

Experimental

Preparation

1: A solution of N-*n*-butyl diethanolamine (0.16 g, 1.0 mmol) in MeOH (5 mL) was slowly added to a solution of Mn(O₂CEt)₂·2H₂O (0.100 g, 0.42 mmol), Dy(NO₃)₃·6H₂O (0.23 g, 0.50 mmol) and HCOONa (0.068 g, 1.0 mmol) in MeOH (20mL). The resulting mixture was stirred for 30 minutes at room temperature then heated at 60 °C for 15 min, resulting in a dark brown solution. The reaction mixture was cooled, filtered and the filtrate was left undisturbed for slow evaporation. Very thin, needle-like pink crystals were harvested after three days. Yield was 20% based on the Dy salt. Elemental analysis (%) calcd. for C₆₈H₁₄₀Dy₄Mn₄N₄O₄₀: C 32.36, H 5.59, N 2.22; found: C 31.75, H 5.40, N 2.21. Selected IR data (KBr) (cm⁻¹): 479 (w), 581 (m), 776 (m), 812 (w), 892 (m), 1009 (w), 1081 (s), 1167 (w), 1291 (m), 1341 (s), 1367 (s), 1408 (s), 1466 (3), 1592 (s), 2874 (s), 2937 (s), 2960 (s), 3429 (b,s).

2: **2** was prepared by similar method as that for **1**, by using Gd(NO₃)₃·6H₂O, in a yield of 33%. Elemental analysis (%) calcd. for C₆₈H₁₄₀Gd₄Mn₄N₄O₄₀: C 32.64, H 5.64, N 2.24; found: C 31.94, H 5.50, N 2.26. Selected IR data (KBr) (cm⁻¹): 580 (m), 774 (m), 812 (w), 892 (m), 1009 (w), 1081 (s), 1291 (m), 1341 (s), 1367 (s), 1408 (s), 1466 (m), 1590 (s), 2874 (s), 2937 (s), 2960 (s), 3420 (b,s).

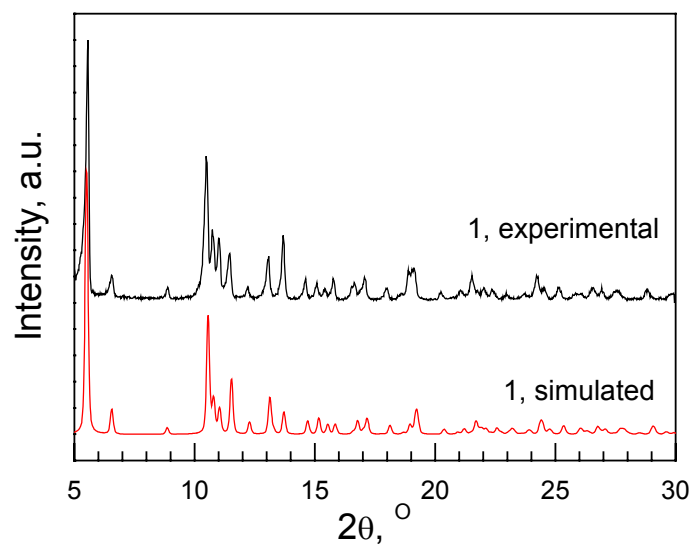
The phase purity of the bulk samples of the two compounds were proved by powder X-ray diffraction (PXRD) patterns, compared to the calculated ones from the single-crystal structures (Fig. S1).

