Supplementary Information

Symmetry Supported Magnetic Blocking at 20 K in the Pentagonal Bipyramidal Dy(III) Single-Ion Magnets

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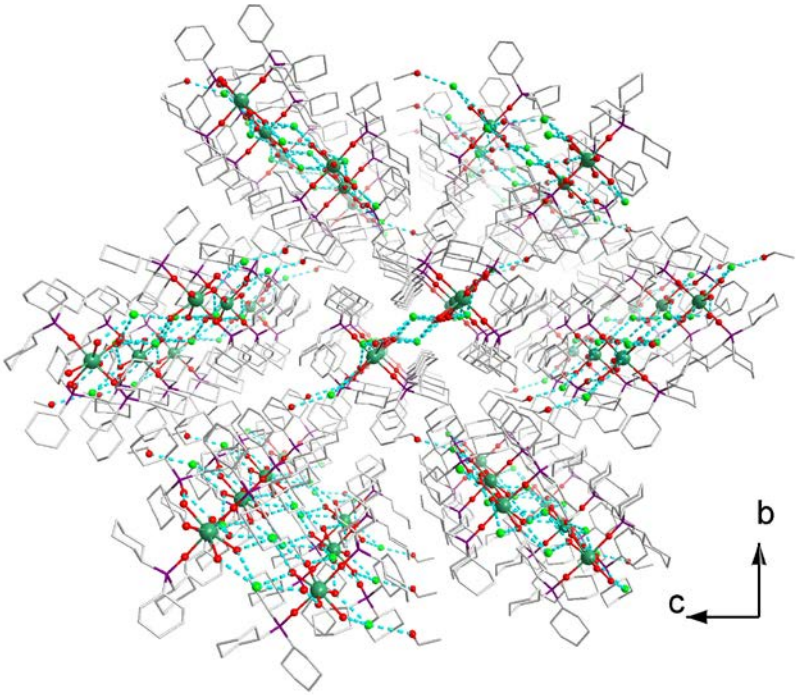

Figure S1. Crystal Structure of 1 viewed along the *a* axis. The dashed lines represent the intermolecular hydrogen bonds. H atoms are omitted for clarity. Color Codes: Dy, cyan; P, purple; Cl, green; O, red; C, gray; H, light gray.

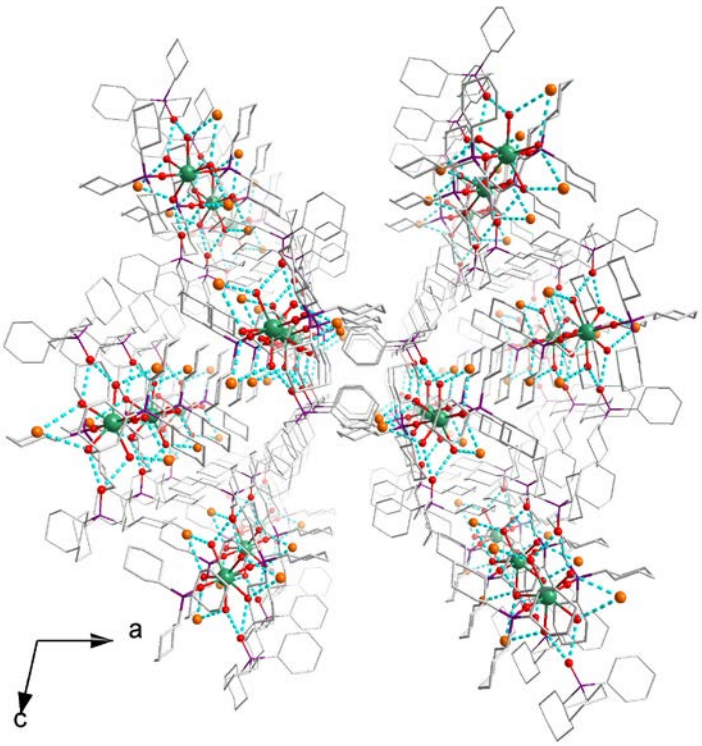

Figure S2. Crystal Structure of 2 viewed along the *b* axis. The dashed lines represent the intermolecular hydrogen bonds. H atoms are omitted for clarity. Colour Codes: Dy, cyan; P, purple; Br, orance; O, red; C, gray; H, light gray.

