

Supporting Information for

**Switching the anisotropy barrier of a single-ion magnet by symmetry change from
quasi- D_{5h} to quasi- O_h**

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1. Synthetic Procedures and Experimental Techniques

Experimental Section

General Remarks:

All chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on an EQUINOX 55 spectrometer.

Synthesis of $[\text{Zn}_2\text{DyL}_2(\text{MeOH})\text{NO}_3\cdot 3\text{MeOH}\cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}_2\text{DyL}_2]\text{NO}_3\cdot \text{H}_2\text{O}$ (**2**)

A mixture of 5-bromo-salicylaldehyde (121 mg, 0.6 mmol), tris(2-aminoethyl)amine (29 mg, 0.2 mmol) and triethylamine (56 mg, 0.55 mmol) in methanol (20 mL) was stirred for 5 min, yielding an orange turbid liquid. NaBH_4 (30 mg, 0.8 mmol) was added to the solution. One hour later, the precipitate and the orange color disappeared. Then $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (46 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (59 mg, 0.2 mmol) was added, and the colorless solution was stirred for additional 10 min. After that the solution was filtered, and the filtrate was left standing at room temperature for evaporation. Colorless crystals available for single crystal diffraction were obtained overnight. Colorless crystals were obtained from the filtration in ~35 % yield based on 5-bromo-salicylaldehyde.

Complex **1** loses easily the solvent molecules and the coordinated methanol. The desolvated complex $[\text{Zn}_2\text{DyL}_2]\text{NO}_3\cdot \text{H}_2\text{O}$ (**2**) was obtained after placing sample **1** into dry air for 1 day. When immersing sample **2** into methanol for 1 day, **2** converted back to **1**.

Anal. Calc. (%) for **1**: N, 6.64; C, 36.70; H, 4.14; for **2**, N, 7.12; C, 36.65; H, 3.53. Found (%) for **1**_{as-synthesis}: N, 6.97; C, 36.10; H, 3.60; for **2**: N, 7.16; C, 36.64; H, 3.43; for **1**_{bath_in_MeOH}: N, 6.96; C, 36.49; H, 3.65.

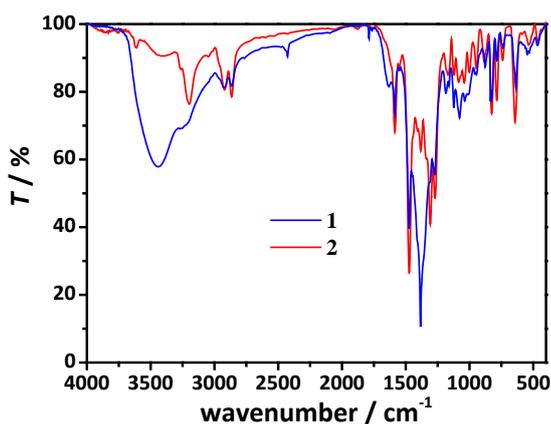


Figure S1. Infra-red spectra for **1** (blue) and **2** (red).

X-ray Crystallographic Study

Diffraction intensities were collected on a Rigaku R-Axis SPIDE IP diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) for **1** and **2** at 150 K. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. For **1**_{bath_in_MeOH}, the program SQUEEZE,¹ a part of the PLATON package of crystallographic software, was used to calculate the solvent area and remove its contribution to the overall intensity data. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms on organic ligands were generated by the riding mode.² CCDC reference numbers 924441 (**1**_{as-synthesis}), 924442 (**2**), and 924443 (**1**_{bath_in_MeOH}).

Magnetic measurements

Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID and a Quantum Design PPMS-XL9 VSM. Polycrystalline samples were embedded in vaseline to prevent torquing. Data were corrected for the diamagnetic contribution calculated using the Pascal constants.

1 P. van der Sluis, A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, 194.

2 a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112; b) G. M. Sheldrick, *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**.

2. Structure and Crystallographic Data

Table S1. Crystallographic Data and Structural Refinements for 1 and 2.

