

Electronic Supporting Information

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Fig. S3 N₂ sorption isotherms at 77 K for **HKUST-1**, **NH₄Br@HKUST-1** and **NH₄Cl@HKUST-1**. The BET surface area of **HKUST-1** in this work is quite similar to that in the published literature.

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Experimental details

Relative humidity (RH) dependence of proton conductivity measurements

The Relative humidity (RH) dependence of the proton conductivity measurements were carried out using a conventional three-electrode method with a CHI 660D electrochemical workstation and the reference electrode has been shortened with auxiliary electrode, the cable connected the copper plate electrodes with the electrochemical workstation is ca. 1.2 m. The copper plate electrode is 13 mm in diameter. The frequency of applied alternating current (ac) field ranges from 100 to 2 MHz with 5 mV of signal amplitude. The DC offset is zero. The powdered sample pellet is suspended in a wide-mouth bottle with a rubber stopper and water solution of salt on the bottom, such a bottle was placed in an oven. The humidity was tuned by the concentration of salt and monitored using a humidity probe.

N₂ adsorption experiments

Low-pressure gas sorption measurements: Glass sample tubes of a known weight were loaded with approximately 200 mg of sample. Samples were outgassed at 95°C for 4h on a Autosorb IQ instrument (Quantachrome, USA) outgas station until the outgas rate was no more than 1 mTorr/min. The outgassed sample and sample tubes were weighed precisely and then transferred back to the outgas station. The outgas rate was again confirmed to be less than 1 mTorr/min. Adsorption isotherms were measured at 77 K in a liquid nitrogen bath for N₂. The isotherm for the adsorption and desorption of N₂ on activated samples at 77 K and the pore size distribution are shown in Fig. S3.

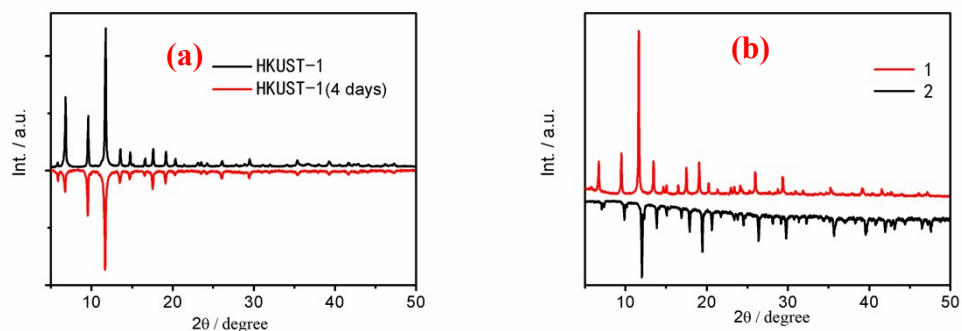


Fig. S1 Experimental PXRD patterns of (a) the samples of **HKUST-1** (as-prepared and immersed in deionized water for four days) (b) **HKUST-1** before (labeled as **1**) and after (labeled as **2**) impedance measurements under various relative humidity, and the diffraction data collection was performed at room temperature.

