Supplemental Information

Low Coordination Water in COF and Acid-free Proton Conduction

1. Materials

All chemicals and solvents used in the syntheses are reagent grade and used without further purification. 1,3,5-triformylbenzene and 2,5-diethoxyterephthalohydrazide were purchased from EXTENSION and TENSUS BIOTECH, respectively.

2. Synthesis

Self-standing and flexible COF membrane was prepared via interfacial polymerization reaction. 2,5-diethoxyterephthalohydrazide (42.2 mg, 0.15 mmol) was dissolved in 25 mL 6M acetic acid aqueous solution, and 1,3,5-triformylbenzene (16.2 mg, 0.1 mmol) were dissolved in 25 mL dichloromethane (DCM). Water phase was slowly dropped to the top of the organic phase. After that, the membrane-forming reaction takes place very quickly. The entire interface aggregation lasted for 3 days.

3.proton conductivity

The proton conduction measurements use one temperature and humidity control box and one Bio-Logic electrochemical workstation. The temperature and humidity control box can maintain humidity levels. The activation energy of proton conductivity (σ) is fitted by Arrhenius equation:

$$\sigma T = A\exp(-\frac{E_a}{k_B T}) \quad (1)$$

where *Ea* is the transport activation energy, k_B is the Boltzmann constant, *T* is temperature, and *A* is a pre-exponential factor.

4.Computational details

The guest molecules of water in framework is simulated by Monte Carlo method with Dreiding forcefield. The cell size used for simulation is 1×1×1. Water molecules are saturatedly placed into the framework. The model of bulk water is established with a density of 1 g/cm³. Molecular dynamics simulation utilizes the Dynamics module in the Forcite Calculation panel, with the ensemble set to NPT.

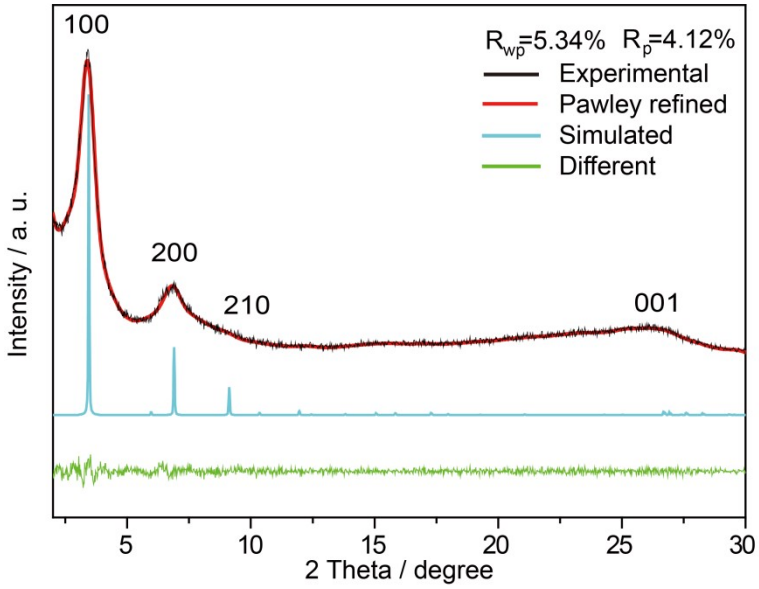

Figure S1. PXRD simulation of COF-42 membrane.

