Supporting Information

Enhancing the Magnetic Anisotropy in Low Symmetric Dy-based Complexes by Tuning the Bond Length

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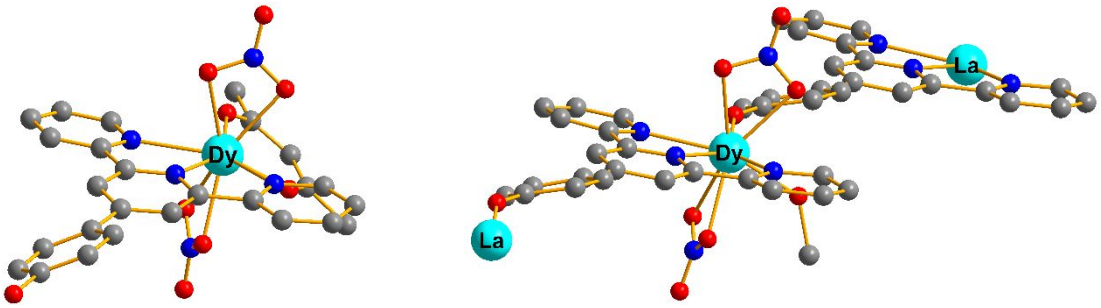
Table S1. Selected Bond Lengths (A) and Angles (deg) for **1**–**2**[a].

	1	**2**
Dy(1)–O(7)	2.257(6)	2.149(17)
Dy(1)–O(8)	2.281(6)	2.383(19)
Dy(1)–O(1)	2.422(7)	2.47(2)
Dy(1)–O(4)	2.467(7)	2.475(19)
Dy(1)–O(2)	2.492(7)	2.536(17)
Dy(1)–O(5)	2.529(7)	2.549(18)
Dy(1)–N(1)	2.491(8)	2.539(18)
Dy(1)–N(2)	2.533(7)	2.545(17)
Dy(1)–N(3)	2.496(8)	2.524(19)
O(1)–Dy(1)–O(2)	51.8(2)	50.7(6)
O(1)–Dy(1)–O(4)	148.4(2)	143.7(6)
O(1)–Dy(1)–O(5)	136.5(2)	146.3(6)
O(1)–Dy(1)–N(1)	73.0(3)	85.0(7)
O(1)–Dy(1)–N(2)	78.8(2)	72.6(5)
O(1)–Dy(1)–N(3)	95.6(3)	76.7(6)
O(2)–Dy(1)–O(5)	145.6(2)	147.4(7)
O(2)–Dy(1)–N(2)	108.1(2)	108.2(6)

O(2)–Dy(1)–N(3)	72.0(2)	124.5(6)
O(4)–Dy(1)–O(2)	146.5(2)	141.9(6)
O(4)–Dy(1)–O(5)	50.7(2)	50.3(7)
O(4)–Dy(1)–N(1)	86.7(2)	76.6(6)
O(4)–Dy(1)–N(2)	70.6(2)	71.3(6)
O(4)–Dy(1)–N(3)	78.2(2)	90.4(6)
O(5)–Dy(1)–N(2)	106.2(2)	104.4(6)
O(8)–Dy(1)–O(1)	82.7(2)	130.0(6)
O(8)–Dy(1)–O(2)	78.4(2)	79.4(6)
O(8)–Dy(1)–O(4)	120.7(2)	76.9(6)
O(8)–Dy(1)–O(5)	71.6(2)	76.3(6)
O(8)–Dy(1)–N(1)	86.5(2)	78.8(6)
O(8)–Dy(1)–N(2)	149.0(2)	135.6(6)
O(8)–Dy(1)–N(3)	143.0(2)	147.1(6)
N(1)–Dy(1)–O(2)	123.9(3)	69.9(6)
N(1)–Dy(1)–O(5)	71.0(2)	125.0(7)
N(1)–Dy(1)–N(2)	64.5(2)	64.4(6)
N(1)–Dy(1)–N(3)	128.5(2)	128.0(6)
N(3)–Dy(1)–O(5)	126.1(2)	72.3(6)
N(3)–Dy(1)–N(2)	64.1(2)	63.8(6)
O(7)–Dy(1)–O(8)	76.5(2)	–
O(7)–Dy(1)–N(1)	145.8(3)	–
O(7)–Dy(1)–N(2)	133.8(2)	–
O(7)–Dy(1)–N(3)	77.7(2)	–
O(7)–Dy(1)–O(5)	75.5(2)	–
O(7)–Dy(1)–O(1)	132.2(2)	–
O(7)–Dy(1)–O(2)	81.8(2)	–
O(7)–Dy(1)–O(4)	77.2(2)	–
O(7)$^{\#1}$–Dy(1)–O(8)	–	83.7(7)
O(7)$^{\#1}$–Dy(1)–N(1)	–	144.7(6)
O(7)$^{\#1}$–Dy(1)–N(2)	–	140.7(6)
O(7)$^{\#1}$–Dy(1)–N(3)	–	81.0(6)
O(7)$^{\#1}$–Dy(1)–O(5)	–	79.1(7)
O(7)$^{\#1}$–Dy(1)–O(1)	–	83.2(7)
O(7)$^{\#1}$–Dy(1)–O(2)	–	76.9(6)
O(7)$^{\#1}$–Dy(1)–O(4)	–	128.6(7)

