Electronic Supplementary Material (ESI) for CrystEngComm.

Synthesis of an ultra-stable metal-organic framework for proton conduction

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Experimental

Materials

Adenine (98%), sodium azide (99%), triethylamine hydrochloride (99%) and zinc nitrate hexahydrate (99%) were purchased from Aladdin (Shanghai, China), Fuchen Chemical Reagent (Tianjin, China), Guangfu Reagent (Tianjin, China) and Sinopharm Chemical Reagent (Shanghai, China). Solvents in this experiment were used as received without any further purification.

Characterizations

Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku D/Max 2550 diffractometer with Cu Kα (λ = 1.5418 Å) at 50 kV and 200 mA. Thermogravimetric analysis curves (TGA) were recorded on a PerkinElmer thermogravimetric analyzer under air flow atmosphere with a heating rate of 10 °C min^{-1} from 30 °C to 800 °C. Single crystal X-ray diffraction data was collected on a Bruker APEX II CCD diffractometer (Mo Kα, λ = 0.71073 Å) at 293 K. Indexing was performed on software APEX2 (difference vectors method). Data integration and reduction were performed on SaintPlus software. An empirical absorption correction was performed using a multi-scan method using the SADABS program. Structures were solved and refined with SHELXL-2014 (direct methods and full-matrix least-squares on F^2). Hydrogen atoms on carbon were calculated in ideal positions with isotropic placement parameters set to 1.2 × Ueq of the attached atoms. ^{1}H NMR spectrum was collected on a Bruker AV 400 spectrometer at 298 K. Elemental analyses (C, H, N) were carried out on a PerkinElmer 240 analyzer. Impedance curves were measured by Solartron 1260+1287 with input voltage amplitude of 30 mV over a frequency range of 1 Hz – 1 MHz. N_2, CO_2 and water vapor adsorption isotherms were measured on Quantachrome Autosorb-IQ2 at 77 K, 273 K and 298 K.

Synthesis of 4,5-bis(tetrazol-5-yl) imidazole ligand (H_3IBT)

The ligand was synthesized according to the literature.[1-2] 2.00 g 4,5-dicyanoimidazole, 6.60 g NaN_3 and 24.70 g triethylamine hydrochloride were added into a mixture of 80 ml toluene and 20 mL methanol. The mixture was heated at reflux for three days. Upon cooling to the room temperature, the mixture was added with 100 ml 1.0 M NaOH in a dropwise manner and stirred for 30 minutes. The aqueous layer was separated from the mixed solution and acidized with 1.0 M HCl until no more white precipitates were formed. Next, the precipitates were filtered and dissolved in aqueous NaOH (1.0 M). And then, the settled solution was acidized with aqueous HCl (1.0 M) until pH = 4 and then filtered. Finally, the precipitate was washed with water until pH = 7 and dried at 100 °C for 12 h. ^{1}H NMR (400 MHz, DMSO) spectrum was displayed in Fig. S1 with δ 8.30 (s, ^{1}H).

Synthesis of Compound 1

Compound **1** was synthesized hydrothermally, and the typical protocol was described in the following: 100 mg of H_3IBT, 200 mg of $Zn(NO_3)_2 \cdot 6H_2O$ and 200 mg of adenine were added in 20 ml H_2O. The resultant solution was sealed in a 50 ml Teflon-lined stainless steel autoclave and then heated at 160 °C for 3 days. After cooling to the room temperature, the brown crystals were washed with water and ethanol, and dried at ambient condition. The product yield is ~138 mg. Elementary analyses (%) for Compound **1**: calc. C 18.93, H 0.954, N 44.16. Found C 18.91, H 0.952, N 44.15.

Proton conductivity

Compound **1** was ground into fine powder and then compressed into a round pellet with a diameter of 6 mm and a thickness of 0.7 mm. Silver colloid was smeared on both sides of the pellet. And silver wires were connected to both sides of the pellet by the silver colloid. The resistances were calculated from the semicircle of the Nyquist plots. ZView software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Nyquist plot and to obtain the resistance values. The conductivity was calculated using the equation below

$$\sigma = \frac{L}{S \times R}$$

where σ (S cm^{-1}) is the conductivity, L (cm) is the thickness of the pellet, R (Ω) is the bulk resistance, and S (cm^2) is the area of the pellet. The activation energy of Compound **1** was estimated according to the Arrhenius equation

$$\sigma = \frac{\sigma_0}{kT} exp(\frac{-E_a}{kT})$$

where σ is the measured conductivity, σ_o is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant, T is the temperature in Kelvin.[3-4] For humidity-dependent measurements, different saturated salt solutions were used to generate the relative humidity of 97% (K_2SO_4), 53% ($Mg(NO_3)_2$) and 33% ($MgCl_2$).

