Supplementary Information

A stable porphyrinic metal-organic framework pore-functionalized by high-density carboxylic groups for proton conduction

Hao Wu, Fan Yang, Xiu-Liang Lv, Bin Wang, Yong-Zheng Zhang, Min-Jian Zhao*

and Jian-Rong Li*

Beijing Key Laboratory for Green Catalysis and Separation and Department of

Chemistry and Chemical Engineering, College of Environmental and Energy

Engineering, Beijing University of Technology, Beijing 100124, P. R. China

Fax: (+86)-10-67392332


E-mail: jrli@bjut.edu.cn

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I. Materials and general characterizations

All general reagents and solvents (AR grade) were commercially available and used as received without further purification. 4-Pyridinecarboxaldehyde and methyl 4-formylbenzoate were purchased from Bide Pharmatech Ltd. ^1H NMR spectra were measured on Bruker Avance 400 MHz with tetramethylsilane as the internal standard. FT-IR spectra were recorded on an IRAffinity-1 instrument. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Smartlab3 X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å) at room temperature. Simulation of the PXRD patterns were carried out by the single-crystal data and the diffraction-crystal module of the Mercury program available free of charge via the Internet at http://www.ccdc.cam.ac.uk/mercury/. TGA datas were obtained on a TGA-60 (SHIMADZU) thermogravimetric analyzer from 30 to 800 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under air atmosphere. Gas adsorption isotherms were measured by the volumetric method using a Micromeritics ASAP2020 surface area and pore analyzer.

II.   Synthesis

Synthesis of [5,15-di[4-carboxyphenyl]-10,20-di[pyridyl]porphyrin] (H₂DCDPP)
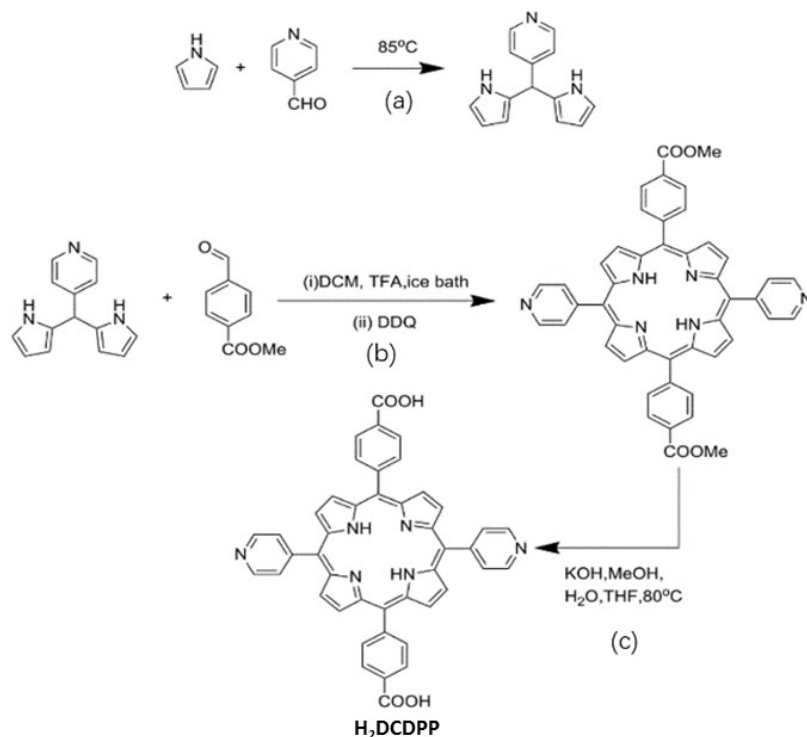
Scheme 1. Synthetic procedure of H₂DCDPP.

(a) 5-(4-Pyridyl)dipyrromethane

A mixture of 4-pyridinecarboxaldehyde (3.0 mL, 31.9 mmol) and pyrrole (20.00 mL, 0.29 mol) was stirred at 85 °C for 8 hours in nitrogen atmosphere. The reaction mixture was dried by evaporation and chromatographed (silica, in dichloromethane/ethyl acetate) from 100/0 to 90/10) affording brown solid. Recrystallization (in ethyl acetate/petroleum ether) afforded 3.557 g of pale yellow crystals. Yield: 65.4%. ^{1}H NMR (400 MHz, δ-CDCl$_3$): 5.45 (s, 1H), 5.88 (m, 2H), 6.18 (d, 2H), 6.75 (m, 2H,), 7.14 (d, 2H), 8.1 (m, 2H), 8.54 (d, 2H).

