

## Supporting Information

### Predictable Self-assembled [2x2] Ln(III)<sub>4</sub> Square Grids (Ln = Dy, Tb) – SMM

#### Behaviour in a New Lanthanide Cluster Motif.

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**Synthesis of Ligand L1.** The ligand L1 was carried out according to a published procedure.<sup>1</sup>

Ligand charge is indicated in terms of the number of protons lost on complexation.

#### Synthesis of [Dy<sub>4</sub>(L1-2H)<sub>2</sub>(L1-H)<sub>2</sub>(OH)<sub>4</sub>]Cl<sub>2</sub>·8H<sub>2</sub>O (1)

Ligand L1 (0.050 g, 0.17 mmol) and DyCl<sub>3</sub>·6H<sub>2</sub>O (0.060 g, 0.16 mmol) were stirred together in MeOH and MeCN mixture (5 mL + 10 mL) for 2-3 min, followed by addition of 5 drops of Et<sub>3</sub>N. After stirring for 30 min at room temperature the solution was filtered and the filtrate was layered with ethyl ether. Dark red crystals appeared in a week (Yield: 38 %). Selected IR data (Nujol, cm<sup>-1</sup>): 1614, 1591 (ν CN), 1162, 1064, 722. Elemental Analysis for bulk vacuum dried sample (%): Calcd for Dy<sub>4</sub>(C<sub>15</sub>H<sub>14</sub>N<sub>6</sub>O)<sub>4</sub>(OH)<sub>4</sub>Cl<sub>2</sub>·8H<sub>2</sub>O: C, 34.15; H, 3.63; N, 15.93. Found: C, 34.13; H, 3.37; N, 15.78.

#### Synthesis of [Dy<sub>4</sub>(L1-2H)<sub>2</sub>(L1-H)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>(O)]·14H<sub>2</sub>O (2)

Ligand L1 (0.050 g, 0.17 mmol), DyCl<sub>3</sub>·6H<sub>2</sub>O (0.060 g, 0.16 mmol), and sodium azide (0.020 g, 0.30 mmol) were stirred together in a MeOH (5 mL) and MeCN (10 mL) mixture for 30 min at room temperature. The solution was filtered and the filtrate was layered with ethyl ether. Dark red crystals appeared after 3 days (Yield: 30 %). The

crystals were washed several times with ethyl ether and then dried. Selected IR data (Nujol,  $\text{cm}^{-1}$ ): 2082 ( $\nu \text{N}_3^-$ ), 1617, 1582 ( $\nu \text{CN}$ ), 1309, 1165, 1066, 721. Elemental Analysis (%): Calcd for  $\text{Dy}_4(\text{C}_{15}\text{H}_{14}\text{N}_6\text{O})_4(\text{N}_3)_4(\text{O}) \cdot 14\text{H}_2\text{O}$ : C, 31.84; H, 3.74; N, 22.28. Found: C, 31.68; H, 3.08; N, 22.01.

### Synthesis of $[\text{Tb}_4(\text{L1-2H})(\text{L1-H})_3(\text{N}_3)_4(\text{O})](\text{NO}_3)(\text{CH}_3\text{CN}) \cdot 2\text{H}_2\text{O}$ (**3**)

Ligand L1 (0.050 g, 0.17 mmol),  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.060 g, 0.14 mmol), and sodium azide (0.020 g, 0.30 mmol) were stirred together in MeOH (5 mL) and MeCN (10 mL) mixture for 24 hours. The solution was then gently heated for 30 min and cooled down to the room temperature, filtered and left undisturbed. Dark red crystals appeared in a few days (Yield: 36 %). Selected IR data (Nujol,  $\text{cm}^{-1}$ ): 2083 ( $\nu \text{N}_3^-$ ), 1615, 1582 ( $\nu \text{CN}$ ), 1305, 1166, 1073, 721. Elemental Analysis (%): Calcd for  $\text{Tb}_4(\text{C}_{15}\text{H}_{14}\text{N}_6\text{O})_4(\text{N}_3)_4(\text{O})(\text{NO}_3)(\text{CH}_3\text{CN})(\text{H}_2\text{O})_5$ : C, 33.98; H, 3.17; N, 24.31. Found: C, 33.42; H, 3.05; N, 25.21. The discrepancy in the N analysis may be due to a small amount of  $\text{NaN}_3$  impurity in the bulk sample.

