

## Supporting information

### **Proton conductors with wide operating temperature domains achieved by applying dual-modification strategy to MIL-101**

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## 1. Experimental Section

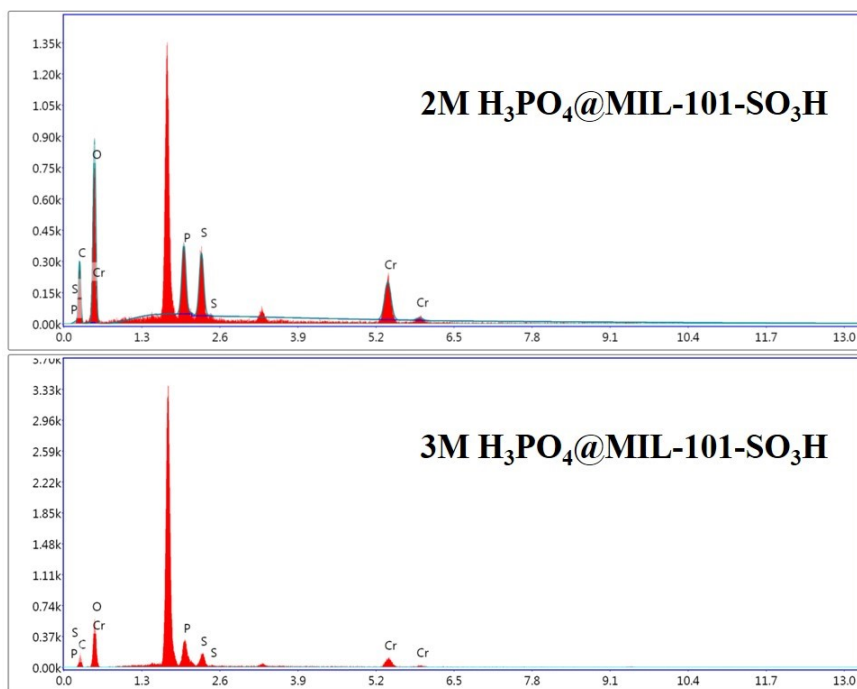
**1.1. Materials.** All the reagents including ethanol absolute ( $\text{CH}_3\text{CH}_2\text{OH}$ ), hydrochloric acid ( $\text{HCl}$ , 36%), methanol ( $\text{CH}_3\text{OH}$ ), N,N-dimethylformamide (DMF), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), Phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%) were obtained from commercial sources and used without further purification. Chromium (III) nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Chromium (VI) oxide ( $\text{CrO}_3$ , 99%), aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ), p-Phthalic acid ( $\text{H}_2\text{BDC}$ , 99%), Monosodium 2-sulfoterephthalate and 2-amino terephthalic acid were purchased from Aladdin.

**1.2. Synthesis of MIL-101(Cr):** MIL-101 (Cr) was synthesized with slight changes to the previously reported procedure in literature<sup>1</sup>.  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (2.0 g) and  $\text{H}_2\text{BDC}$  (0.83 g) were dissolved in 30 mL distilled water. Subsequently, the solution was transferred into a 50 mL Teflon reactor to heat at 180 °C for 20 hours. The resulting precipitate was collected by centrifugation and washed through stirring constantly with ethanol, then dried at 80 °C for 12 hours.

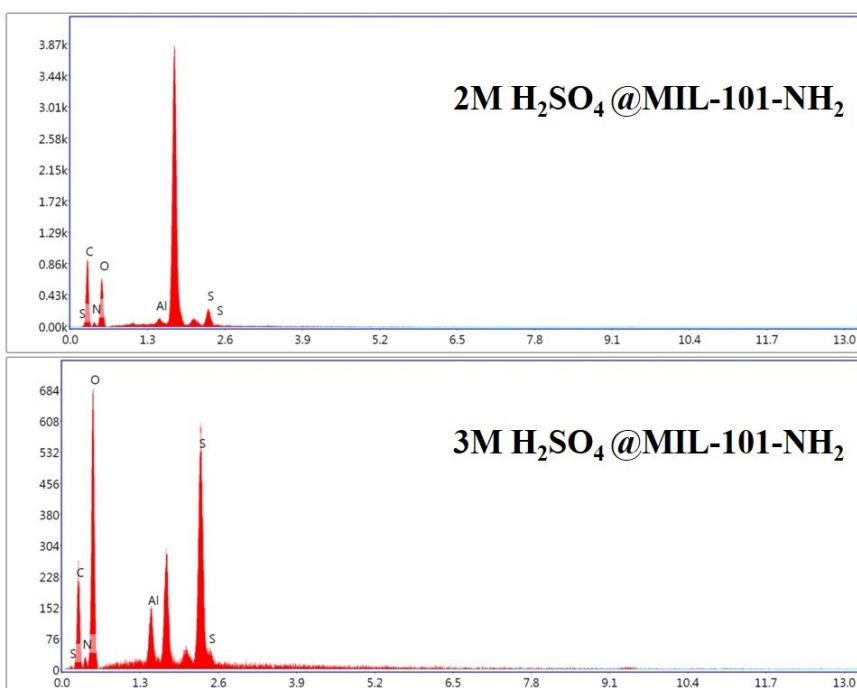
**1.3. Synthesis of MIL-101-SO<sub>3</sub>H(Cr):** MIL-101-SO<sub>3</sub>H was prepared following the method described earlier.<sup>2</sup> Monosodium 2-sulfoterephthalic acid (3.35 g),  $\text{CrO}_3$  (1.25 g) and concentrated aqueous hydrochloric acid (0.8 mL, 12M) were dissolved in 25 mL distilled water. The solution was transferred into a 50 mL Teflon reactor to heat at 180 °C for six days. The resulting solid was collected by centrifugation and washed through centrifugation with distilled water and methanol. After drying in air at room temperature, the green powder was further purified in DMF at 120 °C for 24 hours and then in the mixed solution of methanol.

