Ln-Pt Electron Polarization Effects on the Magnetic Relaxation of Heterometallic Ho- and Er-Pt Complexes

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Experimental.

General Information. Holmium chloride, and Erbium chloride were obtained from Strem Chemicals Inc. and used as received. *S*-potassium thioacetate was obtained from Tokyo chemical industry co., Ltd. and used as received. Every synthetic process were operated under air atmosphere.

Synthesis of $[Ln_2Pt_3(H_2O)_2(SAc)_{12}]$. $[Ln_2Pt_3(H_2O)_2(SAc)_{12}]$ (Ln = Ho, Er) were obtained from aqueous solutions (20 ml) with $Ln(III)Cl_3 \cdot nH_2O$ (55 mg: ~2.2×10^{-1} mmol, n = 6 or 7), K_2PtCl_4 (90 mg: 2.2×10^{-1} mmol), and K(SAc) (100 mg: 8.8×10^{-1} mmol) at 60°C. Half of or one hour later, we got the singe crystals. They were separated from mother liquor by decantation using water and filtered.

$[Ho_2Pt_3(ASc)_{12}(H_2O)_2]$ (1). Yield: 80 mg (39%). Elemental analysis: $C_{24}H_{40}O_{14}S_{12}Ho_2Pt_3$; cal.: C, 15.56; H, 2.18; S, 20.77. Found: C, 15.847; H, 2.014; S, 20.84. IR spectrum (ATR, cm^{-1}): 3548(m), 3495(m), 1579(s), 1528(s), 1419(m), 1351(m), 1137(s), 967(m), 703(m).

$[Er_2Pt_3(ASc)_{12}(H_2O)_2]$ (2). Yield: 45 mg (22%). Elemental analysis: $C_{24}H_{40}O_{14}S_{12}Er_2Pt_3$; cal.: C, 15.52; H, 2.18; S, 20.69. Found: C, 15.686; H, 2.041; S, 20.40. IR spectrum (ATR, cm^{-1}): 3584(m), 3486(m), 1571(s), 1501(s), 1409(m), 1345(m), 1210(s), 1144(s), 976(m), 690(m).

Characterization and Instrumental Procedures. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer with a PHOTON 100 CMOS detector and JAPAN thermal Engineering Co., Ltd Cryo system DX-CS190LD. All of the collection details were written on each CIF file. The elemental analysis performed on J-SCIENCE LAB CO., Ltd. JM-11 microanalyzer. FT-IR spectra of the single crystal were acquired on a JASCO FT/IR 6700 spectrometer using an ATR method. Powder X-ray diffraction patterns were acquired on a Bruker D2 Phaser.

Calculation details. NBO and LOL analyses were performed on Gaussian09 program package. The molecular structure of model made from crystal structure of **2** and simplified on GaussVeiw5.0. The B3LYP functional[S1] was used with Def2-TZVP basis set including Effective Core Potential.[S2] The SCF procedure performed on verytight condition. Ultrafine integration grid was used for integration. Publication materials visualized by GaussVeiw5.0.

X-ray Absorption Fine Structure Measurements. X-ray absorption fine structure was collected on a handmade measurement system on the BL9A beamline in the Photon Factory of the High Energy Accelerator Research Organization (KEK, Proposal No. 2017P016). XANES analysis were done by using Demeter 0.9.25 package.[S3]

Magnetic Susceptibility Measurements. DC and AC magnetic susceptibility measurements were performed on solid polycrystalline and single-crystal samples on Quantum Design MPMS-XL SQUID magnetometer, and a Quantum Design PPMS-6000 physical property measurement system in applied dc fields of 3000 Oe.

Table 1. crystal data of **1** and **2**.

