**Cite this paper:** *Chin. J. Chem.* **2024**, *42*, XXX—XXX. **DOI: 10.1002/cjoc.202400XXX**

**Tuning Hydrophilic Segments to Achieve Acid-free Proton Conduction in COF**

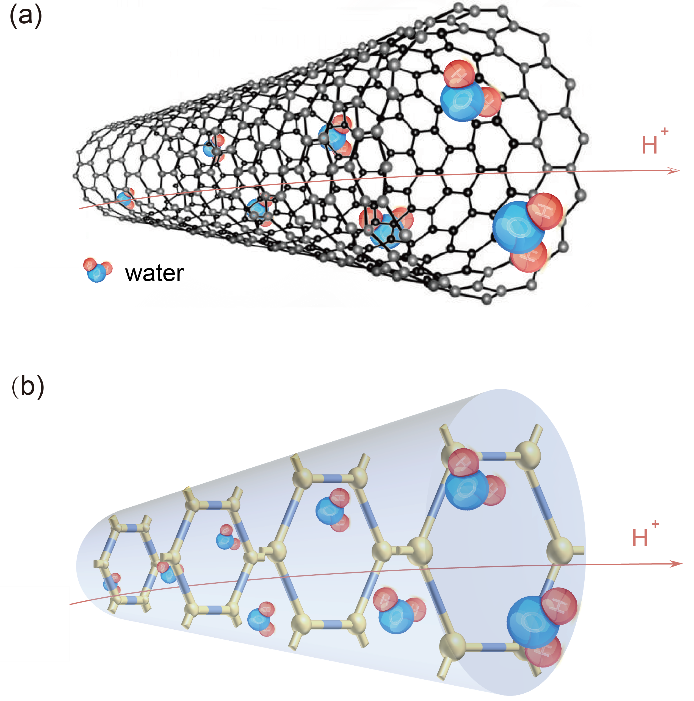
Kun Zhang ,‡,\*,*a* Lei Wu,‡,*a* Yanting Zhang,‡,*a* Hong Zhang,*c*and Dongshuang Wu \*,*b*

a Automotive Engineering Research Institute, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China b School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue 639798, Singapore c School of Energy and Power Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

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| **Keywords** |
| Confined water|Covalent organic frameworks| Acid-free | Proton conduction | Hydrophilic fragment | |
| **Comprehensive Summary** |
| TOC-01  Rapid dynamics and remarkable proton conduction induced byconfined water in nanospaces have attracted much attentions from researchers, which is crucial for advancing the development of innovative proton conductors and deepening comprehension of proton and water transport mechanisms within biological systems. In this aspect, carbon nanotubes (CNTs) are frequently employed as a research platform. However, they possess certain limitations, such as their inherent electronic conductivity and extreme hydrophobicity, which can impede the accurate assessment and precise regulation of proton conduction. We herein prepared two 2D COFs with different hydrophilic fragment, and obtains maximum acid-free proton conductivity of 3.04×10-4 S cm-1 at 70 °C and 100% RH with Grotthuss type activation energy of 0.14 eV. This is mainly due to that the water molecules in the center of channel form strong hydrogen bonds, enhancing proton dissociation and guiding fast directional diffusion. |

Background and Originality Content

Confined water in nanospaces has attracted much at-tentions from researchers, which possesses distinctive structural and dynamical attributes that are notably diver-gent from those of bulk water.[1] Such special characteris-tics dominantly stem from the reduced number of neigh-boring water molecules and restricted hydrogen-bond network cause by size constraints (<3-4 nm).[2] To observe the water under confinement effect, one dimensional car-bon nanotubes (CNTs) are typically utilized as research platform,[3] where the proton conducting property is fre-quently investigated due to its close relationship with wa-ter movement (Figure 1a). These studies are particularly significant in the field of biomimetics, providing crucial insights into the transfer mechanisms of proton pumps and water transport proteins.[4] There are, however, cer-tain limitations in CNTs based system: (1) The poor crys-talline structure and high electronic conductivity compli-cate the precise investigation of confined water's structure and proton conduction. (2) The 1D nanochannels are ab-solutely hydrophobic, differing from aquaporins (AQPs) that have both hydrophilic and hydrophobic groups, which leads to certain deviations from a biomimetic perspective.

