

# Supporting Information

## Field enhanced thermally activated mechanism in a square Dy<sub>4</sub> aggregate

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### 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<sup>-1</sup>). Samples were prepared as KBr disks.

#### Synthesis of the Ligand

The ligand H<sub>2</sub>hpch was prepared in a simple hydrazone condensation reaction of salicylaldehyde with isonicotinoylhydrazine in methanol. Then the mixture was stirred overnight 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%.

#### Synthesis of the Complex 1

[Dy<sub>4</sub>(μ<sub>4</sub>-OH)(Hhpch<sup>-</sup>)<sub>8</sub>]·(ClO<sub>4</sub>)<sub>3</sub>·2CH<sub>3</sub>CN·MeOH·4H<sub>2</sub>O (**1**)

A suspension of Dy(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.2 mmol, 113.8 mg) and H<sub>2</sub>hpch (0.2 mmol, 48.2 mg) in CH<sub>3</sub>OH/CH<sub>3</sub>CN (5 mL/15 mL) was treated with NaHCO<sub>3</sub> (0.4 mmol, 33.6 mg). 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. Yellow plate-shaped single crystals of [Dy<sub>4</sub>(μ<sub>4</sub>-OH)(Hhpch<sup>-</sup>)<sub>8</sub>]·(ClO<sub>4</sub>)<sub>3</sub>·2CH<sub>3</sub>CN·MeOH·4H<sub>2</sub>O (**1**), suitable for X-ray diffraction analysis, formed after 3 days. Yield: 38 mg (25%, based on the metal salt). Anal. Calcd (found) for C<sub>109</sub>H<sub>99</sub>N<sub>26</sub>O<sub>34</sub>Cl<sub>3</sub>Dy<sub>4</sub>: C, 42.59 (42.16); H, 3.24 (3.09); N, 11.85 (11.75). IR (KBr, cm<sup>-1</sup>): 3523(br), 3231(br), 3056(w), 3025(w), 2851(w), 1639(s), 1613(s), 1600(w), 1551(s), 1475(s), 1443(m), 1410(w), 1384(s), 1320(m), 1285(s), 1244(w), 1210(w), 1152(w), 1068(w), 1001(w), 966(w), 890(m), 862(w), 798(w), 763(m), 690(m), 664(w), 623(w), 516(w).

#### X-Ray crystal structure determinations

Crystal data for the complex: C<sub>109</sub>H<sub>99</sub>N<sub>26</sub>O<sub>34</sub>Cl<sub>3</sub>Dy<sub>4</sub>, *M*<sub>r</sub> = 3073.49, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 20.1187(8), *b* = 27.8381(11), *c* = 21.6131(9) Å, α = 90°, β = 103.7340(10)°, γ = 90°, *V* = 11758.7(8) Å<sup>3</sup>, *Z* = 4, *T* = 191(2) K, *D*<sub>c</sub> = 1.736 g cm<sup>-3</sup>, *R*<sub>int</sub> = 0.0754, 59457 reflections collected, *R*<sub>1</sub>(*wR*<sub>2</sub>) = 0.0452 (0.1010) and *S* = 1.030 for 13274 observed reflections out of 20827 unique reflections with *I* > 2σ(*I*). Suitable single crystal with dimensions of 0.25×0.21×0.19 mm<sup>3</sup>, was selected for single-crystal X-ray diffraction analysis. Crystallographic data was collected at a temperature of 191 K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Kα 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*<sup>2</sup> by full-matrix least squares using SHELXTL97.<sup>1</sup> 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 DFIX

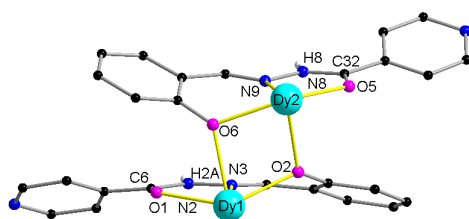
command has been used to refine the C107-C108 distance to be in the reasonable range. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. CCDC-870479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Magnetic measurements

