

Supporting Information

Ionothermal Synthesis and Proton-Conductive Property of NH₂-MIL-53 MOF Nanomaterials

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Experimental Section

1. Chemicals

AlCl₃•6H₂O (Aladdin Reagent, Co., Ltd, Shanghai, China, 99%), 2-aminoterephthalic acid (NH₂-H₂BDC, Energy Chemical, Shanghai, China, 98%), ionic liquid of 1-ethyl-3-methyl-imidazolium bromide (Shanghai Cheng Jie Chemical Co. Ltd, 99%), dimethylformamide (DMF), and ethanol were used as received.

2. Synthesis of NH₂-MIL-53(Al)_{it}

The typical preparation procedure involves firstly dissolving 190 mg NH₂-H₂BDC into 1 g melted 1-ethyl-3-methyl-imidazolium bromide at 100 °C under stirring until a clear solution was obtained; subsequently adding 127 mg AlCl₃•6H₂O into the solution above. The resulted clear precursor in a 10 mL closed glass vessel was heated at 150 °C for 7 days in a preheated oven, and then solid crystals were obtained. After cooling down, the product was cleaned with repeated centrifugations for 5 times using ethanol (10000 r/min, 10 minutes for each cycle) in order to remove the supernatant ionic liquid solvent. The collected powder was dried at 85 °C, and this sample is

designated as NH₂-MIL-53(Al)_{it}. The reference sample (designated as MIL-53(Al)_{it}) was prepared according to the same protocol.³³ NH₂-MIL-53(Al)_{ref(as)} sample was synthesized from a liquid mixture of 493.6 mg AlCl₃•6H₂O and 379.6 mg NH₂-H₂BDC in 5 mL water at 150 °C for 5 h according to our previous procedure.³⁶ The obtained powder was first treated in DMF at 150 °C for 5 h, followed by repetitive washing (10 mL DMF, three times), and then activated under vacuum to remove the solvent at 150 °C overnight prior to further tests (designated as NH₂-MIL-53(Al)_{ref}).

3. Characterizations

The crystalline structures of NH₂-MIL-53(Al)_{it} crystals were determined by X-ray diffraction (XRD) measurements using Rigaku D/MAX2550 diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) running at a voltage of 50 kV and a current of 200 mA. The morphology of this sample was observed on field-emission scanning electron microscope (FE-SEM: Hitachi SU8010) and transmission electron microscope (TEM: JEOL JSM-3010). Fourier transform infrared spectra (FTIR) were collected on a Nicolet Impact 410 FTIR spectrometer at room temperature in the range of 400-4000 cm⁻¹, with potassium bromide pellets. Al content in NH₂-MIL-53(Al) was analyzed by inductively coupled plasma atomic emission spectrometer (ICPAES, Perkin Elmer Optima 3300DV), and C, H, N contents were determined using a Perkin Elmer 2400 Series II CHNS/O analyzer. Simultaneous thermal gravimetric and differential thermal analyses (TG-DTA) were performed on NH₂-MIL-53(Al)_{it} and NH₂-MIL-53(Al)_{ref} samples in air (10 °C min⁻¹) (Netzsch Sta 449c thermal analyzer). Based on the weight loss, the volume of ionic liquid occupied in pores (0.145 cm³) was calculated using the equation $V_{il}=m/\rho$ (V is the volume of ionic liquid, m is its mass, ρ is the density of 1.3 g cm⁻³). The pore volume in NH₂-MIL-53(Al) (0.167 cm³) was estimated from crystallography (Fig. S1)³⁵ using the equation of $V_{\text{pore}}=(m/M)*NA*(\pi r^2 a)$ with the following parameters per unit cell: m is NH₂-MIL-53(Al) mass without ionic liquid, M is the molar mass of 892 g mol⁻¹ with molecular formula of C₃₂N₄Al₄O₂₀H₂₄, NA is Avogadro's number, r is the pore radius (pore diameter of ~0.75 nm), $a=0.692$ nm, $b=1.767$ nm, $c=1.212$ nm. The pore filling factor

(0.87) is estimated from the difference between V_{il} and V_{pore} .

