Supporting Information (SI)

Substituents effect on Synthesis and Magnetic Properties of Carboxylic Acid Ligands Coordinated Dysprosium Complexes

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Experimental

Methods. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex 600 instrument. Elemental analyses (C, H, and N) were performed using an Elemental Vario EL analyzer. Variable-temperature dc magnetic susceptibility measurements and ac magnetic susceptibility measurements were conducted on microcrystalline samples, suspended in eicosane to prevent torquing, using a SQUID-based sample magnetometer, Quantum Design model MPMS-XL instrument. Magnetic susceptibility data (2-300 K) were collected on powdered samples using a SQUID-based sample magnetometer, Quantum Design model MPMS-3 instrument under a 0.1 T applied magnetic field. Data were corrected for diamagnetism using Pascal constants and a sample holder correction.

Crystallographic data and structure refinements. The single crystal-data of all compounds was obtained on a Bruker D8 QUEST diffractometer with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The SAINT program was used for integration of the diffraction profiles.[1] The structures were solved in Olex2 with SHELXT using intrinsic phasing ang refined with SHELXL using least squares minimization.[2-4] All atoms were assigned anistropic thermal parameters. Part of the solvent is disordered, which is removed by the mask program in Olex2, and the type and content of the solvent are determined by elemental analysis; the H-atoms of some of these waters could not be successfully refined. The selected bond lengths and angles are given in Table S1 and S2.

Table S1. Selected bond distances (Å) for compounds **1–3.**

1	**2**	**3**

Dy1–O6$^{\#1}$	2.353(5)	Dy1–O3	2.307(4)	Dy1–O1$^{\#1}$	2.298(5)
Dy1–O3	2.286(4)	Dy1–O4	2.418(4)	Dy1–O3	2.301(4)
Dy1–O4$^{\#1}$	2.338(4)	Dy1–O2	2.358(4)	Dy1–O3$^{\#1}$	2.856(5)
Dy1–N2	2.608(5)	Dy1–O6	2.324(4)	Dy1–O2	2.345(5)
Dy1–O2	2.399(5)	Dy1–N1	2.547(4)	Dy1–O5	2.420(5)
Dy1–O1	2.457(5)	Dy1–O1	2.371(4)	Dy1–O4$^{\#1}$	2.375(5)
Dy1–N1	2.538(5)	Dy1–N2	2.564(4)	Dy1–N2	2.596(6)
Dy1–O5	2.291(5)	Dy1–O5	2.284(4)	Dy1–O6	2.423(6)
Dy2–N6	2.615(5)			Dy1–N1	2.648(5)
Dy2–O9	2.303(5)				
Dy2–O10$^{\#2}$	2.335(4)				
Dy2–O7	2.435(5)				
Dy2–O12$^{\#2}$	2.380(5)				
Dy2–O8	2.421(5)				
Dy2–N5	2.546(5)				
Dy2–O11	2.313(5)				

Symmetry code: compound **1**: 3/2-x, 1/2-y, 3/2-z; compound **2**: 1-x, -y, 1-z; compound **3**: 1-x, 1-y, 1-z.

Table S2. Selected bond angles (°) for compounds **1**–**3**.

