 K[6]

Table S3. Selected Bond Distances (Å) and Bond angles (°) for **1-6**

	Ln = Gd (1)	**Ln = Dy (2)**	**Ln = Ho (3)**
Ln(1)-O(8)	2.321(3)	2.331(3)	2.278(6)
Ln(1)-O(5)	2.338(3)	2.315(3)	2.295(5)
Ln(1)-O(10)	2.382(.3)	2.371(3)	2.341(5)
Ln(1)-O(3)	2.395(3)	2.364(3)	2.363(6)
Ln(1)-O(2)	2.421(3)	2.351(3)	2.364(6)
Ln(1)-O(10)*	2.400(3)	2.367(3)	2.359(5)
Ln(1)-O(11)	2.416(3)	2.372(3)	2.380(5)
Ln(1)-O(7)	2.504(3)	2.489(3)	2.469(6)
Ln(2)-O(6)*	2.339(3)	2.311(3)	2.299(5)
Ln(2)-O(9)	2.360(3)	2.295(3)	2.323(5)
Ln(2)-O(14)	2.379(3)	2.367(3)	2.347(5)
Ln(2)-O(11)	2.391(3)	2.353(3)	2.361(5)
Ln(2)-O(15)	2.397(3)	2.379(3)	2.343(6)
Ln(2)-O(10)	2.411(3)	2.382(3)	2.371(5)
Ln(2)-O(11)*	2.397(3)	2.382(3)	2.355(5)
Ln(2)-O(12)	2.516(3)	2.479(3)	2.477(6)
O(8)-Ln(1)-O(5)	101.58(12)	102.17(12)	100.4(2)
O(8)-Ln(1)-O(10)	85.68(11)	83.33(11)	86.34(19)
O(5)-Ln(1)-O(10)	142.85(11)	144.11(12)	143.42(19)
O(8)-Ln(1)-O(3)	79.90(12)	84.37(12)	84.84(19)
O(8)-Ln(1)-O(10)*	144.28(11)	144.29(11)	144.59(19)
O(5)-Ln(1)-O(10)*	83.56(11)	86.15(11)	84.21(18)
O(10)-Ln(1)-O(10)*	70.87(12)	70.97(13)	70.92(2)
O(3)-Ln(1)-O(10)*	134.55(11)	107.92(11)	108.77(18)
O(8)-Ln(1)-O(11)	77.30(12)	78.36(11)	77.38(19)
O(5)-Ln(1)-O(11)	76.73(11)	77.14(11)	76.76(18)
O(10)-Ln(1)-O(11)	69.37(11)	69.22(11)	69.70(17)
O(6)*1-Ln(2)-O(10)	77.07(11)	77.00(11)	77.34(18)

O(9)-Ln(2)-O(10)	78.05(11)	77.50(12)	78.52(19)
O(14)-Ln(2)-O(10)	138.30(11)	137.73(11)	136.49(17)
O(11)-Ln(2)-O(10)	69.32(11)	69.38(11)	69.52(17)
O(15)-Ln(2)-O(10)	136.27(11)	134.85(11)	137.48(18)
O(11)*-Ln(2)-O(10)	69.60(11)	69.27(11)	69.72(17)
O(14)-Ln(2)-O(12)	76.37(11)	76.70(11)	72.57(19)
O(11)-Ln(2)-O(12)	107.97(11)	68.10(11)	109.01(18)
O(15)-Ln(2)-O(12)	71.77(11)	73.22(12)	75.95(19)
O(11)*-Ln(2)-O(12)	67.34(11)	108.41(11)	67.29(17)
O(10)-Ln(2)-O(12)	134.73(11)	135.29(11)	134.52(18)
Ln(1)-O(10)-Ln(2)	108.18(12)	107.58(12)	108.20(2)
Ln(1)-O(11)-Ln(2)	107.74(12)	108.51(12)	107.27(19)
Ln(1)*-O(10)-Ln(2)	107.71(12)	107.89(12)	107.90(2)
Ln(1)-O(10)-Ln(1)*	104.85(12)	104.82(12)	104.71(19)
Ln(1)-O(11)-Ln(2)*	107.64(12)	107.72(12)	107.68(19)
Ln(2)-O(11)-Ln(2)*	105.02(12)	104.54(12)	104.45(19)

