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Electronic Supplementary Information

Coordination Polymers of Alkali Metal Trithiocyanurates: Structure Determinations and Ionic Conductivity Measurements Using Single Crystals

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Contents

S1. Synthesis

Sodium trithiocyanurate trihydrate (Na-TTC).

1.0 mmol of sodium acetate anhydrous ($NaOOCH_3$, Fisher) and 0.33 mmol of trithiocyanurate (Sigma-Aldrich) were dissolved in 1.0 mL of distilled water (Fisher) at 90°C, and then 0.33 mmol of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Fisher) was added. The solution was kept at 90°C, and then placed at room temperature.

Potassium trithiocyanurate monohydrate (K-TTC)

1.0 mmol of potassium carbonate anhydrous (K_2CO_3, Fisher) and 0.67 mmol of trithiocyanurate (Sigma-Aldrich) were dissolved in 2.0 mL of distilled water (Fisher) at 90°C for 2 h, and then placed at room temperature.

Rubidium trithiocyanurate monohydrate (Rb-TTC-1)

2.0 mmol of rubidium nitrate ($RbNO_3$, Alfa Aesar) and 0.33 mmol of trithiocyanurate (Sigma-Aldrich) were dissolved in 4.0 mL of distilled water (Fisher) at 90°C, and then 0.5 mmol of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Fisher) was added. The solution was kept at 90°C for 2 h, and then placed at room temperature.

Rubidium trithiocyanurate dehydrate (Rb-TTC-2)

1.0 mmol of rubidium nitrate ($RbNO_3$, Alfa Aesar), 1.0 mmol of trithiocyanurate (Sigma-Aldrich) and 1.0 mmol of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Fisher) were dissolved in 4.0 mL of distilled water (Fisher) at 90°C for 2 h, and then placed at room temperature.

Caesium trithiocyanurate (Cs-TTC-1)

1.0 mmol of caesium nitrate ($CsNO_3$, Alfa Aesar) and 0.33 mmol of trithiocyanurate (Sigma-Aldrich) were dissolved in 4.0 mL of distilled water (Fisher) at 90°C, and then 0.5 mmol of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Fisher) was added. The solution was kept at 90°C for 2 h, and then placed at room temperature.

Caesium trithiocyanurate (Cs-TTC-2)

2.0 mmol of caesium nitrate ($CsNO_3$, Alfa Aesar) and 0.33 mmol of trithiocyanurate (Sigma-Aldrich) were dissolved in 5.0 mL of distilled water (Fisher) at 90°C, and then 0.5 mmol of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Fisher) was added. The solution was kept at 90°C for 2 h, and then placed at room temperature.