	1	**2**
Temperature / K	RT	93
formula	$C_{24}H_{40}O_{14}S_{12}Ho_2Pt_3$	$C_{24}H_{40}O_{14}S_{12}Er_2Pt_3$
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a / Å	8.443(5)	8.336(6)
b / Å	11.781(7)	11.594(8)
c / Å	12.701(7)	12.718(9)
α / °	83.155(10)	82.957(2)
β / °	73.837(2)	74.002(2)
γ / °	76.145(10)	75.934(2)
V / Å^3	1176.27(12)	1144.1(14)
Z	1	1
R_1 ($I > 2\sigma(I)$)	3.37%	3.50%
wR_2 ($I > 2\sigma(I)$)	7.46%	5.83%

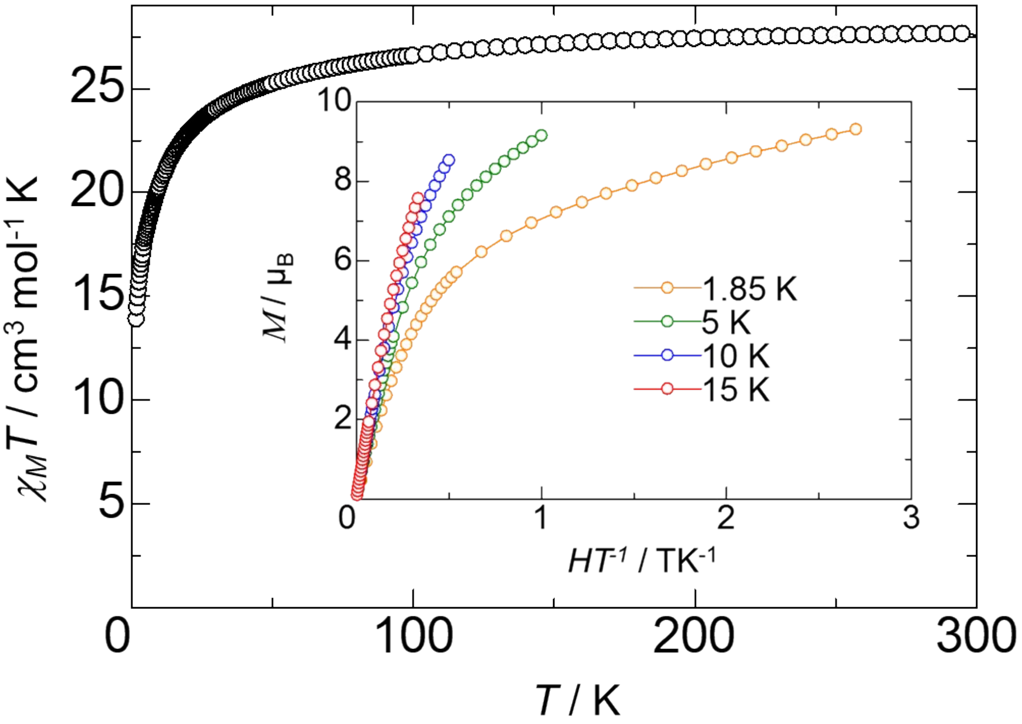


Figure S1. $\chi_M T$ *vs*. T plots for **1** in a *dc* field of 3000 Oe.

