Short hydrogen-bond network confined on COF surfaces enables ultrahigh proton conductivity

Benbing Shi1,7, Xiao Pang1,7, Shunning Li2,7, Hong Wu1,3, Jianliang Shen1, Xiaoya Wang1, Chunyang Fan1, Li Cao1, Tianhao Zhu1, Ming Qiu1, Zhuoyu Yin1, Yan Kong1, Yiqin Liu1, Mingzheng Zhang2,Yawei Liu4, Feng Pan2 & Zhongyi Jiang1,3,5,6

The idea of spatial confinement has gained widespread interest in myriad applications. Especially, the confined short hydrogen-bond (SHB) network could afford an attractive opportunity to enable proton transfer in a nearly barrierless manner, but its practical implementation has been challenging. Herein, we report a SHB network confined on the surface of ionic covalent organic framework (COF) membranes decorated by densely and uniformly distributed hydrophilic ligands. Combined experimental and theoretical evidences have pointed to the confinement of water molecules allocated to each ligand, achieving the local enrichment of hydronium ions and the concomitant formation of SHBs in water-hydronium domains. These overlapped water-hydronium domains create an interconnected SHB network, which yields an unprecedented ultrahigh proton conductivity of 1389 mS cm⁻¹ at 90 °C, 100% relative humidity.

Proton transfer is a ubiquitous process in green energy storage and conversion devices, such as fuel cells and flow batteries1–3. Creating artificial ion channels that confer high proton conductivity has long been an aspirational endeavor for improving their power output4–6. As one of the promising strategies to promote proton conductivity, spatial confinement of water molecules in a laminated/porous architecture has been recently explored, which can yield a proton-rich local environment, leading to higher concentration of charge carriers and more rapid water-mediated proton transfer7–14. It is well recognized that the proton transfer in aqueous systems is governed by the Grotthuss mechanism, which takes place on a water-hydronium network and entails a collective proton motion akin to the Newton’s cradle15–17. Of paramount importance in understanding the Grotthus-type proton conduction is that its efficiency mainly relies on the state of the proton bridges interconnected by hydrogen bonds (H-bonds). Commonly, the intensity of the H-bonds is associated with the distance between the oxygen atoms of the hydrogen-bonded water molecules18, and stronger H-bonds would lead to a more delocalized nature of the protons between donor and acceptor molecules. In particular, short H-bonds (SHBs) with a donor-acceptor distance of below 2.5 Å could generate a superharmonic behavior of proton motion, triggering proton transfer in a nearly barrierless manner19. The confinement of water in either bulk or interfaces of materials can serve as a strategy to favor the formation of a SHB network20, since the excess protons are accommodated in a more constrained space than normal. However, its implementation is still...
focus on a set of ionic covalent organic framework membranes
work via the overlap to share WHD between each pair of neighboring
concentrated hydronium ions and a fully interconnected H-bond net-
ordered distribution, building up a precisely regulated WHD with
the tightly packed counterparts con
observed in loosely packed iCOFMs, and their inferior performance to
observed in other proton exchange membranes. This disruption is also
can circumvent the occasional disruption of H-bond network as
integral SHB network (Fig.1d). We justify that the short H-bonds
conjecture that the concentrated hydronium ions in con
around -SO3
the proton transfer behavior featured by SHBs.

In this work, the iCOFMs with controllable -SO3H group distance were
donor and an enabler for high proton conductivity21
sulfonic acid group (-SO3H) was recognized as a superior proton
resides in the appropriate hydrophilic ligands, among which the

We demonstrate that a high proton conductivity is maintained even at
40% RH, which could be ascribed to the self-adaptation of the surface-
confined H-bond network. We believe that these mechanistic insights
could be extended to other materials or systems, and leveraged for the
rational design of advanced proton exchange membranes.