Compound	1_as-synthesis	2	1_bath_in_MeOH
Molecular formula	C ₅₈ H ₇₈ Br ₆ DyN ₉ O ₁₄ Zn ₂	C ₅₄ H ₆₂ Br ₆ DyN ₉ O ₁₀ Zn ₂	C ₅₈ H ₇₈ Br ₆ DyN ₉ O ₁₄ Zn ₂
Formula weight	1897.99	1769.83	1897.99
Temperature / K		150	
Radiation type		MoK _α	
Crystal system		orthorhombic	
Space group		<i>Pbca</i>	
<i>a</i> / Å	22.0395(5)	20.5186(14)	21.8930(15)
<i>b</i> / Å	16.0165(4)	16.4699(11)	15.9613(15)
<i>c</i> / Å	39.3819(7)	37.585(3)	39.306(3)
<i>V</i> / Å ³	13901.6(5)	12701.4(15)	13734.9(19)
<i>Z</i>		8	
<i>D</i> _{calcd} / g cm ⁻³	1.814	1.851	1.836
<i>μ</i> / mm ⁻¹	5.264	5.749	5.328
GOF	1.089	0.944	1.019
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)] ^(a)	0.0821	0.0725	0.0924
<i>wR</i> ₂ (all data) ^(b)	0.2339	0.1736	0.2621

$$^a)R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b)wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table S2. Selected bond lengths (Å) of Zn^{II} for 1 and 2.

	1_as-synthesis		2		1_bath_in_MeOH	
Zn1	Zn1—O2	2.124(7)			Zn1—O2	2.119(9)
	Zn1—O3	2.068(7)	Zn1—O3	2.069(7)	Zn1—O3	2.012(11)
	Zn1—N1	2.203(9)	Zn1—N1	2.292(9)	Zn1—N1	2.209(14)
	Zn1—N2	2.333(8)	Zn1—N2	2.080(9)	Zn1—N2	2.314(14)
	Zn1—N3	2.126(8)	Zn1—N3	2.090(9)	Zn1—N3	2.123(12)
	Zn1—N4	2.160(9)	Zn1—N4	2.109(8)	Zn1—N4	2.140(14)
Zn2	Zn2—O5	2.062(6)			Zn2—O5	2.081(10)
	Zn2—O6	2.115(7)	Zn2—O6	2.046(7)	Zn2—O6	2.278(12)
	Zn2—N5	2.260(8)	Zn2—N5	2.256(9)	Zn2—N5	2.227(13)
	Zn2—N6	2.269(8)	Zn2—N6	2.073(10)	Zn2—N6	2.278(15)
	Zn2—N7	2.168(8)	Zn2—N7	2.122(9)	Zn2—N7	2.133(14)
	Zn2—N8	2.136(8)	Zn2—N8	2.090(9)	Zn2—N8	2.134(11)

Table S3. The CShM values calculated by SHAPE 2.0 for 1 and 2.

	CN	Coordination Geometry	1_as-synthesis	2	1_bath_in_MeOH
Dy^{III}	7	pentagonal bipyramid (<i>D</i> _{5h})	0.610		0.660
		capped octahedron (<i>C</i> _{3v})	6.622		6.685
	6	octahedron (<i>O</i> _h)		1.879	
		trigonal prism (<i>D</i> _{3h})		10.325	
Zn^{II}	6	octahedron (<i>O</i> _h)	2.845-2.982		3.019-3.072
		trigonal prism (<i>D</i> _{3h})	8.820-9.267		8.627-9.352
	5	trigonal bipyramid (<i>D</i> _{3h})		0.963-1.023	
		square pyramid (<i>C</i> _{4v})		4.770-5.037	