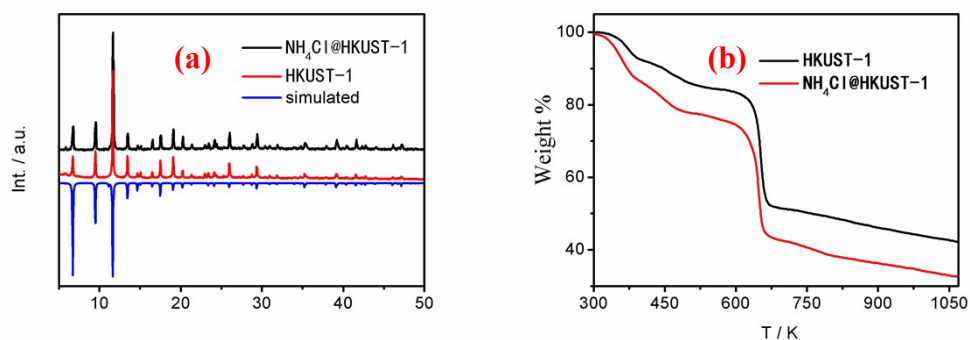
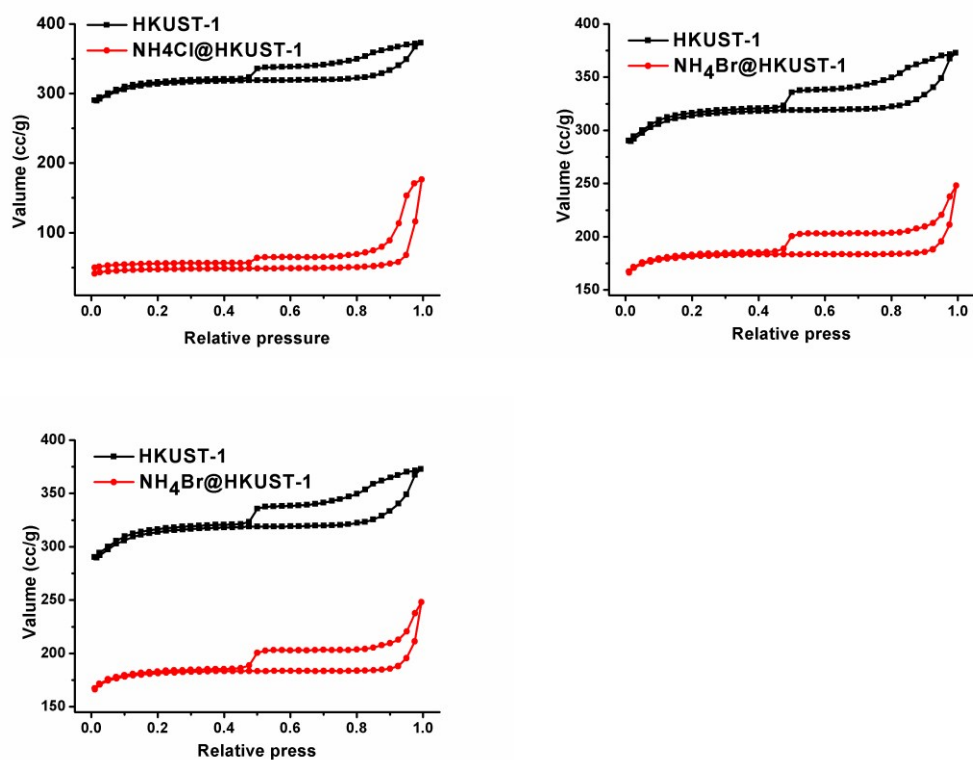
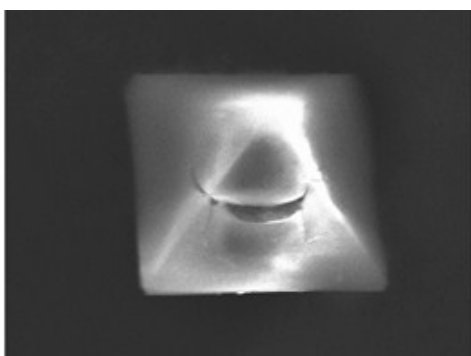


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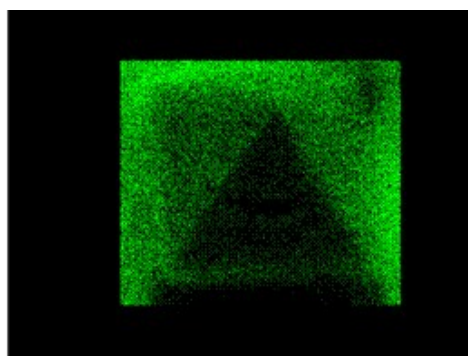


Sample	BET surface area	pore volume
HKUST-1	1098.80m ² /g	0.576 cm ³ /g
NH₄Br@HKUST-1	564.70m ² /g	0.384 cm ³ /g
NH₄Cl@HKUST-1	149.72m ² /g	0.273 cm ³ /g

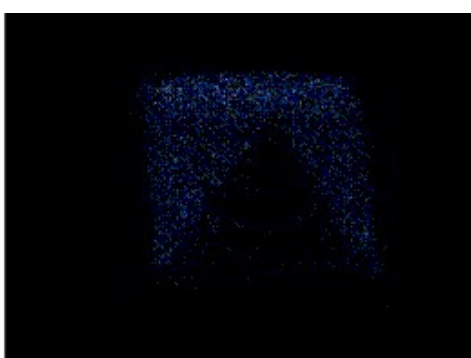
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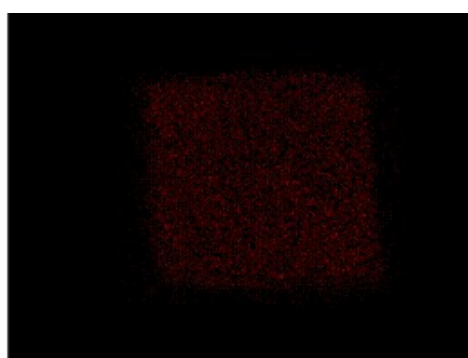
电子图像 1



