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# New strategy to construct single-ion magnets: a unique Dy@$Zn_6$ cluster exhibiting slow magnetic relaxation

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## Experimental Section:

**Materials.** All of reagents are from Tianjin Guangfu Fine chemical research institute. All were used without further purification.

**Measurement techniques.** The FT-IR spectra were measured with a Bruker Tensor 27 Spectrophotometer on KBr disks. The elemental analyses (C, H and N) were carried out applying a Perkin-Elmer 240C elemental analyzer; Powder X-ray diffraction was carried on the Rigaku Ultima IV multipurpose X-ray diffraction system. The magnetic properties were measured on a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Diamagnetic correction was made with Pascal's constants for all the constituent atoms.

### Synthesize, Elemental analysis and FT-IR of 1 and 2

A mixture of 1 mmol glycine, 1 mmol isobutyric lithium and 1mmol lithium hydroxide was dissolved in 2 mL deionized water under stirring, and then the mixture solution of 5 mL methanol and 10 mL acetonitrile was added to the above clarified liquor. 1 mmol $Zn(NO_3)_2{\cdot}6H_2O$ and 0.2 mmol $Ln(NO_3)_3{\cdot}6H_2O$ (Ln=Dy(**1**), Er(**2**)) was added to the above mixture solution one after another, respectively. After stirring about 2 hours, the solution was filtered and the filtrate was placed into a desiccator with phosphorus pentaoxide. After one day, colorless polyhedral crystals were collected with a yield of about 50% for **1** and 53% for **2** (based on the $Ln(NO_3)_3$).

Anal. Calcd. for $C_{12}H_{54}DyN_{11}O_{45}Zn_6$ (%): C 8.86, H 3.34, N 9.47. Found: C 8.79, H 3.30, N 9.42; for $C_{12}H_{54}ErN_{11}O_{45}Zn_6$ (%): C 8.83, H 3.33, N 9.44. Found: C 8.78, H 3.29, N 9.45. IR (KBr disk, υ $cm^{-1}$): for **1**: 3416(br), 3144(br), 1617(s), 1440(s), 1112(m), 1053(m), 858(m), 725(w), 545(m); For 2, 3425(br), 3150(br), 1612(s), 1438(s), 1105(m), 1050(m), 853(m), 721(w), 542(m). For **1**, Weak adsorption peak of 725 $cm^{-1}$ originates from plane swing vibration of $-CH_2$. Strong peaks of 1400 and 1617 $cm^{-1}$ can be referred to asymmetric stretching vibration absorption of $NO_3^-$ anions and carboxyl groups, respectively. Wide and strong adsorption peaks of 3144 and 3416 $cm^{-1}$ can be labeled as the stretching vibration of O-H...O and N-H

**Crystallographic Study**

Crystallographic data of **1** and **2** were collected on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) using the ω - φ scan technique. The data integration and empirical absorption corrections were carried out by SAINT programs.[1] The structures were solved by direct methods (SHELXS 97).[1] All the non-hydrogen atoms were refined anisotropically on $F^2$ by full-matrix least-squares techniques (SHELXL 97).[1] Details of the crystal parameters, data collection, and refinements for **1** and **2** are summarized in TableS1. CCDC: 948391 (**1**) and 949715 (**2**) contain 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.

Table S1. Crystallographic data and structure refinement for complex **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{12}H_{54}DyN_{11}O_{45}Zn_6$ | $C_{12}H_{54}ErN_{11}O_{45}Zn_6$ |
| Formula weight | 1627.38 | 1632.15 |
| Temperature/K | 123(2) | 122.10(10) |
| Crystal system | hexagonal | hexagonal |
| Space group | $P6_3/m$ | $P6_3/m$ |
| a/Å | 14.5144(4) | 14.4193(6) |
| b/Å | 14.5144(4) | 14.4193(6) |
| c/Å | 15.2404(6) | 15.0388(7) |

