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Electronic Supporting Information

Slow magnetic relaxation in five-coordinate spin-crossover cobalt(II) complexes

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1. Materials and Physical Measurements.

All chemicals were purchased from commercial sources and used without further purification. The reactions were carried out using standard Schlenk techniques under nitrogen atmosphere. The solvents used were dried and purified. 1, 4, 7, 10-Tetramethyl-1, 4, 7, 10-tetraazacyclododecane (12-TMC) were synthesized according to literature procedure.[S1] Elemental analyses for C, H, and N were performed on a Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-Kα). Inductively coupled plasma-optical emission spectrometry (ICP OES-Optima 5300DV, PerkinElmer Inc., Waltham, MA, USA) was employed to confirm the ratio of Zn: Co in the diluted samples.

Magnetic susceptibility measurements were performed using a vibrating sample magnetometer (VSM) of Quantum Design MPMS SQUID-VSM system. Measurements on **1**, **2** and the diluted compounds **1’** and **2’** were operated with ground microcrystalline powders within a polycarbonate plastic capsule. Variable temperature direct-current susceptibility data were collected between 1.8 and 400 K under a field of 1000 Oe. The field-dependent magnetizations were measured in a range of 1-7 T between 1.8 and 5.0 K at applied magnetic fields. The alternative-current magnetic susceptibility were measured in the temperature range 1.8 K to 6.0 K under an external dc fields of 2500 Oe using an oscillating ac field of 2.0 Oe at ac frequencies ranging from 1 to 1000 Hz. The data were collected for diamagnetic contribution from the sample holder, as well as for the sample itself estimated from Pascal's constant.[S2]

2. Synthesis

[Co(12-TMC)(CH_3CN)](BF_4)$_2$ (**1**).

A solution of $AgBF_4$ (2.0 mmol, 0.40 g) in 10 mL of CH_3CN was added to a solution of $CoCl_2$ (1.0 mmol, 0.13 g) in 10 mL of CH_3CN. After the resulting solid AgCl was separated, 12-TMC (0.8 mmol, 0.20 g) was added to the filtrate. The reaction mixture was stirred at room temperature for 3 h, filtrated, and allowed the solution to evaporate to give the reddish brown crystals of **1** with a yield of 65 % based on Co. Anal. Calc. for $C_{14}H_{31}B_2CoN_5F_8$: C, 33.50; H, 6.22; N, 13.95. Found: C, 33.11; H, 6.18; N, 13.88.

[Co(12-TMC)(CH_3CN)](PF_6)$_2$ (**2**)

Compound **2** was prepared by the same procedure as **1**, but using $AgPF_6$ (2.0 mmol, 0.50 g) instead of $AgBF_4$ (2.0 mmol, 0.40 g). The reddish brown crystals of **2** were obtained in 70% yield based on Co. Anal. Calcd. for $C_{14}H_{31}CoF_{12}N_5P_2$: C, 27.20; H, 5.05; N, 11.33. Found: C, 26.89; H, 4.96; N, 11.21.

[Zn(12-TMC)(CH_3CN)](BF_4)$_2$ (**3**)

Compound **3** was prepared by the same procedure as **1**, but using ZnI_2 (1.0 mmol, 0.32 g) instead of $CoCl_2$ (1.0 mmol, 0.13 g). The colorless crystals of **3** were obtained in 71% yield based on Zn. Anal. Calcd. for $C_{14}H_{31}B_2F_8N_5Zn$: C, 33.07; H, 6.15; N, 13.77. Found: C, 33.01; H, 6.15; N, 13.69.

[Zn(12-TMC)(CH_3CN)](PF_6)$_2$ (**4**)

Compound **4** was prepared by the same procedure as **3**, but using $AgPF_6$ (2.0 mmol, 0.50 g) instead of $AgBF_4$ (2.0 mmol, 0.40 g). The colorless crystals of **4** were obtained in 75% yield based on Zn. Anal. Calcd. for $C_{14}H_{31}F_{12}N_5P_2Zn$: C, 26.91; H, 5.00; N, 11.21. Found: C, 26.89; H, 5.00; N, 11.20.

[$Co_{0.2}Zn_{0.8}$(12-TMC)(CH_3CN)](A)$_2$ (A = BF_4, **1'**; A = PF_6, **2'**)

The diluted samples **1'** and **2'** were prepared by dissolving the crystals of [Co(12-

TMC)(CH_3CN)](A)$_2$ and [Zn(12-TMC)(CH_3CN)](A)$_2$ with ratio of 1:4. The reaction mixture was stirred at room temperature for 3 h and filtrated. The light reddish brown crystals were obtained from the diffusion of diethyl ether into acetonitrile solution with a yield of 50 %. Successful dilution was confirmed by XRD (Figure S5 and S6) and ICP data.

3. X-ray structure determination

X-ray diffraction data for **1** and **2** were collected using a Bruker D8 ADVANCE diffractometer with a CCD area detector (Mo Kα radiation) at low temperature. The APEXII program was used for collecting frames of data and determining lattice parameters. Data were integrated through the SAINT.[S3] The structures were solved using SHELXS-97 and subsequently completed by Fourier recycling using the SHELXL 97 program.[S4] All non-hydrogen atoms were refined using anisotropic displacement parameters. Crystallographic data and refinement parameters for **1**, **2** are listed in Table S1.

We have attempted to solve the crystal structures of **3** and **4**. Unfortunately, the crystal structures of **3** and **4** were not fully refined due to the high disorder of the carbons atom and the poor quality of diffraction data, but the molecular structures (Figure S2) and crystal parameters have been definitely determined as shown in the following: **3** (a = 8.7620(7) Å, b = 8.7620(7) Å, c = 14.410(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *P4/nmm*) and **4** (a = 9.1402(12) Å, b = 9.1402(12) Å, c = 30.212(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *P4/ncc*).

Table S1. Crystal data of 1 and 2.

	1	**2**
CCDC No.	1546344	1546345
Empirical formula	$C_{14}H_{31}B_2CoN_5F_8$	$C_{14}H_{31}CoF_{12}N_5P_2$
Molecular weight	501.99	618.31
Temperature (K)	155	155
Crystal system	Orthorhombic	Tetragonal
Space group	*Pmn2(1)*	*P-42(1)m*
a / Å	8.794(5)	9.1662(8)
b / Å	14.351(8)	9.1662(8)
c / Å	16.856(9)	14.722(2)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V / Å^3	2127(2)	1237.0(3)
Z	4	2
D_{calc}, g/cm^3	1.567	1.660
μ / mm^{-1}	0.886	0.926
F (000)	1036	630
θ rang (deg)	2.61 /27.29	2.62 /27.39
Goodness-of-fit on F^2	1.185	1.168
$R1$, $wR2$(all data)	0.0754 / 0.2159	0.0770 / 0.2290
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0715 / 0.2127	0.0723 / 0.2242

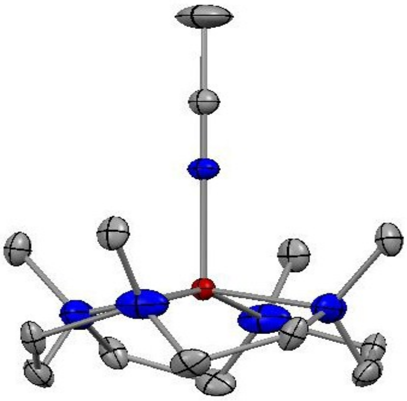


Figure S1 Molecular structure of complex **2**. All hydrogen atoms are omitted for clarity. Red, blue, and gray spheres represent Co, N, and C atoms, respectively.

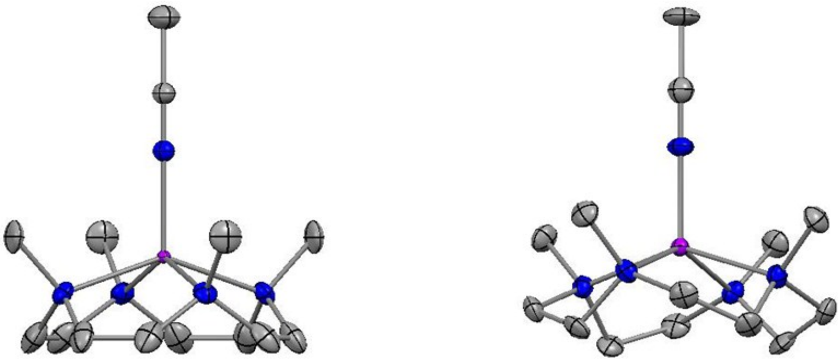


Figure S2 Molecular structure of complexes **3** (left) and **4** (right). All hydrogen atoms are omitted for clarity. Purple, blue, and gray spheres represent Zn, N, and C atoms, respectively.

Table S2. The results of the continuous shape measure (CSM) analyses of Co(12-TMC)$^{2+}$ in **1** and **2** by SHAPE software[S5].

