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Supplementary Information

Incorporation of imidazole within the metal-organic framework UiO-67 for enhanced anhydrous proton conductivity

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Experimental

Synthesis of UiO-67

Synthesis of UiO-67 was performed by dissolving 1.2 mmol of zirconium (IV) chloride ($ZrCl_4$), 1.2 mmol of 4,4'-Biphenyl dicarboxylic acid (H_2BPDC) and 30 equivalents of acetic acid (CH_3COOH) in 30 ml of N,N-dimethyformamide (DMF) at room temperature. The resulting mixture was placed in a 100 ml Teflon-lined stainless steel autoclave and heated at 120°C for 48 hours. The product was cooled to room temperature, washed three times with DMF, and dried at room temperature. Excess H_2BPDC and DMF in the pores were removed using a high temperature treatment at 300°C for one day. A pale yellow powder was obtained.

Synthesis of imidazole@UiO-67

The as-made UiO-67crystal was placed in a tube furnace and evacuated at 120°C for 3 hours, then cooled to room temperature. UiO-67 and imidazole powders were placed in a container and separated by a stainless steel sieve (mesh 2000). The weight ratio of imidazole and UiO-67 is 1:1, 1:2 and 1:4. Imidazole was vapourized into UiO-67 at 120°C for 13 hours under reduced pressure.

Leaching test

The leaching test was performed as follows: the imidazole@UiO-67 powders were placed into a beaker of water. Samples were allowed to sit statically at room temperature for 1 hour. The powders were filtered and dried at room temperature for

analysis. The resulting powders were analyzed using PXRD and AC impedance spectroscopy.

Physical Measurements.

Thermogravimetric analysis (TGA) were performed using a Simultaneous Thermal Analyzer (STA 449C, NETZSCH) in the temperature range between 30^{o}C and 800^{o}C in a N_2 atmosphere. X-ray powder diffraction (XRPD) data were collected on a PANalytical X'PertPowder diffractometer with CuKα radiation. The adsorption isotherms for N_2 at 77 K were measured with 3H-2000PS1 (BeiShiDe Instrument). Transmission electron microscope (TEM) measurement was performed by use of a FEI Tecnai G2 F20. X-ray photoelectron spectroscopy (XPS) was measured with Thermo Escalab 250Xi.

AC impedance spectroscopy was carried out with a ZL5 LCR instrument operated in the frequency range from 10 to 10^5 Hz. For conductivity measurements, the powder was compacted using uniaxial pressing into pellets under a pressure of 900 MPa. AC impedance measurements were carried out using a two-probe method with Ag-paste and Ag-wires. The measurement cell was placed in a tube furnace. The furnace was filled with under dry N_2 before measurement to remove moisture. Measurements were taken under anhydrous conditions and done at thermal equilibrium by holding for 10 min in the temperature range from room temperature to 200 °C. Proton conductivity was calculated using the following equation

$$\sigma = \frac{L}{SR}$$

where L and S are the length (cm) and cross-sectional area (cm^2) of the samples, respectively, and R, which was extracted directly from the impedance plots, is the bulk resistance of the sample (Ω).