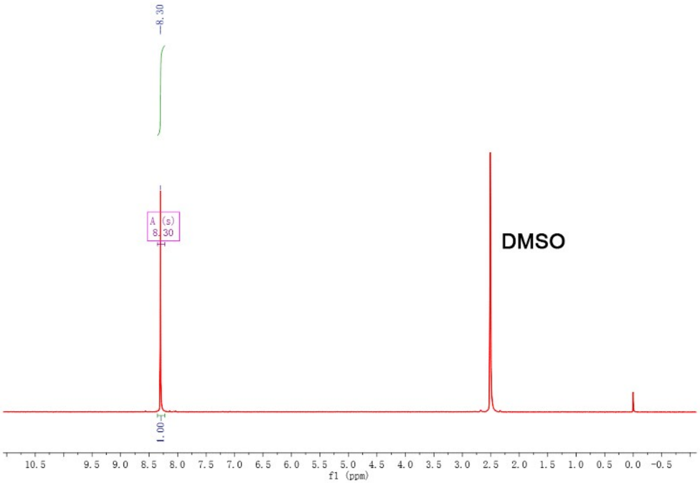

Fig. S1 ^1H NMR spectrum of H_3IBT.

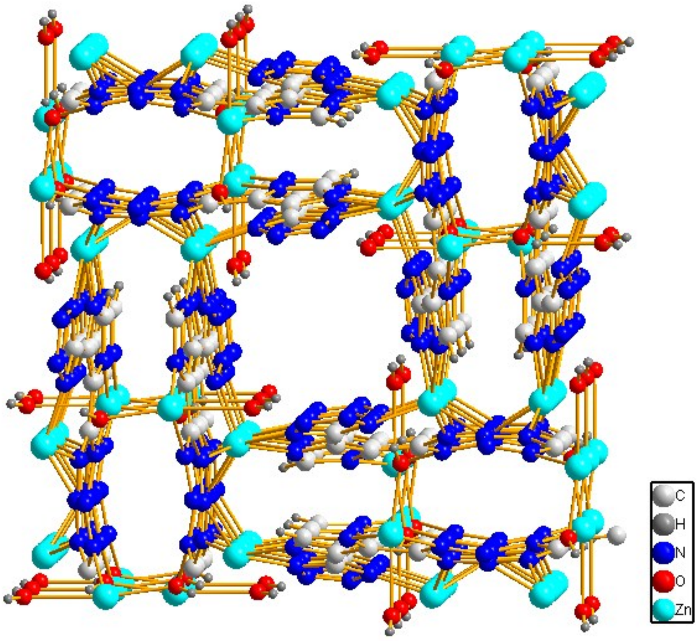

Fig. S2 3D structure of Compound **1**.

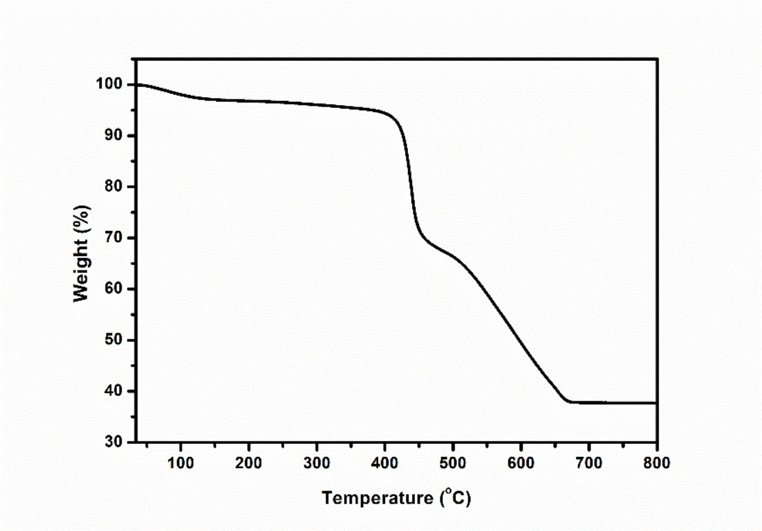

Fig. S3 TGA curve of Compound **1**.

