Electronic Supplementary Material (ESI) for Dalton Transactions.

Self-assembly of fish-bone and grid-like Co^{II}-based single-molecule magnets using dihydrazone ligands with NNN and NNO pockets

Qianqian Yang,[a,b] Guo-Lu Wang,[c] Yi-Quan Zhang*[c] and Jinkui Tang*[a,b]

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: tang@ciac.ac.cn

[b]School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China

[c]Jiangsu Key Lab for NSLSCS, School of Physical Science and Technology, Nanjing Normal University, Nanjing 210023, P. R. China

1. ^{1}H-NMR spectrum

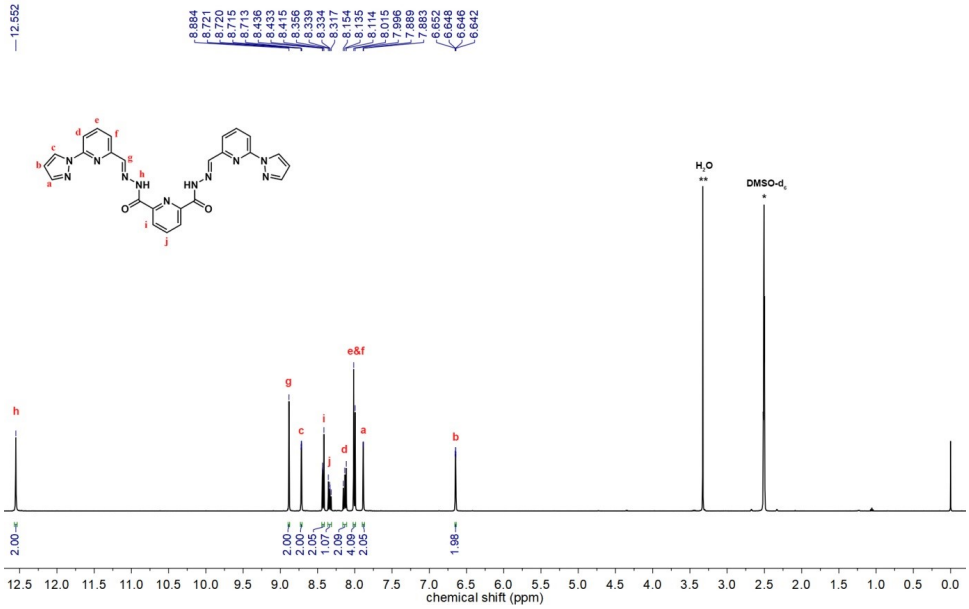

Fig. S1 ^{1}H-NMR spectrum of H_2L^1 in DMSO-d_6 recorded at room temperature. Solvent peaks are marked with asterisks (DMSO-d_6, *; H_2O, **).

2. IR Spectroscopy

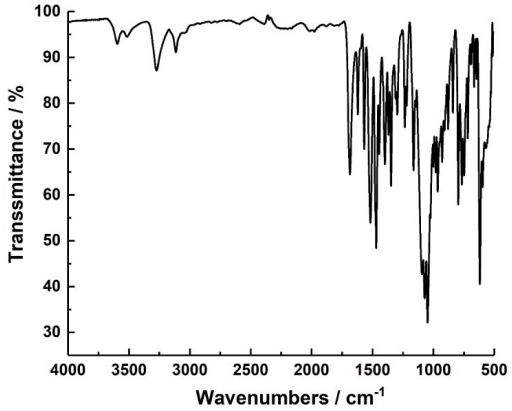

Fig. S2 IR (ATR) spectrum of solid samples for complex **1**.

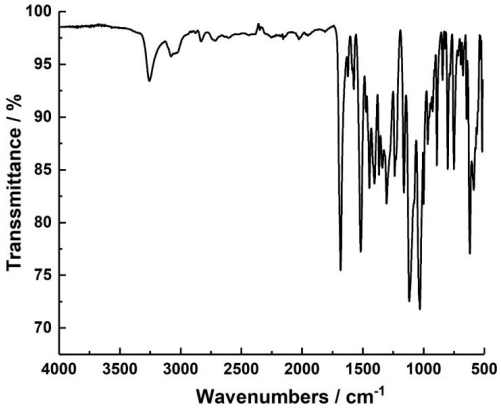

Fig. S3 IR (ATR) spectrum of solid samples for complex **2**.

