

Hydrogen bonding propagated phase separation in quasi-epitaxial single crystals: a Pd-Br molecular insulator

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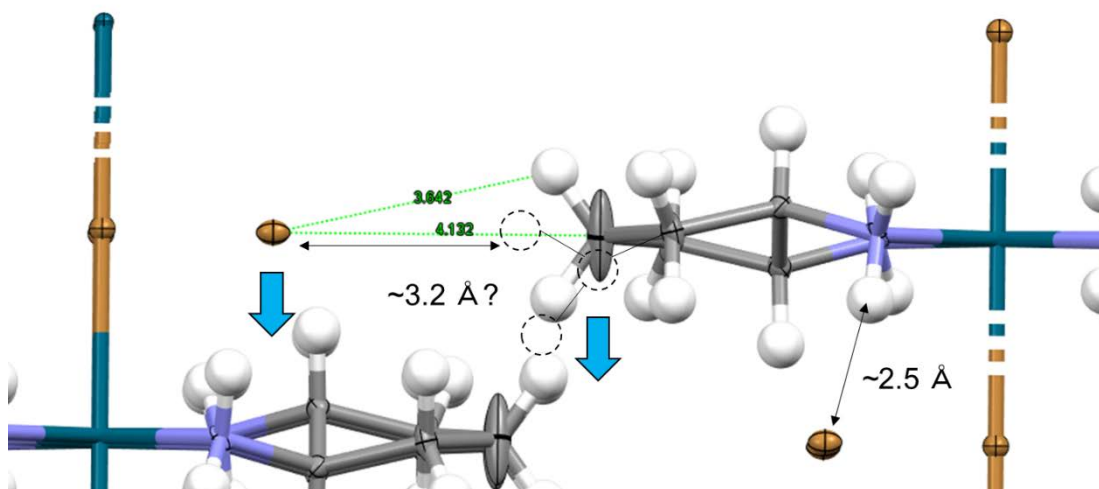
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Table S1. Crystal data of 1.

	1
Temperature / K	93
formula	C ₁₀ H ₂₄ Br ₃ N ₄ Pd
crystal system	Orthorhombic
space group	<i>I</i> 222
<i>a</i> / Å	5.2223(4)
<i>b</i> / Å	6.9660(5)
<i>c</i> / Å	22.6349(17)
<i>V</i> / Å ³	823.42(11)
<i>Z</i>	2
<i>R</i> ₁ (<i>I</i> > 2σ (<i>I</i>))	1.74%
<i>wR</i> ₂ (<i>I</i> > 2σ (<i>I</i>))	3.85%
<i>Flack parameter</i>	0.05 (3)