| | | |
|---|---|---|
| α/° | 90.00 | 90.00 |
| β/° | 90.00 | 90.00 |
| γ/° | 120.00 | 120.00 |
| Volume/Å$^3$ | 2780.51(15) | 2707.9(2) |
| Z | 2 | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.944 | 2.002 |
| F(000) | 1618.0 | 1622.0 |
| Crystal size/mm$^3$ | 0.4 × 0.2 × 0.2 | 0.4 × 0.2 × 0.2 |
| 2θ range for data collection | 7.02 to 50.02° | 6.26 to 49.96° |
| Index ranges | $-16 \le h \le 12$, $-16 \le k \le 17$, $-10 \le l \le 18$ | $-3 \le h \le 15$, $-17 \le k \le 13$, $-17 \le l \le 14$ |
| Reflections collected | 5702 | 5311 |
| Independent reflections | 1684[R(int) = 0.0310] | 1620[R(int) = 0.0405] |
| Data/restraints/parameters | 1684/12/129 | 1620/0/129 |
| Goodness-of-fit on F$^2$ | 1.085 | 1.061 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0305, wR$_2$ = 0.0813 | R$_1$ = 0.0377, wR$_2$ = 0.0919 |
| Final R indexes [all data] | R1 = 0.0347, wR$_2$ = 0.0842 | R$_1$ = 0.0434, wR$_2$ = 0.0961 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.22/-0.70 | 1.61/-0.80 |

Table S2 Bond lengths for **1** and **2** (Å).

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Dy1 | Zn1$^1$ | 3.5644(5) | Zn1 | O6 | 2.059(3) |
| Dy1 | Zn1$^2$ | 3.5644(5) | Zn1 | N1 | 2.043(4) |
| Dy1 | Zn1$^3$ | 3.5644(5) | O1 | Zn1$^4$ | 2.0122(19) |
| Dy1 | O1 | 2.450(4) | O4 | Zn1$^4$ | 2.425(3) |
| Dy1 | O1$^3$ | 2.450(4) | O4 | N2 | 1.267(8) |
| Dy1 | O1$^1$ | 2.450(4) | O5 | N2 | 1.227(6) |
| Dy1 | O2$^4$ | 2.428(3) | O2 | C1 | 1.264(5) |
| Dy1 | O2 | 2.428(3) | O3 | Zn1$^3$ | 2.084(3) |
| Dy1 | O2$^5$ | 2.428(3) | O3 | C1 | 1.250(5) |
| Dy1 | O2$^1$ | 2.428(3) | N2 | O5$^4$ | 1.227(6) |
| Dy1 | O2$^3$ | 2.428(3) | N1 | C2 | 1.443(6) |
| Dy1 | O2$^2$ | 2.428(3) | C2 | C1 | 1.509(6) |
| Zn1 | O1 | 2.0122(19) | O7 | N3 | 1.210(4) |
| Zn1 | O4 | 2.425(3) | N3 | O7$^6$ | 1.210(4) |
| Zn1 | O2 | 2.161(3) | N3 | O7$^7$ | 1.210(4) |
| Zn1 | O3$^5$ | 2.084(3) | | | |
| **2** | | | | | |
| Er1 | Zn1$^1$ | 3.5547(6) | Zn1 | O4 | 2.425(4) |
| Er1 | Zn1$^2$ | 3.5547(6) | Zn1 | N1 | 2.048(4) |
| Er1 | Zn1$^3$ | 3.5547(6) | O3 | Zn1$^3$ | 2.012(2) |

