

Supplementary Information for:

# Remarkable $\text{Ln}^{\text{III}}_3\text{Fe}^{\text{III}}_2$ clusters with magnetocaloric effect and slow magnetic relaxation

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## Experimental section

All reactions were carried out under aerobic conditions. Starting materials were obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-K $\alpha$  radiation. The FT-IR spectra were measured with a Bruker Tensor 27 Spectrophotometer on KBr disks. Magnetic data were measured on microcrystalline samples using a Quantum Design SQUID-VSM magnetometer. Contributions of the sample holder and the diamagnetic correction estimated using Pascal's constants were corrected.

### Synthesis of [Gd<sup>III</sup><sub>3</sub>Fe<sup>III</sup><sub>2</sub>( $\mu_5$ -O)L<sub>2</sub>(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)(MeOH)]·0.5MeOH (1)

To a stirred solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.25 mmol) in 10 mL MeOH was added H<sub>4</sub>L (0.5 mmol) and NEt<sub>3</sub> (1.08 mmol). The resulting red-brown solution was stirred for 15 min and then Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.25 mmol) in 5 mL MeCN was added in and stirred for a further 1h. The solution was filtered and sealed in a vial, which was heated at 60 °C. Yellow rectangular plate-like crystals of **1** suitable for X-ray diffraction were obtained over 2 days. Yield. 43%, based on Gd. Anal. Calcd. For C<sub>21.5</sub>H<sub>48</sub>Gd<sub>3</sub>Fe<sub>2</sub>N<sub>9</sub>O<sub>26.5</sub> (%): C, 17.93; H, 3.36; N, 8.75. Found: C, 18.26; H, 3.42; N, 9.17. IR (KBr), /cm<sup>-1</sup>: 3416 (s, w), 2868 (m, sh), 1635 (m), 1496 (s, sh), 1382 (m, sh), 1299 (s, sh), 1076 (w, sh), 1028, 928 (m, sh), 816 (m, sh), 739 (m, sh), 621 ~ 485 (w, sh).

### Synthesis of [Dy<sup>III</sup><sub>3</sub>Fe<sup>III</sup><sub>2</sub>( $\mu_5$ -O)L<sub>2</sub>(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)(MeOH)]·0.5MeOH (2).

Complex **2** was synthesized in a procedure analogous to that employed for **1**, except that Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was used in place of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. Yield. 40%, based on Dy. Anal. Calcd. for C<sub>21.5</sub>H<sub>48</sub>Dy<sub>3</sub>Fe<sub>2</sub>N<sub>9</sub>O<sub>26.5</sub> (%): C, 17.74; H, 3.32; N, 8.66. Found: C, 17.92; H, 3.21; N, 9.08. IR (KBr), /cm<sup>-1</sup>: 3414 (s, w), 2877 (m, sh), 1630 (m), 1496 (s, sh), 1382 (m, sh), 1293 (s, sh), 1071 (w, sh), 1033 (w, sh), 926 (m, sh), 817 (m, sh), 742 (m, sh), 622 ~ 481 (w, sh).

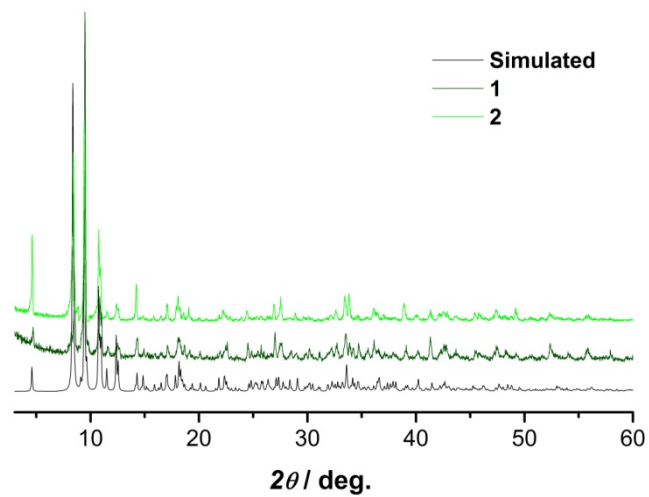
## Crystallographic study:

Diffraction intensity data for single crystals of **1** and **2** were collected at 123(2) K on an Oxford SuperNova diffractometer equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by the full-matrix least-squares method based on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms by using the SHELXS-97<sup>1</sup> and SHELXL-97 programs contained in Olex2.<sup>2</sup> Hydrogen atoms were located geometrically and refined isotropically.