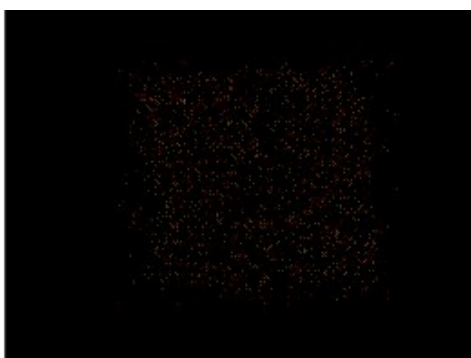
C Ka1_2



O Ka1

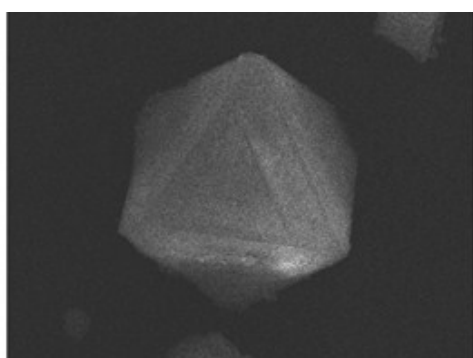


Cu Ka1

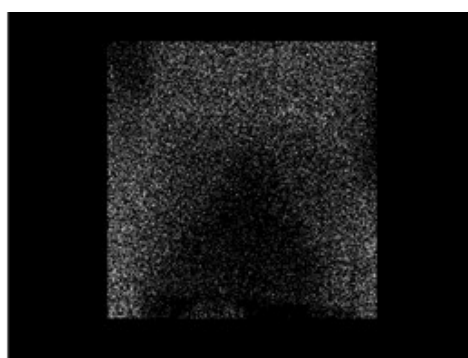


Br Ka1

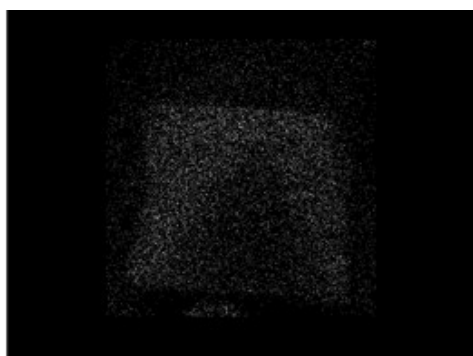
Fig. S4 EDX mapping of C, O, Cu and Br elements for a single crystal of $\text{NH}_4\text{Br}@\text{HKUST-1}$, indicating that the NH_4Br is homogeneously distributed in the pores of the MOF.



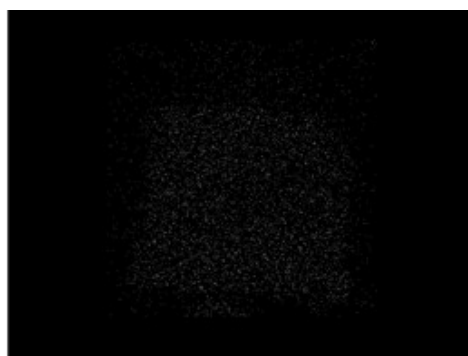
电子图像 1



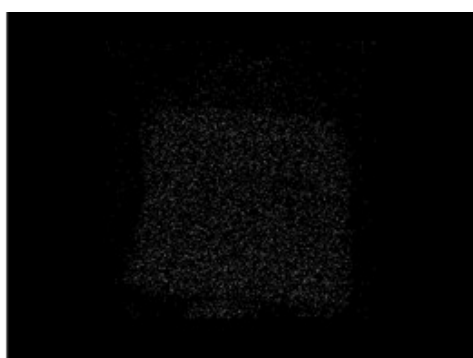
C Ka1_2



O Ka1



Cl Ka1



Cu Ka1

Fig. S5 EDX mapping of C, O, Cu and Cl elements for a single crystal of $\text{NH}_4\text{Cl}@\text{HKUST-1}$, indicating that the NH_4Cl is homogeneously distributed in the pores of the MOF.

