Supporting Information

Giant anisotropic thermal expansion of copper–cyanido flat layers with flexible copper nodes

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Experimental Section

Synthesis

This compound was synthesized as previously reported,[1] with several modifications. $Cu(NO_3)_2 \cdot 3H_2O$ (600 mg, 2.4 mmol) was dissolved in 10 mL H_2O. This solution was mixed with 15 mL of NH_3aq (28 %) and 5 mL of NaCN (200 mg, 5.0 mmol) solutions. After stirring until the solution became colorless, $Cu(NO_3)_2 \cdot 3H_2O$ (300 mg, 1.2 mmol) and NEt_4Cl (198.8 mg, 1.2 mmol) were added. After the reagents entirely dissolved, the solution was slowly evaporated, resulting colorless needle-like single crystals.

Physical measurement

The single-crystal X-ray data of **TEACu** were recorded on a Bruker D8 Venture diffractometer equipped with a PHOTON II detector with Mo Kα radiation (λ = 0.71073 Å). Data integration and reduction were performed with APEX4 Software. Structures were solved with Olex2 and the ShelXT structure solution program by using direct methods and refined with the ShelXL refinement package with least-squares minimization. The temperature was controlled by N2 gas flow with an Oxford Cryosystems 800 Series Cobra Controller. Variable-Temperature X-ray analysis of **TEACu** was conducted using the same single crystal sample at several temperatures. The measurements at respective temperature were performed 60 min after the temperature stabilized. Hydrogen atoms were included in idealized positions and refined by using a riding model. TGA was performed at 10 K min^{-1} by using Rigaku Instrument Thermo plus TG 8120 in a N_2 atmosphere. IR spectral measurement in air was performed on a PerkinElmer Spectrum Two FT-IR equipped with an ATR accessory. Variable-Temperature IR (VT-IR) was measured on FT/IR-4200 with infrared microscopy IRT-5000 under N_2 flow. Temperature control was carried with an LK-600 hot stage (Linkam). The microscopic Raman spectroscopy was carried out by LabRAM HR-800 spectrometer (HORIBA Jobin Yvon Ltd.) at temperatures in the range 100-400 K using an LK-600 hot stage (Linkam). A 785-nm semiconductor laser was used as the excitation source. Powder X-ray diffraction data were collected with Miniflex 600-C (Rigaku) with a D/teX Ultra II detector using CuK α radiation (λ = 1.54184 Å) and a reflection-free single-crystal Si sample holder in ambient air at room temperature.

Computation

Gaussian16[2] was used for optimizing the monomer geometry and for vibrational calculations with B3LYP as the functional and LANL2DZ as the basis set. To obtain the fragment molecular orbital interaction diagram and the Walsh diagram, an extended Hückel calculation

was performed based on the DFT-optimized structure. YAeHMOP[3,4] was used to obtain the former and QuantumATK[5] to obtain the latter. The detailed method for obtaining the Walsh diagram is described in the literature.[6]

Table S1 Crystal parameters of **TEACu** at 100-400 K.

Temp. (K)	100	150	200
CCDC number	2337198	2337199	2337202
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	Ibam	Ibam	Ibam
Formula	$Cu_2C_{11}N_4H_{20}$	$Cu_2C_{11}N_4H_{20}$	$Cu_2C_{11}N_4H_{20}$
a (Å)	14.9083(10)	14.8851(8)	14.8624(4)
b (Å)	8.1008(5)	8.1225(4)	8.1463(2)
c (Å)	12.1620(7)	12.2203(6)	12.2872(3)
V (Å³)	1468.79(22)	1477.49(18)	1487.66(9)
Z	4	4	4
R1	2.54	2.62	2.87
Rwp	6.76	7.17	8.37
G.O.F	1.128	1.092	1.065

Temp. (K)	250	300	350
CCDC number	2337204	2337201	2337200
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	Ibam	Ibam	Ibam
Formula	$Cu_2C_{11}N_4H_{20}$	$Cu_2C_{11}N_4H_{20}$	$Cu_2C_{11}N_4H_{20}$
a (Å)	14.8279(4)	14.8065(7)	14.7778(10)
b (Å)	8.1752(2)	8.2051(3)	8.2376(6)
c (Å)	12.3660(3)	12.4448(5)	12.5337(8)
V (Å³)	1499.02(9)	1511.9(15)	1525.77(24)
Z	4	4	4
R1	2.97	3.02	3.23
Rwp	8.19	8.83	9.30
G.O.F	1.097	1.065	1.049

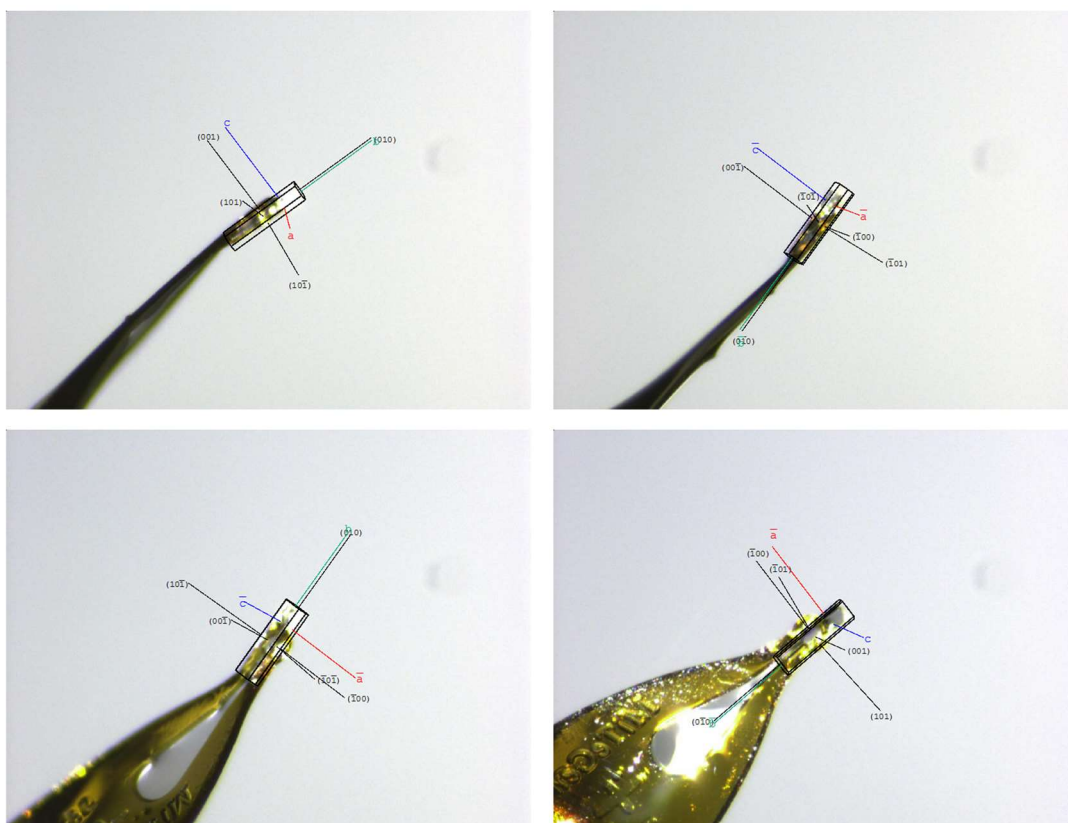| Temp. (K)	400
CCDC number	2337203
Crystal System	Orthorhombic
Space Group	Ibam
Formula	$Cu_2C_{11}N_4H_{20}$
a (Å)	14.7531(7)
b (Å)	8.2731(4)
c (Å)	12.6466(5)
V (Å³)	1543.57(16)
Z	4
R1	3.41
Rwp	9.97
G.O.F	1.063