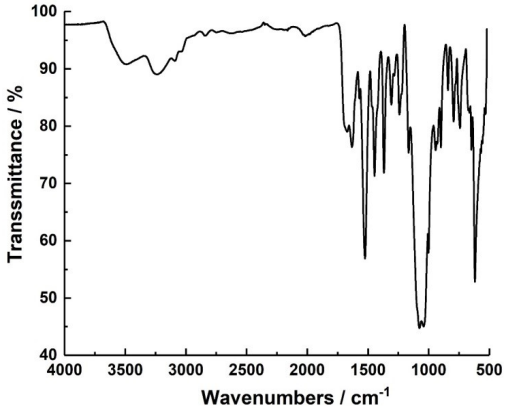

Fig. S4 IR (ATR) spectrum of solid samples for complex **3**.

3. Crystallographic data

Table S1 Crystallographic data for complexes **1-3**.

	1	**2**	**3**
Formula	$C_{54}H_{54}Cl_4Co_2N_{22}O_{24}$	$C_{42}H_{38}Cl_4Co_2N_{14}O_{24}$	$C_{84}H_{76}Cl_8Co_4N_{28}O_{48}$
FW, g·mol^{-1}	1654.85	1382.52	2765.04
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	*P*nma
T, K	173.0	300.0	180.0
λ, Å	1.54178	0.71073	0.71073
a, Å	10.4794(3)	10.4910(14)	36.8996(9)
b, Å	11.2095(3)	9.5103(12)	19.0503(5)
c, Å	15.2781(4)	25.965(4)	21.1241(5)
α, °	89.526(2)	90	90
β, °	75.536(2)	92.001(4)	90
γ, °	72.6610(10)	90	90
V, Å^3	1654.59(8)	2589.0(6)	14849.2(6)
Z	1	2	4
ρ_{calcd}, g·cm^{-3}	1.661	1.773	1.237
GOF on F^2	1.050	1.026	1.682
reflns collected	10996	32854	290382
R_1 ($I \geq 2\,\sigma\,(I)$)	0.0933	0.0895	0.1167
wR_2 (all data)	0.2776	0.3228	0.4058
CCDC	2161940	2161941	2161949

4. Structural details of complexes

Table S2 Selected bond distances (Å) and bond angles (°) for complexes **1**-**3**.