CSM		**1**	**2**
Five-vertex	Pentagon	32.371	33.089
	Vacant octahedron	1.002	1.283
	Trigonal bipyramid	5.541	5.458
	Square pyramid	0.234	0.036
	Johnson trigonal bipyramid	7.868	8.158

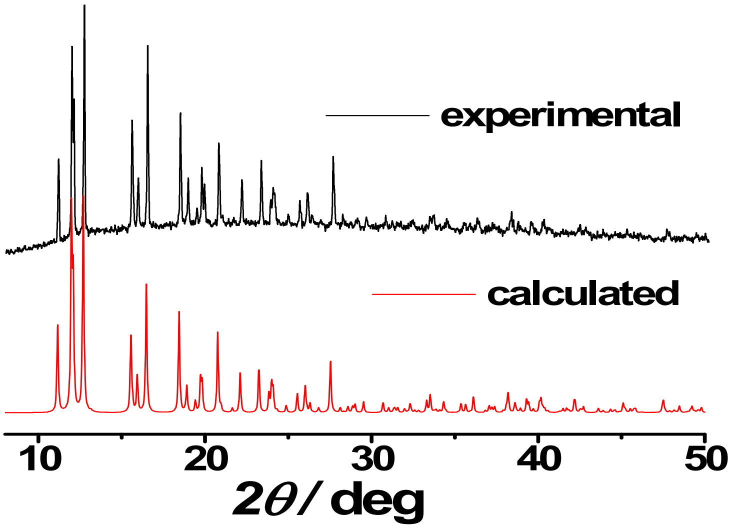


Figure S3 XRD patterns for complex **1**.

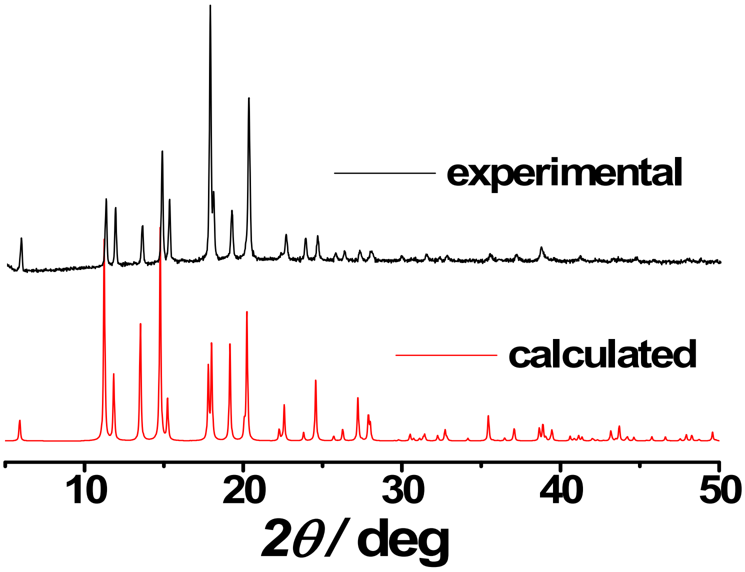


Figure S4 XRD patterns for complex **2**.

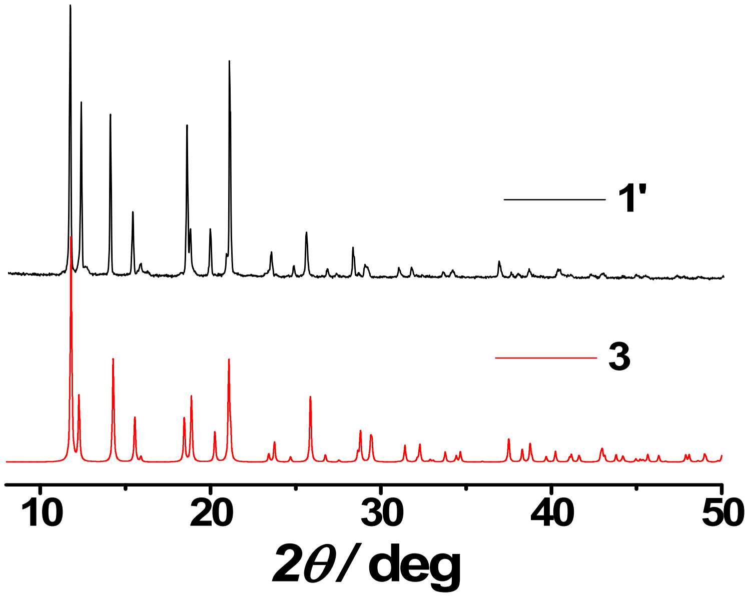


Figure S5 Powder XRD patterns for **1’** and **3**.

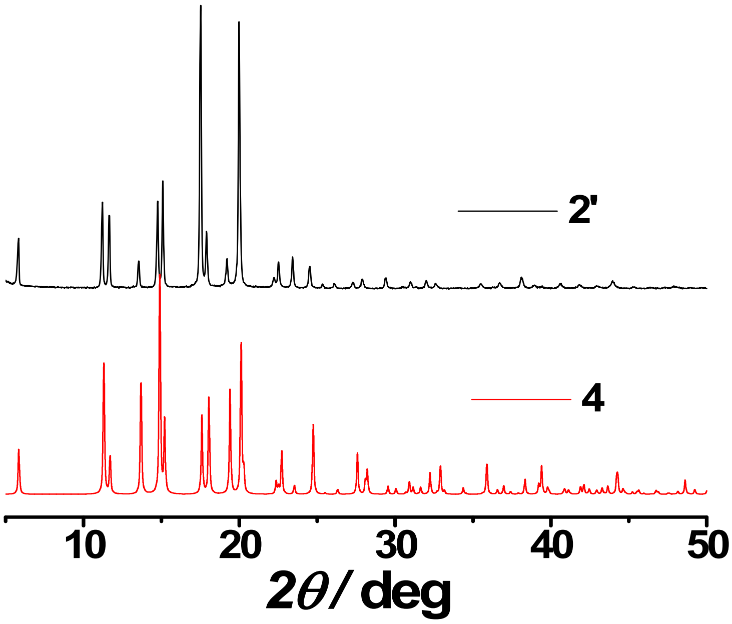


Figure S6 Powder XRD patterns for **2’** and **4.**

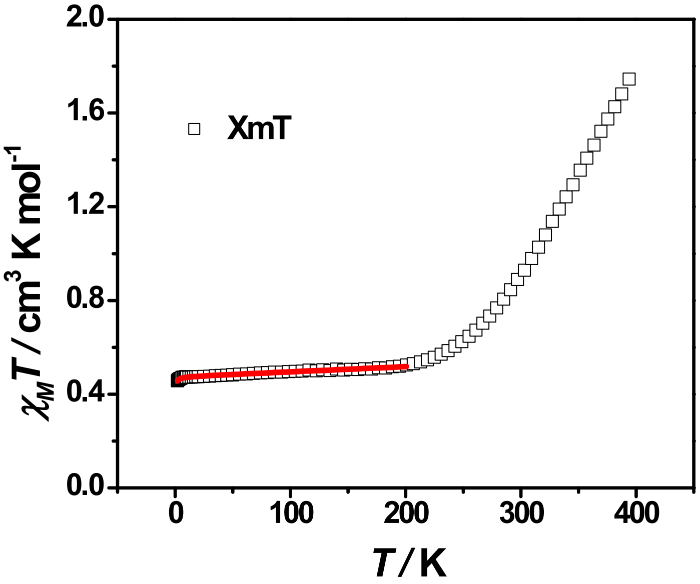


Figure S7 Variable-temperature dc susceptibility data under 1000 Oe applied dc field of **2**. The solid lines are fits to the data with the program PHI.[S6]

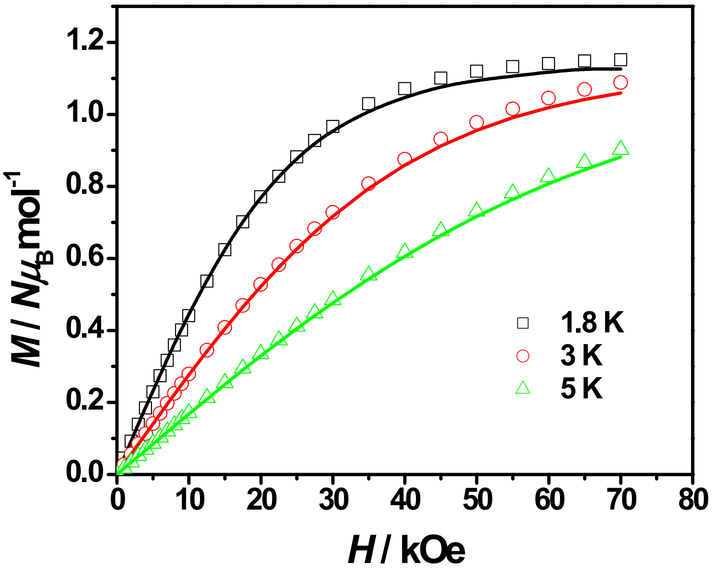


Figure S8 The magnetization measurements in the field range 0-7 T below 5 K for complex **2**. The solid lines are fits to the data with the program PHI.[S6]