Fig. S1 Crystal images with Miller index notations
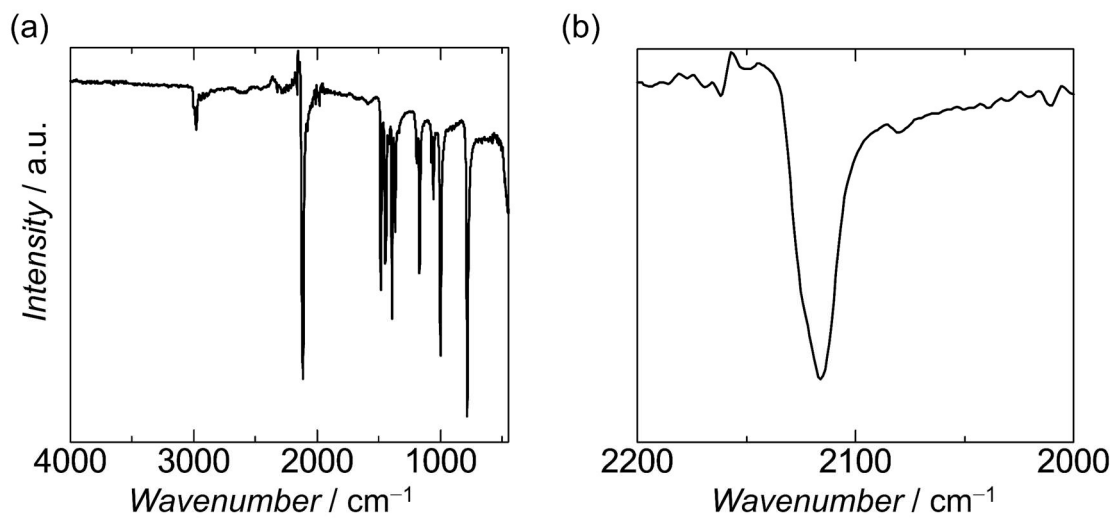
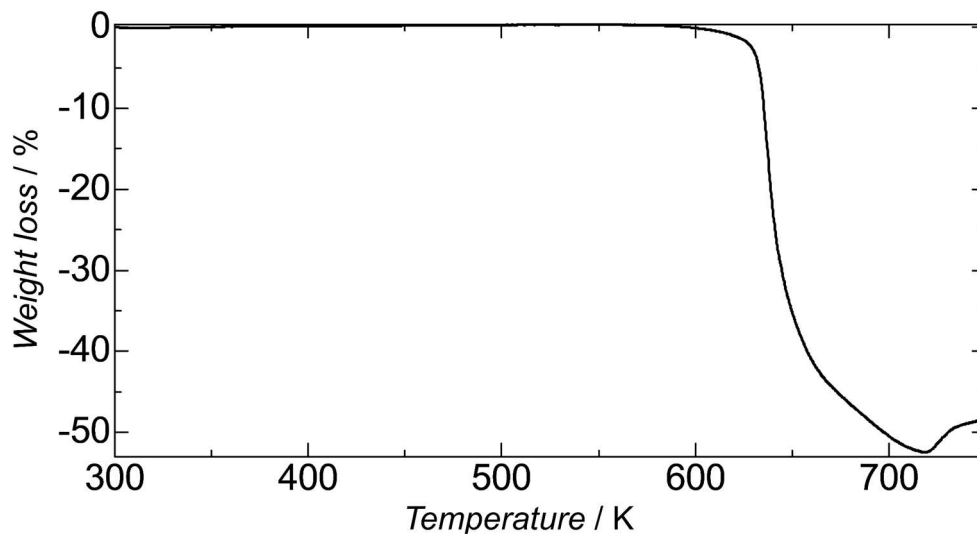Fig. S2 (a) The overall view and (b) the region of cyanido vibration of IR spectra at 300 K.
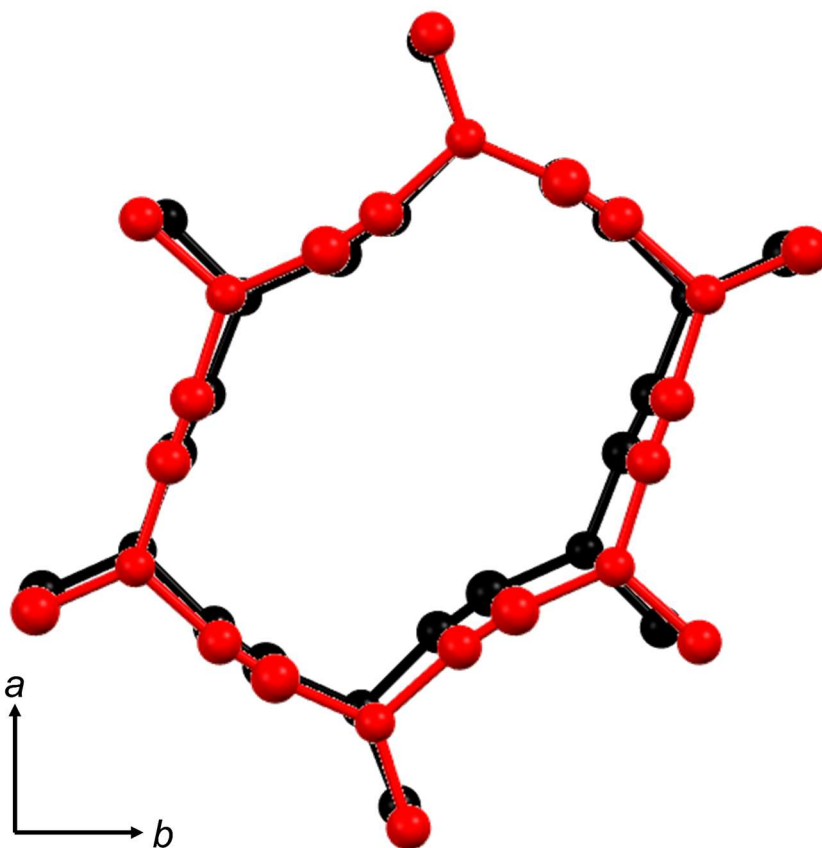