The topological structures of the iCOFs are shown in Fig. 2a. iCOFs
unit with six SO3H groups represents the larger group distance
-2.0 nm and iCOFs unit with twelve SO3H groups represents the
shorter group distance -0.9 nm. The SO3H groups are fixed on the
iCOF skeleton and the group distance can be regulated from 2.5 to
0.8 nm based on the crystal parameter data (Fig. 2b, Supplementary
Figs. 1 and 2, and Tables 1–6). Single-phase and two-phase synthesis
methods were exploited to control the monomer diffusion and chem-
ical assembly processes to fabricate crystalline iCOF nanosheets
(Supplementary Fig. 3). Different synthesis conditions were adopted
based on the reactivity and solubility of amine monomer and aldehyde
monomer (Supplementary Table 7 and Figs. 4 and 5). The transparent
iCOF nanosheets suspensions were obtained after reacting for three to
twenty days and exhibited obvious Tyndall phenomenon (inset of
Fig. 2c and Supplementary Fig. 6). As shown in Supplementary Fig. 7,
the zeta potential value of iCOF nanosheets was positively correlated
with the IEC value. Due to the strong electrostatic repulsion between
iCOF nanosheets, the suspensions kept stable for two years and no
collocation or precipitation was observed. The iCOF nanosheets bore
flake-like morphology and size of several micrometer with thickness of
1.6 nm (Supplementary Fig. 8). High-resolution TEM characterization
of iCOF nanosheets reveals that the long-range ordered lattice fringe
spacing is about 0.34 nm, which is in agreement with the (001) facet
(Supplementary Fig. 9)32,33. The functional groups and chemical
structure of the iCOF nanosheets were characterized by FTIR, XPS, and
NMR (Supplementary Figs. 10–12). The iCOF nanosheets exhibit high-
thermostability up to 300 °C, well satisfying the practical requirement
of electrochemical energy storage and conversion devices (Supple-
mental Fig. 13).

**Results and discussion**

In this work, the iCOFMs with controllable -SO3H group distance were
de novo designed and synthesized based on modular engineering and
vacuum-assisted self-assembly method. The -SO3H groups display an
ordered distribution, building up a precisely regulated WHD with
concentrated hydronium ions and a fully interconnected H-bond net-
work via the overlap to share WHD between each pair of neighboring
domains (Fig. 1c). The perfectly uniform alignment of these domains can
circumvent the occasional disruption of H-bond network as
observed in other proton exchange membranes. This disruption is also
observed in loosely packed iCOFMs, and their inferior performance to
the tightly packed counterparts confirms the essential role of an
integral SHB network (Fig. 1d). We justify that the short H-bonds
emerge in the water domains around -SO3, and find that the limited
number of water molecules not only imparts a high concentration of

![Fig. 1](s41467-022-33868-8)
The iCOFMs were prepared by vacuum-assisted self-assembly method, as shown in Fig. 2d, Supplementary Figs. 14 and 15. The iCOFMs are transparent with high crystallinity, mechanical robustness, and remain stable in water, DMF, and 1 M H2SO4 (60 °C) solution for more than two years, which can be attributed to the strong covalent and π-π interactions between high crystalline nanosheets (Supplementary Figs. 16–18)34,35. Moreover, the iCOFMs display arcs of diffracted intensity respect to (100) facet in the 2D GIWAXs spectrum, manifesting that the iCOF nanosheets are almost parallelly aligned (Fig. 2e and Supplementary Fig. 19)36,37. The surface of iCOFMs is smooth, as observed from the surface SEM image (Fig. 2f). Besides, the strong π-π interaction endows the membrane with compact structure and the membrane keeps intact after being folded for several times (Fig. 2g). No interlayer defects are observed even when the thickness of the membrane decreases to 56 nm (Fig. 2h). Meanwhile, the membrane exhibits in-plane swelling ratio <5% in water with the increase of temperature due to the synergy of covalent, π-π, and electrostatic interactions (Supplementary Fig. 20). The ion exchange content (IEC) values of iCOFMs were determined by acid-base titration method, as shown in Supplementary Fig. 21. The IEC value significantly increase with the decrease of the -SO3H group distance and a value of 5.4 mmol g⁻¹ was achieved, which is the highest IEC values ever reported.

The in-plane proton conductivity of the iCOFMs was measured by two electrode method and calculated according to the resistance (Supplementary Fig. 22), and the proton transfer pathway was illustrated in Fig. 3a. In-plane proton transfer is along the surface groups on the iCOF skeleton. As the -SO3H group distance decreases from 1.4 (TpPa-SO3H) to 1.0 nm (TpBd-SO3H), the proton conductivity increases six folds. The highest proton conductivity reaches 1389 mS cm⁻¹ at 90 °C under 100% RH when the group distance decreases to 0.8 nm (TpPa-SO3H(2), Supplementary Fig. 23), which is the highest proton conductivity ever reported. In sharp contrast, when the group distance is >1.4 nm, the iCOFM displays much lower proton conductivity of <0.2 S cm⁻¹ in spite of the high IEC value (3.42 mmol g⁻¹). Moreover, the proton conductivity remains almost unchanged when further increasing or decreasing the -SO3H group distance. Note that the proton conductivity significantly decreased as the iCOF nanosheets (d~1.0 nm) are loosely packed as characterized by SEM (Fig. 1d, Supplementary Figs. 24 and 25). The water vapor adsorption results indicate that both membranes display similar hydration number (λ) of 6.5 and 6.8 at 30 °C under 100% RH (Fig. 3b), corresponding to the average
number of confined water molecules per -SO₃H for TpPa-SO₃H and TpBd-SO₃H, respectively. Accordingly, the distribution of surface water/hydronium will be constrained in a limited region, outside which the donor-acceptor water bridge is no longer valid. The short group distance in TpBd-SO₃H gives rise to the overlap between these regions and therefore an interconnected H-bond network shared with WHD, while the group distance in TpPa-SO₃H is large enough to allow the isolation of each water domain, leading to a discrete H-bond network.

