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## **RESEARCH ARTICLE**

# Sulfonated 2D Covalent Organic Frameworks for Efficient Proton Conduction

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Abstract: Open 1D channels found in covalent organic frameworks are unique and promising to serve as pathways for proton conduction; how to develop high-rate yet stable transporting systems remains a substantial challenge. Herein, we report a strategy for exploring proton-conducting frameworks by engineering pore walls and installing proton-containing polymers into the pores. Amide-linked and sulfonated frameworks were synthesized from imine-linked precursors via sequentially engineering to oxidize into amide linkages and to further anchor sulfonic acid groups onto the pore walls, enabling the creation of sulfonated frameworks with high crystallinity and channel ordering. Integrating sulfonated polyether ether ketone chains into the open channels enables proton hopping to across the channels, greatly increases proton conductivity and enables a stable continuous run. These results suggest a way to explore protonconducting COFs via systematic engineering of wall and space of the open nanochannels.

#### Introduction

Proton-conducting materials are a burgeoning type of solid electrolyte, which have spurred tremendous interests in recent years. Proton-conducting materials have been utilized as separation membranes for hydrogen evolution via electrocatalytic water splitting, hydrogen sensors, electrochemical reactors and fuel cells, etc.<sup>[1]</sup> Although extensive research efforts have been devoted, the design and synthesis of proton-conducting materials with both high proton conductivity and stability remain challenging. For example, numerous research works have been performed to develop polymeric proton conductors such as polysulfones,<sup>[2]</sup> styrene-ethylene-butylene-styrene (SEBS) and poly(aryl ether ketone)s.<sup>[3,4]</sup> However, such aromatic-based polymers require further functionalization with sulfonic acid groups for efficient proton conduction.[5b] Recently, metal-organic frameworks (MOFs) and conjugated microporous polymer (CMP) have been employed as potential candidates for proton conduction.<sup>[5,6]</sup> Unfortunately, MOFs suffer from poor hydrolytic stability with low acid tolerance of the doped guests, which limits its applicability in operating conditions with high humidity. It is reported that onedimensional ordered channels can further facilitate proton

transport.<sup>[7,8]</sup> Therefore, it is desirable to explore suitable crystalline materials with both high proton conductivity and excellent stability.

Covalent organic frameworks (COFs) represent an emerging class of crystalline porous polymers which have been widely explored in gas separation,<sup>[9,10]</sup> heterogeneous catalysis,<sup>[11]</sup> sensors,<sup>[12]</sup> ionic conduction,<sup>[13]</sup> and many others.<sup>[14]</sup> Noteworthy features including the tunability of the pore size, the modifiability of pore surface and the excellent stability are beneficial for proton conduction. In the past decades, much attention has been paid to employ COFs as a promising platform for proton-conducting materials. In 2014, the first example of proton-conducting COF was reported, where Tp-Azo COF was doped with guest phosphoric acid molecules and applied as proton conductor under both humid and anhydrous conditions.<sup>[7]</sup> Later on, the same group reported another hybrid COF of TpPa-(SO<sub>3</sub>H-Py) with sulfonic acid anchored on the pore surface and phytic acid impregnated in the nanochannel.<sup>[15]</sup> Recently, Zhu and co-workers synthesized a novel cationic COF in which anionic PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> was introduced by static interactions.<sup>[16]</sup> Furthermore, Jiang's group reported an extraordinary stable COF loaded with N-heterocyclic proton carriers and H<sub>3</sub>PO<sub>4</sub> for efficient anhydrous proton conductions at high temperatures.<sup>[8]</sup> All these materials were constructed via de novo syntheses and further incorporation of guest acid molecules/anions such as H<sub>3</sub>PO<sub>4</sub>, phytic acid, PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> etc.. which served as the proton carriers and played pivotal roles in proton conduction. On the other hand, tailed-made functions can be readily introduced to the well-established COFs by postsynthetic modifications, which leads to completely new COFs without "trial and error" processes.<sup>[17]</sup> Sulfonation is a widely used strategy to improve the proton conductivity by introducing abundant sulfonic acid groups, which not only provide proton donors but also facilitate the formation of continuous hydrogen bonding networks for proton migration.<sup>[5c]</sup> However, the reported examples of sulfonated COFs are very rare and all prepared via de novo syntheses using sulfonic acid functionalized monomers because most COFs cannot survive in the harsh conditions of sulfonation reactions.<sup>[15,18]</sup> It is highly challenging to maintain both crystallinity and porosity of COFs upon sulfonation. Thus, direct post-synthetic sulfonation of COFs remains largely unexplored.

