Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Imidazolium cation transportation in a 1-D coordination polymer

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Synthesis of compounds:

$Cu(NO_3)_2{\cdot}3H_2O$ and *N,N*-dimethylformamide (DMF) were obtained from Wako Pure Chemical Industries, Ltd. 4,4'-bypridine (bpy) was obtained from Tokyo Chemical Industries Co., Ltd. 1-Ethyl-3-methylimidazolium dimethyl phosphate (EtMeIm-Me_2PO_4) was obtained from Sigma-Aldrich. All chemicals and deoxidized solvents in the synthesis were purchased from commercial vendors and used without further purification. All manipulations, unless otherwise stated, were performed under an Ar atmosphere in an Ar-filled glove box or using the standard Schlenk technique.

Synthesis of $[EtMeIm][Cu(bpy)(Me_2PO_4)_3]$ (denoted as **1**, $EtMeIm^+$ = 1-ethyl-3-methyl imidazolium cation, bpy = 4,4'-bipyridine, $Me_2PO_4^-$ = dimethyl phosphate): $Cu(NO_3)_2{\cdot}3H_2O$ (0.07 g, 0.3 mmol) was dissolved in a mixture solution of EtMeIm-Me_2PO_4 (2.00 mL, 11 mmol) and deoxidized DMF (1.00 mL, 13 mmol), bpy (0.09 g, 0.6 mmol) was dissolved in a mixture solution of EtMeIm-Me_2PO_4 (2.00 mL, 11 mmol) and deoxidized DMF (1.00 mL, 13 mmol), mix the two prepared solution homogenously in a 20 mL screw glass vial for 24 hours. All the procedure were performed under Ar atmosphere. Blue crystals thus produced were washed with DMF (20 mL × 3) and dried at 25 °C under an Ar atmosphere. On exposure to air, the crystal of **1** lost single crystallinity and became a bluish solid. Therefore, we protected **1** with paratone oil in glove box and transferred it immediately by cryoloop for single crystal X-ray measurement.

Synthesis of **1’**: Exposing **1** to air produced a bluish solid. The SEM image of the **1’** (Fig. S4) displays a rod like shape, suggesting the morphology of **1’** may be influenced by the one-dimensional structure of **1**.

Physical measurements:

Thermogravimetry analysis (TGA) was obtained using a Rigaku TG8120 under flowing N_2 with 10 K min^{-1} ramp rate. The TGA under Ar atmosphere was performed using a Rigaku Thermo plus TG 8121 apparatus at a heating rate of 10 $Kmin^{-1}$. Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC822e/200 at the heating rate of 10 K min^{-1}. Powder X-ray diffraction (PXRD) data were collected on a Rigaku RINT 2200 Ultima diffractometer with Cu*K*α anode. Powder X-ray diffraction under Ar atmosphere was performed on a Rigaku Miniflex 600 diffractometer with CuKα radiation. Infra-red (IR) spectroscopy was obtained using a Nicolet ID5 ATR operating at ambient temperature. The IR under Ar atmosphere was measured on a Bruker Optics ALPHA FT-IR spectrometer with Universal ATR accessory between 4000-500 cm^{-1}. Scanning electron microscope (SEM) images were collected by using a Hitachi S-3000N SEM system operated at an accelerating voltage of 5 kV. The samples were deposited on carbon tape and coated with osmium prior to the measurement. Impedance analysis was performed on powders of **1’** without modification. The powders (ca. 25-30 mg) were pressed at 500 kg N for 2 minutes by a standard 5 mm die and sandwiched between two platinum electrodes under Ar atmosphere. Measurements were performed using an impedance and gain-phase analyser (Solartron SI 1260 Impedance/Gain-Phase analyzer) over frequency range 1 Hz - 1 MHz with an input voltage amplitude of 30 mV, the temperature range is 25 to 110 °C. The measurement cell was filled with an Ar at atmospheric pressure before recording the measurements. We obtained impedance signals of **1** and **1’** as Nyquist plots. ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