Table S1. Continuous Shape Measures calculations (CShM) for **1** and **2**.[a]

Complex	HP-7 (D_{7h})	HPY-7 (C_{6v})	PBPY-7 (D_{5h})	COC-7 (C_{3v})	CTPR-7 (C_{2v})	JPBPY-7 (D_{5h})	JETPY-7 (C_{3v})
1	34.017	24.503	0.239	7.576	5.906	2.833	22.8
2	34.004	25.379	0.142	7.752	5.809	2.642	24.233

HP-7 = Heptagon; HPY-7 = Hexagonal pyramid; PBPY-7 = Pentagonal bipyramid; COC-7 = Capped octahedron; CTPR-7 = Capped trigonal prism; JPBPY-7 = Johnson pentagonal bipyramid J13; JETPY-7 = Johnson elongated triangular pyramid J7.

[a] (a) Alvarez, S.; Alemany, P.; Casanova, D.; Cirera, J.; Llunell, M.; Avnir, D. *Coord. Chem. Rev*., **2005**, *249*, 1693-1708; (b) Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. *Chem. Eur. J*., **2005**, *11*, 1479-1494.

Table S2. Crystal Data and Structural Refinements for **1** and **2**.

Complex	**1**	**2**
Chemical formula	$C_{56}H_{117}Cl_3DyO_{10}P_3$	$C_{72}H_{142}Br_3DyO_9P_4$
Formula Mass	1312.26	1677.97
Crystal system	Monoclinic	Monoclinic
a /Å	11.7472(5)	40.4082(15)
b/Å	29.5882(11)	14.2356(7)
c/Å	19.4338(8)	33.0134(14)
β/°	97.434(2)	102.6630(10)
Unit cell volume/Å^3	6698.0(5)	18528.5(14)
Temperature/K	150(2)	150(2)
Space group	$P2_1/n$	$C2/c$
No. of formula units per unit cell, *Z*	4	8
Radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
Absorption coefficient, μ/mm^{-1}	1.356	2.213
No. of reflections measured	40418	59069
No. of independent reflections	12926	18082
R_{int}	0.1189	0.0747
R_1 [a] ($I > 2\sigma(I)$)	0.0605	0.0545
wR_2 [b] (all data)	0.1324	0.1342
Goodness of fit on F^2	1.018	1.064

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S3. Crystal Data and Structural Refinement for **1**@Y and **2**@Y.

Complex	**1**@Y	**2**@Y
Chemical formula	$C_{56}H_{117}Cl_3Dy_{0.05}O_{10}P_3Y_{0.95}$	$C_{72}H_{142}Br_3Dy_{0.05}O_9P_4Y_{0.95}$
Formula Mass	1242.35	1608.06
Crystal system	Monoclinic	Monoclinic
a /Å	11.7525(8)	40.347(3)
b/Å	29.615(2)	14.3228(11)
c/Å	19.4336(15)	33.253(2)
β/°	97.389(2)	102.448(2)
Unit cell volume/Å^3	6707.8(9)	18764(2)
Temperature/K	150(2)	150(2)
Space group	$P2_1/n$	$C2/c$
No. of formula units per unit cell, *Z*	4	8
Radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
Absorption coefficient, μ/mm^{-1}	1.122	2.019
No. of reflections measured	41947	62011
No. of independent reflections	12943	18323
R_{int}	0.0925	0.1048
R_1 [a] ($I > 2\sigma(I)$)	0.0569	0.0596
wR_2 [b] (all data)	0.1476	0.1457
Goodness of fit on F^2	1.063	0.978

