Supporting Information

Two mononuclear Dysprosium(III) complexes with their slow magnetic relaxation behaviors tuned by coordination geometry

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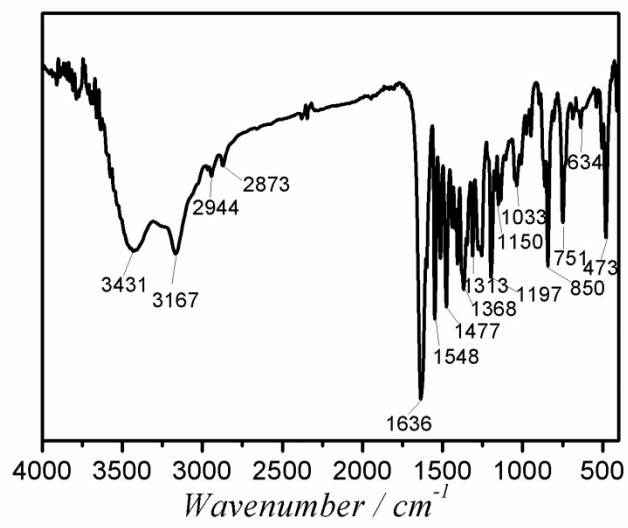


Fig. S1 FT-IR spectrum of **1**.

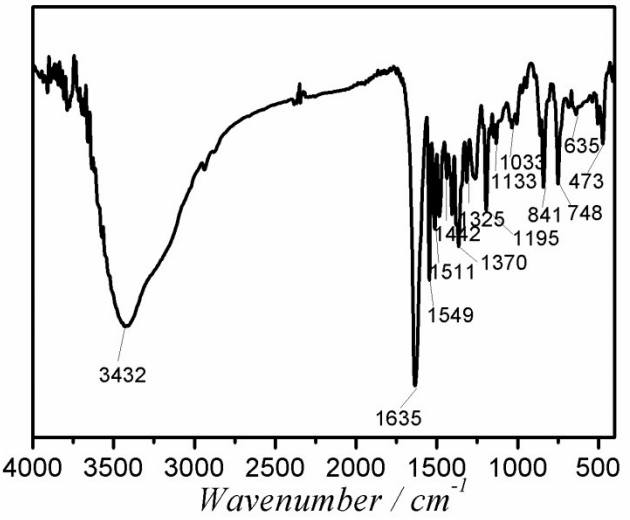


Fig. S2 FT-IR spectrum of **2**.

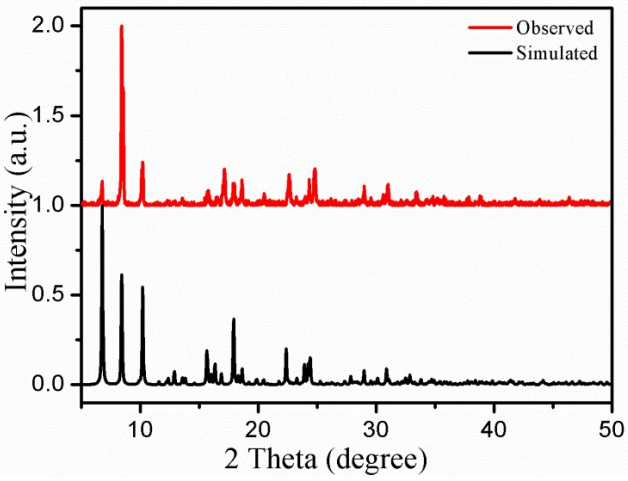


Fig. S3 PXRD patterns of **1**.

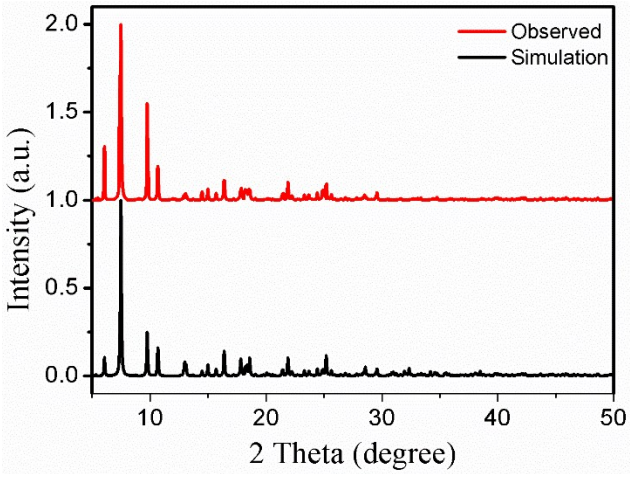


Fig. S4 PXRD patterns of **2**.