(b) [5,15-Di[pyridyl-10,20-di[4-carboxymethylphenyl]]porphyrin (H₂DCOOMeDPP)

5-(4-Pyridyl)dipyrromethane (1.000 g, 4.48 mmol) and methyl 4-formylbenzoate (0.730 g, 4.48 mmol) were dissolved in 600 mL of anhydrous dichloromethane (DCM) under nitrogen atmosphere. The mixture was stirred in an ice bath and trifluoroacetic acid (TFA) (12 mL, 172.0 mmol) was dropwise added. After about 20 minutes, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.030 g, 8.96 mmol) was added, and then it was stirred at room temperature for another 3 hours. The organic phase was washed with saturated aqueous solution of NaHCO₃, and dried over anhydrous Na₂SO₄. Purification by column chromatography (silica, trichloromethane/ethanol from 100/0 to 98/2) afforded a purple solid. Recrystallization (trichloromethane/hexane) afforded 533 mg of purple product. Yield: 32.4%. ¹H NMR (400 MHz, δ-CDCl₃): −2.87 (s, 2H), 4.12 (s, 6H), 8.29–8.32 (m, 8H), 8.47 (4H), 8.82–8.87 (m, 8H), 9.10 (d, 4H).

(c) [5,15-Di[4-carboxyphenyl]-10,20-di[pyridyl]porphyrin] (H₂DCDPP)

H₂DCOOMeDPP (500 mg, 0.126 mmol) was dissolved in tetrahydrofuran/methanol mixture (50 mL). Then, 20 mL 40% KOH solution (w/v) was added and the mixture was heated at 80 °C for 1 hour under stirring. After cooling to room temerature, the mixture was acidified with concentrated HCl aqueous solution (pH = 3) and then 100 mL water was added. The mixture was extracted with chloroform (100 mL × 3). The combining organic phase was washed with water 3 times (100 mL for each time) and dried over anhydrous Na₂SO₄, and filtered. The

solvent was removed and purple solid of H_2DCDPP was obtained (253 mg, 55% yield). ^1H NMR (400 MHz, δ-DMSO-d6): −2.84 (s, 2H), 7.88(d, 4H), 8.05 (d, 4H), 8.17-8.23 (m, 8H), 8.37 (d, 4H), 8.96 (d, 4H), 13.0 (s, 2H).

Synthesis of [Co(DCDPP)]·5H₂O (BUT-83)

$Co(NO_3)_2 \cdot 6H_2O$ (20 mg, 0.07 mmol), H_2DCDPP (30 mg, 0.04 mmol), and tetrafluoroboric acid aqueous solution (48%, 1.5 mL) were ultrasonically dissolved in 10 mL of N,N'-dimethylformamide (DMF) in a 20 mL Pyrex vial and sealed. The vial was then heated at 80 °C for 72 h in an oven. After cooling to room temperature, the resulting deep purple crystals were harvested by filtration and washed with DMF and acetone, and then dried in air (yield 28 mg). For FT-IR and TGA spectra, see Figure S2 and S3, respectively.

Synthesis of Co(DpyDtolP)

The ligand DpyDtolP and its Co-MOF (Co(DpyDtolP)) were synthesized according to literature method.[7] The PXRD is shown in Figure S7, confirming the sucess of obtaining this MOF and the phase purity of the as-synthesized sample.

III.   Single-crystal X-ray diffraction for BUT-83

The crystal data of BUT-83 was collected on a Rigaku Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu Kα radiation (λ = 1.54184 Å) at 100 K. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the *SCALE*3 *ABSPACk*[1] scaling algorithm. The structure of the MOF was solved by direct methods and refined by full-matrix least-squares on F^2 using the *SHELXTL* software package.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of the ligands were calculated in ideal positions with isotropic displacement parameters. There are solvent accessible pore volumes in the crystals of the MOFs, which are occupied by highly disordered solvent molecules. No satisfactory disorder model for these solvent molecules could be assigned, and therefore the *SQUEEZE* program implemented in *PLATON*[3] was used to remove the electron densities of these disordered species. Thus, all of electron densities from free solvent molecules have been "squeezed" out. The details of structural refinement can be found in Table S1 and cif file.

