

## Supporting information for

### **Bulky Schiff-base ligand supported Co(II) single-ion magnets with zero-field slow magnetic relaxation**

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#### **Experimental section**

##### **General Materials and Methods**

All chemicals were commercially available and were used as received without further purification. Elemental analyses (C, H, and N) were conducted on an Elementar vario EL cube elemental analyzer. Fourier transform infrared (IR) spectra were measured on a Nicolet IS10 Spectrum with samples prepared as KBr discs. Powder X-Ray diffraction (PXRD) patterns were recorded at room temperature on a Bruker D8 Advance diffractometer. Direct current (dc) magnetic measurements were

carried out on a Quantum Design PPMS DynaCool-9 magnetometer. The magnetic data were corrected for diamagnetic contribution by using Pascal's constants. Altering current (ac) magnetic measurements were performed on a Quantum Design MPMS3 SQUID magnetometer.

**Synthesis of  $[\text{Co}(\text{L})_2] \cdot \text{C}_2\text{H}_5\text{OH}$  (L = 2-(Adamantan-1-ylimino)methyl-4-methylphenol) (1)**

2-Hydroxy-4-methylbenzaldehyde (0.068g, 0.5mmol), amantadine (0.076g, 0.5mmol) and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.062g, 0.25mmol) were dissolved in  $\text{C}_2\text{H}_5\text{OH}$  (20mL), and then triethylamine (0.07mL, 0.5mmol) was added. The resulting mixture was stirred for 3h at 55°C and then filtered when the solution was cooled. Slow evaporation of the filtrate at room temperature gave crystals after several days. Yield: 59mg (37% based on Co). Calc. (%) for  $\text{C}_{36}\text{H}_{44}\text{CoN}_2\text{O}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ : C 71.12, H 7.85, N 4.37; found: C 70.93, H 7.90, N 4.34. Selected IR data ( $\text{cm}^{-1}$ ): 3357br, 2912m, 2849w, 1589s, 1535w, 1468m, 1389w, 1314w, 1211w, 1159w, 1079w, 825w, 719w, 612w, 535w.

**Synthesis of  $[\text{Co}(\text{L})_2] \cdot \text{C}_2\text{H}_5\text{OH}$  (L = 2-(Adamantan-1-ylimino)methyl-4-bromophenol) (2)**

4-Bromo-2-hydroxybenzaldehyde (0.101g, 0.5mmol), amantadine (0.076g, 0.5mmol) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.073g, 0.25mmol) were dissolved in a mixture of  $\text{CH}_3\text{OH}$  (5mL) and  $\text{C}_2\text{H}_5\text{OH}$  (15mL). The resulting mixture was stirred for

3h at 55°C and then filtered when the solution was cooled. Slow evaporation of the filtrate at room temperature gave crystals after several days. Yield: 21mg (11% based on Co). Calc. (%) for  $C_{34}H_{38}Br_2CoN_2O_2 \cdot C_2H_5OH \cdot 0.5H_2O$ : C 55.40, H 5.81, N 3.59; found: C 55.48, H 5.73, N 3.43. Selected IR data ( $cm^{-1}$ ): 3373br, 2911m, 2849w, 1597s, 1520w, 1459m, 1387w, 1313w, 1169w, 1074w, 823w, 747w, 650w, 550w, 497w.

### Crystal structure determination and refinement

The single-crystal diffraction data of **1** and **2** were collected at 173(2) K on a Bruker APEX II diffractometer with monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). The sorption corrections were conducted using SADABS for both compounds supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least squares analysis on  $F^2$ , using the SHELXTL program package.<sup>S1</sup> Ordered non-H atoms were refined anisotropically, H-atoms were placed in calculated positions and refined using a riding model. The data have been deposited to the Cambridge Crystallographic Data Centre with CCDC 1981887-1981888. Data collection and structural refinement parameters are listed in Table S1.

