Electronic Supplementary Material (ESI)

Encapsulating NH_4Br in metal organic framework: achieving remarkable proton conduction in wide relative humidity range

Yihan Du[aϕ], Kun Zhang[aϕ], Ziya Liu[aϕ], Shaoxian Liu[b], Guoji Huang[a], Yang Huang[c], Qianqian Qin[a], Jiaxin Luo[a], Bingqing Xu[a*], Gen Zhang[a*]

[a.] *Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China*

[b.] *School of Environmental Science, Nanjing Xiaozhuang University, Nanjing, Jiangsu 211171, China*

[c.] *Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, and Joint International Research Lab of Lignocellulosic Functional Materials, Nanjing Forestry University, Nanjing, Jiangsu 210037, China*

* Correspondence authors

E-mail: bingqingxu@njust.edu.cn (B.X)

E-mail: zhanggen@njust.edu.cn (G.Z.)

Experimental section

1.1 Reagents.

$Cr(NO_3)_3 \cdot 9H_2O$ (99%), Terephthalic Acid (99%), HF (40% aqueous solution) and NH_4Br (98%) were supplied by Sinopharm Chemical Reagent Co. Ltd. of China. All chemical reagents were used as received without further purification.

1.2 Synthesis of MIL-101-Cr.

According to the literature,42 1.2 g Cr $(NO_3)_3 \cdot 9H_2O$ and 500 mg Terephthalic Acid were mixed with 15 mL deionized water and 1 mL HF (3mol/L). The reactant was heated to a reaction kettle and heated to 493 K for 6 hours, and the crude product was filtered after cooling. The crude products were heated at 343 K in DMF solution for 3 hours, then heated for 3 hours at 343 K in the ethanol solution. After two times of the above procedure, the sample were placed in DMF solution at 393 K for one week and then filtered. Finally, the product MIL-101-Cr was dried at 353 K.

1.3 Synthesis of NH_4Br@MIL-101-Cr.

200 mg MIL-101-Cr was placed in 10 mL saturated NH_4Br water solution for 24 hours at 298 K. After that, the product was filtered, washed with few water and was finally dried at 353 K.

1.4 General Characterizations.

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer, operated at 40 kV and 40 mA, with Cu Kα radiation (λ = 1.5418 Å), and the measurement was performed at ambient temperature in the range of 2θ = 5-50 degree with 0.02 degree/step. Thermo gravimetric analyses (TG) were performed on a Mettler Toledo TGA/DSC instrument in the range of 303-1073 K under a nitrogen flow (50 mL/min) at a heating rate of 5 K min^{-1}. Gas adsorptions were measured on a BELSORP-Max adsorption analyzer. Samples were pretreated under vacuum and 100 °C for 2 hours before adsorption test. Elemental analyses for C, H and N were performed with an Elementar Vario EL III analytic instrument. Infrared spectrum was tested under environmental conditions with a relatively humidity of 47%.

1.5 Proton Conductivity Measurement.

Powder sample of NH_4Br@MIL-101-Cr were pressed into a disk-shaped pellet with a diameter of 8 mm and a thickness of 0.70 mm at a pressure of 9 MPa. MIL-101-Cr was pressed to a pellet with a diameter of 8 mm and a thickness of 0.52 mm under same pressure. These pellets were then sandwiched between two platinum electrodes for impedance measurement using a Solart 1260A electrochemistry workstation at open

circuit potential with an amplitude of 10 mV. For all the measurements, the range of frequency was set from 1 to 1M Hz. Proton conductivity was calculated by the formula:

$$\sigma = L / (R \times S) \quad (1)$$

where σ represents proton conductivity, L and S is thickness and area of the pellet, R is resistance of the pellet.

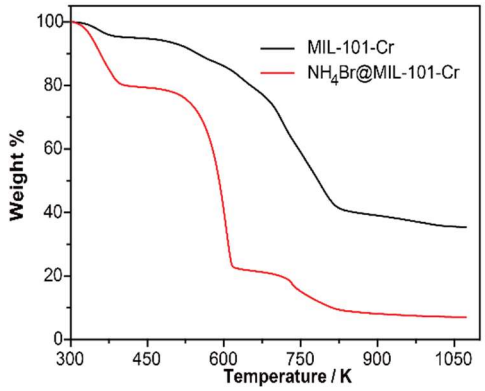

Figure S1. TG plot of MIL-101 and NH_4@MIL-101.

