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Supporting Information

Correlating Magnetic Anisotropy to the Subtle Coordination Geometry Variation of a Series of Cobalt(II)-Sulfonamide Complexes

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1 Experimental Section

Materials and Procedures. All reagents were purchased from commercial suppliers and used as received unless stated otherwise. All the solvents were dehydrated and deoxygenated by using solvent purification systems prior to use. The FT-IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific Instrument).

X-ray Structure Determination. Single crystals suitable for X-ray analysis were coated with deoxygenated Paratone-N oil. All data were collected on a Bruker Apex II DUO area-detector diffractometer with graphite-monochromated MoKα radiation (λ= 0.71073Å). Cell refinement and data reduction were accomplished with the SAINT processing program. The structures were solved by direct methods and refined on F2 using Olex 2.[1] CCDC 1826695 (**1**) , 1826696 (**3**), 1826697 (**5**) and 1826694 (**6**) contain the supplementary crystallographic data for this paper (Tables S2).

Magnetic Measurements. Magnetic measurements were performed on polycrystalline samples sealed in polyethylene bags. Data were collected using a Quantum Design MPMS-XL SQUID magnetometer from 2.0 to 300 K at applied dc fields ranging from 0 to +7 T. Direct-Current (dc) susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of each sample estimated using Pascal's constants. Alternating-Current (ac) magnetic susceptibility data were collected under a dc field of 1000 Oe and an ac field of 3.5 Oe, oscillating at frequencies in the range of 1–1500 Hz. Frequency-dependent ac susceptibility data were used to construct Cole–Cole plots, which were then fitted using a generalized Debye model to estimate relaxation times.

PXRD Measurements. The X-ray powder diffraction (PXRD) measurements for complexes **1**–**6** were performed on a Rigaku SmartLab (3) X-ray diffractometer at room temperature, which was in good agreement with the results simulated from the single crystal data, indicating the high purity of the synthesized samples (Fig. S2-S7).

Computational Details. *Ab initio* multiconfigurational calculations were performed using the ORCA 4.0 computational package.[2] The polarized triple-ζ-quality basis set [def2-TZVPP] proposed by Ahlrichs and co-workers was used for cobalt and def2-TZVP was used for nitrogen atoms, while the basis set def2-SVP was used for other remote atoms.[3] Meanwhile, the scalar relativistic effects were taken into account with a standard second-order Douglas-Kroll-Hess (DKH2)[4] for heavy ion cobalt(II) and the auxiliary basis set def2/J was used in conjunction with the resolution of identity approximation. The state-average (SA)-CASSCF[5] calculations, followed by N-electron valence perturbation theory to second order (NEVPT2)[6] step to account for the major part of the differential dynamic correlation between the ground and the excited states, was composed of 7 metal 3d electrons on 5 3d orbitals [CAS(7,5)] and 7 metal 3d + 4 ligand electrons on 5 3d + 2 ligand + 5 4d orbitals [CAS(11,12)], with 10 states for quartet states and 40 states for doublet states, which has been used by many works.[7]

Syntheses

a) The preparation of ligands

(4-*tert*-butylphenylsulfonyl)-N-(pyridin-2-ylmethyl)-sulfonamide (L_1^-)

0.55g (5.0 mmol) 2-(aminomethyl)pyridine was added to an aqueous solution of NaOH (0.20 g, 5.0 mmol, 5.0 ml). To this solution was added slowly over 15 min a THF (10ml) solution of *p*-tert-butylbenzenesulfonyl chloride with stirring. The resulting mixture was stirred for 4h at room temperature and the THF solution was removed under reduced pressure. The yellow oil thus obtained wan purified by column chromatography(hexanes: ethyl acetate = 4 : 3), yielding pale yellow products (1.2 g, 79.5%) ^{1}H NMR (400 MHz, CD_2Cl_3): δ (ppm) 8.51 (s, 1H), 7.81 (m 1H), 7.65 (d, 2H), 7.57 (d, 2H), 7.24 (d, 1H), 7.15 (d , 1H) 6.23 (s, 2H), 4.23 (s, 2H), 1.56 (s, 9H).

(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-(pyridin-2-ylmethyl)-sulfonamide (L_2^-)

A similar treatment as L_1 was applied by using 2-(aminomethyl)pyridine (0.55 g, 5 mmol) and dansyl chloride (1.4 g, 5 mmol) instead and yields pale yellow products of L_2 (1.3 g, 73%). ^{1}H NMR (400 MHz, CD_2Cl_3): δ (ppm) 8.47 (d, 1H), 8.24-8.36 (m, 3H), 7.81 (m 1H), 7.45-7.59 (m, 3H), 7.24 (d, 1H), 7.15 (d, 2H) 6.23 (s, 2H), 4.23 (d, 2H), 2.52 (s, 6H).

(mesitylsulfonyl)-N-(pyridin-2-ylmethyl)-sulfonamide (L_3^-)

A similar treatment as L_1 was applied by using 2-aminomethylpyridine (0.55 g, 5 mmol) and 2,4,6-trimethylbenzenesulfonate (1.09 g, 5 mmol) instead and yields pale yellow products of L_3 (1.0 g, 68%). ^{1}H NMR (400 MHz, CD_2Cl_3): δ (ppm) 8.39 (d, 1H), 7.74 (d, 1H), 7.45 (d, 1H), 7.22 (d, 1H), 7.15 (s, 1H) 5.82 (s, 2H), 4.26 (s, 2H), 2.64 (s, 6H) 2.18 (s, 3H).

(tosyl)-N-(pyridin-2-ylmethyl)-sulfonamide (L_4^-)

To a stirred solution of *p*-toluenesulfonyl chloride (3.43 g, 0.018 mmol) in pyridine (10 ml) cooled to -10°C was slowly added (2-amino-methyl)pyridine (2.00 g, 0.018 mmol) in pyridine (5 ml). The resulting reaction mixture was stirred at -10 °C for 3 hours and was held at 5 °C overnight. The reaction mixture was poured onto crushed ice resulting in the precipitation pf a yellow solid, which was removed by filtration and washed with water. The precipitate was dissolved in dichloromethane and dried ($NaSO_4$). Pale yellow crystals of L_4 yield (2.12 g, 45%). ^{1}H NMR (400 MHz, CD_2Cl_3): δ (ppm) 8.35 (d, 1H), 7.81 (m 3H), 7.21-7.44 (m, 4H), 6.42 (s, 2H), 4.23 (s, 2H), 1.82 (s, 3H).

(naphthalen-1-ylsulfonyl)-N-(pyridin-2-ylmethyl)-sulfonamide (L_5^-)

The mixture of 2-(aminomethyl)pyridine (0.55 g, 5 mmol) and naphthalenesulfonyl chloride (1.13 g, 5 mmol) was followed by a similar treatment as L_1, yielding pale yellow products (1.1 g, 77%). ^{1}H NMR (400 MHz, CD_2Cl_3): δ (ppm) 8.34-8.51 (m, 6H), 7.79 (m 1H), 7.65 (d, 2H), 7.45-7.57 (m, 3H), 7.24 (d, 1H), 5.89 (s, 2H), 4.50 (s, 2H)

(4-*tert*-butylphenylsulfonyl)-N-(6-methylpyridin-2-ylmethyl)-sulfonamide (L_6^-)

6-methyl-2-pyridinecarboxaldehyde (5 g, 41.2 mmol) and hydroxylamine hydrochloride (3.44 g, 49.5 mmol) were dissolved in methanol (100 ml) at room temperature, and added K_2CO_3 (17 g, 124 mmol) with stirring about 4 hours. Then, Zn (13.5 g, 206 mmol) and NH_4Cl (11 g, 206 mmol) were added. The resulting reaction mixture was stirred overnight at room temperature. After filtration the solvent was evaporated under reduced pressure, and yellow powder of 2-(aminomethyl)-6-methyl-pyridine was obtained (4.5 g, 90%). Then, *p*-tert-butylbenzenesulfonyl chloride (1.13 g, 5 mmol) was used to react with 2-(aminomethyl)-6-methyl-pyridine using a similar treatment as L_1, which yields pale yellow powder of L_6 (0.89 g, 56%). 1H NMR (400 MHz, CD_2Cl_3): δ (ppm) 7.64-7.73 (m, 1H), 7.21 (d, 1H), 7.15 (d, 1H), 5.35 (s, 2H), 4.12 (s, 2H).

b) The preparation of complexes

$Co(C_{16}H_{13}N_2O_2S)_2$ (1): L_1 (152 mg, 0.5 mmol) was dissolved in anhydrous methanol (10 ml), and deprotonated using CH_3ONa (32 mg, 0.5 mmol). The pale yellow solution was stirred about one hour and anhydrous $CoCl_2$ (30 mg, 0.25 mmol) was added into the solution. After heating at 75 °C overnight, the solvent was removed under vacuum and the residue was extracted with methanol. Single crystals suitable for X-ray analysis were obtained by layering the hexane above the methanol extracts and keeping to -35 °C for several days. The crystals were filtered and washed with cold methanol yielding purple crystals (0.135 g, 85%). IR (cm^{-1}):1607, 1442, 1278, 1145, 1085, 947, 760, 668, 554. Anal. Calcd (%) for 1: C, 57.68; H, 5.71; N, 8.41; S, 9.61. Found: C, 56.75; H, 5.77; N, 8.28; S, 8.76.

$Co(C_{18}H_{18}N_3O_2S)_2$ (2): The reaction was followed by a similar treatment as complex **1** by using L_2 (170 mg, 0.5 mmol), CH_3ONa (32 mg, 0.5 mmol) and $CoCl_2$ (30 mg, 0.25 mmol) instead, and yields purple crystals of **2** (0.105 g, 57%). IR (cm^{-1}): 1612, 1437, 1278, 1145, 1085, 947, 760, 672, 560. Anal. Calcd (%) for 2: C, 57.40; H, 4.87; N, 8.65; S, 11.36. Found: C, 57.62; H, 5.07; N, 8.31; S, 10.89.

$Co(C_{15}H_{20}N_2O_2S)_2$ (**3**): The reaction was followed by a similar treatment as complex **1** by using L_3 (138 mg, 0.5 mmol), CH_3ONa (32 mg, 0.5 mmol) and $CoCl_2$ (30 mg, 0.25 mmol) instead, and yields purple crystals of **3** (0.089 g, 54%). IR (cm^{-1}): 1611, 1439, 1278, 1145, 1085, 947, 760, 675, 562. Anal. Calcd (%) for 3: C, 56.93; H, 5.21; N, 8.70; S, 9.94. Found: C, 57.18; H, 5.42; N, 8.56; S, 9.72.

$Co(C_{13}H_{13}N_2O_2S)_2$ (**4**): The reaction was followed by a similar treatment as complex **1** by using L_4 (131 mg, 0.5 mmol), CH3ONa (32 mg, 0.5 mmol) and $CoCl_2$ (30 mg, 0.25 mmol) instead, and yields purple crystals of **4** (0.097 g, 60%). IR (cm^{-1}): 0.08 g, 55%. IR (cm^{-1}): 1609, 1439, 1278, 1145, 1085, 947, 760, 669, 559. Anal. Calcd (%) for 4: C, 54.65; H, 5.44; N, 9.63; S, 9.54. Found: C, 54.28; H, 5.53; N, 9.52; S, 9.39.

$Co(C_{13}H_{13}N_2O_2S)_2$ (**5**): The reaction was followed by a similar treatment as complex **1** by using L_5 (163 mg, 0.5 mmol), CH_3ONa (32 mg, 0.5 mmol) and $CoCl_2$ (30 mg, 0.5 mmol) instead, and yields purple crystals of **5** (0.101 g, 63%). IR (cm^{-1}): 1609, 1478, 1277, 1151, 1104, 970, 762, 670, 556. Anal. Calcd (%) for 5: C, 58.74; H, 3.97; N, 8.57; S, 9.79. Found: C, 58.28; H, 4.61; N, 9.37; S, 9.14.

$Co(C_{17}H_{21}N_2O_2S)_2$ (6): The reaction was followed by a similar treatment as complex **1** by using L_6 (154 mg, 0.5 mmol), CH_3ONa (32 mg, 0.5 mmol) and $CoCl_2$ (30 mg, 0.25 mmol) instead, and yields purple crystals of **6** (0.151 g, 86%). IR (cm^{-1}): 1604, 1425, 1265, 1176, 1095, 965, 758, 675, 547. Anal. Calcd (%) for 6: C, 58.80; H, 6.05; N, 8.07; S, 9.22. Found: C, 59.09; H, 6.03; N, 7.71; S, 9.40.

