

Supporting Information

Chirality detection of two enantiomeric 3D lanthanide coordination polymers by vibrational circular dichroism spectra

Xiu-Ying Zheng, Han Zhang, Ling-Yun Cao, Xiang-Jian Kong,* La-Sheng Long* and Lan-Sun Zheng

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China.

General Considerations. Caution! Perchlorates are potentially explosive. Only a small amount should be used and handled with great care. All reagents were of commercial origin and were used as received. Aqueous solutions of dysprosium perchlorates were prepared by digesting dysprosium oxides in concentrated perchloric acid. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyser. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curve was prepared on a SDT Q600 Thermal Analyzer. The VCD was measured on a Chiral IR-2X Bio Tools with pressed KBr pellets with the mass ratio of crystal to KBr 1:100. The CD was measured on Jasco J-810 with KCl pellets with mass ratio of crystal to KCl 1:100. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Preparation of aqueous solutions of $\text{Ln}(\text{ClO}_4)_3$ (1.0 mol L^{-1}). Dysprosium oxide (0.125 mol, 46.62 g) was dissolved by slowly adding perchloric acid aqueous solution (70.0% - 72.0%, 64.0 ml) at about 80 °C. Aqueous solution of $\text{Dy}(\text{ClO}_4)_3$ (1.0 mol L^{-1}) was obtained by diluting the concentrated solution to 250.00 ml with deionized water.

Synthesis of $\{[\text{Dy}_5(\text{L})_4(\text{H}_2\text{O})_{10}][\text{Dy}(\text{H}_2\text{O})_7][\text{Na}(\text{H}_2\text{O})_5]\} \cdot (\text{ClO}_4)_7 \cdot (\text{H}_2\text{O})_{15}$ (1a** and **1b**).** N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (H_3L , 0.278g, 1mmol) and $\text{Dy}(\text{ClO}_4)_3$ (2ml, 2.0mmol) was added to a mixture of 10ml deionized water. The resulting solution was heated to about 80 °C and a freshly prepared NaOH solution (aq. 1.0 M) was added dropwise to the point of incipient but permanent precipitation. The mixture than brought to and maintained under reflux for 1 hours. The resulting mixture was filtered while hot. Colourless crystals of **1a** and **1b** (yield 50% based on Dy) were obtained in the same solution under ambient conditions after one month. Anal. Calcd. For $\{[\text{Dy}_5(\text{L})_4(\text{H}_2\text{O})_{10}][\text{Dy}(\text{H}_2\text{O})_7][\text{Na}(\text{H}_2\text{O})_5]\} \cdot (\text{ClO}_4)_7 \cdot (\text{H}_2\text{O})_{15}$ (FW = 3353.55, based on 15 crystallization water molecules): C, 14.33; H, 3.67; N,3.34. Found: C: 14.36; H, 3.51; N: 3.30. IR(KBr, cm^{-1}): 2920(s), 1582(s), 1573(s), 1455(m), 1135(s), 1417(s), 824 (s).

Measurements of the solid VCD. We picked a single crystal from a solution containing mixed 1a and 1b crystals, collected the data and determined the space group using single crystal X-ray structure determination. Then the same single crystal for X-ray were pressed one pellet with KBr about the proportion of 1:200, and the pellet were measured on a Chiral IR-2X Bio Tools to obtain the VCD signal. The same methods were performed to obtain another chiral crystal and the distinct VCD signals. So the crystal for VCD is same crystal for x-ray. Notably, the process to choose another chiral crystal may have a certain probability because it is likely to pick up the same chiral crystal to test repeated. Scan three times of VCD measurement and average those data to obtain the VCD spectra. A blank experiment with pure KBr as background was performed. The background data need to deduct when processing the VCD data.