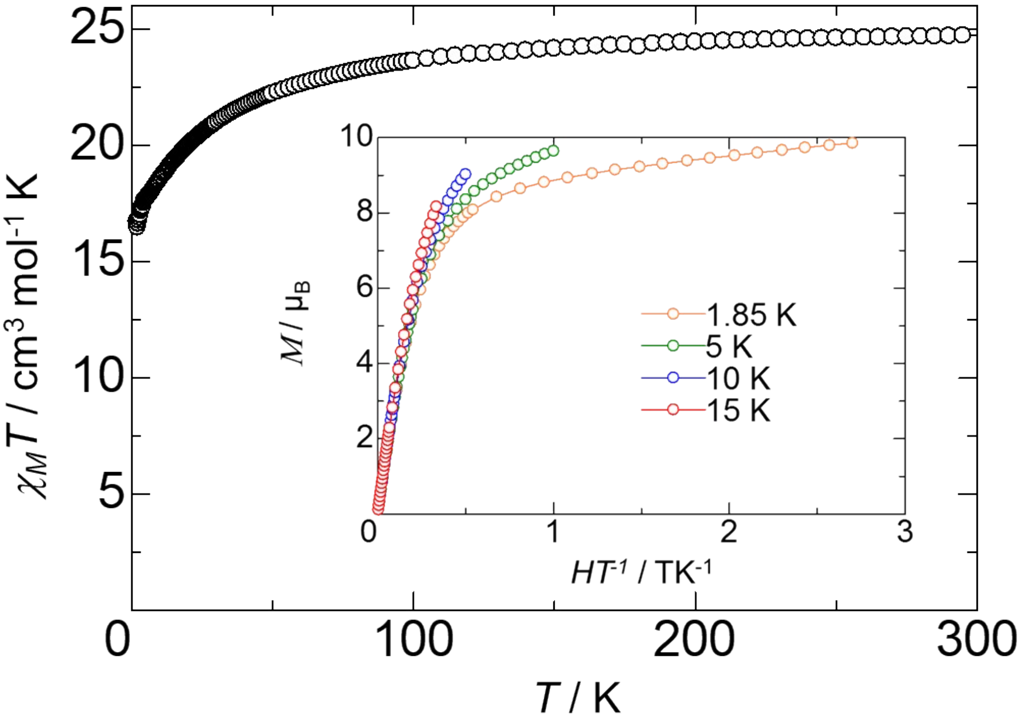


Figure S2. $\chi_M T$ *vs*. T plots for **2** in a *dc* field