

# Supporting Information for:

## **A triangular dysprosium with asymmetric central caps featuring ferromagnetic coupling and single-molecule magnet behaviour**

### **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  $\text{cm}^{-1}$ ). Samples were prepared as KBr disks.

#### **Synthesis of complex 2**

To 3-*p*-methoxyaniline-5-methoxysalicylaldehyde (0.057 g, 0.2 mmol) in ethanol (15 mL) was added 2-aminoethanol (0.8 ml, 0.8 mmol) in a 1:4 molar ratio and the resultant mixture was stirred at room temperature for 30 min. Then  $\text{Dy}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (0.114 g, 0.2 mmol) was added to this solution and stirred at room temperature for 2 h and the resultant solution was left unperturbed to allow for slow evaporation of the solvent. Colourless single crystals of complex **2** were obtained after one month. Yield: 20 mg (27.7%). Elemental analysis (%) Calcd for  $\text{C}_{53}\text{H}_{76}\text{Cl}_2\text{Dy}_3\text{N}_5\text{O}_{29}$ : C, 35.26, H, 4.24, N, 3.88; found C, 34.22, H, 4.18, N, 3.83. IR (KBr,  $\text{cm}^{-1}$ ): 3375 (m), 3058 (w), 2940 (m), 2901 (m), 2842 (w), 1633 (s), 1605 (s), 1550 (w), 1471 (s), 1402 (m), 1301 (s), 1243 (s), 1222 (s), 1169 (m), 1083 (s), 1056 (s), 968 (m), 930 (w), 906 (m), 859 (m), 784 (w), 739 (s), 626 (s), 559 (w), 537 (w), 449 (w), 427 (w).

#### **Physical measurements**

Crystallographic data were collected at a temperature of 191(2) K on a Bruker ApexII CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data processing was accomplished with the SAINT processing program. The structure was solved by the direct methods and refined on  $F^2$  by full-matrix least squares using

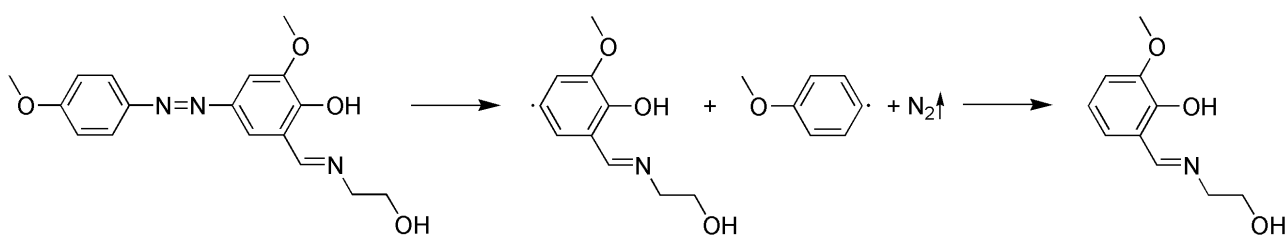
SHELXTL97. The locations of Dy atom were easily determined, and O, N and C atoms were subsequently determined from the difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC 922636 contains the supplementary crystallographic data for this paper. These data 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 were performed in the temperature range 1.9–300 K, using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder. Elemental analysis for C, H and N were carried out on a Perkin-Elmer 2400 analyzer.

