

Supporting Information

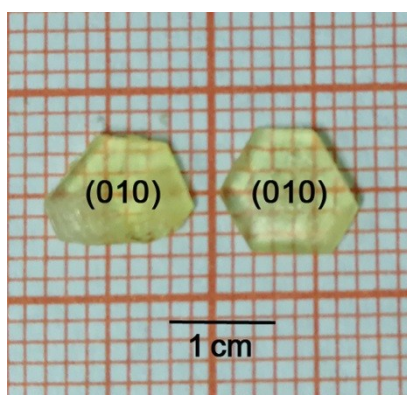


Figure S1. Crystal morphology of **1**.

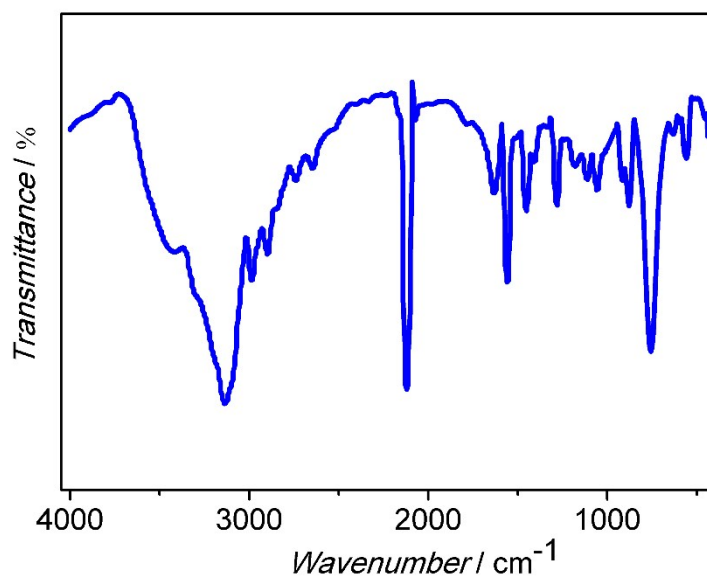


Figure S2. IR spectrum of **1** measured at 293 K.

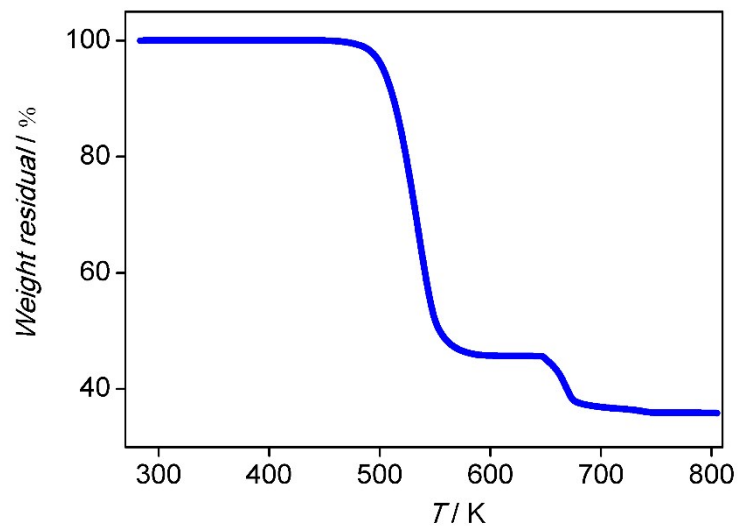


Figure S3. TGA curves of **1**.

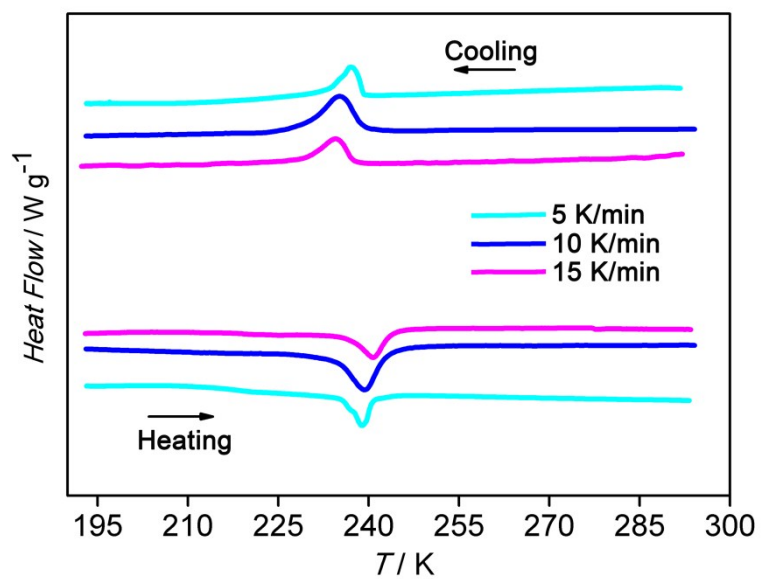


Figure S4. Characterizations of the phase transition behaviours. DSC curves of **1** measured at different scanning rates.

