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Weak interchain interaction-dominated magnetic responses in water-extended cobalt(II)-chains:

from magnetic ordering to single-chain magnet

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Materials and instruments

All initial chemicals were commercially purchased and used as received without further purification. Elemental analyses for C, H, and O were carried out with a CE–440 (Leeman–Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar–370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiment was performed on a Shimadzu simultaneous DTG–60A compositional analysis instrument from room temperature to 800 ^{o}C under N_2 atmosphere at a heating rate of 5 ^{o}C min^{-1}. Powder X–ray diffraction (PXRD) patterns were obtained from a Bruker D8 Advance diffractometer at 40 kV and 40 mA for Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å), with a scan speed of 0.1 sec/step and a step size of 0.01^{o} in 2θ. The simulated PXRD pattern was calculated based on the single–crystal X–ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Magnetic susceptibilities were acquired on a Quantum Design (SQUID) magnetometer MPMS–XL–7 with crystalline samples, in which the phase purity of the samples was determined by PXRD experiments. The diamagnetic corrections were calculated using Pascal's constants. An experimental correction for the sample holder was also applied.

X-ray data collection and structure determination

Diffraction intensities were collected by using the φ-ω scan technique at 296 K on a Bruker SMART CCD diffractometer for **1** and SuperNova, Dual, Cu at home/near, AtlasS2 four-circle diffractometer for **2** equipped with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). There was no evidence of crystal decay during data collection. Semiempirical multiscan absorption corrections were applied by *SADABS* and the program *SAINT* was used for integration of the diffraction profiles of **1**. [1, 2] The programs *CrysAlisPro* were used for integration of the diffraction profiles.[3] Empirical absorption correction of **2** was done using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.[4] The structures of **1** were solved by the direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-2013* programs.[5] Anisotropic thermal parameters were assigned to all non-H atoms. Organic hydrogen atoms were geometrically generated. CCDC 1962614 for **1** contains supplementary crystallographic data for this paper. These data can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.

Table S1. Selected bond lengths (Å) and angles (º) for **1**

Co(1)–O(6)	2.0458(13)	Co(2)–O(1)	2.0231(11)
Co(1)–O(2)	2.0739(11)	Co(2)–O(3)	2.0949(12)
Co(1)–O(5)$^{\#2}$	2.1721(10)	Co(2)–O(5)$^{\#3}$	2.2173(10)
O(6)$^{\#1}$–Co(1)–O(2)$^{\#1}$	90.03(5)	O(1)–Co(2)–O(3)	92.29(5)
O(6)–Co(1)–O(2)	90.02(5)	O(1)–Co(2)–O(1)$^{\#3}$	90.62(5)
O(6)–Co(1)–O(5)$^{\#2}$	88.58(5)	O(1)–Co(2)–O(5)	89.38(5)
O(2)–Co(1)–O(5)$^{\#2}$	90.78(4)	O(3)–Co(2)–O(5)	90.73(5)

[a] Symmetry codes: $^{\#1}$ $1 - x$, $1 - y$, $1 - z$; $^{\#2}$ x, $y + 1$, z; $^{\#3}$ $1 - x$, $- y$, $1 - z$.

Table S2. C–H⋯π and hydrogen-bonding parameters (Å, deg) in **1** and **2**[a]

C–H⋯Cg	d (C–H)	d (X⋯Cg)	d (H⋯Cg)	∠X–H⋯Cg
1				
C5–H5⋯Cg(1)[#1]	0.93	4.113(3)	3.2460	156.06
C24–H24⋯Cg(2)[#2]	0.93	3.863(3)	3.0655	144.91

D–H⋯A	d (D–H)	d (H⋯A)	d (D⋯A)	∠DHA
1				
O5–H5A⋯O7[#3]	0.85	1.861	2.690	164.4
O7–H7B⋯O1[#4]	0.85	2.468	3.115	133.54
O8–H8B⋯O4[#5]	0.85	2.004	2.688	136.63
O6–H6A⋯O8[#6]	0.85	1.910	2.752	170.73
2				
O3–H3⋯N1[#3]	0.85	1.94	2.793(1)	177