1				**2**		**3**	
O2–Dy1–N2	75.31(17)	O6$^{\#1}$–Dy1–N2	68.94(17)	O6–Dy1–O4	128.30(16)	O2–Dy1–O3$^{\#1}$	67.54(16)
O2–Dy1–O1	53.91(18)	O6$^{\#1}$–Dy1–O2	143.36(17)	O6–Dy1–O2	78.23(16)	O2–Dy1–O6	77.64(19)
O2–Dy1–N1	89.69(17)	O6$^{\#1}$–Dy1–O1	146.72(17)	O6–Dy1–N1	74.03(15)	O2–Dy1–O4$^{\#1}$	81.21(18)
O1–Dy1–N2	108.10(17)	O6$^{\#1}$–Dy1–N1	81.47(17)	O6–Dy1–O1	75.68(18)	O2–Dy1–N1	138.26(16)
O1–Dy1–N1	68.84(17)	O3–Dy1–O6$^{\#1}$	81.27(17)	O3–Dy1–O4	73.52(15)	O2–Dy1–O5	130.02(18)
N1–Dy1–N2	63.23(16)	O3–Dy1–O4$^{\#1}$	127.08(16)	O3–Dy1–O2	70.82(15)	O2–Dy1–N2	78.95(17)
O5–Dy1–O6$^{\#1}$	126.11(18)	O3–Dy1–N2	79.24(16)	O3–Dy1–O6	148.55(16)	O3–Dy1–O2	75.27(16)
O5–Dy1–O4$^{\#1}$	78.83(18)	O3–Dy1–O2	84.56(18)	O3–Dy1–N1	137.40(14)	O3–Dy1–O3$^{\#1}$	77.66(17)
O5–Dy1–N2	147.43(18)	O3–Dy1–O1	131.70(17)	O3–Dy1–O1	99.89(17)	O3–Dy1–O6	82.22(19)
O5–Dy1–O2	81.90(18)	O3–Dy1–N1	142.23(17)	O3–Dy1–N2	79.08(14)	O3–Dy1–O4$^{\#1}$	126.08(17)
O5–Dy1–O1	75.08(18)	O3–Dy1–O5	75.68(19)	O4–Dy1–N1	74.83(15)	O3–Dy1–N1	146.42(18)
O5–Dy1–N1	140.35(19)	O4$^{\#1}$–Dy1–O6$^{\#1}$	77.65(17)	O4–Dy1–N2	72.09(14)	O3–Dy1–O5	88.39(18)
O9–Dy2–N6	75.19(16)	O4$^{\#1}$–Dy1–N2	133.51(16)	O2–Dy1–O4	133.59(15)	O3–Dy1–N2	145.32(18)
O9–Dy2–O10$^{\#2}$	132.12(17)	O4$^{\#1}$–Dy1–O2	136.11(18)	O2–Dy1–N1	149.76(15)	O1$^{\#1}$–Dy1–O2	132.97(17)
O9–Dy2–O7	130.87(18)	O4$^{\#1}$–Dy1–O1	83.02(18)	O2–Dy1–O1	72.96(16)	O1$^{\#1}$–Dy1–O3$^{\#1}$	69.65(16)
O9–Dy2–O12$^{\#2}$	88.39(19)	O4$^{\#1}$–Dy1–N1	80.98(15)	O2–Dy1–N2	127.10(16)	O1$^{\#1}$–Dy1–O3	77.49(17)
O9–Dy2–O8	88.33(18)	O7–Dy2–N6	114.59(16)	O6–Dy1–N2	126.11(15)	O1$^{\#1}$–Dy1–O6	134.95(19)
O9–Dy2–N5	138.34(16)	O7–Dy2–N5	70.52(17)	N1–Dy1–N2	64.45(13)	O1$^{\#1}$–Dy1–O4$^{\#1}$	84.88(18)
O9–Dy2–O11	72.07(17)	O12$^{\#2}$–Dy2–N6	66.54(16)	O1–Dy1–O4	142.75(15)	O1$^{\#1}$–Dy1–N1	77.09(17)

O10$^{\#2}$–Dy2–N6	134.17(16)	O12$^{\#2}$–Dy2–O7	140.57(17)	O1–Dy1–N1	88.56(15)	O1$^{\#1}$–Dy1–O5	86.19(18)
O10$^{\#2}$–Dy2–O7	77.30(17)	O12$^{\#2}$–Dy2–O8	140.05(16)	O1–Dy1–N2	70.66(15)	O1$^{\#1}$–Dy1–N2	137.04(17)
O10$^{\#2}$–Dy2–O12$^{\#2}$	77.12(18)	O12$^{\#2}$–Dy2–N5	76.85(18)	O5–Dy1–O3	97.23(18)	O6–Dy1–O3$^{\#1}$	143.11(17)
O10$^{\#2}$–Dy2–O8	130.85(16)	O8–Dy2–N6	74.14(15)	O5–Dy1–O4	68.86(16)	O6–Dy1–N1	100.85(19)
O10$^{\#2}$–Dy2–N5	82.59(16)	O8–Dy2–O7	53.60(16)	O5–Dy1–O2	87.13(18)	O6–Dy1–N2	69.80(19)
N5–Dy2–N6	63.17(15)	O11–Dy2–O12$^{\#2}$	126.8(2)	O5–Dy1–O6	75.35(18)	O4$^{\#1}$–Dy1–O3$^{\#1}$	48.48(14)
O11–Dy2–N6	143.74(17)	O11–Dy2–O8	89.64(19)	O5–Dy1–N1	97.19(17)	O4$^{\#1}$–Dy1–O6	138.32(18)
O11–Dy2–O10$^{\#2}$	80.78(18)	O11–Dy2–N5	146.35(18)	O5–Dy1–O1	147.57(18)	O4$^{\#1}$–Dy1–N1	72.72(18)
O11–Dy2–O7	77.38(18)			O5–Dy1–N2	140.10(16)	O4$^{\#1}$–Dy1–O5	141.09(17)
				O6–Dy1–N2	126.11(15)	O4$^{\#1}$–Dy1–N2	71.15(19)
						N1–Dy1–O3$^{\#1}$	113.01(16)
						O5–Dy1–O3$^{\#1}$	154.10(16)
						O5–Dy1–O6	53.21(18)
						O5–Dy1–N1	68.37(18)
						O5–Dy1–N2	90.75(19)
						N2–Dy1–O3$^{\#1}$	113.13(18)
						N2–Dy1–N1	62.16(18)
						Dy1–O3–Dy1$^{\#1}$	102.34(17)

Symmetry code: compound **1**: 3/2-x, 1/2-y, 3/2-z; compound **2**: 1-x, -y, 1-z; compound **3**: 1-x, 1-y, 1-z.

Table S3. The CShM values calculated by SHAPE 2.1 for **1** and **2**.