	Ln = Gd (4)	**Ln = Dy (5)**	**Ln = Ho (6)**
Ln(1)-O(3)	2.375(11)	2.301(2)	2.294(2)
Ln(1)-O(6)	2.335(10)	2.321(2)	2.3128(18)
Ln(1)-O(6)*	2.356(10)	2.313(2)	2.3029(18)
Ln(1)-O(2)	2.332(11)	2.343(2)	2.3372(19)
Ln(1)-O(10)	2.357(11)	2.336(2)	2.3134(19)
Ln(1)-O(9)	2.350(11)	2.324(2)	2.323(2)
Ln(1)-O(5)	2.455(11)	2.438(2)	2.4216(19)
Ln(1)-O(7)	2.463(11)	2.436(2)	2.294(2)
O(3)-Ln(1)-O(6)*	146.94(4)	141.19(8)	141.15(7)
O(3)-Ln(1)-O(6)	140.19(4)	84.45(7)	84.24(7)
O(3)-Ln(1)-O(2)	71.78(4)	72.34(8)	72.69(7)
O(6)-Ln(1)-O(2)	84.50(4)	140.57(7)	145.69(7)
O(6)*-Ln(1)-O(2)	140.60(4)	145.94(7)	140.59(7)

O(3)-Ln(1)-O(10)	119.26(4)	69.74(8)	106.41(7)
O(6)-Ln(1)-O(10)	78.95(4)	78.80(7)	85.83(7)
O(6)*-Ln(1)-O(10)	79.05(4)	79.70(8)	142.88(7)
O(2)-Ln(1)-O(10)	69.58(4)	119.70(8)	75.58(7)
O(3)-Ln(1)-O(9)	75.80(4)	105.98(8)	69.85(8)
O(6)-Ln(1)-O(9)	142.720(4)	142.72(7)	79.66(7)
O(6)*-Ln(1)-O(9)	86.00(4)	85.86(7)	78.66(7)
O(2)-Ln(1)-O(9)	105.20(4)	75.65(8)	120.08(7)
O(10)-Ln(1)-O(9)	71.48(4)	72.03(8)	72.42(7)
O(3)-Ln(1)-O(5)*	75.87(4)	144.98(8)	144.75(7)
O(6)-Ln(1)-O(5)*	115.65(4)	115.84(7)	115.96(7)
O(6)*-Ln(1)-O(5)*	73.00(4)	73.40(7)	73.61(6)
O(2)-Ln(1)-O(5)*	146.10(4)	74.43(7)	73.93(7)
O(10)-Ln(1)-O(5)*	138.02(4)	139.08(8)	75.53(7)
O(9)-Ln(1)-O(5)*	75.85(4)	75.76(8)	139.32(7)
O(3)-Ln(1)-O(7)	74.14 (4)	80.18(8)	80.11(8)
O(6)-Ln(1)-O(7)	70.56(4)	70.86(7)	70.98(6)
O(6)*-Ln(1)-O(7)	111.45(4)	110.94(7)	110.90(7)
O(2)-Ln(1)-O(7)	80.20(5)	74.02(7)	73.82(7)
O(10)-Ln(1)-O(7)	138.71(4)	138.94(8)	145.04(7)
O(9)-Ln(1)-O(7)	145.92(4	145.39(7)	139.00(7)

