Supporting Information for

A rare chloride-bridged dysprosium chain with slow magnetic relaxation: thermally activated mechanism via the second excited state promoted by the magnetic interactions[†]

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Experimental Section

All the starting materials were commercially available reagents for analytical grade and used without further purification.

Syntheses of H_2L : The H_2L Schiff-base ligand was synthesized by the condensation of pyrazine-N-oxide-2-carbohydrazide and 5-bromosalicylaldehyde in 1:3 ratios in methanol under reflux reaction. All the reagents and solvents were commercially available and utilized without further purification.

 $[Dy(L)Cl(CH_3OH)]_n$: H₂L (0.05 mmol, 16.9 mg) was dissolved in 10.0 mL mixture solvent of methanol and acetonitrile (7:3 in volume ratio), then methanolic solution of NaOH (1.0 mL, 0.05 mol·L⁻¹) was added to the solution. The reaction mixture was stirred for 2 min, after that solid DyCl₃·6H₂O (0.05 mmol, 18.8 mg) was added and the orange solution was continually stirred for 15 min. The mixture was transferred to a 20 mL Teflon reactor and heated to 80 °C for 48 h under autogenous pressure, then cooled to room temperature at a rate of 5 °C ·h⁻¹. The yellow flake crystals of **1** were obtained. Yield: 13.7 mg (48.5% based on the metal salt). Elemental analysis (%) calcd for $C_{13}H_{11}DyClBrN_4O_4$: C, 27.63, H, 1.95, N, 9.91; found C, 27.57, H, 2.01, N, 9.89. IR (KBr, cm⁻¹): 3367(br), 1612(s), 1560(s), 1475(s), 1458(s), 1348(s), 1178(m), 1022(m), 879(m), 829(m), 698(m).

X-ray crystallography and physical measurement

Intensity data for crystals of **1** was collected on a rigaku SuperNova, Dual, AtlasS2 diffractometer with graphite-monochromated Mo K α radiation at 100 K. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculation positions. The details of crystallographic data and selected bond parameters for complex **1** are listed in Table S1 and Table S2, respectively.

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL analyzer. FTIR spectra were recorded in the range of 4000 to 400 cm⁻¹ on an AVATAR 360 Nicolet 380 FT/IR spectrometer using KBr pellets.

Powder X-ray diffraction (XRD) analyses were performed on a Rigaku Dmax-2000 X-ray diffractometer with Cu K α ($\lambda = 1.54059$ Å) radiation. Variable-temperature magnetic susceptibility measurements of **1** were performed on Quantum Design PPMS magnetometer (100~10000 Hz) and Quantum Design SQUID-MPMS3 (1~1000 Hz) magnetometer.

Computational details

Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{3+} fragment have been carried out with MOLCAS 8.2 program package.¹ For complex **1**, there is only one type of Dy^{3+} ion within the dinuclears, and thus we only need to calculate one Dy^{3+} ion fragment. During the calculations, the close Dy^{3+} ion was replaced by diamagnetic Lu^{3+} . And the influence of distant Dy^{3+} ions were taken into account by the closed-shell La^{3+} ab initio embedding model potentials (AIMP; La.ECP.deGraaf.0s.0s.0e-La-(LaMnO3.).² SINGLE_ANISO ³ program was used to obtain the *g* tensors, energy levels, magnetic axes, *et al.*, based on the above CASSCF/RASSI calculations.

In the CASSCF calculations, the basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy^{3+} ion; VTZ for close O, N and Cl; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For the fragment of individual Dy^{3+} ion, active electrons in 7 active spaces include all *f* electrons (CAS(9 in 7)) in the CASSCF calculation. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets, 130 from 490 doublets).

Magnetic interaction analysis

For the total magnetic interaction in complex **1**, we used sixty-four points of $\chi_M T$ -T data to fit the three total coupling constants. And the dipole-dipole interaction between two sites can be described with $J_{dip} = \frac{\mu_B^2}{|r|^3} [\overline{g_{1z}} \cdot \overline{g_{2z}} \cdot 3(\overline{g_{1z}} \cdot \vec{r})(\vec{r} \cdot \overline{g_{2z}})]$ (\vec{r} is the unit vector at the direction from site i to site j, \vec{g}_{iz} is the vector of the dipole at site i, which could be calculated using the program SINGLE_ANISO³ with the results of ab initio calculations). After that, the constants of exchange coupling can be obtained from the formula $J_{exchange} = J_{total} - J_{dipole}$.