[a] Symmetry codes for **2**: $^{\#1}$ $x, y, z - 1$.



1 **2**

Figure S1. Calculated structures of complexes **1** and **2**; H atoms are omitted.

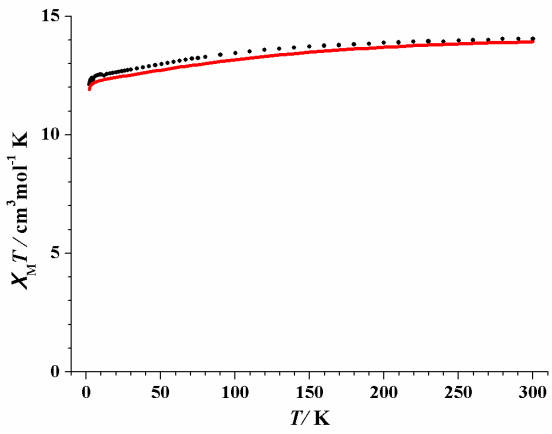


Figure S2. Calculated (red solid line) and experimental (circle dot) data of magnetic susceptibility of complex **2**. The intermolecular interaction zJ' of **2** was fitted to 0.01cm^{-1}.

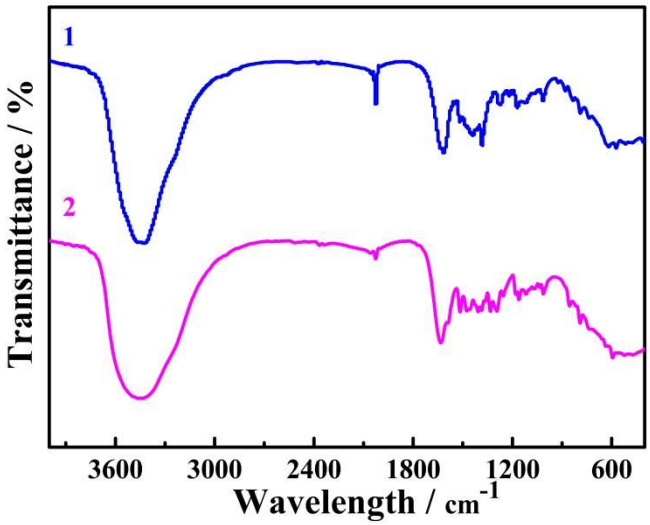


Figure S3. FT-IR spectra for **1**−**2**.

Table S2. Calculation of the Agreement Between the Coordination Polyhedron of Dy^{III} in **1** and **2** with Various Ideal Polyhedra Using the SHAPE Program.*

Ideal polyhedron geometry	MFF-9 (C_s)	CSAPR-9 (C_{4v})	JCSAPR-9 (C_{4v})	TCTPR-9 (D_{3h})
Agreement factor for Dy^{III} in **1**	1.764	2.150	2.809	2.931
Agreement factor for Dy^{III} in **2**	1.613	1.838	2.693	2.412

* MFF = Muffin; CSAPR = Spherical capped square antiprism; JCSAPR = Capped square antiprism J10; TCTPR = Spherical tricapped trigonal prism.