of 3000 Oe.

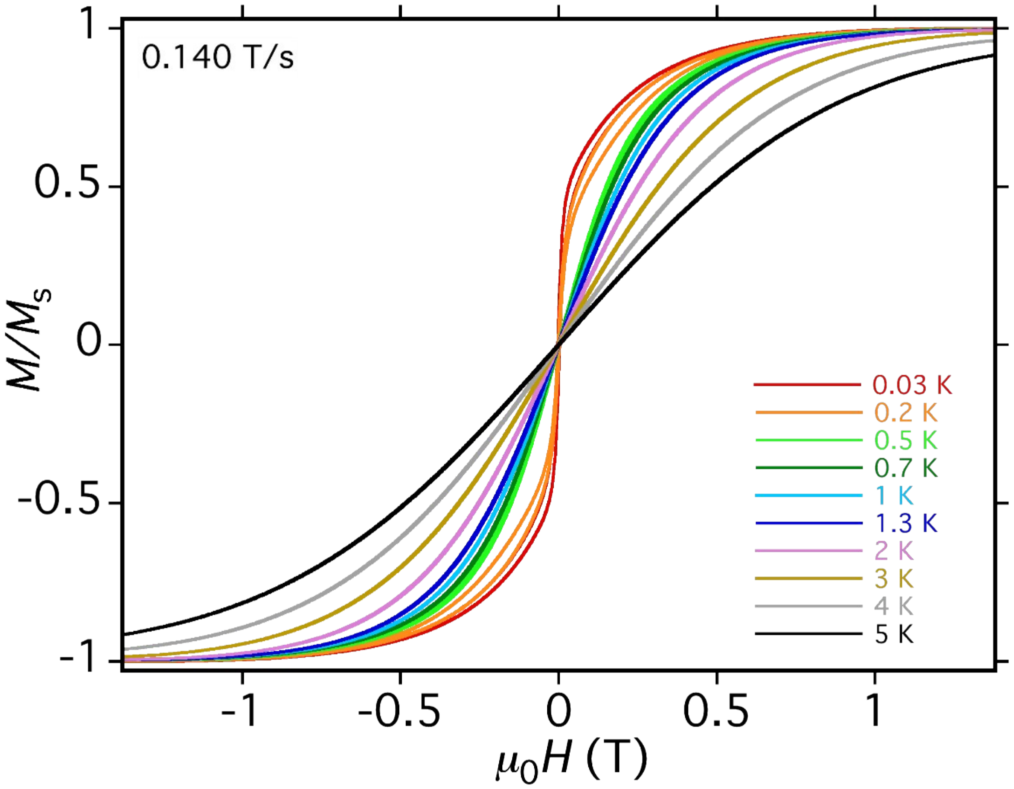
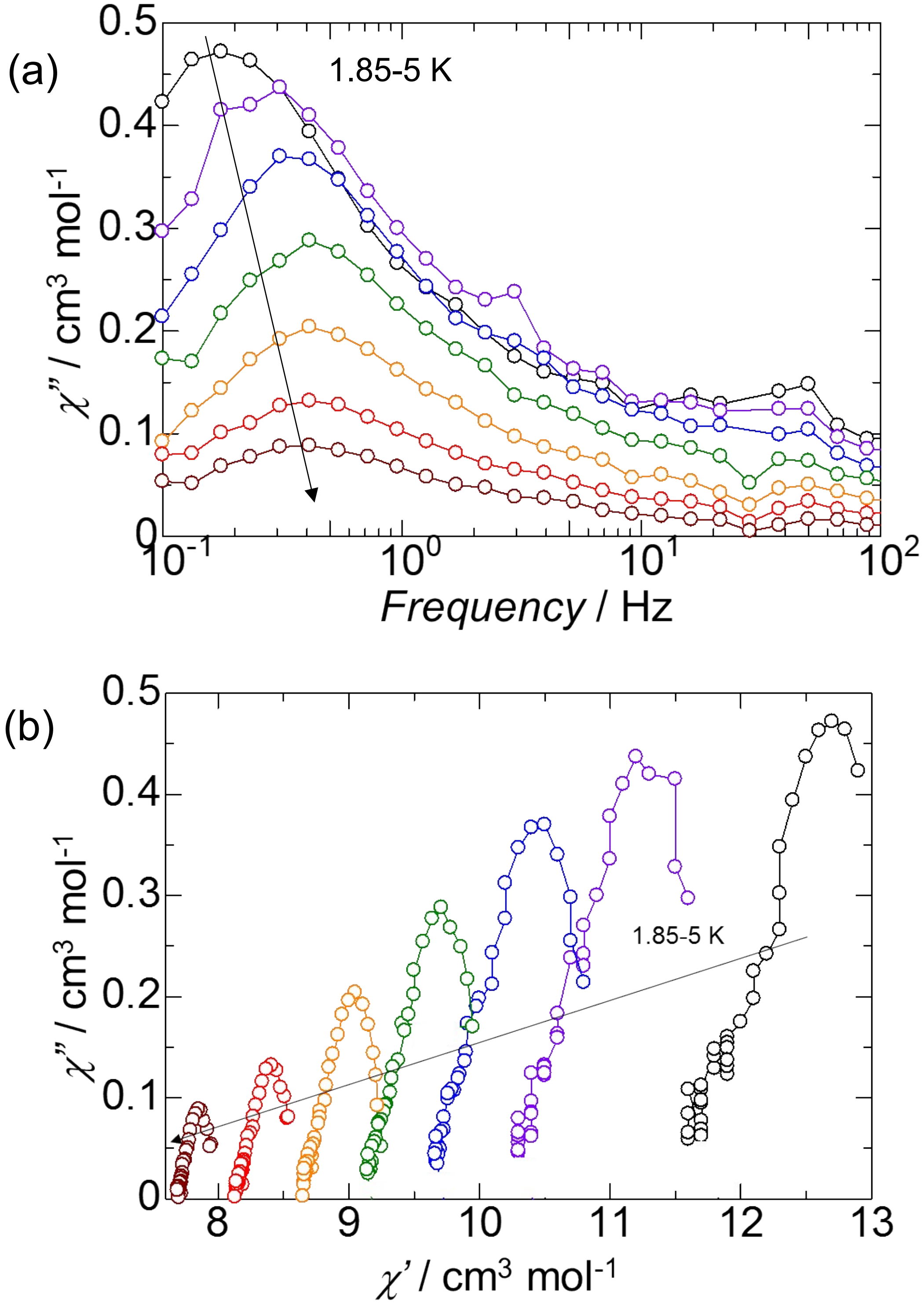