### EA and IR spectroscopy.

Elemental analyses were carried out by Canadian Microanalytical Service, Delta, BC, Canada. Infrared spectra were obtained as Nujol mulls on a Bruker TENSOR 27 infrared spectrometer.

### Single Crystal X-ray Diffraction Studies.

Crystals of **1** – **3** were mounted on low temperature diffraction loops and measured on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K $\alpha$  radiation. Structures were solved by direct methods<sup>2</sup> and expanded using Fourier techniques<sup>3</sup>. Neutral atom scattering factors were taken from Cromer and Waber<sup>4</sup>. Anomalous dispersion effects were included in  $F_{\text{calc}}$ <sup>5</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley<sup>6</sup>. The values for the mass attenuation coefficients are those of Creagh and Hubbell<sup>7</sup>. All calculations were performed using Crystal Structure<sup>8,9</sup> and Platon<sup>10</sup> crystallographic software packages, except for refinement, which was performed using

SHELXL-97<sup>2</sup>. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced in calculated positions and refined on a riding model, unless otherwise indicated.

For **1**, H5- H8, and H13- H16 (the bridging hydroxide H-atoms) were located in difference map positions and refined positionally with distance restraints, and with  $U_{\text{iso}} = 1.5U_{\text{eq}}$  of their parent oxygen-atom. The Platon<sup>10</sup> SQUEEZE procedure was applied to **1** and **2**. For **1**, 840 electrons per unit cell were recovered in one void (total volume 3684 Å<sup>3</sup>); that is 210 electrons per formula unit. For **2**, 1014 electrons per unit cell were recovered in one void (total volume 4097 Å<sup>3</sup>); that is 253.5 electrons per formula unit. Disordered, partial-occupancy lattice solvent water molecules were present for both, prior to the application of SQUEEZE; the recovered electrons were assigned as 21 and 25 lattice solvent water molecules per formula unit, respectively. The water molecules omitted from the model by SQUEEZE were included in the formula for the calculation of intensive properties.

For **3**, collection, solution and refinement proceeded normally. Distance, angle and similarity restraints were applied to the nitrate anion. Similarity restraints were also applied to the lattice solvent acetonitrile molecule. O10 and O11 are partial occupancy, disordered lattice solvent water molecules. Their occupancies were refined (summed to one), however, the corresponding hydrogen atoms were omitted from the model as these could not be located from examination of difference Fourier maps.

**Table S1. Crystallographic Data for Complexes 1-3.**

	<b>1</b>	<b>2</b>	<b>3</b>
formula	C <sub>60</sub> H <sub>104</sub> Cl <sub>2</sub> Dy <sub>4</sub> N <sub>24</sub> O <sub>29</sub>	C <sub>60</sub> H <sub>108</sub> Dy <sub>4</sub> N <sub>36</sub> O <sub>30</sub>	C <sub>62</sub> H <sub>66</sub> N <sub>38</sub> O <sub>10</sub> Tb <sub>4</sub>
Fw	2346.53	2463.82	2139.15
temp. (K)	163(2)	163(2)	163(2)
crystal system	Triclinic	Triclinic	Monoclinic
space group	P $\bar{1}$ (#2)	P $\bar{1}$ (#2)	P2 <sub>1</sub> /c (#14)
a/Å	17.7717(7)	19.806(9)	17.275(3)
b/Å	22.2755(8)	20.037(9)	20.969(4)
c/Å	27.8431(19)	27.326(15)	26.506(5)
$\alpha$ /°	110.343(8)	84.31(3)	90.00
$\beta$ /°	95.225(7)	86.78(2)	128.219(3)
$\gamma$ /°	106.955(8)	71.967(18)	90.00
vol/Å <sup>3</sup>	9655.4(12)	10257(9)	7543(2)
Z	4	4	4
D <sub>c</sub> /mg m <sup>-3</sup>	1.614	1.595	1.884
$\mu$ (MoK $\alpha$ )/cm <sup>-1</sup>	32.00	29.65	37.87
reflns collected	39537	40060	97349
reflns unique (I>2.00 $\sigma$ (I))	28920	24602	14814
R <sub>merge</sub>	0.0545	0.0948	0.0419
R1 <sup>a</sup> , wR2 <sup>b</sup>	0.0492,0.1360	0.1146,0.3419	0.0635, 0.1859

a:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , I > 2 $\sigma$ I

b:  $wR2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum w(F_o^2)^2]^{1/2}$ , all reflections