Table S3. Hydrogen-Bonding Parameters (A, deg) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
O9—H9···O6	0.82	2.03	2.8376(3)	167
C3—H3···O4	0.93	2.45	3.2066(3)	128

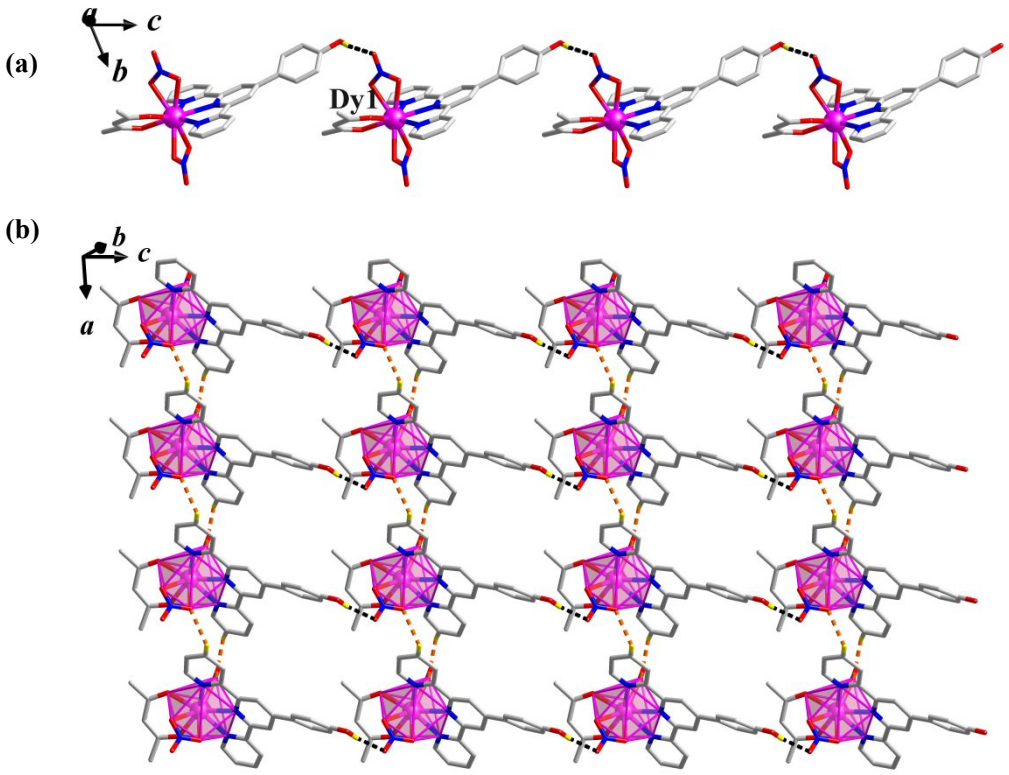


Figure S4. 1D supramolecular chain (a) and 2D sheet (b) of **1** extended by different hydrogen-bondings.