S2. Thermogravimetric analyses

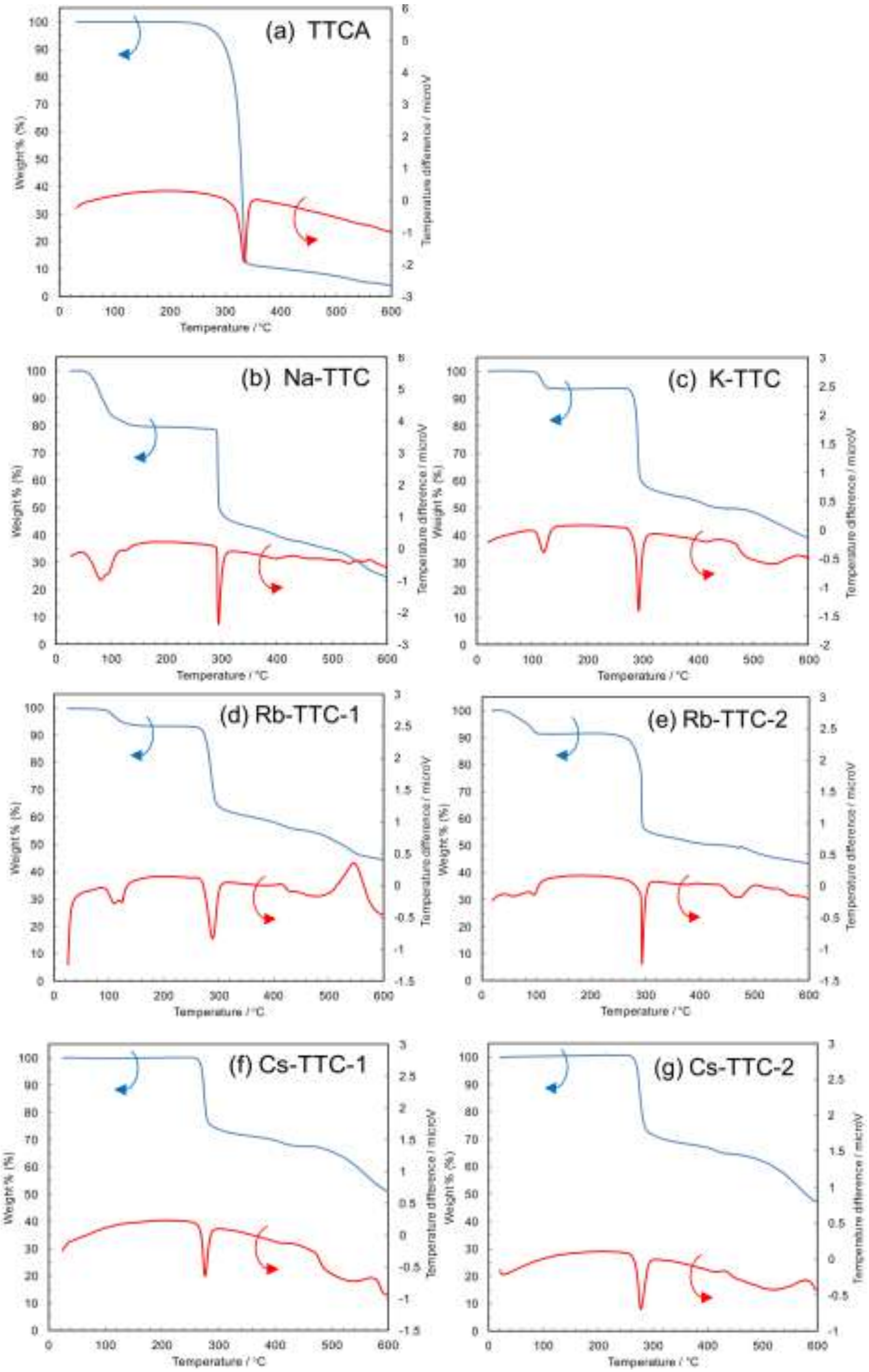

Fig. S1 Simultaneous differential scanning calorimetry (DSC)-thermogravimetric analysis (TGA) of trithiocyanuric acid (a) and alkali metal trithiocyanurates: (b) Na-TTC, (c) K-TTC, (d) Rb-TTC-1, (e) Rb-TTC-2, (f) Cs-TTC-1 and (g) Cs-TTC-2. N_2 flow: 100 mL min^{-1}. Scan rate: 5 °C min^{-1}.

