Experiment

All reagents were commercially available and used without further purification.

Synthesis

$PPh_4CN{\cdot}0.8MeCN$[S1]: A solution of KCN (1.55 g, 23.80 mmol) in 10 ml of MeOH was treated dropwise with a solution of PPh_4Br (6.44 g, 15.36 mmol) in 10 ml of MeOH. The resulting suspension was evaporated to dryness, and the residue was extracted with 20 ml of MeCN. The solution was evaporated after filtration. Light brown powder of PPh_4CN was obtained. Yield 92.01 %. Anal. Found (cald) for $PC_{26.6}H_{22.4}N_{1.8}$ (397.84): C 75.43 (75.41); H 5.43 (5.03); N 2.49 (3.52) %.

$K[Cu_2(CN)_3]{\cdot}2.2\ H_2O$[S2]: KCN (0.65 g, 10.0 mmol) was dissolved in H_2O (5 ml). CuCN (1.79 g, 20.0 mmol) was added into the water solution with stirring at 363 K. After 24 hours, the water suspension was filtered and the filtrate was evaporated. White powder of $K[Cu_2CN)_3]$ was obtained. Yield 15.44 %. Anal. Found (cald) for $C_4N_3H_{2.2}O_{1.1}KCu_2$ (244.19): C 13.42 (13.63); H 0.10 (0.84); N 15.60 (15.90) %.

Single crystals of $PPh_4[Cu_2(CN)_3]$: 5 mM water solution of $K[Cu_2(CN)_3]$ and 5 mM methanol solution of PPh_4Cl are mixed. After 3 months, single crystal of $PPh_4[Cu_2(CN)_3]$ formed as colorless crystals.

Powder samples of $PPh_4[Cu_2(CN)_3]{\cdot}0.6H_2O$: CuCN (179.1mg, 2.0 mmol) was added to a suspension of PPh_4CN (365.4 mg, 1.0 mmol) in 200 ml of DMF and stirred for 1 day. The residue was dried under reduced pressure for 1 day after wash with DMF. Pale yellow powder was obtained. Yield 52.65 %. Anal. Found (cald) for $PC_{27}H_{21.2}N_3Cu_2O_{0.6}$ (554.87): C 58.33 (58.39); H 3.72 (3.60); N 7.83 (7.57) %.

Physical measurements

Single-crystal X-ray data for **1** at 150 – 400 K 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 undertaken with APEX3 Software. Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Hydrogen atoms were included in idealized positions and refined using a riding model. Variable-temperature powder X-ray diffraction data (VT-PXRD) at 100 – 500 K were obtained using the SAGA-LS, BL-15 (λ = 1.08 Å) in the 2θ range of 2.00 ° – 57.355 ° with a step width of 0.02° at each temperature. The powder samples with homogeneous granularity were sealed in a glass capillary of 0.2 mm internal diameter. The sample temperatures were controlled by a dry dinitrogen flow using a Rigaku GN_2 apparatus. Thermogravimetric analysis (TGA) was performed at 10 K min^{-1} using a Rigaku Instrument Thermo plus TG 8120 in a nitrogen atmosphere. Infrared (IR) spectra measurements were performed on a PerkinElmer Spectrum Two FT-IR equipped with an ATR accessory.

