Supporting Information for

A 3D MOF constructed from dysprosium(III) oxalate and capping ligand: ferromagnetic coupling and field-induced two-step magnetic relaxation

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1. Experimental

Materials and instrumentation

All chemicals are reagent grade and commercial available. The elemental analyses were determined on a Varlo ELIII elemental analyser. The infrared spectra were performed on a Bruker/Tensor-27 spectrophotometer with pressed KBr pellets in the range 4000–400 cm^{-1}. The X-ray powder diffraction (XRD) spectra were recorded on a PANalytical /Empyrean-1 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation. The magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants of all components.

Synthesis of 1

A mixture of $Dy(NO_3)_3{\cdot}5H_2O$ (1.0 mmol), oxalic acid(2.0 mmol), 1,10-phenanthroline(1.0 mmol) and H_2O(15 mL) in a Teflon-lined stainless steel autoclave (25 mL) was kept at 170 °C for seven days. Light yellow rod crystals of **1** were harvested after the autoclave had cooled to room temperature overnight, these crystals were washed with water and dried at ambient temperature. 80% yield based on Dy. Elemental analysis (%): calc. for $C_{15}H_9DyN_2O_{6.50}$ (**1**): C, 37.24; H, 1.88; N, 5.79. Found: C, 37.29; H, 1.91; N 5.73. IR (KBr pellet, cm^{-1}): 3683(w), 3441(b, s), 3091(w), 3068(w), 2927(w), 1685(m), 1631(s), 1615(s), 1521(w), 1426(w), 1364(w), 1347(w), 1316(m), 1226(w),

1212(w), 1147(w), 1106(w), 1089(w), 1052(w), 1038(w), 1005(w), 854(w), 797(m), 728(m), 640(w).

Crystallography

A single crystal with dimensions 0.21× 0.06 × 0.05 mm^3 of **1** was selected to collect data on a Rigaku MM007HF Saturn724+ diffractometer with *Mo-Kα* radiation (λ = 0.71073 Å) in the φ-scan mode. Cell parameters were obtained by the global refinement of the positions of all collected reflections. The structure was solved by direct methods and refined with the ShelXL refinement package using least squares minimisation. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms but those in the solvent hydrate molecule were set in calculated positions and refined as riding atoms.

Table S1. Continuous Shape Measures calculation for the Dy(III) ion in **1**.

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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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Dy structures

OP-8             1 D8h    Octagon
HPY-8            2 C7v    Heptagonal pyramid
HBPY-8           3 D6h    Hexagonal bipyramid
CU-8             4 Oh     Cube
SAPR-8           5 D4d    Square antiprism
TDD-8            6 D2d    Triangular dodecahedron
JGBF-8           7 D2d    Johnson gyrobifastigium J26
JETBPY-8         8 D3h    Johnson elongated triangular bipyramid J14
JBTPR-8          9 C2v    Biaugmented trigonal prism J50
BTPR-8          10 C2v    Biaugmented trigonal prism
JSD-8           11 D2d    Snub diphenoid J84
TT-8            12 Td     Triakis tetrahedron
ETBPY-8         13 D3h    Elongated trigonal bipyramid