Cu *K*-edge XAS spectra of **1** and **1’** were measured at the BL5S1, hard X-ray XAFS beamline, at Aichi Synchrotron Radiation Center (AichiSR; Aichi Science and Technology Foundation, Aichi, Japan). The XAS spectra of their powder samples were recorded in transmission mode under ambient conditions, using a Si(111) double crystal monochromator. The photon energy was calibrated with the pre-edge peak (8980.3 eV) observed in the Cu *K*-edge XANES spectrum of Cu foil. Incident and transmitted X-ray fluxes were measured with ion chambers filled with N_2 (100%) and N_2/Ar (25/75%). Higher harmonic X-ray was cut off with proper glancing angle of Rhcoated collimating and focusing mirrors. Fourier transformation was k^3-weighted in the k range from 3 to 13 Å^{-1}. The RDF of **1** and **1'** were fitted by a model in which the copper ions are surrounded by three oxygen atoms and two nitrogen atoms. The following equation was used to calculate and fit RDF of **1** and **1'**:

$$\chi(k) = S_0^2 \sum \frac{N_j f_j(k) \exp\left[-2k^2 \sigma_j^{\,2}\right]}{k r_j^{\,2}} \sin\left[2k_j r_j + \delta(k)\right]$$

Where r is distance from the target to neighboring atom, N is coordination number of the neighboring atom, and σ^2 is Debye-Waller factor. The photoelectron wavenumber k is given as $k = \sqrt{2\mathrm{m}(E - E_0)/\hbar^2}$, $f(k)$ is the scattering amplitude, and $\delta(k)$ is the phase shift. S_0, amplitude reduction factor, was empirically determined from EXAFS of **1** (crystalline state) as 1.085. EXAFS spectrum of **1** and **1'** were fitted in r range from 1 to 2 Å. The final values of these parameters are summarized in Table S1 and S2.

Single crystal X-ray diffraction measurements of **1** were performed at −50 °C and 25 °C with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated Mo$K\alpha$ radiation. Data were processed by a direct method (SIR97) and refined by full-matrix least-squares refinement using the SHELXL-2016 computer program. The refinement of the disordered dimethyl phosphate group and ethyl group were made anisotropically using PART restrictions. The deposited number of Cambridge Crystallographic Data Centre (CCDC) are 1530651 (−50 °C) and 1530702 (25 °C).

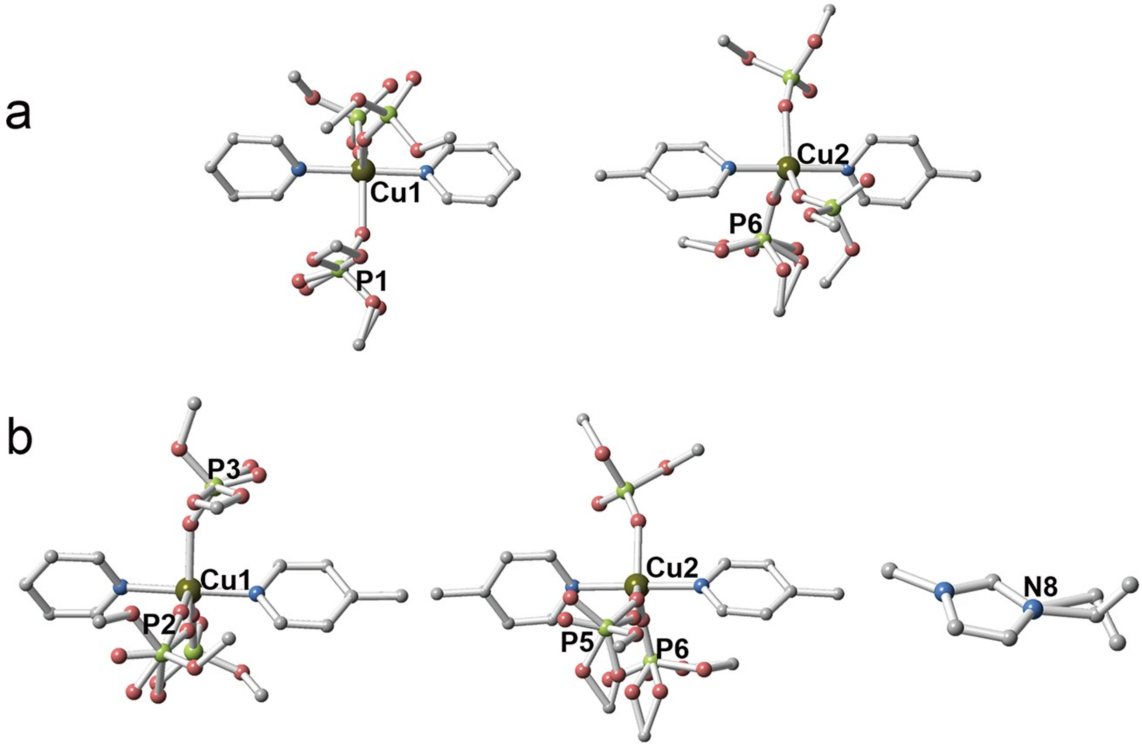

Figure S1. (a) Crystal structures in **1** at −50 °C with the disorder treatment around P(1) and P(6). (b) Crystal structures in **1** at 25 °C with the disorder treatment around P(2), P(3), P(5), P(6) and ethyl group attached to N(8). H atoms are omitted for clarity. Cu, P, O, N and C atoms are shown in brown, green, red, blue and gray.

