Multiple-Decker Phthalocyaninato Dinuclear Lanthanoid(III) Single-Molecule Magnets with Dual-Magnetic Relaxation Processes

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Supporting Information Contents:

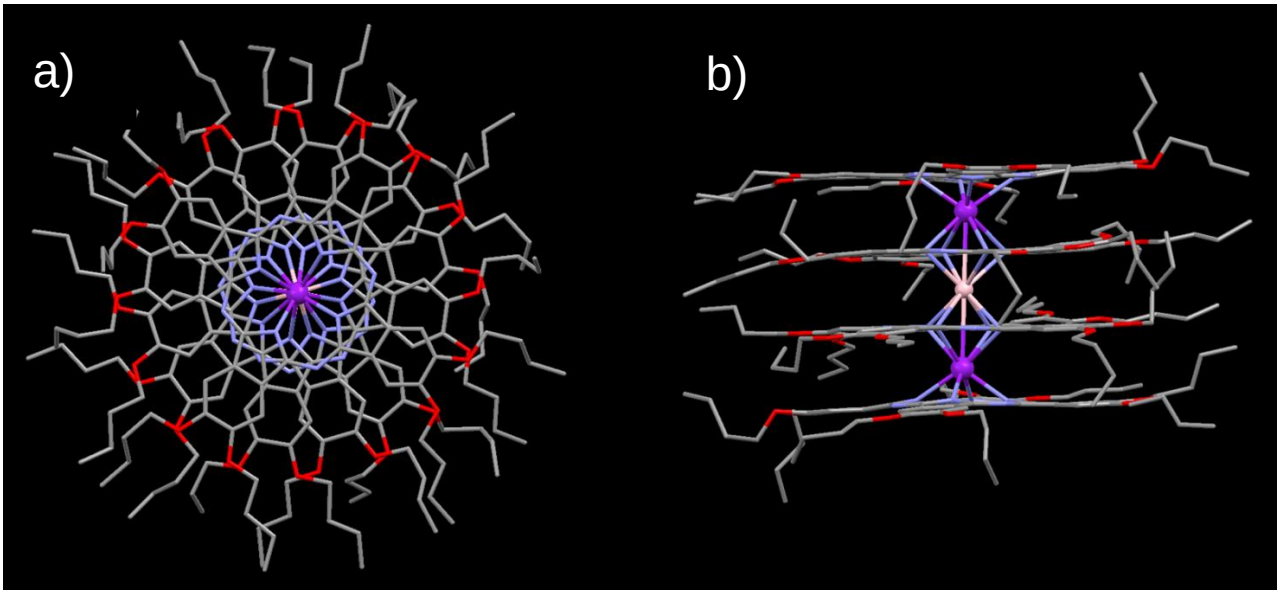

Fig. S1-1 Crystal structure of **1** in top view (a) and side view (b) with all hydrogen atoms omitted for clarity. Tb(III): purple, Cd(II): pink, C: gray, N: pale purple, O: red.

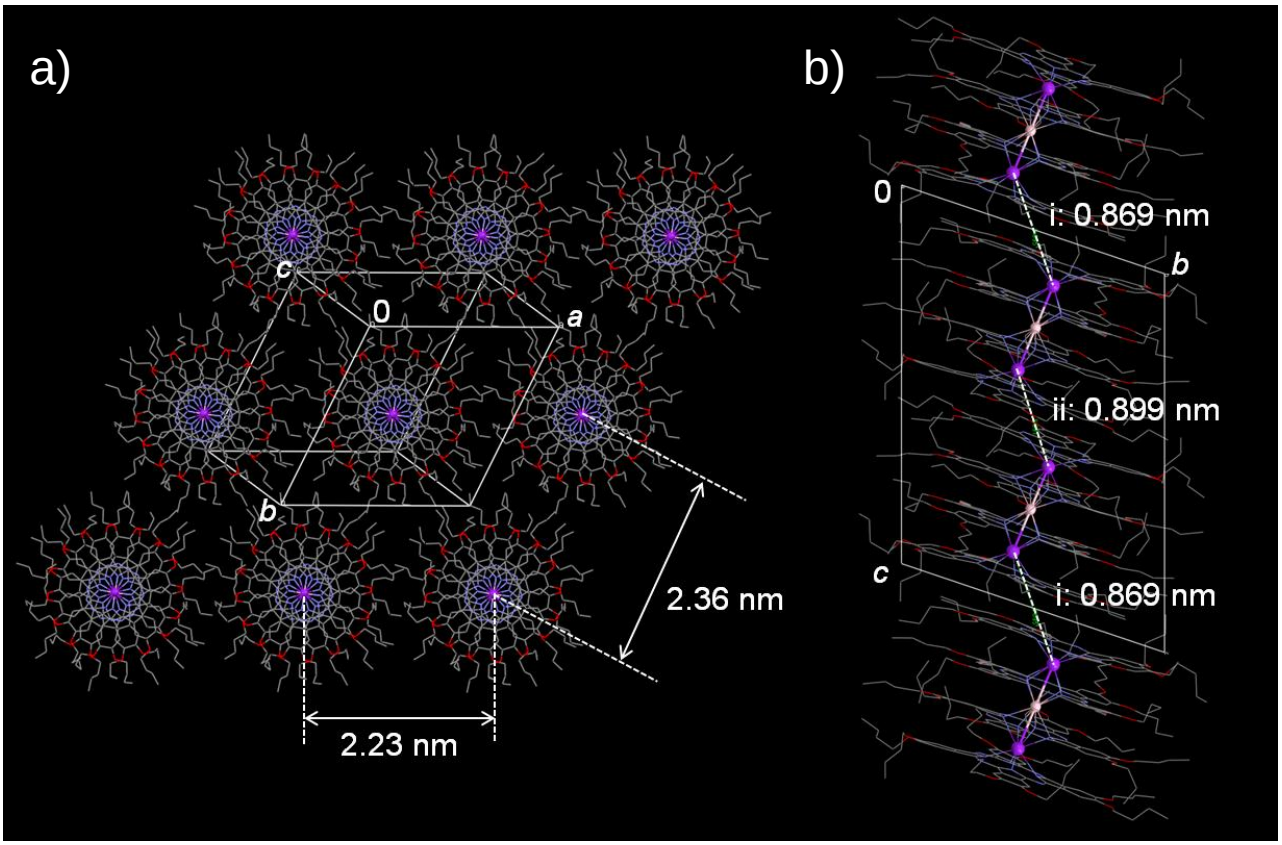

Fig. S1-2 Packing diagram of **1**. Solvent molecules (H_2O) located between the *n*-butoxy chains omitted for clarity.

