Supporting Information for:

The Use of a Versatile *o*-Vanilloyl Hydrazone Ligand to Prepare SMM-like Dy_3 Molecular Cluster Pair

Shufang Xue,[a,b], Lang Zhao,[a], Yun-Nan Guo,[a,b] Peng Zhang,[a,b] and Jinkui Tang*[a]

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_2**apovh** was synthesized by condensation reaction of *o*-vanilloyl hydrazine with the methyl ester of imino-picolinic acid, generated by addition 2-cyanopyridine to sodium methoxide in dry methanol[1]. Then the mixture was stirred overnight with the formation of a light yellow suspended solid. The fine yellow precipitate was filtered off and washed with methanol. The crude product was obtained as yellow powder in 60%. Anal. Calcd (found) for $C_{14}H_{14}N_4O_3$: C, 58.73 (58.20); H, 4.93 (4.82); N, 19.57 (19.41). IR (KBr, cm^{-1}): 3385(w), 3312(w), 3260(m), 3122(s), 2928(w), 2830(w), 1684(s), 1627(m), 1587(m), 1574(m), 1550(s), 1471(s), 1438(s), 1396(s), 1360(s), 1314(m), 1302(w), 1256(s), 1169(w), 1108(w), 1091(m), 1075(m), 1058(w), 997(w), 952(w), 833(w), 799(m), 792(w), 741(w), 728(w), 719(w), 678(w), 646(w), 622(w), 581(m), 464(w).

Synthesis of the Complex 1

$[Dy_6$(**apovh**$)_4$(H**apovh**$)_4(CO_3)_2(SCN)_2]\cdot 6CH_3CN\cdot 8CH_3OH\cdot 2H_2O$ (**1**)

To a solution of the ligand H_2**apovh** (0.20 mmol, 0.057 g) and triethylamine (0.07 mL, 0.5 mmol) in MeOH/ CH_3CN (1:3), solid $Dy(SCN)_3\cdot 6H_2O$ (0.045 g, 0.1 mmol) was added and the resulting mixture was stirred for six hours. The yellow solution was left unperturbed to allow the slow evaporation of the solvent. Yellow single crystals, suitable for X-ray diffraction analysis, were formed after one week. These crystals were collected by filtration, washed with cold methanol, and dried in air.Yield: 38 mg (19%, based on the metal salt). Anal. Calcd (found) for $C_{136}H_{154}N_{40}O_{40}S_2Dy_6$: C, 40.55 (40.16); H, 3.85 (3.79); N, 13.91 (13.75). IR (KBr, cm^{-1}): 3324(br), 3183(br), 2993(w), 2835(w), 2058(m), 1635(s), 1570(s), 1528(s), 1476(s), 1438(m), 1378(s), 1251(s), 1199(w), 1163(w), 1100(w), 1068(w), 1009(w), 952(w), 853(m), 794(m), 745(s), 691(m), 653(w), 634(w), 535(w).

X-Ray crystal structure determinations

Crystal data for the complex: $C_{136}H_{154}N_{40}O_{40}S_2Dy_6$, *M*r = 4028.11, monoclinic, space group $P2_1/n$, a = 15.3269(8), b = 27.9952(13), c = 18.0851(8) Å, α = 90°, β = 91.4970(10)°, γ = 90°, V = 7757.3(6) $Å^3$, Z = 2, T = 191(2) K, D_c = 1.725 g cm^{-3}, R_{int} = 0.0594, 39361 reflections collected, R_1 (wR_2) = 0.0577 (0.1353) and S = 1.109 for 9538 observed reflections out of 13722 unique reflections with $I >$

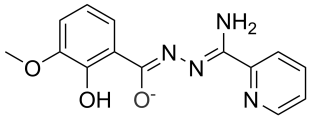
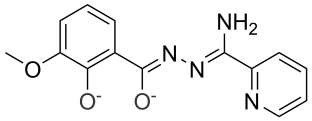
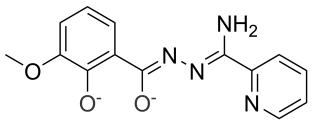
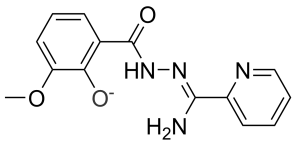
$2\sigma(I)$. Suitable single crystal with dimensions of 0.25 × 0.21 × 0.19 mm^3, was selected for single-crystal X-ray diffraction analysis. Crystallographic data was collected at a temperature of 191 K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). 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-881629 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.