Single crystal X-ray structure determination: Data of compounds **1a** and **1b** were collected on an Oxford Gemini S Ultra CCD area detector with monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 123 K. Absorption corrections were applied by using the multi-scan program CrysAlis Red. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the

SHELXTL–2013 program. The hydrogen atoms of the organic ligand were generated geometrically (C–H, 0.96 Å). Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1. Selected bond are showed in Table S2 and Table S3. CCDC contains the supplementary crystallographic data for this paper with a deposition number of nos. 1029797 for **1a** and 1029798 for **1b**, respectively. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

According to the charge balance, there are 2 ClO₄⁻ counter anions per formula units. Based on the EA and TGA analysis, there are 15 guest water molecules per formula units. However, they are however severely disordered and were therefore removed by SQUEEZE in structural refinement. The SQUEEZE analysis estimate the electron count to be 3396 within 19941 Å³ void per formula unit for **1a**, and 3375 electron counts within 19345 Å³ void per formula unit for **1b**. According to the electron counts and the void per formula unit, the number of guest water is 18, which is consistent with the number calculated from EA and TGA results.

Table S1 Crystal data and details of data collection and refinement for **1a** and **1b**

Compound	Compound 1a	Compound 1b
Formula	C ₄₀ H ₁₂₂ Cl ₇ Dy ₆ N ₈ NaO ₈₇	C ₄₀ H ₁₂₂ Cl ₇ Dy ₆ N ₈ NaO ₈₇
<i>Mr</i>	3353.59	3353.59
Crystal system	Cubic	Cubic
Space group	<i>P4₁32</i>	<i>P4₃32</i>
<i>a</i> /Å	35.491(4)	35.3561(3)
<i>b</i> /Å	35.491(4)	35.3561(3)
<i>c</i> /Å	35.491(4)	35.3561(3)
<i>V</i> /Å ³	44706(8)	44197.0(6)
<i>Z</i>	12	12
ρ_{calc} [g/cm ³]	1.495	1.512
μ (Mo K α)/mm ⁻¹	3.188	3.225
F(000)	19680	19680
θ /°	3.29 – 25.00	3.31 – 25.00
Observed reflections	325513	43807
Independent reflections	13128	12951
Data/parameters	13128/628	12949 /628
GOF	1.088	1.039
R_1 [$I > 2\sigma(I)$] ^a	0.0600	0.0754
wR_2 (All data) ^b	0.1747	0.2119

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ^b $wR_2 = \{ \sum [w (F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

Table S2 Selected bonds for **1a**.

Dy1-N1	2.609(9)	Dy2-N3	2.629(8)
Dy1-N2	2.618(12)	Dy2-N4	2.668(8)
Dy1-O1	2.286(8)	Dy2-O6	2.357(6)
Dy1-O3	2.318(8)	Dy2-O8	2.358(6)
Dy1-O5	2.387(7)	Dy2-O10	2.394(6)
Dy1-O7	2.366(7)	Dy2-O12	2.459(7)
Dy1-O12 ¹	2.717(7)	Dy2-O3W	2.406(9)
Dy1-O13 ¹	2.430(8)	Dy3-O9	2.270(6)
Dy1-O1W	2.418(9)	Dy3-O11	2.305(6)
Dy2-O14	2.429(8)	Dy3-O4W	2.426(7)
Dy2-O2W	2.471(7)	Dy3-O5W	2.420(6)

Symmetry transformations used to generate equivalent atoms: #1 $y+1/4, -x+5/4, z-1/4$

Table S3 Selected bonds for **1b**.

Dy1-O1	2.284(10)	Dy2-O14	2.439(9)
Dy1-O3	2.338(11)	Dy2-N3	2.659(11)
Dy1-O5	2.394(10)	Dy2-N4	2.680(10)
Dy1-O7	2.359(8)	Dy2-O2W	2.418(10)
Dy1-O12 ¹	2.716(10)	Dy2-O3W	2.485(9)
Dy1-O13 ¹	2.423(10)	Dy2-O12	2.456(10)
Dy1-N1	2.625(14)	Dy2-O10	2.327(8)
Dy1-N2	2.643(11)	Dy3-O4W	2.460(10)
Dy1-O1W	2.435(11)	Dy3-O5W	2.409(9)
Dy2-O6	2.357(8)	Dy3-O11	2.274(9)
Dy2-O8	2.394(9)	Dy3-O9	2.294(8)

Symmetry transformations used to generate equivalent atoms: #1 $x+1/4, z+3/4, -y+3/4$

