Supplementary Information for

Effects of ligand substituent on single-molecule magnet behavior of quinonoid-bridged dicobalt compounds

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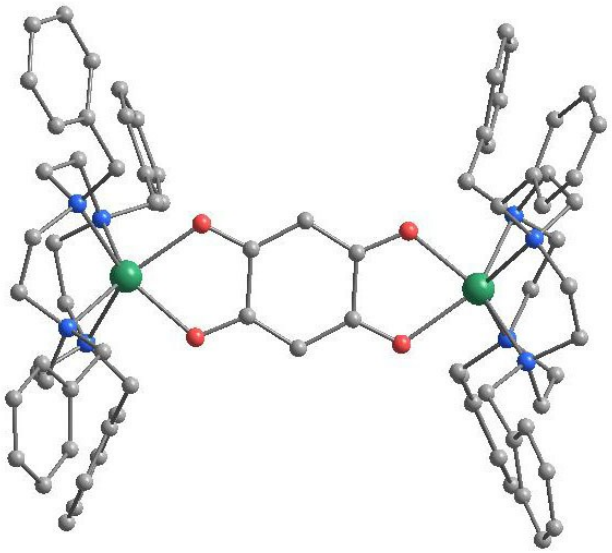

Figure S1. Crystal structure of the cation $[(N_4Co)_2L^H]^{2+}$ in **1·CH$_3$CN·0.5H$_2$O**. Green, blue, red and gray spheres represent Co, N, O and C atoms, respectively. H-atoms are omitted for clarity.

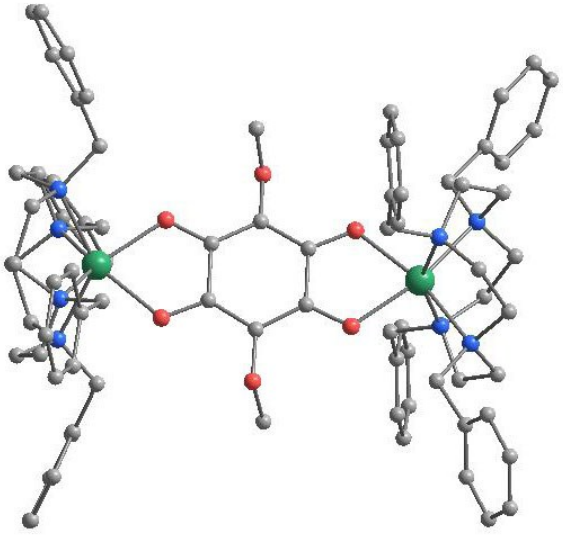

Figure S2. Crystal structure of the cation $[(N_4Co)_2L^{OMe}]^{2+}$ in **4·3CH$_3$CN·0.5CH$_2$Cl$_2$**. Green, blue, red and gray spheres represent Co, N, O and C atoms, respectively. H-atoms are omitted for clarity.

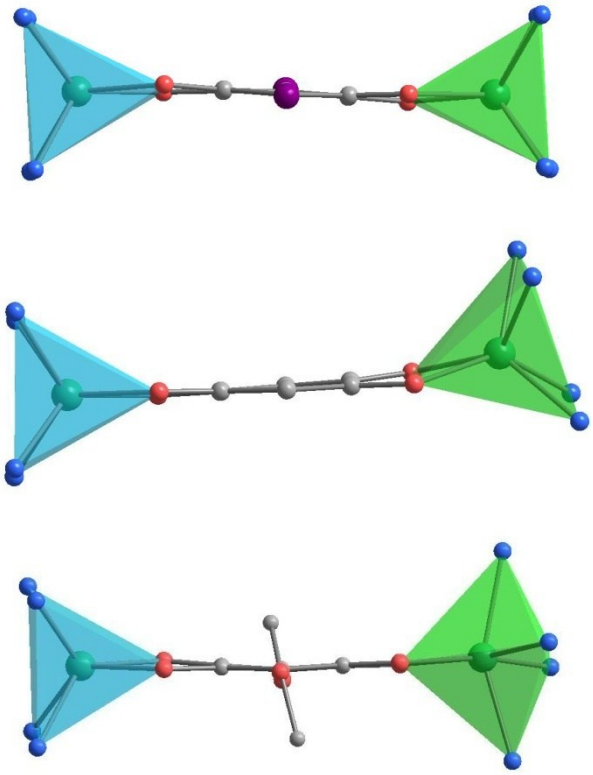

Figure S3. The coordination geometries of Co ions in compounds **3** (top), **1** (middle), **4** (bottom). Green, purple, blue, red and gray spheres represent Co, Br, N, O and C atoms, respectively.