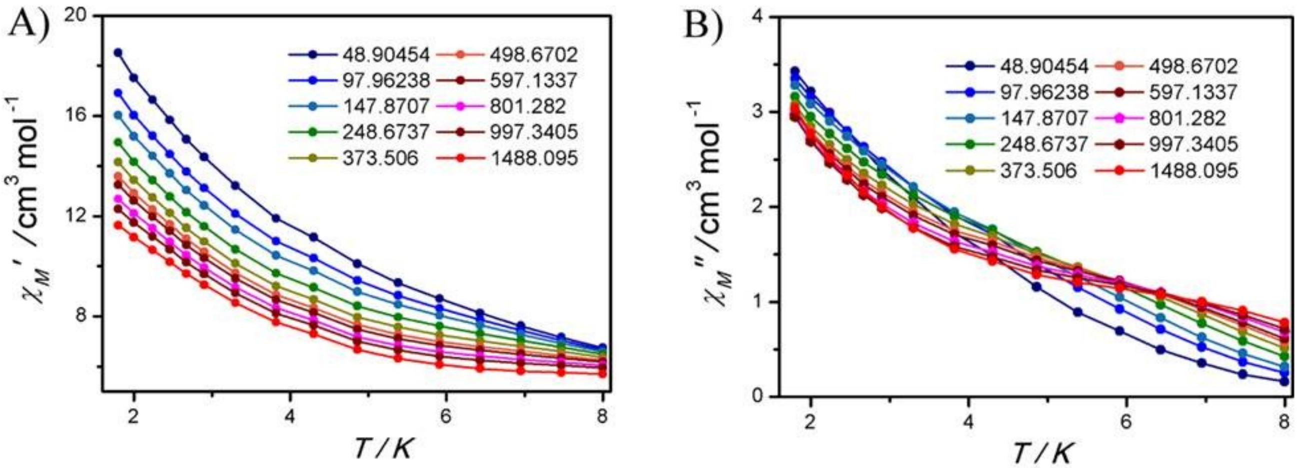

Figure S6. Alternating current magnetic susceptibility measurement performed on polycrystalline samples of **2** showing the temperature dependent in-phase (($\chi_M{'}$) (panel A) and out-of-phase susceptibility signals ($\chi_M{''}$) (panel B) in the absence of external magnetic field.

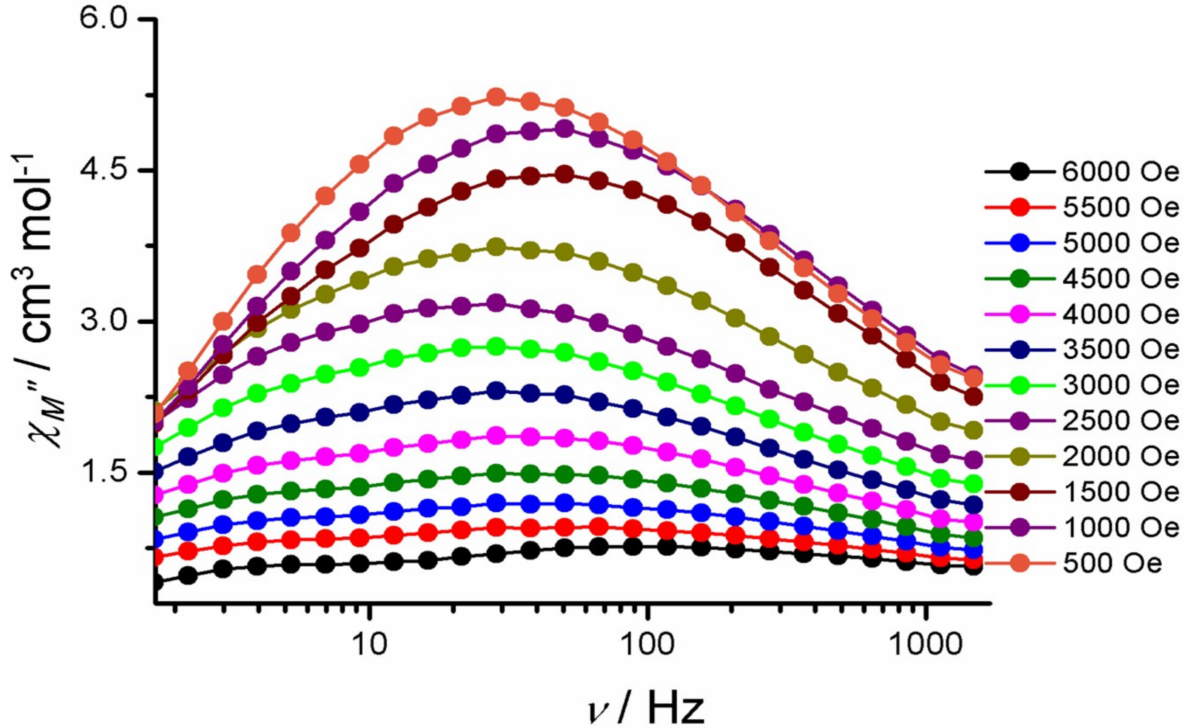

Figure S7. Isothermal field sweep measurement performed on polycrystalline sample of complex **2**.