**1.4. Synthesis of MIL-101-NH<sub>2</sub>(Al):** NH<sub>2</sub>-MIL-101(Al) was synthesized according to a modified procedure.<sup>3</sup> A mixture of 2-aminoterephthalic acid (112 mg), aluminum chloride hexahydrate (102 mg) and N,N-dimethylformamide (DMF) (8 mL) was heated in a Teflon-lined autoclave at 130 °C for 3 days. After cooling to room temperature, the product was separated from the solution by centrifugation and washed with DMF and methanol. After re-dispersing in methanol and refluxing overnight, the yellow solid was dried under 80 °C for 12 hours.

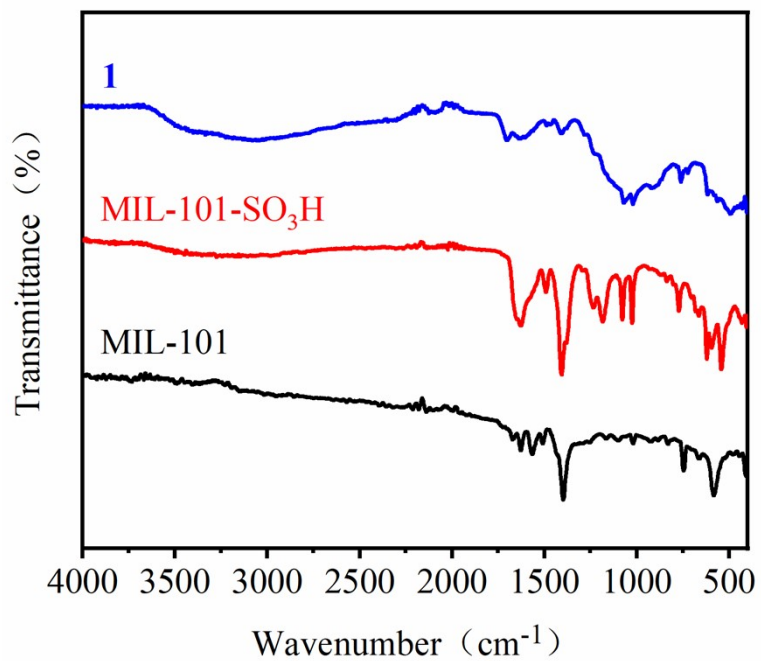
**1.5. Synthesis of H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub>@MIL-101:** H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub>@MIL-101 were synthesized according to a modified procedure.<sup>4</sup> MIL-101 (0.135 g) was immersed in the diluted H<sub>2</sub>SO<sub>4</sub> (1.35 mL, 3M), or MIL-101 (0.5 g) were added to H<sub>3</sub>PO<sub>4</sub> solution (2.5 mL, 3M), and the resulting suspension was stirred 30 min at room temperature. The suspension was treated by filtration and then the solid was dried at 60 °C overnight to get H<sub>2</sub>SO<sub>4</sub>@MIL-101 and H<sub>3</sub>PO<sub>4</sub>@MIL-101.



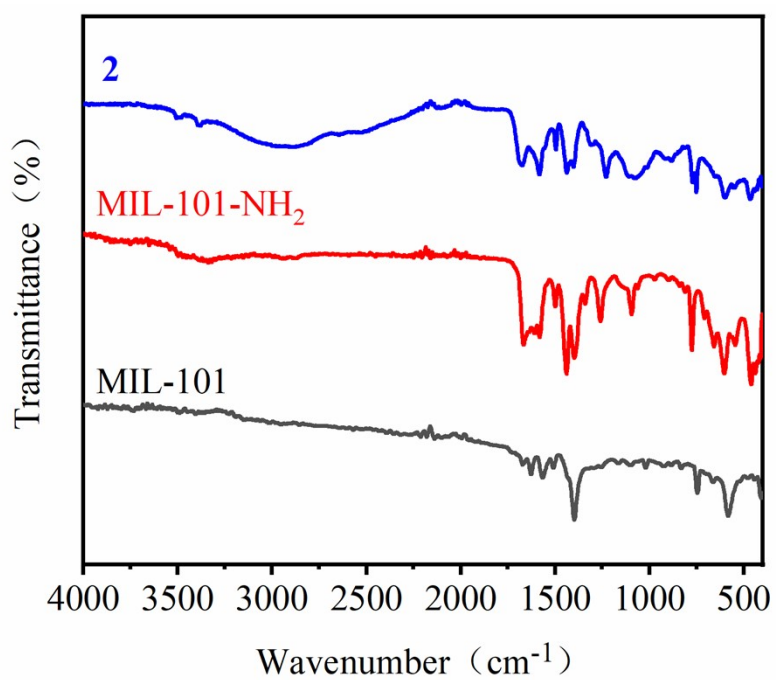
**Figure S1 EDS spectrum of 2M and 3M H<sub>3</sub>PO<sub>4</sub>@MIL-101-SO<sub>3</sub>H**



