Electronic Supplementary Information

Reversible Transformation between Chiral and Achiral Dy_6Mo_4 Clusters through a Symmetric Operation

Yong Zheng, Yin-Yin Pan, Yan-Ping Ren, La-Sheng Long,* Rong-Bin Huang, and Lan-Sun Zheng

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

Email: lslong@xmu.edu.cn, ypren@xmu.edu.cn

1. General Experimental. All chemicals were of commercial origin and were used as received, except $(n\text{-}Bu_4N)_4Mo_8O_{26}$, which was prepared using a previously reported procedure.[1] C, H, and N microanalyses were performed with a CE Instruments EA 1110 elemental analyzer. The infrared (IR) spectra were recorded on a Nicolet AVATAR FT-IR330 spectrophotometer using pressed KBr pellets. Magnetic measurements were performed with a Quantum Design SQUID MPMS magnetometer working in the 2-300 K range. X-ray powder diffraction (PXRD) studies were performed using a Panalytical X-Pert PRO diffractometer equipped with a Cu-Kα radiation source (λ = 0.15418 nm, 40.0 kV, 30.0 mA). The calculated PXRD patterns were produced using the Mercury 3.1 software package and single-crystal reflection data.

2. Syntheses of complexes I-III.

$(NH_4)_2[Dy_6Mo_4O_{12}(rac\text{-}L^{3-})_4(OOCCH_3)_8]\cdot 4CH_3OH\cdot 6H_2O$ (I)

A mixture of *rac*-3-aminopropane-1,2-diol (23 mg, 0.25 mmol) and 2-hydroxybenzaldehyde (26 μl, 0.25 mmol) in methanol (18 mL) was refluxed for 2 hours. To the solution of Schiff-base (*rac*-H_3L) formed *in situ* was added $Dy(CH_3COO)_3\cdot 3H_2O$ (157 mg, 0.40 mmol), $(^nBu_4N)_4Mo_8O_{26}$ (50 mg, 0.023 mmol), $NH_3\cdot H_2O$ (34□ μL, 0.60 mmol), and CH_3COONH_4 (123 mg, 1.6 mmol) under stirring at room temperature. The mixture was stirred for another 30 minutes, and was subsequently sealed in a 23 ml Teflon-lined Parr bomb. The sample was heated to 70 °C for 12 hours and then cooled to 30 °C at a rate of 4 °C h^{-1}. The filtrate was layered with *n*-hexane, and pale-yellow block-shaped crystals were collected after a few days. **I**, Yield: 60% (based on Dy). Elemental analysis (%) calcd for $Dy_6Mo_4C_{60}H_{100}N_6O_{50}$ (FW = 3064.21): C 23.52, H 3.28, N 2.74; found: C 23.57, H 3.36, N 2.64. IR (KBr, cm^{-1}): 3442(b,s), 2899(w), 2361(w), 2343(w), 2026(w), 1633(vs), 1561(s), 1468(m), 1446(m), 1407(m), 1340(m), 1283(w), 1221(w), 1193(w), 1149(w), 1124(w), 1092(w), 1066(w), 1026(w), 938(w), 872(w), 838(s), 812(m), 761(m), 718(w), 670(w), 647(w), 599(w), 548(w), 512(w), 478(w), 445(w).

$(Et_3NH)_2[Dy_6Mo_4O_{12}($*rac*$-L^{3-})_4(OOCCH_3)_8]\cdot 18H_2O$ (II)

Compound **II** was prepared in a manner similar to that described for compound **I**, except with Et_3NH and $CH_3COOHNEt_3$ used in place of $NH_3\cdot H_2O$ and CH_3COONH_4, respectively. **II**, Yield: 35% (based on Dy). Elemental analysis (%) calcd for $Dy_6Mo_4C_{68}H_{132}N_6O_{58}$ (FW = 3320.55): C 24.60, H 4.01, N 2.53; found: C 24.66, H 4.01, N 2.56. IR (KBr, cm^{-1}): 3438(b,s), 2932(w), 2360(w), 2343(w), 2026(w), 1631(vs), 1570(s), 1469(m), 1451(m), 1412(m), 1385(m), 1346(m), 1220(w), 1190(w), 1147(w), 1124(w), 1092(w), 1071(w), 1025(w), 944(w), 870(w), 835(s), 812(m), 759(m), 718(w), 670(w), 648(w), 598(w), 550(w), 516(w) , 474(w) , 420(w).