Table S1 Crystallographic data for complexes **1** – **6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{32}H_{38}CoN_4O_4S_2$	$C_{36}H_{36}CoN_6O_4S_2$	$C_{30}H_{40}CoN_4O_4S_2$	$C_{26}H_{26}CoN_4O_4S_2$	$C_{32}H_{26}CoN_4O_4S_2$	$C_{34}H_{42}CoN_4O_4S_2$
F.w.	665.71	739.76	643.71	581.56	653.62	693.76
T (K)	293	296	293	296	293	296
Space group	*Cc*	$P2_1/c$	*C2/c*	*C2/c*	*C2/c*	*P-1*
a (Å)	15.8779(4)	19.669(11)	26.3121(9)	30.34(2)	17.1468(5)	10.6946(5)
b (Å)	10.3508(4)	11.086(6)	6.7700(2)	7.971(5)	9.9155(2)	12.6058(6)
c (Å)	19.6797(8)	17.161(9)	16.7692(7)	26.850(14)	17.9855(5)	15.0981(7)
α (◦)	90	90	90	90	90	96.063(3)
β (◦)	99.798(2)	113.850(7)	102.255(3)	122.21(3)	106.784(3)	108.146(3)
γ (◦)	90	90	90	90	90	110.295(3)
V (Å^3)	3187.2(2)	3423(3)	2919.08(18)	5494(6)	2927.61(14)	1761.24(15)
Z	4	4	4	4	4	2
Dc (g cm^{-3})	1.387	1.436	1.465	1.406	1.483	1.308
M (mm^{-1})	0.712	0.673	6.299	0.815	6.304	0.647
Data collected/unique	12067/5203	28118/6845	11845 / 2778	20948 / 4734	7589 / 2908	16491/6467
R_1 (> 2σ/all data)	0.0441/0.0463	0.0301/0.0403	0.0456/0.0465	0.0494/0.0670	0.0671/0.0711	0.039/0.06
wR_2 (> 2σ/all data)	0.1073/0.1090	0.0781/0.0837	0.1279/0.1290	0.1019/0.1019	0.1949/0.1975	0.095/0.103
GOF	1.047	1.036	1.019	1.054	1.163	1.119
Residues (e Å^3)	0.337/-0.477	0.280/-0.294	0.724/-0.463	0.640/-0.248	0.774/-1.625	0.487/-0.248

Table S2 Selected bond lengths (Å) for complex **1** - **6**.

	1	**2**	**3**	**4**	**5**	**6**
Co – N1	1.95(3)	1.94(2)	1.95(2)	1.94(3)	1.93(3)	1.93(2)
Co – N2	1.95(4)	1.95(2)	1.95(2)	1.95(3)	1.93(3)	1.94(2)
Co – N3	2.03(3)	2.03(2)	2.03(2)	2.03(3)	2.03(3)	2.03(2)
Co – N4	2.04(4)	2.05(2)	2.03(2)	2.04(3)	2.03(3)	2.04(2)

Table S3 Selected bond angles (°) for complexes **1** – **6.**

	1	**2**	**3**	**4**	**5**	**6**
N1–Co–N2	81.86(2)	81.74(7)	81.79(8)	82.14(2)	82.15(1)	81.79(8)
N3–Co–N4	81.54(1)	81.71(3)	81.79(8)	81.37(1)	82.15(1)	83.02(9)
N1–Co–N3	146.9(2)	135.82(7)	132.1(1)	136.8(1)	133.9(2)	134.65(9)
N1–Co–N4	115.3(1)	128.67(7)	127.33(9)	120.1(1)	120.9(1)	118.53(8)
N2–Co–N3	112.8(2)	107.62(7)	127.33(9)	119.3(1)	120.9(1)	117.88(8)
N2–Co–N4	124.9(1)	125.33(7)	110.3(1)	122.8(1)	122.4(2)	124.23(9)

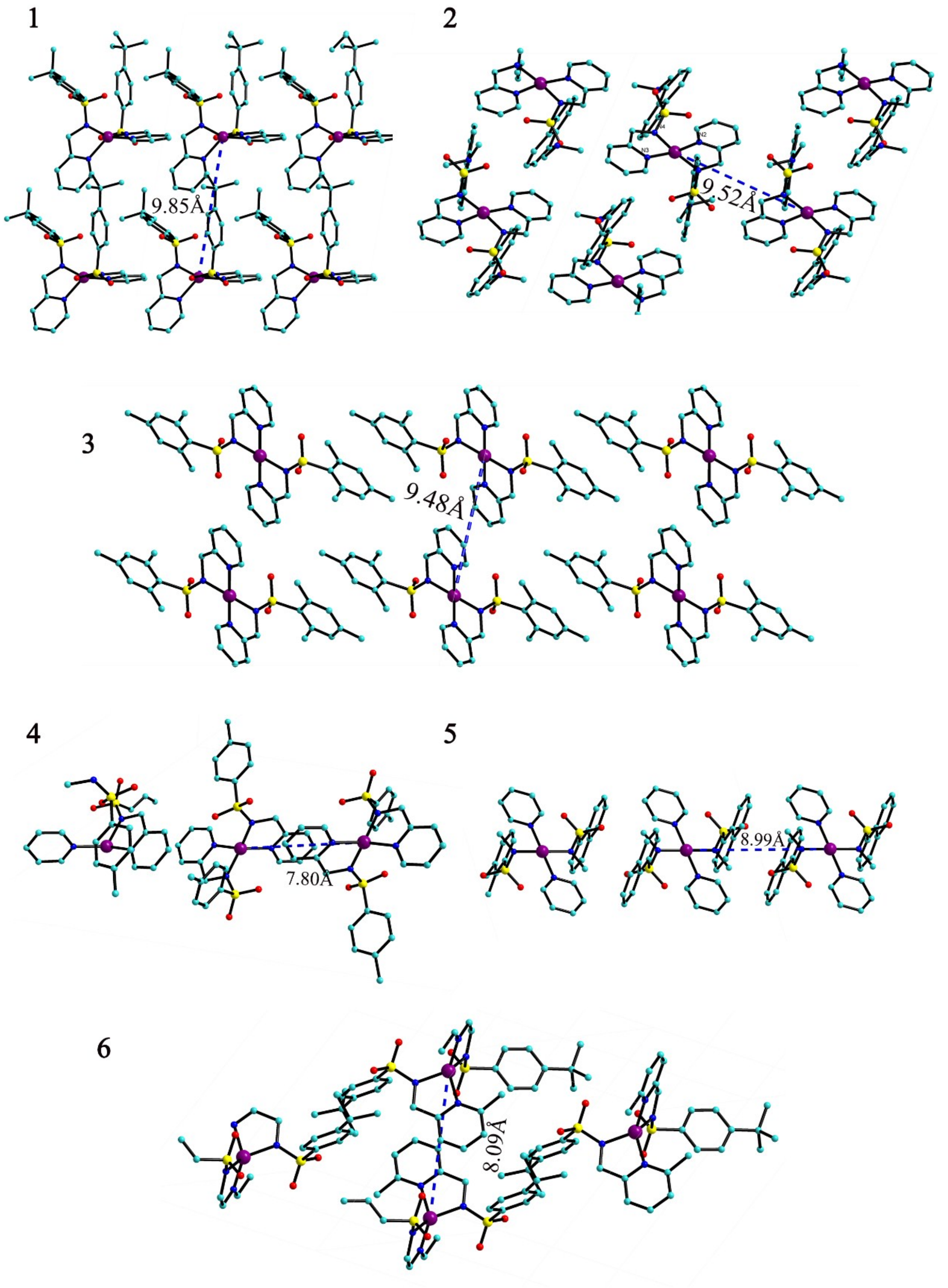

Fig. S1 The diagrams of molecular packing for complexes **1** - **6**. The dashed lines indicate the shortest Co···Co distances.

