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SUPPORTING INFORMATION

A luminescent Schiff-base heterotrinuclear Zn_2Dy Single-Molecule Magnet with an Axial Crystal Field.

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Experimental Section

Syntheses

All experiments were carried out under aerobic conditions. All the solvents in these experiments were analytical grade. The lanthanide chloride salts were purchased from Alfa Aesar. The ligand *H_2L* (H_2L = N,N'-bis(3-methoxysalicylidene)-1,2-diaminoethane) has been synthesized according to a well-established procedure from the literature.[1]

*Synthesis of **1**.*

Triethylamine (0.1 mmol) was added to a stirred solution of H_2L (0.2 mmol, 0.0656 g) and $ZnCl_2{\cdot}2H_2O$ (0.2 mmol, 0.0266 g) in methanol (15 mL). After 10 minutes of stirring, solid $Dy(NO_3){\cdot}5H_2O$ was added (0.1 mmol, 0.0348 g), the mixture was refluxed 5 hours at 60°C. A clear yellow solution is obtained and was then cooled down to room temperature. Small yellow fragile platelet crystals suitable for X-ray determination were obtained by slow evaporation during two days. Elemental Anal. Calcd. $C_{144}H_{152}C_{l16}Dy_4N_{16}O_{37}Zn_{10}$ C, 37.85 %; H, 3.35 %; N, 4.90 % Found: C, 37.03; H 3.62; N,5.29.

Single-Crystal X-ray Diffraction Studies

Diffraction intensities for complex **1** was collected on a Bruker-AXS APEX II CCD diffractometer at 293(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo Kα radiation (λ = 0.71073 Å). Data processing, Lorentz-polarization were performed using APEX.[2] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXL-2104[3] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. Molecular plots were performed with the ATOMS and MERCURY programs.[4,5] Selected bond lengths and angles are summarized in the Table S1. Table S3 lists of the hydrogen bond interactions in complexes 1–2. Geometrical calculations were carried out with PLATON.[6] CCDC 1575686 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

Magnetic Measurements

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working between 1.8 and 350 K with the magnetic field up to 7 Tesla. The data were corrected for the sample holder and for the diamagnetic contributions calculated from Pascal's constants. The AC magnetic susceptibility measurements were carried out in the presence of a 3 Oe oscillating field in zero or applied external DC field.

Photoluminescence Measurements

The photoluminescence spectra were recorded at in solid state 77 K and at 300 K with a Edinburg FLS 920 spectrofluorimeter. All the emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter.