Structure [ML8 ]  OP-8     HPY-8     HBPY-8    CU-8     SAPR-8    TDD-8     JGBF-8    JETBPY-8   JBTPR-8    BTPR-8    JSD-8     TT-8      ETBPY-8
 ABOXIY          ,31.222,  22.757,  14.954,  7.538,  1.056,  1.250,  16.006,  28.569,     2.838,     2.114,    4.618,  8.275,  23.387
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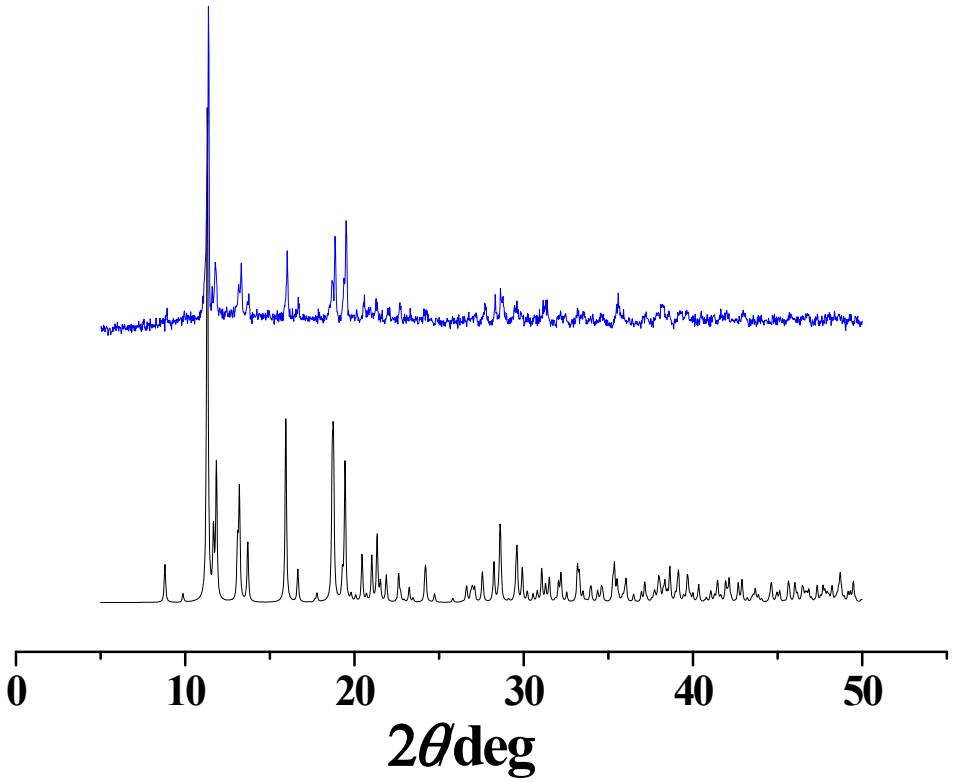

Fig. S1. The simulative (black) and experimental (blue) powder X-ray diffraction patterns for **1**.

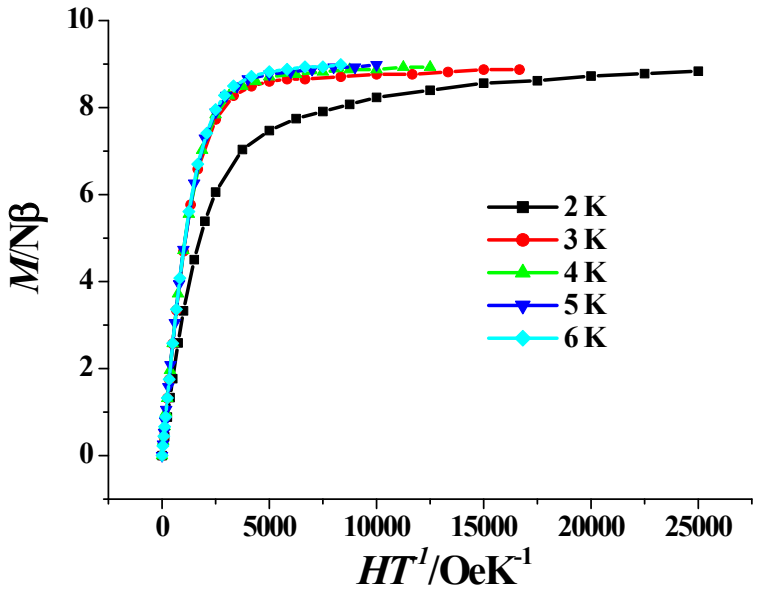

Fig. S2. *M* versus *H*/*T* plots at 2–6 K of **1**.