| | | | | | |
|---|---|---|---|---|---|
| Er1 | O3$^{4}$ | 2.421(4) | O3 | Zn1$^{2}$ | 2.012(2) |
| Er1 | O3 | 2.421(4) | O1 | C2 | 1.271(6) |
| Er1 | O3$^{2}$ | 2.421(4) | O2 | C2$^{1}$ | 1.242(6) |
| Er1 | O1$^{4}$ | 2.411(3) | O4 | Zn1$^{5}$ | 2.425(4) |
| Er1 | O1$^{5}$ | 2.411(3) | O4 | N2 | 1.294(9) |
| Er1 | O1 | 2.411(3) | N3 | O7$^{6}$ | 1.231(5) |
| Er1 | O1$^{3}$ | 2.411(3) | N3 | O7$^{7}$ | 1.231(5) |
| Er1 | O1$^{2}$ | 2.411(3) | N3 | O7 | 1.231(5) |
| Er1 | O1$^{1}$ | 2.411(3) | C2 | O2$^{2}$ | 1.242(6) |
| Zn1 | O3$^{4}$ | 2.012(2) | C2 | C1 | 1.512(7) |
| Zn1 | O1 | 2.159(3) | N1 | C1 | 1.430(7) |
| Zn1 | O2 | 2.072(3) | N2 | O5$^{5}$ | 1.202(7) |
| Zn1 | O6 | 2.043(4) | N2 | O5 | 1.202(7) |

Symmetry operation code: For **1**, $^{1}$1+Y-X,1-X,1/2-Z; $^{2}$1-Y,+X-Y,1/2-Z; $^{3}$1-Y,+X-Y,+Z; $^{4}$X,+Y,1/2-Z; $^{5}$1+Y-X,1-X,+Z; $^{6}$Y-X,1-X,+Z; $^{7}$1-Y,1+X-Y,+Z.; For **2**, $^{1}$+Y-X,1-X,+Z; $^{2}$1-Y,1+X-Y,+Z; $^{3}$1-Y,1+X-Y,3/2-Z; $^{4}$+Y-X,1-X,3/2-Z; $^{5}$+X,+Y,3/2-Z; $^{6}$1+Y-X,1-X,+Z; $^{7}$1-Y,+X-Y,+Z.

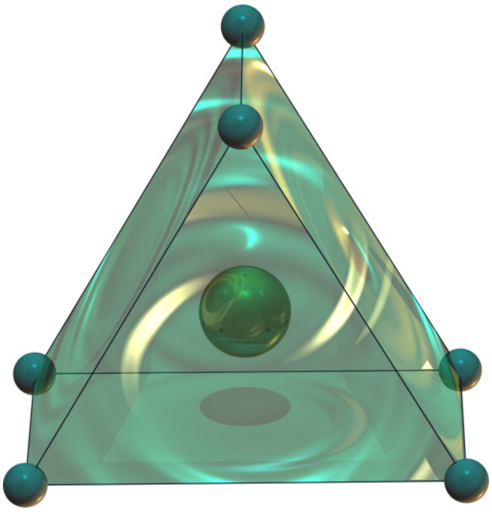

Fig.S1 The triangular prism constructed by six Zn cations as apexes and Dy(III) locate in the center.

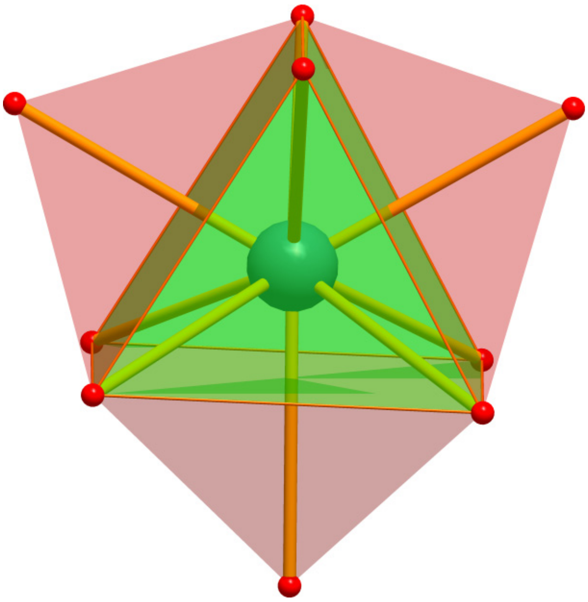

Fig.S2 The coordination environment of Dy(III).