**Figure S1.** Crystal structure of **1** at 93 K. C–H···Br···H–C hydrogen bonding.

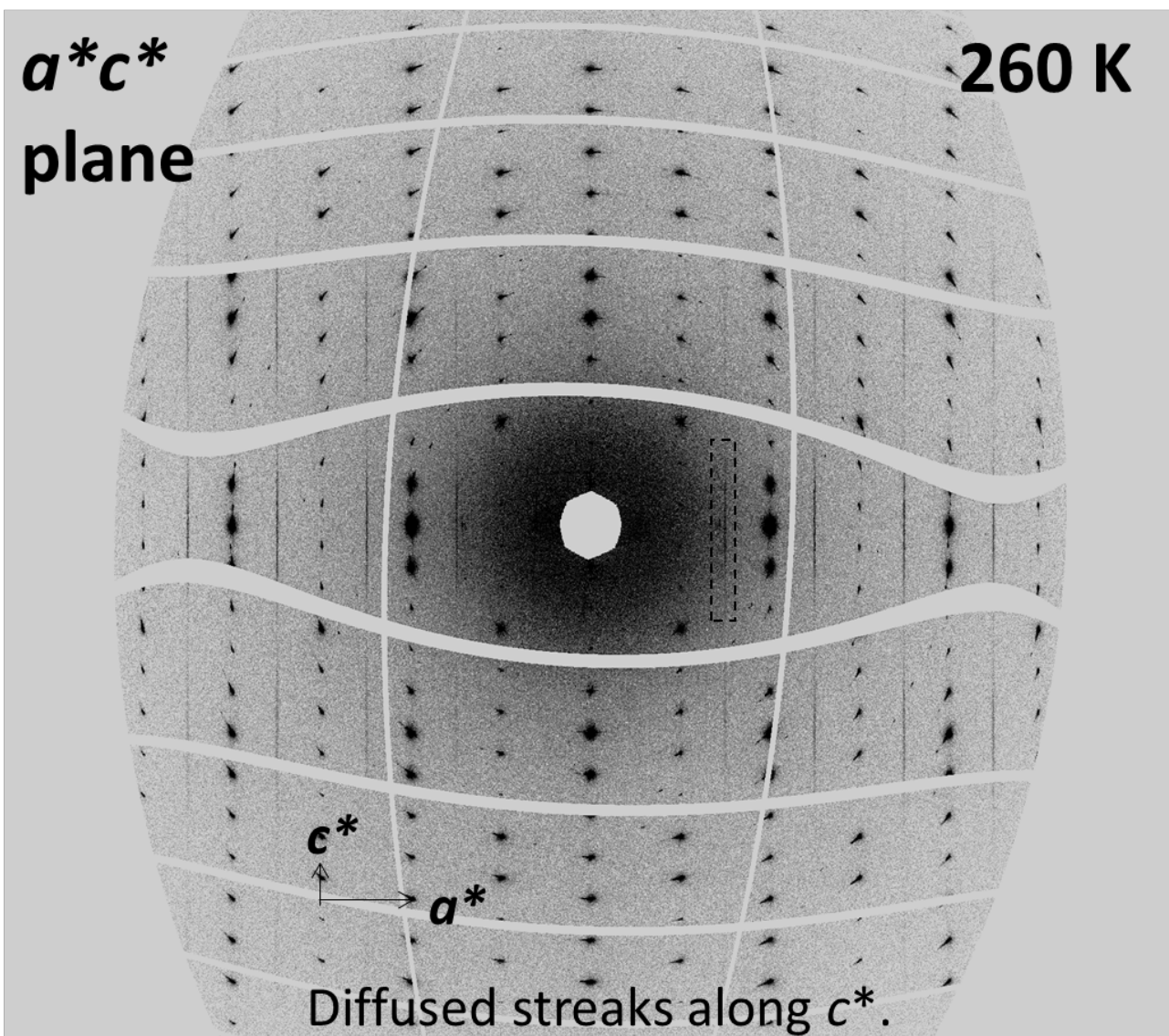


Figure S2. Reconstructed diffraction image and Diffused streaks of **1** along c^* at 260 K.

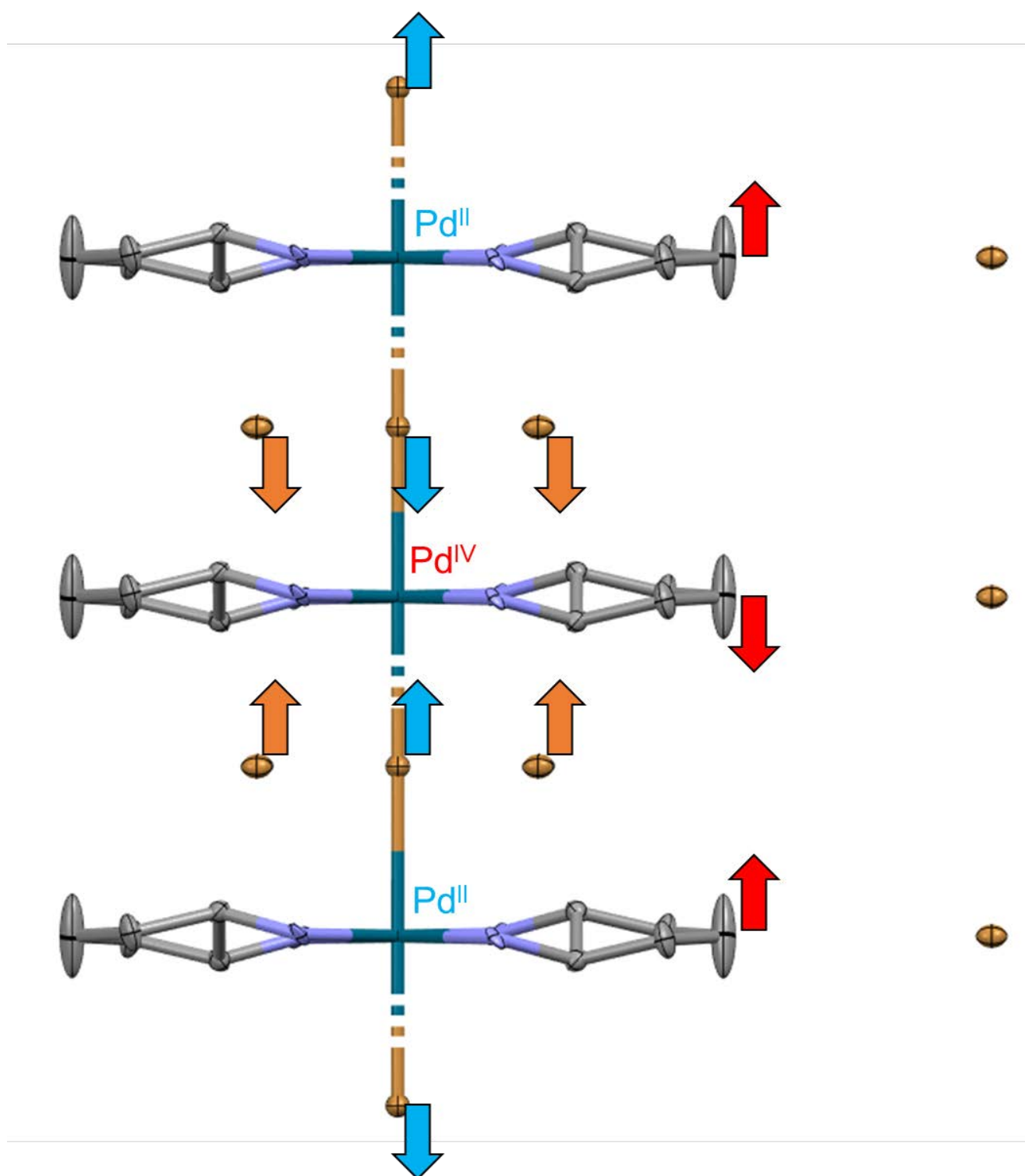


Figure S3. Crystal structure of **1** in the CDW state (RT).