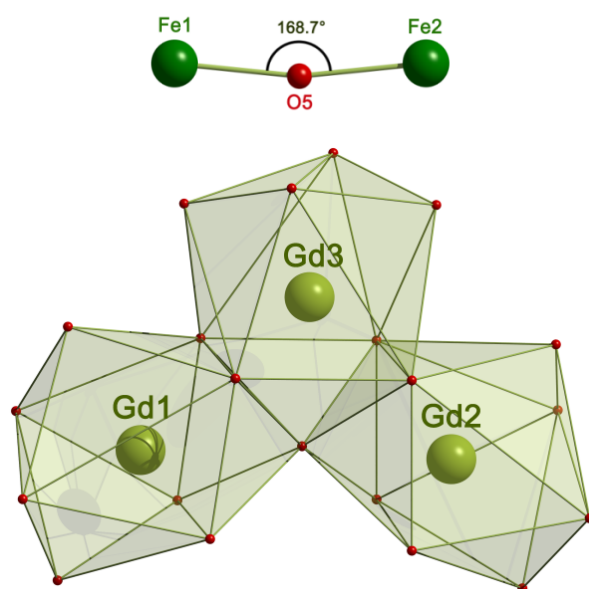
The carbon atoms of one of the ligands (C1-C7, C9-C10, C1'-C7', C9'-C10') are disordered over two positions, as well as the coordinated methanol molecules (O19, C21 and O19', C21') and oxygens from the nitrate anions (O9, O11, O12, O22 and O9', O11', O12', O22') in complexes **1** and **2**. All of the disordered atoms were refined to suitable site occupancies. Therefore restricted instructions were employed in the refinement of the crystal data, such as ISOR, EADP and SADI, in order to constrain the disordered parts. For example, restraints (ISOR) are placed on C1, C3-C5, C10, O22 in **1** and C4', C5, C6, C10, O11, O11', O12, O12', O22' etc. in **2**. EADP are also placed on C1-C2, C4-C7, C9-C10, C21, O19, O22 in **1** and C2-C4, C6, C9-C10 in **2**. Restraints (SADI) are placed on N2-C4 and N2'-C4', N2-C9 and N2'-C9', C9-C10 and C9'-C10' etc. in **1**, N2-C9 and N2-C9', O19-C21 and O19'-C21' etc. in **2** as well. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1. CCDC: 1024368- 1024369 for **1** and **2**, respectively.

**Table S1.** Crystal data and structure refinements for complexes **1** and **2**.

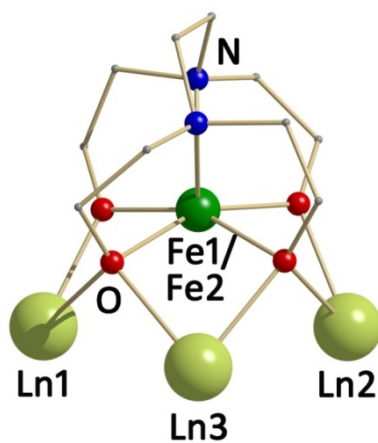
	<b>1</b> (Gd <sub>3</sub> Fe <sub>2</sub> )	<b>2</b> (Dy <sub>3</sub> Fe <sub>2</sub> )
formula	C <sub>21.5</sub> H <sub>48</sub> Gd <sub>3</sub> Fe <sub>2</sub> N <sub>9</sub> O <sub>26.5</sub>	C <sub>21.5</sub> H <sub>48</sub> Dy <sub>3</sub> Fe <sub>2</sub> N <sub>9</sub> O <sub>26.5</sub>
M, g mol <sup>-1</sup>	1440.14	1455.89
cryst syst	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / Å	37.7638(12)	37.7598(17)
<i>b</i> / Å	10.7465(4)	10.7635(3)
<i>c</i> / Å	21.2240(8)	21.2450(6)
$\alpha$ / deg	90.00	90.00
$\beta$ / deg	104.809(4)	104.773(4)
$\gamma$ / deg	90.00	90.00
<i>V</i> / Å <sup>3</sup>	8327.2(6)	8349.4(5)
<i>Z</i>	8	8
reflns collected	16083	30181
unique reflns	7331	7344
<i>R</i> / [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0373	0.0421
<i>wR</i> 2(all data)	0.0770	0.1081