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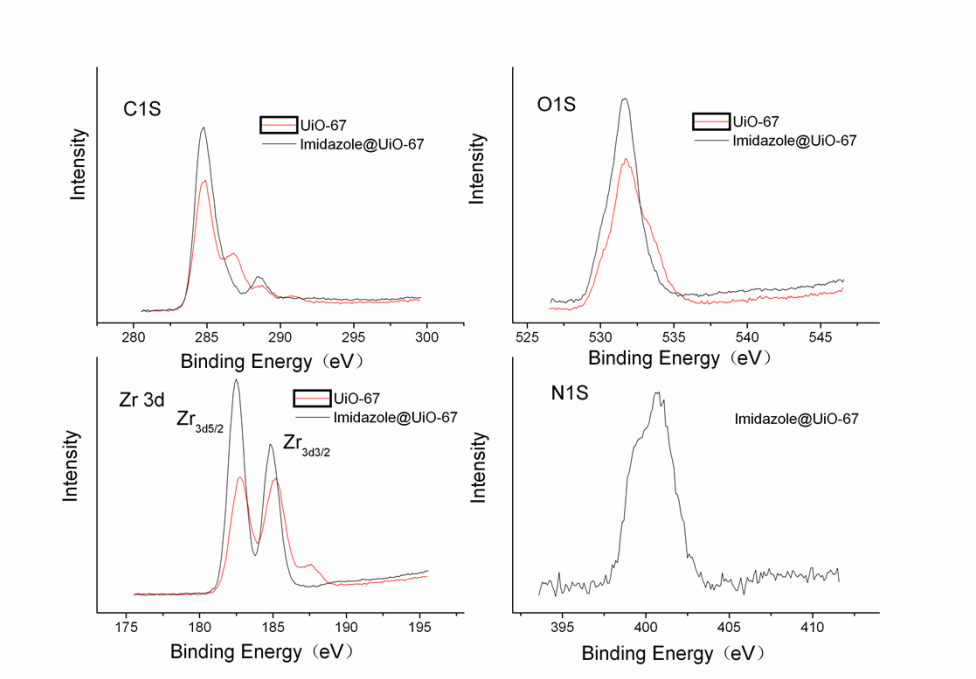

Fig. S1 XPS of UiO-67 and imidazole@UiO-67

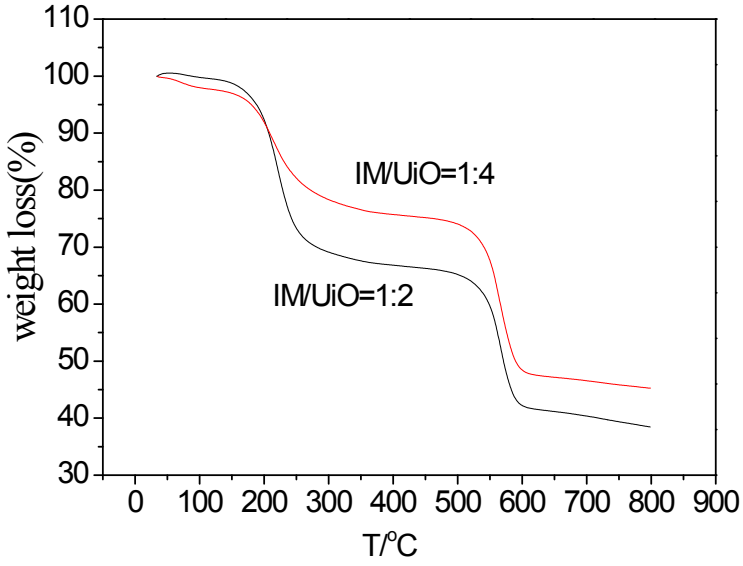

Fig. S2 TGA of imidazole@UiO-67 with different imidazole loading amount (IM/UiO=1:4 indicates the 21 % imidazole content; IM/UiO=1:2 indicates the 30 % imidazole content)