*Symmetry codes for **2**: [#1] $1 - x, y - 1/2, 1/2 - z$; [#2] $- x, 1/2 + y, 1/2 - z$; [#3] $1/2 - x, 1/2 + y, 3/2 - z$. Cg(1) and Cg(2) refer to the centers of two six-member rings generated by C2, C3, C8, C9, C10 and C15 as well as by C25, C26, C27, C28, C29 and C15 in **1**. Symmetry codes for **1**: [#3] $x, y - 1, z$; [#4] $x, y + 1, z$; [#5] $x, y + 1, z$; [#6] $- x + 1, - y + 1, - z + 1$.
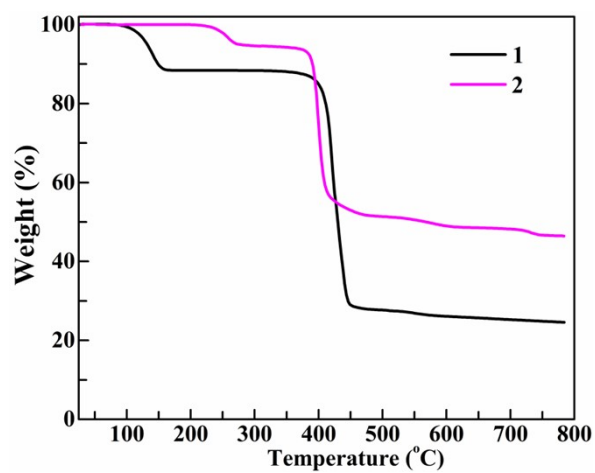
Table S3. Selected bond lengths (Å) and angles (º) for **2**

Co(1)–O(3)	2.2358(10)	Co(1)–O(1)	2.0199(13)
Co(1)–O(2)$^{\#2}$	2.0870(13)		
O(2)$^{\#2}$–Co(1)–O(3)	90.92(5)	O(1)–Co(1)–O(3)	88.87(5)
O(1)$^{\#}$–Co(1)–O(2)$^{\#3}$	91.62(6)	Co(1)–O(3)–Co(1)$^{\#2}$	115.02(8)

