

## **Electronic Supporting Information**

# **Dy(III) zig-zag chains assembled in a 3D framework with single-molecule magnet behavior**

Chao Bai, Chuan-Ti Li, Huai-Ming Hu\*, Bin Liu, Jin-Dian Li and Ganglin Xue

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China

\*To whom correspondence should be addressed.

Prof. Dr. Huai-Ming Hu

College of Chemistry and Materials Science

Northwest University

Xi'an 710127, China

Tel/Fax: +86-29-81535026

Email: [chemhu1@nwu.edu.cn](mailto:chemhu1@nwu.edu.cn)

## Experimental Section

### Materials and physical measurements

All chemicals were commercially available sources of analytical grade and employed without further purification. Hydrated dysprosium (III) nitrate was prepared in the usual way by evaporating the solution of the corresponding oxide (99.9%) in HNO<sub>3</sub>. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform Infrared spectrometer in the 400-4000 cm<sup>-1</sup> region. Elemental analyses (C, H, N) were carried out with an ElementarVario EL analyzer. Thermal gravimetry analyse (TGA) was carried out with a Universal V2.6 DTA system at a rate of 10 °C/min in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurement was measured on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K<sub>α</sub>, 1.5418 Å). Magnetic data were collected on a Quantum Design MPMS-7 SQUID magnetometer using crushed samples (in the powdered form).

### Synthesis of sodium 2-(2,2':6',2''-terpyridin-4'-yl)benzenesulfonate (NaSTP)

Sodium 2-formylbenzenesulfonate (5.2 g, 25 mmol) and 2-acetylpyridine (5.6 mL, 50 mmol) were dissolved in 80 ml ethanol. Then the 30% NH<sub>3</sub>·H<sub>2</sub>O (5mL) and NaOH (2 g, 50 mmol) were added. The solution was stirred vigorously at 0-5°C for 3h and then at room temperature for 12h, after which yellow precipitate appeared. The stirring was continued at 50°C for 12h and more precipitate was obtained. The precipitate was collected by filtration, washed with methanol, and dried at 60°C overnight (5.45 g, yield: 45.13% based on sodium 2-formylbenzenesulfonate). Anal. Calc for NaSTP·4H<sub>2</sub>O: C, 61.31; H, 3.43; N, 10.21%. Found: C, 61.21; H, 3.55; N, 10.27%. IR (KBr, cm<sup>-1</sup>): 3389 (m), 3058 (W), 1590 (s), 1567 (m), 1463 (s), 1426 (m), 1407 (m) 1217 (s), 1140 (s), 1084 (m), 1021 (m), 770 (m), 725(w), 658(w), 613 (m). <sup>1</sup>H NMR (400 MHz, DMSO): δ 8.80-8.64 (m, 4H), 8.56 (s, 2H), 8.12-7.98 (m, 3H), 7.59-7.44 (m, 4H), 7.34-7.26 (m, 1H).

### Synthesis of [Dy(STP)(1,2-bdc)]<sub>n</sub> (**1**)

A mixture of NaSTP (0.010g, 0.025 mmol), Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.024g, 0.05 mmol) and H<sub>2</sub>(1,2-bdc) (0.004g, 0.025 mmol) in distilled water (2 mL) was stirred for 30 min in air. After the pH value of the mixture was adjusted to 5.0 with 0.5 M NaOH, then sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 180°C for 3 days. After cooling to room temperature, yellow block-shaped crystals were obtained by filtration in 54.2% yield based on NaSTP. Anal. Calc (%) for C<sub>29</sub>H<sub>18</sub>DyN<sub>3</sub>O<sub>7</sub>S (714): C, 48.71; H, 2.53; N, 5.88%. Found: C, 48.78; H, 2.35; N, 5.77%. IR (KBr, cm<sup>-1</sup>): 3451 (m), 1635 (s), 1547 (s), 1485 (m), 1418 (s), 1259 (s), 1184 (s), 1015 (m), 788 (w), 751 (w), 720 (m), 613 (m).

