Supporting Information

Experimental

Sample preparation. Aqueous solution (30 mL) containing $Na_3[Co(CN)_6]$ (2.84 g, 10 mmol) and (HIm)Cl (3.14 g, 30 mmol) was evaporated slowly at room temperature over two weeks, affording pale yellow crystals of **Na**. Block yellow crystal of **Rb** was collected by the similar method but using $Rb_3[Co(CN)_6]$ (4.71 g, 10 mmol) instead of $Na_3[Co(CN)_6]$.

Na: yield 90% (based on Co). Elemental analysis calcd (%) for $C_{12}H_{12}CoN_{10}NaO$ (394.24): C 35.65, H 5.48, N 34.64; found: C 35.30, H 5.79, N 34.84. FTIR for **Na** (KBr): 3160, 2135, 2116, 1590, 1427, 1198, 1050, 762, 622 cm^{-1}.

Rb: yield 85% (based on Co). Elemental analysis calcd (%) for $C_{12}H_{10}CoN_{10}Rb$ (438.70): C 32.12, H 4.49, N 32.21; found: C 32.09, H 4.98, N 32.62. FTIR for **Rb** (KBr): 3165, 2121, 1586, 1090, 1046, 751, 621 cm^{-1}.

Measurements. Elemental analysis of C, H and N was conducted on a vario MICRO analyzer. Thermal gravimetric analysis (TGA) was performed on a TA Instruments Q500 in air flow. A Nicolet 5700 spectrometer was used to receive the infrared (IR) spectra. Powder X-ray diffraction (PXRD) was measured by a Rigaku SmartLab X-ray diffraction instrument to confirm the purity of the samples. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 200F3 instrument with a cooling/heating rate of 5 K min^{-1} in the temperature ranges of 103−293 K. Dielectric constant curves were collected by a Tonghui TH2828A impedance analyzer within an applied electric field of 1.0 V.

Single-crystal X-ray crystallography. A Rigaku Saturn 724^+ diffractometer using Mo-Kα (λ = 0.71073 Å) radiation from a graphite monochromator equipped with gas spray cooler device was used to collect single-crystal dates of compound **Na** and **Rb**. The bonds of C−H and N−H were placed in calculated positions, with C−H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C) for imidazolium H atoms and N−H = 0.86 Å and U_{iso}(H) =

1.2 U_{eq}(N). The water H atoms were located in difference Fourier syntheses and refined with an O−H distance restraint of 0.85 Å and with U_{iso}(H) = 1.5 U_{eq}(O). Crystallographic data and structural refinement details, selected bond lengths and bond angles, details of hydrogen bonding interactions are given in Table S1−2.

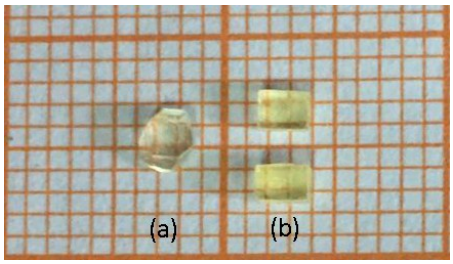

Figure S1. Crystal morphology of (a) **Na** and (b) **Rb**.