According to the Nernst-Einstein equation \( (\sigma = DCF_2/RT) \), the proton diffusion coefficient \( D \) in TpBd-SO₃H is 4.48 folds higher than that of TpPa-SO₃H. Moreover, the proton conductivity was normalized by IEC value to exclude the influence of the amount of -SO₃H group on proton transfer (Supplementary Fig. 26). It is found that the -SO₃H group distance plays vital role in proton transfer, especially when the -SO₃H group distance decreases from 1.4 nm to 1.0 nm (Fig. 3c). For -SO₃H group with specific position, localized WHD forms in water domain around -SO₃H group, in which proton shuttles with a nearly barrierless manner. As the -SO₃H groups distance decrease to 1.0 nm, the water domains are overlapped and the WHDs can be shared among -SO₃H groups on iCOF nanosheet surface. When the iCOF nanosheets are tightly packed, WHDs can be shared between iCOF nanosheets, which enables ultrafast proton transfer in iCOFMs. Furthermore, benefiting from the covalent, π-π, electrostatic interactions, as well as high IEC values, our iCOFMs acquired significant superiorities in overcoming the trade-off between proton conductivity and mechanical stability, as compared with the membranes reported in literatures (Fig. 3d, Supplementary Table 8, and Fig. 27).

The relative humidity (RH) dependent in-plane proton conductivities of the iCOFMs at 30 °C and 90 °C were shown in Fig. 3e and Supplementary Fig. 28. The TpPa-SO₃H(2), TpBd-SO₃H, and TpPa-SO₃H exhibit lower proton conductivity with the decrease of RH at both 30 °C and 90 °C due to the reduction of the hydration number. Notably, the proton conductivities of TpPa-SO₃H(2), TpBd-SO₃H maintain at \( 10^{-3} \) S cm⁻¹ even when the RH decreases to 40%, while TpPa-SO₃H displays inferior proton conductivity of about \( 10^{-4} \) S cm⁻¹, indicating that the surface confinement endows the H-bond network with high flexibility for self-adaptation rearrangement, thus facilitating the preservation of high proton conductivity at low RH. This finding can help accelerate the exploitation of weakly humidity-dependent proton exchange membranes.

The through-plane proton conductivities of the iCOFMs were measured by sandwiching the iCOFMs between two 1 M HCl solutions. The proton conductivity of iCOFMs can be derived based on the I-V curves, the thickness and effective area of the membranes (Supplementary Fig. 29). In the through-plane direction of iCOFMs, the short -SO₃H group distance (0.68 nm) and straight proton transfer pathway endow the iCOFMs with proton conductivity of hundreds of mS cm⁻¹ at 30 °C, which is several times higher than that of Naion 117 (Supplementary Fig. 30). Moreover, the through-plane proton conductivity of iCOFMs is positively correlated with -SO₃H group density (Fig. 3f). Finally, the TpPa-SO₃H and TpBd-SO₃H nanosheets were packed into membrane electrode assemblies (MEAs) to evaluate the potential applications in fuel cells (Supplementary Fig. 31). Both of the MEA exhibit open circuit voltage (OCV) of 0.95 V (theoretical value, 1.22 V) ascribed to higher gas permeability. However, the maximum power density and current density of TpBd-SO₃H reach about 423.4 mW cm⁻² and 1280 mA cm⁻², which can be attributed to the higher through-plane proton conductivity. Despite the high gas permeability, the iCOFMs exhibit comparable fuel cell performance than that of Naion 117 under the same condition. Further optimizing the topological structure of iCOFMs based on the surface-confined concentrated hydronium ions would be an efficient way to simultaneously facilitate the gas barrier property, proton conductivity, and fuel cell performance.