Table S1. Crystal data and structure refinement for BUT-83.

BUT-83 (CCDC: 1524129)	Before squeeze	After squeeze
Empirical formula	$C_{44}H_{26}CoN_6O_4$	$C_{44}H_{26}CoN_6O_4$
Formula weight	761.64	761.64
Measurement temperature	100 K	100 K
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}$
a (Å)	33.0267(7)	33.0267(7)
b (Å)	33.0267(7)	33.0267(7)
c (Å)	9.1815(3)	9.1815(3)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
Volume ($Å^3$)	8673.1(5)	8673.1(5)
Z	9	9
Calculated density(mg m^{-3})	1.312	1.312
Absorption coefficient (mm^{-1})	0.496	0.496
Independent reflections ($I > 2\sigma(I)$)	3792 [R_{int} = 0.0857]	3792 [R_{int} = 0.0857]
$F(000)$	3519.0	3519.0
Reflections collected	10911	10911
Crystal size (mm^3)	0.220 × 0.200 × 0.200	0.220 × 0.200 × 0.200
θ range for data collection	4.268 to 52.494	4.268 to 52.494
Data / restraints / parameters	3792/12/250	3792/12/250
	$-39 \le h \le 29$	$-39 \le h \le 29$
Limiting indices	$-36 \le k \le 38$	$-36 \le k \le 38$
	$-5 \le l \le 11$	$-5 \le l \le 11$
Goodness-of-fit on F^2	1.037	1.045
$R_1{}^a$, $wR_2{}^b$ [I > 2σ(I)]	R_1 = 0.0806, wR_2 = 0.2239	R_1 = 0.0860, wR_2 = 0.2375
$R_1{}^a$, $wR_2{}^b$ (all data)	R_1 = 0.1193, wR_2 = 0.2561	R_1 = 0.1208, wR_2 = 0.2669
Largest diff. peak and hole (e/$Å^3$)	0.94/–0.95	0.82/–0.97

[a] $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$.
[b] $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/\Sigma w(F_0^2)$

IV. Activation of the BUT-83 sample

As-synthesized sample of BUT-83 was firstly soaked in fresh DMF for 24 h and then the extract was discarded. Fresh acetone was subsequently added, and the sample was allowed to stay in it for 8 h. This procedure was repeated three times over one day. After removing the acetone, the sample was dried under a dynamic vacuum (< 10^{-3} Torr) at room temperature for 3 h. Before adsorption measurement, the sample was further activated using the "outgas" function of the adsorption analyzer for 10 h at 70 °C. Before proton conductivity measurement, the sample was further dried for 10 h at 80 °C.

V.   Proton conduction measurement

The given MOF powder (*ca.* 80-100 mg) was pressed under 1000 kg cm^{-2} pressure for 2 min to make a plate (length 1.0 cm and width 0.4 cm) (Fig. S1), then the thickness was measured by a micrometer. Both sides of the plate were attached to silver wires with silver paste and then put in a sealed double-walled glass chamber. The relative humidity (RH) inside the chamber was controlled through using standard saturated aqueous solutions of $MgCl_2$, $Mg(NO_3)_2$, $NaNO_2$, NaCl, KCl, and K_2SO_4 (corresponding RH are about 33, 53, 65, 75, 85, and 97%, respectively).[4] The proton conductivities of the plate were then tested by a quasi-four-probe method in the chamber connected with a temperature controlled circulation water bath. The impedance measurements were carried out by using a Zennium electrochemical workstation with tuned frequencies from 1 Hz to 4 MHz and alternating potentials of 100 mV at 298-353 K. The bulk conductivities (σ, S cm^{-1}) of the sample were estimated by using the following equation(1):

$$\sigma = L / (RA) \tag{1}$$

where L (cm) is the lenth of the block, R (Ω) is the impedance, and A (cm^2) is the face area of the plate (A = thickness × width). All measurements were repeated three times to get reproducible results.