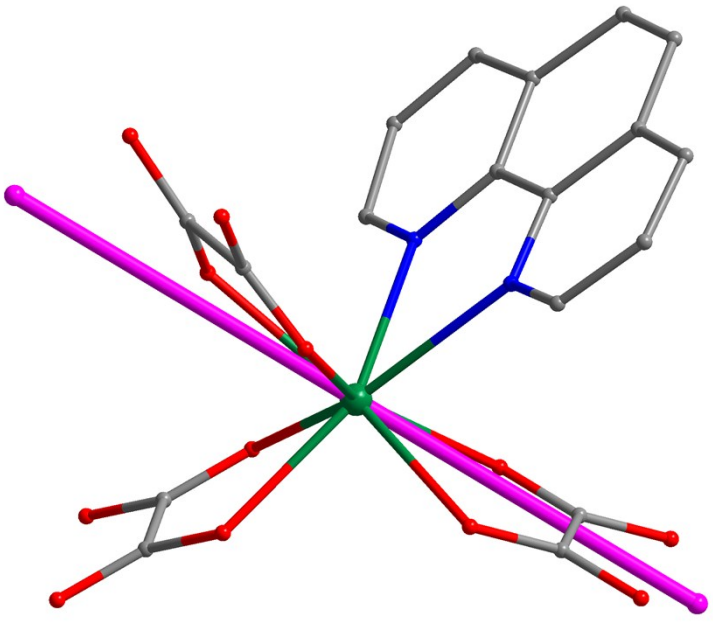

Fig. S3. Magnetic axis of the Dy^{3+} ion in **1** calculated by an electrostatic method

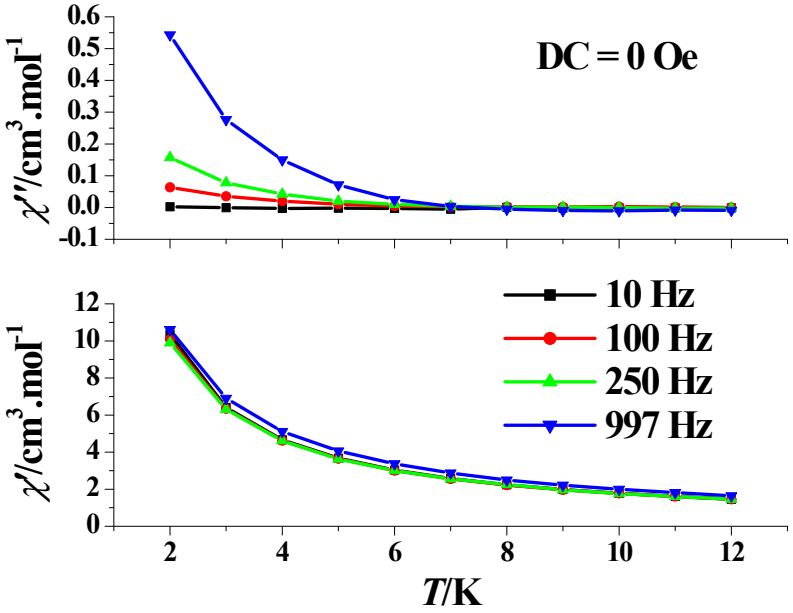

Fig. S4. AC susceptibilities measured in a 2.5 Oe ac magnetic field with a zero dc field for **1.**