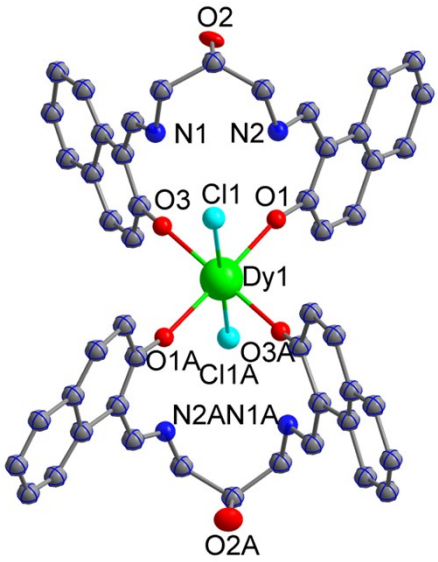


Fig. S5 The structure of **1** with 30 % probability ellipsoid and selected atoms labelled. Hydrogen atoms are omitted for clarity. Symmetry code: A) *–x* + 1, *-y* + 1, *-z* + 1.

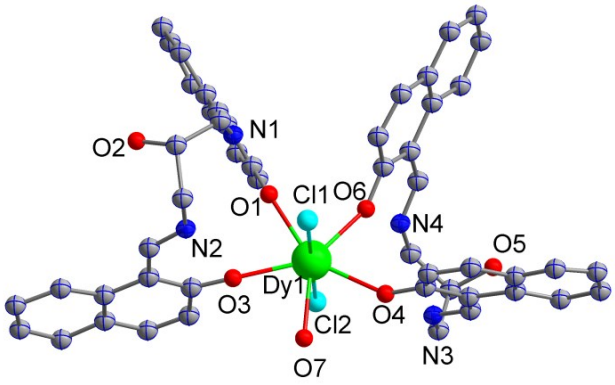
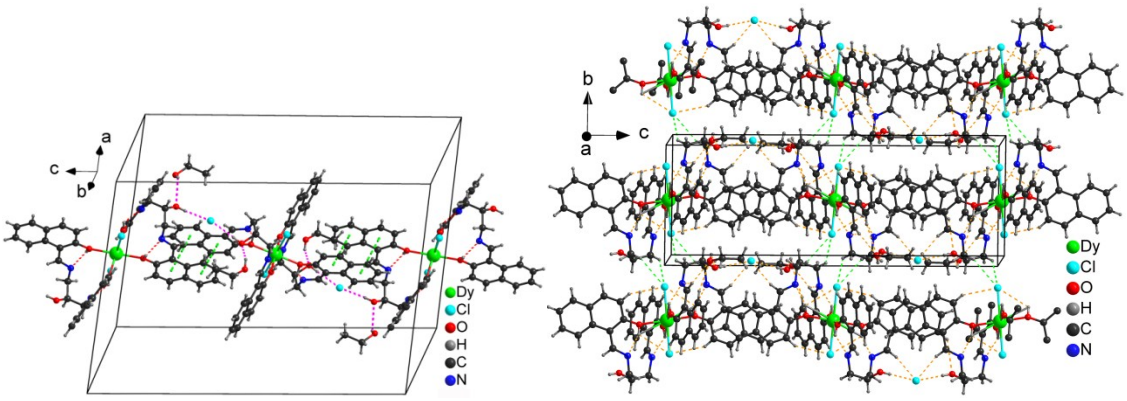
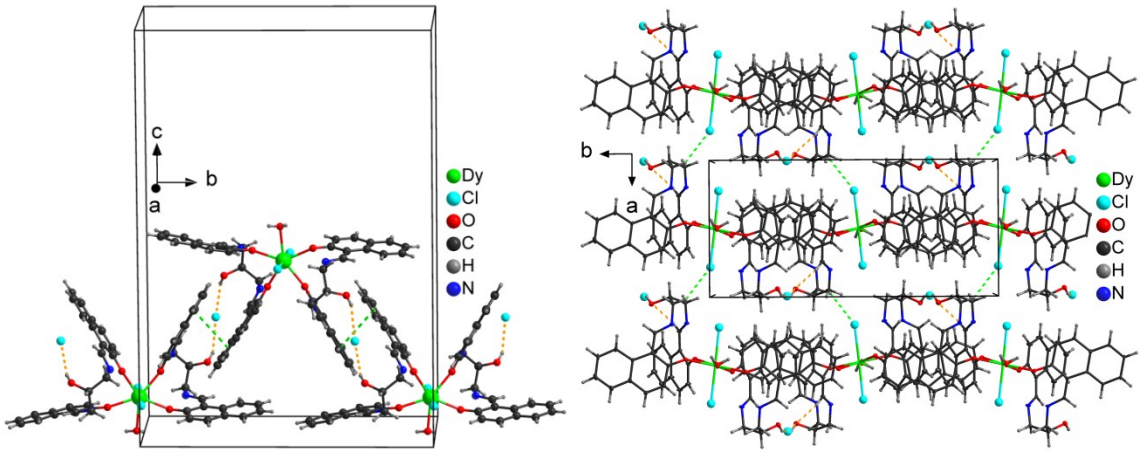


Fig. S6 The structure of **2** with 30 % probability ellipsoid and selected atoms labelled. Hydrogen atoms are omitted for clarity.