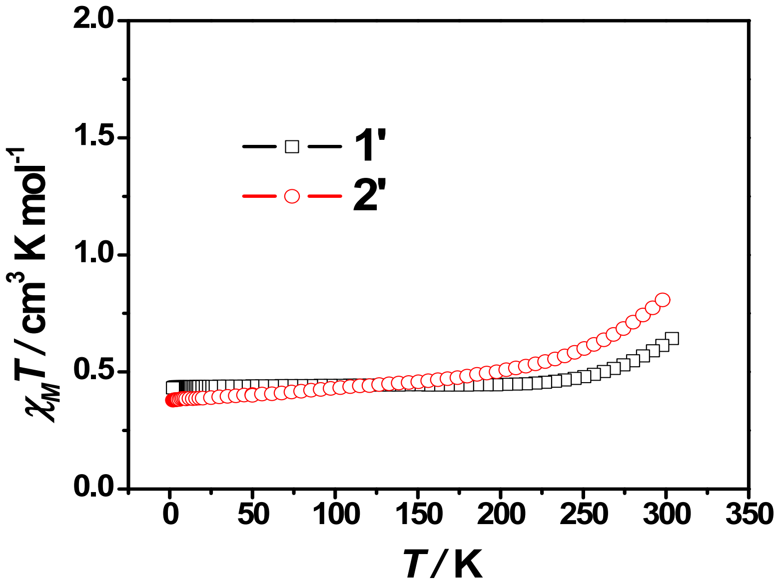


Figure S9 Variable-temperature dc susceptibility data under 1000 Oe applied dc field of **1’** and **2’**.

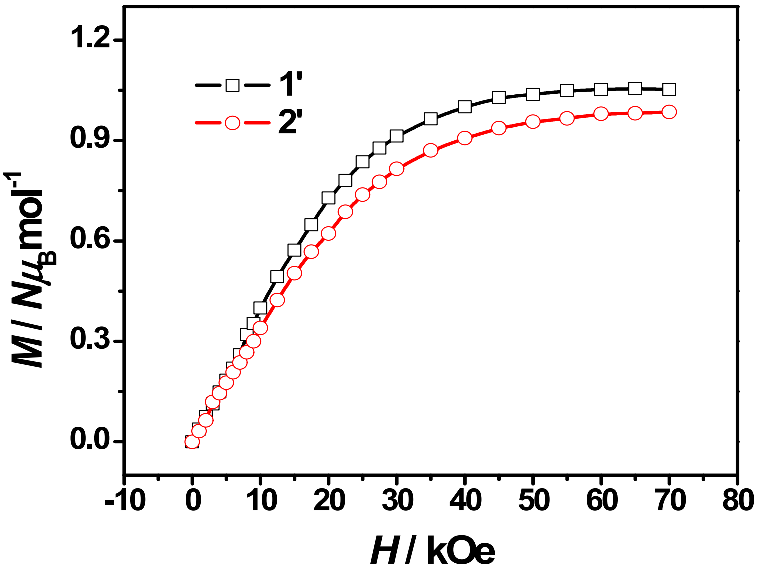


Figure S10 The magnetization measurements in the field range 0-7 T at 1.8K for complexes **1’** and **2’**. The solid lines are for eye guide.

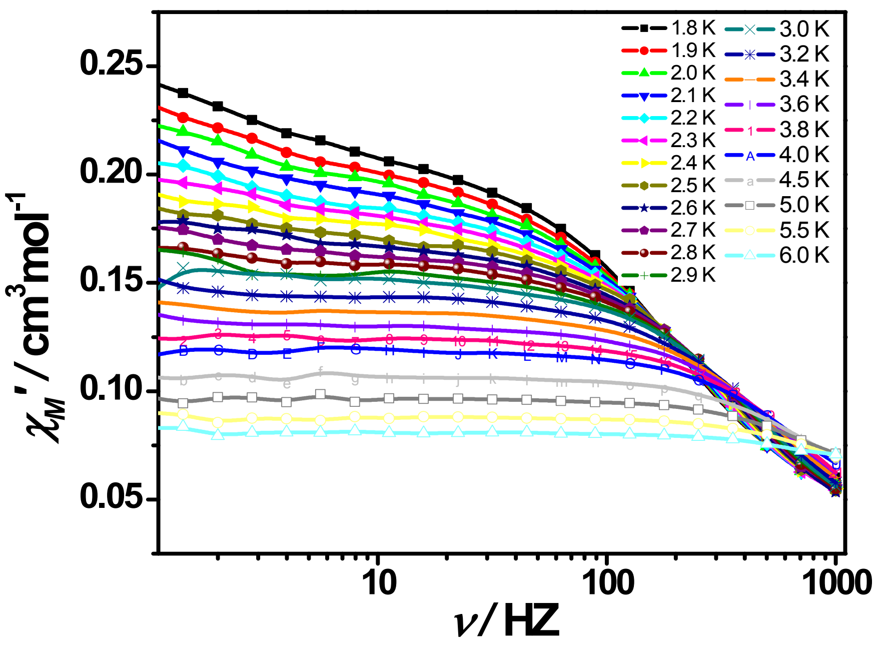


Figure S11 Temperature dependence of in-of-phase ($\chi_M{}'$) at different temperature under a 2500 Oe dc field for **1**. The solid lines are for eye guide.

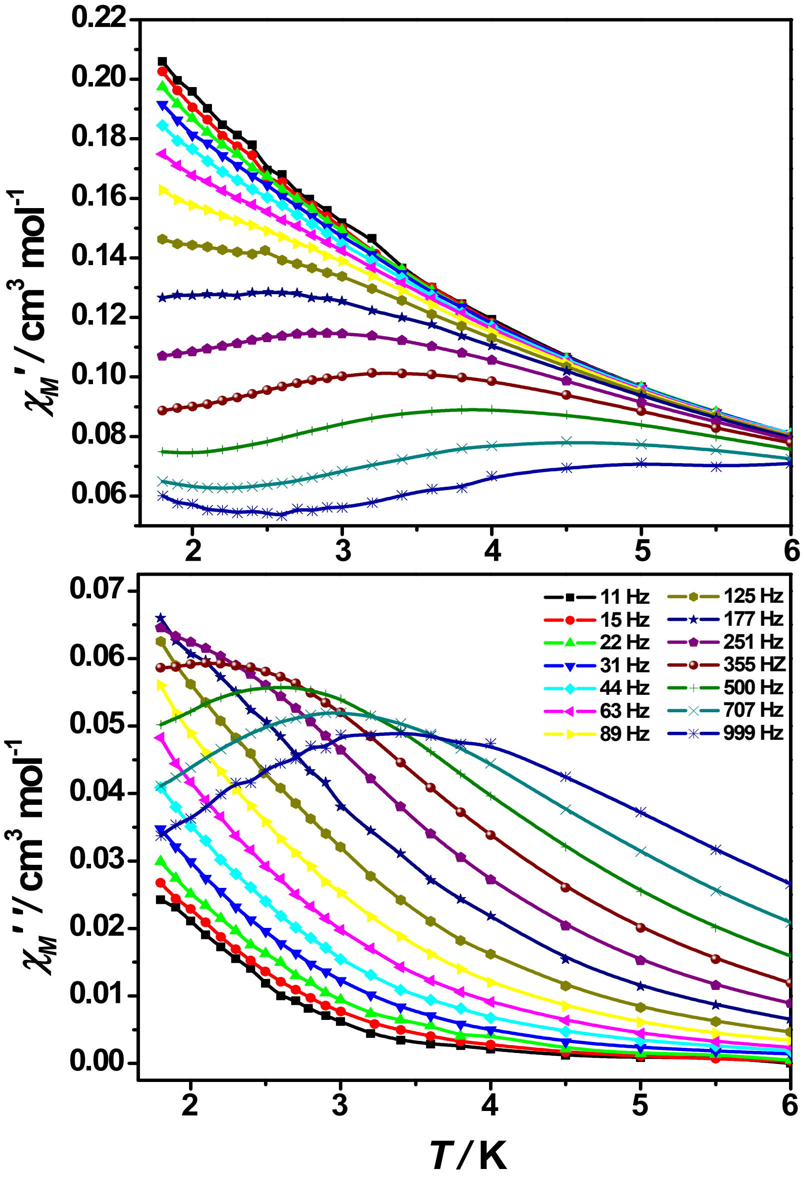


Figure S12 Temperature dependence of in-of-phase ($\chi_M{}'$) and out-of-phase ac susceptibility ($\chi_M{}''$) at different ac frequency under a 2500 Oe dc field for **1**. The solid lines are for eye guide.