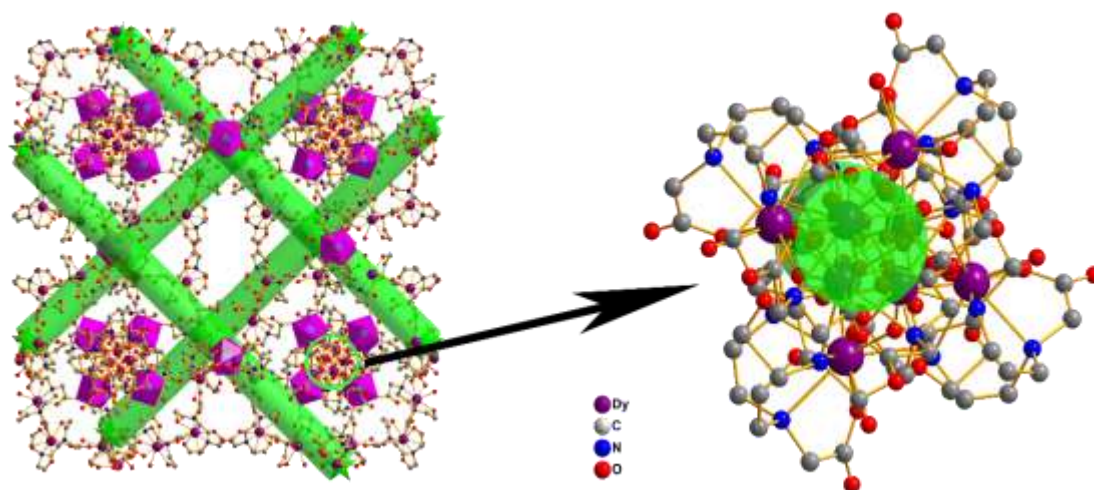


Figure S1 The 3D structure of compound 1 and the 1D chiral chain.

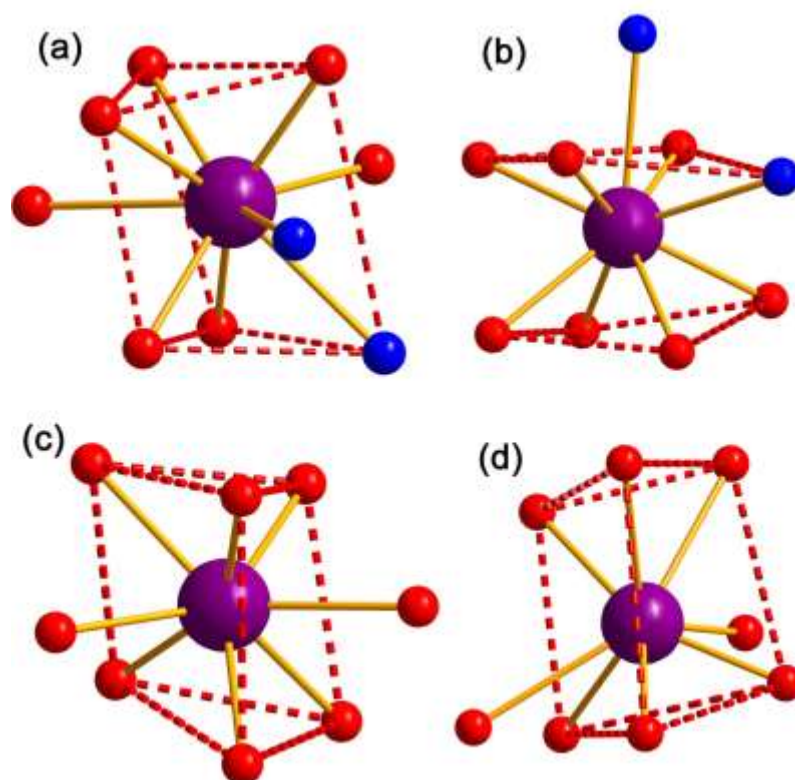


Figure S2 Ball and stick view of the coordination geometry of Dy1(a), Dy2(b), Dy3(c) and Dy4(d).