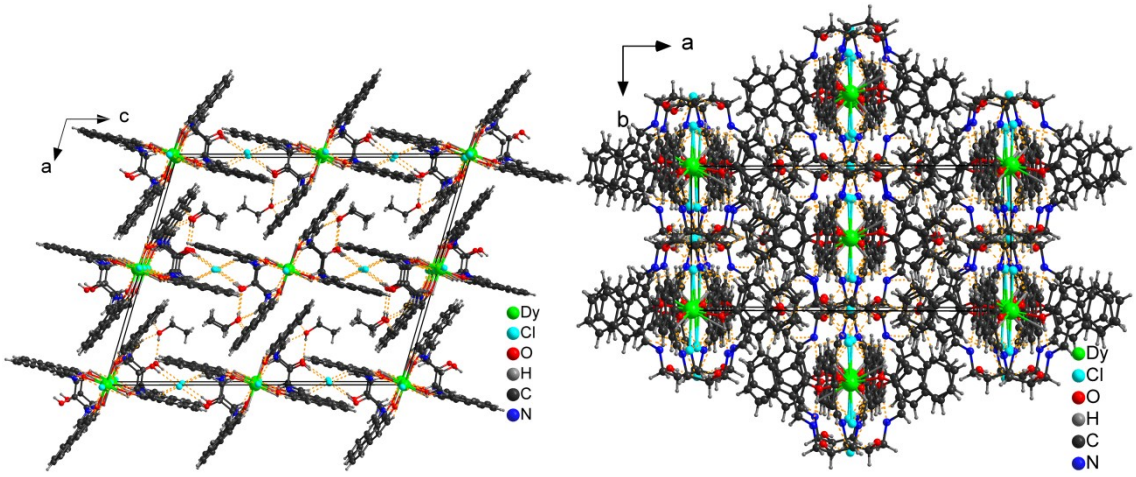
(a) (b)

Fig. S7 (a) 1D supramolecular chain of **1** formed through hydrogen bonds of O2-H2A···Cl2 and $\pi\cdots\pi$ stacking interactions between the two naphthalene planes as revealed by a dihedral angle of 5.508(12)° and a ring-to-ring distance of 3.8071(13) Å. (b) 2D supramolecular framework of **1** formed from 1D supramolecular chains through non-classic hydrogen bonds of C-H···Cl (C12-H12B···Cl1(-x+1, -y, -z+1), C14-H14A···Cl1(-x+1, -y, -z+1)).



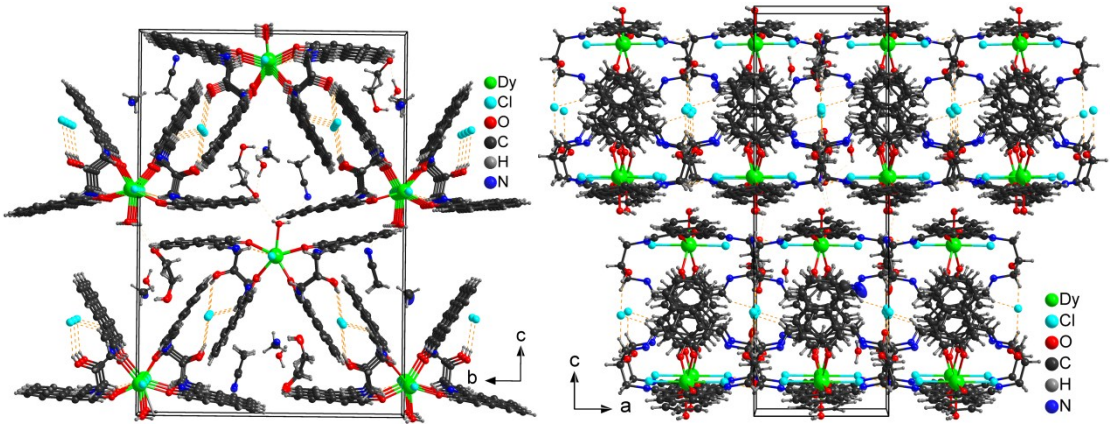
(a) (b)

Fig. S8 (a) 1D supramolecular chain of **2** formed by hydrogen bonds of O-H···Cl (O2-H2A···Cl3(-x+1,y+1/2,-z+1/2), O5-H5A···Cl3) and $\pi\cdots\pi$ stacking interactions between the two naphthalene planes as revealed by a dihedral angle of 4.655(12)° and a ring-to-ring distance of 3.5743(1) Å. (b) 2D supramolecular framework of **2** formed from 1D supramolecular chains through non-classic hydrogen bonds of C-H···Cl (C12-H12A···Cl2(x-1,y,z)).



(a) (b)

Fig. S9 A stacking diagram of 1D supramolecular chain of **1** seen along the axis b (a) and along the axis c (b).



(a) (b)

Fig. S10 A stacking diagram of 1D supramolecular chain of **2** seen along the axis b (a) and along the axis c (b).