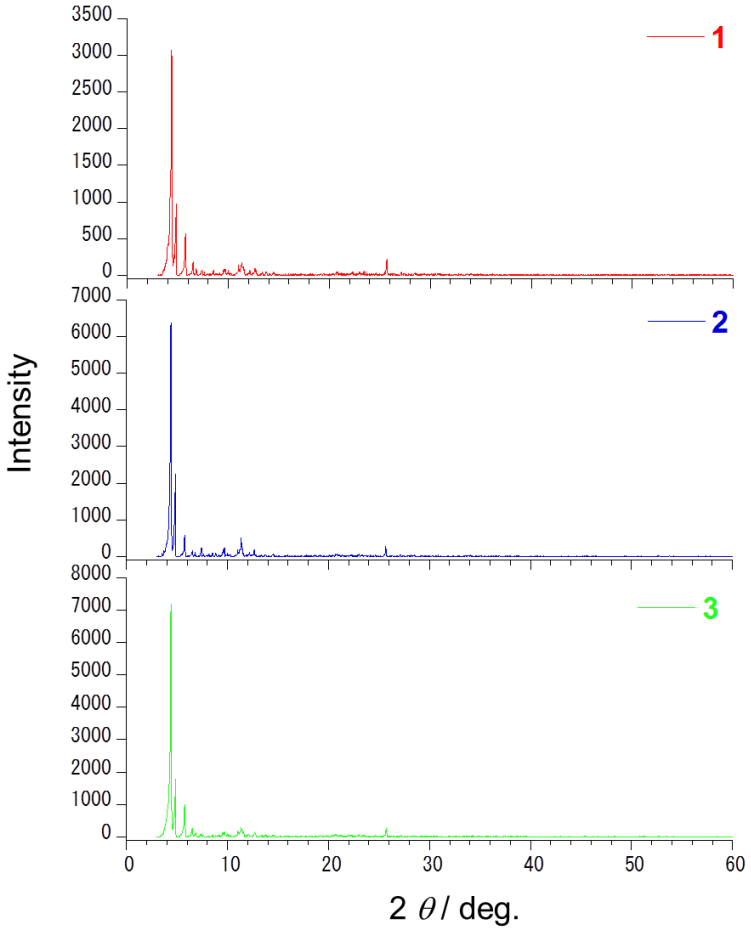

Fig. S1-3 Powder XRD patterns for **1**, **2** and **3** at room temperature.

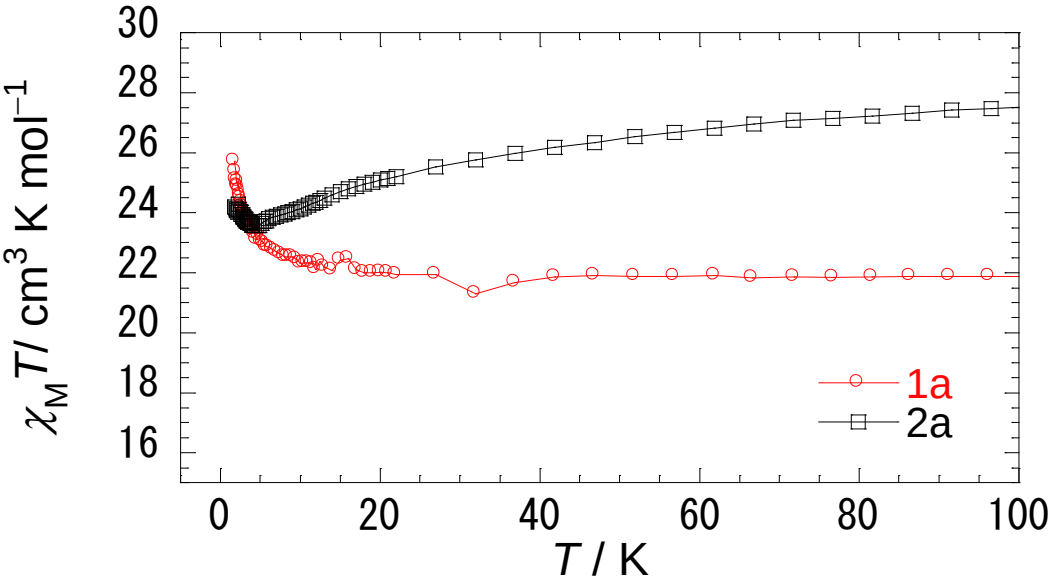

Fig. S2 $\chi_M T$ versus T plots for **1a** [the molar ratio of sample **1** (5 mg, 1.04×10^{-6} mol) and **3** (50 mg, 1.08×10^{-5} mol) is 1:10] and **2a** [the molar ratio of sample **2** (5 mg, 1.04×10^{-6} mol) and **3** (50 mg, 1.08×10^{-5} mol) is 1:10]. Open red circles represent the powder sample (**1a**), and the open black squares represent the isolated sample (**2a**). The solid lines are guides only.

