

Electronic Supplementary Information for:

Proton conduction of an ionic HOF with multiple water molecules and application as membrane filler in direct methanol fuel cells

Fang Zhao^a, Li-Hui Cao^{a,}, Can Ji^b*

^aShaanxi Key Laboratory of Chemical Additives for Industry, College of Chemistry and

Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, China

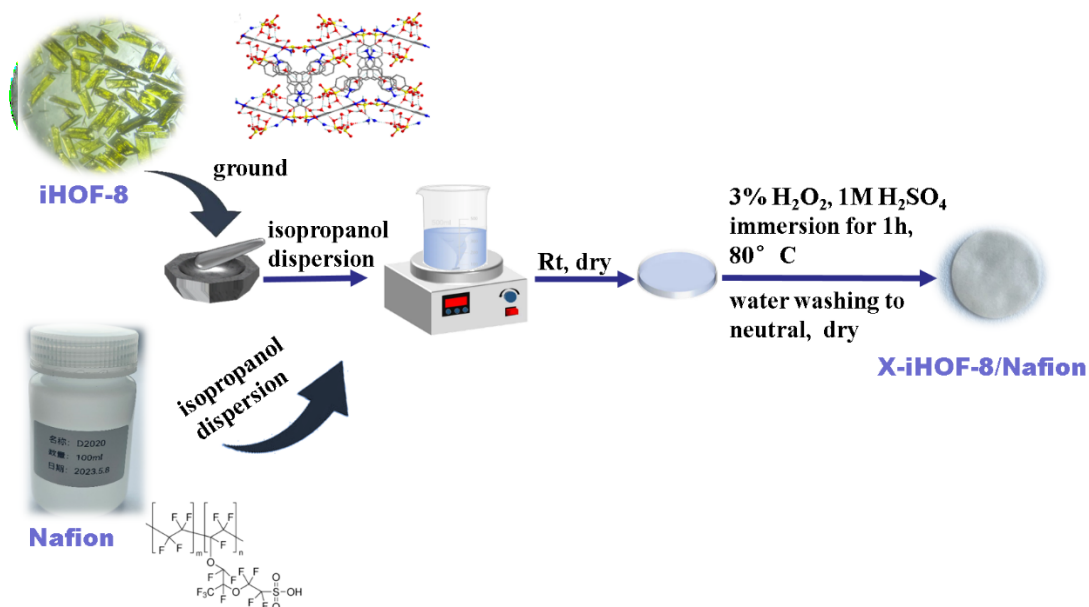
^bXi'an Manareco New Materials Co., Ltd., Xi'an 710077, China

*E-mail: caolihui@sust.edu.cn

Section S1. Experimental section.

Synthesis of iHOF-8: 10 mg of the ligand H₃SPB powder was measured and dissolved in 2 mL of H₂O and 2 mL of methanol, and 11.2 mg of DBpy·2I^[S1] was calculated and dissolved in 2 mL of H₂O. The two clarified solutions were mixed and left to stand for about a week, and yellowish needle-like crystals were precipitated, which fluoresced orange under a UV lamp. The yield of the crystals was: 68%. IR (cm⁻¹, KBr): 613 (w), 825 (w), 1180 (s), 1490 (w), 3068 (w), 3498 (w).

Preparation of X-iHOF-8/Nafion composite membranes: Preparation of **X-iHOF-8/Nafion** composite membranes (X = 3%, 6%, 9%): **iHOF-8** crystals (9 mg) were well powdered, added to isopropanol (3 mL) and then well dispersed for 3 h. 1.5 g (10%) of Nafion was diluted in water to dissolve it in 5 mL of isopropanol and then kept stirring for 3 h. Finally, the above two solutions were mixed and stirred for 6 h. The solution is then poured onto a transparent glass plate and dried at room temperature for 24 h to create a **3%-iHOF-8/Nafion** composite membrane. In addition, **6%-iHOF-8/Nafion** and **9%-iHOF-8/Nafion** composite membranes have also been fabricated using this method. The flow chart for the preparation of the composite membrane is shown in Scheme S1.



Scheme S1 Flow chart for the preparation of composite membranes.

Synthesis of ligands:

1) 1 g (3.26 mmol) of 1,3,5-triphenylbenzene powder was dissolved in 100 mL of dichloromethane, chlorosulfonic acid (2 mL, 29.3 mmol) was added slowly and dropwise under the protection of N_2 atmosphere, and stirred uniformly, and the above mixed solution was refluxed in an oil bath at $40\text{ }^\circ\text{C}$ for 1.5 h, and then continued to be refluxed for another 8 h. The remaining chlorosulfonic acid was quenched by measuring 10 mL of water, and then partitioned into liquid, and then dichloromethane phase was spin-dried. phase was spun dry, hydrolyzed by adding 1 M NaOH (36 h, $50\text{ }^\circ\text{C}$), extruded with methanol, filtered out as a white-gray powder, dried, and the yield was calculated to be 78%^[S16].

2) Hydroxylamine-O-sulfonic acid (15 g) was dissolved in 25 mL of water, cooled to $-5\text{ }^\circ\text{C}$ with ice brine, neutralized with 8.2 g, 30 mL of KOH, and the above solution was added to water (35 mL) containing 4,4-bipyridine (13 g) at $30\text{ }^\circ\text{C}$, and the suspension

was stirred in a steam bath until dissolved, and then refluxing was continued at 100 °C for 2 h. After cooling, the solution was treated with saturated K₂CO₃ solution, the yellow solution was diluted with methanol until no more precipitate was precipitated, the precipitate was filtered, and the filtrate was acidified with concentrated hydriodic acid (pH = 3-4) and allowed to stand in the refrigerator for 30 min. The solids were filtered out, washed several times with acetone, and finally recrystallized from distilled water (80 °C), filtered, and dried naturally to give a yield of 53%^[S1].