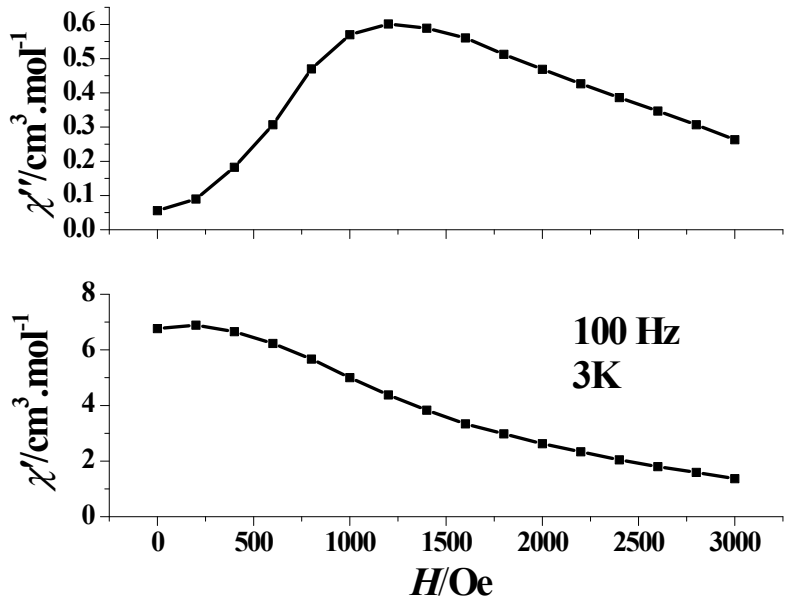

Fig. S5. AC susceptibilities measured in a 2.5 Oe ac magnetic field with variable dc fields at 100 Hz and 3 K for **1.**

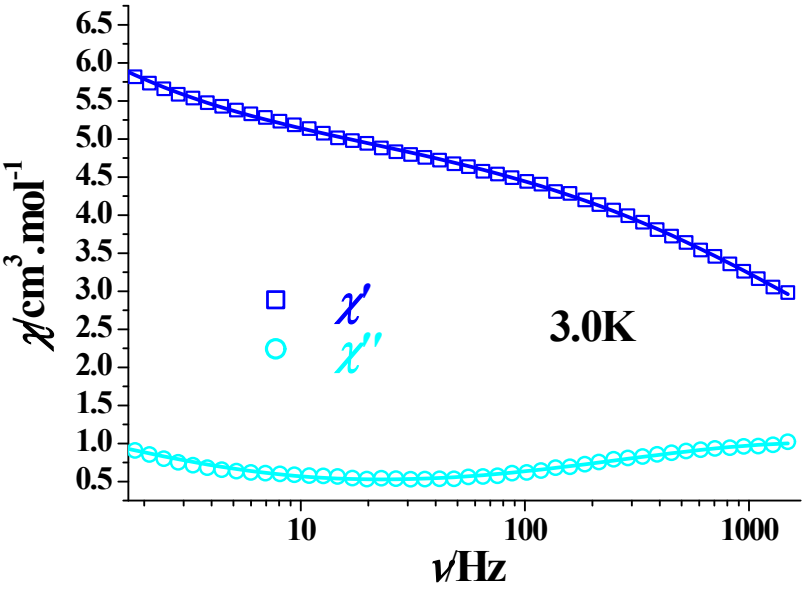

Fig. S6 Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility of **1** at 3.0 K. the solid lines represent the best fitting with the sum of two modified Debye functions.

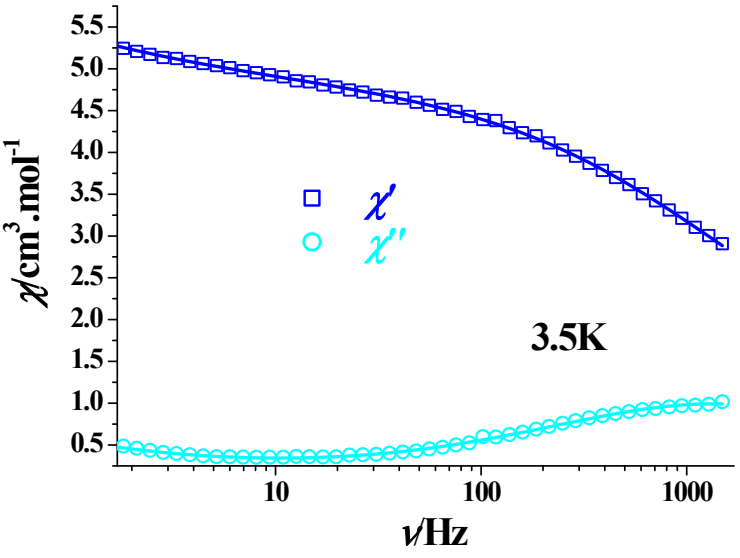

Fig. S7 Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility of **1** at 3.5 K. the solid lines represent the best fitting with the sum of two modified Debye functions.