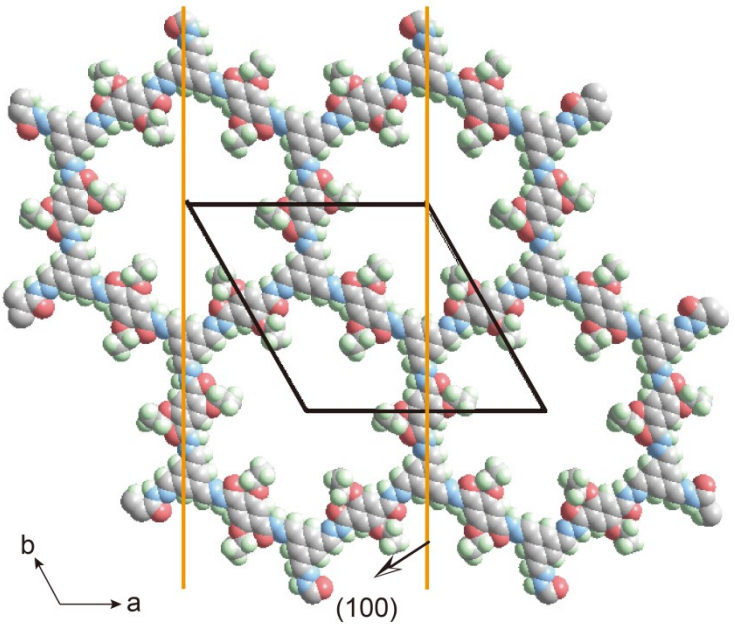

Figure S2. Structural model of COF-42 along c-axis with unit cell (black box), orientation displaying lattice plane (100) (orange).

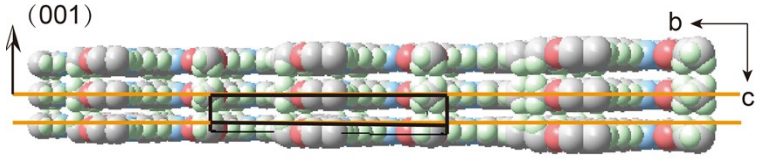

Figure S3. Structural model of COF-42 along a-axis with unit cell (black box), orientation displaying lattice plane (001) (orange).

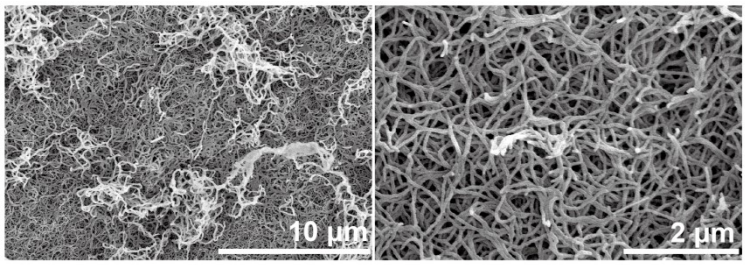

Figure S4. SEM photograph of COF-42-M with different rulers from front side.

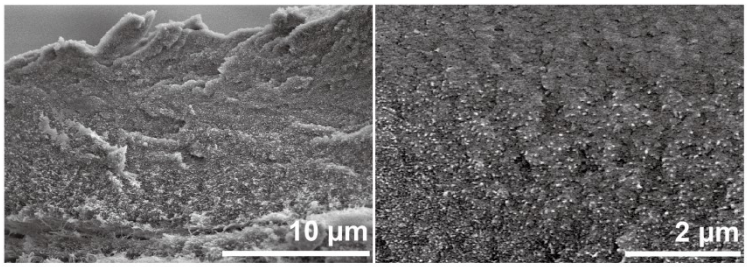

Figure S5. SEM photograph of COF-42-M(dry) with different rulers from section side.

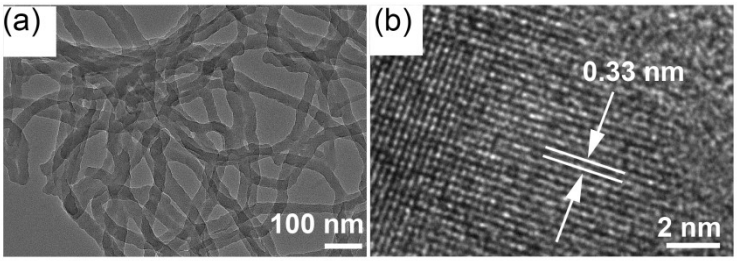

Figure S6. (a) TEM image of COF-42 membrane. (b) HR-TEM image of COF-42 membrane crystallite displaying the (001) plane, fringes represent π-π stacking (0.33 nm).

