Supporting Information

Table S1 Crystal data and structure refinements for **1** at 293 K and 203 K.

T/K	293	203
formula	$C_{12}H_{11}CoN_8S_2$	$C_{12}H_{11}CoN_8S_2$
M_w	406.34	406.34
crystal system	orthorhombic	orthorhombic
space group	*Pna*2$_1$ (No. 29)	*Pca*2$_1$ (No. 33)
a / Å	15.03(1)	15.71(6)
b / Å	8.92(1)	8.70(3)
c / Å	13.21(1)	13.25(4)
α / °	90	90
β / °	90	90
γ / °	90	90
V / Å^3	1771(3)	1811(11)
Z	4	4
ρ_{calcd} / g cm^{-3}	1.524	1.490
μ / mm^{-1}	1.221	1.195
Refls. collected /unique	12203 / 4032	12170 / 4109
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0955, 0.2817	0.1198, 0.3049
GOF	1.153	1.095
$\Delta\rho$[c] / e Å^{-3}	1.249, −1.126	2.700, −1.121

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

Table S2 Hydrogen bonds of **1** at 293 K and 203 K.

	D–H···*A*	*D*–H	H···*A*	*D*···*A*	∠*D*–H···*A*
293K	N(7)–H(7A)···N(3)#1	0.86	2.43	3.22(5)	152.9
	N(7')–H(7A')···N(3)#1	0.86	2.39	3.20(3)	156.8
	N(8)–H(8A)···N(5)#2	0.86	2.59	3.35(4)	146.7
	N(8')–H(8A')···N(3)#3	0.86	2.45	3.14(2)	137.6
	O(1)–H(1A)···N(4)#2	0.85	1.77	2.62(1)	176.5
	O(1)–H(1B)···N(6)	0.85	1.77	2.62(1)	173.4
	O(1)–H(1C)···N(2)#3	0.85	1.75	2.59(1)	172.2
203K	N(7)–H(7B)···N(4)#4	0.86	2.16	3.01(2)	166.5
	N(8)–H(8B)···N(5)#5	0.86	1.98	2.83(2)	173.5
	O(1)–H(1A)···N(6)#6	0.85	1.81	2.66(2)	176.4
	O(1)–H(1B)···N(1)	0.85	1.79	2.63(2)	176.0
	O(1)–H(1C)···N(2)#7	0.85	1.79	2.63(2)	171.8

Symmetry codes: #1–x+1, –y, z–1/2; #2 x, y+1, z; #3 x+1/2, –y+1/2, z; #4 –x, –y+2, z–1/2; #5 –x+1/2, y, z–1/2; #6 x+1/2, –y+1, z; #7 x+1/2, –y+2, z.

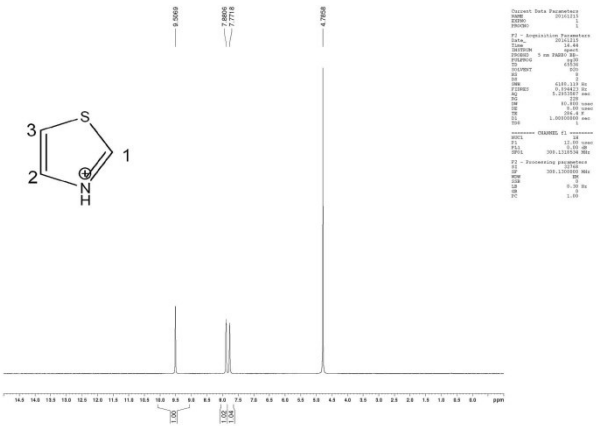

Figure S1 ^{1}H NMR (D_2O) spectrum of **1**.

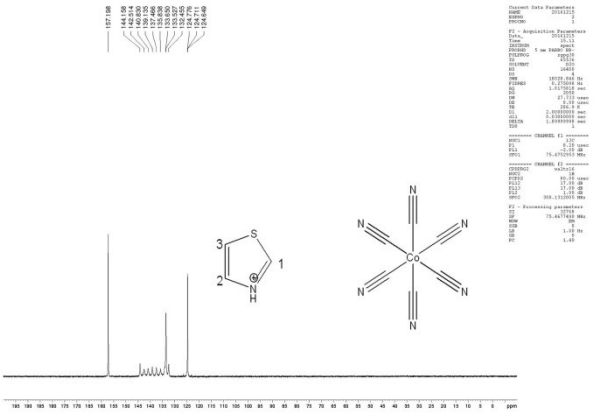

Figure S2 ^{13}C NMR (D_2O) spectrum of **1**.