In contrast to CNTs, covalent organic frameworks (COFs) are constructed through the versatile linking of organic covalent ligands, which endows them with crystal-linity, porosity, insulation, adjustable hydrophilicity and structural diversification.[5] Particularly, 2D COFs provide one-dimensional channels that are structurally similar to those found in CNTs and biomass, and within which re-markable proton conduction has been achieved (Figure 1b).[6] However, such proton conducting property is typi-cally obtained through the cooperation of acidic species and guest water,[7] a process distinctly different from the acid-free proton conduction observed in CNTs, where the process is solely governed by confined water.[8] To date, research on proton conduction in acid-free COFs is still scarce,[9] which aids in the construction of novel proton conductors and in understanding the confined state of water within biological systems.

**Figure 1** (a) Proton conduction in water-filled one dimensional carbon nanotubes. (b) Schematic illustration of water mediated proton conduction in 2D-COFs.

Considering the role of hydrophilic residues of amino acids on the AQP surface in guiding the molecular orientation and dynamics of water,[10] we have prepared two acid-free 2D COFs featuring distinct hydrophilic segments and investigated the confined water’s proton conduction. The COF sample with strong interaction with water (COF-H) achieves superior proton conduction, with maximum value of 3.04×10-4 S cm-1 and Grotthuss type activation energy of 0.14 eV. This is primarily because interfacial water molecules are more tightly bound near the channel surface of COF-H, which makes the central channel water molecules (core water) relatively independent. Consequently, these core water can form strong hydrogen bonds internally, facilitating proton dissociation and rapid diffusion.

