Supporting Information

Exchange-Bias Quantum Tunnelling in CO₂-based Dy₄-Single Molecule Magnet

Eufemio Moreno Pineda,^[a] Yanhua Lan,^[b] Olaf Fuhr,^[a] Wolfgang Wernsdorfer*^[a,b] and Mario Ruben*^[a,c]

a. Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany. E-mail: mario.ruben@kit.edu

b. Institut Néel, CNRS / Université Grenoble Alpes,, 25 rue des Martyrs, F-38000 Grenoble, France.

c. Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

A. Synthetic Method

Synthesis of **1** and **2**: A 100 mL Schlenk tube containing anhydrous LnCl₃ (6 mmol) (where Ln = Dy(III) or Gd(III)) was heated to 120 °C for 2 under vacuum ~ 10⁻³ mbar for a period of 1.5 h. After this time, the Schlenk tube was led to cool down to room temperature followed by the addition of 50 mL of dried toluene. To the slurry was posteriorly added 5 mL of freshly distilled NH/Pr₂ and the suspension was stirred for 1.5 h. Following, dried CO₂ was bubbled into the solution for approximately 20 min and finally the Schlenk tube was closed with an atm. of CO₂. The slurry was then kept under stirring for 4 days. After the CO₂ absorption was completed, the cloudy solution was filtered and both the precipitate and filtrate were kept. The clear solution obtained from filtration was then kept at 5°C leading to the formation to big block crystals after 1 day. The reactions were carried employing standard Schlenk technique under Argon atmosphere. Anhydrous lanthanide sources were obtained from Alfa-Aesar and used as purchased. Toluene and di-isopropyl amine (NHPr₂) were freshly dried and distilled over sodium metal and CaH2 before use. CO₂ gas was dried over CaH₂. Elemental analysis: for Dy₄N₁₂O₂₄C₈₄H₁₆₈·2C₇H₈ calculated (found) (%): C 45.90 (46.02), H 7.23 (7.27), N, 6.55 (6.49).

B. Crystallography

The single crystal X-ray diffraction data of **1** was collected employing STOE StadiVari 25 diffractometer with a Pilatus300 K detector using GeniX 3D HF micro focus with MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved using direct methods and was refined by full-matrix least-squares methods on all F^2 using SHELX-2014 implemented in Olex2. The crystals were mounted on a glass tip using crystallographic oil and placed in a cryostream. Data were collected using ϕ and ω scans chosen to give a complete asymmetric unit. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated geometrically riding on their parent atoms. Full

crystallographic details can be found in CIF format: see the Cambridge Crystallographic Data Centre database (CCDC 1483884).

C. Magnetic Measurements

Magnetic susceptibility measurements were collected using Quantum Design MPMS[®]3 and MPMS-XL SQUID magnetometers on polycrystalline material in the temperature range 2 – 300 K under an applied DC magnetic field (H) of 1 kOe. Magnetisation as a function of applied field was investigated in the field and temperature ranges 0 – 7 T and 2–3 K, respectively. AC data was collected using an oscillating magnetic field of 3.5 Oe and frequencies between 0.1 and 1.5 kHz. DC data were corrected for diamagnetic contributions from the eicosane and core diamagnetism employing Pascal's constants. Low temperature (0.03 – 5 K) magnetisation measurements were performed on single crystals using a μ -SQUID apparatus at different sweep rates between 0.280 and 0.002 T s⁻¹. The time resolution is approximately 1 ms. The magnetic field can be applied in any direction of the micro-SQUID plane with precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure good thermalisation, each sample was fixed with apiezon grease.

D. Supplementary Tables

1. Crystallographic Tables

	1
formula	$Dy_4 N_{12}O_{24}C_{105}H_{192}$
$FW / g mol^{-1}$	2656.69
crystal system	monoclinic
space group	C2/c
a/Å	28.1117(11)
b/Å	20.1279(6)
c/Å	22.8674(10)
a/°	90
$\beta/^{\circ}$	105.985(3)
$\gamma/^{\circ}$	90
$V/Å^3$	12438.7(8)
Ζ	4
ho calcd/g cm ⁻³	1.419
<i>T</i> /K	180.15
$\mu \left(Mo K_{\alpha} \right) / mm^{-1}$	2.442
$\mathrm{R}_{1}(I \!\!>\! 2\sigma)(I))^{a}$	0.0723
wR_2^a	0.1870

Table S1. Crystallographic information for clusters 1.

	Distance / A		Angles / °
C1-O11	1.28(1)	O1-C36-O2	119.3(7)
C1-O12	1.28(1)	O3-C29-O4	122.7(7)
C15-O9	1.25(1)	O5-C22-O6	120.4(6)
C15-O10	1.278(8)	O7-C8-O8	121.3(6)
C22-O5	1.300(7)	O10-C15-O9	124.2(7)
C22-O6	1.278(9)	O11-C1-O12	119.0(7)
C29-O3	1.27(1)		
C29-O4	1.275(8)		
C36-O1	1.30(1)		
C36-O2	1.26(1)		
C8-O7	1.293(9)		
C8-O8	1.25(1)		
C1-N1	1.34(1)		
C8-N2	1.372(8)		
C15-N3	1.35(1)		
C19-N3	1.47(1)		
C22-N4	1.33(1)		
C29-N5	1.36(1)		
C36-N6	1.36(1)		

Table S2. Selected angles and bond distances for compound 1.

2. SHAPE analysis

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Table S3. Continuous shaped measures (CShM) for compound 1 obtained using SHAPE.