Fig. S3 TG curve of **TEACu**.

Fig. S4 The overlap view of hexagons in **TEACu**. Black and red structures represent that at 100 K and 400 K, respectively.
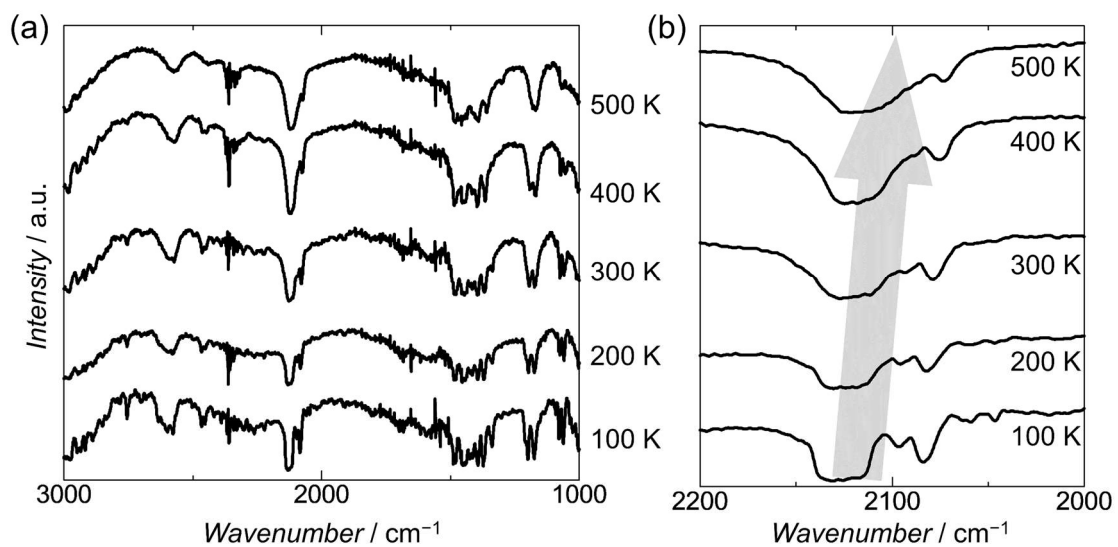
Fig. S5 (a) Overall view and (b) the region of cyanido vibration of variable temperature FT-IR spectra for **TEACu** at 100–500 K.
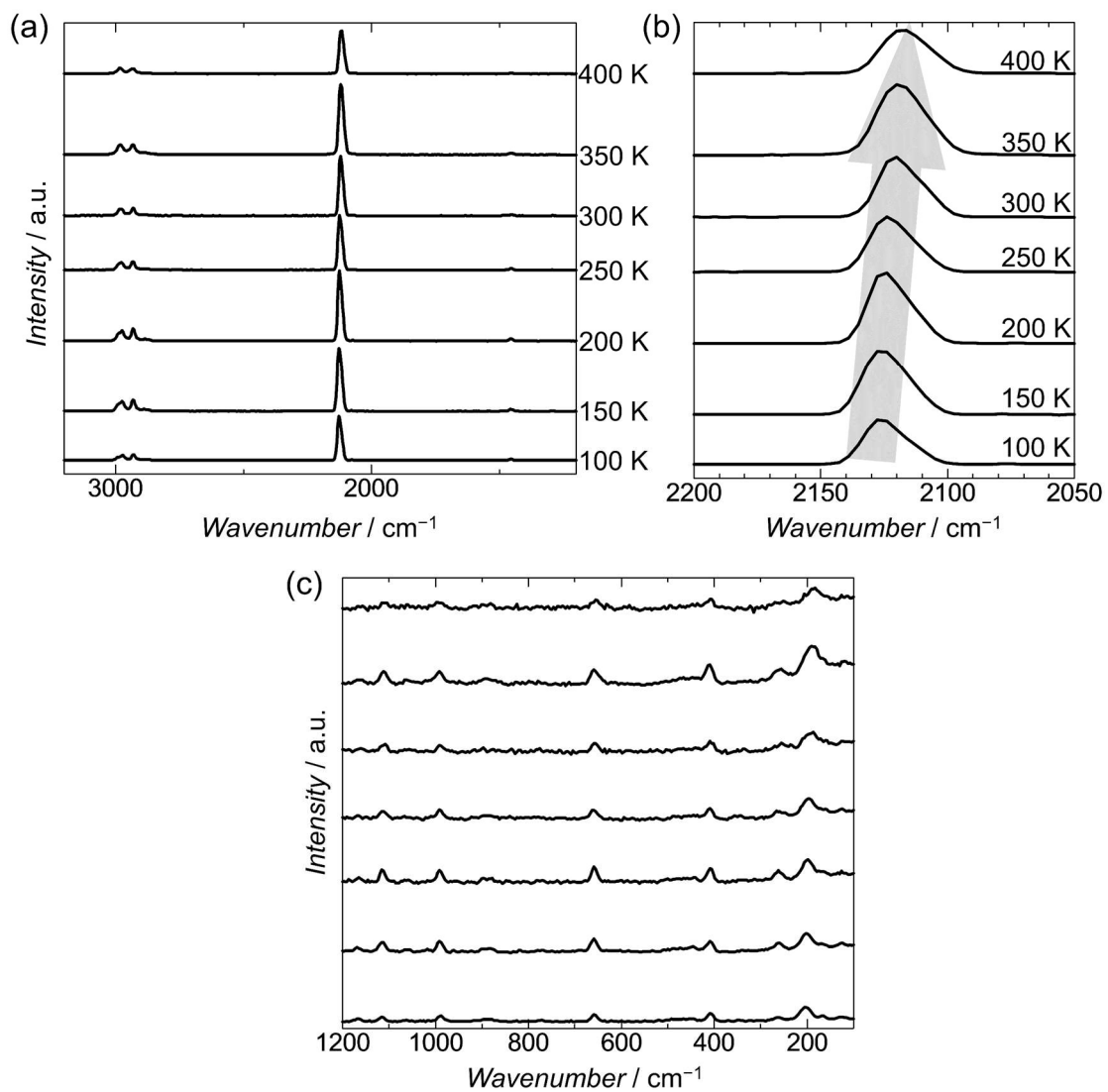
