Supporting Information

A high-temperature hybrid bimetal nitrite perovskite ferroelectric: [(R)-3-quinuclidinol]$_2$[LiCo(NO$_2$)$_6$]

Zhi-Yuan Yue†, Rong-Meng Liao†, Wang Luo, Na Wang, Le-Ping Miao,*

Heng-Yun Ye and Chao Shi*

Chaotic Matter Science Research Center, Department of Materials,

Metallurgy and Chemistry, Jiangxi University of Science and Technology,

Ganzhou 341000, P. R. China.
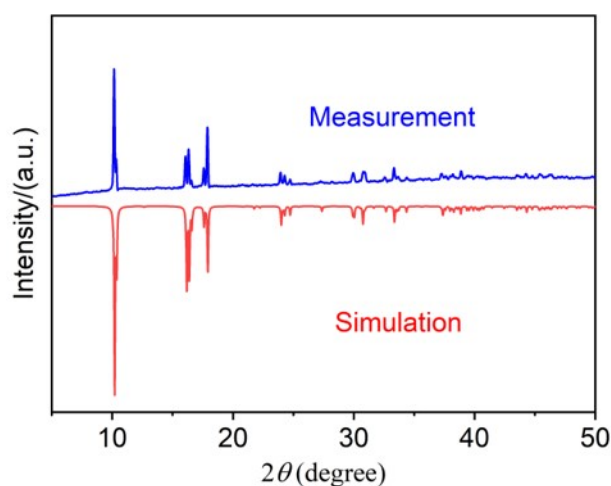
Corresponding authors:
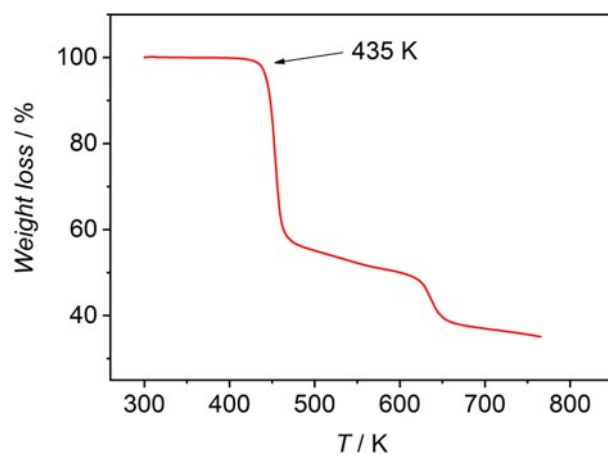*15150517670@163.com

Figure. S1 PXRD patterns of **1** 297 K.

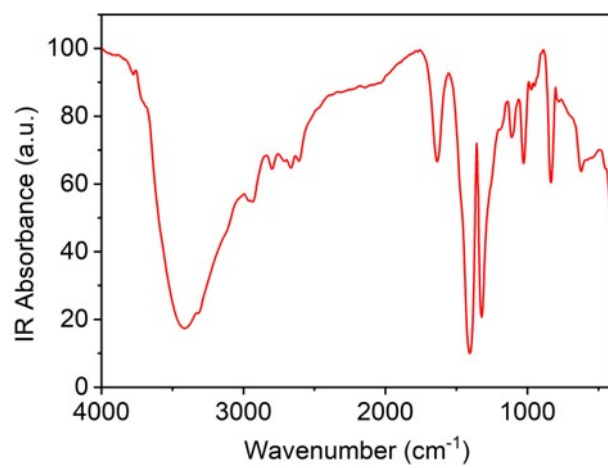**Figure. S2** The thermogravimetric analysis of **1**.

Figure. S3 Infrared (IR) spectra for **1**.

Table S1 Crystal Data and Structure Refinement Details for **1** at 297 K and 350 K.

	1_297 K	**1_350 K**
Empirical formula	$C_{14}H_{28}CoLiN_8O_{14}$	
Formula weight	596.30	
Crystal system	monoclinic	trigonal
Space group	$C2$	$P321$
a / Å	17.0535(6)	9.9786(3)
b / Å	10.0663(4)	9.9786(3)
c / Å	6.9926(2)	7.0265(3)
α / °	90	90
β / °	91.543(3)	90
γ / °	90	120
Volume / Å³	1199.95(7)	605.91(4)
Z	2	1
ρcalcg/cm³	1.650	1.530
μ / mm⁻¹	0.800	0.780
$F(000)$	620.0	276.0
Radiation	Mo Kα (λ=0.71073)	
2θ range	4.7−61.764	4.714−62.03
Reflns collected	7378	9310
Independent reflns (Rint)	3795 (0.043)	1285 (0.0564)
No. of parameters	174	59
GOF	1.073	2.313
R_1[a], wR_2[b] [I>2σ(I)]	0.0972, 0.2772	0.1063, 0.2911
R_1, wR_2 [all data]	0.1029, 0.2864	0.1146, 0.2937
Δρ[c] / e·Å⁻³	1.63, −0.76	1.04, −0.63
Flack parameter	0.72 (6)	0.44 (11)