### X-ray crystallography

Intensity data for **1** was conducted on a Bruker Smart Apex II CCD diffractometer using Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296(2) K. The structure was solved using the direct methods and refined by full-matrix least-squares technique based on  $F^2$  by SHELXL-97 and SHELXS-97. Non-hydrogen atoms were refined anisotropically. Pertinent crystal data and structural refinement results, and selected bond distances and angles for **1** are listed in Tables S1 and S2, respectively. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre.

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

Compound	<b>1</b>
empirical formula	C <sub>29</sub> H <sub>18</sub> DyN <sub>3</sub> O <sub>7</sub> S
formula weight	715.02
crystal system	Monoclinic
space group	P2(1)/n
<i>a</i> (Å)	9.096(4)
<i>b</i> (Å)	13.463(7)
<i>c</i> (Å)	20.685(10)
$\alpha$ (°)	90
$\beta$ (°)	97.556(10)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	2511(2)
<i>Z</i>	4
$\rho_{\text{calcd}}$ (mg·m <sup>-3</sup> )	1.891
$\mu$ (mm <sup>-1</sup> )	3.116
<i>F</i> (000)	1404
collected / unique	12203 / 4436
<i>R</i> <sub>(int)</sub>	0.1356
parameters	370
<i>S</i> on <i>F</i> <sup>2</sup>	0.962
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0657, 0.1135
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>a</sup> (all data)	0.1360, 0.1412
$\Delta\rho_{\text{max and min}}$ (e·Å <sup>-3</sup> )	1.186 and -1.026
CCDC	1860308

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR_2 = \frac{\sum [(w(F_o^2 - F_c^2)^2)]}{\sum [w(F_o^2)^2]}^{1/2}$$

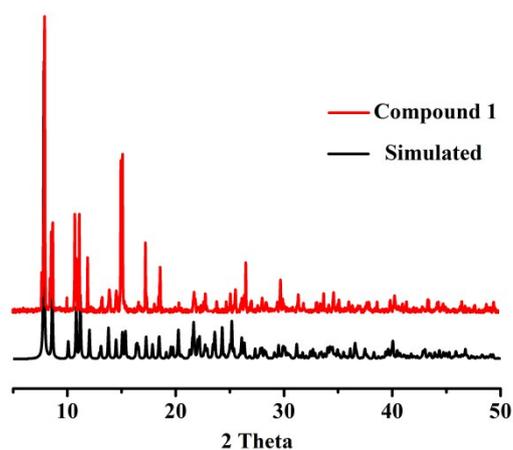
**Table S2.** Selected bond lengths (Å) and angles (deg) of **1**.

Dy(1)-O(7)#1	2.258(8)	Dy(1)-O(4)	2.285(9)
Dy(1)-O(6)	2.325(9)	Dy(1)-O(5)#2	2.325(8)
Dy(1)-O(1)#3	2.381(8)	Dy(1)-N(2)	2.501(10)
Dy(1)-N(3)	2.534(9)	Dy(1)-N(1)	2.546(10)
O(7)#1-Dy(1)-O(4)	100.2(3)	O(7)#1-Dy(1)-O(6)	78.8(3)
O(4)-Dy(1)-O(6)	70.1(3)	O(7)#1-Dy(1)-O(5)#2	147.7(3)
O(4)-Dy(1)-O(5)#2	93.3(3)	O(6)-Dy(1)-O(5)#2	78.4(3)
O(7)#1-Dy(1)-O(1)#3	70.5(3)	O(4)-Dy(1)-O(1)#3	87.4(3)
O(6)-Dy(1)-O(1)#3	137.9(3)	O(5)#2-Dy(1)-O(1)#3	139.9(3)
O(7)#1-Dy(1)-N(2)	103.6(3)	O(4)-Dy(1)-N(2)	146.1(3)
O(6)-Dy(1)-N(2)	138.3(3)	O(5)#2-Dy(1)-N(2)	79.3(3)
O(1)#3-Dy(1)-N(2)	78.1(3)	O(7)#1-Dy(1)-N(3)	136.2(3)
O(4)-Dy(1)-N(3)	81.5(3)	O(6)-Dy(1)-N(3)	139.3(3)
O(5)#2-Dy(1)-N(3)	74.6(3)	O(1)#3-Dy(1)-N(3)	65.8(3)
N(2)-Dy(1)-N(3)	64.5(3)	O(7)#1-Dy(1)-N(1)	74.5(3)
O(4)-Dy(1)-N(1)	147.1(3)	O(6)-Dy(1)-N(1)	77.0(3)
O(5)#2-Dy(1)-N(1)	78.3(3)	O(1)#3-Dy(1)-N(1)	119.5(3)
N(2)-Dy(1)-N(1)	64.1(3)	N(3)-Dy(1)-N(1)	125.1(3)