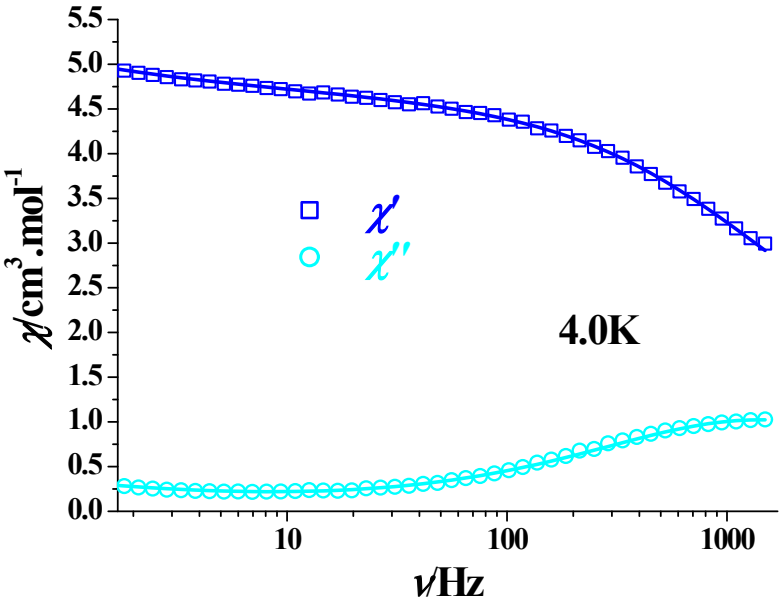

Fig. S8. Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility of **1** at 4.0 K. the solid lines represent the best fitting with the sum of two modified Debye functions.

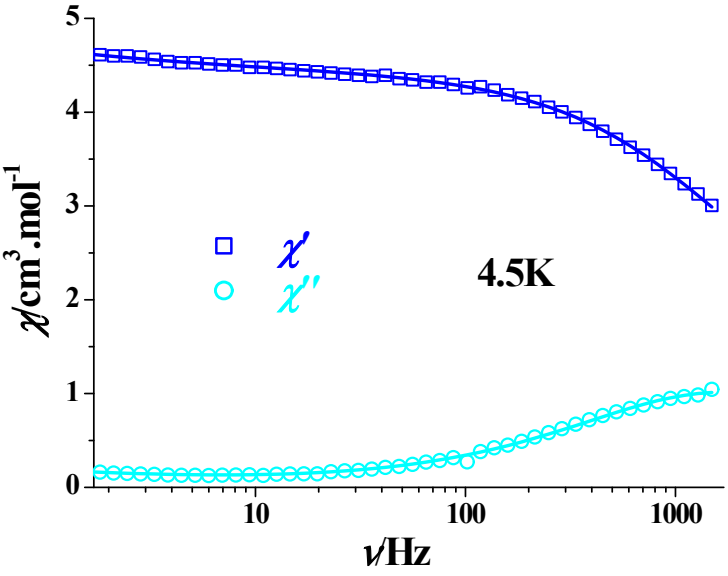

Fig. S9. Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility of **1** at 4.5 K. the solid lines represent the best fitting with the sum of two modified Debye functions.