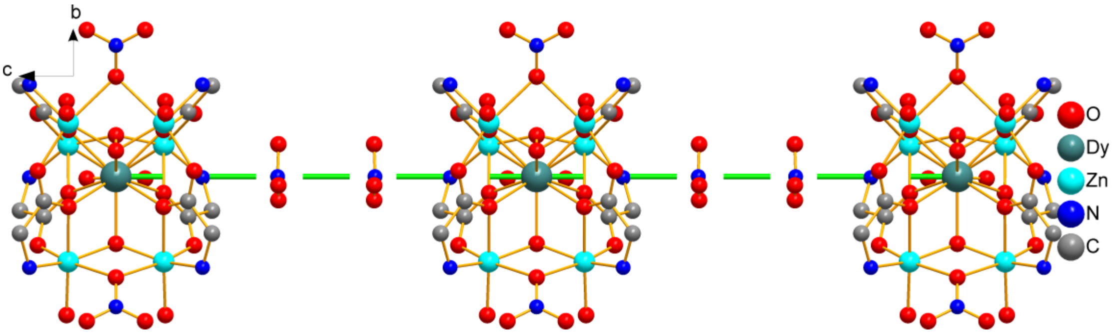

Fig.S3 The sites of uncoordinated nitrate groups.

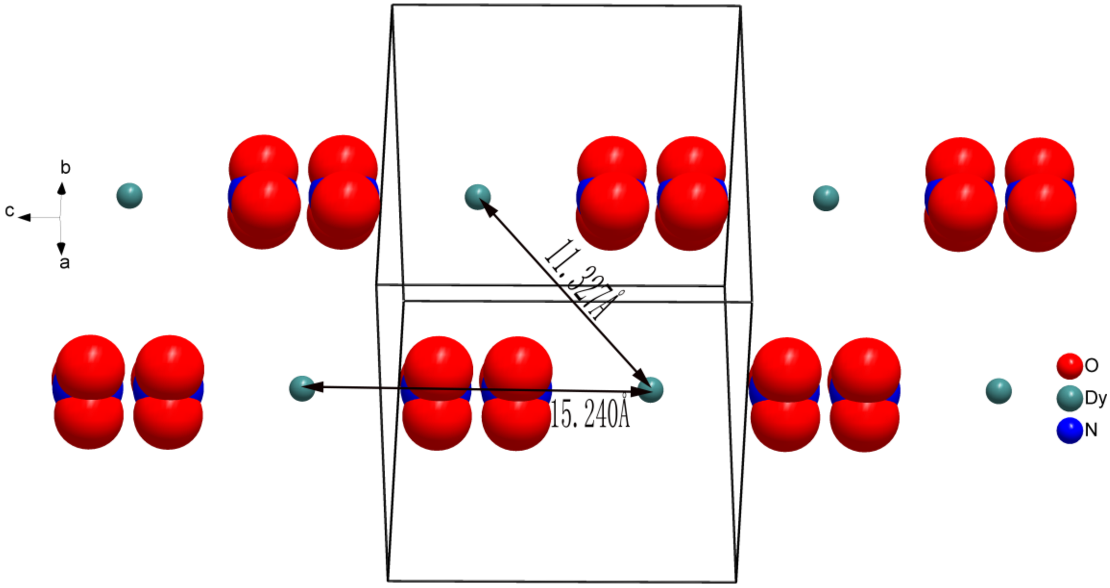

Fig.S4 The sites of uncoordinated nitrate groups and $Dy^{3+}$ cations and the distances of adjacent $Dy^{3+}$ cations .