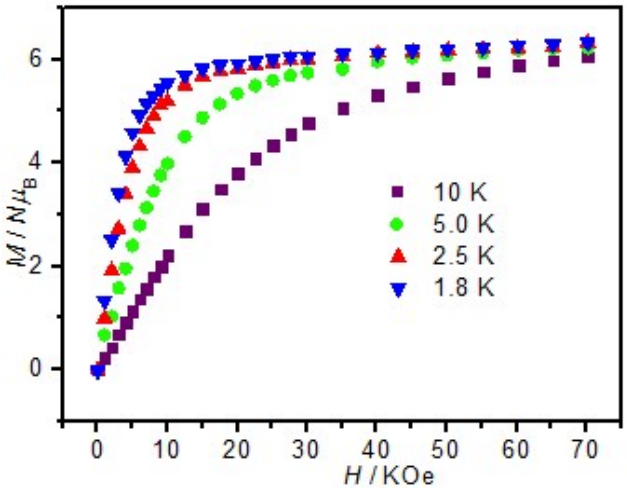


Fig. S11 Plots of *M vs*. *H* for complex **1** measured at 1.8, 2,5, 5.0, and 10 K.

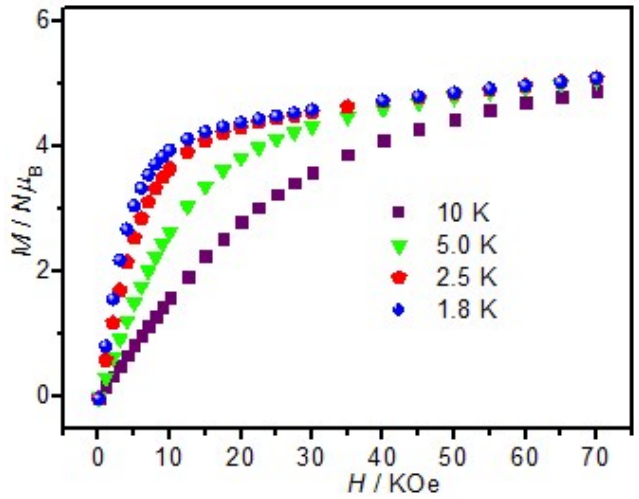


Fig. S12 Plots of *M vs*. *H* for complex **2** measured at 1.8, 2, 5, 5.0, and 10 K.

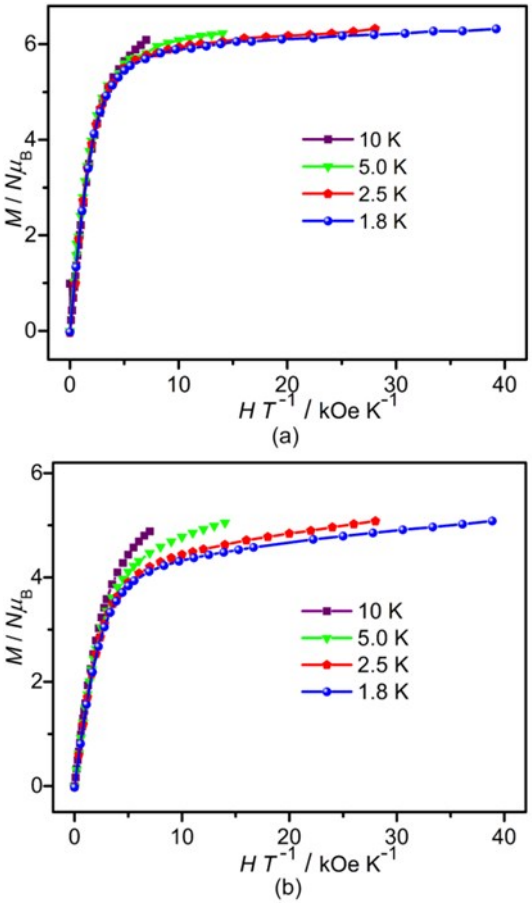


Fig. 13 Plots of M vs $H\ T^{-1}$ for **1** (a) and **2** (b) measured at 1.8, 2.5, 5.0, and 10 K.

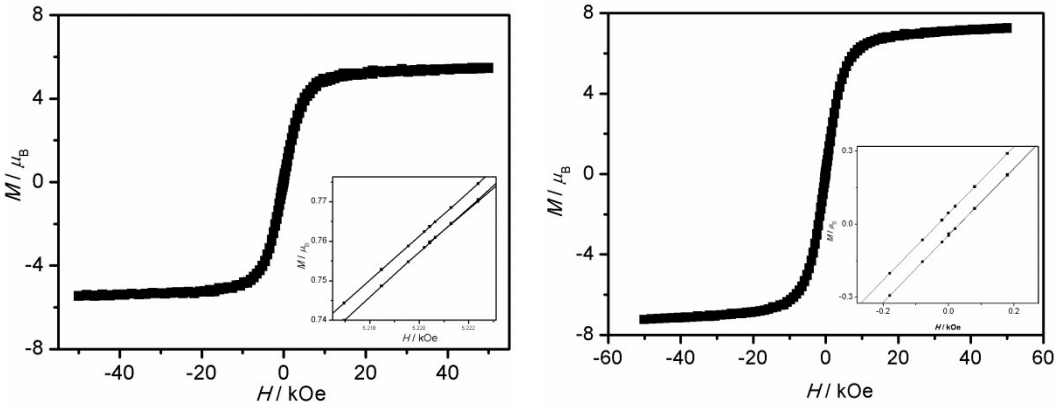


Fig. S14 Plots of Magnetic hysteresis loops for **1** (left) and **2** (right)**.**