Table S1. Crystallographic data for compounds **1**, **3** and **4**

	1·CH$_3$CN·0.5H$_2$O	**3·2CH$_3$CN**	**4·3CH$_3$CN·0.5CH$_2$Cl$_2$**
Empirical formula	$C_{80}H_{91}Cl_2Co_2N_9O_{12.5}$	$C_{82}H_{94}Br_2Cl_2Co_2N_{10}O_{12}$	$C_{346}H_{416}Cl_{12}Co_8N_{44}O_{56}$
Color and Habit	red Prism	red Prism	red Prism
Crystal Size (mm)	0.67×0.25×0.20	0.63×0.54×0.31	0.506×0.352×0.280
Temperature(K)	123(2)	123(2)	123(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	23.12(2)	16.539(3)	18.947(5)
b (Å)	16.952(13)	16.867(5)	16.237(4)
c (Å)	25.161(17)	17.917(4)	31.011(6)
alpha (deg.)	90	75.33(2)	90
beta (deg.)	121.52(6)	65.839(18)	114.933(12)
gamma (deg.)	90	71.128(19)	90
Volume(A^3)	8406(12)	4272.8(19)	8651(4)
Z	2	2	2
Formula weight	1567.38	1760.25	6984.07
ρ(cal.)(Mg/m^3)	1.238	1.368	1.341
μ(mm^{-1})	0.520	1.449	0.545
F(000)	3287	1820	3667
Theta range (deg.)	2.136 to 25.000	2.401 to 27.516	2.056 to 27.490
Reflections measured	58557	50082	70192
Index ranges	-27<=h<=23, -19<=k<=20, -29<=l<=29	-21<=h<=21, -21<=k<=21, -22<=l<=23	-24<=h<=24, -21<=k<=16, -40<=l<=40
Independent reflections	14769 (R_{int} = 0.0554)	19418 (R_{int} = 0.0423)	19757 (R_{int} = 0.0519)
Parameter/Restraints/Data(obs.)	956 / 0 / 10899	1018 / 39 / 12551	1067 / 15 / 16507
Final R indices (obs.)	R_1 = 0.0846, wR_2 = 0.1915	R_1 = 0.0658, wR_2 = 0.1605	R_1 = 0.0679, wR_2 = 0.1830
R indices (all)	R_1 = 0.1053, wR_2 = 0.2078	R_1 = 0.1053, wR_2 = 0.1859	R_1 = 0.0775, wR_2 = 0.1950
Goodness-of-fit	1.013	0.994	1.011

$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$;

$wR_2 = [\Sigma w(|F_0^2| - |F_c^2|)^2/\Sigma w|F_0^2|^2]^{1/2}$

Table S2. Selected bond lengths (Å) for compounds **1**, **3** and **4**

	1	**3**[a]	**4**
Co(1)-O(1)	2.110(3)	2.117(3)	2.1112(19)
Co(1)-O(2)	2.123(4)	2.108(3)	2.092(2)
Co(2)-O(3)	2.163(4)	2.116(3)	2.0924(19)
Co(2)-O(4)	2.114(3)	2.107(3)	2.1137(19)
Ave. Co-O	2.128(4)	2.112(3)	2.102(2)
Co(1)-N(1)	2.212(4)	2.302(3)	2.225(2)
Co(1)-N(2)	2.305(5)	2.186(3)	2.165(2)
Co(1)-N(3)	2.202(5)	2.315(3)	2.211(2)
Co(1)-N(4)	2.341(5)	2.175(3)	2.156(2)
Ave. Co(1)-N	2.265(5)	2.244(3)	2.189(2)
Co(2)-N(5)	2.217(4)	2.307(4)	2.189(2)
Co(2)-N(6)	2.267(5)	2.199(3)	2.270(2)
Co(2)-N(7)	2.267(5)	2.284(3)	2.201(2)
Co(2)-N(8)	2.283(5)	2.193(3)	2.293(2)
Ave. Co(2)-N	2.258(5)	2.246(3)	2.238(2)
Co(1)…Co(2)	8.0590(67)	8.0448(26)	7.9972(21)

a: Co(1) and Co(2) of compound **3** are in two $[(N_4Co)_2LBr]^{2+}$ cations respectively, different with compounds **1** and **4**.