S3. Powder X-ray diffraction patterns

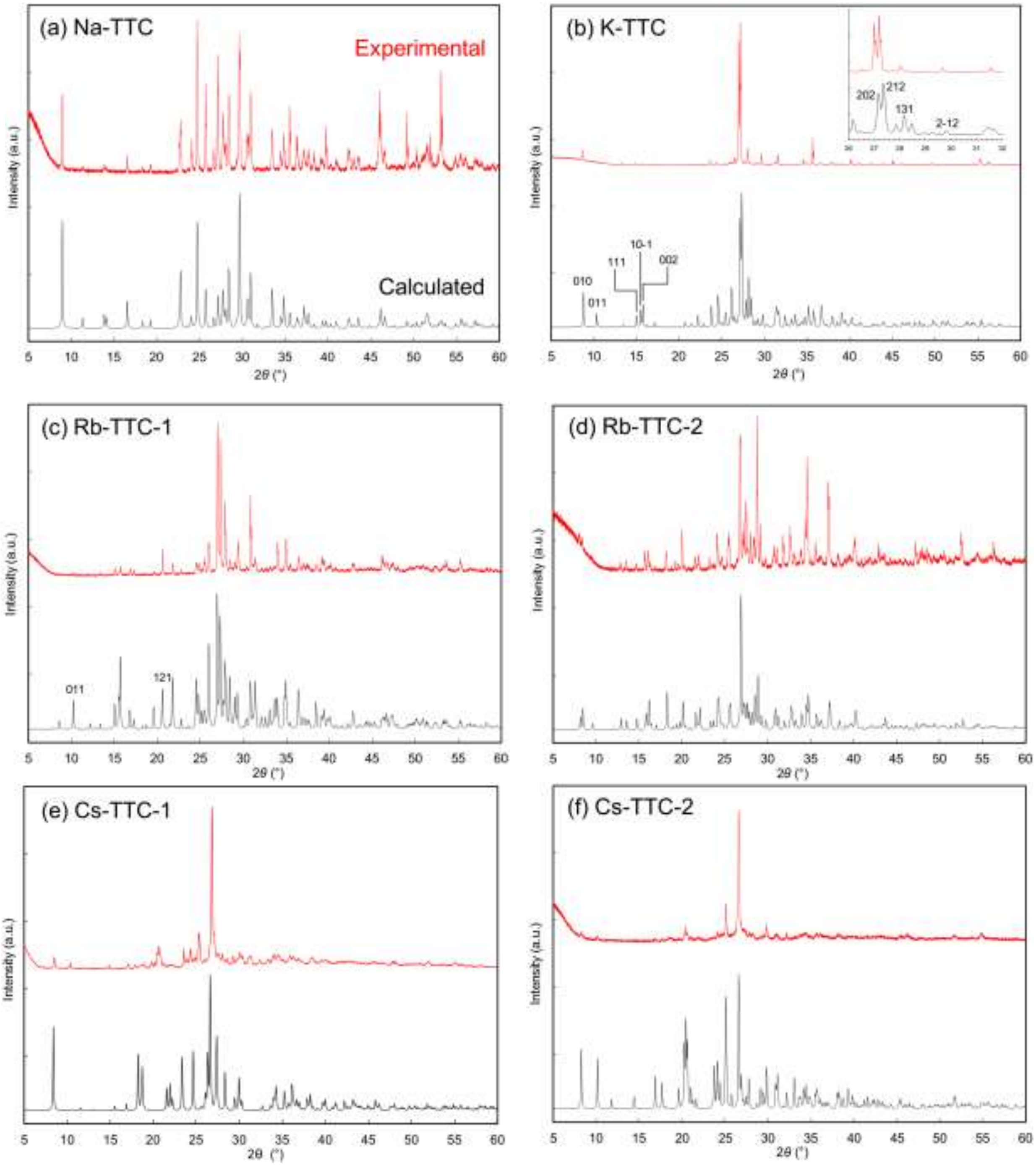

Fig. S2 Powder X-ray patterns of alkali metal trithiocyanurates measured at room temperature: (a) Na-TTC, (b) K-TTC, (c) Rb-TTC-1, (d) Rb-TTC-2, (e) Cs-TTC-1, and (f) Cs-TTC-2. The powder pattern of Cs-TTC-1 suggest that the bulk phase is composed of both polymorphs; Cs-TTC-1 and Cs-TTC-2.

S4. FTIR spectra

The FTIR spectrum of pure trithiocyanuric acid has major bands observed at 1524, 1115, and 737 cm^{-1}, which are assignable to non-aromatic, trithioketone form of triazine ring [Chem. Sci., 2011, 2, 1826-1830]. The 1115 cm^{-1} band is assignable to C=S stretching vibration. The peaks located at 2900, 3040, 3080 and 3130 cm^{-1} are attributed to N-H stretching vibration.

