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Supporting Information

Missing Metal-Linker Connectivities in a 3-D Robust Sulfonate-Based Metal-Organic Framework for Enhanced Proton Conductivity

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General Methods

Starting materials and solvents were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, *et al*) and used without further purification. Elemental analysis (EA) for C, H, and N were operated on a FLASH EA 1112 element analyzer. Thermogravimetric analysis (TGA) were carried out in N_2 stream (60 mL/min) on a NETZSCH STA 409 PC/PG differential thermal analyzer running from room temperature to 800 ℃ with a heating rate of 5 ℃/min. Fourier-transform infrared spectrum (FT-IR) were recorded using a Nicolet iS10 spectrophotometer with KBr pellets in 4000~400 cm^{-1} region.

Experimental Section

Hydrothermal Synthesis of TMOF-2. A mixture of 0.34 g $Cu(NO_3)_2$ $3H_2O$ (1.4 mmol), 0.22 g 4,4’-bipyridine (4,4’-bipy, 1.4 mmol), 0.43 g disodium 1,4-benzenedimethylsulfonate (1,4-$BDMSNa_2$, 1.4 mmol), and 10 mL deionized water were added into a 15 mL teflon-lined autoclave reactor followed by 30 min sonication for sufficient dispersion. The autoclave was then sealed into a stainless steel vessel and heated at 150 ℃ for 72 h, which was then cooled down to room temperature at a rate of 10 ℃/h. Skyblue cubic crystals of TMOF-2 suitable for single-crystal X-ray diffraction were obtained and collected by filtration. The crystals were rinsed with distilled water (2×20 mL), ethyl acetate (2×20 mL) and dried in air, giving a yield of 65 % (0.29 g) based on 4,4’-bipy. Elemental analysis calculated for $C_{28}H_{25}CuN_4O_{6.5}S_2$: C, 51.76; H, 3.85; N, 8.63, found: C, 51.26; H, 3.65; N, 8.90 (%, after activation).

Single-Crystal X-ray Diffraction. A single crystal of TMOF-2 suitable for X-ray analysis was chosen under an optical microscope and mounted onto a glass fiber. The diffraction data were collected at room temperature using graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) from a fine-focus sealed tube operated at 50 kV and 30 mA on a Bruker SMART APEX II CCD area detector X-ray diffractometer. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Thermal parameters for hydrogen atoms were tied to the isotropic thermal parameter of the atom to which they are bonded. Programs used were APEX-II v2.1.4,[S1] SHELXTL v6.14,[S2] and Diamond v3.1e.[S3] Further details of crystallographic data and structural refinement are summarized in Table S1. CCDC 1534326 contains the supplementary crystallographic data for TMOF-2. These data can be obtained freely from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray Diffraction. ~20 mg TMOF-2 crystals were grinded into uniform powder and then tiled onto the sample holder. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu K_α (λ=1.5418 Å), with a scan speed of 1 s per step, a step size of 0.02 ° in 2θ, and a 2θ range of 4~40 °. The experimental backgrounds were corrected using Jade 5.0 software package.

Activation of TMOF-2. Freshly prepared crystals were soaked in 20 mL ethyl acetate for 3 days, in which the solvent was exchanged with fresh ethyl acetate (20 mL) every 12 h. Then the crystals were filtrated and dried overnight under vacuum at 105 ℃.

Gas Sorption. ~150 mg of activated TMOF-2 was transferred to a pre-weighed sample tube and degassed at 105 ℃ on a Micromeritics ASAP 2020 adsorption analyzer for a minimum of 12 h or until the outgas rate was less than 5 mm Hg. The sample tube was re-weighed to obtain a consistent mass for the degassed sample. Brunauer-Emmett-Teller (BET) surface area data were collected volumetrically at 87 K by Ar or 77K by N_2. The exact surface area was averaged by the analyses of three independent samples. H_2 sorption experiments were performed at 77K in liquid N_2 bath or 87K in liquid Ar bath, respectively. CO_2 sorption experiments were performed at 200K, 273K, or 298K in dry ice-ethanol bath, ice-water bath or heating jacket, respectively. Isosteric heat of adsorption (Q_{st}) for H_2 and CO_2 were calculated by applying the Clausius-Clapeyron equation to two sets of adsorption data collected at two different temperatures.

