Supporting Information

Experimental

Synthesis. Compounds **1**−**3** were prepared by mixing $H_3[Co(CN)_6]$ (1.09 g, 5 mmol), $CaCl_2$ (0.55 g, 5 mmol) and the corresponding organic salt (10 mmol) in acidic aqueous solution. Pale-yellow crystals were obtained after two weeks through slow evaporation at room temperature.

1: yield 72% (based on $H_3[Co(CN)_6]$). FT–IR (KBr, cm^{-1}): 2147(s), 2150(m), 2153(vs), 1546(s), 1558(m), 1643(m), 3402(m), 3440 (vs), 3453(w). Elemental analysis calcd (%) for $C_7H_6CaCoN_9$ (315.22): C 26.67, H 1.92, N 39.99. Found: C 27.14, H 2.22, N 39.70.

2: yield 68% (based on $H_3[Co(CN)_6]$). FT-IR (KBr, cm^{-1}): 2153(vs), 919(w), 1545(s), 1645(s), 1702(s), 3361(m), 3454(m), 3496 (m), 3607 (w). Elemental analysis calcd (%) for $C_7H_5CaCoN_8O$ (316.21): C 26.59, H 1.59, N 35.44. Found: C 26.94, H 2.00, N 35.11.

3: yield 69% (based on $H_3[Co(CN)_6]$). FT-IR (KBr, cm^{-1}): 2147(s), 643(w), 849(w), 1643(s), 3403(s). Elemental analysis calcd (%) for $C_7H_5CaCoN_8S$ (315.22): C 25.31, H 1.52, N 33.73. Found: C 25.67, H 1.96, N 33.50.

General measurements. Thermogravimetric analysis (TGA) was performed on a DSC/DTA-TG SDT-Q600 instrument at the rate of 10 $K \cdot min^{-1}$ under nitrogen atmosphere in the temperature range of 300−870 K. Differential scanning calorimetry (DSC) measurements upon heating and cooling scans were recorded on a TA Instruments SDT-Q10 with the crystals in the temperature range of 100−270 K with a heating/cooling rate of 10 $K \cdot min^{-1}$ under nitrogen at atmospheric pressure in aluminum crucible. Specific heat (C_p) measurements were carried out on a Quantum Design PPMS. Powder X-ray diffraction (PXRD) was measured on a Rigaku SmartLab X-ray diffraction instrument at various temperatures. CHN elemental analysis was determined by the VARIO EL Ⅲ Elemental Analyzer.

Single Crystal X-ray Diffraction. Variable-temperature X-ray single-crystal diffraction data of **1**–**3** were collected at 298 and 93 K on a Rigaku Saturn 724$^+$ CCD diffractometer equipped with Rigaku low-temperature gas spray cooler device, by using Mo-Kα (λ = 0.71075 Å) radiation from a graphite monochromator. Data processing including empirical absorption corrections was performed using the Crystal clear software package (Rigaku, 2005). The structures were solved by direct methods and refined by the full-matrix method based on F^2 by means of the SHELXTL software package. Non-H atoms were refined anisotropically using all reflections with $I > 2\sigma$ (I). All H atoms were not added due to the highly disordered state of the cations and the complex symmetry elements. Crystallographic data and structure refinements at 298 and 93 K of **1**–**3** are listed in Table S1.

Dielectric measurements. Dielectric measurements were applied on the pellets of the powder samples with silver conduction paste depositing on both sides. The measurements were performed on a TongHui 2828A impedance analyzer at frequencies of 1000 kHz with an applied electric field of 0.5 V in the temperature range of 100−280 K.

Table S1 Crystal data and structure refinements for **1**−**3** at 298 K and 93 K.