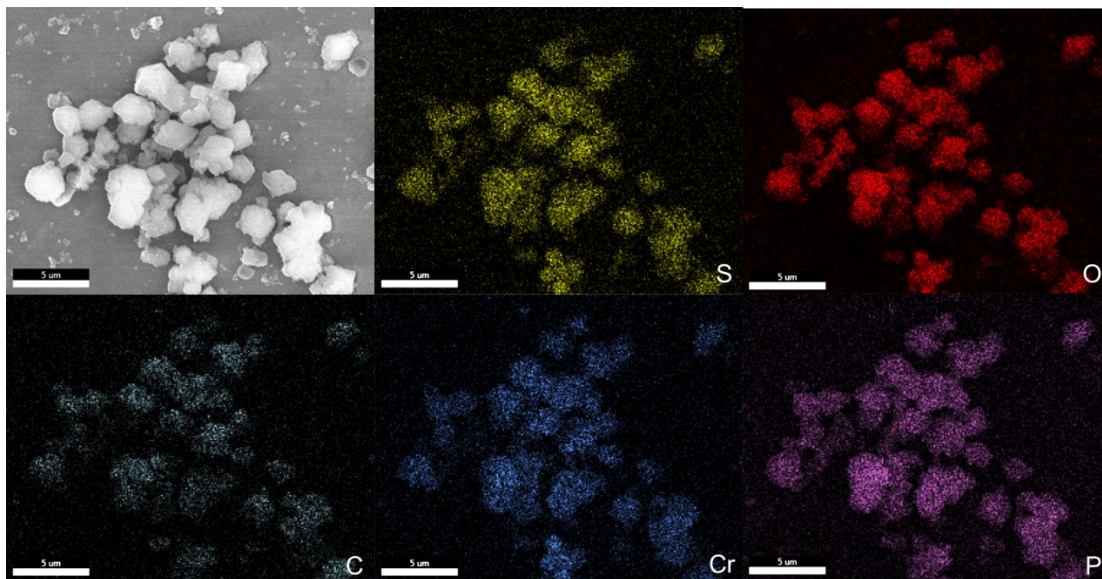
**Figure S2 EDS spectrum of 2M and 3M H<sub>2</sub>SO<sub>4</sub>@MIL-101-NH<sub>2</sub>.**



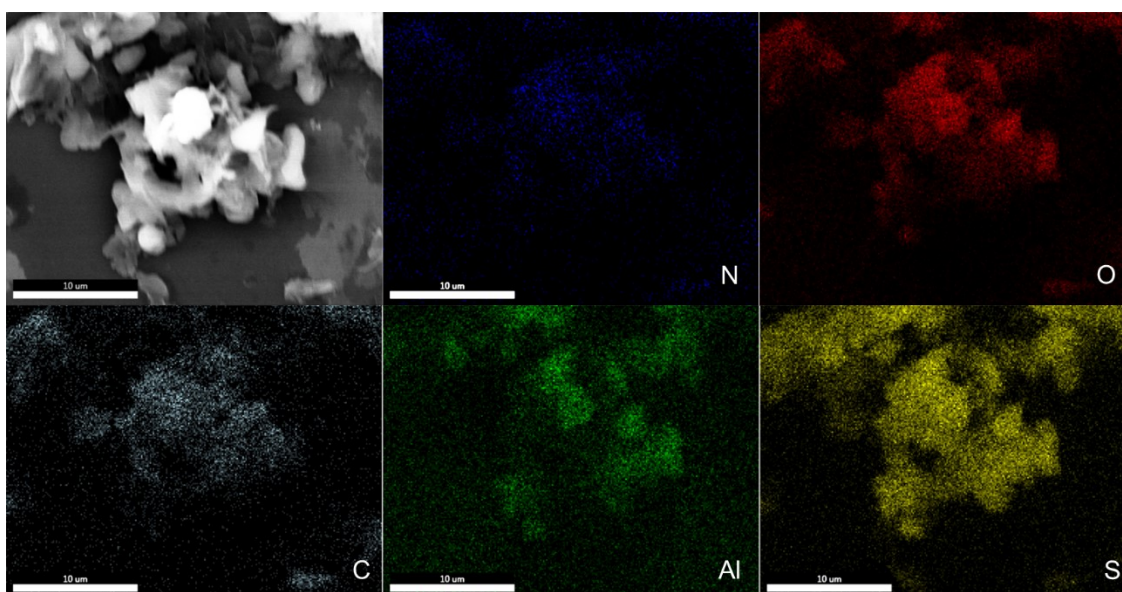
**Figure S3 FT-IR spectra of as-synthesized 1.**



**Figure S4 FT-IR spectra of as-synthesized 2.**



**Figure S5 Element mapping images of 1.**



**Figure S6 Element mapping images of 2.**

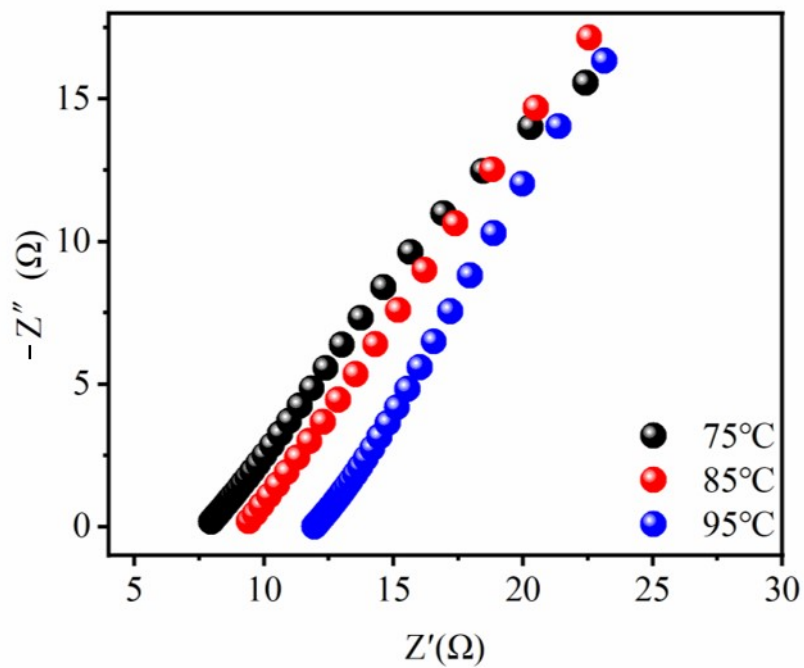


Figure S7 Nyquist plots of 1 at 75-95 °C and 95% RH.