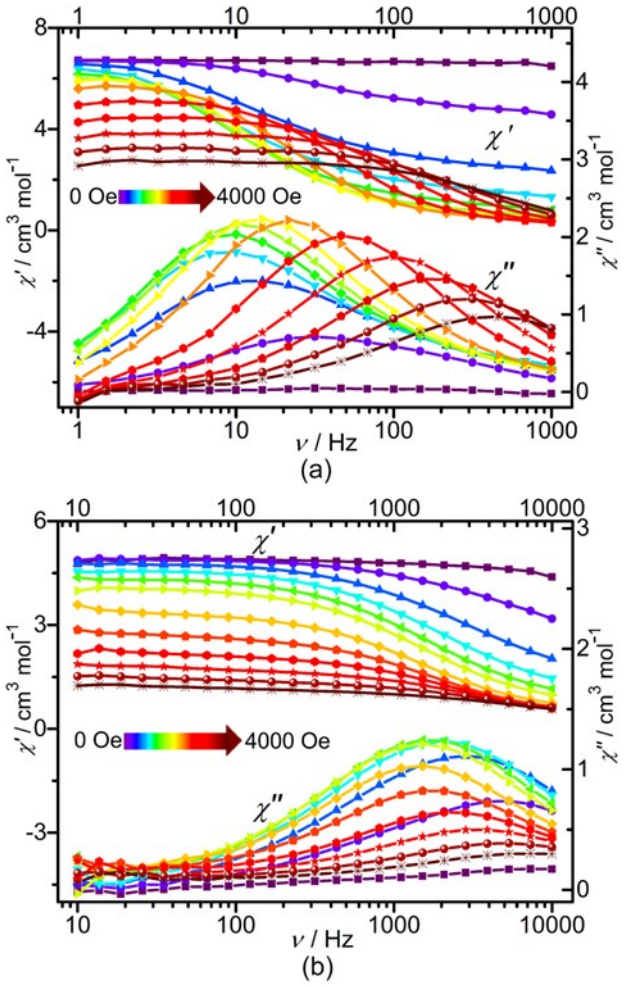


Fig. S15 Frequency-dependent in-phase (χ') and out-of phase (χ") ac susceptibilities under different dc fields for **1** (a) at 2 K and **2** (b) at 1.8 K.

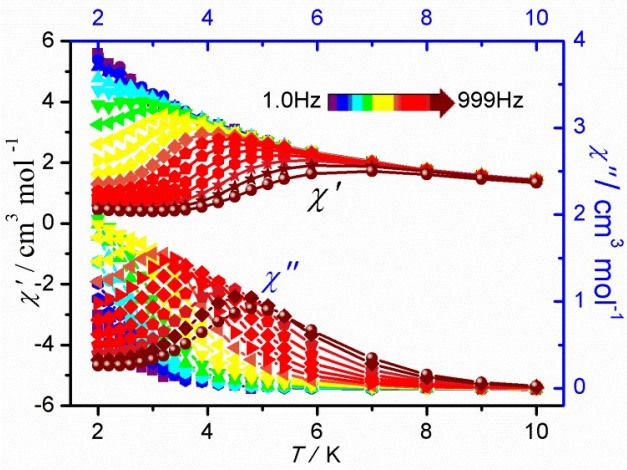


Fig. S16 Plots of χ' and χ'' vs T (1.8-10 K) at various frequencies under 1200 dc field for **1**.