**Table S1** Crystallographic data and structure refinement for complexes **1** and **2**.

	1	2
Formula	$C_{38}H_{50}CoN_2O_3$	$C_{36}H_{44}Br_2CoN_2O_3$
$M_r$ (g mol <sup>-1</sup> )	641.73	771.48
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
$T$ (K)	173(2)	173(2)

<i>a</i> (Å)	9.4856(4)	9.9489(7)
<i>b</i> (Å)	26.4577(14)	25.4584(17)
<i>c</i> (Å)	13.9175(7)	13.7446(10)
$\alpha$ (°)	90	90
$\beta$ (°)	108.917(2)	107.112(2)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	3304.2(3)	3327.2(4)
<i>Z</i>	4	4
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.290	1.540
$\mu$ (mm <sup>-1</sup> )	0.559	2.956
<i>F</i> (000)	1372	1580
Reflns collected	23901	19635
Unique reflns	5970	6063
<i>R</i> <sub>int</sub>	0.0769	0.0741
GOF	1.023	1.036
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ )	0.0444	0.0489
w <i>R</i> <sub>2</sub> (all data)	0.1011	0.1056
Max. diff. peak / hole (e Å <sup>-3</sup> )	0.422 / -0.273	0.692 / -0.583

**Table S2** Selected bond lengths (Å) and angles (°) for **1** and **2**.

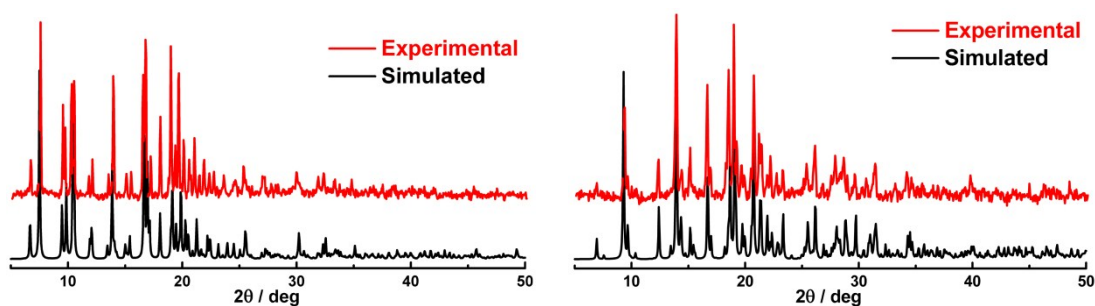
	1	2
Co(1)-O(1)	1.9008(19)	1.909(3)
Co(1)-O(2)	1.9197(18)	1.924(3)
Co(1)-N(1)	1.999(2)	1.993(4)
Co(1)-N(2)	2.004(2)	2.007(4)
O(1)-Co(1)-O(2)	112.98(8)	111.89(14)
O(1)-Co(1)-N(1)	97.53(8)	97.17(14)
O(2)-Co(1)-N(1)	109.80(8)	111.97(14)
O(1)-Co(1)-N(2)	114.87(8)	117.39(14)
O(2)-Co(1)-N(2)	96.35(8)	97.35(14)
N(1)-Co(1)-N(2)	125.92(9)	121.76(15)

**Table S3** Continuous shape measures (CShM) for complexes **1** and **2**

	1	2
SP-4 ( <i>D</i> <sub>4h</sub> )	26.045	28.200
<b>T-4 (<i>T</i><sub>d</sub>)</b>	<b>1.603</b>	<b>1.334</b>
SS-4 ( <i>C</i> <sub>2v</sub> )	5.679	6.822
vTBPY-4 ( <i>C</i> <sub>3v</sub> )	3.686	3.706

SP-4 = Square, T-4 = Tetrahedron, SS-4 = Seesaw,  
vTBPY-4 = Vacant trigonal bipyramid

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**Fig. S1** Experimental and simulated PXRD patterns for complexes **1**(left) and **2** (right).

**Table S4** Zero field splitting parameters for complexes **1** and **2** extracted from magnetic data and theoretic calculations.

		$D / \text{cm}^{-1}$	$E / \text{cm}^{-1}$	$g_x$	$g_y$	$g_z$	$\text{TIP} \times 10^5 / \text{cm}^3 \text{mol}^{-1}$
Experimental	<b>1</b>	-19.3	-0.05	2.179	2.179	2.250	78.9
	<b>2</b>	-19.2	1.2	2.255	2.255	2.316	9.73
Theoretic	<b>1</b>	-26.1	1.0	2.148	2.178	2.487	-
	<b>2</b>	-24.1	0.2	2.163	2.169	2.466	-

