Three Dy(III) single-ion magnets bearing tropolone ligand: structure, magnetic property and theoretical elucidation

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Gerneral Materials and methods

All chemicals and solvents were used as obtained without purification. Elemental analyses were made on an Elementar Micro cube CHN elemental analyzer. IR data (KBr disks) were collected on a Perkin-Elmer Spectrum Two FT/IR spectrometer in the wavenumber range of 4000-400 cm⁻¹. The powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/max 2500v/pc diffractometer equipped with Cu-K α radiation ($\lambda = 1.5418$ Å).

Magnetic Measurements

All magnetic measurements for titled complexes were made on a Quantum Design MPMS SQUID-XL-7 magnetometer. The samples for magnetic measurements were prepared by separating the pure crystals from the corresponding reaction solutions, subsequently washed by methanol to remove the reaction solution absorbed on the crystals, and at last dried in air to get rid of the methanol. The crystalline samples of **1** (23.19 mg), **2** (29.73 mg), **3** (13.38 mg) were wrapped by thin film and fixed on the sample rod for magnetic measurements. The magnetic susceptibilities were measured under 1000 Oe from 2 to 300 K. Data were corrected with the diamagnetic contribution of the sample and the sample holder from Pascal's Tables. The field-dependent magnetizations were measured from 0 to 70 kOe at different temperatures of 10, 5, 2.5, and 2 K. The magnetic hysteresis was measured with a sweep rate from 1.4 Oe/s to 97 Oe/s upon the field rising from 0 to high field, then the same sequence in reverse to complete the loop. This gave an average sweep rate of 67 Oe/s over the whole measurement. The alternating current (ac) susceptibility measurements in different applied static fields ($H_{dc} = 0$ Oe or the optimal external dc field) were performed with an oscillating

ac field of 2 Oe and ac frequencies ranging from 0 to 1000 Hz. Their Cole–Cole diagrams were fitted by Debye model in the software of Origin. The derived relaxation time (τ) at different temperatures were drawn into their ln(τ /s) versus T^{-1} plots which were simulated in the software of Origin according to the equation of $\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_{\text{B}}T) + CT^n + \tau_{\text{QTM}}^{-1} +$ AH^mT by considering one or more terms in the equation.



Fig. S1 PXRD patterns of 1.



Fig. S2 PXRD patterns of 2.



Fig. S3 PXRD patterns of 3.



Fig. S4 Coordination polyhedron of Dy(III) ion in 1.



Fig. S5 Coordination polyhedron of Dy(III) ion in **2**.



Fig. S6 Coordination polyhedrons of Dy(III) ions in 3.



Fig. S7 $\chi_{\rm M}$ versus *T* curve of **1**.



Fig. S8 $\chi_{\rm M}$ versus *T* curve of **2**.



Fig. S9 $\chi_{\rm M}$ versus *T* curve of **3**.



Fig. S10 M versus H curves for 1 at 2, 2.5, 5 and 10 K.



Fig. S11 M versus H curves for 2 at 2, 2.5, 5 and 10 K.



Fig. S12 M versus H curves for **3** at 2, 2.5, 5 and 10 K.



Fig. S13 Plots of Magnetic hysteresis loops for 1 with an average sweep rate of 67 Oe/s.



Fig. S14 Plots of Magnetic hysteresis loops for 2 with an average sweep rate of 67 Oe/s.



Fig. S15 Plots of Magnetic hysteresis loops for 3 with an average sweep rate of 67 Oe/s.



Fig. S16 a) Frequency-dependent χ " for 1 under different dc fields with a 2 Oe oscillating ac field, b) Dependence of τ with the applied DC fields for 1 at 2 K. Solid lines are guides for the eye.



Fig. S17 Plots of χ' and χ'' vs T (1.8-10 K) at various frequencies for 1 under 1000 Oe.



Fig. S18 Plots of χ' and χ'' vs T(1.8-15 K) at various frequencies for **2** under 0 Oe.



Fig. S19 Plots of χ' and χ'' vs T(1.8-15 K) at various frequencies for 2 under 1000 Oe.



Fig. S20 Frequency-dependent χ " for 2 under different dc fields with a 2 Oe oscillating ac field.



Fig. S21 Frequency-dependent χ' components of ac susceptibilities of 2 at different temperatures under 800 Oe dc fields with the solid lines guiding for eyes.



Fig. S22 Frequency-dependent χ " for **3** under different dc fields with a 2 Oe oscillating ac field at 2 K.

Theoretical methods and computational details

Multiconfigurational *ab initio* calculations, including spin-orbit coupling (SOC), were performed on the experimental structures of **1**, **2** and **3** to explore their SMM properties. This type of calculation includes two steps:¹ 1) a set of spin eigenstates are obtained by the state-averaged (SA) CASSCF method;² 2) the low-lying SOC states, i.e., Kramers doublets (KD) herein, are obtained by state interaction which is the diagonalization of the SOC matrix in the space spanned by the spin eigenstates from the first step. All the calculations were carried out with the MOLCAS@UU, a version of MOLCAS 8.0^{3, 4} which is freely distributed for academic users.