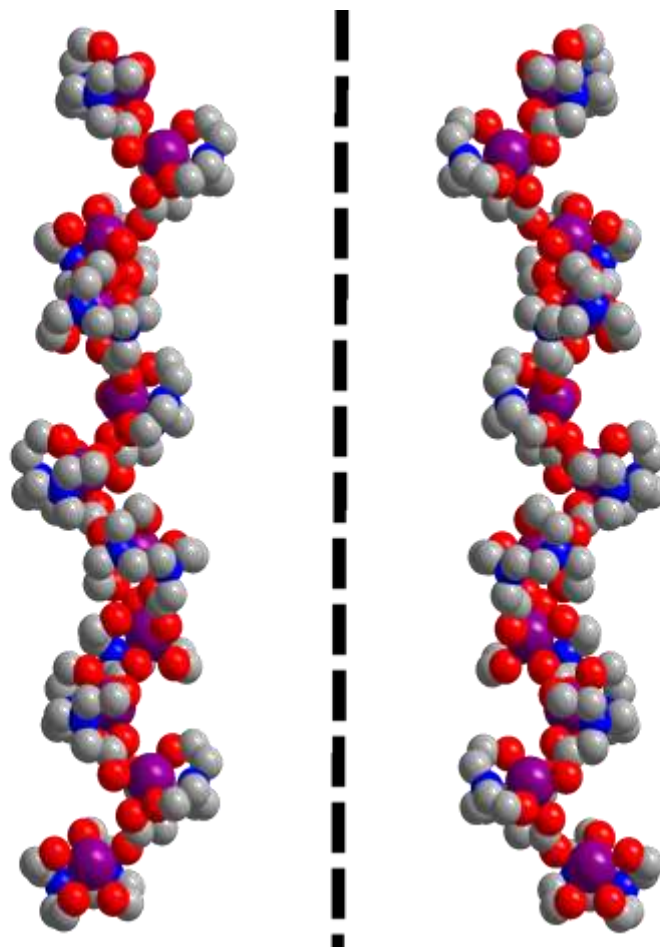


Figure S3 The spacefill view of chiral chains in compounds **1a** and **1b**.

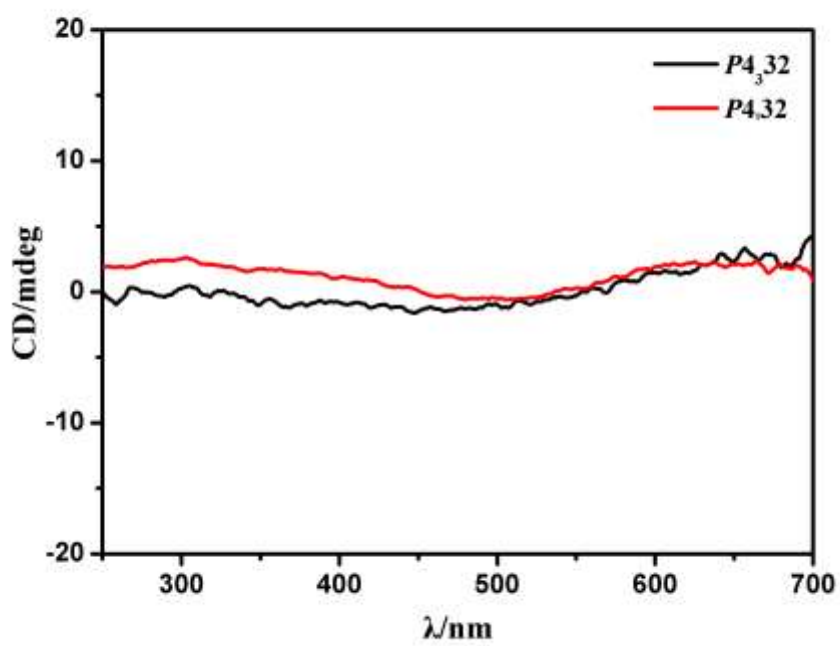


Figure S4 The ECD spectra of compounds **1a** and **1b**.

