Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A Novel Windmill-typed Dy^{III} [2×2] Grid Exhibiting Slow Magnetic Relaxation

Experimental Section

General

All chemicals were of reagent grade and were used without any further purification. Elemental analysis for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. FTIR spectra were recorded with a Perkin-Elmer Fourier transform infrared spectrophotometer using the reflectance technique (4000–300 cm^{-1}). Samples were prepared as KBr disks.

Synthesis of the Ligand

The ligand H_4L were prepared in a simple hydrazone condensation reaction of two equivalent 2-hydroxy-3-methoxybenzoic acid hydrazide generated according to the previous literature[1] with one equivalent butane-2,3-dione in methanol. Then the mixture refluxed for several hours with the formation of a white suspended solid. The fine white precipitate was filtered off and washed with methanol. The crude product was obtained as white powder in 60%. Anal. Calcd (found) for $C_{20}H_{22}N_4O_6$: C, 57.97 (57.82); H, 5.31 (5.26); N, 13.53 (13.37). IR (KBr, cm^{-1}): 3426(s), 3248(s), 3076(w), 3011(w), 2939(w), 2842(w), 1652(s), 1607(m), 1582(s), 1544(s), 1481(s), 1443(m), 1428(w), 1369(w), 1347(w), 1291(s), 1248(s), 1190(w), 1163(w), 1139(m), 1091(w), 1077 (m), 973(w), 927(m), 894 (w), 883(w), 810(w), 742 (s), 725(m), 592(w), 516(w), 488(w).

Synthesis of the Complex 1

$[Dy_4(HL^{3-})_4(MeOH)_4]_2\cdot 7CH_2Cl_2\cdot MeOH$ (**2**)
A suspension of $Dy(NO_3)_3\cdot 6H_2O$ (0.1 mmol, 88.48 mg) and H_4L (0.2 mmol, 53.02 mg) in MeOH/CH_2Cl_2 (5 mL/15 mL) was treated with Et_3N (0.5 mmol, 0.07 mL). The ensuing orange solution was stirred for 6 h and subsequently filtered. The filtrate was left undisturbed to allow the slow evaporation of the solvent. Orange block-shaped single crystals of $[Dy_4(HL^{3-})_4(MeOH)_4]_2\cdot 7CH_2Cl_2\cdot MeOH$ (**2**), suitable for X-ray diffraction analysis, formed after 3 days. Yield: 38 mg, (55%, based on the metal salt). Anal. Calcd (found) for $C_{176}H_{202}N_{32}O_{57}Cl_{14}Dy_8$: C, 38.58 (38.42); H, 3.71 (3.66); N, 8.18 (8.03). IR (KBr, cm^{-1}): 3437(br), 2939(w), 2839(w), 1598(w), 1554(s), 1496(s), 1461(m), 1438 (m), 1379(s), 1321(m), 1248(s), 1197(w), 1162(w), 1089(s), 999(m), 953(w), 851(w), 799(w), 748(m), 694(w), 656(w), 629(w), 457(w).

X-Ray crystal structure determinations

Crystal data for the complex: $C_{176}H_{202}N_{32}O_{57}Cl_{14}Dy_8$, M_r = 5474.00, triclinic, space group P-1, a = 17.4258(8), b = 22.2181(10), c = 27.5838(13) Å, α =84.5860(10), β = 77.4380(10), γ = 88.3570(10), V = 10377.0(8) Å^3 , Z = 2, T = 191(2) K, D_c = 1.752 g cm^{-3}, 53386 reflections collected with 36522 unique (R_{int} = 0.0377), S = 1.017, R_1 (wR_2) = 0.0560 (0.1379) for 36522 reflections with $I > 2\sigma(I)$. The final wR was 0.1713 (all data). Suitable single crystal with dimensions of 0.25 × 0.20 × 0.18 mm^3, was selected for single-crystal X-ray diffraction analysis. Crystallographic data was collected at a temperature of 191(2) K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT processing program. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL97.[2] The location of Dy atom was easily determined, and O, N, and C atoms were subsequently determined from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. CCDC-839284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic measurements

Magnetic susceptibility measurements were performed in the temperature range 2–300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The magnetisation isotherm was collected at 1.9 K between 0 and 7 T. Samples were restrained in eicosane to prevent torquing. The diamagnetic corrections for the compounds were estimated using Pascal's constants,[3] and magnetic data were corrected for diamagnetic contributions of the sample holder.

