

Supporting information for

Integration of Intrinsic Proton Conduction and Guest-accessible Nanospace into a Coordination Polymer

Daiki Umeyama, Satoshi Horike, Munehiro Inukai, Susumu Kitagawa

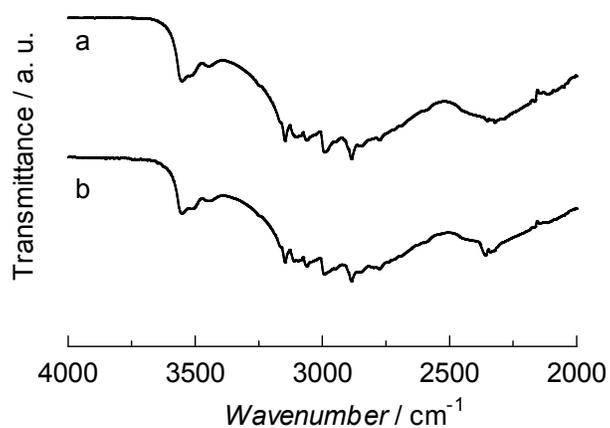


Figure S1. Infrared spectra of (a) **1** and (b) benzimidazole.

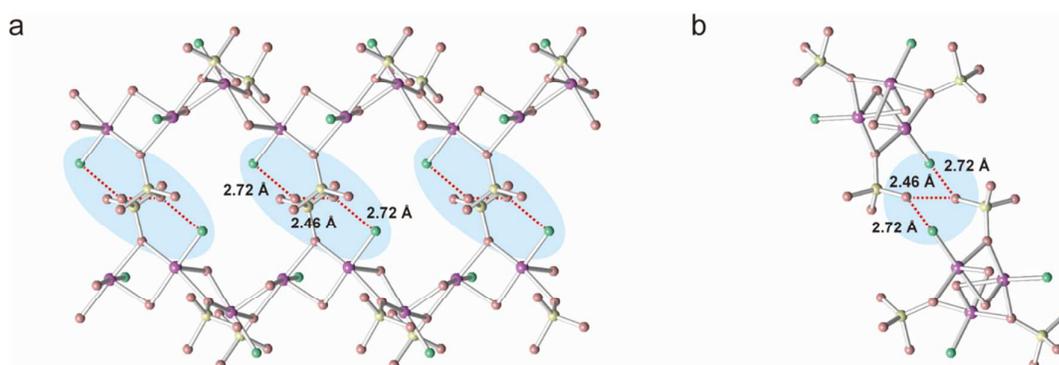


Figure S2. (a, b) Hydrogen bonds between the two chains of **1** (a) along the *a* direction and (b) viewed from the *a* direction. Zn, P, O, N, C, are purple, yellow, red, blue, and gray, respectively. H atoms have been omitted. O-O distances in hydrogen-bonding length are represented by red dashed lines. Hydrogen-bonding domains are represented by blue ellipses.

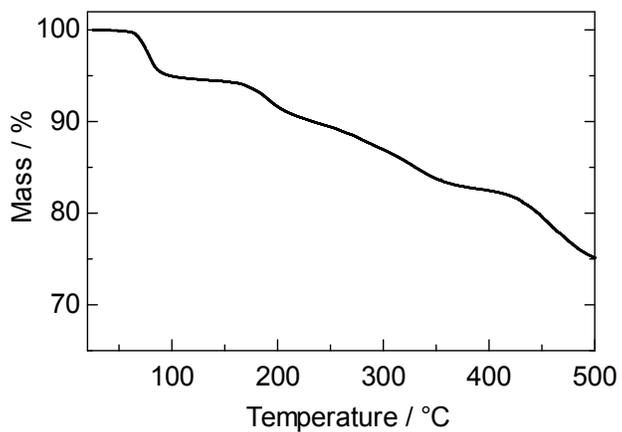


Figure S3. Thermogravimetric analysis of **1** from 25 to 500 °C under N₂.