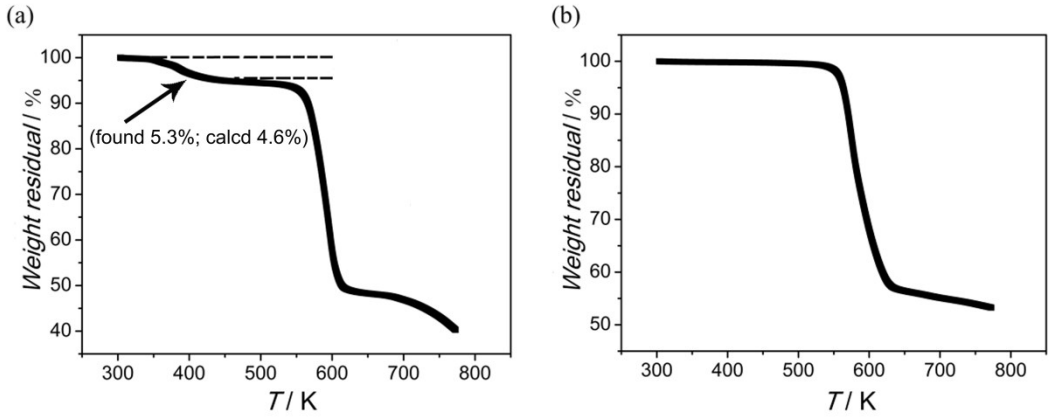

Figure S2. TGA curves of (a) **Na** and (b) **Rb**.

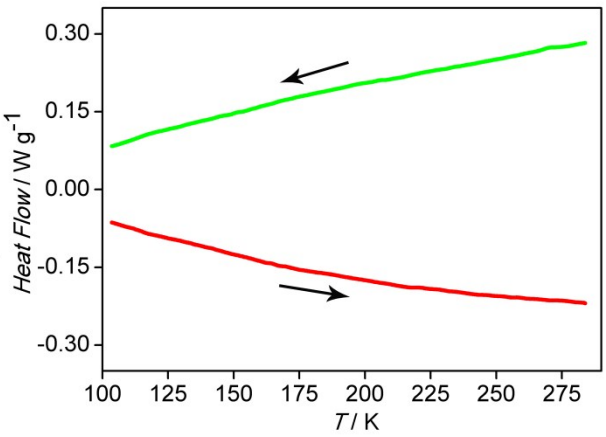

Figure S3. DSC curves of **Na** measured in the temperature range 100−290 K.

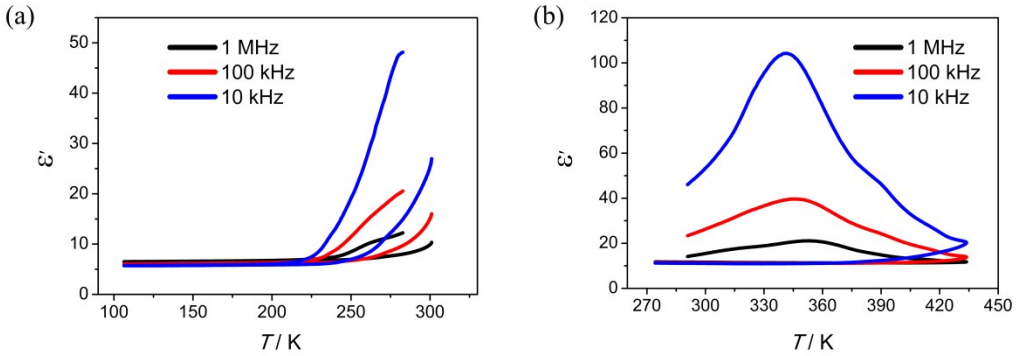

Figure S4. The ε' vs T of **Na** on the power state in the different frequency and temperature ranges of 100−430 K.

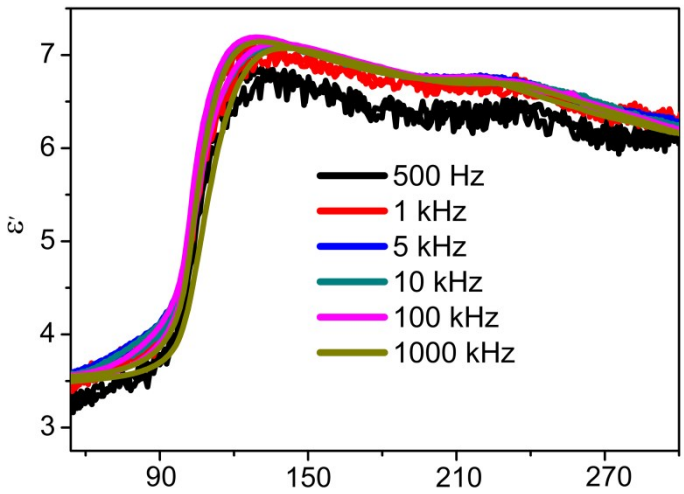

Figure S5. The ε' vs T of **Rb** on the power state in the different frequency and temperature ranges of 63−293 K.