This 1115 cm^{-1} peak was shifted to a large wavenumber when alkali metal trithiocyanurates formed: 1150 cm^{-1} (Na-TTC), 1142 cm^{-1} (K-TTC), 1130 cm^{-1} and 1157 cm^{-1} (Rb-TTC-1), 1130 cm^{-1} (Rb-TTC-2), 1146 cm^{-1} (Cs-TTC-1), 1142 cm^{-1} (Cs-TTC-2). As the increase of coordinating water molecules, intensity of O-H stretching vibration observed in the range of 3200–3650 cm^{-1} increased. The O-H bands of K-TTC and Rb-TTC-1 are identical. These two structures contain M-O-M bridging oxygen atoms. The O-H bands of Rb-TTC-2, whose H_2O molecules are M-O-M bridging oxygen atoms, are similar to those of Rb-TTC-1, except for a peak located at 3370 cm^{-1}. Probably, this is attributable to the unique proton shared by two H_2O molecules (H3 in Fig. 2c). The O-H bands of Na-TTC are different from these, because of the presence of non-bridging H_2O molecules.

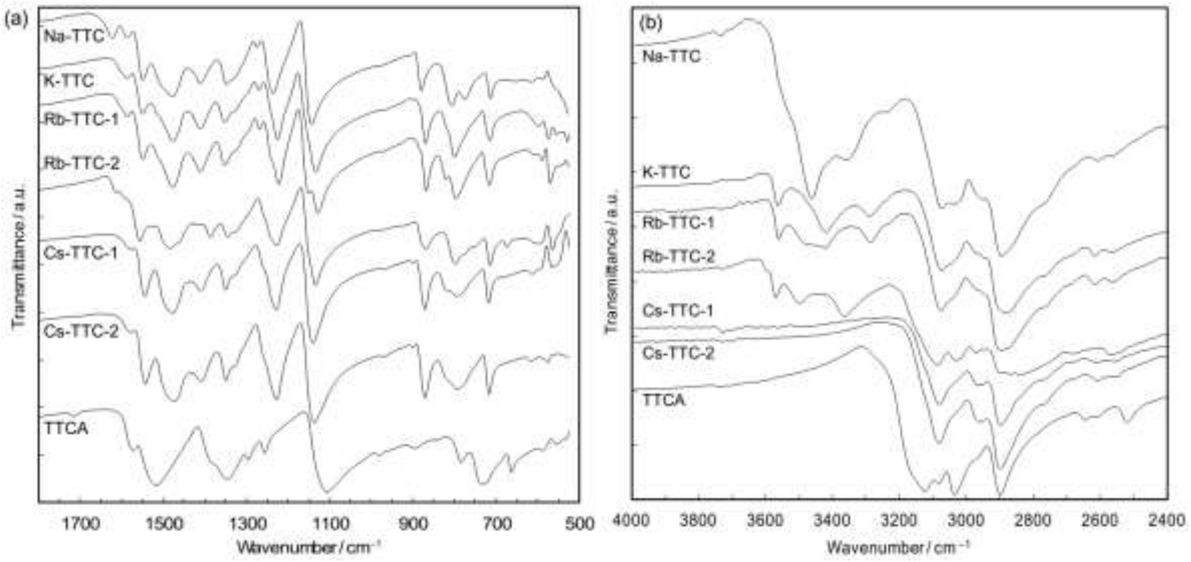

Fig. S3 FTIR spectra of alkali metal trithiocyanurates: sodium trithiocyanurate of Na-TTC, K-TTC, Rb-TTC-1, Rb-TTC-2, Cs-TTC-1 and Cs-TTC-2. in comparison to the spectrum of pure trithiocyanuric acid. (a) 500–1800 cm^{-1}. (b) 2400–4000 cm^{-1}. The transmittance was normalized relative to the peaks assignable to C=S stretching vibration (1100 to 1160 cm^{-1}) and plotted with shifts.