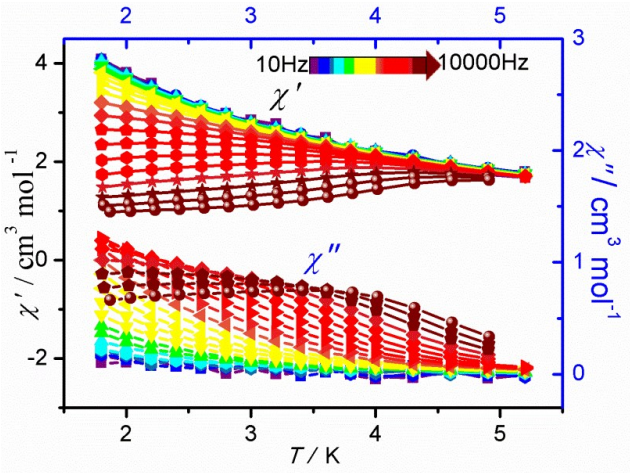
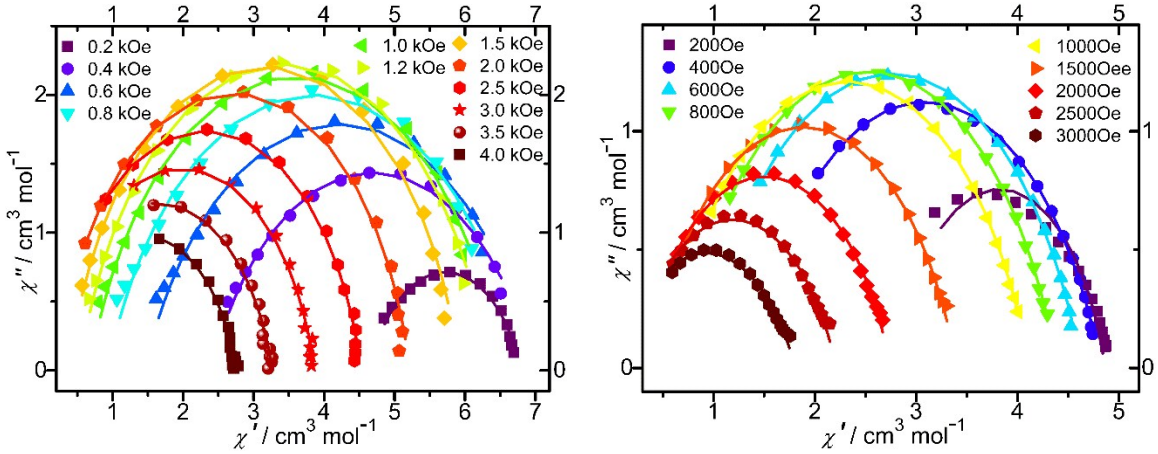
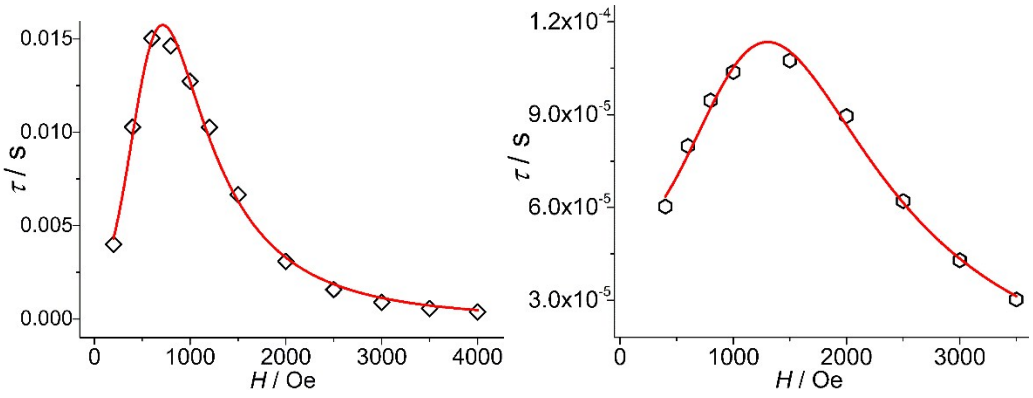


Fig. S17 χ' and χ'' vs T (1.8-5 K) plots at various frequencies under 1000 Oe for **2**.



(a) (b)

Fig. S18 Cole–Cole drawings at different dc fields for **1** (a) and **2** (b) with the best fit to Debye model designated by solid lines.



(a) (b)

Fig. S19 τ versus H curves of **1** (a) and **2** (b) with the fit to the equation $\tau^{-1} = B_1 / (1 + B_2H^2) + A_1H^4T + A_2H^2T$.

Table S1. Selected bond lengths / Å and bond angles / ° for **1.**

Dy1-O1	2.224 (3)	Dy1-O3A	2.237 (4)
Dy1-O1A	2.224 (3)	Dy1-Cl1A	2.6656 (17)
Dy1-O3	2.237 (4)	Dy1-Cl1	2.6656 (17)
O1-Dy1-O1A	180.0	O1A-Dy1-Cl1A	84.81 (9)
O1-Dy1-O3	84.50 (15)	O3-Dy1-Cl1A	95.49 (10)
O1A-Dy1-O3	95.50 (15)	O3A-Dy1-Cl1A	84.51 (10)
O1-Dy1-O3A	95.50 (15)	O1-Dy1-Cl1	84.81 (9)
O1A-Dy1-O3A	84.50 (15)	O1A-Dy1-Cl1	95.19 (9)
O3-Dy1-O3A	180.0	O3-Dy1-Cl1	84.51 (10)
O1-Dy1-Cl1A	95.19 (9)	O3A-Dy1-Cl1	95.49 (10)
		Cl1A-Dy1-Cl1	180.0