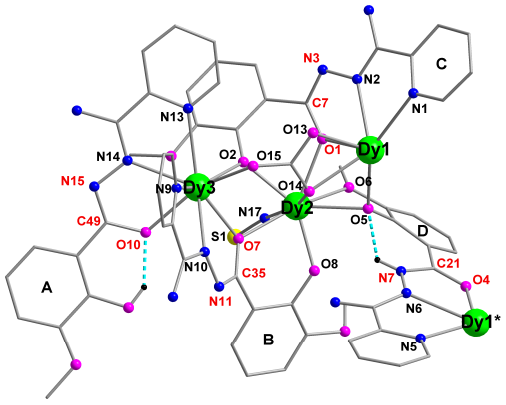
Magnetic measurements

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.

Table S1 The keto-enol tautomerism and deprotonated form of H_2**apovh** ligand in **1** judging by crystallography

Keto form Enol form

Ligand	O-C	N-C	Keto-enol tautomerism	Deprotonated form
A	O(10)-C(49) 1.346(12)	N(15)-C(49) 1.282(13)	Enol form	
B	O(7)-C(35) 1.307(11)	N(11)-C(35) 1.304(12)	Enol form	
C	O(1)-C(7) 1.299(11)	N(3)-C(7) 1.309(13)	Enol form	
D	O(4)-C(21) 1.239(11)	N(7)-C(21) 1.333(12)	Keto form	



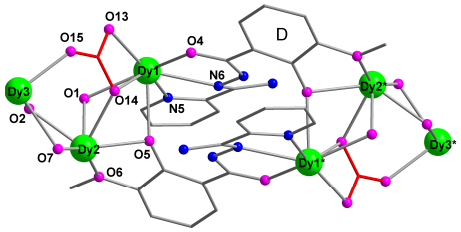


Fig. S1 (top) Partially labeled Structure of the Dy_3 motif, with each type of H_2**apovh** ligand marked as A, B, C and D. The bond lengths involving red label atoms were shown in Table S1 for judging keto-enol tautomerism and deprotonated form of H_2**apovh** ligands. (bottom) Structure of the pair of Dy_3 cores covalently linked by two H_2**apovh** ligands. Red bonds represent carbonato ligands fixed by the absorption of carbon dioxide from air.

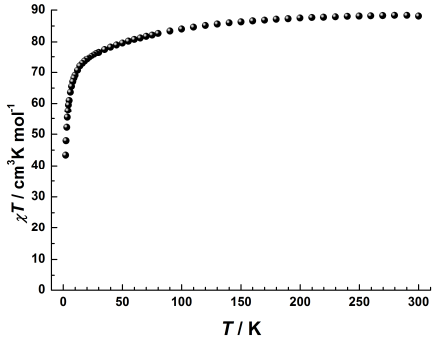


Fig. S2 Temperature dependence of the $\chi_M T$ product at 1000 Oe with χ defined as M/H.