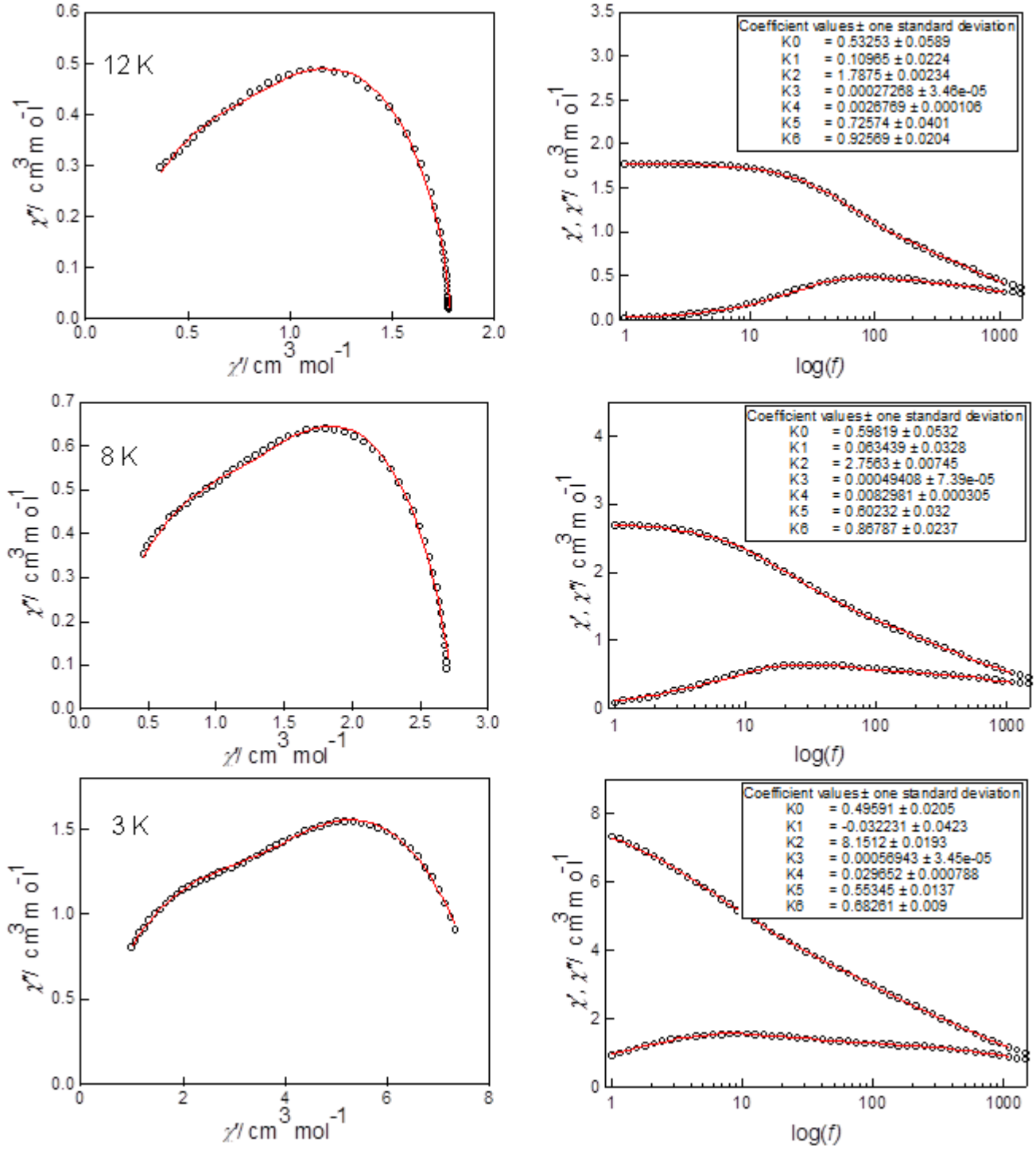

Fig. S3 Selected frequency dependence of the ac magnetic susceptibility for **1** measured in the *T* range of 3–21 K (right) and Argand plots (left). The red solid lines were fitted by using an extended Debye model (eq. 1). The fitting parameters are listed in Table S1.

Table S1 Extended Debye Model Fitting Parameters in the *T* Range of 3–21 K for a Powder Sample **1** at 0 T.

T / K	χ_S/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	τ_1 / s	α_1	τ_2 / s	α_2	β
3	-0.032	8.151	5.694×10^{-4}	0.553	2.965×10^{-2}	0.683	0.495
4	-0.046	5.884	6.187×10^{-4}	0.536	2.467×10^{-2}	0.725	0.559
5	-0.044	4.603	6.737×10^{-4}	0.525	2.013×10^{-2}	0.769	0.613
6	-0.031	3.768	6.501×10^{-4}	0.543	1.551×10^{-2}	0.809	0.626
7	0.029	3.186	5.724×10^{-4}	0.569	1.142×10^{-2}	0.841	0.617
8	0.063	2.756	4.941×10^{-4}	0.602	8.298×10^{-3}	0.868	0.598
9	0.080	2.429	4.148×10^{-4}	0.636	6.050×10^{-3}	0.884	0.575
10	0.102	2.170	3.758×10^{-4}	0.672	4.625×10^{-3}	0.907	0.566
11	0.109	1.963	3.133×10^{-4}	0.700	3.461×10^{-3}	0.914	0.542
12	0.109	1.788	2.677×10^{-4}	0.726	2.677×10^{-3}	0.926	0.533
15	0.114	1.413	1.880×10^{-4}	0.792	1.430×10^{-3}	0.948	0.511
18	0.109	1.181	1.335×10^{-4}	0.830	8.372×10^{-4}	0.963	0.505
21	0.114	1.009	9.963×10^{-5}	0.905	5.362×10^{-4}	0.973	0.488