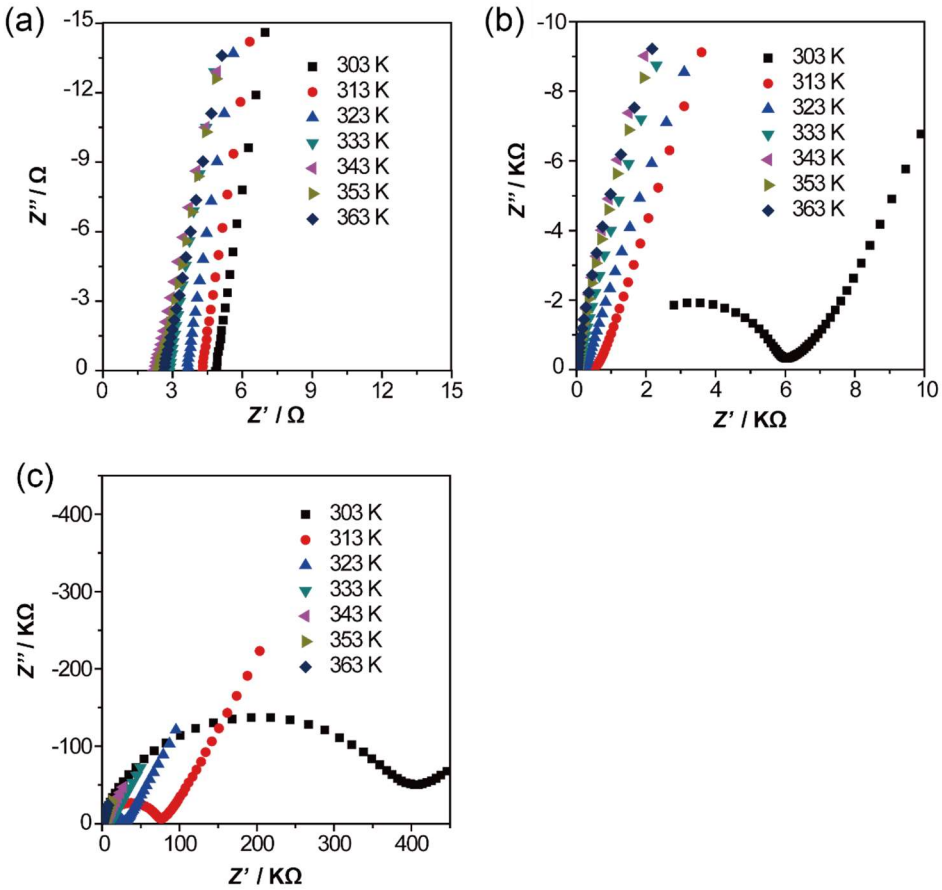

Figure S2. (a-c) Variable temperature impedance curves of NH_4Br@MIL-101-Cr under 75% RH, 60% RH and 45% RH.

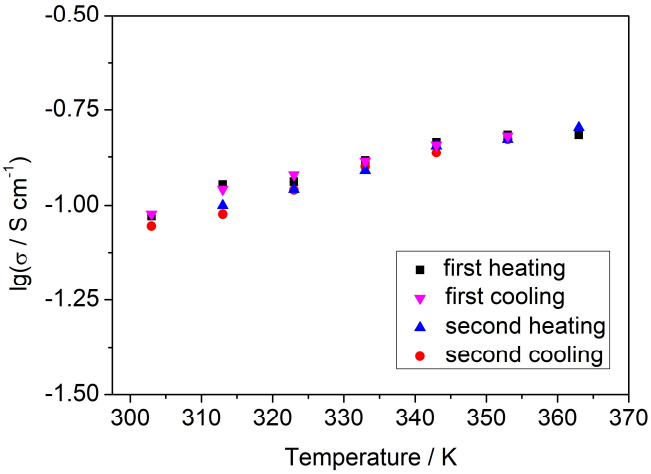

Figure S3. Two heating and cooling cycle proton conducting test of NH_4Br@MIL-101 in 100% RH

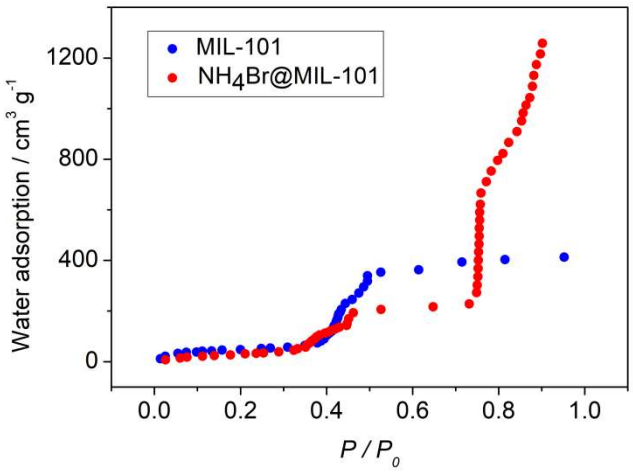

Figure S4. Water adsorption of MIL-101 and NH_4Br@MIL-101.