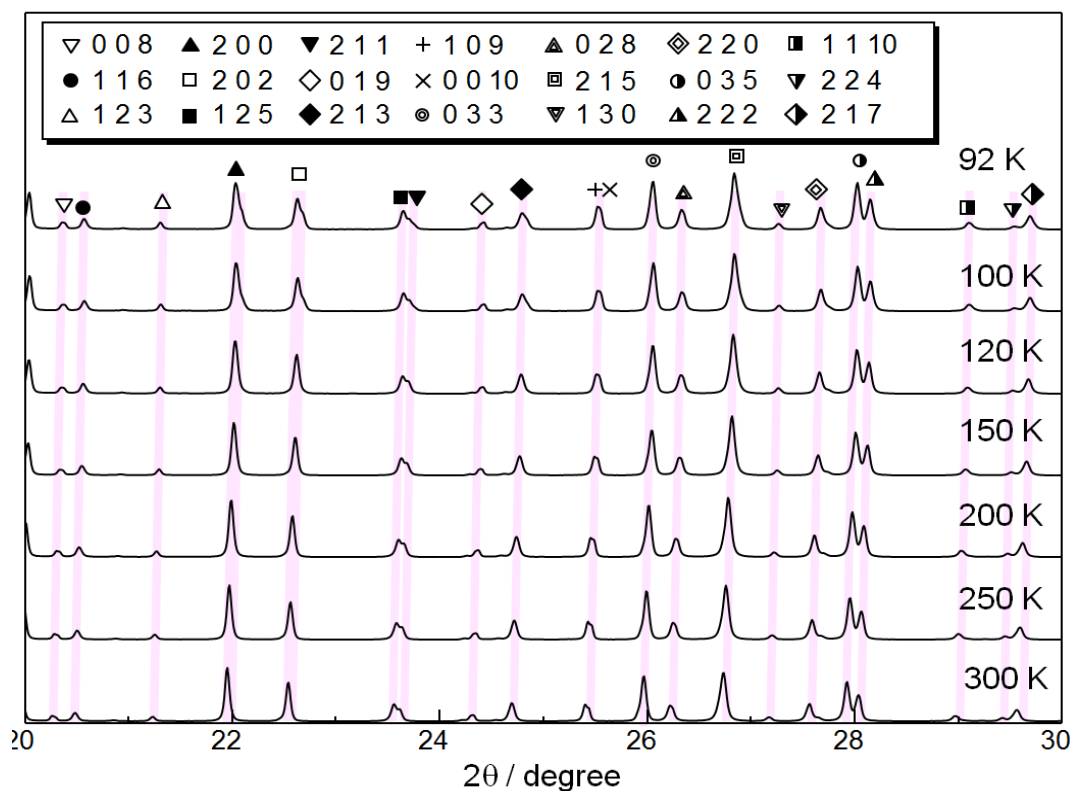


Figure S4. Synchrotron powder X-ray diffraction pattern (PXRD) of **1** at various temperatures.

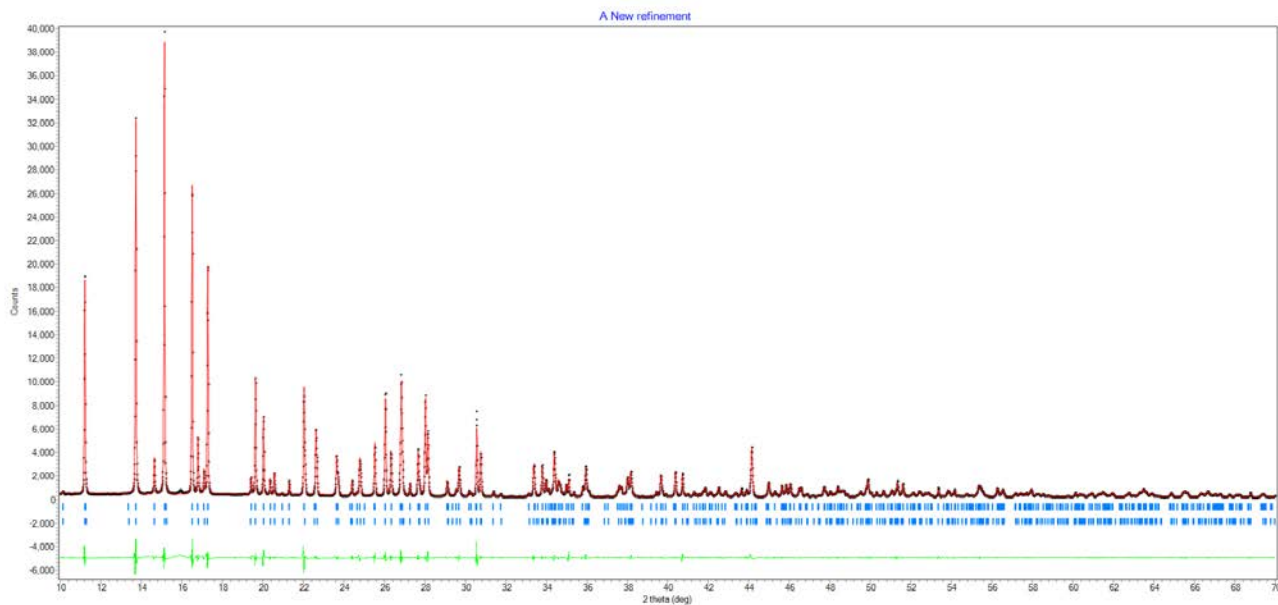


Figure S5. The results of two-phase Le Bail fitting for synchrotron powder X-ray diffraction pattern of **1** at 92 K.