3 Powder X-ray diffraction

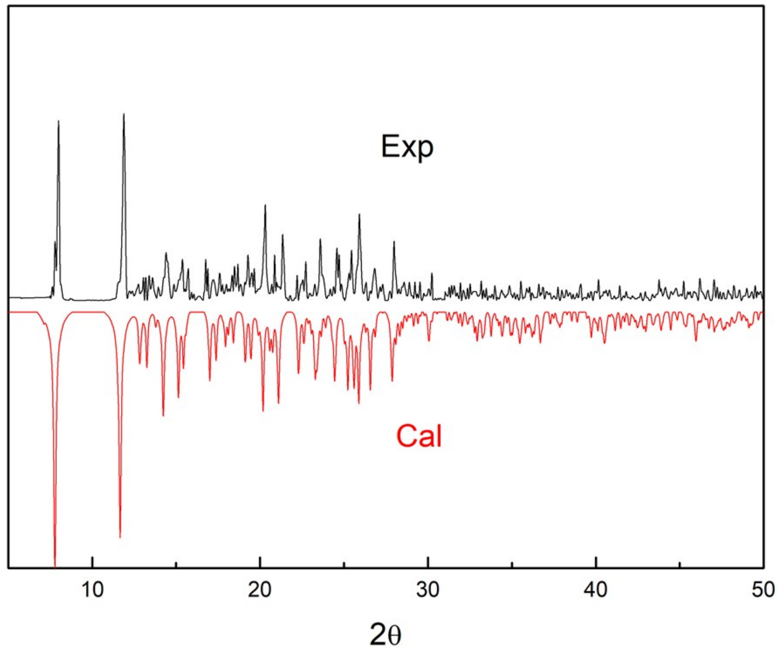

Fig. S2 Experimental and calculated PXRD patterns for complex **1**

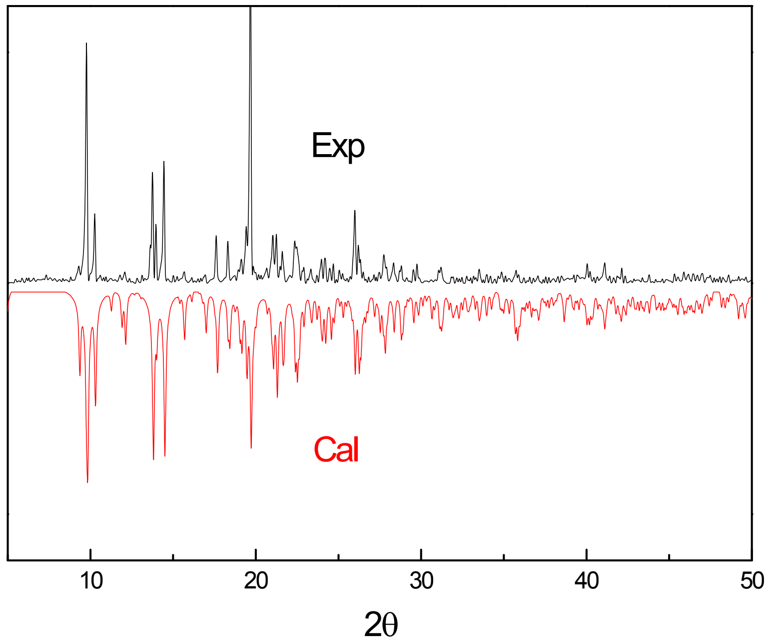

Fig. S3 Experimental and calculated PXRD patterns for complex **2**

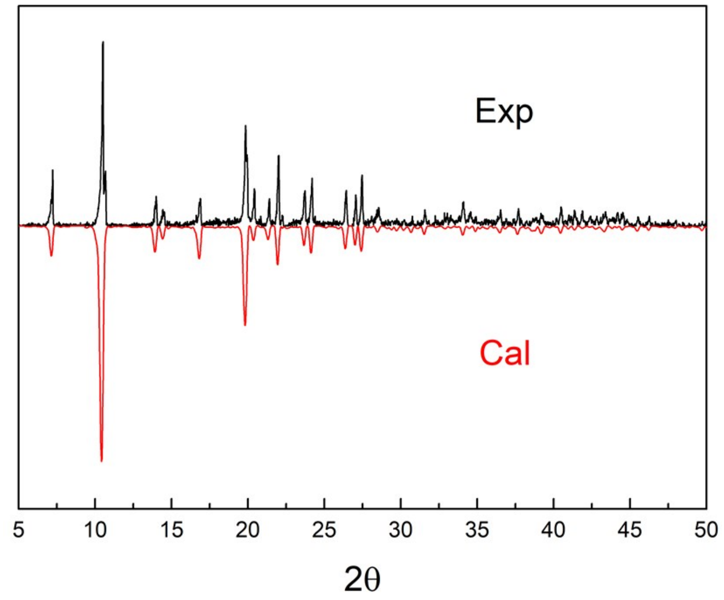

Fig. S4 Experimental and calculated PXRD patterns for complex **3**

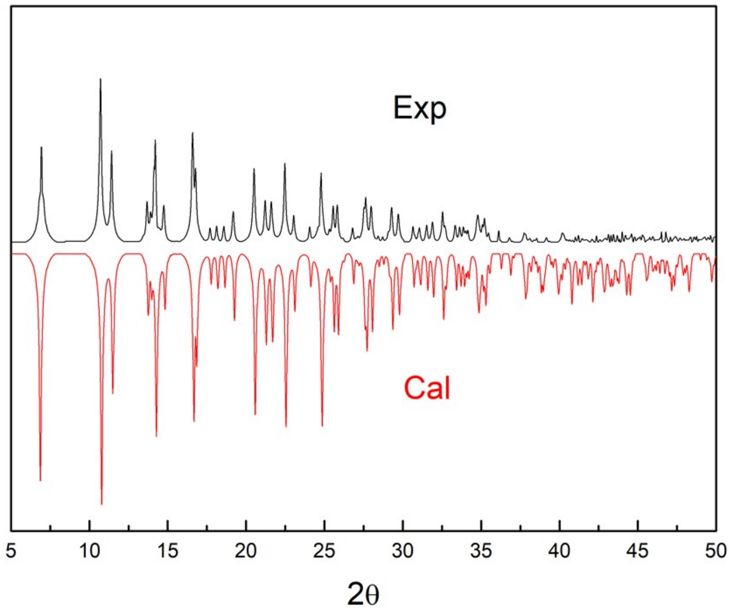

Fig. S5 Experimental and calculated PXRD patterns for complex **4**

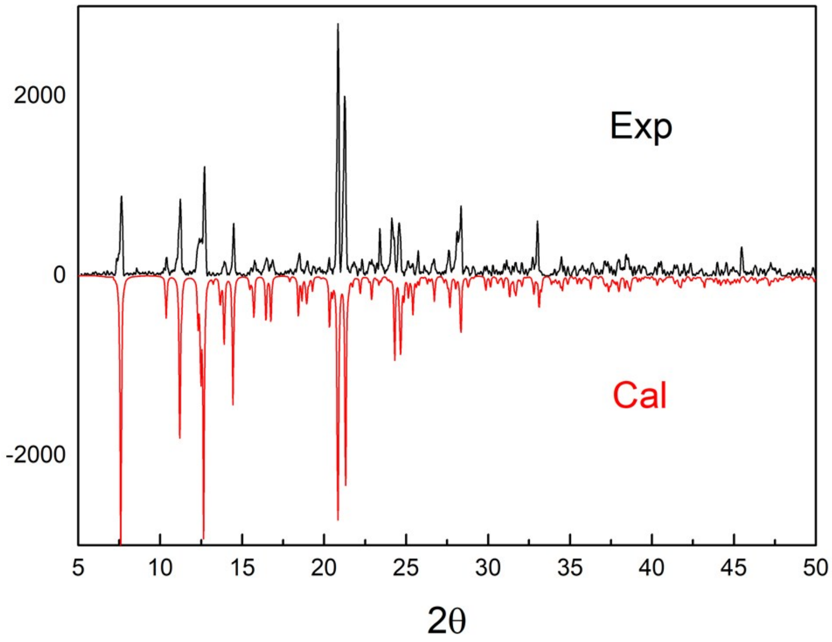

Fig. S6 Experimental and calculated PXRD patterns for complex **5**

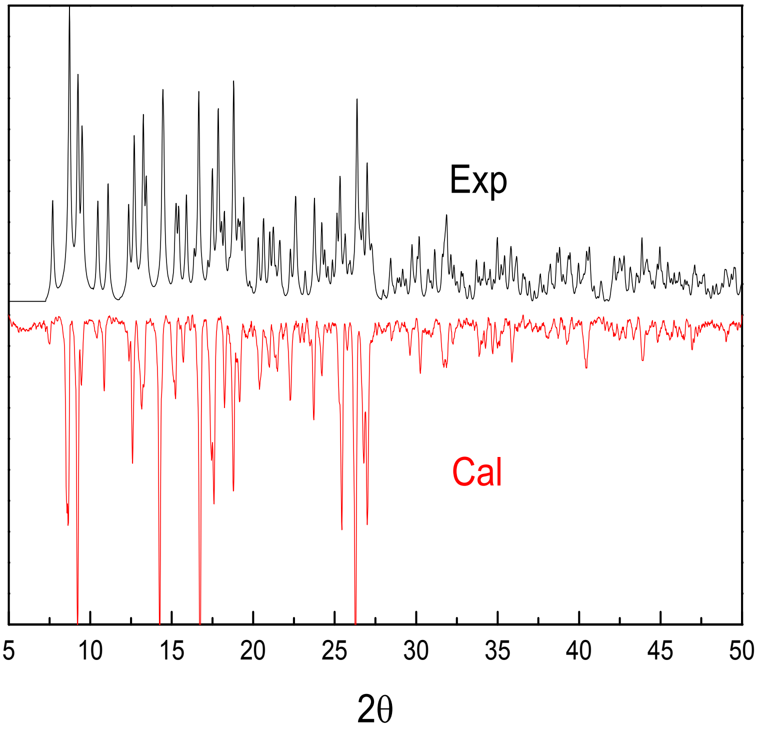

Fig. S7 Experimental and calculated PXRD patterns for complex **6**

4 Magnetic data

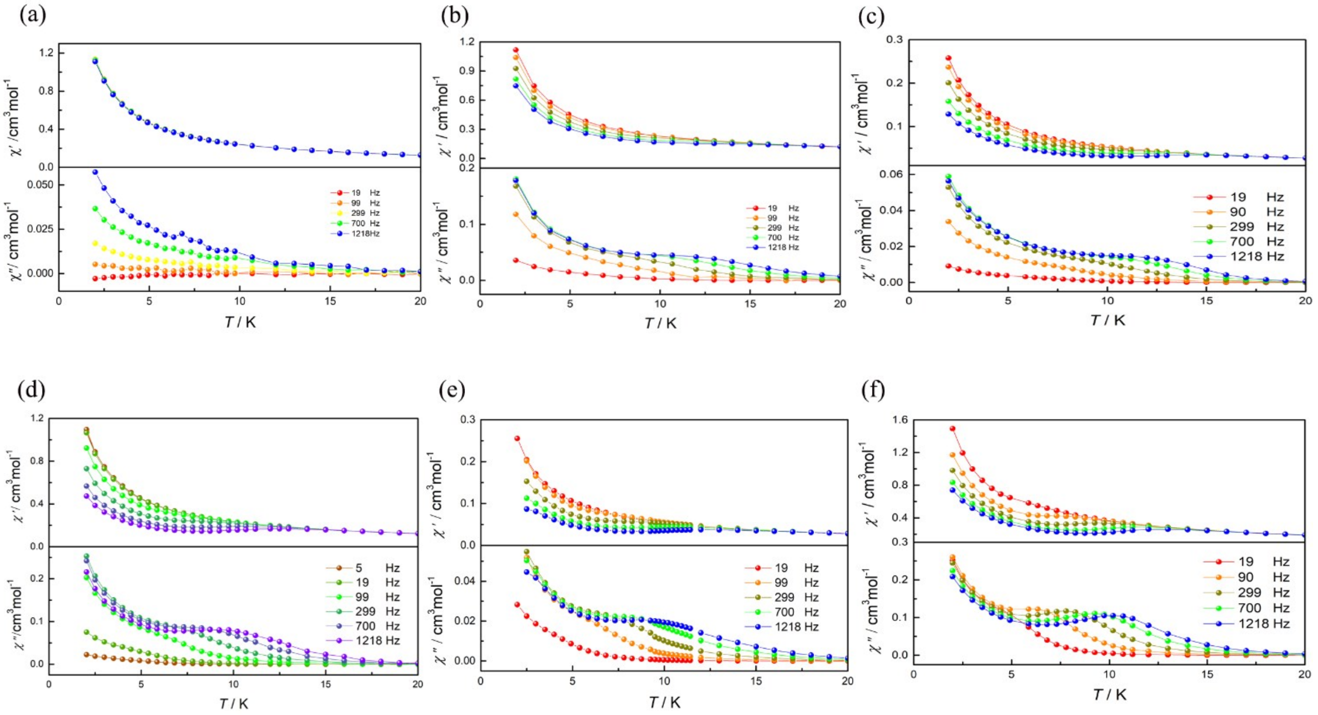

Fig S8 Temperature-dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility signals under 0 Oe dc field at the indicated frequencies for complexes **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f). Lines are visual guides only.

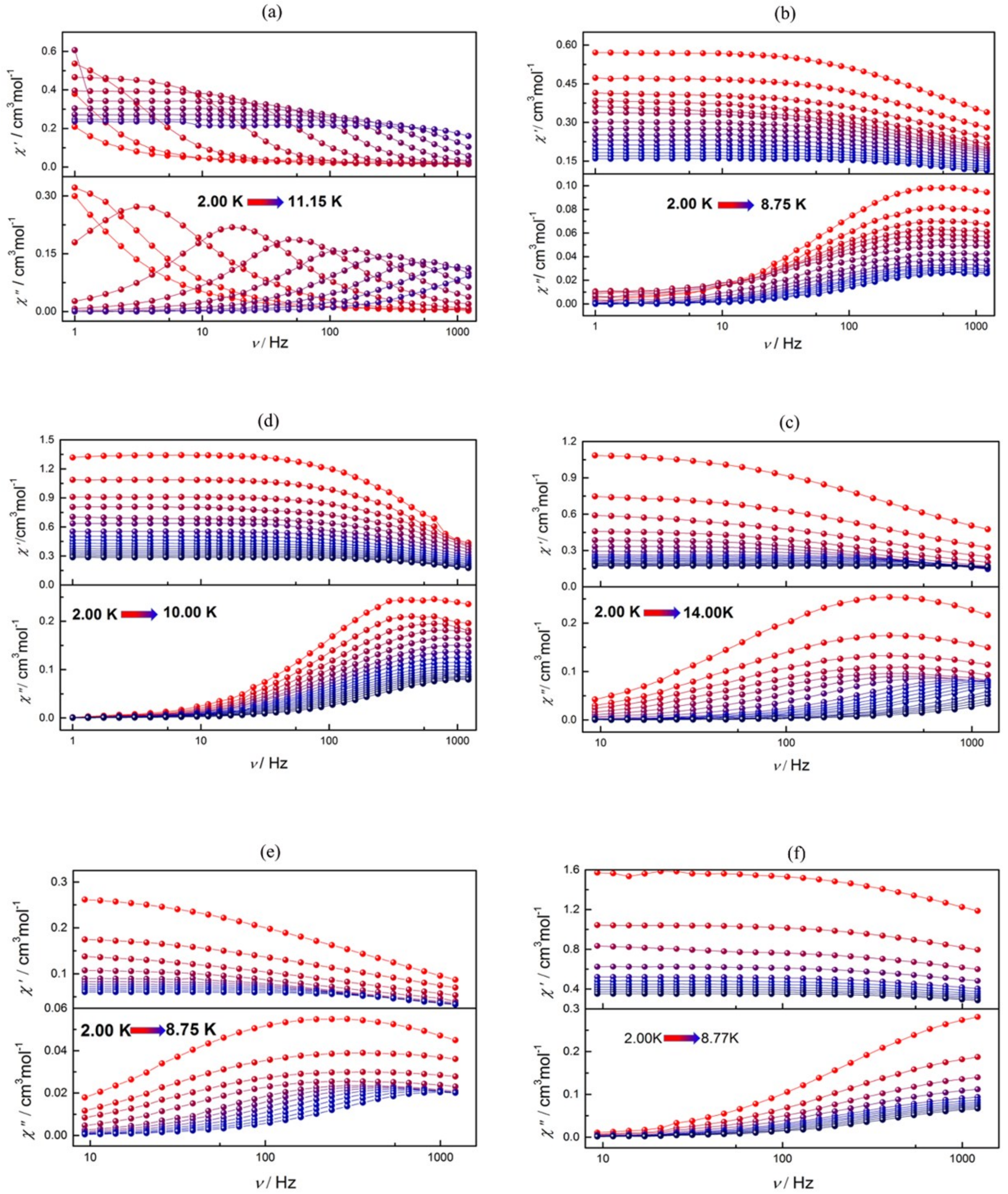

Fig. S9 Frequency-dependent ac susceptibility data measured under a dc field of 0 Oe at indicated temperature for **2**(b), **3**(c), **4**(d), **5**(e) and **6**(f), and 2600 Oe for **1**(a). Lines are visual guides only.