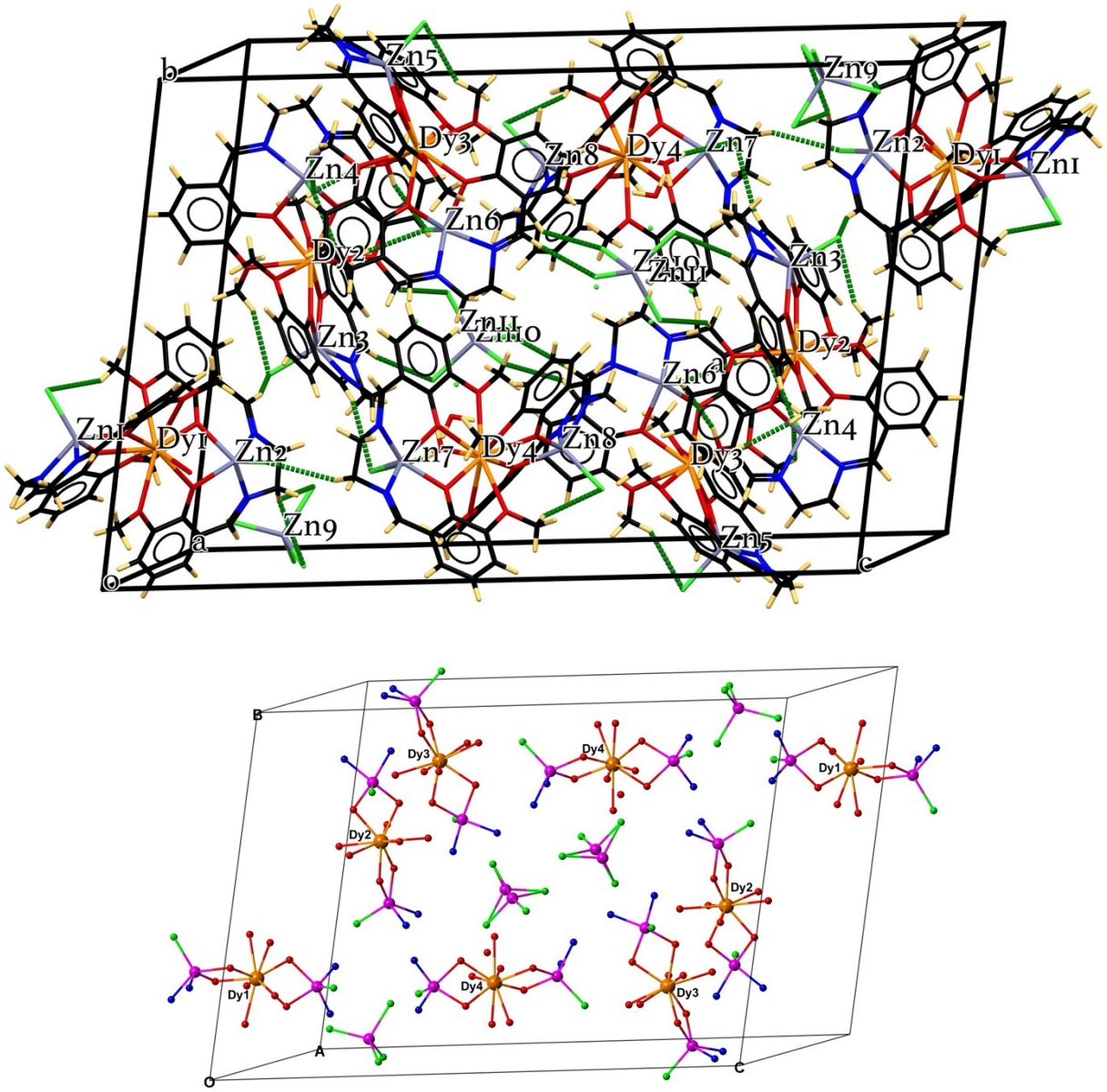

Figure S1: Perspective views of the crystal packing for **1** showing the hydrogen bonds as dashed green lines. For bottom picture, the carbon and hydrogen atoms have been omitted for clarity. Bottom picture: perspective views

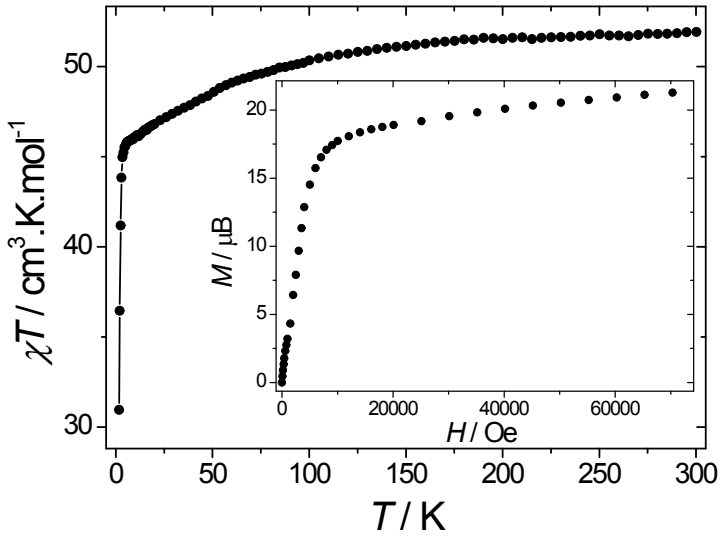

Figure S2: Temperature dependence of χT under a 1000 Oe DC field for **1**. Inset: field dependence of the magnetization at 1.8 K.