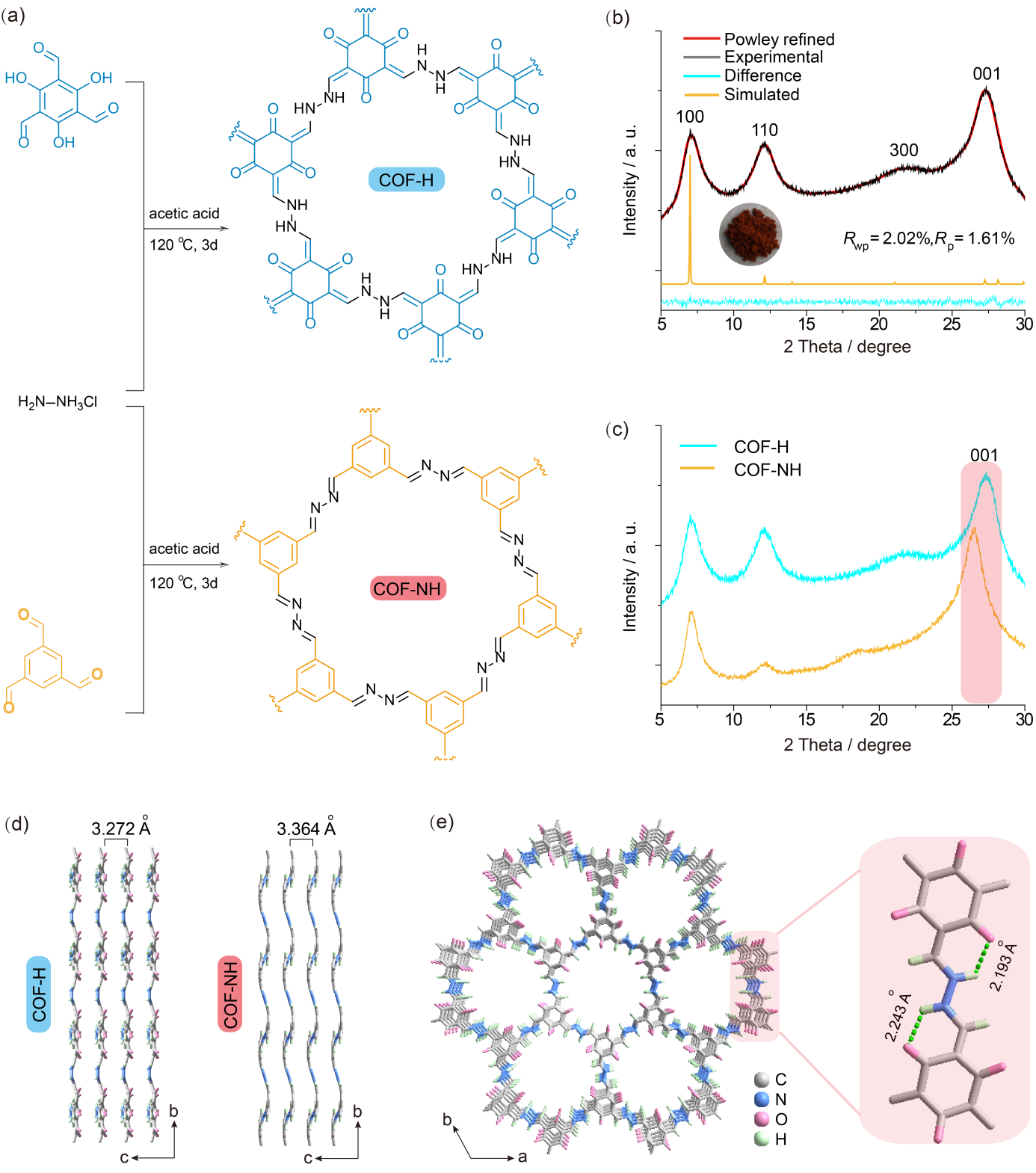
Results and Discussion

The 2D COFs, designated as COF-H and COF-NH, are synthesized through the condensation of hydrazine monohydrochloride with either 1,3,5-triformylphloroglucinol or 1,3,5-triformylbenzene (Figure 2a). Characteristic broad peak around 1480-1700 cm-1 in COF-H and new peak indicative of C=N stretching vibration in COF-NH are observed (Figure S1-S2), confirming the formation of the COFs’ structures. The crystallinity of COFs are evaluated by powder X-ray diffraction simulation (Figure 2b, Figur S3-S4). It is observed that both COF-H and COF-NH adopt a same space group of P3(143) and similar pore size of ~11 Å (Table S4-S5). The 001 peaks are 27.360o and 26.560o for COF-H and COF-NH (Figure 2c), with corresponding interlayer distance of 3.272 Å and 3.364 Å (Figure 2d), indicating that the layer stacking of COF-H is much tighter. This is because COF-H has strong intralayer H-bond rings (Figure 2e), which facilitates the formation of coplanar layers and layer stacking. Given the shorter interlayer distance in COF-H, the effect of H- bond rings is even stronger than that of the π-π stacking induced by the benzene rings in COF-NH. The detailed hydrogen bonding (N-H…O) is shown in Figure 2e, which is formed between the hydrogen atom on the secondary amine and the oxygen atom on the ketone group in same layer. The H-bonds have distance about 2.2 Å, forming six membered rings with adjacent atoms. According to the XPS analysis (Figure S6, Table S1), the mole ratio of N/Cl is 83.38 and 75.23 to COF-H and COF-NH, whereas the corresponding value for hydrazine monohydrochloride, based on its molecular formula, is 2. This indicates that almost all chloride ions escaped during the synthesis process, and that no nitrogen atom is protonated within the framework.

The proton conductivity values were derived from the Nyquist plots (Figure S7-S9). COF-NH exhibits notably low proton conductivity, peaking at a mere 1.36×10-6 S cm-1 at 70 °C and 100% RH. In stark contrast, COF-H demonstrates significantly higher proton conductivity, exceeding ~10-4 S cm-1 at 100% RH, with its peak value reaching 3.04×10-4 S cm-1 at 70 °C (Figure 3a). This performance is on par with other COFs and metal-organic frameworks (MOFs), as detailed in Tables S2 and S3. More importantly, COF-H is acid-free, differing from those proton conductors that typically possess acid species such as -SO3H and H3PO4.[11] The activation energy is fitted by Arrhenius equation:

 (1)

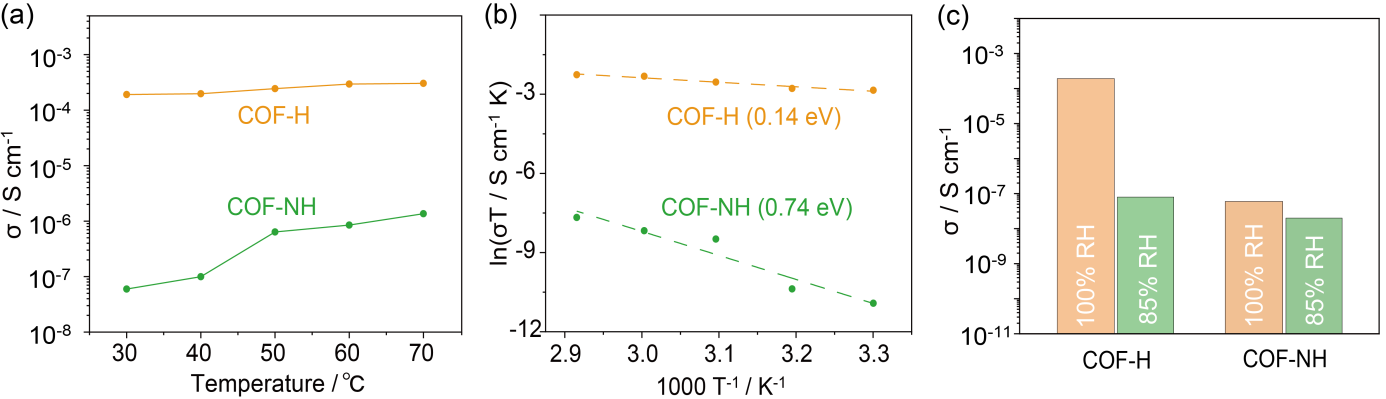
where *Ea* is the transport activation energy, *kB* is the Boltzmann constant, *T* is temperature, and *A* is a pre-exponential factor. The best fitting provides activation energy values of 0.14 eV for COF-H and 0.74 eV for COF-NH (Figure 3b), implying the



