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Electronic Supplementary Information (ESI)

Reversible Structural Transformation Induced Switchable Single-

Molecule Magnet Behavior in Lanthanide Metal-Organic

Frameworks

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1. Syntheses, Structure and Crystallographic Studies

Materials and Physical Measurements. All chemicals and solvents are commercially available, and used without further purification. Elemental analyses (C, H and N) were measured by a Perkin-Elmer elemental analyzer. The phase purities of all the samples are demonstrated by powder X-ray diffraction at room temperature. The powder X-ray diffraction patterns were obtained on a Rigaku D/Max-2500 X-ray diffractometer using Cu- $K\alpha$ radiation. The experimental PXRD patterns of synthesized samples match well with their simulated spectra based on single-crystal X-ray diffraction data (Fig. S4-S7), indicating the high purity of samples, which are essential for the subsequent magnetic analysis. An accurate yttrium/dysprosium ratio was determined using the inductively coupled plasma atomic emission spectra (ICP-AES) analyzed by ICP-9000(N+M) (Thermo Jarrell-Ash Corp, USA). Magnetic susceptibilities were performed on a Quantum Design SQUID MPMS VSM magnetometer. Diamagnetic corrections were carried out with Pascal's constants for all constituent atoms and sample holders. Thermogravimetric analyses (TGA) were measured on a NETZSCH TG 209 Setaram apparatus by heating rate of 10 °C/min in Nitrogen atmosphere. Fourier-transform Infrared(FT-IR) spectra (4000-400 cm⁻¹) measurements were implemented on a Bruker ALPHA FT-IR Spectrometer with directly loading powder samples onto the platinum ATR single reflection diamond module.

X-ray Crystal Structure Analysis. Crystallographic data of **1** and **2** were performed on an Oxford Supernova diffractometer equipped with graphite-monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) using ω -scan technique. The structures were solved by direct methods using SHELXL and refined by means of full-matrix least-squares procedures on F^2 with the SHELXS-97 and SHELXL-97 programs.¹ All non-hydrogen atoms were refined anisotropically. Other details of crystal data, data collection parameters, and refinement statistics are given in Table S1. Synthesis of 1 and 2. A mixture of H₂OBA (H₂OBA = 4, 4'-oxybis(benzoate) acid) (0.6 mmol, 154.5 mg), Dy(NO₃)₃·6H₂O (0.4 mmol, 182.5 mg) and 8 mL of DMF/H₂O (1:1, v/v) was placed into a Parr Teflon-lined stainless steel vessel (25 ml) and heated at 160 °C and 80 °C respectively for 3 days under autogenous pressure. After the mixture was cooled to 25 °C for 2 days, colourless block-like crystals of 1 and 2 suitable for single-crystal X-ray structural determination were collected, washed with DMF and dried in air.

 $[Dy_3(OBA)_4(HCOO)(H_2O)(DMF)]_n$ (1). Yield: 48% based on $Dy(NO_3)_3 \cdot 6H_2O$. Elem anal. Calcd (%) for $C_{60}H_{35}NO_{24}Dy_3$: C, 43.86; H, 2.13; N, 0.85. Found: C, 43.92; H 2.52; N 1.00.

 $[Dy_{0.16}Y_{2.84}(OBA)_4(HCOO)(H_2O)(DMF)]_n$ (1'). The synthetic process of 1' is similar to that of 1, except $Dy(NO_3)_3 \cdot 6H_2O$ was replaced by a mixture of $Dy(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ in a molar ratio of 1:30. Colorless block crystals were obtained after filtration and dried in air. Yield: 47% based on $Dy(NO_3)_3 \cdot 6H_2O$. Elem anal. Calcd (%) for $C_{60}H_{35}NO_{24}Dy_{0.16}Y_{2.84}$: C, 50.31; H, 2.44; N, 0.97. Found: C, 50.28; H, 2.85; N, 1.19. ICP-OES anal (wt%). Found: Dy, 2.11; Y, 20.1.

{[Dy(OBA)(HOBA)(H₂O)₂]·3DMF}_n (**2**). Yield: 70% based on H₂OBA. Elem anal. Calcd (%) for $C_{37}H_{42}N_3O_{15}Dy$: C, 47.72; H, 4.55; N, 4.51. Found: C, 47.44; H, 4.92; N, 4.16.

{[Dy_{0.027}Y_{0.972}(OBA)(HOBA)(H₂O)₂]·3DMF}_n (**2'**). The synthetic process of **2'** is similar to that of **2**, except Dy(NO₃)₃·6H₂O was replaced by a mixture of Dy(NO₃)₃·6H₂O and Y(NO₃)₃·6H₂O in a molar ratio of 1:30. Colorless block crystals were obtained after filtration and dried in air. Yield: 52% based on H₂OBA. Elem anal. Calcd (%) for C₃₇H₄₂N₃O₁₅Dy_{0.027}Y_{0.972}: C, 51.64; H, 4.92; N, 4.88. Found: C, 51.44; H, 5.13; N, 4.50. ICP-OES anal (wt%). Found: Dy, 0.54; Y, 10.6.