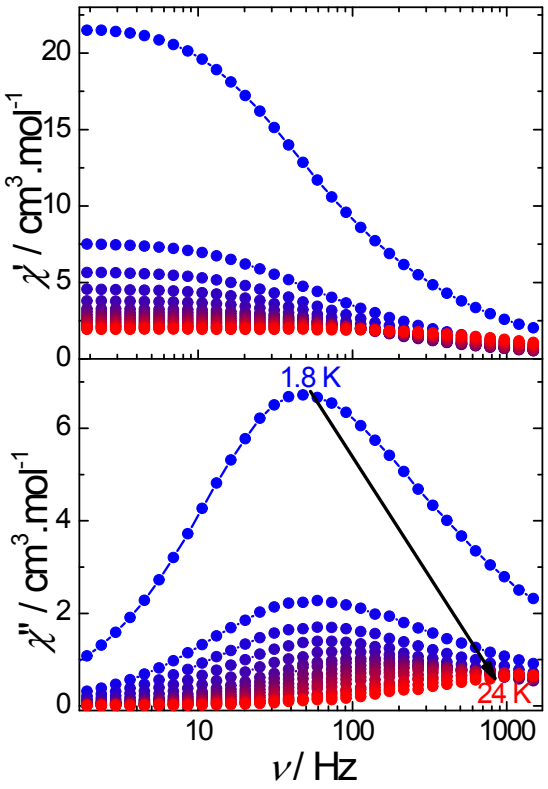

Figure S3. Frequency dependence of χ' and χ'' under a zero-dc field for **1.** Line is a guide for the eyes.

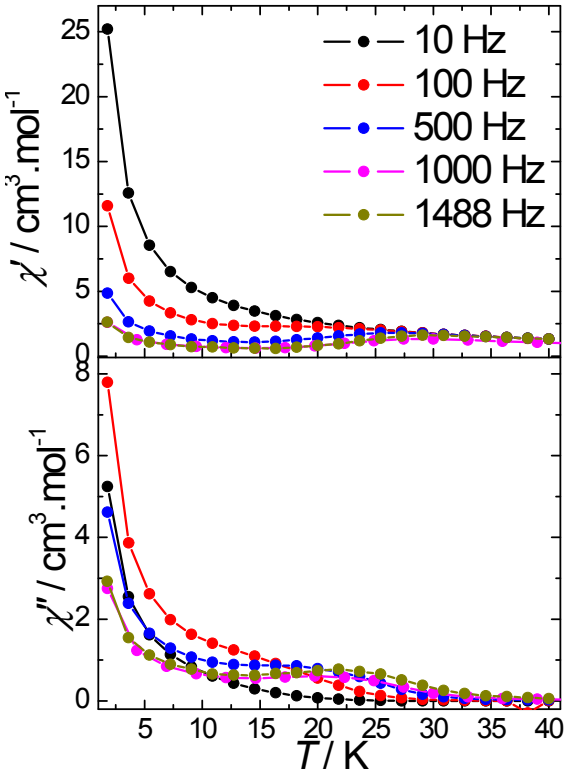

Figure S4. Temperature dependence of χ' and χ'' under a zero-dc field for **1.** Line is a guide for the eyes.

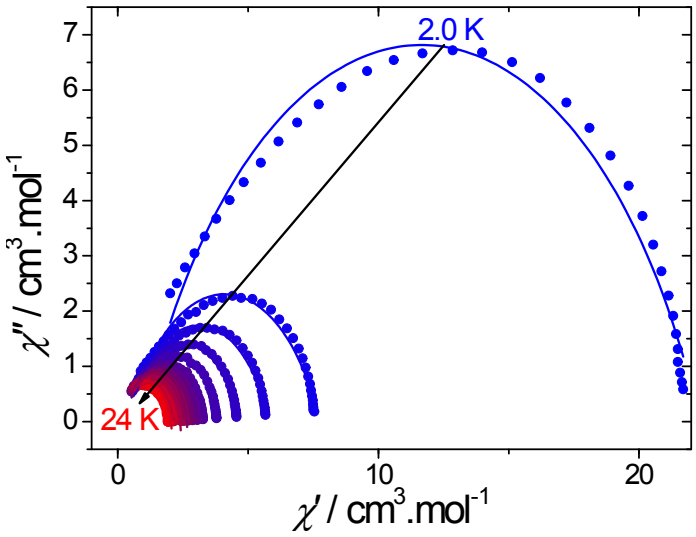

Figure S5: Cole-Cole (Argand) plot obtained using the ac susceptibility data (0 Oe) for **1**. The solid lines correspond to the best fit obtained with a generalized Debye model.