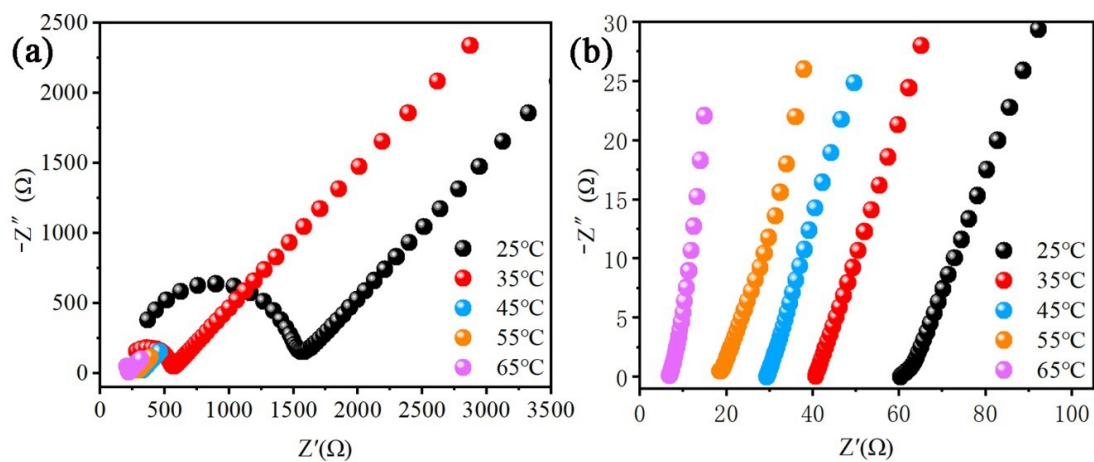


Figure S8 Nyquist plots of (a) MIL-101-SO<sub>3</sub>H (b) H<sub>3</sub>PO<sub>4</sub>@MIL-101 at 25-65 °C and 95% RH.

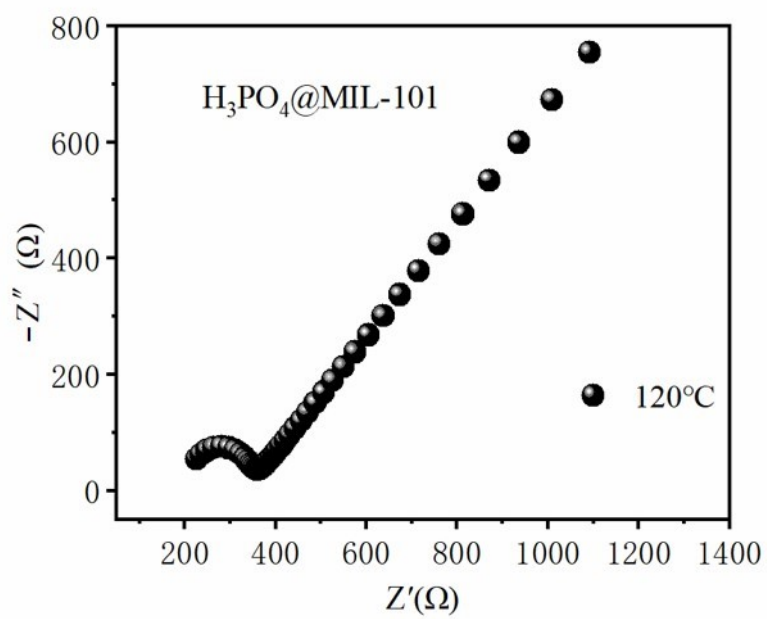


Figure S9 Nyquist plots of  $\text{H}_3\text{PO}_4@\text{MIL-101}$  at 120 °C.

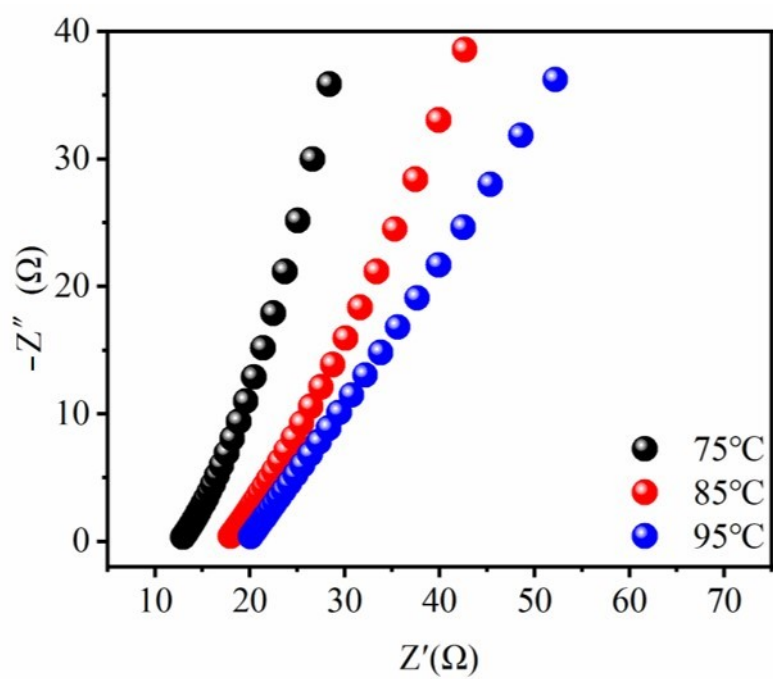


Figure S10 Nyquist plots of 2 at 75-95 °C and 95% RH.



