


Title	Accumulation of Sulfonic Acid Groups Anchored in Covalent Organic Frameworks as an Intrinsic Proton-Conducting Electrolyte
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Citation	Macromolecular rapid communications, 43(1): 2100590
Issue Date	2021-10-06
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/18092
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Description	 <p>JAPAN ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY</p>

Accumulation of sulfonic acid groups anchored in covalent organic frameworks as an intrinsic proton-conducting electrolyte

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Keywords: Covalent organic frameworks, stability, **nanochannel**, proton conductivity.

Abstract: Covalent organic frameworks (COFs) are a novel class of crystalline porous polymers, which possessed high porosity, excellent stability, and regular nanochannels. Two-dimensional (2D) COFs **provided** 1D **nanochannel** to form the proton transport **channels**. **The abovementioned features afforded a powerful potential platform for designing materials as proton transportation carriers.** Herein, we incorporated sulfonic acid groups on the pore walls **as** proton **sources** for enhancing proton transport conductivity in the 1D channel. Interestingly, the sulfonic acid COFs (S-COFs) **electrolytes** with binder free exhibited excellent proton conductivity about $1.5 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C and 95% relative humidity (RH), which ranked the excellent performance in standard proton-conducting **electrolytes**. The S-COFs **electrolytes** kept the high proton conduction over the 24 h. The activation energy was estimated to be as low as 0.17 eV, which was much lower than most reported COFs. This research opens **a** new window to evolve great potential of structural design for COFs as the high proton-conducting **electrolytes**.

1. Introduction

Due to the rapid progress and development of society, social modernization and industrial development, fossil fuels are the main source of the utilized energy leading a major greenhouse gas pollution and global warming. Therefore, developing novel and clean energy is an effective and reasonable way to tackle these issues. Currently, owing to the lower or zero emissions compared to fossil fuels, fuel cell has attracted scientists' wide attention. Meanwhile, developing materials with outstanding proton conductivity is essential and attractive for fabricating proton exchange membranes in electronic devices and fuel cells. In the past few decades, owing to their distinct advantages including excellent physical and chemical stability and outstanding proton conductivity, Nafion or Flemion is considered to be the widely proton-conducting materials.¹ However, inadequate durability and high water/methanol permeability still restrict their further applications, which inspire us to explore and design new materials as potential proton-conducting electrolyte candidates for replacing Nafion or Flemion.²⁻⁵

Owing to the high crystallinity, excellent porosity, remarkable stability, and pre-designable structures, a rapid development and great progress were achieved for covalent organic frameworks (COFs).⁶⁻¹¹ Besides, COFs provided an ideal platform for precisely integrating organic units into two- (2D) or three-dimensional (3D) structures with long-range periodic skeletons and high-ordered porous structures. Therefore, these superiorities enable them possessing wide areas including molecules storage and separation, catalysts, light-emitting materials and sensing, and proton/ion conduction.¹²⁻³⁵

Two-dimensional (2D) COFs possessed high-ordered π -structure and uniform 1D columns, which provided effective channels for proton transportation. In this respect, COFs have achieved a milestone using as proton-conducting electrolytes. However, up to now, most researchers have focused on employing COFs as carriers to provide proton resources such as imidazole, phosphoric acid, and *p*-toluene sulfonic acid.³⁰⁻³⁷ In this strategy, host-guest interactions lead to the inevitable leaching of protons from the pore structures. Long-term

excellent performance is hard to achieve since these molecules were aligned the channel. Recently, in order to solve these issues, constructing proton-conducting COFs without adding extra proton sources for directly fabricating electrolytes has been developed. Zhao and co-authors reported intrinsic proton-conducting COFs under water conditions with binder due to their fragile style COFs pellet itself.³⁸ Banerjee and co-authors constructed COFs as intrinsic proton-conduction under anhydrous process.³⁹ However, the intrinsic proton-conducting COFs as effective electrolytes with high stability, good durability and binder free has not been explored under the humidity conditions. In this project, the electronic cloud of high-density methoxy units over the vertexes delocalized from vertex to the imine-linkage through the p- π conjugation in Scheme 1, which therefore enhanced the stability of frameworks. The rich sulfonic acid groups have been anchored on the walls via the bottom-up strategy in Scheme 1. These features afforded 2D sulfonic functionalized frameworks as excellent candidates for proton conduction. The remarkable proton conductivity of S-COFs was as well as high 1.5×10^{-2} S cm⁻¹ at 25 °C and 95% relative humidity (RH). Meanwhile, S-COFs not only possessed low activation energy, but also achieved high durability for proton conduction in this work.

