

Supporting Information

A [Mn₁₈Dy] SMM Resulting from the Targeted Replacement of the central Mn^{II} in the $S = 83/2$ [Mn₁₉]-Aggregate with Dy^{III}

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Experimental:

Preparation of **2**

A slurry of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 g, 2 mmol), NaN_3 (0.22 g, 3.38 mmol), $\text{NaO}_2\text{CMe} \cdot 3\text{H}_2\text{O}$ (0.28 g, 2 mmol) and 2,6-bis(hydroxymethyl)-4-methylphenol (1.12 g, 6.66 mmol) in 25 mL MeCN and 5 mL MeOH was stirred for 30 minutes at room temperature, then a solution of the corresponding $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) in 5 mL of MeCN was added. The resulting mixture was stirred for additional 1 h then heated at reflux for 2 h, cooled and filtered. X-ray quality crystals formed within a few days. Yield: 151 mg, 37.43 % (based on Mn). Elemental analysis (%) calcd for $\text{C}_{118}\text{DyH}_{160}\text{Cl}_{9.5}\text{Mn}_{18}\text{N}_{4.5}\text{O}_{54}$ (dried): C 35.49; H 4.04; N 1.58 %; found: C 35.21; H 3.76; N 1.88. Selected IR data (KBr (cm^{-1})): $\tilde{\nu} = 475$ (w), 546 (m), 632 (s), 809 (m), 862 (w), 986 (m), 1022 (m), 1160 (m), 1223 (m), 1253 (m), 1384 (s), 1470 (s), 1564 (w), 2076 (m), 2849 (s), 3385 (b,s).

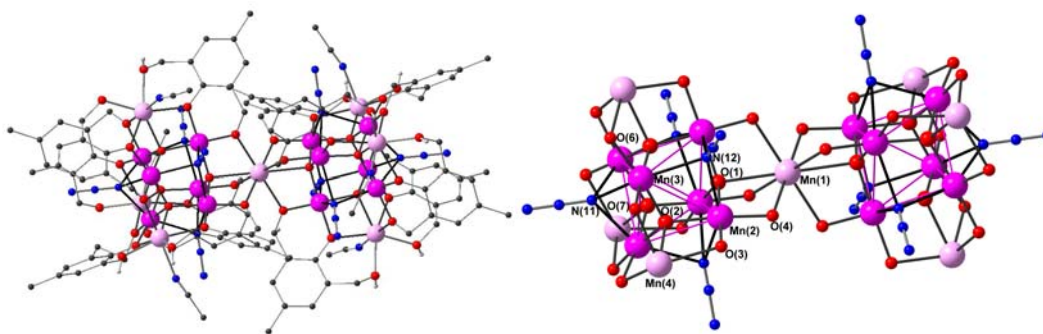


Figure S1. Molecular structure of **1** (left) in the crystal and metallic core with partial atom numbering scheme (right). Carbon-bound hydrogen atoms, counter ions, and noncoordinated solvent molecules have been omitted for clarity. Colour code: Mn^{III} , dark pink; Mn^{II} , pale pink; O, red; N, blue.

X-ray Crystallography

Crystals for X-ray diffraction analyses were maintained in contact with the mother liquor. The structure of **2** was determined using a conventional Mo- $K\alpha$ rotating-anode source. Data were collected at 150K, using Bruker SMART Apex CCD diffractometer, and were corrected semi-empirically^{1,2} for absorption. Structure solution by direct methods and