^{a} Symmetry codes: $^{\#1}$ $1 - x, 1 - y, 1 - z$; $^{\#2}$ $1 - x, y, 3 / 2 - z$; $^{\#3}$ $x, 1 - y, 1/2 + z$.
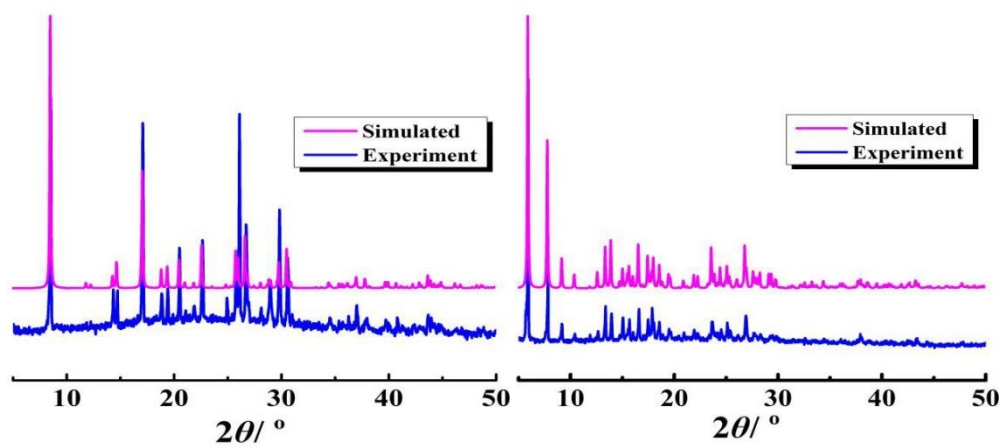
Fig. S1 Simulated and experimental PXRD patterns for **1** (left) and **2** (right).
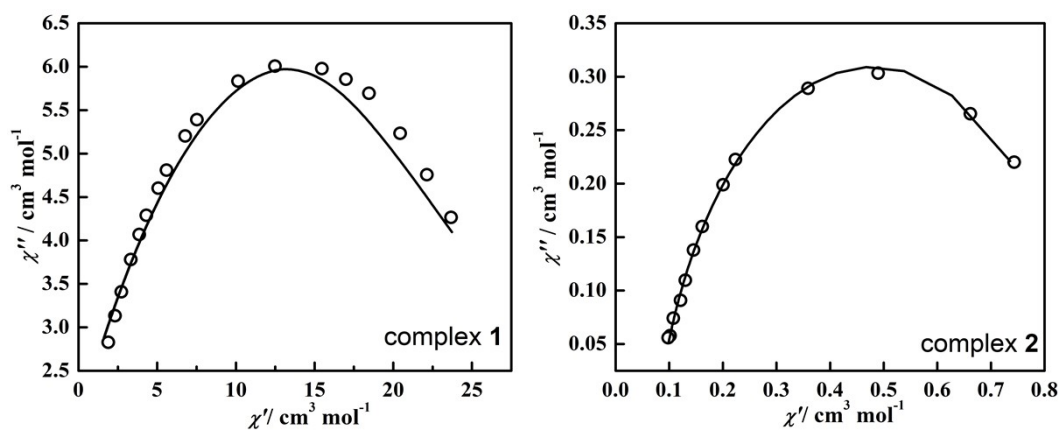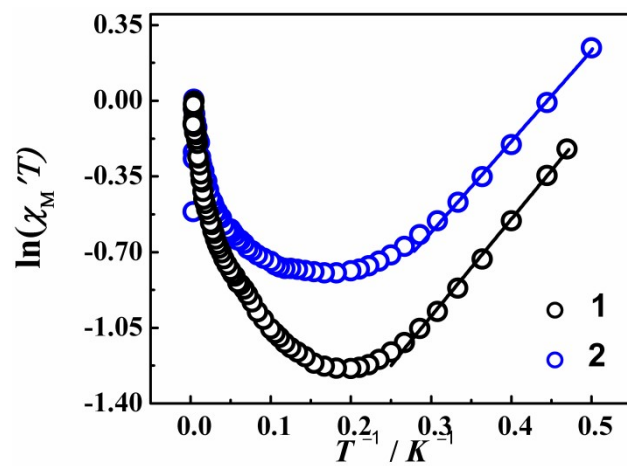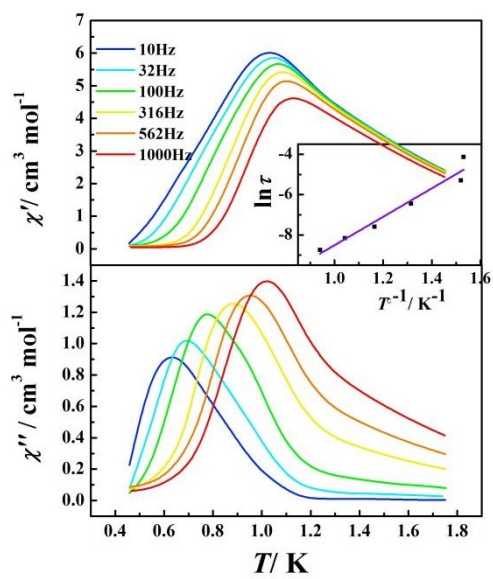
Fig. S2 TG curves for **1** and **2**.

Fig. S3 Cole–Cole plots for **1** (left) and **2** (right) measured at 0.5 K under zero dc field (The solid lines represent the best fits to the generalized Debye model).

Fig. S4. Plots of $\ln(\chi_M'T)$ versus T^{-1} for **1** and **2** measured at 1.0 Hz under $H_{dc} = 0$ and $H_{ac} = 3.5$ Oe. The
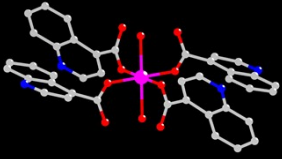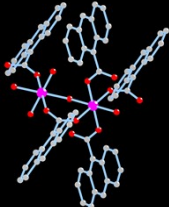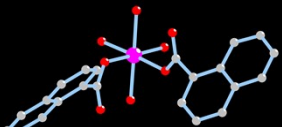
solid lines represent the best fit to 1D Ising model.