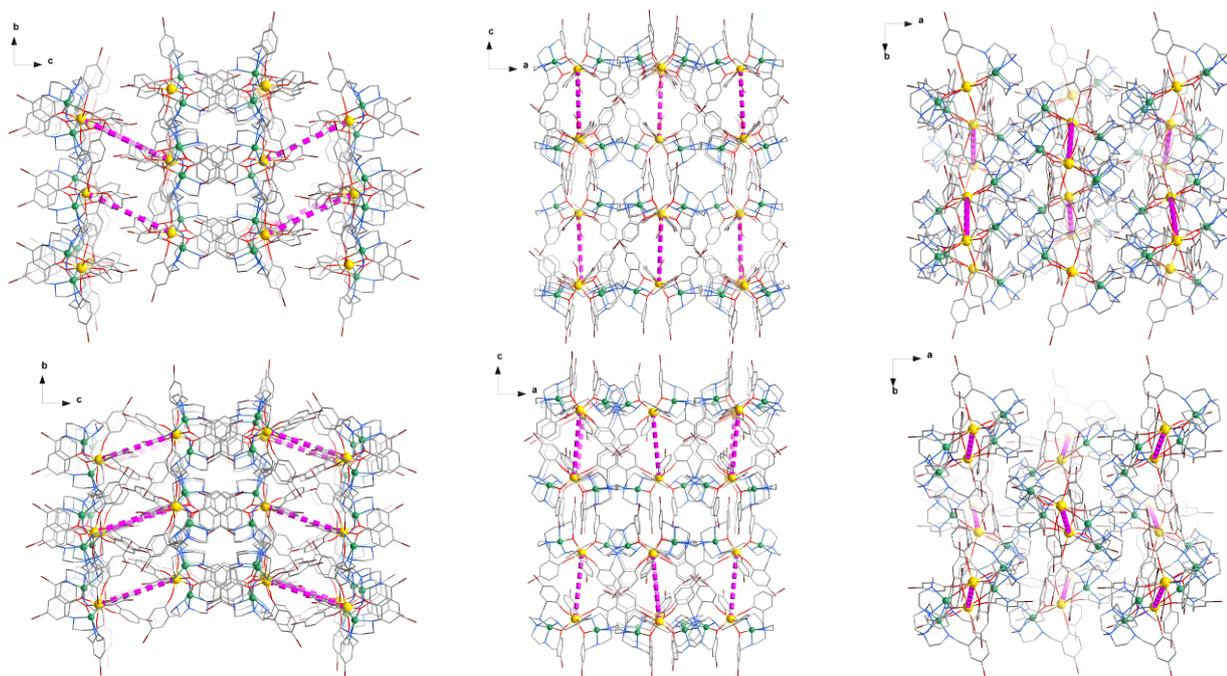


Figure S2. View along indicated axis for **1** (*top*) and **2** (*bottom*). The dash lines correspond the nearest neighboring [Zn-Dy-Zn] cores.