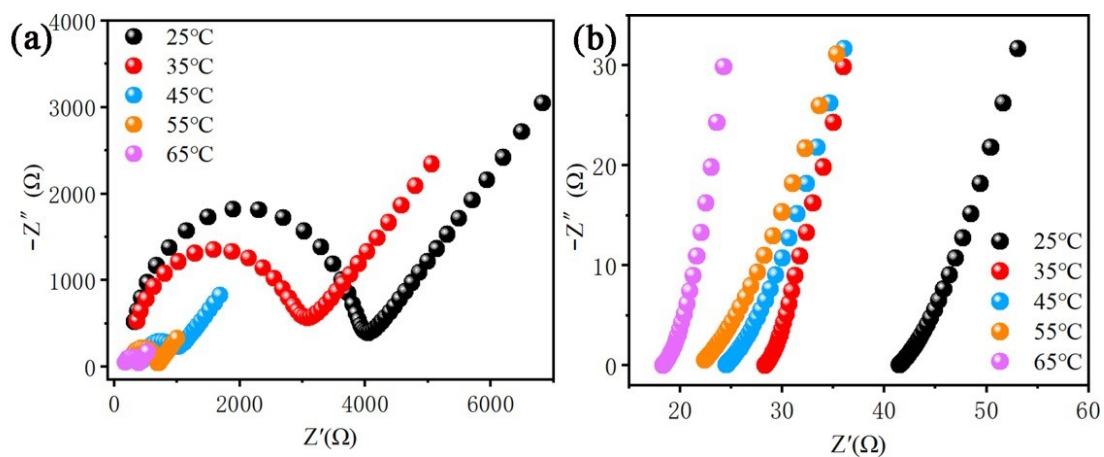


Figure S11 Nyquist plots of (a) MIL-101-NH<sub>2</sub> (b) H<sub>2</sub>SO<sub>4</sub>@MIL-101 at 25-65 °C and 95% RH.

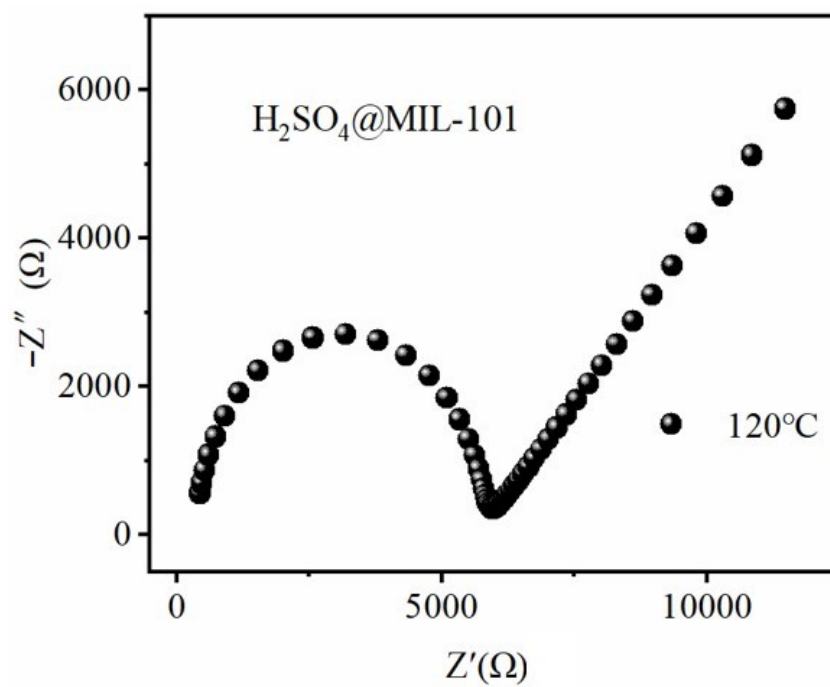
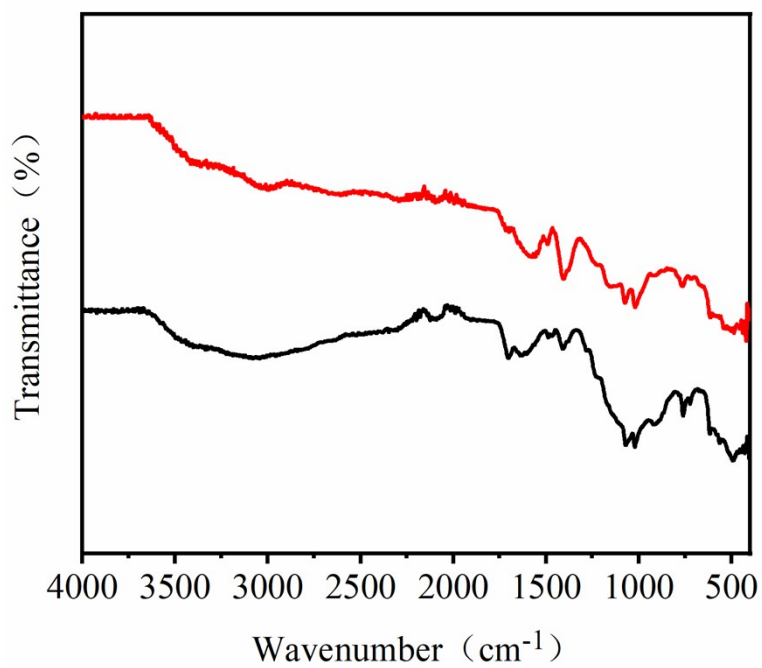
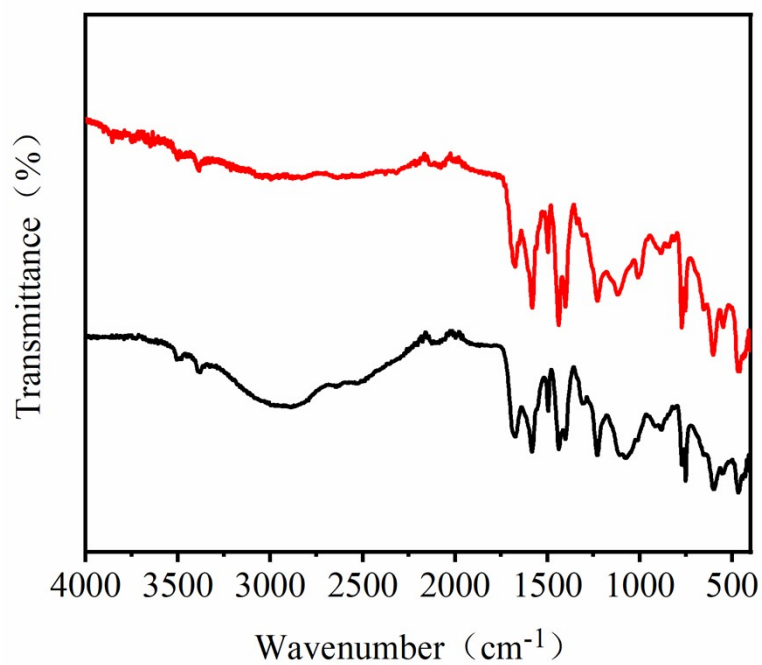


