

Supplementary Material for:

Organotemplate-Free Synthesis of an Open-Framework Magnesium Aluminophosphate with Proton Conduction Property

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Synthesis

The reagents and solvents employed in the synthesis were commercially available and used as received without further purification. JU102 was prepared under hydrothermal condition in the reaction system of $\text{MgO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. Typically, pseudoboehmite (Al_2O_3 , 62%) and magnesium acetate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were dispersed in a solution of orthophosphoric acid (85 wt%) in water under vigorous stirring at room temperature. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0\text{Al}_2\text{O}_3 : 2.0\text{MgO} : 1.45\text{P}_2\text{O}_5 : 290\text{H}_2\text{O}$ was formed, which was heated under autogenous pressure at 180°C in a 7 mL Teflon-lined stainless steel autoclave for 12 hours. The crystals were washed in distilled water and dried at room temperature overnight.

Characterization

Powder X-ray diffraction (PXRD) was collected on a Rigaku D/max-2550 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric analysis (TG) was carried out on a TA Q500 analyzer in air with a heating rate of $10^\circ\text{C min}^{-1}$ from RT to 800°C . The circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter with KBr pellets. Nitrogen adsorption isotherm at -196°C was performed in an apparatus of Micromeritics ASAP 2020. The ^1H MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probehead whose channel was tuned to 400.18 MHz, using a magnetic field of 9.39T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 12 kHz rate. The experiments were conducted at a contact time of 2 ms. Total of 16 scans were recorded with 6 s recycle delay for each sample. All ^1H MAS chemical shifts were referenced to the resonances of adamantane ($\text{C}_{10}\text{H}_{16}$) standard ($\delta=1.91$). Vacuum in-situ variable temperature XRD was collected on a D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The as-synthesized sample was smeared on a platinum filament and data were collected from room temperature to 550°C with a heating rate of $10^\circ\text{C min}^{-1}$.

Several tablets of JU102 and JU102-c (9.4~10.4 mm in diameter and 1.28~1.30 mm in thickness) were prepared by pressing samples on a tableting machine for the proton conductivity. The measurement was carried out via impedance spectroscopy on a Solartron 1260 impedance analyzer over the frequency range from 1(or 10) Hz to 1 MHz and an applied a.c. voltage of 500 (or 1000) mV. The humidity was obtained by continuously ventilating wet nitrogen. The measurements on pellets in direct contact with water were carried out after 24 h of immersion in deionised water, and the various temperature were obtained by using water bath. The Conductivity was calculated using the following equation : $\sigma = l / (\text{RsS})$, where l and S are the thickness(cm) and cross-sectional area (cm^2) of the pellet respectively, and Rs that was extracted directly from the impedance plots, is the bulk resistance of the sample (Ω).

Structural Determination

Suitable single crystal of JU102 with dimensions of $0.210 \times 0.200 \times 0.180 \text{ mm}^3$ was selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Bruker SMART APEX II CCD diffractometer by oscillation scans using graphite-

monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at temperature of $23 \pm 2 \text{ }^\circ\text{C}$. Cell refinement and data reduction were accomplished with the SAINT processing program. The structure was solved in the space group $P2_1$ by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package. The heaviest atoms of Al, Mg, P and O could be unambiguously located, and the H atoms were subsequently located in the difference Fourier maps. All non-hydrogen atoms were refined anisotropically.