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Figure 1. a) Synthetic strategy for the sulfonated COFs through sequential imine formation, amide formation and sulfonation. b) Synthetic routes of the sulfonated 2D COFs of BD-COF (black), Ox-BD-COF (red), Ox-BD-COF-SO<sub>3</sub>H (blue). c) PXRD patterns and d) Nitrogen adsorption (solid) and desorption (open) isotherms of BD-COF (black), Ox-BD-COF (red), Ox-BD-COF-SO<sub>3</sub>H (blue). e) TEM images of Ox-BD-COF-SO<sub>3</sub>H (scale bar: 20 nm).

Herein, we designed and synthesized two ultrastable imine COFs annulated with cyclic ether moieties and further oxidized and sulfonated by post-synthetic modification approach (Figure 1). To our delight, these sulfonated COFs not only retain high crystallinity but also exhibit enhanced proton conductivity. In addition, an isostructural contrastive COF based on 1,2dimethoxybenzene (MB-COF) was synthesized for comparison to explore the effect of the cyclic ether moieties on the crystallinity and stability. The cyclic ether based imine COFs exhibited excellent chemical stability toward strong acid (12 M HCI) and base (9 M NaOH). In order to guarantee the COF skeletons can retain both crystallinity and porosity upon sulfonation, the dynamic imine linkages were further oxidized to more stable amide linkages. Due to the presence of electron-donating cyclic ether moieties, sulfonic acid groups were facilely grafted to the amide COFs. Sulfonated polyether ether ketone (SPEEK) featuring abundant sulfonic acid groups was infiltrated to the nanochannels of these two sulfonated amide-linked COFs to further enhance the proton conductivity. The hybrid composites of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H and 50 wt% SPEEK@Ox-DBD-COF-SO<sub>3</sub>H exhibit much higher proton conductivity (6.22 × 10<sup>-3</sup> S cm<sup>-1</sup> and  $3.87 \times 10^{-3}$  S cm<sup>-1</sup> at 90 °C and 98% RH, respectively) than the pristine sulfonated COFs.

#### **Results and Discussion**

Tri(4-aminophenyl)benzene (TAPB) was employed to synthesize imine COFs (BD-COF, DBD-COF and MB-COF) with three different dialdehydes (benzo[d][1,3]dioxole-4,7-dicarbaldehyde; 2,3-dihydrobenzo[b][1,4]dioxine-5,8-dicarbaldehyde and 2,3-dimethoxybenzene-1,4-dicarboxaldehyde) under solvothermal conditions at 120 °C for three days. The two cyclic ether decorated imine-linked COFs (BD-COF and DBD-COF) were further oxidized to corresponding amide COFs (Ox-BD-COF and Ox-DBD-COF) using sodium chlorite (NaClO<sub>2</sub>) as the oxidant. Finally, these two amide COFs were directly sulfonated by chlorosulfonic acid to afford the target sulfonated COFs (Ox-BD-COF) COF-SO<sub>3</sub>H and Ox-DBD-COF-SO<sub>3</sub>H, Figure 1b).

Fourier transform infrared spectroscopy (FT-IR), solid-state NMR spectroscopy and elemental analysis were employed to confirm the chemical composition and transformation of these imine COFs, amide COFs and sulfonated COFs. In terms of BD-COF, the disappearance of C=O stretching bands at 1674 cm<sup>-1</sup> and N-H stretching bands at 3431 cm<sup>-1</sup> compared to their corresponding monomer reveals the high condensation efficiency of these building units (Figure S1). The new appearance of vibration bands at 1622 cm<sup>-1</sup> demonstrates the formation of imine linkages which was also confirmed by the <sup>13</sup>C cross-polarization magic-angle spinning (CP-MAS) NMR spectra (Figure S5). The chemical shift at 153 ppm is attributed to the carbon of C=N double bonds. The verification of successful oxidation and sulfonation of BD-COF can be collectively concluded by the

