Supporting Information

Cooperative proton transportation based on the reversible single crystal–single crystal transformation in a highly water-stable Cu-MOF with its facile and scalable preparation

Jun Zhang,*[a,b,c1] Xiaofan Ma,[b,1] Weili Kong, [a] Guodong Lu, [b] Xiaopeng Xuan[*,b]

[a] New Energy Photovoltaic Industry Research Center, Qinghai University, Xining 810006, P. R. China
[b] School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Henan Normal University, Xinxiang, Henan 453007, P. R. China.
[c] School of Materials and Chemical Engineering, Anhui Jianzhu University, Hefei 230601, P. R. China.

[1] J. Zhang and X. Ma contributed equally to this work.

Experiment section

1.1 Measurements and apparatus

All reagents are commercially available and used without any further purification. IR spectrum was carried out on a NEXUS 870 (Nicolet) infrared spectrometer in the 400-4000 cm^{-1} region using a KBr pellet with a resolution of 2 cm^{-1}. The Power X-ray diffraction (PXRD) was performed on a Bruker D8 (40kV, 40 mA) advance diffractometer with Cu-K_α radiation (λ=1.5418 Å). Thermogravimetric (TG) analysis data was obtained on a Netzsch STA 409 PC analyzer at a heating rate of 10 °C·min^{-1} under N_2 atmosphere. The optical absorption properties were determined on a UV-vis diffuse reflectance spectrometer (UV-3700, Shimadzu, Japan). Single crystal X-diffraction data were collected on a Bruker Smart APEX II diffractometer with a CCD area detector or on an Agilent SuperNova Dual diffractometer.

The Gamry Reference 600+ electrochemical workstation and the conventional three-electrode methods were used to measure the AC impedance spectrum, with the frequency range of 10^5 Hz ~ 10^{-2} Hz and the signal amplitude of 5mv. Impedance spectra at different temperature and different relative humidity (RH) were recorded, respectively. Different relative humidity (RH) is prepared with saturated salt solutions. The calculation formula of proton conductivity is σ= L/RS, where L is the sample thickness, S is the section area, and R is the resistance. The activation energy (Eα) derived from the Arrhenius equation: ln(σT)=lnA- Eα/(k_BT), where σ, T, A and k_B represent respectively the proton conductivity, temperature, the pre-exponential factor and the Boltzmann constant.

1.2 Representative synthesis of HNNU-2 {$[Cu_2(\mu_3\text{-}O)(BTTC)]^{2-}$•$2[H_3O]^+$}

$CuNO_3$·$3H_2O$ (0.20 mml) and 1,2,4,5-benzenetetracarboxylic acid (H_4BTC) (0.10 mmol) were respectively dissolved in 1 mL H_2O and 4 ml DMF. After mixing the two solutions, 7 drops of hydrochloric acid (6 M) were added. This solution was refluxed at 60 °C for 3 days and cooled to room temperature, then filtrated. The filter was washed with ethanol three times and dried at 60 °C for 24 hours, resulting in the dark green crystal (0.031 g) with a 67.4% yield. Elemental analysis based on Cu salt: Calcd.: H: 1.44%; C: 28.65%. Found: H: 1.23%; C: 29.21 %.

$Cu(OH)_2$ (0.20 mml) was dissolved in 1 mL H_2O, and mixed with 4 mL DMF containing 0.10 mmol 1,2,4,5-benzenetetracarboxylic acid, 7 drops of hydrochloric acid (6M) was added into this mixture, and the obtained solution was heated at 60 °C for 24 hours, and cooled to room temperature, filtrated, and washed with ethanol three times. The filter cake was dried at 60 °C for 24 hours, getting the dark green crystal.

$CuNO_3$•$3H_2O$ (96.0 g) was dissolved in 200 mL H_2O, and H_4BTC (50.0 g) was dissolved in 800 mL DMF. After mixing these two solutions in one liter flask, hydrochloric acid (6 M) was added to adjust pH value within 2~3. The flask was heated at 60 °C for 3 days and cooled to room temperature, then filtrated, and the dark green crystal

(56.1g) was obtained.