Fig. S6 (a) Overall view, (b) the region of cyanido vibration and (c) low wavenumber region (100 – 1200 cm^{-1}) of variable temperature Raman spectra for **TEACu** at 100–500 K.
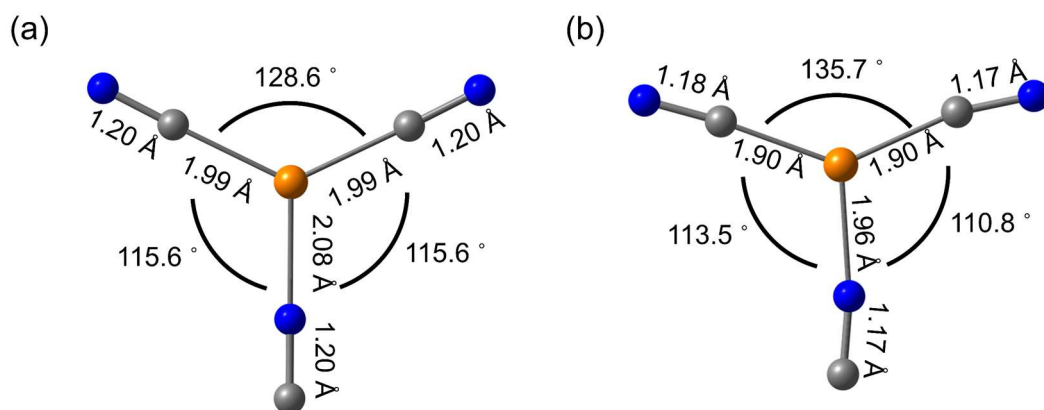
Fig. S7 The structure of $Cu(CN)_3$ moiety (a) optimized with DFT (B3LYP/LANL2DZ implemented in Gaussian 16)[1] calculation and (b) obtained with SCXRD measurement at 100 K.
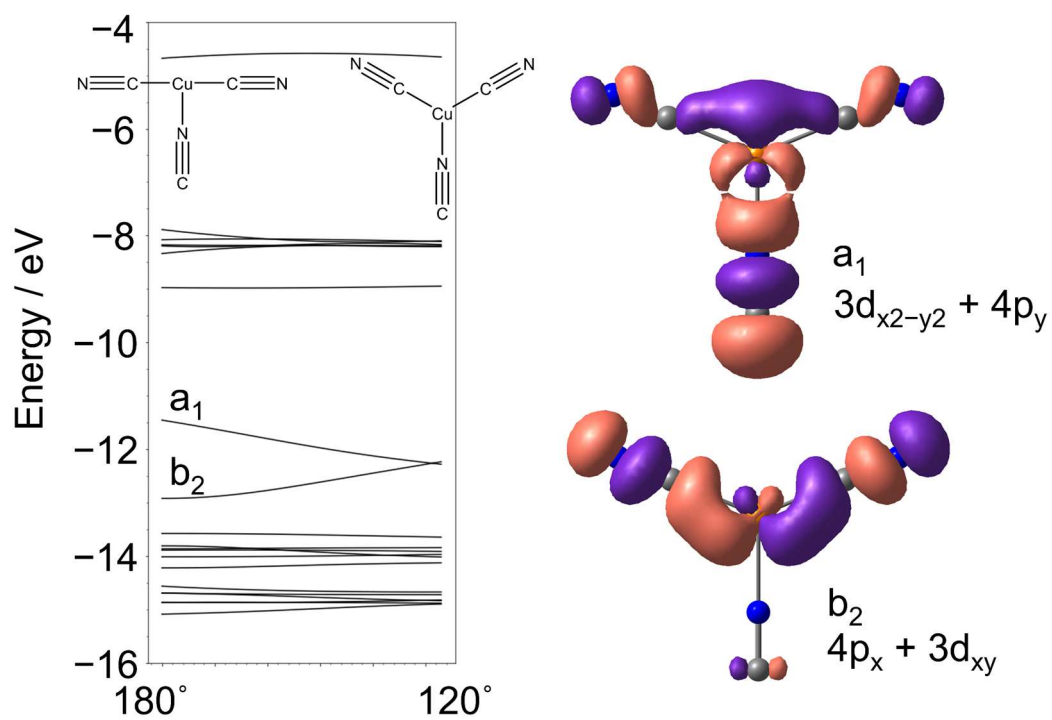