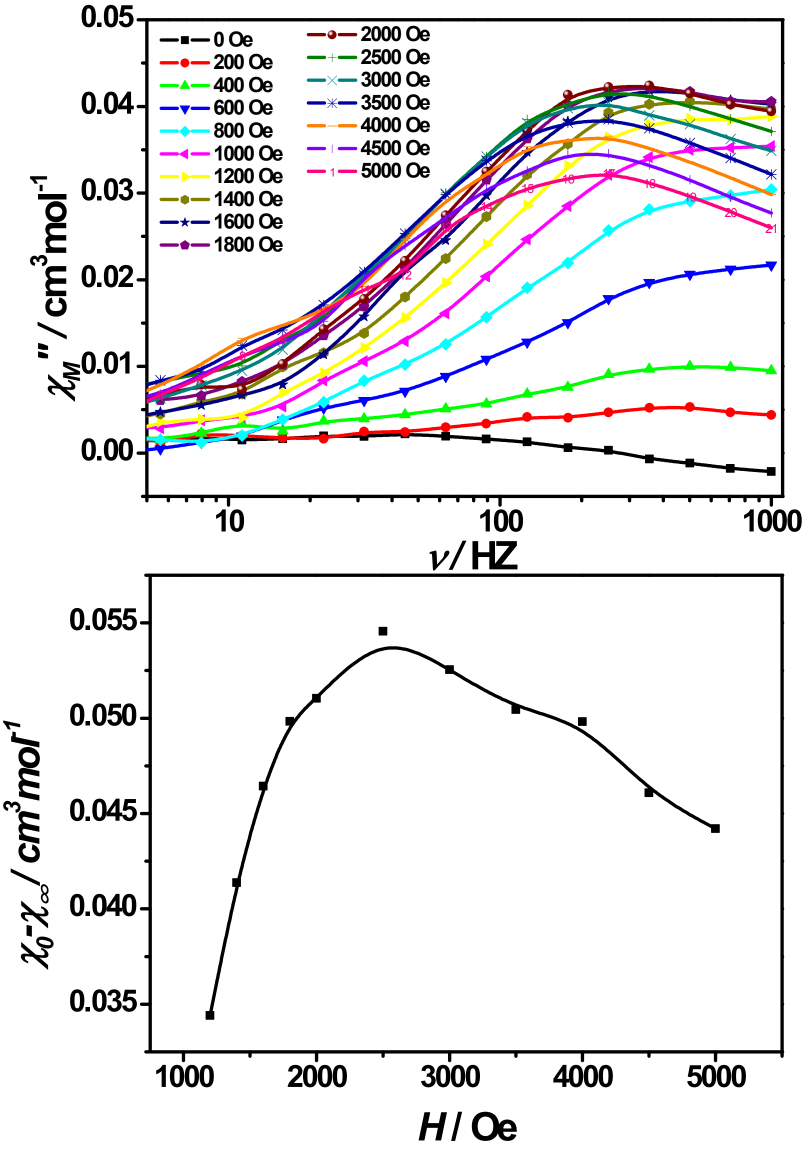


Figure S13 Frequency dependence of out-of-phase (χ_M'') ac susceptibility at 1.8 K under the different applied static fields from 0 to 5000 Oe and field dependence of the magnetic parameters collected from the χ_M' vs. ν for **2**. The solid lines are for eye guide.

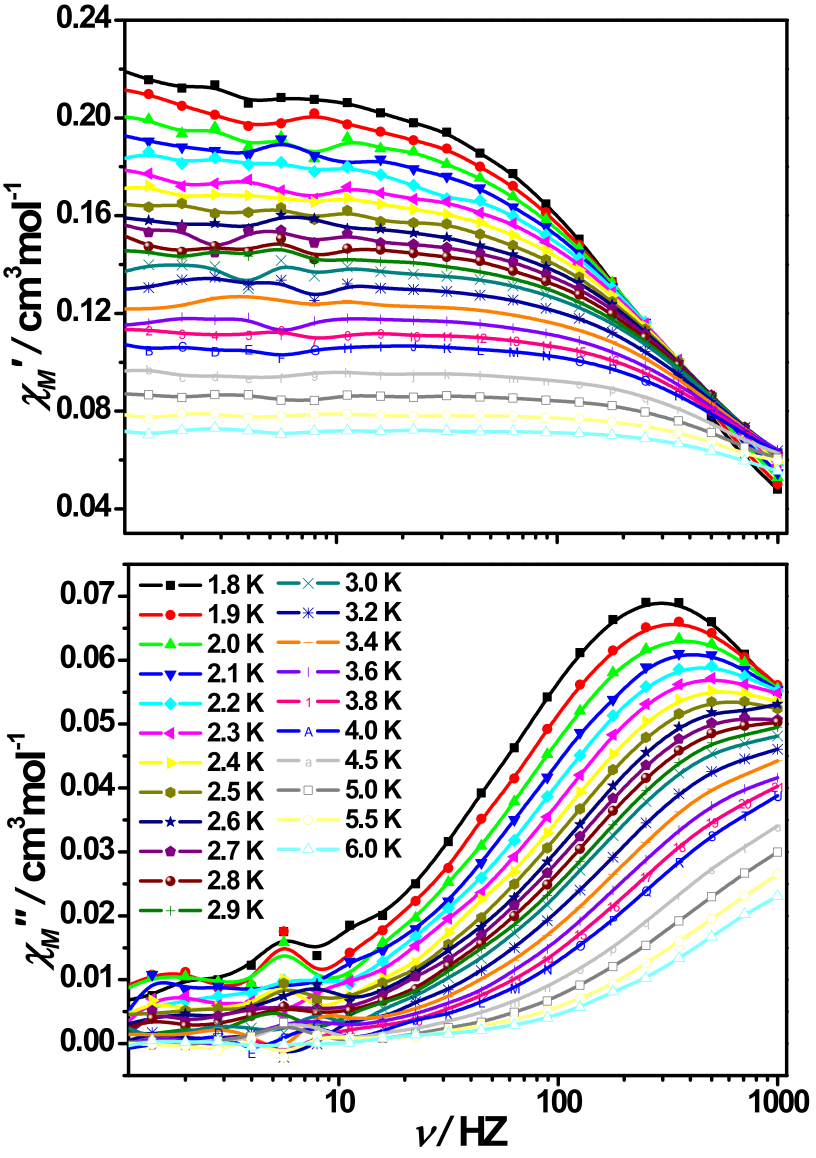


Figure S14 Frequency dependence of the ac susceptibility from 1.8 to 6.0 K under 2500 Oe dc field for **2**. The solid lines are for eye guide.

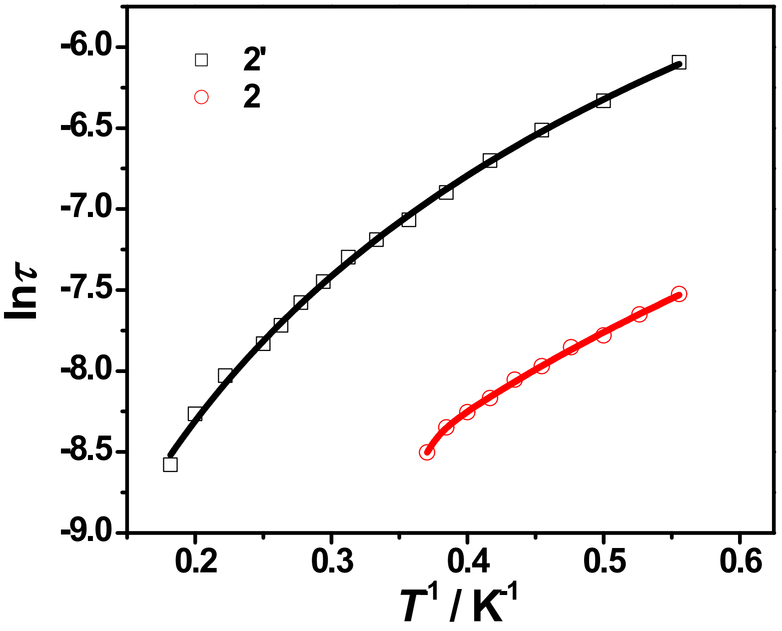


Figure S15 Relaxation time of the magnetization ln(τ) vs T^{-1} plot under 2500 Oe for **2** and those diluted in a matrix of [Zn(12-TMC)(CH_3CN)]$(X)_2$ under the same field. The solid lines fit by eqn (1). The data was collected from the maximum of χ_M'' against frequency at different temperature.