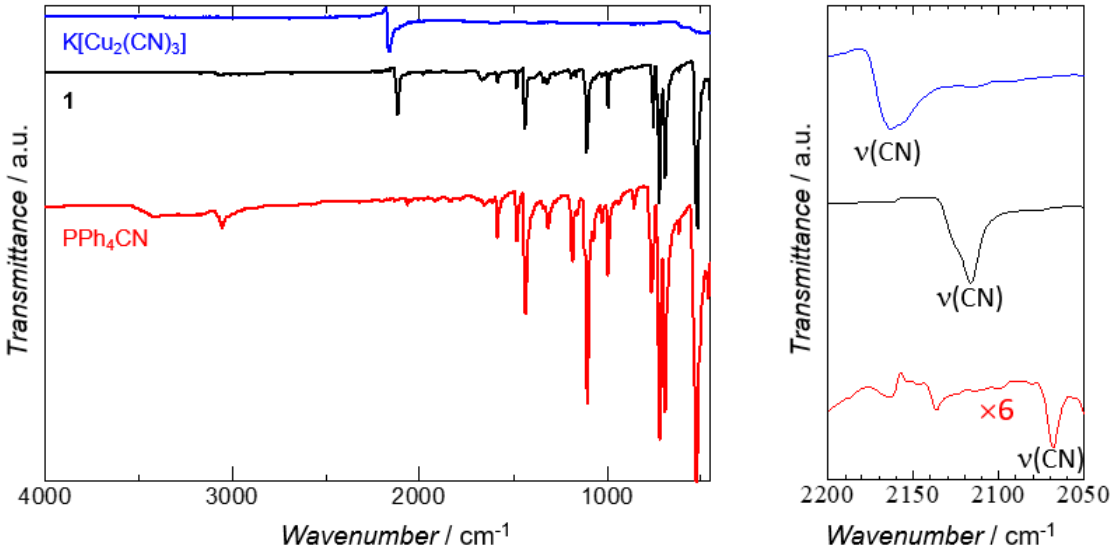

Fig. S1 IR spectra of $K[Cu_2(CN)_3]$ (blue), **1** (black) and PPh_4CN (red)

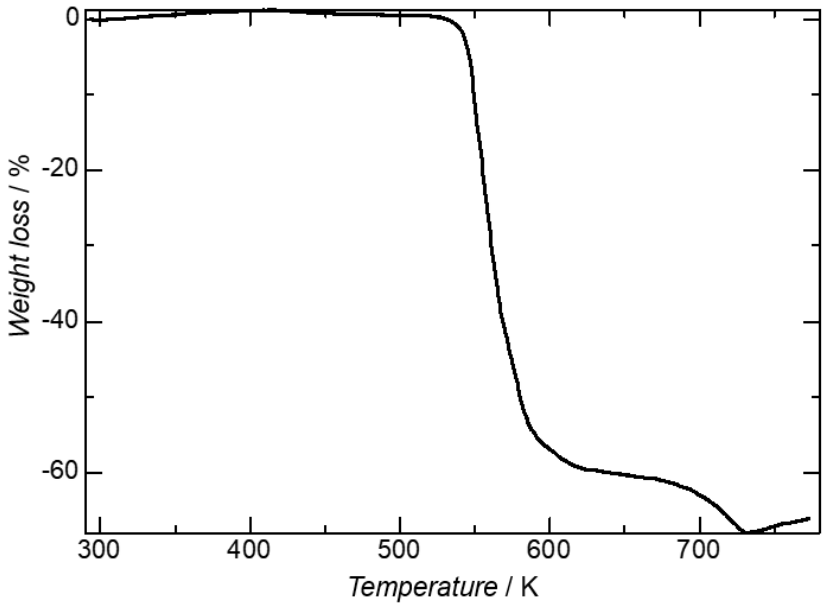

Fig. S2 A TG result for **1** under N_2 flow.