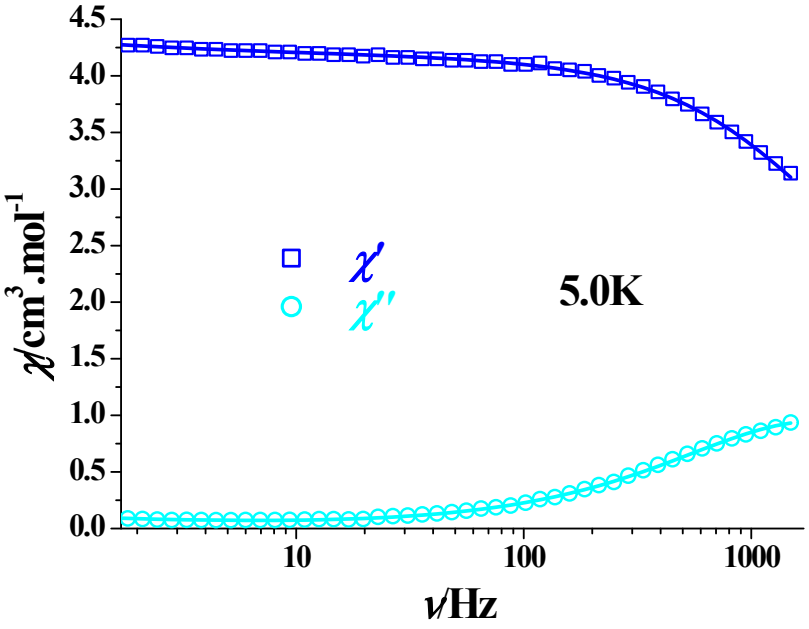

Fig. S10. Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility of **1** at 5.0 K. the solid lines represent the best fitting with the sum of two modified Debye functions.

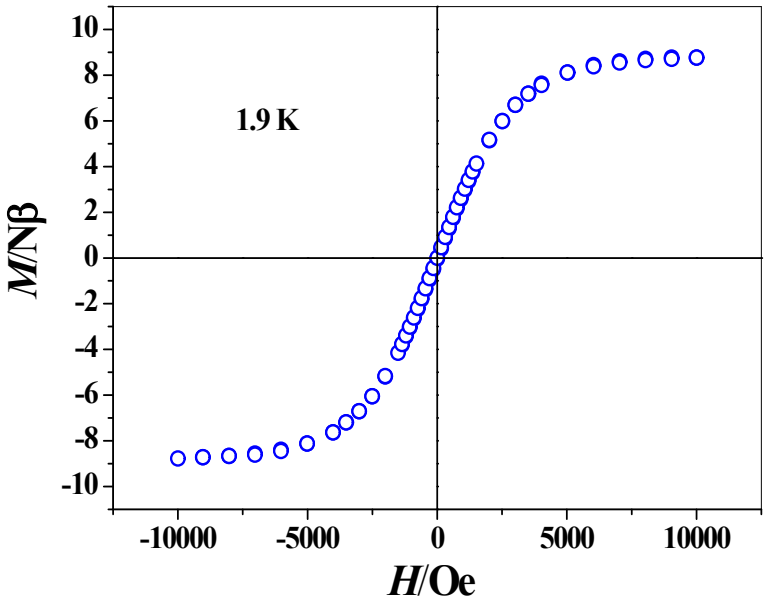

Fig. S11. Plot of *M* versus *H* at 1.9 K from −10000 to 10000 Oe for **1**.

Table S2. Some examples of high-dimensional DyMOFs behaving as SMMs.