Fig. S8 Walsh diagram for bending C-Cu-C angle, HOMO (a1), and HOMO−1 (b2) of the $[Cu(CN)_3]^{2-}$ moiety.
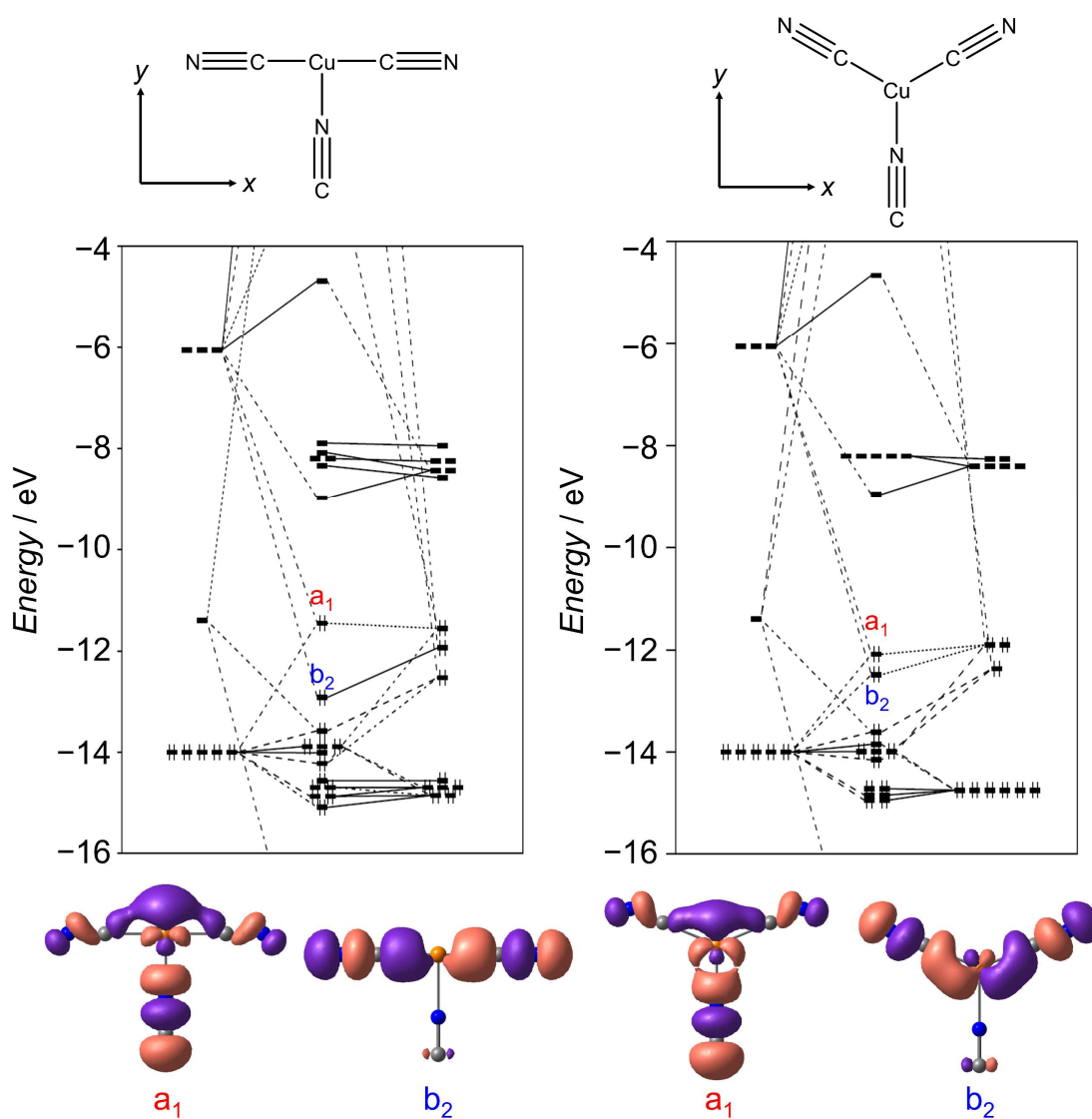
Fig. S9 Fragment molecular orbital interaction diagrams for the formation of T-shaped and Y-shaped $[Cu(CN)_3]^{2-}$ moieties from Cu^+ and $(CN^-)_3$ fragments generated by using YAeHMOP.[2,3]
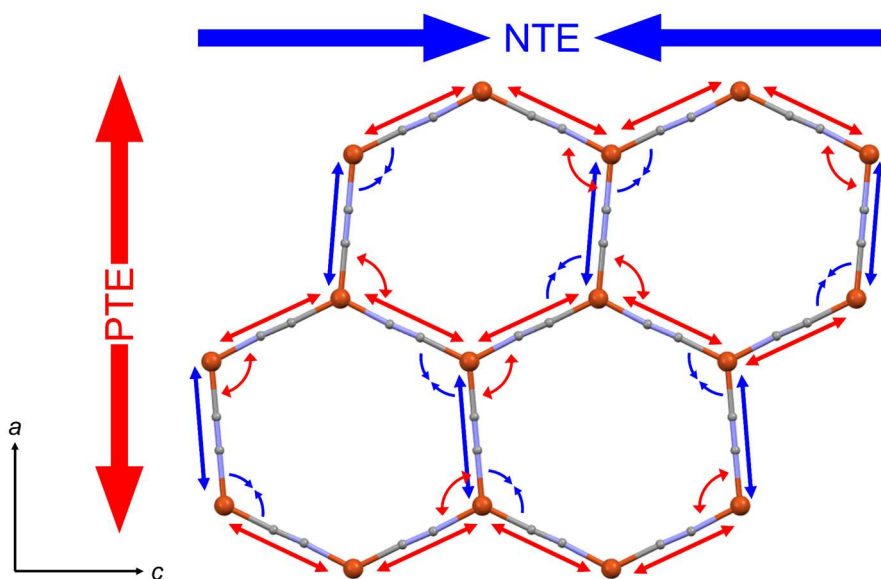
Fig. S10 Schematic image of the shape change of hexagons in **PPh₄Cu**.