Figure S12 Nyquist plots of H<sub>2</sub>SO<sub>4</sub>@MIL-101 at 120 °C.

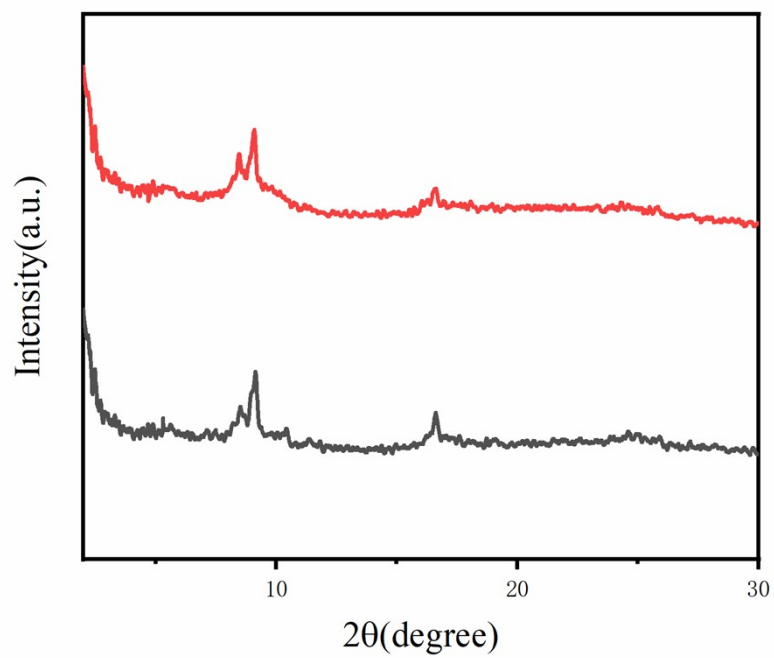




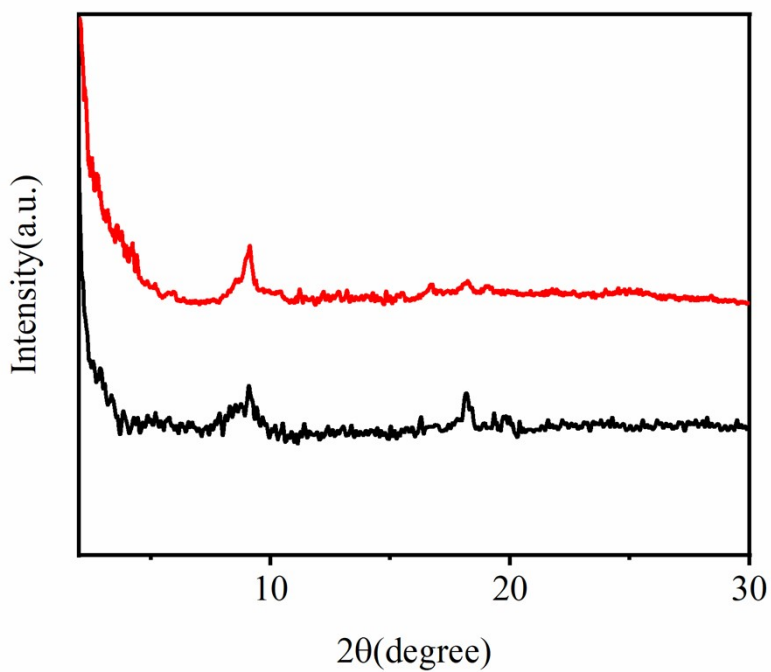
**Figure S14** FT-IR spectra of as-synthesized **1** (black) and **1** (red) after time-dependent proton conductivity test.



**Figure S15** FT-IR spectra of as-synthesized **2** (black) and **2** (red) after time-dependent proton conductivity test.



**Figure S16 PXRD patterns of as-synthesized 1 (black) and 1 (red) after time-dependent proton conductivity test.**



**Figure S17 PXRD patterns of as-synthesized 2 (black) and 2 (red) after time-dependent proton conductivity test.**

**Table S1 Comparison of proton conductivities measured at moderate temperature between our work and reported proton conductors.**

Compounds	$\sigma$ (S cm <sup>-1</sup> )	Temperature (°C)	Relative humidity (%)	Ea (eV)	Ref.
H <sub>2</sub> SO <sub>4</sub> @MIL-101-SO <sub>3</sub> H	0.9×10 <sup>-1</sup>	65	95	0.33	This work
H <sub>3</sub> PO <sub>4</sub> @MIL-101-NH <sub>2</sub>	5.8×10 <sup>-2</sup>	65	95	0.30	This work
P-PA55-PW40	1.0×10 <sup>-2</sup>	25	32	0.15	5
3DGO	3.5×10 <sup>-2</sup>	70	100	0.29	6
ML-UiO-66-(NH <sub>2</sub> )(SO <sub>3</sub> H)-5:5	2.8×10 <sup>-2</sup>	80	75	0.20	7
Zr-TCPBP-HCl	1.2×10 <sup>-3</sup>	70	98	0.17	8
Eu <sup>3+</sup> (Eu[P <sub>5</sub> W <sub>30</sub> O <sub>110</sub> K] <sup>11-</sup> )	1.0×10 <sup>-2</sup>	95	90	0.23	9
Eu-I-230	3.6×10 <sup>-2</sup>	80	95	0.11	10