The activation energy (E_a) was determined by the equation (2) in previous literature.

$$\sigma = \frac{\sigma^0}{kT} \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where σ^0 is a constant, k is the Boltzmann constant, T is the temperature (K), E_a is the activation energy (eV).
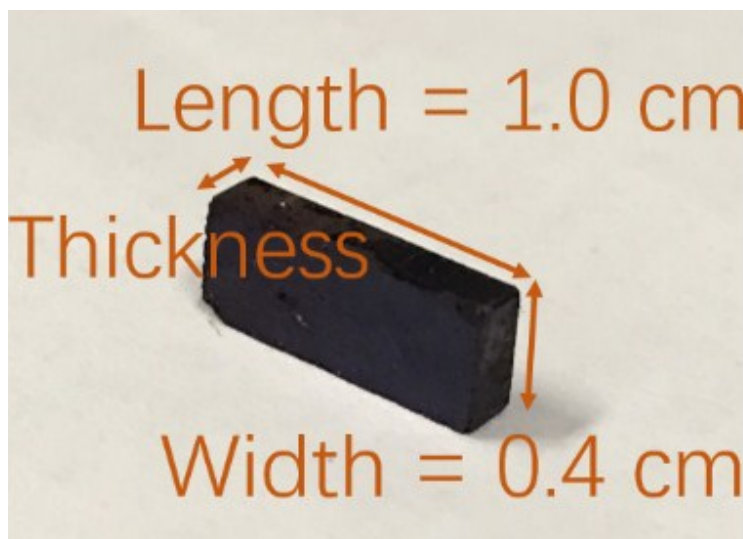
Fig. S1. Pressed sample for conductivity measurement.

The density of –COOH groups was calculated by the equation (3) below:

$$D_{-COOH} = n_{-COOH}/(V_{pore} \times M)$$ (3)

Where n_{-COOH} is the number of carboxylic acid groups per formula of the MOFs, V_{pore} is the pore volume (cm^3 g^{-1}) of MOFs, M is the molecular mass (g mol^{-1}) of MOFs. The pore volume of BUT-83 (0.10 cm^3 g^{-1}) was calculated from N_2 uptake, and that of UiO-66-(COOH)$_2$ (0.26 cm^3 g^{-1}) was obtained from reported literature.[5] Due to the unavailable data for N_2 uptake in MIL-53(Fe)-(COOH)$_2$, the pore volume of it used the approximate value of MIL-53(Al)-(OH)$_2$ (0.42 cm^3 g^{-1}) calculated by H_2O uptake.[6]

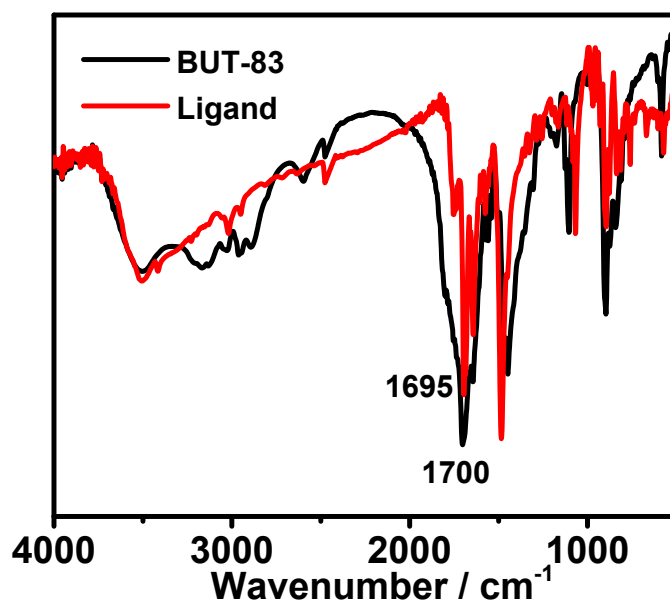## VI. Supplementary tables and figures

Fig. S2. FT-IR spectra of as-synthesized BUT-83 and its corresponding ligand.