**Table S1** Crystal data and structure refinement for compound **2**.

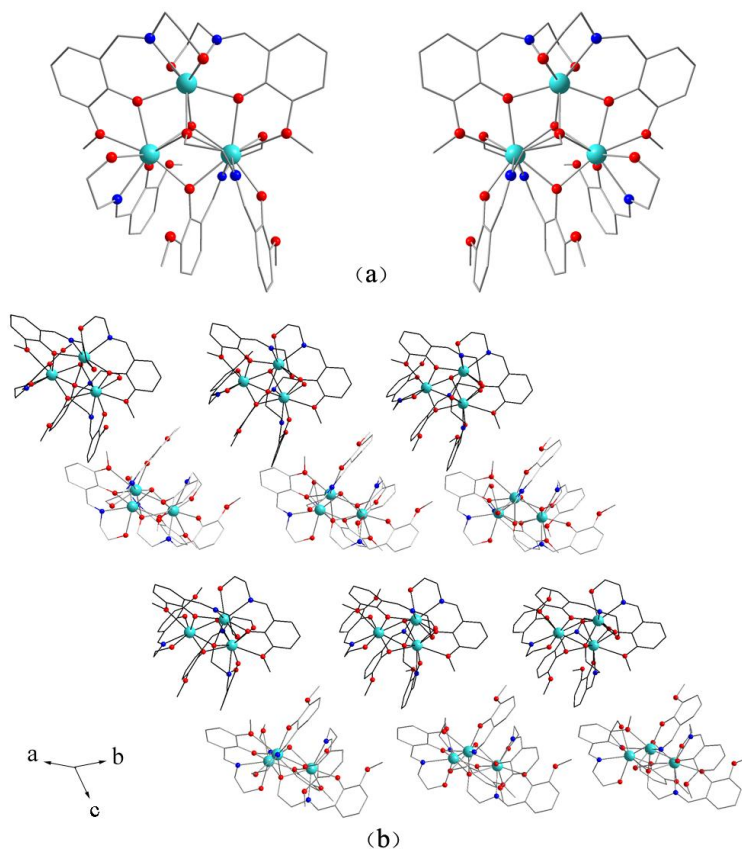
Compound <b>2</b>	
Empirical formula	C <sub>106</sub> H <sub>152</sub> Cl <sub>4</sub> Dy <sub>6</sub> N <sub>10</sub> O <sub>58</sub>
Fw (g/mol)	3611.18
Crystal system	Monoclinic
Space group	<i>Cc</i>
Temperature (K)	191(2)
<i>Z</i>	2
<i>a</i> (Å)	26.076(2)
<i>b</i> (Å)	14.2392(11)
<i>c</i> (Å)	22.762(3)
$\alpha$ (°)	90.00
$\beta$ (°)	122.8220(10)
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	7102.4(12)
$\rho_{\text{calcd}}$ (Mg/m <sup>3</sup> )	1.689
<i>F</i> (000)	3572
<i>R</i> <sub>int</sub>	0.0391
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0540, 0.1326
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0670, 0.1412
Flack parameter	0.020(16)
GOF	1.033

**Table S2** Structural parameters for the Dy<sub>3</sub>(μ<sub>3</sub>-O)<sub>2</sub> core in compounds **1** and **2**.

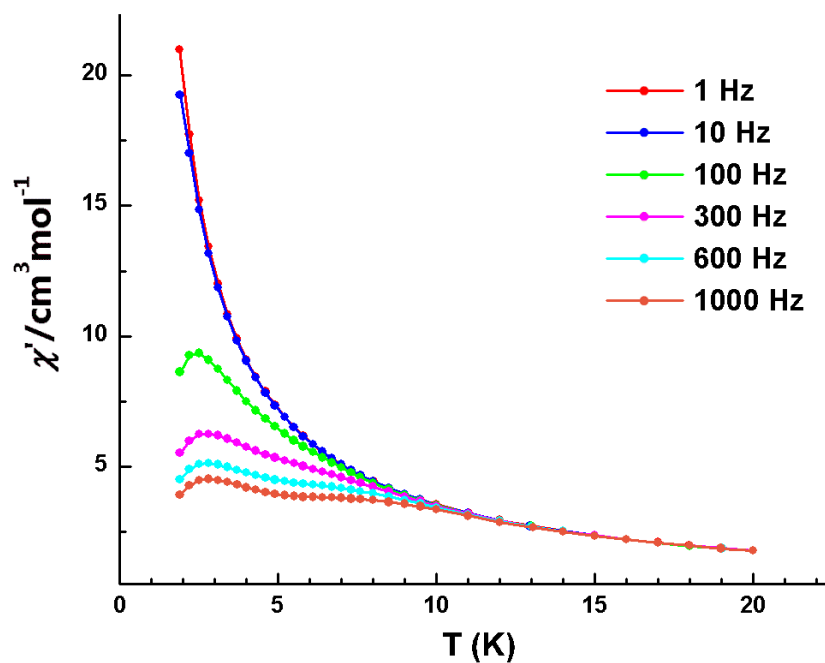
Compound 1			
Dy(1)-O(1)	2.3978(23) Å	Dy(1)-O(1)-Dy(3)	96.308(72) °
Dy(2)-O(1)	2.3713(18) Å	Dy(1)-O(1)-Dy(2)	95.853(77) °
Dy(3)-O(1)	2.3251(24) Å	Dy(2)-O(1)-Dy(3)	96.857(79) °
Dy(1)-O(2)	2.3477(20) Å	Dy(1)-O(2)-Dy(3)	96.127(72) °
Dy(2)-O(2)	2.3330(25) Å	Dy(1)-O(2)-Dy(2)	98.281(80) °
Dy(3)-O(2)	2.3823(20) Å	Dy(2)-O(2)-Dy(3)	96.339(78) °
O2 to Dy <sub>3</sub> plane	1.1839 Å	O1 to Dy <sub>3</sub> plane	-1.2047 Å
Compound 2			
Dy(1)-O(12)	2.399(9) Å	Dy(1)-O(12)-Dy(3)	95.3(3) °
Dy(2)-O(12)	2.509(9) Å	Dy(1)-O(12)-Dy(2)	92.6(3) °
Dy(3)-O(12)	2.315(8) Å	Dy(2)-O(12)-Dy(3)	96.7(3) °
Dy(1)-O(16)	2.357(8) Å	Dy(1)-O(16)-Dy(3)	96.3(3) °
Dy(2)-O(16)	2.369(8) Å	Dy(1)-O(16)-Dy(2)	97.3(3) °
Dy(3)-O(16)	2.324(9) Å	Dy(2)-O(16)-Dy(3)	100.5(3) °
O12 to Dy <sub>3</sub> plane	1.2637 Å	O16 to Dy <sub>3</sub> plane	-1.1507 Å