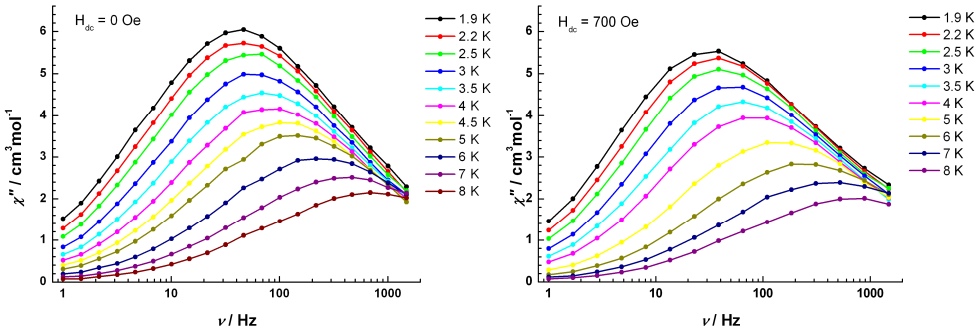


Fig. S3 Frequency dependence of the out-of-phase ac susceptibilities of **1** measured in zero static field (left) and a 700 Oe dc-field (right) at the indicated temperatures.

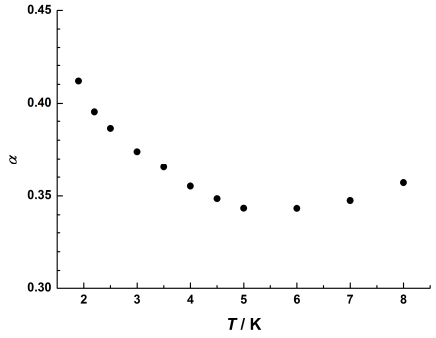


Fig. S4 Temperature dependence of α parameter from fits to Cole-Cole plots as shown in Fig. 3 of main text.

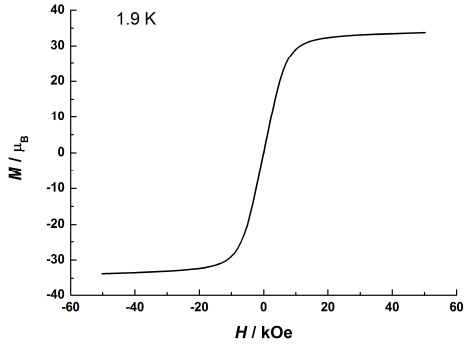


Fig. S5 *M vs. H* data of **1** at 1.9 K. The value of 33.7 μ_B at 7 T is lower than the expected saturation value

of 60 μ_B (10 μ_B for each Dy^{III} ion), which is most likely due to anisotropy and the crystal-field effect at the Dy^{III} ion that eliminates the 16-fold degeneracy of the $^6H_{15/2}$ ground state. Indeed, the maximum of *M* is agree with the expected value (31.38 μ_B) for six uncorrelated Dy^{III} ions with a value of 5.23 μ_B per Dy^{III} ion assuming the presence of considerable ligand-field effects.[4]

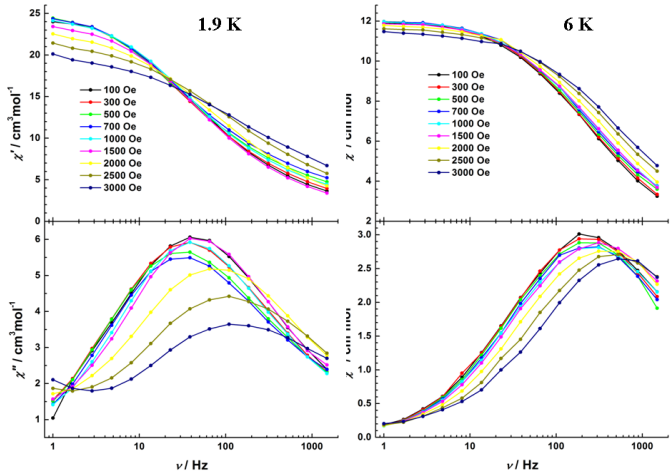


Fig. S6 Frequency dependence of the ac susceptibility at 1.9 K (left) and 6 K (right) performed at different dc fields for **1**.

Reference

1 L. Zhao, V. Niel, L. K. Thompson, Z. Xu, V. A. Milway, R. G. Harvey, D. O. Miller, C. Wilson, M. Leech, J. A. K. Howard, S. L. Heath, *Dalton Trans.* 2004, 1446.

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.

4 J. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.* 2006, **45**, 1729.