$(Me_4N)_2[Dy_6Mo_4O_{12}($*rac*$-L^{3-})_4(OOCCH_3)_8]\cdot CH_3OH\cdot 14H_2O$ (III)

Compound **III** was prepared in a manner similar to that described for compound **I**, except with $Me_4N\cdot OH$ and $CH_3COONMe_4$ used in place of $NH_3\cdot H_2O$ and CH_3COONH_4, respectively. **III**, Yield: 40% (based on Dy). Elemental analysis (%) calcd for $Dy_6Mo_4C_{65}H_{120}N_6O_{55}$ (FW = 3224.43): C 24.21, H 3.75, N 2.61; found: C 24.23, H 3.79, N 2.78; IR (KBr, cm^{-1}): 3423(b, s), 3196(b, s), 3021(m), 2896(w), 2026(w), 1633(vs), 1560(s), 1469(s), 1451(s), 1432(m), 1342(m), 1244(w), 1221(w), 1193(w), 1149(m), 1124(m), 1093(m), 1068(w), 1025(w), 935(w), 871(m), 837(s), 810(m), 759(m), 719(w), 673(w), 649(w), 614(w), 599(w), 565(w), 550(w), 515(w), 473(w), 473(w), 447(w), 419(w).

$(Me_4N)_2[Gd_6Mo_4O_{12}($*rac*$-L^{3-})_4(OOCCH_3)_8]\cdot CH_3OH\cdot 14H_2O$ (III-Gd analogue)

Compound **III-Gd** was prepared in a manner similar to that described for compound **I**, except with $Me_4N\cdot OH$, $Gd(CH_3COO)_3\cdot 3H_2O$, and $CH_3COONMe_4$ used in place of $NH_3\cdot H_2O$, $Dy(CH_3COO)_3\cdot 3H_2O$, and CH_3COONH_4, respectively. **III-Gd**, Yield: 35% (based on Gd). Elemental analysis (%) calcd for $Gd_6Mo_4C_{65}H_{120}N_6O_{55}$ (FW = 3192.93): C 24.45, H 3.79, N 2.63; found: C 24.33, H 3.70, N 2.72; IR (KBr, cm^{-1}): 3420(b, s), 3166(b, s), 2930(m), 2892(w), 2026(w), 1631(vs), 1560(s), 1467(s), 1450(s), 1343(m), 1244(w), 1221(w), 1192(w), 1148(m), 1124(m), 1093(m), 1068(w), 1043(w), 1025(w), 932(w), 898(w), 870(m), 835(s), 808(m), 760(m), 718(w), 671(w), 647(w), 616(w), 598(w), 562(w), 547(w), 510(w), 475(w), 446(w), 418(w).

3. X-ray Structure Determination.

Intensity data for **I** and **II(b)** were collected on a Bruker SMART CCD using graphite-monochromated Mo-Kα radiation □ (λ = 0.71073 Å) at 173 K and 123 K. The frames were integrated with the Bruker SAINT© program in the APEX II software package using a narrow-frame integration algorithm, which also corrects for Lorentz and polarization effects. Absorption corrections were applied using SADABS.

Intensity data for **II(a)** and **III** were collected on an Oxford Gemini S Ultra system using graphite-monochromated Mo-Kα□ radiation (λ = 0.71073 Å) at 133 K and 153 K. Data reductions were performed using the CrysAlis RED program.