2. Results and discussion

The S-COF-1 and S-COF-2 were synthesized from 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde and 2,5-diaminobenzenesulfonic acid or 2,5-diaminobenzene-1,4-disulfonic acid using 1,4-dioxane and 1,3,5-trimethylbenzene as solvents and 6 M acetic acid as catalyst under solvothermal reaction, respectively. The S-COF-1 and S-COF-2 were characterized by Fourier-transform infrared spectroscopy (FT IR), Field emission scanning electron microscope (FE SEM), X-ray photoelectron spectroscopy (XPS), nitrogen sorption isotherm, elemental analysis, water vapor sorption, and powder X-ray diffraction (PXRD).

Firstly, the chemical structure information of S-COFs was investigated by FT IR measurement (Figure S1). The S-COF-1 and S-COF-2 showed the C=N bonds at 1580 and 1581 cm⁻¹, respectively. The S-COF-1 and S-COF-2 displayed the methoxy units signals in 2917 and

2925 cm^{-1} , respectively. The obvious peaks were found at 1441 and 1443 cm^{-1} for S-COF-1 and S-COF-2, respectively, which were assigned to the O=S=O groups stretching.

XPS analysis was further employed to investigate the structure information of these two COFs (Figure 1). Based on the XPS spectra results, S-COF-1 and S-COF-2 displayed C 1s, O 1s, N 1s, S 2s, and 2p signals. S-COF-1 and S-COF-2 showed the bonding energies of S 2p_{3/2} and S 2p_{1/2} around 168.2 and 169.3 eV, and 168.2 and 169.3 eV, respectively. The element analysis results displayed the sulfonic element of 9.76 and 15.88 wt% in Table S1, which is very close to the theoretical values. The contents of sulfonic units for S-COF-1 and S-COF-2 were calculated to be 24.7% and 40.2%, respectively. The EDS analysis was observed for S-COF-1 (Figure S2) and S-COF-2 (Figure S3), which indicated a uniform distribution of elemental Sulphur. FE-SEM images demonstrated that S-COF-1 and S-COF-2 exhibited micrometerscale morphology (Figure S4).

Nitrogen (N₂) adsorption-desorption isotherms at 77 K were utilized to investigate the porosity of S-COF-1 and S-COF-2 (Figure S5a-b). S-COF-1 and S-COF-2 exhibited type-1 sorption curves, which was typical of the microporous characteristics. The Brunauer-Emmett-Teller (BET) surface areas were calculated to be 351 and 139 $\text{m}^2 \text{g}^{-1}$ for S-COF-1 and S-COF-2, respectively. The pore size distribution of S-COFs was explored using non-local density functional theory (NLDFT) method (Figure S5c-d). The S-COF-1 and S-COF-2 showed the pore size centered at 1.30 and 1.26 nm, respectively.

The crystallinity of S-COFs was observed by PXRD measurement (Figure 2a-b). The experimental PXRD pattern of S-COF-1 showed the strong peaks at 4.68, 8.78, 11.40, and 26.60° (Figure 2a, red), which were assigned to 100, 200, 300, and 001 facets, respectively. As shown in Figure 2a, the observed diffraction peaks were assigned by using the Pawley refined pattern. Simulations based on the space group with $a = b = 25.32 \text{ \AA}$, $c = 4.97 \text{ \AA}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ can reproduce the PXRD pattern that was in good agreement with the AA-stacking experimentally observed pattern (Figure 2a, green). In contrast, the AB staggered stacking

mode does not match the PXRD experimental result (Figure 2a, orange). The experimental PXRD pattern of S-COF-2 displayed obvious peaks at 4.52, 7.64, and 25.43° (Figure 2b, purple), which associated with 100, 200, and 001 facets, respectively. The S-COF-2 matched the AA-stacking model (Figure 2b and 2c). After the Pawley refinement the optimize the lattice parameters was gave for S-COF-2 with $a = b = 25.35 \text{ \AA}$, $c = 5.23 \text{ \AA}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