**Table S2. Ranges of selected bond distances (Å) and angles (°) for 1-3.**

#	Ln <sup>III</sup> -Ln <sup>III</sup> (Å)	Ln <sup>III</sup> -N (Å)	Ln <sup>III</sup> -O (Å)	Ln <sup>III</sup> -N <sub>3</sub> -Ln <sup>III</sup> (°)	Ln <sup>III</sup> -O-Ln <sup>III</sup> (°)
<b>1</b>	3.768(3)-3.786(3)	2.500(6)-2.566(5)	2.251(4)-2.357(4)		107.40(18)- 108.44(17)(O <sub>hyd</sub> ) 112.50(19)- 113.83(17)(OH)
<b>2</b>	3.664(3)-3.690(3)	2.356(12)-2.571(9)	2.260(7)-2.308(8) (O <sub>hyd</sub> ) 2.546(8)-2.674(9) ( $\mu_4$ -O)	95.2(3)-99.3(3)	106.4(3)-108.7(3)(O <sub>hyd</sub> ) 88.5(2)-91.4(3) ( $\mu_4$ -O)
<b>3</b>	3.681(3)-3.704(3)	2.455(7)-2.566(6)	2.264(5)-2.331(5) (O <sub>hyd</sub> ) 2.557(7)-2.710(6) ( $\mu_4$ -O)	95.8(2)-96.2(2)	105.6(2)-107.8(2) (O <sub>hyd</sub> ) 88.6(2)-92.4(2) ( $\mu_4$ -O)

### Magnetic Measurements.

Magnetic susceptibility measurements were obtained using Quantum Design SQUID magnetometers, MPMS-5S and MPMS-XL7, operating between 2.0 and 300 K for dc applied fields from -7 to 7 T. DC analyses were performed on polycrystalline samples of **1** and **2** supported in polyethylene membranes under fields of 0 to 7 T, between 1.8 and 300 K. **3** was examined in a gel cap, in the temperature range 2.0 to 300 K, in fields from 0 to 5 T. AC susceptibility measurements were carried out under an oscillating field of 3 Oe and ac frequencies in the range 1 to 1500 Hz. Field dependent magnetization data were collected at 100 K to check for ferromagnetic impurities, which were found to be absent. Diamagnetic corrections were applied for the sample holder and the core diamagnetism of the sample (from Pascal constants).

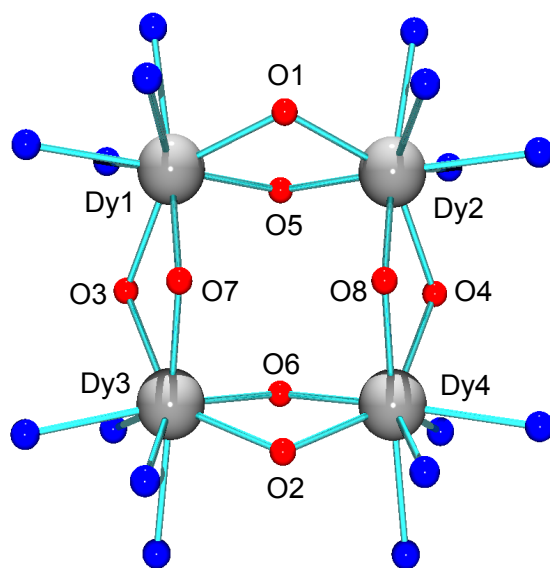


Fig. S1. Core structural representation in **1**.