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analysis of FT-IR and solid-state NMR spectra. For example, compared to BD-COF, the C=O stretching band (1651 cm<sup>-1</sup>) was newly appeared and the C=N imine stretching band (1622 cm<sup>-1</sup>) was disappeared in the FT-IR spectrum of Ox-BD-COF. In addition, in the case of Ox-BD-COF-SO<sub>3</sub>H, new O=S=O stretching bands at 1005, 1031, and 1058 cm<sup>-1</sup> were observed which verified the presence of sulfonic acid groups. As illustrated in Figure S5a, a new peak around 161-162 ppm in the CP-MAS <sup>13</sup>C NMR spectra assignable to amide carbonyl was observed for Ox-BD-COF, which is consistent with the reported results.<sup>[19]</sup> Indeed, a new carbon signal attributed to the C-SO<sub>3</sub>H bond was observed at 166 ppm in CP-MAS <sup>13</sup>C NMR spectra for Ox-BD-COF-SO<sub>3</sub>H. Furthermore, small shifts in the frequencies of the aromatic carbon resonances among BD-COF, Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H further support the conversion of imine to amide, and final substitution of sulfonic acid groups. Similar results were observed for the DBD-COF, Ox-DBD-COF and Ox-DBD-COF-SO<sub>3</sub>H as well, which confirmed the successful transformation of DBD-COF to the target Ox-DBD-COF-SO3H (Figures S2 and S5). On the other hand, the content of grafted sulfonic acid groups in sulfonated COFs were further estimated by the elemental analysis (Table S1), which revealed a sulfonated degree of 6.2 and 5.8 wt% (X wt% is the mass ratio of sulfonic acid groups in the sulfonated COFs) for Ox-BD-COF-SO<sub>3</sub>H and Ox-DBD-COF-SO<sub>3</sub>H, respectively.<sup>[6a]</sup>



Figure 2. a) TEM images and corresponding EDX elemental mapping images of b) C, c) O, d) S for Ox-BD-COF-SO<sub>3</sub>H. e) UV-visible spectra of BD-COF (black line), Ox-BD-COF (blue line) and Ox-BD-COF-SO<sub>3</sub>H (red line), inset shows photographs of the three COFs under ambient light.

Solid-state UV/Vis spectra exhibit broad adsorption bands with similar absorption maxima at 436 nm for BD-COF, Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H (Figure 2e). Interestingly, the absorption region of amide-linked and sulfonated COFs is broader than the pristine imine COFs with increasing shoulder absorption around 520-530 nm, which are also corresponding to the color change from imine COF (yellow) to amide COF (orange) and sulfonated COF (red) as shown in the inset of Figure 2e.

The crystallinities of all imine COFs, amide COFs and sulfonated COFs were evaluated by powder X-ray diffraction (PXRD) measurements (Figure 1b, Figure S26). The PXRD pattern of BD-COF showed prominent peaks at 2.75°, 4.78°, 5.53°, 7.34°, 9.59° and 25.23° corresponding to the (100), (110), (200), (210), (220) and (001) facets, respectively (Figure S28a, black line). BD-COF was determined to be fitted in *P3* space group with unit cell parameters of *a* = *b* = 36.9244 Å, *c* = 3.5369 Å, *a* = *β* = 90° and *γ* = 120° (Table S2) upon Pawley refinement. The simulated PXRD pattern based on the AA stacking mode (Figure S28a, magenta line) is in good agreement with the experimental results with the *R*<sub>p</sub> and *R*<sub>wp</sub> converged to 5.29% and 4.05%, respectively. Ox-BD-COF retained the same space group and eclipsed stacking configuration, but with slight difference in the unit cell parameters (*a* = *b* = 36.7132 Å, *c* = 3.8793 Å) comparing with BD-COF (Figure S30a). The nearly identical PXRD pattern of the sulfonated Ox-BD-COF-SO<sub>3</sub>H indicates that the covalent

network remains intact and adopts the same structure as BD-COF and Ox-BD-COF upon sulfonation (Figure 1b). Similar structures were also observed for DBD-COF, Ox-DBD-COF and Ox-DBD-COF-SO<sub>3</sub>H (Figures S29 and S31).