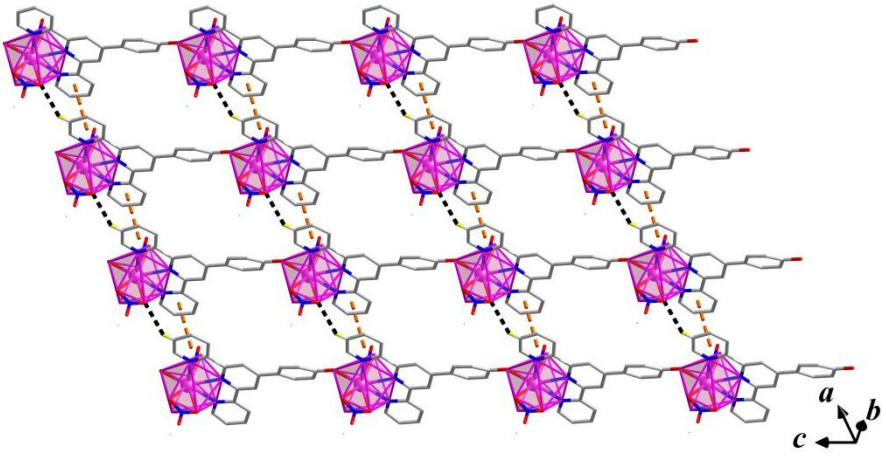


Figure S5. 2D supramolecular sheet of **2** expanded by hydrogen-bonding and π···π stacking interactions.

Table S4. Hydrogen-Bonding Parameters (A, deg) for **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
C14—H14···O1	0.93	2.58	3.3887(13)	145

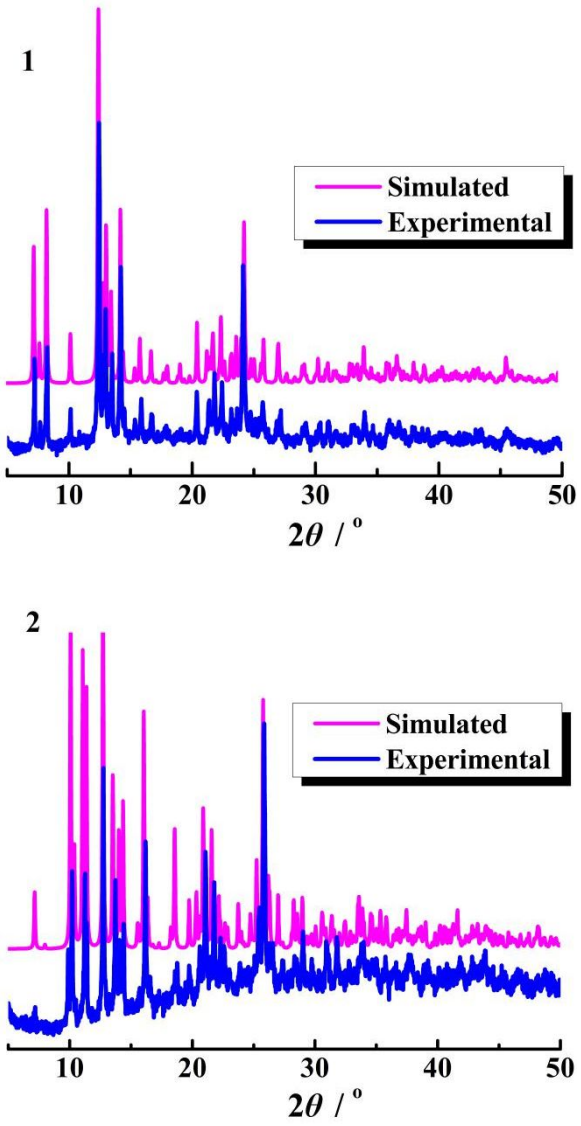


Figure. S6 Simulated and experimental PXRD patterns for **1**−**2**.

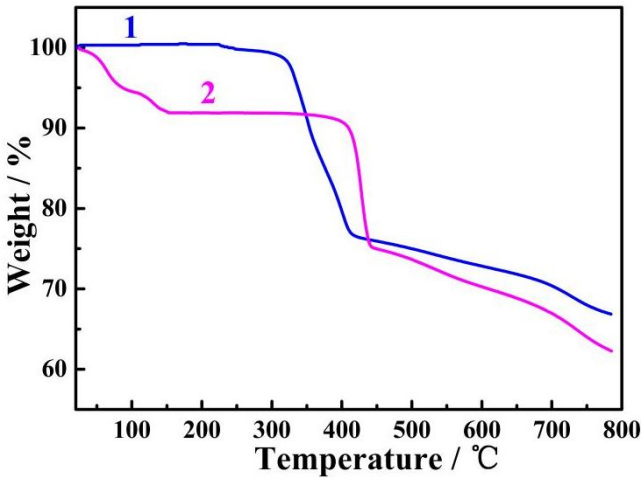


Figure. S7 TG curves for **1** and **2**.