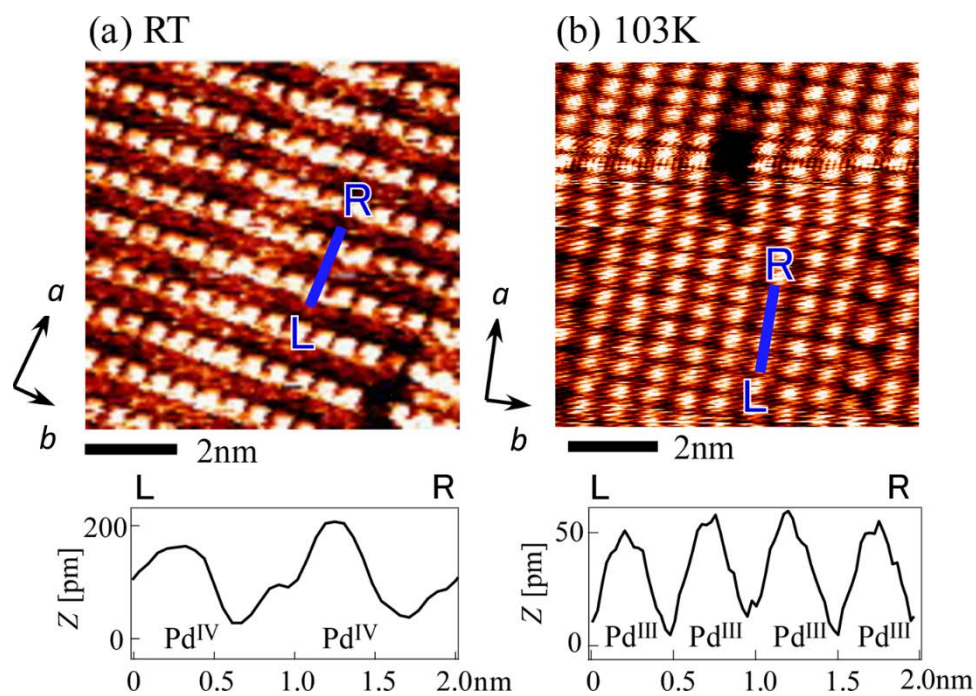
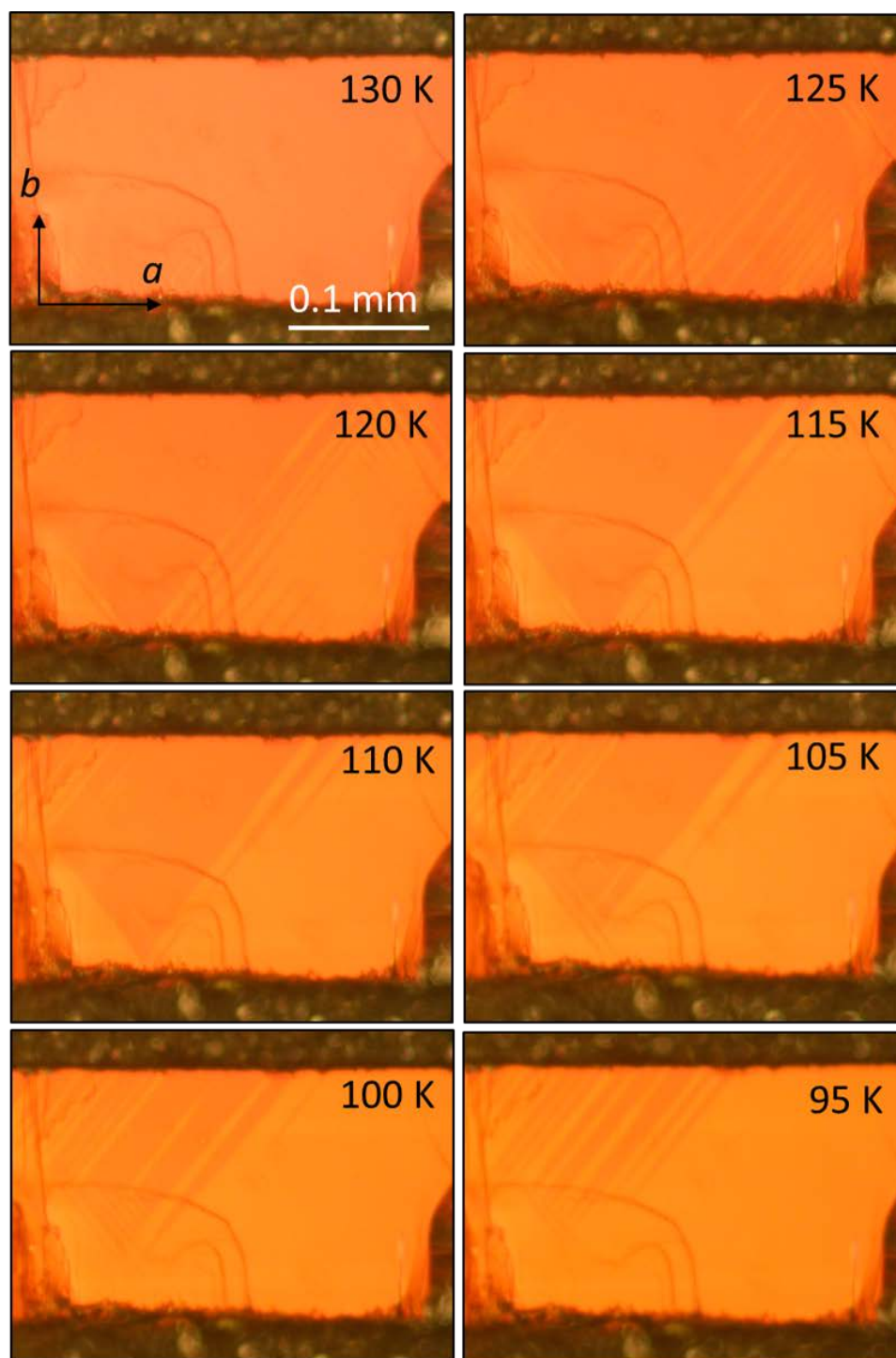


Figure S6. STM images of **1** at (a) RT (CDW) (b) 103 K (MH). Copyright (2016) The Japan Society of Applied Physics.