Figure S3. The magnetization *vs.* field plots of **1** in the *T* range of 0.03–5 K at a scan rate of 0.140 T/s.


(a)
1.85-5 K
χ'' / cm³ mol⁻¹
0
0.1
0.2
0.3
0.4
0.5
10⁻¹
10⁰
10¹
10²
Frequency / Hz
(b)
1.85-5 K
χ'' / cm³ mol⁻¹
0
0.1
0.2
0.3
0.4
0.5
8
9
10
11
12
13
χ' / cm³ mol⁻¹

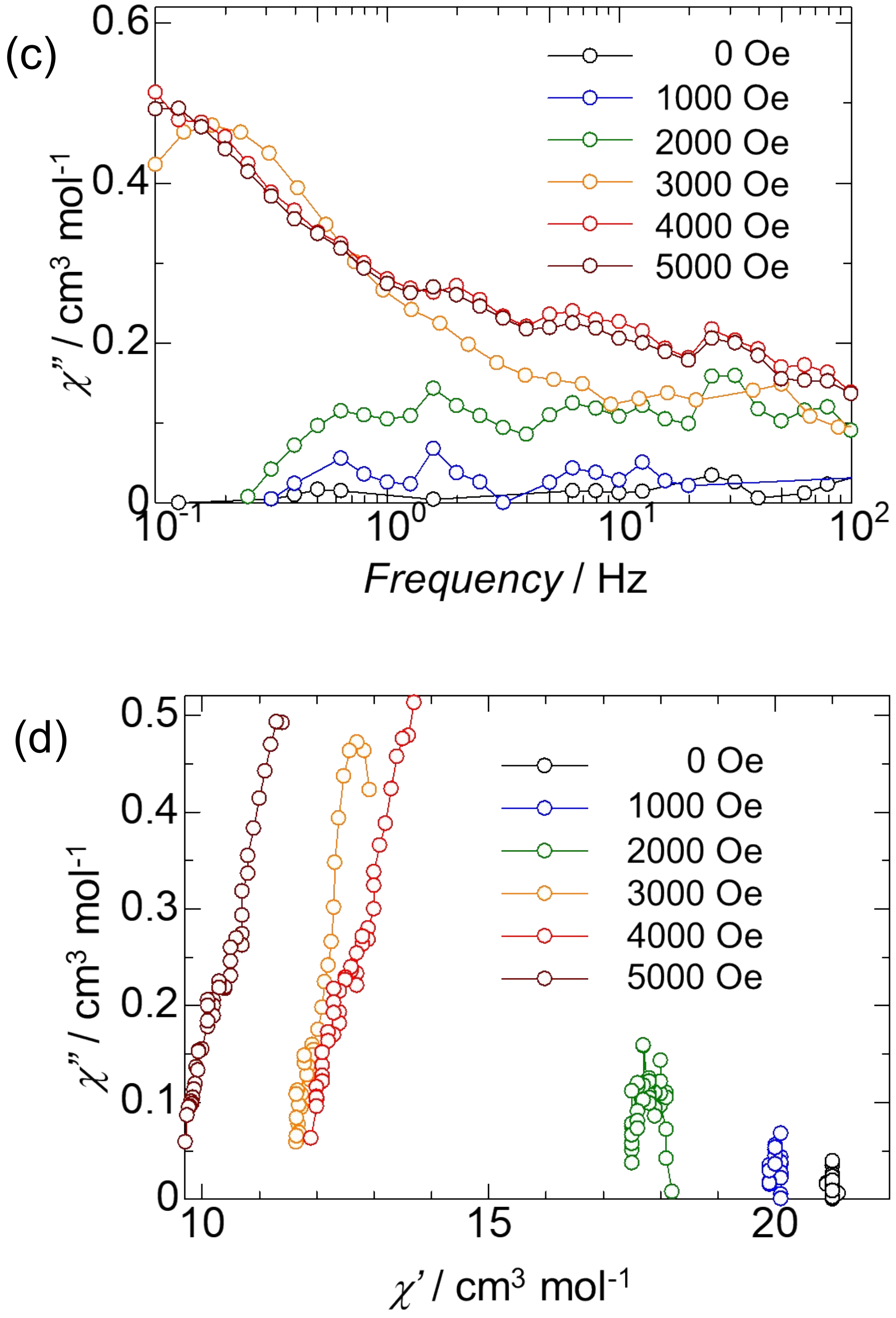
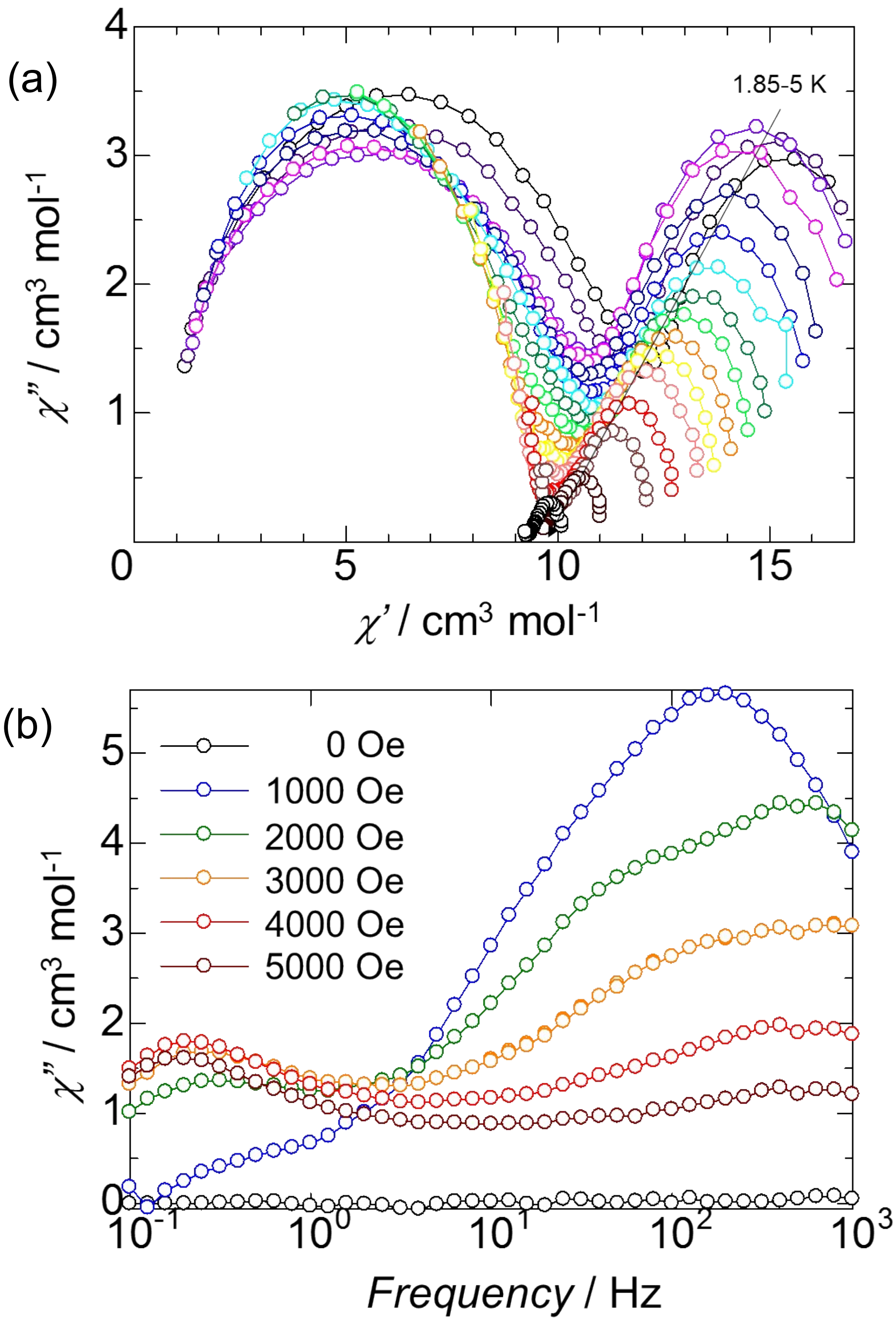