**Figure 2** (a) Schematic representation of the synthesis of COF-H and COF-NH. (b) Simulated and experimental PXRD patterns of COF-H. (c) PXRD comparison of COF-H and COF-NH. (d) Layer structures of COF-H and COF-NH with different stacking distance. (e) AA manner along c-axis generating one-dimensional channels of COF-H (left) and H-bond ring on the framework (right).

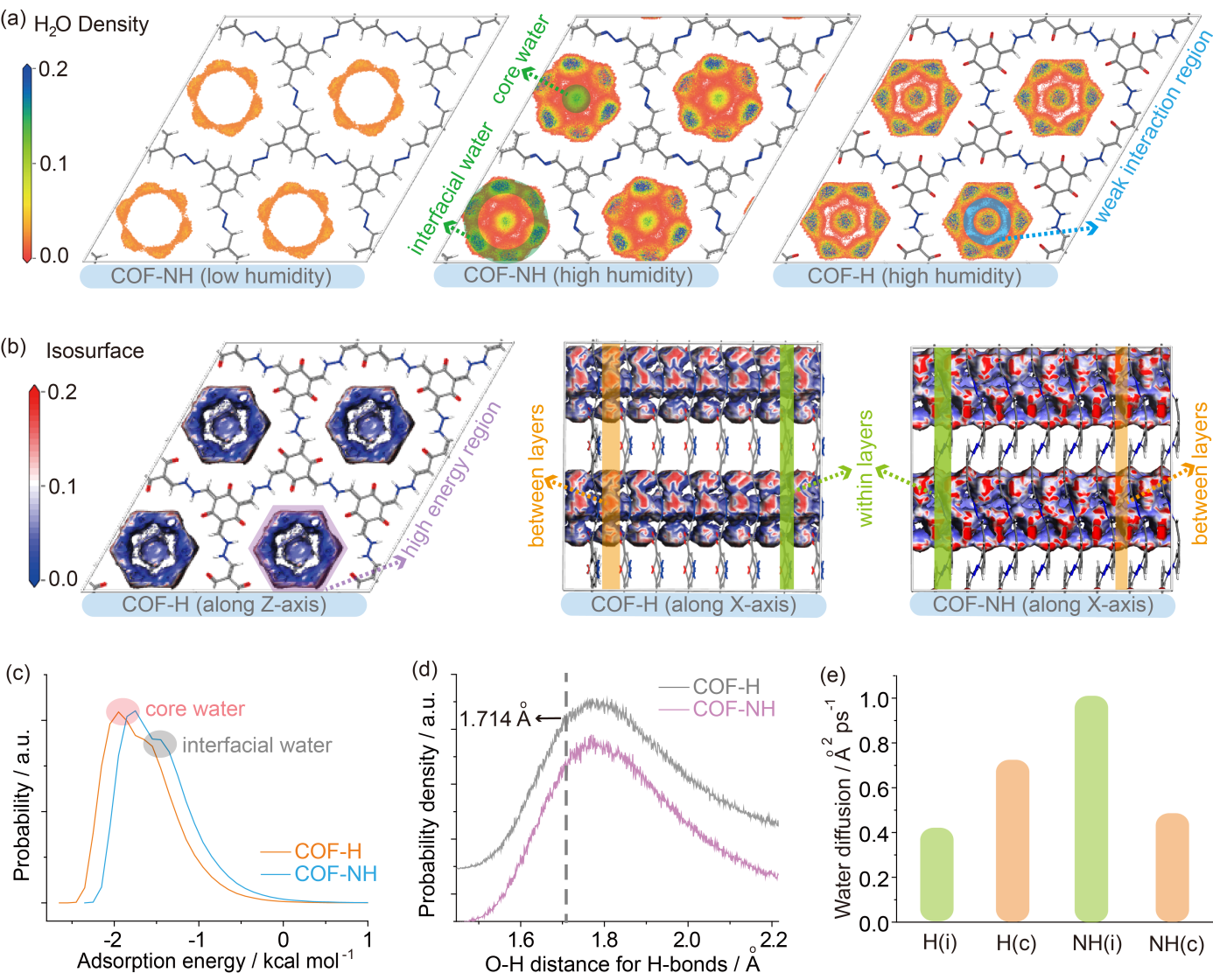
Grotthuss and Vehicle mechanisms, respectively. Therefore, the proton conduction processes in COF-H and COF-NH are distinct: protons in COF-H jump along the hydrogen bonding network, while in COF-NH, they move with hydronium ions as a whole. The proton conductivity decreases significantly with decreased relative humidity. For instance, it is 8×10-8 S cm-1 and 1×10-8 S cm-1 for COF-H and COF-NH at 30 °C and 85% RH (Figure 3c), demonstrating that the proton conduction is highly correlated with the amount of loaded water in COFs’ channel.