Table S3. The CShM values calculated by *SHAPE 2.1* for compounds **1**, **3** and **4**

	Coordination Geometry	**1**	**3**[a]	**4**
Co(1)	Trigonal prism (D_{3h})	5.550	4.493	14.264
	Octahedron (O_h)	19.357	19.515	10.215
Co(2)	Trigonal prism (D_{3h})	4.896	4.518	6.354
	Octahedron (O_h)	20.685	19.777	22.084

a: Co(1) and Co(2) of compound **3** are in two $[(N_4Co)_2LBr]^{2+}$ cations respectively, different with compounds **1** and **4**.

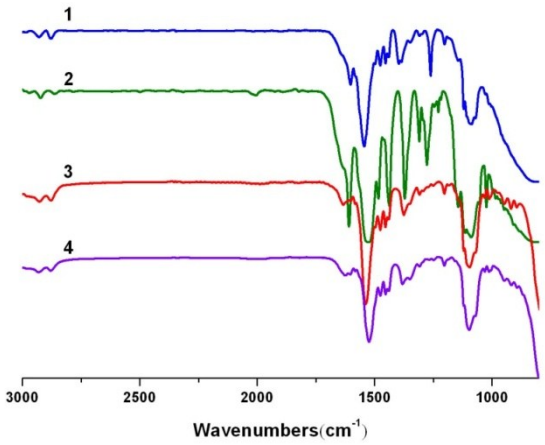

Figure S4. IR spectra of **1** (blue), **2** (green), **3** (red) and **4** (purple).

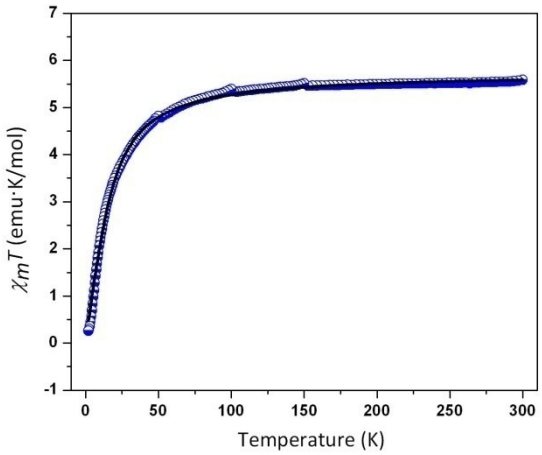

Figure S5. DC magnetic susceptibility of compound **1** (blue) and the fit curve (solid line).

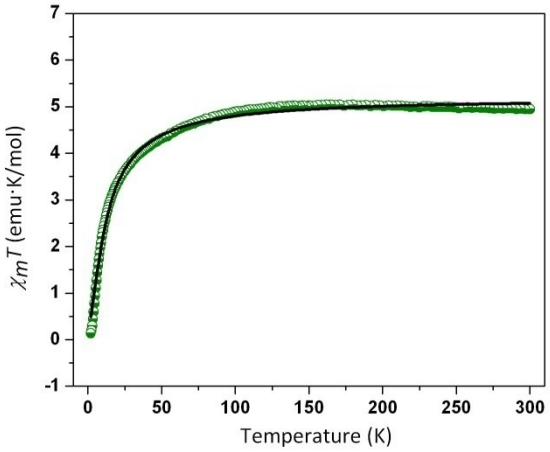

Figure S6. DC magnetic susceptibility of compound **2** (green) and the fit curve (solid line).

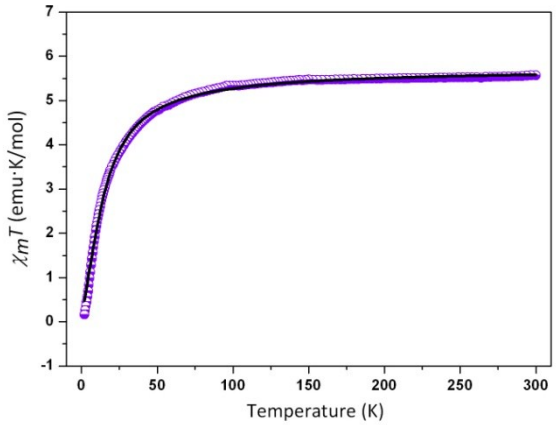

Figure S7. DC magnetic susceptibility of compound **4** (purple) and the fit curve (solid line).