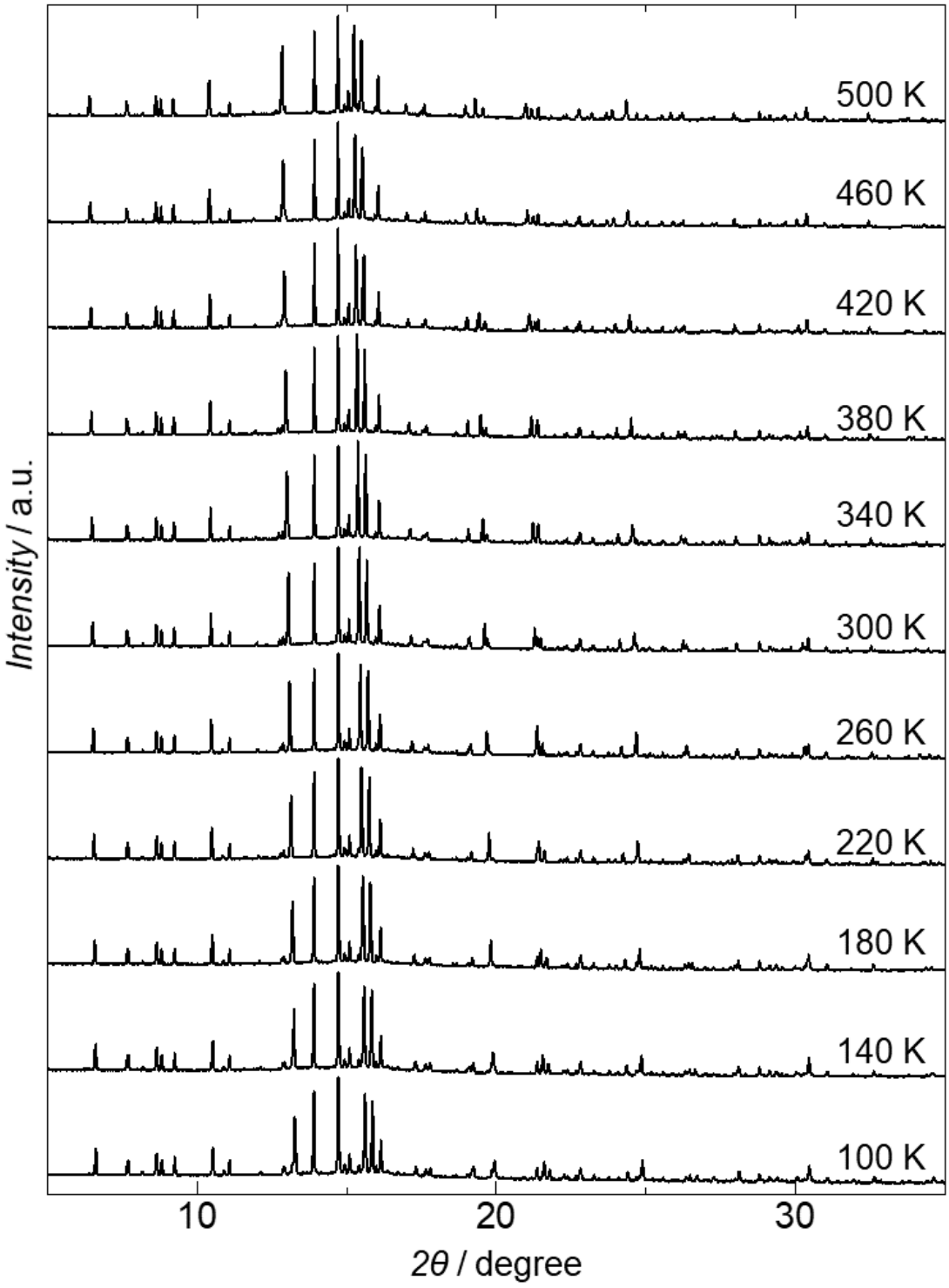

Fig. S3 PXRD patterns of **1** at 100 – 500 K (λ = 1.08 Å)

Table S1. Cell parameters of **1** at 100 – 500 K determined by the LeBail fitting for PXRD patterns.

Temp. (K)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*area* (Å^2)
100	14.3438(5)	18.7017(4)	8.93038(2)	2395.61	128.10
140	14.3465(5)	18.7540(6)	8.93111(3)	2402.95	128.13
180	14.3468(5)	18.8217(5)	8.93007(3)	2411.40	128.12
220	14.3442(5)	18.8817(6)	8.92654(3)	2417.69	128.04
260	14.3586(5)	18.9647(5)	8.93168(3)	2432.16	128.25
300	14.3609(7)	19.0323(6)	8.92728(3)	2440.01	128.20
340	14.3650(5)	19.0968(6)	8.92473(3)	2448.28	128.20
380	14.3661(5)	19.1511(7)	8.92292(3)	2454.93	128.19
420	14.3716(7)	19.2110(7)	8.91993(3)	2462.73	128.19
460	14.3694(6)	19.2692(7)	8.91541(3)	2468.56	128.10
500	14.3937(6)	19.3560(8)	8.92144(3)	2485.55	128.41