The contribution of channel surface groups to proton transfer was further explored by experiment and molecular simulation. The absorbed water in iCOF nanochannel includes bound water and free water according to DSC and molecular simulation results...
Due to the strong molecular affinity between H₂O and -SO₃H group, water molecule forms a denser adsorption layer (i.e. hydration shell) near the -SO₃H group, whose outer edge is away from the central S atom by 0.5 nm (Supplementary Fig. 34). When the -SO₃H group distance is set as 2.0 nm, the adsorption layers are almost isolated. However, as the -SO₃H group distance decreases to 1.0 nm, the hydration shells are overlapped. The water molecule distribution in iCOFs nanochannel was obtained by molecular simulation, as shown in Supplementary Figs. 35 and 36. The results demonstrate that the water molecule density on channel surface is much higher than that in bulk water, which confers high hydrogen bond density on channel surface. Moreover, the water molecules along channel surface keep frequent exchanges with bulk water, suggesting the flexible rearrangement of the water/hydronium network (Supplementary Fig. 37)

Ab initio molecular dynamics (AIMD) simulation was performed to elucidate the microscopic picture of proton transfer in surface-confined water. We first evaluate the hopping frequency of protons in the confined region of seven water molecules surrounding each -SO₃H. Here, the single-layer TpPa-SO₃H was taken as a model system. Two kinds of hopping events are discriminated: shuttle events which are associated with the consecutive to-and-from motions of a proton between two neighboring water molecules, and transfer events where the proton keeps forward motion (Fig. 4a)

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The simulation results reveal that the former event dominates in the confined region. This can be attributed to the attraction of the negatively charged -SO₃⁻ species to protons, which prevails after the prompt dissociation of proton from the -SO₃H group, as verified by the short period (<3 ps) for proton to reach an adjacent water molecule and form a hydronium ion (Fig. 4b and Supplementary Fig. 38). We note that this proton would no longer recombine to the -SO₃⁻ species after its detachment. Given the low kinetic barrier for Grotthuss-type proton transport in water-hydronium network (Supplementary Fig. 39), the electrostatic interaction between protons and -SO₃⁻ species will be major contributing factor for the spatial confinement of the hydronium ions. Similar situation is found in H₂SO₄ aqueous solution (Supplementary Figs. 40 and 41). This interaction will pose hindrance to the transport of hydronium ions between two adjacent separate water domains.

In comparison to the pattern of isolated water domains on TpPa-SO₃H, the confined regions on TpBd-SO₃H is interconnected with each other, as revealed by the probability density distribution of hydronium ions displayed in Fig. 4c. The establishment of the interconnected water-hydronium network permits facile Grotthuss-type proton transport between the confined regions, which is reminiscent to the electron delocalization in conjugated systems. The overlap of the confined regions also leads to a more vague boundary for each of these regions, as illustrated by the more prevalent smearing of peaks in the radial distribution functions between O in hydronium ions and S in the -SO₃H species (Supplementary Fig. 42).

Owing to the electrostatic interactions, protons quickly shuttle between the surface-confined water molecules rather than transport to bulk water, thus affording a high concentration of hydronium ions in the H-bond network. This feature may benefit the emergence of SHBs as each hydronium ion tends to engage in a SHB with one of its neighboring water molecules. FTIR was utilized to characterize the H-bonds in bulk water, acid solution, and surface confined water in...
iCOFMs (Fig. 4d). Pure water exhibits absorption bond at around 3500 cm$^{-1}$ ascribed to the stretching vibration of H-bond. By comparison, the absorption bond shifts to 3200 cm$^{-1}$ in H$_2$SO$_4$ solution and wet iCOFMs attributed to emergence of SHBs (Supplementary Fig. 43). This is in good agreement with the AIMD results of the distribution of O–O distance for all the H-bonds (Fig. 4e and Supplementary Fig. 44). The SHB allows proton sharing between donor and acceptor, which renders low proton transfer resistance. We note that 44% H$_2$SO$_4$ aqueous solution possesses approximately one hydrated proton for every seven water molecules and exhibits a proton conductivity on the scale of ~1600 mS cm$^{-1}$ at 90 °C (Supplementary Fig. 45). The proton conductivity of TpBd$_2$SO$_4$H is close to this value, suggesting that the essence of facile proton transfer in surface-confined water lies in the local concentration of hydronium ions and SHBs. The overlap of water confined regions triggers the delocalization of protons such that a fast proton transfer network is built on the surface. Based on the above results, the prerequisite for this delocalization is a short distance between the hydrophilic groups (no larger than 1.0 nm). The proton transfer isotope effect of the iCOFMs was probed by measuring the proton conductivity under H$_2$O or D$_2$O vapor, respectively. The $\sigma_{H_2O}$/$\sigma_{D_2O}$ ratios fall into the range of 1.6–2 and the activation energy ($E_a$) of iCOFMs is less than 10 kJ mol$^{-1}$, indicating that the proton transfer in the surface confined water regions obeys the Grotthuss mechanism (Supplementary Figs. 46 and 47$^{31-32}$).