Characterization

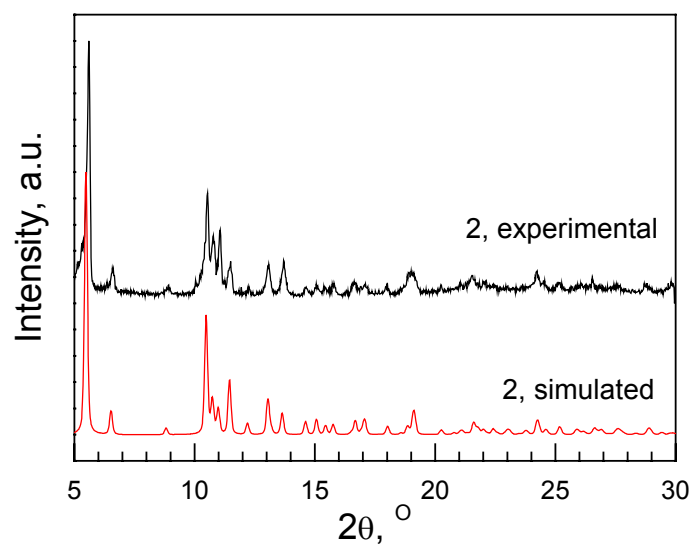
The crystallographic data were measured at 100K on a Bruker SMART Apex CCD diffractometer using a conventional Mo K α rotating-anode source (**1**), or at 150 K on a Stoe IPDS II area detector diffractometer using Si-monochromated synchrotron radiation of wavelength $\lambda = 0.80000$ Å on the SCD beamline of the ANKA synchrotron at the Karlsruhe Institute of Technology (**2**). Intensity data were corrected for Lp factors and absorption. The structures were solved by direct methods, and refined by full-matrix least-squares on F^2 using SHELXTL. All non-H atoms were refined anisotropically, and organic H-atoms were placed in calculated positions. PXRD data for the two

compounds were collected in the range of $5^{\circ} < 2\theta < 30^{\circ}$ at room temperature against the bulk samples on a Rigaku RINT2000 diffractometer with Cu K α radiation in a flat plate geometry.

DC and AC magnetization measurements were performed on a Quantum Design MPMS-XL7 SQUID system for polycrystalline samples. Diamagnetic corrections were estimated using Pascal constants and background correction by experimental measurement on sample holder. The magnetization study of **1** at temperatures down to 40 mK was carried out on an array of micro-SQUIDS against a single crystal of **1**.

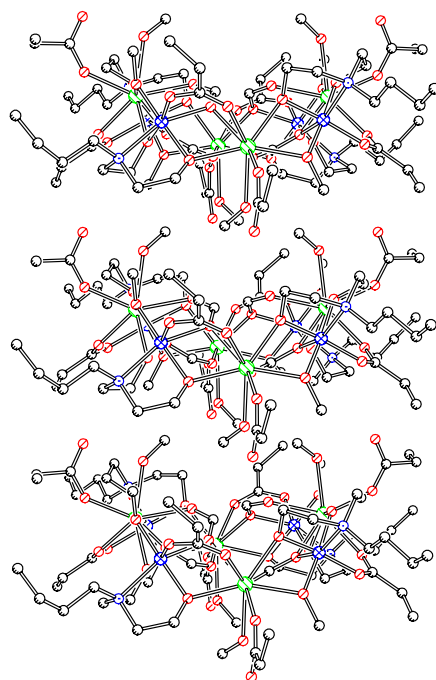


(a)

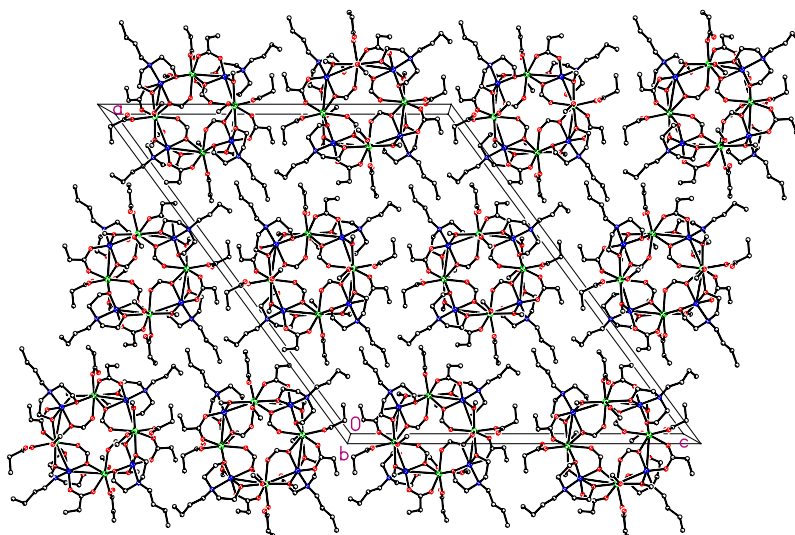


(b)

Fig. S1 Powder X-ray patterns of the two compounds **1** (a) and **2** (b). The simulated patterns were calculated based on the single-crystal structures.