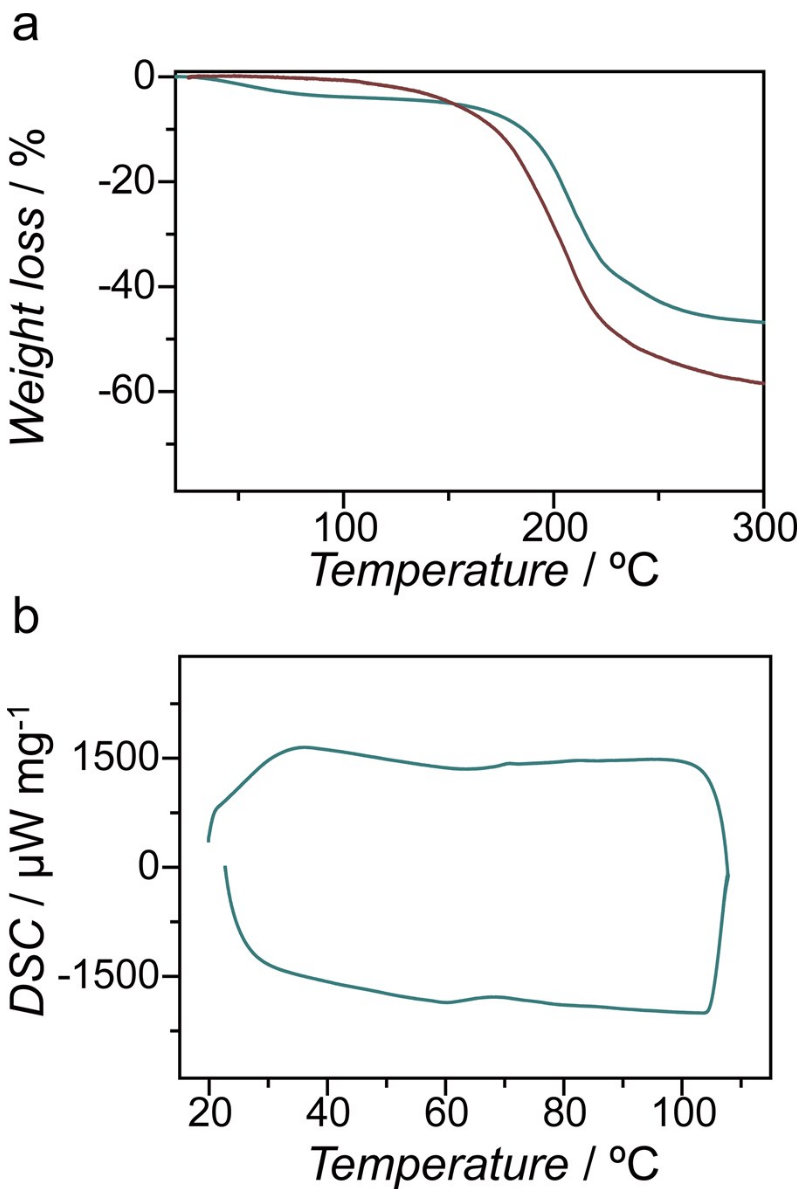

Figure S2. (a) Thermogravimetric analysis profiles of **1** inside glove box under Ar atmosphere (brown) and **1’** under N_2 flow (green). (b) Differential scanning calorimetry profile of **1’** under N_2 atmosphere.