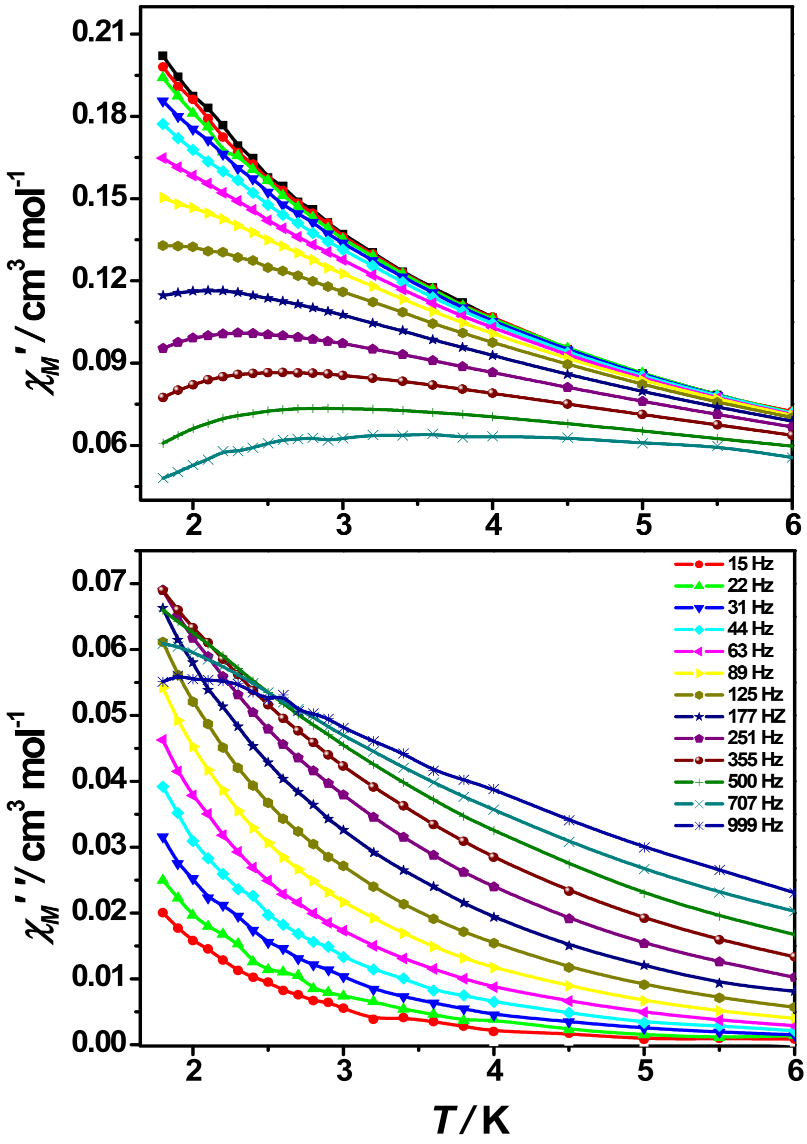


Figure S16 Temperature dependence of in-of-phase (χ_M') and out-of-phase ac susceptibility (χ_M'') at different ac frequency under a 2500 Oe dc field for **2**. The solid lines are for eye guide.

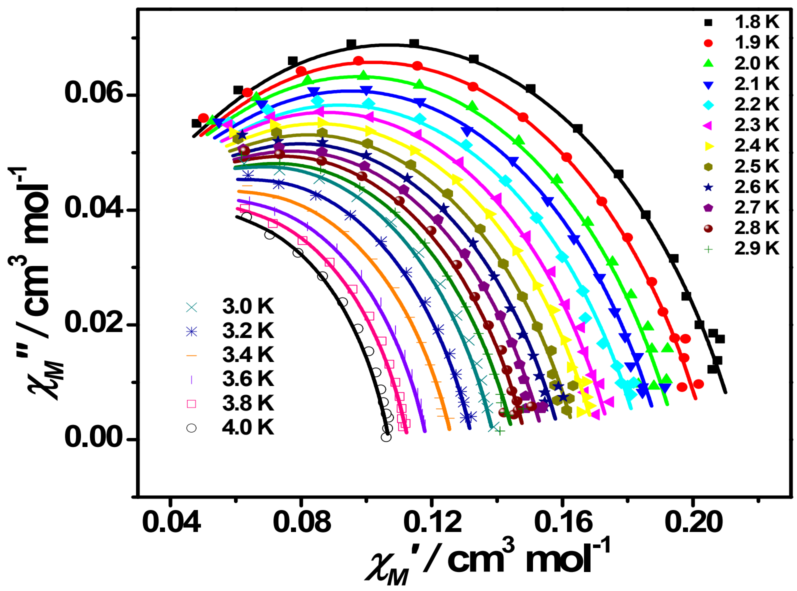


Figure S17 Cole-Cole plot obtained from the ac susceptibility data under 2500 Oe dc field in the temperature range of 1.8-4.0 K for **2**. Solid lines represent the best fits to a generalized Debye model.

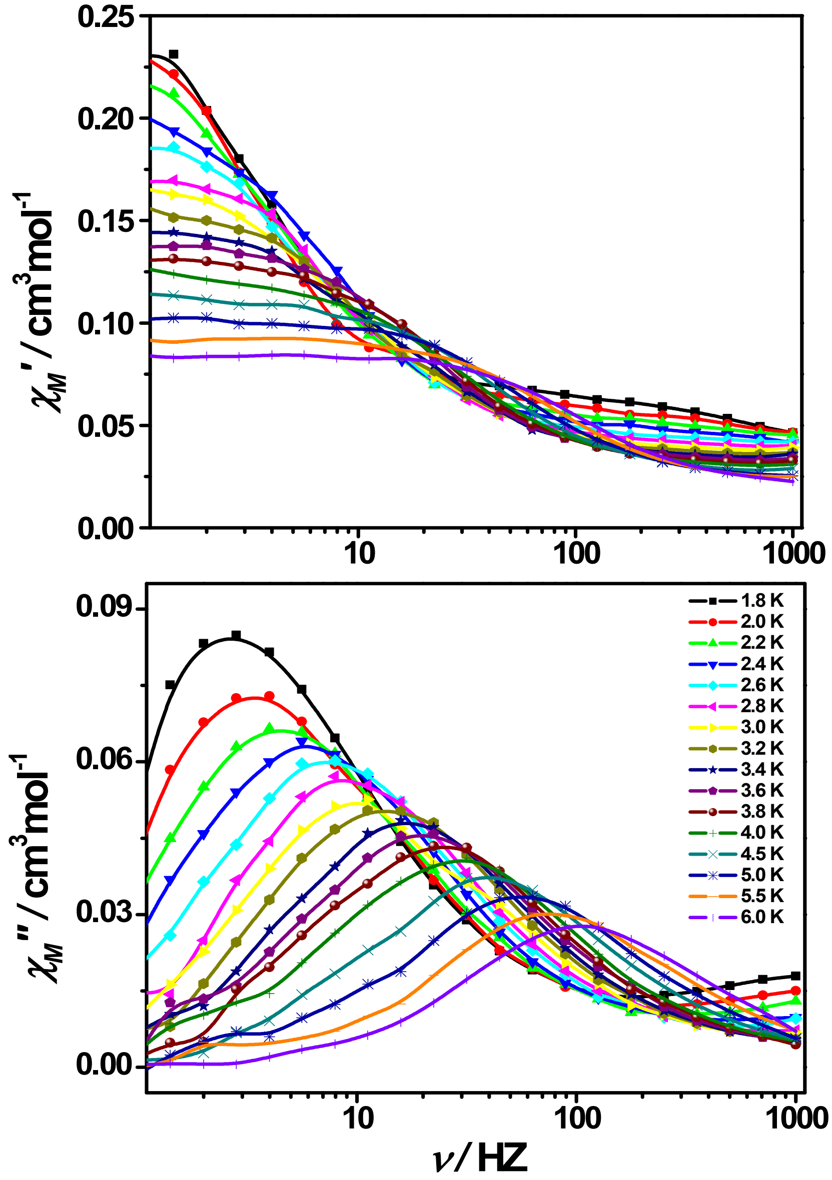


Figure S18 Frequency dependence of the ac susceptibility from 1.8 to 6.0 K under 2500 Oe dc field for **1'**. The solid lines are for eye guide.