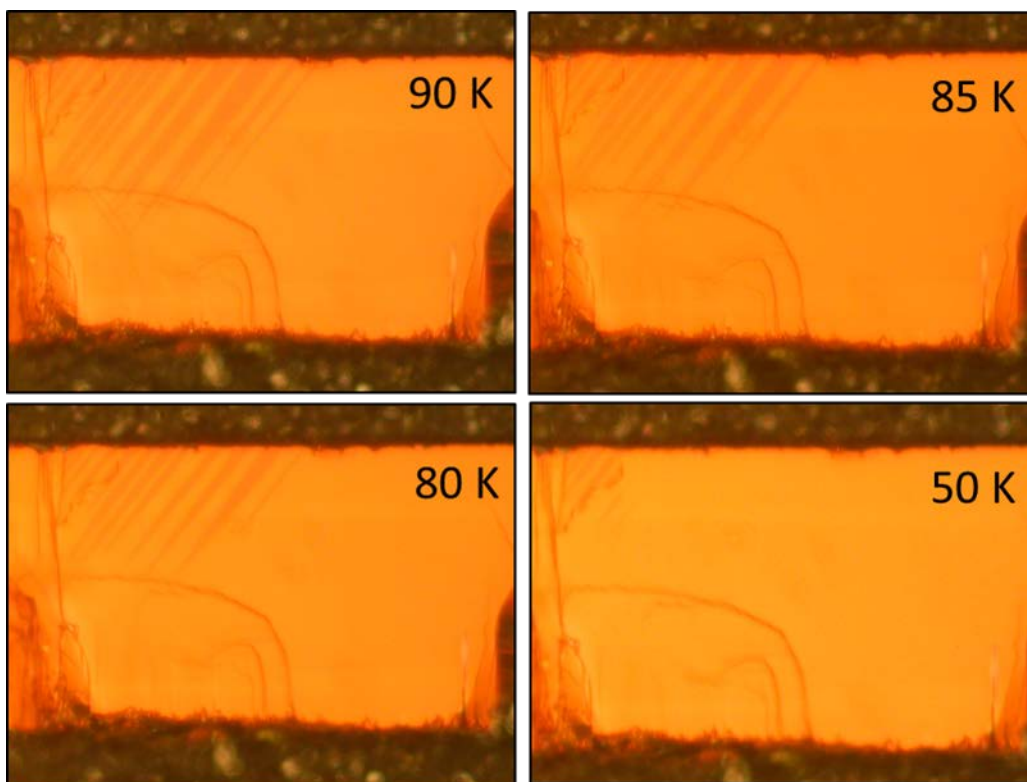


Figure S7. Images of a single crystal of **1** at various temperatures.

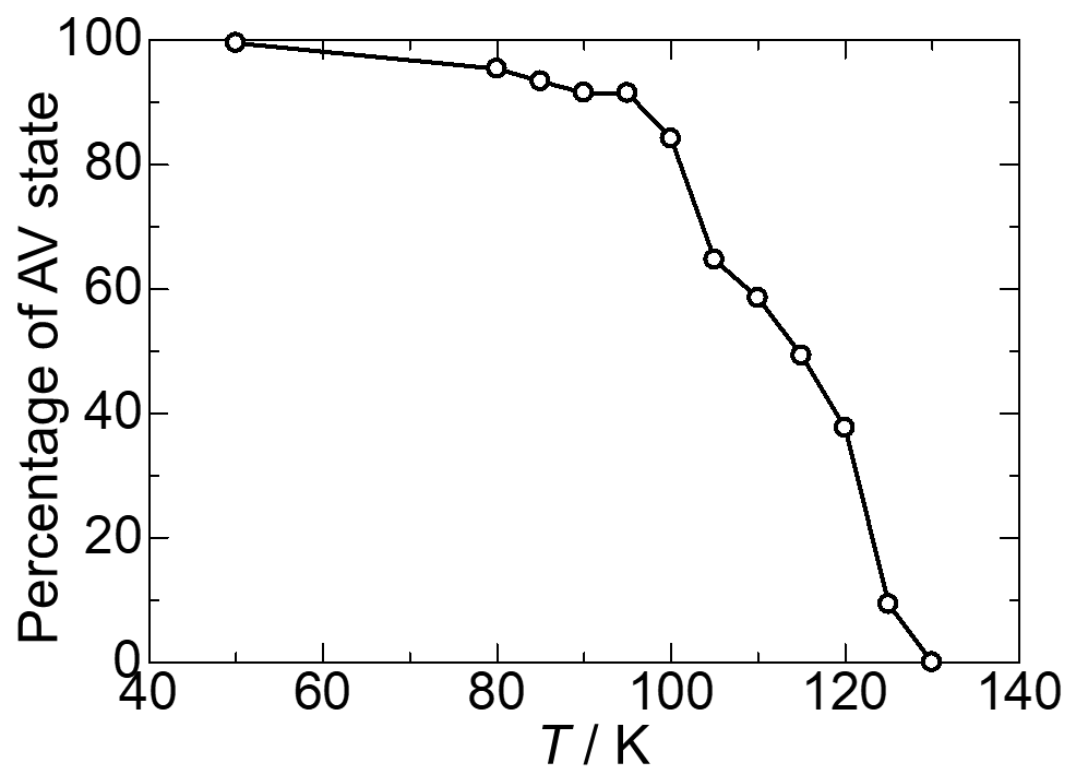


Figure S8. Ratio of the AV-MH state of **1** at various temperatures.