Humidity is an essential factor for proton transport system, which is beneficial to tune and promote proton-exchange/transport efficiency. We investigated water vapor sorption isotherms of S-COFs at 298 K (Figure S6). The water adsorption capacities of S-COF-1 were 15.4 mmol g^{-1} at $P/P_0 = 0.95$ and 298 K (Figure S6a). The higher water uptake of S-COF-2 were found to be 23.3 mmol g^{-1} (Figure S6b) due to its high sulfonic acid density in the frameworks compared with S-COF-1. To consider the long term for proton-conducting electrolyte, we kept the S-COFs samples in the water under the water system for 72 h. Then, the S-COFs were filtered, washed by water, and dried under the vacuum. As shown in Figure S7a-b, FT IR spectra and PXRD patterns for S-COF-1-W and S-COF-2-W were also checked, the same characteristic signals were found for as-synthesized COFs and S-COF-Ws. The good crystal peaks have been shown in Figure S8a-b. The good stability of S-COFs was on the grounds that the electronic cloud of the high-density methoxy units on the vertexes delocalized from vertex to the imine-linkage through the p- π conjugation to improve the stability of frameworks.²⁶ These results provided a guarantee for S-COFs using as electrolytes to work for a long time.

The S-COF-1 and S-COF-2 possessed high-density sulfonic acid groups on the wall and an opened uniform 1D channel (Figure 3), which inspire us to explore the proton conductivity under various humidity condition. Firstly, the humidity dependence on proton conductivity were observed for S-COF-1 with binder free. The lower proton-conducting result was found at $1.4 \times 10^{-7} \text{ S cm}^{-1}$ under 40% and 25 °C (Figure 4a). With increasing humidity conditions, the conductivities of S-COF-1 were also enhanced to be 1.4×10^{-6} , 2.4×10^{-5} , and $1.8 \times 10^{-4} \text{ S cm}^{-1}$, respectively, under 60%, 80%, and 90% RH at 25 °C (Figure 4a). The higher proton

conductivity value reached $7.5 \times 10^{-4} \text{ S cm}^{-1}$ at 95% RH. The proton-conducting values of S-COF-2 were also promoted with the increasing of humidity (Figure 4b). The excellent proton conductivity of $1.5 \times 10^{-2} \text{ S cm}^{-1}$ were achieved for S-COF-2, which was 20 times than that of S-COF-1. The remarkable conductivity of S-COF-2 was attributed to high-density proton source on the walls, which among the excellent performance in the reported COFs and sulfonic porous polymers.⁴⁰⁻⁴²

We also investigated the proton conductivity of S-COFs under different temperatures and 95% RH. With improvement of temperature, the proton conductivities of S-COF-1 and S-COF-2 were slightly enhanced. For example, the proton conductivity values of S-COF-1 increased slightly to 1.1×10^{-4} (35 °C), 1.4×10^{-4} (45 °C), 1.7×10^{-4} (55 °C), and $5.1 \times 10^{-3} \text{ S cm}^{-1}$ (65 °C) under 95% RH (Figure 5a). The highest value was as high as $2.9 \times 10^{-2} \text{ S cm}^{-1}$ for S-COF-2 (Figure 5b). To our best knowledge, this result shows similarly high conductivity performance, which could be comparable to the standard materials such as Nafion 115 ($4.5 \times 10^{-2} \text{ S cm}^{-1}$, 65 °C, water)^{43a} and Nafion 112 ($3.1 \times 10^{-2} \text{ S cm}^{-1}$, 65°C, water).^{43b} With the consideration of durability, we inspected the time-dependent proton conduction for S-COF-2 for 24 h in Figure S9. **There was no obvious decline in proton conductivity values for S-COF-2.** The remarkable proton-conducting performance not only **dependent on the** high-density sulfonic acid groups on the wall contributed the proton source, but also an opened 1D channel formed effective proton transportation **pathway**.