CShM	Dy(1)	Dy(2)
HP-7	31.248	31.415
HPY-7	18.862	19.912
PBPY-7	4.059	3.217
COC-7	2.406	3.307
CTPR-7	2.312	2.233
JPBPY-7	7.143	6.145
JETPY-7	21.392	20.787

HP-7 = (D_{7h}) Heptagon

HPY-7 = (C_{6v}) Hexagonal pyramid

PBPY-7 = (D_{5h}) Pentagonal bipyramid

 $COC-7 = (C_{3v})$ Capped octahedron

 $CTPR-7 = (C_{2v})$ Capped trigonal prism

JPBPY-7 = (D_{5h}) Johnson pentagonal bipyramid J13

JETPY-7 = (C_{3v}) Johnson elongated triangular pyramid J7

3. Euler Angles

Table S4. Euler angles of anisotropy axes obtained from electrostatic analysis.

	α / °	β / °	γ/°
Dy(1)	59.3	68.30	0
Dy(2)	237.4	71.3	0
Dy(1)'	329.3	68.3	0
Dy(2)'	122.6	71.3	0

E. Dipolar matrices for complex 1

Dipolar matrix obtained from $\hat{H} = -2\hat{S}_1 \cdot J_i^{dip} \cdot \hat{S}_2$ employing the Euler rotation angles from the electrostatic anistropic axes and Dy…Dy distances obtained from crystallographic data. The dipolar couplings were obtained using an spin effective formalism ($S_{eff} = \frac{1}{2}$) employing $g_x = g_y = 0$ and $g_z = 0$ 20.

$$J_{a}^{dip} = \begin{pmatrix} 0.913285 & 1.42806 & -0.573769 \\ 1.53815 & 2.40513 & -0.966337 \\ 0.71187 & 1.11312 & -0.447231 \end{pmatrix} \mathbf{K}$$
$$J_{b}^{dip} = \begin{pmatrix} -0.450739 & 0.704801 & 0.283176 \\ -0.759131 & 1.18702 & 0.476922 \\ -0.351333 & 0.549365 & 0.220724 \end{pmatrix} \mathbf{K}$$

where J_a^{dip} is the dipolar matrix between $Dy(1)\cdots Dy(2)$ and $Dy(1)'\cdots Dy(2)'$; whilst J_b^{dip} accounts for the interaction along $Dy(1)\cdots Dy(2)$ ' and $Dy(1)'\cdots Dy(2)$. Note that the dipolar couplings are strongly anisotropic due to the non- collinearity of the Dy(III) ions. The values are small compared to the obtained from simulation using isotropic exchange values, i.e. $J_1 = -4.95$ K and $J_2 = 6.75$ K.

F. Supplementary Figures







Figure S2. Three different coordination modes of carbamate groups observed in compound 1.



2. Magnetic measurements

Figure S3. Dynamic magnetic data for compound 1 at zero field with an oscillating field of 3.5 Oe. (a) $\chi_{M'}(T)$; (b) $\chi_{M'}T(T)$; (c) $\chi_{M}T'(\nu)$ and (d) $\chi_{M}T''(\nu)$ experimental data and fits to a single relaxation process (solid lines).



Figure S4. Out-of-phase component of compound **1** at different applied fields (0 to 2 kOe) and optimal field versus relaxation time (inset). A field of 1.5 kOe was found to be the optimal field for following dynamic investigations of compound **1**.



Figure S5. Dynamic magnetic data for compound **1** under 1.5 kOe applied DC field. (a) $\chi_{M}'(T)$; (b) $\chi_{M}''(T)$; (c) $\chi_{M}'T(T)$ experimental data.



Figure S6. Dynamic magnetic data for compound 1 at zero field with an oscillating field of 3.5 Oe. (a) $\chi_{M}"(\nu)$; (b) $\chi_{M}'(\nu)$; (c) $\chi_{M}'(\nu)$ vs. $\chi_{M}"(\nu)$ (Cole-Cole plots) experimental data and fits to a single relaxation process (solid lines). (d) U_{eff} calculated from AC data at zero field (red circles) and upon application of 1.5 kOe DC field (green circles).



Figure S7. (a) Experimental $\chi_M T$ and (b) M(H) (open circles) and Brillouin function (dashed line) for four Gd(III) ions with g = 2.00. Fittings of the $\chi_M T$ (a) and $M_\beta(H)$ (b) data having in mind crystallographic considerations i.e. two different crystallographic Gd…Gd distances with two exchange pathways employing a Hamiltonian of the form: $H = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - 2J_2(\hat{S}_2\hat{S}_3 + \hat{S}_4\hat{S}_1) + g\mu_B H \sum_{i=1}^4 \hat{S}_i$. Simulataneous ftting yields $J_1 = -0.058(1)$ and $J_2 = +0.012(1)$ K. In panels c and d fittings were performed assuming a single exchange interaction using the following Hamiltonian: $H = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_4\hat{S}_1) + g\mu_B H \sum_{i=1}^4 \hat{S}_i$. Best fits was obtained employing J = -0.029(1) K. (e and f) To verify the possibility of the downturn in $\chi_M T$ at low temperature being a solely consequence of individual zero field splitting (D) we model the $\chi_M T$ and M(H) employing a single Gd(III) with D = -0.69 cm⁻¹ and a Hamiltonian of the form: $H = +D_{Gd}\hat{S}_{Gd_z}^2 + g\mu_B H \hat{S}_i^2$.



Figure S8. Zeeman digram employing only dipolar couplings with (a) **B** applied perpendicular to easy axis and (b) with **B** parallel to the easy axis. As observed no reasonable agreement is found employing uniquely the dipolar values obtained in section E.