Permanent porosities of these imine COFs, amide COFs and sulfonated COFs were assessed by nitrogen sorption measurements at 77 K. The sorption profiles (Figures 1d and S7) of all COFs exhibit typical characteristics of type IV isotherms,<sup>[20]</sup> which reveal that these COFs are mesoporous. BD-COF exhibits a Brunauer-Emmett-Teller (BET) surface area of 1580 m<sup>2</sup> g<sup>-1</sup> calculated from the N<sub>2</sub> adsorption isotherms in the low pressure region ( $P/P_0 < 0.15$ ) with a pore volume up to 2.10 cm<sup>3</sup> g<sup>-1</sup> ( $P/P_0$ = 0.99). Upon oxidation and sulfonation, although the BET surface areas of Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H decreased to 853 and 630 m<sup>2</sup> g<sup>-1</sup>, respectively. However, the uptake of water vapor of Ox-BD-COF-SO<sub>3</sub>H greatly increased due to the hydrophilicity of the sulfonic acid substituents (Figure S11). The corresponding pore volumes reasonably decreased to 0.96 and 0.82 cm<sup>3</sup> g<sup>-1</sup> for Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H, respectively. Interestingly, the pore size distribution (PSD) calculated based on the nonlocal density functional theory (NLDFT) method shows similar dominant pore size centered at 3.2, 3.1 and 3.0 nm for BD-COF, Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H (Figure S9a) which match well with the theoretical value (3.2 nm, Figure S28b). On the other hand, DBD-COF, Ox-DBD-COF and Ox-DBD-COF-SO<sub>3</sub>H show comparable BET surface areas of 1228, 620 and 524 m<sup>2</sup> g<sup>-1</sup>, respectively (Figure S7). The pore size distribution analyses of the DBD-COF, Ox-DBD-COF and Ox-DBD-COF-SO<sub>3</sub>H also indicated a dominant pore size distribution of 3.2, 3.1 and 3.0 nm (Figure S9b), and the corresponding pore volumes are 1.67, 0.72 and 0.64 cm<sup>3</sup> g<sup>-1</sup>, respectively. In sharp contrast, the contrastive MB-COF exhibits a much lower BET surface area of 228 m<sup>2</sup> g<sup>-1</sup> (Figure S10). Unfortunately, such a low BET surface impedes further post-functionalization on MB-COF.

The morphologies of these COFs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As revealed by SEM images (Figures S15–S17), BD-COF and DBD-COF exhibit rod-like morphology while MB-COF showcases sheet-like structures. Upon oxidation and sulfonation, the morphologies of cyclic ether decorated COFs still retained. Surprisingly, TEM images of all the imine COFs, amide COFs and sulfonated COFs disclose clear lattice stripes, which further reflected that these COFs are highly crystalline (Figures S18–S20). As shown in Figure 2a-d, the EDX elemental mapping demonstrated a homogeneous distribution of C, N, O and S, indicating that the sulfonic acid groups were evenly distributed on the pore walls of OX-BD-COF-SO<sub>3</sub>H.

The thermal stabilities of these COFs were evaluated by thermogravimetric analysis (TGA). TGA profiles reveal that BD-COF could be thermally stable up to about 400 °C and retained 73% of its initial mass even at 800 °C under N<sub>2</sub> atmosphere (Figure S22a). In contrast, the amide-linked COF (Ox-BD-COF) and sulfonated COF (Ox-BD-COF-SO<sub>3</sub>H) exhibit lower thermostability and showcase weight loss started at around 300 °C and 200 °C, respectively. This is probably due to the less conjugated skeleton and the grafted sulfonic acid groups. Similar results were also observed for DBD-COF, Ox-DBD-COF and Ox-DBD-COF-SO<sub>3</sub>H (Figure S22b). However, the contrastive MB-COF showcased weight loss below 350 °C (Figure S22c), indicative of a worse thermostability. On the other hand, the chemical stability tests of imine COFs were performed by soaking

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Figure 3. a) PXRD patterns and b) Nitrogen adsorption (solid) and desorption (open) isotherms of BD-COF before (black) and after 12 M HCl (red), 9 M NaOH (blue) and boiling water (magenta) treatments.

these COFs in boiling water, strong acid (12 M HCl, 25 °C), and corrosive base (9 M NaOH, 25 °C) for 3 days. After treatments in these harsh conditions, the isolated COF samples were again characterized by PXRD, N2 sorption, FT-IR spectroscopy (Figures 3, S23, S24 and S25). All COFs maintained their crystallinity, porosity and chemical composition in these harsh conditions except the contrastive MB-COF which exhibited severe decomposition. Furthermore, for justifying the chemical stability of cyclic ether moieties, monomer 3 and 4 were treated in same conditions (12 M HCl and 9 M NaOH, 25 °C) for 3 days. The resulting mixtures were extracted with ethyl acetate, dried over anhydrous MgSO<sub>4</sub> and evaporated without purification. Solution state <sup>1</sup>H NMR spectra show that cyclic ether moieties are stable in these conditions. These results indicate that the COFs with cyclic ether moieties are much more stable than MB-COF bearing o-methoxy groups in terms of both thermal and chemical stability.