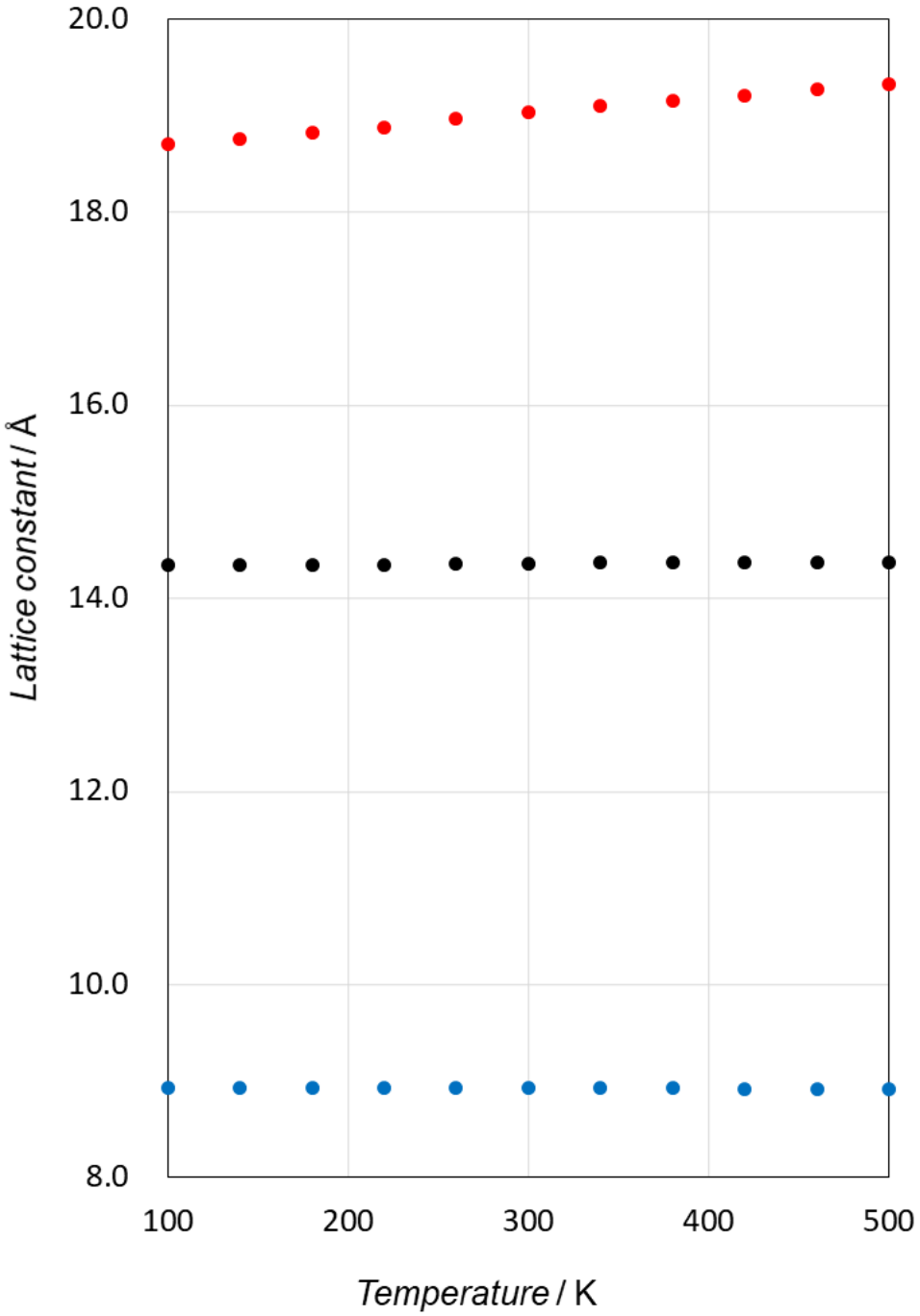

Fig. S4 Temperature variations of lattice constants of **1** at 100 – 500 K determined by Le-bail fitting.

Table S2. Crystal parameters of **1** at 150 – 400 K obtained by SCXRD.

CCDC Number	2165051	2165052	2165053
***T*/ K**	150	200	250
Formula	$C_3Cu_2N_3C_{24}H_{20}P$	$C_3Cu_2N_3C_{24}H_{20}P$	$C_3Cu_2N_3C_{24}H_{20}P$
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
***a* / Å**	14.3168(8)	14.3204(9)	14.3252(5)
***b* / Å**	18.7687(11)	18.8505(13)	18.9350(7)
***c* / Å**	8.9267(5)	8.9253(6)	8.9216(3)
V / Å³	2368.67	2409.36	2419.96
Z	4	4	4
***R*1**	3.78	4.26	3.79
***wR*2**	9.20	10.67	8.89
G.O.F	1.0967	1.0581	1.0801

CCDC Number	2165054	2165056	2165055
***T*/ K**	300	350	400
Formula	$C_3Cu_2N_3C_{24}H_{20}P$	$C_3Cu_2N_3C_{24}H_{20}P$	$C_3Cu_2N_3C_{24}H_{20}P$
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
***a* / Å**	14.3250(6)	14.3334(8)	14.3364(17)
***b* / Å**	19.0152(8)	19.0929(11)	19.170(2)
***c* / Å**	8.9170(4)	8.9152(5)	8.9148(11)
V / Å³	2428.93	2439.79	2450.17
Z	4	4	4
***R*1**	4.23	3.96	3.87
***wR*2**	9.47	9.54	9.62
G.O.F	1.0671	1.0850	1.0949