3. Plots of Magnetic Data

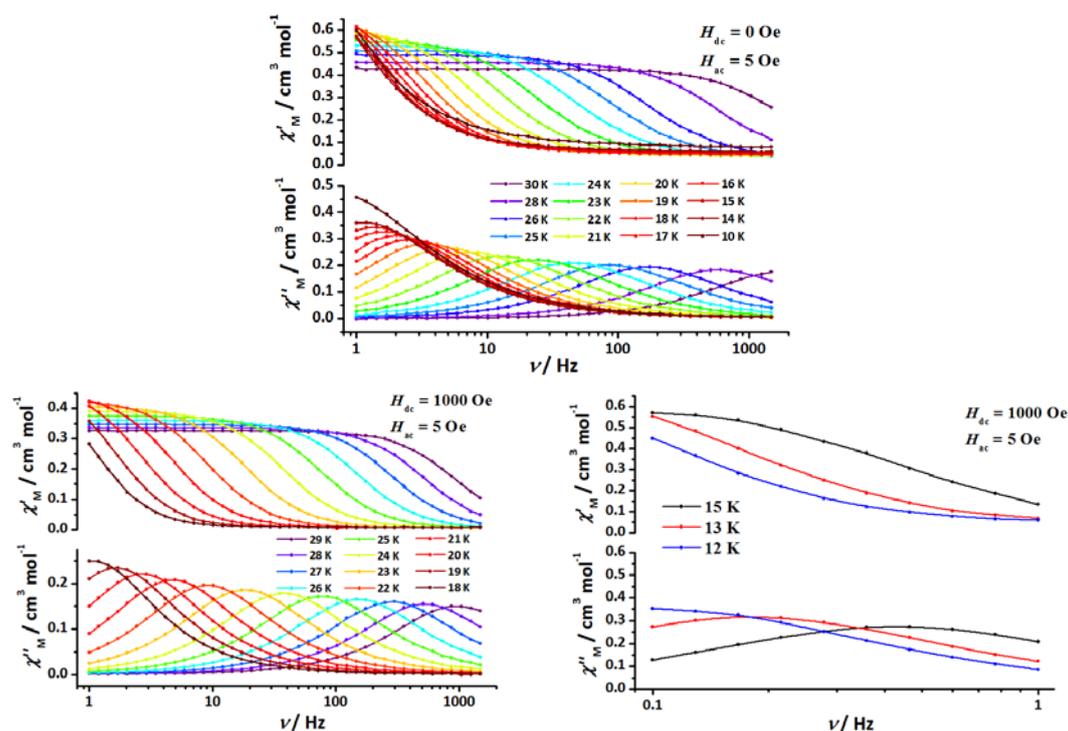


Figure S3. Plots of ac susceptibility vs. frequency at $H_{ac} = 5$ Oe, $H_{dc} = 0$ Oe (top) and $H_{ac} = 5$ Oe, $H_{dc} = 1000$ Oe (bottom), oscillating at 1–1488 Hz (left) and 0.1–1.0 Hz (right) for **1** at the indicated temperatures. The solid line is a guide for the eye.

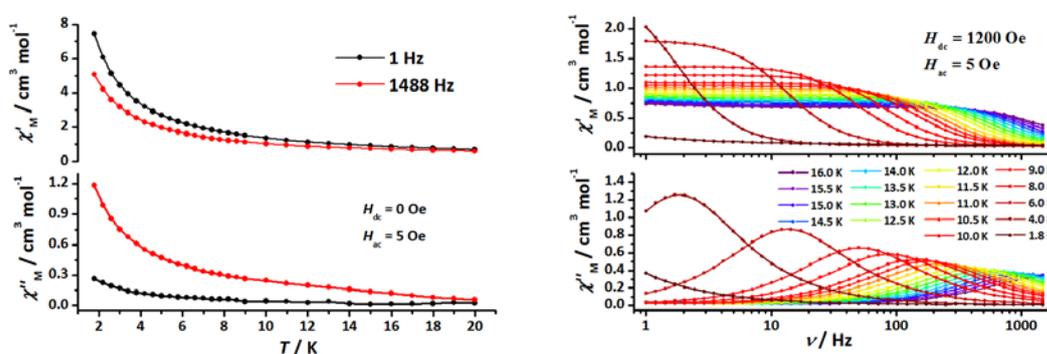


Figure S4. Left: Plot of ac susceptibility vs. temperature oscillating at 1 Hz and 1488 Hz at $H_{ac} = 5$ Oe and $H_{dc} = 0$ Oe for **2**. Right: Plot of ac susceptibility vs. frequency oscillating at 1–1488 Hz at $H_{ac} = 5$ Oe and $H_{dc} = 1200$ Oe in the temperature range of 1.8–16.0 K for **2**. The solid line is a guide for the eye.

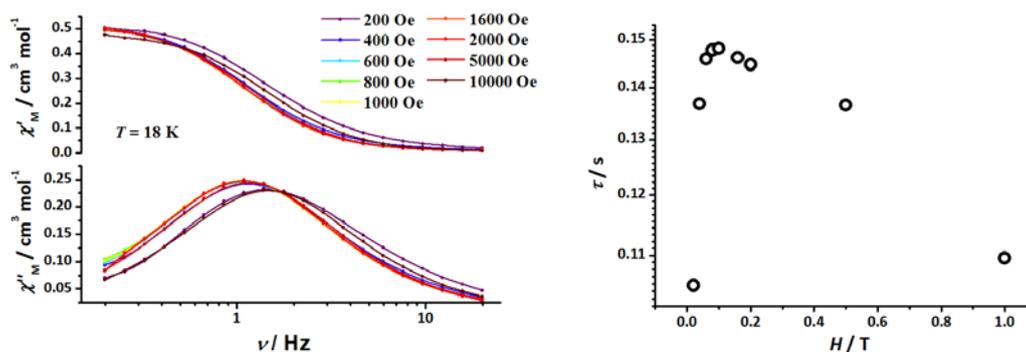


Figure S5. Left: Plot of ac susceptibility vs. frequency oscillating at 0.2–20 Hz at the indicated applied fields at 18 K for **1**; Right: Dc field dependence of the relaxation time at 18 K for **1**. The solid line is a guide for the eye.