Table S1 Crystal data and structure refinement for JU102

Compound	JU102		
Empirical formula	Al H ₅ Mg O ₁₀ P ₂		
Formula weight	278.27		
Temperature	296(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	<i>P</i> 2 ₁		
Unit cell dimensions	<i>a</i> = 5.0119(11) Å	<i>α</i> = 90°	
	<i>b</i> = 7.7690(17) Å	<i>β</i> = 102.595(3)°	
	<i>c</i> = 9.995(2) Å	<i>γ</i> = 90°	
Volume	379.81(14) Å ³		
<i>Z</i>	2		
Density (calculated)	2.433 g/cm ³		
Absorption coefficient	0.812 mm ⁻¹		
<i>F</i> (000)	280		
Theta range for data collection	2.088 to 28.328°.		
Index ranges	-6≤ <i>h</i> ≤5, -10≤ <i>k</i> ≤10, -11≤ <i>l</i> ≤13		
Reflections collected	2795		
Independent reflections	1689 [<i>R</i> (int) = 0.0159]		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.8677 and 0.8480		
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data / restraints / parameters	1689 / 6 / 143		
Goodness-of-fit on <i>F</i> ²	1.114		
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0243, <i>wR</i> ₂ = 0.0616		
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0252, <i>wR</i> ₂ = 0.0623		
Absolute structure parameter	-0.02(16)		

Table S2 Hydrogen bonds for JU102 [\AA and $^\circ$]

D-H \cdots A	d(D-H)	d(H \cdots A)	d(D \cdots A)	\angle (DHA)
O(8)-H(8) \cdots O(5)#7	0.962(14)	1.713(18)	2.659(4)	167(4)
O(9)-H(9A) \cdots O(1)#7	0.955(14)	2.57(4)	3.254(4)	129(4)
O(9)-H(9A) \cdots O(6)	0.955(14)	2.47(4)	3.161(4)	129(4)
O(9)-H(9B) \cdots O(3)#8	0.960(14)	2.225(19)	3.168(4)	167(5)
O(10)-H(10A) \cdots O(7)#9	0.967(14)	1.717(16)	2.678(4)	172(4)
O(10)-H(10B) \cdots O(4)#6	0.956(14)	1.927(16)	2.873(4)	170(5)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, y+1/2, -z+2$ #2 $x-1, y, z$ #3 $-x+1, y-1/2, -z+1$
#4 $x+1, y, z$ #5 $-x+1, y+1/2, -z+1$ #6 $-x+1, y-1/2, -z+2$
#7 $-x+2, y-1/2, -z+2$ #8 $x, y, z+1$ #9 $-x, y+1/2, -z+2$

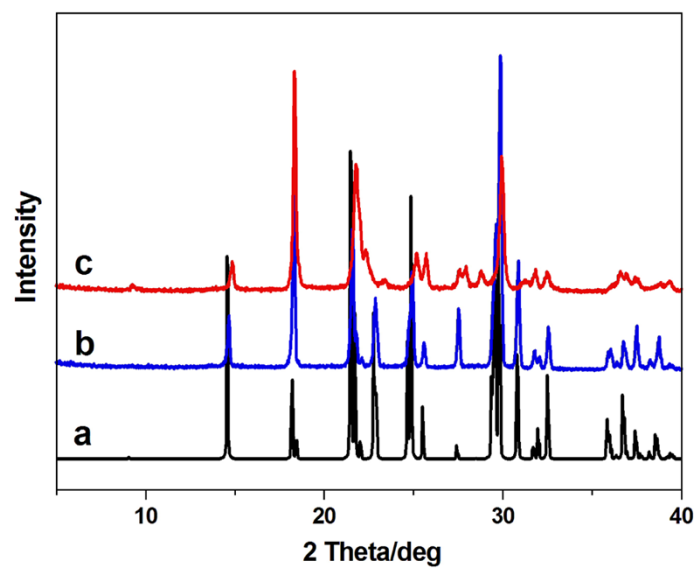


Fig S1 Powder X-ray diffraction patterns of (a) simulated JU102 and experimental (b) JU102 and (c) JU102-c.

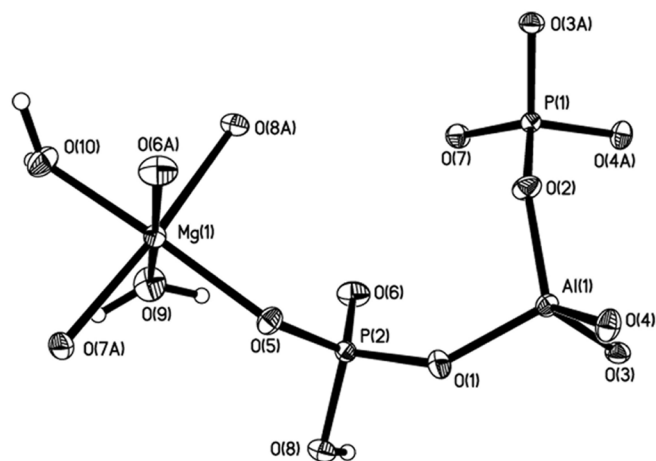


Fig S2 Thermal ellipsoid of JU102 given at 50% probability, showing the atomic labeling scheme.

