# A Square Antiprism Dysprosium Single-Ion Magnet with Energy Barrier over 900 K

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# **EXPERIMENTAL SECTION**

### **General Procedure.**

All reactions and manipulations described below were performed under aerobic conditions. The ligand *N*,*N*'-bis(2-hydroxybenzyl)-*N*,*N*'-bis(2-methylpyridy1)ethylenediamine (H<sub>2</sub>bbpen) was prepared in excellent yield according to the reported methods. Metal salts and other reagents were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on an EQUINOX 55 spectrometer. Thermogravimetric analysis was carried out on a NETZSCH TG209F3 thermogravimetric analyzer. X-ray powder diffraction intensities for polycrystalline samples were measured at 293 K on Bruker D8 Advance Diffratometer (Cu-*Ka*,  $\lambda = 1.54178$  Å).

# Synthesis of [Dy(bbpen)(Ph<sub>3</sub>PO)<sub>2</sub>][BPh<sub>4</sub>]

 $Dy(NO_3)_3 \cdot 6H_2O$  (0.01 mmol),  $H_2bbpen$  (0.01 mmol) and  $Et_3N$  (0.02 mmol) were added to a solution of 6 mL acetonitrile and then the mixture was stirred for 10 minutes. Then add 0.02 mmol of  $Ph_3PO$  and stirred for another 10 mins. 0.01 mmol of  $NaBPh_4$  was added and mixture was stirred for 10 minutes. Finally the mixture was transferred to a teflon sealed autoclave and heated for 72 hours. Block shaped colorless crystals were obtained and dried in the air for days.

The sample can be synthesized in a different method.  $[Dy(bbpen)]NO_3 (0.01 \text{ mmol})^1$  and Ph<sub>3</sub>PO (0.02 mmol) were added to a solution of 6 mL acetonitrile, and then the mixture was stirred for 10 minutes. After NaBPh<sub>4</sub> (0.01 mmol) was added, the mixture was stirring for another 10 minutes. Finally the mixture was transferred to a teflon sealed autoclave and heated for 72 hours. Block shaped colorless crystals were obtained and dried in the air for days. Colorless crystals were obtained. Elemental analysis: anal. calcd for C<sub>88</sub>H<sub>78</sub>BDyN<sub>4</sub>O<sub>4</sub>P<sub>2</sub>: C, 70.82; H, 5.23; N, 3.75. Found: C, 70.98; H, 5.30; N, 3.65. IR (KBr, cm<sup>-1</sup>): 3423(b), 3054(s), 2830(s), 1823(ms), 1590(s), 1479(s), 1432(s), 1306(s), 1162(s), 1115(s).

**Computational Details.** All *ab initio* calculations were carried out with Open MOLCAS version  $18.09^2$  and are of the CASSCF/RASSI type. The Cholesky decomposition threshold was set to  $1 \times 10^{-8}$  to save disk space. An entire molecule was included, and the coordinates of atoms were extracted from the experimentally determined crystal structure. ANO-RCC-VTZP basis set approximations have been employed for Dy, P, O and N atoms, ANO-RCC-

VTZP for C atoms and ANO-RCC-VTZ for H atoms.<sup>3-5</sup> Active space of the CASSCF method included nine electrons in seven 4f orbitals of Dy(III). 21 sextets, 224 quartets and 490 doublets were optimized in state-averaged calculations, and then 21 sextets, 128 quartets and 130 doublets were mixed by spin–orbit coupling using RASSI approach.<sup>6</sup> The *g*-tensors, energies, main magnetic axis as well as the magnetizations were obtained by SINGLE\_ANISO routine<sup>7</sup>.

## **Magnetic Measurements**

Magnetic susceptibility measurements were collected using a Quantum Design MPMS-XL7 SQUID magnetometer and a Quantum Design PPMS VSM. Polycrystalline samples were embedded in vaseline to prevent torqueing. AC magnetic susceptibility data measurements were performed with a 5 Oe oscillating field at frequencies between 1 and 1488 Hz. All data were corrected for the diamagnetic contribution.