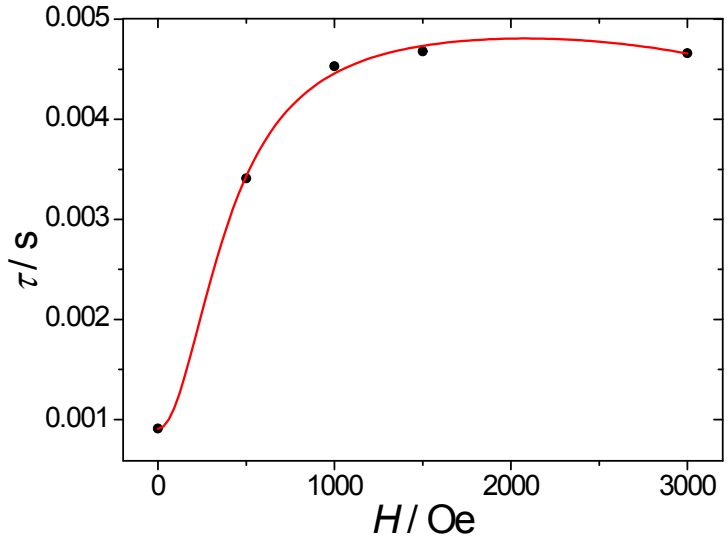

Figure S6. Field dependence of the relaxation time for **1** at 15 K. The red solid line represents the fit with Equation 2.

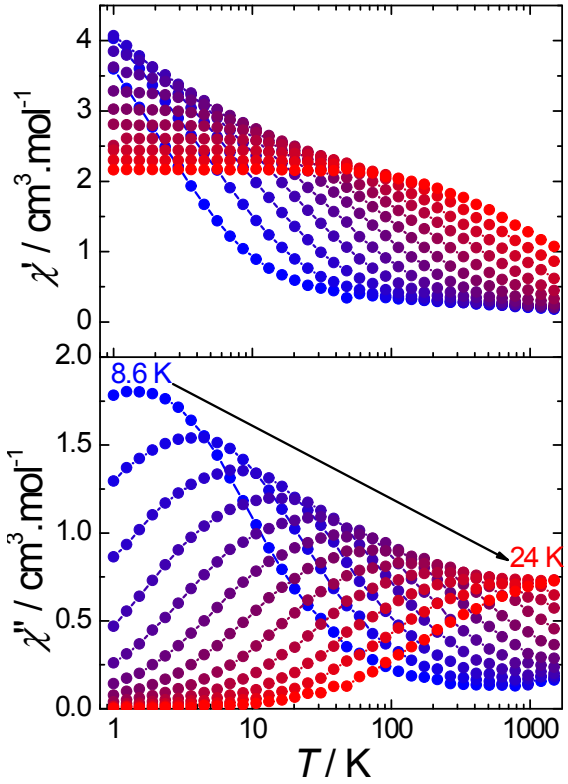

Figure S7. Frequency dependence of χ' and χ'' under a 1000 Oe DC field for **1.**

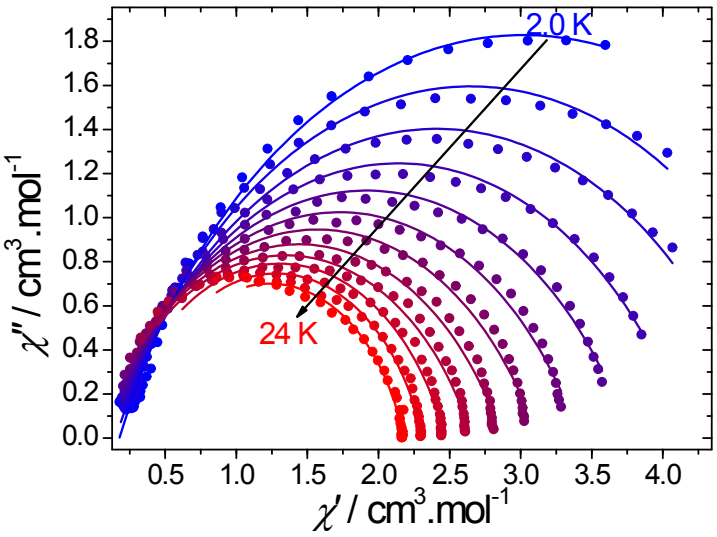

Figure S8. Cole-Cole plots under a 1000 Oe DC field for **1.** The solid lines represent the fit with a Debye model.