S5. Asymmetric units

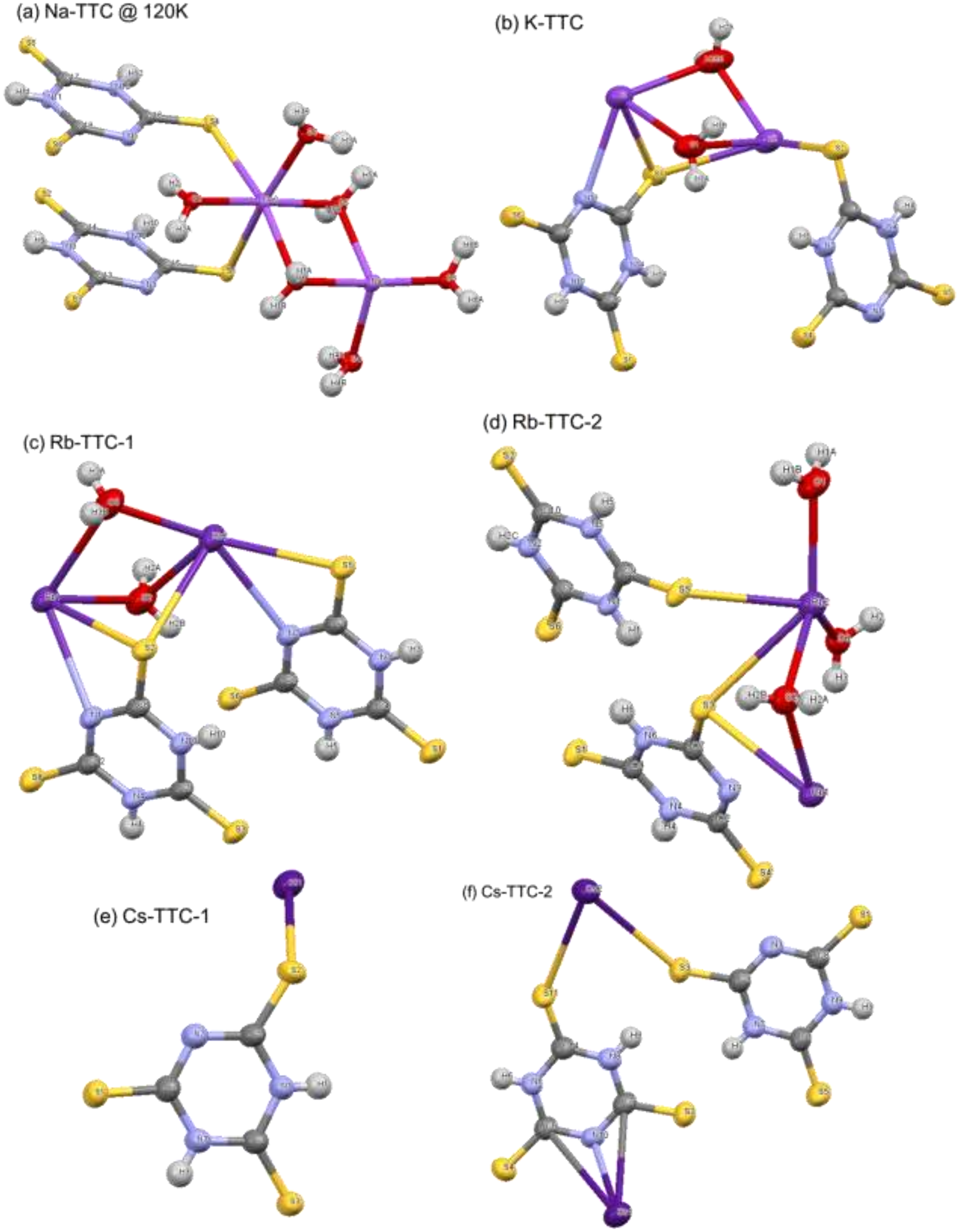

Fig. S4 Asymmetric units of (a) Na-TTC (120 K), (b) K-TTC, (c) Rb-TTC-1, (d) Rb-TTC-2, (e) Cs-TTC-1 and (f) Cs-TTC-2. These were visualized using Mercury from Cambridge Structural Database System (CSDS).