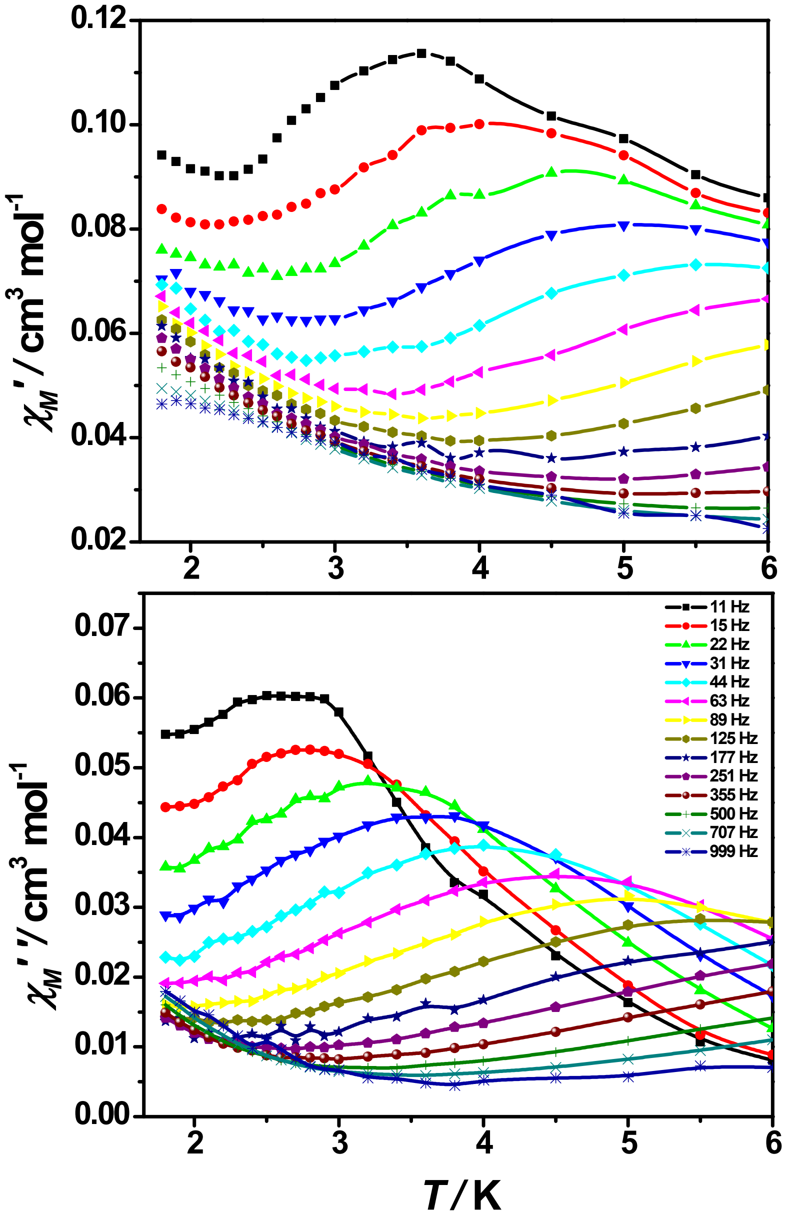


Figure S19 Temperature dependence of in-of-phase (χ_M') and out-of-phase (χ_M'') at different ac frequency under a 2500 Oe dc field for **1'**. The solid lines are for eye guide.

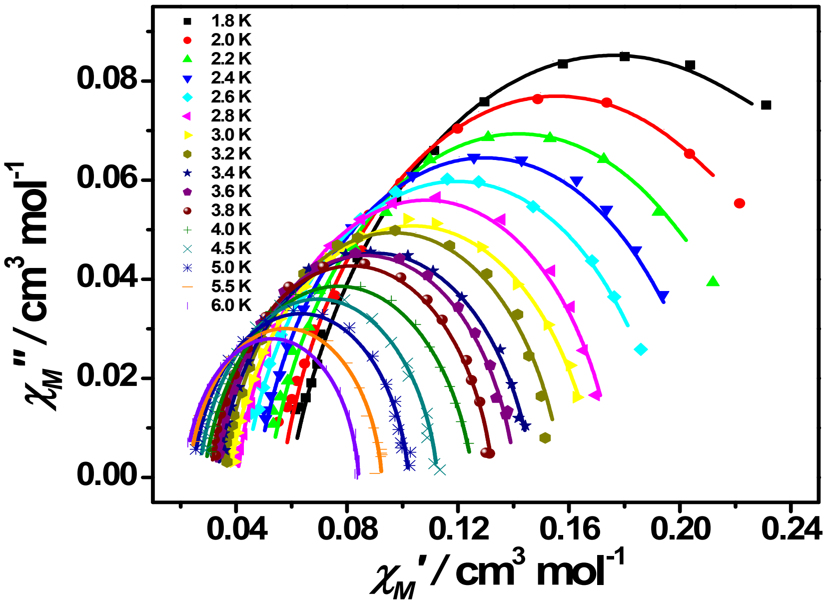


Figure S20 Cole-Cole plot obtained from the ac susceptibility data under 2500 Oe dc field in the temperature range of 1.8-6.0 K for **1'**. Solid lines represent the best fits to a generalized Debye model.

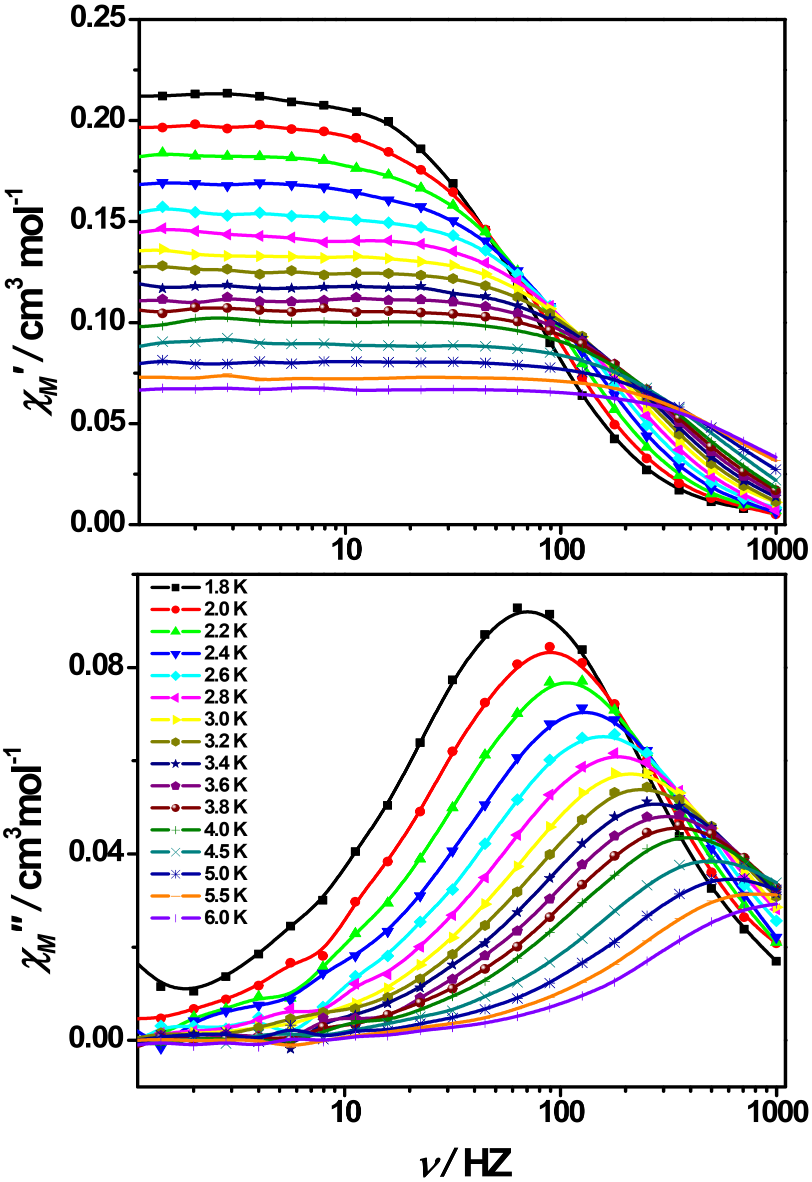


Figure S21 Frequency dependence of the ac susceptibility from 1.8 to 6.0 K under 2500 Oe dc field for **2’**. The solid lines are for eye guide.

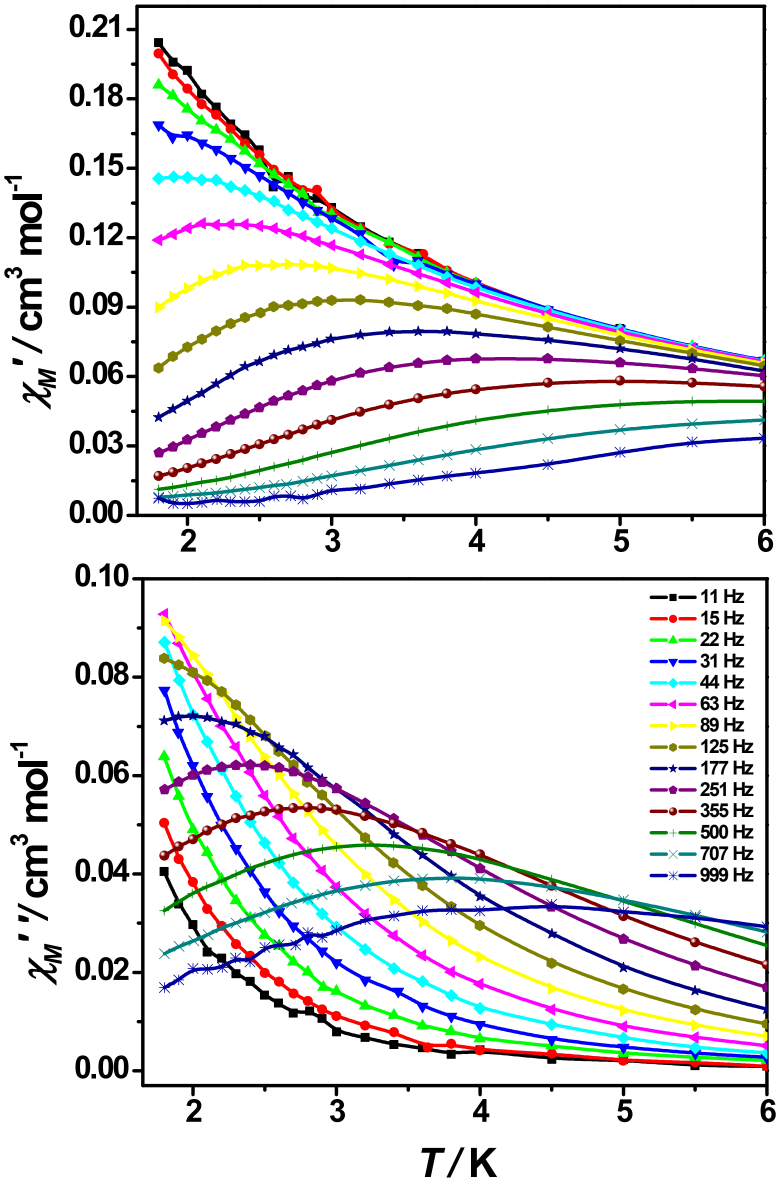


Figure S22 Temperature dependence of in-of-phase ($\chi_M{}'$) and out-of-phase ($\chi_M{}''$) at different ac frequency under a 2500 Oe dc field for **2'**. The solid lines are for eye guide.