SPEEK, featuring high mechanical and thermal stability, low price and high proton conductivity, has been widely used as proton-conducting materials and proton exchange membranes.<sup>[21]</sup> However, SPEEK exhibits large solubility in water attributed to the high sulfonation degree, which hinders its practical application as proton conductors at high temperatures and humidity. On the other hand, COFs are normally obtained as insoluble powders which is difficult for direct processing. Fortunately, the large porosity and excellent stability enable COFs as a versatile platform for post-synthetic hybridization with various guest polymers, which afford processable composites for tailor-made applications.<sup>[22]</sup> As a kind of hydrophilic polymer, the ability of SPEEK to hinder the loss of proton (H<sup>+</sup>) under high humidity is much better than commonly used guest acid molecules/anions such as H<sub>3</sub>PO<sub>4</sub>, phytic acid and PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>. Stable protonconducting materials under high humidity were prepared by infiltration of SPEEK into the one-dimensional nanochannels of sulfonated COFs. The successful incorporation of SPEEK into sulfonated COFs was clearly demonstrated by SEM, PXRD and N<sub>2</sub> sorption measurements. SEM images indicated that the morphology of the hybrid composites obviously changed when increases the amount of SPEEK (Figures S16 and S17). As for the PXRD patterns (Figure 4c), the peak at 2.75° corresponding to the (100) facets is significantly weakened for 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H, which could be reasonably



**Figure 4.** a) Nitrogen sorption profiles, b) pore size distribution and c) PXRD patterns of Ox-BD-COF-SO<sub>3</sub>H, 50 wt% Ox-BD-COF-SO<sub>3</sub>H, Ox-BD-COF-SO<sub>3</sub>H-MIX and Ox-BD-COF-SO<sub>3</sub>H-WAS.

attributed to the disorder induced by the flexible SPEEK chains inside the 1D channels. However, the peak at 2.75° in the PXRD pattern of Ox-BD-COF-SO<sub>3</sub>H-MIX (i.e. mechanically mixed sample of 50 wt% SPEEK and Ox-BD-COF-SO<sub>3</sub>H) is basically same with that of the pristine Ox-BD-COF-SO<sub>3</sub>H, because the SPEEK is mainly located outside the one-dimensional channels and causes little effect on the periodicity of Ox-BD-COF-SO<sub>3</sub>H. After removal of SPEEK from the COF by thoroughly washing with solvent (denoted as Ox-BD-COF-SO<sub>3</sub>H-WAS), the peak intensity of (100) facets is recovered, illustrating the structure of the COF was retained during the whole process (Figure 4c). N2 adsorption measurements were further carried out to confirm the successful incorporation of SPEEK inside the regular channels. N2 uptake and BET surface area of Ox-BD-COF-SO3H-MIX exhibited a significant reduction (248 m<sup>2</sup> g<sup>-1</sup>) but are still much higher than that of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H (21 m<sup>2</sup> g<sup>-1</sup>). The nearly nonporous feature of 50 wt% SPEEK@Ox-BD-COF-SO3H revealed that the channels of sulfonated COFs were almost fully occupied by SPEEK. After the removal of SPEEK, the N<sub>2</sub> uptake and BET surface area can be recovered up to 401 m<sup>2</sup> g<sup>-1</sup>. The loss in the BET surface area compared to that of the pristine Ox-BD-COF-SO<sub>3</sub>H (630 m<sup>2</sup> g<sup>-1</sup>) might be attributed the SPEEK residue remained in the channels (Figure 4a). In order to investigate the effect of SPEEK content on proton conductivity, different amounts of SPEEK were loaded to prepare corresponding hybrid composites (Figures S25 and S28). The hybrid composites were denoted as X wt% SPEEK@Ox-BD-COF (X is the mass ratio of SPEEK in the hybrid material). The results demonstrate that the proton conductivity increased rapidly and gradually saturated as the content increased (Figures S34d and S36e). Considering the cost-effectiveness, we selected and fixed the loading amount of 50 wt% SPEEK into the hybrid composites for systematical investigation.

The proton conductivity of the hybrids was evaluated by alternating current impedance measurements. Figure 5b shows the Nyquist plots of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H at 98% RH from 50 to 90 °C. The proton conductivity increases with elevating the temperature and reaches  $6.22 \times 10^{-3}$  S cm<sup>-1</sup> at 90 °C. To illustrate the universality of this doping approach, the same test was also performed for other hybrid composite 50 wt% SPEEK@Ox-DBD-COF-SO<sub>3</sub>H and comparable conductivity of 3.87 ×  $10^{-3}$  S cm<sup>-1</sup> at 90 °C was obtained (Figure S35c). Repeated conductivity measurements were conducted and confirmed that the conductivity of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H basically remained unchanged on a 48-h-continuous run at

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90 °C under 98% RH (Figure S34d). It is well accepted that the Grotthuss and vehicular mechanisms are two main mechanisms for proton transport, which are primarily identified by the activation energy.<sup>[23]</sup> Based on the temperature-dependent conductivity profiles (Figures 5c and S36d), the activation energy of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H and 50 wt% SPEEK@Ox-DBD-COF-SO<sub>3</sub>H for the proton conduction was calculated to be as low as 0.199 eV and 0.336 eV, respectively. Such low barriers (< 0.4 eV) imply a Grotthuss-type hopping mechanism for the proton conduction in these SPEEK@sulfonated COFs.