	1(298 K)	**1**(93 K)	**2**(298 K)	**2**(93 K)	**3**(298 K)	**3**(93 K)
Formula	$C_7H_6CaCoN_9$	$C_7H_6CaCoN_9$	$C_7H_5CaCoN_8O$	$C_7H_5CaCoN_8O$	$C_7H_5CaCoN_8S$	$C_7H_5CaCoN_8S$
Formula weight	315.22	315.22	316.21	316.21	332.27	332.27
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
Space group	*P*6$_3$/*mmc*	*P*6$_3$/*mmc*	*P*6$_3$/*mmc*	*P*6$_3$/*mmc*	*P*6$_3$/*mmc*	*P*6$_3$/*mmc*
a/Å	7.573(1)	7.575(7)	7.549(1)	7.529(6)	7.524(1)	7.505(7)
b/Å	7.573(1)	7.575(7)	7.549(1)	7.529(6)	7.524(1)	7.505(7)
c/Å	13.338(3)	13.31(2)	13.313(3)	13.243(14)	13.576(3)	13.575(18)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	120	120	120	120	120	120
V/Å^3	662.3(2)	661.6(16)	657.0(2)	650.1(13)	665.5(2)	662.1(16)
Z	2	2	2	2	2	2
D_{calc}/g·cm^{-3}	1.580	1.583	1.598	1.615	1.658	1.666
μ/mm^{-1}	1.679	1.681	1.696	1.714	1.825	1.834
F(000)	414	414	430	414	425	425
θ range/°	3.055−27.472	3.060−27.475	3.060−27.416	3.124−27.471	3.001−27.420	3.001−27.418
Reflns. collected	4347	4404	4303	4233	3869	4404
Indep. reflns(R_{int})	324(0.0362)	320(0.0358)	322(0.0419)	311(0.0281)	328(0.0325)	321(0.0302)
no.parameters	29	27	27	27	27	27
R_1[a],wR_2[b][$I>2\sigma(I)$]	0.0531,0.1888	0.0702,0.2052	0.0828,0.2428	0.0870,0.2299	0.0751,0.2424	0.0697,0.2136
R_1,wR_2[alldata]	0.0534,0.1891	0.0718,0.2072	0.0831,0.2429	0.0874,0.2302	0.0753,0.2425	0.0703,0.2140
GOF	1.326	1.205	1.244	1.135	1.229	1.259
$\Delta\rho$[c]/e·Å^{-3}	1.238,−1.352	2.140,−0.840	1.778,−2.700	2.627,−2.127	1.912,−1.794	1.937,−0.948

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c]Maximum and minimum residual electron density.

Table S2 Bond lengths (Å) and bond angles (°) for **1**−**3** at 298 K and 93 K.

1(298 K)			
Ca(1)−N(1)	2.463(5)	Ca(1)−N(1)−C(1)	175.4(4)
Co(1)−C(1)	1.895(5)	Co(1)−C(1)−N(1)	180.0(5)
C(1)−N(1)	1.145(7)	C(1)−Co(1)−C(1)#1	180.0(2)
C(2)−N(2)	1.357(10)	N(1)−Ca(1)−N(1)#2	79.8(2)
C(2)−N(3)	1.357(10)	N(1)−Ca(1)−N(1)#3	134.89(8)
		N(1)−Ca(1)−N(1)#4	83.27(17)

Symmetry codes: #1 –x, –y+2, –z; #2 x, y, –z+1/2; #3 –x+y, –x+1, –z+1/2; #4 –y+1, x–y+1, z

1(93 K)

Ca(1)−N(1)	2.452(6)	Ca(1)−N(1)−C(1)	175.2(5)
Co(1)−C(1)	1.904(6)	Co(1)−C(1)−N(1)	179.8(6)
C(1)−N(1)	1.144(8)	C(1)−Co(1)−C(1)#1	90.0(3)
C(2)−N(2)	1.443(10)	N(1)−Ca(1)−N(1)#2	83.34(19)
C(2)−N(3)	1.453(10)	N(1)−Ca(1)−N(1)#3	134.85(9)
		N(1)−Ca(1)−N(1)#4	79.7(3)

Symmetry codes: #1 x–y, x–1, –z; #2 –y+1, x–y, z; #3 –x+y+1, –x+1, –z+1/2; #4 x, y, –z+1/2