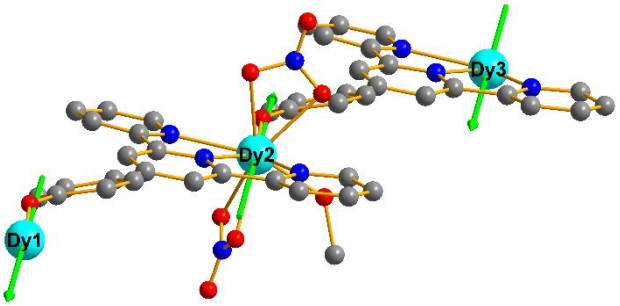


Figure S8. Calculated orientations of the local main magnetic axes of the ground Kramers doublet on neighboring Dy^{III} ions of complex **2**.

Table S5. Fitted Exchange Coupling Constant J_{exch} (cm^{-1}), the Calculated Dipole-Dipole Interaction J_{dip} (cm^{-1}) and the Total J_{total} (cm^{-1}) Between Dy^{III} Ions in **2**. The Intermolecular Interaction zJ' of **2** was Fitted to 0.01 cm^{-1}.

2	J_{dip}	J_{exch}	J_{total}
	0.11	−0.75	−0.64

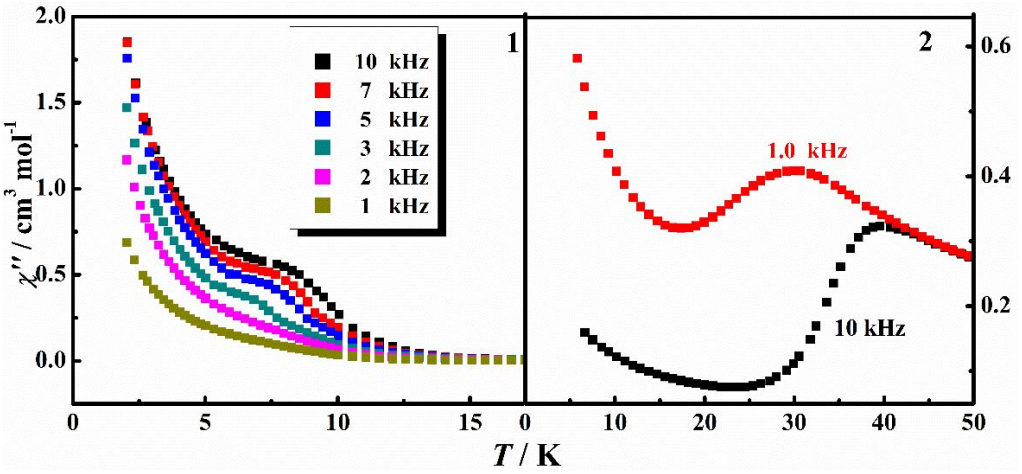


Figure S9. Temperature dependence of the out-of-phase ac susceptibilities for **1** (1.0 to 10 kHz) and **2** (1.0 kHz and 10.0 kHz) measured under 3.5 *ac* field with a zero *dc* field.

Table S6. Fitting Results for the Cole–Cole Plots of **1** to the Generalized Debye Model Under Zero Field.

T/ K	χ_S /cm^3 mol^{-1}	χ_T /cm^3 mol^{-1}	τ / s	α
2	6.53271	1.78182	2.27×10^{-5}	0.11622
2.5	5.23252	1.44205	2.14×10^{-5}	0.11356
3	4.3648	1.22732	2.05×10^{-5}	0.11164
3.5	3.7435	1.08054	1.96×10^{-5}	0.10996
4	3.27856	0.97596	1.87×10^{-5}	0.10847
4.5	2.91658	0.89052	1.77×10^{-5}	0.10699
5	2.62809	0.82787	1.70×10^{-5}	0.10413
5.5	2.39282	0.77232	1.62×10^{-5}	0.10218
6	2.19612	0.72051	1.55×10^{-5}	0.09978
6.5	2.02978	0.68047	1.48×10^{-5}	0.09473
7	1.88696	0.64526	1.40×10^{-5}	0.08806
7.5	1.76447	0.61063	1.31×10^{-5}	0.08162
8	1.65683	0.57609	1.18×10^{-5}	0.07306
8.25	1.60789	0.56004	1.11×10^{-5}	0.06847
8.5	1.56241	0.54159	1.04×10^{-5}	0.06433
8.75	1.52156	0.52168	9.49×10^{-6}	0.0627
9	1.48674	0.50323	8.61×10^{-6}	0.06451