Figure 5. a) Schematic illustrations of H<sup>+</sup> transport in the hybrid material. b) EIS spectra of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H. c) Arrhenius plots of 50 wt% SPEEK@OX-BD-COF-SO<sub>3</sub>H.

To differentiate the contributions of sulfonic acid groups in the COF skeletons and the infiltrated guest SPEEK on the proton conduction, the conductivity of 50 wt% SPEEK@Ox-BD-COF and Ox-BD-COF-SO<sub>3</sub>H were investigated and compared under the same conditions. The proton conductivities of Ox-BD-COF-SO<sub>3</sub>H (i.e. sulfonated COF without SPEEK) and 50 wt% SPEEK@Ox-BD-COF (i.e. amide-linked COF without sulfonic acid groups but infiltrated with SPEEK) are  $1.79 \times 10^{-6}$  S cm<sup>-1</sup> and  $6.27 \times 10^{-4}$  S cm<sup>-1</sup> at 90 °C and 98% RH, respectively (Figure S34). Both conductivities are much lower than that of 50 wt% SPEEK@Ox-BD-COF-SO<sub>3</sub>H (6.22  $\times$  10<sup>-3</sup> S cm<sup>-1</sup>) which suggested that the sulfonic acid groups and SPEEK play synergistic effect in enhancing the proton conductivity. Furthermore, the conductivity of the physically mixture of Ox-BD-COF-SO<sub>3</sub>H and corresponding amount of SPEEK (50 wt%) was measured under the same conditions. The proton conductivity of the physically mixed material was  $5.01 \times 10^{-4}$  S cm<sup>-1</sup> (Figure S34a), which is more than one order of magnitude lower than that of 50 wt% SPEEK@Ox-DBD-COF-SO<sub>3</sub>H (6.22 × 10<sup>-3</sup> S cm<sup>-1</sup>). This result suggests that SPEEK in the nanochannels of COFs might exert more predominant effect on improving the proton conductivity than that of SPEEK outside the channels. Furthermore, the conductivity of Ox-BD-COF measured by direct-current measurements was lower than  $10^{-12}$  S cm<sup>-1</sup>, which suggests that post-sulfonation of COFs is crucial for proton conduction enhancement. To further confirm the versatility of the post-modification strategy, the same tests were carried out for 50 wt% SPEEK@Ox-DBD-COF-SO<sub>3</sub>H and similar results of proton conductivity enhancement was confirmed (Figure S36).

#### Conclusion

In summary, two highly crystalline and sulfonated 2D covalent organic frameworks with cyclic ether moieties on the pore walls were synthesized by sequential post-synthetic oxidation and sulfonation of the corresponding imine COFs. Integrating SPEEK into the nanochannels of sulfonated COFs triggers a profound synergistic effect on proton conductivity. The 2D imine-linked COFs with cyclic ether moieties exhibited higher porosity and are much more stable than the isostructural imine COF with odimethoxy groups. Further introduction of sulfonic acid groups and SPEEK are conducive for releasing more protons for proton conduction, therefore leading to a great enhancement of proton conductivity. Owing to the synergistic effect of sulfonic acid groups and SPEEK, the resulting 50 wt% SPEEK@Ox-BD-COF- $SO_3H$  showcases excellent proton conductivity up to  $6.22 \times 10^{-3}$ S cm<sup>-1</sup> at 90 °C and 98% RH, which is higher than many protonconducting COFs (Table S7). The current work thus shows the importance of engineering pore walls and open space of the nanochannels to create stable high-rate transporting systems and offers a new phase in developing proton-conducting molecular frameworks.