**Fig. S5** Temperature dependence of ac susceptibilities of **2** over various frequencies under H_{dc} = 200 Oe

and H_{ac} = 3.5 Oe (Inset: linear fit of τ vs. T^{-1} to the Arrhenius law).

**Table S4.** Parameters for the coordination geometries of Co^{II} ions used for the distortion calculations

Ligand	2-naphthoate	4-quinolinecarboxylate	9-anthracenecarboxylate		1-naphthoate
Local Coordination Environment					
d_z	2.2297(9)	2.2358(10)	2.1721(10)	2.2173(10)	2.2312(15), 2.2395(15)
d_x	2.0491(17)	2.0870(13)	2.0739(11)	2.0949(12)	2.0726(15), 2.0657(15)
d_y	2.0292(15)	2.0199(13)	2.0458(13)	2.0231(11)	2.0398(15), 2.0274(15)
$\angle O_{ax}CoO_{ax}$	180.0	180.0	180.0	180.0	179.122(47)
φ_i	86.31(9)	90.92	92.29(5)	90.02(5)	92.17(6)
	93.69(9)	89.08	87.71(5)	89.98(5)	89.76(6)
	93.69(9)	90.92	87.71(5)	89.98(5)	90.66(6)
	86.31(9)	89.08	92.29(5)	90.03(5)	87.49(6)
	93.11(5)	91.13	90.62(5)	88.58(5)	87.65(6)
	86.89(5)	88.87	89.38(5)	91.42(5)	92.45(6)
	85.91(6)	88.87	89.27(5)	90.78(4)	94.32(5)
	94.09(6)	91.13	90.73(5)	89.22(4)	85.45(6)