Table S2 Calculated vibration mode energies of $Cu(CN)_3$ moiety in wavenumber and temperature.

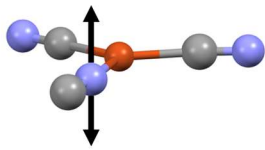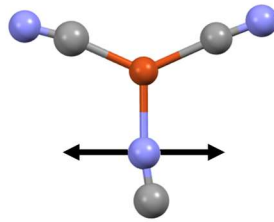| #	Wavenumber (cm⁻¹)	Temperature (K)	#	Wavenumber (cm⁻¹)	Temperature (K)
1	64.6633	93.0	9	292.9937	421.6
2	68.8813	99.1	10	307.0290	441.7
3	79.4933	114.4	11	334.6925	481.6
4	159.4251	229.4	12	335.2458	482.3
5	191.1637	275.0	13	2041.4970	2937.3
6	221.8933	319.3	14	2067.7300	2975.0
7	226.1289	325.4	15	2077.738	2989.4
8	278.0508	400.1			
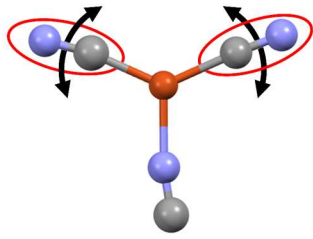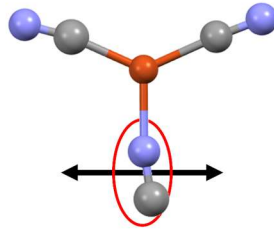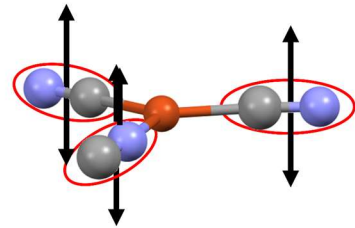
Angular vibrations of CN group(s)
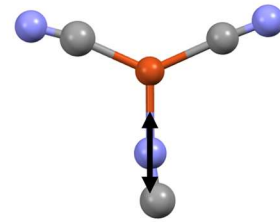
#1   #2   #3
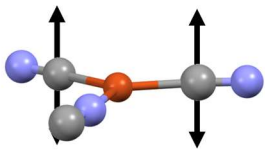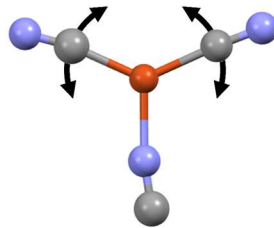
Angular vibrations of N   Stretching vibration of N
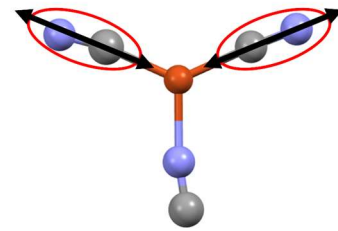
#4   #5   #6

Transverse angular vibration of C atoms   Stretching vibration of CN.

#7   #8   #9

Angular vibrations of C   Transverse stretching   Angular vibrations of C
vibration of CN.

#10   #11   #12

Stretching vibration of CN.   Transverse stretching   Stretching vibration of CN
vibration of CN.

