Electronic Supplementary Material (ESI) for Dalton Transactions.

Dy(III)-Carboxylate Chain Containing Quasi-D_{5h} Sites Exhibits Enhanced Energy Barrier for Magnetisation Reversal

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Experimental section:

Materials and measurements:

The reagents were used as they are received from commercial source. Ultrapure water was generated by Thermo Scientific BARNSTEAD NANOPURE system. The C and H microanalyses were carried out with an Elementar Vario-ELCHNS elemental analyzer. The FT-IR spectra were recorded using a NICOLET 6700 spectrometer. Inductively coupled plasma (ICP) analysis was performed on a PerkinElmer Optima 3300DV spectrometer. Magnetic measurements were performed with samples on a Quantum Design MPMS-XL7 SQUID, and the data were corrected for the diamagnetic contribution calculated with Pascal constants. Ac magnetic susceptibility data are collected applying 3.5 Oe alternating field on crushed crystalline samples wrapped by eicosane.

Synthesis

Caution: Lanthanide perchlorates are potentially explosive! Only a small amount of the salt should be prepared and handled with great care.

1: A mixture of $Dy(ClO_4)\cdot XH_2O$ (0.3 g, ~0.5 mmol), isobutyric acid (0.26g, ~3 mmol) and benzotriazole (0.12g, 1 mmol) was dissolved in mixed solvent of MeCN (4 mL). After stirred for 10 minutes, to this clear solution, trimethylamine (0.2 mL) was added drop by drop. Under continuously stirring, precipitate caused by the base disappeared rapidly. The final nearly clear solution was filtered. The filtrate was sealed by film and left undisturbed for 3 days before colorless stick-like crystals of **1** came out. Yield: 0.12g, ~ 45%, based on the metal. Anal. calcd. for $Dy_3ClC_{44}H_{76}N_6O_{25}$ (FW = 1612.05): C, 32.78; H, 4.75; N, 5.21. Found: C, 33.40; H, 4.73; N, 6.89 %. IR: 3328 (w), 2974 (w), 1523 (S), 1482 (s), 1434 (s), 1380 (w), 1363 (w), 1302 (m), 1285 (m), 1218 (m), 1142 (w), 1097 (m), 1049. (w), 1013 (m), 928 (w), 856 (m), 780 (m), 755 (m).

1': $Dy(ClO_4)\cdot XH_2O$/ $Y(ClO_4)\cdot XH_2O$ (0.05 mmol/ 0.45 mmol) was applied instead of pure Dy perchlorate salt to prepare the diluted sample. Colorless stick-like crystals were collected by filtration. Yield: 0.31 g, ~ 44%, based on the metal. Anal. calcd. for $Dy_{0.28}Y_{2.72}ClC_{44}H_{76}N_6O_{25}$ (FW = 1425.86): C, 32.78; H, 4.75; N, 5.21. Found: C, 33.51; H, 4.77; N, 6.48%. IR: 3310 (w), 2974 (w), 1524 (s), 1483 (s), 1435 (s), 1303 (m), 1218 (w), 1096 (m), 1013 (m), 929 (w), 857 (w), 779 (w), 757 (m). The Dy/Y ratio of the product based on ICP analysis (in wt.%) Dy: 2.994, Y: 15.96, gave the molecular formula of $[Dy_{0.28}Y_{2.72}(C_4H_7O_2)_8(C_6H_5N_3)_2(ClO_4)(H_2O)_5]_n$.

2: Nearly the same recipe as **1** was applied to isolate the colorless block crystals of **2** only using mixed solvent MeCN/H2O (4mL/2mL) as solvent instead of above pure MeCN. Yield: 0.19 g, ~ 60% based on the metal. Anal. calcd. for $Dy_3C_{52}H_{89}N_6O_{24}$ (FW = 1867.96): C, 33.44; H, 5.99; N, 5.00. Found: C, 34.36; H, 4.77; N, 4.53%. IR: 2969 (w), 1686 (w), 1537 (s), 1481 (s), 1428 (s), 1303 (m), 1283 (w), 1216 (w), 1095 (m), 1013 (w), 930 (w), 854 (m), 754 (m).

Crystallography:

The single crystal reflection data of **1** and **2** were collected on a Bruker ApexII CCD diffractometer with the graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. All the structures were solved by direct methods with the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically with isotropic temperature factors. Data collection parameters and structure solution details are listed in Table S1. Selected bond distances and angles are listed in Table 2. CCDC **1509701** (for **1**) and **1509702** (for **2**) contain the crystallographic data that can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam. ac.uk).