Reference

1 Y.-N. Guo, G.-F. Xu, P. Gamez, L. Zhao, S.-Y. Lin, R. Deng, J. Tang, H.-J. Zhang, *J. Am. Chem. Soc.* 2010, **132**, 8538.
2 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.
3 E. A. Boudreaux, L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, John Wiley & Sons, New York, **1976**.

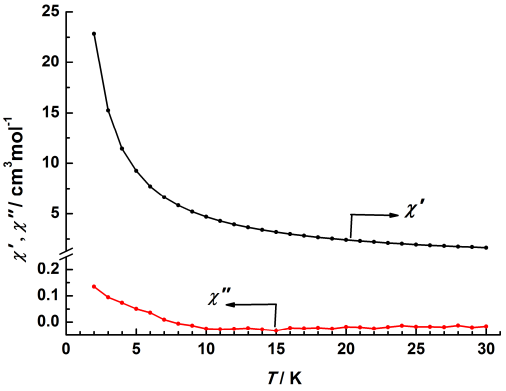

Fig. S1. Temperature dependences of χ' (black) and χ'' (red) of **2** measured at 1000 Hz in an 0 Oe external dc field.

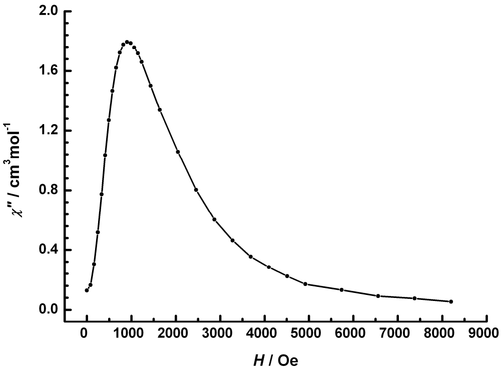

Fig. S2. Dependence of the out of phase signal of **2** on applied dc field strength at 1.9 K, 1000 Hz. χ'' signal with a significant sharp peak around 900 Oe dc field indicate field-enhanced slow magnetic relaxation operating in **2**.

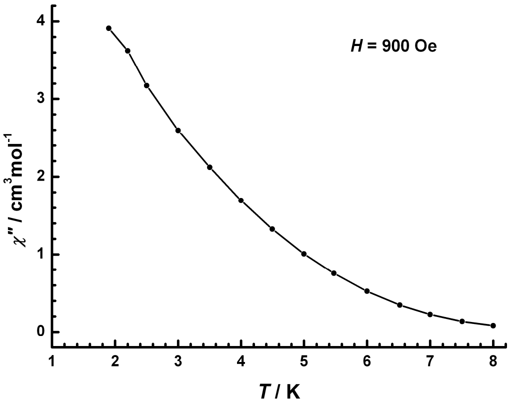

Fig. S3. Temperature dependences of χ'' component of **2** measured in a 900 Oe dc field. As compared with the zero dc field (Figure S1), the intensity of out-of-phase susceptibility under the applied external dc field is dramatically enhanced.

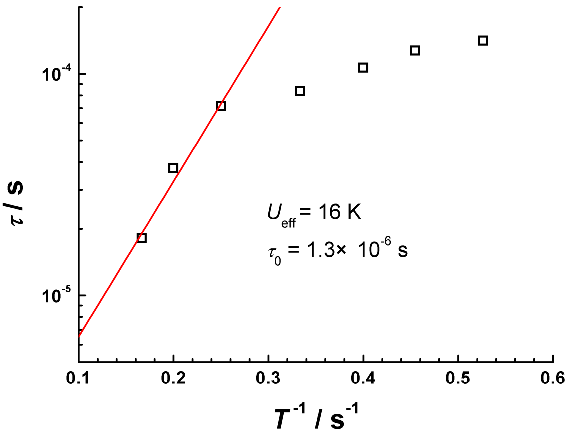

Fig. S4. Magnetization relaxation time (τ) versus T^{-1} plot for **2** under 900 Oe dc-field. The solid line represents the best fits to the Arrhenius law of the thermally-activated region.