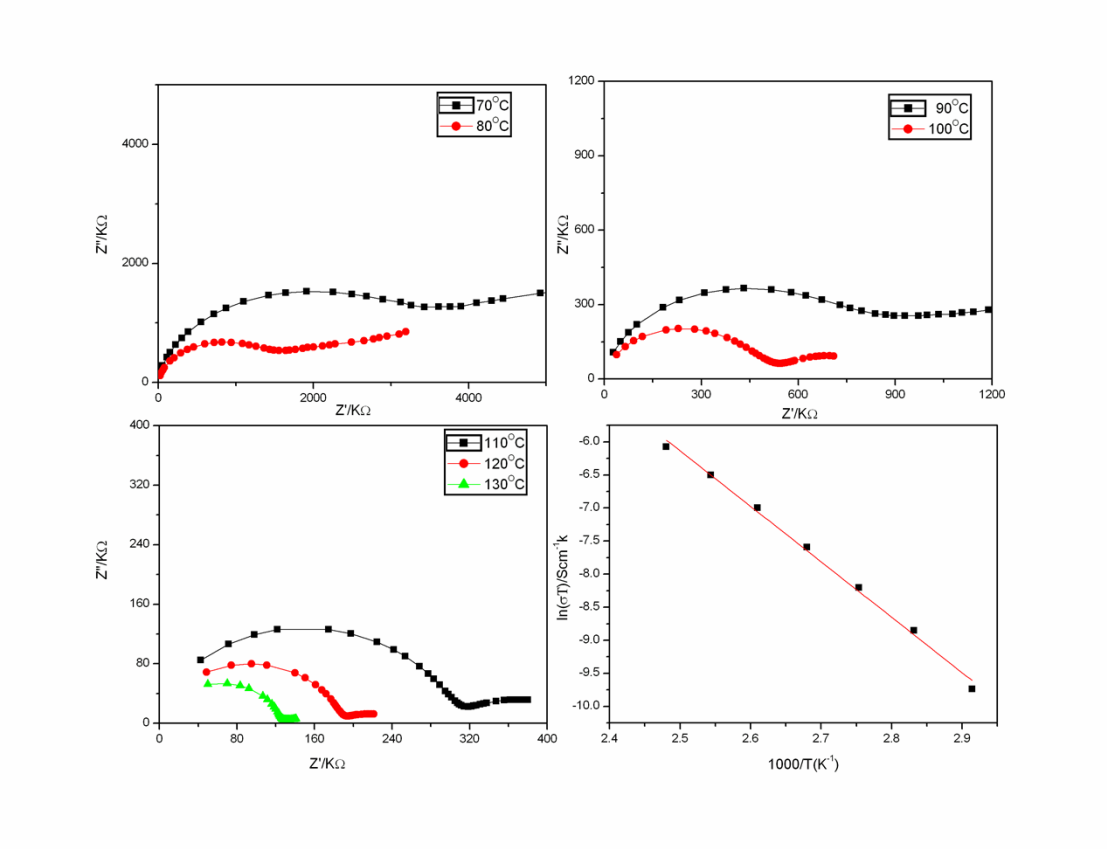

Fig. S3 AC impedance spectra (a-c) and Arrhenius curves (d) of imidazole@UiO-67 with 21 % imidazole content