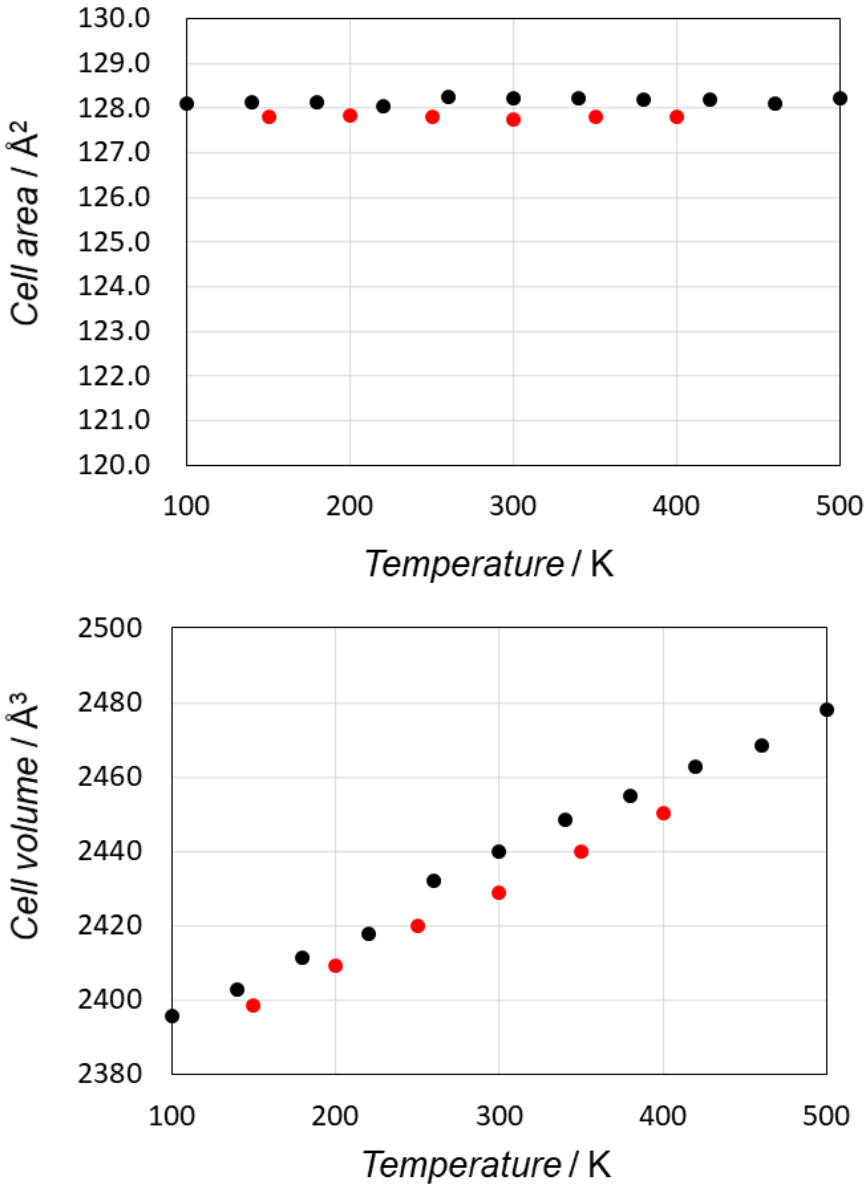

Fig. S5 (a) Thermal variations of cell area (products of *a*- and *c*-axis lengths) and (b) cell volume of **1**. Red and Black circles are results of the SCXRD and the LeBail fitting, respectively.