### X-ray Crystallography

Diffraction intensities were collected on a Bruker D8 QUEST diffractometer with Mo-*K* $\alpha$  radiation ( $\lambda = 0.71073$  Å) for **1** at 120 K. The structures were solved by SHELXT and all non-hydrogen atoms were refined by least-squares on *F*<sup>2</sup> utilizing the SHELXTL program suite and Olex2.<sup>8</sup> All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Data have been deposited at the Cambridge Structural Database with the following CCDC numbers: 1920897.



Figure S1. Molecular structure of 1 with its anion.



Figure S2. Thermogravimetric analysis for 1 under N<sub>2</sub> atmosphere (10 K min<sup>-1</sup>).



Figure S3. Experimental and simulated X-ray powder diffraction (PXRD) patterns for 1.

Table S1. Dy(III) geometry analysis by using Continuous Shape Measurements (CShM).9

ОР	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8
( <b>D</b> <sub>8h</sub> )	(C <sub>7v</sub> )	( <b>D</b> <sub>6h</sub> )	( <b>O</b> <sub>h</sub> )	( <b>D</b> <sub>4d</sub> )	( <b>D</b> <sub>3d</sub> )	( <b>D</b> <sub>3d</sub> )
31.58845	22.19258	12.38895	7.59553	1.39626	2.81764	12.57748
JETBPY-8	<b>JBTPR-8</b>	BTPR-8	JSD-8	TT-8	ETBPY-8	
( <b>D</b> <sub>3h</sub> )	(C <sub>2v</sub> )	(C <sub>2v</sub> )	( <b>D</b> <sub>2d</sub> )	(T <sub>d</sub> )	( <b>D</b> <sub>3h</sub> )	
27.95271	3.10116	2.85671	4.77044	8.47343	23.22614	

OP-8 = Octagon, HPY-8 = Heptagonal pyramid, HBPY-8 = Hexagonal bipyramid, CU-8 = Cube, SAPR-8 = Square antiprism, TDD-8 = Triangular dodecahedron, JGBF-8 = Johnson gyrobifastigium J26, JETBPY-8 = Johnson elongated triangular bipyramid J14, JBTPR-8 = Biaugmented trigonal prism J50, BTPR-8 = Biaugmented trigonal prism, JSD-8 = Snub diphenoid J84, TT-8 = Triakis tetrahedron, ETBPY-8 = Elongated trigonal bipyramid

	1
Empirical formula	$C_{88}H_{78}BDyN_4O_4P_2$
Formula weight	1490.79
Temperature/K	120
Crystal system	monoclinic
Space group	C2/c
a/Å	20.8027(9)
$b/\text{\AA}$	19.3411(9)
$c/\text{\AA}$	18.5062(8)
β/°	106.428(2)
Volume/Å <sup>3</sup>	7141.9(5)
Ζ	4
$ ho_{ m calc}/ m g\  m cm^{-3}$	1.386
$\mu/\mathrm{mm}^{-1}$	1.148
F(000)	3068
Radiation	Mo- <i>K</i> $\alpha$ ( $\lambda$ = 0.71073)
Reflections collected	24156
Independent reflections	$8112 [R_{int} = 0.0349, R_{sigma} = 0.0416]$
Goodness-of-fit on $F^2$	1.064
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0497, wR_2 = 0.1020$
Final R indexes [all data]	$R_1 = 0.0654, wR_2 = 0.1106$
Largest diff. peak/hole/eÅ <sup>-3</sup>	1.475/-1.480
CCDC no.	1920897
$\underline{a R_1 = \sum  F_0  -  F_c   / \sum  F_o ; b wR_2} = \{ \sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2 - F_c^2) / \sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2 - F_c^2) / \sum w(F_0^2 - F_c^2$	$[w(F_0^2)^2]\}^{1/2}.$