**Table S2 Comparison of proton conductivities measured above 100°C temperature between our work and reported proton conductors.**

Compounds	$\sigma$ (S cm <sup>-1</sup> )	Temperature (°C)	Ea (eV)	Ref.
H <sub>2</sub> SO <sub>4</sub> @MIL-101-SO <sub>3</sub> H	4.4×10 <sup>-5</sup>	120	0.35	This work
H <sub>3</sub> PO <sub>4</sub> @MIL-101-NH <sub>2</sub>	7.1×10 <sup>-4</sup>	120	0.21	This work
FJU-17	1.1×10 <sup>-2</sup>	100	0.29	11
LiBr@1	1.0×10 <sup>-2</sup>	110	0.36	12
CS/A-6 + B-15	3.8×10 <sup>-3</sup>	120	0.19	13
FJU-31@Hq	2.6×10 <sup>-4</sup>	125	0.18	14
[ImH <sub>2</sub> ][Cu(H <sub>2</sub> PO <sub>4</sub> ) <sub>1.5</sub> (HPO <sub>4</sub> ) <sub>0.5</sub> ·Cl <sub>0.5</sub> ]	2.0×10 <sup>-2</sup>	130	1.10	15
[Zn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (TzH) <sub>2</sub> ] <sub>n</sub>	1.1×10 <sup>-4</sup>	130	0.60	16
F6-[dema]HSO <sub>4</sub> -1.5	1.3×10 <sup>-2</sup>	140	0.34	17
H <sub>2</sub> SO <sub>4</sub> @MIL-101	1.0×10 <sup>-2</sup>	150	0.42	4
CNC/Im	2.0×10 <sup>-3</sup>	150	0.28	18
CsK-PEG400	1.3×10 <sup>-4</sup>	150	1.80	19
Im@sPMO	7.1×10 <sup>-3</sup>	180	0.17	20

**Table S3 Comparison of proton conductivities measured at freezing temperature between our work and reported proton conductors.**

Compounds	$\sigma$ (S cm <sup>-1</sup> )	Temperature (°C)	Ea (eV)	Ref.
H <sub>3</sub> PO <sub>4</sub> @MIL-101-SO <sub>3</sub> H	4.4×10 <sup>-5</sup>	-40	0.35	This work
H <sub>2</sub> SO <sub>4</sub> @MIL-101-NH <sub>2</sub>	7.1×10 <sup>-4</sup>	-40	0.21	This work
Im@Td-PPI	2.2×10 <sup>-6</sup>	-40	0.30	21
Im@Td-PNDI	4.6×10 <sup>-7</sup>	-40	0.33	21
FJU-31@Hq	3.2×10 <sup>-6</sup>	-40	0.18	14
FJU-31@Ch	1.2×10 <sup>-6</sup>	-40	0.29	14
H <sub>2</sub> SO <sub>4</sub> @MIL-101-SO <sub>3</sub> H	9.2×10 <sup>-3</sup>	-40	0.21	22
COG-10P	3.8×10 <sup>-4</sup>	-40	0.18	23
Im@sPMO	1.1×10 <sup>-6</sup>	-40	0.50	20

3HPW-HSN@SBA-15	$6.8 \times 10^{-5}$	-40	0.22	24
CTF-Mx	$1.2 \times 10^{-3}$	-40	0.13	25
FJU-17	$9.1 \times 10^{-5}$	-40	0.29	11

**Table S4 List of MIL-101 samples featured in this work and their conductivity profiles.**

Names	Conductivity (S cm <sup>-1</sup> )	Condition
<b>H<sub>3</sub>PO<sub>4</sub>@MIL-101-SO<sub>3</sub>H(Cr)</b> <sup>a</sup>	$0.9 \times 10^{-1}$	65°C, 95%RH
	$7.5 \times 10^{-5}$	-40°C
	$1.4 \times 10^{-2}$	150°C
<b>H<sub>2</sub>SO<sub>4</sub>@MIL-101-NH<sub>2</sub>(Al)</b> <sup>a</sup>	$5.8 \times 10^{-2}$	65°C, 95%RH
	$7.1 \times 10^{-4}$	-40°C
	$2.5 \times 10^{-4}$	170°C
<b>H<sub>2</sub>SO<sub>4</sub>@MIL-101-SO<sub>3</sub>H(Cr)</b> <sup>b</sup>	1.8	70°C, 90%RH
	$9.2 \times 10^{-3}$	-40°C
<b>H<sub>3</sub>PO<sub>4</sub>@MIL-101-NH<sub>2</sub>(Al)</b> <sup>a</sup>	$2.1 \times 10^{-2}$	65°C, 95%RH
	$1.5 \times 10^{-5}$	160°C
<b>H<sub>3</sub>PO<sub>4</sub>@MIL-101 (Cr)</b> <sup>c</sup>	$1.1 \times 10^{-2}$	65°C, 95%RH
	$4.6 \times 10^{-4}$	120°C
<b>H<sub>2</sub>SO<sub>4</sub>@MIL-101 (Cr)</b> <sup>c</sup>	$2.7 \times 10^{-2}$	65°C, 95%RH
	$2.0 \times 10^{-5}$	120°C

<sup>a</sup>New compounds and new conductivity data. <sup>b</sup>Compounds previously synthesized by Lan et al. <sup>22</sup> <sup>c</sup>Compound and conductivity previously reported by Fedin et al.<sup>4</sup>; conductivity was measured under new conditions.