Configuration	1	2
Octagon (D_{8h})	31.89039	31.57856
Heptagonal pyramid (C_{7v})	20.89381	23.40498
Hexagonal bipyramid (D_{6h})	15.09888	16.15843
Cube (O_h)	9.44792	8.86781
Square antiprism (D_{4h})	1.49748	2.49296
Triangular dodecahedron (D_{2d})	2.13002	**0.49752**
Johnson gyrobifastigium J26 (D_{2d})	15.30449	13.08964
Johnson elongated triangular bipyramid J14 (D_{3h})	28.40257	28.76164
Biaugmented trigonal prism J50 (C_{2v})	2.16034	3.11554
Biaugmented trigonal prism (C_{2v})	**1.41008**	2.47212

Snub diphenoid J84 (D_{2d})	4.87859	3.03991
Triakis tetrahedron (T_d)	9.92971	9.62351
Elongated trigonal bipyramid (D_{3h})	22.72250	23.54764

Table S4. The CShM values calculated by SHAPE 2.1 for **3**.

Configuration	**3**
Enneagon(D_{9h})	33.60716
Octagonal pyramid(C_{8v})	21.80493
Heptagonal bipyramid(D_{7h})	16.92366
Johnson triangular cupola J3(C_{3v})	15.80398
Capped cube J8(C_{4v})	9.95250
Spherical-relaxed capped cube(C_{4v})	10.08543
Capped square antiprism J10(C_{4v})	2.40558
Spherical capped square antiprism(C_{4v})	2.42875
Tricapped trigonal prism J51(D_{3h})	3.37991
Spherical tricapped trigonal prism(D_{3h})	3.47303
Tridiminished icosahedron J63(C_{3v})	13.49781
Hula-hoop(C_{2v})	9.51351
Muffin(C_s)	**1.60517**

Table S5. Relaxation fitting parameters for **3** under 1.5 kOe dc field obtained from CCFIT2.

T / K	χ_s / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	τ / s	α	Residual
2.0	0.47763	4.5548	0.03283	0.39951	0.02351
2.4	0.44653	4.1518	0.02218	0.35204	0.02439
2.8	0.43466	3.3553	0.01144	0.27198	0.01481
3.2	0.41915	3.0623	0.00718	0.22327	0.01310
3.4	0.39699	2.8783	0.00518	0.19951	0.01881
3.6	0.39903	2.7761	0.00392	0.17106	0.01375
3.8	0.40558	2.6487	0.00280	0.13035	0.02779
4.0	0.36276	2.5193	0.00197	0.13870	0.01605
4.2	0.37305	2.4074	0.00136	0.10496	0.01313
4.4	0.33943	2.3361	0.00094	0.11333	0.01644
4.6	0.34819	2.2358	0.00062	0.08897	0.01153
4.8	0.35779	2.1597	0.00042	0.07437	0.02103
5.0	0.32990	2.0949	0.00027	0.08373	0.02358
5.2	0.37067	2.0008	0.00018	0.05377	0.02664

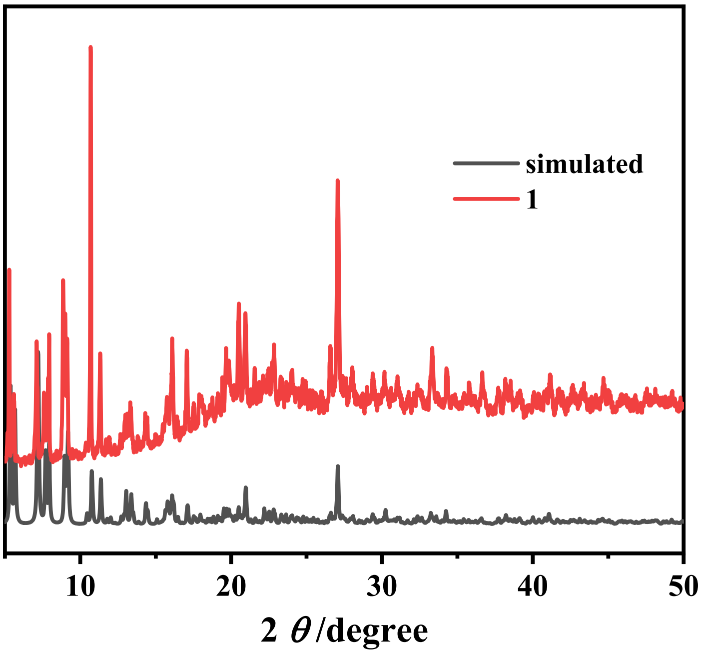

Fig. S1 Experimental and simulated XRD patterns for compound **1**.