1.3 Crystallographic Data

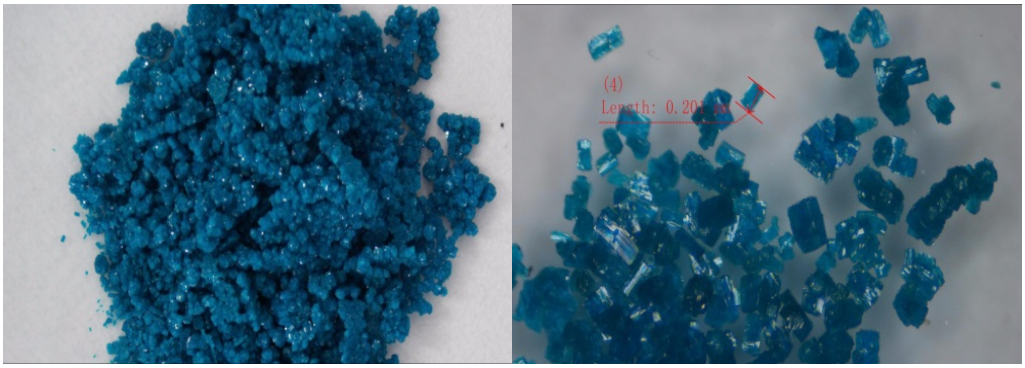
Single-crystal X-ray diffraction data at 298(2) K and 358 K were respectively collected on a Bruker SMART APEX Ⅱ diffractometer and on an Agilent SuperNova Dual diffractometer, equipped with a CCD area-detector using graphite-monochromated Mo-Ka radiation (0.71073 Å), then data reductions and absorption corrections were carried out by the SAINT [1] and SADABS [2] programs under APEX2 [3] software package, respectively. The structure at 298(2) was solved by dual space algorithm using SHELXT [4] routine and refined by SHELXL[4] routine with full-matrix least squares on F^2 under SHELXTL[5] software package. In the final refinement circle, the O atoms of guest water molecules with a fixed occupancy factor of 0.25 are refined isotropically, while the other non-hydrogen atoms were refined anisotropically. All the hydrogen atoms positions were generated geometrically and refined isotropically using a riding model. The carboxyl of C5O3O4 and O2 are disordered and refined over two sets of site with site occupancy actor of 0.54:0.46 and 0.47:0.53, respectively. The displacement parameters of these disordered atoms are restrained by simu, rigu, isor orders, while the other atoms are refined normally. In this structure as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms, the refinement was completed with no allowance for these water H atoms in the model. Summary of structural parameters and crystal data for **HNNU-2** were given in Table S1. Crystallographic data at 298 K have been deposited in the Cambridge Crystallographic Date Centre (CCDC No. 1873665).

1.4 Proton Conduction of HNNU-2

Alternating current impedance analysis was performed on the compressed powder samples to evaluate the proton conductivity of **HNNU-2**. In these measurements, the AC frequency range is 10^{-2}~10^{5} Hz and the temperature range is 298~368 K at different humidity conditions (RH). In Fig. S4-5, all Nyquist plots present incomplete arcs at high frequencies and tails at low frequencies, and the resistance of proton-conducting materials of **HNNU-2** is estimated by z' intercept values. The temperature-dependent proton conductivity of **HNNU-2** is shown in Fig. S5, indicating that the proton conductivity increases with the increase of temperature. At 85℃, the proton conductivity increases dramatically. The proton conductivity is only 1.9×10^{-6} S cm^{-1} at 298 K, but reaches to 9.4×10^{-4} S cm^{-1} at 358 K, and to the maximum value of 1.2×10^{-3} S cm^{-1} at 363 K.