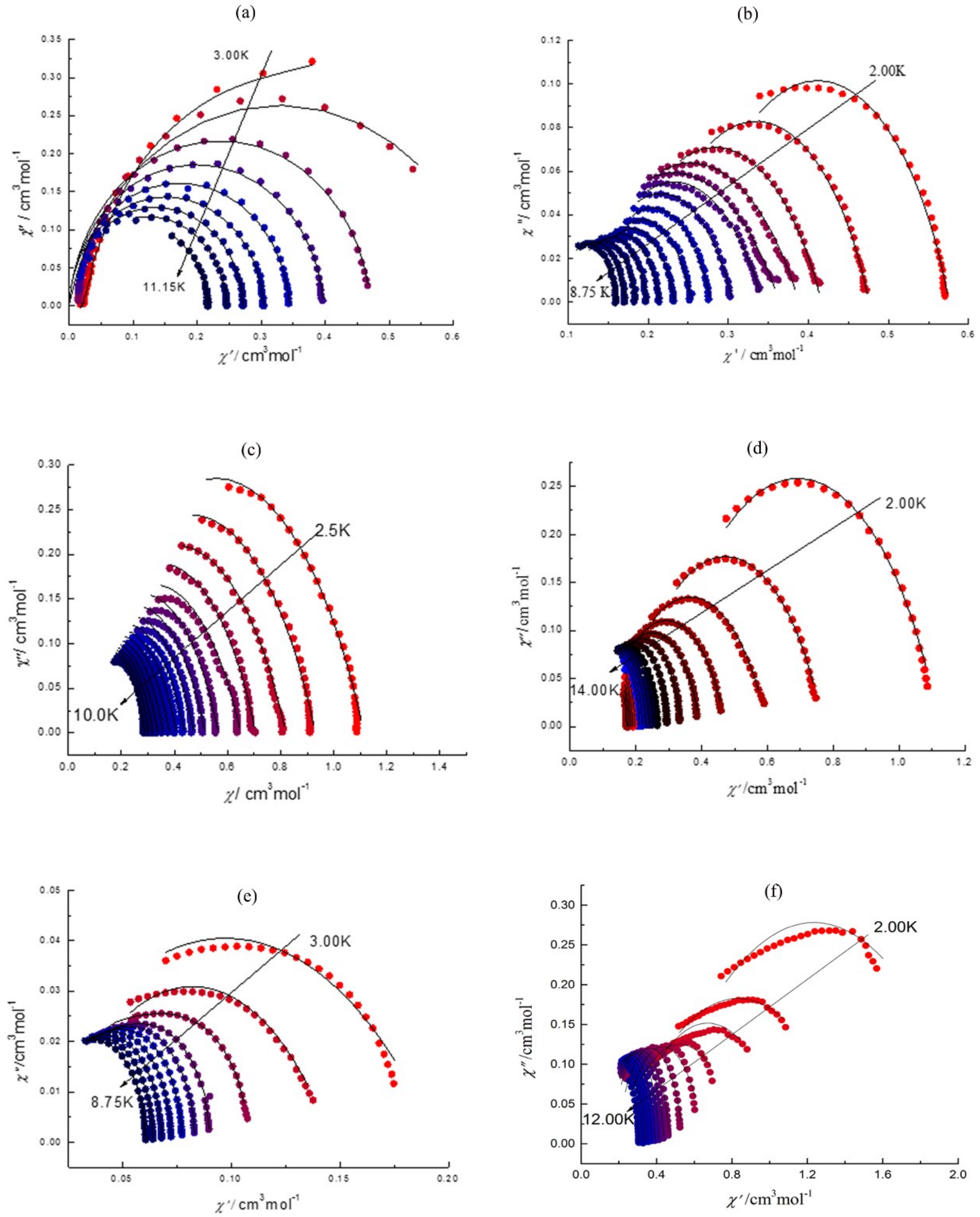

Fig. S10 Cole-Cole plots using the frequency-dependence ac susceptibility data under a dc field of 0 Oe for **2, 3, 4, 5** and **6,** and 2600Oe for **1** The solid lines are the best fits.

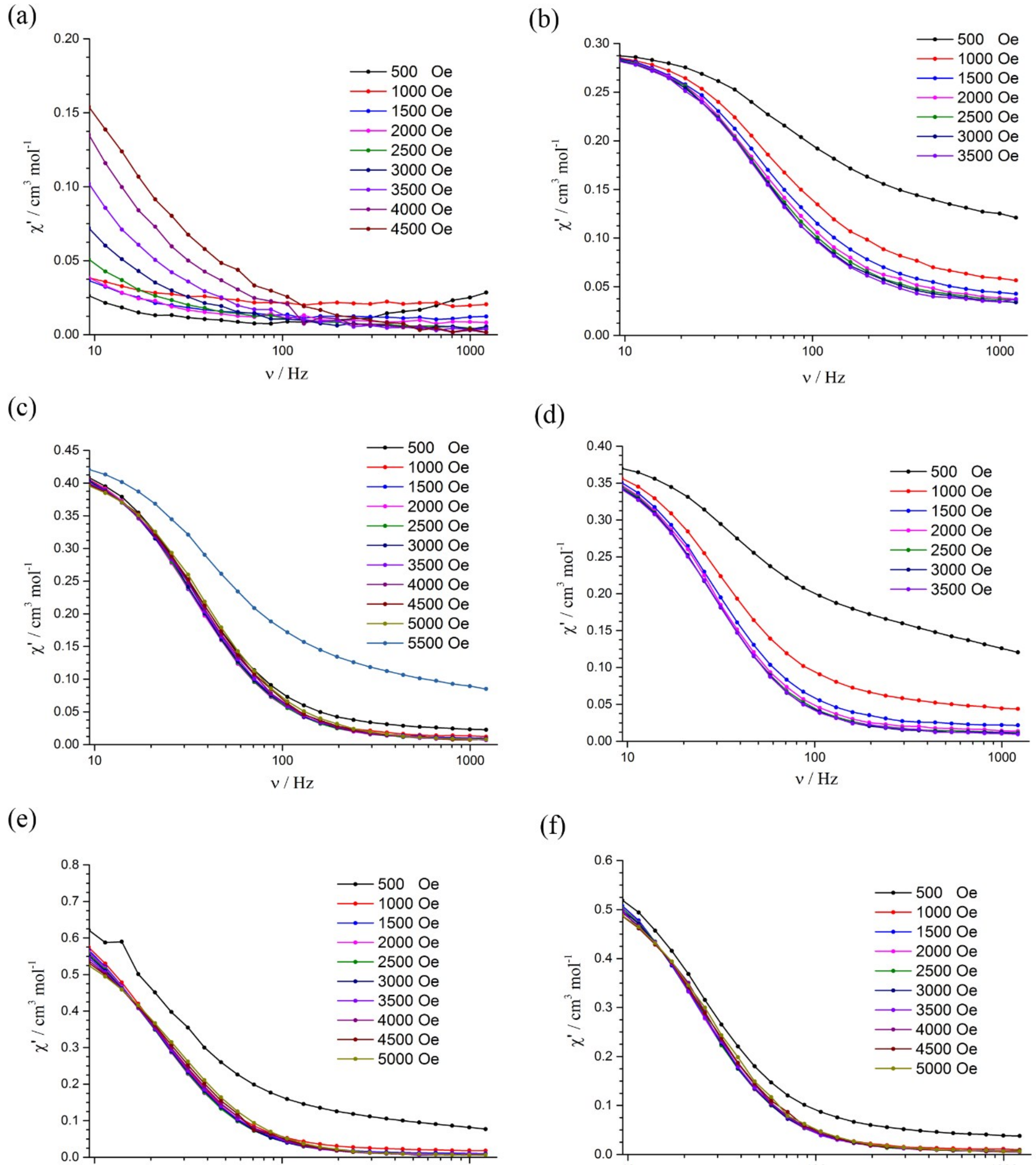

Fig. S11 Frequency dependent of the in-phase ac susceptibility for **1**, **2, 3, 4, 5** and **6** (a - f) under different dc field. The solid lines are the best fits.

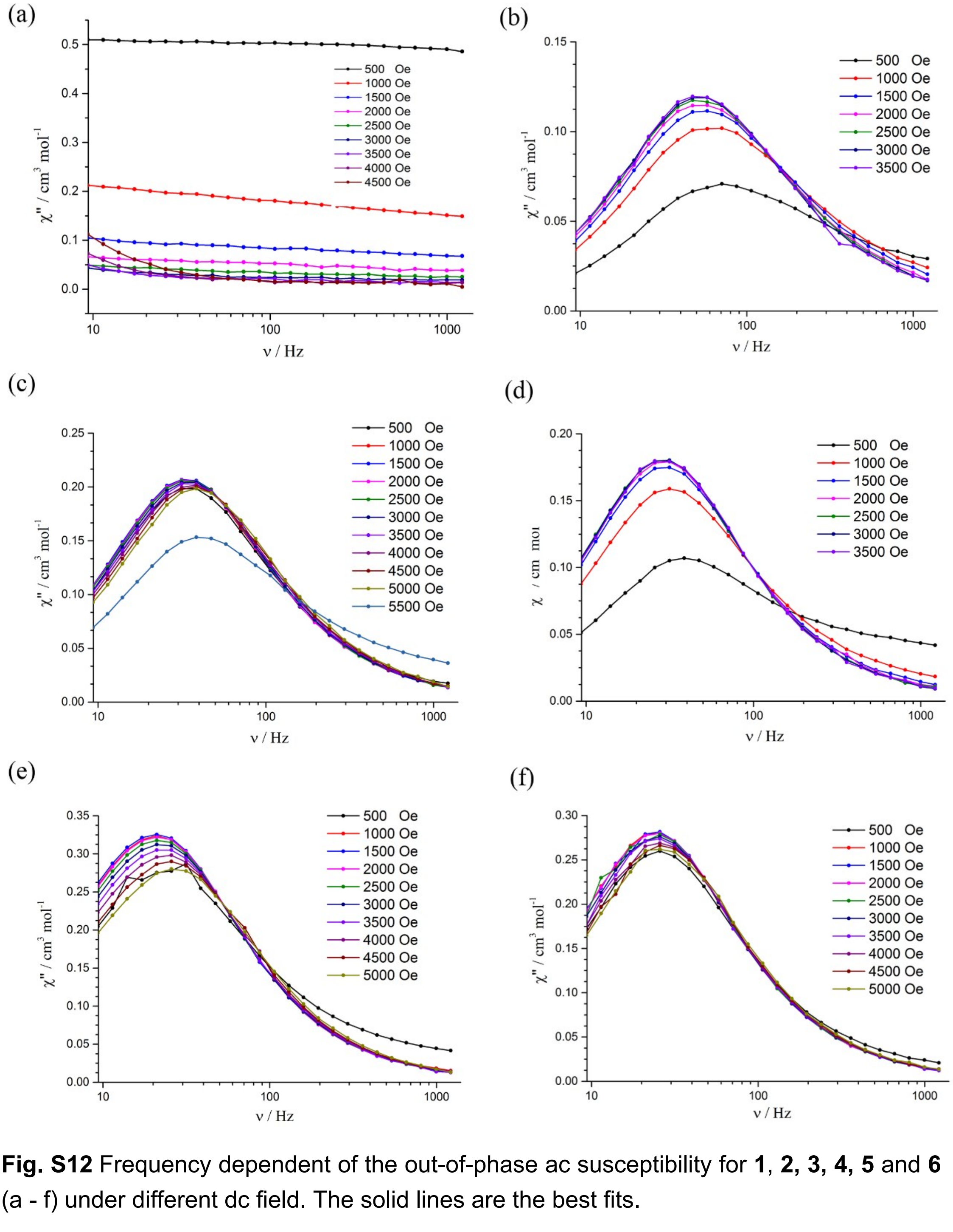

Fig. S12 Frequency dependent of the out-of-phase ac susceptibility for **1**, **2**, **3**, **4**, **5** and **6** (a - f) under different dc field. The solid lines are the best fits.