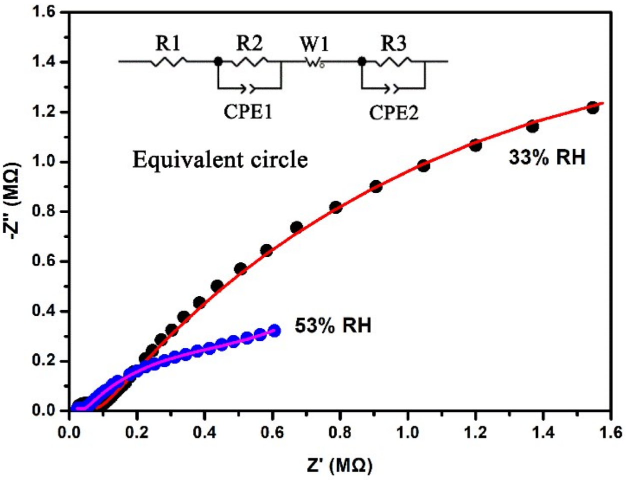

Fig. S4 Nyquist plots of Compound **1** at 30 ℃ and 33% RH (black) and at 30 ℃ and 53% RH (blue) and their equivalent electrical-circuit fitting lines (red for 33% RH and pink for 53% RH).

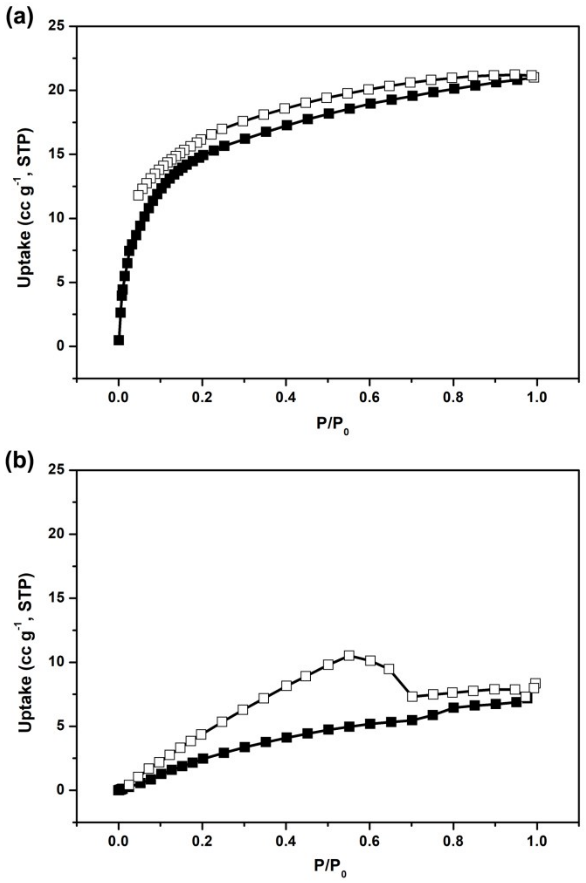

Fig. S5 (a) CO_2 and (b) N_2 sorption isotherms of Compound **1** at 273 K and 77 K. P_0 is 760 torr.

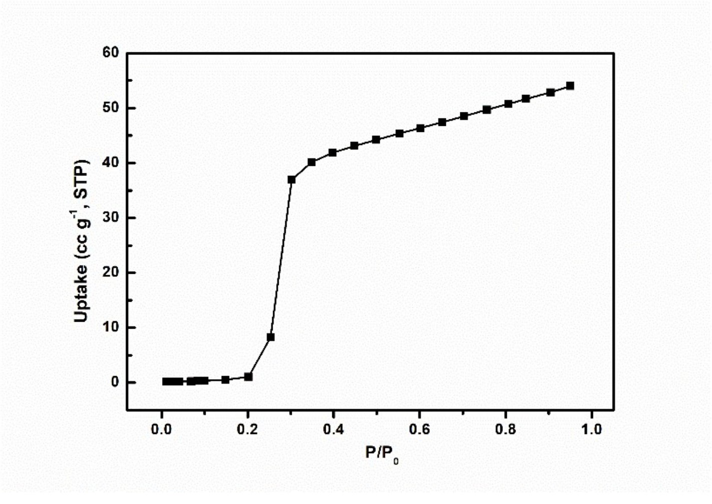

Fig. S6 Water adsorption isotherm of Compound **1**. P_0 is the saturated vapor pressure of water at 298 K.

References

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