Proton Conductivity Measurement. Proton conductivity of the pelletized samples were measured using a CHI 760e electrochemical workstation over a frequency range of 10 Hz~10 MHz with an input voltage amplitude of 500 mV. As-synthesized samples of TMOF-1 and TMOF-2 were grinded into uniform powder and made pellets under 8000 MPa for 2 min. The diameter of the pellets are 6.50 mm for both; the thickness of the pellets are 0.96 mm for TMOF-1 and 1.03 mm for TMOF-2, respectively (measured by a vernier caliper). Silver pastes were painted uniformly onto both sides of the pellets and copper wire electrodes were affixed into the paste. The measurements were taken in a temperature range of 20~90 ℃ and a relative humidity range of 30~98%. The temperature and humidity were controlled by a climate chamber. Before each measurement, the samples were put in the chamber at specified temperature and humidity for 6 hours for sufficient diffusion and equilibration of the water molecules. The grain interior resistance (R) was extrapolated by fitting the semicircles of the Niquist plots using a proposed equivalent circuit *via* Zview software package and the conductivity (σ) was acquired by the equation of $\sigma = l/AR$ where l and A represent the thickness and the area of the pellets, respectively.

Supporting Figures and Tables

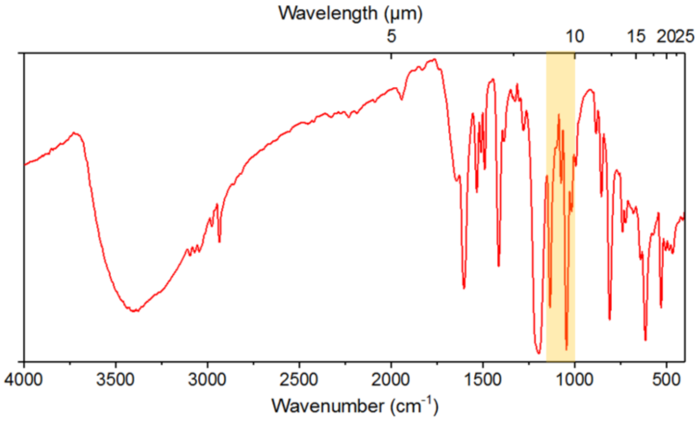

Fig. S1. FT-IR spectrum of TMOF-2 in which the absorption peaks of sulfonate group are highlighted.

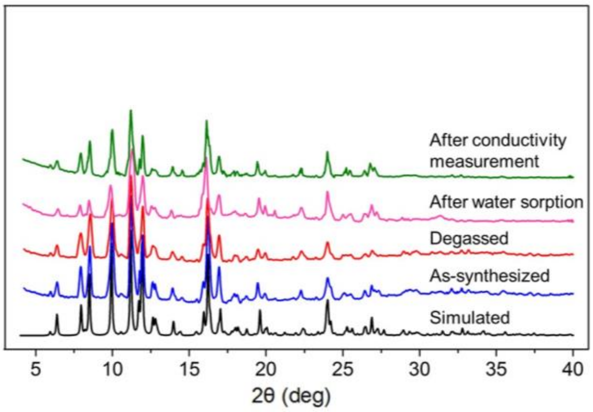

Fig. S2. PXRD patterns of TMOF-2.

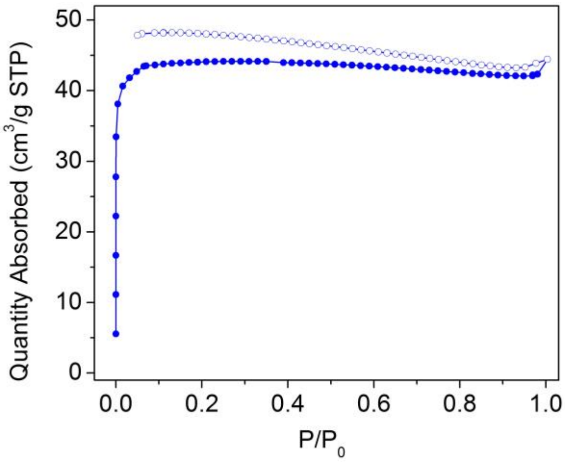

Fig. S3. N_2 sorption isotherm of TMOF-2 at 77K.