Table S1. Crystallographic data for compound **1** and **2**.

Complex	**1**	**2**
Formula	$C_{44}H_{75}N_6ClDy_3O_{25}$	$C_{52}H_{111}N_6Dy_3O_{35}$
fw	1615.51	1867.9572
T/K	296(2)	296(2)
Space group	$C2/c$	P-1
a/Å	31.340(8)	13.335(6)
b/Å	13.874(3)	16.628(7)
c/Å	20.741(10)	18.090(8)
α/°	90	77.468(7)
β/°	129.133(2)	70.836(6)
γ/°	90	68.592(6)
V/ Å^3	6996(4)	3506(3)
Z	4	2
$D_{calcd.}$/g·cm^{-3}	1.435	1.582
μ/mm^{-1}	3.234	3.237
R_1[a)]	0.0700	0.0484
wR_2[b)]	0.0987	0.1037

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

XRD measurements:

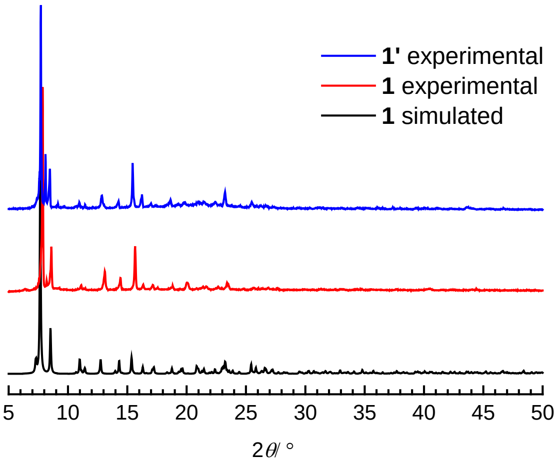

Fig. S1. Experimental and simulated X-ray powder diffraction (XRPD) patterns for compound **1** and **1’**.

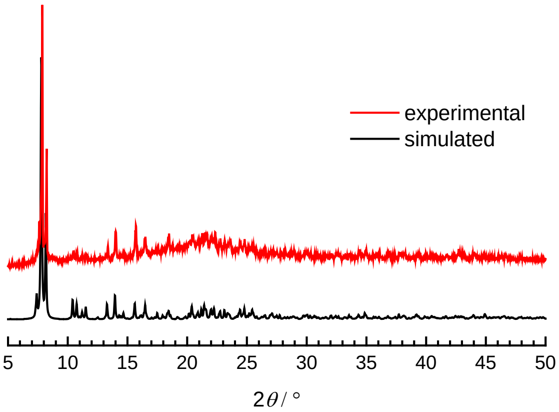

Fig. S2. Experimental and simulated X-ray powder diffraction (XRPD) patterns for compound **2**.

Structural details of 1 and 2:

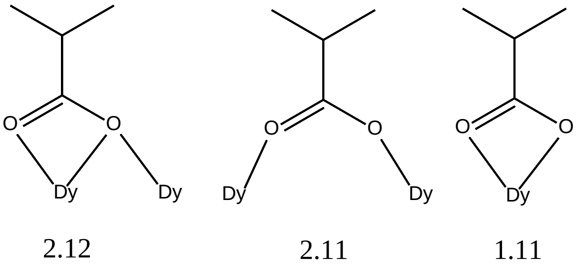

Fig. S3. Coordination modes (Harris notation) in both compounds.

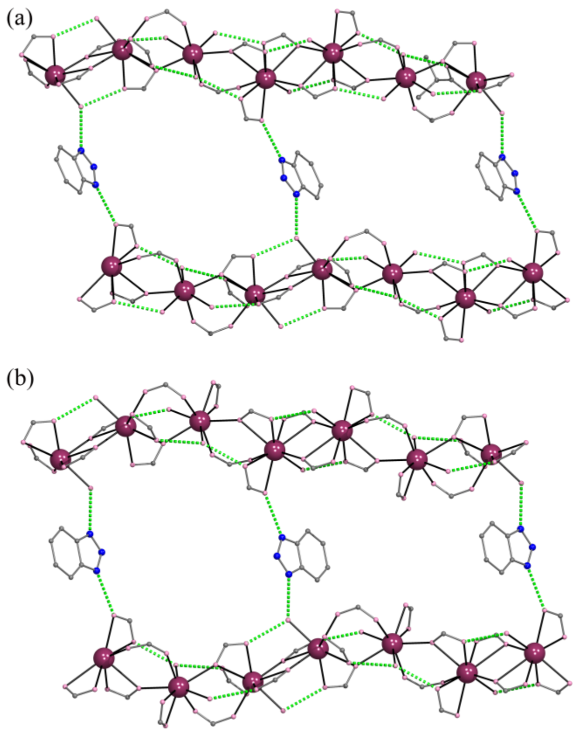

Fig. S4. The intra-chain and inter-chain hydrogen bonds in compound **1** (a) and **2** (b).