2(298 K)

Ca(1)−N(1)	2.458(7)	Ca(1)−N(1)−C(1)	173.9(7)
Co(1)−C(1)	1.889(8)	Co(1)−C(1)−N(1)	179.5(7)
C(1)−N(1)	1.143(11)	C(1)−Co(1)−C(1)#1	89.5(3)
C(2)−N(2)	1.348(10)	N(1)−Ca(1)−N(1)#2	81.2(4)
C(2)−O(1)	1.263(5)	N(1)−Ca(1)−N(1)#3	82.2(3)
		N(1)−Ca(1)−N(1)#4	135.38(13)

Symmetry codes: #1 y–1, –x+y, –z; #2 x, y, –z+1/2; #3 –y+1, x–y+1, z; #4 –x+y, –x+1, –z+1/2

2(93 K)

Ca(1)−N(1)	2.441(7)	Ca(1)−N(1)−C(1)	173.8(6)
Co(1)−C(1)	1.888(8)	Co(1)−C(1)−N(1)	179.5(7)
C(1)−N(1)	1.143(10)	C(1)−Co(1)−C(1)#1	89.5(3)
C(2)−N(2)	1.336(5)	N(1)−Ca(1)−N(1)#2	81.1(4)
C(2)−O(1)	1.255(5)	N(1)−Ca(1)−N(1)#3	135.34(13)
		N(1)−Ca(1)−N(1)#4	82.3(3)

Symmetry codes: #1 x–y, x–1, –z; #2 x, y, –z+1/2; #3 –y+1, x–y, –z+1/2; #4 –x+y+1, –x+1, z

3(298 K)

Ca(1)−N(1)	2.464(6)	Ca(1)−N(1)−C(1)	178.1(5)
Co(1)−C(1)	1.897(6)	Co(1)−C(1)−N(1)	178.1(6)
C(1)−N(1)	1.154(8)	C(1)−Co(1)−C(1)#1	90.9(3)
C(2)−N(2)	1.327(9)	N(1)−Ca(1)−N(1)#2	79.4(3)
C(2)−S(1)	1.708(10)	N(1)−Ca(1)−N(1)#3	134.75(9)
		N(1)−Ca(1)−N(1)#4	83.6(2)

Symmetry codes: #1 y–1, –x+y, –z; #2 x, y, –z+1/2; #3 –x+y, –x+1, –z+1/2; #4 –x+y, –x+1, z

3(93 K)

Ca(1)−N(1)	2.458(6)	Ca(1)−N(1)−C(1)	177.6(5)
Co(1)−C(1)	1.899(7)	Co(1)−C(1)−N(1)	178.5(6)
C(1)−N(1)	1.150(9)	C(1)−Co(1)−C(1)#1	91.1(3)
C(2)−N(2)	1.321(9)	N(1)−Ca(1)−N(1)#2	79.8(3)
C(2)−S(1)	1.709(10)	N(1)−Ca(1)−N(1)#3	83.2(2)

	N(1)−Ca(1)−N(1)#4	134.90(9)

Symmetry codes: #1 x−y, x−1, −z; #2 x, y, −z+1/2; #3 −y+1, x−y, z; #4 −y+1, x−y, −z+1/2

Table S3 The α values correlated with different temperatures of **2**.

T / K	170	180	190	200	210
α	0.46	0.45	0.41	0.31	0.25

Table S4 The α values correlated with different temperatures of **3**.