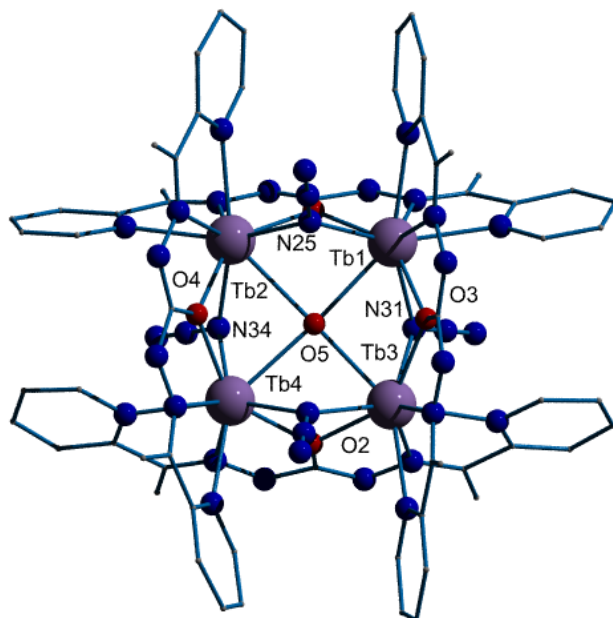


Fig. S2. Structural representation of **3**.

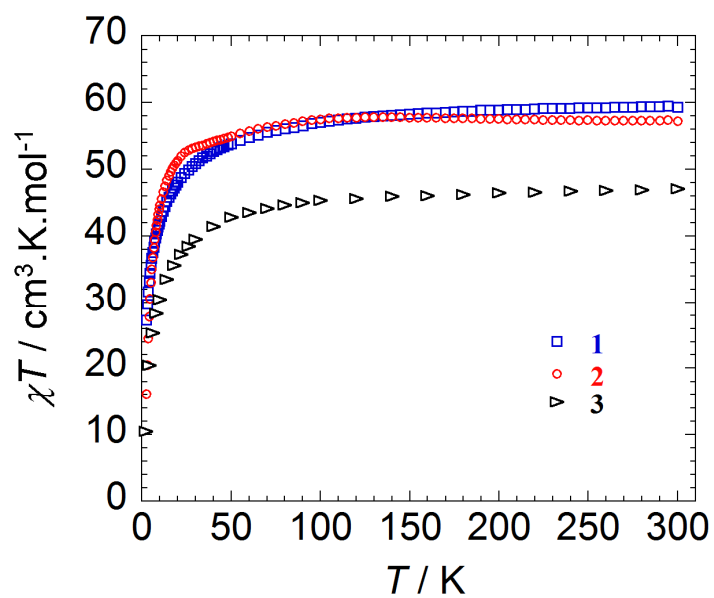


Figure S3. Variable temperature DC magnetic data for **1-3** (Red; **1**, blue; **2**, black; **3**).

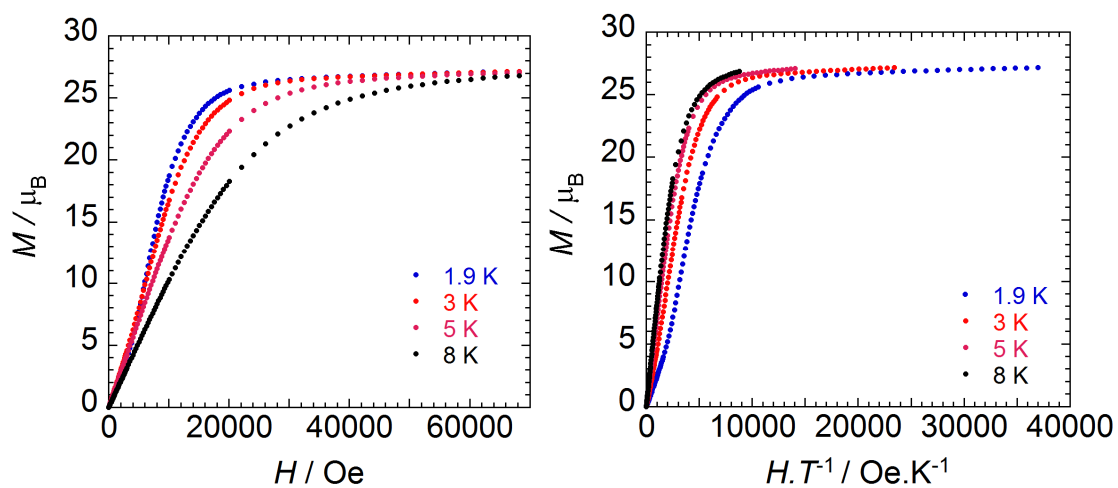


Figure S4. Magnetization data versus H and H/T at indicated temperatures for **1**.