 Table S2. Crystal data and structure refinement parameters for 1

 Table S3. Selected bond lengths [Å] and angles [°] for 1

Bond le	engths	Bond a	ngles	
Dy <sub>1</sub> —O <sub>1</sub>	2.343(3)	O <sub>1</sub> —Dy <sub>1</sub> —O <sub>1</sub>	76.17(14)	
$Dy_1 - O_1$	2.343(3)	$O_2 - Dy_1 - O_1$	83.63(10)	
$Dy_1 - O_2$	2.208(3)	$O_2$ — $Dy_1$ — $O_1$	83.63(10)	
$Dy_1 - O_2$	2.208(3)	$O_2$ — $Dy_1$ — $O_1$	81.94(11)	
$Dy_1 - N_1$	2.689(3)	$O_2$ — $Dy_1$ — $O_1$	81.94(11)	
$Dy_1 - N_1$	2.689(3)	$O_2$ — $Dy_1$ — $O_2$	161.64(15)	
$Dy_1 - N_2$	2.598(3)	$N_1$ — $Dy_1$ — $O_1$	149.30(11)	
$Dy_1 - N_2$	2.598(3)	$N_1$ — $Dy_1$ — $O_1$	116.68(10)	
		$N_1$ — $Dy_1$ — $O_1$	149.30(11)	
		$N_1$ — $Dy_1$ — $O_1$	116.68(10)	
		$N_1$ — $Dy_1$ — $O_2$	125.41(11)	
		$N_1$ — $Dy_1$ — $O_2$	125.41(11)	
		$N_1$ — $Dy_1$ — $O_2$	71.69(10)	
		$N_1$ — $Dy_1$ — $O_2$	71.69(10)	
		$N_1$ — $Dy_1$ — $N_1$	67.49(14)	
		$N_2$ — $Dy_1$ — $O_1$	145.92(11)	
		$N_2$ — $Dy_1$ — $O_1$	73.69(11)	
		$N_2$ — $Dy_1$ — $O_1$	73.69(11)	
		$N_2$ — $Dy_1$ — $O_1$	145.92(11)	
		$N_2$ — $Dy_1$ — $O_2$	79.29(11)	
		$N_2$ — $Dy_1$ — $O_2$	107.27(10)	
		$N_2$ — $Dy_1$ — $O_2$	79.29(11)	
		$N_2$ — $Dy_1$ — $O_2$	107.27(10)	
		$N_2$ — $Dy_1$ — $N_1$	61.95(11)	

$N_2$ — $Dy_1$ — $N_1$	61.95(11)
$N_2$ — $Dy_1$ — $N_1$	83.79(10)
$N_2$ — $Dy_1$ — $N_1$	83.79(10)
$N_2 - Dy_1 - N_2$	139.29(15)



Figure S4. Square-antiprismatic environment with skew angle  $\Phi$  between the diagonals of the two squares.



**Figure S5**. Angle  $\alpha$  between the pseudo- $S_8$  axis and a Dy-N/Dy-O vector.



in steady fields. The solid lines correspond to the ab initio calculations.



**Figure S7.** Frequency dependence of the  $\chi'_{M}T$  and out-of-phase ( $\chi''_{M}$ ) components of the ac magnetic susceptibility for 1 under zero applied dc field.



**Figure S8.** Temperature-dependence of the in-phase ( $\chi'_M T$ ) and out-of-phase ( $\chi''_M$ ) products under zero dc field.



Figure S9. Cole–Cole plots of 1 at 25-55 K (*left*) and 11-25 K (*right*) under zero dc field.



**Figure S10.** Frequency dependence of the in-phase ( $\chi'_M T$ ) and out-of-phase ( $\chi''_M$ ) products under 2 kOe dc field with the ac frequency of 1-1488 Hz.