In summary, a strategy of constructing a surface-confined SHB network via a precisely regulated alignment of hydrophilic ligands was proposed to develop high-performance proton exchange membranes. Crystalline iCOFMs with tunable group distance were de novo designed and fabricated, which exhibited a maximum proton conductivity of 1389 mS cm$^{-1}$ at 90 °C (Supplementary Fig. 45). The proton conductivity ($\sigma$) of membranes was measured by a Shimadzu TGA-50 from 40 to 800 °C with a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere.

**Methods**

**Materials and reagents**

2,5-diaminobenzene sulfonic acid (Pa-SO$_3$H), 2,5-diaminobenzene-1,4-disulfonic acid (Pa-SO$_3$H(2)), 1,3,5-trihydroxy homobenzaldehyde (Tp), 4,4′,4″-nitrilotribenzenaldehyde (NTBA), 5′-(4-formyphenyl)-1′,3′,1″-terphenyl-4,4″-dicarbaldehyde (TFPB), and 4,4′,4″,4‴-(1,3,5-triazine-2,4,6-triytris(1,1′-biphenyl)-4-carbaldehyde) (CABPTZ) were purchased by Aladdin Reagents Co., Ltd. (Jilin, China). 4′-diamino-[1,1′,3′-biphenyl]-3,3′-disulfonic acid (Bd-SO$_3$H) was obtained from Henan Alpha Technology Co. Ltd.

**Preparation of iCOFMs**

The iCOFMs were prepared by vacuum-assisted assembly method. First, the iCOF nanosheets were assembled on the surface of PAN driven by vacuum pressure of ~0.025 MPa and ~0.08 MPa. Then, the composite iCOF membranes were immersed into DMF to peel off the PAN substrate and a freestanding iCOF was obtained. At last, the iCOF was placed in 1 M H$_2$SO$_4$ solution at 60 °C for 3 days.

**Characterization of iCOFMs**

The chemical structure and the element contents of iCOF nanosheets and iCOFMs were characterized by FTIR, NMR, and XPS. The morphology, lattice fringe, and element distribution of iCOF nanosheets and iCOFMs were characterized by TEM (Tecnai G220 S-TWIN) and SEM (Nanosem 430). The thickness of the iCOF nanosheets and the roughness of the membranes were recorded by a Bruker Dimension FastScan. The crystallinity of iCOFMs was characterized by XRD using a Bruker D8 Advance X-ray diffractometer equipped with Cu Ka radiation ($\lambda = 1.5406$ Å) at a scanning rate of 8° min$^{-1}$. The thermal stability of iCOFMs was measured by a Shimadzu TGA 50 from 40 to 800 °C with a ramp rate of 10 °C min$^{-1}$.

**Swelling ratio of iCOFMs**

The iCOFMs were dried at 100 °C under vacuum conditions for 24 h before testing the swelling ratio. Then, the dry iCOFMs were immersed into water at the temperature ranging from 30 to 90 °C. The swelling ratio of iCOFMs was calculated by equation as follows:

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

where, the $A_{\text{wet}}$ and $A_{\text{dry}}$ were the area of dry and wet iCOFMs, respectively.

**IEC values of iCOFMs**

The IEC values of iCOFMs were obtained by a titration method. The dry membranes (0.2 g) were immersed into NaCl solution (0.01 g/mL, 20 mL) and stirred for 24 h. Then, the solutions were titrated using a 0.01 M NaOH solution, and phenolphthalein was used as indicator. The IEC values (mmol g$^{-1}$) of the samples were calculated by Eq. (2):

\[
\text{IEC} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}}
\]

where, the $C_{\text{NaOH}}$ and $V_{\text{NaOH}}$ were the concentration and consumed volume of NaOH solution, and $W_{\text{dry}}$ (g) was the weight of the dry iCOFMs.