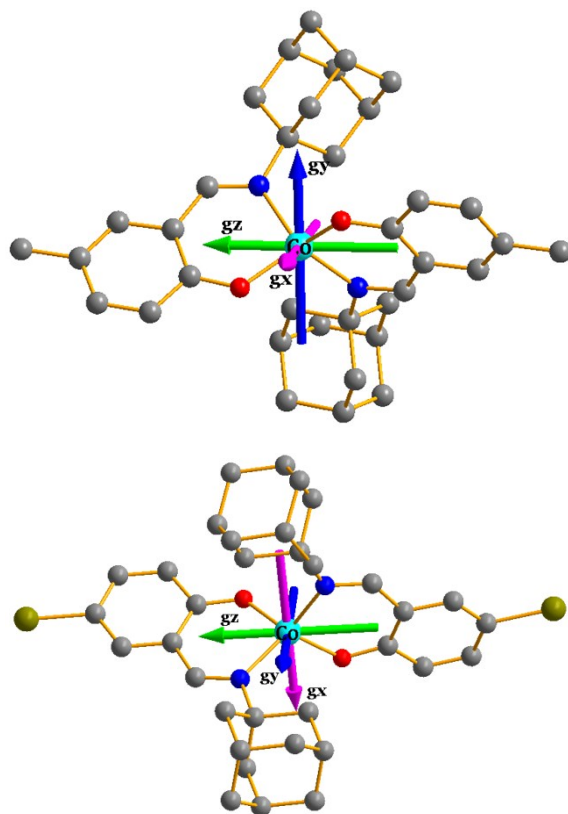
### Ab initio calculation

Complete-active-space self-consistent field (CASSCF) calculations on mononuclear complexes **1** and **2** (see Figure 1 for the molecular structures of **1** and **2**) on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.2<sup>S2</sup> program package.

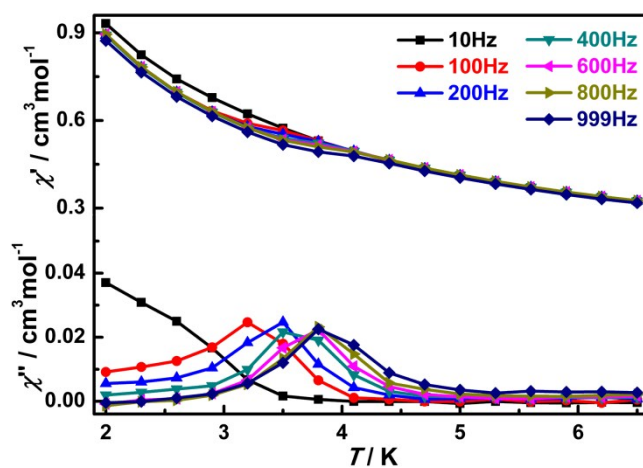
The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Co(II); VTZ for close O; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. And then, the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 10 active spaces considering the  $3d$ -double shell effect ( $5+5'$ ) include all seven  $3d$  electrons (CAS(7 in  $5+5'$ )), and the mixed spin-free states are 30 (all from 10 quadruplets and 20 from 40 doublets). And then, SINGLE\_ANISO<sup>S3</sup> program was used to obtain the  $g$  tensors, energy levels, magnetic axes, *et al.*, based on the above CASSCF/RASSI calculations.

**Table S5** Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of complexes **1** and **2** using CASSCF/RASSI with MOLCAS 8.2.

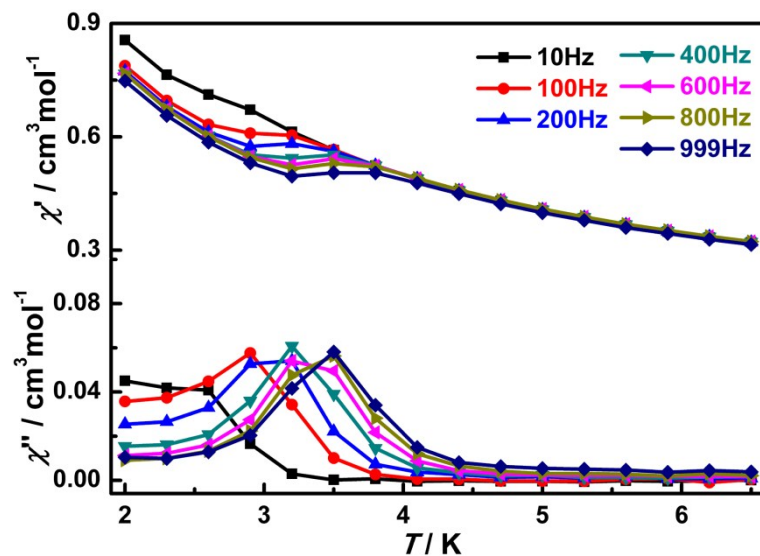
	Spin-orbit states	Energy (cm <sup>-1</sup> )	Spin-free states, Spin, Weights				
<b>1</b>	1	0.0	1,1.5,0.9587	2,1.5,0.0367	3,1.5,0.0022	4,1.5, 0.0013	19,0.5, 0.0003
	2	52.3	1,1.5,0.9859	2,1.5,0.0047	3,1.5,0.0046	4,1.5, 0.0033	17,0.5, 0.0006
<b>2</b>	1	0.0	1,1.5,0.9617	2,1.5,0.0337	3,1.5,0.0019	4,1.5 0.0017	19,0.5 0.0003
	2	48.3	1,1.5,0.9863	2,1.5,0.0043	3,1.5,0.0042	4,1.5, 0.0040	17,0.5, 0.0007