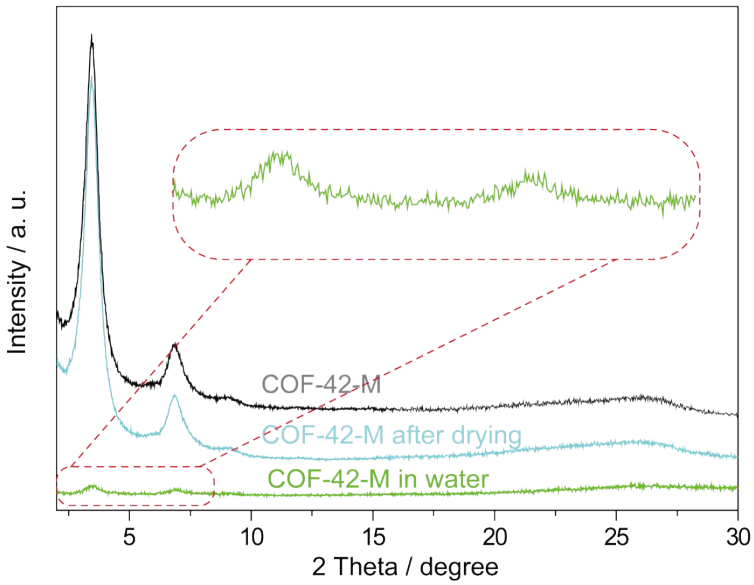

Figure S7. PXRD of COF-42-M in different conditions, with an inset showing the enlarged image.

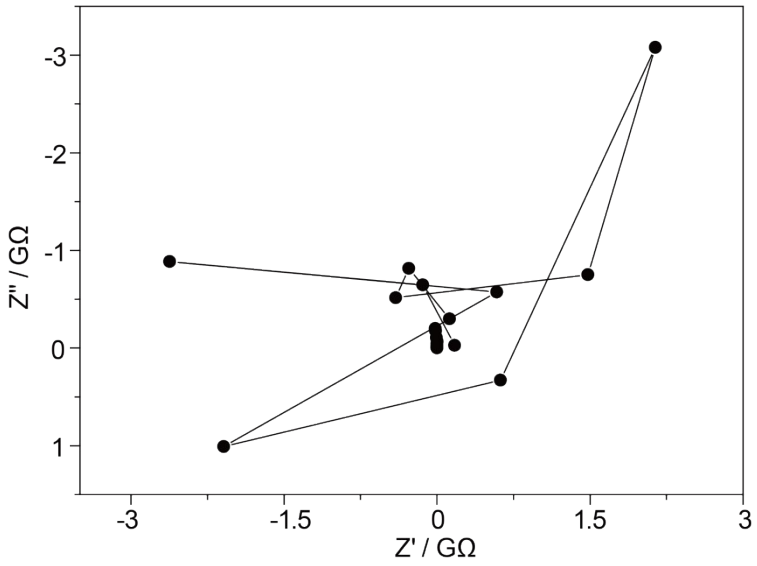

Figure S8. Nyquist plot of COF-42-M under 30 °C and nitrogen atmosphere.

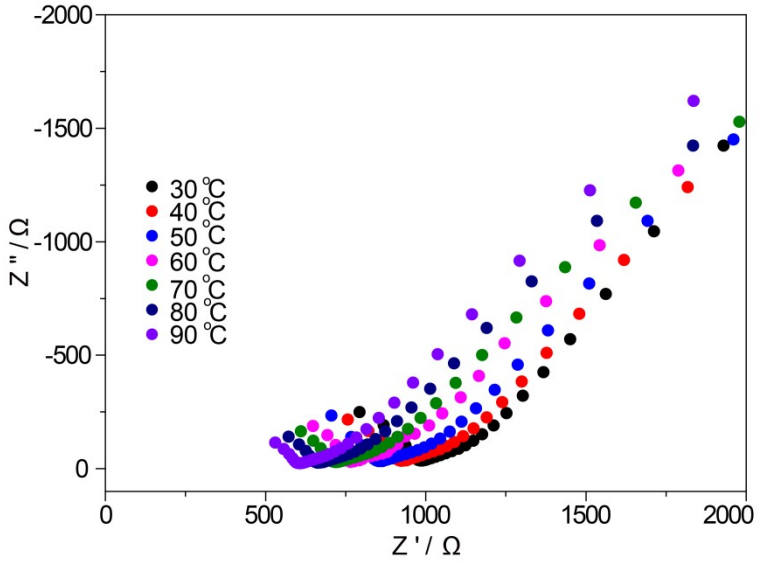

Figure S9. Nyquist plots of COF-42-M in water versus different temperatures.