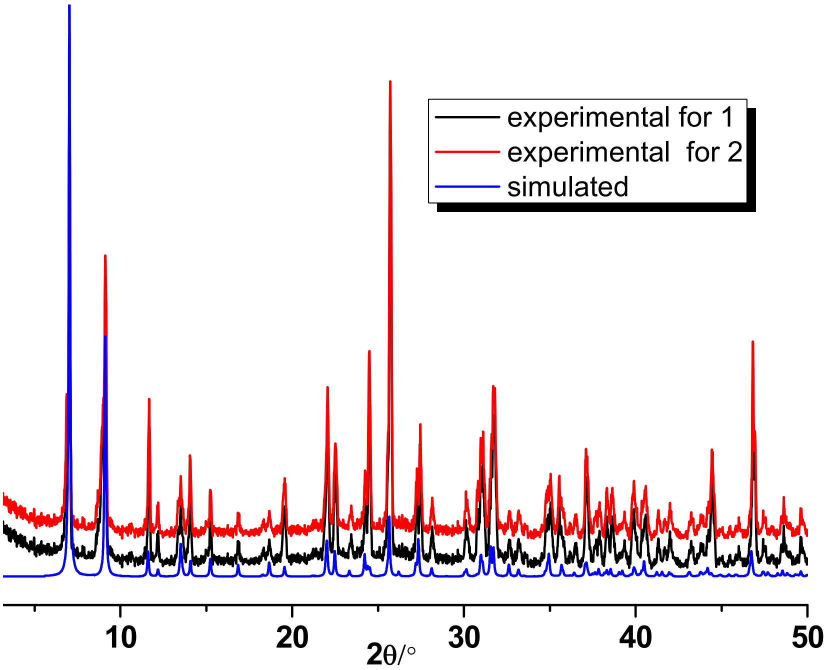

Fig. S5 PXRD pattern and the simulated spectrogram of **1** and **2**.

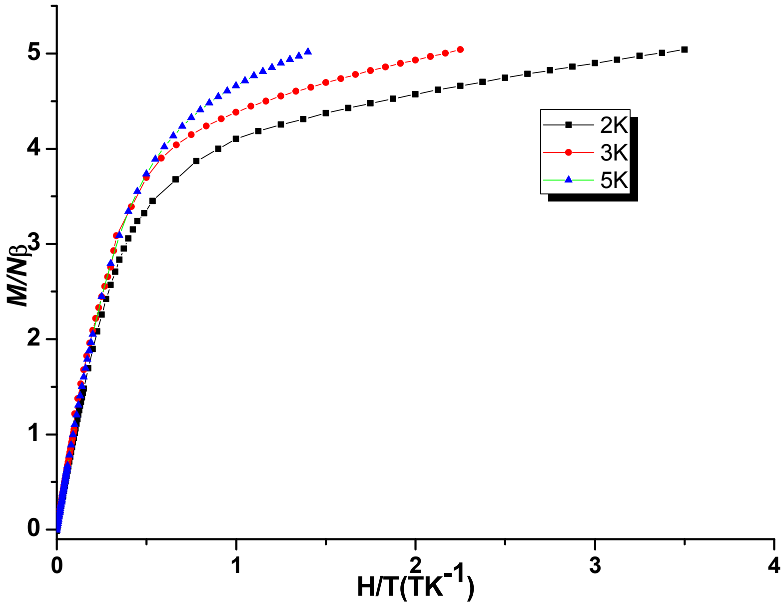

Fig.S6 Field dependence of the magnetization drawn as *M* vs *H*/*T* plots for **2** under the temperature of 2, 3 and 5 K.

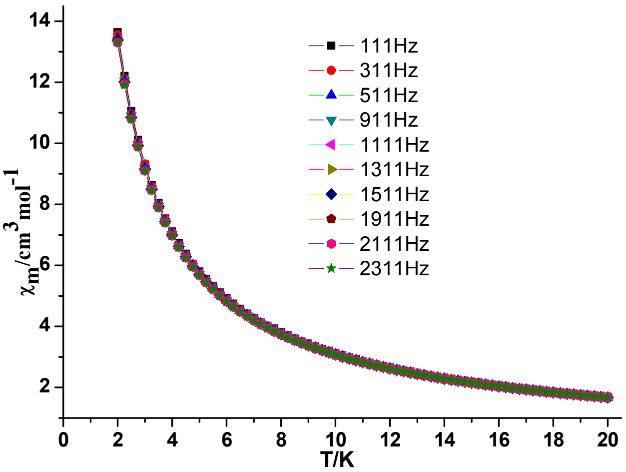

Fig.S7 Temperature dependence of in-phase (χ′) ac susceptibility components at different frequencies for **1** with zero dc field and an oscillation of 3 Oe.