#13   #14   #15
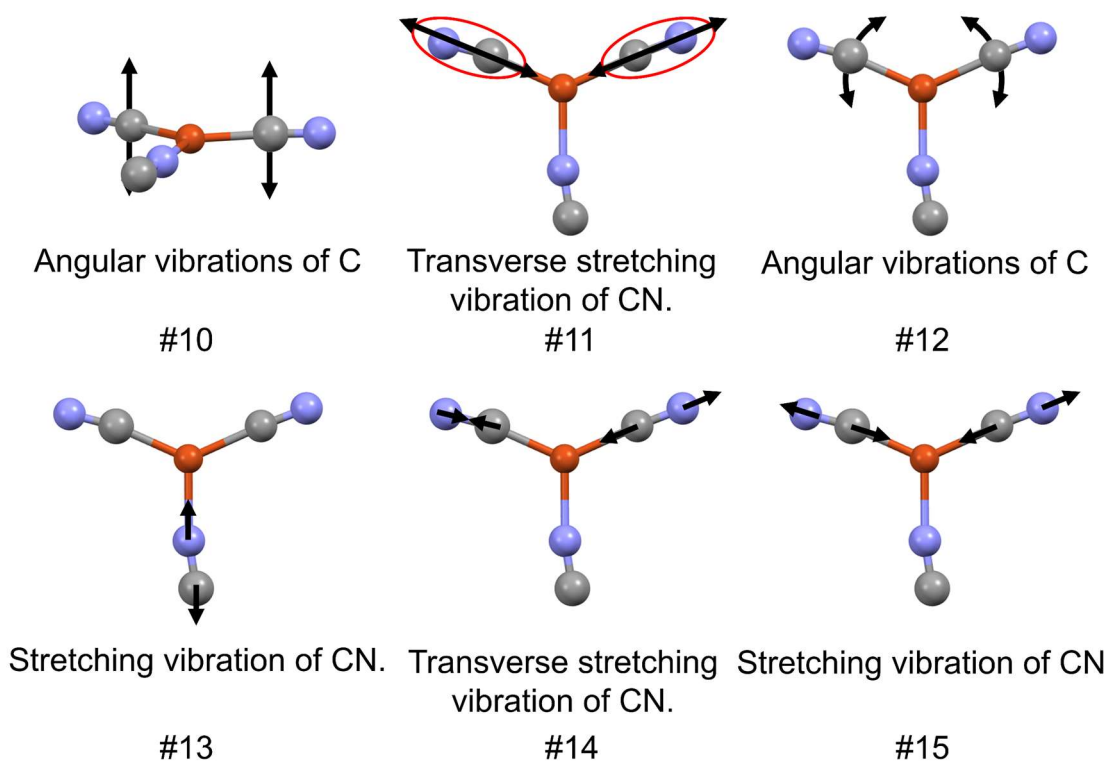
Fig. S11 Vibration modes of the [Cu(CN)$_3$] moiety at the B3LYP/LANL2DZ level of theory.
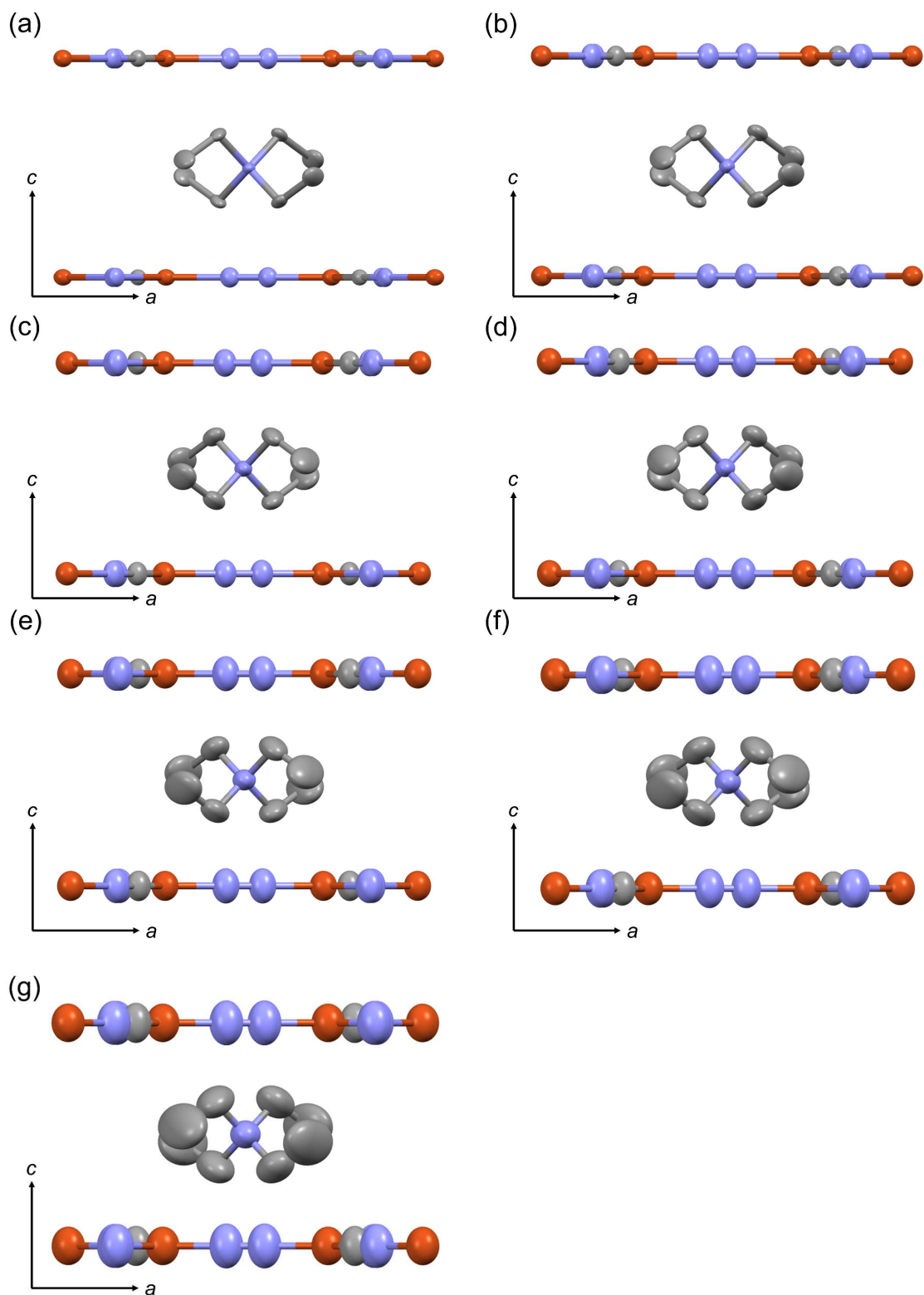
Fig. S12 Views of **TEACu** with an ellipsoid style at (a) 100 K, (b) 150 K, (c) 200 K, (d) 250 K, (e) 300 K, (f) 350K, and (g) 400 K.
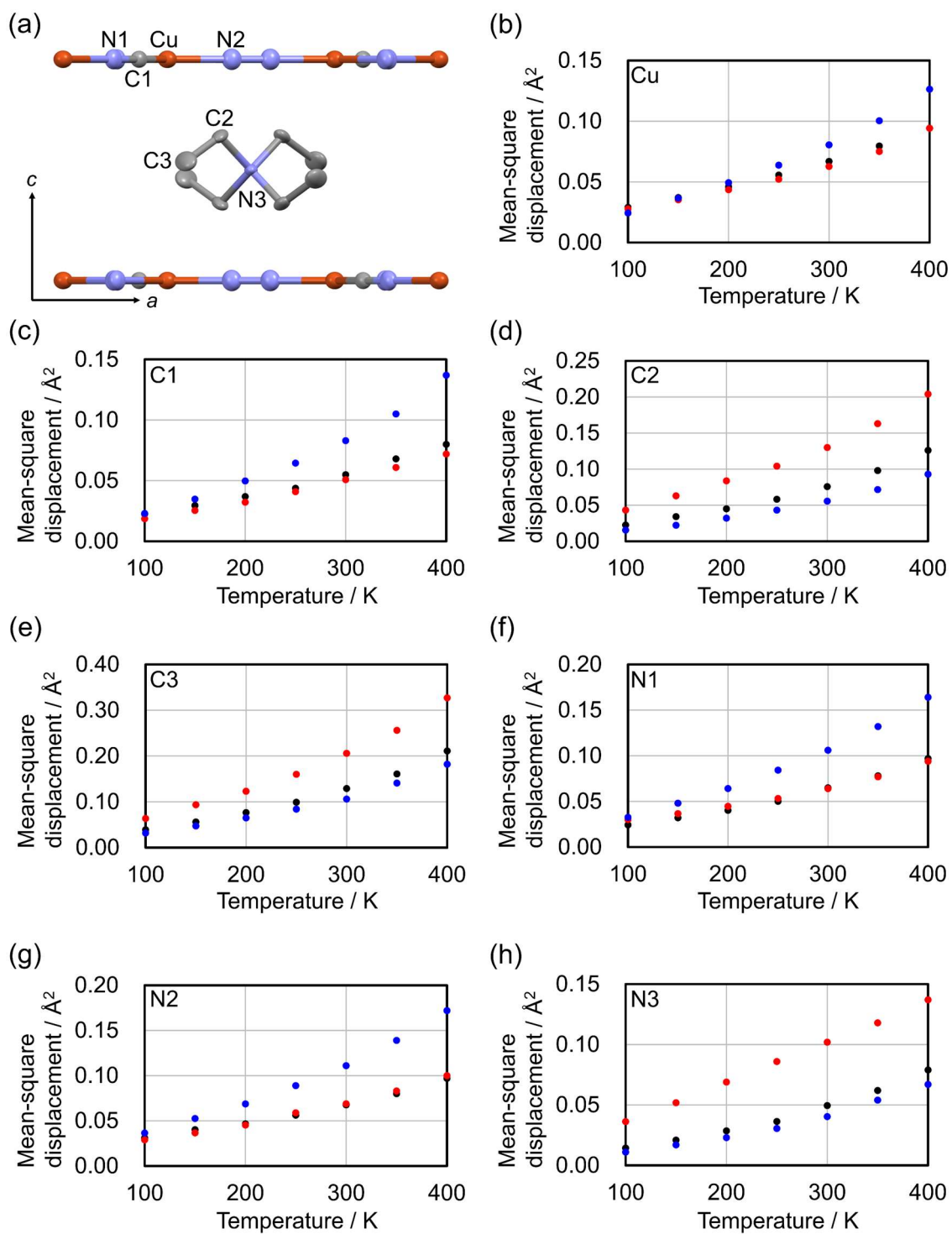
Fig. S13 Thermal variation of Mean-square distributions for each atom in **TEACu**. Black, red, and blue points indicate *a*-, *b*-, and *c*-axis, respectively.
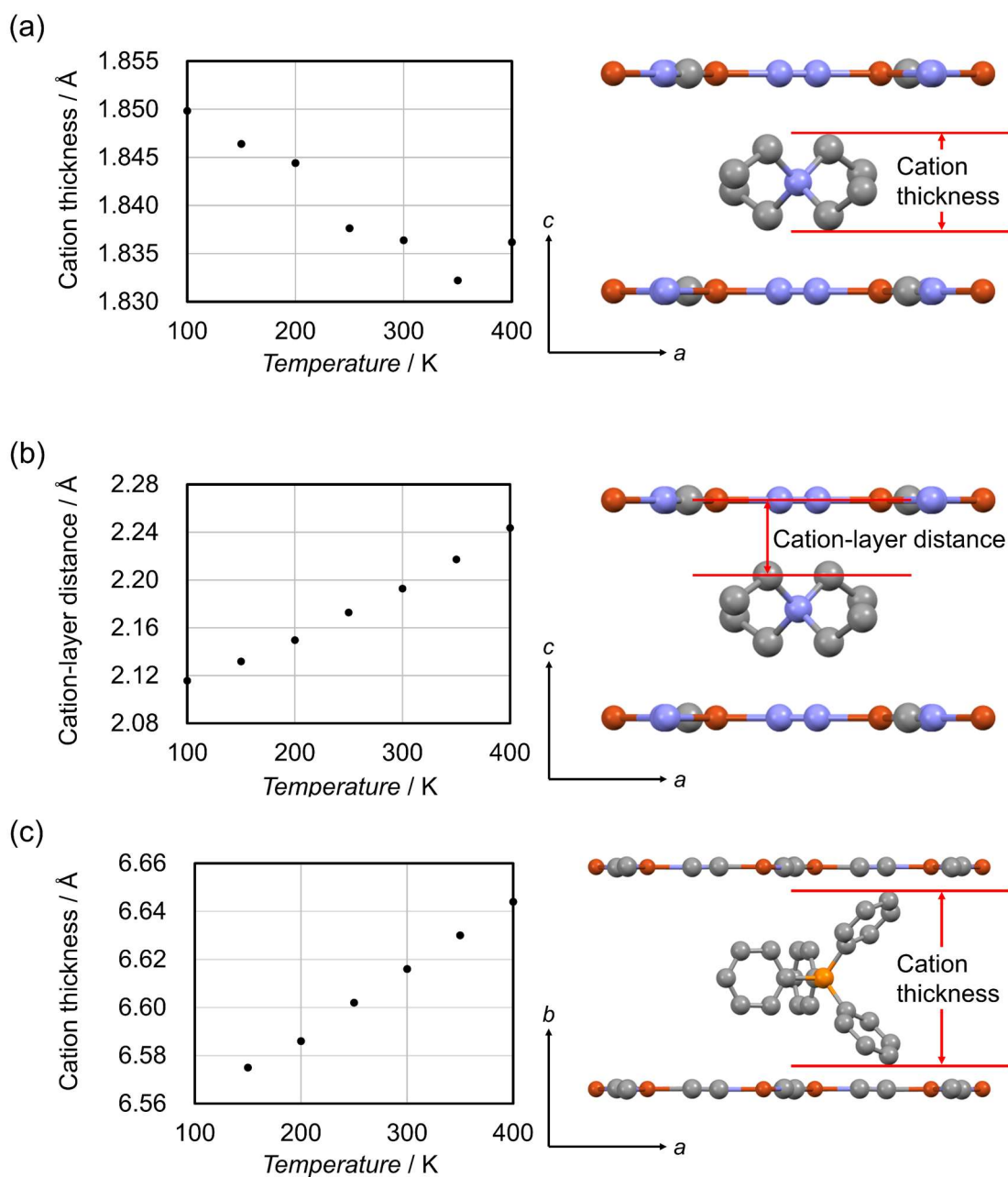
Fig. S14 Thermal variation of (a) cation thickness and (b) cation-layer distance for **TEACu**. (c) Thermal variation of cation thickness for **PPh₄Cu**.

Reference

1. E. Colacio, R. Kivekäs, F. Lloret, M. Sunberg, J. S.-Varela, M. Bardaji and A. Laguna, *Inorg. Chem.*, 2002, **41**, 5141-5149.

2. M. J.Frisch, et al., Gaussian16 Revision C.01, 2016.

3. G. A. Landrum, YAeHMOP: Yet Another extended Hückel Molecular Orbital Package, Version 3.0.

4. YAeHMOP is freely available on the WWW at URL: http://sourceforge.net/projects/yaehmop/.

5. K. Stokbro, D. E. Petersen, S. Smidstrup, A. Blom, M. Ipsen, K. Kaasbjerg, *Phys. Rev. B*, 2010, **82**, 075420.

6. Y. Tsuji, M. Yoshida, T. Kamachi, K. Yoshizawa, *J. Am. Chem. Soc.* 2022, **144**, 18650-18671.