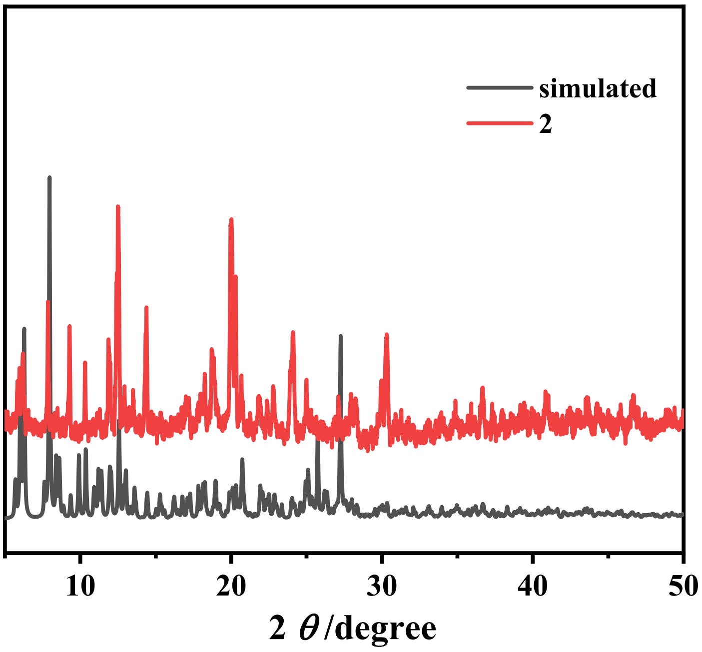

Fig. S2 Experimental and simulated XRD patterns for compound **2**.

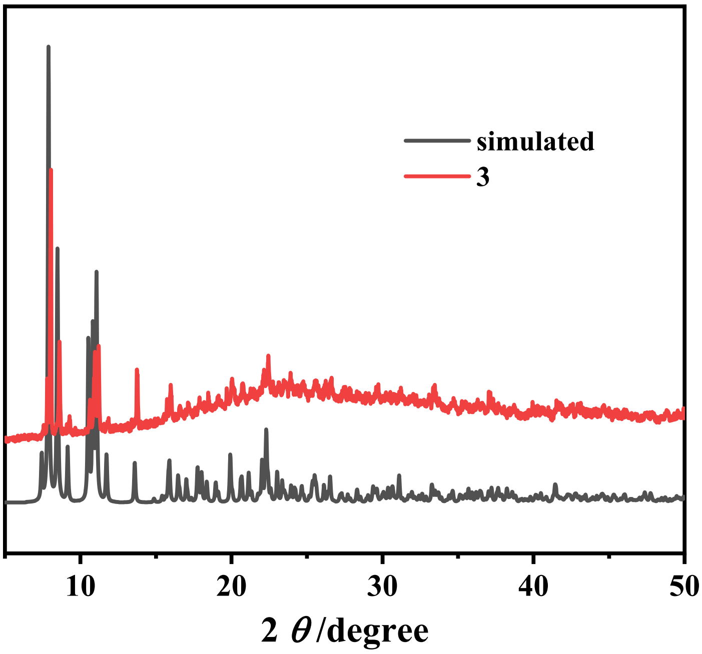

Fig. S3 Experimental and simulated XRD patterns for compound **3**.

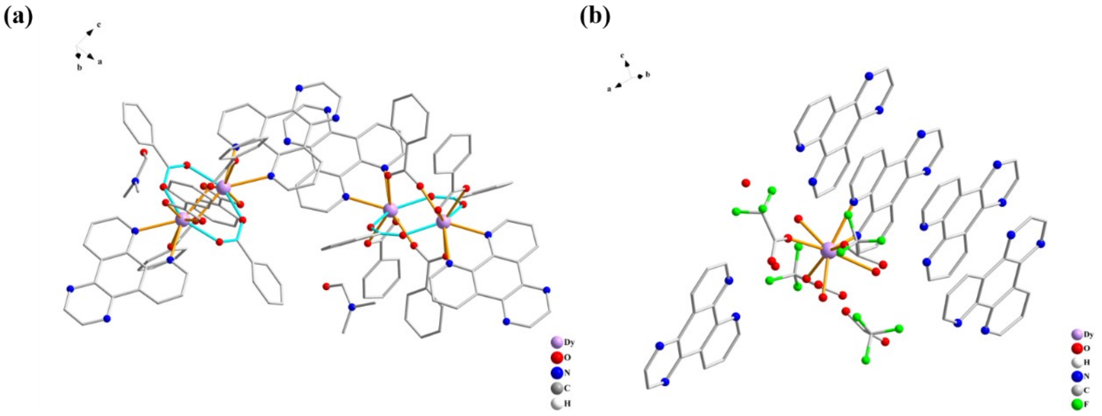

Fig. S4 Molecular structures of **1** (a) and **2** (b). Hydrogen atoms and disorder components are omitted for clarity

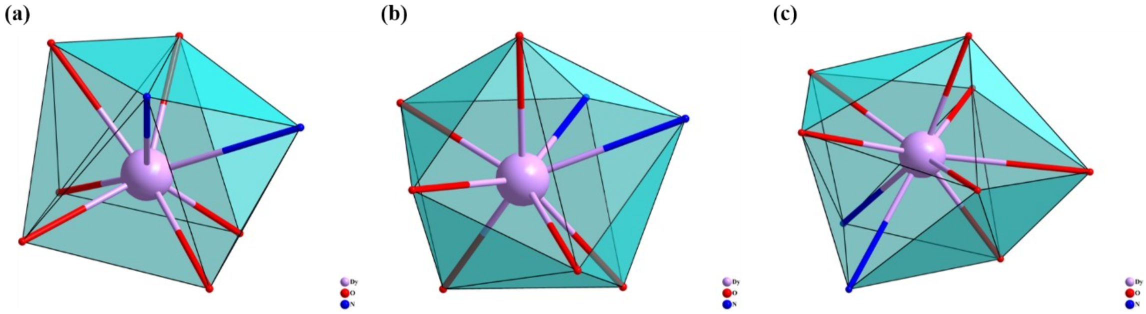

Fig. S5 Coordination geometries of Dy^{III} in compounds **1** (a), **2** (c), **3** (d).