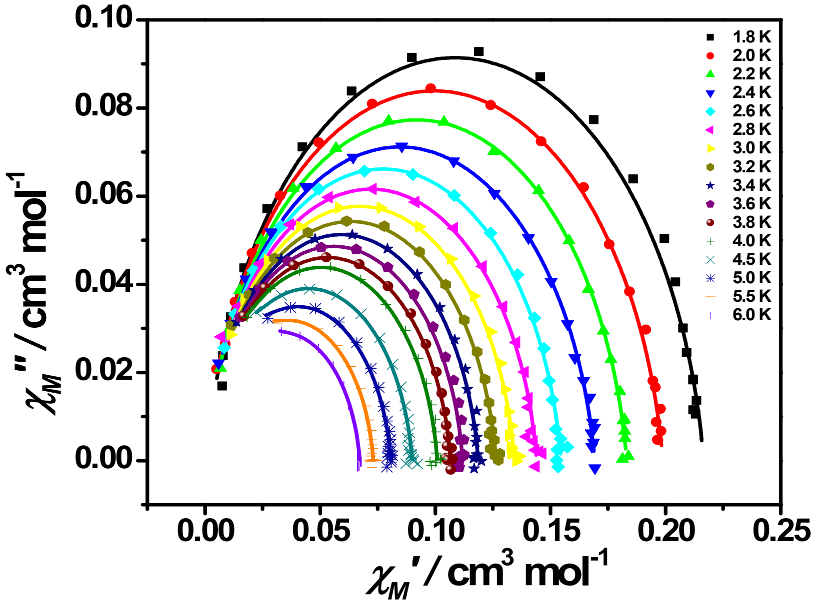
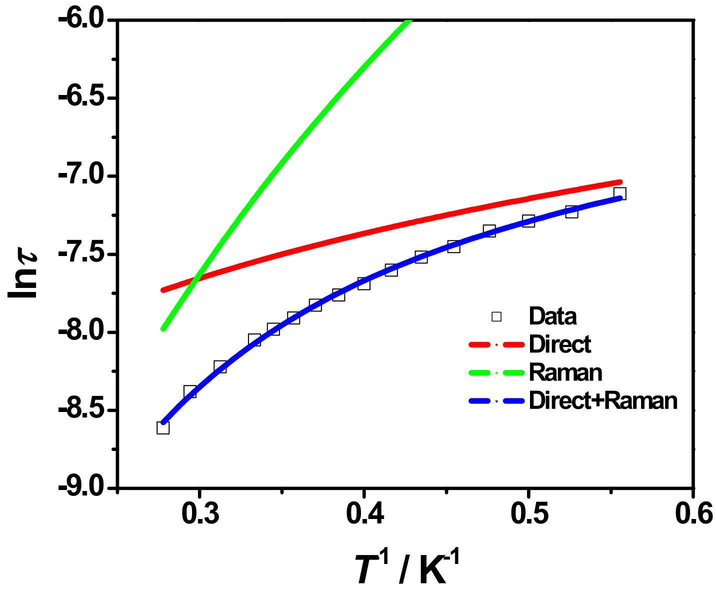


Figure S23 Cole-Cole plot obtained from the ac susceptibility data under 2500 Oe dc field in the temperature range of 1.8-6.0 K for **2'**. Solid lines represent the best fits to a generalized Debye model.



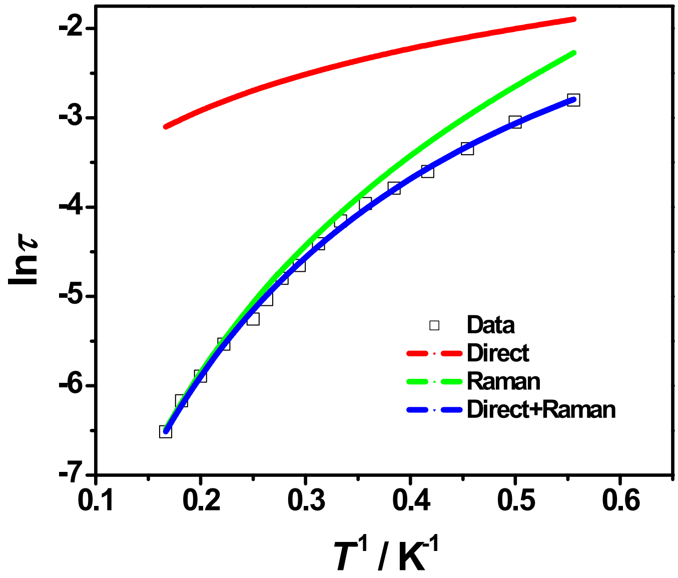
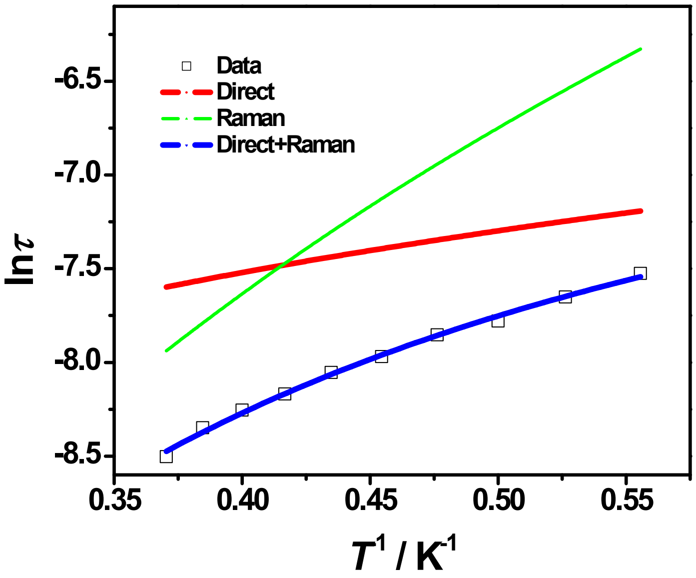


Figure S24 Temperature dependence of the magnetization relaxation rates of **1** (top) and **1’** (bottom) under the applied dc field of 2500 Oe. The solid blue lines represent the best fit by using eqn (1). The other solid lines represent data fits using direct process (red) and Raman process (green), respectively.



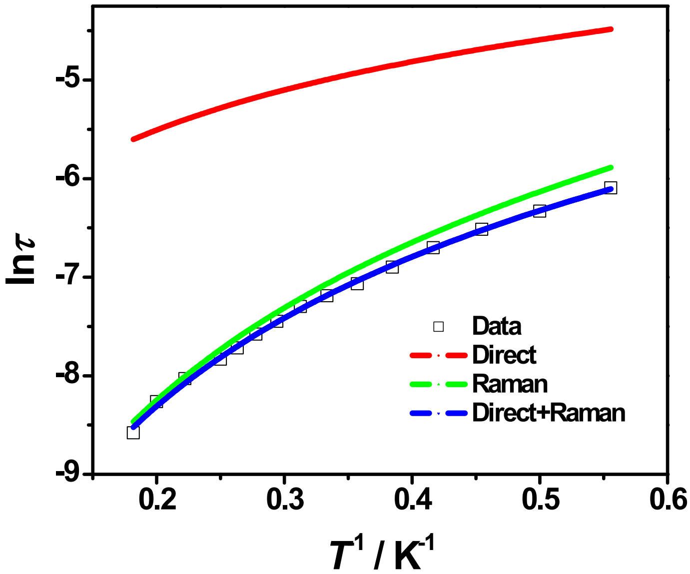


Figure S25 Temperature dependence of the magnetization relaxation rates of **2** (top) and **2’** (bottom) under the applied dc field of 2500 Oe. The solid blue lines represent the best fit by using eqn (1). The other solid lines represent data fits using direct process (red) and Raman process (green), respectively.

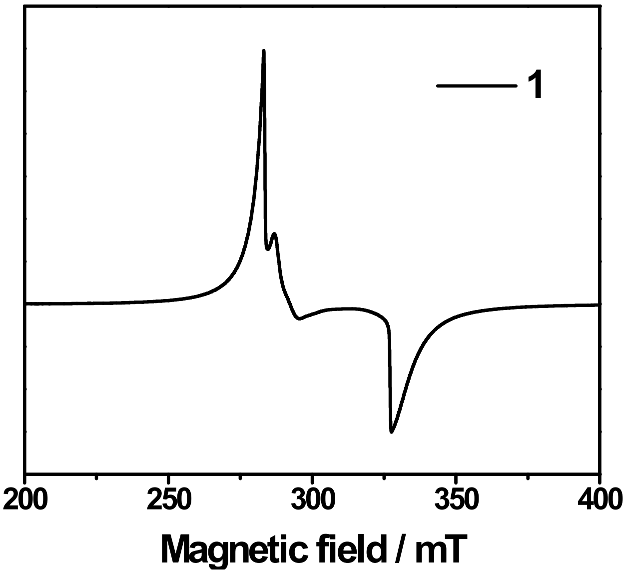


Figure S26 X-band EPR spectra of **1** with $g_x = 2.38$, $g_y = 2.34$, $g_z = 2.06$ at 91 K.