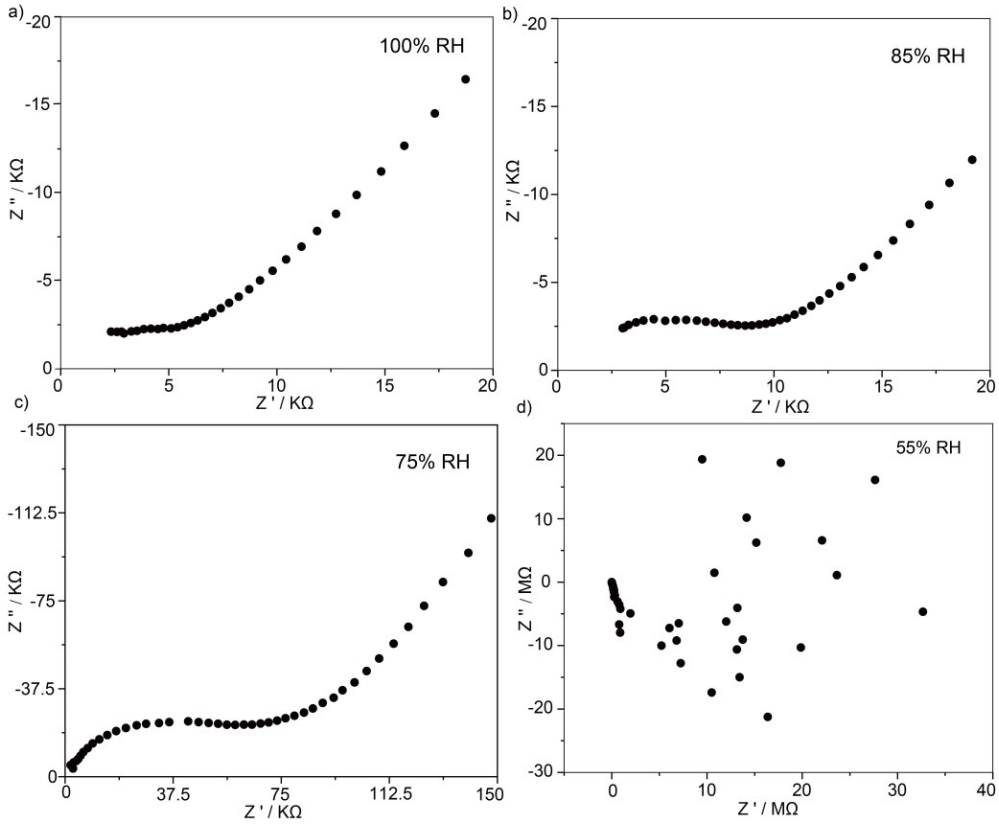

Figure S10. Nyquist plots of COF-42-M at different humidity.