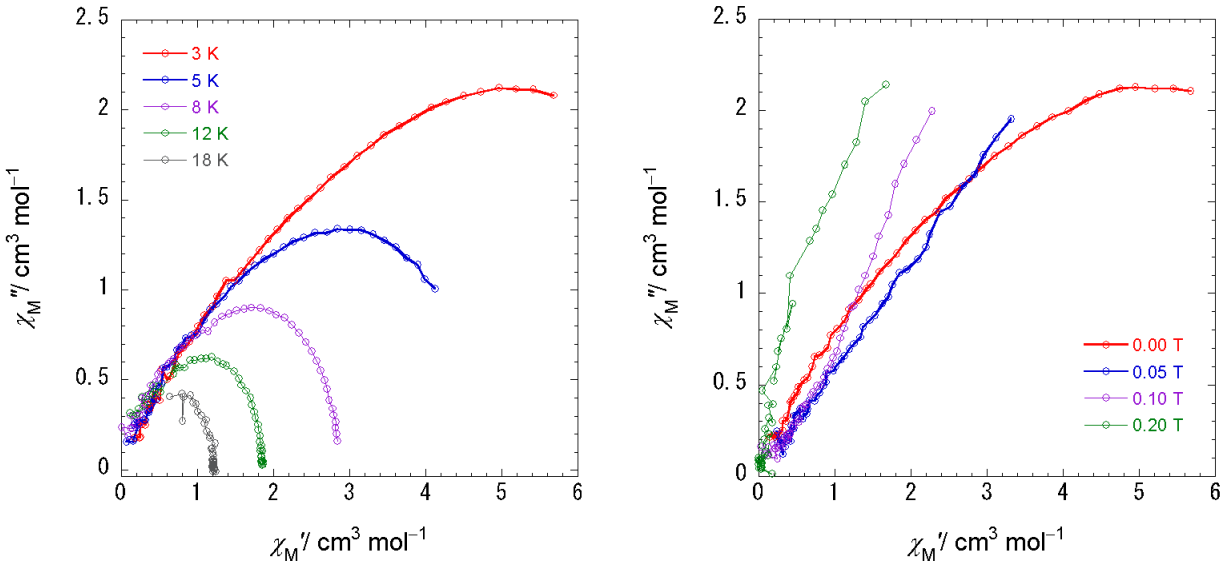

Fig. S4 Argand plot of **1a** (the molar ratio of sample **1** (5 mg, 1.04×10^{-6} mol) and **3** (25 mg, 1.08×10^{-5} mol) is 1:10) measured in the T range of 3–18 K in a zero dc field (left) and an Argand plot of **1a** measured in fields between 0 and 0.2 T at 3 K (light). The solid lines are guides only.

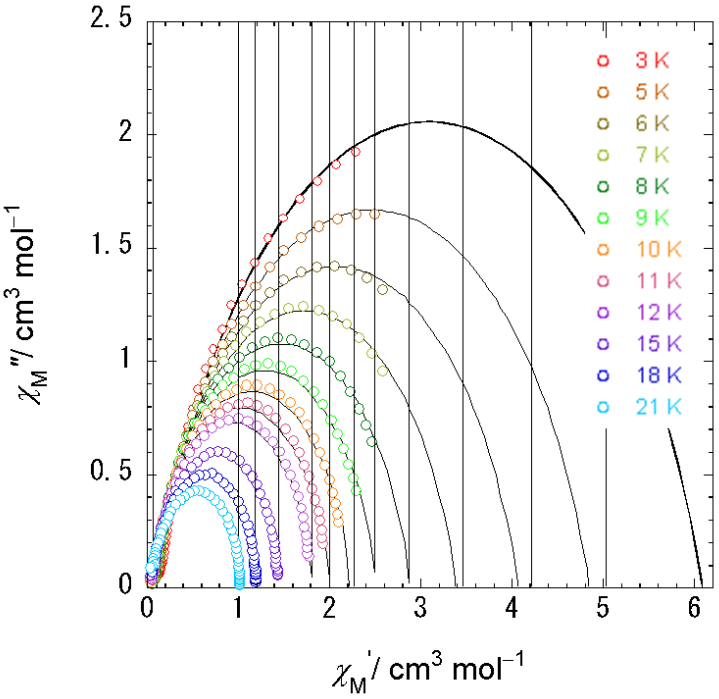

Fig. S5 Argand plot for **1** measured in the *T* range of 3–21 K in a dc field of 0.2 T. The solid lines were fitted by using a generalized Debye model (eq. 5). The fitting parameters are listed in Table S3.

Table S2 Generalized Debye Model (Argand plot analysis) Fitting Parameters in the *T* Range of 3–21 K for a Powder Sample **1** at 0.2 T

T / K	χ_S/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	α
3	0.102	6.091	0.233
5	0.074	4.854	0.224
6	0.061	4.077	0.217
7	0.057	3.397	0.195
8	0.057	2.886	0.171
9	0.052	2.524	0.159
10	0.047	2.244	0.149
11	0.047	2.015	0.136
12	0.046	1.827	0.126
15	0.041	1.451	0.111
18	0.041	1.199	0.091
21	0.037	1.025	0.088

Table S3 Generalized Debye Model Fitting Parameters in the *T* Range of 3–21 K for a Powder Sample **1** at 0.2 T

T / K	χ_S/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	τ / s	α
3	-0.059	5.454	2.150×10^{-1}	0.214
5	0.161	4.816	1.503×10^{-1}	0.213
6	0.213	4.055	9.843×10^{-2}	0.193
7	0.165	3.370	6.307×10^{-2}	0.569
8	0.129	2.866	4.154×10^{-2}	0.143
9	0.311	2.289	2.868×10^{-2}	0.186
10	0.085	2.224	2.041×10^{-2}	0.117
11	0.073	2.005	1.504×10^{-2}	0.109
12	0.066	1.822	1.128×10^{-2}	0.104
15	0.055	1.453	5.615×10^{-3}	0.095
18	0.121	1.134	3.115×10^{-3}	0.136
21	0.041	1.032	1.860×10^{-3}	0.089