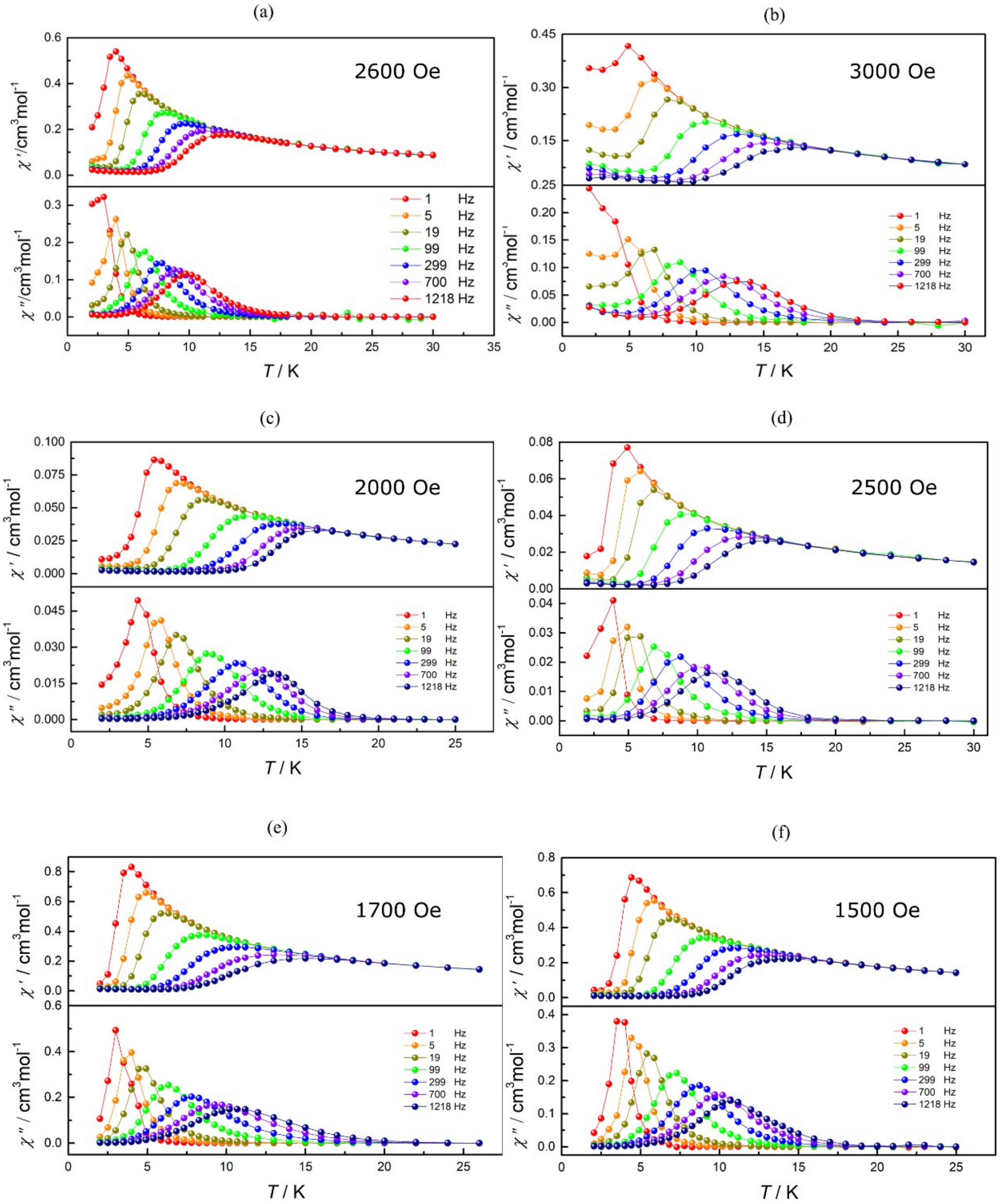

Fig. S13 Temperature-dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility signals under different applied dc field at the indicated frequencies for complexes **1** – **6** (a - f). Lines are visual guides only.

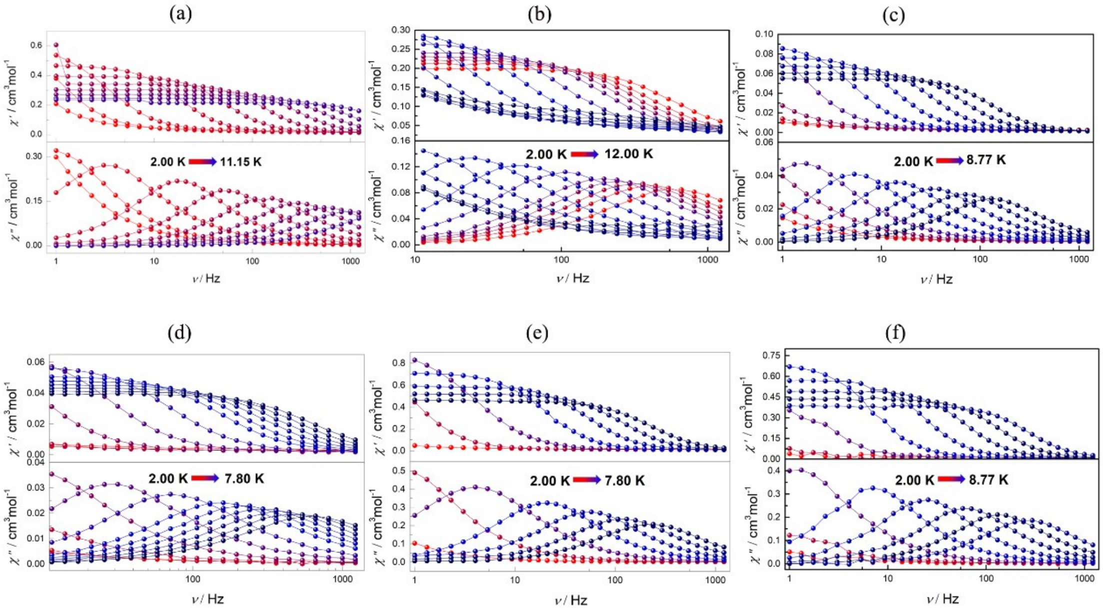

Fig. S14 Frequency-dependent ac susceptibility data measured under different dc field at indicated temperature for **1**(a), **2**(b), **3**(c), **4**(d), **5**(e) and **6**(f). Lines are visual guides only.

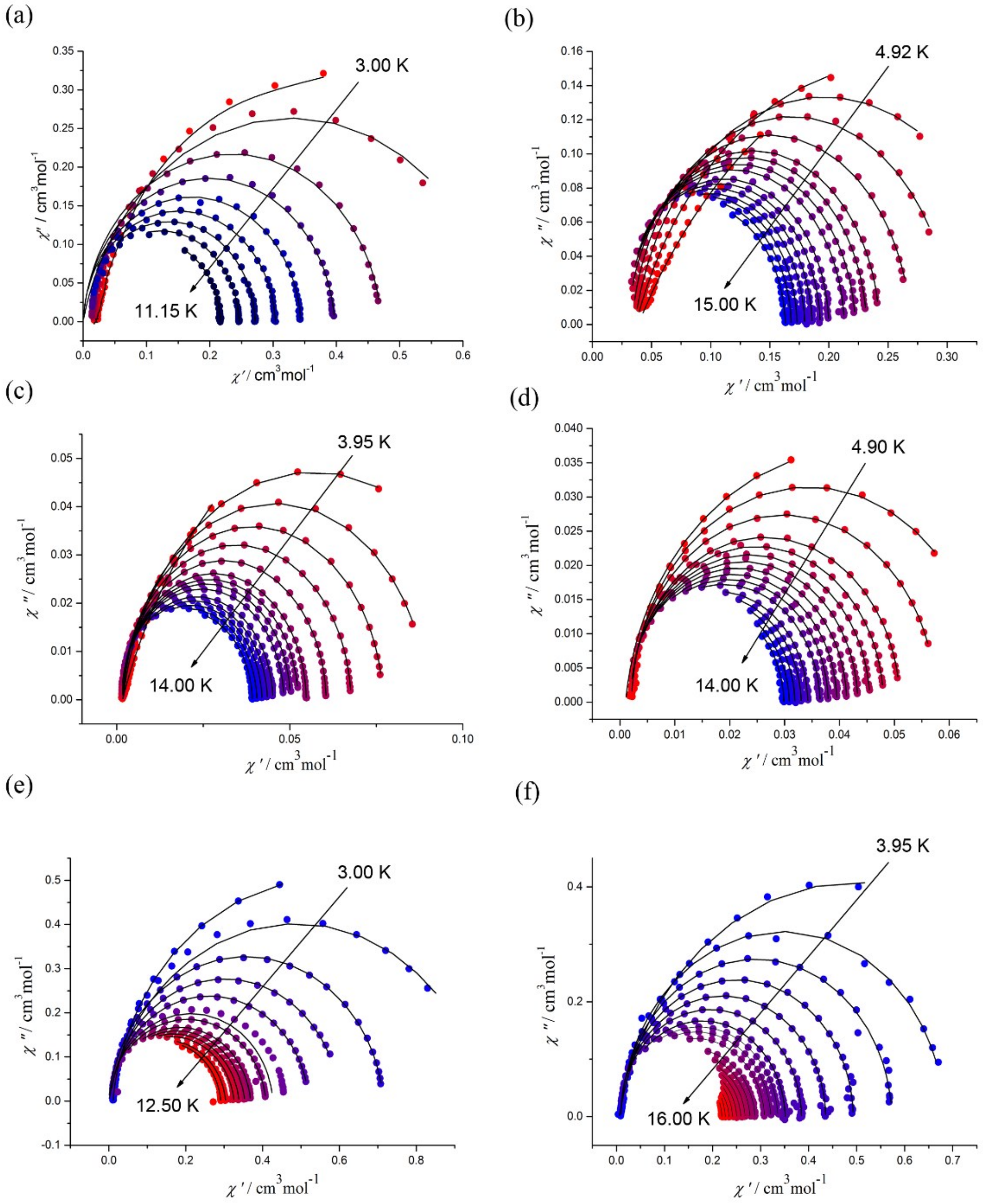

Fig. S15 Cole-Cole plots using the frequency-dependence ac susceptibility data under different dc field of 2600 Oe for **1**; 3000 Oe for **2**; 2000 Oe for **3**; 2500 Oe for **4**; 1700 Oe for **5** and 1500 Oe for **6**. The solid lines are the best fits.

Table S4 Relaxation Fitting Parameters of a generalized Debye model for **2** under zero dc field.

T	*τ*	*α*
2.00	3.50626E-4	0.29
2.50	3.3487E-4	0.32
3.00	3.12562E-4	0.37
3.5	3.00887E-4	0.43
4.00	2.73548E-4	0.46
4.35	3.62112E-4	0.41
4.90	2.92764E-4	0.35
5.45	2.92171E-4	0.31
5.88	2.96634E-4	0.29
6.37	3.06492E-4	0.28
6.88	3.12552E-4	0.25
7.30	3.10977E-4	0.23
7.78	3.11764E-4	0.20
8.24	2.80185E-4	0.19
8.75	2.61689E-4	0.17
9.20	2.41231E-4	0.15
9.70	2.17406E-4	0.13
10.2	1.87864E-4	0.12
10.7	1.70389E-4	0.09
11.15	1.54353E-4	0.08
12.00	1.19224E-4	0.06
12.5	1.09963E-4	0.04
13.00	8.97049E-5	0.04
13.50	9.04536E-5	0.01
14.00	6.52569E-5	0.03
14.50	5.92938E-5	0.02

Table S5 Relaxation Fitting Parameters of a generalized Debye model for **3** under zero dc field.

T	*τ*	*α*
2.5	1.56793E-4	0.39
3	1.29345E-4	0.38
3.5	1.16832E-4	0.39
4	1.06532E-4	0.37
4.5	1.10712E-4	0.39
5	1.0267E-4	0.35
5.5	1.01874E-4	0.35
6	1.01266E-4	0.35
6.5	1.0059E-4	0.35
7	9.99381E-5	0.34
7.5	9.84114E-5	0.33

8	9.70626E-5	0.32
8.5	9.44184E-5	0.31
9	9.16886E-5	0.29
9.5	8.8607E-5	0.27
10	8.39598E-5	0.26

Table S6 Relaxation Fitting Parameters of a generalized Debye model for **4** under zero dc field.