1		**2**		**3**			
Co1-N1[1]	2.256(6)	Co1-O1	2.156(6)	Co1-O1	2.171(5)	Co2-O4	2.204(5)
Co1-N3[1]	2.106(6)	Co1-O4[1]	2.164(7)	Co1-O8	2.207(5)	Co2-O5	2.169(5)
Co1-N4[1]	2.178(6)	Co1-N1	2.045(7)	Co1-N1	2.063(5)	Co2-N6	2.168(5)
Co1-N8	2.206(6)	Co1-N2	2.217(7)	Co1-N2	2.197(5)	Co2-N7	2.086(6)
Co1-N9	2.055(6)	Co1-N6[1]	2.171(7)	Co1-N14	2.202(5)	Co2-N8	2.058(5)
Co1-N11	2.135(7)	Co1-N7[1]	2.046(8)	Co1-N15	2.061(5)	Co2-N9	2.236(5)
N3[1]-Co1-N1[1]	72.2(2)	O1-Co1-O4[1]	90.5(3)	O1-Co1-O8	94.1(2)	O4-Co2-N9	87.1(2)
N3[1]-Co1-N4[1]	73.4(2)	O1-Co1-N2	148.3(3)	O1-Co1-N2	149.63(19)	O5-Co2-O4	94.1(2)
N3[1]-Co1-N8	108.7(2)	O1-Co1-N6[1]	97.5(3)	O1-Co1-N14	90.26(19)	O5-Co2-N9	150.32(18)
N3[1]-Co1-N11	99.3(2)	O4[1]-Co1-N2	102.1(3)	N1-Co1-O1	74.48(19)	N6-Co2-O4	147.2(2)
N4[1]-Co1-N1[1]	144.7(2)	O4[1]-Co1-N6[1]	149.1(3)	N1-Co1-O8	83.60(19)	N6-Co2-O5	91.8(2)
N4[1]-Co1-N8	88.0(2)	N1-Co1-O1	75.4(3)	N1-Co1-N2	75.74(19)	N6-Co2-N9	103.07(18)
N8-Co1-N1[1]	95.5(2)	N1-Co1-O4[1]	93.3(3)	N1-Co1-N14	127.3(2)	N7-Co2-O4	73.0(2)
N9-Co1-N1[1]	81.6(2)	N1-Co1-N2	75.0(3)	N2-Co1-O8	88.35(19)	N7-Co2-O5	85.4(2)
N9-Co1-N3[1]	153.8(2)	N1-Co1-N6[1]	117.7(3)	N2-Co1-N14	103.20(18)	N7-Co2-N6	75.4(2)
N9-Co1-N4[1]	132.6(2)	N1-Co1-N7[1]	160.4(3)	N14-Co1-O8	148.62(18)	N7-Co2-N9	122.9(2)
N9-Co1-N8	74.7(2)	N6[1]-Co1-N2	86.5(3)	N15-Co1-O1	88.0(2)	N8-Co2-O4	85.7(2)
N9-Co1-N11	76.6(3)	N7[1]-Co1-O1	89.1(3)	N15-Co1-O8	73.71(18)	N8-Co2-O5	74.54(18)
N11-Co1-N1[1]	85.4(2)	N7[1]-Co1-O4[1]	74.7(3)	N15-Co1-N1	150.3(2)	N8-Co2-N6	126.82(19)
N11-Co1-N4[1]	108.0(2)	N7[1]-Co1-N2	122.1(3)	N15-Co1-N2	121.49(19)	N8-Co2-N7	149.7(2)
N11-Co1-N8	150.9(2)	N7[1]-Co1-N6[1]	75.6(3)	N15-Co1-N14	75.41(18)	N8-Co2-N9	75.99(18)

[1]1-X,1-Y,1-Z

Table S3 The BVS values for complexes **1-3.**

BVS value	**1**	**2**	**3**	
	Co1	Co1	Co1	Co2
Co^{II}	2.171	2.183	2.090	2.069
Co^{III}	1.954	1.965	1.881	1.862

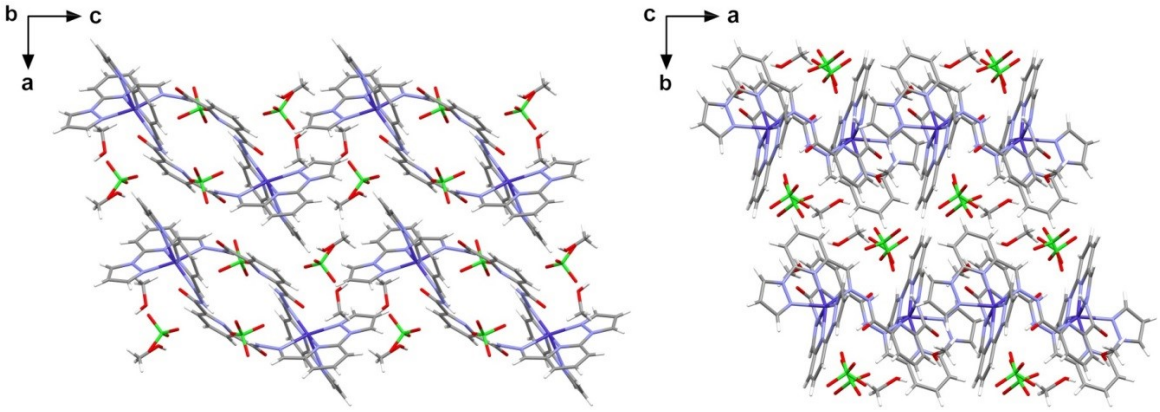

Fig. S5 Packing model along with *b* (left) and *c* axes (right) of complex **1**. Color code: Co^{II}, dark-blue; N, light-blue; C, gray; O, red; Cl, bright green; H, white.