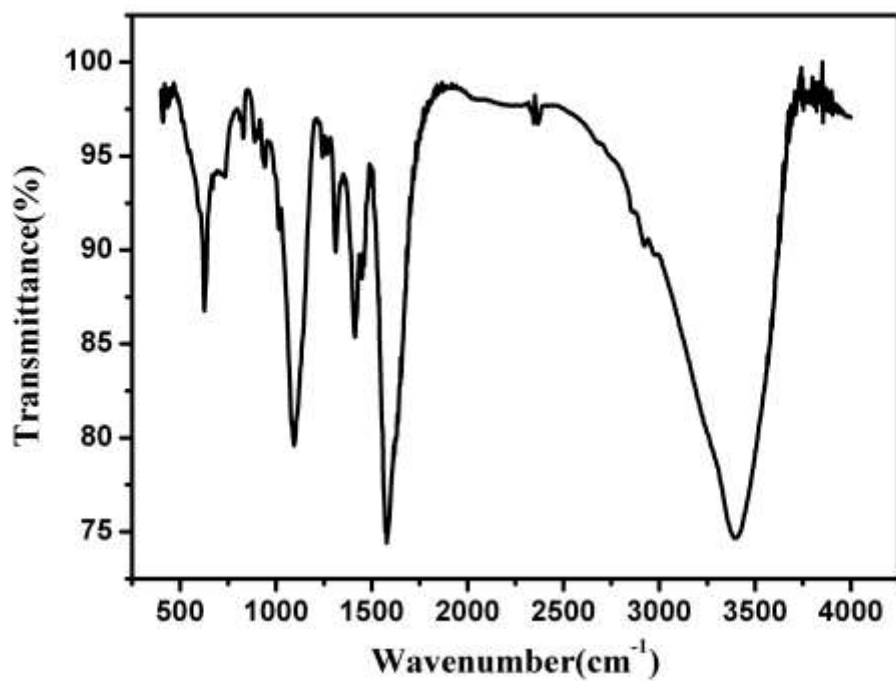


Figure S5 IR spectra in 4000-400 cm⁻¹ for compound 1.

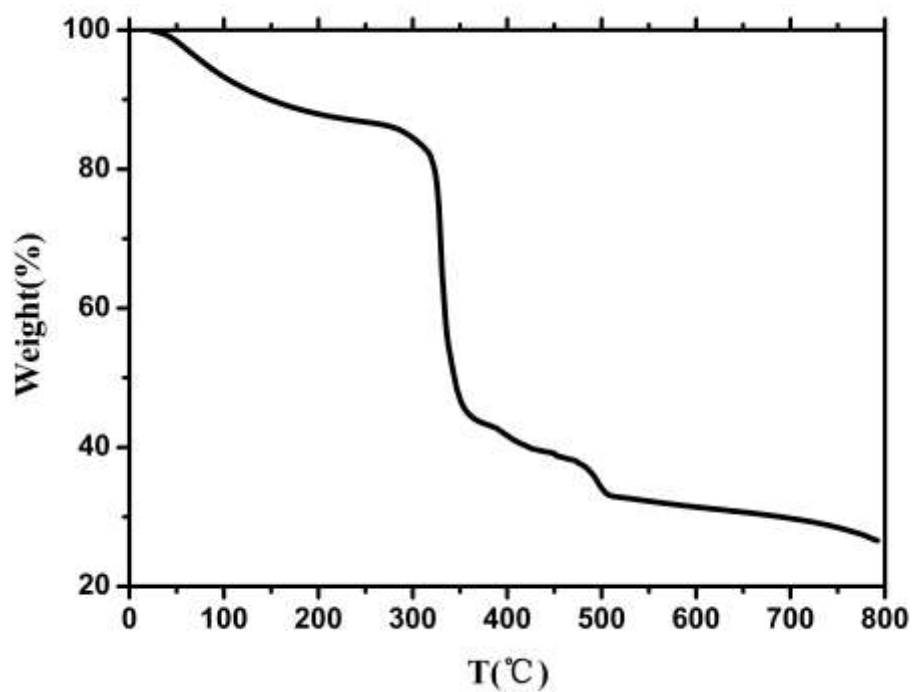


Figure S6 TG Curve between 30 and 800 °C for compound 1.