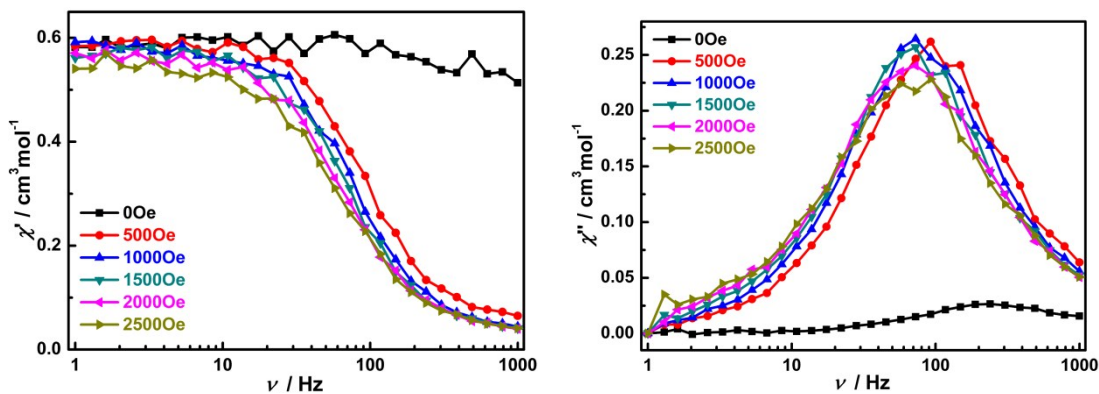
**Fig. S2** Orientations of the local magnetic axes (red:  $g_x$ ; blue:  $g_y$ ; green:  $g_z$ ) of the ground doublet on Co(II) ions of complexes **1** (up) and **2** (down).



**Fig. S3** Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility under zero dc field for **1**. The solid lines are guides for the eyes.

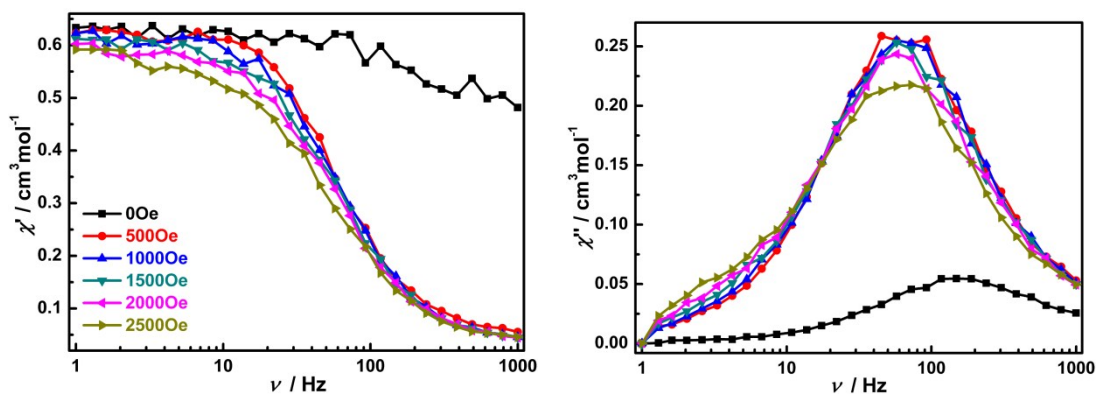


**Fig. S4** Temperature dependence of the in-phase and out-of-phase ac magnetic susceptibility under zero dc field for **2**. The solid lines are guides for the eyes.