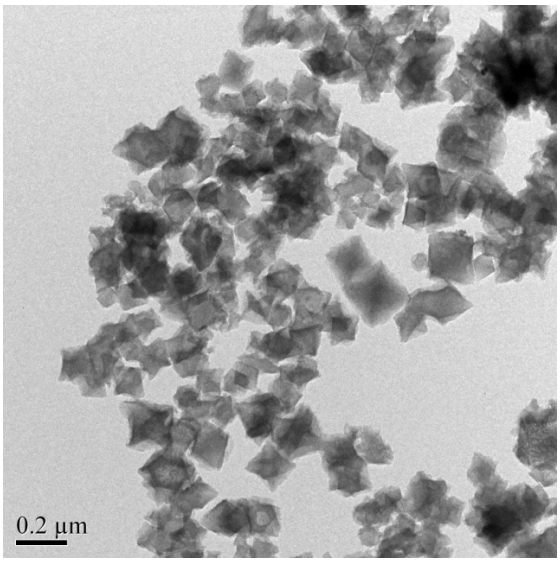

Fig. S4 TEM of UiO-67

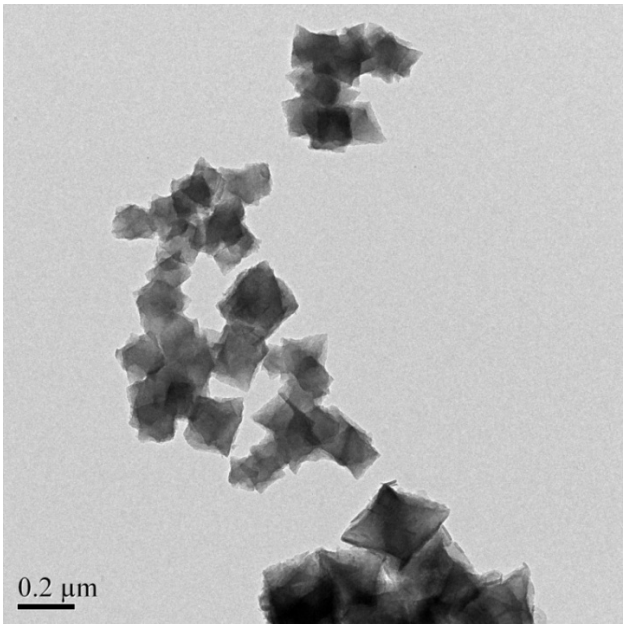

Fig. S5 TEM of imidazole@UiO-67

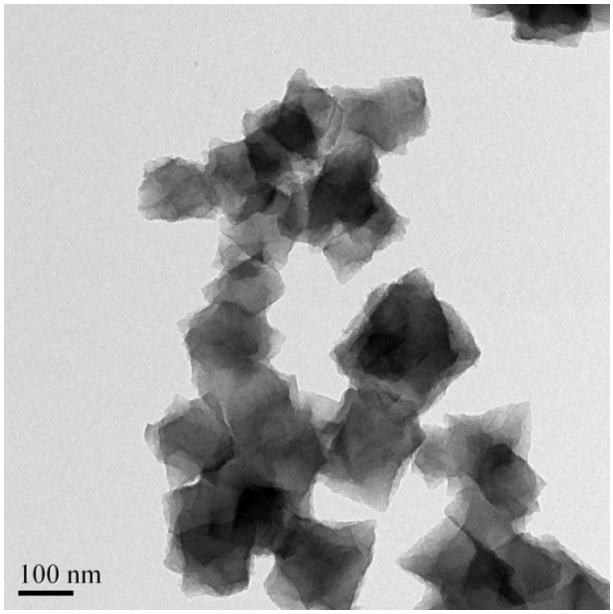

Fig. S6 TEM of imidazole@UiO-67

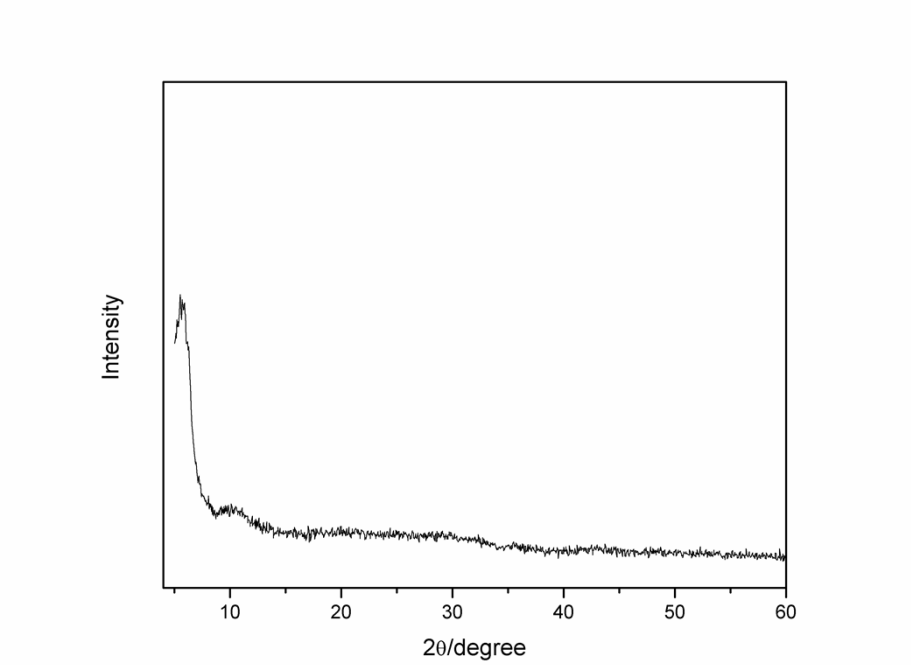

Fig. S7 XRD of imidazole@UiO-67 after treated with water for 1 hour