86.89(5)	88.38	89.38(5)	91.42(5)	92.19(6)
93.11(5)	91.62	90.62(5)	88.58(5)	88.42(6)
94.09(6)	91.62	90.73(5)	89.22(4)	85.80(5)
85.91(6)	88.38	89.27(5)	90.78(4)	93.69(6)
$(\sum|\Phi_i - 90|)/12$	3.63	1.22	1.21	0.74	2.58
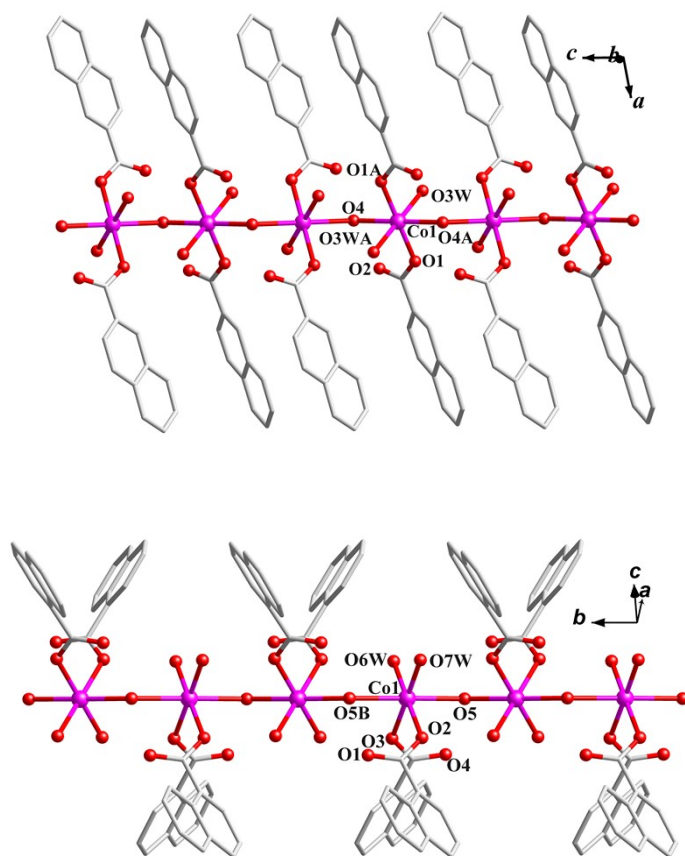
Fig. S6 Water-extended cobalt(II)-chains with isomeric naphthoate ligands.
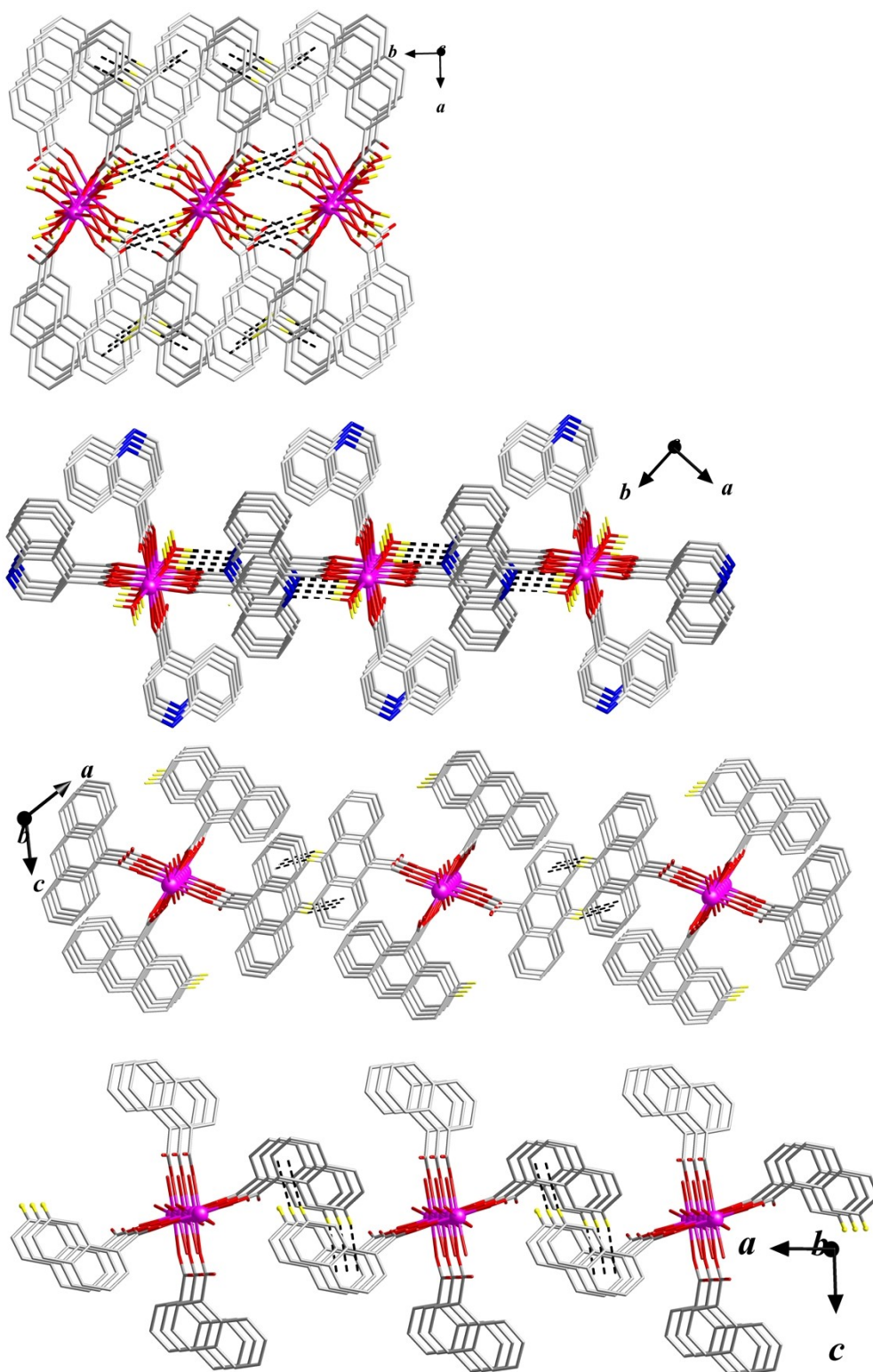
Fig. S7 Stacking manners of four water-extended cobalt(II)-chains with different carboxylate-modified aromatic ligands.

References

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Ltd., Oxford, England, **2006**.

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