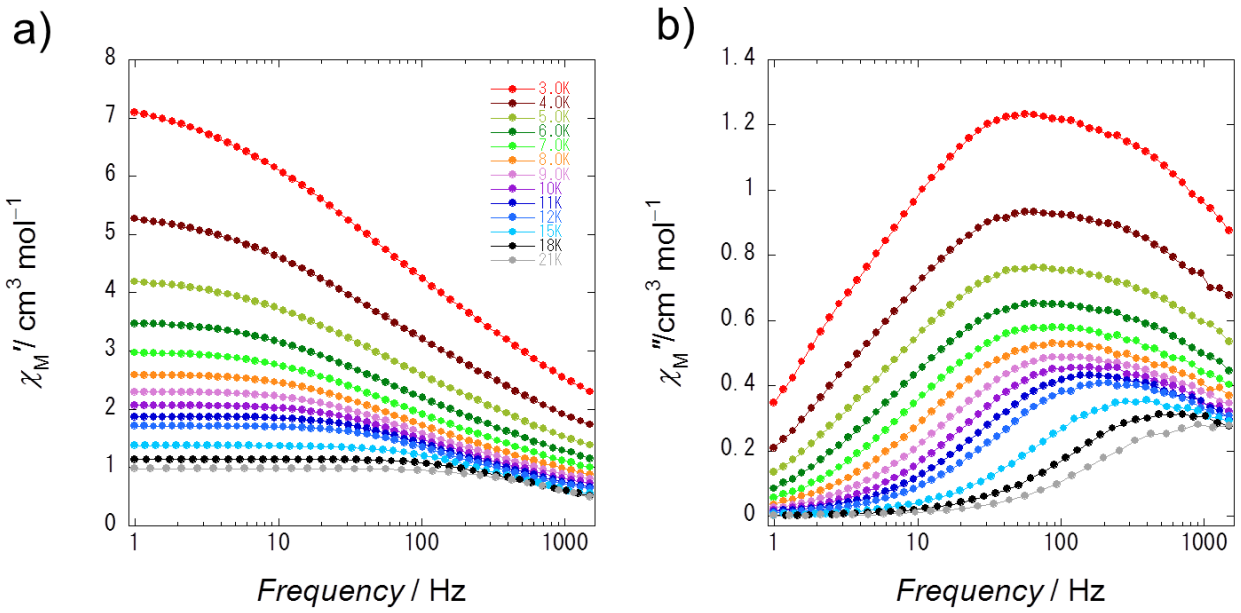

Fig. S6-1 Frequency (*f*) dependence of (a) the real (χ_M') and (b) imaginary (χ_M'') parts of the ac susceptibility of **10** measured between 3 and 21 K in a H_{dc} of zero. The solid lines are guides only.

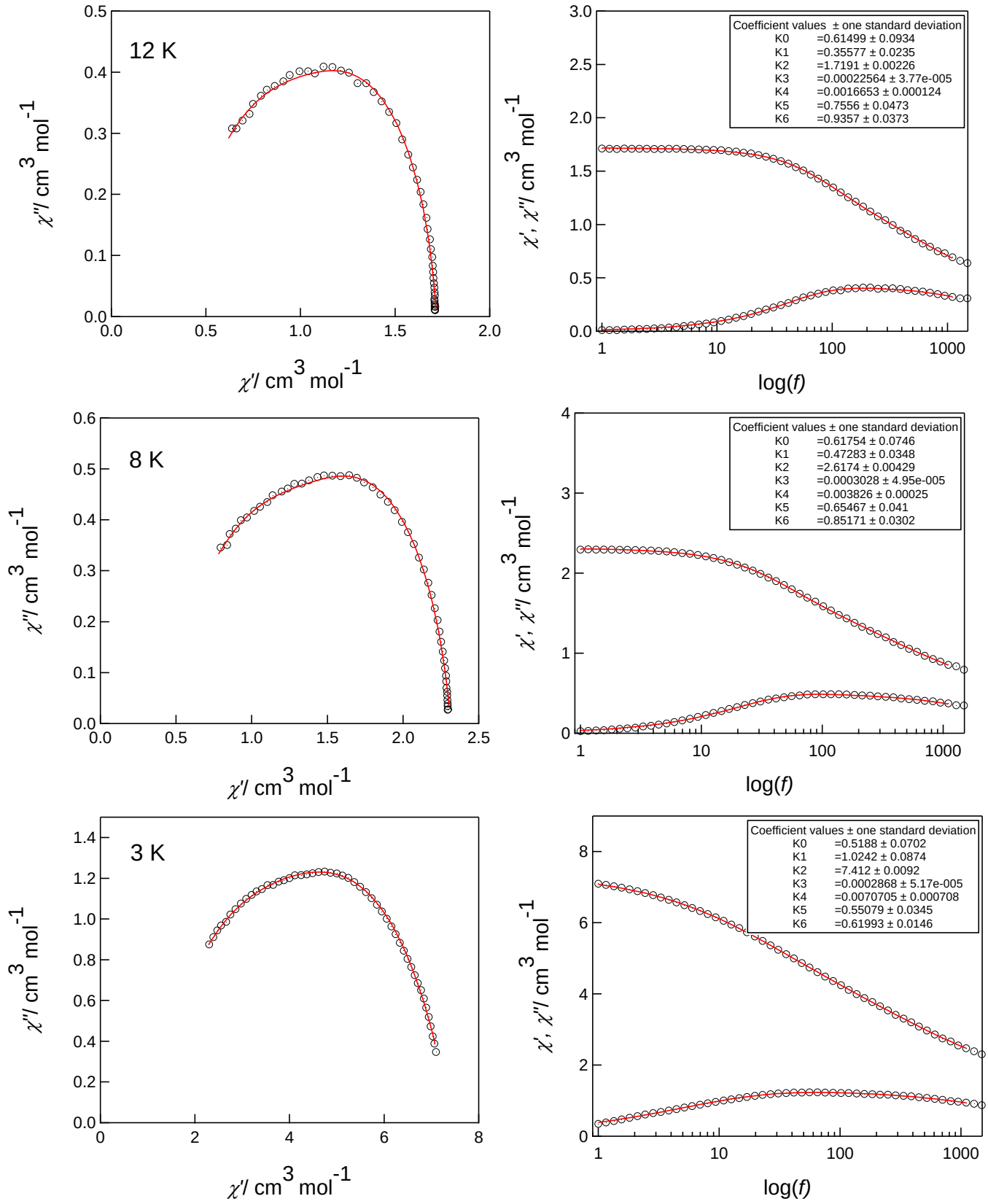

Fig. S6-2 Selected frequency dependence of the ac magnetic susceptibility for **10** measured in the *T* range of 3–21 K (right) and Argand plots (left). The red solid lines were fitted by using an extended Debye model (eq. 1). The fitting parameters are listed in Table S4.

Table S4 Extended Debye Model Fitting Parameters in the *T* Range of 3–21 K for a Powder Sample **10** at 0 T.

T / K	χ_s/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	τ_1 / s	α_1	τ_2 / s	α_2	β
3	1.024	7.412	2.868×10^{-4}	0.551	7.071×10^{-3}	0.619	0.519
4	0.743	5.369	3.666×10^{-4}	0.534	7.121×10^{-3}	0.691	0.631
5	0.647	4.286	3.537×10^{-4}	0.565	6.283×10^{-3}	0.730	0.626
6	0.618	3.536	3.822×10^{-4}	0.604	5.815×10^{-3}	0.783	0.637
7	0.532	3.009	3.345×10^{-4}	0.626	4.703×10^{-3}	0.819	0.625
8	0.473	2.617	3.028×10^{-4}	0.655	3.826×10^{-3}	0.852	0.618
9	0.438	2.317	2.816×10^{-4}	0.684	3.092×10^{-3}	0.879	0.610
10	0.421	2.078	2.832×10^{-4}	0.710	2.545×10^{-3}	0.912	0.621
11	0.393	1.883	2.491×10^{-4}	0.746	2.067×10^{-3}	0.921	0.604
12	0.356	1.719	2.256×10^{-4}	0.756	1.665×10^{-3}	0.936	0.615
15	0.307	1.375	1.534×10^{-4}	0.847	9.229×10^{-4}	0.945	0.552
18	0.281	1.143	1.536×10^{-4}	0.874	7.111×10^{-4}	1.015	0.702
21	0.297	0.979	9.698×10^{-5}	1.102	4.028×10^{-4}	0.967	0.452