**Fig. S1** Powder X-ray diffraction patterns for **1** and **2**.

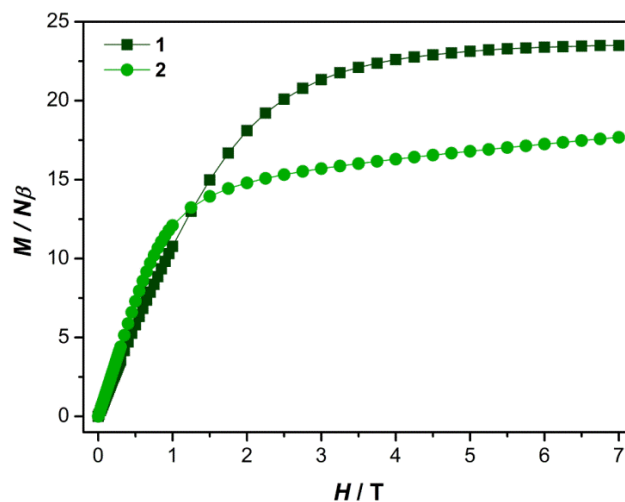


**Fig. S2** The Fe<sub>2</sub> (top) and Gd<sub>3</sub> (bottom) units of complex **1**.

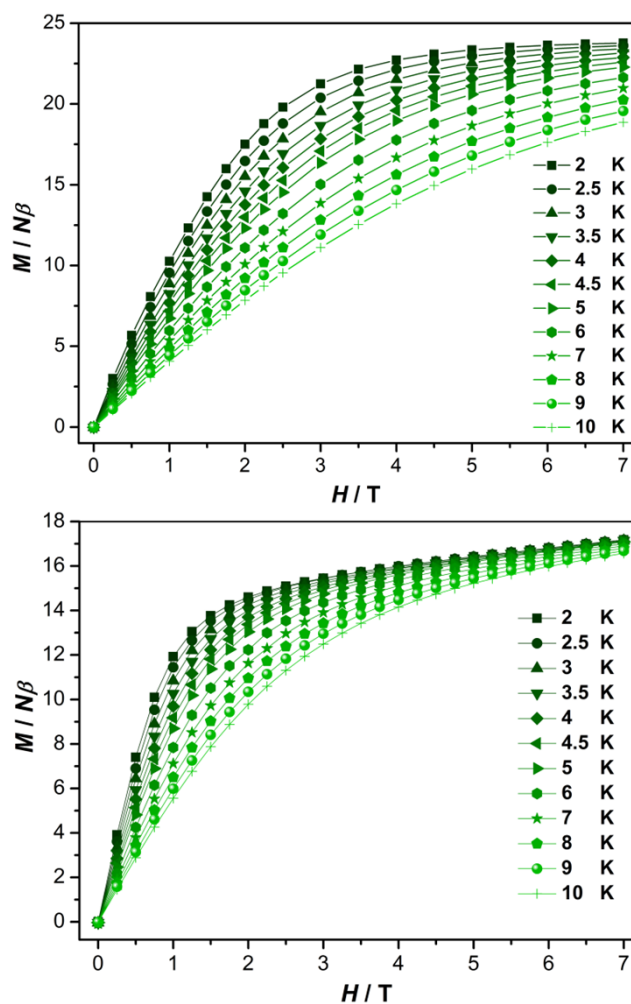


**Scheme S1** Coordination mode of H<sub>4</sub>L in Ln<sub>3</sub>Fe<sub>2</sub>.

## Magnetic Properties:

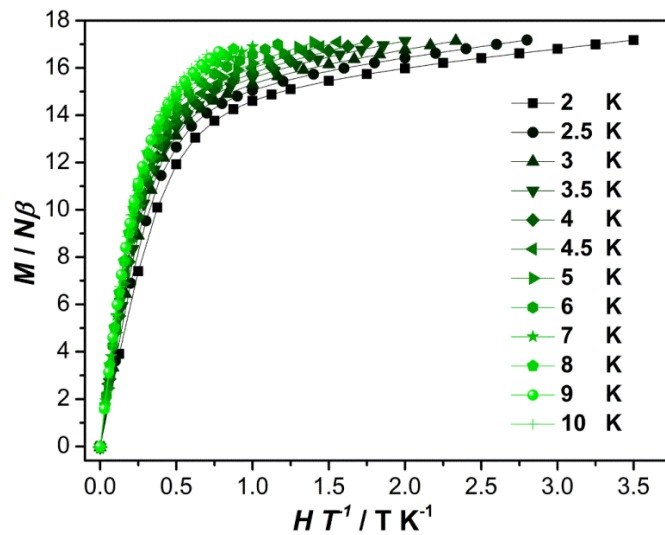