In the CASSCF step, the active space consisted of 9 electrons in 7 orbitals and a total number of 21 sextets were included. Due to the hardware limitation, other highly excited spin states were not considered. The step of state interaction were performed by the RASSI-SO module⁵ with the SOC integrals from the AMFI method.⁶ The ANO-RCC basis sets,⁷⁻⁹ including VTZP for Dy, VDZ for C and H as well as VDZP for other atoms, were used. The SINGLE ANISO module,^{10, 11} developed by Chibotaru et al, was used to obtain the g-tensors, transition magnetic moments and other parameters characterizing the magnetic anisotropy.

$$\Delta_{\text{tun}} = [(\mu_{\text{X}}H_{\text{X}})^2 + (\mu_{\text{Y}}H_{\text{Y}})^2]^{1/2} = [\beta(g_{\text{X}}^2H_{\text{X}}^2 + g_{\text{Y}}^2H_{\text{Y}}^2)^{1/2}]/2$$
(S1a)

$$\mu_{\alpha} = -\langle -n|\beta g_{\alpha}S_{\alpha}|n\rangle = -g_{\alpha}\beta/2, \qquad \alpha = X, Y, Z$$
(S1b)

$$g_{\alpha} = 2 \langle -n | \mu_{\alpha} | n \rangle / \beta = -g_{\alpha} \beta / 2, \qquad \alpha = X, Y, Z$$
(S1c)

$$g_{XY} = ((g_X)^2 + (g_Y)^2)^{1/2}$$
(S2a)

 $\mu_{QTM} = (|\mu_X| + |\mu_Y| + |\mu_Z|)/3 \tag{S2b}$

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Table S	1 The	negative	charges	$(in \epsilon)$	e) fron	ı ab	initio	calculations	and	the	related	Dy-O/N
bond ler	i gths (i	in Å) of th	ne atoms	in the	e first sp	ohere	ð.					

1	01	02	03	04	O6	07	N1	N2	N3	N4
Charge	-0.7395	0.7596	-0.6420	-0.6404	-0.6238	-0.6573	-0.3330	-0.3143	-0.3028	-0.3298
Dy-O/N	2.3625	2.3386	2.5499	2.4896	2.7867	2.4940	2.5306	2.6171	2.6640	2.5293
2	01	02	03	04	05	06	N1	N2		
Charge	-0.7353	-0.7453	-0.7501	-0.7565	-0.7654	-0.7235	-0.3248	-0.3026		
Dy-O/N	2.3648	2.3558	2.3449	2.3312	2.3210	2.3627	2.5588	2.5841		
3	01	02	03	04	05	06	07	013		
Charge	-0.7004	-0.7686	-0.7565	-0.7225	-0.7217	-0.7734	-0.6223	-0.7022		
Dy-O/N	2.3283	2.3920	2.2997	2.3438	2.3243	2.3827	2.4181	2.3722		

CFP	1	2	3
B(2-2)	$0.4803 \times 10^{+00}$	$-0.7880 \times 10^{+00}$	0.5543×10^{-01}
B(2-1)	0.9496×10^{-01}	$0.1341 \times 10^{+00}$	$0.2189 \times 10^{+00}$
B(20)	-0.1357×10 ⁺⁰¹	$-0.1667 \times 10^{+01}$	$-0.2208 \times 10^{+01}$
B(21)	$-0.1181 \times 10^{+00}$	$0.2858 \times 10^{+00}$	$-0.3965 \times 10^{+00}$
B(22)	$0.1427 \times 10^{+01}$	$0.1182 \times 10^{+01}$	$0.1792 \times 10^{+01}$
B(4-4)	-0.2771×10^{-03}	-0.7231×10^{-03}	-0.7718×10^{-02}
B(4-3)	0.4738×10^{-02}	0.2069×10^{-01}	-0.8410×10^{-02}
B(4-2)	-0.1320×10^{-01}	0.2082×10^{-01}	0.1230×10^{-01}
B(4-1)	0.9453×10^{-03}	0.3135×10^{-02}	-0.3211×10^{-02}
B(40)	-0.1838×10^{-03}	-0.5506×10^{-02}	-0.5731×10^{-02}
B(41)	-0.1481×10^{-03}	0.1779×10^{-02}	0.2992×10^{-02}
B(42)	0.3367×10^{-02}	0.2110×10^{-01}	0.2617×10^{-01}
B(43)	0.4280×10^{-02}	-0.3216×10^{-02}	-0.3305×10^{-02}
B(44)	0.4525×10^{-02}	-0.7397×10^{-02}	-0.2219×10 ⁻⁰²
B(6-6)	0.1134×10^{-03}	0.2432×10^{-03}	0.2782×10^{-04}
B(6-5)	0.2288×10^{-03}	0.3680×10^{-04}	-0.2634×10^{-03}
B(6-4)	-0.9386×10^{-04}	0.1544×10^{-03}	0.6310×10^{-04}
B(6-3)	0.7648×10^{-04}	0.1149×10^{-03}	-0.4920×10^{-04}
B(6-2)	-0.4403×10^{-04}	-0.4279×10^{-04}	-0.3992×10^{-04}
B(6-1)	-0.4226×10^{-05}	-0.1871×10^{-04}	0.7518×10^{-05}
B(60)	-0.2333×10^{-04}	-0.4981×10 ⁻⁰⁶	0.6910×10^{-05}
B(61)	-0.4059×10^{-04}	-0.3175×10 ⁻⁰⁴	-0.2490×10 ⁻⁰⁵
B(62)	0.1432×10^{-03}	0.5844×10^{-04}	0.6071×10^{-04}
B(63)	-0.2902×10^{-04}	-0.5499×10 ⁻⁰⁴	0.4071×10^{-04}
B(64)	-0.2328×10 ⁻⁰³	0.6490×10^{-04}	0.1700×10^{-03}
B(65)	0.8544×10^{-04}	-0.2014×10^{-03}	0.8106×10^{-04}
B(66)	0.4922×10^{-03}	-0.1340×10^{-03}	0.2227×10^{-03}

Table S2 Ab initio Computed Crystal-Field Parameters for the Investigated Compounds.



Fig. S23 Direction of the *ab initio* magnetic easy axis of the ground KDs of the titled compounds.