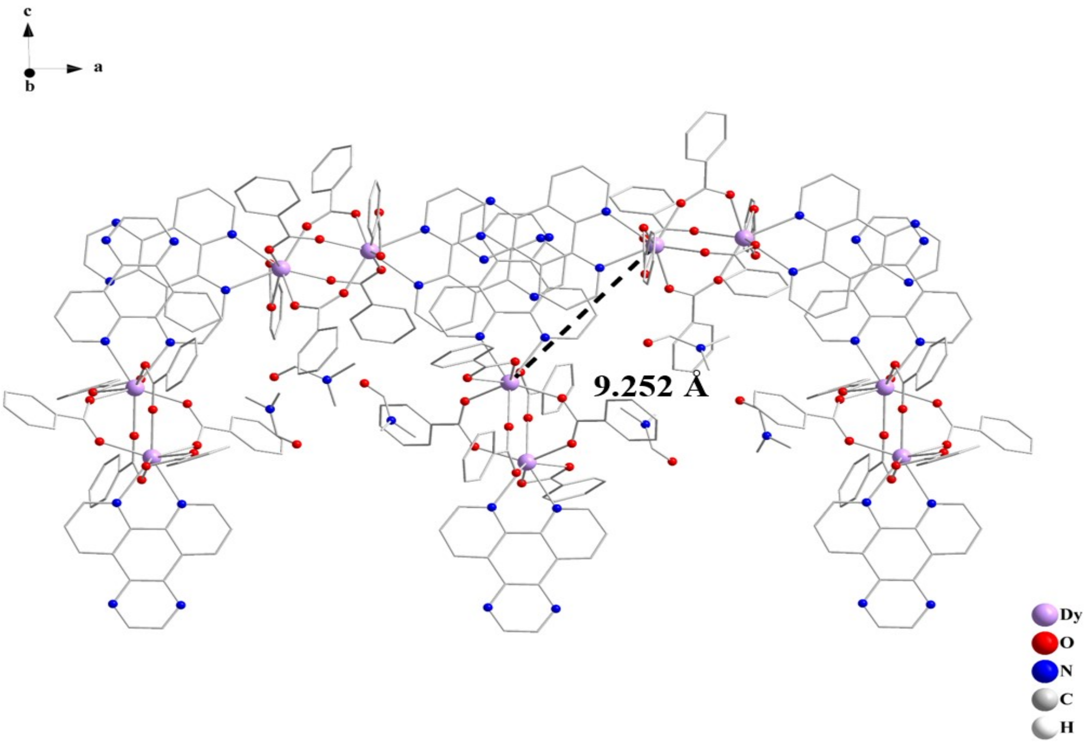

Fig S6. Packing of compound **1**. Dash lines are the shortest distance of intermolecular Dy-Dy distances