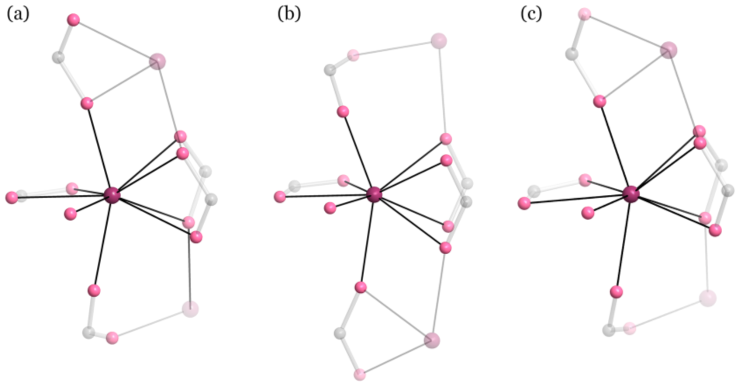

Fig. S5. The nona-coordinated cites for compound **1** (a) and **2** ((b) and (c)).

Magnetic measurements:

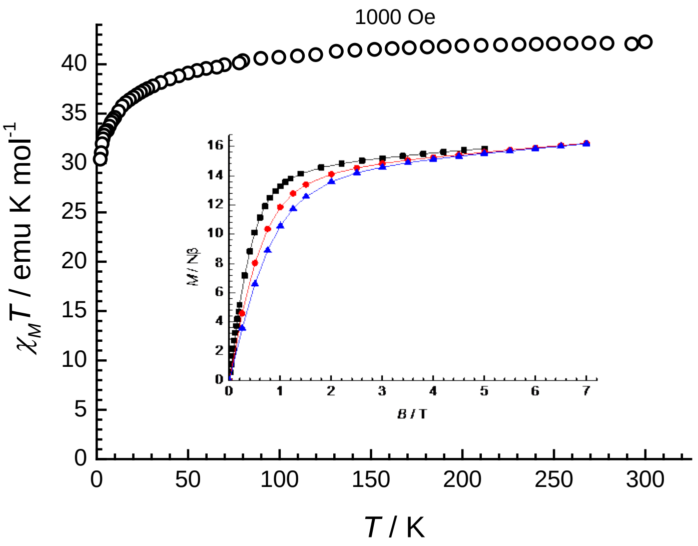

Fig. S6. The dc magnetic susceptibility and magnetization (inset) for compound **1**.

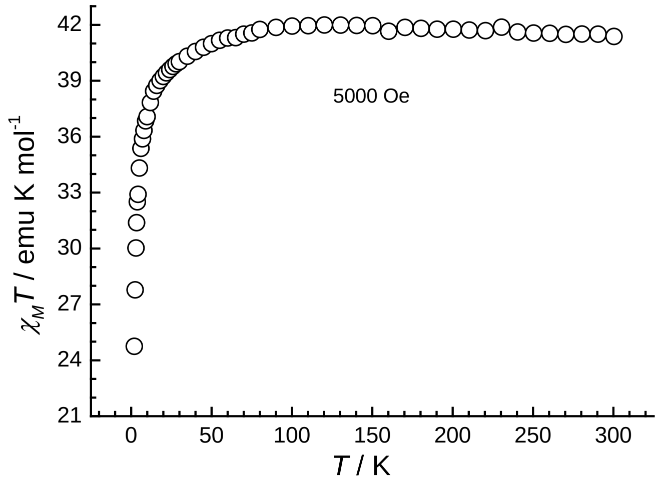

Fig. S7. Dc susceptibility data for compound **2** under 5 KOe field.