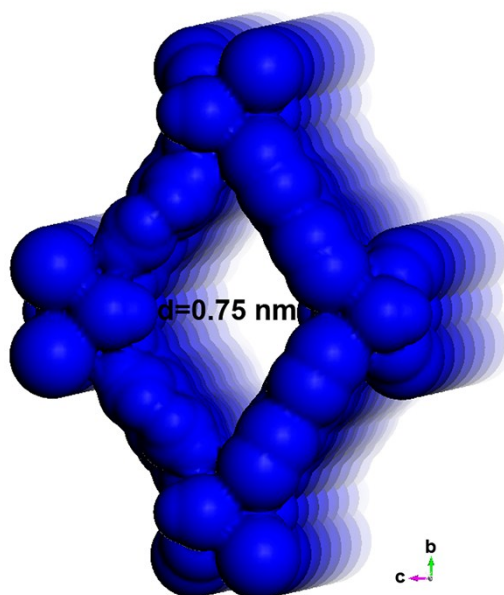


Fig. S1 Crystallographic structure of $\text{NH}_2\text{-MIL-53(Al)}$ unit cell.

4. Proton conductivity

Pellets with 13 mm in diameter and 0.85-0.95 mm thick were prepared by pressing material (about 150 mg) at 40 kN cm^{-2} . The proton conductivities of $\text{NH}_2\text{-MIL-53(Al)}_{it}$, $\text{NH}_2\text{-MIL-53(Al)}_{ref}$ and MIL-53(Al)_{it} samples were estimated in a quasi-four-probe method conductivity cells by the AC impedance spectroscopy technique. The impedances were measured with a frequency response analyzer/potentiostat (Princeton Applied Research PAR 2273, EG&GPARC, Princeton, NJ) over a frequency range from 0.1 Hz to 1 MHz, 10 mV ac perturbation and 0.0 V dc rest voltage. The samples were covered with silver paint to improve contact with the two copper blocking electrodes in a measurement cell, and placed in a temperature and humidity controlled environment. The Nyquist plot obtained from impedance measurement comprises a depressed semicircular arc at high frequency and a spur at low frequency. The conductivity (σ , S cm^{-1}) of the sample was calculated from the impedance data, using the relation $\sigma = L/RA$, where L (cm) is the thickness of the sample, A (cm^2) is the face area and R (Ω) is the sample resistance estimated by extrapolation of the high-frequency arc crossing to the real axis.⁹ The measurements

have been repeated three times to get reproducible results.