- 1 G. Férey, C. Serre, F. Millange, J. Dutour, S. Surble´ and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
- 2 Y. X. Zhou, Y. Z. Chen, Y. Hu, G. Huang, S. H. Yu and H. L. Jiang, *Chem. Eur. J.*, 2014, **20**, 14976-14980.
- 3 P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *Chem. Mater.*, 2011, **23**, 2565-2572.
- 4 V. G. Ponomareva, K. A. Kovalenko, A. P. Chupakhin, D. N. Dybtsev, E. S. Shutova and V. P. Fedin, *J. Am. Chem. Soc.*, 2012, **134**, 15640-15643.
- 5 H. K. Guo, M. H. Zeng, X. Li, H. B. He, L. X. Wu and H. L. Li, *ACS Appl. Mater. Interfaces*, 2021, **13**, 30039-30050.
- 6 J. Yagyu, M. S. Islam. Y. Shudo, M. Fukuda, H. Ushijima, J. Ohyama, S. Ida, L. F. Lindoy and S. Hayami, *ACS Appl. Energy Mater.*, 2021, **4**, 6296-6301.
- 7 Q. H. Wang, X. F. Zheng, H. X. Chen, Z. K. Shi, H. Tang, P. W. Gong, L. H. Guo, M. T. Li, H. L. Huan and Z. Liu, *Microporous and Mesoporous Materials*, 2021, **323**, 111199.
- 8 S. L. Yang, G. Li, M. Y. Guo, W. S. Liu, R. Bu and E. Q. Gao, *J. Am. Chem. Soc.*, 2021, **143**, 8838-8848.
- 9 T. Iwano, K. Shitamatsu, N. Ogiwara, M. Okuno, Y. Kikukawa, S. Ikemoto, S. Shirai, S. Muratsugu, P. G. Waddell, R. J. Errington, M. Sadakane and S. Uchida, *ACS Appl. Mater. Interfaces*, 2021, **13**, 19138-19147
- 10 I. R. Salcedo, R. M. P. Colodrero, M. Bazaga-Garcia, M. Lopez-Gonzalez, C. Del Rio, K. Xanthopoulos, K. D. Demadis, G. B. Hix, A. D. Furasova, D. Choquesillo-Lazarte, P. Olivera-Pastor and A. Cabeza, *ACS Appl. Mater. Interfaces*, 2021, **13**, 15279-15291.
- 11 L. Z. Liu, Z. Z. Yao, Y. X. Ye, Q. J. Lin, S. M. Chen, Z. J. Zhang and S. C. Xiang, *Cryst. Growth Des.*, 2018, **18**, 3724-3728.
- 12 K. Zhang, G. H. Wen, X. J. Yang, D. W. Lim, S. S. Bao, M. Donoshita, L. Q. Wu, H. Kitagawa and L. M. Zheng, *ACS Materials Lett.*, 2021, **3**, 744-751.
- 13 X. Y. Dong, J. H. Wang, S. S. Liu, Z. Han, Q. J. Tang, F. F. Li and S. Q. Zang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 38209-38216.
- 14 Y. X. Ye, X. Z. Wu, Z. Z. Yao, L. Wu, Z. T. Cai, L. H. Wang, X. L. Ma, Q. H. Chen, Z. J. Zhang and S. C. Xiang, *J. Mater. Chem. A.*, 2016, **4**, 4062-4070.
- 15 S. Horike, W. Chen, T. Itakura, M. Inukai, D. Umeyama, H. Asakura and S. Kitagawa, *Chem. Commun.*, 2014, **50**, 10241-10243.
- 16 V. G. Ponomareva, K. A. Kovalenko, A. P. Chupakhin, D. N. Dybtsev, E. S. Shutova and V. P. Fedin, *J. Am. Chem. Soc.*, 2012, **134**, 15640-15643.
- 17 X. W. Wu, Z. Y. Liu, H. Guo, Y. L. Hong, B. Q. Xu, K. Zhang, Y. Nishiyama, W. Jiang, S. Horike, S. Kitagawa and G. Zhang, *ACS Appl. Mater. Interfaces*, 2021, DOI: 10.1021/acsami.1c09157.
- 18 O. Danyliv, M. Strach, O. Nechyporchuk, T. Nypelö, A. Martinelli, *ACS Appl. Energy Mater.*, 2021, **4**, 6474-6485.
- 19 N. Ogiwara, M. Tomoda, S. Miyazaki, Z. W. Weng, H. Takatsu, H. Kageyama, T. Misawa, T. Ito and S. Uchida, *Nanoscale*, 2021, **13**, 8049-8057.
- 20 L. Wu, Y. S. Yang, Y. X. Ye, Z. J. Yu, Z. J. Song, S. M. Chen, L. J. Chen, Z. J. Zhang and S. C. Xiang, *ACS Appl. Energy Mater.*, 2018, **1**, 5068-5074.
- 21 Y. X. Ye, L. Q. Zhang, Q. F. Peng, G. E. Wang, Y. C. Shen, Z. Y. Li, L. H. Wang, X. L. Ma,

- Q. H. Chen, Z. J. Zhang and S. C. Xiang, *J. Am. Chem. Soc.*, 2015, **137**, 913-918.
- 22 X. M. Li, L. Z. Dong, S. L. Li, G. Xu, J. Liu, F. M. Zhang, L. S. Lu and Y. Q. Lan, *ACS Energy Lett.*, 2017, **2**, 2313-2318.
- 23 H. Zhong, Z. H. Fu, J. M. Taylor, G. Xu and R. H. Wang, *Adv. Funct. Mater.*, 2017, **27**, 1701465.
- 24 X. W. Sun, S. M. Liu, S. Zhang, T. Y. Dang, H. R. Tian, Y. Lu and S. X. Liu, *ACS Appl. Energy Mater.*, 2020, **3**, 1242-1248.
- 25 W. Huang, B. Li, Y. Wu, Y. Zhang, W. Zhang, S. Chen, Y. Fu, T. Yan and H. Ma, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13604-13612.