full-matrix least-squares refinement against F^2 (all data) were carried out using SHELXTL.¹ Atomic form factors for $\lambda = 0.80000 \text{ \AA}$ (15.510 keV) were obtained by the method of Brennan and Cowan³ as implemented on http://skuld.bmsc.washington.edu/scatter/AS_periodic.html. All ordered non-H atoms were refined anisotropically. The solvent molecules were disordered, and some or all could not be refined satisfactorily and were handled using the SQUEEZE option in PLATON.⁴ Full details can be found in the accompanying CIF files. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 698065. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi>, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Crystal data for **2**: $C_{139}H_{244}Cl_{9.5}DyMn_{18}N_{4.5}O_{75}$ $M_r = 4666.58 \text{ g mol}^{-1}$; trigonal, space group $R\bar{3}$, $a = 20.1038(10) \text{ \AA}$ $c = 39.313(2) \text{ \AA}$, $V = 13760.1(12) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 3$, $\mu = 1.820 \text{ mm}^{-1}$, $F(000) = 7161$ $\rho_{\text{calcd}} = 1.689 \text{ Mg m}^{-3}$; 12533 data measured, 4965 unique ($R_{\text{int}} = 0.0253$), final $wR_2 (F^2, \text{ all data}) = 0.1486$, $S = 0.961$, $R_1 (2593 \text{ with } I > 2\sigma(I)) = 0.0652$.

Magnetic Measurements

The magnetic susceptibility measurements of **2** were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements of M versus H were performed at 100 K to check for the presence of ferromagnetic impurities, which were found to be systematically absent. Measurements of ac susceptibility were made with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz without applied dc fields. Measurements were performed on finely ground crystalline samples of 6.06 mg. The magnetic data were corrected for the sample holder and the diamagnetic contribution. Before any measurement, the sample has been checked for the presence of ferromagnetic impurities by measuring the magnetization as a function of the field at 100

K. For pure paramagnetic or diamagnetic systems, a perfect straight line is expected and is indeed observed for this compound indicating the absence of any ferromagnetic impurities.

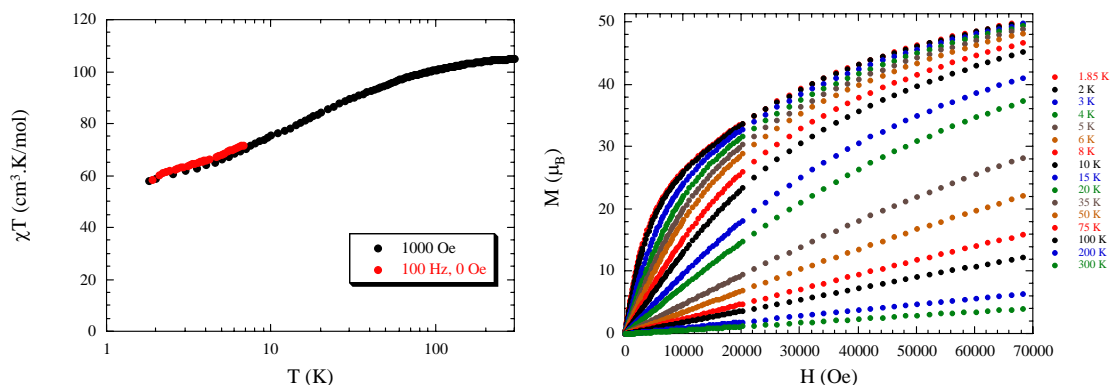


Figure S2. (left) Temperature dependence of (i, black dots) the χT product in semi-log plot for **2** at 1000 Oe (with $\chi = M/H$) and (ii, red dots) the $\chi' T$ products for **2** without dc field and with 3 Oe of ac field modulation at 100 Hz (with $\chi' = dM/dH$); (right) Field dependence of the magnetization for **2** between 1.85 and 300 K.