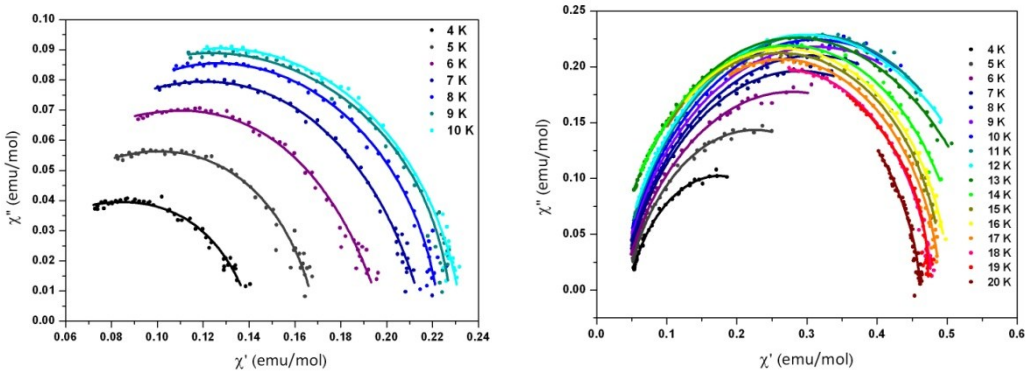

Figure S8. Cole-Cole plots for **1** (left) and **3** (right), solid lines are the best fits to the Debye model.

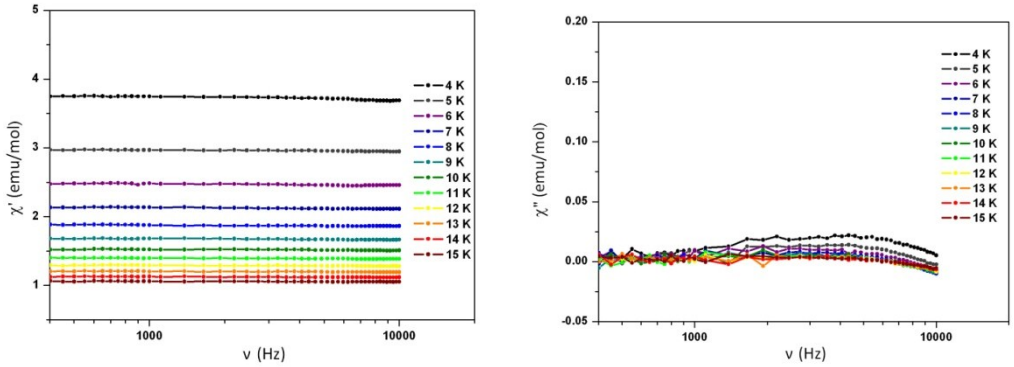

Figure S9. In-phase (left) and out-of-phase (right) AC magnetic susceptibility vs. frequency for compound **2** under zero DC field.

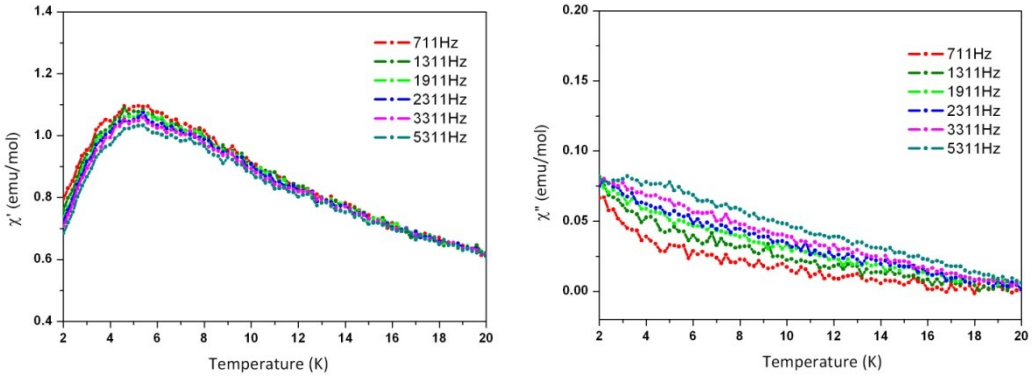

Figure S10. In-phase (left) and out-of-phase (right) AC magnetic susceptibility vs. temperature for compound **4** under zero DC field.