**Fig. S3** Plots of magnetization vs. field for 1 and 2 at 2 K. The lines are guides for the eyes.

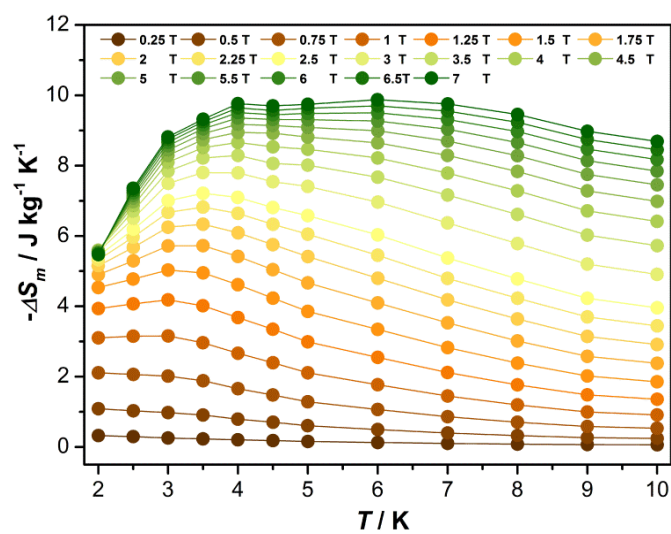


**Fig. S4** The field-dependent magnetization plots at indicated temperatures for 1 (top) and 2 (bottom).

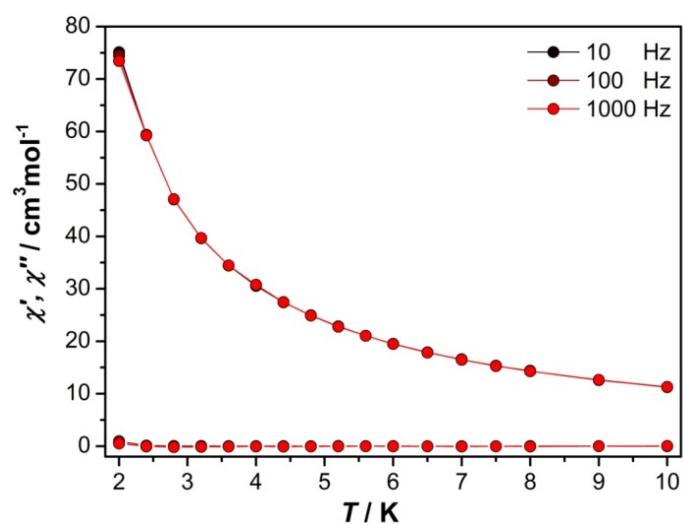
Lines are visual guides.