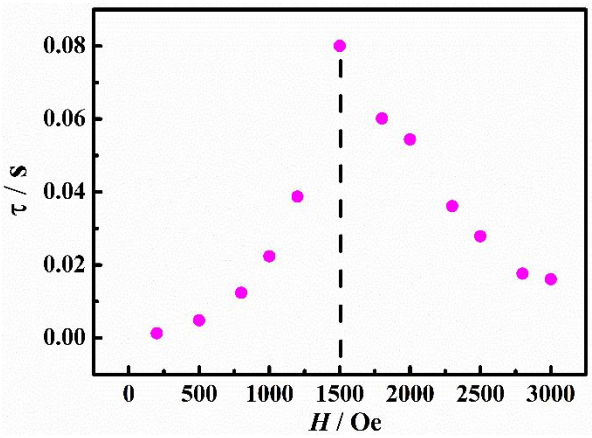


Figure S10. The dc field-dependence of the relaxation time for **2** at 2.0 K.

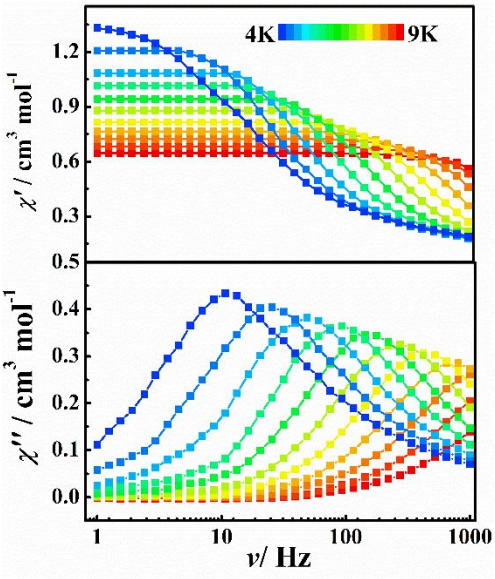


Figure S11. Frequency dependence of ac susceptibility measured under 1.5 kOe external field for complex **2**.

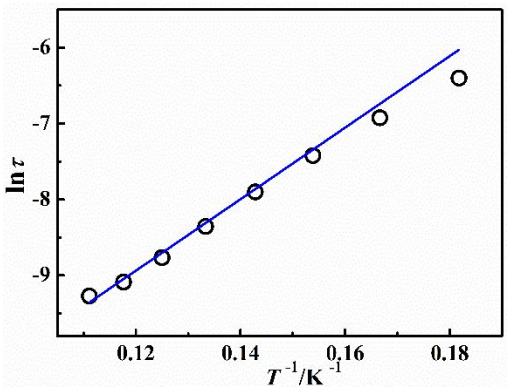


Figure S12. The plot of ln τ vs 1/T for **1** under 1.5 kOe dc field (the solid lines represent the best fits to Arrhenius law).

Table S7. Fitting Results for the Cole–Cole Plots of **2** to the Generalized Debye Model Under Zero Field.

