Supporting information for

Glass-phase coordination polymer displaying proton conductivity and
guest-accessible porosity

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Table S1. Crystallographic data for 1
S1. Syntheses

Syntheses of \( [\{\text{Zn}_2(\text{HPO}_4_2)(\text{H}_2\text{PO}_4)\} (\text{ClbimH}^+)_2 \cdot (\text{H}_2\text{PO}_4) \cdot (\text{MeOH})]_n \) (1), activated 1 (1a), and glass-form 1 (1g)

All chemicals employed were obtained from commercial suppliers and used without further purification. ZnO (81 mg, 1 mmol), 5-Chloro-1H-benzimidazole (153 mg, 1 mmol), phosphoric acid (85% solution, 205 µl, 3 mmol) and MeOH (200 µl) were stirred in a mortar until the mixture become paste. The obtained red paste was washed with MeOH three times to get dry pure-phase. 1 was heated at 120°C under vacuum for 6 hours to obtain activated 1a. Glass-form 1 was prepared by melt-quenching. 1a was put in an oven preheated at 150 °C and stayed for 30 min. The molten 1a was cooled in air at room temperature to obtain 1g. ZnO (81 mg, 1 mmol), 5-Chloro-1H-benzimidazole (153 mg, 2 mmol), phosphoric acid (85% solution, 205 µl, 3 mmol) and MeOH (200 µl) were stirred in a vial and let the reagents react at room temperature for 6 h to obtain single crystals.
S2. Physical measurements

X-ray powder diffraction (XRPD) patterns were collected on a Rigaku SmartLab and Rigaku MiniFlex II with CuKα radiation. Thermogravimetry analysis (TGA) in the temperature range of 303-773 K was performed using a Rigaku Thermo plus EVO2 under flowing nitrogen with 20 K min⁻¹ ramp rate. The adsorption and desorption of water and methanol 298 K were measured by a BELSORP-aqua instrument. ¹H-³¹P MAS and ¹H-³¹P cross polarization MAS (CP-MAS) NMR spectra of 1 and 1a were recorded on a Bruker ADVANCE 400 MHz spectrometer. Static magnetic field and MAS frequency were 9.4 T and 10 kHz. The signals were acquired under two-pulse phase modulating (TPPM) proton decoupling. The recycle delay and contact time were 15 s and 2 ms. All MAS NMR of 1g were performed on a JNM-ECA600. Static magnetic field and MAS frequency were 14.1 T and 70 kHz. The recycle delay and contact time were 20s and 2 ms. Two-dimensional ¹H-¹H double-quantum filter (2D ¹H-¹H DQNMR) spectra were obtained with back-to-back (BaBa) pulse sequence. To assign peaks in the ¹H MAS spectra, ¹H-¹⁴N multiple Quantum Coherence (HMQC) and ¹H-³¹P double cross polarization (double CP) spectra were carried out. WALTZ-16 was used as decoupling pulse sequence. The contact time for double CP was 3 ms. Single crystal X-ray diffraction data at 223 K were collected using a Rigaku X-ray diffractorometer with a confocal monochromated MoKα radiation. The deposited number of Cambridge Crystallographic Data Centre (CCDC) is 1907325.
S3. Powder X-ray diffraction patterns (PXRD)

Fig. S1. PXRD patterns of (a) 1, (b) 1a, (c) 1g, (d) 1a after heating at 80 °C under 95 % relative humidity, (e) 1g after heating at 80 °C under 95 % relative humidity, and (f) calculation from crystal structure of 1. The PXRD patterns after the heating under the humid condition display large differences compared to those of original CPs, suggesting structural transition to another crystal structure.
**Fig. S2** PXRD patterns of 1 (black), 1a (red), and 1a after adsorption of MeOH (green) in the range of 4-15°. After the removal of MeOH, some peaks related 2-D frameworks (e.g. 5.5° and 11.2° indicating [010] and [020]) are slightly shifted, indicating shrinkage of the distance between 2-D frameworks. After adsorption of MeOH in 1a, the peaks back to the original positions. This indicates that the layer distance expands and backs to the original on during the adsorption of MeOH.
S4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Fig. S3. TGA profiles of 1 (black) and 1a (red). The weight loss in the profile of 1a at 130°C is 3.6%, which is well corresponding to that of MeOH (calculated weight loss 3.6%).
Fig. S4. DSC curves of (a) 1a and (b) 1g.
S5. Adsorption isotherms

Fig. S5. Adsorption isotherms of methanol at 298 K for 1a (circle) and 1g (square). Closed and open circles represent adsorption and desorption, respectively.
S6. AC impedance measurement

![Graph showing proton conductivity of 1g under various humidity conditions at 298 K.](image)

**Fig. S6.** Proton conductivity of 1g under various humidity conditions at 298 K.
S7. Extended X-ray absorption fine structure analyses (EXAFS)

Fig. S7. RDFs from Zn K-edge EXAFS spectra of 1 (black), 1a (red), and 1g (blue) at room temperature.
**S8. Solid-state NMR analyses**

![Solid-state NMR spectra](image)

**Fig. S8.** $^{31}$P MAS NMR of (a) 1a and 1g at room temperature. Black and blue lines correspond to the experimental and fitted spectra, respectively. The fitted spectra are composed of the spectra of the uncoordinated phosphate (red) and the coordinated phosphates (gray). The ratio of peak intensities between uncoordinated phosphates and coordinated phosphates is 24:76 (1a) and 23:77 (1g), respectively. The ratios are approximately equal to the stoichiometric ratio of 1a (25:75), suggesting that uncoordinated phosphates are tightly encapsulated as well as the crystal structure of 1.
Fig. S9. (a) 1D $^1$H–$^{31}$P double CP-MAS and (b) 1D $^1$H–$^{14}$N hetero-nuclear multiple quantum coherence (HMQC) spectrum of 1g. The $^1$H–$^{31}$P double CP-MAS and $^1$H–$^{14}$N HMQC spectrum includes peaks at 9.5 and 10.5–13.0 ppm assigned to the O–H moiety of the phosphate ions within the 2D frameworks and a peak at 14.5 ppm assigned to the N–H moiety of Clbim. Other large peaks in the spectrum can are assigned to the C–H moiety of Clbim.
Fig. S10. 2D $^1$H–$^1$H DQNMR spectrum of 1g at room temperature. The red lines connect the correlation peaks between O–H and C–H (green), N–H and C–H (blue), and N–H and O–H (yellow). The 2D $^1$H–$^1$H DQNMR spectrum of 1g is characterized by the presence of three peaks pointing to a correlation between Clbim (N–H and C–H) and the 2D frameworks (O–H). These correlations reflect the homogenous distribution of Clbim molecules in the 2D frameworks.
### S9. Single crystal X-ray diffraction

**Table S1.** Crystallographic data for 1.

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<tr>
<th>Compound</th>
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