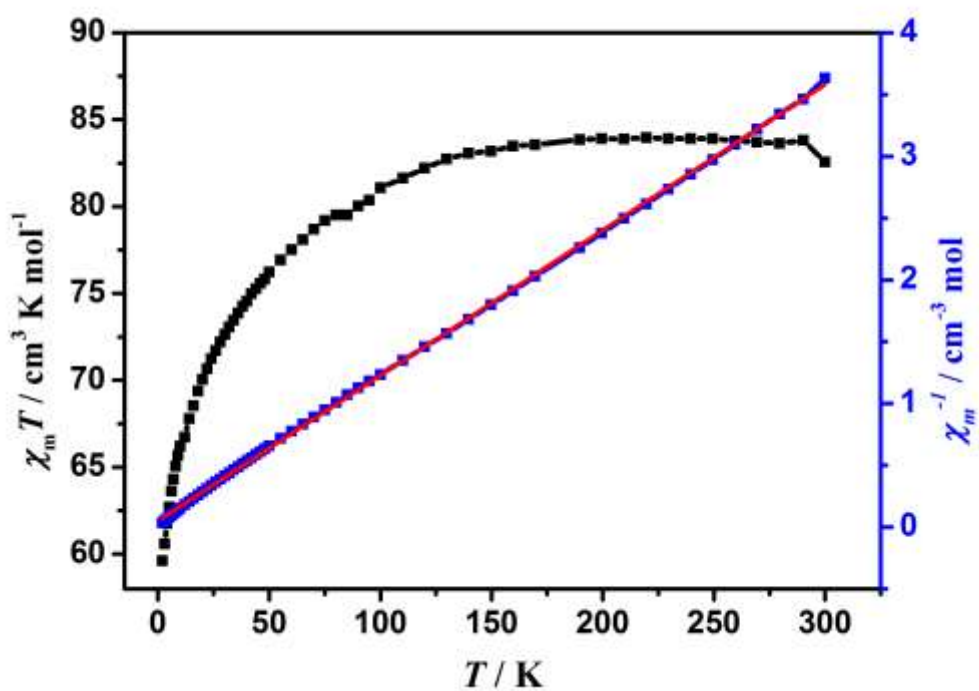


Figure. S7 Plots of temperature dependence of $\chi_M T$ and χ_M^{-1} for **1** under 1000 Oe dc field between 2 and 300 K.

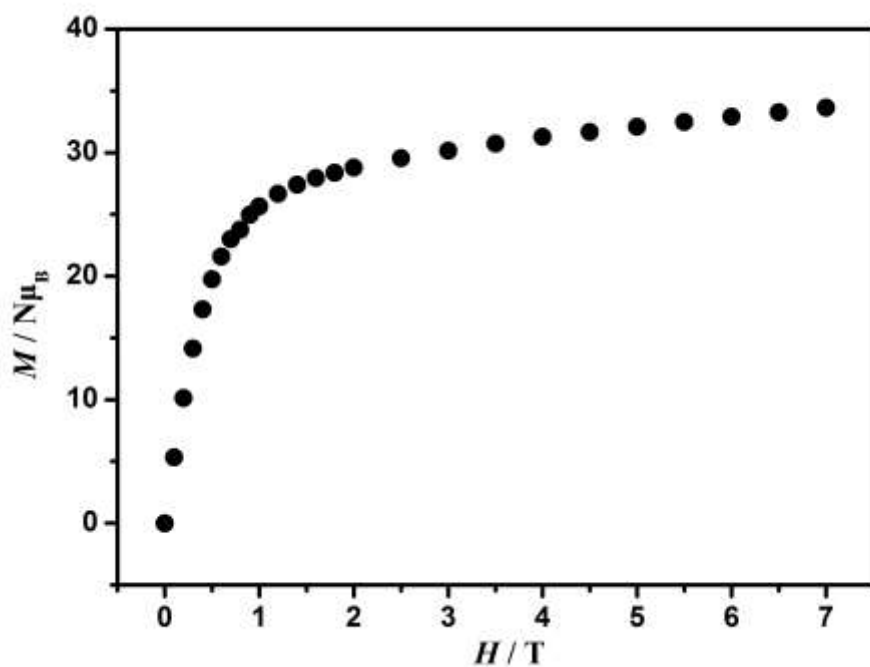


Figure S8 Magnetization versus H/T for **1** at 2.0 K and at indicated fields.