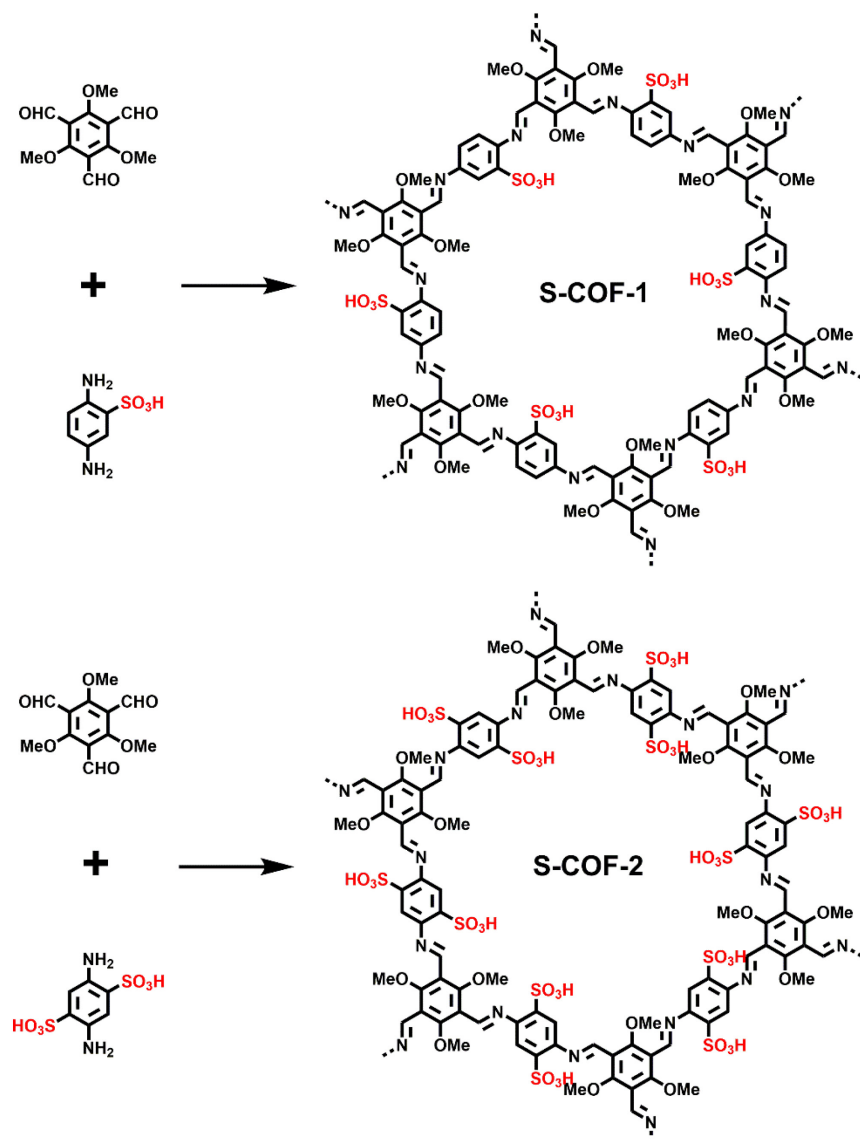
Linear least-squares fitting of the slopes of Arrhenius plots at different temperatures were employed to investigate the activation energy (E_a) of proton-conducting electrolyte. The E_a values were found to be 0.25 eV for S-COF-1 (Figure 5c) and 0.17 eV for S-COF-2 (Figure 5d), **respectively**. Therefore, the mechanism for proton conduction is transported by the hopping pathway through extended hydrogen-bonding interaction between sulfonic acid units on the walls and water molecules. **In the respect, the proton-transfer in the 1D channel of 2D COFs was great improvement.**

3. Conclusion

In summary, we designed and synthesized two new sulfonated COFs as intrinsic proton-conducting electrolytes. The 2D S-COFs had rich sulfonic acid groups on the wall and a uniform 1D channel to afford the excellent proton-conducting performance with binder free. The S-COF-2 exhibited excellent proton conductivity of $1.5 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C and 95% relative humidity (RH), which ranked the excellent performance in standard proton-conducting electrolytes. The S-COF-2 electrolyte kept the high proton conduction during the 24 h. Moreover, S-COF-2 also displayed the lower activation energy at 0.17 eV. This research opens the new design of proton-conducting COFs electrolytes for a new benchmark that combines high conductivity, durability, and binder free.

Author Contributions

L. Zhai and Y. Yao contributed equally. L. Z. and Y. Yao, B. Ma, N. Qin, Y. Han, Md. M. Hasan, and Z. Li conducted experiments and collected data collection. L. Zhai, L. Mi, Y. Nagao and Z. Li wrote the manuscript and discussed the results with all authors.



Scheme 1. Design and synthesis of S-COF-1 and S-COF-2.