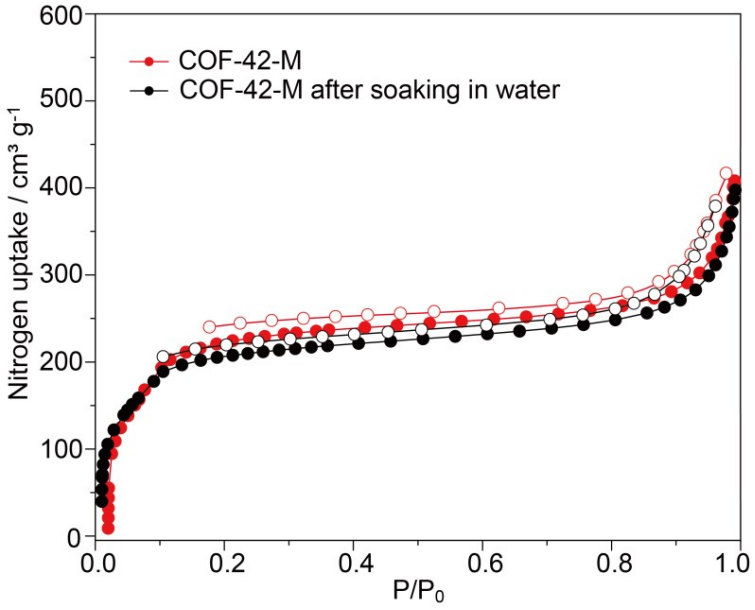

Figure S11. Nitrogen adsorption of COF-42-M before and after water immersion.

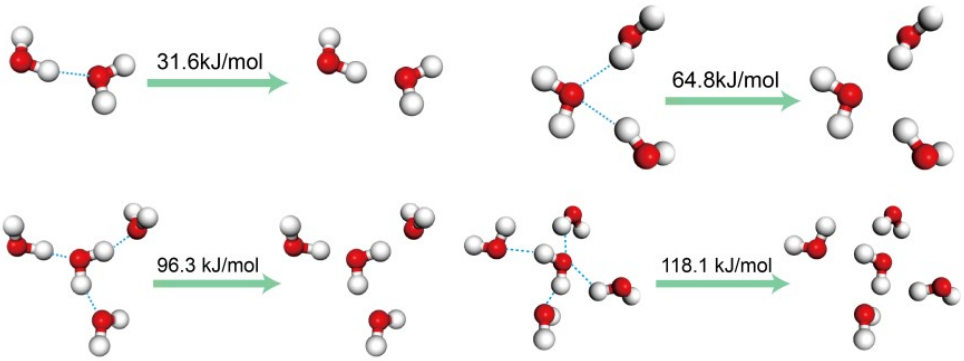

Figure S12. The H-bond breaking energy for water with different coordination numbers.

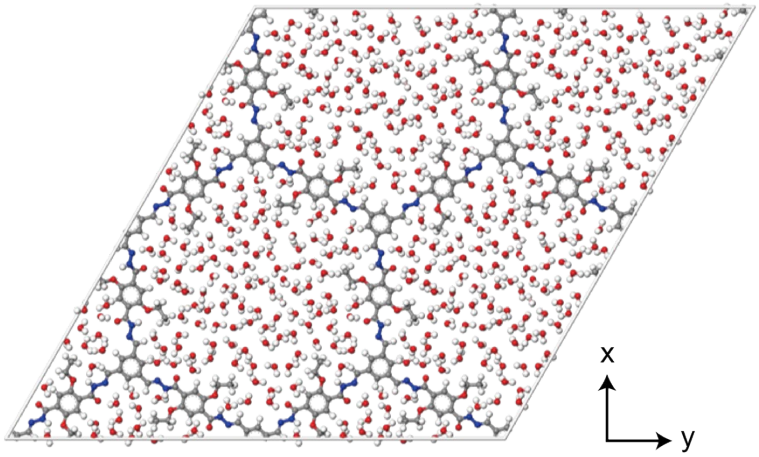

Figure S13. Model schematic diagram of COF-42-M with water.

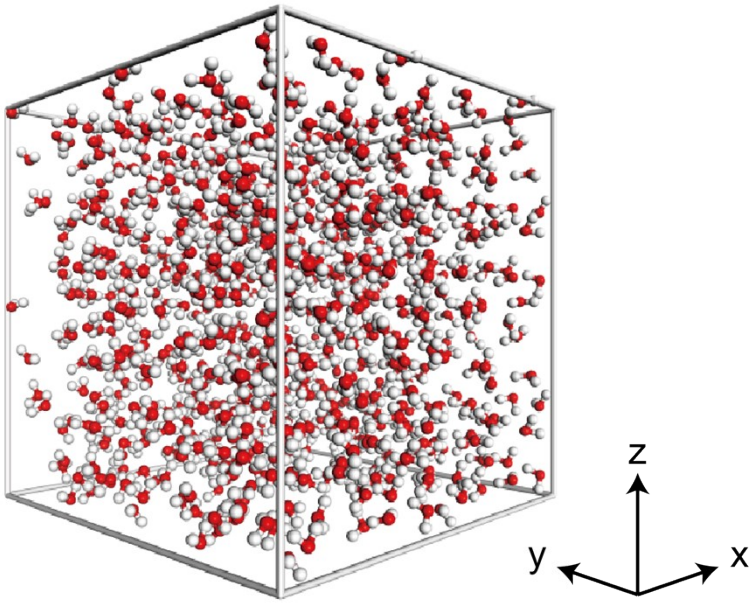

Figure S14. Model schematic diagram of bulk water.