Table S4. Fitting parameters for Cole-Cole plot for complex **2** (Optimum field of 500 Oe)

S. No.	Temperature (K)	χ_S	χ_T	τ	α	residual
1	2.0	0.485583E+01	0.213361E+02	0.102857E-02	0.371419E+00	0.734713E+01
2	2.2	0.489822E+01	0.199923E+02	0.908660E-03	0.352661E+00	0.677026E+01
3	2.4	0.483345E+01	0.185235E+02	0.791095E-03	0.337465E+00	0.545196E+01
4	2.6	0.475222E+01	0.173092E+02	0.706296E-03	0.325677E+00	0.444805E+01
5	2.8	0.467057E+01	0.162357E+02	0.638803E-03	0.314907E+00	0.375707E+01
6	3.0	0.458311E+01	0.152866E+02	0.582108E-03	0.305846E+00	0.311194E+01
7	3.2	0.450158E+01	0.144405E+02	0.533096E-03	0.297002E+00	0.263548E+01
8	3.4	0.442209E+01	0.136805E+02	0.489626E-03	0.289195E+00	0.221655E+01
9	3.6	0.434306E+01	0.129886E+02	0.448673E-03	0.281722E+00	0.185598E+01
10	4.0	0.421539E+01	0.117968E+02	0.376768E-03	0.266478E+00	0.127939E+01
11	5.0	0.396428E+01	0.956903E+01	0.222501E-03	0.229217E+00	0.403521E+00
12	6.0	0.376298E+01	0.804631E+01	0.110622E-03	0.200699E+00	0.700955E-01
13	7.0	0.344384E+01	0.694132E+01	0.452781E-04	0.203925E+00	0.816926E-02
14	8.0	0.409642E+01	0.610494E+01	0.340558E-04	0.182404E+00	0.692859E-02

Table S5. Fitting parameters for Cole-Cole plot for complex **5** (absence of bias field)

S. No.	Temperature (K)	χ_S	χ_T	τ	α	residual
1	2.0	0.614221E+00	0.183188E+02	0.710361E-02	0.208097E+00	0.824204E+00
2	2.2	0.581461E+00	0.164895E+02	0.649717E-02	0.209542E+00	0.612107E+00
3	2.4	0.560337E+00	0.146505E+02	0.586349E-02	0.210852E+00	0.114670E+01
4	2.6	0.446823E+00	0.132122E+02	0.518833E-02	0.210901E+00	0.491779E+00
5	2.8	0.485631E+00	0.120152E+02	0.474652E-02	0.207704E+00	0.381005E+00
6	3.0	0.458659E+00	0.110055E+02	0.425951E-02	0.204777E+00	0.329082E+00
7	3.2	0.441390E+00	0.101555E+02	0.379568E-02	0.203325E+00	0.169764E+00
8	3.4	0.424599E+00	0.941623E+01	0.339249E-02	0.200194E+00	0.129646E+00
9	3.6	0.406443E+00	0.877422E+01	0.301435E-02	0.196792E+00	0.944658E-01
10	4.0	0.372370E+00	0.771428E+01	0.235163E-02	0.188963E+00	0.446970E-01
11	5.0	0.290246E+00	0.590085E+01	0.118066E-02	0.172061E+00	0.565398E-02
12	6.0	0.224505E+00	0.478510E+01	0.575295E-03	0.163180E+00	0.572334E-03
13	7.0	0.178637E+00	0.401860E+01	0.280481E-03	0.167784E+00	0.830973E-03
14	8.0	0.188554E+00	0.346312E+01	0.134422E-03	0.183680E+00	0.103577E-02

References:

1) S. Das, A. Dey, S. Biswas, E. Colacio and V. Chandrasekhar, *Inorg. Chem.,* 2014, **53***,* 3417-3426.

2) Y. J. Gao, G. F. Xu, L. Zhao, J. Tang and Z. L. Liu, *Inorg. Chem.* 2009, **48**, 11495−11497.

3) H. S. Ke, P. Gamez, L. Zhao, G. F. Xu, S. F. Xue and J. Tang, *Inorg. Chem.* 2010, **49**, 7549−7557.

4) Y. Li, J.-W. Yu, Z.-Y. Liu, E.-C. Yang and X.-J. Zhao, *Inorg. Chem.* 2015, **54**, 153-160.

5) D. Savard, P.-H. Lin, T. J. Burchell, I. Korobkov, W. Wernsdorfer, R. Clérac and M. Murugesu, *Inorg. Chem.,* 2009, **48**, 11748−11754.

6) C.-M. Liu, D.-Q. Zhang, X. Hao and D.-B. Zhu, *Cryst. Growth Des.,* 2012, **12**, 2948−2954.