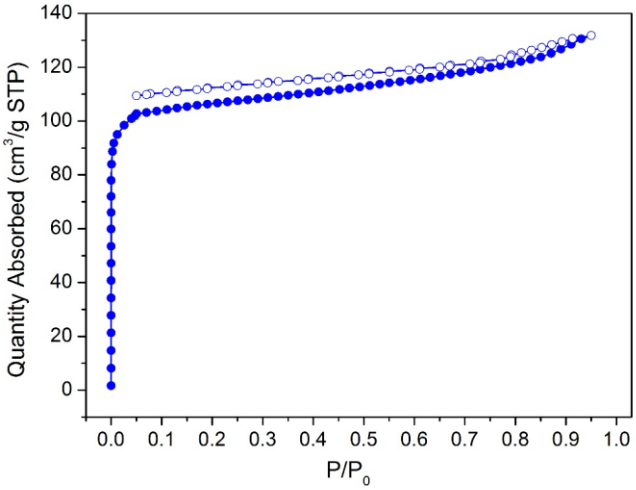

Fig. S4. Ar sorption isotherm of $[Cu_2(bpy)(bdc)_2]_n$ at 87K.

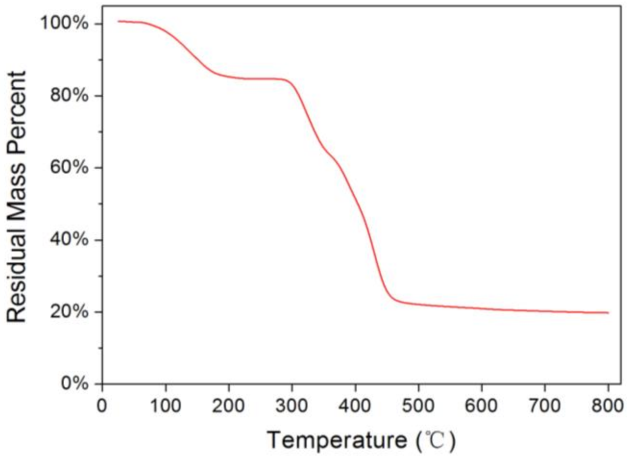

Fig. S5. Thermogravimetric analysis curve of TMOF-2 in N_2 flow.

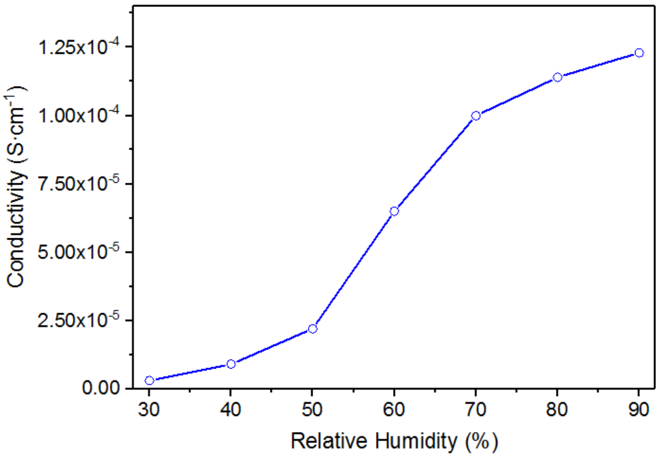

Fig. S6. Humidity dependence of the proton conductivity of TMOF-2 at 90℃.

Table S1. Crystal data and structure refinement for TMOF-2.