The water adsorption models in COFs are established based on DTF calculation. From water density distribution map, water molecules are preferentially adsorbed at channel interfaces at low humidity (Figure S11 and left in Figure 4a), which aligns with the mechanism where guest molecules are adsorbed first at pore interfaces.[12] At high humidity, the adsorbed water molecules can be divided into core water (water at center of channel) and interfacial water (water near the channel surface) (marked with green background in the middle of Figure 4a). Besides this, the energy distribution shows that the interfacial water’s energy is relatively high (marked with purple background in Figure S13 and left of Figure 4b), which is red color near the edge of frameworks. Figure 4c gives two water adsorption energy peaks for both COF-H and COF-NH (-1.95 kcal/mol and -1.65 kcal/mol for COF-H, -1.75 kcal/mol and -1.45 kcal/mol for COF-NH). Combining energy distribution, the high absolute values belong core water while low absolute values belong to interfacial water. The higher adsorption energy of core water (-1.95 kcal/mol for COF-H, -1.75 kcal/mol for COF-NH) is also beneficial for water molecules aggregating at the



**Figure 3** (a) Proton conductivity of COF-H and COF-NH at 100% RH versus different temperature. (b) Arrhenius plot of the proton conductivity of COF-H and COF-NH under 100% RH. (c) Proton conductivity of COF-H nad COF-NH at 100% RH and 85% RH (30 °C).

center of channel, thus greater density distribution of core water can be seen in COF-H (seen from comparison of core water in middle and right of Figure 4a), and will further contribute to the formation of denser H-bond networks. According to radial distribution function (RDF), water molecules themselves in COF-H form one type of strong hydrogen bonds with a distribution of distance of 1.714 Å (Figure 4d). Considering the higher adsorption energy of core water in COF-H (-1.95 kcal/mol), such strong hydrogen bonds are present at center of channel in COF-H. Ab initio molecular dynamics (AIMD) simulation further gives local diffusion of water along Z-axis direction (parallel to the direction of channel) (Figure 4e). The diffusion constant is 0.42 Å2/ps, 0.72 Å2/ps, 1.01 Å2/ps and 0.49 Å2/ps for interfacial water of COF-H, core water of COF-H, interfacial water of COF-NH and core water of COF-NH, implying proton conduction mainly occurs in core water of COF-H and interfacial water of COF-NH.

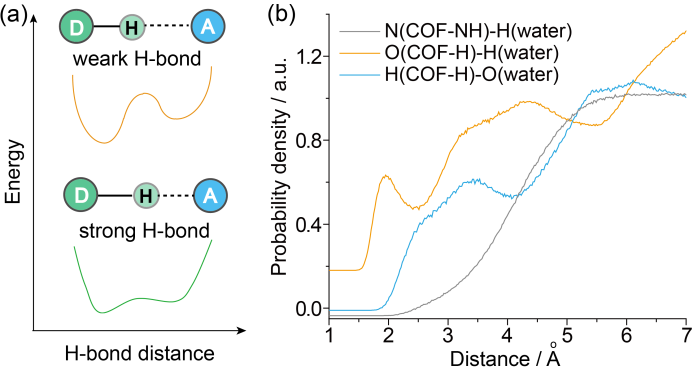


**Figure 4** (a) Water density distribution of COFs in different relative humidity. (b) Energy distribution of water in COFs at high RH. (c) Water adsorption energy of COFs. (d) Distribution of O-H distance of H-bonds between water molecules. (e) Diffusion of different types of water along distinct axes. COF-H’s interfacial water and core water, COF-NH’s interfacial water and core water are abbreviated as H(i), H(c), NH(i) and NH(c) respectively.

