Supplementary Information (SI) for Journal of Materials Chemistry A.

Deciphering the Role of Sulfonated Side-Chain Length in Modulating Proton Transport in TpBd-COFs

Supporting Information

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S1. Calculations of Distances between sulfonic acid groups and the channel center

To accurately determine the position of the channel center in each simulation frame, the coordinates of the nitrogen atoms in the COF backbone were tracked. The *xy* coordinates of these nitrogen atoms were averaged to define the channel center for each frame. For each frame, the distances from the six sulfur atoms of the sulfonic acid groups to this center were calculated and then averaged. Finally, the time-averaged distance was obtained over all frames. Note that all reported distances are projected in the *xy* plane and do not include any contribution from the *z* direction.

$$r_c^{(t)} = (x_c^{(t)}, y_c^{(t)}), \begin{cases} x_c^{(t)} = \frac{1}{N_N}\sum_{j=1}^{N_N} x_{N_j}^{(t)} \\ y_c^{(t)} = \frac{1}{N_N}\sum_{j=1}^{N_N} y_{N_j}^{(t)} \end{cases} \tag{1}$$

$$d_k^{(t)} = \sqrt{(x_{S_k}^{(t)} - x_c^{(t)})^2 + (y_{S_k}^{(t)} - y_c^{(t)})^2}, k = 1,\ldots,6 \tag{2}$$

$$d^{(t)} = \frac{1}{6}\sum_{k=1}^{6} d_k^{(t)} \tag{3}$$

$$\overline{d} = \frac{1}{T}\sum_{t=1}^{T} d^{(t)} \tag{4}$$

To determine the center of the pore in each simulation frame, the xy-coordinates of all nitrogen atoms on the COF backbone were averaged, yielding the in-plane pore center $r_c^{(t)} = (x_c^{(t)}, y_c^{(t)})$ at frame t. The positions of six sulfur atoms were then used to calculate their Euclidean distances to the pore center, denoted as $d_k^{(t)}$. The average of these six distances, $d^{(t)}$, represents the pore radius for that frame. Finally, the overall average pore radius $\overline{d}$ was obtained by averaging $d^{(t)}$ over all T frames. All calculations were restricted to the xy-plane, excluding the z-component.

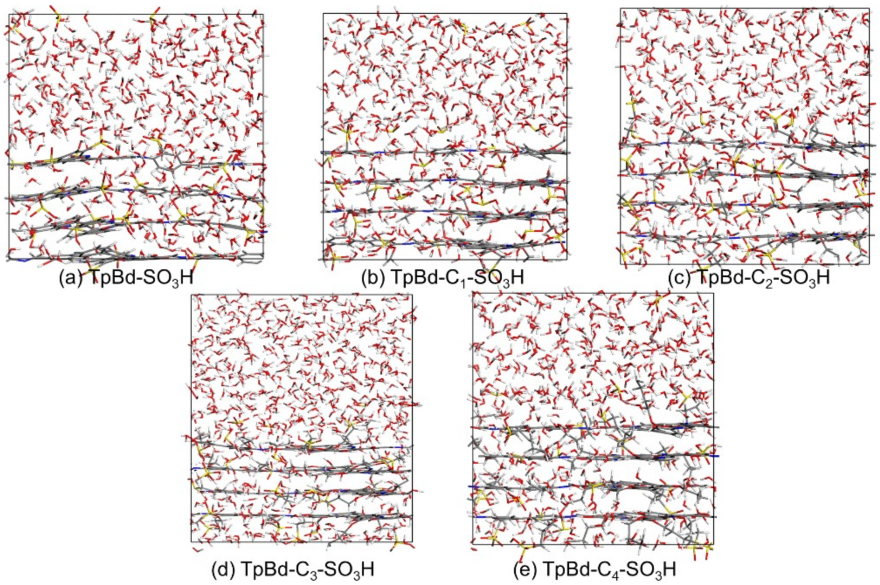

(a) TpBd-SO_3H (b) TpBd-C_1-SO_3H (c) TpBd-C_2-SO_3H (d) TpBd-C_3-SO_3H (e) TpBd-C_4-SO_3H

Figure S1. Snapshots of water permeation experiments of the five systems.