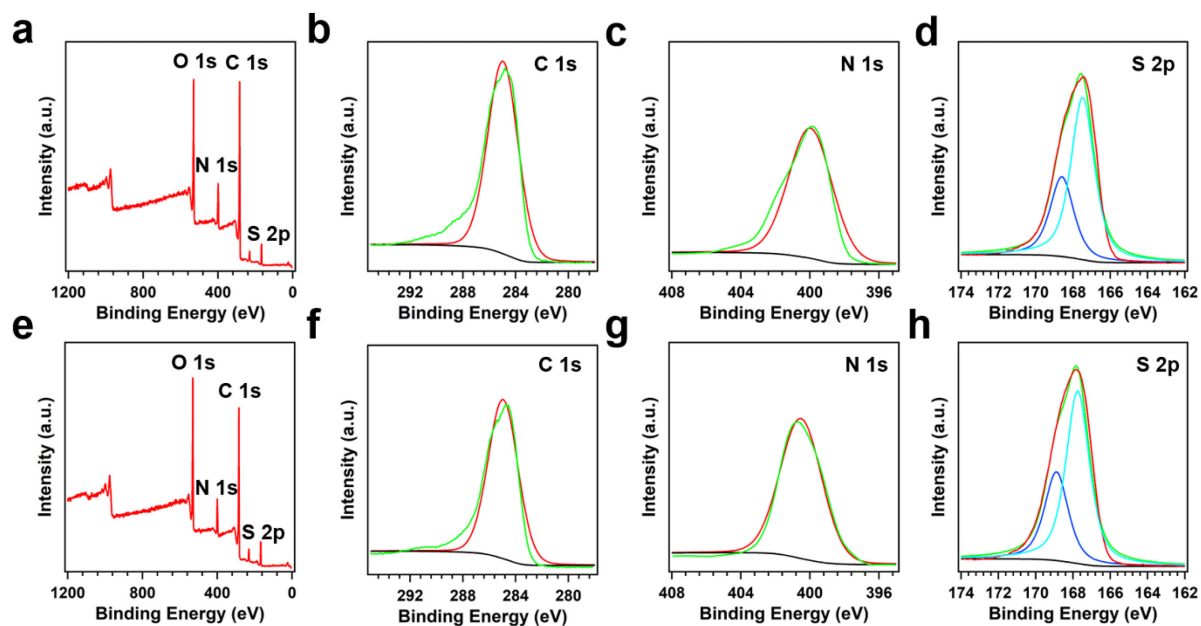


Figure 1. X-ray photoelectron spectroscopy spectrum of (a) S-COF-1 and (e) S-COF-2. XPS analysis of C 1s of (b) S-COF-1 and (f) S-COF-2. XPS analysis of N 1s of (c) S-COF-1 and (g) S-COF-2. XPS analysis of S 2p of (d) S-COF-1 and (h) S-COF-2.