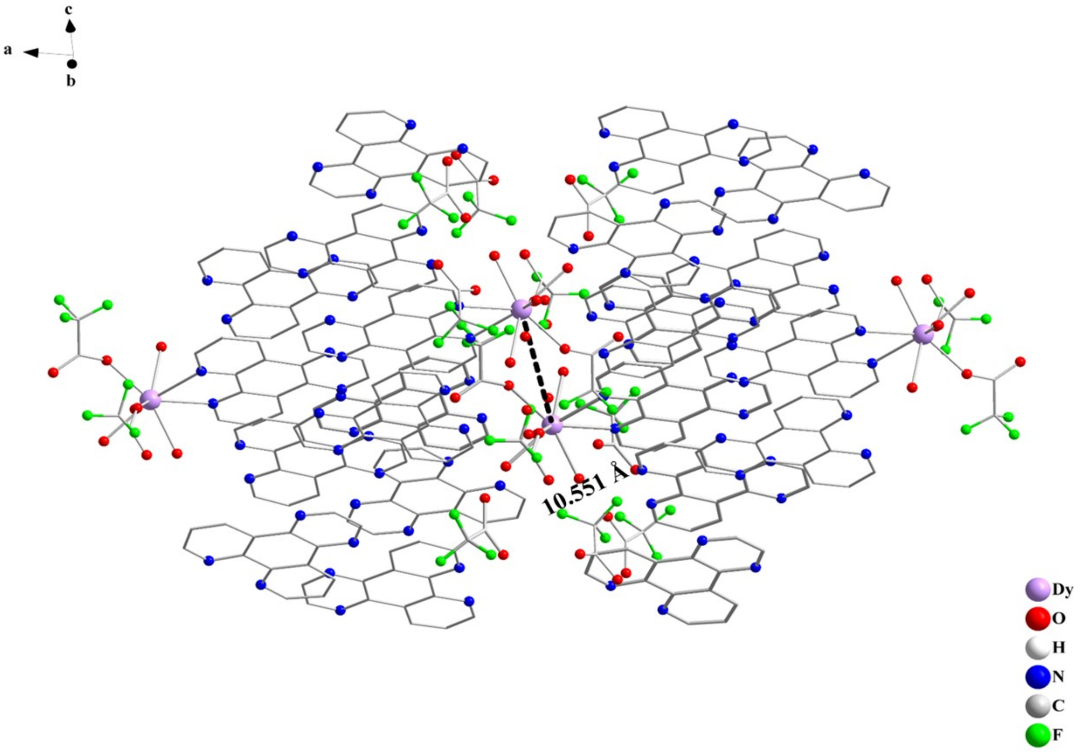

Fig S7. Packing of compound **2**. Dash lines are the shortest distance of intermolecular Dy-Dy distances

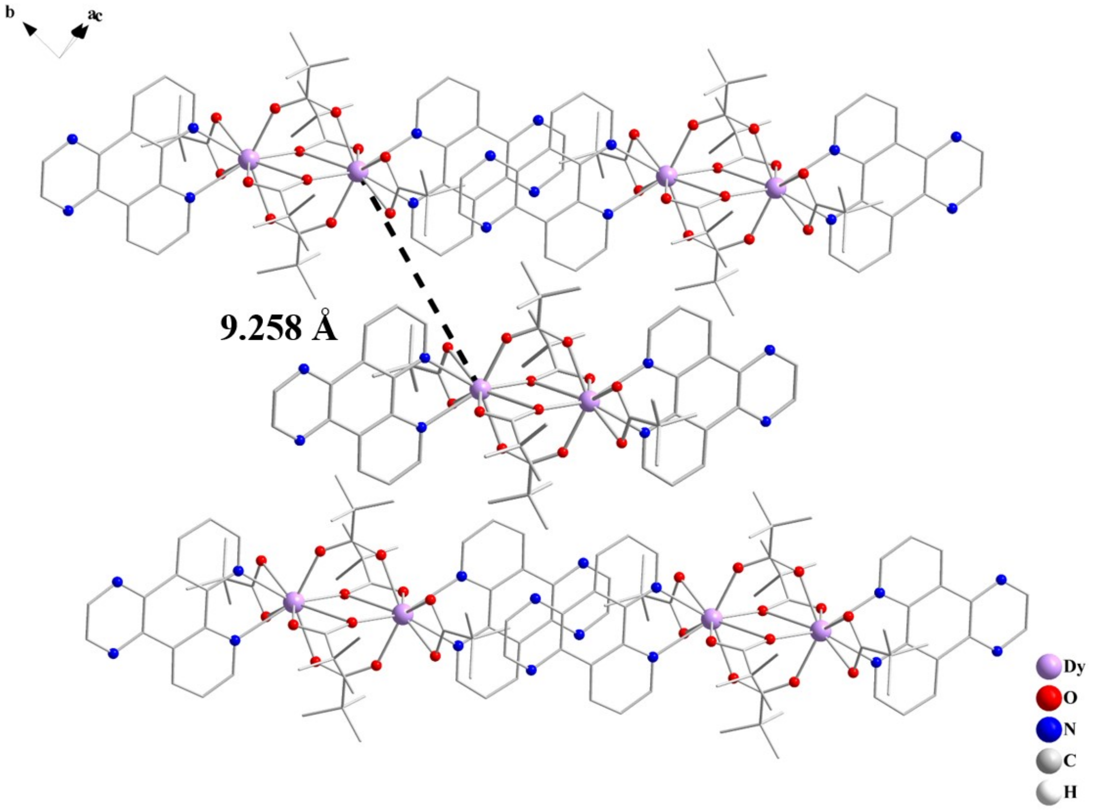

Fig S8. Packing of compound **3**. Dash lines are the shortest distance of intermolecular Dy-Dy distances

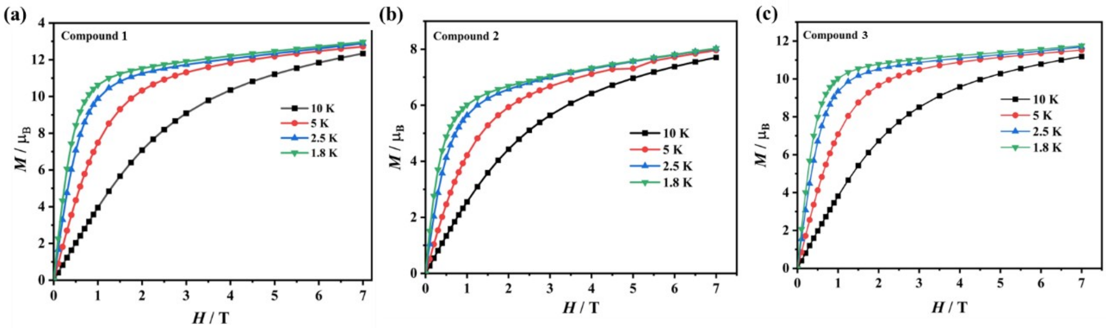

Fig. S9 Field dependence of the magnetization for **1** (a), **2** (b) and **3** (c) at corresponding temperatures.

