Supporting information for

Order-to-disorder structural transformation of a coordination polymer and its influence on proton conduction

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Synthesis of compounds

All of the chemicals and solvents used in the syntheses were reagent-grade and used without further purification. Synthesis of powder samples of 1 and 1’: Copper chloride dihydrate (170 mg, 1 mmol), imidazole (68 mg, 1 mmol), and phosphoric acid (85%, 134 μL, 2 mmol) were put into a 10 mL Teflon jar with two steel-cored 10 mm Teflon balls. The mixture was ground for 60 minutes in a Retch MM200 grinder mill operating at 25 Hz. The powder obtained was washed with ethanol to get dry pure phase 1. We heated 1 at 130 °C for 6 hours under vacuum condition to prepare 1’. Deuterated 1 and deuterated 1’ were synthesized by imidazole-D4.

Other physical measurements

Thermogravimetry analysis (TGA) was obtained using a Rigaku TG8120 under flowing nitrogen with 10 K min^{-1} ramp rate. Sample preparations for TGA were conducted under air. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT 2200 Ultima diffractometer with CuKα anode. Infra-red (IR) Spectroscopy was obtained using a Nicolet ID5 ATR operating at ambient temperature. Solid state 2H static NMR spectra were recorded on a Bruker ADVANCE 400 MHz spectrometer, using a quadrupole echo pulse sequence.

Impedance analyses were performed as following. Sample powders (ca. 25-30 mg) were pressed at 500 kg N for 2 minutes and sandwiched between two gold electrodes with 5 mm of diameter. 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 measurement cell was filled with nitrogen at atmospheric pressure before recording the measurements. ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

Cu K-edge XAFS spectra of these materials were measured at the BL5S1, hard X-ray XAFS
beamline, at Aichi Synchrotron Radiation Center (AichiSR; Aichi Science and Technology Foundation, Aichi, Japan). The XAFS 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\textsubscript{2} (100%) and N\textsubscript{2}/Ar (25/75%). Higher harmonic X-ray was cut off with proper glancing angle of Rh-coated collimating and focusing mirrors.

Temperature programmed desorption-mass spectrometry (TPD-MS) was performed by using a Rigaku TPD type R Photo. Sample (ca. 10mg) in silica capillary was set into a furnace, and heated from room temperature to 400°C at the rate of 10 K min\textsuperscript{-1} under He gas flow of 300 cm\textsuperscript{3} min\textsuperscript{-1}. The MS uses an electron impact ionization and Quadrupole mass analyzer. TPD-MS data were obtained by monitoring a range of 1 to 200 amu. Elemental analyses (C, N, H, Cl) were performed on a MICRO CORDER JSL JM10 apparatus. An automatic quick furnace (AQF-100, MITSUBISHI Chemical Corporation) and an ion chromatography system (ICS-1000, Dionex Corporation) were used to examine the total amount of chloride in 1 and 1’.

Figure S1. Powder X-ray diffraction patterns of (a) simulation from the crystal structure of 1 (b) 1 at 70 °C (c) 1 at 90 °C (d) 1 at 130 °C under N\textsubscript{2} (e) 1’ at 25 °C.
Figure S2. TGA profiles of (black line) 1 and (dot line) 1’ from 25 to 500 °C under N₂.

Figure S3. Infrared spectra of (a) bulk imidazole (b) 1 and (c) 1’.
Figure S4. Temperature programmed desorption (TPD) (gray line) and mass spectrometry (black line) traces of 1, emission of (a) H$_2$O, (b) HCl and (c) ImH$_2$ from 25 to 400 °C, heated under argon at 5 °C min$^{-1}$.

Figure S5. Powder X-ray diffraction patterns of (a) deuterated 1 and (b) deuterated 1’ at 25 °C.
**Figure S6.** TGA profiles of (black line) deuterated 1 and (dot line) deuterated 1’ from 25 to 500 °C under N₂.

**Figure S7.** Arrhenius plot of H⁺ conductivity of deuterated 1’ under N₂ atmosphere from 30 °C to 130 °C. Pellet thickness is 0.72 mm.
Figure S8. Time dependence on H$^+$ conductivity of 1' at under N$_2$ atmosphere at 100 °C.

Table S1. Results of elemental analyses of 1 and 1’.

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<tr>
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<th>1 / mol%</th>
<th>1’ / mol%</th>
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<tbody>
<tr>
<td>C</td>
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