Stability experiments. The crystals of **iHOF-8** were soaked in water for 24 hours as well as refluxed in boiling water for 24 hours for hydrothermal stability, after the water-treated, the solids were filtered out and dried at room temperature for PXRD measurements. The chemical stability of **iHOF-8** was test as follows: the crystal of samples was dispersed in HCl or NaOH aqueous solutions with different pH values for 24 hours (pH = 2, 12), respectively. After that, the solids were filtered out and dried at room temperature for PXRD to determine its stability. We also performed a PXRD test on the crystal to determine the stability after the electrochemical impedance test.

Proton conductivity. Electrochemical impedance test of the crystal samples was determined by sandwiching the pellets of iHOFs between two copper sheets and then by two-electrode AC impedance spectroscopy using an electrochemical work-station (CHI 660E) in the frequency range from 1 Hz to 0.1 MHz with an alternating voltage of 5 mV.

The samples were pressed into a circular cylinder with a diameter of about 13

mm on a tableting machine for 5 min under 10.00 MPa pressure. Their thicknesses and diameter were determined by a Vernier caliper. The thickness of the crystal pressed into a pellet is about 1.5-2.0 mm. The temperature and relative humidity conditions are in the range of 30-100 °C at 68% RH to 98% RH and the humidity are controlled using high and low temperature and humidity test chamber. The thickness of our experimentally prepared composite membranes is generally around 50-100 μm . The proton conductivity of crystal samples was obtained from the following equation: $\sigma = L/RS$, where σ is the value of proton conductivity ($\text{S}\cdot\text{cm}^{-1}$), L is the thickness (cm) of the pellet, R is the value of electrochemical impedance and S is the flat surface area (cm^2) calculated by the diameter of the circular cylinder. Activation energy (E_a) values were calculated from the Arrhenius equation: $T\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is the pre-exponential factor, T is temperature, k is Boltzmann constant.

Water uptake and area swelling. Water uptake and area swelling test were measured to investigate the dimensional stability and hydrophilic ability of membrane. The weights (W_{dry} , g) and area (A_{dry} , cm^2) were pre-measured before testing. The area was measured by the length of the composite membrane. The composite membrane was cut into pieces ($1 \times 1 \text{ cm}^2$) and then immersed into deionized water for 48 h at room temperature. After that, the weights (W_{wet} , g) and areas (A_{wet} , cm^2) of the membrane were calculated immediately after wiping off the moisture on the surface. The water uptake and swelling rates were calculated using the following equations:

$$\text{Water uptake} = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100\%$$

$$\text{Swelling} = [(A_{\text{wet}} - A_{\text{dry}})/A_{\text{dry}}] \times 100\%$$

Ion exchange capacity. Take a sample with a mass of not less than 0.5 g, cut it into pieces, place it in a 0.1 MPa, 80 °C vacuum drying oven for 8 hours, take it out of the vacuum drying oven and quickly weigh its weight W , put the sample in a sealed, stir in a reagent bottle filled with saturated sodium chloride solution for 24 hours, titrate it with 0.01 mol/L sodium hydroxide solution until it is neutral, and record the volume V of sodium hydroxide solution consumed.

$$IEC = (V_{NaOH} \times C_{NaOH})/W_{Dry}$$

where C_{NaOH} (mol L⁻¹) is the molar concentration of the NaOH solution; V_{NaOH} (L) is the consumed volume of the NaOH solution during the titration process; and W_{Dry} (g) is the weight of the dry samples.

Methanol permeability measurement Methanol permeability of membranes was measured using liquid permeation equipment in two rooms. The membrane was cut into a round piece and sandwiched between two rooms which contained 2 M or 8 M aqueous methanol solution and deionized water, respectively (shown in the figure below). The two rooms were continuously stirred during the test. The concentration of methanol in the deionized water was periodically determined by gas chromatography (GC). Methanol permeability was calculated using the following equation:

$$C_B(t) = APC_A(t - t_0)/V_B L$$

Where A (cm²), L (cm) and V_B (cm³) are the diffusion area, the thickness of the membrane and the volume of permeated reservoirs, respectively. C_A and C_B (mol·L⁻¹) are the methanol concentration in donor and receptor reservoirs, respectively. P

($\text{cm}^2 \cdot \text{s}^{-1}$) and $t-t_0$ are the methanol permeability and the time of methanol penetration, respectively.

SEM and mechanical properties: Scanning electron microscope test were performed on a SU8100. The mechanical properties of the membrane are tested on CMT4202 for tensile tester.

Section S2: Single crystal X-ray diffraction analyses.

Single-crystal X-ray diffraction data for compounds **iHOF-8** was collected on a Bruker SMART APEX CCD diffractometer^[S2] equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique. Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine.^[S3] All the structures were solved with direct methods (SHELXS)^[S4] and refined by full-matrix least squares on F^2 using OLEX2,^[S5] which utilizes the SHELXL-2015 module^[S6]. All non-hydrogen atoms were refined anisotropically. Displacement parameter restraints were used in modeling the ligands. Hydrogen atoms were placed geometrically on their riding atom where possible. Crystal data containing space group, lattice parameters and other relevant information for the title complex are summarized in Table S1. More details on the crystallographic data are given in the X-ray crystallographic files in CIF format. Full details of the structure determinations have been deposited with Cambridge Crystallographic Data Center under reference number CCDC 2268869 and for **iHOF-8** and is available free of charge from CCDC.