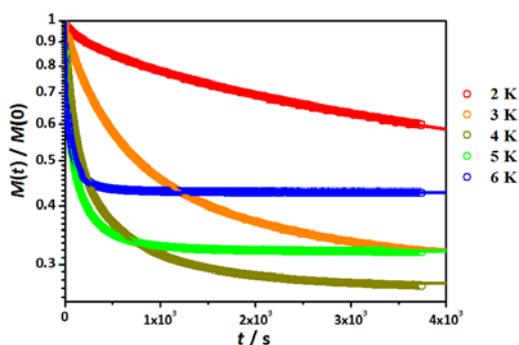


Figure S6. Plot of time vs. normalized magnetization used to derive relaxation times for **1** at the indicated temperatures. The measurements were first going from an initial field ($H_0 = 2$ T) to a final field ($H_f = 0.01$ T) and then measuring continuously for 3740 s. The obtaining data were fit to a function of $M(t) = M_f + (M_i - M_f) \exp[-(t/\tau)^\beta]$ (where τ is the relaxation time). The solid lines correspond to the best fit.

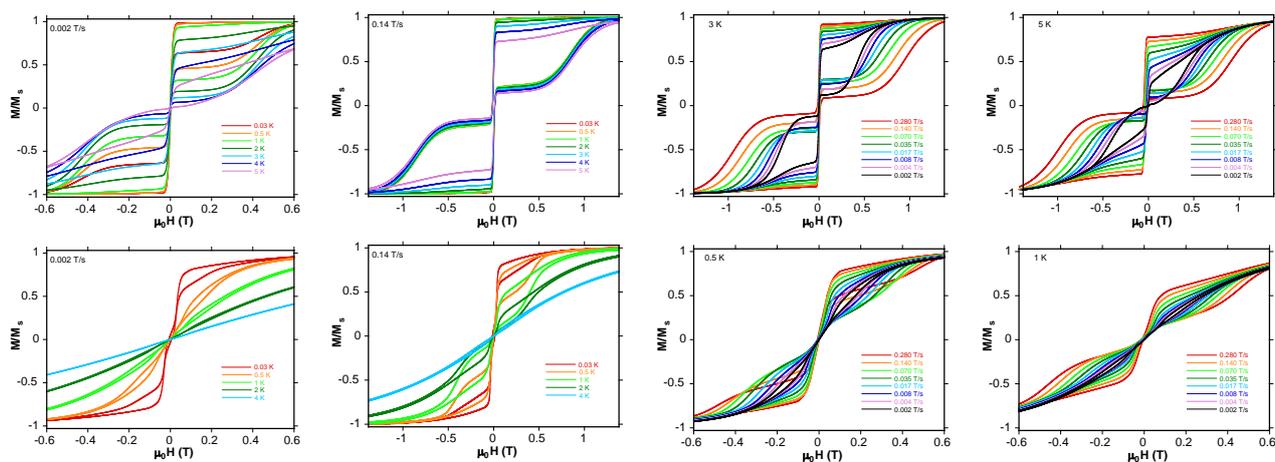


Figure S7. The normalized magnetization (M/M_s) vs applied dc field sweeps at the indicated sweep rates and temperatures on a micro-SQUID magnetometer for the single crystal samples of **1** (top) and **2** (bottom), applying the magnetic fields along the easy axis.

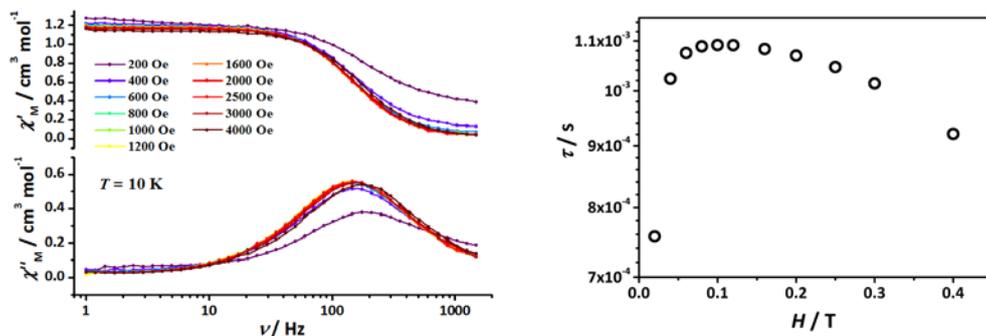


Figure S8. Left: Plot of ac susceptibility vs. frequency oscillating at 1–1488 Hz at the indicated applied fields at 10 K for **2**; Right: Dc field dependence of the relaxation time at 10 K for **2**. The solid line is a guide for the eye.