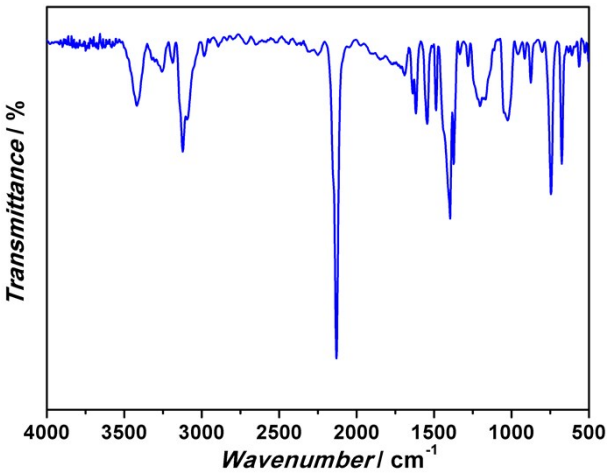

Figure S3 Infrared (IR) spectra of **1** measured at room temperature.

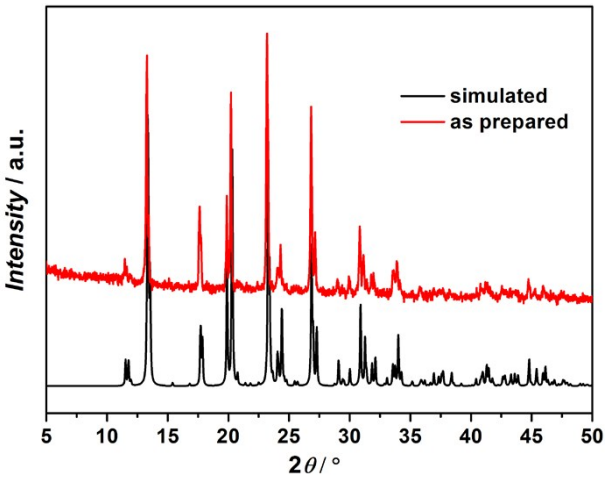

Figure S4 PXRD pattern for the as-prepared samples of **1** and the simulated one based on the single crystal structure at 293 K.

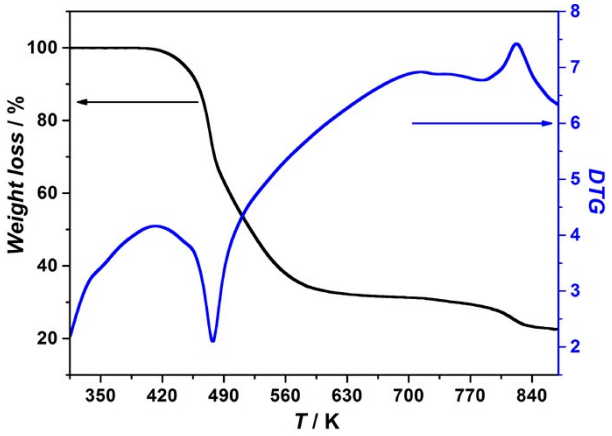

Figure S5 TGA measurement of **1** in the temperature range of 315−870 K.

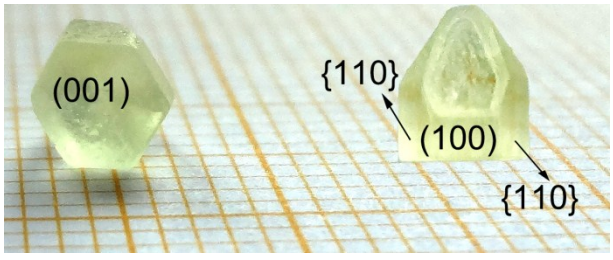

Figure S6 Crystal morphology and orientation of **1** based on the structure at 293 K.

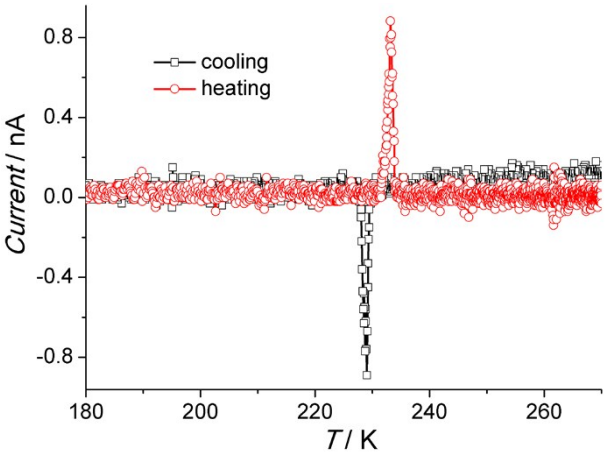

Figure S7 Pyroelectric current of **1** measured in a cooling-heating run.