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

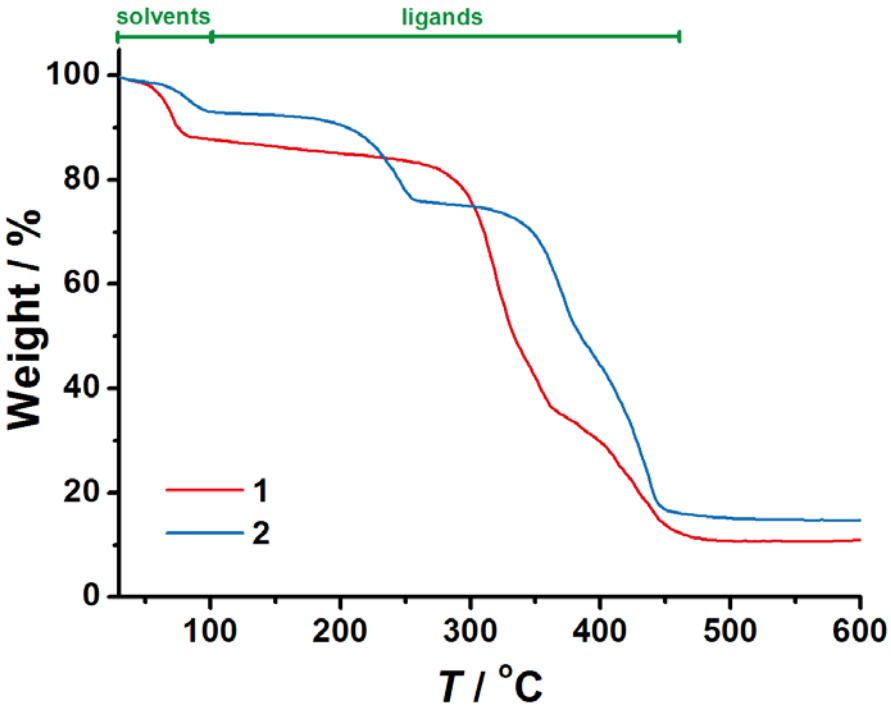

Figure S3. Thermogravimetric analysis of 1 (red) and 2 (blue) under N_2 atmosphere.

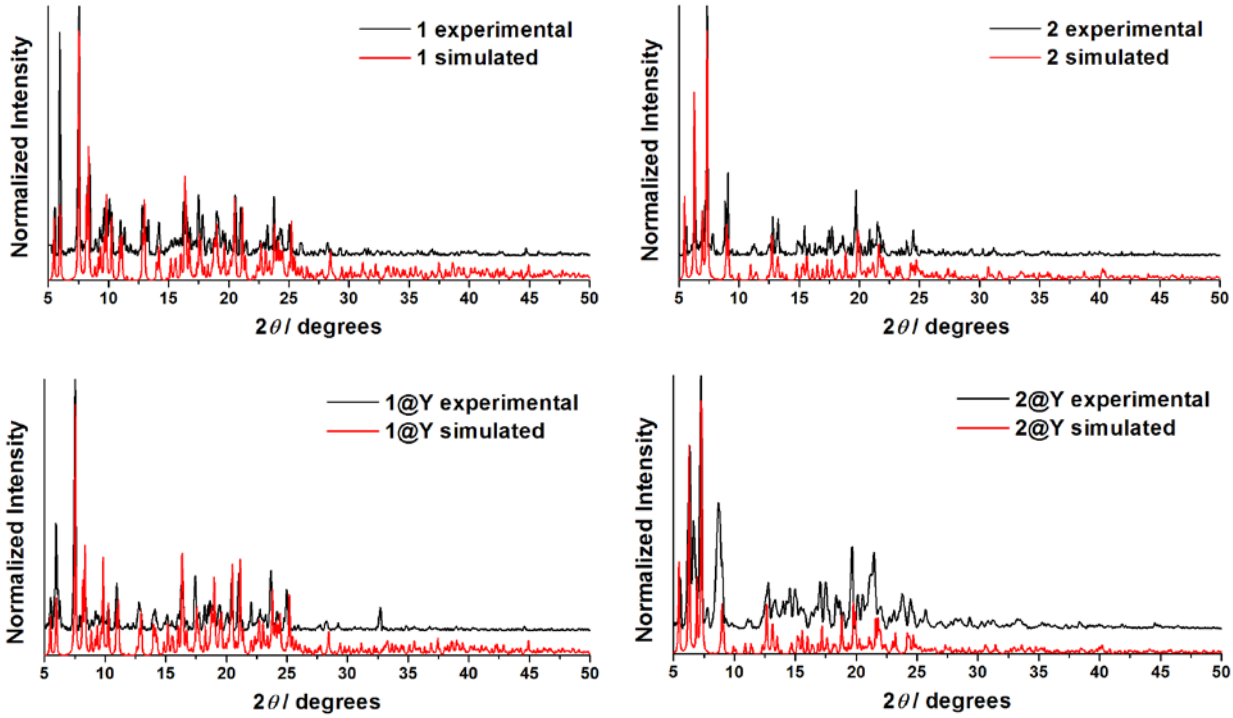

Figure S4. PXRD patterns of 1, 2, 1@Y and 2@Y compared with the simulated pattern from the single crystal structure.