**Proton conductivity of iCOFMs**

The in-plane proton conductivities of iCOFMs were measured using a two-electrode ac impedance spectroscopy technique. The resistance value ($\Omega$) was tested over the frequency range of 1 M–1 Hz with an oscillating voltage of 15 mV. Proton conductivity measurements were carried out in a thermo-controlled chamber equipped with water and D$_2$O vapor. The proton conductivities ($\sigma$, mS cm$^{-1}$) of membranes were...
performed at 60 °C under 100% RH.

Applying back pressure. The performance evaluation of fuel cells was measured by sandwiching the iCOFs between 1 M HCl solutions. The through-plane proton conductivities of the iCOFs were calculated by Eq. (3):

$$\sigma = \frac{I}{R \times A}$$  (3)

where I (cm), R (Ω), and A (cm²) represent the membrane thickness, resistance, and contact area, respectively.

The through-plane proton conductivities of the iCOFs were measured by sandwiching the iCOFs between 1 M HCl solutions. The samples were prepared by assembling the iCOFs onto polyethylene diaphragm (100 μm) with pore size of 0.5 mm × 0.5 mm. The resistance with and without iCOFs was both measured. The resistances of iCOFs were obtained by removing the resistance of HCl solution from the total resistance. The through-plane proton conductivities (σ, mS cm⁻¹) of the iCOFs were calculated by Eq. (3).

**Single-cell performance evaluation**

Membrane electrode assemblies (MEA) were fabricated by sandwiching the iCOFs between two catalytic electrodes without hot pressing. Then, the MEAs were sandwiched between two graphite electrodes and assembled into single cells. The flow rates of hydrogen and oxygen were both controlled at 100 mL min⁻¹ and 400 mL min⁻¹ without applying back pressure. The performance evaluation of fuel cells was performed at 60 °C under 100% RH.

**H₂O aggregate state in the iCOF nanochannel**

The isolated -SO₃H group is simply represented by the rigid tetrahedral SO₃²⁻ with one O atom being replaced by C atom. The atomic charges on S atom, O atom, C atom are +2e, −1e and 0e, respectively, so that the single -SO₃ group has a net charge of −1e. The Lennard-Jones (LJ) potential parameters were used for S-S pairs and O-O pairs and the DREIDING field was used for C-C pairs. The water molecules were represented by the SPC/E model. The atomic structure of the TpPa-SO₃H nanosheets with -SO₃ groups from Ref. 2 was used. The atomic charges of atoms were calculated by the DFT method with the PBE0 and def2tzvp basis set using Gaussian 16. DREIDING field was used for the LJ potential parameters. In the simulations, hydroniums (H₃O⁺) were added to maintain the neutralization of the system, and the model in Ref. 35 was used for H₂O.

All simulations were carried out using the parallel MD software package LAMMPS. Periodic boundary conditions were imposed in all three directions. The velocity-Verlet algorithm with a time step of 1 fs was used to integrate the equation of motion, and a Nosé-Hoover thermostat with a time constant of 100 fs was used to maintain the liquid pressure at 1 atm. All simulations were performed with a Nosé-Hoover thermostat, and the time step was set to 1 fs. To prevent flipping of the benzene rings, the z-coordinates of all sulfate atoms were fixed. The following simulation scheme was applied: thermalizing the system to 300 K within 1 ps, equilibrating the structure for 4 ps, and collecting the structural data in a sufficiently long period (40 ps for TpPa-SO₃H, 25 ps for TpBd-SO₃H). The climbing-image nudged elastic band method (CI-NEB) was employed to calculate the migration barriers for proton hopping within water molecules in different configurations. Excess electrons were compensated with a homogeneous background charge. All the graphs of atomic structures were plotted using VESTA, and the probability densities of protons were obtained using Pymatgen.

**Data availability**

All data supporting the findings of this work are available within the article and the Supplementary Information file, or available from the corresponding authors upon request. Source data are provided with this paper.

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Author contributions

Z.J., H.W., F.P., S.L., and B.S. conceived the idea and designed the research. B.S. and X.P. carried out the experiment. X.Y., X.P., J.S., X.W., C.F., L.C., T.Z., M.Q., Y.K., and Y.L. prepare the COF nanosheets and membranes. S.L., M.Z., and Y.L. carried out density functional theory calculations and classical molecular dynamics simulations. H.W., X.P., F.P., and X.W. provided constructive suggestions for results and discussion. All authors participated in the discussion. B.S., X.P., H.W., S.L., F.P., and Z.J. co-wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Feng Pan or Zhongyi Jiang.

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