Supporting Information

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Contents

Experimental

General. DSC was performed using a TA Instrument Q100 differential scanning calorimeter with sweep rates of 10–30 °C min^{-1} under a nitrogen atmosphere. TG analyses were performed at 10 °C min^{-1} under a nitrogen atmosphere using a Rigaku TG8120 analyzer. Infrared (IR) spectra were recorded via attenuated total reflectance (ATR diamond) using a Thermo Scientific Nicolet iS 5 FT-IR spectrometer. Raman spectra were measured using a Renishaw Ramascope System 1000 spectrometer (λ_{ex} = 780 nm). PXRD measurements were performed using Bruker APEX II Ultra and Rigaku Smartlab diffractometers. FSC measurements were conducted using a Mettler Toledo Flash DSC 1 instrument under a nitrogen atmosphere. A single crystal of **1** was heated to 250 °C at 100 °C min^{-1}, maintained at this temperature for 5 s, and then cooled to −80 °C at various cooling rates (20–500 °C s^{-1}). Subsequently, FSC traces were recorded upon heating the sample to 250 °C at 1000 °C s^{-1}. The measurements at various cooling rates were conducted using the same sample.

Synthesis of 1. The recrystallization of a mixture of [Emim][TCM][S1] (16.8 mg, 0.08 mmol) and K[TCM] (11 mg, 0.08 mmol) from Et_2O–EtOH yielded the desired complex as colorless needle crystals, which were collected by filtration and dried under vacuum (9.7 mg, 35%). Grinding equimolar amounts of [Emim][TCM] and K[TCM] using a mortar and pestle also produced **1** quantitatively. Anal. Calcd. for $C_{14}H_{11}N_8K$: C, 50.90; H, 3.36; N, 33.92. Found: C, 50.90; H, 2.99; N, 33.51. IR (cm^{-1}): 2160 (CN), 1572, 1236, 1167, 840, 746, 702, 621, 563, 526. The material was not hygroscopic and completely stable under atmospheric condition.

X-ray structure determination. The X-ray diffraction data were collected on a Bruker APEX II Ultra CCD diffractometer at −173 °C and 20 °C with MoKα radiation (λ = 0.71073 Å). All calculations were performed using SHELXTL.[S2] The crystallographic parameters are shown in **Table S1**. CSD number: CCDC 1869226 (data at −173 °C) and 2169840 (data at 20 °C).

References

[S1] Y. Yoshida, K. Muroi, A. Otsuka, G. Saito, M. Takahashi, T. Yoko, *Inorg. Chem.* 2004, **43**, 1458–1462.

[S2] G. M. Sheldrick, *Acta Crystallogr*. 2008, **C64**, 112–122.

[S3] J. R. Witt, D. Britton, *Acta Cryst.* 1971, **27**, 1835–1836.

Table S1. Crystallographic parameters of **1** at −173 and 20 °C

	−173 °C	20 °C
Empirical formula	$C_{14}H_{11}N_8K$	
Formula weight	330.41	
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	8.5703(8)	8.6092(12)
b (Å)	9.7142(10)	9.8641(14)
c (Å)	10.2374(10)	10.4829(15)
α (°)	83.6370(10)	83.222(2)
β (°)	83.0040(10)	82.672(2)
γ (°)	81.1040(10)	81.215(2)
V (Å^3)	832.09(14)	868.2(2)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.319	1.264
F (000)	340	340
Reflns collected	4019	4433
Independent reflns	2878	3222
Parameters	210	230
Temperature (K)	100	293
R_1[a], R_w[b] ($I > 2\sigma$)	0.0336, 0.0878	0.0481, 0.1287
R_1[a], R_w[b] (all data)	0.0342, 0.0883	0.0557, 0.1357
Goodness of fit	1.076	1.045
$\Delta\rho_{max,min}$ [e Å^{-3}]	0.376, –0.380	0.334, −0.22

[a]$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b]$R_w = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