The diffusion constant of COFs has not reached a difference of more than an order of magnitude. Therefore, it is not the key factor for the distinct proton conductivity (1.36×10-6 S cm-1 and 3.04×10-4 S cm-1 for COF-NH and COF-H at 70 °C and 100% RH) according to Einstein relation:[13]

 (2)

where *D,* *n,* *kB,* and *T* represent the diffusion constant, concentration, Boltzmann constant and absolute temperature. The key factor is considered to be mobile proton concentration, which can be improved by the strong H-bonds of core water in COF-H. As the hydrogen bond distance becomes shorter, the double potential well in which the proton resides will gradually transition to a single potential well, which facilitates proton dissociation and generates large amount of mobile proton. The reason for the strong H-bonds formed in core of COF-H’s channel is further discussed. It can be seen that the channel surface of COFs can be divided into two parts: (1) the space between layers, marked with orange background and abbreviated as space-b; (2) the space within layers, marked with green background and abbreviated as space-w (middle and right in Figure 4b). The space-b and space-w of COF-H and COF-NH is further abbreviated as space-b-H, space-b-NH, space-w-H and space-w-NH for the convenience of narration. The Space-b is similar to vacuum (no atoms in it), almost having no interaction with water. Therefore, it can be approximately considered that the larger the volume of space-b, the weaker the binding effect on water molecules. Due to the greater interlayer distance of COF-NH, the volume of space-b-NH is larger than that of space-b-H, thus the interfacial water in space-b-NH is weakly bound and has high energy (The energy distribution of space-b-NH exhibits a more vibrant red color compared to that of space-b-H in the middle and right in Figure 4b ). On the other hand, COF-NH’s distribution of N…H (N from C=N, H from water) distance (5.61 Å) is longer than COF-H’s distribution of O…H (O from C=O, H from water) and H…O (H from N-H, O from water) distance (1.950 Å and 2.511 Å). Therefore, space-w-NH possesses weaker H-bond attraction to interfacial water compared to space-w-H, leading to higher energy of interfacial water. Taken overall of space-b and space-w, the channel surface of COF-NH has frail attraction to interfacial water, making the interfacial water relatively loose and easily interact with the core water. This interaction between core water and interfacial water occurs in the direction perpendicular to Z-axis, which weakens the dynamics of core water along the Z-axis. This also leads to a weakening of the internal interactions of the core water and a reduction in the strength of hydrogen bonds, which is unfavorable for the dissociation of protons. In contrast, the channel surface of COF-H produces strong attraction to interfacial water, further generates weak interaction between interfacial water and core water (a clear boundary marked with blue background in Figure 4a), and finally causes strong internal interaction among core water, leading to fast diffusion along Z-axis and strong proton ionization ability of core water.



**Figure 5** (a) Schematic diagram of potential well for strong H-bond and short H-bond. (b) Distance distribution between wa-ter and hydrophilic groups on COFs’ framework (C=O, N-H from COF-H, C=N from COF-NH).

Conclusions

In summary, we prepared two 2D COFs with different hydrophilic fragment and studied acid-free proton conduction within them. The COF-H acquires higher proton conductivity, with Grotthuss type proton conducting process and maximum value of 3.04×10-4 S cm-1 at 70 °C and 100% RH. The channel surface of COF-H produces strong interaction with interfacial water, making core water more independent and improving its dynamics and proton dissociation capability. Our research has guiding significance for the development of acid-free proton conductors and helps to understand biomass such as water and protons transport in biological systems.

Experimental

All experimental details are listed in Supporting Information.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202400xxx.

Acknowledgement

This work was supported by National Natural Science Foundation of China (52207238), China Postdoctoral Science Foundation (2023M731361) and Jiangsu University Senior Talent Launch Fund. The author is grateful to Mr. Yang from Huasuan for the discussion of DFT calculation. Kun Zhang, Lei Wu and Yanting Zhang contribute equally and are marked with ‡.

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| Manuscript received: XXXX, 2024  Manuscript revised: XXXX, 2024  Manuscript accepted: XXXX, 2024  Version of record online: XXXX, 2024 |  |

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| ***The Authors*** | | |
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**Entry for the Table of Contents**

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