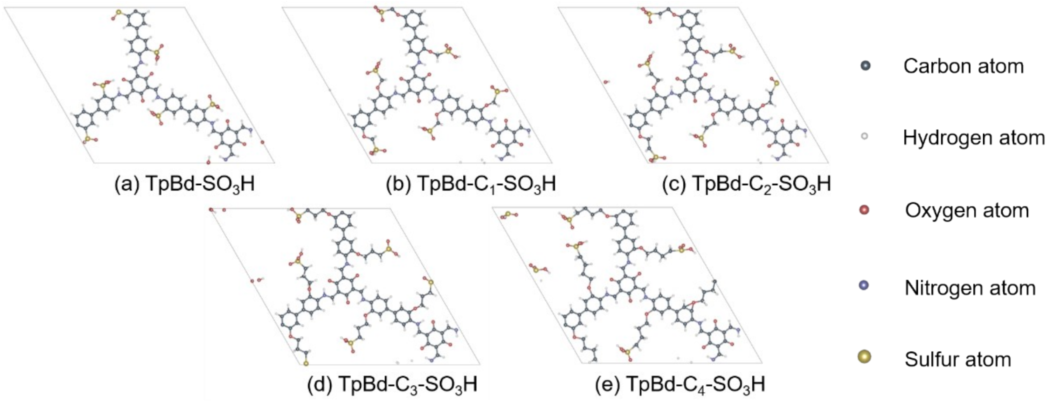

(a) TpBd-SO_3H (b) TpBd-C_1-SO_3H (c) TpBd-C_2-SO_3H (d) TpBd-C_3-SO_3H (e) TpBd-C_4-SO_3H

Figure S2. The hexagonal crystalline structures of Sulfonated side chain modified COFs.

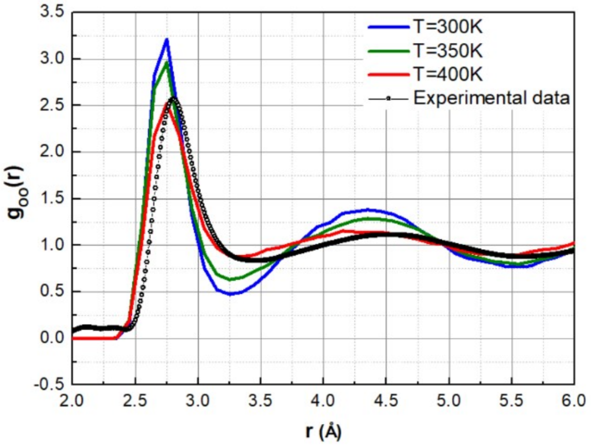


Figure S3. Experimental and simulated oxygen-oxygen pair-correlation functions at different simulation temperature. [1]

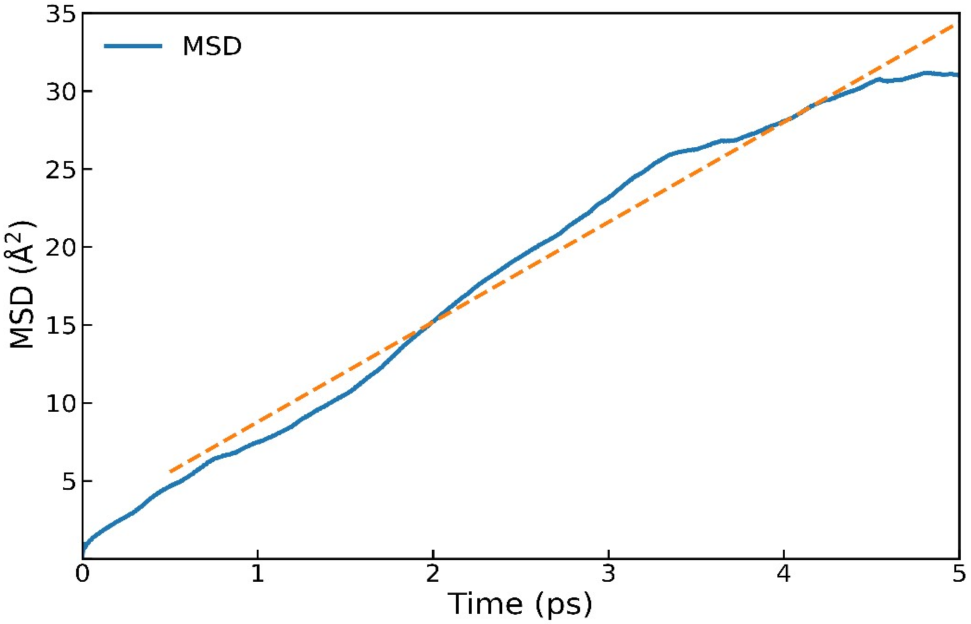


Figure S4. Validation of the AIMD-based proton-conductivity calculation using an aqueous H2SO4 benchmark system. The benchmark system contains one H2SO4 molecule and 33 water molecules, corresponding to an H2SO4 mole fraction of 0.029 and a mass fraction of approximately 14.2 wt%. The solid line shows the MSD of the proton tracked from the AIMD trajectory, while the dashed line shows the linear fit used to determine the proton diffusion coefficient. The proton conductivity estimated from the fitted MSD slope using the Nernst–Einstein equation is 0.662 S cm^{-1}, which is comparable to reported experimental values, supporting the reliability of the AIMD-based proton-transport analysis. [2]