To check the population of the domain inside of crystal, we studied the diffraction patterns, including diffuse scattering of exactly same crystal of movie 2, 3 (135 K), integrated equivalence diffraction and diffuse scattering (integrate as spot), averaged intensity of Bragg diffraction (I_B), and diffuse scattering (I_D) and calculated I_D/I_B value to ignore scaling on each crystal position. (When we integrated by $(2a, b, c)$ unitcell (superlattice), $(h = \text{odd}, k, l)$ is correspond to Bragg spots (i_B), whereas $(h = \text{even}, k, l)$ is correspond to diffuse scattering (i_D). $I = (\sum i_n)/n$). As the results, top: ($I_D, I_B, I_D/I_B$) = (16.6, 9465, 0.18); bottom: ($I_D, I_B, I_D/I_B$) = (4.15, 3397, 0.12) at RT. However, top: ($I_D, I_B, I_D/I_B$) = (0.40, 5866, 0.007); bottom: ($I_D, I_B, I_D/I_B$) = (5.3, 5801, 0.09) at 100 K. At RT, I_D/I_B values were slimier to each position because the crystal only had a CDW domain. In contrast, at 100 K, decrease in the I_D/I_B value at the top (96% off) was much larger than that at the bottom (25% off). These results indicate that domain (not only surface but also the interior) at the top is mainly in an MH state, whereas the bottom is still in a CDW state. The result is consistent with the results of movie. Therefore, the possibility of phase separation along the c axis can be excluded.

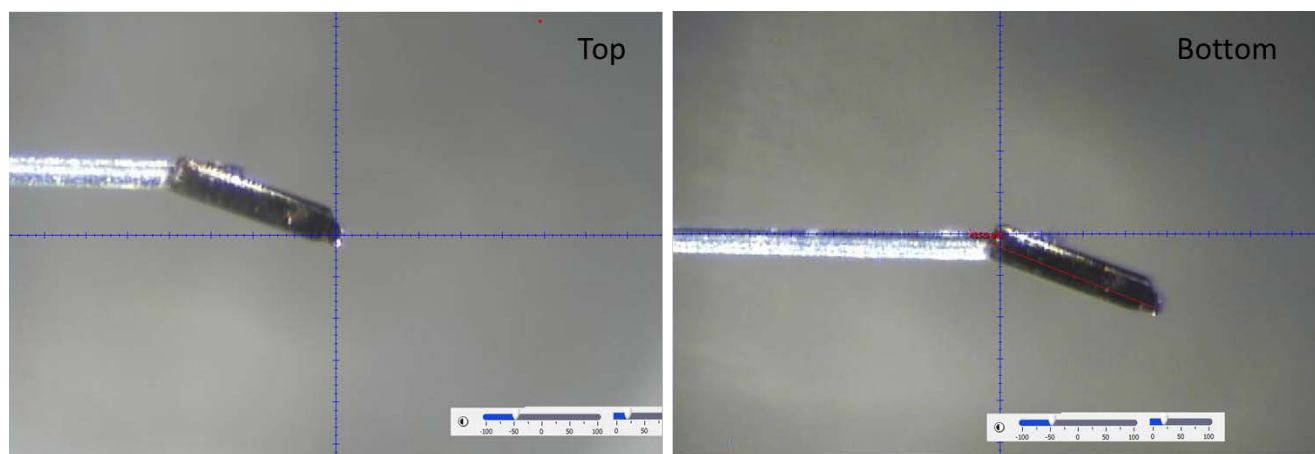
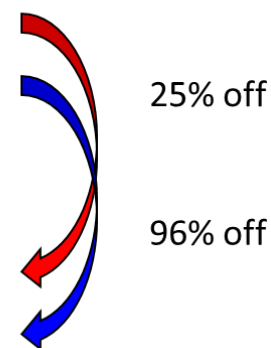


Figure S9. Images of single a crystal of **1**.

Table S2. Integrate equivalence diffraction and diffuse scattering.

RT	super AVER. (s)	Bragg AVER. (B)	s/B
bottom	4.159048	3397.075	0.12%
top	16.57745	9465.981	0.18%
100 K	super AVER. (s)	Bragg AVER. (B)	s/B
bottom	5.366667	5801.942	0.09%
top	0.400	5866.437	0.007%