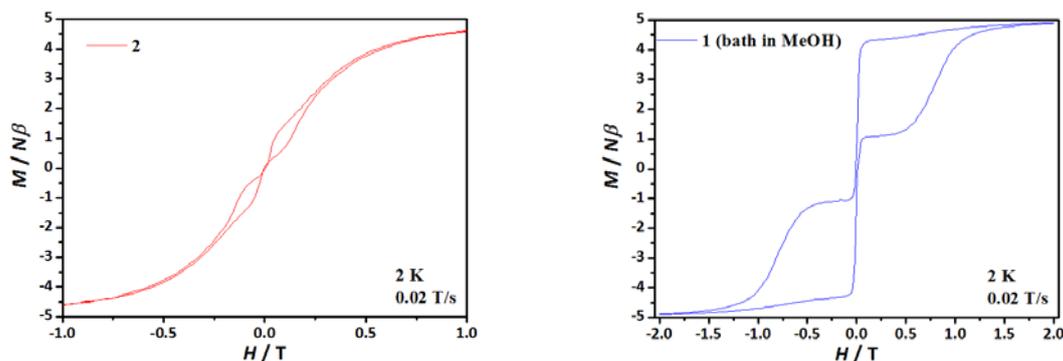


Figure S9. Hysteresis loop of the powder samples for **2** (left) and **1_bath_in_MeOH** (right) at 2 K at an average sweep rate of 0.02 T/s.

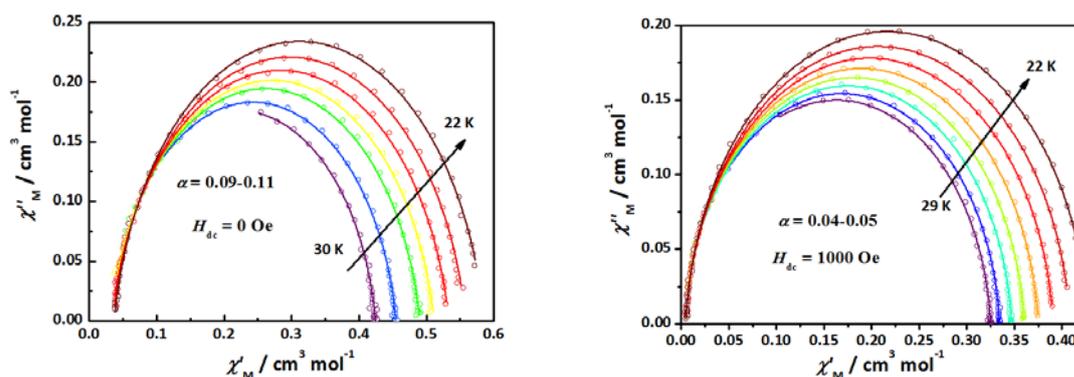


Figure S10. Cole-Cole plots in the temperature range of 22–30 K in the absence of dc field (*left*) and 22–29 K at an applied field of 1000 Oe (*right*) for **1**. The solid lines represent the best fitting of the experimental data to a generalized Debye model.

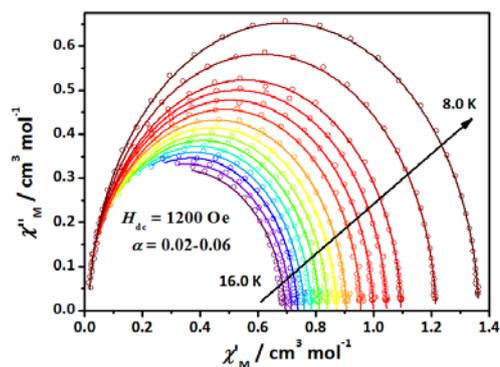


Figure S11. Cole-Cole plots in the temperature range of 8.0–16.0 K at an applied field of 1200 Oe for **2**. The solid lines represent the best fitting of the experimental data to a generalized Debye model.