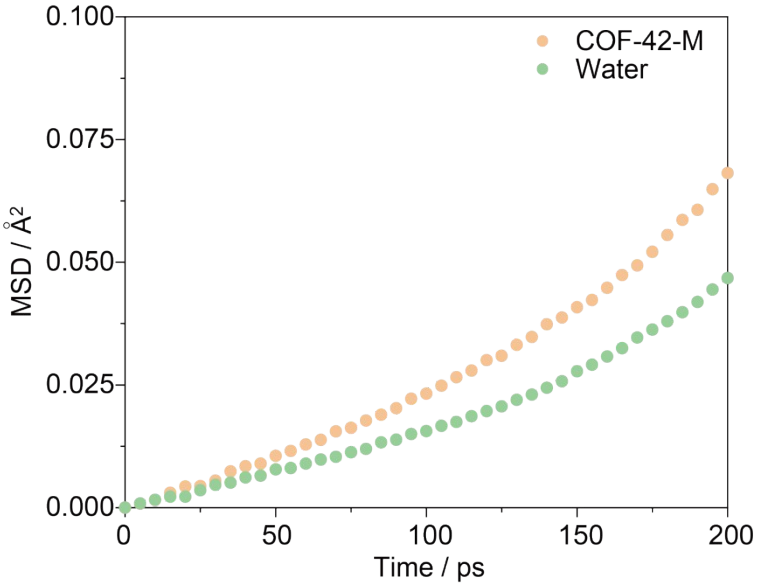

Figure S15. The results of MSD of COF-42-M and water.

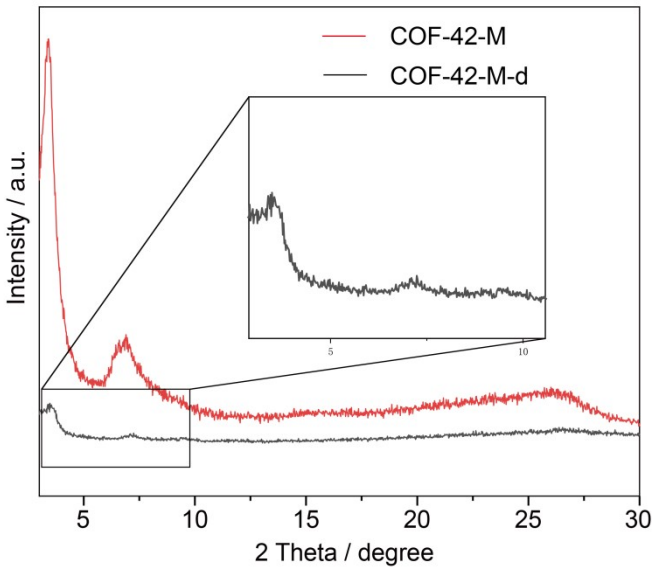

Figure S16. PXRD of COF-42-M and COF-42-M-d.

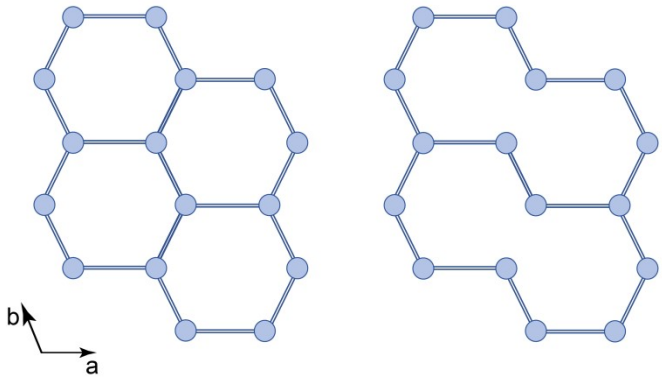

Figure S17. Structure diagram of COF-42-M and COF-42-M-d.