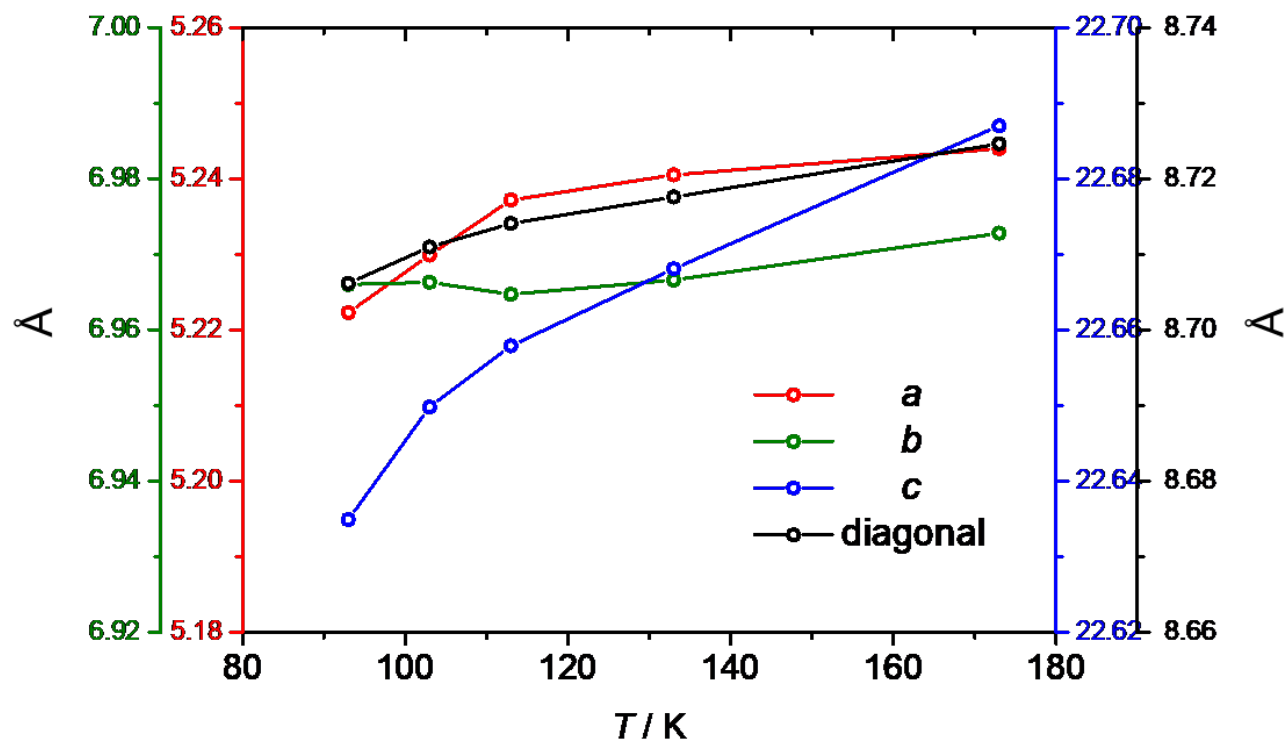


Figure S10. Unit cell parameters for **1** at various temperatures (diagonal = $(a^2 + b^2)^{1/2}$).

Equations S1

$$100 \text{ } \mu\text{m} / (a = \sim 5 \text{ } \text{\AA} \text{ or } b = \sim 7 \text{ } \text{\AA}) = 2.0 \times 10^4 \text{ units or } 2.0 \times 10^4 \text{ units.}$$

$$10 \text{ } \mu\text{m} / (c = \sim 22 \text{ } \text{\AA}) = 4.5 \times 10^3 \text{ units.}$$

$$|\Delta a| \times 2.0 \times 10^4 \text{ units} = 0.24 \text{ } \mu\text{m}, |\Delta b| \times 2.0 \times 10^4 \text{ units} = 0.14 \text{ } \mu\text{m}, |\Delta c| \times 4.5 \times 10^3 \text{ units} = 7.2 \text{ nm}$$