Table S1. Crystal structure data and refinement details of **iHOF-8**.

Compounds	iHOF-8
Empirical formula	C ₃₉ H ₄₇ N ₆ O ₁₆ S ₃
Formula weight	953.01
Temperature / K	273.15
Wavelength / Å	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.9951(14)
<i>b</i> /Å	23.069(2)
<i>c</i> /Å	14.7334(16)
<i>α</i> /°	90
<i>β</i> /°	102.688(6)
<i>γ</i> /°	90
Volume/Å ³	4309.0(10)
<i>Z</i>	4
Density (calculated)g/cm ³	1.469
Absorption coefficient/mm ⁻¹	0.252
F (000)	1996.0
Reflections collected	37888
Independent reflections	7598 (R _{int} = 0.0318, R _{sigma} = 0.0242)
Data/restraints/parameters	7598/0/601
Goodness-of-fit on <i>F</i> ²	1.041
^a R ₁ , ^b wR ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0572/0.1487
^a R ₁ , ^b wR ₂ (all data)	0.0643/0.1527
Largest diff. peak and hole	0.92/-0.47
CCDC number	2268869

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

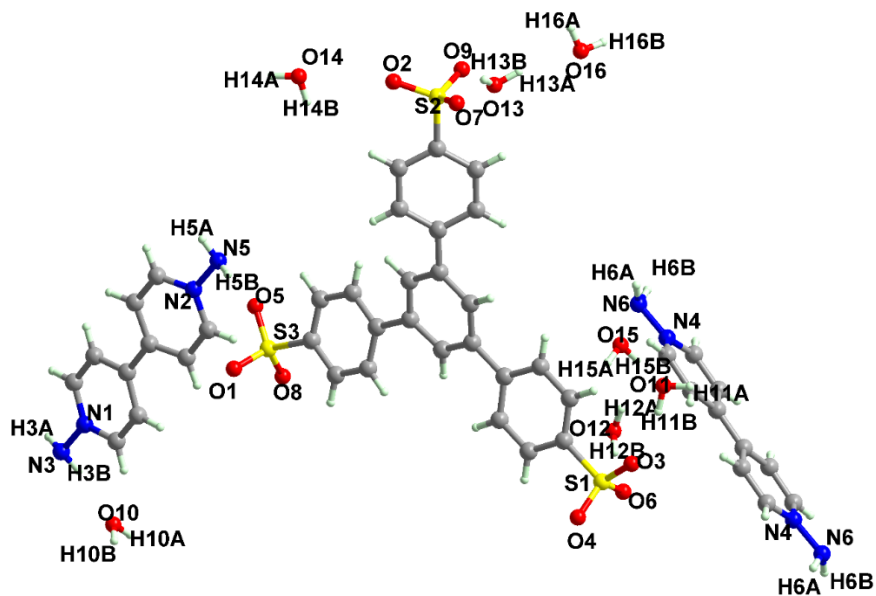


Fig. S1 Asymmetric unit structure diagram of iHOF-8.

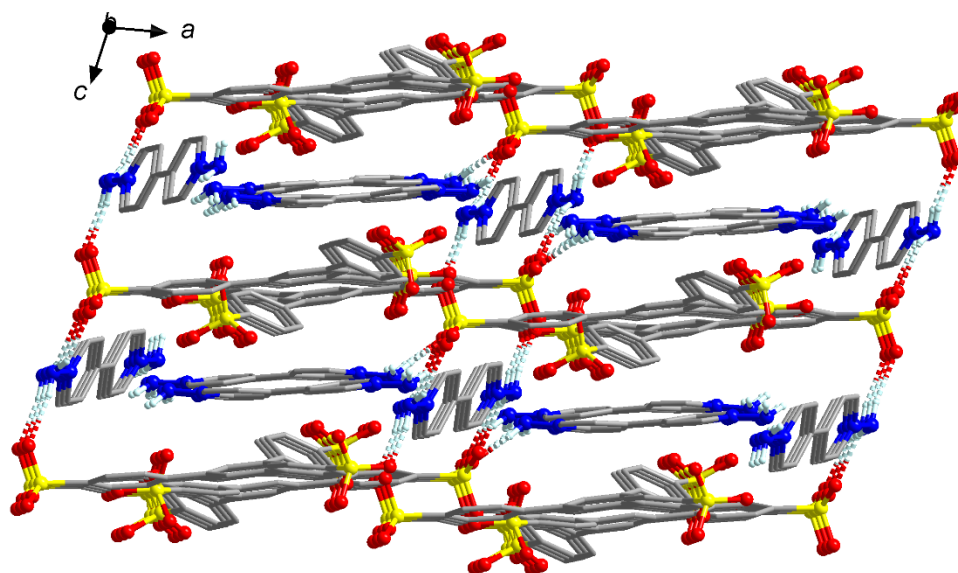


Fig. S2 SPB³⁻ and DBpy²⁺ are stacked layer by layer in the structure of iHOF-8.