	1	
Formula	C ₁₃ H ₁₁ BrClDyN ₄ O ₄	
Mr	565.11	
Crystal system	Triclinic	
Space group	$P \overline{1}$	
a(Å)	6.974(6)	
b(Å)	9.067(7)	
c(Å)	13.062(9)	
$a(^{\circ})$	99.132(6)	
β (°)	92.118(6)	
γ(°)	104.300(7)	
$V(Å^3)$	787.7(11)	
Ζ	1	
μ (mm ⁻¹)	7.475	
<i>F</i> (000)	534	
GOF	0.977	
Data collected	4984	
Unique	3212	
R _{int}	0.0568	
$R1, wR2[I > 2\sigma(I)]$	0.0516, 0.0842	
R1, wR2 [all data]	0.0711, 0.0934	

Table S1. Crystallographic Data and Structure Refinement for complex 1.

Table S2. The calculated results for Dy^{3+} ions configuration of complex 1 by *SHAPE* 2.0 software.^a

	BTPR-8	JBTPR-8	TDD-8
Dy	2.521	3.275	3.834

^aBTPR-8: biaugmented trigonal prism. JBTPR-8: biaugmented trigonal prism J50. TDD-8: triangular dodecahedron.

Table S3. Selected Bond Distances (Å) in complex 1.

]	[
Dy1-O1	2.163(6)	Dy1-O2	2.353(6)	Dy1-O2#1	2.353(6)
Dy1-O4	2.395(6)	Dy1-N1	2.474(7)	Dy1-N3#1	2.608(7)
Dy1-Cl1	2.822(2)	Dy1-Cl1#2	2.807(2)		

Symmetry code for 1:#1: -x+1, -y+1, -z, #2: x-1, y, z

Table S4. Hydrogen Bonds in 1.

D-H	d(D-H) (Å)	<dha(°)< th=""><th>d(DA) (Å)</th><th>A</th></dha(°)<>	d(DA) (Å)	A
C10-H10	0.930	95.49	3.453	N1 [3-x, 1-y, 1-z]
C10-H10	0.930	23.64	2.403	N3 [1-x, 2-y, 1-z]
С3-Н3	0.930	177.52	3.462	O3 [-x, 2-y, 1-z]

T (K)	χt	χs	α	$\tau(s)$
10	1.72	0.022	0.13	0.16
10.5	1.55	0.022	0.12	0.098
11	1.43	0.022	0.11	0.079
11.5	1.34	0.022	0.098	0.059
12	1.27	0.022	0.095	0.046
12.5	1.19	0.024	0.082	0.035
13	1.13	0.025	0.070	0.028
13.5	1.07	0.028	0.057	0.023
14	1.02	0.031	0.039	0.018
14.5	0.99	0.028	0.051	0.015
15	0.96	0.028	0.048	0.013
15.5	0.89	0.028	0.040	0.010
16	0.86	0.028	0.036	0.0087
16.5	0.86	0.028	0.041	0.0074
17	0.83	0.028	0.035	0.0063
17.5	0.81	0.028	0.034	0.0053
18	0.78	0.028	0.030	0.0046
18.5	0.76	0.027	0.038	0.0039
19	0.73	0.020	0.036	0.0034
20	0.70	0.018	0.045	0.0026
21	0.66	0.018	0.044	0.0019
22	0.63	0.020	0.029	0.0015
23	0.61	0.018	0.042	0.0011
24	0.58	0.019	0.040	8.52E-4
25	0.55	0.019	0.039	6.39E-4
26	0.53	0.019	0.041	4.76E-4
27	0.51	0.020	0.036	3.48E-4
28	0.49	0.019	0.042	2.47E-4
29	0.48	0.018	0.051	1.72E-4
30	0.46	0.018	0.051	1.18E-4
31	0.44	0.020	0.033	7.88E-5
32	0.43	0.010	0.065	5.13E-5
33	0.41	0.0075	0.063	3.32E-5
34	0.40	0.0010	0.068	2.17E-5
35	0.39	1E-5	0.060	1.41E-5
36	0.37	1E-5	0.050	9.44E-6
37	0.37	1E-5	0.075	6.32E-6

Table S5. Relaxation fitting parameters from Least-Squares Fitting of $\chi(f)$ data under zero dc field of **1**.

	Value	Standard Error
$ au_0$	2.10×10 ⁻¹²	6×10 ⁻¹³
$U_{\rm eff}$	556	8
С	1.30×10 ⁻⁵	1×10-6
n	5.76	0.03

Table S6. The parameters of fitting $ln(\tau)$ versus T^{-1} plots and standard deviations for **1**.

Table S7. Some similiar examples of lanthanide-based molecular nanomagnets featuring slow magnetic relaxation.