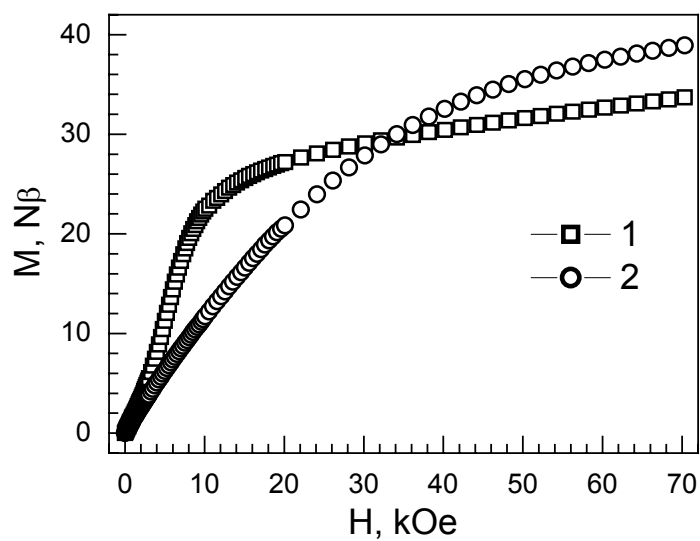


(a)

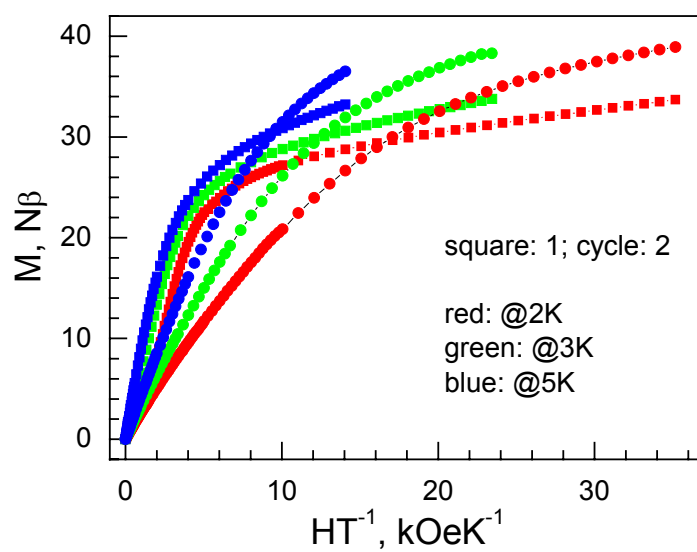


(b)

Fig. S2 (a) Molecular column and (b) the nearly hexagonal closest packing of the columns (one molecular layer) viewed along *b* direction in the crystal structure of **1**. H atoms were omitted.



(a)



(b)

Fig. S3 (a) Field dependence of the magnetization for **1** and **2** at 2K, (b) M vs H/T plots at 2 K, 3 K and 5 K.

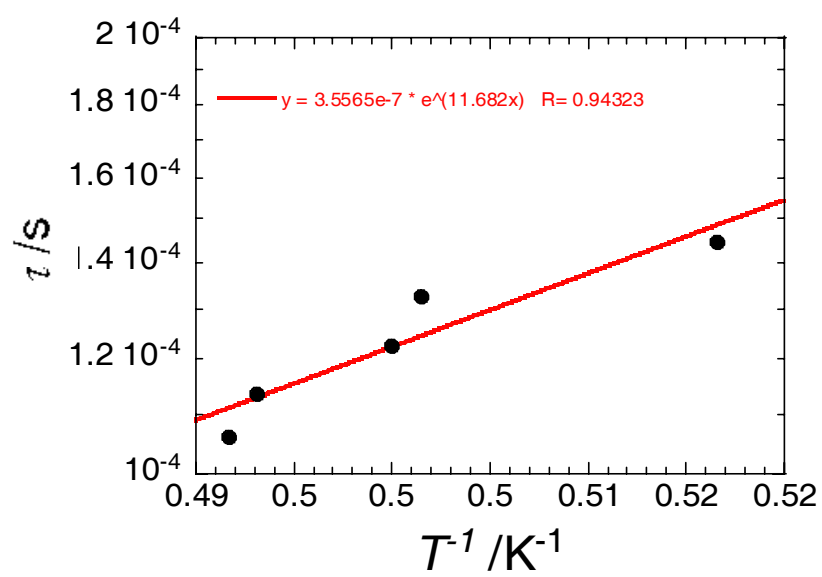


Fig. S4 Arrhenius law plot of 1.