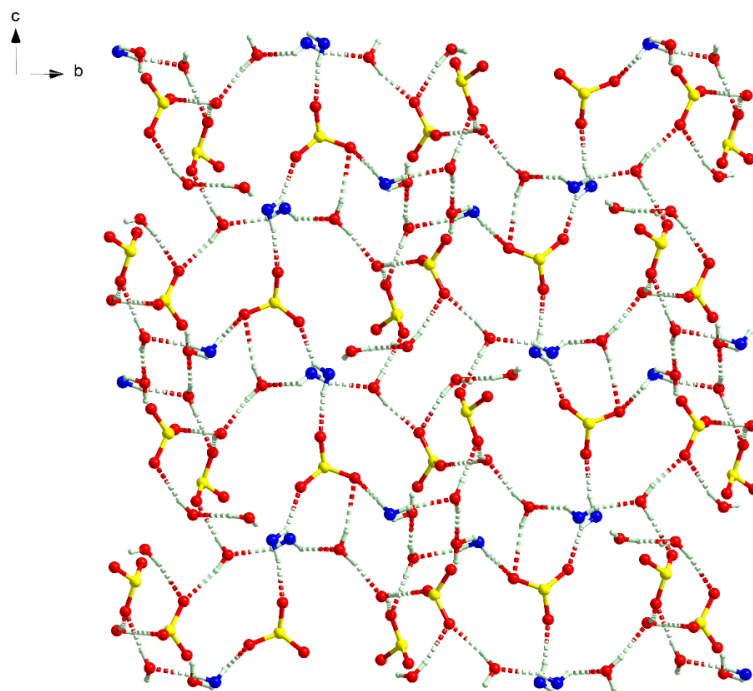


Fig. S3 2D hydrogen bonding network diagram of **iHOF-8**.

Section S3. PXRD and TG patterns.

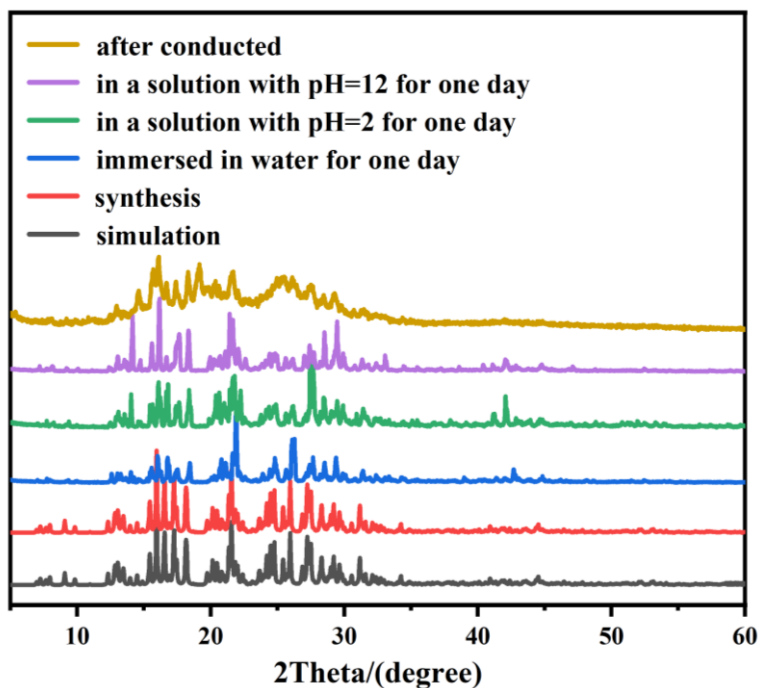


Fig. S4 PXRD Patterns: solution stability graph of **iHOF-8**.

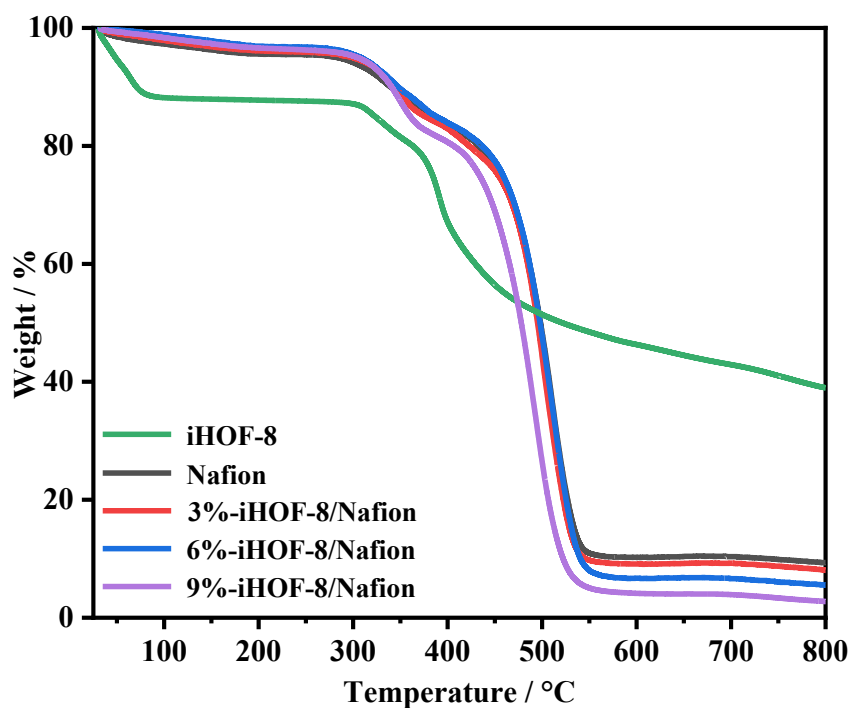


Fig. S5 TGA Pattern: thermal stability graph of **iHOF-8**, Nafion, and composite membranes.