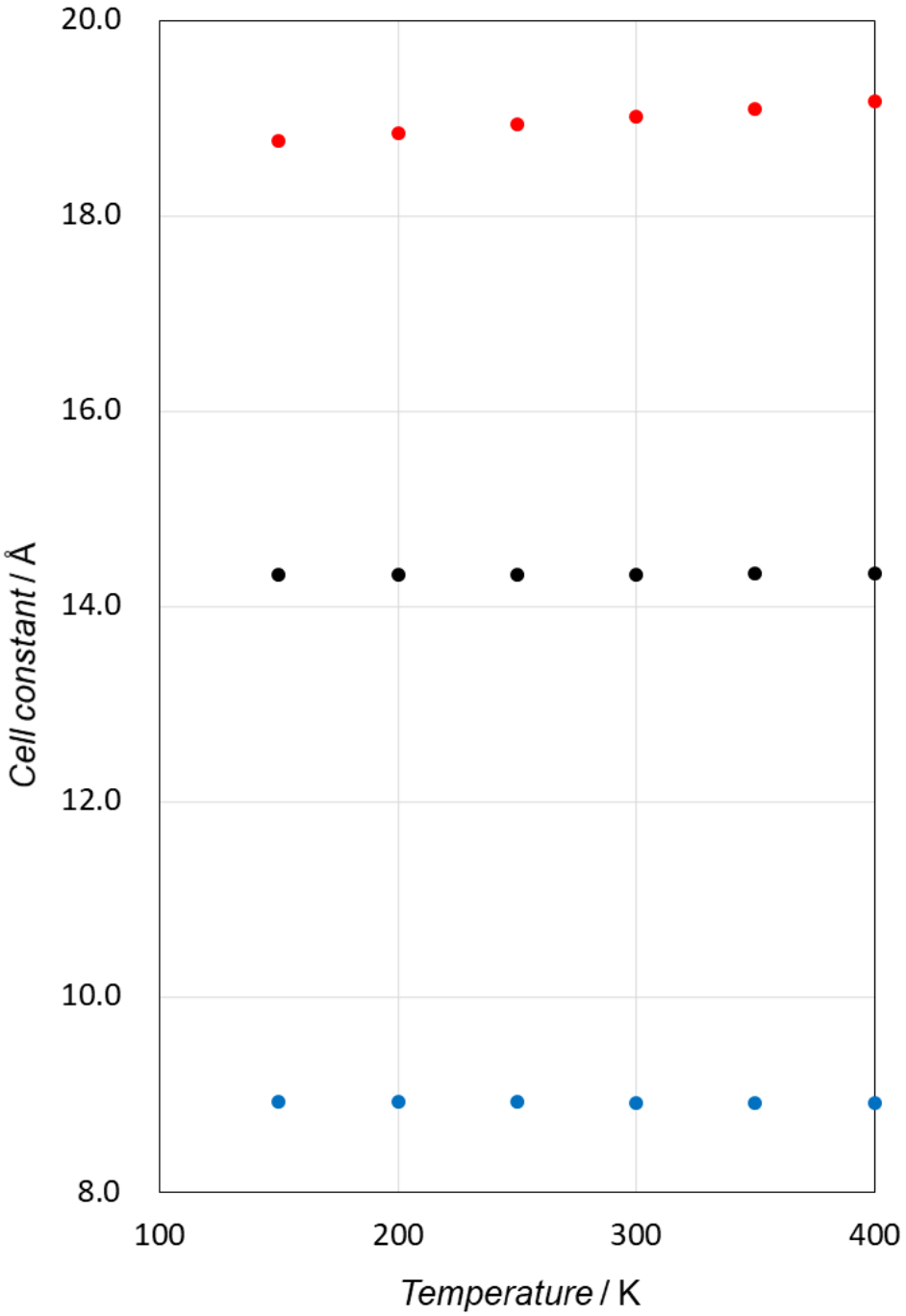

Fig. S6 Thermal variation of lattice constants of **1** at 100 – 500 K obtained by SCXRD. Red, black and blue correspond to cell constant of *b*-, *a*- and *c*-axis.