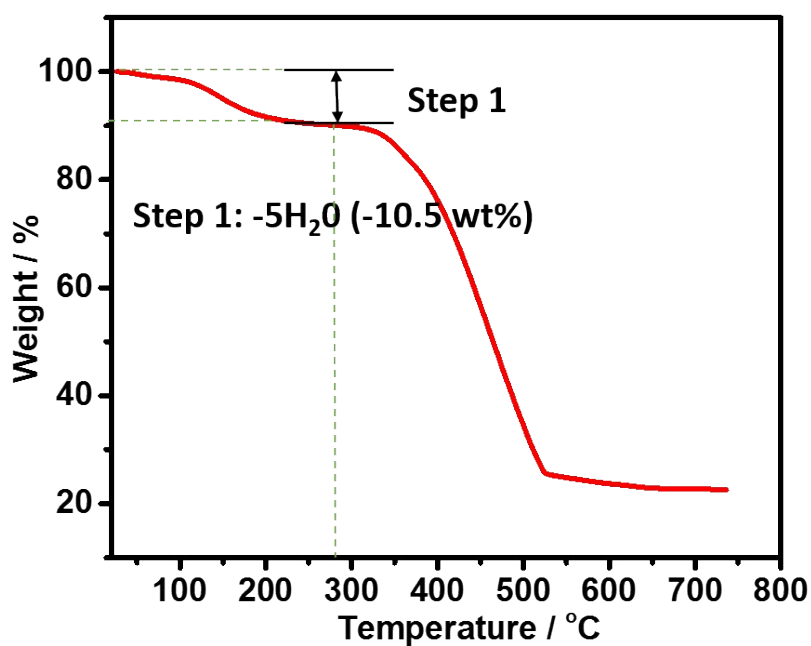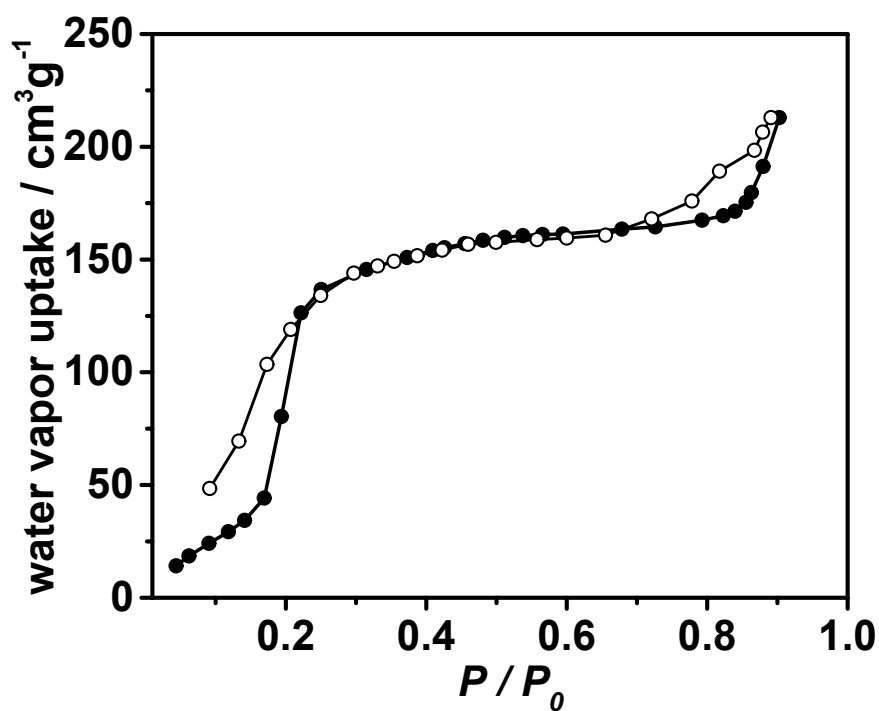**Fig. S3.** TGA curve of BUT-83.