Intensity data for the **III-Gd analogue** were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 nm) at 173 K. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.

All structures were solved by direct methods and refined to convergence by the least-squares method on F^2 using the SHELXTL software suite and Olex2.[2,3] Hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 × □Ueq of the attached atom (1.5 × □Ueq for methyl hydrogen atoms). The severely disordered guest molecules in **II** and **III** were removed by SQUEEZE during the structural refinement.[4] Other disordered atoms were refined with commands of AFIX, DFIX, ISOR, SIMU, and DELU. CCDC 967301-967305 contain the supplementary crystallographic data for **I**, **II(a)**, **II(b)**, **III-Gd**, and **III(b)**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tab. S1. Crystal data and structure refinements for **I-III**.

Complex	**I**	**II(a)**	**II(b)**	**III-Gd**	**III(b)**
Formula	$Dy_6Mo_4C_{60}H_{100}N_6O_{50}$	$Dy_6Mo_4C_{68}H_{132}N_6O_{58}$	$Dy_6Mo_4C_{68}H_{132}N_6O_{58}$	$Gd_6Mo_4C_{65}H_{120}N_6O_{55}$	$Dy_6Mo_4C_{65}H_{120}N_6O_{55}$
Mr	3064.21	3320.55	3320.55	3192.93	3224.43
Temperature/K	173(2)	133(2)	123(2)	173(2)	153(2)
Crystal size/mm^3	0.50 × 0.40 × 0.30	0.35 × 0.35 × 0.3	0.50 × 0.40 × 0.30	0.15 × 0.10 × 0.10	0.40 × 0.10 × 0.08
Crystal system	Tetragonal	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$P4_2/n$	$P3_121$	$P3_221$	$P3_121$	$P3_221$
a/Å	14.510(2)	21.969(1)	22.087(2)	21.761(3)	21.983(1)
b/Å	14.510(2)	21.969(1)	22.087(2)	21.761(3)	21.983(1)
c/Å	20.196(3)	19.099(1)	19.183(3)	19.354(4)	19.146(1)
V/Å^3	4252.2(11)	7982.7(2)	8103.9(13)	7937(2)	8012.4(4)
Z	2	3	3	3	3
Dc/g cm^{-3}	2.393	2.072	2.041	2.004	2.005
μ/mm^{-1}	5.874	4.708	4.637	4.253	4.685
Data/restraints/params	4179/0/281	10454/96/562	10621/15/561	10380/151/535	10486/147/537
θ /deg	1.73- 26.00	2.83-26.00	1.50-26.00	3.02-26.00	2.82-26.00
Obs reflns	4060	9516	10194	5726	8291
Goof on F^2	1.169	1.065	1.137	1.009	1.161
Flack parameters	Null	0.002(12)	0.000(11)	-0.02(2)	0.00(3)
$R_1[I> 2\sigma(I)]$[a]	0.0304	0.0384	0.0490	0.0795	0.1015
wR_2(all data)[b]	0.0724	0.0859	0.1129	0.1967	0.2257

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

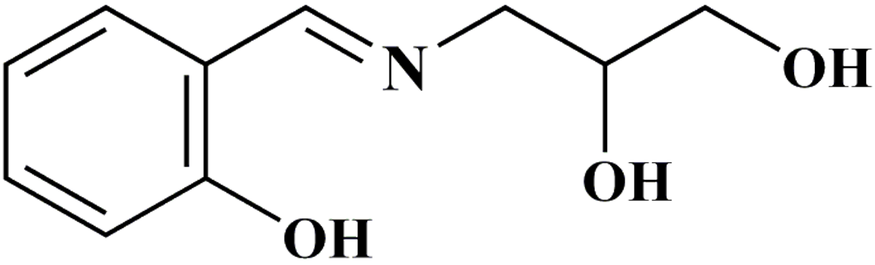
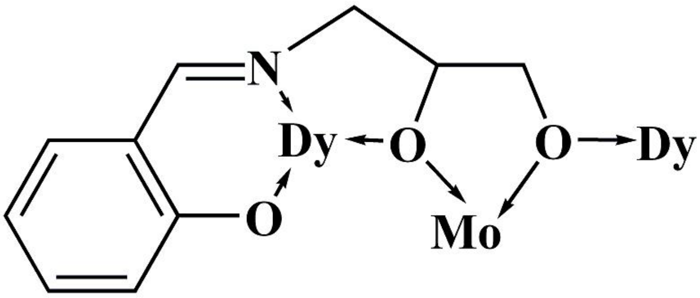