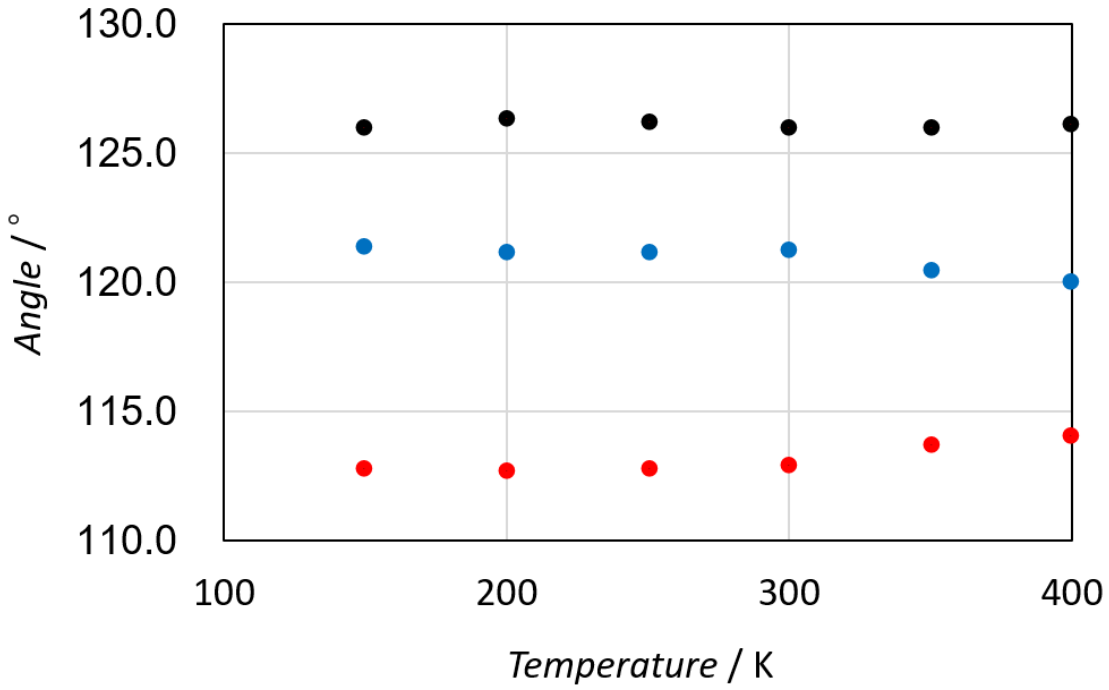

Fig. S7 Thermal variation of angles of Cu-Cu-Cu at 150 – 400 K. Red blue and black points correspond to Fig. 1(b) in the main manuscript.

Table S3 Selected angles of Cu-Cu-Cu and bond distances of Cu-C/N at 150 – 400 K. The angles of red, blue and black correspond to Fig. S7 as well as Fig. 1(b).

	Angle of Cu-Cu-Cu (°)			Coordination length between Cu - C/N (Å)		
T (K)	Red	blue	black			
150	112.7(2)	121.3(2)	126.0(2)	1.920(5)	1.911(5)	1.896(5)
200	112.6(2)	121.1(2)	126.3(2)	1.919(6)	1.911(5)	1.906(6)
250	112.7(2)	121.1(2)	126.2(2)	1.920(5)	1.914(5)	1.903(5)
300	112.9(2)	121.2(2)	126.0(2)	1.918(5)	1.909(5)	1.908(5)
350	113.6(2)	120.4(2)	126.0(2)	1.924(5)	1.916(5)	1.906(5)
400	114.0(2)	120.0(2)	126.1(2)	1.921(5)	1.921(5)	1.902(4)