Fig. S4. Water vapor adsorption/desorption isotherms of BUT-83 at 298 K.
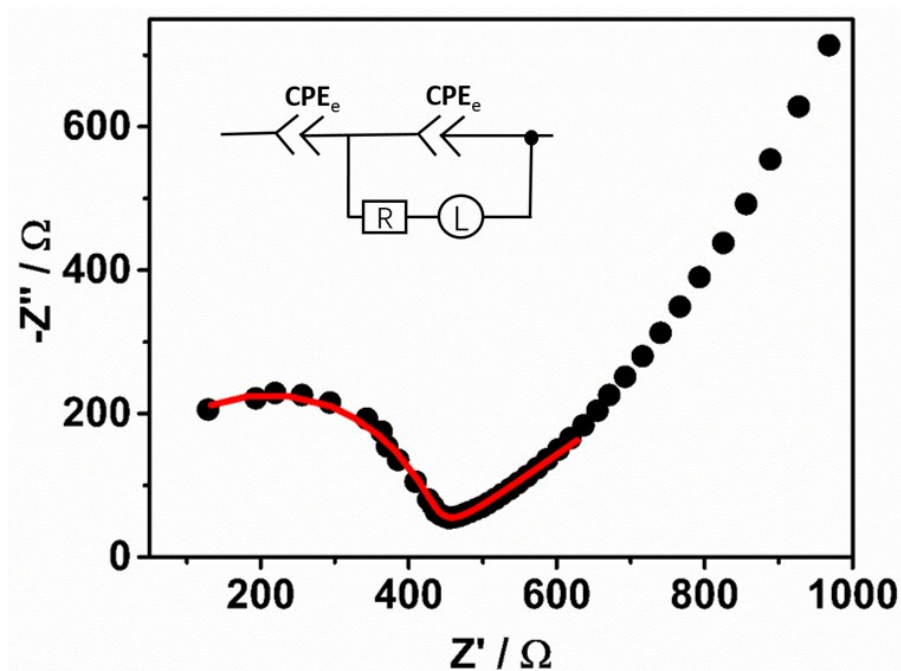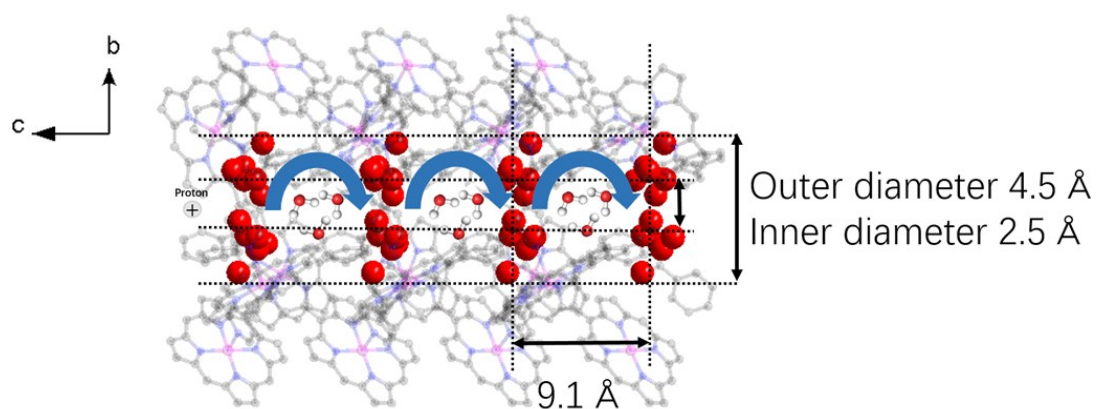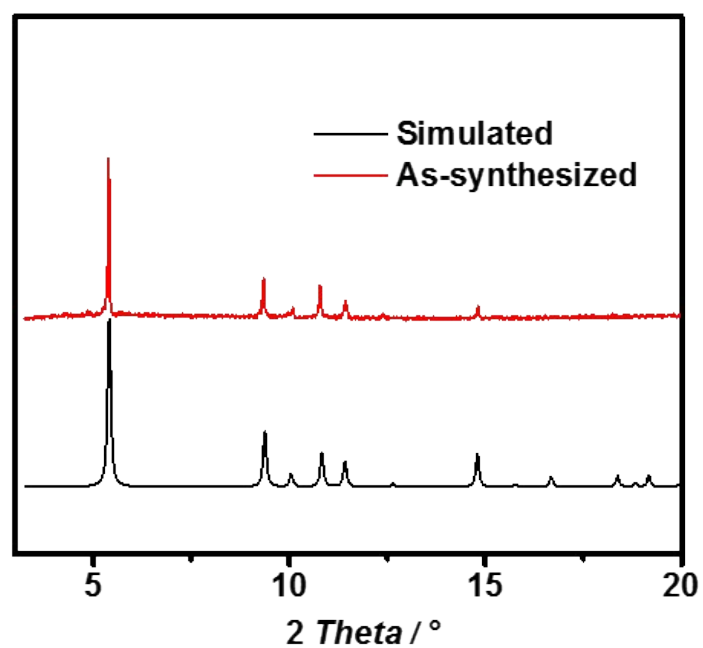