4. Ab initio Calculations

4.1. Computational approximations

All calculations on individual magnetic centers were done with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type.

Active space of the CASSCF included 9 electrons in seven 4f orbitals of the Dy³⁺.

The spin-orbit coupling included the mixing of 21 sextets, 128 quartets and 130 doublet states.

The structure of the calculated ZnDyZn corresponded to the reduced molecule: all distant Br ions were computationally replaced by hydrogens.

Table S4. Contractions of the employed ANO-RCC basis sets in computational approximations A1 and A2.

Basis 1	Basis 2
Dy.ANO-RCC...7s6p4d3f1g.	Dy.ANO-RCC...8s7p5d4f2g1h.
Zn.ANO-RCC...5s4p2d1f.	Zn.ANO-RCC...6s5p3d2f1g.
O.ANO-RCC...3s2p1d.	O.ANO-RCC...4s3p2d1f.
N.ANO-RCC...3s2p.	N.ANO-RCC...3s2p.
C.ANO-RCC...3s2p.	C.ANO-RCC...3s2p.
H.ANO-RCC...2s.	H.ANO-RCC...2s.

4.2. Electronic and magnetic properties of the complex 1

Table S5. Energies of the lowest Kramers doublets (cm^{-1}) of the **1**.

Kramers doublets (cm^{-1})	
A1	A2
0.000	0.000
249.999	289.911
288.935	303.369
327.723	369.468
393.849	433.459
431.768	464.063
465.793	504.373
507.221	542.533
3693.196	3700.532
3805.307	3824.580
3840.879	3877.338
3874.903	3907.282
3903.351	3937.414
3938.065	3974.396
3967.669	4005.448
6290.088	6310.066
6322.762	6337.400
6349.579	6375.263
6394.256	6426.450
6436.612	6472.606
6484.442	6524.712
8243.094	8264.902
8292.177	8309.581
8311.152	8336.313
8374.429	8407.863
8425.451	8463.895
9779.002	9800.371
9823.888	9840.871
9884.202	9914.632
9947.189	9984.422
...	...

Table S6. Energies (cm^{-1}) and g tensors of the lowest Kramers doublets (KD) of the **1**.

KD		A1		A2	
		E	g	E	g
1	g_x		0.000151		0.000102
	g_y	0.000	0.000199	0.000	0.000130
	g_z		19.868853		19.870388
2	g_x		0.223162		0.382147
	g_y	249.999	0.405080	289.911	0.822461
	g_z		18.782700		18.052916
3	g_x		0.163439		0.195937
	g_y	288.935	0.226374	303.369	0.655172
	g_z		16.620541		16.021798
4	g_x		1.233534		1.122614
	g_y	327.723	1.381285	369.468	1.359527
	g_z		14.327818		14.730118
5	g_x		4.310371		4.173696
	g_y	393.849	6.235691	433.459	6.139064
	g_z		8.916654		9.366774
6	g_x		1.804588		1.722385
	g_y	431.768	2.299802	464.063	2.488901
	g_z		12.335452		12.449911
7	g_x		0.499558		0.659288
	g_y	465.793	0.574532	504.373	0.869183
	g_z		16.971749		16.714235
8	g_x		0.016579		0.067046
	g_y	507.221	0.066232	542.533	0.110423
	g_z		17.830754		17.783671

Table S7. Angles between the main magnetic axes of the lowest Kramers doublet of the **1** obtained in different computational approximations (degrees).

	A1	A2
A1	0.0000	0.1644

A2	0.1644	0.0000
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Table S8. Angles between the main magnetic axes of the lowest Kramers doublet and the shortest DyO bond (with oxygen O1 in the structure file).

	A1	A2
angle (degrees)	4.010	4.113

4.3. Electronic and magnetic properties of the complex 2

Table S9. Energies of the lowest Kramers doublets (cm^{-1}) of the **2**.

Kramers doublets (cm^{-1})	
A1	A2
0.000	0.000
280.973	294.832
317.244	330.498
391.938	413.581
469.732	491.751
548.650	560.210
679.746	710.061
801.661	838.492
3710.710	3716.203
3855.600	3868.110
3904.542	3919.332
3947.667	3960.477
3999.663	4015.906
4089.849	4115.254
4224.540	4257.823
6314.641	6327.223
6376.083	6381.395
6430.052	6442.443
6491.424	6506.225
6568.321	6589.481
6696.903	6727.364
8281.356	8293.628
8336.517	8340.988
8414.344	8428.794
8481.537	8498.611
8617.521	8644.851
9818.246	9829.654
9874.636	9878.756
9984.968	10000.785
10128.674	10154.212
...	...

