#### **Supporting Information**

# Single-molecule magnet behaviour in a dysprosium-triradical

# complex

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# **1.** Physical Measurements

IR data were measured on KBr pellets using a Bruker Vector 27 FT-IR spectrometer in the 4000-400 cm<sup>-1</sup> range. Elemental analyses for C, H, and N were performed at Elementar Vario MICRO analyzer. Magnetic measurements were performed using Quantum Design SQUID MPMS/VSM magnetometers on the microcrystalline sample of **1** embedded in eicosane. Direct current (dc) measurements were conducted from 300 to 2 K under an external magnetic field of 1000 Oe. The field dependence of the magnetization was measured at 2 K with dc magnetic field between 0 and 7 T. All magnetic data were corrected for the sample holder, the eicosane and for the diamagnetic contribution of the sample.

## 2. Synthesis

All preparations and manipulations were performed under ambient conditions. The solvents were obtained from commercial sources (AR grade) and used as received. The starting material 1,3,5-benzenetricarboxaldehyde was synthesized following a published method.<sup>S1</sup> Dy(hfac)<sub>3</sub> 2H<sub>2</sub>O was prepared according to the literature method.<sup>S2</sup>

**Synthesis of triradical BTR**. This triradical ligand BTR was prepared by refluxing of 2,3-bis(hydroxyamino)-2,3-dimethylbutane with 1,3,5-benzenetricarboxaldehyde in toluene, followed by oxidation with NaIO<sub>4</sub> according to the reported Ullman's method<sup>S3</sup> and then purified by recrystallization. Yield 57%, dark blue powder. Elemental analysis (%) calculated for **BTR** (C<sub>27</sub>H<sub>39</sub>N<sub>6</sub>O<sub>6</sub>, M = 543.65): C, 59.65; H, 7.23; N, 15.46. Found: C, 59.53; H, 7.21; N, 15.41. Selected FT-IR (KBr, cm<sup>-1</sup>): 3408 (w), 3110 (w), 2982 (m), 2942 (m), 2918 (m), 1463 (m), 1400 (s), 1376 (s), 1367 (s), 1354 (s), 1268 (m), 1212 (m), 1173 (s), 1137 (s), 867 (m), 754 (m), 674 (m), 536 (m), 453 (m).

**Synthesis of compound 1.** A solution of  $Dy(hfac)_3 2H_2O$  (0.15 mmol) in 32 mL dry heptane was heated to reflux for 3 h then cooled to 75 °C, to which the powder of triradicals BTR (27.18 mg, 0.05 mmol) was added in one portion, then 8 mL CH<sub>2</sub>Cl<sub>2</sub> was added. The resulting solution was stirred for an hour at 75 °C, and then cooled to

room temperature and filtered. The filtrate was allowed to stand in air for slow evaporation. After a week, dark blue block-shaped crystals suitable for single-crystal X-ray analysis were obtained. Yield: 38%. Elemental analysis (%) calculated for **1** ( $C_{57}H_{45}F_{36}N_6O_{18}Dy_2$ , M = 2110.99): C, 32.43; H, 2.15; N, 3.98. Found: C, 32.37; H, 2.16; N, 3.95. Selected FT-IR (KBr, cm<sup>-1</sup>): 3001 (w), 1650 (s), 1558 (m), 1531 (m), 1497 (m), 1358 (m), 1258 (s), 1209 (s), 1145 (s), 1098 (m), 800 (m), 739 (w), 660 (m), 584 (m), 544 (w), 527 (w), 456 (w).

# **3.** X-ray crystallography

Single crystal X-ray data were collected on a Bruker APEX II diffractometer with a CCD area detector (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT.<sup>S4</sup> Absorption corrections were applied with SADABS.<sup>S5</sup> The structure was solved by direct method and refined by full-matrix least-squares method on  $F^2$  using the SHELXTL crystallographic software package.<sup>S6</sup> All the non-hydrogen atoms were refined an isotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Additional details of the data collections and structural refinement parameters are provided in Table S1. Selected bond lengths and angles of **1** are listed in Table S2. CCDC-1835455 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

Complex	1
Formula	$C_{57}H_{45}F_{36}N_6O_{18}Dy_2$
Formula weight	2110.99
T/K	296
Crystal system	Monoclinic
Space group	<i>P</i> 2/c
<i>a</i> / Å	10.927(3)
<i>b</i> / Å	12.297(3)
<i>c</i> / Å	30.796(7)
$\alpha$ / deg	90
$\beta$ / deg	100.219(2)
γ / deg	90
V / Å3	4072.5(16)
Z	2
F(000)	2058
Collected refl.	18846
Unique refl.	7042
R <sub>int</sub>	0.0556
$\frac{R_1^a, wR_2^b}{(I > 2\sigma(I))}$	0.0572, 0.1330
$\begin{array}{c} R_1, wR_2 \\ (all data) \end{array}$	0.0970, 0.1430
GOF	0.999

 Table S1. Crystallographic data and structure refinement parameters for 1.