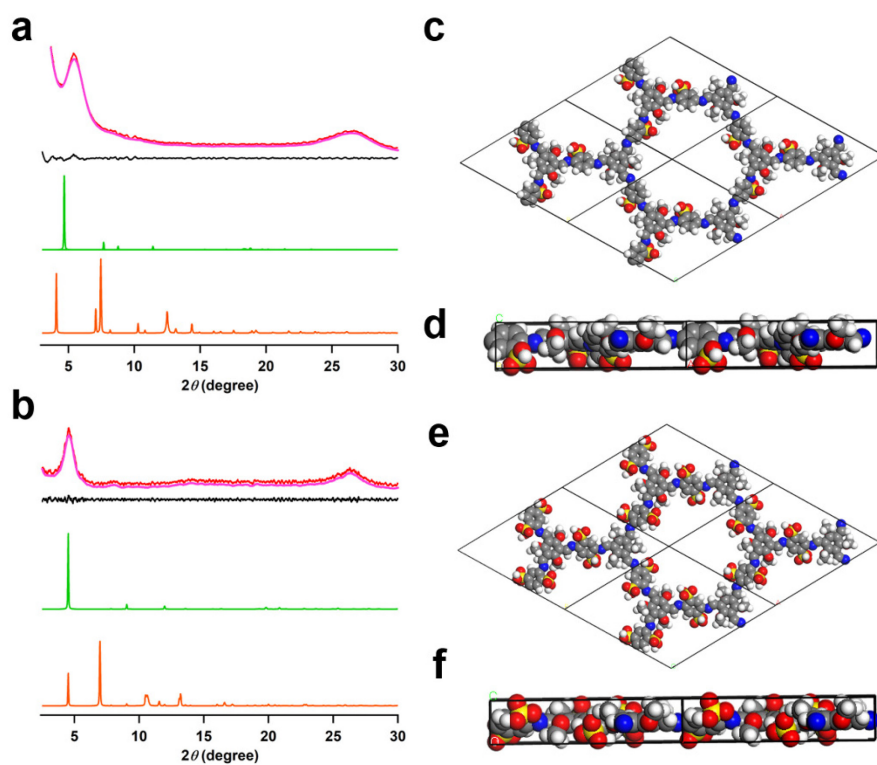


Figure 2. PXRD patterns of (a) S-COF-1 and (b) S-COF-2 (Observed pattern: purple; Pawley refinement: red; Their difference: black; AA-stacking model: green; AB-stacking model: orange). The unit cell structure of (c) (d) S-COF-1 and (e) (f) S-COF-2.

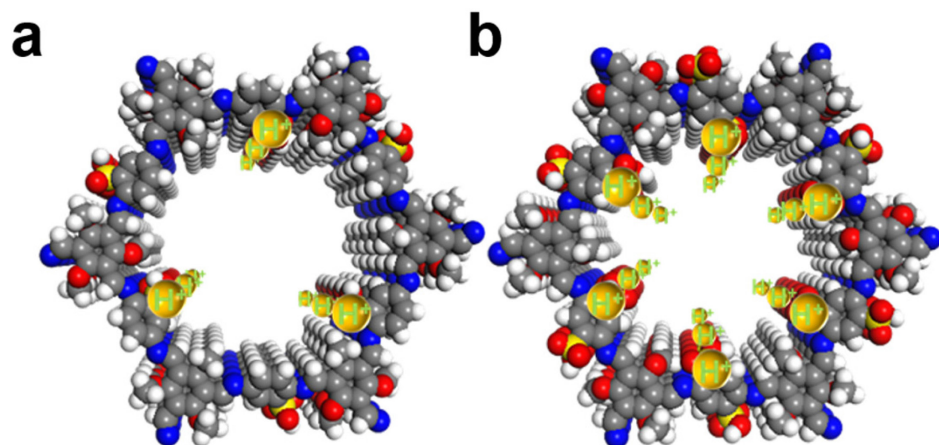


Figure 3. Proton framework in 1D channel of (a) S-COF-1 and (b) S-COF-2.