Symmetry code: A) −x+1, −y+1, −z+1

Table S2. Selected bond lengths / Å and bond angles / ° for **2.**

Dy(1)-O(4)	2.290(5)	Dy(1)-O(7)	2.402(5)
Dy(1)-O(1)	2.294(6)	Dy(1)-Cl(1)	2.6628(19)
Dy(1)-O(3)	2.296(6)	Dy(1)-Cl(2)	2.669(2)
Dy(1)-O(6)	2.308(6)		
O(4)-Dy(1)-O(1)	146.9(2)	O(1)-Dy(1)-Cl(1)	84.64(15)
O(4)-Dy(1)-O(3)	74.5(2)	O(3)-Dy(1)-Cl(1)	81.68(15)
O(1)-Dy(1)-O(3)	73.3(2)	O(6)-Dy(1)-Cl(1)	96.06(16)
O(4)-Dy(1)-O(6)	73.3(2)	O(7)-Dy(1)-Cl(1)	89.3(2)
O(1)-Dy(1)-O(6)	139.5(2)	O(4)-Dy(1)-Cl(2)	81.55(16)
O(3)-Dy(1)-O(6)	147.0(2)	O(1)-Dy(1)-Cl(2)	95.20(15)
O(4)-Dy(1)-O(7)	142.6(2)	O(3)-Dy(1)-Cl(2)	97.45(15)
O(1)-Dy(1)-O(7)	70.00(19)	O(6)-Dy(1)-Cl(2)	84.62(16)
O(3)-Dy(1)-O(7)	142.9(2)	O(7)-Dy(1)-Cl(2)	91.4(2)
O(6)-Dy(1)-O(7)	69.5(2)	Cl(1)-Dy(1)-Cl(2)	179.13(6)
O(4)-Dy(1)-Cl(1)	98.11(16)		

Table S3. Hydrogen bonds for **1** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(1)	0.85	2.02	2.659(5)	131.0
C(2)-H(2)...Cl(1)#1	0.93	2.90	3.721(6)	147.6
C(11)-H(11)...Cl(2)	0.93	2.82	3.697(5)	156.8
C(12)-H(12B)...Cl(1)#2	0.97	2.97	3.759(5)	138.7
O(2)-H(2A)...Cl(2)	0.82	2.29	3.113(4)	175.9
C(14)-H(14A)...Cl(1)#2	0.97	2.96	3.750(6)	138.9
C(15)-H(15)...O(4)#3	0.93	2.49	3.384(14)	162.4
C(24)-H(24)...Cl(1)#1	0.93	2.95	3.720(7)	140.7
O(3)-H(3A)...Cl(1)	0.85	2.92	3.312(4)	110.5
O(3)-H(3A)...N(2)	0.85	1.98	2.659(5)	136.5
O(4)-H(4)...O(2)#4	0.82	2.44	2.893(16)	115.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+1 #3 x,-y,z+1/2 #4 x,-y,z-1/2 #5 x-1/2, -y + 1/2, z

Table S4. Hydrogen bonds for **2** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...Cl(2)	0.93	2.91	3.663(9)	139.1
C(12)-H(12A)...Cl(2)#1	0.97	2.86	3.626(9)	137.1
O(2)-H(2A)...Cl(3)#2	0.81	2.57	3.175(7)	132.9
C(15)-H(15)...Cl(3)#2	0.93	2.81	3.642(9)	149.9
C(24)-H(24)...Cl(2)	0.93	2.97	3.817(9)	151.4
C(27)-H(27)...Cl(1)	0.93	2.96	3.807(10)	151.6
C(36)-H(36)...Cl(3)	0.93	2.92	3.780(9)	154.7
C(37)-H(37B)...Cl(1)#3	0.97	2.97	3.754(9)	138.5
O(5)-H(5A)...Cl(3)	0.81	2.44	3.154(7)	147.1
C(39)-H(39A)...Cl(1)#3	0.97	2.88	3.685(8)	140.5
C(49)-H(49)...Cl(1)	0.93	2.93	3.761(9)	149.6
O(7)-H(71)...O(8)#4	0.73	2.38	2.763(14)	114.9
O(7)-H(72)...N(5)	0.85	2.47	2.984(9)	120.0
C(52)-H(52B)...N(6)#5	0.96	2.57	3.52(3)	170.7
C(52)-H(52C)...O(10)#4	0.96	2.55	3.21(6)	125.8
O(8)-H(81)...O(7)#6	0.79	2.37	2.763(14)	111.2
C(53)-H(53A)...O(10)	0.96	2.26	3.01(6)	134.1
O(9)-H(9)...N(6)#1	0.82	2.23	2.80(4)	127.4
C(54)-H(54C)...O(10)	0.96	2.06	2.61(6)	114.7
O(10)-H(101)...O(9)	0.84	2.37	2.80(6)	112.3
O(10)-H(102)...O(8)	0.87	2.53	3.03(5)	117.0

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,y+1/2,-z+1/2 #3 x+1,y,z #4 -x+1/2,-y+2,z-1/2 #5 -x+3/2,-y+2,z-1/2 #6 -x+1/2,-y+2,z+1/2