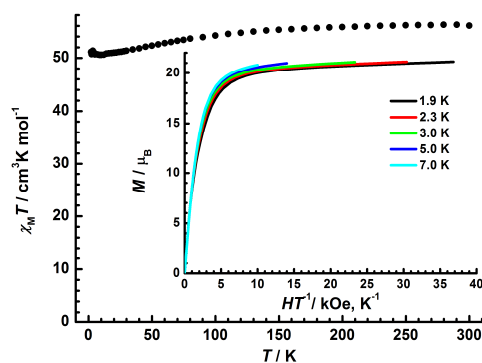
Magnetic susceptibility measurements were performed in the temperature range 2–300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The magnetisation isotherm was collected at 1.9 K between 0 and 7 T. Samples were restrained in eicosane to prevent torquing. The diamagnetic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

### Reference

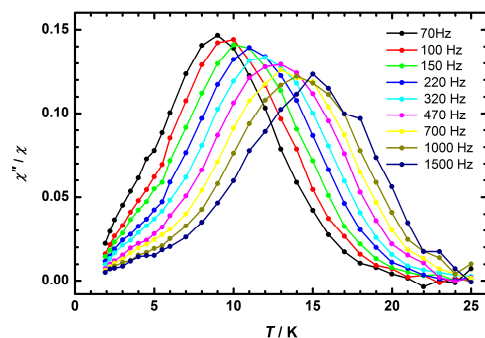
1. Sheldrick, G. M., *SHELXS-97, Program for Crystal Structure Solution*. University of Göttingen, Germany, 1997.
2. Boudreaux, E. A.; Mulay, L. N., *Theory and Applications of Molecular Paramagnetism*. John Wiley & Sons, New York, 1976.



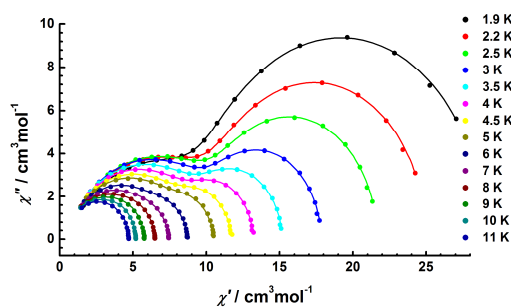
**Fig. S1** The coordination of a pair of the  $\text{Hhpch}^-$  ligands to two dysprosium (III) centers in an antiparallel or “head-to-tail” fashion. The carbonyl oxygen atoms (O1 and O5) remain in original keto form with C-O distance 1.238(10) and 1.240(10) Å.



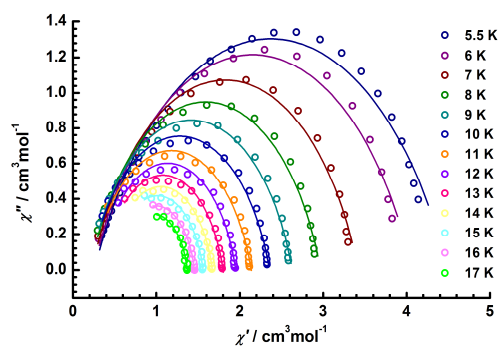
**Fig. S2** Temperature dependence of  $\chi_M T$  at 1 kOe for **1** (with  $\chi = M/H$  normalized per mol). Inset:  $M$  vs.  $H/T$  plot at various temperatures between 1.9 and 7 K.



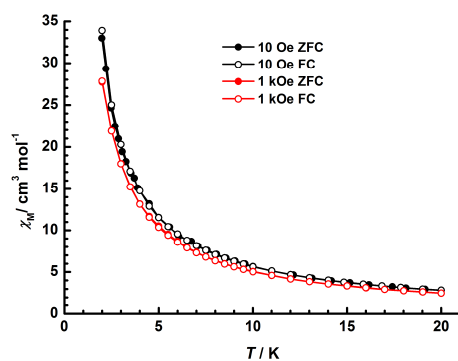
**Fig. S3** The plot of  $\chi''/\chi$  against temperature  $T$ , where  $\chi''$  and  $\chi$  are out-of-phase-ac and dc molar magnetic susceptibilities of **1** under an applied dc field of 1 kOe, respectively. Solid lines are guides for the eye.



**Fig. S4** The Cole-Cole plots as well as its evolution from faster relaxation to slower relaxation according to the temperature rise. Solid lines were performed using the sum of two modified Debye functions.



**Fig. S5** Cole-Cole plots measured at 5.5-17 K under 1 kOe dc field. The solid lines are the best fits to the experimental data, obtained with the generalized Debye model with  $\alpha$  parameters below 0.30.



**Fig. S6** The zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities at 10 Oe and 1 kOe.