[a] $R_1 = \Sigma \, ||F_o|-|F_c||/|F_o|$; [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 Selected bond lengths [Å] for **1** at 297 K and 350 K.

297 K		**350 K**	
Co1−N2¹	1.965(6)	Co1−N1	1.943(6)
Co1−N2	1.965(6)	Co1−N1¹	1.943(6)
Co1−N4	1.964(10)	Co1−N1²	1.943(6)
Co1−N4¹	1.964(10)	Co1−N1³	1.943(6)
Co1−N3	1.937(12)	Co1−N1⁴	1.943(6)
Co1−N3¹	1.938(12)	Co1−N1⁵	1.943(6)
O7−C5	1.431(3)	O3−N1	1.217(8)
O6−Li1	2.07(3)	O3−Li1	2.042(5)

N2−O1	1.225(8)	N1−O1	1.273(16)
N2−O2	1.227(11)	N1−O2	1.48(3)
N4−O3	1.200(12)	O1−O2	1.20(3)
N4−O4	1.221(10)	C2−C1	1.554(2)
O1−Li1[2]	2.064(6)	C2−O4	1.4349(16)
Li1−O4	1.97(2)	C2−C3	1.515(3)
Li1−O4[3]	1.97(2)	C1−N2	1.509(3)

Symmetry codes: [1]1−X, +Y,1−Z; [2]+X, +Y, −1+Z; [3]1−X, +Y, 2−Z

Symmetry codes: [1]+Y−X, −X, +Z; [2]−X, −X+Y, 1−Z; [3]−Y, +X−Y, +Z; [4]+Y, +X,1−Z; [5]−Y+X, −Y, 1−Z

Table S3 Selected bond angles [°] for **1** at 297 K.

1_297 K			
N2−Co1−N2[1]	176.7(11)	O6[3]−Li1−O6	89.5(15)
N4[1]−Co1−N2	91.2(6)	O1[4]−Li1−O6[3]	87.5(8)
N4−Co1−N2	86.4(5)	O1[1]−Li1−O6	87.5(8)
N4[1]−Co1−N2[1]	86.3(5)	O1[4]−Li1−O6	89.4(8)
N4−Co1−N2[1]	91.2(6)	O1[1]−Li1−O6[3]	89.4(8)
N4[1]−Co1−N4	86.3(7)	O1[1]−Li1−O1[4]	176(2)
N3−Co1−N2	87.0(6)	O4−Li1−O6[3]	178.2(11)
N3−Co1−N2[1]	95.4(6)	O4[3]−Li1−O6[3]	89.1(3)
N3[1]−Co1−N2[1]	87.0(6)	O4−Li1−O6	89.1(3)
N3[1]−Co1−N2	95.4(6)	O4[3]−Li1−O6	178.2(11
N3[1]−Co1−N4[1]	92.6(4)	O4−Li1−O1[1]	89.4(8)
N3−Co1−N4[1]	178.0(8)	O4−Li1−O1[4]	93.7(7)
N3[1]−Co1−N4	178.0(8)	O4[3]−Li1−O1[4]	89.4(8)
N3−Co1−N4	92.6(4)	O4[3]−Li1−O1[1]	93.7(7)
N3−Co1−N3[1]	88.4(9)	O4[3]−Li1−O4	92.4(15)
C6−C4−C1	110.3(13)	N4−O4−Li1	127.2(10)
N1−C1−C4	108.3(13)	C1−N1−C3	105.4(13)
N3−O6−Li1[1]	125.6(12)	C2−N1−C1	113.4(13)
O1−N2−Co1[1]	123.3(5)	C2−N1−C3	97.5(12)
O1−N2−O2	116.1(8)	C5−C6−C4	110.7(13)
O2−N2−Co1[1]	118.1(6)	C7−C6−C4	97.7(14)
O3−N4−Co1[1]	115.8(8)	C7−C6−C5	116.4(13)
O3−N4−O4	119.7(11)	N1−C2−C7	113.8(13)
O4−N4−Co1	123.5(9)	O7−C5−C6	104.0(10)
O6−N3−Co1	122.7(10)	O7−C5−C3	113.2(14)
O5−N3−Co1	121.4(10)	C6−C5−C3	105.0(12)

