Supporting Information

Field enhanced thermally activated mechanism in a square Dy₄ 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⁻¹). Samples were prepared as KBr disks.

Synthesis of the Ligand
The ligand H₂hpch 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
\[
[Dy_4(\mu_4-\text{OH})(\text{Hhpch})_8] \cdot (\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN} \cdot \text{MeOH} \cdot 4\text{H}_2\text{O} \quad (1)
\]
A suspension of Dy(ClO₄)₃·6H₂O (0.2 mmol, 113.8 mg) and H₂hpch (0.2 mmol, 48.2 mg) in CH₃OH/CH₃CN (5 mL/15 mL) was treated with NaHCO₃ (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 [Dy₄(µ₄-OH)(Hhpch)₈]·(ClO₄)₃·2CH₃CN·MeOH·4H₂O (1), suitable for X-ray diffraction analysis, formed after 3 days. Yield: 38 mg (25%, based on the metal salt). Anal. Calcd (found) for C₁₀₉H₉₉N₂₆O₃₄Cl₃Dy₄: C, 42.59 (42.16); H, 3.24 (3.09); N, 11.85 (11.75). IR (KBr, cm⁻¹): 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: C₁₀₉H₉₉N₂₆O₃₄Cl₃Dy₄, Mr = 3073.49, monoclinic, space group P2₁/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) Å³, Z = 4, T = 191(2) K, Dₓ = 1.736 g cm⁻³, Rint = 0.0754, 59457 reflections collected, R₁ (wR₂) = 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 mm³, 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 F² by full-matrix least squares using SHELXTL.¹ 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.

**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, and magnetic data were corrected for diamagnetic contributions of the sample holder.

**Reference**


**Fig. S1** The coordination of a pair of the 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.