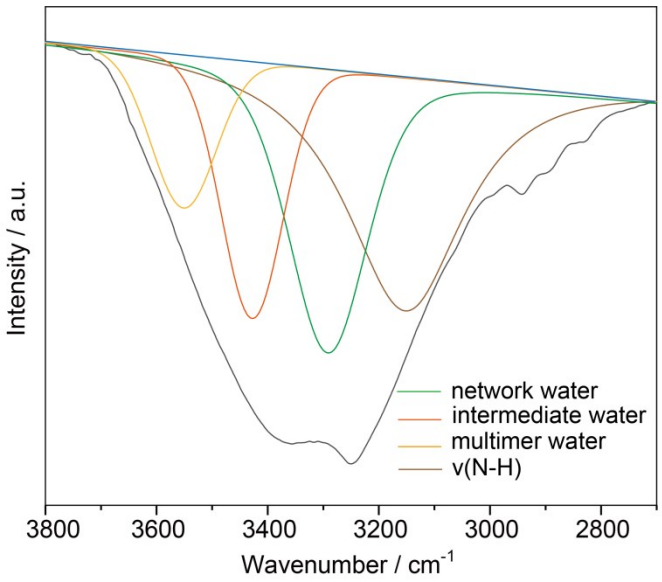

Figure S18. IR plot of COF-42-M-d with water.

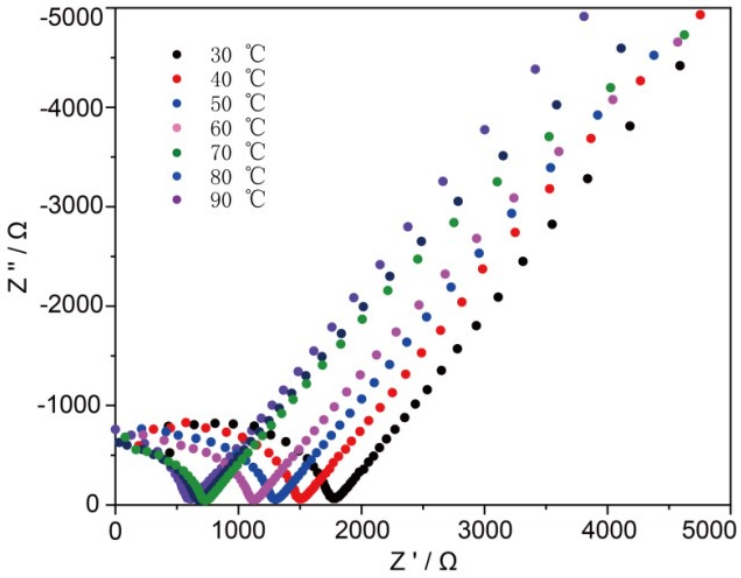

Figure S19. Nyquist plots of COF-42-M-d in water versus different temperatures.