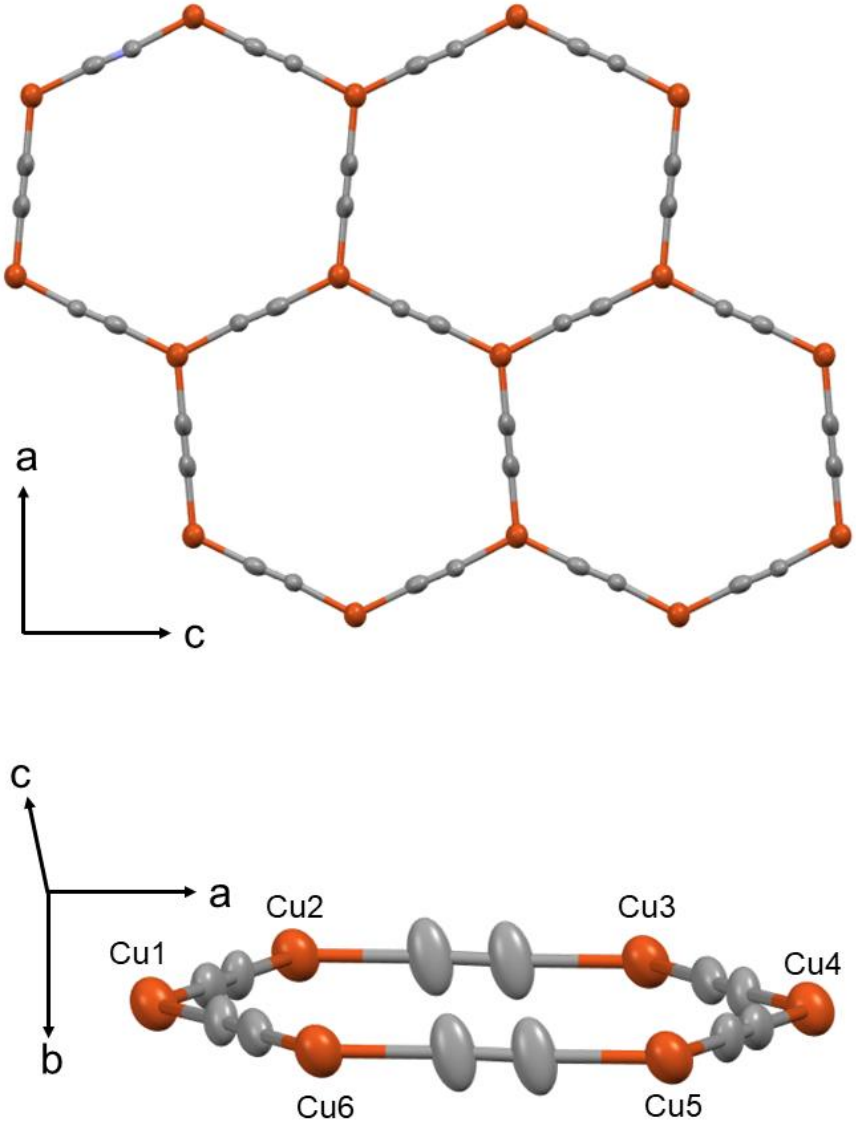

Fig. S8 Views of a $[Cu_2(CN)_3]^-$ layer of **1** with an ellipsoid style at 150 K.

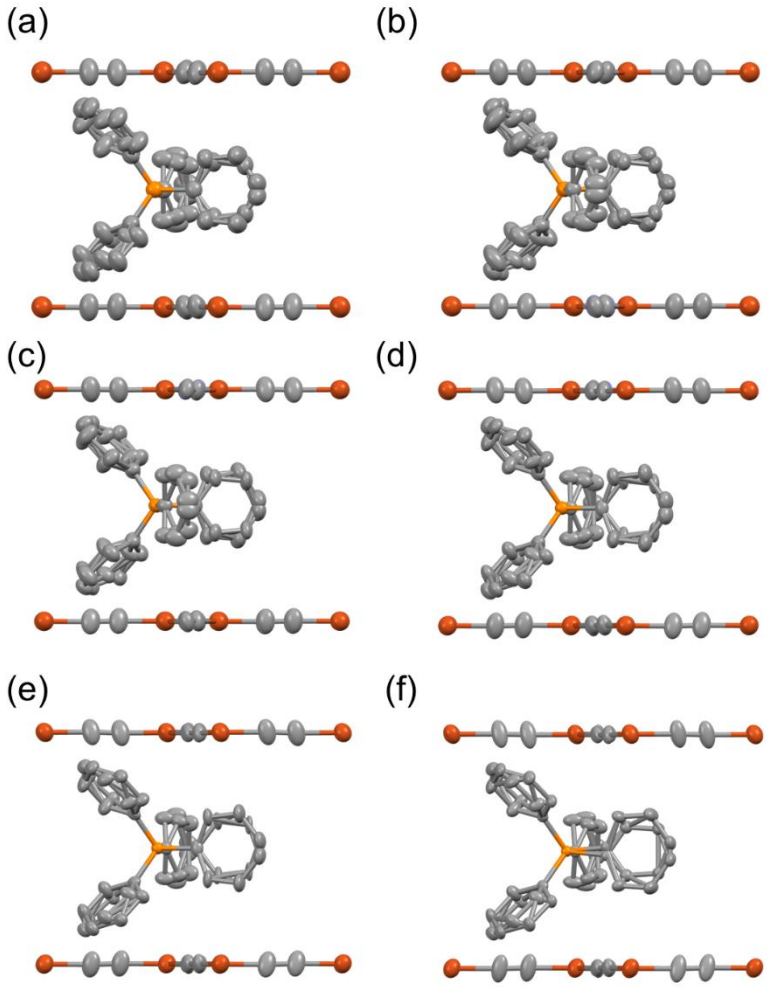

Fig. S9 Views of **1** with an ellipsoid style at (a) 400 K (b) 350 K (c) 300 K (d) 250 K (e) 200 K (f) 150K. These image include the structural disorder of PPh_4^+ between layers.

Reference

[S1] F. Gloaguen, J. D. Lawrence, M. Schmidt, S. R. Wilson and T. B. Rauchfuss, *J. Am. Chem. Soc.*, **2001,** *123,* 12518-12527.

[S2] B. D. T. Cromer and A. C. Larson, *Acta Cryst.*, **1962**, *15*, 397-402.