2. Magnetic Characterization

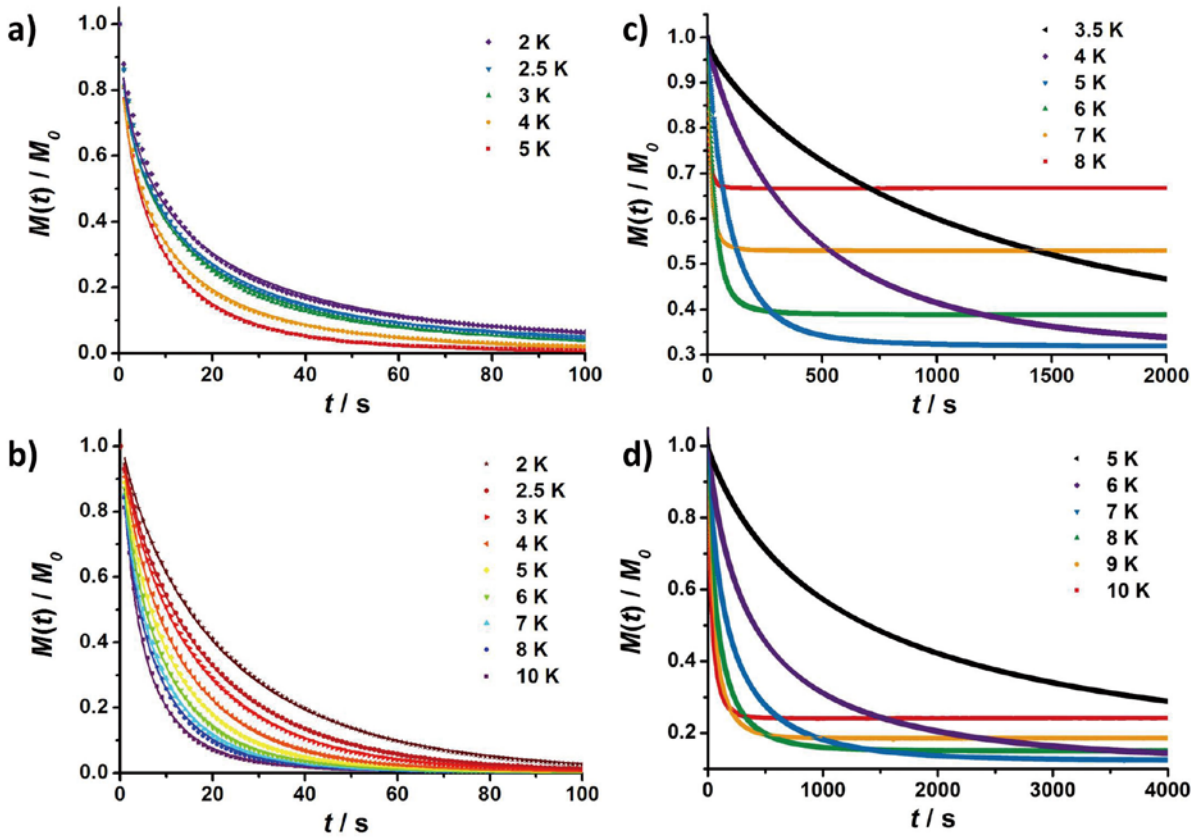

Figure S5. DC relaxation of 1 (a, c) and 2 (b, d) with the final field of 0 Oe (a, b) and 1 kOe (c, d). The magnetizations are plotted as normalized to M_0 (the starting value at t = 0) for clarity. The solid lines are the best fit to the exponential decay as $M(t) = M_f + (M_f - M_0) \exp[(-t/\tau)^{\beta}]$, where τ is the relaxation time. Note the different scale of the time axis (x).