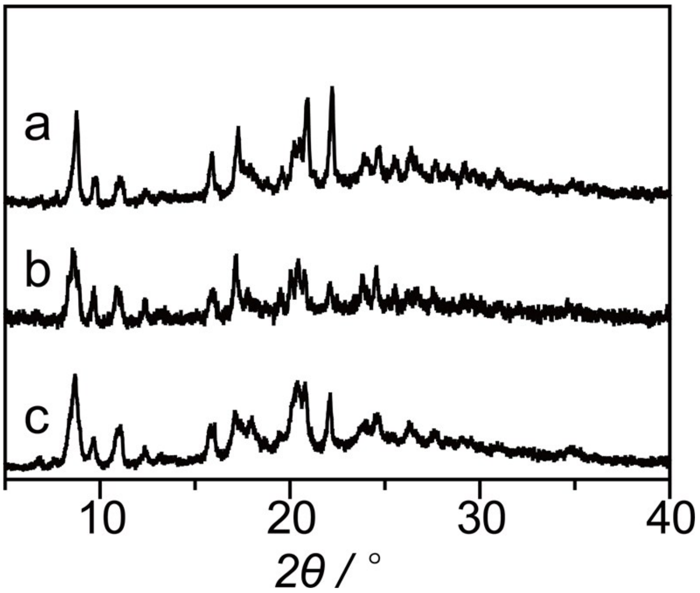

Figure S3. PXRD patterns at 25 °C for (a) **1’** after the heat treatment at 110 °C for 10 hours, (b) **1’** after the impedance measurement at 110 °C, and (c) **1’**. All measurements were performed under the air.

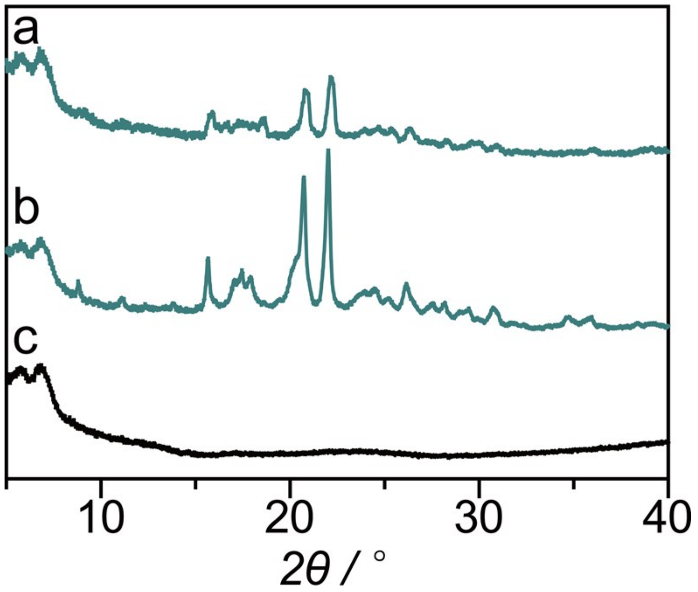

Figure S4. PXRD patterns at 25 °C for (a) **1’** after the heat treatment at 110 °C under vacuum for 5 hours, (b) **1’** and (c) background from the sample holder. All the measurements were performed under the Ar.

Figure S5. Photographs of (a) **1** under the Ar atmosphere, (b) **1’** under the air. (c) Scanning electron microscope (SEM) image of **1’**.

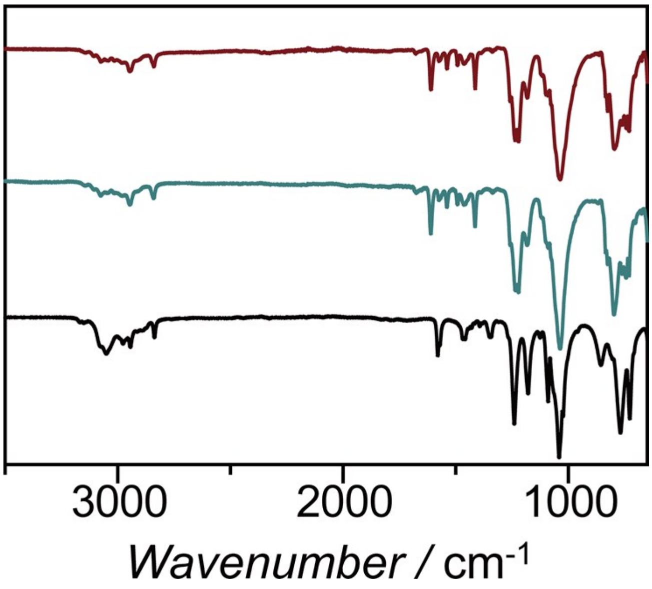

Figure S6. IR spectra of **1** (brown) under the Ar and **1’** (green) under the air and EtMeIm-Me_2PO_4 (black) under the air.