Structural formula	Dimension	Coordination configuration	Magnetic interaction	DC field (Oe)	U_{eff} (K)	Ref.
[Dy(3-py-4-pmc)$(C_2O_4)_{0.5}$(OH)(H_2O)]	2D	square antiprism	ferromagnetic	0	186	5d
[Dy_2(HCAM)$_3(H_2O)_4]_2$·H_2O	2D	spherical tricapped trigonal prism; square antiprism	ferromagnetic	2000	63.5, 57.1	5q
[Ln_2(glu)$_2(\mu_3$-OH$)_2$ $(H_2O)]$ ·H_2O	2D	triangular dodecahedron	ferromagnetic	0	112	5k
{[Ln(NNO)(glu)] ·0.25H_2O	2D	spherical capped square antiprism	anti-ferromagnetic (possible)	2000	44.2	5p
(EMIM)[Dy_3(BDC$)_5$	3D	triangular dodecahedron	anti-ferromagnetic (possible)	2000	39.3	5l
[Dy_2(1H-5-Cl-6-Opy-3-$CO_2)_2(C_2O_4)_2(H_2O)]$·2H_2 O	3D	monocapped square antiprism; pentagonal bipyramid	anti-ferromagnetic (possible)	2000	37.6	5o
Dy_2(dcps$)_3(H_2O)_5$	2D	square antiprism; bicapped trigonal prism	anti-ferromagnetic (possible)	2000	12.5	5n
$Dy_2(INO)_4(NO_3)_2$ ·2MeCN	3D	square antiprism	anti-ferromagnetic (possible)	0	110	5a
(H_3O)[Ln$(NA)_2]$·H_2O	2D	octahedron	anti-ferromagnetic (possible)	1000	75	5b
[Ln$(bipyNO)_4](TfO)_3$·x solvent	3D	square antiprism	anti-ferromagnetic (possible)	1000	17.9	5c
[Dy(hip)phen]	3D	pentagonal bipyramid	ferromagnetic	0	131	5g
[Ln$(hfac)_3]_2$ (4,4′ -BipyNO$)_2$	3D	capped square antiprism	anti-ferromagnetic (possible)	1900	10.3	5h
Dy(BTC)	3D	trigonal prism	anti-ferromagnetic (possible)	1000	45.9	5s
[Dy$(C_2O_4)_{1.5}(H_2O)_3$] ·$2H_2O$	2D	tricapped trigonal prism	anti-ferromagnetic (possible)	700	3.8, 10.7	9
Dy$(C_2O_4)_{1.5}$phen] ·0.5H_2O	3D	square antiprism	ferromagnetic	1200	35.5, 32.6	this work

Abbreviations: 3-py-4-pmc = 2-(3-pyridyl)pyrimidine-4-carboxylate; CAM = 4-hydroxypyridine-2,6 -dicarboxylate; H_2glu = 2,2-dimethylglutaric acid; HNNO = nicotinic acid N-oxide, H_2glu = glutaric acid; H_2BDC = 1,4-benzenedicarboxylic acid，EMIM = 1-ethyl-3-methylimidazolium；1H-5-Cl-6-Opy-3-CO_2 = 1-hydro-5-chloro-6-oxopyridine-3-carboxylate; H_2dcps = 4,4'-dicarboxybiphenyl sulfone; HINO = isonicotinic acid N-oxide; H_2NA = 5-hydroxynicotinic acid; bipyNO = 4,4'-bipyridine-N,N'-dioxide, TfO = triflate; H_3hip = 5-hydroxyisophthalic acid, phen = 1,10-phenanthroline; 4,4′ -BipyNO = 4,4′ -bipyridine N,N'-dioxide; BTC = 1,3,5-benzenetricarboxylate.

Table S3. Linear combination of two modified Debye model fitting parameters at 3-5 K of **1** under 1.2 kOe dc field.

T(K)	χ_2(cm^3.mol^{-1})	χ_1(cm^3.mol^{-1})	χ_0(cm^3.mol^{-1})	τ_1(s)	α_1	τ_2(s)	α_2
3.0	11.51064	4.88819	0.68109	0.00009	0.4534	1.34619	0.46814
3.5	14.56681	4.80332	0.97193	0.00011	0.40169	26.0164	0.53083
4.0	8.33111	4.63746	1.23079	0.00010	0.31772	7.50116	0.52176
4.5	5.78684	4.43113	1.33996	0.00009	0.26464	2.30764	0.50525
5.0	4.88441	4.18072	1.55955	0.00008	0.20261	1.80177	0.46836