	1	2
CCDC	1849050	1849051
Formula	$C_{60}H_{35}NO_{24}Dy_{3}$	$C_{37}H_{41}N_3O_{15}Dy$
Formula wt	1641.39	931.24
Temperature (K)	120.00(1)	130.25(1)
Crystal System	orthorhombic	triclinic
Space Group	$Cmc2_1$	P^{1}
a (Å)	27.7738(15)	9.4019(5)
<i>b</i> (Å)	10.6809(5)	13.8627(6)
<i>c</i> (Å)	19.1423(8)	16.5461(8)
α (deg)	90.00	85.355(4)
β (deg)	90.00	76.826(4)
γ (deg)	90.00	72.112(4)
Z	4	2
V (Å ³)	5678.5(5)	1998.15(16)
$\rho_{\rm calc}$ (g/cm ³)	1.920	1.548
$\mu (\mathrm{mm}^{-1})$	3.995	1.942
F(000)	3168.0	942.0
$R_{ m int}$	0.0565	0.0546
S	1.040	1.047
$R_1, wR_2(I \ge 2\sigma(I))^a$	0.0333, 0.0709	0.0370, 0.0840
R_1, wR_2 (all data) ^b	0.0354, 0.0725	0.0422, 0.0887
$_{a}R_{1} = \sum F_{0} - F_{c} ,$	$/\sum F_0 _{,b} wR_2 = \left \sum w($	$ F_0 ^2 - F_c ^2 /\sum w(F_o)^2 ^{1/2}$

 Table S1. Crystal Data and Structure Refinement Details for 1 and 2.



Fig. S1 The Dy-COO chain structure of 1.



Fig. S2 The 3D structure of 1 and coordination modes of the ligand in 1.







Fig. S3 The simplified diagrams of **1** in different directions (The ligands were simplified for clarity).



Fig. S4 Comparison of the experimental PXRD patterns of **1** and **1'** with the simulated pattern from the single crystal data of **1**.



Fig. S5 Comparison of the experimental PXRD patterns of 2 and 2' with the simulated pattern from the single crystal data of 2.



Fig. S6 Comparison of the experimental PXRD patterns of **1** and **1**' standing for 48h in the mother solution with the simulated pattern from the single crystal data of **2**.



Fig. S7 Comparison of the experimental PXRD patterns of **2** and **2**' heating for 72 h in the mother solution with the simulated pattern from the single crystal data of **1**.



Fig. S8 IR spectra of 1 and 2.



Fig. S9 TGA of 1 and 2.



Fig. S10 The Dy-COO chain structure of 2.



Fig. S11 The 2D network architecture structure of 2 and coordination modes of the ligand in 2.



Fig. S12 The 3D supramolecular structure connected by hydrogen bonds of 2.



Fig. S13 The hydrogen bonds between the layers of 2.



Fig. S14 The $\pi \cdots \pi$ stacking between benzene ring of adjacent layers in **2**.



Fig. S15 (a-c) The separation/convergence of the adjacent layers during the transformation processes between 1 and 2; (d) The change of coordination environment of Dy^{III} ions during the transformation processes between 1 and 2 (The dotted lines are cracked/new generated bonds).

In ions	Coordination	Symmetry	Deviated
number	Symmetry	parameters	
1- Dy1	7	Capped trigonal prism (C_{2v})	0.623
1-Dy2	7	Capped trigonal prism (C_{2v})	0.590
1-Dy3	9	Spherical capped square antiprism (C_{4v})	1.964
1 Der1	Dy1 8 Biaugmented trigonal p Square antiprism	Biaugmented trigonal prism (C_{2v})	1.705
2-Dy1 8		Square antiprism (D_{4d})	1.777

 Table S2. Symmetries and Deviated Parameters for 1 and 2.

2. Other Magnetic Data



Fig. S16 The temperature dependence of $\chi_{\rm M}T$ curves for 1 and 1' under 1000 Oe dc field.



Fig. S17 The field dependence of magnetization for 1 and 1' at 2 K.



Fig. S18 The field dependence of magnetization for 2 and 2' at 2 K.



Fig. S19 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') of ac susceptibilities for 1 under the indicated frequencies.



Fig. S20 Temperature dependence of the (left) in-phase (χ') and (right) out-of-phase (χ'') of ac susceptibilities for 2 under variable frequencies.



Fig. S21 The τ versus T^{-n} plot shown in log-log scale for **2**.



Fig. S22 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') of ac susceptibilities for 1' under the indicated frequencies.



Fig. S23 Temperature dependence of the (left) in-phase (χ') and (right) out-of-phase (χ'') of ac susceptibilities for 2' under variable frequencies.



Fig. S24 The τ versus T^{-n} plot shown in log-log scale for **2'**.



Fig. S25 Magnetization hysteresis at 2 K within ±70 kOe for **2**.



Fig. S26 Magnetization hysteresis at 2 K within ± 70 kOe for 2'.



Fig. S27 FC/ZFC for 2.



Fig. S28 FC/ZFC for for 2'.

5. Tables of Magnetic Data

Т / К	$\chi_{ m S}$ / cm ³ mol ⁻¹	$\chi_{\rm T}$ / cm ³ mol ⁻¹	α
2.0	0.3418	6.3696	0.3539
2.5	0.3455	5.3399	0.3226
3.0	0.3721	4.4965	0.2554
3.3	0.3769	3.9961	0.2166
3.6	0.4287	3.7538	0.2196
3.9	0.3705	3.4566	0.2269
4.2	0.2863	3.1779	0.2303
4.5	0.4612	3.1547	0.2241
4.8	0.8796	3.2756	0.2069
5.1	1.4345	3.4261	0.1889

 Table S3. Debye Model Fitting Parameters for 2.

Table S4. Debye Model Fitting Parameters for 2'.

<i>T /</i> K	$\chi_{\rm S}$ / cm ³ mol ⁻¹	$\chi_{\rm T}$ / cm ³ mol ⁻¹	α
2.0	0.3320	5.8896	0.3109
2.3	0.2817	5.4645	0.5197
2.5	0.4689	4.6664	0.2359
2.8	0.4830	3.9478	0.1969
3.1	0.4691	3.5008	0.1532
3.4	0.3675	3.1880	0.1434
3.7	0.2945	2.9370	0.1083

References

 (a) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997; (b) Sheldrick, G. M. SHELXS-97, Program for Solution of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.