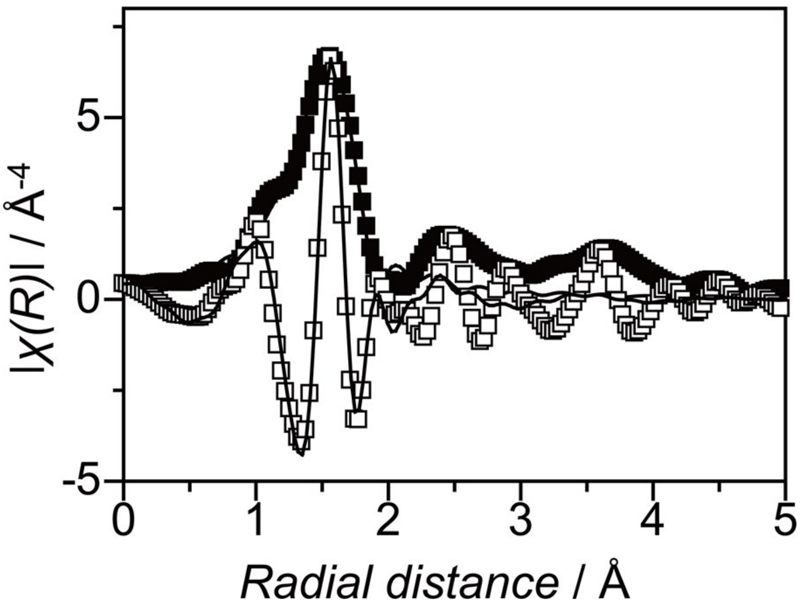

Figure S7. Comparison between experimental EXAFS data (squares) and best fits (line) for **1**, displayed in R-space contacting both magnitude of Fourier Transform (close squares) and real components (open squares).

Table S1. Parameters refined by fitting the EXAFS spectrum of **1**.

Shell	*N*	*r* / Å	σ^2 / Å^2	E_0 / eV	*R*-factor	S_0
Cu-O	3	1.989 (±0.011)	0.007 (±0.002)	6.3 (±1.6)	0.00542	1.085(±0.137)
Cu-N	2	2.000(±0.011)	0.007 (±0.002)	6.3 (±1.6)	0.00542	1.085(±0.137)

Table S2. Parameters refined by fitting the EXAFS spectrum of **1'**.

Shell	*N*	*r* / Å	σ^2 / Å^2	E_0 / eV	*R*-factor	S_0
Cu-O	2.7(±0.4)	1.981 (±0.013)	0.006 (±0.002)	6.5 (±2.0)	0.00830	1.085
Cu-N	1.8(±0.3)	1.991(±0.013)	0.006 (±0.002)	6.5 (±2.0)	0.00830	1.085

Table S3. Crystal data and structure refinement for **1** at 223 K and 298 K.

Compound	**1**	**1**
Empirical formula	$C_{22}H_{37}CuN_4O_{12}P_3$	$C_{22}H_{37}CuN_4O_{12}P_3$
Formula weight (g mol^{-1})	706.00	706.00
Temperature (K)	223(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
Unit cell dimensions	a = 22.221(4) Å	a = 22.240(4) Å
	b = 23.702(5) Å	b = 23.915(5) Å
	c = 23.882(5) Å	c = 24.189(5) Å
	α = 90°	α = 90°
	β =90°	β =90°
	γ = 90°	γ = 90°
Volume (Å^3)	12578(4)	12865(4)
Z	16	16
ρ (g cm^{-3})	1.491	1.458
F(000)	5872	5872
Theta range for data collection	3.005° to 27.520°	2.998° to 27.471°
Limiting indices	$-28 \leq h \leq 28$	$-28 \leq h \leq 28$
	$-29 \leq k \leq 30$	$-29 \leq k \leq 31$
	$-30 \leq l \leq 30$	$-31 \leq l \leq 30$
Reflections collected / unique	97211 / 14423	100286 / 14683
Data / restraints / parameters	14423 / 14 / 806	14683 / 13 / 879
GOF	1.007	1.127
R_1,wR_2 [I□2σ(I)]	R_1 = 0.0853	R_1 = 0.0959
	wR_2 = 0.1696	wR_2 = 0.2488
R_1,wR_2 (all data)	R_1 = 0.1930	R_1 = 0.1441
	wR_2 = 0.2097	wR_2 = 0.2843
Largest diff. peak and hole (e Å^3)	0.867 and −0.441	1.311 and −1.845