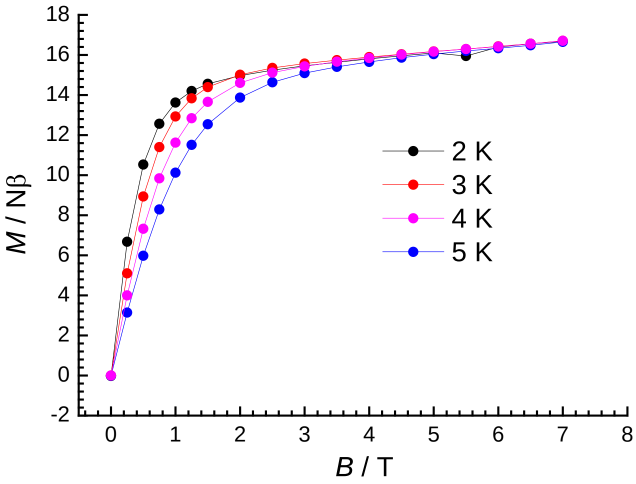

Fig. S8. Magnetization results for compound **2**.

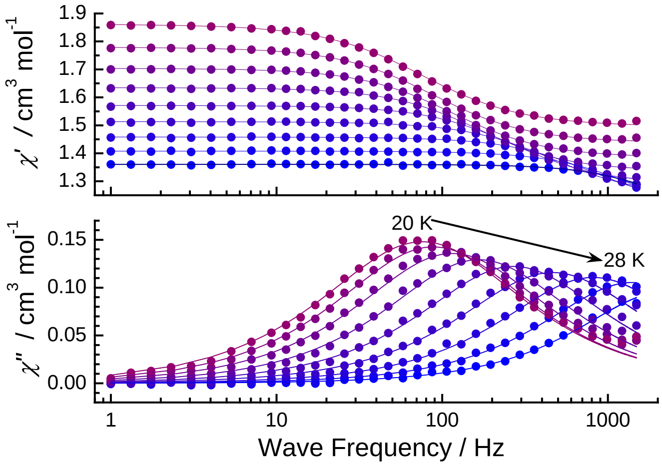

Fig. S9. Frequency dependent ac susceptibility for compound **1**.

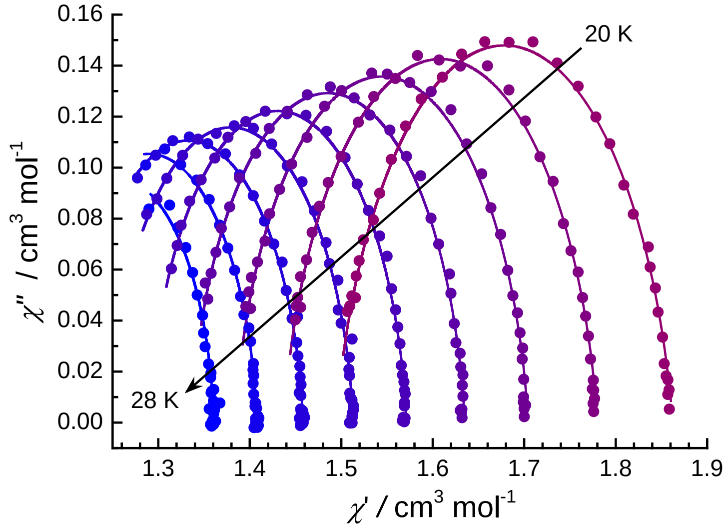

Fig. S10. The cole-cole plot applying generalized Debye model for compound **1**.

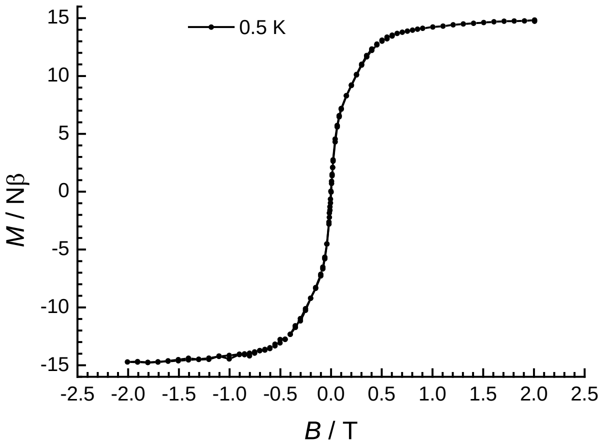

Fig. S11. Magnetic hysteresis loop measurement at the temperature of 0.5 K for compound **1**.