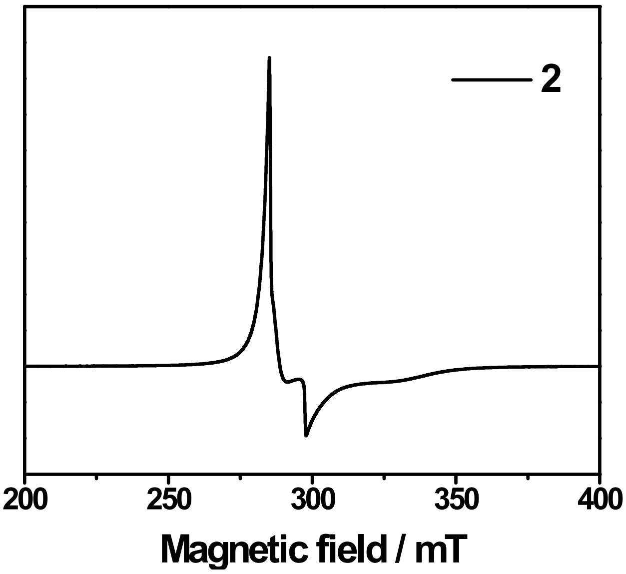


Figure S27 X-band EPR spectra of **2** with $g_x = 2.37$, $g_y = 2.28$, $g_z = 2.04$ at 91 K.

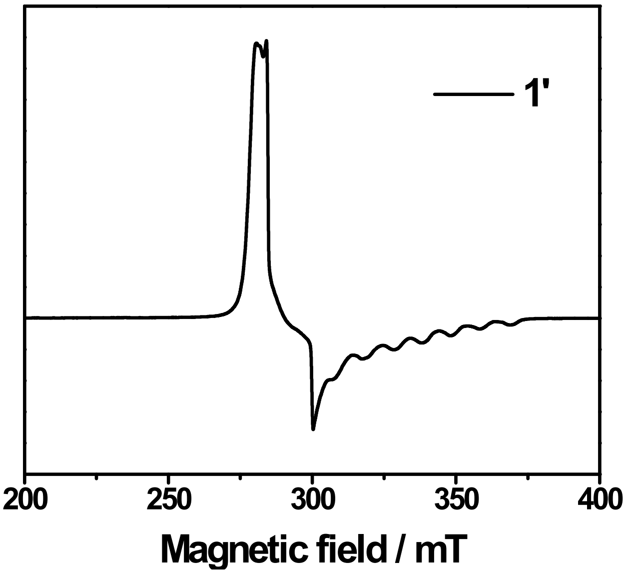


Figure S28 X-band EPR spectra of **1'** with $g_x = 2.39$, $g_y = 2.26$, $g_z = 1.99$ at 91 K.

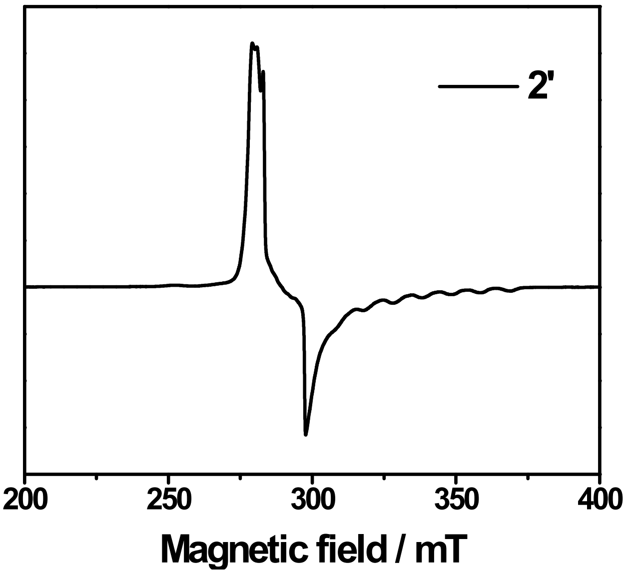


Figure S29 X-band EPR spectra of **2'** with $g_x = 2.40$, $g_y = 2.27$, $g_z = 1.99$ at 91 K.

Table S3. Relaxation times τ (s) and α values for **1**

T (K)	χ_S	χ_T	τ (s)	α
1.8	0.034	0.22	0.00089	0.23
1.9	0.029	0.21	0.00079	0.24
2.0	0.027	0.20	0.00072	0.24
2.1	0.024	0.20	0.00065	0.23
2.2	0.022	0.19	0.00058	0.23
2.3	0.020	0.19	0.00053	0.22
2.4	0.019	0.18	0.00049	0.21
2.5	0.019	0.17	0.00044	0.19
2.6	0.018	0.17	0.00041	0.18
2.7	0.017	0.16	0.00038	0.18
2.8	0.015	0.16	0.00034	0.18
2.9	0.014	0.16	0.00032	0.17
3.0	0.012	0.15	0.00029	0.17
3.2	0.011	0.14	0.00025	0.16
3.4	0.009	0.14	0.00022	0.15
3.6	0.007	0.13	0.00019	0.14
3.8	0.008	0.12	0.00017	0.13
4.0	0.51E-14	0.12	0.00014	0.14
4.5	0.31E-14	0.11	0.00011	0.12
5.0	0.62E-14	0.10	0.000088	0.09

Table S4. Relaxation times τ (s) and α values for **2**

T (K)	χ_S	χ_T	τ (s)	α
1.8	0.40E-16	0.21	0.00055	0.27
1.9	0.73E-16	0.20	0.00049	0.27
2.0	0.87E-16	0.20	0.00043	0.26
2.1	0.98E-16	0.19	0.00040	0.27
2.2	0.15E-15	0.18	0.00036	0.27
2.3	0.18E-15	0.18	0.00032	0.26
2.4	0.23E-15	0.17	0.00030	0.26
2.5	0.38E-15	0.16	0.00028	0.26
2.6	0.50E-15	0.16	0.00026	0.26
2.7	0.42E-15	0.15	0.00024	0.26
2.8	0.69E-15	0.15	0.00023	0.25
2.9	0.10E-14	0.15	0.00022	0.25
3.0	0.18E-14	0.14	0.00020	0.23
3.2	0.27E-14	0.13	0.00018	0.23
3.4	0.39E-14	0.13	0.00017	0.23
3.6	0.55E-14	0.12	0.00015	0.22
3.8	0.76E-14	0.11	0.00014	0.21
4.0	0.10E-13	0.10	0.00013	0.19

Table S5. Relaxation times τ (s) and α values for **1'**

T (K)	χ_S	χ_T	τ (s)	α
1.8	0.059	0.29	0.054	0.19
2.0	0.056	0.26	0.043	0.15
2.2	0.052	0.23	0.033	0.16
2.4	0.048	0.21	0.024	0.15
2.6	0.043	0.20	0.021	0.15
2.8	0.040	0.18	0.016	0.12
3.0	0.037	0.17	0.015	0.16
3.2	0.035	0.16	0.012	0.13
3.4	0.033	0.15	0.0097	0.13
3.6	0.032	0.14	0.0077	0.11
3.8	0.030	0.13	0.0065	0.11
4.0	0.028	0.12	0.0056	0.13
4.5	0.026	0.11	0.0038	0.11
5.0	0.024	0.10	0.0027	0.096
5.5	0.023	0.09	0.0020	0.084
6.0	0.022	0.08	0.0015	0.059

Table S6. Relaxation times τ (s) and α values for **2'**

T (K)	χ_S	χ_T	τ (s)	α
1.8	0.64E-03	0.22	0.0023	0.097
2.0	0.13E-03	0.20	0.0018	0.098
2.2	0.50E-03	0.18	0.0015	0.096
2.4	0.49E-11	0.17	0.0013	0.10
2.6	0.74E-11	0.15	0.0010	0.090
2.8	0.10E-10	0.14	0.00089	0.090
3.0	0.17E-10	0.13	0.00075	0.087
3.2	0.31E-10	0.13	0.00066	0.087
3.4	0.35E-10	0.12	0.00057	0.083
3.6	0.59E-10	0.11	0.00050	0.080
3.8	0.90E-10	0.11	0.00045	0.083
4.0	0.12E-09	0.10	0.00040	0.080
4.5	0.25E-09	0.09	0.00031	0.080
5.0	0.31E-09	0.08	0.00024	0.082
5.5	0.58E-09	0.07	0.00020	0.079
6.0	0.13E-08	0.06	0.00017	0.083

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