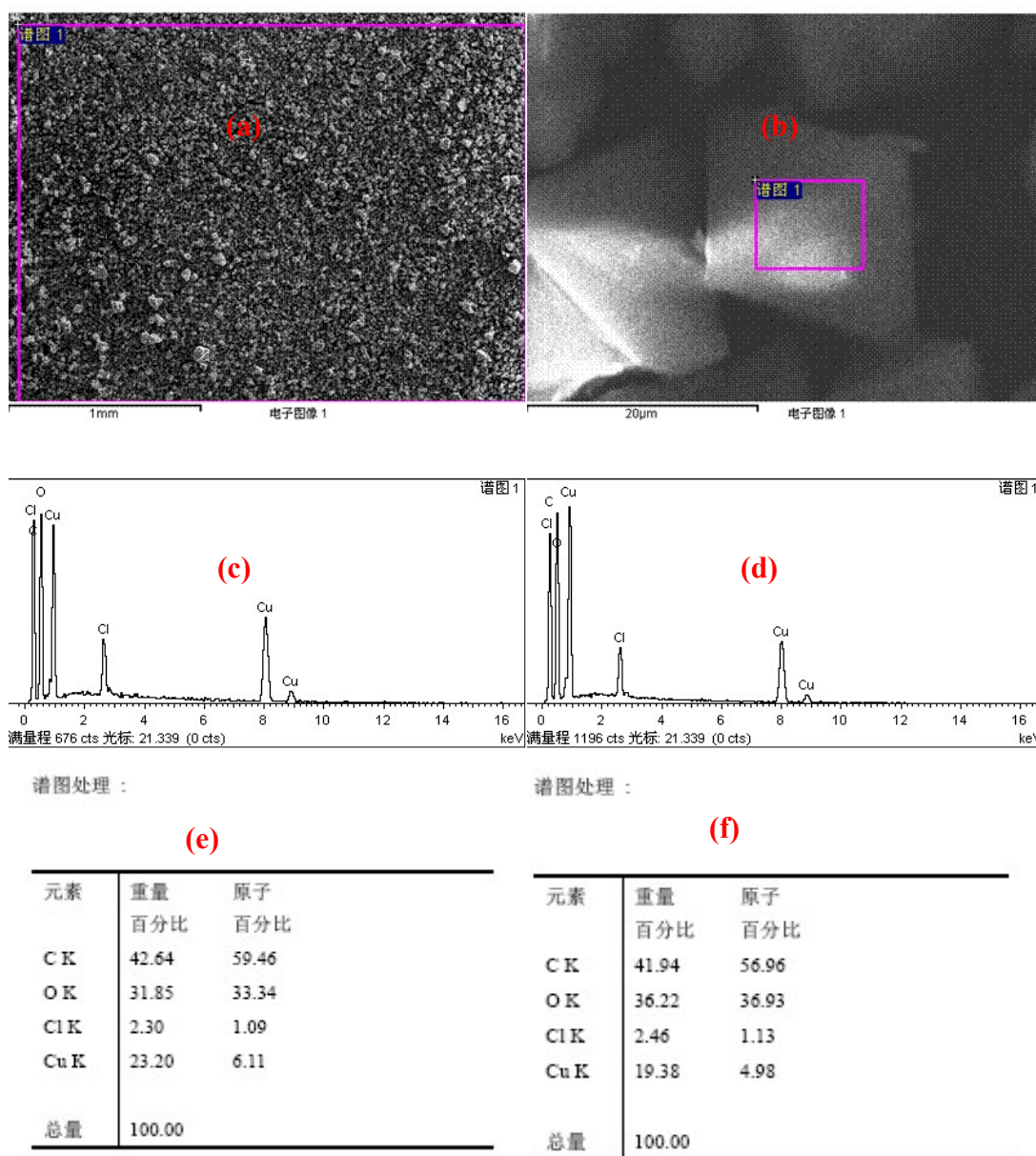


Fig. S6 SEM images of $\text{NH}_4\text{Cl}@\text{HKUST-1}$ and EDX analysis of (a, c, e) power sample and (b, d, f) single crystal.

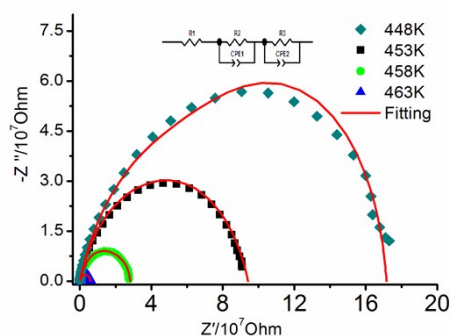


Fig. S7 The fits of impedance spectra for **NH₄Br@HKUST-1** at selected temperatures and under anhydrous condition, where CPE = constant phase element, R1, R2, R3 represent the resistances of bulk, grain boundary and external circuit, respectively.