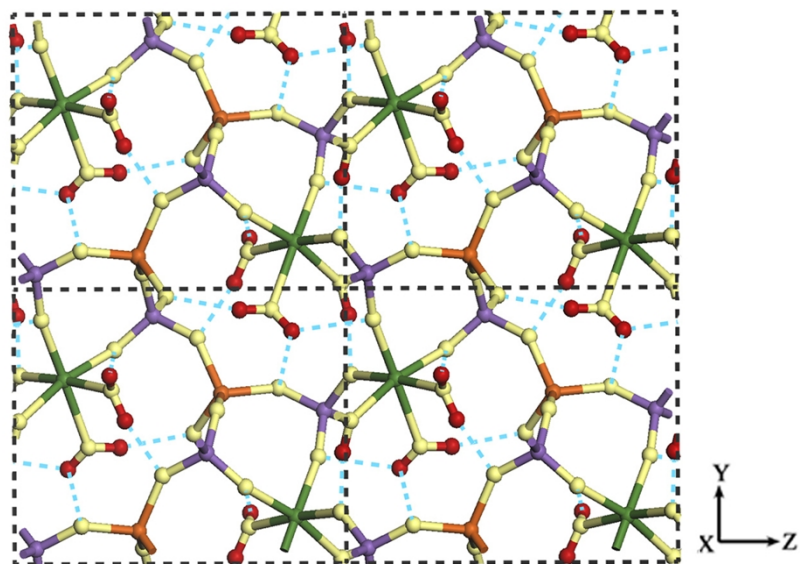


Fig S3 The H-bonding network in JU102.

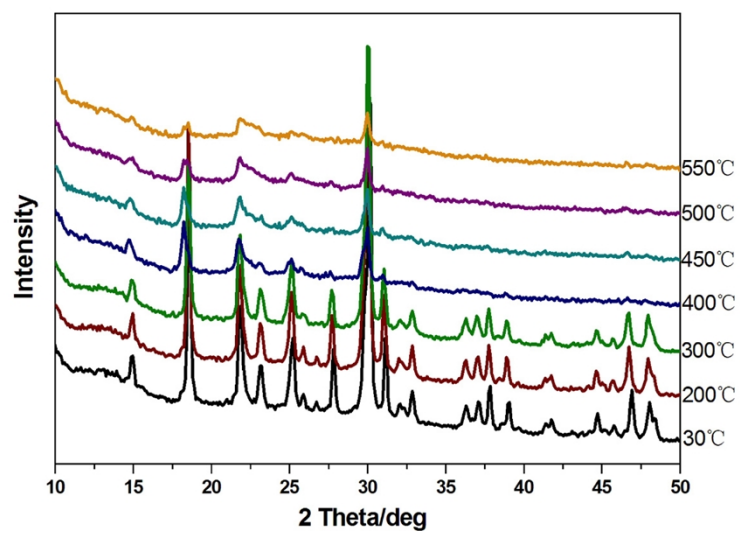


Fig S4 Vacuum in-situ variable temperature XRD patterns of JU102.