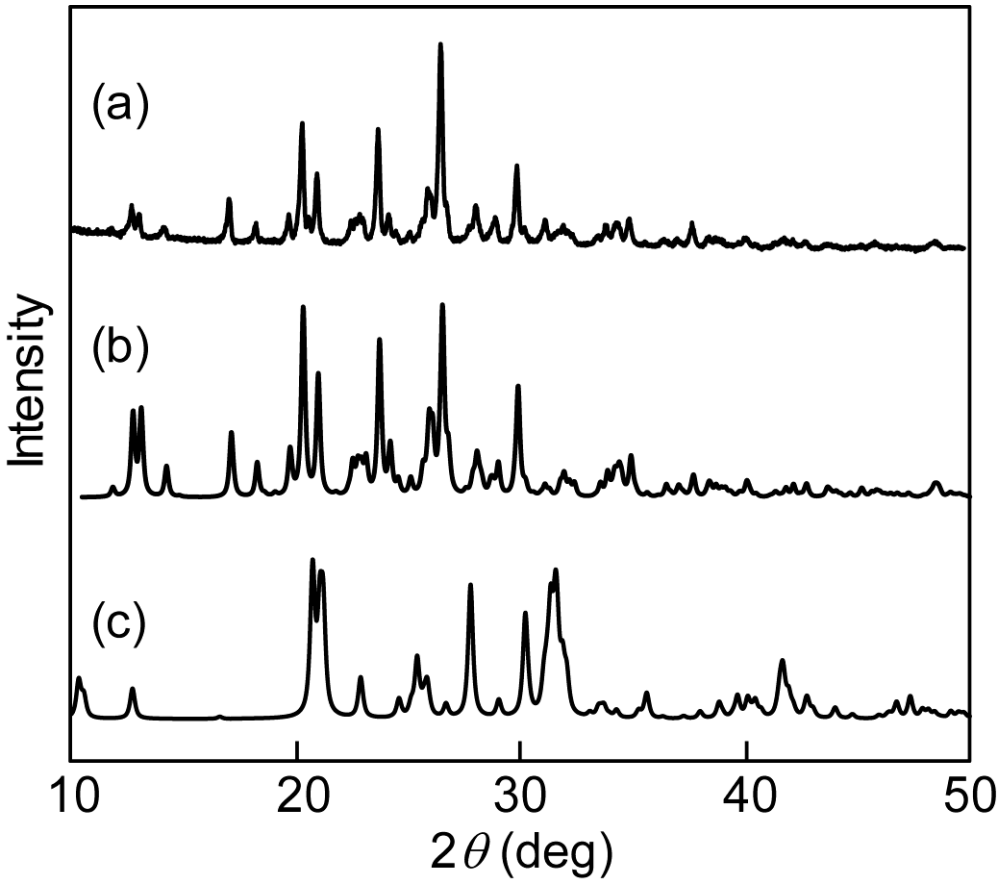

Fig. S1. PXRD patterns of (a) **1** formed by grinding [Emim][TCM] and K[TCM] for 1 h at 22 °C, (b) **1** simulated from the single crystal data at 20 °C, and (c) K[TCM] simulated from the single crystal data.[S3]

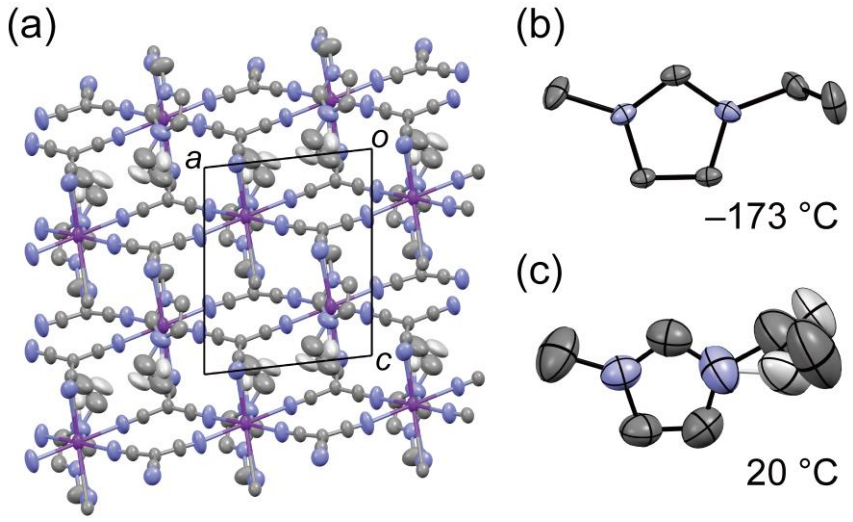

Fig. S2. (a) Packing diagram of **1** determined at 20 °C. (b) ORTEP drawings of the molecular structures of the cations determined at −173 °C (top) and 20 °C (bottom, occupancy ratio = 0.7:0.3).

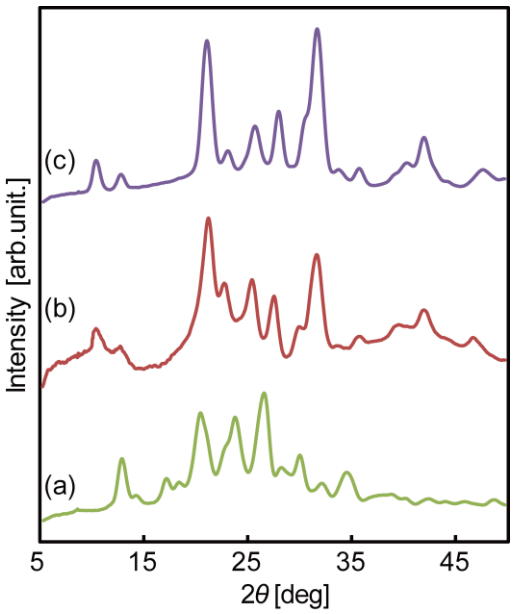

Fig. S3. PXRD patterns of (a) **1** at 22 °C, (b) **1** after incongruent melting at 150 °C, and (c) K[TCM] at 22 °C (Cu*K*α radiation).