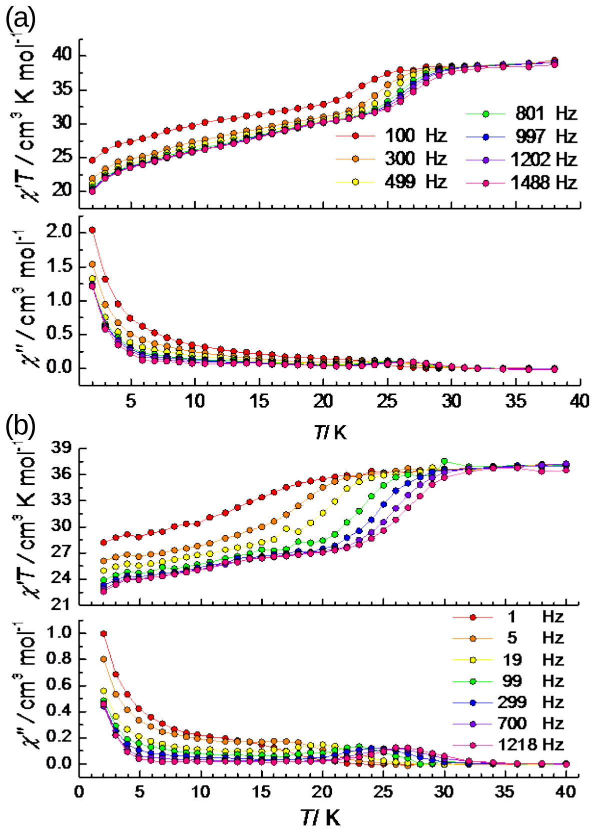

Fig. S12. The temperature dependent ac susceptibility data for compound **1** (a) and **1'** (b) under zero dc field in the temperature range of 2 K to 40 K. The solid lines are the guide for the eyes.

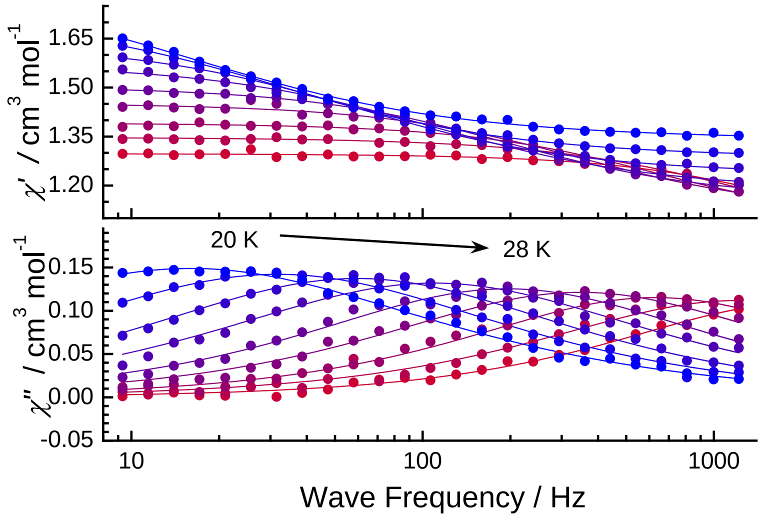

Fig. S13. The frequency dependent ac susceptibility data for compound **1'** under zero dc field. The solid lines are fitting results using generalized Debye model.

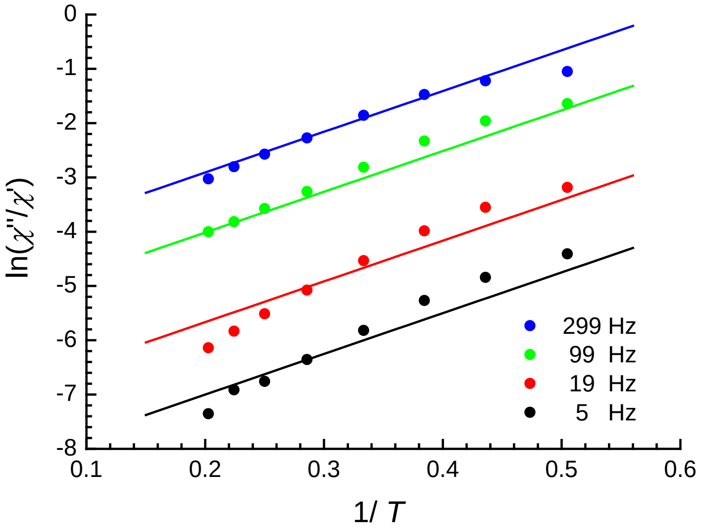

Fig. S14. Natural logarithm of the ratio of *χ*'' to *χ*' vs. 1/*T* for **2**.