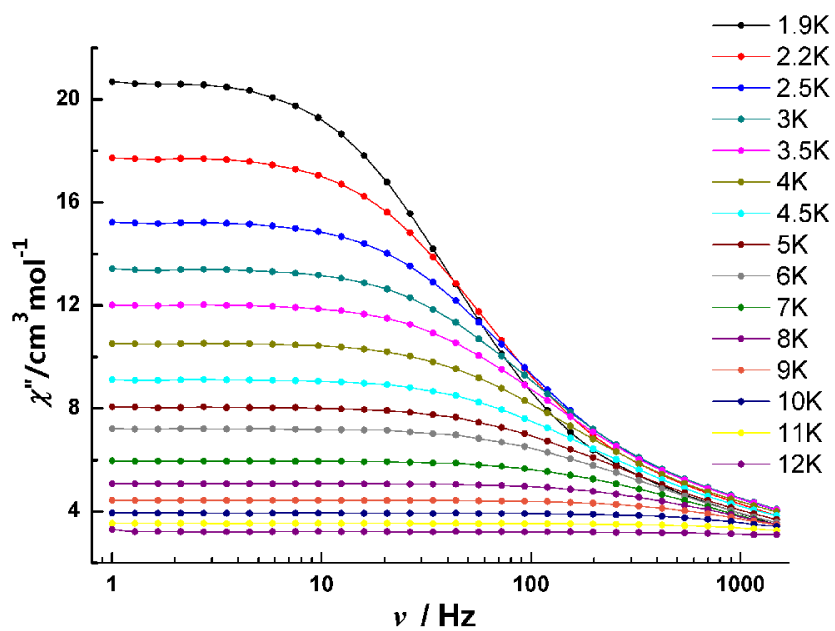
**Scheme S1** Proposed mechanism for the decomposition of H<sub>2</sub>L'.



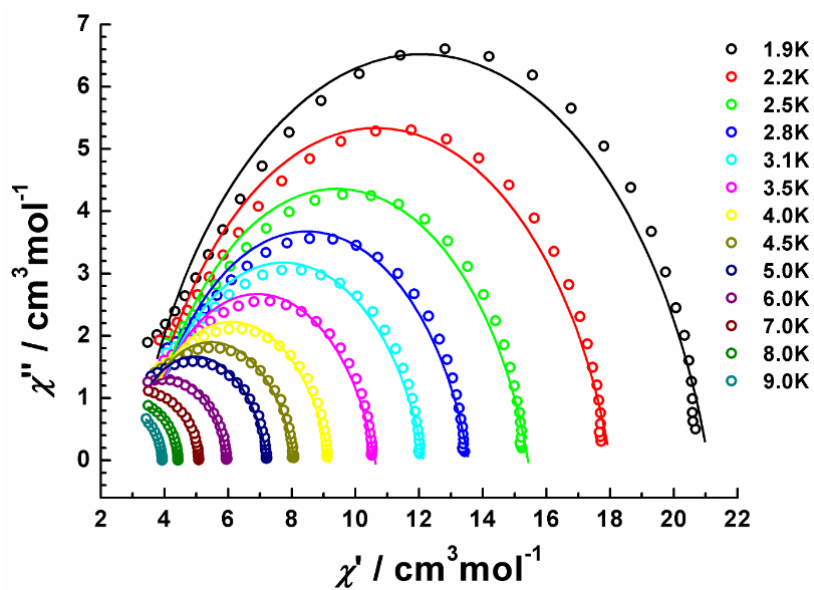
**Fig. S1** (a) Views of the two opposite configurations for **2**; (b) Molecular packing in single crystal **1** without hydrogen atoms and solvent molecules omitted for clarity.



**Fig. S2** Temperature dependence of the in-phase ac susceptibility of **2** under zero dc field.



**Fig. S3** Frequency dependence of the in-phase ac susceptibility of **2** below 12 K under zero-dc field.



**Fig. S4** Cole-Cole plots measured below 9 K under zero-dc field.