T	*τ*	*α*
2.00	0.44E-03	0.30
3.13	4.35E-4	0.31
3.88	4.59E-4	0.33
4.91	4.28E-4	0.29
5.86	4.06E-4	0.24
6.84	3.43E-4	0.17
7.80	2.60E-4	0.11
8.75	1.88E-4	0.07
9.22	1.61E-4	0.05
9.75	1.38E-4	0.04
10.2	1.18E-4	0.02
10.7	9.80E-5	0.03
11.18	8.43E-5	0.02
12.00	6.30E-5	0.02
12.50	5.21E-5	0.02
13.00	4.47E-5	0.02
13.5	3.87E-5	0.01
14.00	3.34E-5	0.01

Table S7 Relaxation Fitting Parameters of a generalized Debye model for **5** under zero dc field.

T	*τ*	*α*
3	3.56046E-4	0.49
3.9	5.22083E-4	0.42
4.92	1.42304E-4	7.02656E-7
5.88	2.16949E-4	1.1858E-6
6.33	2.05244E-4	1.9311E-6
6.85	1.90222E-4	2.8096E-6
7.32	1.60878E-4	0.27
7.79	1.47212E-4	0.24
8.31	1.28707E-4	0.21
8.75	1.12382E-4	0.18

Table S8 Relaxation Fitting Parameters of a generalized Debye model for **6** under zero dc field.

T	*τ*	*α*
2	0.00214	0.60
3	0.00212	0.63
3.89	0.00282	0.58
4.9	0.0021	0.53
5.87	0.00135	0.36
6.82	8.17985E-4	0.23
7.79	5.00875E-4	0.15
8.29	3.95813E-4	0.12
8.76	3.15622E-4	0.08
9.26	2.48922E-4	0.08
9.72	1.96399E-4	0.06
10.21	1.56041E-4	0.05
10.68	1.23464E-4	0.05
11.18	9.60289E-5	0.05
12	7.00506E-5	0.04

Table S9 Relaxation Fitting Parameters of a generalized Debye model for **1** under 2600 Oe dc field.

T	*τ*	*α*
3.00	0.22627	0.19
3.74	0.05127	0.14
4.92	0.00847	0.05
5.88	0.0028	0.04
6.87	0.00123	0.09
7.82	5.28402E-4	0.03
8.79	2.75392E-4	0.02
9.75	1.52597E-4	0.02
11.19	7.35746E-5	0.07

Table S10 Relaxation Fitting Parameters of a generalized Debye model for **2** under 3000 Oe dc field.

T	*τ*	*α*
4.92	0.08278	0.33
5.88	0.02185	0.22
6.85	0.0068	0.11
7.82	0.00297	0.06
8.74	0.00148	0.04
9.74	8.16639E-4	0.03
10.23	6.25788E-4	0.02
10.71	4.89362E-4	0.02

11.19	3.8751E-4	0.02
12	2.67889E-4	0.01
12.5	2.1754E-4	0.01
13	1.76901E-4	0.02
13.5	1.47932E-4	0.01
14	1.22273E-4	0.01
14.5	1.00819E-4	0.01
15	8.48701E-5	0.01

Table S11 Relaxation Fitting Parameters of a generalized Debye model for **3** under 2000 Oe dc field.

T	τ	α
3.95	0.85574	0.21
4.92	0.10136	0.09
5.88	0.02898	0.05
6.84	0.01071	0.03
7.78	0.00467	0.01
8.76	0.00228	0.01
9.7	0.00122	0.01
10.21	9.13231E-4	0.01
10.71	7.00144E-4	0.01
11.17	5.29398E-4	0.02
12	3.27324E-4	0.01
12.5	2.43613E-4	0.02
13	1.80405E-4	0.02
13.49	1.31863E-4	0.02
14	9.44534E-5	0.03

Table S12 Relaxation Fitting Parameters of a generalized Debye model for **4** under 2500 Oe dc field.

T	τ	α
4.9	0.01961	0.07
5.91	0.00553	0.01
6.85	0.00218	0.01
7.82	0.00103	0.01
8.3	7.42926E-4	0.01
8.78	5.51583E-4	0.01
9.27	4.22245E-4	0.01
9.74	3.26397E-4	0.01
10.19	2.56446E-4	0.01
10.71	2.07637E-4	0.01
11.19	1.66094E-4	0.02

12	1.20073E-4	0.01
12.5	9.45435E-5	0.02
13	7.41933E-5	0.02
13.5	5.95104E-5	0.02
14	4.85331E-5	0.01

Table S13 Relaxation Fitting Parameters of a generalized Debye model for **5** under 1700 Oe dc field.

T	τ	α
3	0.20572	0.07
3.76	0.04189	0.12
4.89	0.0078	0.05
5.88	0.00296	0.04
6.82	0.00137	0.05
7.8	6.74027E-4	0.04
8.78	4.18051E-4	0.06
9.73	2.57739E-4	0.06
10.19	2.09479E-4	0.06
10.69	1.72622E-4	0.06
11.19	1.44318E-4	0.06
12	1.06751E-4	0.06
12.5	8.9883E-5	0.05

Table S14 Relaxation Fitting Parameters of a generalized Debye model for **6** under 1500 Oe dc field.

T	τ	α
3.95	0.15008	0.12
4.9	0.0222	0.03
5.9	0.00657	0.02
6.85	0.00255	0.01
7.81	0.00118	0.01
8.77	5.96566E-4	0.01
9.73	3.2306E-4	0.02
10.2	2.4106E-4	0.03
10.69	1.86565E-4	0.03
11.17	1.47891E-4	0.03
12	1.02659E-4	0.04
12.5	8.50659E-5	0.05
13	7.19525E-5	0.04
13.5	5.84925E-5	0.04
14	4.96422E-5	0.04
14.5	3.8786E-5	0.04

15	3.04765E-5	0.05

5 Theoretical Analysis

Table S15 The relative energies of ground and low-lying quartet spin eigenstates (cm^{-1})

	1	**2**	**3**	**4**	**5**	**6**
$^4\Psi_0$	0.0	0.0	0.0	0.0	0.0	0.0
$^4\Psi_1$	644.3	558.7	608.4	643.2	781.0	859.4
$^4\Psi_2$	5326.3	5592.1	5406.1	5347.4	6514.8	7138.4
$^4\Psi_3$	6529.6	6359.5	6690.0	6778.4	7922.6	7789.9
$^4\Psi_4$	7925.3	8879.8	7323.2	8230.8	8572.8	8475.8
$^4\Psi_5$	8448.4	9000.2	9519.8	9185.8	8932.5	8828.2
$^4\Psi_6$	10179.8	10872.5	11096.3	11328.8	11180.4	11625.2
$^4\Psi_7$	17683.8	17954.2	17893.8	17931.7	18163.9	17933.7
$^4\Psi_8$	20183.6	19192.3	21383.2	20312.4	21155.2	20773.4
$^4\Psi_9$	22661.3	22593.2	22841.8	22487.0	22025.4	21996.6

Table S16 Individual contribution to *D*-tensor calculated by CASSCF/NEVPT2 (cm^{-1})[a]

Multiplicity	Root	**1**	**2**	**3**	**4**	**5**	**6**
4	1	-67.2	-100.3	-73.7	-69.3	-60.7	-59.4
	2	5.1	4.5	5.3	4.1	7.3	5.2
	3	/	/	/	1.0	/	2.1
	5	1.0	/	1.2	1.4	/	/
2	all	/	2.3	/	1.5	/	1.9

[a] Only the values larger than 1 cm^{-1} are shown here.

Table S17 The relative energies (cm^{-1}) of d-orbitals for **1** - **6**.

	1	**2**	**3**	**4**	**5**	**6**

d_{z2}	0.0	0.0	0.0	0.0	0.0	0.0
d_{x2-y2}	461.2	775.4	433.3	561.8	520.0	497.2
d_{xy}	1111.4	1223.7	1097.8	1161.8	1112.6	1286.6
d_{xz}	5451.4	5830.0	5049.8	5257.0	5562.8	5575.0
d_{yz}	7224.1	7329.3	8259.1	7165.1	7088.4	6803.4

Table S18 The calculated xyz coordinates of complex **1.**

Co	5.66324	5.35012	7.96456
N	3.94052	6.43302	7.86508
N	7.14339	6.34815	8.75888
N	7.01233	5.14849	6.44418
N	4.40492	3.88051	8.15946
S	4.75408	2.33866	8.27620
O	6.14242	2.18505	7.91686
O	3.79399	1.51225	7.56798
C	4.60077	1.88902	9.99051
S	7.26860	6.26772	10.33240
O	5.90414	6.15045	10.80171
O	8.20740	5.27270	10.78328
C	7.91697	7.81485	10.90294
C	3.84270	7.76517	7.70334
C	2.81868	5.71882	8.06133
C	8.37924	6.41232	7.98706
C	8.18559	5.76747	6.64528
C	6.81335	4.48086	5.28585
C	2.99227	4.24072	8.29734
C	9.17054	5.79334	5.66673
C	9.06012	7.82520	11.69396
H	9.50233	7.03026	11.89157
C	9.53291	9.02486	12.18343
C	5.03759	2.74710	10.98981
H	5.35138	3.59483	10.77262
C	5.00128	2.33411	12.31259
C	4.10088	0.63761	10.32736
H	3.77698	0.07039	9.66530
C	4.08432	0.23910	11.64606
H	4.62311	8.25890	7.58834
C	2.64297	8.42555	7.69966
H	5.28974	2.91686	12.97756
C	4.54265	1.06510	12.67251
C	1.56845	6.32434	8.06502
H	9.08677	5.95585	8.46877
H	8.64247	7.33768	7.86954

C	7.76928	10.19657	11.08697
H	7.33458	10.99048	10.87346
C	7.27396	8.99899	10.59925
C	8.91141	10.23798	11.89312
H	6.01254	4.02646	5.16038
C	7.75925	4.45498	4.28616
H	9.96885	6.24567	5.81586
C	8.95212	5.13814	4.46748
H	2.68123	4.01197	9.18824
H	2.46344	3.74181	7.65428
H	3.75864	-0.60656	11.85861
H	10.28911	9.02486	12.72352
C	4.51179	0.55687	14.11727
H	6.50977	8.99174	10.06866
C	9.49411	11.53907	12.46327
C	3.05689	0.28879	14.51540
H	2.56051	1.10961	14.48437
H	3.02861	-0.06832	15.40552
H	2.66858	-0.34261	13.90453
C	5.33004	-0.73801	14.22451
H	4.92942	-1.41599	13.67570
H	5.34378	-1.03301	15.13790
H	6.22915	-0.57447	13.92780
C	5.10657	1.57436	15.10474
H	0.79943	5.81404	8.18758
C	1.47568	7.69064	7.88505
H	9.59379	5.15573	3.79514
H	7.60121	3.98506	3.50037
H	0.64618	8.11192	7.88893
H	2.60737	9.34677	7.57477
C	9.42059	11.47179	14.00149
H	8.50134	11.44384	14.27687
H	9.84499	12.24707	14.37577
H	9.87100	10.68099	14.30790
C	8.74116	12.78220	11.99629
C	10.95571	11.66328	12.00793
H	8.77482	12.83603	11.03830
H	9.14710	13.56472	12.37639
H	7.82500	12.72734	12.28137
H	11.44758	10.89111	12.29494
H	11.34509	12.45305	12.39190
H	10.98777	11.72435	11.04993
H	6.01659	1.75860	14.86447
H	5.07542	1.21311	15.99312

H	4.59620	2.38689	15.07197

Table S19 The calculated xyz coordinates of complex **2.**

Co	2.34247	12.83814	6.00779
N	3.77465	12.12709	7.10696
N	3.82533	14.08421	5.39645
N	0.66831	13.97712	6.33018
N	1.11415	11.87521	4.82655
S	3.53285	11.28754	8.41958
O	4.57889	11.49241	9.39160
O	2.17458	11.54651	8.83629
C	3.56704	9.55225	7.98277
S	1.74472	11.05806	3.63023
O	1.16316	11.40328	2.35857
O	3.17520	11.17591	3.76961
C	1.35524	9.32676	3.87100
C	5.12567	12.49570	6.68396
C	3.69837	15.15667	4.59362
C	5.04675	13.70751	5.79826
C	0.55238	15.04614	7.14321
C	-0.39943	13.59820	5.60301
C	-0.24128	12.39758	4.71495
N	3.24287	4.82330	9.21032
C	4.61040	4.39782	8.90300
C	2.62348	3.87677	10.13573
C	3.17215	6.18832	9.61542
N	1.33262	4.70490	2.23332
C	-0.09101	4.55080	1.94766
C	2.11272	3.67944	1.53299
C	1.81689	6.03356	2.09803
C	3.34364	7.19736	8.61043
C	2.93065	6.55914	10.91046
C	3.50328	6.87842	7.23896
C	3.33897	8.57014	9.00094
C	3.70570	7.84301	6.30193
C	3.75275	9.19938	6.67956
C	3.10660	8.89385	10.36253
C	2.89337	7.90631	11.27507
C	4.77527	15.87094	4.14332
C	6.03064	15.47827	4.53775
C	6.17360	14.40071	5.37825
C	-0.61769	15.75465	7.26548
C	-1.60354	14.28986	5.69106
C	-1.71031	15.37074	6.52606