Section S4. Proton conductivity.

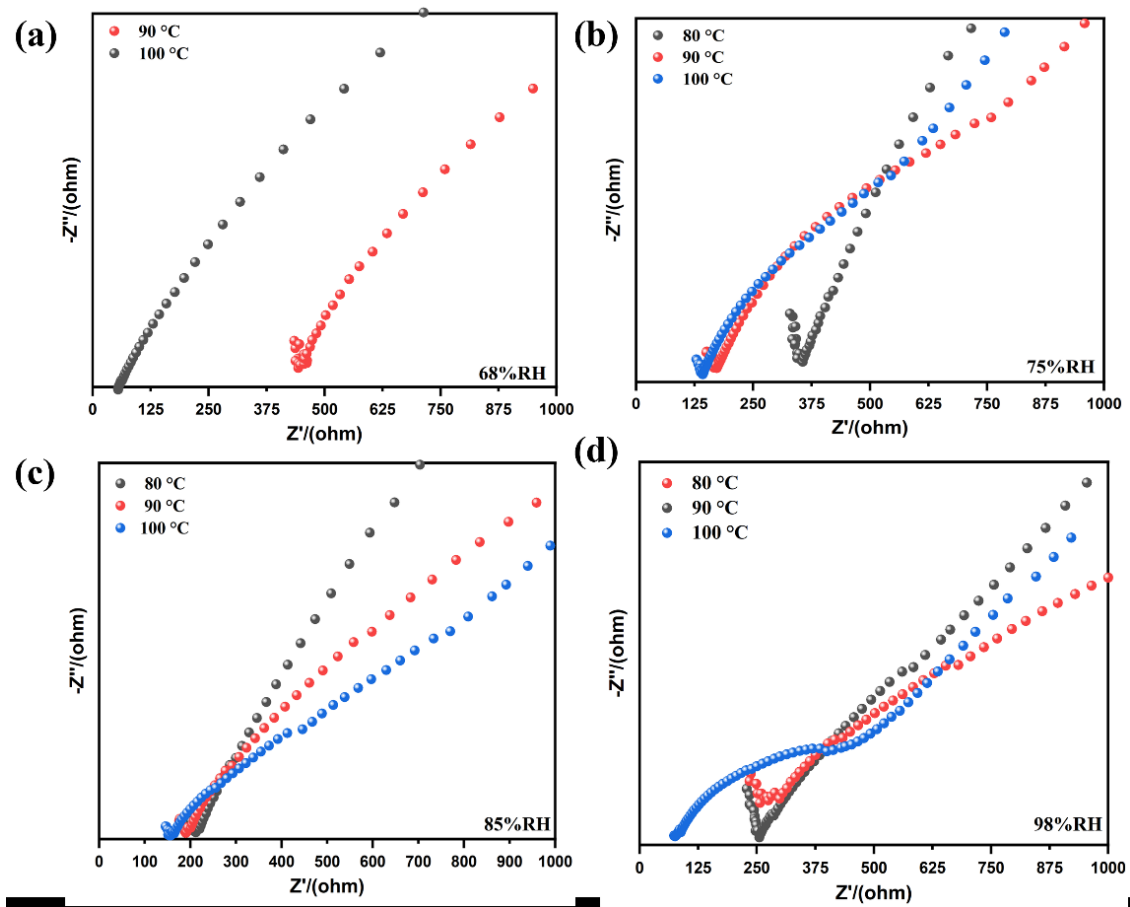


Fig. S6 Impedance diagram of **iHOF-8** at different humidity and temperature.

Table S2 Proton conductivity values ($\text{S}\cdot\text{cm}^{-1}$) of **iHOF-8** at different humidity temperatures.

	70 °C	80 °C	90 °C	100 °C
68%RH	8.5×10^{-4}	9.4×10^{-4}	9.8×10^{-4}	1.1×10^{-3}
75%RH	9.6×10^{-4}	1.0×10^{-3}	2.0×10^{-3}	2.5×10^{-3}
85%RH	1.2×10^{-3}	2.1×10^{-3}	3.0×10^{-3}	2.65×10^{-3}
98%RH	3.8×10^{-3}	4.5×10^{-3}	4.9×10^{-3}	5.02×10^{-3}

Section S5. Mechanical stability and macroscopic pattern.

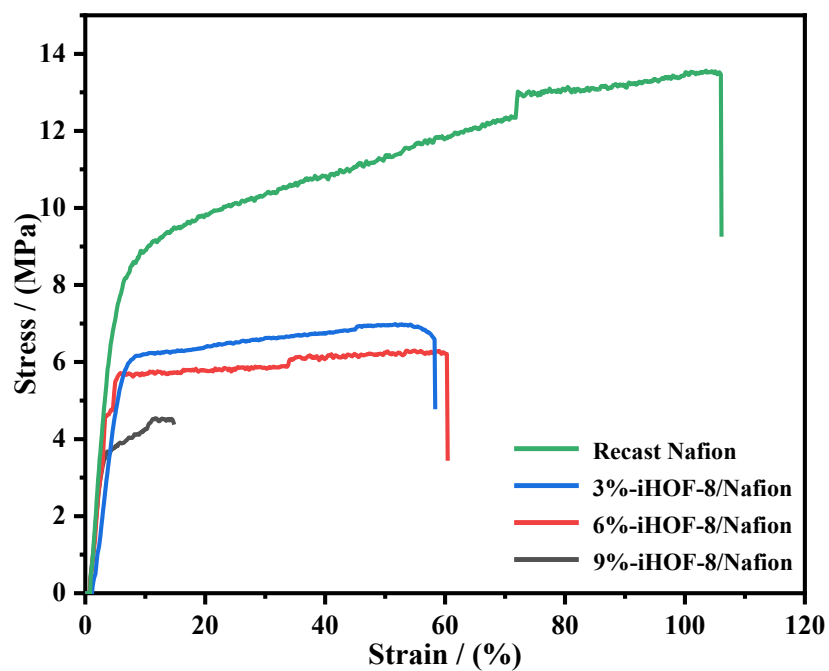


Fig. S7 Stress-strain curves of different composite membranes.