T / K	145	150	155	160	165
α	0.35	0.30	0.17	0.19	0.09

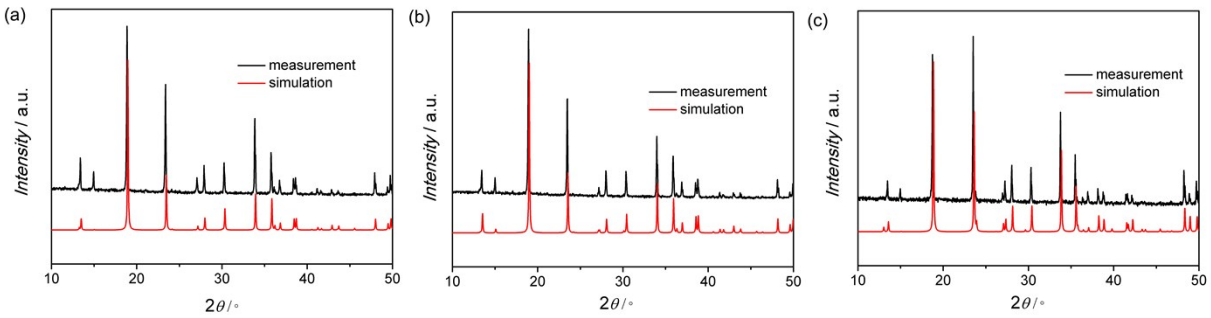

Figure S1 PXRD patterns measured on the crystalline samples of **1**–**3** (a–c) and the simulated ones based on the single crystal structures at 298 K.

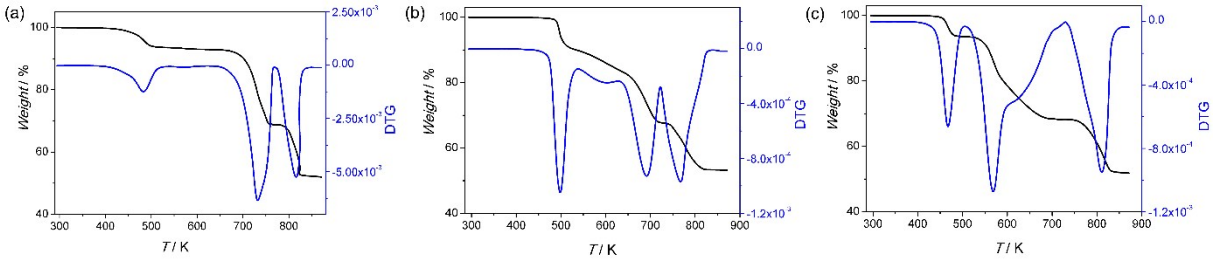

Figure S2 TGA curves of **1**–**3** (a–c) measured between 300−870 K.

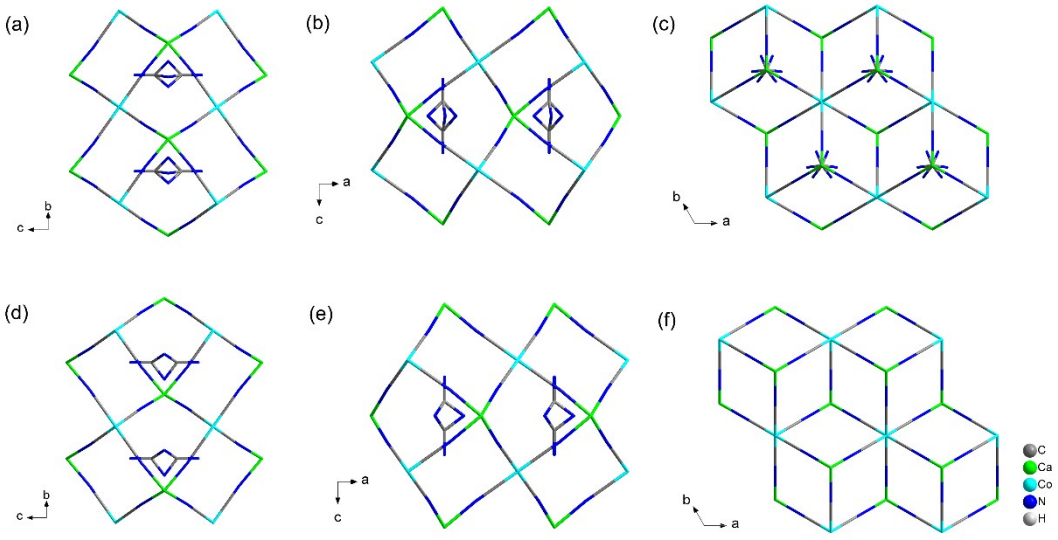

Figure S3 Packing views of **1** at 298 K (a−c) and 93 K (d−f) along three axes.