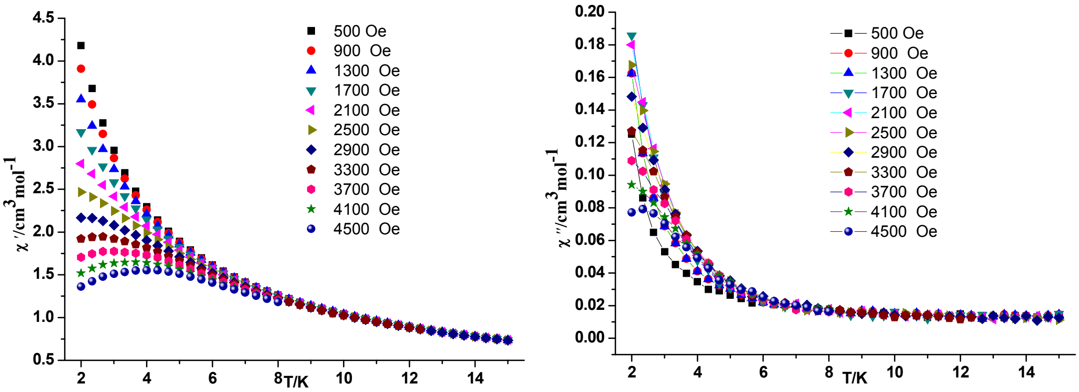

Fig.S8 Temperature dependence of in-phase (χ′) (Left) and the out-of-phase (χ″) (Right) ac susceptibility components for **1** measured at 500 Hz with different dc fields and an oscillation of 3 Oe.

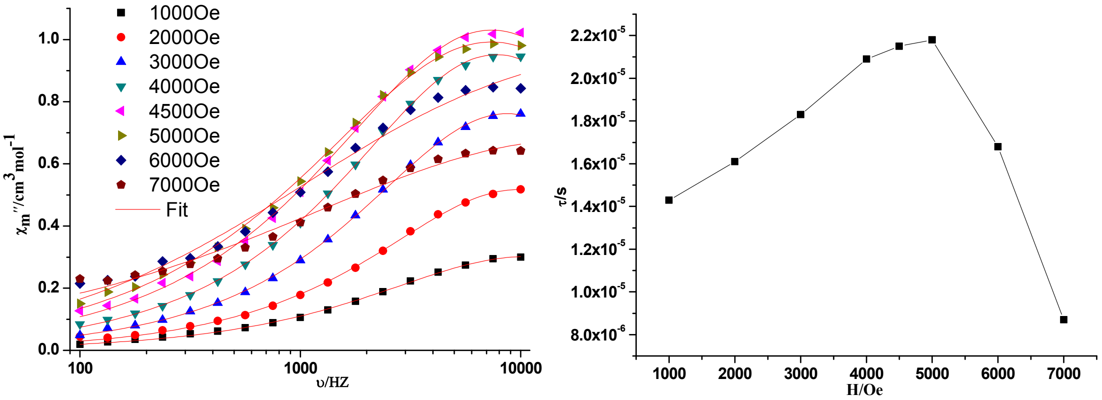

Fig.S9 Left: Frequency dependence of the out-of-phase (χ″) ac susceptibility components for **1** measured at 2.5 K with several dc fields and an oscillation of 3 Oe. Right: Field dependence of the relaxation time from χ″ vs υ data fitted to eqn 1.