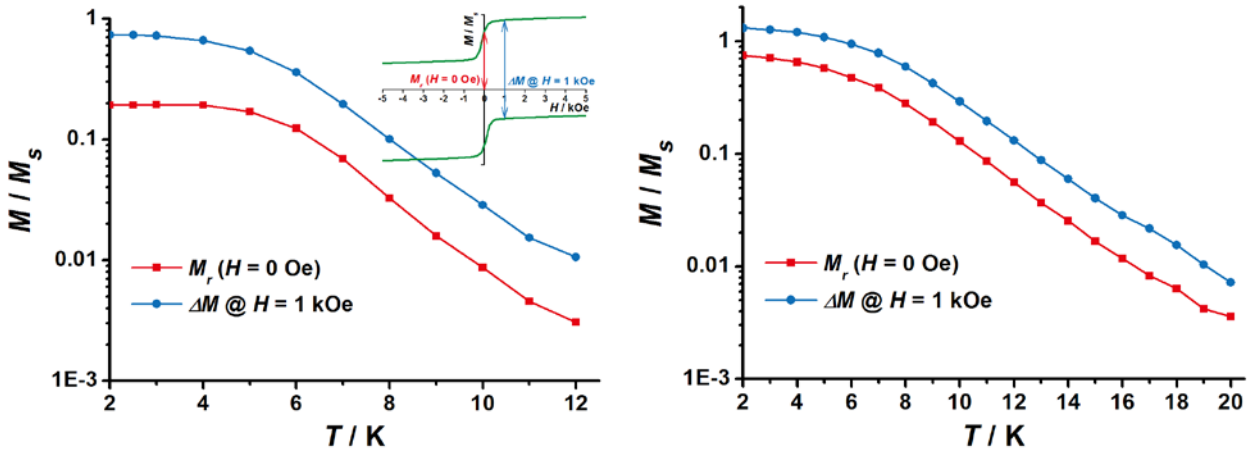

Figure S6. Temperature dependence of the remnant magnetization (M_r) at H = 0 Oe and the opening of the hysteresis loops (ΔM) at H = 1 kOe for 1 (left) and 2 (right). The magnetizations are normalized to the saturated magnetization (M_s) and the inset shows the schematic explanation of these two parameters. All lines are guides to the eyes.

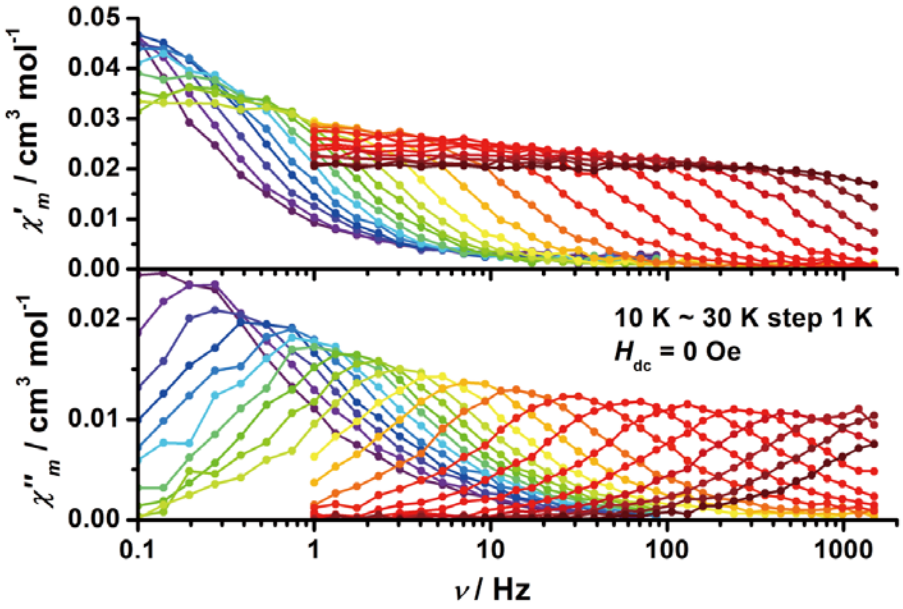

Figure S7. Frequency dependence of the alternating-current molar magnetic susceptibilities for 1@Y in zero dc field. Lines are guides to the eyes.