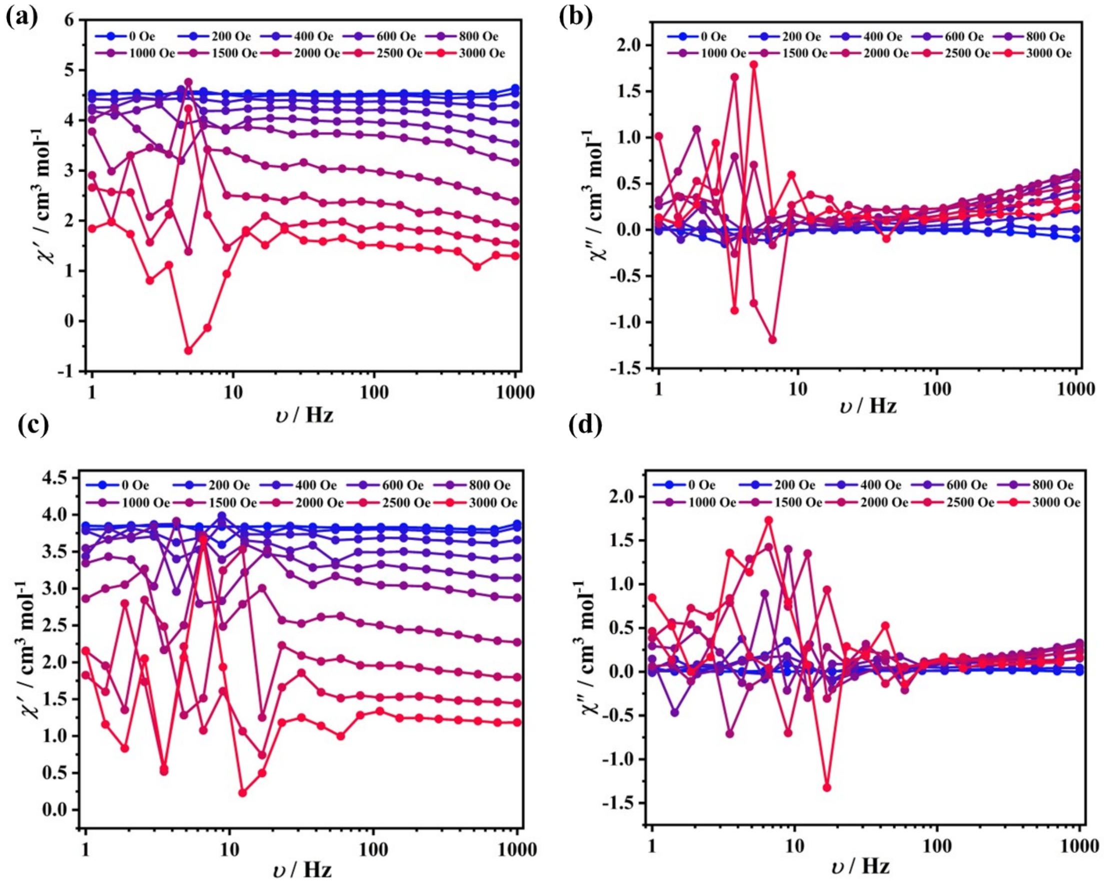

Fig. S10 Field-dependent real (χ′) and imaginary (χ″) ac signals maps for compounds **1** (a, b) and **2** (c, d).

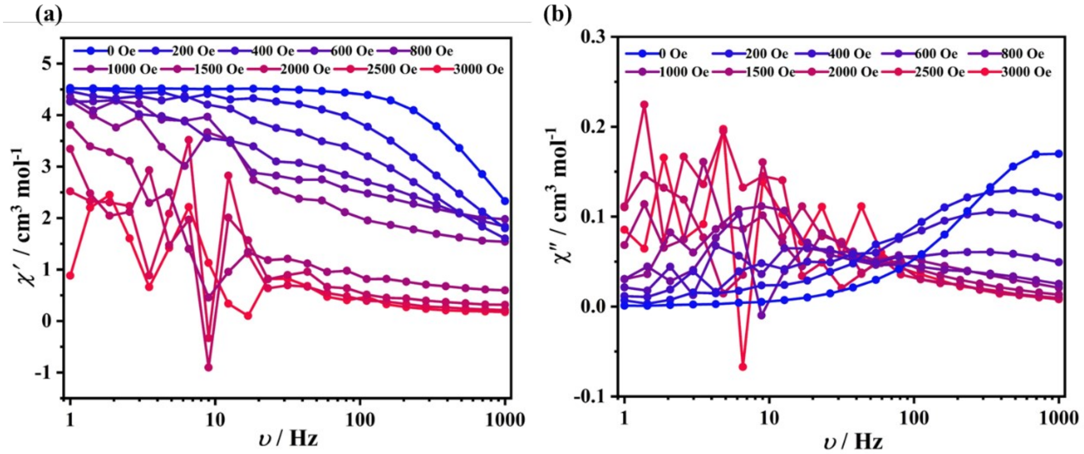

Fig. S11 Field-dependent real (χ′) (a) and imaginary (χ″) (b) ac signals for compound **3**.