Fig. S1. The molecular structure of the Schiff-base ligand H_3L.



3.2211

Fig. S2. Schematic presentation of the coordination mode for the L^{3-} ligand with Harris notation.[5]

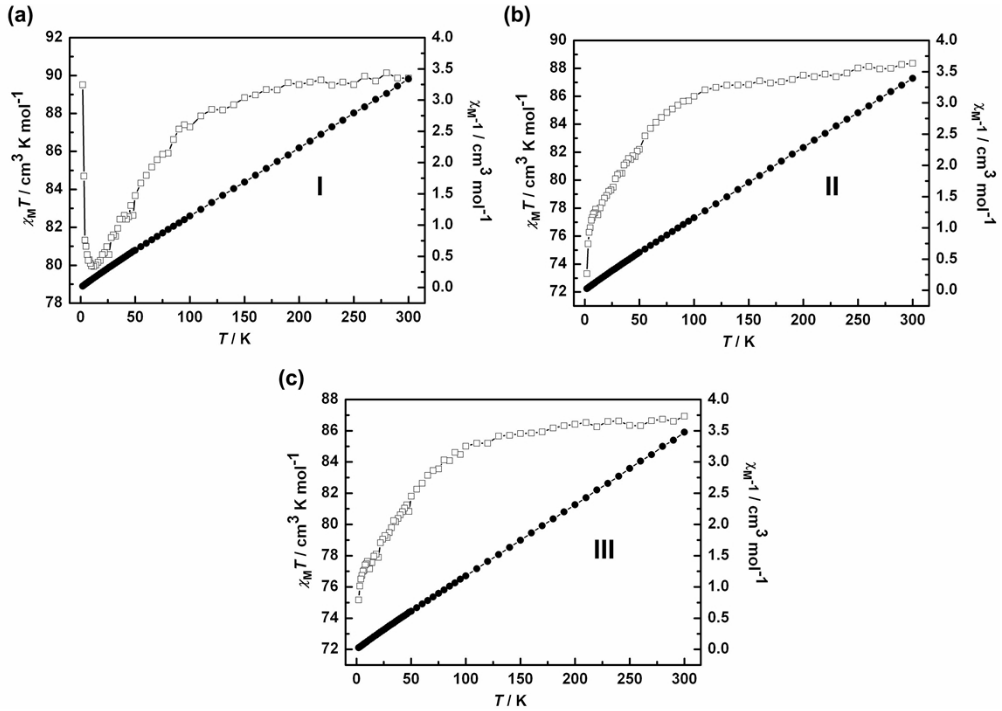


Figure S3. Plots of the temperature dependence of χ_MT *vs.* T and χ_M^{-1} *vs.* T for **I-III** under a 1000 Oe DC field at temperatures between 2 and 300 K.