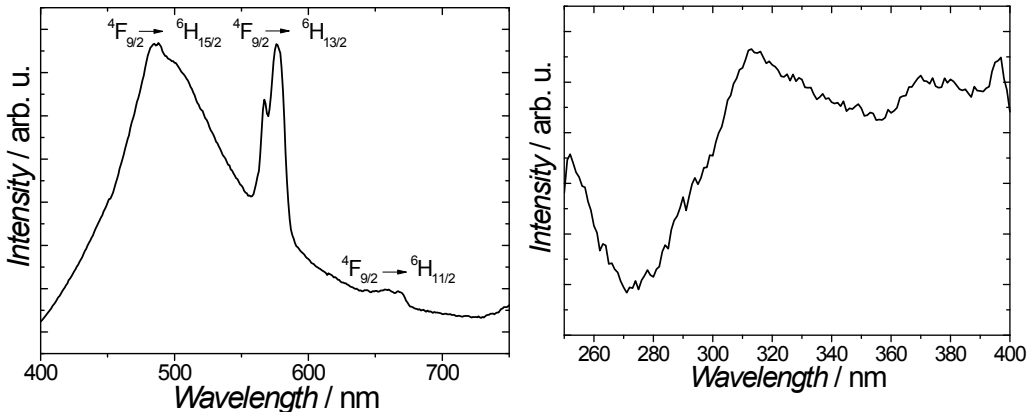

Figure S9. Room temperature photoluminescence (left, λ_{exc} = 380 nm) and excitation (λ_{em} = 576 nm right) spectra for **1**.