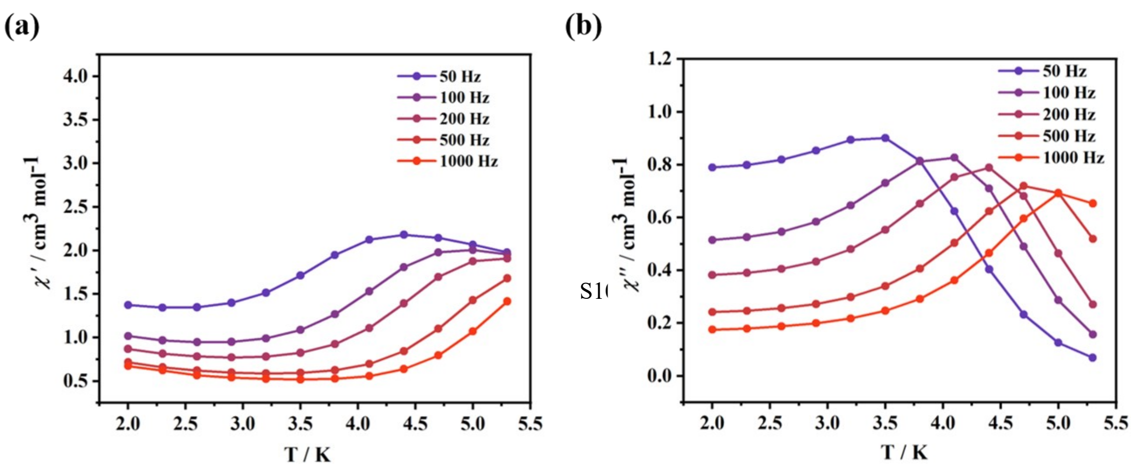

Fig S12. Plots of χ' (left) and χ'' (right) vs temperature under different frequency for compound **3**.

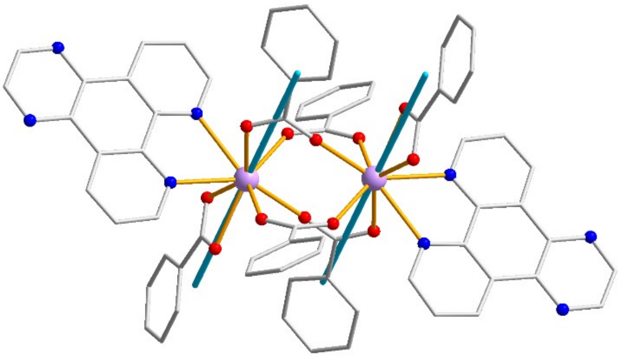

Fig S13. The magnetic anisotropy axis (blue) of compound **1**

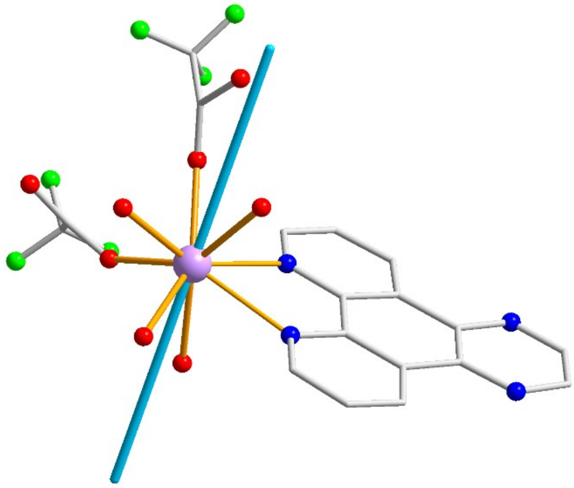

Fig S14. The magnetic anisotropy axis (blue) of compound **2**

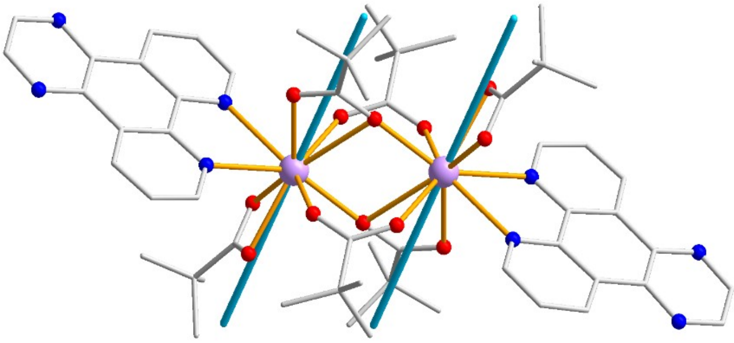

Fig S15. The magnetic anisotropy axis (blue) of compound **3**

References

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