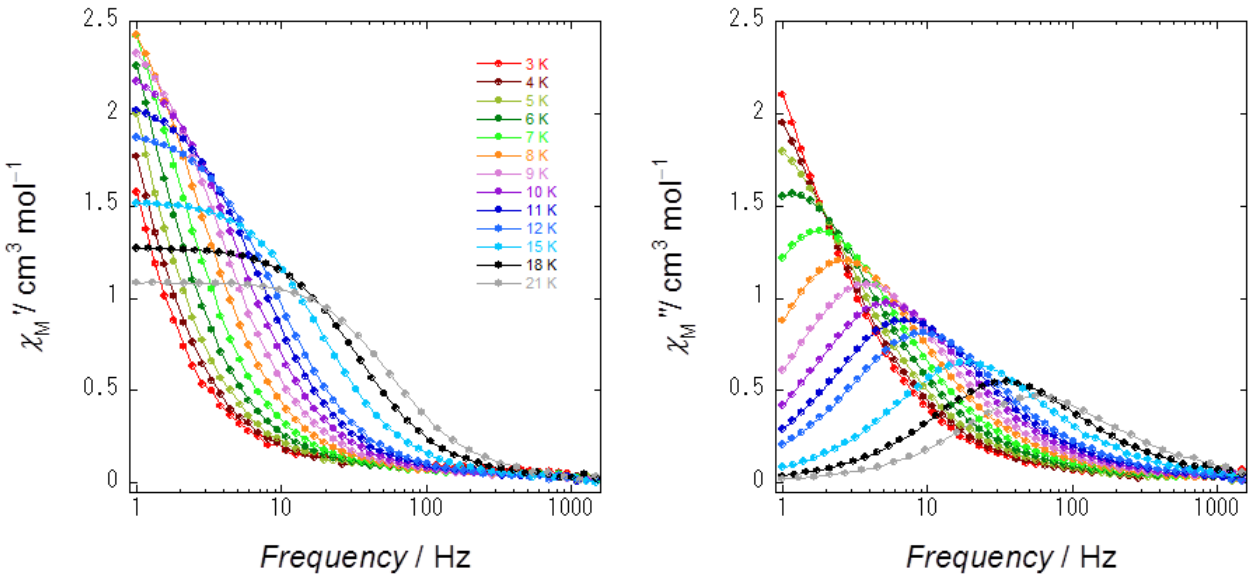

Fig. S6-3 Frequency (*f*) dependence of (a) the real (χ_M') and (b) imaginary (χ_M'') parts of the ac susceptibility of **10** measured between 3 and 21 K in a H_{dc} of 0.2 T. The solid lines are guides only.

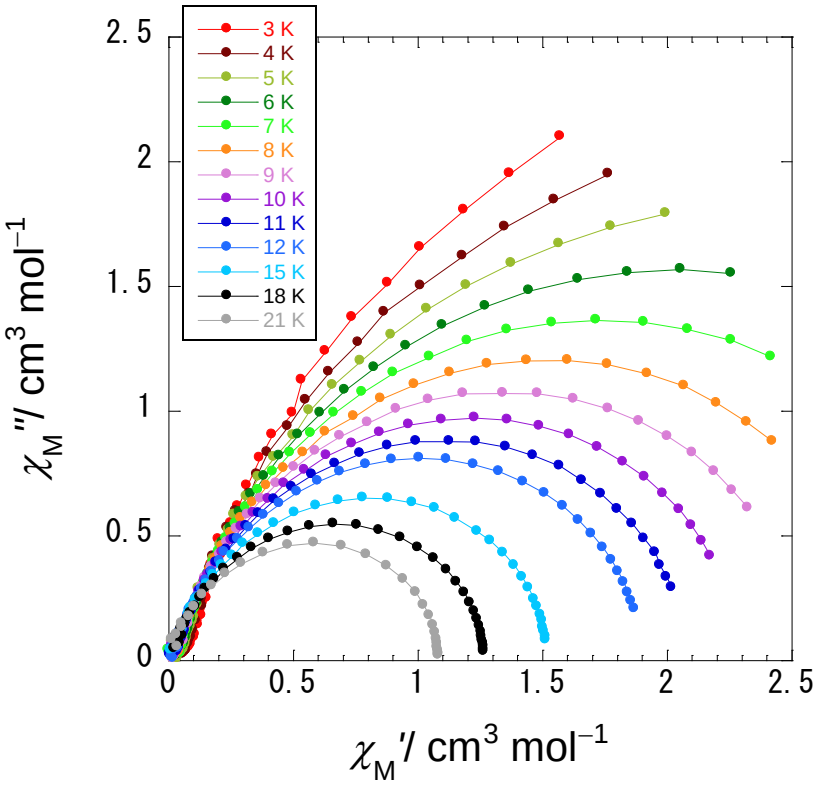

Fig. S6-4 Argand plot for **10** measured in the *T* range of 3–21 K in a dc field of 0.2 T. The solid lines are guides only. These datas are fitted by using a generalized Debye model (eq. 5) and the fitting parameters are listed in Table S3.