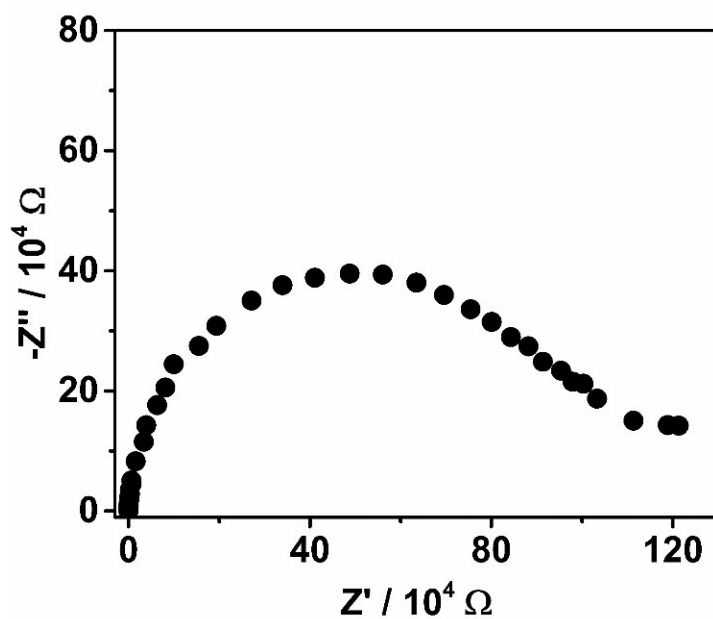**Fig. S5.** Nyquist plots (black circles) and fitted line (red curve) of BUT-83 at 80 °C

and 97% RH (the inset shows schematic representation of an equivalent circuit).

Outer diameter 4.5 Å
Inner diameter 2.5 Å

9.1 Å

Fig. S6. Proposed Grotthuss proton hopping pathway in BUT-83 (color code: Co, magenta; N, blue; C, black; H, white; and O, red).

Fig. S7. PXRD patterns of Co(DpyDtolP).

Fig. S8. Nyquist plot of Co(DpyDtolP) measured at 25 °C and 97% RH.

Table S2. Proton conductivities of BUT-83 and Co(DpyDtolP).

MOF	Conductivity (S cm^{-1})	T (°C)	RH (%)
BUT-83 powder	5.0×10^{-3}	25	97
Co(DpyDtolP) powder	4.7×10^{-7}	25	97
Co(DpyDtolP) single crystal[7]	6.4×10^{-7}	RT	–

Table S3. Proton conductivities ($> 10^{-2}$ S cm^{-1}) of selected MOFs.

Compounds	Conductivity (S cm^{-1})	T (°C)	RH (%)	Ref.
UiO-66(-SO$_3$H)$_2$	8.4×10^{-2}	80	90	8
TfOH@MIL-101	8×10^{-2}	60	15	9
Fe-CAT-5	5×10^{-2}	25	98	10
[(Me$_2$NH$_2$)$_3$(SO$_4$)]$_2$[Zn$_2$(ox)$_3$]$_n$	4.2×10^{-2}	80	95	11
BUT-83	3.9×10^{-2}	80	97	This work
PCMOF-10	3.55×10^{-2}	70	95	12
VNU-15	2.90×10^{-2}	95	60	13
H$^+$@Ni$_2$(dobdc)(H$_2$O)$_2$ (pH = 1.8)	2.2×10^{-2}	80	95	14
PCMOF2$^1/_2$	2.1×10^{-2}	85	90	15
[ImH][Cu(HPO4)$_{1.5}$(HPO$_4$)$_{0.5}$·Cl$_{0.5}$]	2.0×10^{-2}	130	0	16
HOF-GS-11	1.8×10^{-2}	30	95	17
H$_3$PO$_4$@MIL-101	1.0×10^{-2}	140	1.1	18
H$_2$SO$_4$@MIL-101	1.0×10^{-2}	150	0.13	18
CsHSO$_4$@Cr-MIL-101	10^{-2}	200	0	19

VII. References

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