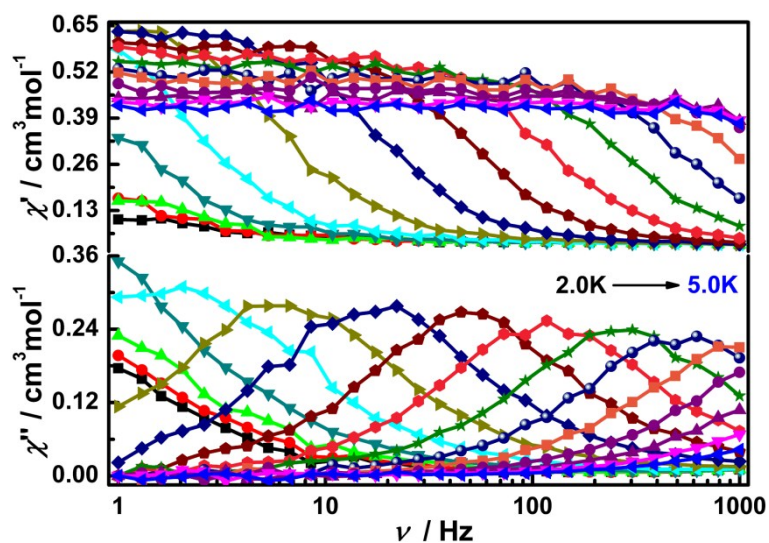


**Fig. S5** Frequency dependence of in-phase (left) and out-of-phase (right) ac susceptibility under various dc fields at 3.5 K for **1**. The solid lines are guides for the eyes.

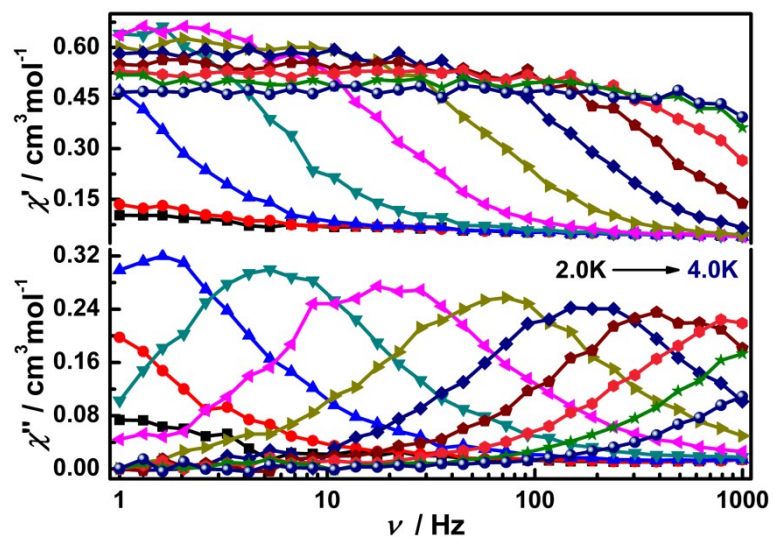




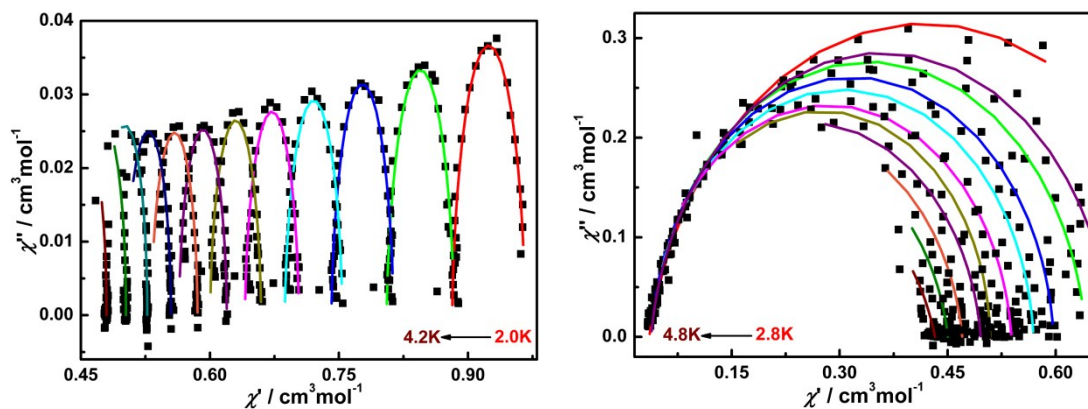
**Fig. S6** Frequency dependence of in-phase (left) and out-of-phase (right) ac susceptibility under various dc fields at 3K for **2**. The solid lines are guides for the eyes.