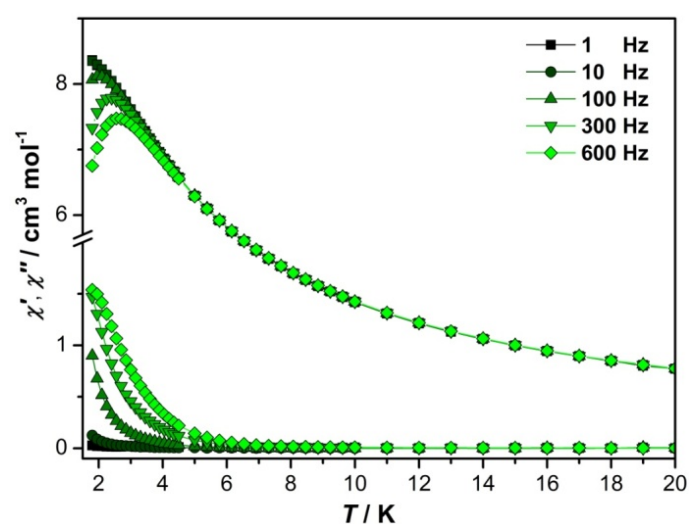
**Fig. S5** Plots of magnetization vs. field for **2** at 2 - 10 K. The lines are guides for the eyes.



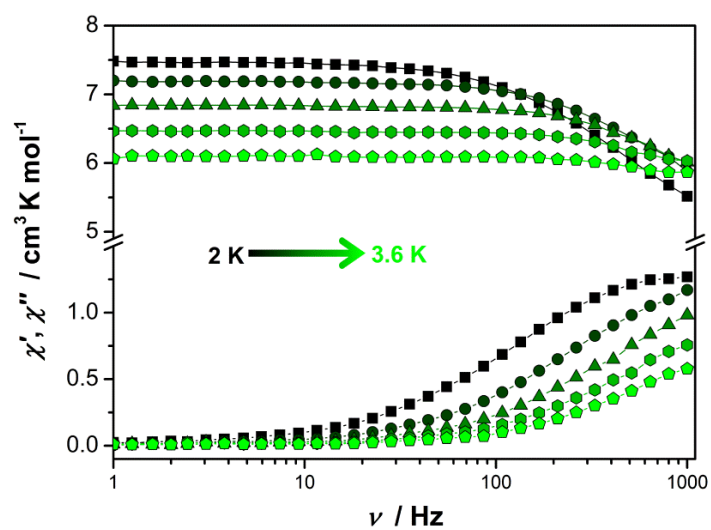
**Fig. S6** Experimental  $-\Delta S_m$  obtained from magnetization data at various temperatures and magnetic field changes for **2**.