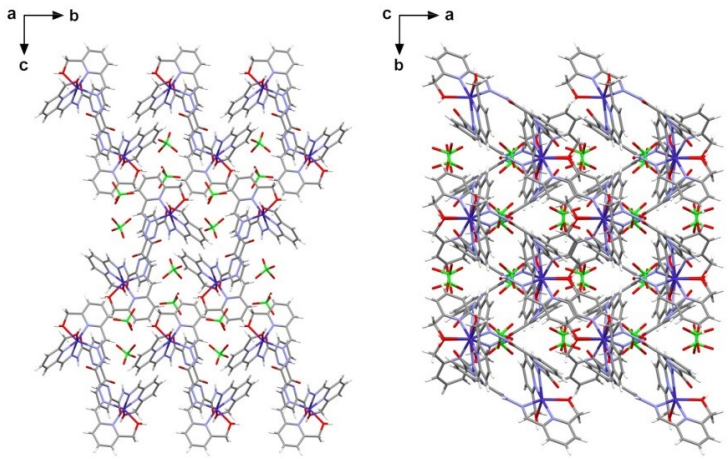

Fig. S6 Packing model along with *a* (left) and *c* axes (right) of complex **2**. Color code: Co^{II}, dark-blue; N, light-blue; C, gray; O, red; Cl, bright green; H, white.

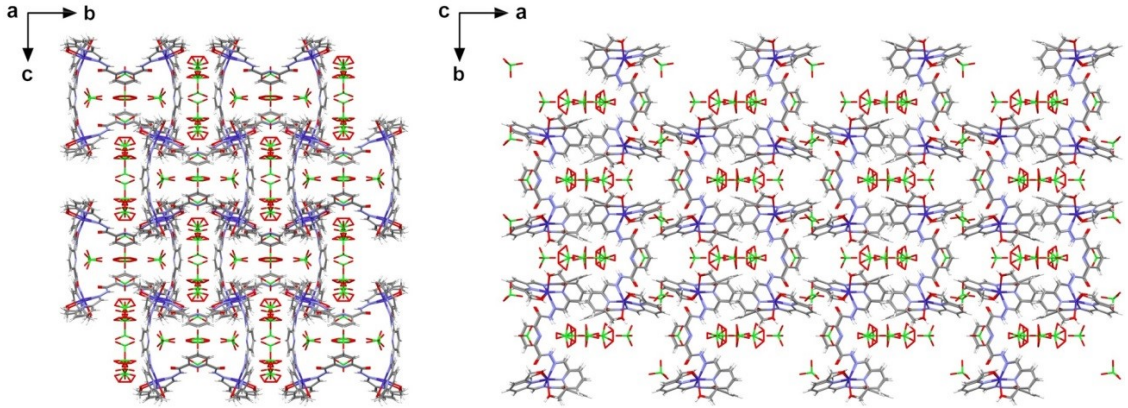

Fig. S7 Packing model along with *a* (left) and *c* axis (right) of complex **3**. Color code: Co^{II}, dark-blue; N, light-blue; C, gray; O, red; Cl, bright green; H, white.

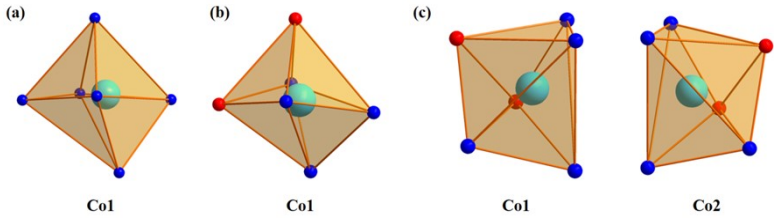

Fig. S8 Coordination polyhedrons of Co^{II} ions in complexes **1** (a), **2** (b) and **3** (c). Color code: Co^{II}, sky-blue; N, blue; O, red.

Table S4 The *CShM* values calculated by *SHAPE* 2.1[1] for **1-3.**

Coordination Geometry	**1**	**2**	**3**	
	Co1	Co1	Co1	Co2
Hexagon (D_{6h})	29.080	29.648	32.551	32.692
Pentagonal pyramid (C_{5v})	15.327	15.773	17.863	17.488
Octahedron (O_h)	7.128	6.557	7.035	7.290
Trigonal prism (D_{3h})	8.637	7.227	5.941	5.816
Johnson pentagonal pyramid J2 (C_{5v})	18.976	19.091	21.303	20.796