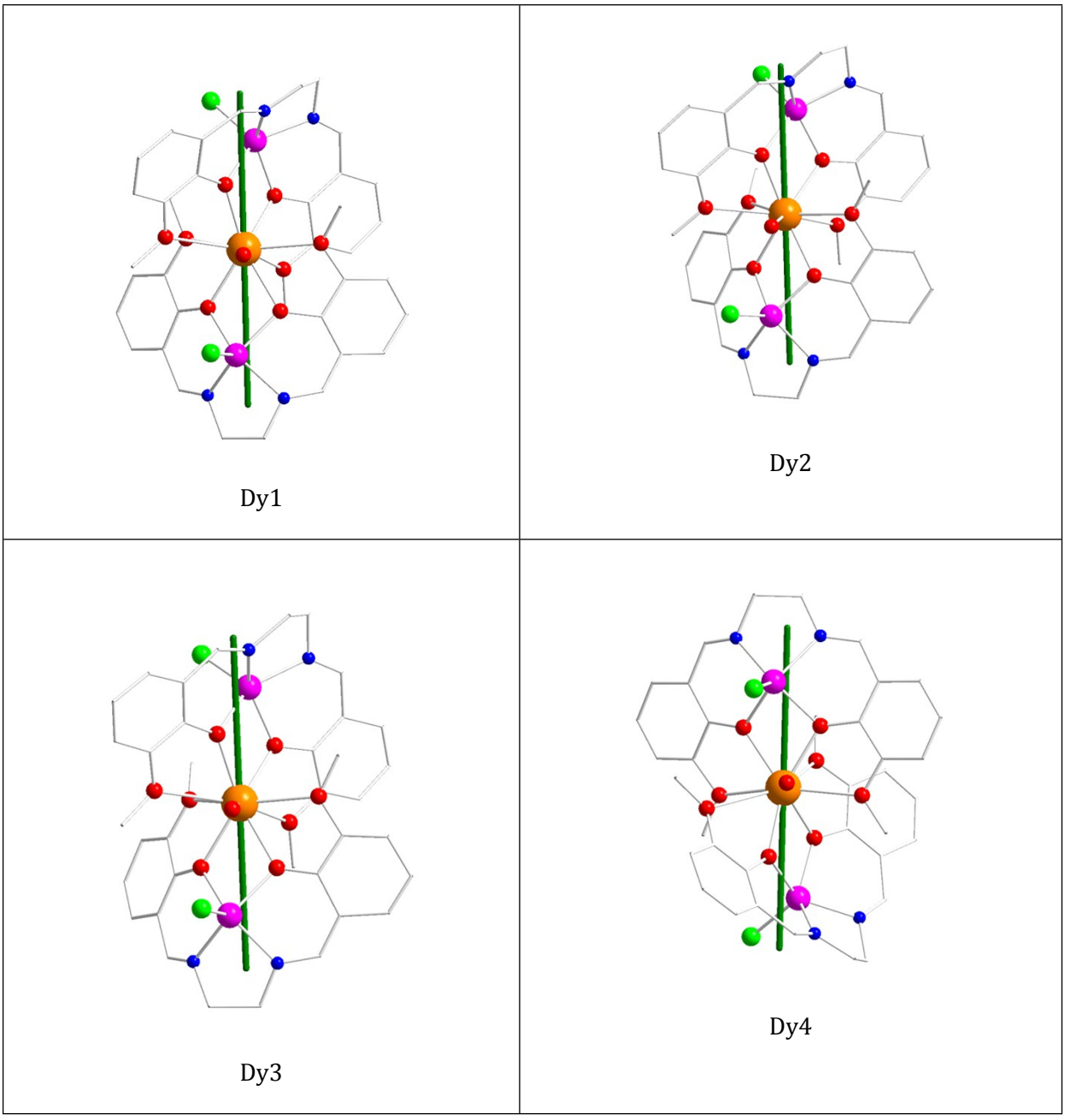

Figure S10. Orientation of the anisotropic axes (green) obtained with the MAGELLAN software in **1**.

Table S1. Crystal and structure refinement data for **1**.

	1
Empirical formula	$C_{144}H_{154}Cl_{16}Dy_4N_{16}O_{37}Zn_{10}$
Formula weight	4571.72
Temperature/K	296
Crystal system	triclinic
Space group	P-1
a/Å	15.581(3)
b/Å	20.331(4)
c/Å	29.683(5)
α/°	82.897(9)
β/°	80.573(9)
γ/°	74.654(10)
Volume/Å^3	8913(3)
Z	2
ρ_{calc}g/cm^3	1.703
μ/mm^{-1}	3.283
F(000)	4524.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.01 to 50.054
Index ranges	-18 ≤ h ≤ 18, -24 ≤ k ≤ 24, -35 ≤ l ≤ 35
Reflections collected	114686
Independent reflections	31138 [R_{int} = 0.0785, R_{sigma} = 0.0888]
Data/restraints/parameters	31138/128/2061
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0658, wR_2 = 0.1835
Final R indexes [all data]	R_1 = 0.1107, wR_2 = 0.2134
Largest diff. peak/hole / e Å^{-3}	2.22/-1.62

[a] $R1 = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; [b] $wR2 = \sqrt{\sum \left[w\left(F_o^2 - F_c^2\right)^2 \right] / \sum \left[w\left(F_o^2\right)^2 \right]}$