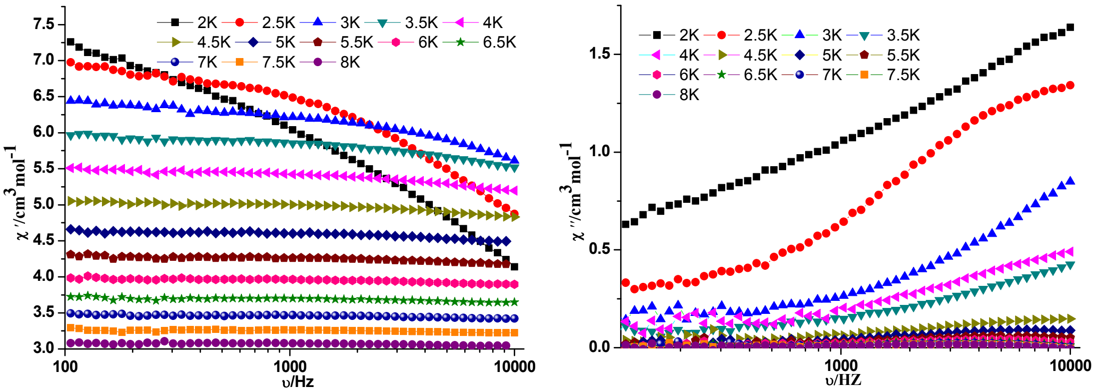

Fig.S10 Frequency dependence of in-phase (χ′) (Left) and the out-of-phase (χ″) (Right) ac susceptibility components for **1** measured in a static field of 5000 Oe and in the frequency range from 100 to 10000 Hz and oscillation of 3 Oe.

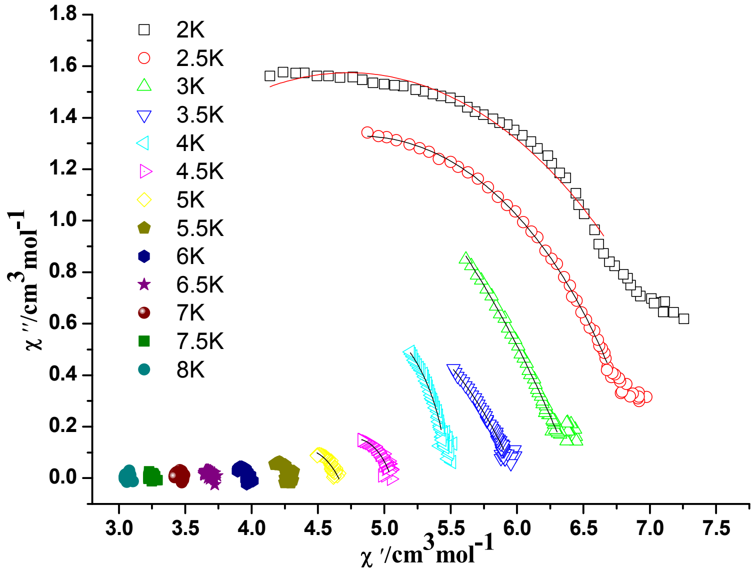

Fig. S11 Cole-Cole diagram extracted by plotting χ′ vs χ″ and fitted by an extended Debye model for the temperature in the 2-4.5 K ranges.

Table S2 The α values obtained from Cole-Cole plots of **1** using the Debye model.

| *T*(K) | α | *T*(K) | α |
|---|---|---|---|
| 2 | 0.34 | 3.5 | 0.36 |
| 2.5 | 0.29 | 4 | 0.35 |
| 3 | 0.38 | 4.5 | 0.34 |