5. Direct current (dc) magnetic measurements

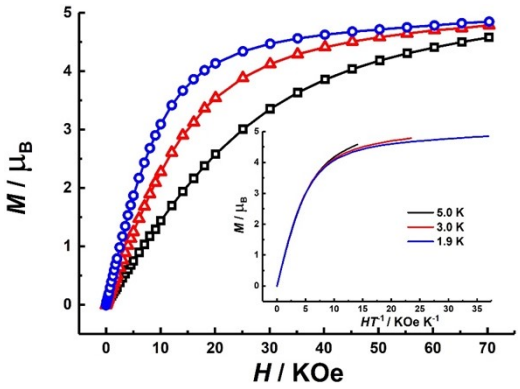

Fig. S9 Magnetization (*M*) versus *H* for **1** at indicated temperatures. Inset represents the plots of *M* versus *H*/*T*.

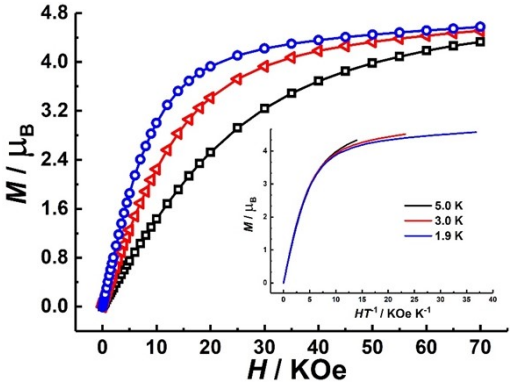

Fig. S10 Magnetization (*M*) versus *H* for **2** at indicated temperatures. Inset represents the plots of *M* versus *H*/*T*.

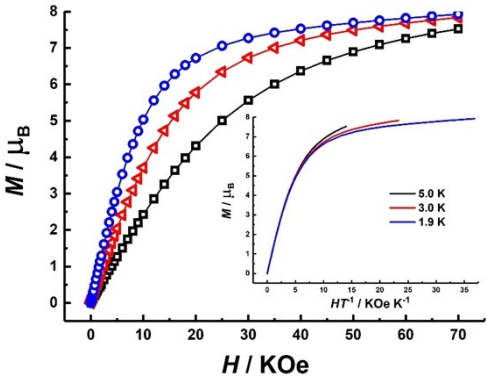

Fig. S11 Magnetization (*M*) versus *H* for **3** at indicated temperatures. Inset represents the plots of *M* versus *H*/*T*.

6. Theoretical study

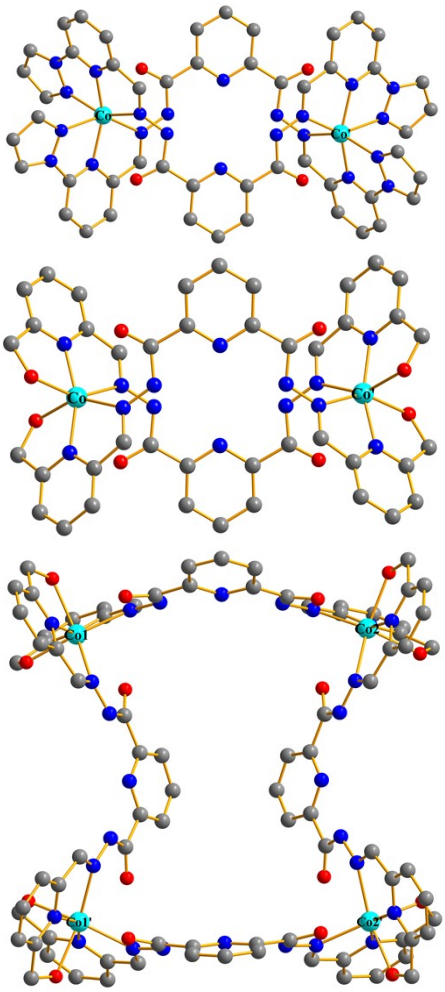

Fig. S12 Molecular structures of complexes **1** (up), **2** (middle) and **3** (down). Color code: Co^{II}, sky-blue; C, dark-gray; N, blue; O, red. Hydrogen atoms, solvents and counter ions have been omitted for clarity.