Table S5 Generalized Debye Model (Argand plot analysis) Fitting Parameters in the *T* Range of 3–21 K for a Powder Sample **10** at 0.2 T

T / K	χ_s/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	α
3	0.054	7.965	0.186
4	0.045	6.062	0.181
5	0.036	4.993	0.179
6	0.033	4.172	0.169
7	0.026	3.602	0.172
8	0.027	3.048	0.151
9	0.022	2.687	0.148
10	0.021	2.388	0.140
11	0.017	2.163	0.144
12	0.018	1.954	0.128
15	0.007	1.555	0.132
18	0.021	1.281	0.097
21	0.009	1.094	0.097

Table S6 Generalized Debye Model Fitting Parameters in the *T* Range of 1.8–5 K for a Powder Sample **2** at zero

T / K	χ_s/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	τ / s	α
1.8	0.494	15.006	4.379×10^{-3}	0.278
2.0	0.487	13.014	3.869×10^{-3}	0.272
2.2	0.623	11.877	3.412×10^{-3}	0.267
2.4	0.459	10.541	2.833×10^{-3}	0.264
2.6	0.567	9.733	2.252×10^{-3}	0.264
2.8	0.540	8.960	1.716×10^{-3}	0.269
3.0	0.349	8.151	1.262×10^{-3}	0.280
3.2	0.365	7.635	9.066×10^{-4}	0.293
3.4	0.357	7.143	6.439×10^{-4}	0.304
3.6	0.340	6.659	4.603×10^{-4}	0.312
3.8	0.425	6.275	3.339×10^{-4}	0.315
4.0	0.564	5.936	2.500×10^{-4}	0.314
4.2	0.709	5.590	1.944×10^{-4}	0.307
4.4	0.971	5.329	1.590×10^{-4}	0.294
4.6	1.069	4.930	1.343×10^{-4}	0.279
4.8	1.046	4.454	1.152×10^{-4}	0.265
5.0	1.055	4.045	1.019×10^{-4}	0.248

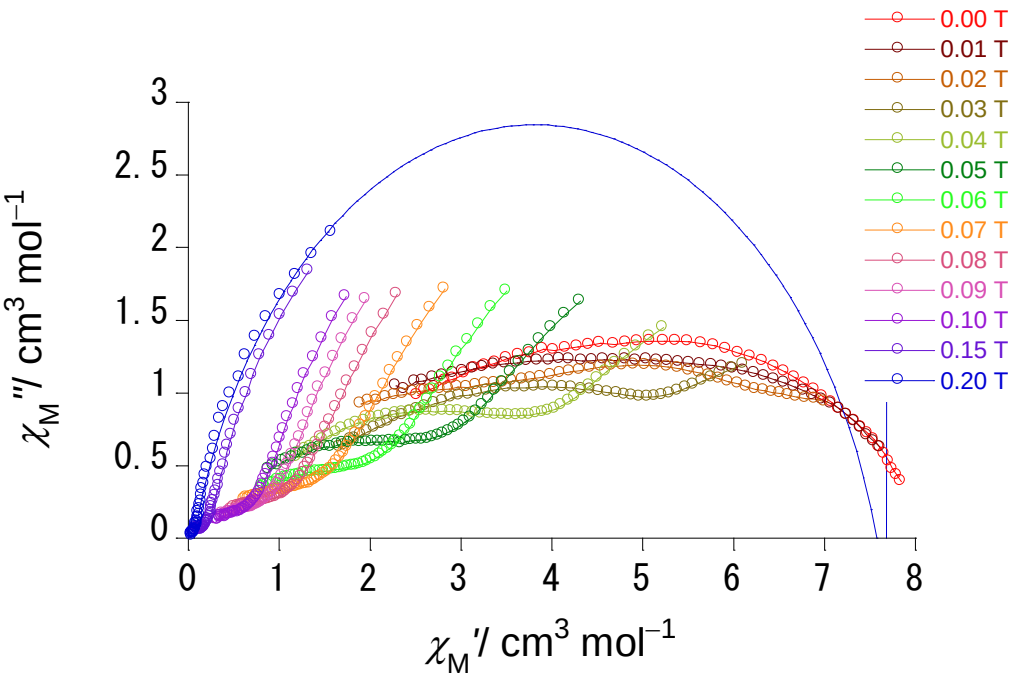

Fig. S6-5 An Argand plot of **10** measured in fields between 0 and 0.2 T at 3 K. The solid lines are guides only. In the case of a H_{dc} of 0.2 T, the solid line was fitted by using a generalized Debye model (eq. 5).

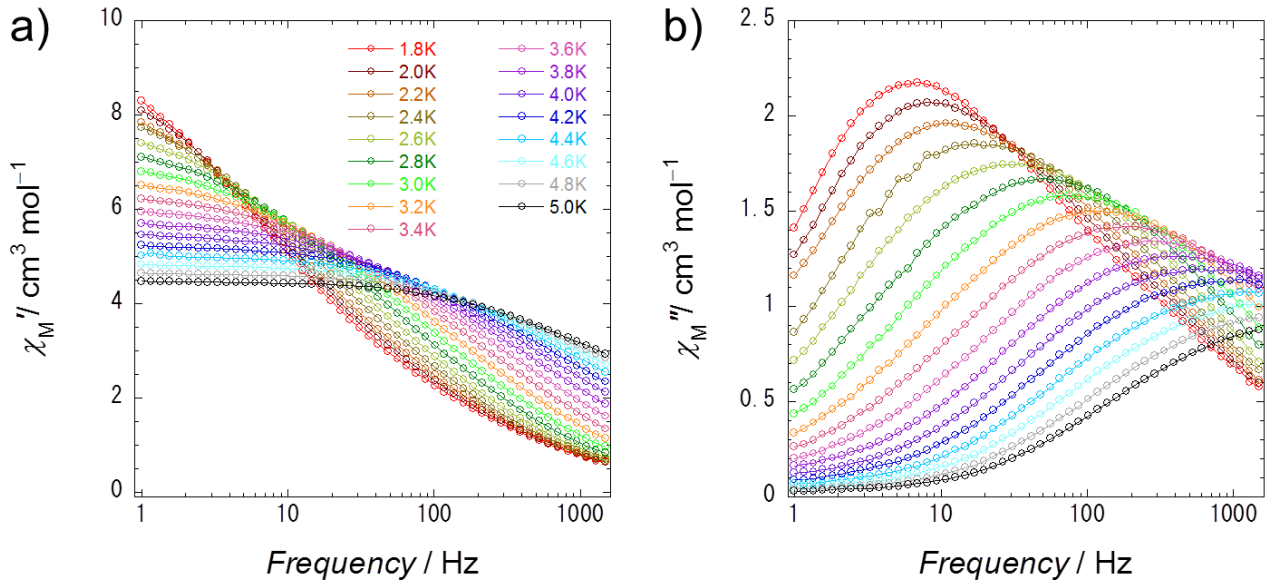

Fig. S7 Frequency (f) dependence of (a) the real (χ_M') and (b) imaginary (χ_M'') parts of the ac susceptibility of **2** measured between 3 and 21 K in a H_{dc} of 0.2 T. The solid lines are guides only.