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**Keywords:** covalent organic frameworks • sulfonation • proton conduction • post-synthesis • stability

- a) M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* 2004, 104, 4587; b) Q. Li, R. He, J. O. Jensen, N. J. Bjerrum, *Chem. Mater.* 2003, 15, 4896; c) R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, *Chem. Rev.* 2007, 107, 3904.
- [2] J. Kerres, W. Cui, S. Reichle, J. Polym. Sci. Part A 1996, 34, 2421.
- [3] J. M. Serpico, S. G. Ehrenberg, J. J. Fontanella, X. Jiao, D. Perahia, K. A. McGrady, E. H. Sanders, G. E. Kellogg, G. E. Wnek, *Macromolecules* 2002, 35, 5916.
- [4] D. J. Jones, J. Rozière, J. Membrane Sci. 2001, 185, 41.
- [5] a) P. Ramaswamy, N. E. Wong, G. K. Shimizu, *Chem. Soc. Rev.* 2014, 43, 5913; b) W. J. Phang, H. Jo, W. R. Lee, J. H. Song, K. Yoo, B. Kim, C. S. Hong, *Angew. Chem.* 2015, *127*, 5231; *Angew. Chem. Int. Ed.* 2015, 54, 5142; c) F. Yang, G. Xu, Y. Dou, B. Wang, H. Zhang, H. Wu, W. Zhou, J. Li, B. Chen, *Nat. Energy* 2017, *2*, 877; d) Y. Ye, L. Gong, S. Xiang, Z. Zhang, B. Chen, *Adv. Mater.* 2020, 1907090.
- [6] a) S. Yang, X. Ding, B. Han, *Langmuir* **2018**, *34*, 7640; b) S. Bhunia, B. Banerjee, A. Bhaumik, *Chem. Commun.* **2015**, *51*, 5020; c) P. Samanta,

## **RESEARCH ARTICLE**

A. V. Desai, B. Anothumakkool, M. M. Shirolkar, A. Karmakar, S. Kurungot, S. K. Ghosh, *J. Mater. Chem. A* **2017**, *5*, 13659; d) C. Klumpen, S. Gödrich, G. Papastavrou, J. Senker, *Chem. Commun.* **2017**, *53*, 7592.