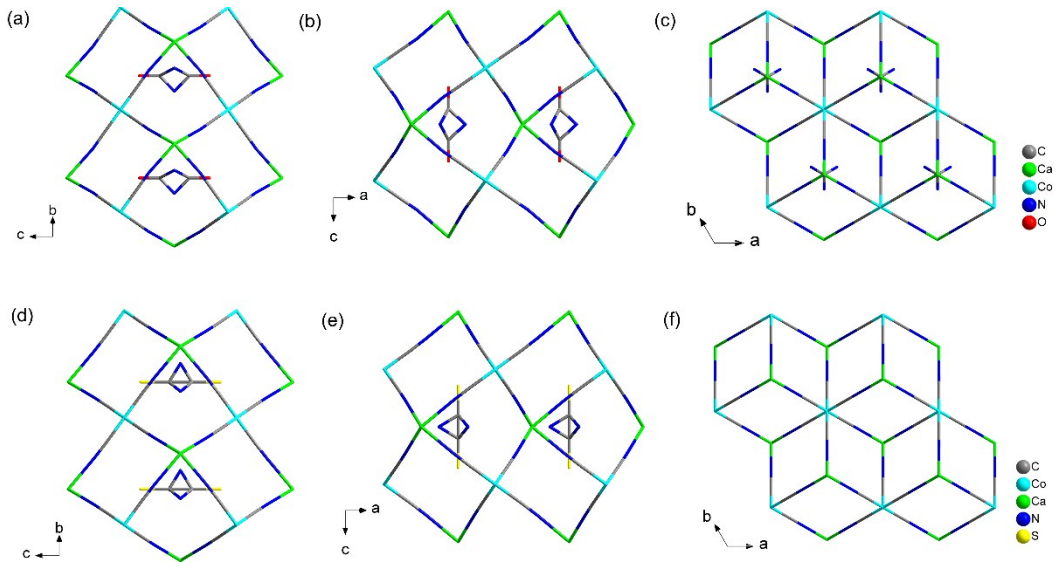

Figure S4 Packing views of **2** (a–c) and **3** (d–f) at 298 K along three axes.

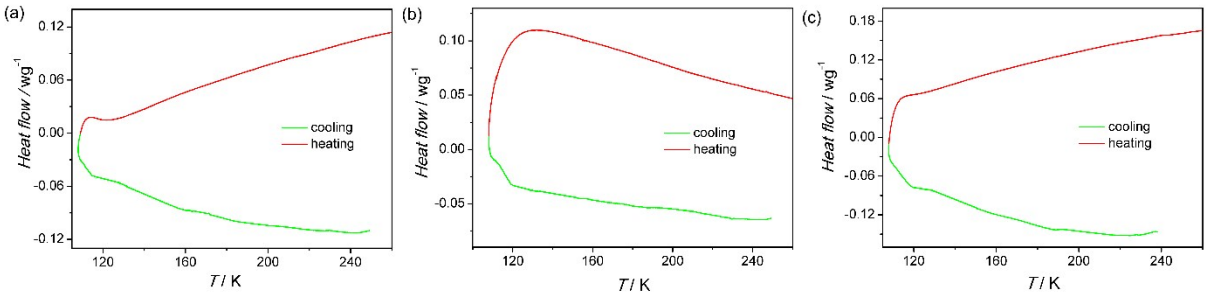

Figure S5 DSC curves of **1**–**3** (a–c) in a cooling-heating run.