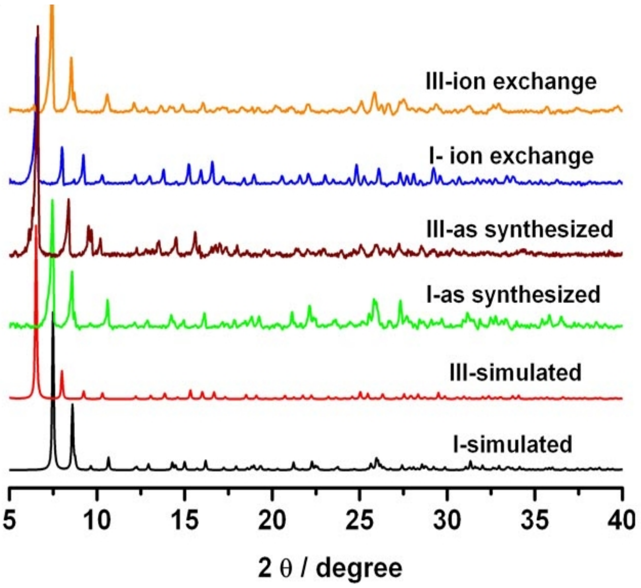


Fig 4. Simulated PXRD patterns for **I** and **III** and experimental PXRD patterns for **I** and **III** synthesized and for **I** and **III** prepared through ion exchange.

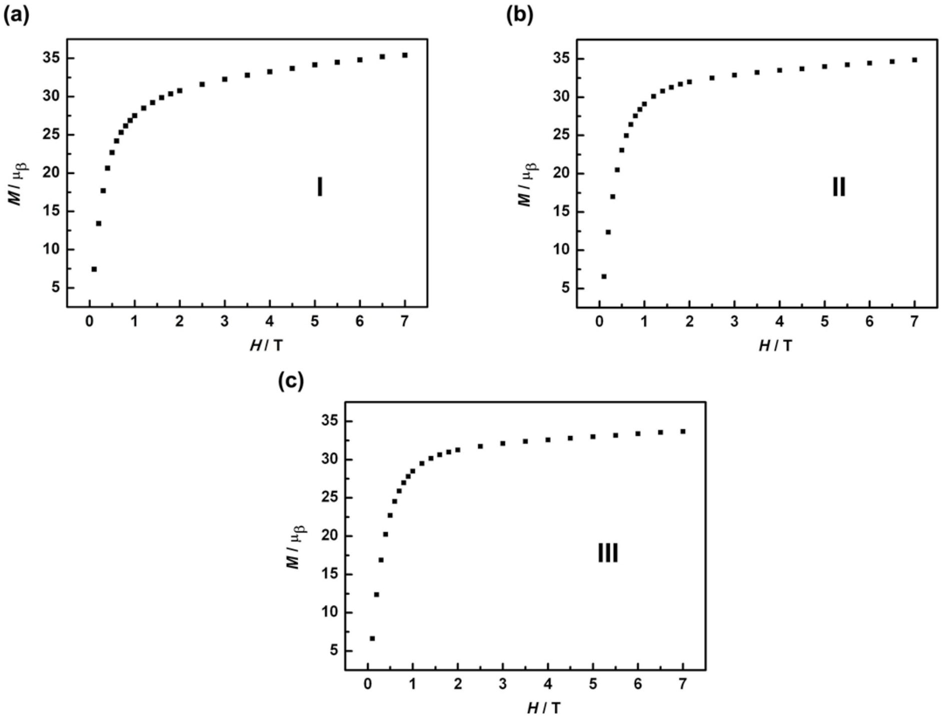


Fig. S5. Field dependence of the magnetization of **I-III** at 2 K.