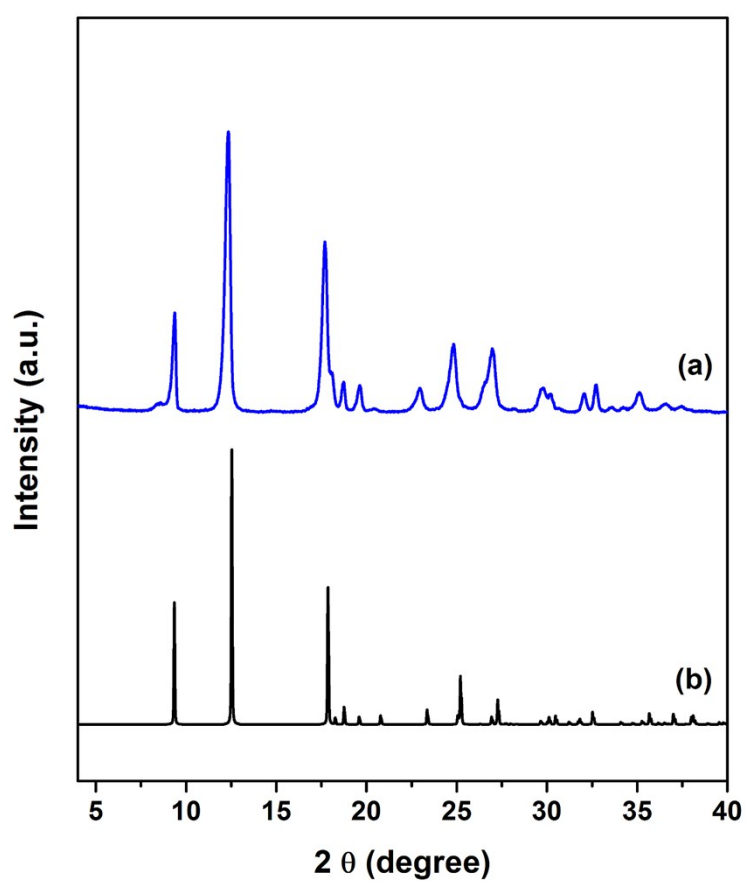


Fig. S2 XRD patterns of (a) $\text{NH}_2\text{-MIL-53(Al)}_{\text{ref}}$ and (b) simulated one from $\text{Al(OH)[NH}_2\text{-BDC]}\cdot\text{H}_2\text{O}$ single crystal.³⁵

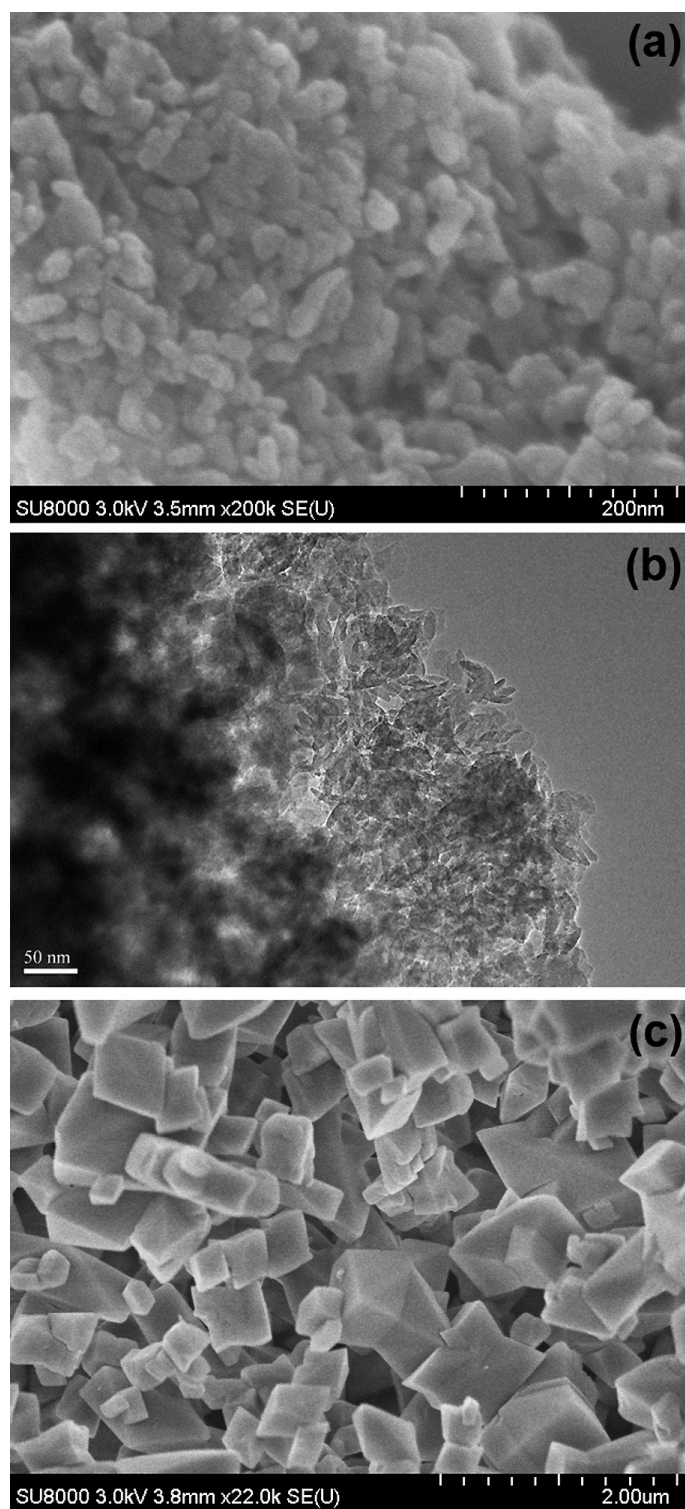


Fig. S3 Representative SEM (a) and TEM (b) pictures of $\text{NH}_2\text{-MIL-53(Al)}_{\text{it}}$, and SEM picture (c) of $\text{NH}_2\text{-MIL-53(Al)}_{\text{ref(as)}}$ samples.