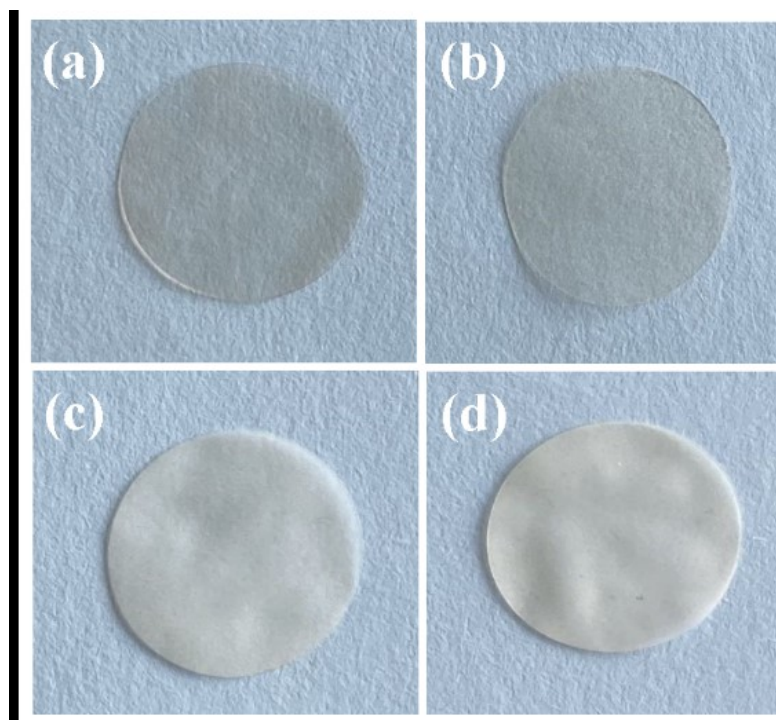


Fig. S8 The photographs of Membranes. (a) Recast Nafion; (b) 3%-iHOF-8/Nafion; (c) 6%-iHOF-8/Nafion; (d) 9%-iHOF-8/Nafion.

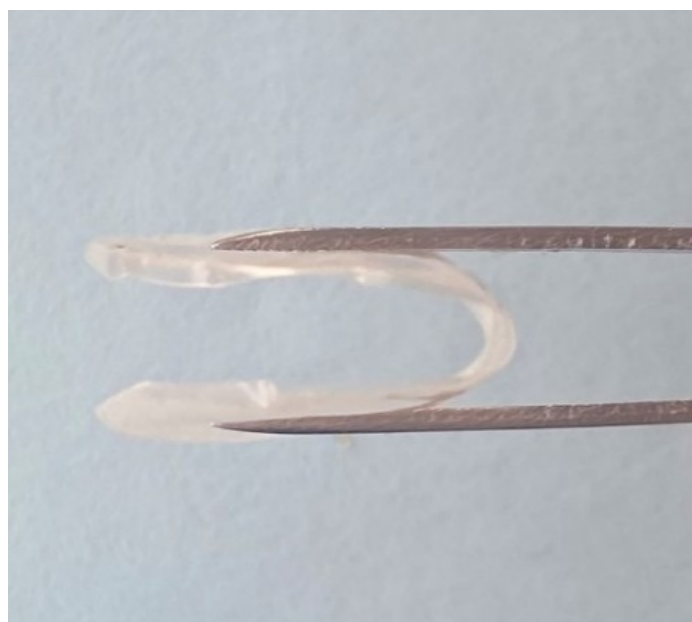
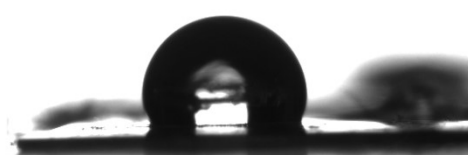
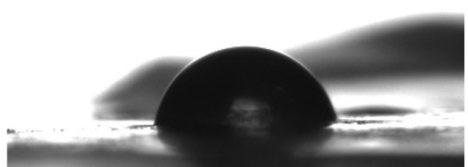


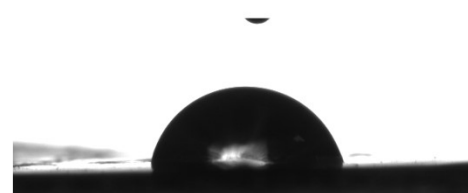
Fig. S9 Bending diagram for composite membrane.



3%-iHOF-8/Nafion 115.4°



6%-iHOF-8/Nafion 89.5°



9%-iHOF-8/Nafion 85.4°

Fig. S10 Water contact angle of composite membranes

Section S6. Scanning Electron Microscope, and AFM.