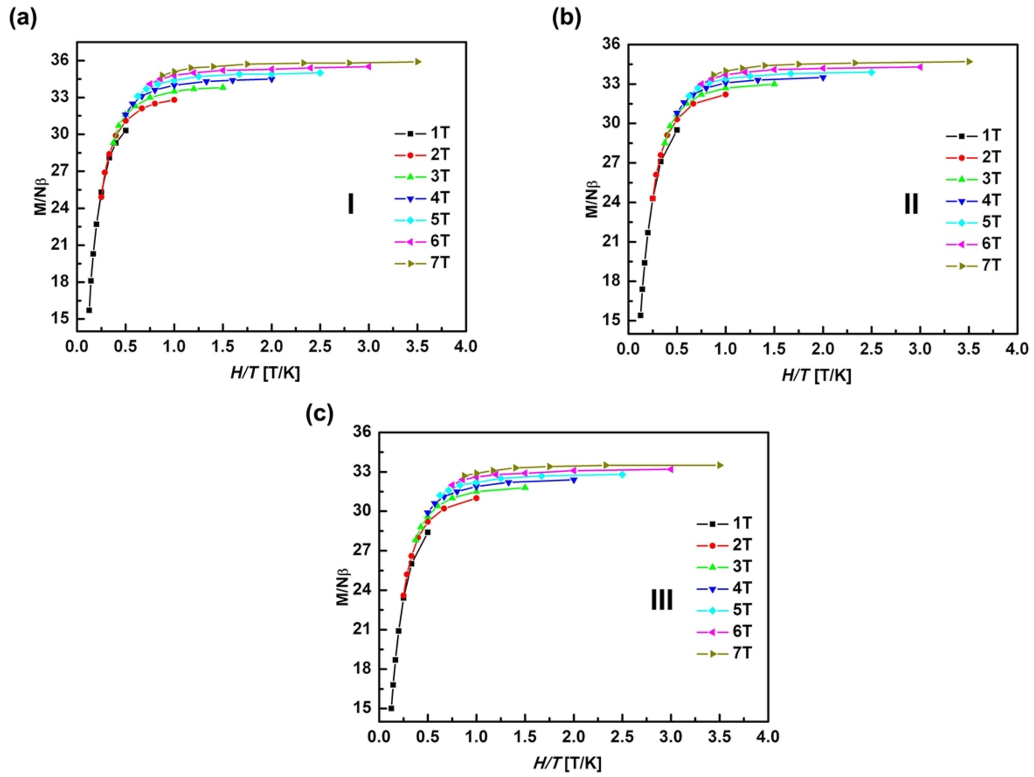


Fig. S6. Experimental field-dependent magnetization plots of **I-III** at indicated temperatures.

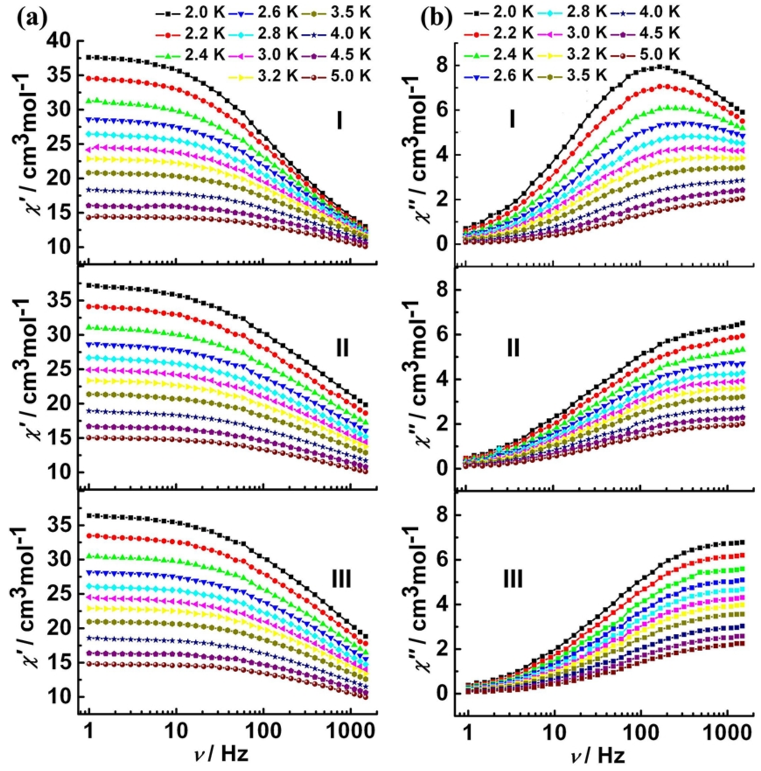


Figure S5. a) In-phase susceptibility (χ') as a function of frequency (υ) for **I-III** in the temperature range 2.0−5.0 K at zero dc field. b) Out-of-phase susceptibility (χ'') as a function of frequency (υ) for **I-III** in the temperature range 2.0−5.0 K at zero dc field.