T/ K	χ_S /cm^3 mol^{-1}	χ_T /cm^3 mol^{-1}	τ / s	α
6	2.23841	0.07958	5.98×10^{-4}	0.2323
7	1.91174	0.07326	5.45×10^{-4}	0.22958
8	1.66865	0.06809	5.04×10^{-4}	0.22688
9	1.47882	0.06373	4.71×10^{-4}	0.22352
10.0	1.41036	0.08367	4.19×10^{-4}	0.21995
11.0	1.2815	0.07919	3.97×10^{-4}	0.2149
12.0	1.17098	0.07636	3.73×10^{-4}	0.20588
14.0	0.99785	0.07186	3.26×10^{-4}	0.18437
16.0	0.86561	0.06818	2.77×10^{-4}	0.15884
18.0	0.76142	0.0648	2.29×10^{-4}	0.13181
20.0	0.68262	0.06228	1.87×10^{-4}	0.11052
22.0	0.61614	0.05794	1.49×10^{-4}	0.09247
24.0	0.5626	0.05383	1.16×10^{-4}	0.08042
26.0	0.5184	0.05082	8.76×10^{-5}	0.07411
28.0	0.48142	0.05024	6.41×10^{-5}	0.06887
30.0	0.44868	0.05141	4.41×10^{-5}	0.06212
32.0	0.42149	0.05259	2.80×10^{-5}	0.06325
34.0	0.39586	0.06082	1.68×10^{-5}	0.05877
36.0	0.37398	0.08064	1.01×10^{-5}	0.05086
38.0	0.35501	0.1048	6.13×10^{-6}	0.04686
40.0	0.33785	0.13468	3.91×10^{-6}	0.04432

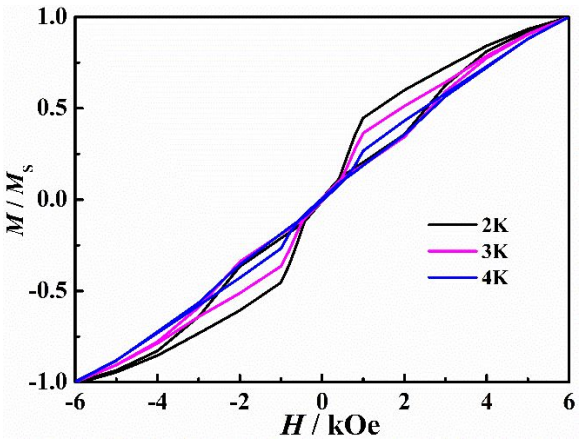


Figure S13. Magnetic hysteresis loops of **2** measured at a sweep rate of 200 Oe s^{-1}.

Table S8. Calculated Energy Levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) Tensors and m_J Values of the Lowest Kramers Doublets (KDs) of Individual Dy^{III} Fragments of Complexes **1** and **2**.

KDs	**1**				**2**			
	E/cm^{-1}	$\boldsymbol{g}$		m_J	E/cm^{-1}	$\boldsymbol{g}$		m_J
1	0.0	g_x	0.071	±15/2	0.0	g_x	0.004	±15/2
		g_y	0.125			g_y	0.006	
		g_z	19.494			g_z	19.785	
2	55.3	g_x	0.537	±13/2	254.5	g_x	0.070	±13/2
		g_y	0.733			g_y	0.118	
		g_z	17.644			g_z	16.733	
3	127.9	g_x	1.922	±11/2	379.3	g_x	0.501	±11/2
		g_y	3.477			g_y	0.721	
		g_z	12.463			g_z	13.864	
4	189.3	g_x	1.398	±7/2	436.0	g_x	0.489	±9/2
		g_y	4.427			g_y	1.805	
		g_z	11.337			g_z	10.558	
5	256.1	g_x	7.493	±9/2	491.4	g_x	8.101	±7/2
		g_y	5.602			g_y	5.924	
		g_z	1.126			g_z	3.119	
6	329.5	g_x	3.377	±5/2	524.4	g_x	1.809	±5/2
		g_y	5.133			g_y	3.981	
		g_z	10.094			g_z	13.555	
7	381.9	g_x	0.936	±3/2	574.2	g_x	0.277	±1/2
		g_y	1.823			g_y	0.519	
		g_z	15.366			g_z	16.647	
8	408.6	g_x	0.882	±1/2	664.7	g_x	0.054	±3/2
		g_y	4.114			g_y	0.142	
		g_z	15.166			g_z	19.303	

Table S9. Exchange Energies E (cm^{-1}), the Transversal Magnetic Moments Between Each Exchange Doublets Δ_t (μ_B) and the Main Values of the g_z for the Lowest Four Exchange Doublets of **2**.