- [7] S. Chandra, T. Kundu, S. Kandambeth, R. BabaRao, Y. Marathe, S. M. Kunjir, Rahul Banerjee, J. Am. Chem. Soc. 2014, 136, 6570.
- [8] a) H. Xu, S. Tao, D. Jiang, *Nat. Mater.* 2016, *15*, 722; b) S. Tao, L. Zhai, A. D. D. Wonanke, M. A. Addicoat, Q. Jiang, D. Jiang. *Nat. Commun.* 2020, *11*, 1981.
- [9] a) C. S. Diercks, O. M. Yaghi, *Science* 2017, *355*, 923; b) K. Geng, T. He, R. Liu, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang, D. Jiang, *Chem. Rev.* 2020, *120*, 8814–8933; c) S. Y. Ding, W. Wang, *Chem Soc Rev.* 2013, *42*, 548; d) Y. Li, W. Chen, G. Xing, D. Jiang, L. Chen, *Chem. Soc. Rev.* 2020, *49*, 2852.
- [10] a) N. Huang, X. Chen, R. Krishna, D. Jiang, *Angew. Chem.* 2015, 127, 3029; b) N. Huang, R. Krishna, D. Jiang, *J. Am. Chem. Soc.* 2015, 137, 7079.
- a) H. Xu, J. Gao, D. Jiang, *Nat. Chem.* 2015, *7*, 905; b) X. Wang, X. Han,
   J. Zhang, X. Wu, Y. Liu, Y. Cui, *J. Am. Chem. Soc.* 2016, *138*, 12332.
- [12] a) S. Ding, M. Dong, Y. Wang, Y. Chen, H. Wang, C. Su, W. Wang, J. Am. Chem. Soc. 2016, 138, 3031; b) Z. Li, Y. Zhang, H. Xia, Y. Mu, X. Liu, Chem. Commun. 2016, 52, 6613.
- [13] a) Y. Hu, N. Dunlap, S. Wan, S. Lu, S. Huang, I. Sellinger, M. Ortiz, Y. Jin, S. Lee, W. Zhang, J. Am. Chem. Soc. 2019, 141, 7518; b) K. Jeong, S. Park, G. Y. Jung, S. H. Kim, Y. Lee, S. K. Kwak, S. Lee, J. Am. Chem. Soc. 2019, 141, 5880; c) G. Zhang, Y. Hong, Y. Nishiyama, S. Bai, S. Kitagawa, S. Horike, J. Am. Chem. Soc. 2019, 141, 1227; d) H. Chen, H. Tu, C. Hu, Y. Liu, D. Dong, Y. Sun, Y. Dai, S. Wang, H. Qian, Z. Lin, L. Chen, J. Am. Chem. Soc. 2018, 140, 896.
- [14] a) P. Wang, X. Chen, Q. Jiang, M. Addicoat, N. Huang, S. Dalapati, T. Heine, F. Huo, D. Jiang, Angew. Chem. 2019, 131,16069–16074; Angew. Chem. Int Ed. 2019, 58, 15922; b) F. Yu, W. Liu, B. Li, D. Tian, J. Zuo, Q. Zhang, Angew. Chem. 2019, 131,16247; Angew. Chem. Int Ed. 2019, 58, 16101; c) A. C. Jakowetz, T. F. Hinrichsen, L. Ascherl, T. Sick, M. Calik, F. Auras, D. D. Medina, R. H. Friend, A. Rao, T. Bein, J. Am. Chem. Soc. 2019, 141, 11565; d) S. Ghosh, A. Nakada, M. A. Springer, T. Kawaguchi, K. Suzuki, H. Kaji, I. Baburin, A. Kuc, T. Heine, H. Suzuki, R. Abe, S. Seki, J. Am. Chem. Soc. 2020, 142, 9752. e) D. Sakamaki, S. Ghosh, S. Seki, Mater. Chem. Front. 2019, 3, 2270. f) S. Ghosh, Y. Tsutsui, K. Suzuki, H. Kaji, K. Honjo, T. Uemura, S. Seki, Mol. Syst. Des. Eng. 2019, 4, 325.
- [15] S. Chandra, T. Kundu, K. Dey, M. Addicoat, T. Heine, R. Banerjee, *Chem. Mater.* 2016, 28, 1489.
- [16] H. Ma, B. Liu, B. Li, L. Zhang, Y. G. Li, H. Q. Tan, H. Y. Zang, G. Zhu, J. Am. Chem. Soc. 2016, 138, 5897.
- [17] a) J. L. Segura, S. Royuela, M. M. Ramos, *Chem. Soc. Rev.* 2019, *48*, 393; b) Y. Yusran, X. Guan, H. Li, Q. Fang, S. Qiu, *Natl. Sci. Rev.* 2020, 7, 170.
- [18] a) H. S. Sasmal, H. B. Aiyappa, S. N. Bhange, S. Karak, A. Halder, S. Kurungot, R. Banerjee, *Angew. Chem.* 2018, *130*,11060; *Angew. Chem. Int. Ed.* 2018, *57*, 10894; b) Y. Peng, Z. Hu, Y. Gao, D. Yuan, Z. Kang, Y. Qian, N. Yan, D. Zhao, *ChemSusChem* 2015, *8*, 3208; c) Y. Peng, G. Xu, Z. Hu, Y. Cheng, C. Chi, D. Yuan, H. Cheng, D. Zhao, *ACS Appl. Mater. Inter.* 2016, *8*, 18505.
- [19] P. J. Waller, S. J. Lyle, T. M. O. Popp, C. S. Diercks, J. A. Reimer, O.M. Yaghi, *J. Am. Chem. Soc.* **2016**, *138*, 15519.
- [20] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.* 2015, 87, 1051.
- [21] T. Higashihara, K. Matsumoto, M. Ueda, Polymer 2009, 50, 5341.
- [22] a) Z. Xie, B. Wang, Z. Yang, X. Yang, X. Yu, G. Xing, Y. Zhang, L. Chen, *Angew. Chem.* **2019**, *131*,15889; *Angew. Chem. Int. Ed.* **2019**, *58*, 15742; b) Z. Guo, Y. Zhang, Y. Dong, J. Li, S. Li, P. Shao, X. Feng, B. Wang, *J. Am. Chem. Soc.* **2019**, *141*, 1923.
- [23] a) O. F. Mohammed, D. Pines, J. Dreyer, E. Pines, T. J. N. Erik, *Science* 2005, *310*, 83; b) X. Meng, H. Wang, S. Song, H. Zhang, *Chem. Soc. Rev.* 2017, *46*, 464.

## **RESEARCH ARTICLE**

#### **Entry for the Table of Contents**



Highly crystalline sulfonated COFs annulated with cyclic ether moieties were constructed by direct post-synthetic sulfonation for the first time. Sulfonated polyether ether ketone (SPEEK) was further infiltrated into the 1D regular channels of these sulfonated COFs to improve the proton conductivity and reduce the loss of protons (H<sup>+</sup>). The resulting hybrid material achieves excellent proton conductivity up to  $6.22 \times 10^{-3}$  S cm<sup>-1</sup>.