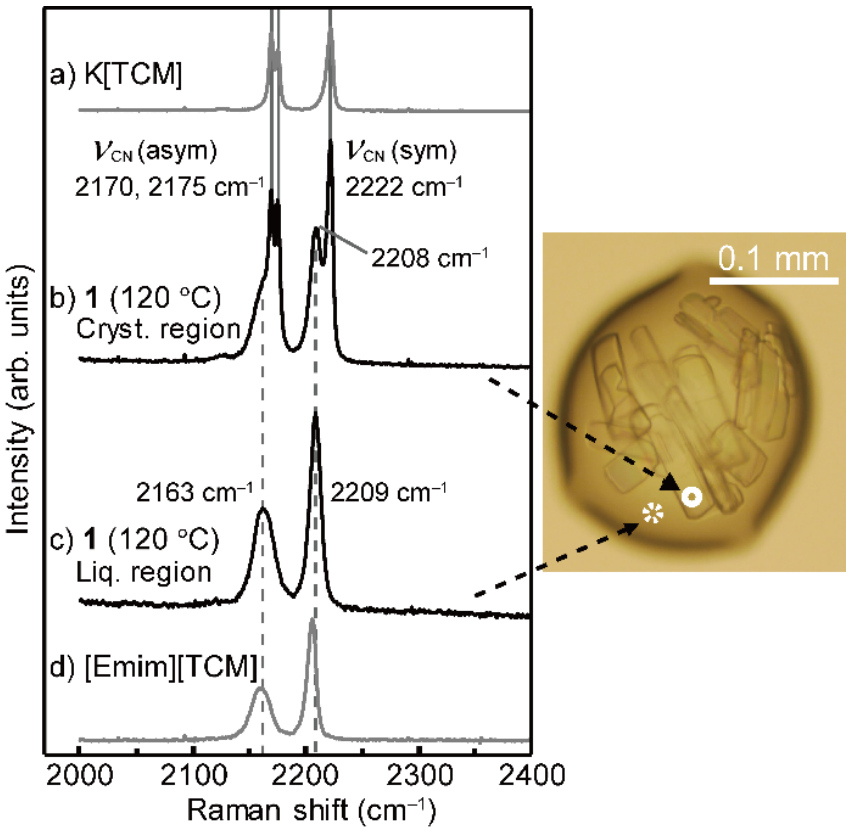

Fig. S4. Raman spectra of (a) K[TCM] (20 °C), (b) **1** after incongruent melting (120 °C, solid-rich region), (c) **1** after incongruent melting (120 °C, liquid region), and (d) [Emim][TCM] (20 °C). In the photograph of the sample at 120 °C shown on the right, the circles represent the regions for which the Raman spectra were recorded.

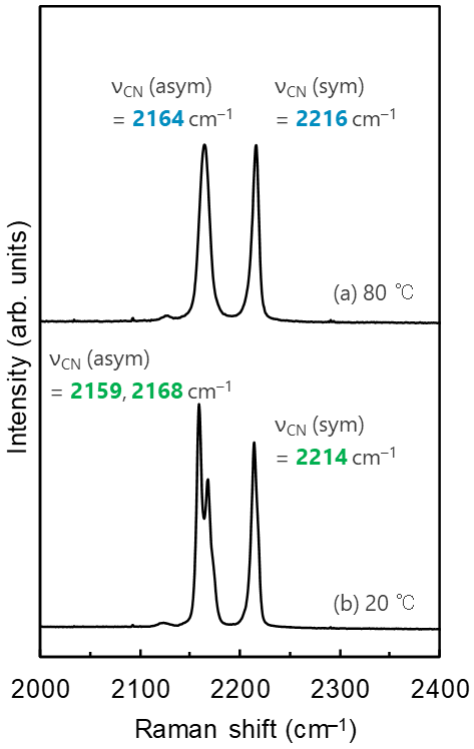

Fig. S5. Raman spectra of **1** measured at (a) 80 °C and (b) 20 °C.

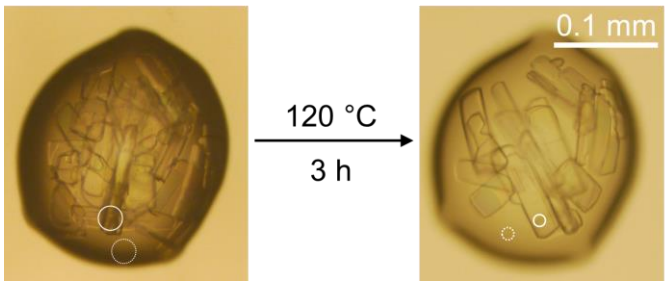

Fig. S6. Photographs of **1** taken at 120 °C after incongruent melting (left) and after standing at the same temperature for 3 h (right).