**Fig. S7** In-phase and out-of-phase ac susceptibility at various frequencies for **1** under zero dc field.

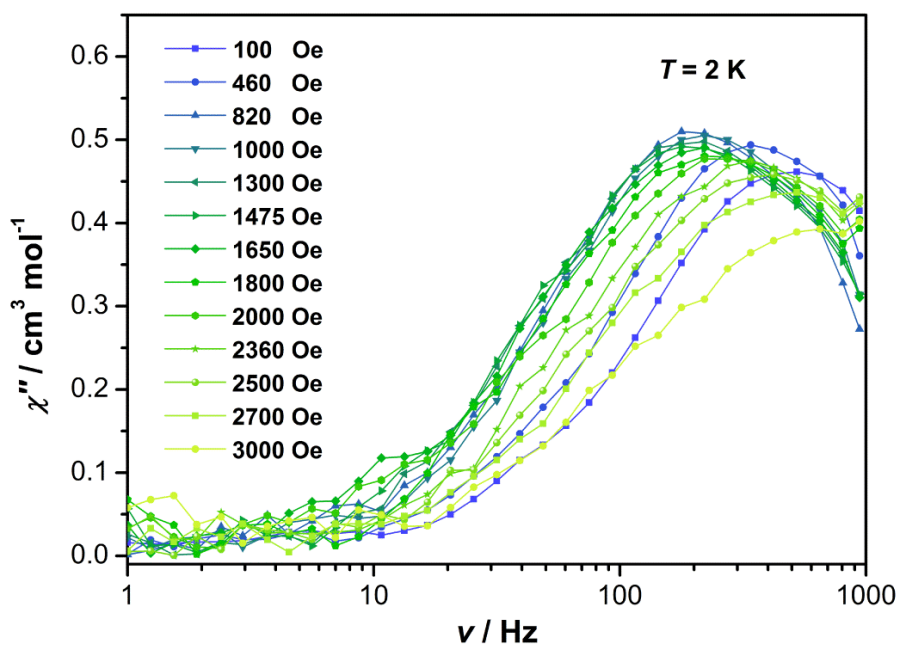
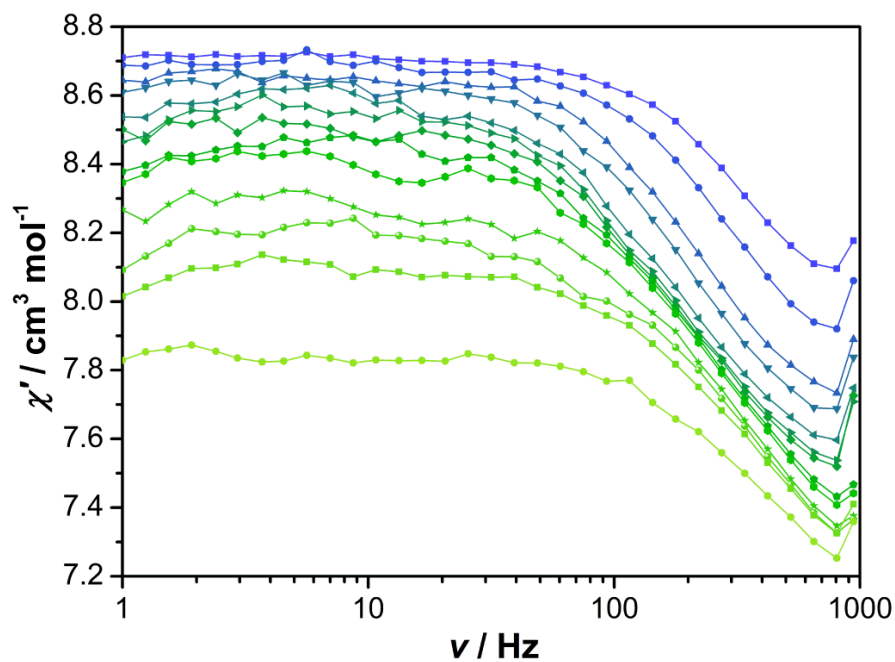