Table S5 Calculated spin-free energies (cm^{-1}) of the lowest ten terms (S = 3/2) of the Co^{II} ion of complexes **1-3** using CASSCF/RASSI-SO with OpenMolcas.

	1_Co1	**2_Co1**	**3_Co1**	**3_Co2**
	E	*E*	*E*	*E*
1	0.0	0.0	0.0	0.0
2	1306.1	901.8	497.5	793.0
3	2744.4	2482.9	2619.1	2833.5
4	5185.9	5894.2	5292.4	5370.9
5	7016.2	6429.0	6076.2	5982.2
6	8410.6	8155.1	6202.2	6325.6
7	13049.2	13246.1	11157.4	11028.5
8	22242.6	21717.9	21044.6	21141.2
9	24280.9	24498.5	23932.9	23873.9
10	25333.5	25759.6	24374.5	24506.1

Table S6 Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states individual Co^{II} fragments for **1-3** using CASSCF/RASSI-SO with OpenMolcas.

	Spin-orbit states	Energy (cm^{-1})	Spin-free states, Spin, Weights				
1_Co1	1	0.0	1, 1.5, 0.9019	2, 1.5, 0.0832	3, 1.5, 0.0077	4, 1.5, 0.0039	5, 1.5, 0.0017
	2	114.2	1, 1.5, 0.9676	2, 1.5, 0.0153	3, 1.5, 0.0089	4, 1.5, 0.0042	5, 1.5, 0.0026
2_Co1	1	0.0	1, 1.5, 0.8294	2, 1.5, 0.1556	3, 1.5, 0.0112	5, 1.5, 0.0013	4, 1.5, 0.0011
	2	135.7	1, 1.5, 0.9529	2, 1.5, 0.0263	3, 1.5, 0.0119	5, 1.5, 0.0039	4, 1.5, 0.0029
3_Co1	1	0.0	1, 1.5, 0.7232	2, 1.5, 0.2624	3, 1.5, 0.0095	4, 1.5, 0.0019	6, 0.5, 0.0012
	2	217.3	1, 1.5, 0.8970	2, 1.5, 0.0828	3, 1.5, 0.0109	6, 1.5, 0.0041	4, 1.5, 0.0025
3_Co2	1	0.0	1, 1.5, 0.8101	2, 1.5, 0.1762	3, 1.5, 0.0082	4, 1.5, 0.0028	6, 1.5, 0.0008
	2	170.8	1, 1.5, 0.9407	2, 1.5, 0.0407	3, 1.5, 0.0089	5, 1.5, 0.0042	4, 1.5, 0.0036

Table S7 Calculated ZFS parameters D (E) (cm^{-1}) and $\boldsymbol{g}$ (g_x, g_y, g_z) tensors of complexes **1-3** using CASSCF/RASSI-SO with OpenMolcas.

1_Co1		**2_Co1**		**3_Co1**		**3_Co2**	
D (E)	$\boldsymbol{g}$	D (E)	$\boldsymbol{g}$	D (E)	$\boldsymbol{g}$	D (E)	$\boldsymbol{g}$
	2.077		2.117		1.996		2.045
−53.5 (11.6)	2.266	−66.4 (8.1)	2.230	−107.5 (9.5)	2.123	−83.6 (9.9)	2.223
	2.737		2.897		3.214		3.031

Table S8 Calculated dipole-dipole interactions $\mathcal{J}_{dip}$ (cm^{-1}) between Co^{II} in **1-3** with respect to the pseudospin $\tilde{S}$ = 1/2 of the Co^{II} ion.