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ . <sup>b</sup>  $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$ 

 Table S2. Selected bond lengths [Å] and angles [°] for 1.

Dy(1)-O(3)	2.317(6)
Dy(1)-O(1)	2.327(5)
Dy(1)-O(2)	2.323(6)
Dy(1)-O(6)	2.349(5)
Dy(1)-O(5)	2.379(5)
Dy(1)-O(4)	2.371(7)
Dy(1)-O(8)	2.433(6)
Dy(1)-O(7)	2.454(5)
N(2)-O(8)	1.316(7)
O(7)-N(1)	1.288(7)
N(3)-O(9)	1.303(8)
N(2)-O(8)-Dy(1)	138.8(4)
N(1)-O(7)-Dy(1)	143.5(5)



Fig. S1 ORTEP view of 1 with thermal ellipsoids at 30% probability.



Fig. S2 Packing diagram of 1. All hydrogen and fluorine atoms are omitted for clarity.

Label Deviation Symmetry Shap		Shape	
<b>OP-8</b> 29.446 <i>D</i> <sub>8h</sub>		$D_{8\mathrm{h}}$	Octagon
HPY-823.462C7vHeptagonal pyramid		Heptagonal pyramid	
HBPY-8	13.884	884 <i>D</i> <sub>6h</sub> Hexagonal bipyramid	
<b>CU-8</b>	9.218	$O_{ m h}$	Cube
<b>SAPR-8</b> 1.386 D <sub>4d</sub>		$D_{ m 4d}$	Square antiprism

Table S3. Detailed geometry analysis results by Continuous Shape Measures (CShMs).

TDD-8	1.677	$D_{2d}$	Triangular dodecahedron	
JGBF-8	12.216	$D_{2d}$	Johnson - Gyrobifastigium	
<b>JETBPY-8</b>	27.467	$D_{3\mathrm{h}}$	Johnson - Elongated triangular bipyramid	
JBTP-8	2.022	$C_{2\mathrm{v}}$	Johnson - Biaugmented trigonal prism	
BTPR-8	1.154	$C_{2v}$	Biaugmented trigonal prism	
JSD-8	4.422	$D_{2d}$	Snub disphenoid	
<b>TT-8</b>	10.055	$T_{d}$	Triakis tetrahedron	
ETBPY-8	23.026	$D_{3\mathrm{h}}$	Elongated trigonal bipyramid	



**Fig. S3** Powder X-ray diffraction pattern of **1** at room temperature, together with the calculated pattern from the single crystal data.

# 4. Magnetic measurements



**Fig. S4** Temperature dependent magnetic susceptibility data for **1** measured at 1 kOe; insert: field dependent magnetization at 2 K.



Fig. S5 a) Frequency dependence of the out-of-phase ( $\chi''$ ) magnetic susceptibilities of 1 (1-1000 Hz) measured at 2.0 K in various applied fields from 0 to 4500 Oe. b) Field dependence of the magnetic relaxation time at 2.0 K for 1.



Fig. S6 Cole-Cole plots of  $\chi''$  vs.  $\chi'$  of 1 at 2.0 K under various applied dc fields. The solid lines represent the best fit of the experimental results with the generalized Debye model.

**Table S4**. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots at 2 K under various dc fields according to the generalized Debye model.

H (Oe)	χo	χt	τ	α
0	0.98421	21.97012	0.00016	0.09363

200	0.93687	25.19972	0.00017	0.08574
400	1.08641	25.20000	0.00019	0.09943
600	1.59888	24.54387	0.00024	0.10047
800	1.55326	23.22347	0.00026	0.09728
1000	1.71622	21.55822	0.00027	0.09421
1200	1.60001	19.19976	0.00025	0.09230
1500	1.38104	16.80000	0.00023	0.10968
2000	0.94078	11.79896	0.00019	0.10223
2500	0.79757	7.99993	0.00017	0.10260



Fig. S7 Frequency dependence of the in-phase  $(\chi')$  and out-of-phase  $(\chi'')$  parts of the ac magnetic susceptibilities in zero (a) and the optimum 1 kOe (b) dc fields with an oscillation of 2 Oe.

Table S5.	Relaxation	fitting paramet	ers from the	least-square	fitting of the	Cole-Cole
plots of 1	under 1.8 K	-2.5 K accordin	ig to the gene	eralized Deby	ye model.	