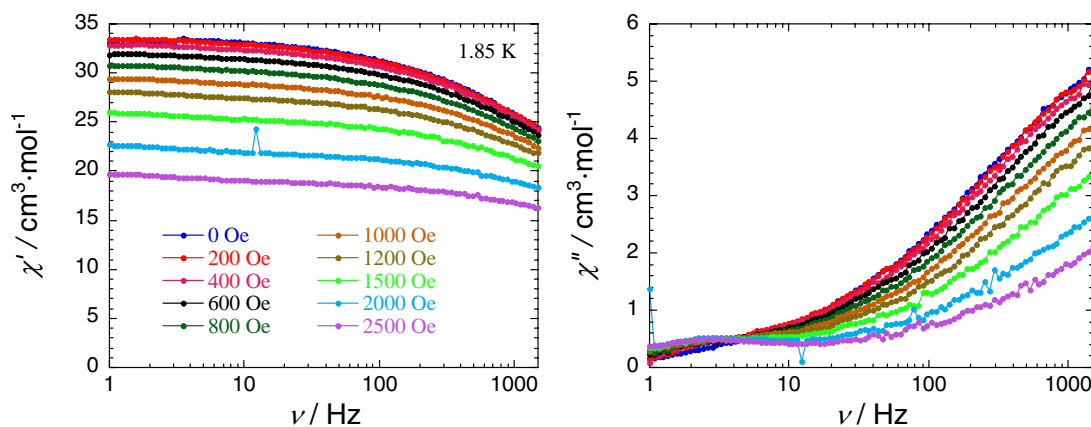


Figure S3. (left) Frequency dependence at 1.85 K of the in-phase (χ' , left) and the out-of-phase (χ'' , right) ac susceptibility component at different dc fields for **2**

Magnetization measurements on single crystals of **2** were performed with an array of micro-SQUIDs.⁵ This magnetometer works in the temperature range of 0.04–7 K and in fields of up to 1.4 T with sweeping rates as high as $10 \text{ T}\cdot\text{s}^{-1}$, along with a field stability of

μT . The time resolution is approximately 1 ms. The field can be applied in any direction of the $\mu\text{-SQUID}$ plane with precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure good thermalization, the single crystals were fixed with Apiezon grease.

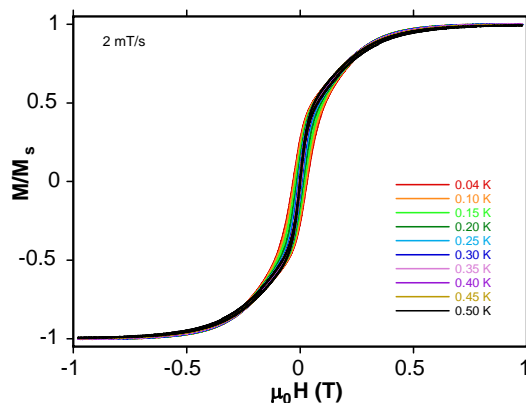


Figure S4. Field hysteresis loops of the normalized magnetization at a field scan rate of 2 mT/s in the temperature range 0.5-0.04 K for a single crystal of complex **2** oriented in its easy direction of magnetization.

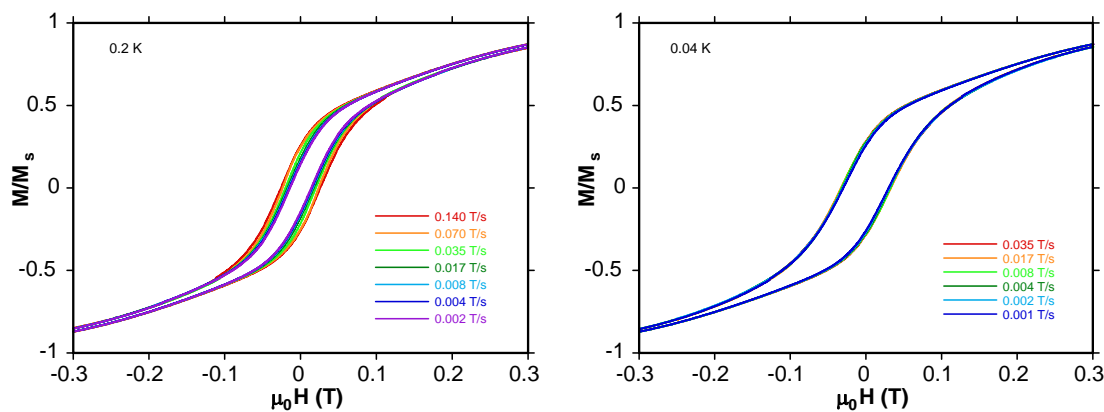


Figure S5. Field hysteresis loops of the normalized magnetization at different field scan rate at 0.2 K (left) and 0.04 K (right) for a single crystal of complex **2** oriented in its easy direction of magnetization.

References

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