(a)

(b)



(c)

Fig. S1 (a): The reaction process. (b): The quality of HNNU-2. (c): Shape and size of the **HNNU-2**

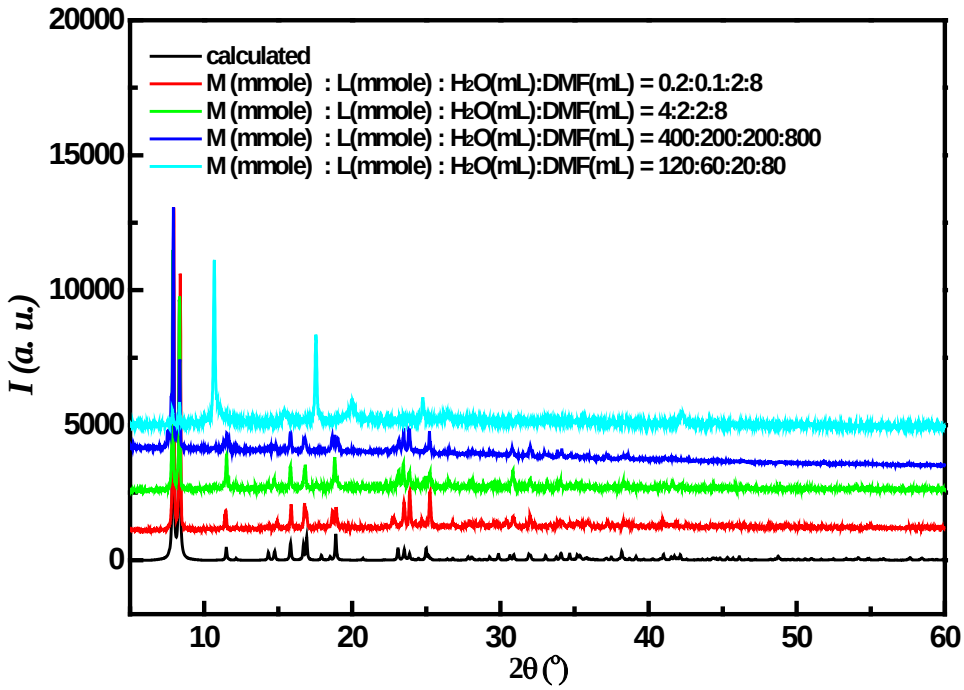


Fig. S2 PXRDs of HNNU-2 at the different multiples of reactants. A fail example is also given.