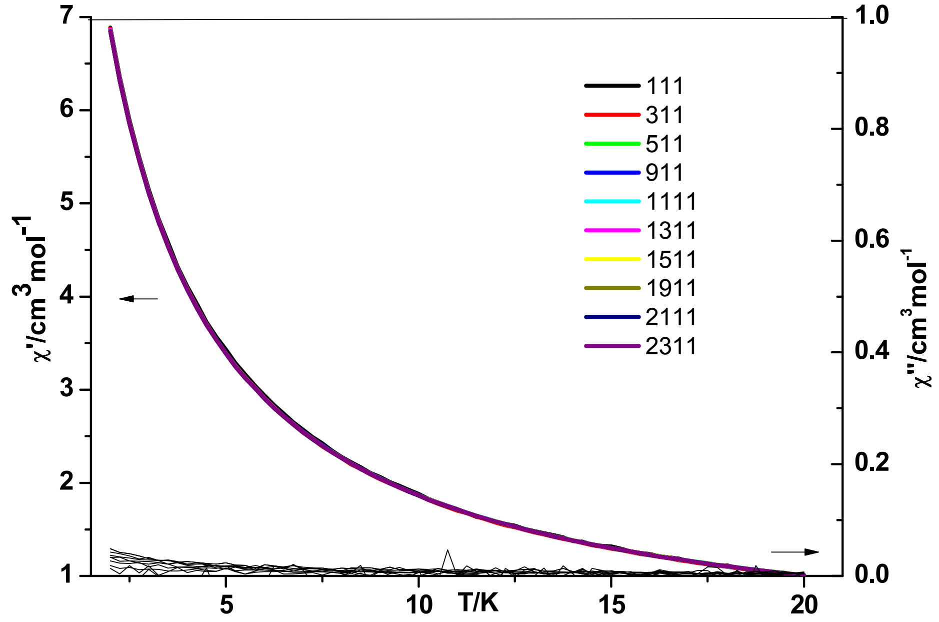

Fig.S12 Temperature dependence of in-phase (χ′) and the out-of-phase (χ″) ac susceptibility components at different frequencies for **2** with zero dc field and an oscillation of 3 Oe.

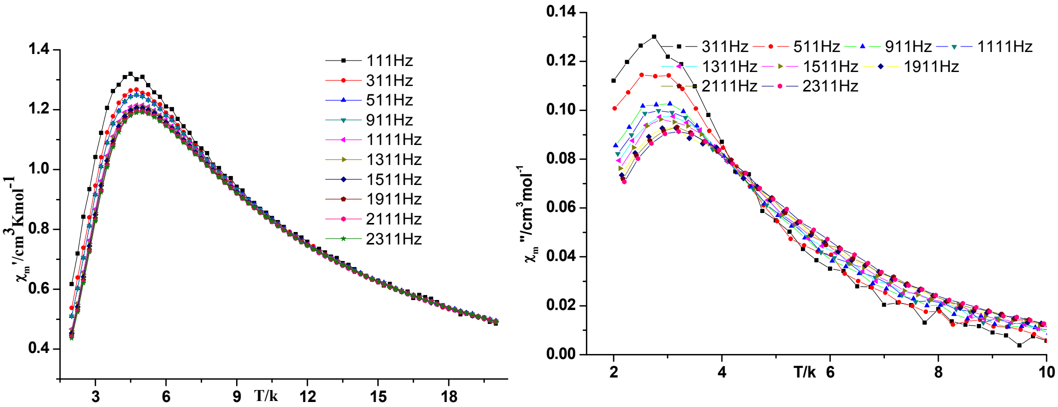

Fig.S13 Temperature dependence of in-phase (χ′) (Left) and the out-of-phase (χ″) (Right) of the ac susceptibility components at different frequencies for **1** under 5000 Oe dc field and an oscillation of 3 Oe.

$$\chi''(\omega) = \frac{(\chi_T - \chi_S)(\omega\tau)^{1-\alpha}\cos\frac{1}{2}\alpha\pi}{1 + 2(\omega\tau)^{1-\alpha}\sin\frac{1}{2}\alpha\pi + (\omega\tau)^{2(1-\alpha)}} \qquad \text{eqn } 1^{[2,3]}$$

$\chi_T$ is the isothermal susceptibility χ (ω→0)

$\chi_S$ is the adiabatic susceptibility χ (ω→∞)

ω=2πυ is angular frequency

τ is relaxation time

α is a measure of the distribution of relaxation

## References

[1] G. M. Sheldrick, *Acta Cryst.*, **2008**. *A64*, 112-122.

[2] R. J. Blagg, F. Tuna, E. J. L. McInnes and R. E. P. Winpenny, *Chem. Commun.*, **2011**, *47,* 10587-10589

[3] S.M. J. Aubin, Z. Sun, L.Pardi, J. Krzystek, K. Folting, L. C. Brunel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Inorg. Chem.* **1999**, 38, 5329-5340