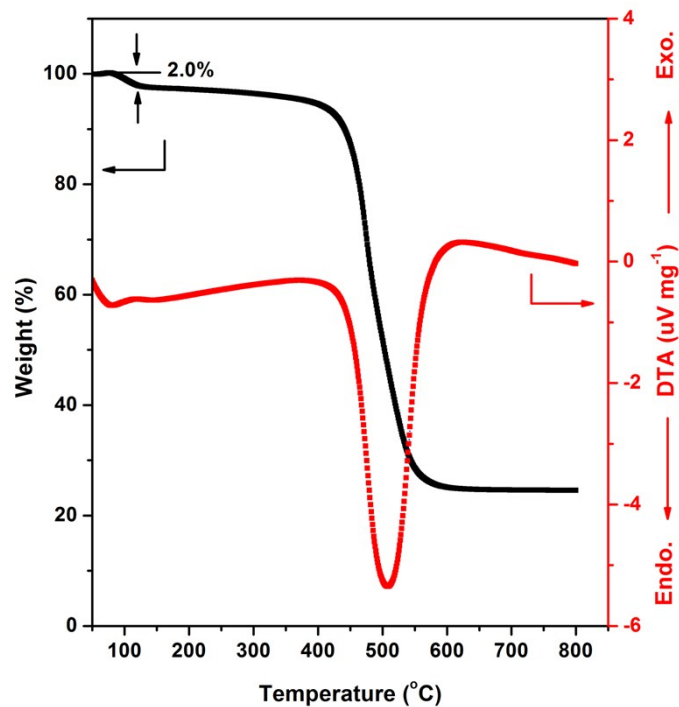


Fig. S4 TG-DTA curves of $\text{NH}_2\text{-MIL-53(Al)}_{\text{ref}}$ reference sample.

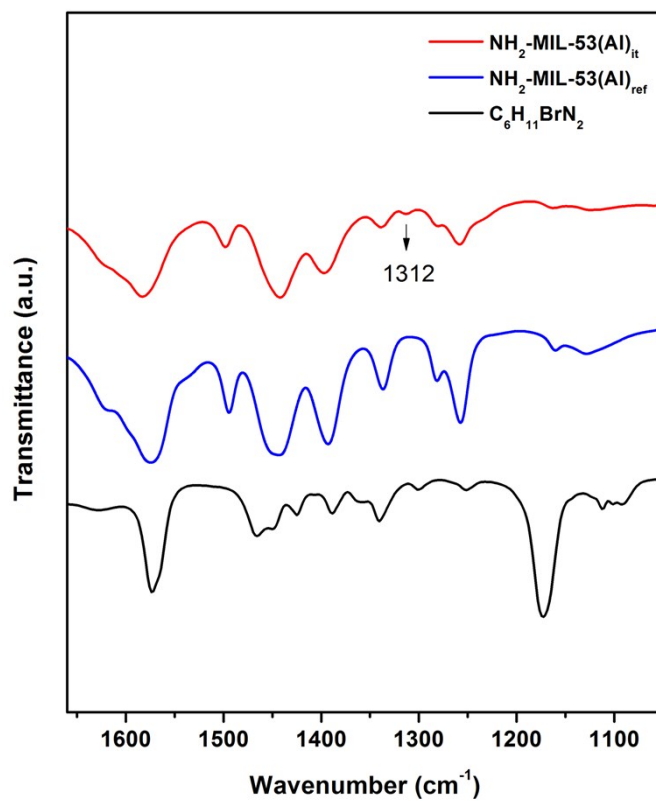


Fig. S5 IR spectra of $\text{NH}_2\text{-MIL-53(Al)}_{\text{it}}$, $\text{NH}_2\text{-MIL-53(Al)}_{\text{ref}}$ and 1-ethyl-3-methyl-

imidazolium bromide.