1	**2**	**3**	
		Co1-Co1	Co1-Co2
−0.02	−0.03	−0.04	−0.03

7. Alternating current (ac) magnetic measurements

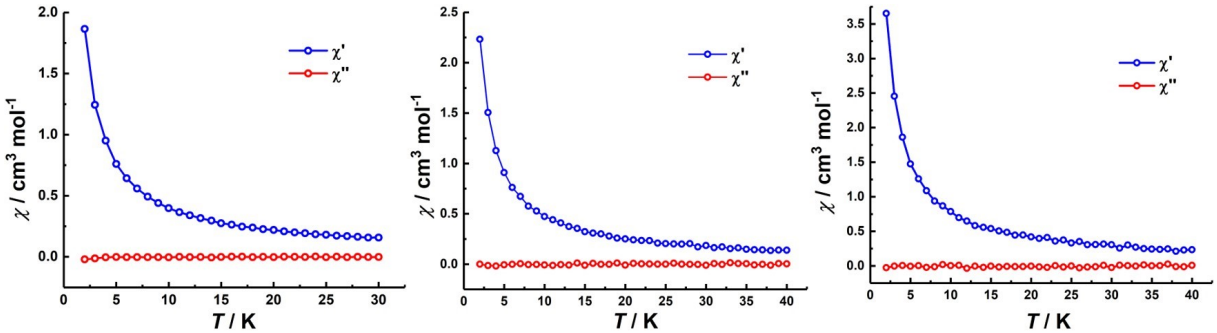

Fig. S13 Temperature-dependent ac susceptibility of complexes **1** (left), **2** (middle) and **3** (right) at 997 Hz under zero dc field.

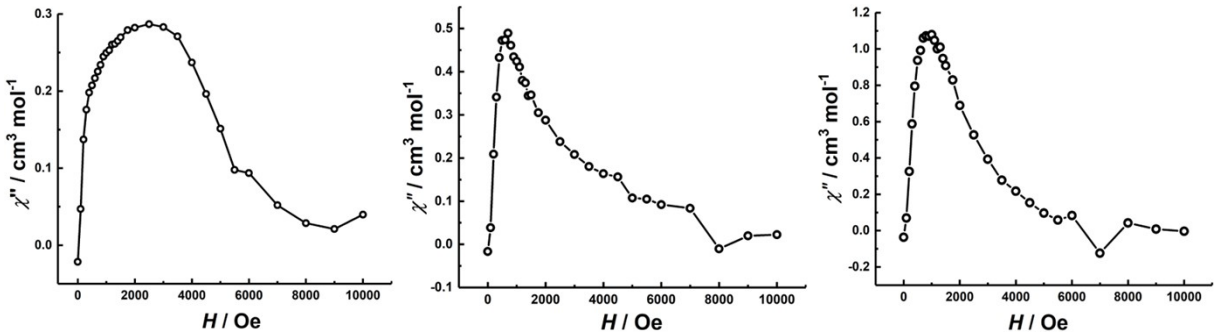

Fig. S14 Field-dependent ac susceptibility of complexes **1** (left), **2** (middle) and **3** (right) at 1.9 K and 997 Hz.

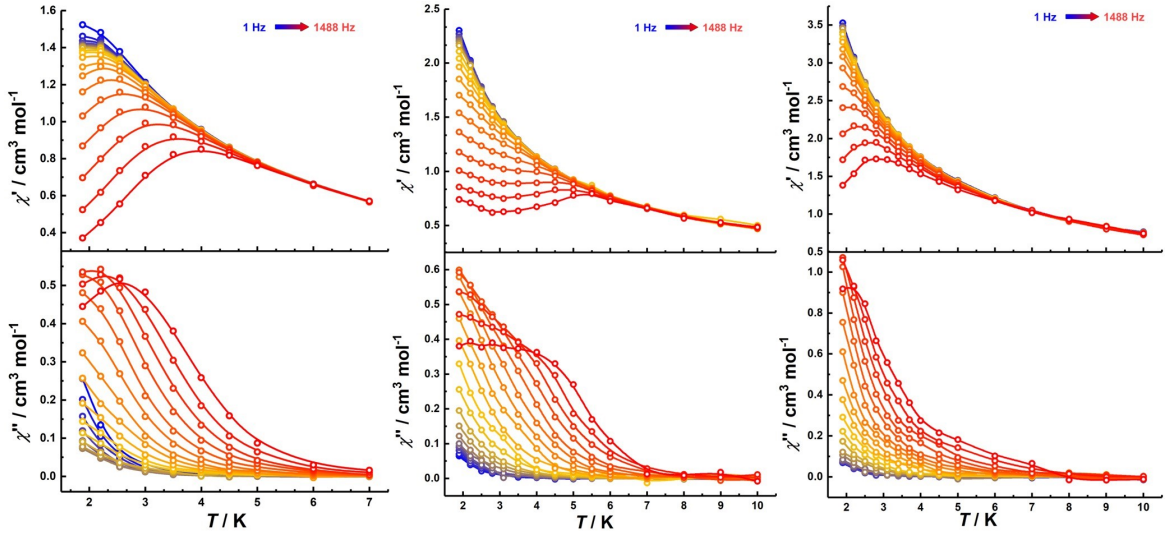

Fig. S15 Temperature-dependent ac susceptibility of complexes **1** under 2000 Oe (left), **2** under 700 Oe (middle) and **3** under 800 Oe dc field (right).