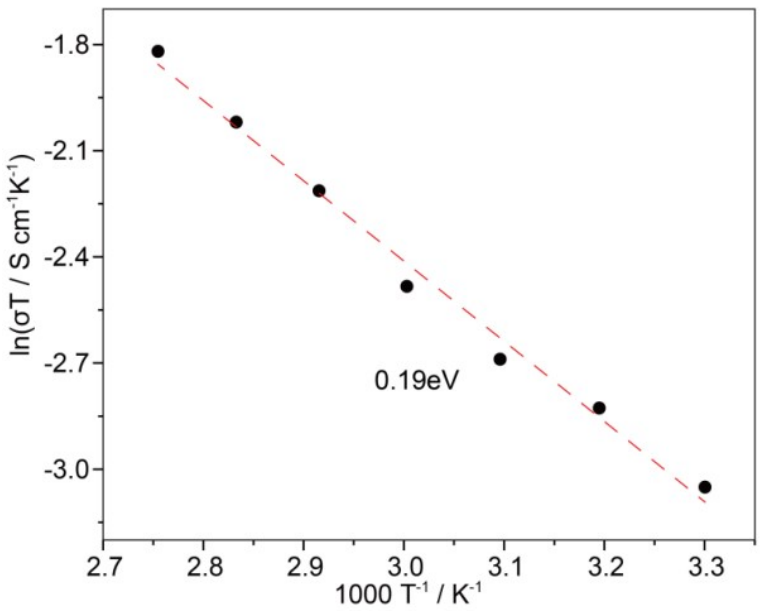

Figure S20. Arrhenius plot of COF-42-M-d.

Table S1. Summary of MOFs/COFs based proton conduction.

Materials	**σ (S cm^{-1})**	**Ea (eV)**	**Condition**	**Ref.**
COF-42-M	7.56×10^{-4}	0.11	90 °C, in water	This work
$(NH_4)_3Zr(H_{2/3}PO_4)_3$	1.21×10^{-2}	0.26	90 °C, 95% RH	J. *Am. Chem. Soc.* **2018**, *140*, 6146-6155.
Im–Fe–MOF	1.21×10^{-2}	0.436	60 °C, 98% RH	*J. Am. Chem. Soc.* **2017**, *139*, 6183-9.
$(Me_2NH_2)[Eu(L)]$	3.76×10^{-3}	0.72	100 °C, 98% RH	*J. Am. Chem. Soc.* **2017**, *139*, 3505-3512.
Z-TpPa	1.80×10^{-1}	0.20	98%	*Small.* **2024**, *20*, 2308499.
MOF-74(Mg)–Urea	2.64×10^{-2}	0.10	25 °C, 95% RH	*J. Am. Chem. Soc.* **2020**, *142*, 6861-6865
BUT-8(Cr)A	1.27×10^{-1}	0.11	80 °C, 100% RH	*Nature. Energy.* **2017**, *2*, 877-883.
SCOF	5.40×10^{-1}	0.19	Pure water	*Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 14875-14880.
H_3PO_4@PyTFB-1-SO_3H	1.15×10^{-1}	0.17	98%	*Nano. Lett.* **2024**, *24*, 5075–5084.
HPW@TAPT-DHTA	5.30×10^{-1}	0.15	80 °C, 100% RH	*Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 18051-18058.
SCOF membrane	5.40×10^{-1}	0.19	80°C, in water	*Angew. Chem. Int. Ed. Engl.* **2021**, *60,* 14875-14880.
H_3PO_4@GS-COF-2-COOH	4.35×10^{-2}	0.21	80 °C, 90% RH	*J. Am. Chem. Soc.* **2020**, *142,* 13316-13321.
Aza-COF-2_H	4.80×10^{-3}	0.45	50 °C, 97% RH	*Chem. Mater.* **2018**, *31*, 819-825.
BIP	3.20×10^{-2}	0.31	95 °C, 95% RH	*J. Am. Chem. Soc.* **2019**, *141,* 14950-14954.
KAUST-7'	2.00×10^{-2}	0.19	90 °C, 95% RH	*J. Am. Chem. Soc.* **2018**, *140,* 13156-13160.
$Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 15H_2O$	1.31×10^{-1}	0.26	25 °C, 95% RH	*Angew. Chem. Int. Ed. Engl.* **2017**,5531-5535.
MIP-202(Zr)	1.10×10^{-2}	0.22	90 °C, 95% RH	*Nat. Commun.* **2018**, *9,* 4937.
$[Pt(dach)(bpy)Br]_4(SO_4)_4 \cdot 32H_2O$	1.72×10^{-2}	0.22	55 °C, 95% RH	*Nat. Commun.* **2020**, *11*, 843.

Table S2. Elemental analysis of different samples.

Sample	C	H	O	N	C/N
COF-M-42 before water immersion	55.34%	5.64%	24.59%	14.35%	3.86
COF-M-42 after water immersion	51.82%	5.95%	28.12%	13.22%	3.92
COF-42-M-d	45.07%	6.01%	33.05%	15.77%	2.86