Table S1 Elemental analyses of $\text{NH}_2\text{-MIL-53(Al)}_{it}$ and $\text{NH}_2\text{-MIL-53(Al)}_{ref}$ samples.

Sample	N (wt.%) ^a	C (wt.%) ^a	H (wt.%) ^a	Al (wt.%) ^b	N/C	Al/C
$\text{NH}_2\text{-MIL-53(Al)}_{it}$	6.74	38.7	2.90	9.6	0.174	0.248
$\text{NH}_2\text{-MIL-53(Al)}_{ref}$	5.44	38.3	2.92	11.8	0.142	0.308

^a measured on CHNS/O analyzer.

^b measured on ICP spectrometer.

Elemental analysis cal. for $\text{NH}_2\text{-MIL-53(Al)}$ ($\text{Al(OH)[NH}_2\text{-BDC]}\cdot\text{H}_2\text{O}$): C, 39.83%; H, 3.32%; N, 5.81%; Al, 11.2%; N/C, 0.146; Al/C, 0.282. The similar values in N/C and Al/C ratios for $\text{NH}_2\text{-MIL-53(Al)}_{ref}$ and $\text{NH}_2\text{-MIL-53(Al)}$ suggest that $\text{NH}_2\text{-MIL-53(Al)}_{ref}$ has the same structure of $\text{Al(OH)[NH}_2\text{-BDC]}\cdot\text{H}_2\text{O}$.

Table S2 A summary of proton-conducting performances of different MOF materials tested under high temperatures and low humidity in recent reports.

MOFs	Temperature (°C)	RH (%)	Conductivity (S cm^{-1})	Ref.
$\text{NH}_2\text{-MIL-53(Al)}$	80	26	3.0×10^{-5}	This work
MOF-74	146	anhydrous	4.3×10^{-9}	15
In-IA-2D	90	anhydrous	1.18×10^{-5}	7
$\text{Zn(H}_2\text{PO}_4)_2(\text{TzH})_2$	45-150	anhydrous	$10^{-7}\sim 10^{-4}$	S1
Al(OH)(1, 4-ndc)	25-120	anhydrous	$10^{-8}\sim 10^{-5}$	27
$\text{Zn}_2(\text{ox})_3$	30-150	anhydrous	$10^{-5}\sim 10^{-4}$	S2
UiO-67	50-120	anhydrous	$10^{-7}\sim 10^{-3}$	S3
ZIF-8	80	20	10^{-8}	S4
$\text{La}_3\text{PP}_4(\text{H}_2\text{O})_6$	90-110	20	10^{-7}	8
Mg, Sr, Ba-BPTC	23-100	43-98	$10^{-8}\sim 10^{-4}$	12
$\text{Eu}_2(\text{CO}_3)(\text{ox})_2(\text{H}_2\text{O})_2$	25-100	40-90	$10^{-6}\sim 10^{-4}$	S5

Supplementary references:

1. D. Umeyama, S. Horike, M. Inukai, T. Itakura and S. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 12780-12785.
2. S. S. Nagarkar, S. M. Unni, A. Sharma, S. Kurungot and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2014, **53**, 2638-2642.
3. S. C. Liu, Z. F. Yue and Y. Liu, *Dalton Trans.*, 2015, **44**, 12976-12980.
4. P. Barbosa, N. C. Rosero-Navarro, F. N. Shi and F. M. L. Figueiredo, *Electrochim. Acta*, 2015, **153**, 19-27.
5. Q. Tang, Y. W. Liu, S. X. Liu, D. F. He, J. Miao, X. Q. Wang, G. C. Yang, Z. Shi and Z. P. Zheng, *J. Am. Chem. Soc.*, 2014, **136**, 12444-12449.