Table S10. Energies (cm^{-1}) and g tensors of the lowest Kramers doublets (KD) of the **2**.

KD		A1		A2	
		E	g	E	g
1	g_x		0.014718		0.012148
	g_y	0.000	0.016509	0.000	0.013777
	g_z		19.759367		19.763169
2	g_x		2.240673		2.397632
	g_y	280.973	5.591768	294.832	6.713330
	g_z		12.968551		11.963338
3	g_x		8.781177		3.226131
	g_y	317.244	5.351794	330.498	5.286081
	g_z		1.809328		8.272749
4	g_x		0.399162		0.230993
	g_y	391.938	2.506125	413.581	2.370181
	g_z		14.051065		14.083157
5	g_x		9.536617		9.819921
	g_y	469.732	7.366826	491.751	6.507633
	g_z		2.138286		1.483853
6	g_x		2.122602		2.430646
	g_y	548.650	2.403658	560.210	3.218625
	g_z		15.486645		14.669848
7	g_x		0.450758		0.385514
	g_y	679.746	0.752029	710.061	0.603227
	g_z		16.383299		16.481817
8	g_x		0.081834		0.074725
	g_y	801.661	0.176593	838.492	0.149914
	g_z		19.031665		19.059782

Table S11. Angles between the main magnetic axes of the lowest Kramers doublet of the **2** obtained in different computational approximations (degrees).

	A1	A2
A1	0.0000	0.3794

A2	0.3794	0.0000
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Table S12. Angles between the main magnetic axes of the lowest Kramers doublet and the shortest DyO bond (with oxygen O1 in the structure file).

	A1	A2
angle (degrees)	4.198	4.320

4.4. *Ab initio* calculations on symmetrized models with D_{5h} and O_h symmetries

We have performed similar *ab initio* calculations of CASSCF/RASSI/SINGLE_ANISO type for two symmetrized complexes:

- $[Dy(OCH)_6]^{3-}$ having exact O_h symmetry;
- $[Dy(OCH)_7]^+$ having exact D_{5h} symmetry ;

We have obtained these models by cutting the Dy with the oxygens and carbons from the first and second coordination spheres. The neighbouring Zn atoms were removed, since the O-Zn bond is much weaker than O-C bond. The ligand comes usually with a small negative charge, therefore we have added one electron per O-C bond, and in order to compensate the charge on the ligand, we added one H connected to the C atom.

For the O_h model the Dy-O bonds were set to the average value 2.26050 Å, O-C was set to 1.33758 Å.

For the D_{5h} model two Dy-O distances were set: the axial Dy-O was 2.20785 Å, while the equatorial Dy-O was 2.393594 Å. All seven O-C bonds were set to 1.35823 Å.

All O-H bonds were set to 1.0700 Å for both symmetrized models.

We have employed the Basis 2 (Table S4) for all atoms of these models.

Table S13. Energies of the low-lying Kramers doublets and the corresponding *ab initio* calculated parameters of the crystal field B_q^k for the idealized crystal environment (D_{5h} and O_h).

B_q^k parameters		Ab initio energies (cm^{-1})	
Model D_{5h}	Model O_h	Model D_{5h}	Model O_h
$B_2^0 = -0.181E+01$	---	0.000	0.000
		199.197	23.278
		302.577	23.278
		336.718	148.678
		352.689	264.106
$B_4^0 = -0.829E-02$	$B_4^0 = -0.968E-02$ $B_4^4 = -0.485E-01$	390.487	264.106
		431.267	339.523
		434.446	339.523
		g tensor of the ground Kramers doublet	
$B_6^0 = 0.235E-04$	$B_6^0 = 0.955E-05$ $B_6^4 = -0.198E-03$	$g_x = 0.00$	$g_x = 6.582$
		$g_y = 0.00$	$g_y = 6.582$
		$g_z = 19.886$	$g_z = 6.582$