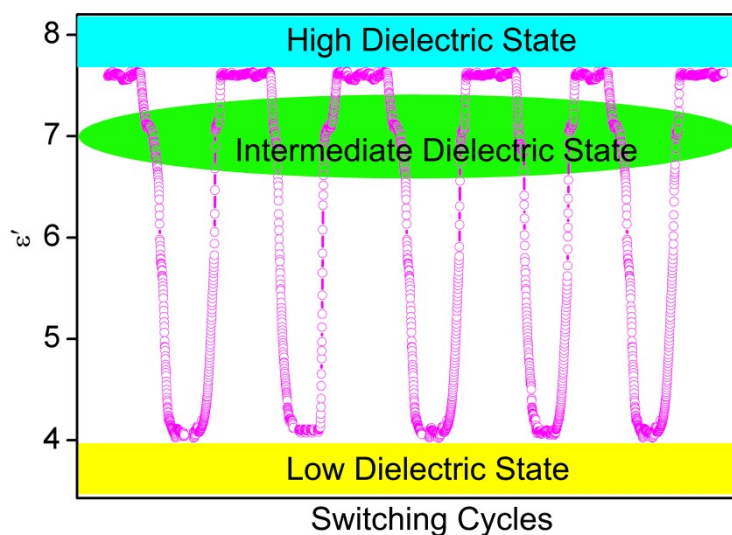


Figure S5. The ϵ' -switching cycles of dielectric response of **1** at 1000 kHz.

Table S1. Crystallographic data and structure refinements for **1** at ITP (220 K) and HTP (293 K).

	1	
	ITP	HTP
<i>T</i> / K	ITP	HTP
Formula	C ₁₂ H ₈ CoN ₈ KS ₂	C ₁₂ H ₈ CoN ₈ KS ₂
Formula weight	426.37	426.37
Crystal system	orthorhombic	orthorhombic
Space group	<i>Cmcm</i>	<i>Cmcm</i>
<i>a</i> / Å	9.1037(18)	9.0903(18)
<i>b</i> / Å	16.085(3)	16.188(3)
<i>c</i> / Å	11.716(2)	11.776(2)
<i>V</i> / Å ³	1715.6(6)	1732.9(6)
<i>Z</i>	4	4
<i>D</i> _{calc} / g·cm ⁻³	1.302	1.289
μ / mm ⁻¹	1.360	1.346
Reflections collected unique	5739	6133
<i>R</i> _{int}	0.0979	0.0236
<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] [<i>I</i> > 2σ(<i>I</i>)]	0.1523, 0.4403	0.1099, 0.3473
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.1610, 0.4572	0.1131, 0.3558
GOF	1.985	1.726
$\Delta\rho$ ^[c] / e·Å ⁻³	3.415 / -1.235	3.404 / -0.418

[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. Bonds lengths (Å) and angles (°) for **1** at ITP (220 K) and HTP (293 K).

1 (220 K)			
Co1–C1	1.884(10)	N1–K1–N1#5	176.1(4)
Co1–C1#4	1.884(10)	N1–K1–N2#1	91.41(16)
Co1–C2	1.873(11)	N1–K1–N2#8	91.41(16)
Co1–C2#3	1.873(11)	N1#5–K1–N2#1	91.41(16)
Co1–C3	1.915(9)	N1#5–K1–N2#8	91.41(16)
Co1–C3#3	1.915(9)	N1–K1–N3#6	88.83(13)
K1–N1	2.822(9)	N1–K1–N3#7	88.83(13)
K1–N1#5	2.822(9)	N1#5–K1–N3#6	88.83(13)
K1–N2#1	2.940(12)	N1#5–K1–N3#7	88.83(13)
K1–N2#8	2.940(12)	N2#1–K1–N2#8	88.5(5)
K1#1–N2	2.940(12)	N2#1–K1–N3#6	82.3(3)
K1–N3#6	2.841(9)	N2#1–K1–N3#7	170.8(4)
K1–N3#7	2.841(9)	N2#8–K1–N3#6	170.8(4)
K1#7–N3	2.841(9)	N2#8–K1–N3#7	82.3(3)
		N3#6–K1–N3#7	106.9(4)

Symmetry codes: #1 $-x, 1-y, 1-z$; #2 $-x, y, z$; #3 $-x, y, 1/2-z$; #4 $x, y, 1/2-z$; #5 $x, y, 3/2-z$; #6 $-1/2+x, 1/2-y, 1/2+z$; #7 $1/2-x, 1/2-y, 1-z$; #8 $x, 1-y, 1/2+z$.

1 (293 K)			
Co1–C1	1.901(7)	N1–K1–N1#5	178.1(2)
Co1–C1#4	1.901(7)	N1–K1–N2#1	90.69(9)
Co1–C2	1.894(6)	N1–K1–N2#8	90.69(9)
Co1–C2#3	1.894(6)	N1#5–K1–N2#1	90.69(9)
Co1–C3	1.896(6)	N1#5–K1–N2#8	90.69(9)
Co1–C3#3	1.896(6)	N1–K1–N3#6	89.42(7)
K1–N1#5	2.858(6)	N1–K1–N3#7	89.42(7)
K1–N2#1	2.997(8)	N1#5–K1–N3#6	89.42(7)
K1–N2#8	2.997(8)	N1#5–K1–N3#7	89.42(7)
K1#1–N2	2.997(8)	N2#1–K1–N2#8	89.1(3)
K1–N3#6	2.871(5)	N2#1–K1–N3#6	82.23(17)
K1–N3#7	2.871(5)	N2#1–K1–N3#7	171.3(2)
K1#7–N3	2.872(5)	N2#8–K1–N3#6	171.3(2)
		N2#8–K1–N3#7	82.23(17)
		N3#6–K1–N3#7	106.5(3)

Symmetry codes: #1 $-x, 1-y, 1-z$; #2 $-x, y, z$; #3 $-x, y, 1/2-z$; #4 $x, y, 1/2-z$; #5 $x, y, 3/2-z$; #6 $-1/2+x, 1/2-y, 1/2+z$; #7 $1/2-x, 1/2-y, 1-z$; #8 $x, 1-y, 1/2+z$.