Table S1. Bond lengths (Å) and bond angles (°) for **Na and Rb**.

Na (293 K)			
Na(1)−N(1)	2.4140(17)	N(1)#5−Na(1)−N(1)	134.94(9)
Na(1)−N(1)#5	2.4139(17)	N(1)−Na(1)−N(2)#2	102.25(5)
Na(1)−N(2)#2	2.477(2)	N(1)−Na(1)−O(1)	78.46(5)
Na(1)−N(5)#4	2.371(2)	N(2)#2−Na(1)−O(1)	65.08(7)
Na(1)−O(1)	2.955(2)	N(5)#4−Na(1)−N(1)	99.39(5)
		N(5)#4−Na(1)−N(2)#2	121.17(10)
		N(5)#4−Na(1)−O(1)	173.75(8)
Symmetry codes: #2 −x, −y, −z; #4 −x+1/2, −y, z−1/2; #5 x, −y−1/2, z.			
Rb (293 K)			
Rb(1)−N(1)	2.994(4)	N(1)−Rb(1)−N(1)#6	83.00(12)
		N(1)−Rb(1)−N(1)#7	97.00(12)
		N(1)−Rb(1)−N(1)#9	180.0
Symmetry codes: #6 x−y+2/3, x+1/3, −z+4/3; #7 x−y+2/3, x+1/3, −z+4/3; #9 x−y+2/3, x+1/3, −z+4/3.			
Rb (193 K)			
Rb(1)−N(1)	2.979(6)	N(1)−Rb(1)−N(1)#6	82.36(18)
		N(1)−Rb(1)−N(1)#8	97.64(18)
		N(1)−Rb(1)−N(1)#10	180.0
Symmetry codes: #6 y−1/3, −x+y+1/3, −z+1/3; #8 −y+1, x−y+1, z; #10 −x+2/3, −y+4/3, −z+1/3.			
Rb (93 K)			
Rb(1)−N(1)	2.972(6)	N(1)−Rb(1)−N(1)#8	93.2(3)
Rb(1)−N(2)	2.968(5)	N(1)−Rb(1)−N(2)	82.65(18)
Rb(1)−N(3)	2.995(6)	N(1)−Rb(1)−N(2)#8	105.9(2)
		N(1)−Rb(1)−N(3)	95.55(17)
		N(1)−Rb(1)−N(3)#8	169.5(2)
		N(2)−Rb(1)−N(2)#8	167.7(3)
		N(2)−Rb(1)−N(3)	81.1(2)
		N(2)−Rb(1)−N(3)#8	89.28(18)
		N(3)−Rb(1)−N(3)#8	76.4(3)
Symmetry codes: #8 −x+1, y, −z+1/2.			

Table S2. Hydrogen bonds (Å, °) for **Na and Rb**.

	H···A	D···A	D−H···A
D−H···A			
Na (293 K)			
N7−H7A···N3#3	2.18	2.955(2)	149.0
N8−H8A···O1#4	2.08	2.872(2)	149.9
O1−H1WA···N6#6	1.91(2)	2.765(3)	170(2)
Symmetry codes: #3 −x+1/2, −y, z+1/2; #4 −x+1/2, −y, z−1/2; #6 −x, −y, −z+1.			
Rb (93 K)			
N(4)−H(4B)···N(1)#4	2.19	3.015(10)	161
N(5)−H(5B)···N(3)#9	2.60	3.248(11)	133
Symmetry codes: #4 −x+1/2, −y+1/2, −z; #9 −x+1/2, y−1/2, −z+1/2.			