Table S2: Selected bond distances (Å) for complex **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Dy1	O1	2.553(7)	Dy2	O2W	2.424(7)	Zn9	Cl9	2.263(8)
Dy1	O1W	2.362(8)	Dy2	O9	2.753(7)	Zn9	Cl10	2.307(8)
Dy1	O2	2.280(7)	Dy2	O10	2.262(6)	Zn9	Cl11	2.258(7)
Dy1	O3	2.364(7)	Dy2	O11	2.305(7)	Zn9	Cl12	2.236(6)
Dy1	O4	2.567(7)	Dy2	O12	2.531(8)	Zn10	Cl13	2.313(5)
Dy1	O5	2.585(7)	Dy2	O13	2.579(7)	Zn10	Cl14	2.313(5)
Dy1	O6	2.331(7)	Dy2	O14	2.313(6)	Zn10	Cl15	2.313(5)
Dy1	O7	2.261(6)	Dy2	O15	2.326(7)	Zn10	Cl16	2.313(5)
Dy1	O8	2.750(8)	Dy2	O16	2.562(7)	Zn11	Cl20	2.307(6)
Zn1	Cl2	2.234(3)	Zn3	Cl3	2.246(3)	Zn11	Cl17	2.307(6)
Zn1	O6	2.059(7)	Zn3	O10	2.047(7)	Zn11	Cl18	2.307(6)
Zn1	O7	2.035(7)	Zn3	O11	2.036(7)	Zn11	Cl19	2.307(6)
Zn1	N3	2.028(10)	Zn3	N5	2.026(10)			
Zn1	N4	2.087(10)	Zn3	N6	2.037(10)			
Zn2	Cl1	2.241(4)	Zn4	Cl4	2.271(4)			
Zn2	O2	2.099(7)	Zn4	O14	2.059(7)			
Zn2	O3	1.995(7)	Zn4	O15	2.008(7)			
Zn2	N1	1.990(12)	Zn4	N7	2.009(8)			
Zn2	N2	2.070(11)	Zn4	N8	2.050(10)			
Dy3	O3W	2.418(7)	Dy4	Zn7	3.4226(13)			
Dy3	O17	2.592(7)	Dy4	Zn8	3.5429(13)			
Dy3	O18	2.316(6)	Dy4	O4W	2.390(7)			
Dy3	O19	2.292(6)	Dy4	O25	2.551(6)			
Dy3	O20	2.766(7)	Dy4	O26	2.287(6)			
Dy3	O21	2.550(7)	Dy4	O27	2.291(6)			
Dy3	O22	2.338(6)	Dy4	O28	2.588(7)			
Dy3	O23	2.323(7)	Dy4	O29	2.790(7)			
Dy3	O24	2.576(7)	Dy4	O30	2.273(6)			
Zn5	Cl5	2.235(3)	Dy4	O31	2.317(7)			
Zn5	O18	2.044(7)	Dy4	O32	2.557(7)			
Zn5	O19	2.045(6)	Zn7	Cl7	2.257(3)			
Zn5	N9	2.027(9)	Zn7	O26	2.054(6)			
Zn5	N10	2.042(10)	Zn7	O27	2.043(6)			
Zn6	Cl6	2.278(3)	Zn7	N15	2.045(9)			
Zn6	O22	2.084(7)	Zn7	N16	2.055(9)			
Zn6	O23	2.033(7)	Zn8	Cl8	2.224(3)			
Zn6	N11	2.066(9)	Zn8	O30	2.058(7)			
Zn6	N12	2.069(10)	Zn8	O31	2.064(6)			

Table S3: Selected angles (deg) for **1**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Zn2	Dy1	Zn1	177.39(3)		Zn4	Dy2	Zn3	176.75(4)
Zn2	O2	Dy1	104.1(3)		Zn3	O10	Dy2	109.8(3)
Zn2	O3	Dy1	104.6(3)		Zn3	O11	Dy2	108.6(3)
Zn1	O6	Dy1	107.0(3)		Zn4	O14	Dy2	103.9(3)
Zn1	O7	Dy1	110.5(3)		Zn4	O15	Dy2	105.1(3)
Zn6	Dy3	Zn5	175.69(3)		Zn7	Dy4	Zn8	177.04(3)
Zn5	O18	Dy3	108.5(3)		Zn7	O26	Dy4	103.9(3)
Zn5	O19	Dy3	109.3(3)		Zn7	O27	Dy4	104.2(3)
Zn6	O22	Dy3	103.5(3)		Zn8	O30	Dy4	109.7(3)
Zn6	O23	Dy3	105.7(3)		Zn8	O31	Dy4	107.8(3)

Table S4 Hydrogen-bond geometry (Å, °) of structures **1.**

D*—*H*···*A	***D*—*H***	***H*···*A***	***D*···*A***	***D*—**
O2W—H2WA···Cl6	1.0100	2.4200	3.409	166.00
O2W—H2WB···Cl4	1.0000	2.4400	3.287	141.00
O3W—H3WA···Cl6	0.9500	2.2700	3.194	163.00
O3W—H3WB···Cl4	0.9500	2.1900	3.088	157.00
O4W—H4WA···Cl7	0.8500	2.3600	3.172	161.00
O4W—H4WB···O5W	0.8500	2.4500	2.733	101.00
O4W—H4WB···O28	0.8500	2.4900	2.899	111.00
O5W—H5WA···O4W	0.8500	2.4400	2.733	101.00
O5W—H5WB···Cl13	0.8500	2.8200	3.231	112.00
C1—H1C···Cl2	0.9600	2.5700	3.46	153.00
C8—H8···Cl3i	0.9300	2.6000	3.449	153.00
C108—H10D···Cl4	0.9600	2.6900	3.416	133.00
C109—H10F···O26	0.9600	2.6000	3.219	123.00
C127—H12F···Cl8	0.9600	2.7800	3.518	134.00
C135—H13B···Cl1i	0.9700	2.8100	3.563	136.00
C32—H32···Cl3ii	0.9300	2.8200	3.459	127.00
C47—H47···Cl15	0.9300	2.7300	3.638	164.00
C53—H53···Cl19	0.9300	2.5500	3.37	147.00
C54—H54C···O14	0.9600	2.5500	3.272	132.00
C55—H55A···Cl3	0.9600	2.6500	3.531	153.00
C90—H90C···O22	0.9600	2.5100	3.202	129.00
C91—H91C···Cl5	0.9600	2.7300	3.514	140.00
C91—H91C···O18	0.9600	2.5200	3.197	128.00
C112—H112···Cl20iii	0.9300	2.8200	3.61	143.00
C113—H113···Cl18iii	0.9300	2.6200	3.49	155.00
C134—H134···Cl5iv	0.9300	2.6700	3.475	146.00
C137—H137···Cl19v	0.9300	2.7800	3.659	157.00
Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) −x, −y+1, −z+2; (iii) −x+1,				