Identification code	TMOF-2	
Empirical formula	$C_{28}H_{25}CuN_4O_{6.5}S_2$	
Formula weight	649.20	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 15.6139(12) Å	α = 90 °
	b = 15.7965(13) Å	β = 90 °
	c = 29.712(2) Å	γ = 90 °
Volume	7328.3(10) $Å^3$	
Z	4	
Density (calculated)	1.275 g/cm^3	
F(000)	2912	
Crystal size	0.07×0.06×0.05 mm^3	
θ range for data collection	2.89~27.58 °	
Limiting indices	$-20 \le h \le 20$, $-20 \le k \le 20$, $-38 \le l \le 38$	
Reflections collected	16902	
Independent reflections	11515	
Completeness to θ = 27.58 °	100 %	
Absorption correction	Empirical	
Data / restraints / parameters	16902/759/869	
Goodness-of-fit on F^2	1.030	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1171, wR_2 = 0.2457	
R indices (all data)	R_1 = 0.0779, wR_2 = 0.2783	
Largest diff. peak and hole	1.014 and -1.120e.$Å^{-3}$	

Table S2. Representative proton-conducting MOFs reported in recent two years.

Material	Temperature (℃)	Humidity (% RH)	Conductivity (S/cm)	E_a (eV)
$(NH_4)_2[ZrF_2(HPO_4)_2]$ [S4]	90	95	1.5×10^{-2}	0.19
$\{[Mg(4,4'\text{-bpdc})(H_2O)_3](H_2O)\}_n$ [S5]	30	0	1.4×10^{-5}	0.28
Cu^I-MOF⊃DEA [S6]	55	95	2.4×10^{-3}	0.60
$(Hpy)_2[Zn_2(ox)_3]\cdot nH_2O$ [S7]	25	98	2.2×10^{-3}	0.36
$Mg(C_8O_4H_4)(C_5NOH_5)$ [S8]	90	90	8.3×10^{-6}	0.38
$Cd(C_8O_4H_4)(C_5NOH_5)$ [S8]	90	90	2.3×10^{-3}	0.22
$Nd_2(C_8O_4H_4)_3(C_5NOH_5)_2\cdot(DMF)_n$ [S8]	90	90	1.7×10^{-3}	0.23
$\{[K_8(PTC)_2(H_2O)_{1.5}]\cdot 4H_2O\}_n$ [S9]	25	98	1.0×10^{-3}	0.23
POMOF [S10]	80	75	1.0×10^{-2}	0.22
NENU-530 [S11]	75	98	1.5×10^{-3}	0.33
NENU-531 [S11]	75	98	1.7×10^{-4}	0.36
$(NH_4)_3[Co_2(bamdpH)_2(HCOO)(H_2O)_2]$ [S12]	25	95	8.0×10^{-6}	0.69
$[Co(bamdpH_2)(H_2O)_2]\cdot 2H_2O$ [S12]	25	95	1.9×10^{-6}	0.75
$[Me_2NH_2][Eu(ox)_2(H_2O)]\cdot 3H_2O$ [S13]	55	95	2.7×10^{-3}	0.40
Cu(HL)L [S14]	25	97	1.1×10^{-3}	0.23
NH_4Br@HKUST-1 [S15]	25	99	9.0×10^{-4}	1.42
HKUST-1 [S15]	25	99	1.0×10^{-8}	0.69
VNU-15 [S16]	95	60	2.9×10^{-2}	0.22
UiO-66-SO_3H [S17]	30	97	3.0×10^{-1}	0.27
UiO-66-2COOH [S17]	30	97	1.0×10^{-1}	0.18
$\{[Zn(C_{10}H_2O_8)_{0.5}(C_{10}S_2N_2H_8)]\cdot 5H_2O]\}_n$ [S18]	80	95	2.6×10^{-7}	0.96
$\{[Zn(C_{10}H_2O_8)_{0.5}(C_{10}S_2N_2H_8)]\cdot 2H_2O]\}_n$ [S18]	80	95	4.4×10^{-4}	0.84
$[Nd(mpca)_2Nd(H_2O)_6Mo(CN)_8]\cdot nH_2O$ [S19]	90	44	1.4×10^{-4}	0.39
imidazole@UiO-67 [S20]	120	0	1.4×10^{-3}	0.36
JUK-2 [S21]	25	60	4.5×10^{-5}	0.28
$[Cu(H_2L)(DMF)_4]_n$ [S22]	95	95	3.5×10^{-3}	0.68

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