Table S9 Parameters for the best fit of frequency-dependent ac susceptibility of complex **1** in the temperature range of 1.9-2.5 K under 2000 Oe dc field.

T/K	$\chi_{S,tot}$	$\Delta\chi_1$	$\tau_{1/s}$	α_1	$\Delta\chi_2$	$\tau_{2/s}$	α_2
1.9	1.3626E-10	0.138044E+01	2.54815E-4	0.15487E+00	0.54621E+00	0.2579E+00	1.96401E-16
2.2	8.3390E-11	0.133007E+01	2.05745E-4	0.12324E+00	0.27777E+00	0.24602E+00	7.29043E-16
2.5	7.3601E-12	0.126619E+01	1.49667E-4	0.11351E+00	0.16428E+00	0.26858E+00	8.61464E-16

Table S10 Parameters for the best fit of frequency-dependent ac susceptibility of complex **1** in the temperature range of 3.0-5.0 K under 2000 Oe dc field.

T/K	χ_S	χ_T	τ	α
3.0	7.88804E-14	0.120332E+01	9.08732E-5	0.910E-01
3.5	2.50005E-15	0.106854E+01	5.60793E-5	0.863E-01
4.0	8.31092E-15	0.95118E+00	1.49118E-5	0.562E-01
4.5	2.57364E-16	0.8576E+00	1.00486E-6	0.508E-01
5.0	9.99556E-17	0.78029E+00	2.95485E-7	0.482E-01

Table S11 Parameters for the best fit of frequency-dependent ac susceptibility of complex **2** under 700 Oe dc field.

T/K	χ_S	χ_T	τ	α
1.9	0.418409E+00	0.228259E+01	0.491737E-03	0.273611E+00
2.2	0.405979E+00	0.202314E+01	0.411760E-03	0.230072E+00
2.5	0.393410E+00	0.178172E+01	0.345981E-03	0.191897E+00
2.8	0.344963E+00	0.160177E+01	0.280147E-03	0.173251E+00
3.1	0.339927E+00	0.145476E+01	0.238929E-03	0.149195E+00
3.5	0.340165E+00	0.129439E+01	0.187155E-03	0.111747E+00
4.0	0.316122E+00	0.113762E+01	0.131713E-03	0.731204E-01
4.5	0.319607E+00	0.101515E+01	0.920839E-04	0.295014E-01
5.0	0.171286E+00	0.917934E+00	0.460148E-04	0.502116E-01
5.5	0.223217E-20	0.838770E+00	0.223226E-04	0.610448E-01
6.0	0.762738E-21	0.770644E+00	0.124564E-04	0.119567E+00
7.0	0.111197E-20	0.664433E+00	0.208573E-05	0.182253E+00

Table S12 Parameters for the best fit of frequency-dependent ac susceptibility of complex **3** under 800 Oe dc field.

T (K)	χ_S	χ_T	τ	α
1.9	0.470630E+00	0.349090E+01	0.210850E-03	0.217710E+00
2.2	0.373338E+00	0.306773E+01	0.129410E-03	0.220567E+00
2.5	0.182835E-01	0.274202E+01	0.653620E-04	0.267101E+00
2.8	0.568434E-01	0.246565E+01	0.449573E-04	0.281996E+00
3.1	0.151398E-01	0.224224E+01	0.319595E-04	0.280224E+00
3.4	0.572606E-14	0.205315E+01	0.233610E-04	0.288021E+00
3.7	0.684589E-14	0.189649E+01	0.176289E-04	0.291805E+00
4.0	0.879608E-14	0.176204E+01	0.131778E-04	0.300371E+00

8. References

1. (a) D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. Eur. J.*, 2005, **11**, 1479-1494; (b) D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, *Chem. Eur. J.*, 2003, **9**, 1281-1295.