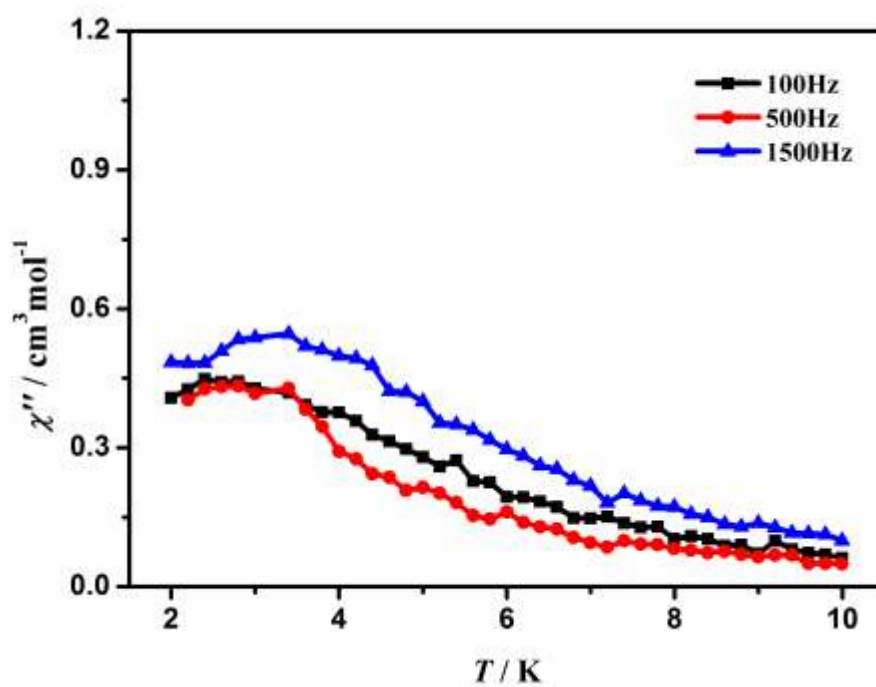
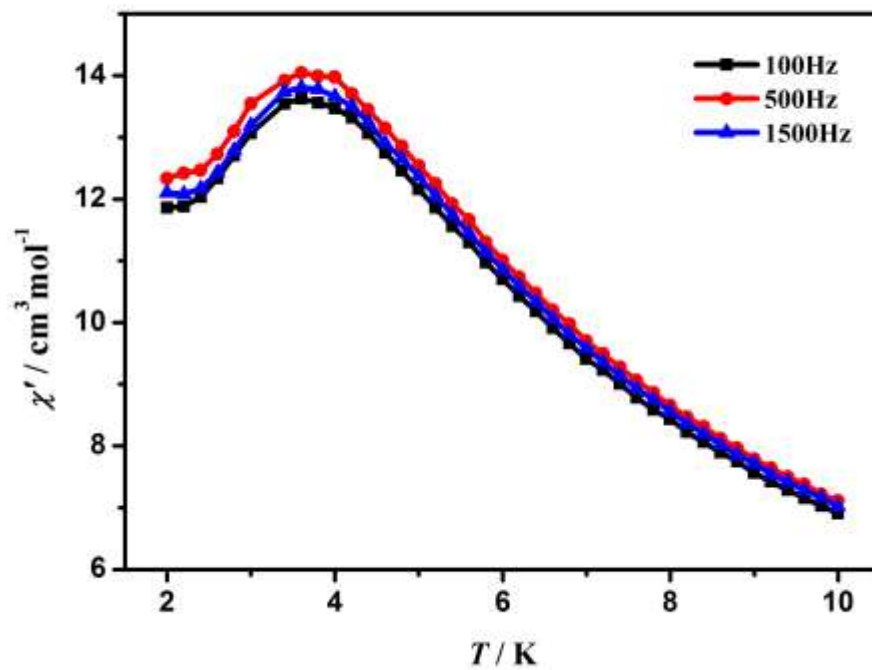


Figure.S9 Temperature dependence of the in phase (top) and out-of-phase (bottom) ac susceptibilities in $H_{dc}=1.5$ kG at the indicated frequencies for **1**.