					$J(\text{cm}^{-1})$		$U_{\rm eff}({\rm K})$	Ref
	structu	Dy-Cl/ Å	Dy-Dy/ Å	J_{dip}	J _{exch}	J		
	re			-				
[Dy(L)Cl(CH ₃ OH	1D	2.807(9)	4.629(13)	-1.67	2.25	0.58	556	This
)]n		2.822(7)						work
[(PyCp ₂)Dy-(μ-	dinucl	2.683(3)	4.252(1)	0.0892	-0.138	-0.05	70	7f
Cl)]2	ear	2.785(3)						
Dy ₂ (opch) ₂ (m-	tetran	2.774(2)	4.630(1)	-1.33	2.25	0.92	43	7g
$Cl)Cl(MeOH)_2]_2$	uclear	2.851(2)					89	-
Abbreviations: $L = N' - (5-bromo-2-hydroxybenzylidene)$ pyrazine-N-oxide-carbohydrazide;								
$(PvCp_2^2 = [2,6-(CH_2C_5H_3)_2C_5H_3N]^2)$; H ₂ opch = (E)-N ² -(2-hydroxy-3-methoxybenzylidene)pyrazine-2-								
carbohydrazide;					-			

		1	
KDS	E/cm^{-1}	g	m_J
		0.001	
1	0.0	0.002	$\pm 15/2$
		19.748	
		0.062	
2	261.0	0.089	$\pm 13/2$
		16.998	
		1.862	
3	464.8	4.038	$\pm 11/2$
		11.947	
		0.611	
4	541.6	5.241	±7/2
		11.408	
		3.082	
5	650.7	5.310	$\pm 9/2$
		9.361	
		1.629	
6	754.2	2.271	$\pm 3/2$
		13.559	
		0.056	
7	836.1	0.294	$\pm 1/2$
		17.127	
		0.149	
8	875.5	0.236	$\pm 5/2$
		19.740	

Table S8. Calculated energy levels (cm⁻¹), $g(g_x, g_y, g_z)$ tensors and m_J values of the lowest Kramers doublets (KDs) of individual Dy³⁺ fragment of complex 1.

Table S9. Fitted exchange coupling constant J_{exch} , the calculated dipole-dipole interaction J_{dip} and the total J between two close Dy³⁺ ions in 1 (cm⁻¹). The fitted intermolecular interactions zJ' of 1 is -0.02 cm⁻¹.

	1				
	J_1	J_2	J_3		
$J_{ m dip}$	4.64	-1.67	0.04		
$J_{ m exch}$	6.75	2.25	0.50		
J	11.39	0.58	0.54		

Table S10. Exchange energies (cm^{-1}) and main values of the g_z for the lowest eight exchange doublets of **1**.

	1		
	E	gz	
1	0.000	78.993	
2	0.483	0.853	
3	0.483	0.853	
4	0.966	0.016	
5	5.967	0.000	
6	5.994	39.496	
7	5.994	39.496	
8	6.020	0.000	

Table S11. Included angle (θ) between the local main magnetic axis of the ground Kramers doublet and the vector connecting the two Dy³⁺ ions for complex **1**.

	1			
	Dy1-Dy2	Dy1-Dy3	Dy1-Dy4	
θ	17.0°	85.6°	53.3°	



Fig. S1 The hydrogen-bonded 2D layer (a) and the connection of the hydrogen bonds between the layers (b) in 1.



Fig. S2. Powder X-ray diffraction profiles of 1 together with simulations from the single crystal data



Fig. S3 Temperature dependence of $\chi_M T$ for 1 (open circles represent experimental data while the red line indicates the simulation from *ab* initio calculation). The intermolecular interactions zJ' of 1 was fitted to -0.02 cm^{-1} .



Fig. S4 the zero-field-cooled/field-cooled (ZFC-FC) magnetic susceptibilities under 500 Oe dc field with a sweep rate of 3 K/min were measured for 1.



Fig. S6 *Ac-f* curves measured under 0 kOe *dc* fields for 1. Solid lines were fitted using a generalized Debye relaxation model, simultaneously to $\chi'(f)$ and $\chi''(f)$ curves.





Fig. S8 Calculated model structure of individual Dy^{3+} fragment of complex 1.



Fig. S9 The magnetization blocking barriers of individual Dy^{3+} fragment in complex **1**. The thick black lines represent the Kramers doublets as a function of their magnetic moment along the magnetic axis. The green lines correspond to the diagonal matrix element of the transversal magnetic moment; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represents the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.



Fig. S10 Structure of the labeled exchange coupling constants in complex 1.

Notes and references

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