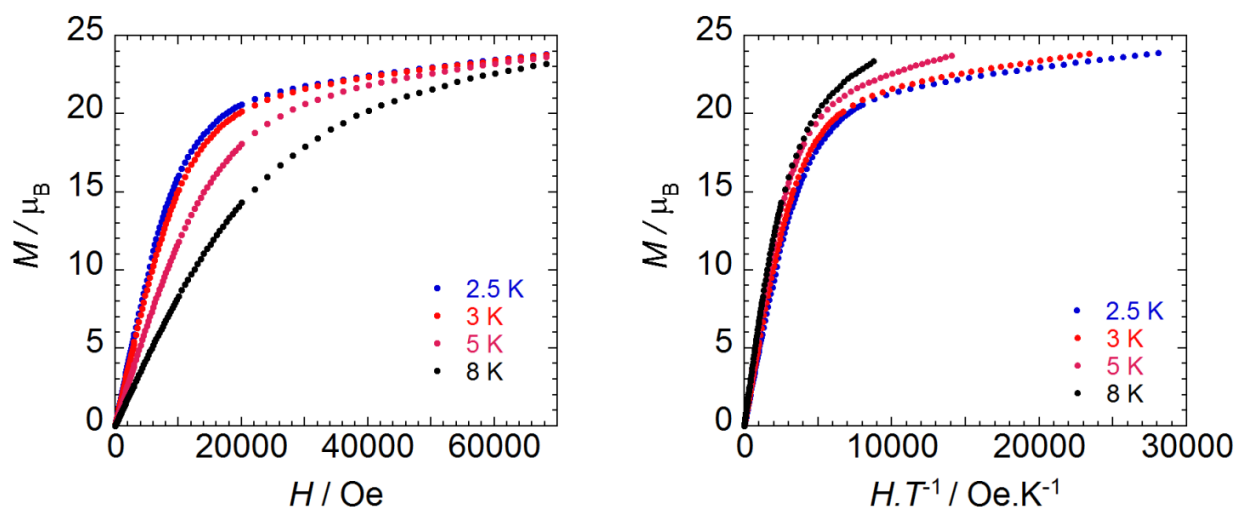


Figure S5. Magnetization data versus H and H/T at indicated temperatures for **2**.

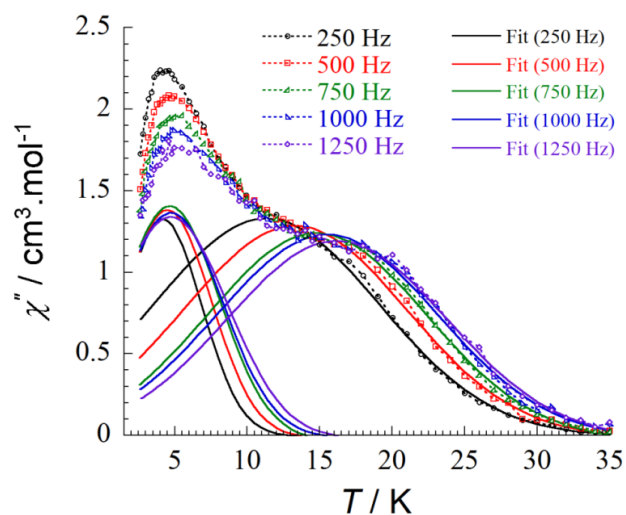


Fig. S6. Gaussian fit of two peaks in **2**.

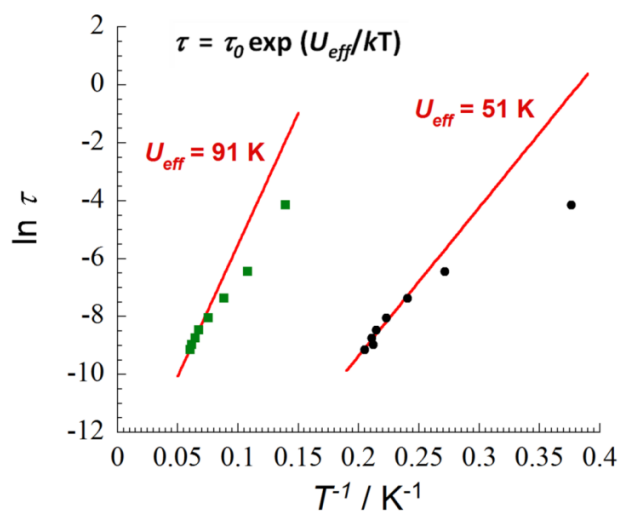


Figure S7. Energy barriers for reversal of magnetization in **2**.