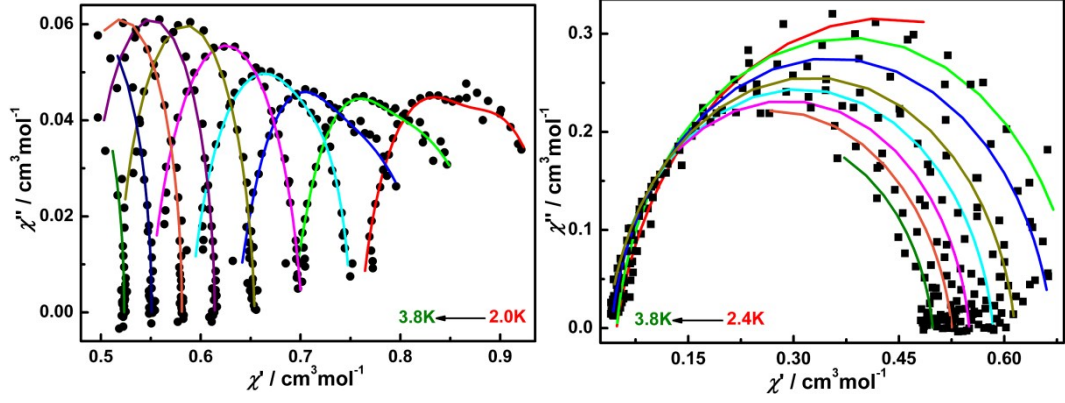
**Fig. S7** Frequency dependence of in-phase and out-of-phase ac susceptibility under 1000 Oe dc field for **1**. The solid lines are guides for the eyes.



**Fig. S8** Frequency dependence of in-phase and out-of-phase ac susceptibility under 1000 Oe dc field for **2**. The solid lines are guides for the eyes.



**Fig. S9** The Cole-Cole plots of **1** under zero (left) and 1000 Oe (right) dc field. The solid lines are the best fits to a generalized Debye model.



**Fig. S10** The Cole-Cole plots of **2** under zero (left) and 1000Oe (right) dc field. The solid lines are the best fits to a modified/generalized Debye model.

**Table S6** Cole-Cole parameters of **1** under zero dc field.

$T / \text{K}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$	$R$
2.0	8.81E-01	9.67E-01	1.52E-02	9.50E-02	5.18E-04
2.2	8.05E-01	8.84E-01	1.27E-02	1.04E-01	4.19E-04
2.4	7.41E-01	8.13E-01	1.02E-02	8.93E-02	3.64E-04
2.6	6.87E-01	7.54E-01	8.06E-03	8.73E-02	3.39E-04
2.8	6.41E-01	7.04E-01	5.96E-03	8.10E-02	2.93E-04
3.0	6.00E-01	6.60E-01	3.75E-03	7.29E-02	2.49E-04
3.2	5.64E-01	6.20E-01	1.91E-03	6.36E-02	2.38E-04
3.4	5.32E-01	5.86E-01	8.69E-04	4.90E-02	2.05E-04
3.6	5.02E-01	5.55E-01	3.86E-04	3.32E-02	1.78E-04
3.8	4.76E-01	5.27E-01	1.84E-04	1.12E-09	1.55E-04
4.0	4.50E-01	5.02E-01	9.28E-05	1.09E-09	1.87E-04
4.2	4.32E-01	4.80E-01	5.75E-05	2.93E-09	1.70E-04

**Table S7** Cole-Cole parameters of **1** under 1000 Oe dc field.

$T / \text{K}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$	$R$
2.8	3.55E-02	8.00E-01	8.35E-02	1.23E-01	3.18E-03
3.0	3.80E-02	6.80E-01	2.54E-02	7.48E-02	3.36E-03
3.2	3.90E-02	6.42E-01	8.70E-03	5.54E-02	4.33E-03
3.4	3.87E-02	5.97E-01	3.18E-03	4.34E-02	2.66E-03