Table S7 Generalized Debye Model Fitting Parameters in the T Range of 1.8–5 K for a Powder Sample **2** at 0.2 T

T / K	χ_s/cm^3 mol^{-1}	χ_T/cm^3 mol^{-1}	τ / s	α
1.8	-0.018	10.631	1.895×10^{-2}	0.520
2.0	-0.085	10.085	1.410×10^{-2}	0.517
2.2	-0.148	9.648	1.069×10^{-2}	0.518
2.4	-0.378	8.578	6.741×10^{-3}	0.497
2.6	-0.474	7.974	4.486×10^{-3}	0.494
2.8	-0.123	7.823	2.917×10^{-3}	0.488
3.0	-0.311	7.171	1.903×10^{-3}	0.484
3.2	-0.012	7.042	1.248×10^{-3}	0.481
3.4	0.049	6.682	8.309×10^{-4}	0.477
3.6	0.034	6.196	5.767×10^{-4}	0.468
3.8	0.188	5.912	4.078×10^{-4}	0.459
4.0	0.108	5.332	3.115×10^{-4}	0.443
4.2	0.173	4.907	2.479×10^{-4}	0.425
4.4	0.265	4.504	2.049×10^{-4}	0.404
4.6	0.302	4.098	1.727×10^{-4}	0.384
4.8	0.414	3.766	1.522×10^{-4}	0.361
5.0	0.203	3.197	1.322×10^{-4}	0.341

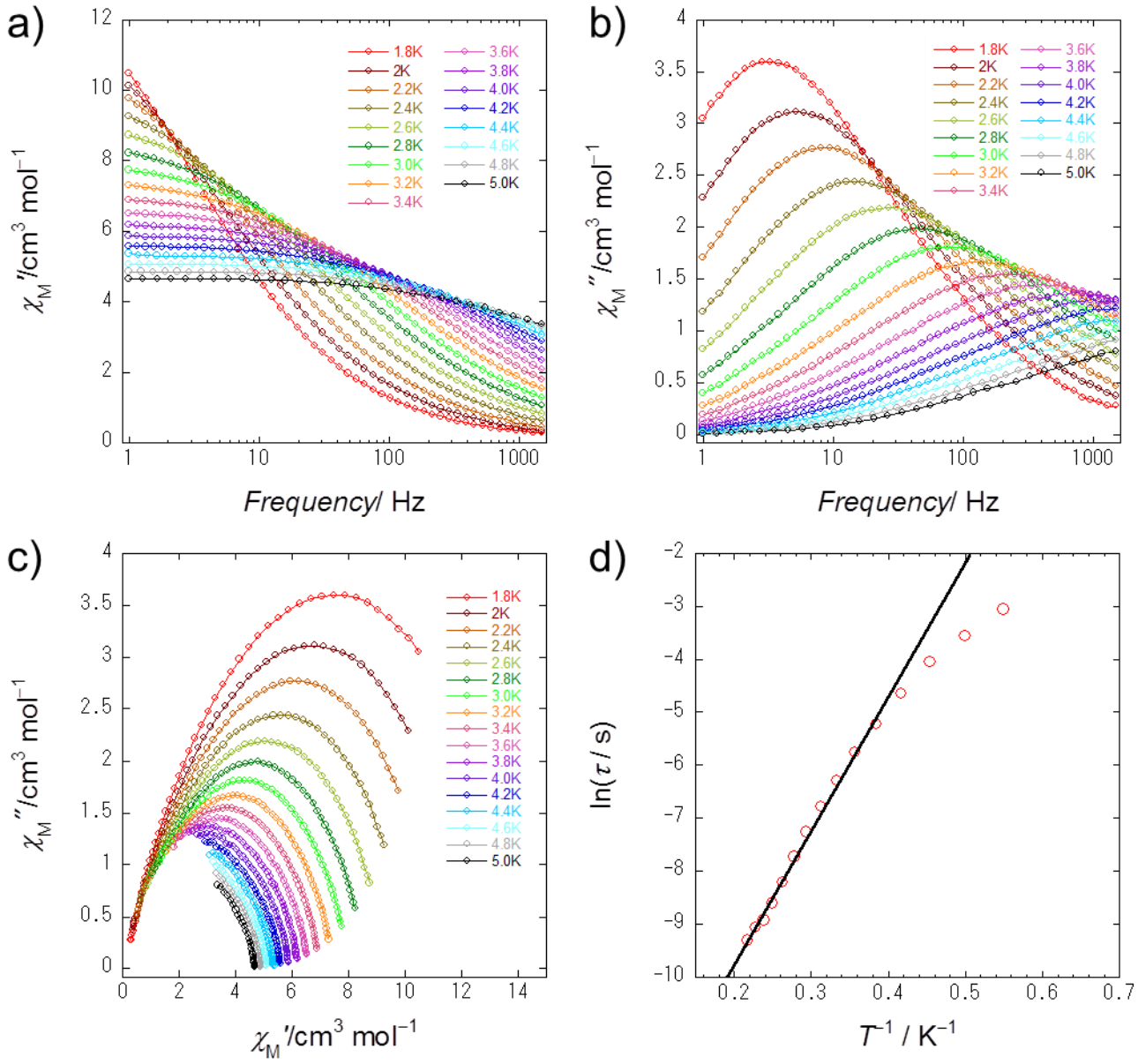

Fig. S8 Frequency (f) dependence of (a) the real (χ_M') and (b) imaginary (χ_M'') parts of the ac susceptibility of **2** measured between 1.8 and 5 K in a H_{dc} of zero. The solid lines are guides only. (c) Argand plot for **2** measured in the T range of 1.8–5 K in a dc field of zero. The solid lines are guides only. (d) τ was obtained from least-squares fitting using the generalized Debye model (eq. 5). The solid lines represents a least-square fit of the data in the high temperature region using the equation $\tau = \tau_0 \exp(\Delta/k_B T)$ with kinetic parameters (Δ/hc = 17 cm^{-1} with $\tau_0 = 4.6 \times 10^{-7}$ s).