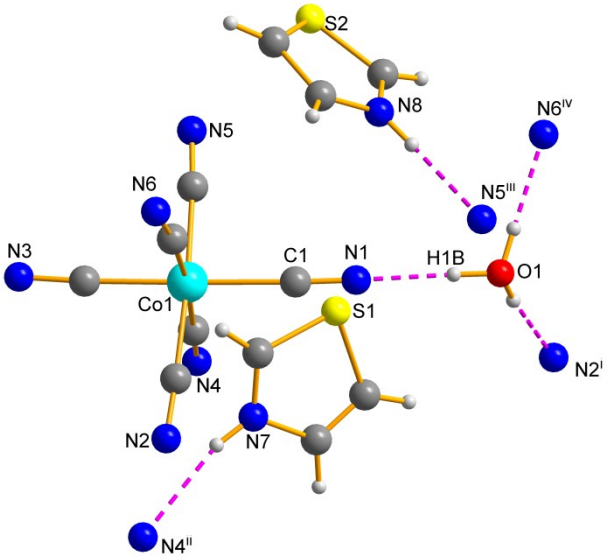

Figure S8 Basic structure unit of **1** in the LTP with hydrogen bonding interactions. Symmetry codes: i 0.5+x, 2–y, z; ii –x, 2–y, –0.5+z; iii 0.5–x, y, –0.5+z; iv 0.5+x, 1–y, z.

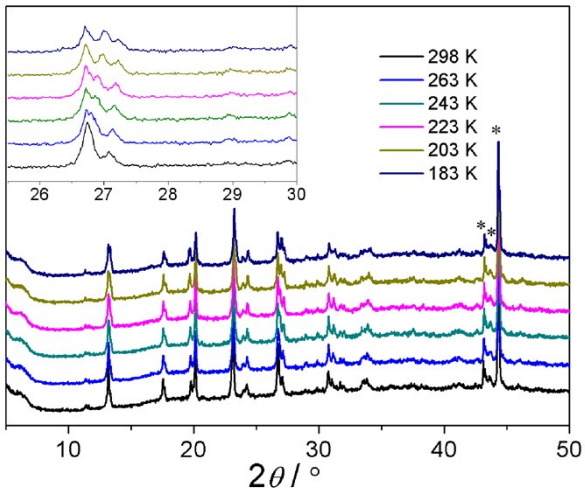

Figure S9 Variable temperature PXRD patterns of **1** upon cooling in the temperature range of 298−183 K. The asterisked peaks arise from the sample holder.

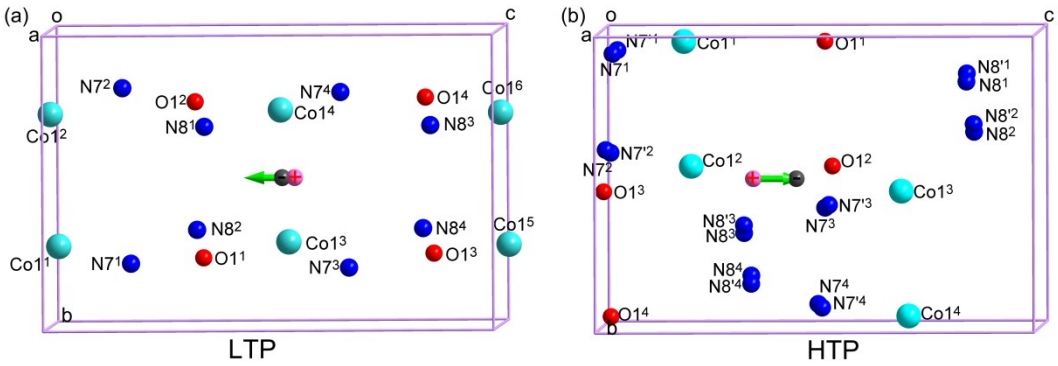

Figure S10 Arrangements of the dipole moments in the cell unit of **1** in the (a) 203 K (LTP) and (b) 293 K (HTP). The inserted atoms with pink and black colors present the centers of the positive charge and negative charge, respectively. The arrows in green denote the dipole moments of **1**.