Figure S4. (a) χ''_M *vs*. T plots for **1** in a field of 3000 Oe and T range of 1.85–5K at 0.5 K per step. (b) Cole-Cole plots for **1** in a field of 3000 Oe and T range of 1.85–5K at 0.5 K per step. (c) χ" versus frequency plots for powder sample for **1** in various fields at 1.85 K. (d) Cole-Cole plots for **1** in various fields at 1.85 K.


(a)
4
3
2
1
0
5
10
15
1.85-5 K
χ'' / cm³ mol⁻¹
χ' / cm³ mol⁻¹
(b)
0 Oe
1000 Oe
2000 Oe
3000 Oe
4000 Oe
5000 Oe
5
4
3
2
1
0
10⁻¹
10⁰
10¹
10²
10³
χ'' / cm³ mol⁻¹
Frequency / Hz

(c)

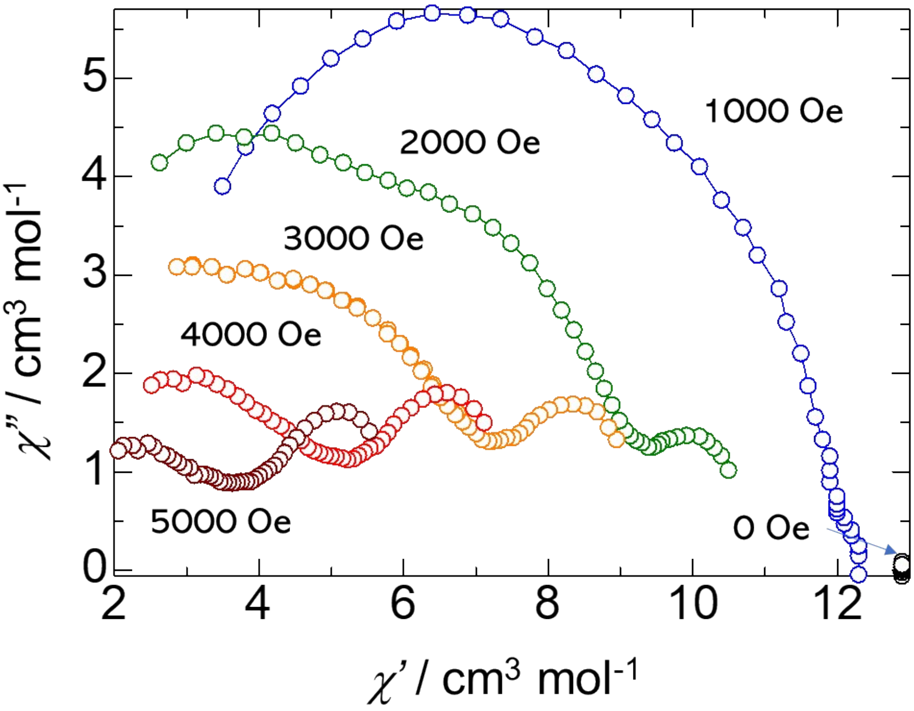


Figure S5. (a) Cole-Cole plots for **2** in a field of 3000 Oe and *T* range of 1.85–3.5K at 0.15 K per step, 3.75–4 K at 0.25 K per step, and 4–5 K at 0.5 K per step. (b) χ“ versus frequency plots for powder sample for **2** in various fields at 1.85 K. (c) Cole-Cole plots for **2** in various fields at 1.85 K.

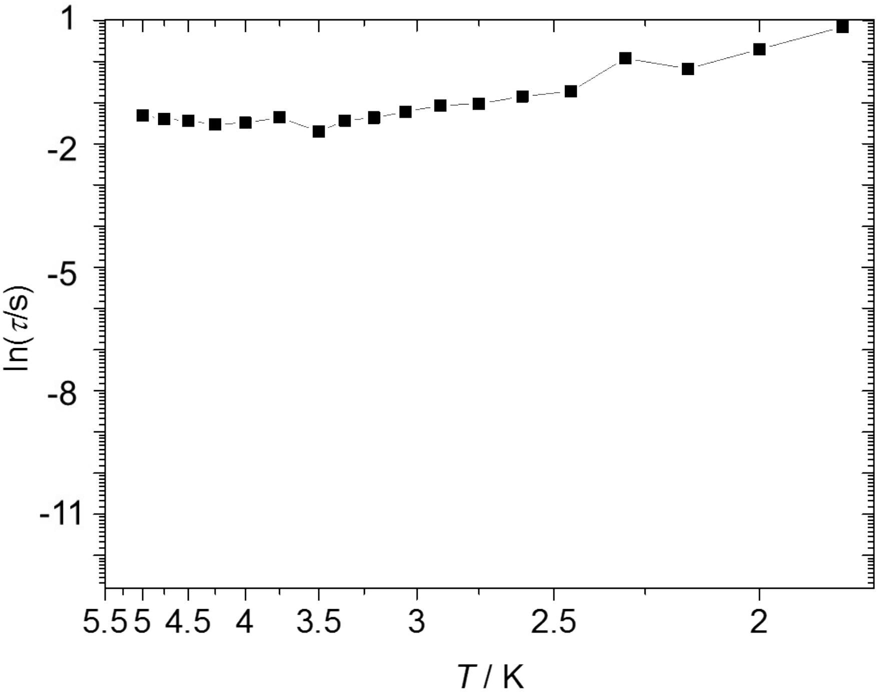


Figure S6. ln(τ) *vs*. T^{-1} plots for **1**.

References

[S1] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.,* 1994, **98**, 11623-11627.

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[S3] B. Ravel and M. Newville, *J. Synchrotron Rad.,* 2005, **12**, 537-541.