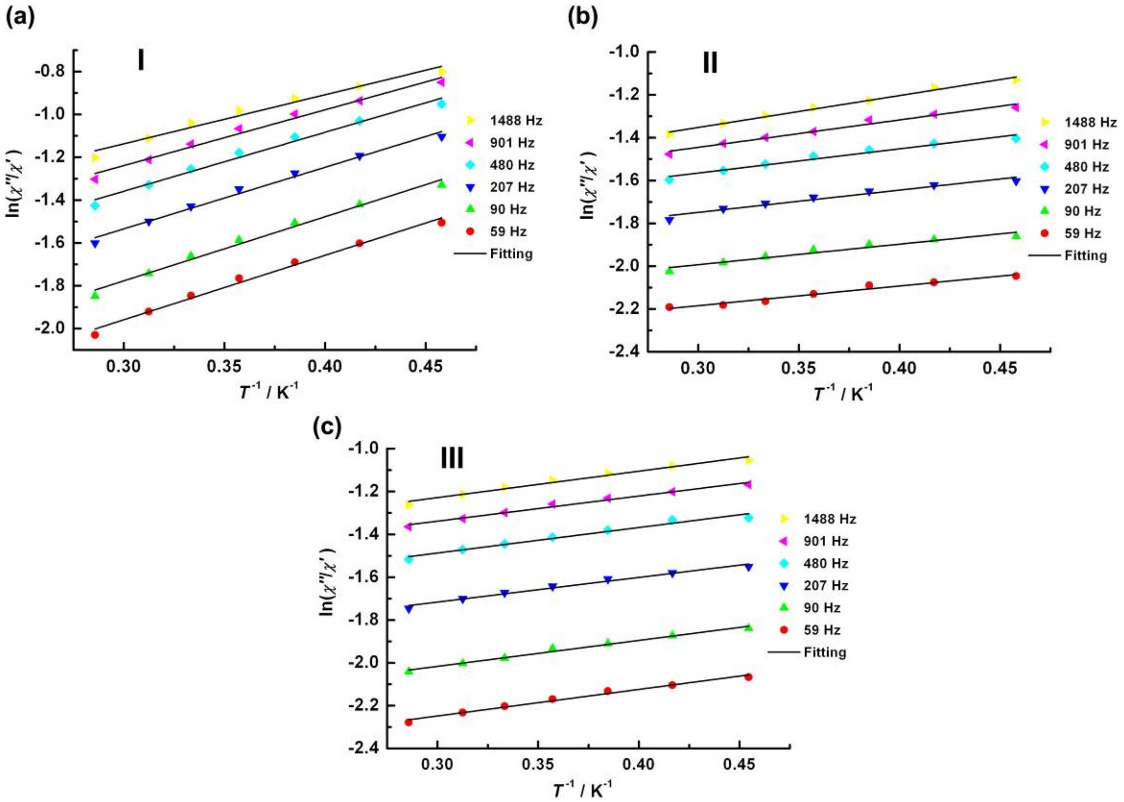


Fig. S8. Plots of $\ln(\chi''/\chi')$ *vs.* $1/T$ for **I**, **II**, and **III**. The solid lines represent the fitting results over the range 2.2–3.5 K.

[1] N. H. Hur, W. G. Klemperer and R.-C. Wang, *Inorg. Synth.*, 1990, **27**, 78.
[2] Bruker AXS SHELXTL version 6.12. Structure Determination Package. Bruker AXS 2000. Madison, WI, USA.
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst., 2009, **42**, 339-341.
[4] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
[4] R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans*. 2000, 2349.