Table S5. A list of some SIMs and their performances

SIM	U_{eff} [K]	τ_0 [s]	local symmetry	dc field [Oe]	Ref
$[Dy^{III}(L)_2(NO_3)](ClO_4)_2$	44.3	5.17×10^{-7}	C_{2v}	1000	1
$Dy(Hthd)_3(MeOH)\cdot2,5\text{-}Py$	26.6	2.76×10^{-6}	C_{2v}	1000	2
$[Dy(Hthd)_3(Tppo)]$	35.9	1.12×10^{-6}	C_{3v}	1000	2
$[Dy(Hthd)_3(PyNO)]$	42.7	5.53×10^{-6}	C_{3v}	1000	2
$[Dy(Hthd)_3(4\text{-}PyNO)]$	55.8	1.58×10^{-6}	C_{3v}	1000	2
$[Dy(TFNB)_3(bpy)]$	23.44	5.01×10^{-6}	D_{4d}	1200	3
$[Dy(TTA)_3Lz]$	32	5.55×10^{-5}	D_{4d}	0	4
$[Dy(acac)_3Lz]\cdot CH_3OH\cdot0.5H_2O$	162	4.38×10^{-6}	D_{4d}	0	4
$[Dy(MQ)_2Lz_2]Br\cdot CH_3OH$	80	1.25×10^{-6}	D_{4d}	0	4
$(^nBu_4N)[Ga^{III}_8\ Dy^{III}(OH)_4(shi)_8]$	39	$2.3(5)\times10^{-8}$	D_{4d}	1000	5
$[Dy(Phen)(Cl\text{-}tcpb)_3]$	151.1	1.44×10^{-8}	D_{4d}	0	6
$[Dy(Im^{Dipp}N)Cl_2(THF)_3]$	803	1.4×10^{-12}	D_{4d}	0	7
$[Ln(hfac)_3(NIT\text{-}Pyz)]_2$	53	1.85×10^{-7}	D_{4d}	0	8
$Dy(btfa)_3\cdot2H_2O$	95.4	2.8×10^{-8}	D_{4d}	0	9
$\{(H_3O)[Dy(NA)_2]\cdot H_2O\}n$	75	4.21×10^{-5}	D_{5h}		10
$[(^tBuPO(NH^iPr)_2)_2Dy(H_2O)_5][I]_3\cdot L_2\cdot(H_2O)$	651.0	5.63×10^{-12}	D_{5h}	0	11
$[Dy(CyPh_2PO)_2(H_2O)_5]Br_3\cdot2(CyPh_2PO)\cdot EtOH\cdot 3H_2O$	508	8.6×10^{-12}	D_{5h}	0	12
$[Dy(Bpen)(Cl)_3]$	22.4	3.72×10^{-6}	D_{5h}	800	13
$[Dy(Bpen)Cl(OPhCl_2NO_2)_2]$	85.8	4.65×10^{-7}	D_{5h}	100	13
$[Dy(Bpen)\ (OPhCl_2NO_2)_3]$	34.2	2.40×10^{-6}	D_{5h}	800	13
$[Dy(Bpen)(OPhNO_2)_3]$	26.8	1.12×10^{-6}	D_{5h}	800	13
$[(H_2L)Dy^{III}Cl_2]$	70	1.9×10^{-6}	D_{5h}	500	14
$[Dy(bbpen)Br]$	1025	4.21×10^{-12}	D_{5h}	2000	15
$[Dy(Cy_3PO)_2(H_2O)_5]Br_3\cdot2(Cy_3PO)\cdot2H_2O\cdot2EtOH$	543	2.0×10^{-10}	D_{5h}	0	16
$[Dy(Cy_3PO)_2(H_2O)_5]Cl_3\cdot(Cy_3PO)\cdot H_2O\cdot EtOH$	472	8.7×10^{-12}	D_{5h}	0	16
$[Dy(OtBu)_2(py)_5][BPh_4]$	1815	$1.170X\ 10^{-12}$	D_{5h}	0	17
$Dy(bpad)_3\cdot CH_3OH\cdot H_2O$	106.93	2.28×10^{-8}	C_{4v}	1200	18
$[DyH_4L_{RRRRRR}(SCN)_2](SCN)_2\cdot xCH_3OH\cdot yH_2O$	34.5	1.1×10^{-6}	C_{4V}	200	19
$[Dy(bbpen)(tpeCOOH)]\cdot2MeOH$	77	5.07×10^{-6}	D_{2d}	0	20
$[Dy(dbpy)(tcpb)_3]\cdot0.5(1,4\text{-dioxane})$	149.87	1.42×10^{-15}	D_{2d}	0	21
$[(Cp^{iPr5})Dy(Cp^*)]^+$	2217	$4.2(6)\times10^{-12}$	metallocene	0	22
$[(Cp^{ttt})_2Dy][B(C_6F_5)_4]$	1837	8.12×10^{-12}	metallocene	0	23
$[Dy(bbpen)(tpo)_2][BPh_4]$	944	$1.73(9)\times10^{-12}$	D_{4d}	0	24

References:

[1] Q. Q. Su, K. Fan, X. X. Jin, X. Da Huang, S. C. Cheng, L. J. Luo, Y. J. Li, J. Xiang, C. C. Ko, L. M. Zheng, and T. C. Lau, *Inorg. Chem. Front.*, 2019, 6, 1442-1452.

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