**Figure S11.** Temperature dependence of the in-phase  $(\chi'_M T)$  and out-of-phase  $(\chi''_M)$  products under 2 kOe dc field with the ac frequency of 1-1488 Hz.



Figure S12. Field dependence of the relaxation time for 1.



Figure S13. Dc magnetic relaxation data for 1 collected at 2-8 K. Solid lines represent the best fits to the data using  $m = m_0 \exp[-(t/\tau)^{\beta}]$ .

KD	<i>E</i> (cm <sup>-1</sup> )	g	Angle (°)
		0.0000181	
1	0	0.0000690	0
		19.8323852	
		0.0273252	
2	301.342	0.0280360	2.77
		16.9868599	
		0.4871115	
3	579.116	0.9102843	2.58
		13.4563920	
		0.5807272	
4	670.967	2.3469784	89.96
		16.1680453	
		0.9275015	
5	738.432	3.0925891	89.96
		12.2377993	
		1.5100804	
6	768.011	2.7546342	36.74
		9.1929459	
		1.9698607	
7	815.827	3.1337639	64.94
		14.4809716	
		0.0848631	
8	979.953	0.1379032	66.45
		19.4946445	

**Table S4.** Energies (cm<sup>-1</sup>), *g*-tensors ( $g_X$ ,  $g_Y$ ,  $g_Z$ ) and angles (°) between the main magnetic axes of the lowest Kramers doublets for the local Dy(III) sites of the complex.

Table S5. Weight of individual crystal field parameters on the crystal field splitting for the local Dy(III) sites of 1<sup>17b</sup>

k	q	$B_{k}^{q}$ (cm <sup>-1</sup> )	Weight (%)
2	0	-10.3221	21.70807
4	0	-0.07653	13.00893
6	0	0.00111	7.11575
2	2	3.27988	6.89781
2	1	2.78512	5.85729
4	3	0.02925	4.97162
4	4	0.02228	3.78728
6	-5	5.60935E-4	3.58342
6	5	5.40083E-4	3.45021
6	2	4.59366E-4	2.93457
4	-4	0.01672	2.84205
4	-3	0.01552	2.63769
6	1	-3.72557E-4	2.38001
6	3	3.69989E-4	2.3636
6	4	3.6034E-4	2.30196
2	-2	1.06065	2.23061
4	2	0.01065	1.81063
6	-4	2.53803E-4	1.62137
6	-3	1.99207E-4	1.27259
2	-1	0.47612	1.00131
6	-2	1.42981E-4	0.91341
4	1	-0.00398	0.6774

6	-1	-7.32371E-5	0.46786
4	-2	0.00273	0.46426

The parameters with weight <0.3% are not shown.  $\hat{H} = \sum B_k^q \hat{O}_k^q$ , where  $\hat{O}_k^q$  is the extended Steven operators.



**Figure S14.** Molecular structure for the complex with the orientation of the main magnetic axis of the ground Kramers doublet (green arrow). Color code: Dy, orange; P, pink; O, red; N, blue; C, grey.



**Figure S15.** Magnetization blocking barriers for complex 1. The lowest 16 spin-orbit states are arranged according to the magnitude of their magnetic moments on the horizontal axis. The numbers next to arrows connecting two states display the average transition magnetic moment matrix element between the respective states. Since the tunneling transition rate ( $\Gamma_{i\pm}$ ) is roughly proportional to  $\mu^2 \exp(-E_i/k_BT)$ , the relative transition rate of 4th and 3rd KDs ( $\Gamma_{4\pm}/\Gamma_{3\pm}$ ) is 11.7 at 50 K, suggesting the magnetization mainly relaxes through the 4th KD at 50 K. This is consistent with the extracted effective energy barrier from ac magnetic susceptibilities.

$U_{\rm eff}/k_{\rm B}$ [K] under 0 dc field	Hysteresis temperature [K]	References
189	2 (diluted sample)	10
128	4	11
136	1.9	12
187	1.9	12
102	5	13
149	5	14
151	2	15
190	2	16
696	7	17
944	6	This work

Table S6. Some examples of Dy-SIMs with square antiprism (SAP) coordination environment.