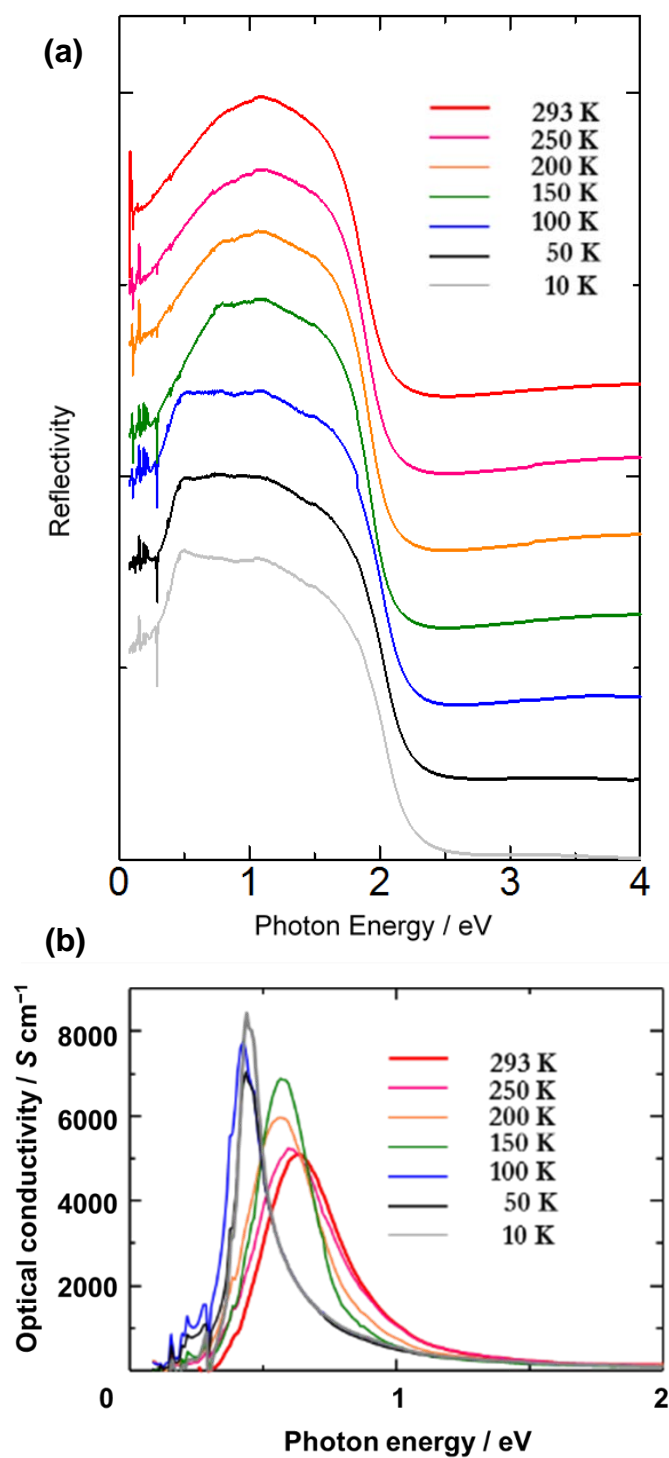


Figure S11. (a) Reflectivity spectra of **1** at various temperatures. (b) Optical conductivity which calculated by reflectivity spectra of **1** at various temperatures.

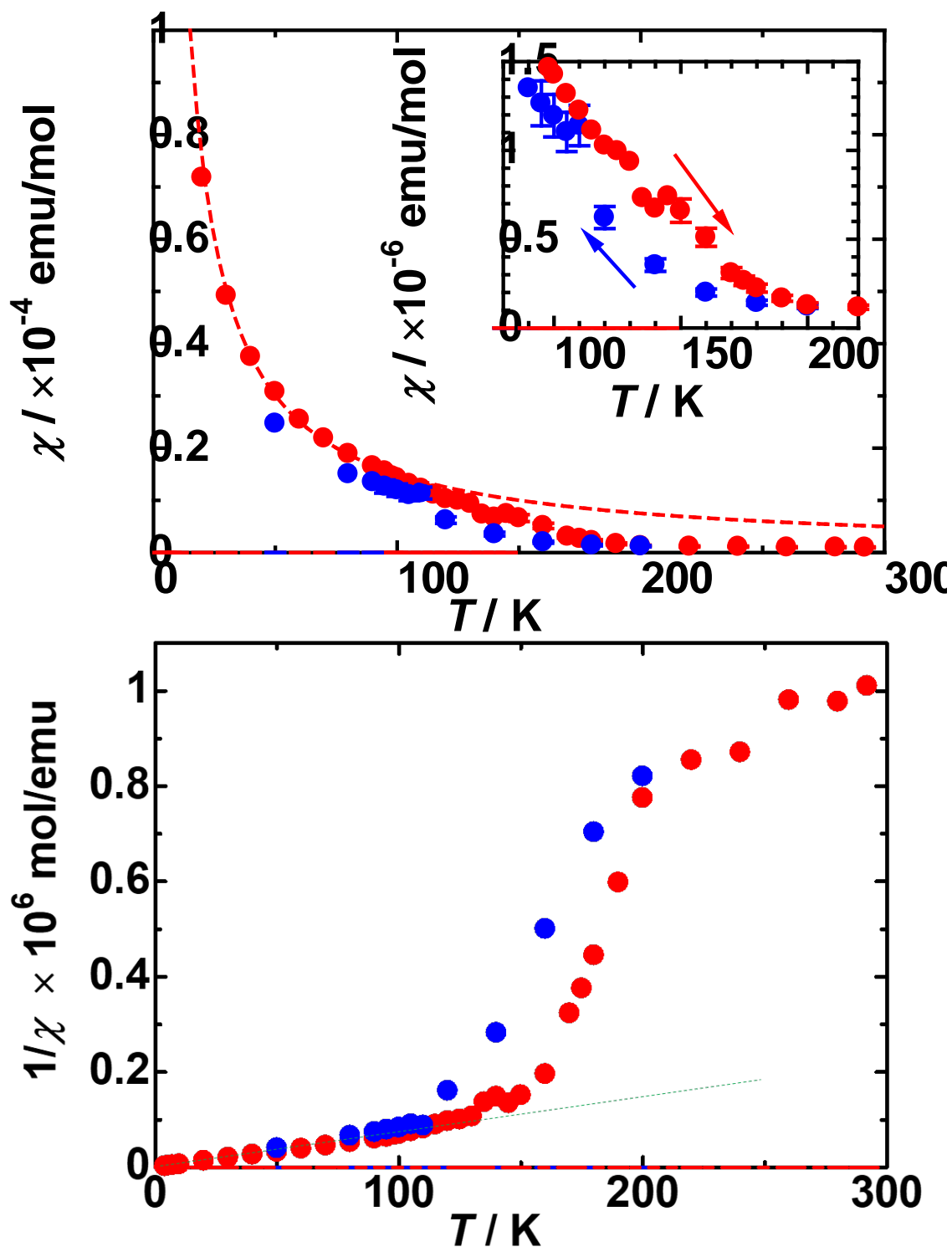


Figure S12. (a) χ vs. T plots for **1**. (b) $1/\chi$ vs. T plots for **1**. Green broken line are Curie curves with spin concentration of 0.36%. The electron spin resonance spectra were measured at X-band in the range of 2700–3800 G.