According to the crystal structure data collected at 203 K and 293 K, we select a unit cell and make an assumption that the positive charge of $(C_3H_4NS)^+$ and $(H_3O)^+$ and the negative charge of $[Co(CN)_6)]^{3-}$ is on the N atom, O atom and Co atom, respectively.

1. 203 K

Atoms	Coordinate		Center coordinate
Co	$Co1^1$(0.4109, 0.7323, 0.0152)	$Co1^4$(0.5891, 0.2677, 0.5152)	(0.5,0.5,0.51524)
	$Co1^2$(0.9109, 0.2677, 0.0947)	$Co1^5$(0.4109, 0.7323, 1.0152)	
	$Co1^3$(0.0891, 0.7323, 0.5152)	$Co1^6$(0.9109, 0.2677, 1.0152)	
N	$N7^1$(0.0182, 0.8060, 0.1620)	$N7^2$(0.5182, 0.1940, 0.1620)	(0.5,0.5,0.5429)
	$N7^3$(0.4818, 0.8060, 0.6620)	$N7^4$(0.9818, 0.1940, 0.6620)	
	$N8^1$(0.2783, 0.3348, 0.3352)	$N8^2$(0.7783, 0.6652, 0.3352)	
	$N8^3$(0.2217, 0.3348, 0.8352)	$N8^4$(0.7217, 0.6652, 0.8352)	
O	$O1^1$(0.4162, 0.7730, 0.3372)	$O1^2$(0.9162, 0.2270, 0.3372)	
	$O1^3$(0.0838, 0.7730, 0.8372)	$O1^4$(0.5838, 0.2270, 0.8372)	

$P = lim\frac{1}{V}\sum q_i r_i$

$= (q_-r_- + q_+r_+) / V$

= [(−3e×0.51524)×4+ (3e×0.5429)×4]×c/V

= [0.33192×(−1.6 × 10^{-19})×13.25 × 10^{-10} C m] / (1811 × 10^{-30} m^3)

= −0.0389×10^{-2}C m^{-2}

= −0.0389 μC cm^{-2}

2. 293 K

Atoms	Coordinate		Center coordinate
Co	$Co1^1$(0.6685, 0.02898, 0.1934)	$Co1^3$(0.8315, 0.5290, 0.6934)	(0.5,0.5,0.4434)
	$Co1^2$ (0.1685, 0.4710, 0.1934)	$Co1^4$(0.3315, 0.9710, 0.6934)	
N	$N7^1$(-0.0004, 0.098, 0.009)	$N7'^1$(-0.0433, 0.087, 0.019)	(0.5,0.5,0.3451)
	$N7^2$(0.496, 0.402, 0.009)	$N7'^2$(0.4567, 0.413, 0.019)	
	$N7^3$(0.504, 0.598, 0.509)	$N7'^3$(0.5433, 0.587, 0.519)	
	$N7^4$(1.004, 0.902, 0.509)	$N7'^4$(1.0433, 0.913, 0.519)	
	$N8^1$(0.634, 0.168, 0.836)	$N8'^1$(0.6128, 0.141, 0.8363)	
	$N8^2$(0.134, 0.332, 0.836)	$N8'^2$(0.1128, 0.359, 0.8363)	
	$N8^3$(0.866, 0.668, 0.336)	$N8'^3$(0.8872, 0.641, 0.3363)	
	$N8^4$(0.366, 0.832, 0.336)	$N8'^4$(0.3872, 0.859, 0.3363)	
O	$O1^1$(0.6675, 0.0290, 0.5151)	$O1^2$(0.1675, 0.4710, 0.5151)	
	$O1^3$(0.8325, 0.5290, 0.0151)	$O1^4$(0.3325, 0.9710, 0.0151)	

$P = lim\frac{1}{V}\sum q_i r_i$

= (q_-r_-+ q_+r_+) / V

= [(−3e×0.4434)×4+ (3e×0.3451)×4]×c/V

= [−1.1796×(−1.6 × 10^{-19})×13.21 × 10^{-10} C m] / (1771 × 10^{-30} m^3)

= 0.1408×10^{-2}C m^{-2}

= 0.1408 μC cm^{-2}

$|\Delta P| = |P_{203K} - P_{293K}|$

= |–0.0389 μC cm^{-2} – 0.1408 μC cm^{-2}|

= 0.1797 μC cm^{-2}