<i>T</i> (K)	χo	χt	τ	α
1.8	0.70126	20.39960	0.00062	0.14862
1.9	0.49913	20.06053	0.00040	0.15025
2.0	0.74666	19.42591	0.00026	0.13529
2.1	0.59623	19.20033	0.00018	0.14657
2.2	0.55530	18.56577	0.00012	0.13479
2.3	0.55372	18.04579	0.00008	0.12577
2.5	1.25856	17.21556	0.00004	0.11969

# **5.** Theoretical calculations

## 5.1 Ab initio Calculations for 1.

Complete-active-space self-consistent field (CASSCF) calculations on the Dy<sup>III</sup> fragment (see Fig. S7 for the calculated model structure) extracted from **1** on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.2 program package.<sup>S7</sup> The Dy<sup>III</sup> fragment was calculated keeping the experimentally determined structure of **1** while replacing the neighboring Dy<sup>III</sup> ion by the diamagnetic Lu<sup>III</sup> ion.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy<sup>III</sup> ions; VTZ for close O; 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 Dy<sup>III</sup> fragment, active electrons in 7 active spaces include all *f* electrons CAS(9 in 7) in the CASSCF calculation. 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 for the Dy<sup>III</sup> fragment). Single\_Aniso<sup>S8</sup> program was used to obtain the energy levels, *g* tensors, *m<sub>J</sub>* values, magnetic axes, *et al.*, based on the above CASSCF/RASSI calculations.



Fig. S8 Calculated structure of Dy<sup>III</sup> fragment of 1; H atoms are omitted.

KDs	$E/cm^{-1}$	g	тJ
		0.025	
1	0.0	0.157	$\pm 15/2$
		18.259	
		0.124	
2	20.9	0.353	$\pm 3/2$
		18.175	
		0.010	
3	77.2	0.744	±13/2
		15.676	
		4.204	
4	114.3	5.825	$\pm 9/2$
		10.378	
		8.626	
5	174.3	4.798	$\pm 7/2$
		0.391	
		1.110	
6	203.9	3.455	$\pm 1/2$
		14.061	
		0.251	
7	271.4	0.593	$\pm 5/2$
		17.833	
		0.251	
8	400.4	0.593	$\pm 11/2$
		17.833	

**Table S6**. Calculated energy levels (cm<sup>-1</sup>),  $g(g_x, g_y, g_z)$  tensors and  $m_J$  values of the lowest eight Kramers doublets of the Dy<sup>III</sup> ion of **1**.

**Table S7.** Wave functions with definite projection of the total moment  $|m_J\rangle$  for the lowest two Kramers doublets (KDs) of individual Dy<sup>III</sup> fragment for complex **1**.

$E/cm^{-1}$	wave functions
0.0	86% ±15/2>+5% ±9/2>
20.9	5% ±15/2>+5% ±9/2>+11% ±7/2>+21% ±5/2>+28% ±3/2>+27% ±1/2>



**Fig. S9** Orientations of the local main magnetic axes of the ground doublets on Dy<sup>III</sup> ions of **1**.



**Fig. S10** Calculated (red solid line) and experimental (circle black dot) data of magnetic susceptibilities of **1**. The intermolecular interactions zJ' was fit to 0.08 cm<sup>-1</sup>.

**Table S8.** Exchange energies  $(cm^{-1})$  and main values of the  $g_z$  for the lowest sixteen exchange doublets of **1**.

	$E/cm^{-1}$	$g_{ m z}$		$E/cm^{-1}$	$g_{\mathrm{z}}$
1	0.0	30.526	9	32.7	5.359
2	16.3	31.452	10	33.5	21.990
3	18.1	2.734	11	33.8	0.077
4	21.9	2.162	12	39.2	21.699
5	24.0	1.044	13	40.4	20.850
6	26.0	17.774	14	40.8	13.609
7	26.7	11.932	15	41.1	13.405
8	27.3	0.392	16	46.4	20.835

**5.2 Estimation of the radical-radical exchange interactions by BS-DFT calculation** To calculate the Radical-Radical exchange couplings, we used diamagnetic Lu<sup>III</sup> ion to replace Dy<sup>III</sup>. Tight convergence criteria were selected to ensure the results to be well converged with respect to technical parameters. Through calculating the energies of three spin states: the high-spin state ( $S_{HS} = S_{radical1} + S_{radical2} + S_{radical3}$ ), the first low-spin state (flip the spins on Radical1;  $S_{LS1} = -S_{radical1} + S_{radical2} + S_{radical3}$ ), and the second lowspin state (flip the spins on Radical2;  $S_{LS2} = S_{radical1} - S_{radical2} + S_{radical3}$ ), the isotropic Radical-Radical coupling constants  $J_2$  and  $J_3$  were obtained as eqs. 3-4 using the spinprojected approach<sup>S9-S11</sup> according to the Heisenberg exchange Hamiltonian:

$$\hat{H} = -2J_{2}(\hat{S}_{radical1}\hat{S}_{radical2} + \hat{S}_{radical1}\hat{S}_{radical3}) - 2J_{3}\hat{S}_{radical2}\hat{S}_{radical3}.$$

$$J_{2} = \frac{E_{LS1} - E_{HS}}{4}$$

$$J_{3} = \frac{E_{LS2} - E_{HS}}{2} - J_{2}$$
(4)

$$=\frac{1}{2} - J_2 \tag{4}$$

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