Table S5. SHAPE analysis for compounds **1**.

		JJCU	CCU	JCSAPR	CSAPR	JTCTPR	TCTPR
1	**Dy1**	8.244	7.851	3.373	1.925	3.428	2.478
	Dy2	8.105	7.391	3.776	2.370	4.293	2.990
	Dy3	7.685	7.056	3.927	2.495	3.915	2.659
	Dy4	7.615	7.235	3.532	2.443	3.647	2.309

JJCU:Capped cube
CCU: Spherical-relaxed capped cube
JCSAPR: Capped square antiprism
CSAPR: Spherical capped square antiprism
JTCTPR: Tricapped trigonal prism
TCTPR: Spherical tricapped trigonal prism

Table S6. Fitting of the Cole-Cole plots with a generalized Debye model for temperature ranging from 2 to 24 K under a zero dc field for **1**.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
2	4.34962	18.96071	0.37836
6	1.63518	6.55988	0.38871
8	1.2345	4.96754	0.37319
10	0.97013	4.03838	0.3434
12	0.76941	3.41079	0.29805
14	0.63913	2.96559	0.27213
15	0.59032	2.799	0.24384
16	0.54658	2.62104	0.24833
17	0.48717	2.49405	0.15364
18	0.48682	2.34524	0.23747
19	0.46224	2.23905	0.16875
21.5	0.45727	1.97971	0.23262
22	0.3974	1.92056	0.16724
23	0.58782	1.9432	0.08244
24	0.38257	1.78913	0.21074

Table S7. Fit parameters of the field dependence of the relaxation time obtained using the Eq. 2

Compound	*D* ($s^{-1}K^{-1}Oe^{-4}$)	B_1 (s^{-1})	B_2 (Oe^{-2})	*K*
1	1.08×10^{-14}	904	3.52×10^{-5}	199.14

Table S8. Fitting of the Cole-Cole plots with a generalized Debye model under a 1000 Oe dc field for **1**.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
8.6	1.05261	4.9828	0.36995
10	0.93781	4.35967	0.37756
11.4	0.93316	3.88284	0.42586
12.8	0.83266	3.44533	0.43183
14.2	0.74354	3.09018	0.43753
15.6	0.65449	2.79719	0.43639
17	0.57648	2.56168	0.42984
18.4	0.51631	2.36981	0.42024
19.8	0.46363	2.23619	0.38769
21.2	0.44758	2.16785	0.31071
22.6	0.47049	2.09533	0.25016
24	0.47707	1.99774	0.22458
15.6	0.65449	2.79719	0.43639
17	0.57648	2.56168	0.42984
18.4	0.51631	2.36981	0.42024

Table S9. Angles of the anistropic axis for **1**.

Compound	*Dy site*	*Dy-anistropic axis-Zn angle 1*	*Dy-anistropic axis-Zn angle 2*	*Shortest Dy-O distance*	*Privileged Dy-axis-O angle*
1	Dy1	25.38	25.46	Dy1-O7 (2.256)	15.46
	Dy2	23.11	26.60	Dy2-O10 (2.259)	16.59
	Dy3	22.14	27.07	Dy3-O19 (2.294)	17.23
	Dy4	26.89	29.26	Dy4-O30 (2.275)	14.50

Table S10. Deviation of the hard plane from the D_{5h} symmetry obtained by SHAPE analysis. [7]

	Dy1	*Dy2*	*Dy3*	*Dy4*
1	1.929	1.187	1.433	2.700

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