Table S1. Elemental analysis for NH_4Br@MIL-101-Cr (%).

NH_4Br@MIL-101-Cr		
C	H	N
11.46	4.28	9.26
11.10	3.95	9.57
11.32	4.19	9.41
NH_4Br@MIL-101-Cr after impedance test		
11.51	4.03	9.33
MIL-101-Cr		
35.71	3.28	0.14

Table S2. Comparison of proton conductivities in some reported MOFs (conductivity over 10^{-2} S cm^{-1}) and Nafion.

Compound	**σ / S cm^{-1}**	**Conditions**	**Ref.**
H_2SO_4@MIL-101	**1.0×10^{-2}**	**423 K,0.13% RH**	**1**
PCMOF2$_{1/2}$	**2.1×10^{-2}**	**358 K, 90% RH**	**2**
H^+@Ni_2(dobdc)(H_2O)$_2$	**2.2×10^{-2}**	**353 K, 95% RH**	**3**
PCMOF10	**3.55×10^{-2}**	**343 K, 95% RH**	**4**
[(Me_2NH_2)$_3$(SO_4)]$_2$[Zn_2(ox)$_3$]	**4.2×10^{-2}**	**298 K, 98% RH**	**5**
Fe-CAT-5	**5×10^{-2}**	**298 K, 98% RH**	**6**
TfOH@MIL-101	**8×10^{-2}**	**288 K, 60% RH**	**7**
UiO-66-(SO_3H)$_2$	**8.4×10^{-2}**	**353 K, 90% RH**	**8**
BUT-8(Cr)A	**1.27×10^{-1}**	**353 K, 100% RH**	**9**
NH_4Br@MIL-101-Cr	**1.53×10^{-1}**	**363 K, 100% RH**	**This work**

Reference:

1. Ponomareva, V. G.; Kovalenko, K. A.; Chupakhin, A. P.; Dybtsev, D. N.; Shutova, E. S.; Fedin, V. P. *J. Am. Chem. Soc* 2012, **134**, 15640-15643.

2. Kim, S.; Dawson, K. W.; Gelfand, B. S.; Taylor, J. M.; Shimizu, G. K. *J Am Chem Soc* 2013, **135**, 963-6.

3. Phang, W. J.; Lee, W. R.; Yoo, K.; Ryu, D. W.; Kim, B.; Hong, C. S.*Angew Chem Int Ed Engl* 2014, **53**, 8383-7.

4. Otake, K.-i.; Otsubo, K.; Komatsu, T.; Dekura, S.; Taylor, J. M.; Ikeda, R.; Sugimoto, K.; Fujiwara, A.; Chou, C.-P.; Sakti, A. W.; Nishimura, Y.; Nakai, H.; Kitagawa, H. *Nat. Com* 2020, **11** .

5. Nagarkar, S. S.; Unni, S. M.; Sharma, A.; Kurungot, S.; Ghosh, S. K. *Angew Chem Int Ed Engl* 2014,

53, 2638-42.

6. Nguyen, N. T.; Furukawa, H.; Gandara, F.; Trickett, C. A.; Jeong, H. M.; Cordova, K. E.; Yaghi, O. M. *J Am Chem Soc* 2015, **137**, 15394-7.

7. Dybtsev, D. N.; Ponomareva, V. G.; Aliev, S. B.; Chupakhin, A. P.; Gallyamov, M. R.; Moroz, N. K.; Kolesov, B. A.; Kovalenko, K. A.; Shutova, E. S.; Fedin, V. P. *ACS Appl Mater Interfaces* 2014, **6**, 5161-7.

8. Phang, W. J.; Jo, H.; Lee, W. R.; Song, J. H.; Yoo, K.; Kim, B.; Hong, C. S. *Angew Chem Int Ed Engl* 2015, *54* (17), 5142-6.

9. Dong, X. Y.; Wang, R.; Li, J. B.; Zang, S. Q.; Hou, H. W.; Mak, T. C. *Chem Commun (Camb)* 2013, *49* (90), 10590-2.