**Fig. S8** In-phase and out-of-phase ac susceptibilities at various frequencies for **2** under zero dc field.

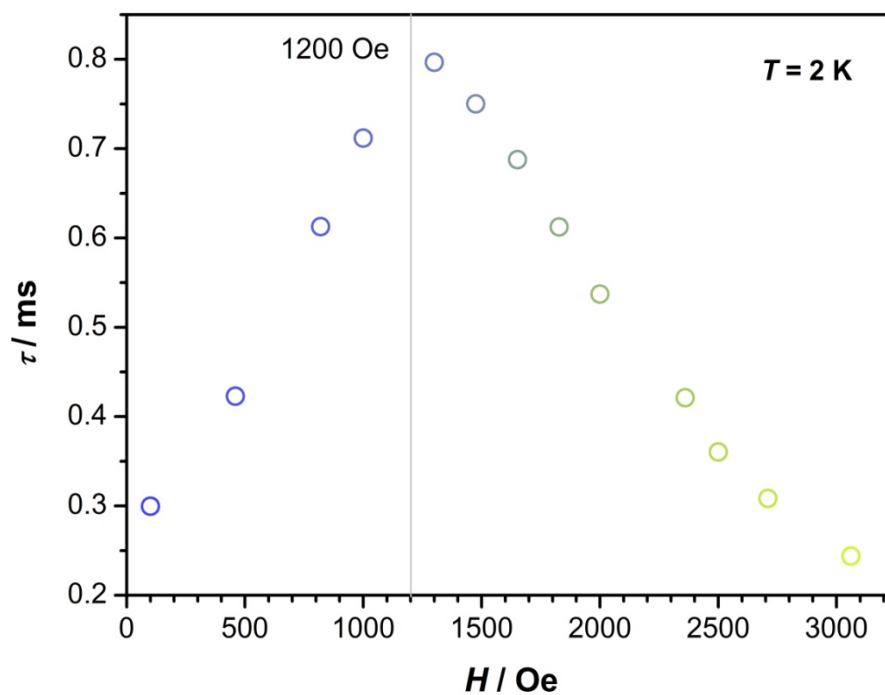


**Fig. S9** In-phase and out-of-phase ac susceptibilities at various temperatures for **2** under zero dc field.

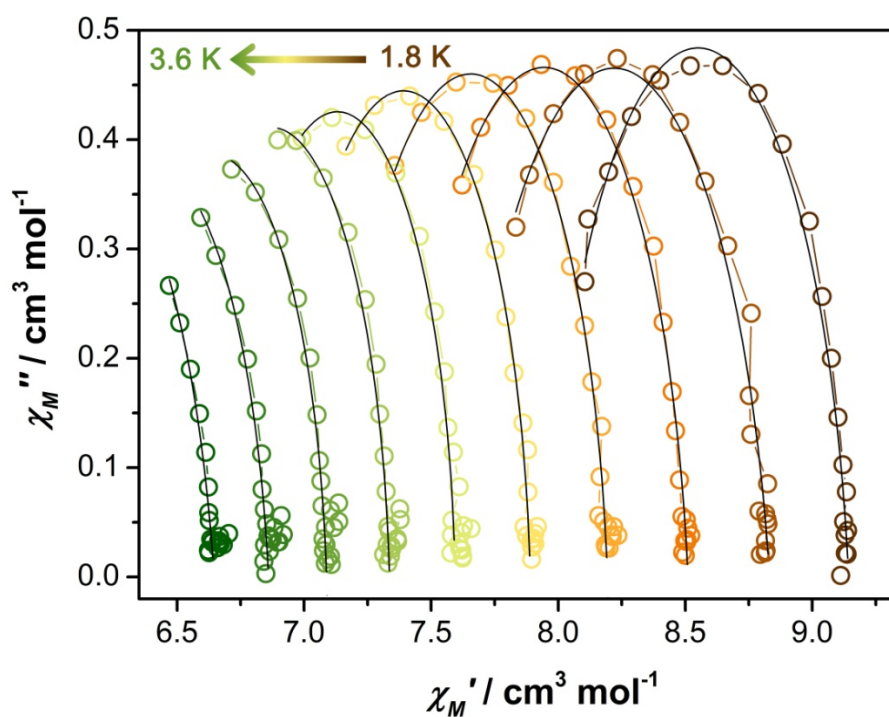




**Fig. S10** Frequency dependence of the in-phase ( $\chi'$ , top) and out-of-phase ( $\chi''$ , bottom) components of the ac magnetic susceptibility for **2** at 2 K at different dc field between 100 and 3000 Oe. The solid lines are guides for the eye.



**Fig. S11** Dc field dependence of the relaxation time for **2** at 2.0 K. The solid line is a guide for the eye.



**Fig. S12** Cole-Cole plots for **2** from 1.8-3.6 K under 1200 Oe. Solid lines represent the best fitting by using Debye function.

**Table S2** Fitting parameters by Debye model (1.8 K to 3.6 K) of **2** under 1200 Oe.

T/K	$\chi_s/\text{cm}^3\text{mol}^{-1}$	$\chi_t/\text{cm}^3\text{mol}^{-1}$	$\alpha_1$
1.80	7.95	9.14	0.1278
2.0	7.61	8.83	0.1719
2.2	7.38	8.51	0.1233
2.4	7.12	8.19	0.0996
2.6	6.89	7.89	0.0730
2.8	6.67	7.59	0.0537
3.0	6.41	7.34	0.0750
3.2	6.21	7.09	0.0851
3.4	6.03	6.87	0.1182
3.6	5.81	6.65	0.1445

## REFERENCES

1. Sheldrick, G. *Acta Crystallogr. A*, **2008**, *64*, 112.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.