	2		
	E	Δ_t	g_z
1	0.000	0.709×10^{-9}	19.785
2	0.300	0.352×10^{-8}	19.785
3	0.300	0.289×10^{-8}	19.785
4	0.600	0.224×10^{-9}	59.355

Table S10. The Included θ Angles of Main Magnetic Axes Between the Ground and Excited KDs of **1** and Individual Dy^{III} Fragment of **2**.

Complex	KD	θ/*degree*
1	1	0.0
	2	35.4
	3	7.2
	4	63.9
	5	75.3
	6	70.0
	7	76.6
	8	86.0
2	1	0.0
	2	4.2
	3	41.1
	4	24.2
	5	81.2
	6	71.8
	7	83.9
	8	84.0

Table S11. Calculated Crystal-field Parameters *B(k,q)* for **1** and Individual Dy^{III} Fragment of **2**.

k	*q*	**1**	**2**
	–2	0.4022	-0.2975×10^{1}
	–1	0.7107×10^{1}	−0.7041
2	0	-0.3874×10^{1}	-0.7116×10^{1}
	1	0.5057	0.4052
	2	0.3846×10^{1}	0.2784×10^{1}
	–4	0.1362×10^{-1}	-0.4025×10^{-2}
	–3	−0.1628	0.6678×10^{-1}
	–2	-0.3696×10^{-1}	-0.1436×10^{-1}
	–1	-0.3888×10^{-1}	-0.2754×10^{-1}
4	0	-0.5158×10^{-2}	-0.3522×10^{-1}
	1	−0.1510	-0.3191×10^{-2}
	2	0.6619×10^{-1}	-0.1013×10^{-1}
	3	–0.3882	−0.2366
	4	0.2640×10^{-1}	0.5967×10^{-1}
	–6	-0.4701×10^{-2}	0.4202×10^{-2}
	–5	0.1014×10^{-1}	-0.1134×10^{-1}
	–4	0.7257×10^{-3}	0.5961×10^{-3}
	–3	0.1023×10^{-1}	-0.2999×10^{-4}
	–2	-0.3666×10^{-4}	-0.3096×10^{-2}
	–1	0.2508×10^{-3}	0.3251×10^{-2}
6	0	-0.9280×10^{-4}	-0.2771×10^{-3}
	1	0.7924×10^{-3}	-0.4907×10^{-3}
	2	0.1339×10^{-4}	0.1714×10^{-2}
	3	0.6322×10^{-2}	0.1108×10^{-1}
	4	0.6081×10^{-2}	0.8870×10^{-3}
	5	-0.1921×10^{-1}	-0.1224×10^{-1}
	6	0.3677×10^{-3}	-0.7300×10^{-3}

Table S12. Natural Bond Order (NBO) Charges Per Atoms in the Ground State of Complexes **1** and **2** Calculated within CASSCF.

Atom	**1**	Atom	**2**
Dy1	2.505	Dy1	2.509
N1	−0.351	N1	−0.362
N2	−0.362	N2	−0.336
N3	−0.361	N3	−0.353
O1	−0.672	O1	−0.678
O2	−0.626	O2	−0.652
O4	−0.659	O4	−0.675
O5	−0.612	O5	−0.611
O7	−0.782	O7	−0.953
O8	−0.788	O8	−0.705

Table S13 In Wave Functions with Definite Projection of theTotal Moment | *JM* > for the Lowest Three Kramers Doublets (KDs) of the Dy^{III} for Complexes **1** and **2**.

	***E*/cm^{-1}**	**wave functions**
1	0.0	94.76%|±15/2>
	55.3	49.87%|±13/2>+16.74%|±11/2>+19.54%|±9/2>
	127.9	34.55%|±13/2>+29.05%|±11/2>+13.54%|±7/2>+10.86%|±5/2>
2	0.0	98.43%|±15/2>
	254.5	94.09%|±13/2>
	379.3	54.14%|±11/2>+12.03%|±1/2>