Impedance spectra of HKUST-1 and NH₄Br@HKUST-1 samples exposure to MeOH vapor at room temperature.

To assess proton conductivity of the samples following exposure to MeOH vapor further, ac impedance analysis was carried out on powdered sample of **HKUST-1** and **NH₄Br@HKUST-1**. At following exposure to MeOH vapor 48h, the proton conductivities are 4.57×10^{-8} and 5.46×10^{-6} S cm⁻¹ for **HKUST-1** and **NH₄Br@HKUST-1** at 298k, respectively.

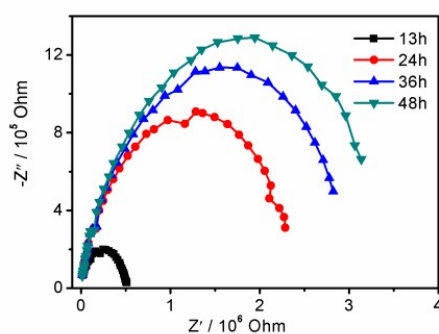


Fig. S8 Impedance spectra of **HKUST-1** sample following exposure to MeOH vapor at 298K.

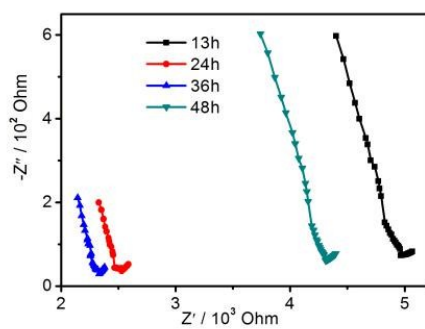


Fig. S9 Impedance spectra of $\text{NH}_4\text{Br}@\text{HKUST-1}$ sample following exposure to MeOH vapor at 298K.

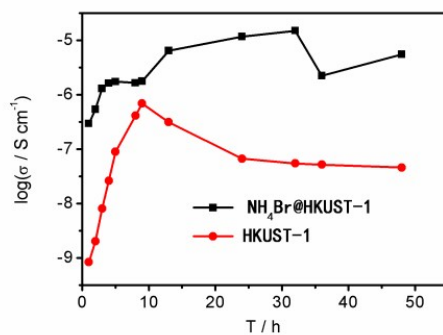


Fig. S10 Time dependence of the proton conductivity, and the sample exposed to MeOH vapor at 298K. Red circles and black squares correspond to HKUST-1 and $\text{NH}_4\text{Br}@\text{HKUST-1}$, respectively.

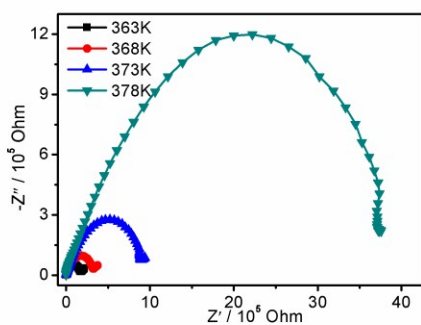
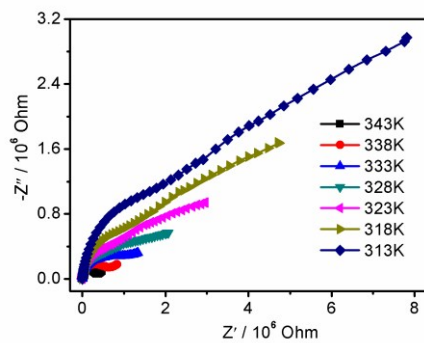
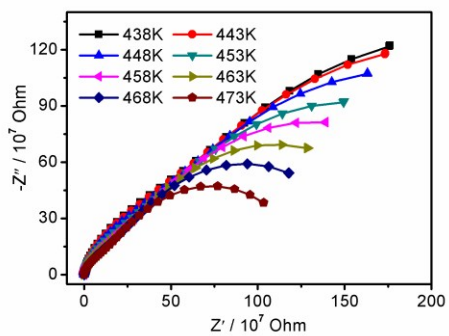


Fig. S11 Impedance spectra of $\text{NH}_4\text{Cl}@\text{HKUST-1}$ at selected temperatures and under anhydrous condition.