C	0.58835	8.95749	4.93610
C	1.83627	8.36683	2.91953
C	0.23892	7.60378	5.11786
C	0.62636	6.66768	4.20767
C	1.40330	7.01289	3.06958
C	2.75258	8.68366	1.88394
C	3.19110	7.71031	1.03795
C	2.71422	6.39950	1.12851
H	4.99893	5.00422	8.26843
H	4.59519	3.51315	8.53211
H	5.13365	4.39893	9.70771
H	3.15727	3.81026	10.93040
H	2.56002	3.01539	9.71870
H	1.74238	4.18497	10.36693
H	3.46877	5.98755	6.97354
H	3.81244	7.60610	5.40869
H	3.91184	9.85435	6.03809
H	3.10029	9.78340	10.63218
H	2.72016	8.13380	12.15936
H	2.78993	5.90551	11.55665
H	4.65878	16.60461	3.58330
H	2.84533	15.42284	4.33512
H	7.01819	14.13798	5.66296
H	6.78085	15.94056	4.23780
H	1.29224	15.31309	7.63904
H	-0.66907	16.48377	7.83994
H	-2.51045	15.83968	6.59057
H	-2.33520	14.01825	5.18425
H	-0.57712	5.27583	2.34649
H	-0.40184	3.71824	2.31039
H	-0.22889	4.55745	0.99824
H	1.96898	3.75815	0.58701
H	1.83385	2.80919	1.82696
H	3.04464	3.79917	1.72651
H	0.29565	9.59826	5.54211
H	-0.25895	7.34891	5.86230
H	0.37560	5.78135	4.33355
H	3.05506	9.55724	1.78302
H	3.82014	7.92206	0.38611
H	3.01177	5.76361	0.51952
H	-0.87719	11.71347	4.97393
H	-0.42099	12.64580	3.79519
H	5.53317	11.76003	6.20132
H	5.67295	12.69015	7.46011

Table S20 The calculated xyz coordinates of complex **3.**

Co	-0.88987	1.17561	4.09677
N	-0.88902	0.01286	2.42725
N	-0.89072	0.01286	5.76628
N	0.65437	1.96736	4.98839
N	-2.43411	1.96736	3.20515
S	1.61693	3.09078	4.41271
O	1.53518	3.01603	2.97327
O	1.36034	4.39373	4.97741
C	3.24609	2.56922	4.95217
C	-0.02666	0.42786	6.70887
C	-1.57266	-1.13398	5.95736
C	0.73118	1.69724	6.41669
C	0.15460	-0.28705	7.88644
C	3.94082	3.24892	5.98505
C	3.51511	4.56569	6.59907
C	5.09611	2.65790	6.48928
H	0.34537	2.43517	6.91371
H	1.65782	1.59907	6.68593
H	-2.15519	-1.42779	5.29466
C	-1.43135	-1.88341	7.10445
H	4.15919	4.83378	7.25947
H	2.65526	4.46278	7.01203
H	3.46244	5.23592	5.91246
C	3.75870	1.35942	4.43106
H	0.74849	0.01896	8.53439
C	-0.55565	-1.45894	8.08669
C	3.08512	0.56056	3.33837
C	4.93811	0.84896	4.95873
H	3.59364	-0.23492	3.16434
H	3.03498	1.08997	2.53836
H	2.19786	0.32022	3.61827
H	5.54415	3.08644	7.18245
C	5.61063	1.46503	6.01029
H	5.29016	0.06838	4.59657
H	-1.92018	-2.66670	7.21687
C	6.83635	0.83677	6.60940
H	-0.44466	-1.95179	8.86705
H	7.33324	1.49888	7.11035
H	6.55580	0.10561	7.22506
H	7.39489	0.44750	5.90590
C	-1.75308	0.42786	1.48467
C	-0.20708	-1.13398	2.23618

S	-3.39667	3.09078	3.78083
C	-2.51092	1.69724	1.77685
C	-1.93434	-0.28705	0.30709
H	0.37545	-1.42779	2.89887
C	-0.34839	-1.88341	1.08909
O	-3.31492	3.01603	5.22027
O	-3.14008	4.39373	3.21613
C	-5.02583	2.56922	3.24136
H	-2.12510	2.43517	1.27983
H	-3.43756	1.59907	1.50761
H	-2.52823	0.01896	-0.34085
C	-1.22409	-1.45894	0.10684
H	0.14044	-2.66670	0.97667
C	-5.72056	3.24892	2.20849
C	-5.53844	1.35942	3.76247
H	-1.33508	-1.95179	-0.67351
C	-5.29485	4.56569	1.59446
C	-6.87585	2.65790	1.70426
C	-4.86486	0.56056	4.85516
C	-6.71785	0.84896	3.23481
H	-5.93893	4.83378	0.93406
H	-4.43500	4.46278	1.18151
H	-5.24218	5.23592	2.28108
H	-7.32389	3.08644	1.01108
C	-7.39036	1.46503	2.18325
H	-5.37338	-0.23492	5.02919
H	-4.81471	1.08997	5.65518
H	-3.97760	0.32022	4.57527
H	-7.06990	0.06838	3.59696
C	-8.61609	0.83677	1.58414
H	-8.69488	1.07846	0.66040
H	-8.56398	-0.11441	1.65673
H	-9.39702	1.14142	2.05166

Table S21 The calculated xyz coordinates of complex **4.**

Co	3.53059	6.36588	0.43164
N	4.09589	5.51434	-1.21699
N	5.22229	5.49282	1.13680
N	3.07445	8.17187	1.01844
N	1.67991	5.97745	1.20404
S	3.37449	5.66459	-2.59982
C	5.33914	4.75470	-1.17496
C	5.90178	4.79854	0.19787
C	5.71371	5.53028	2.37514

S	4.02637	9.43073	0.91803
C	1.70740	8.38151	1.48211
C	0.97702	7.07107	1.55980
C	1.06908	4.78180	1.28219
O	3.51320	4.48767	-3.42153
O	2.04019	6.12412	-2.30131
C	4.17123	6.98100	-3.47491
O	5.22792	9.01440	0.24990
O	3.33853	10.58230	0.39938
C	4.46790	9.84976	2.57847
C	4.85812	6.78332	-4.66351
C	4.05073	8.26354	-2.96626
H	4.97504	5.92405	-4.99791
C	5.37167	7.88172	-5.35299
H	5.83271	7.74383	-6.14743
C	5.20949	9.16585	-4.88364
C	5.65669	10.36708	-5.67490
C	4.55839	9.33643	-3.66711
H	6.35868	10.10962	-6.27920
H	5.98244	11.04143	-5.07515
H	4.91541	10.71462	-6.17470
H	4.46353	10.19332	-3.31907
H	3.62778	8.40143	-2.15137
H	5.97415	5.13173	-1.80152
H	5.17047	3.83405	-1.43122
C	7.08871	4.15608	0.49979
H	7.54865	3.68738	-0.15902
C	7.57701	4.21347	1.75609
H	8.37249	3.78224	1.97190
C	6.88546	4.91890	2.71705
H	7.21376	4.97789	3.58487
H	5.24196	5.98941	3.03055
C	5.58609	9.30295	3.13687
C	3.69450	10.71621	3.33656
H	6.11490	8.71549	2.64662
C	5.92755	9.62339	4.42543
H	6.69224	9.24955	4.79800
C	5.16989	10.48266	5.18647
C	5.57570	10.85172	6.60406
C	4.04470	11.00875	4.62761
H	4.94015	11.47266	6.96755
H	6.44754	11.25665	6.59270
H	5.59773	10.06100	7.14702
H	3.50693	11.57628	5.12968

H	2.93515	11.10121	2.96467
H	1.24352	8.97614	0.87236
H	1.72138	8.79839	2.35811
C	-0.33243	6.98499	1.98213
H	-0.80073	7.75419	2.21498
C	-0.93903	5.75745	2.05551
H	-1.82175	5.68093	2.33312
C	-0.21062	4.63434	1.70883
H	-0.59160	3.78862	1.76744
H	1.54543	4.02296	1.03366

Table S22 The calculated xyz coordinates of complex **5.**

Co	-1.29839	4.95735	4.30483
N	-3.07184	3.97612	4.50991
N	0.47506	3.97612	4.09975
N	-0.77399	5.71331	2.60597
N	-1.82279	5.71331	6.00369
S	-0.87682	6.62861	6.86672
O	-0.96626	6.32510	8.26958
O	0.43302	6.55712	6.26525
C	-1.45549	8.29729	6.69608
C	1.17905	4.34200	3.01579
C	0.99261	3.07182	4.95228
C	-3.12988	5.33950	6.52268
C	2.42417	3.78475	2.75854
C	0.53309	5.33950	2.08698
C	2.95288	2.87351	3.62639
C	2.23277	2.49672	4.74048
C	-3.77584	4.34200	5.59387
C	-2.46993	8.54617	5.81841
C	-0.86787	9.35428	7.46526
C	-3.03194	9.83717	5.73748
C	-2.54611	10.84756	6.49168
C	-1.43935	10.64726	7.34748
C	-0.89174	11.72012	8.08447
C	0.17589	11.52379	8.89378
C	0.76851	10.24569	9.00398
C	0.25385	9.18374	8.31693
H	2.89601	4.03065	1.99572
H	3.79508	2.50961	3.46625
H	2.57262	1.86907	5.33627
H	0.50331	2.82790	5.70476
H	-3.68942	6.12778	6.59844
H	-3.03280	4.95081	7.40603

H	-2.79107	7.86497	5.27428
H	-3.74273	9.99383	5.16063
H	-2.94585	11.68641	6.44691
H	-1.26602	12.56889	8.01215
H	0.52274	12.23672	9.38109
H	1.51317	10.12670	9.54811
H	0.64076	8.34290	8.40992
C	-3.58940	3.07182	3.65738
S	-1.71997	6.62861	1.74294
H	1.09264	6.12778	2.01122
H	0.43601	4.95081	1.20363
C	-5.02095	3.78475	5.85113
C	-4.82955	2.49672	3.86918
H	-3.10010	2.82790	2.90490
O	-1.63052	6.32510	0.34008
O	-3.02981	6.55712	2.34441
C	-1.14129	8.29729	1.91358
H	-5.49280	4.03065	6.61394
C	-5.54966	2.87351	4.98327
H	-5.16940	1.86907	3.27339
C	-0.12686	8.54617	2.79125
C	-1.72891	9.35428	1.14440
H	-6.39186	2.50961	5.14341
H	0.19428	7.86497	3.33538
C	0.43515	9.83717	2.87218
C	-1.15744	10.64726	1.26218
C	-2.85064	9.18374	0.29273
H	1.14594	9.99383	3.44903
C	-0.05067	10.84756	2.11798
C	-1.70505	11.72012	0.52519
C	-3.36530	10.24569	-0.39432
H	-3.23755	8.34290	0.19974
H	0.34906	11.68641	2.16275
H	-1.33077	12.56889	0.59751
C	-2.77268	11.52379	-0.28412
H	-4.10996	10.12670	-0.93845
H	-3.11953	12.23672	-0.77143

Table S23 The calculated xyz coordinates of complex **6.**

Co	5.38446	3.61346	3.03525
N	3.87433	4.12411	4.14232
N	5.36332	4.17737	1.07601
N	6.02752	1.93871	2.29298
N	6.43159	4.75984	4.37173