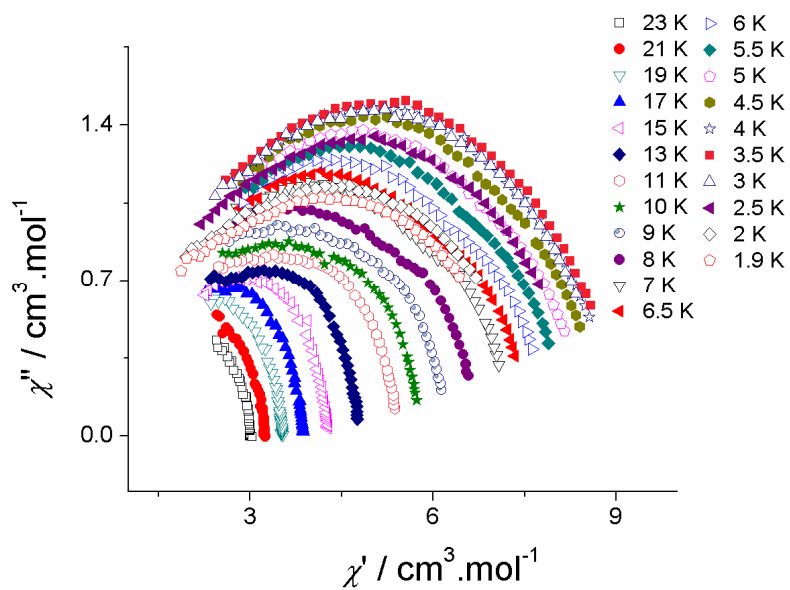


Fig. S8. Cole-Cole plots for **2** obtained using the ac data susceptibility data in 0 Oe external field.

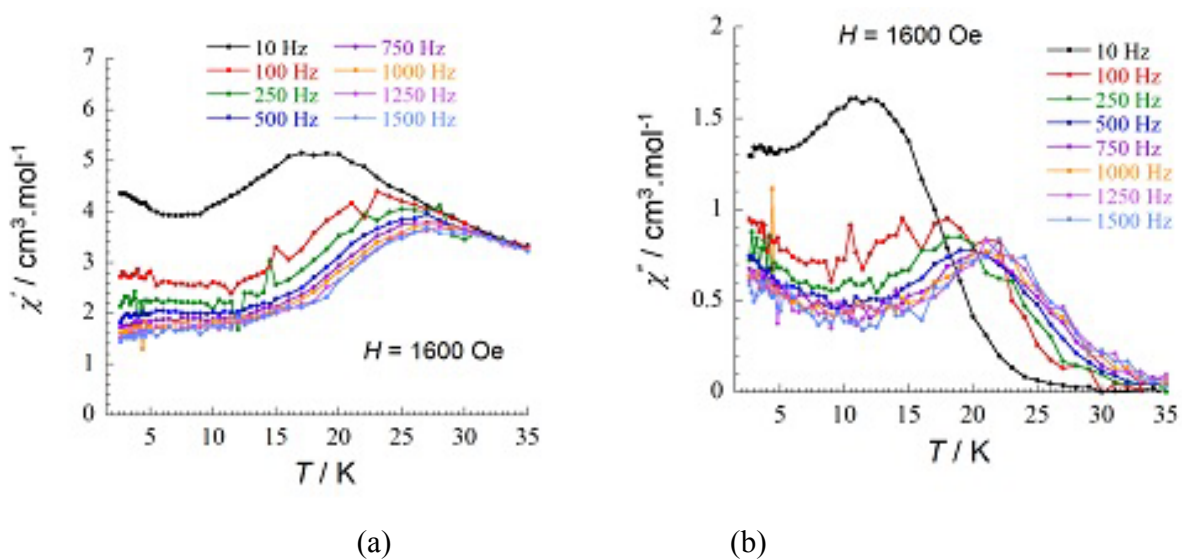


Fig. S9.  $\chi'$  vs. T data for **2** in 1600 Oe external field.

## References

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