Table S7. Some examples of Dy-SIMs with phosphine oxide derivatives

$U_{\rm eff}/k_{\rm B}$ [K] under 0 dc field	Hysteresis temperature [K]	References
734	12	17
556	12	18
508	19	19
543	20	20
944	6	This work

## References

- (a) T. Gregorio, A. L. Rudiger, G. G. Nunes, J. F. Soares and D. L. Hughes, *Acta Crystallogr. E*, 2015, 71, 65-68; (b) I. A. Setyawati, S. Liu, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 2000, 39, 496-507; (c) Y. Yamada, S.-I. Takenouchi, Y. Miyoshi and K.-I. Okamoto, *J. Coord. Chem.*, 2010, 63, 996-1012.
- F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.*, 2016, 37, 506-541.
- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark and A. C. Borin, J. Phys. Chem. A, 2008, 112, 11431-11435.
- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, J. Phys. Chem. A, 2004, 108, 2851-2858.
- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, J. Phys. Chem. A, 2005, 109, 6575-6579.
- 6. P. Å. Malmqvist, B. O. Roos and B. Schimmelpfennig, Chem. Phys. Lett., 2002, 357, 230-240.
- 7. L. F. Chibotaru and L. Ungur, J. Chem. Phys., 2012, 137, 064112.
- (a) G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3; (b) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2015, 71, 3; (c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339.
- (a) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, 249, 1693-1708; (b) D. Casanova, M. Llunell, P. Alemany and S. Alvarez, *Chem. Eur. J.* 2005, 11, 1479-1494.
- 10. C. Gao, Q. Yang, B.-W. Wang, Z.-M. Wang and S. Gao, CrystEngComm, 2016, 18, 4165–4171.
- 11. X. Yao, P. Yan, G. An, C. Shi, Y. Li and G. Li, New J. Chem., 2018, 42, 8438-8444.
- 12. G. J. Chen, Y. N. Guo, J. L. Tian, J. Tang, W. Gu, X. Liu, S. P. Yan, P. Cheng and D. Z. Liao, *Chem. Eur. J.*, 2012, **18**, 2484-2487.
- S. Zhang, H. Ke, L. Sun, X. Li, Q. Shi, G. Xie, Q. Wei, D. Yang, W. Wang and S. Chen, *Inorg. Chem.*, 2016, 55, 3865-3871.
- 14. S. Zhang, W. Mo, B. Yin, G. Zhang, D. Yang, X. Lu and S. Chen, Dalton Trans., 2018, 47, 12393-12405.
- 15. S. Zhang, W. Mo, J. Zhang, H. Wu, M. Li, X. Lü, B. Yin and D. Yang, RSC Adv., 2018, 8, 29513-29525.
- 16. J. f. Wu, J. Jung, P. Zhang, H. Zhang, J. Tang and B. L. Guennic, Chem. Sci., 2016, 7, 3632-3639.
- 17. S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, Chem. Sci., 2016, 7, 5181-5191.
- 18. L-L. Li, H-D. Su, S. Liu, Y-C. Xu and W-Z. Wang, Dalton Trans., 2019, 48, 2213-2219.
- Y-C. Chen, J-L. Liu, Y. Lan, Z-Q. Zhong, A. Mansikkam-ki, L. Ungur, Q-W. Li, J-H. Jia, L. F. Chibotaru, J-B. Han, W. Wernsdorfer, X-M. Chen and M-L. Tong, *Chem. Eur. J.*, 2017, 23, 5708-5715.
- Y.-C. Chen, J.-L. Liu, L. Ungur, J. Liu, Q.-W. Li, L.-F. Wang, Z.-P. Ni, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, J. Am. Chem. Soc., 2016, 138, 2829.