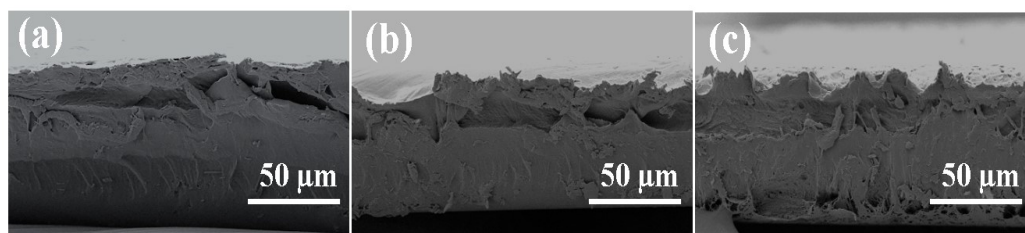


Fig. S11 The SEM of cross section of the composite membranes.

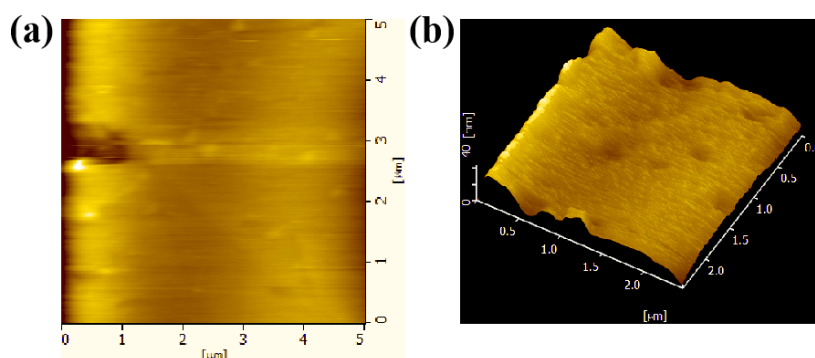


Fig. S12 The AFM phase images of recast Nafion.

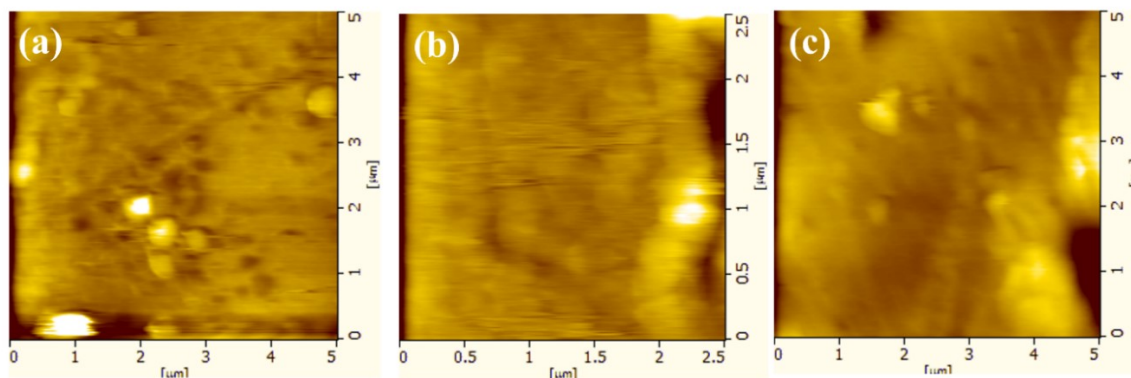


Fig. S13 The AFM phase images. (a) **3%-iHOF-8/Nafion** membrane; (b). **6%-iHOF-8/Nafion** membrane; (c). **9%-iHOF-8/Nafion** membrane.

Section S7. Methanol permeability.

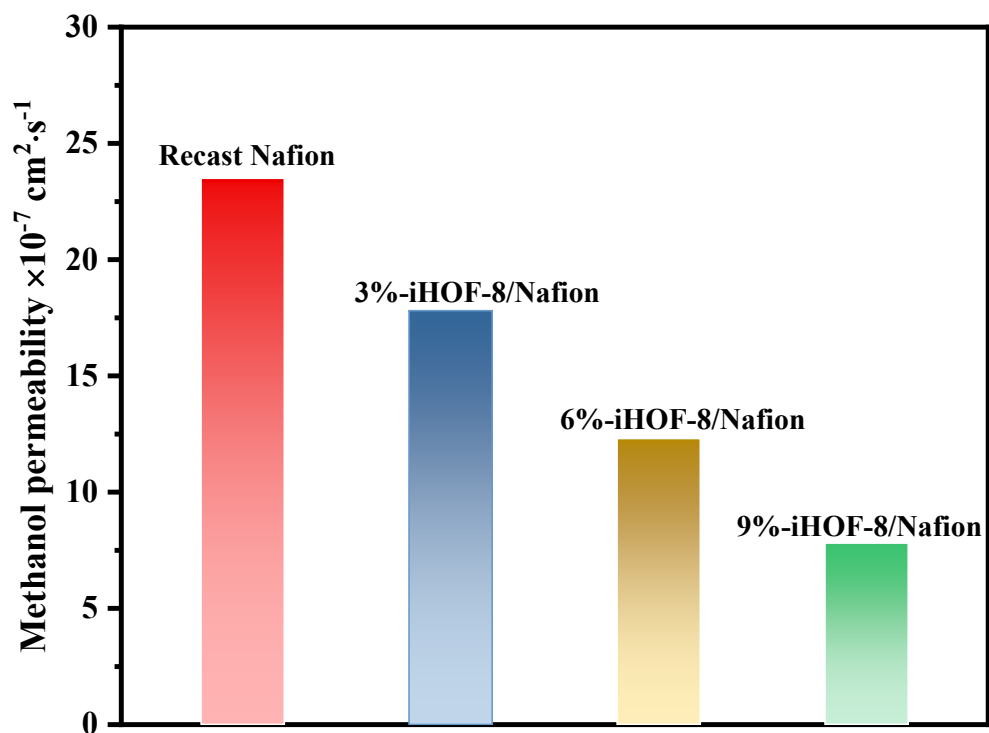


Fig. S14 Methanol permeability (in 8 M methanol solution) of pure Nafion, **3%-iHOF-8/Nafion**, **6%-iHOF-8/Nafion** and **9%-iHOF-8/Nafion** membranes at ambient temperature.