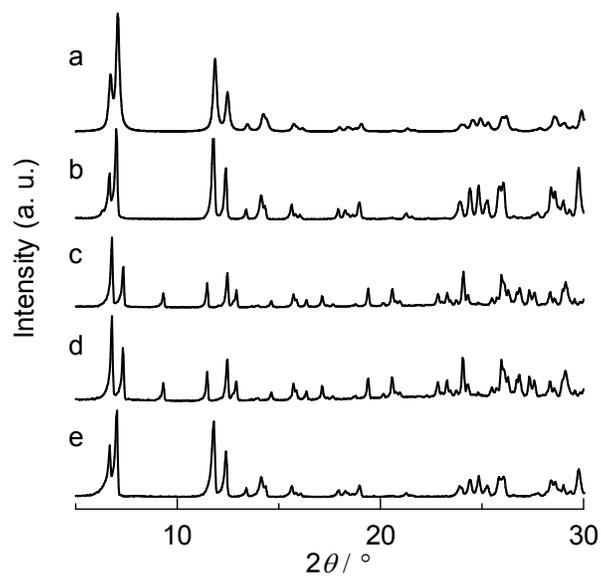


Figure S4. Powder X-ray diffraction of (a) simulation from the crystal structure of **1**, (b) **1** at 60 °C, (c) **1** at 80 °C, (d) **1** at 140 °C under N₂, (e) **1'** after kept under humid condition for one day.

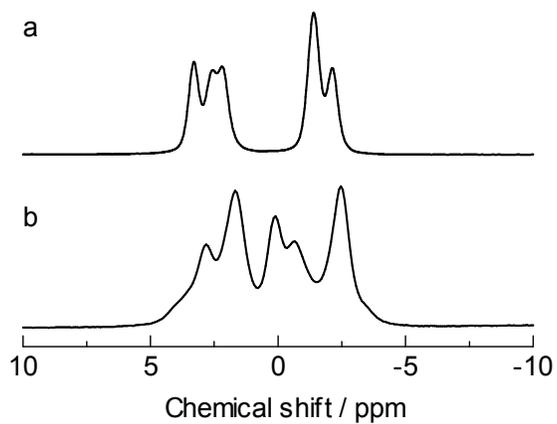


Figure S5. ^{31}P CPMAS solid-state NMR spectra of (a) **1** at 25 °C and (b) **1'** at 25 °C.

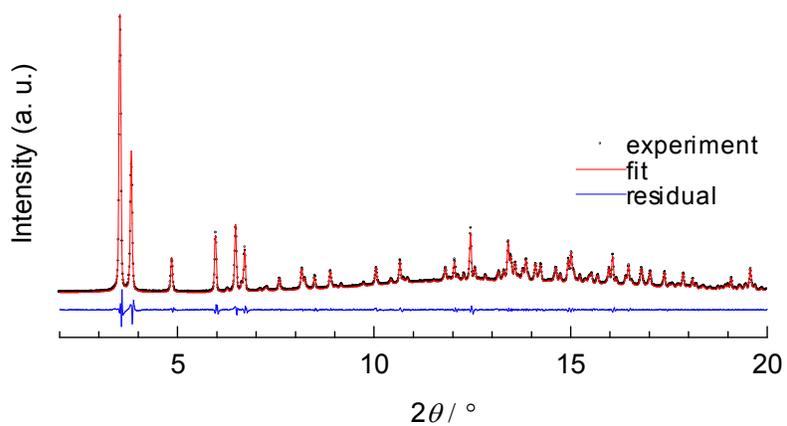


Figure S6. Pawley fitting analysis of **1'**. Space group is $P2_1/c$. $a = 7.7007(1) \text{ \AA}$, $b = 15.3296(3) \text{ \AA}$, $c = 24.1360(6) \text{ \AA}$, $\beta = 98.507(2)^\circ$, $V = 2817.9 \text{ \AA}^3$. $R_p = 1.49\%$, $R_{wp} = 2.34\%$