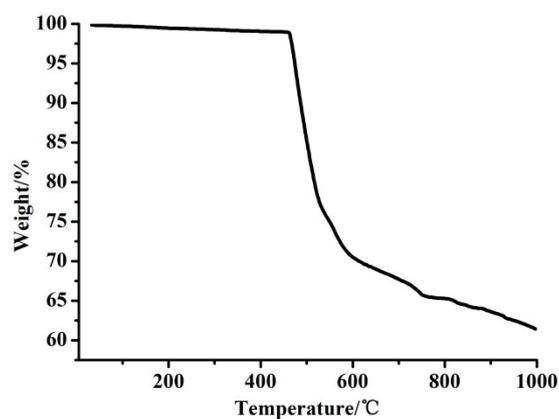
**Table S3.** Continuous Shape Measures (CShMs)<sup>1</sup> of the coordination geometry for Dy<sup>3+</sup> ion in **1**.

Label	Symmetry	Shape	
OP-8	D <sub>8h</sub>	Octagon	31.262
HPY-8	C <sub>7v</sub>	Heptagonal pyramid	24.014
HBPY-8	D <sub>6h</sub>	Hexagonal bipyramid	15.832
CU-8	O <sub>h</sub>	Cube	11.813
SAPR-8	D <sub>4d</sub>	Square antiprism	2.997
<b>TDD-8</b>	<b>D<sub>2d</sub></b>	<b>Triangular dodecahedron</b>	<b>1.371</b>
JGBF-8	D <sub>2d</sub>	Johnson gyrobifastigium J26	12.414
JETBPY-8	D <sub>3h</sub>	Johnson elongated triangular bipyramid J14	27.548
JBTPR-8	C <sub>2v</sub>	Biaugmented trigonal prism J50	2.375
BTPR-8	C <sub>2v</sub>	Biaugmented trigonal prism	1.909
JSD-8	D <sub>2d</sub>	Snub diphenoid J84	2.967
TT-8	T <sub>d</sub>	Triakis tetrahedron	12.232
ETBPY-8	D <sub>3h</sub>	Triakis tetrahedron	23.338

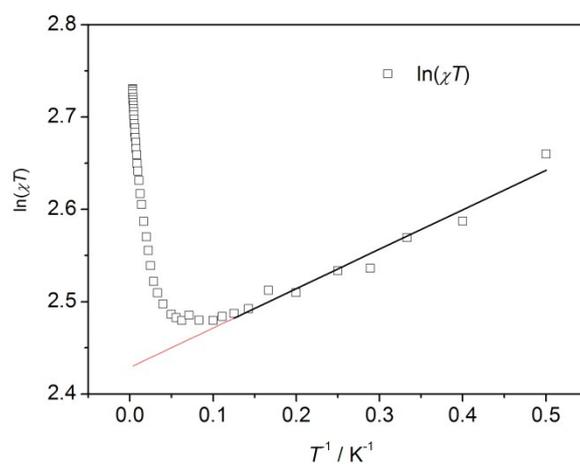
<sup>1</sup>M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, Shape 2.0, Universitat de Barcelona, 2010.



**Fig. S1.** Experimental and simulated powder XRD patterns of **1**.



**Fig. S2.** TGA curve of **1**.



**Fig. S3.** The plots of  $\ln(\chi T)$  vs  $T^{-1}$  of **1** in the linear regime of temperature range of 10-16 K.