O5−N3−O6	115.0(13)	N1−C3−C5	114.9(13)
N2−O1−Li1[2]	125.0(5)	C6−C7−C2	108.5(14)

Symmetry codes: [1]1−X, +Y, 1−Z; [2]+X, +Y, −1+Z; [3]1−X, +Y, 2−Z; [4]+X, +Y, 1+Z

Table S4 Selected bond angles [°] for **1** and 350 K.

1_350 K			
N1−Co1−N1[1]	174.0(12)	O2−O1−N1	73.4(19)
N1[2]−Co1−N1[3]	92.7(10)	O3[5]−Li1−O3	87.60(19)
N1−Co1−N1[3]	84.1(9)	O3[5]−Li1−O3[6]	88.4(6)
N1[4]−Co1−N1[3]	91.8(2)	O3[2]−Li1−O3	87.60(19)
N1[4]−Co1−N1[2]	174.0(12)	O3[2]−Li1−O3[6]	96.7(6)
N1[2]−Co1−N1[5]	91.8(2)	O3[5]−Li1−O3[7]	174.0(8)
N1−Co1−N1[2]	91.8(2)	O3[6]−Li1−O3	174.0(8)
N1−Co1−N1[4]	92.7(10)	O3[8]−Li1−O3[2]	174.0(8)
N1[1]−Co1−N1[2]	84.1(9)	O3[8]−Li1−O3[6]	87.60(19)
N1[1]−Co1−N1[5]	92.7(10)	O3[8]−Li1−O3[7]	87.60(19)
N1[3]−Co1−N1[5]	174.0(12)	O3[6]−Li1−O3[7]	87.59(19)
N1[1]−Co1−N1[4]	91.8(2)	O3[8]−Li1−O3[5]	96.7(6)
N1−Co1−N1[5]	91.8(2)	O3[8]−Li1−O3	88.4(6)
N1[1]−Co1−N1[3]	91.8(2)	O3−Li1−O3[7]	96.7(6)
N1[4]−Co1−N1[5]	84.1(9)	O3[2]−Li1−O3[5]	87.60(19)
N1−O3−Li1	124.7(6)	O3[2]−Li1−O3[7]	88.4(6)
O3−N1−Co1	123.8(6)	O4−C2−C1	104.53(19)
O3−N1−O1	119.2(10)	O4−C2−C3	110.2(2)
O3−N1−O2	101.3(14)	C3−C2−C1	103.27(19)
O1−N1−Co1	117.0(9)	N2−C1−C2	96.05(16)
O1−N1−O2	51.1(11)	O1−O2−N1	55.5(14)
O2−N1−Co1	113.7(13)		

Symmetry codes: [1]−Y+X, −Y,1−Z; [2]+Y−X, −X, +Z; [3]+Y, +X,1−Z; [4]−X, −X+Y,1−Z; [5]−Y, +X−Y, +Z; [6]−Y+X, −Y,2−Z; [7]+Y, +X,2−Z; [8]−X, −X+Y,2−Z

Table S5 Bond lengths [Å] and bond angles [°] of the hydrogen bond at 297 K of **1**.

D	H	A	d(D−H)/Å	d(H−A)/Å	d(D−A)/Å	D−H−A/°
O7	H7	O4[1]	0.82	2.41	2.737(13)	104.6
C1	H1B	O7	0.97	2.52	2.91(2)	103.8
C2	H2B	O5	0.97	2.69	3.048(17)	102.1
C3	H3A	O1[2]	0.97	2.69	3.497(15)	141.1

Symmetry codes: [1]+X, −1+Y, −1+Z; [2]1/2−X, −1/2+Y, −Z; [3]1/2−X,1/2+Y, −Z

Calculations of ΔS and N

$$\Delta S = \int_{T_1}^{T_2} \frac{QdT}{T} \approx \frac{\Delta T}{T_C} = \frac{\dfrac{30.66 + 28.77}{2} \times 596.30}{342} = 51.81 j \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S = RlnN$$

$$N = e^{\frac{\Delta S}{R}} = e^{\frac{51.81}{8.314}} = 521.55$$