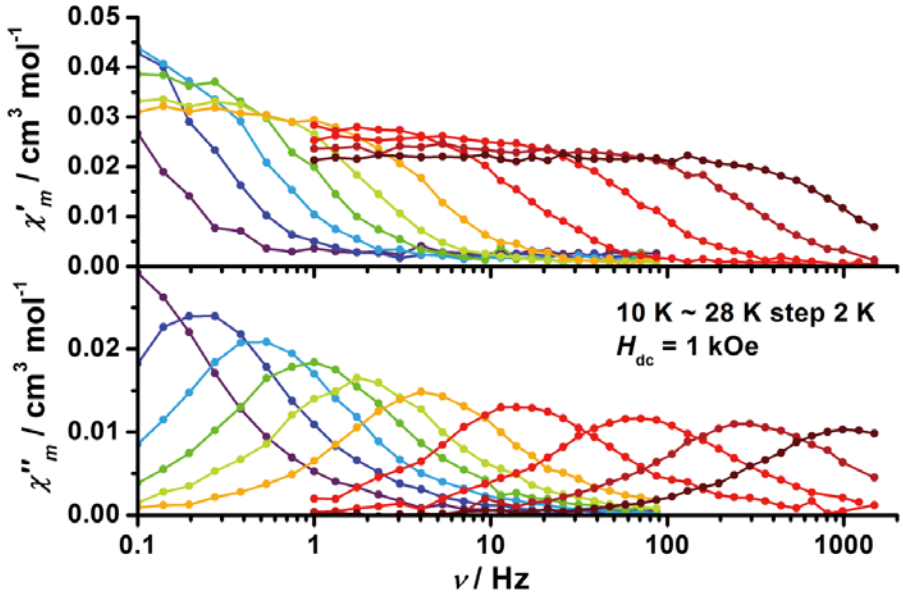

Figure S8. Frequency dependence of the alternating-current molar magnetic susceptibilities for 1@Y in 1 kOe dc field. Lines are guides to the eyes.

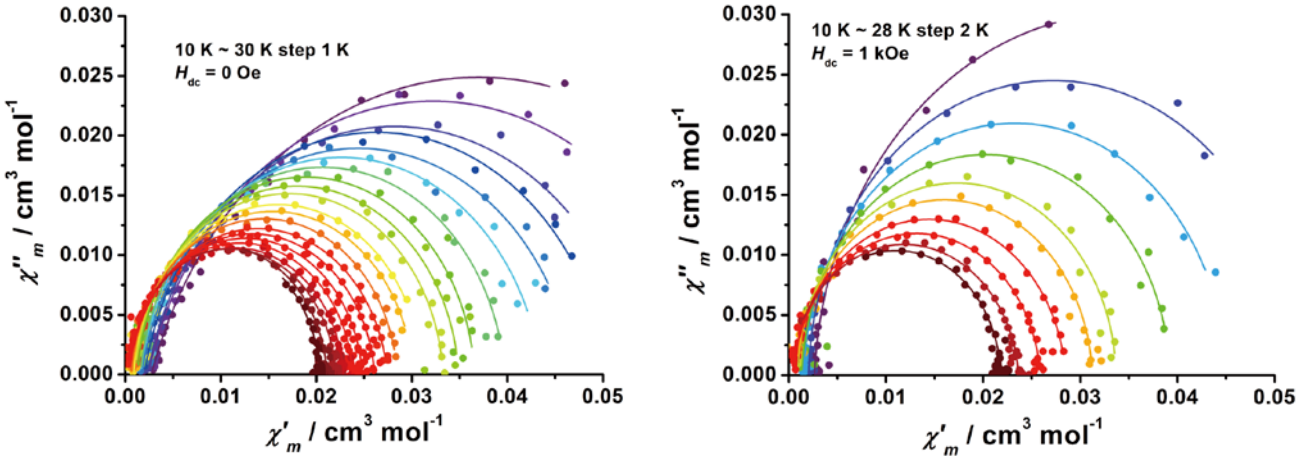

Figure S9. Cole-Cole plots for the ac susceptibilities for 1@Y in zero dc field (left) and in 1 kOe dc field (right). The solid lines are the best fit to the Debye's law.