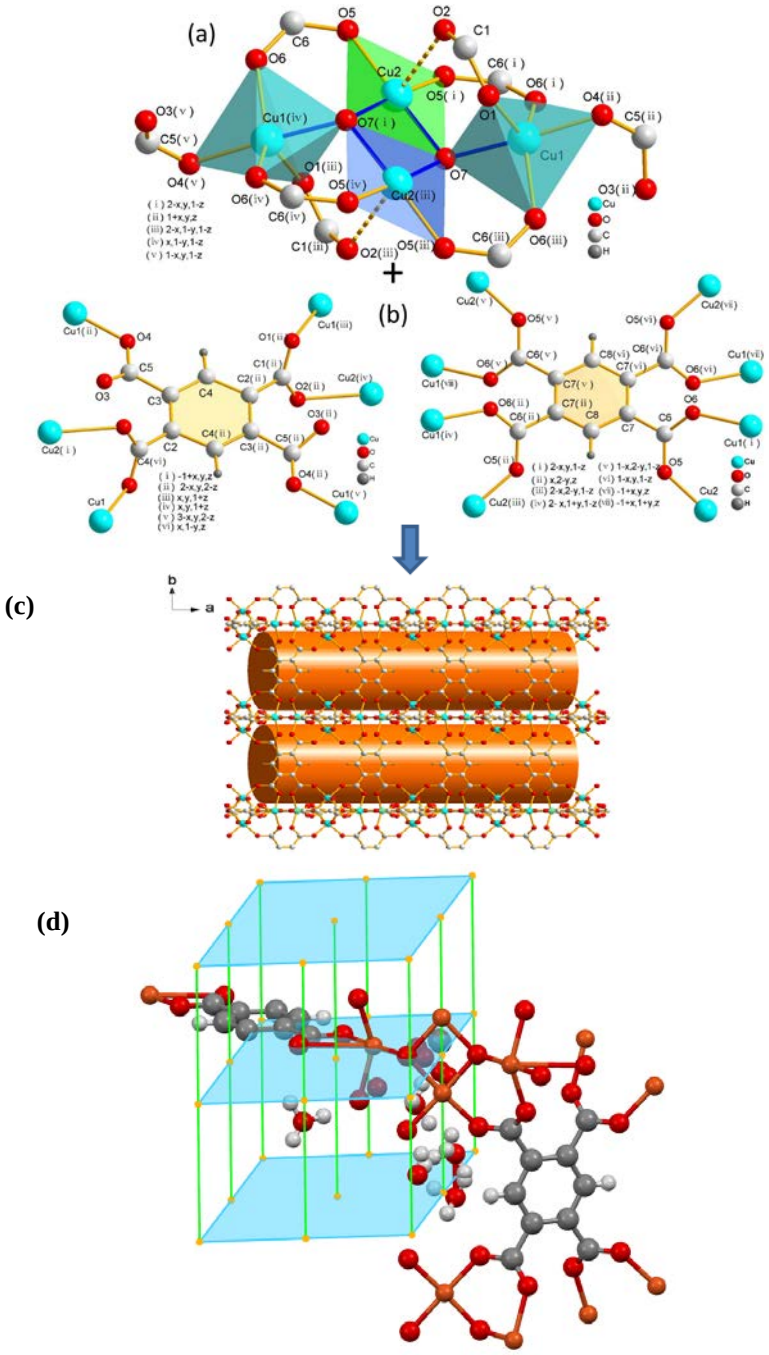


Fig. S3 (a): The coordination environments of Cu^{2+} ions in HNNU-2, symmetry code: (i) 2-x,y,1-z; (ii) 1+x,y,z; (iii) 2-x,1-y,1-z; (iv) x,1-y,1-z; (v) 1-x,y,1-z. (b): The coordination modes of BTC^{4-} ligands. (c): View of 1D straight channel of HNNU-2 along a-axis, symmetry code: (i) -1+x,y,z; (ii) 2-x,y,2-z; (iii) x,y,1+z; (iv) x,y,1+z; (v) 3-x,y,2-z; (vi) x,1-y,z for left figure of b and (i) 2-x,y,1-z; (ii) x,2-y,z; (iii) 2-x,2-y,1-z; (iv) 2- x,1+y,1-z; (v) 1-x,2-y,1-z; (vi) 1-x,y,1-z; (vii) -1+x,y,z; (viii) -1+x,1+y,z. (d): The symmetric operations in the structure of **HNNU-2**: inversion (orange dots); 2-fold axes (green lines) and mirror (blue planes).