S6. Structure determination of sodium trithiocyanurate, Na-TTC

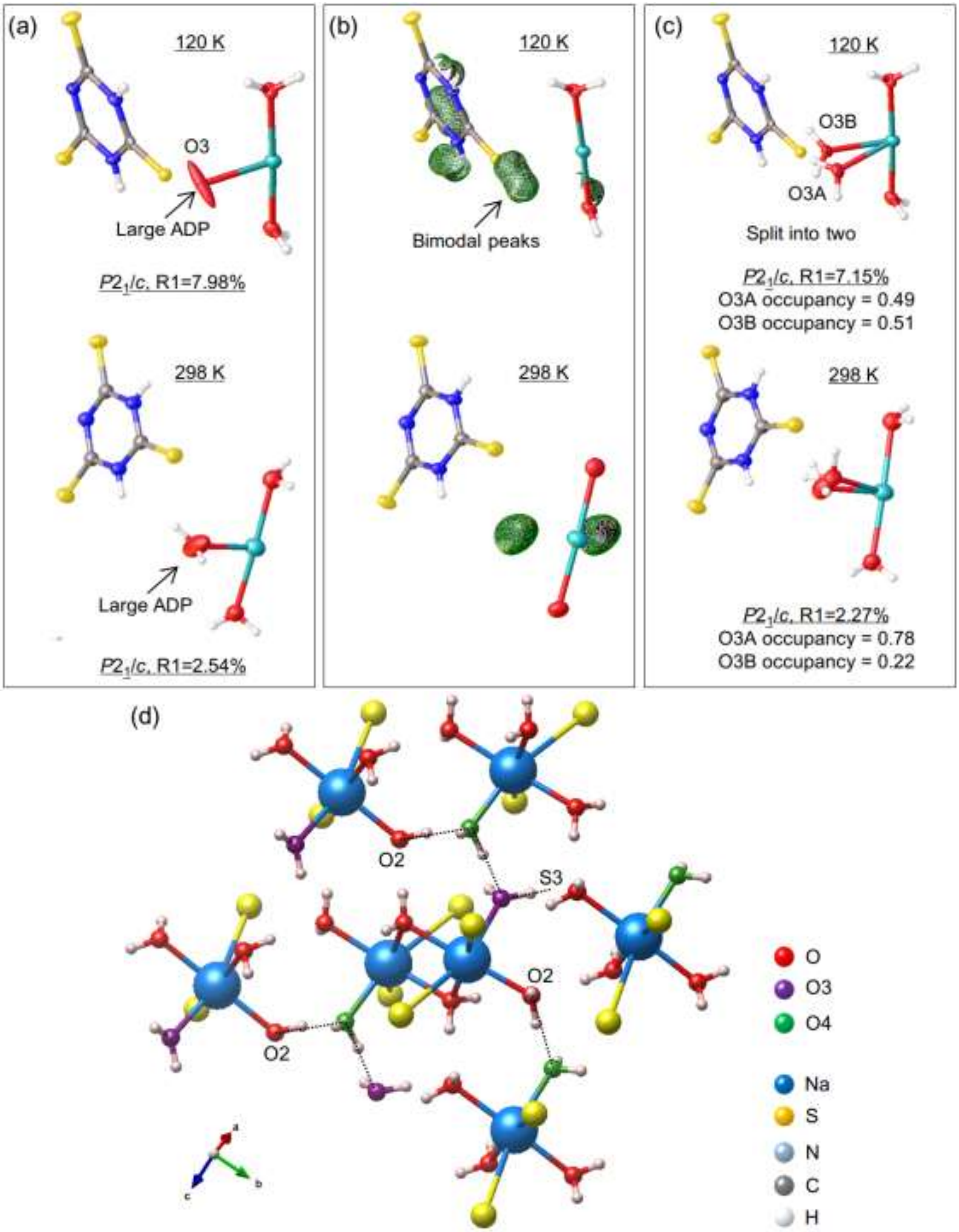

Fig. S5 Structure determination of Na-TTC. Data were measured at both 120 K and 298 K. (a) The asymmetric unit in $P2_1/c$, $NaC_3H_8O_3N_3S_3$, has an oxygen atom (O3) with a large atomic displacement parameter. (b-c) The electron density map shows that O3 has a bimodal peak at 120 K and a distorted ellipse at 298 K, which can be refined by two oxygen atoms of 50% occupancies for the former, and 80% & 20% for the latter. (d) The two oxygen positions at 120 K are refined as independent positions (O3 and O4) in $P2_1$. In terms of hydrogen bonding, these positions are clearly different.

Table S1 Summary of crystal data for sodium trithiocyanurate measured at 298 K and 120 K.

Abbreviated formula [a]	Na(ttcH_2)(H_2O)$_3$	Na(ttcH_2)(H_2O)$_3$
Empirical formula of asymmetric unit	$NaC_3H_8O_3N_3S_3$	$Na_2C_6H_{16}O_6N_6S_6$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