Section S8. Proton conductivity of membrane and battery performance.

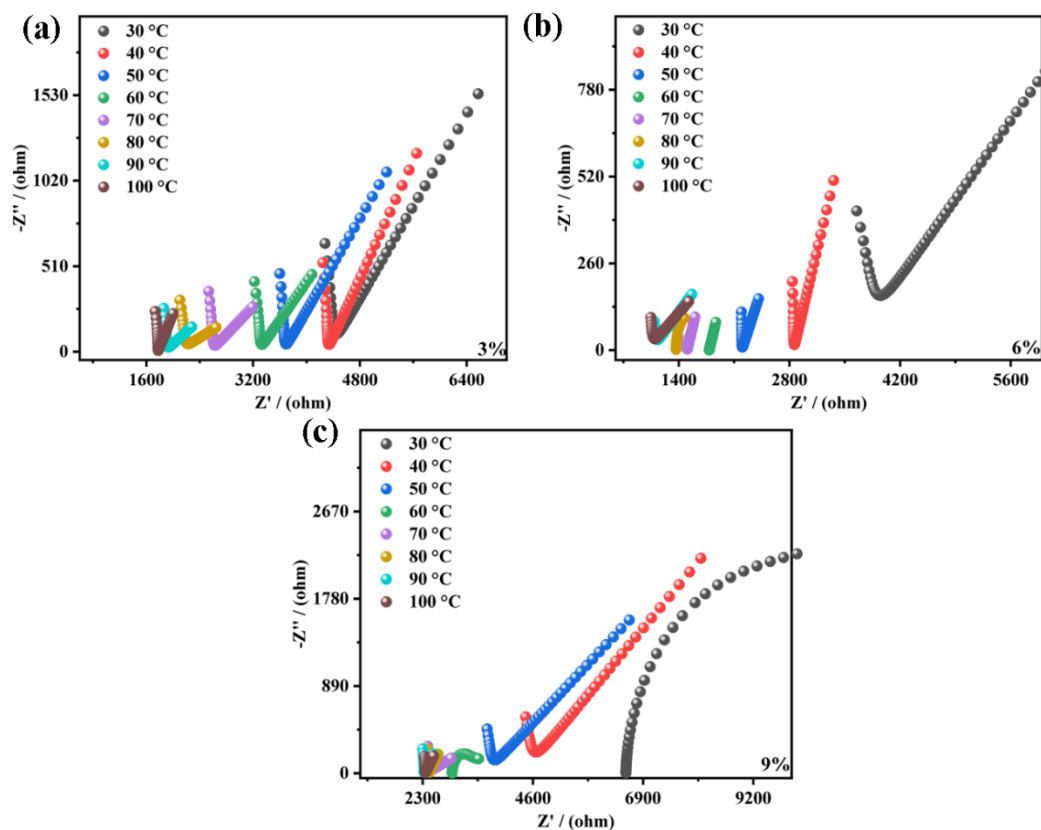


Fig. S15 (a)-(c) The Nyquist plot of **3%-iHOF-8/Nafion**, **6%-iHOF-8/Nafion** and **9%-iHOF-8/Nafion** membranes at 98% RH and 100 °C.

Table S3 Proton conductivity of composite membranes ($\text{S}\cdot\text{cm}^{-1}$) with different doping ratios at different temperatures.

membranes	70 °C	80 °C	90 °C	100 °C
3%-iHOF-8/Nafion	5.1×10^{-2}	6.8×10^{-2}	7.3×10^{-2}	8.1×10^{-2}
6%-iHOF-8/Nafion	8.0×10^{-2}	8.5×10^{-2}	9.2×10^{-2}	9.8×10^{-2}
9%-iHOF-8/Nafion	1.2×10^{-1}	1.3×10^{-1}	1.5×10^{-1}	1.6×10^{-1}

Table S4. The maximum power density and proton conductivity of modified Nafion membrane for DMFC from this study compared to other works.

Samples	Proton conductivity/ [S cm⁻¹]	T /(°C)	Power density/ (mW/cm⁻²)	Methanol Concentration/ (M)	Reference
p-BPAF@ Nafion-7.5	0.256	80	111.53	2	7
Nafion-Bi₁₂-3%	0.386	80	110.2	1	8
Nafion/CS-CNT	0.104	25	110	5	9
9%-iHOF-8/Nafion	0.16	100	73.5	2	This work
CBA/Nafion-PVA	0.110	80	68.7	2	10
Recast Nafion	0.062	100	50	2	This work
NF/S-GO-MOR 0.05	0.0865	70	29.55	1.84	11
Nafion-PDDA-GO	0.023	25	28	2	12
Nafion 117	0.108	80	12.05	4	13
MOR/NF	0.0494	70	10.75	2	14
Nafion/Pd-SiO₂-3	0.1292	75	8.30	4	15
ANA/NF	0.0501	70	7.16	2	14

Section S9. References.

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