S	6.13581	0.60108	3.14849
C	7.72226	-0.10446	2.78383
O	6.14135	1.00092	4.53679
O	5.16272	-0.38385	2.74121
S	2.34894	3.87554	3.77669
C	1.76273	2.61036	4.88515
O	2.32590	3.32553	2.43923
O	1.53335	5.04178	4.03911
C	4.18954	4.91753	5.31903
C	5.63525	3.16577	0.22704
C	5.08449	5.41493	0.59421
C	5.86969	1.80815	0.84604
C	5.65083	5.23373	5.36960
C	7.76140	5.04531	4.35139
C	5.66401	3.36546	-1.14677
C	5.10915	5.66148	-0.77305
C	4.74348	6.47108	1.60322
C	5.40593	4.62637	-1.64222
C	10.25042	-1.13576	2.11469
C	9.11311	-1.51755	1.41518
C	11.65362	-1.69943	1.79265
C	10.07988	-0.24323	3.15908
C	8.83937	0.28180	3.48919
C	7.85560	-1.01858	1.75504
C	12.06258	-2.65532	2.92507
C	11.68123	-2.44621	0.45965
C	12.66058	-0.54415	1.72022
C	6.18172	6.01716	6.39616
C	7.51180	6.30535	6.38780
C	8.31264	5.82745	5.36403
C	2.43438	1.39176	4.94588
C	0.66750	2.81954	5.68996
C	1.98329	0.40941	5.80237
C	0.87509	0.58701	6.62975
C	0.43891	-0.52318	7.60658
C	0.23572	1.81790	6.54798
C	-0.87147	-0.19560	8.31974
C	1.53705	-0.65192	8.69304
C	0.31026	-1.85634	6.87671
C	8.54633	4.51255	3.20504
H	5.85290	2.66119	-1.72301
H	5.43142	4.78172	-2.55874
H	4.92967	6.51199	-1.10038
H	4.01426	6.16872	2.14784

H	4.49146	7.27722	1.14914
H	5.50891	6.64161	2.15759
H	8.76248	0.89372	4.18564
H	7.10324	-1.30147	1.28703
H	9.19090	-2.11608	0.70759
H	5.11811	1.22744	0.65048
H	6.66718	1.40915	0.46523
H	10.82231	0.01234	3.65634
H	11.42801	-3.37408	2.98218
H	12.07992	-2.17725	3.75663
H	12.93544	-3.01260	2.74400
H	11.05787	-3.17618	0.49030
H	12.56515	-2.78569	0.30226
H	11.43757	-1.84587	-0.24793
H	13.54647	-0.89921	1.61158
H	12.61946	-0.03289	2.53228
H	12.44731	0.02055	0.97502
H	3.93706	4.42833	6.11758
H	3.68125	5.74312	5.29856
H	5.63371	6.33763	7.07589
H	7.88198	6.82090	7.06753
H	9.22043	6.02883	5.35288
H	3.18152	1.24202	4.41268
H	2.43560	-0.40239	5.82925
H	0.21646	3.63227	5.65932
H	-0.50576	1.97447	7.08703
H	-1.57857	-0.12385	7.67483
H	-0.78110	0.63638	8.79054
H	-1.07948	-0.89472	8.94376
H	1.31084	-1.36564	9.29476
H	1.60119	0.17051	9.18333
H	2.38010	-0.84196	8.27517
H	0.04209	-2.53704	7.49793
H	1.15633	-2.09297	6.48948
H	-0.34841	-1.77931	6.18165
H	8.39959	3.56669	3.12843
H	9.48005	4.67945	3.35269
H	8.26774	4.94646	2.39577

Table S24 The SH parameters extracted from dc magnetic experiment and *ab* initio calculations for complexes **7** - **8**.

Complex	D [a] (cm^{-1})	D [b] (cm^{-1})	$\lvert E/D\rvert$ [a] (cm^{-1})	$\lvert E/D\rvert$ [b] (cm^{-1})	g_x, g_y, g_z [a]	g_x, g_y, g_z [b]	CSM
7	-115	-121	$<$ 0.01	0.01	2.20,2.20,3.03	2.03,2.04,3.23	6.29

8	-58.0	-59	0.15	0.05	2.17,1.90,2.94	2.19,2.24,2.81	10.05

[a] Extracted from the PHI fitting. [b] Computed from the *ab initio* calculation (recalculated by us).

Table S25 The local symmetry defined by the program SHAPE for complexes **7** – **8**.

Structure	SP-4	T-4	SS-4	vTBPY-4
7	23.290	6.286	9.356	9.341
8	23.885	10.630	12.863	13.456

*SP-4 stands for the distortion degree away from the square-planar coordination.

*T-4 presents distortion degree away from tetrahedral coordination.

*SS-4 stands for the distortion degree away from the seesaw or sawhorse coordination.

*vTBPY-4 stands for the distortion degree away from the axially vacant trigonal bipyramid coordination.

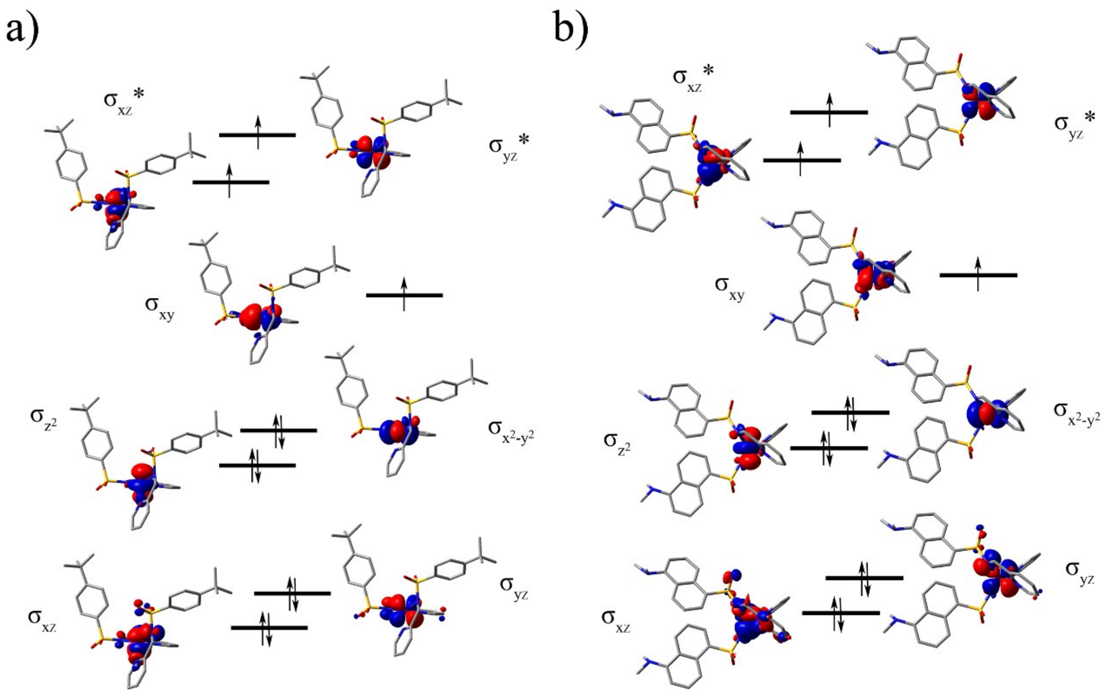

Fig. S16 The energy diagram, electronic configuration, and the perspective views of the calculated active molecular orbitals for complex **1**(a) and **2**(b).

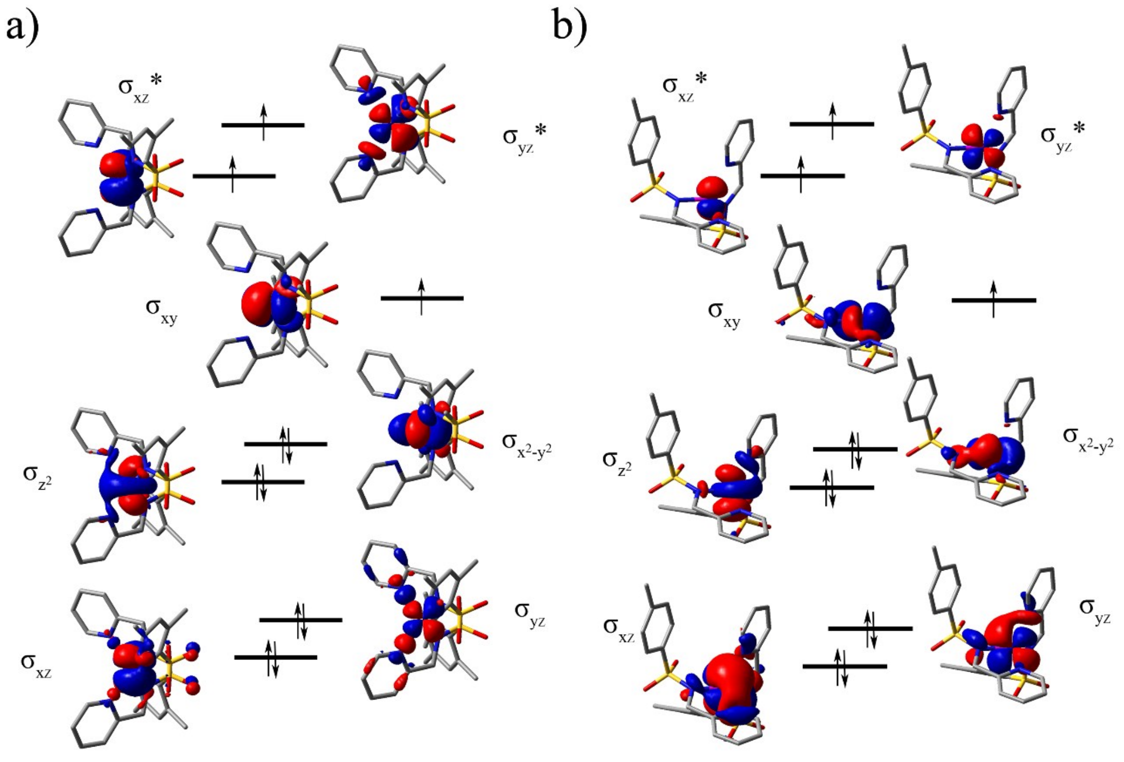

Fig. S17 The energy diagram, electronic configuration, and the perspective views of the calculated active molecular orbitals for complex **3**(a) and **4**(b).

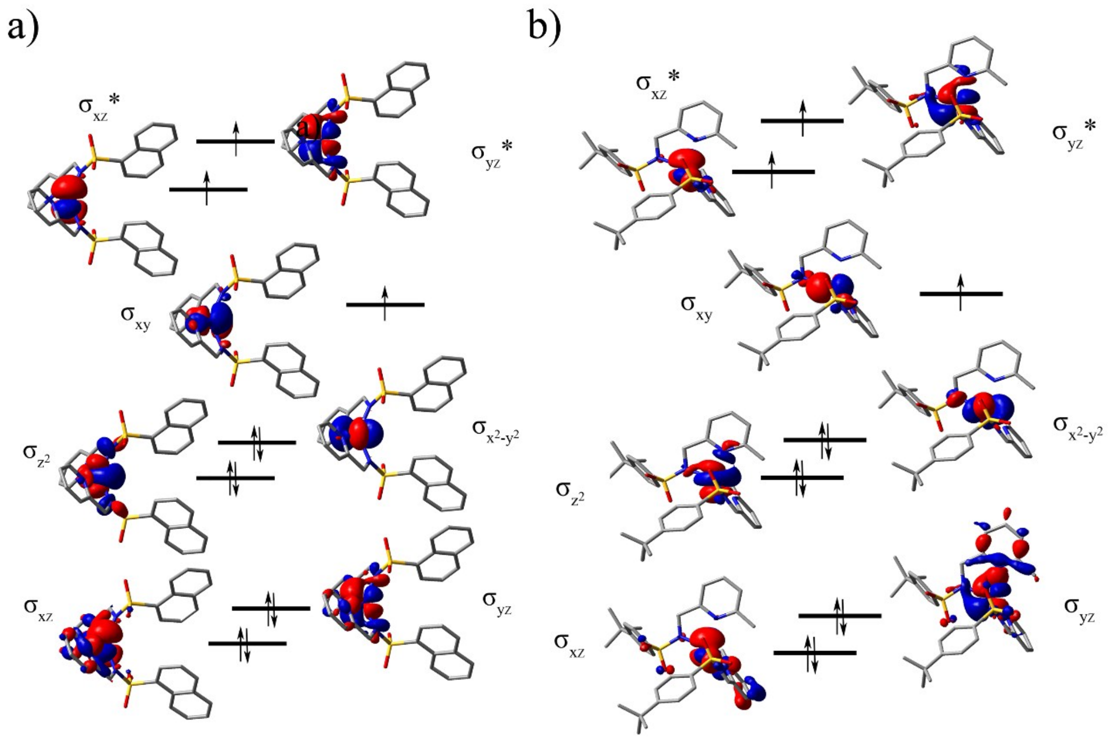

Fig. S18 The energy diagram, electronic configuration, and the perspective views of the calculated active molecular orbitals for complex **5**(a) and **6**(b).

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