3.6	3.96E-02	5.69E-01	1.32E-03	4.08E-02	3.86E-03
3.8	3.10E-02	5.38E-01	5.76E-04	5.50E-02	3.23E-03
4.0	4.25E-02	5.09E-01	2.85E-04	1.83E-02	6.60E-03
4.2	1.65E-02	4.96E-01	1.41E-04	6.94E-02	5.33E-03
4.4	3.43E-11	4.70E-01	7.25E-05	8.27E-02	3.98E-03
4.6	4.99E-11	4.50E-01	3.99E-05	1.03E-01	4.33E-03
4.8	4.95E-11	4.33E-01	1.98E-05	1.73E-01	2.74E-03

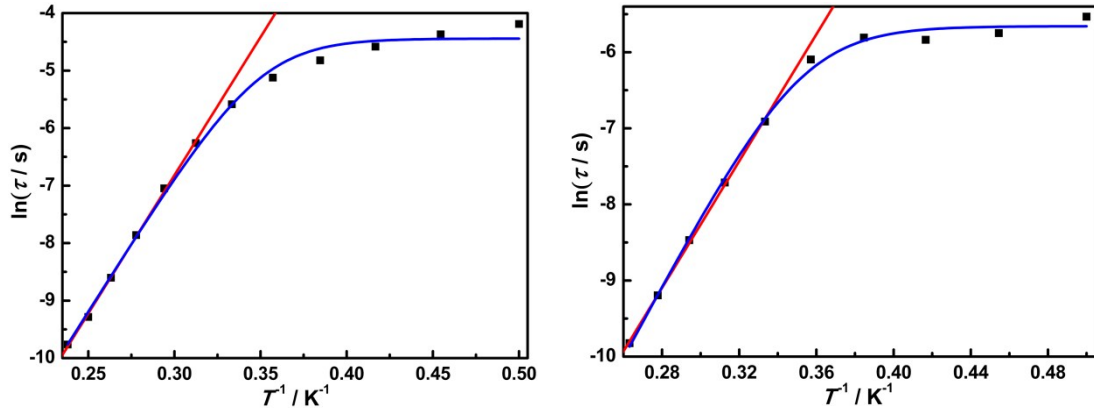
**Table S8** Cole-Cole parameters of **2** under zero dc field.

$T / \text{K}$	$\chi_S / \text{cm}^3 \cdot \text{mol}^{-1}$	$\Delta\chi_1 / \text{cm}^3 \cdot \text{mol}^{-1}$	$\tau_1 / \text{s}$	$\alpha_1$	$\Delta\chi_2 / \text{cm}^3 \cdot \text{mol}^{-1}$	$\tau_2 / \text{s}$	$\alpha_2$	$R$
			3.95E-03	2.39		8.65	2.66	
2	7.60E-01	1.03E-01	03	E-01	9.54E-02	E-02	E-01	3.90E-04
			3.18E-03	6.05		3.71	5.07	
2.2	6.88E-01	4.40E-02	03	E-02	1.68E-01	E-02	E-01	3.02E-04
			2.91E-03	6.97		2.96	4.97	
2.4	6.33E-01	5.08E-02	03	E-02	1.52E-01	E-02	E-01	2.41E-04
			3.00E-03	2.21		2.34	3.65	
2.6	5.90E-01	1.29E-01	03	E-01	3.13E-02	E-02	E-03	2.24E-04
			2.25E-03	1.99		2.73	5.45	
2.8	5.49E-01	1.53E-01	03	E-01	2.36E-17	E-02	E-03	2.43E-04
			9.96E-03	8.85		4.12	5.68	
3	5.17E-01	1.37E-01	04	E-02	2.87E-17	E-02	E-03	2.37E-04
			4.47E-03	2.75		1.04	7.50	
3.2	4.87E-01	1.27E-01	04	E-02	5.54E-17	E-01	E-03	2.44E-04
			2.10E-03	2.92		2.00	2.14	
3.4	4.59E-01	1.22E-01	04	E-15	6.91E-17	E-01	E-03	1.70E-04
			1.01E-03	3.77		2.10	2.63	
3.6	4.33E-01	1.18E-01	04	E-15	8.16E-17	E-01	E-03	1.79E-04
			5.42E-03	4.70		2.45	3.28	
3.8	4.13E-01	1.10E-01	05	E-15	1.02E-16	E-01	E-03	2.68E-04