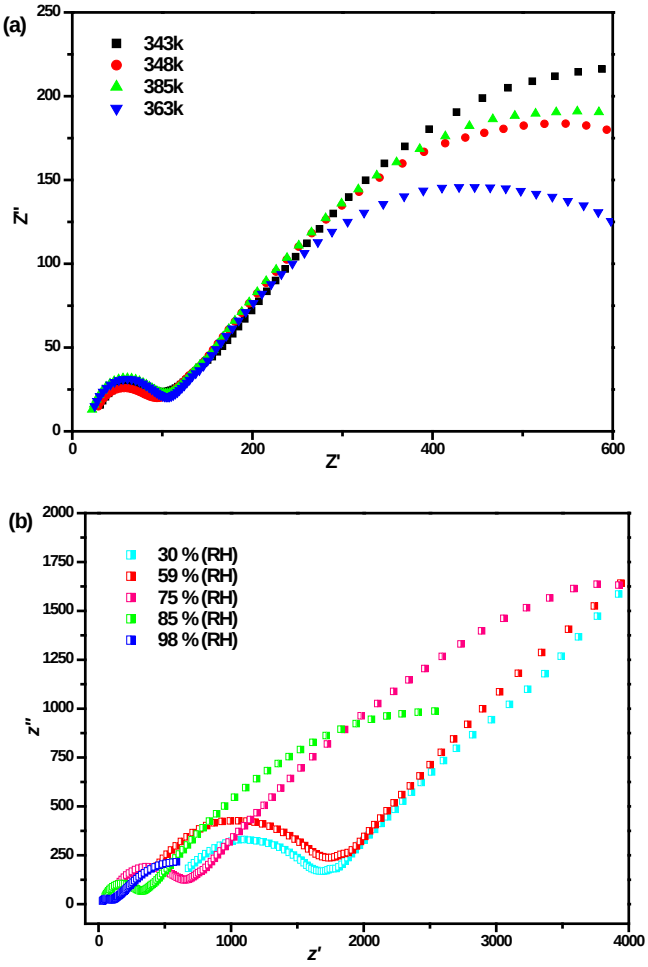


Fig. S4 (a): Temperature-dependent impedance plots of **HNNU-2** at different temperatures with 98% RH. (b): Humidity- dependent impedance plots of **HNNU-2** at 358 K with different RHs.

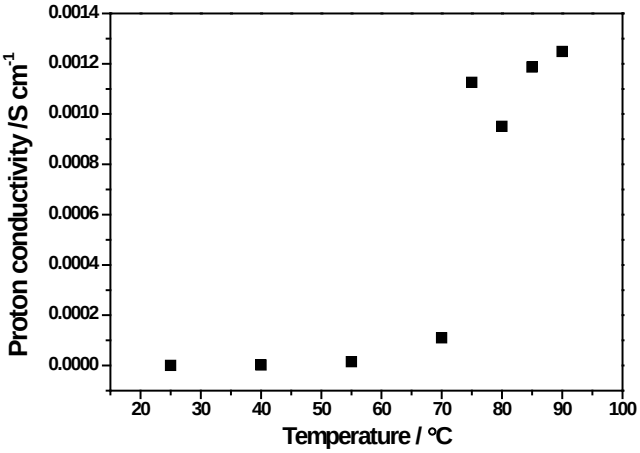


Fig. S5 Proton conductivity of **HNNU-2** under 98% RH at different temperature.

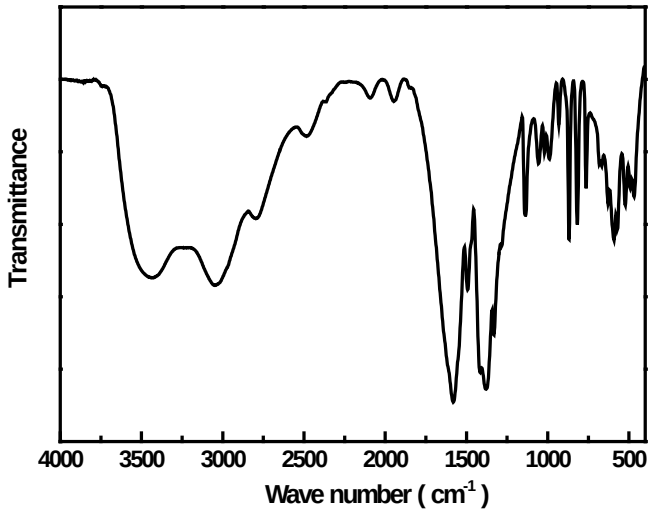


Fig. S6 IR spectrum of **HNNU-2**.

Table S1. Crystal data and structure refinement for HNNU-2 at 298K.

Empirical formula	C10 H8 Cu2 O11	
Formula weight	431.24	
Temperature	298.3(1) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 2/m 1	
Unit cell dimensions	a = 7.8682(3) Å	a= 90°.
	b = 10.5629(4) Å	b= 106.552(5)°.
	c = 11.6070(5) Å	g = 90°.
Volume	924.70(7) Å3	
Z	2	
Density (calculated)	1.549 Mg/m3	
Absorption coefficient	3.285 mm-1	
F(000)	428	
Crystal size	0.2 x 0.18 x 0.18 mm3	
Theta range for data collection	4.185 to 71.337°.	
Index ranges	-8<=h<=9, -12<=k<=12, -13<=l<=14	
Reflections collected	4226	
Independent reflections	1848 [R(int) = 0.0256]	
Completeness to theta = 67.684°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.75474	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	1848 / 171 / 177	
Goodness-of-fit on F2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1692	
R indices (all data)	R1 = 0.0554, wR2 = 0.1721	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.117 and -0.640 e.Å-3	

References:

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