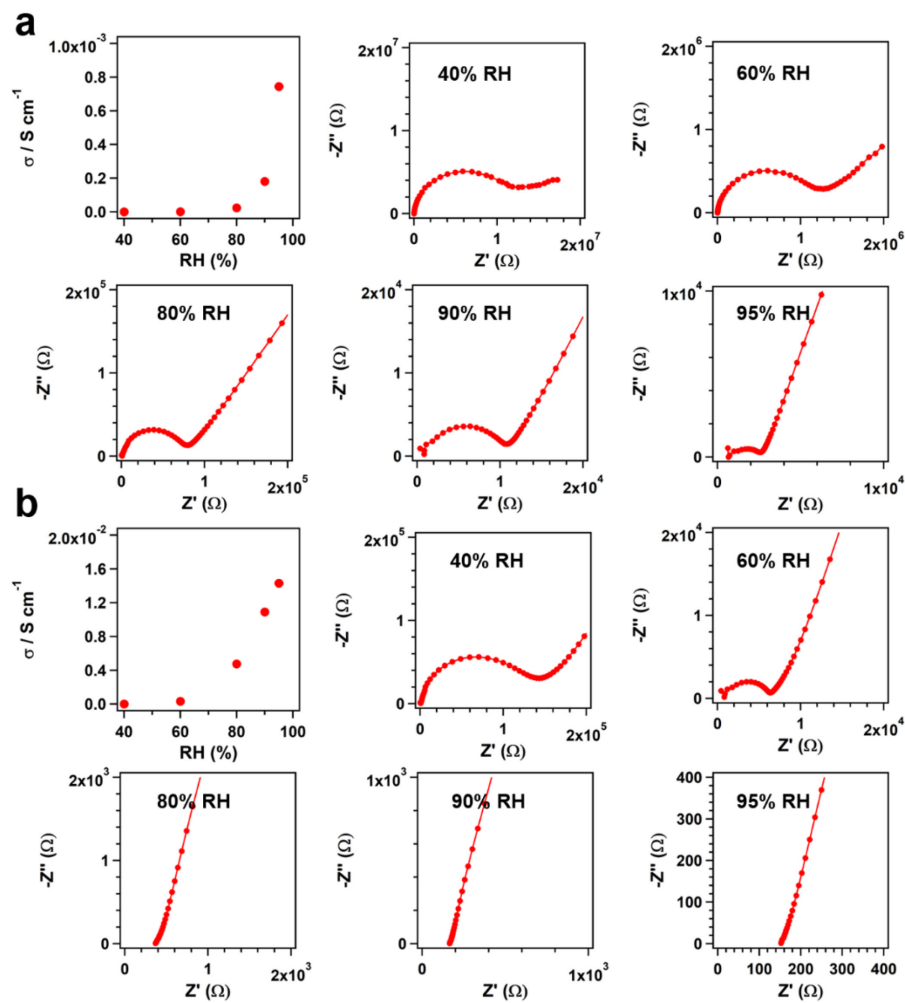


Figure 4. Proton conductivities and Nyquist plots of (a) S-COF-1 and (b) S-COF-2 under different RH and 25 °C.

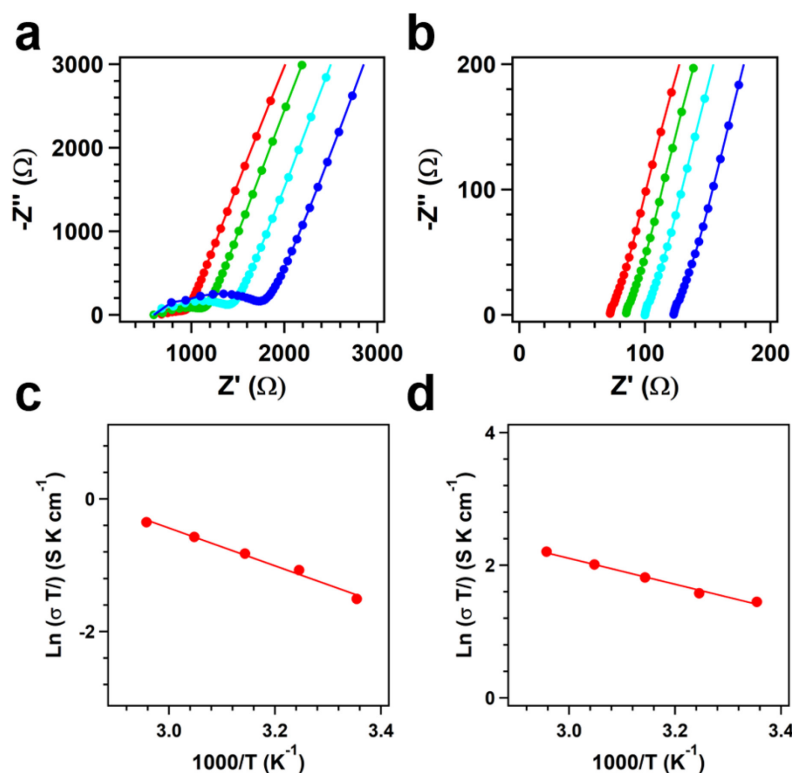


Figure 5. Nyquist plots of (a) (c) S-COF-1 and (b) (d) S-COF-2 under 95% RH and different temperature. (308 K: blue curves; 318 K: sky-blue curves; 328 K: green curves; 338 K: red curves).

Acknowledgements

L. Z. appreciates support from National Natural Science Foundation of China (52103277), Key Projects of Science and Technology of Henan Province (No. 212102210208), N. Q. appreciates support Key Projects of Science and Technology of Henan Province (No. 202102210054). L. M. thanks the National Natural Science Foundation of China (Grant No. 21671205, U1804126, 21771164, and U1804129). Y. N. appreciated the support by JSPS KAKENHI grant numbers JP21H00020 and JP21H01997 and The Murata Science Foundation. Y. H. appreciates support from Shandong Provincial Natural Science Foundation (No. ZR2020QB023).

Received: ((will be filled in by the editorial staff))
 Revised: ((will be filled in by the editorial staff))
 Published online: ((will be filled in by the editorial staff))

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Two new sulfonated COFs as intrinsic proton-conducting electrolyte were constructed. The 2D COFs have rich sulfonic acid groups on the uniform 1D channel to afford the excellent proton-conducting performance with binder free. Excellent proton conductivity of $1.5 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C and 95% relative humidity (RH) were achieved, which ranked the excellent performance in proton-conducting electrolyte.

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Accumulation of sulfonic acid groups anchored in covalent organic frameworks as an intrinsic proton-conducting electrolyte