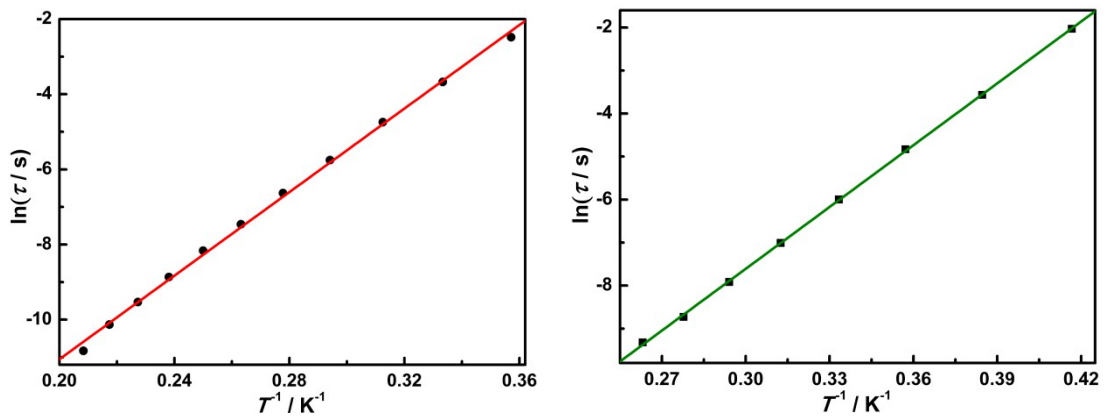
**Table S9** Cole-Cole parameters of **2** under 1000 Oe dc field.

$T / \text{K}$	$\chi_S / \text{cm}^3 \cdot \text{mol}^{-1}$	$\chi_T / \text{cm}^3 \cdot \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$	$R$
2.4	4.81E-02	8.14E-01	1.31E-01	1.22E-01	2.75E-03
2.6	4.85E-02	7.07E-01	2.83E-02	6.77E-02	5.76E-03
2.8	4.05E-02	6.68E-01	7.96E-03	8.32E-02	5.72E-03
3	3.59E-02	6.15E-01	2.48E-03	7.96E-02	3.18E-03

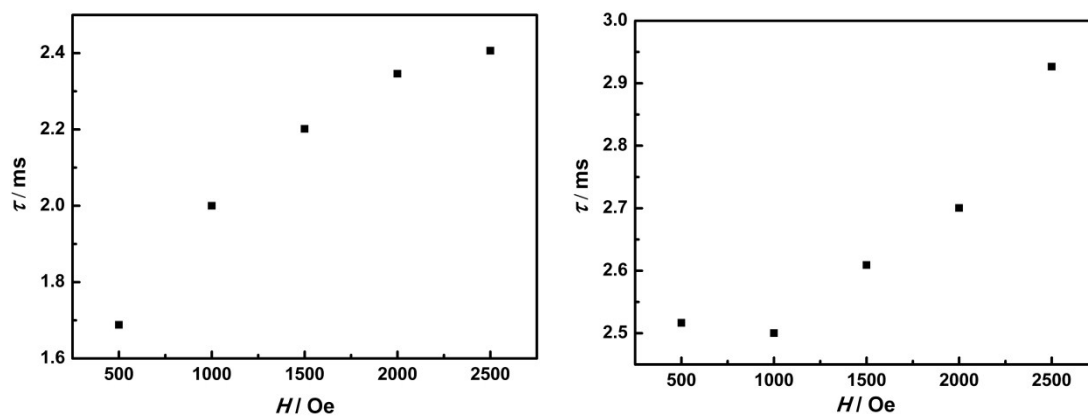
3.2	3.45E-02	5.84E-01	9.02E-04	7.63E-02	4.67E-03
3.4	2.88E-02	5.50E-01	3.64E-04	7.49E-02	5.00E-03
3.6	1.42E-02	5.25E-01	1.62E-04	9.11E-02	2.92E-03
3.8	5.22E-02	4.98E-01	8.95E-05	8.27E-02	3.98E-03



**Fig. S11** Temperature dependence of the relaxation times for **1** (left) and **2** (right) under zero dc field. The red line is the best fits to an Arrhenius law, while the blue line is fit for Orbach plus QTM processes.



**Fig. S12** Temperature dependence of the relaxation times for **1** (left) and **2** (right) under 1000 Oe dc field. The solid line is the best fits to an Arrhenius law.



**Fig. S13** Field dependence of the relaxation times for **1** at 3.5 K (left) and **2** at 3 K (right).

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