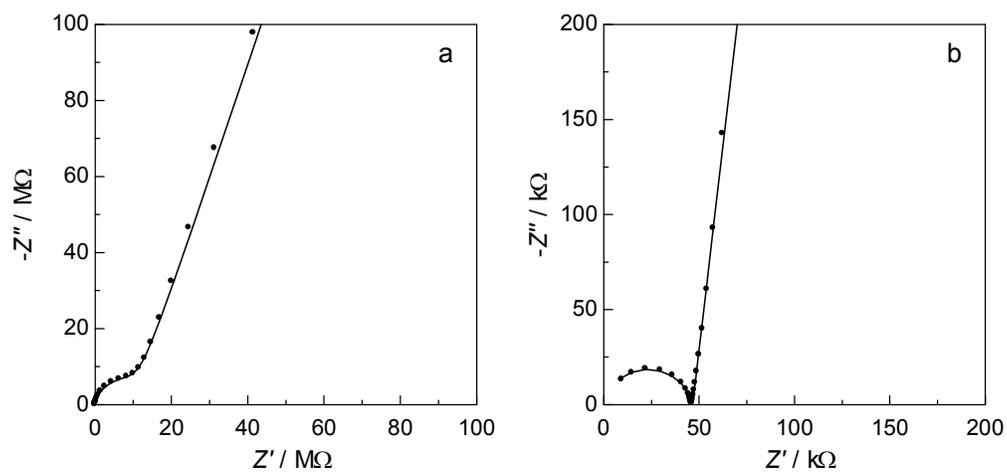


Figure S7. Nyquist plots for (a) **1** at 60 °C and (b) **1'** at 30 °C. Black • are experimental data, and lines are simulated values from equivalent circuits.

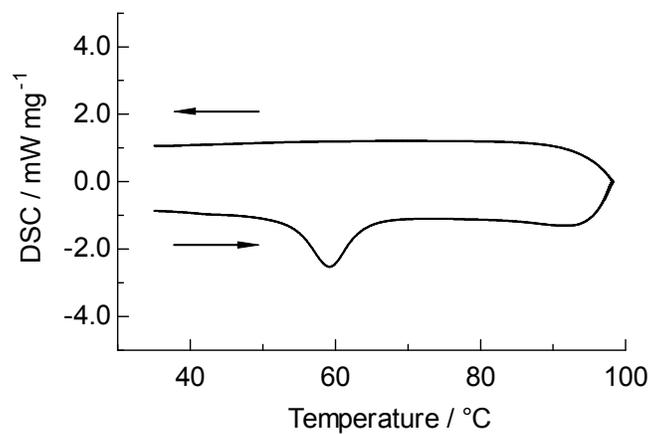


Figure S8. DSC profile of **1'** from 30 °C to 100 °C.

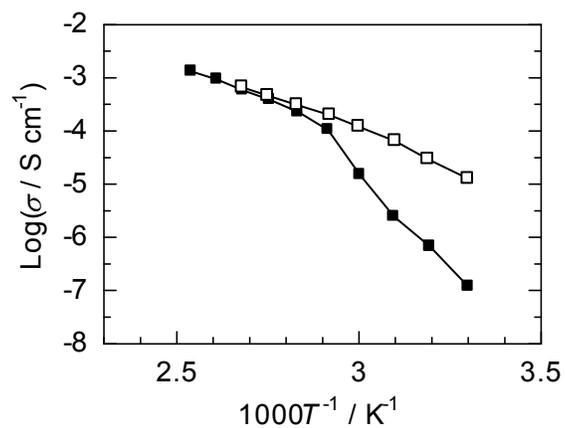


Figure S9. Arrhenius plots of the anhydrous conductivity of **1'** under atmospheric N₂. Heating (■) and cooling (□) processes.