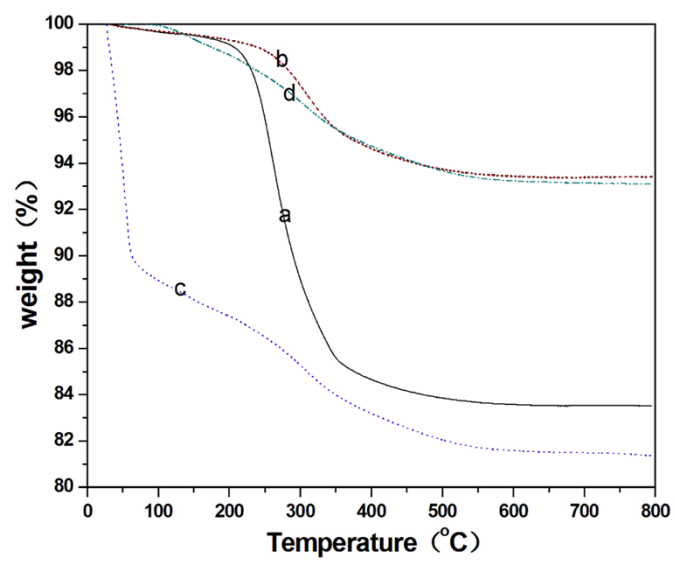


Fig S5 TG curves of (a) JU102, (b) JU102-c, (c) JU102-c immersed in water and (d) JU102-c immersed in water treated by heating at 80 °C.

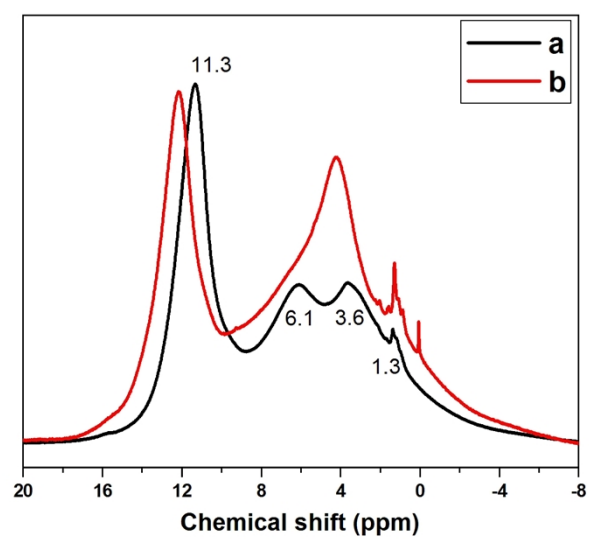


Fig S6 ^1H MAS NMR spectra of (a) JU102 and (b) JU102-c. The small signals around 1.3 ppm may be caused by the little adsorption water.

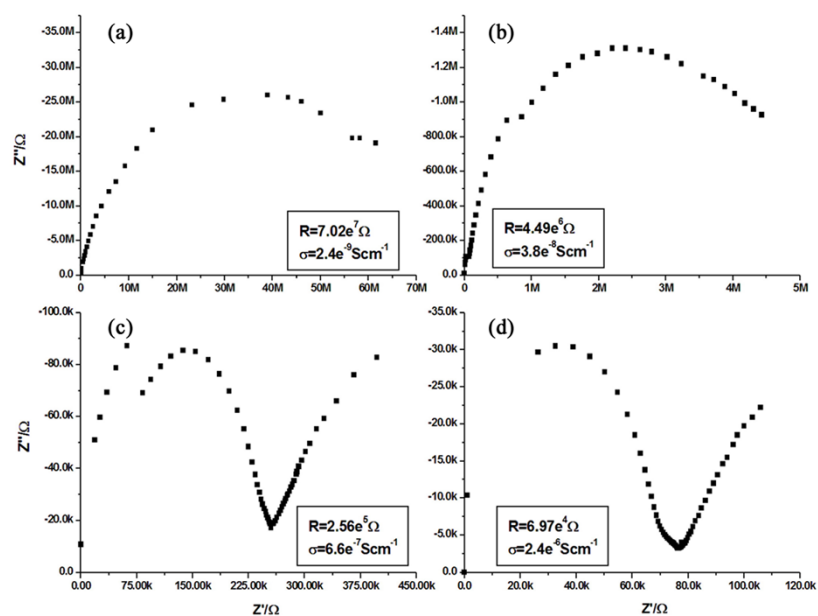


Fig S7 a.c. impedance plots of JU102 at different humidities by ventilating wet nitrogen for (a) 0h, (b) 1h, (c) 4h and (d) 12h.