Formula weight of asymmetric unit	253.29	506.59
a / Å	10.45030(2)	10.3697(4)
b / Å	12.7369(2)	12.6801(3)
c / Å	7.86207(17)	7.7756(2)
α (°)	90	90
β (°)	109.644(2)	109.059(4)
γ (°)	90	90
V / Å^3	985.83(3)	966.37(5)
Z	4	2
R_1,wR_2	2.54%, 7.08%	2.90%, 7.97%
GOF	1.077	1.160
Temperature / K	298	120
Coordination number	6	Na1: 6 Na2: 6
Coordination environment of alkali metals [b]	2S + 4O	1: 2S + 4O 2: 2S + 4O

[a] ttc is trithiocyanurate anion ($C_3N_3S_3^{3-}$). [b] Coordination bond lengths are defined as ≤3.3 Å for Na-S and ≤2.5 Å for Na-N and Na-O.

S7. Conductivity measurement of Rb-TTC-2

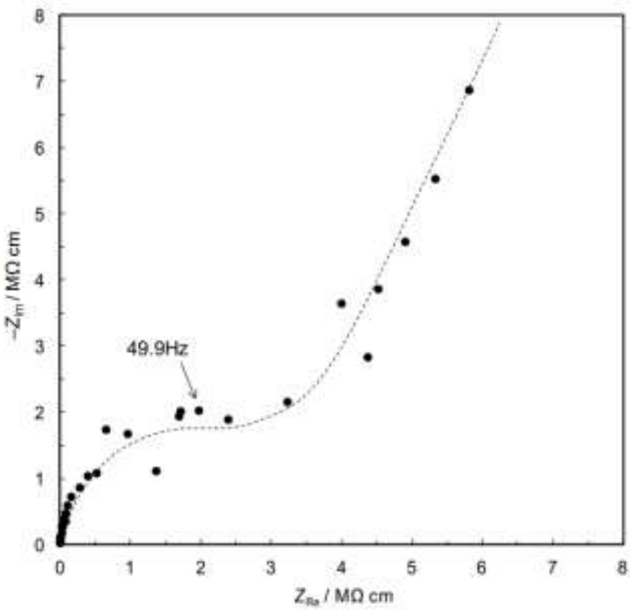

Fig. S6 Complex-plane impedance plots of single crystal Rb-TTC-2 along the [3 -1 0] direction measured at 25°C in air. The *c* facet was placed in contact with microelectrodes patterned on a SiO_2 substrate. AC amplitude: 100 mV. Frequency range: 1 M Hz to 1 Hz. The dotted lines are for better visualization of the spectra.