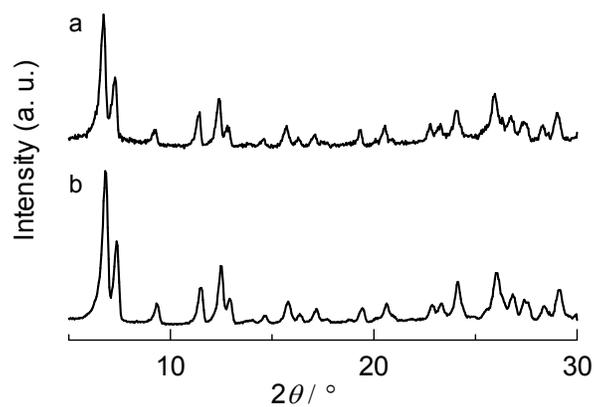


Figure S10. Powder X-ray diffraction of **1'** at 25 °C under methanol pressure at (a) 0 kPa, (b) 10 kPa.

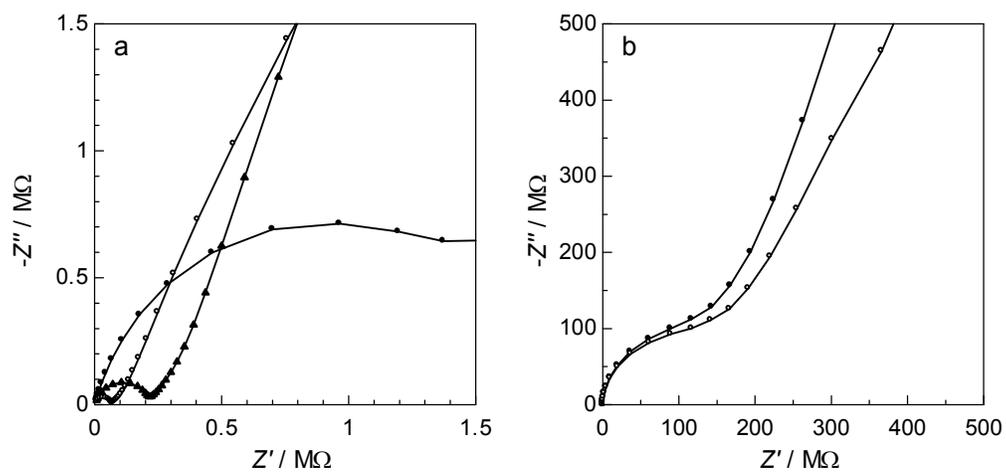


Figure S11. Nyquist plots under methanol pressure at 25 °C. (a) **1'** at 0 kPa (black circle), 4 kPa (black triangle), 8 kPa (white circle) and (b) **1** at 0 kPa (black circle), 8 kPa (open circle)

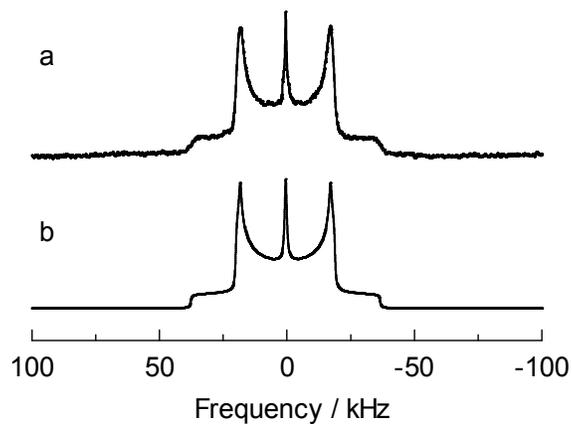


Figure S12. ^2H solid state NMR spectra of (a) **1'** \supset CD_3OH (static) and (b) fitting with $Q_{\text{eff}} = 50$ kHz and $\eta = 0.048$ for Pake doublet.