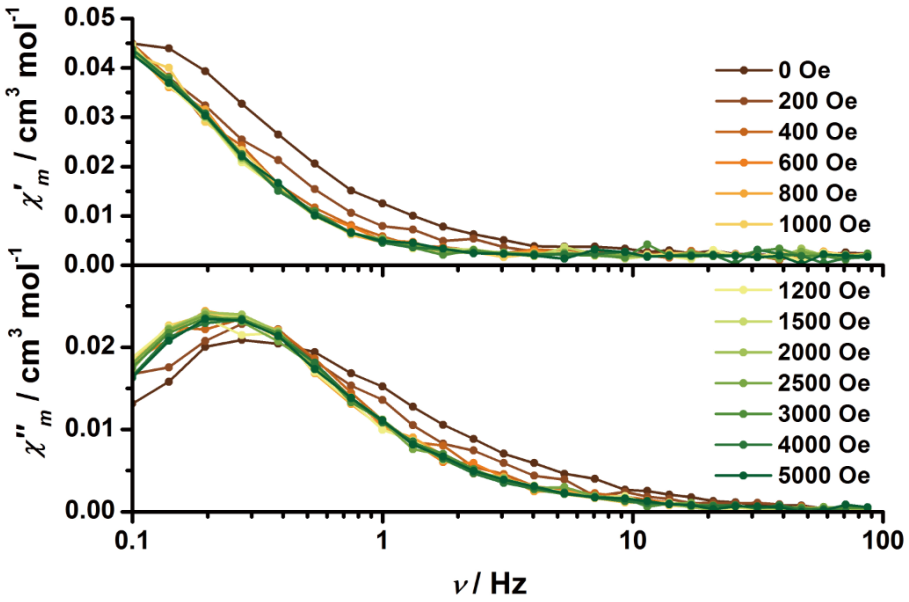

Figure S10. Field dependence of the alternating-current molar magnetic susceptibilities for 1@Y at 12 K. Lines are guides to the eyes.

3. Ab Initio Calculations

Table S4. Spin-orbital energies and corresponding ***g*** tensors of the **2-no-water** model system (The structure of the model compound **2-no-water** is identical to the structure of **2,** in which the five coordinated water molecules of the Dy site were removed from the *ab initio* calculations (vide infra) while all bromide counter-ions and Cy_3PO ligands were present.). Note the large excitation energies and the very small values of the g_X and g_Y of the four low-lying Kramers doublets.

2-no-water			
Energy (cm^{-1})	g_X	g_Y	g_Z
0	1.65×10^{-7}	2.41×10^{-7}	19.91
520	0.32×10^{-8}	1.80×10^{-7}	17.01
1004	7.33×10^{-6}	7.60×10^{-6}	14.19
1377	7.91×10^{-4}	8.74×10^{-4}	11.54
1593	0.61	0.85	8.76
1654	2.17	6.18	13.27
1692	1.41	3.74	14.49
1732	2.13×10^{-2}	0.21	19.22

Table S5. Some magneto-structural correlations in the investigated compounds. Angles between the main anisotropy axis and the shortest chemical bond (degrees).

Contraction	**1**	**2**	**2-no-water**
Angles between the main anisotropy axis and the shortest chemical bond (O1)	0.44	3.05	0.90
Angles between the main anisotropy axis and the O1-O2 direction	2.42	3.28	0.51

Table S6. Angles between main anisotropy axes of the low-lying Kramers doublets.

Compound **1**:

	1	**2**	**3**	**4**
1	0.00	2.56	88.12	86.76
2	2.56	0.00	85.56	84.92
3	88.12	85.56	0.00	41.68
4	86.76	84.92	41.68	0.00

Compound **2**:

	1	**2**	**3**	**4**
1	0.00	89.43	3.35	87.43
2	89.43	0.00	86.87	6.18
3	3.35	86.87	0.00	84.67
4	87.43	6.18	84.67	0.00

Compound **2-no-water**:

	1	**2**	**3**	**4**	**5**	**6**
1	0.00	0.10	0.40	1.68	7.25	88.27
2	0.10	0.00	0.35	1.67	7.28	88.38
3	0.40	0.35	0.00	1.32	6.96	88.31
4	1.68	1.67	1.32	0.00	5.70	87.80
5	7.25	7.28	6.96	5.70	0.00	83.93
6	88.27	88.38	88.31	87.80	83.93	0.00