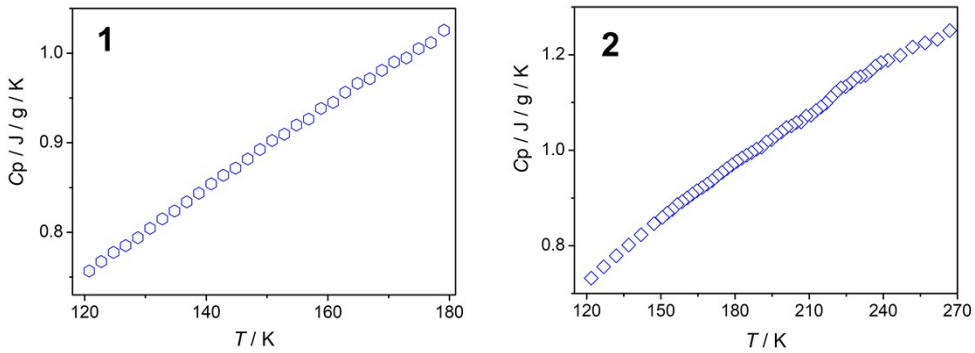

Figure S6 Specific heat measurements of **1** and **2** in a cooling run.

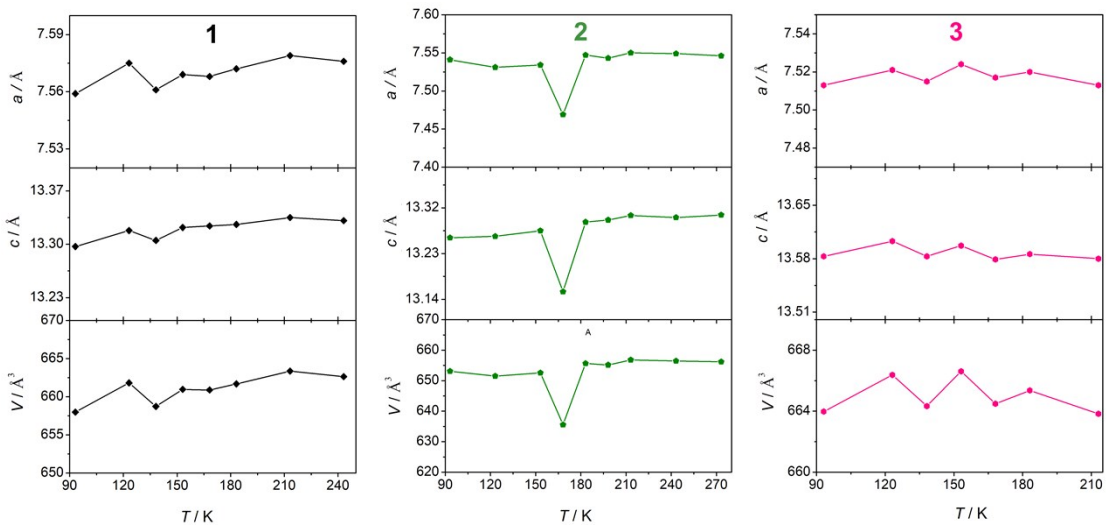

Figure S7 Variable-temperature cell parameters of **1**–**3**. The point at 168 K in **2** would be an experimental error.

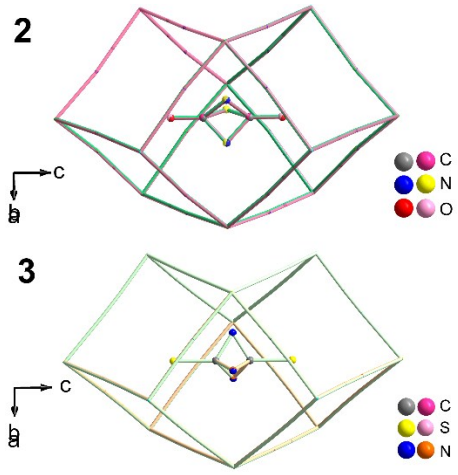

Figure S8 Superposition of the unit cages at 298 K (pink and light yellow) and 93 K (green and light green) for **2** and **3**, drawn at the thermal ellipsoids of 30 %.