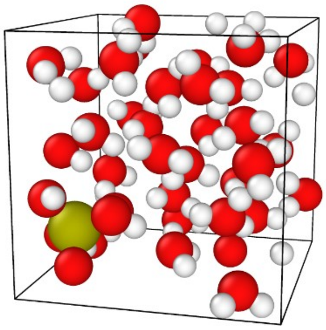
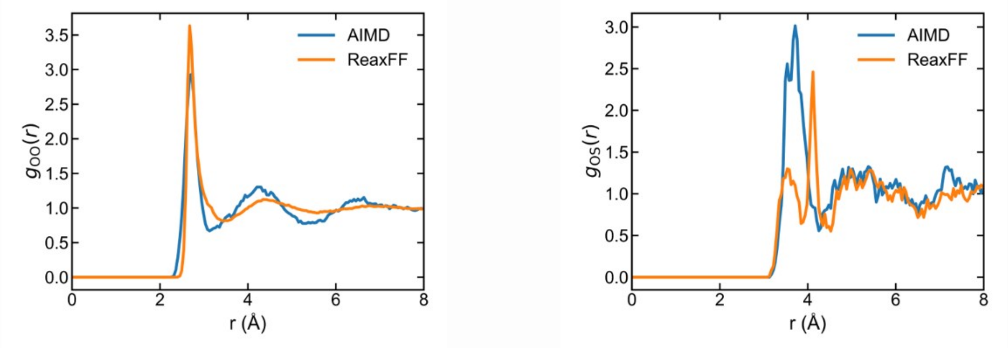
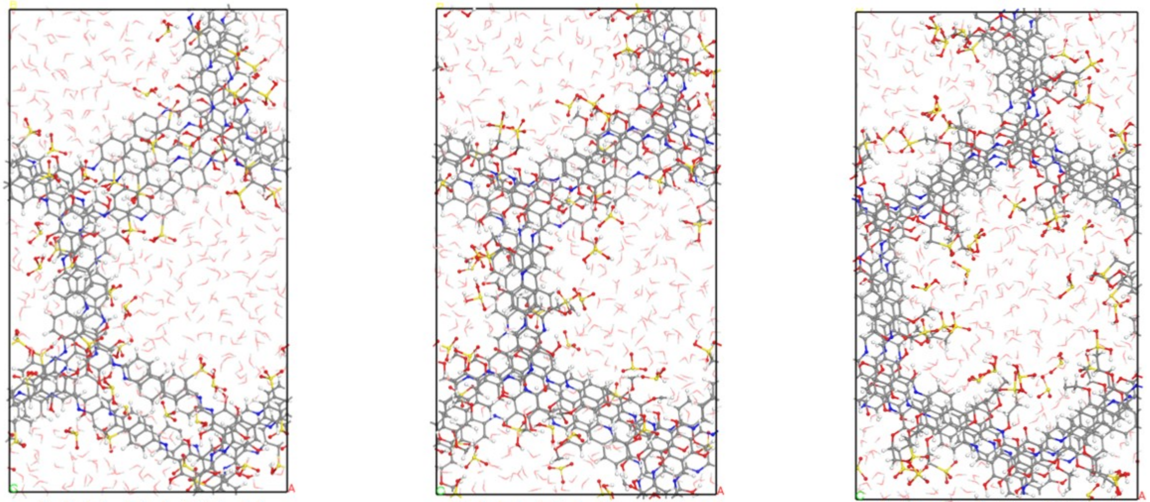


Figure S5. Initial configuration of the aqueous H2SO4 model system for force-field validation. One H2SO4 molecule was placed in a periodic water box to represent the local hydration environment of sulfur-containing acid groups. This model was simulated using both AIMD and ReaxFF MD, and the resulting trajectories were used to compare the water distribution and the hydration environment around the sulfur-containing acid group through O–O and O–S radial distribution functions.

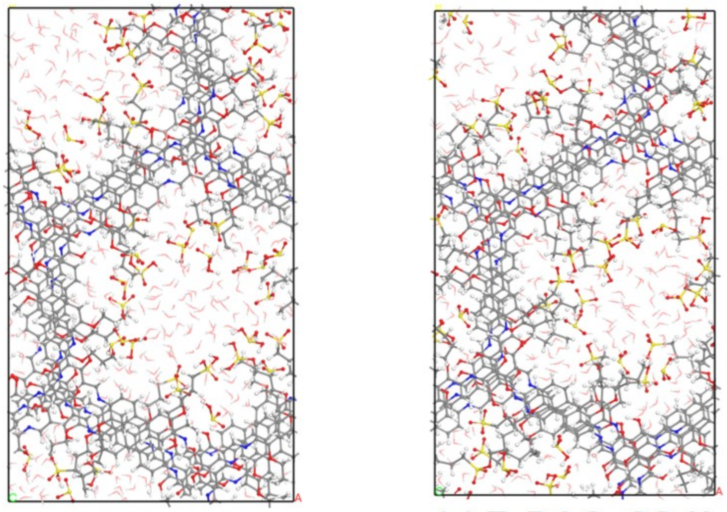


(a) O-O RDF **(b) O-S RDF**

Figure S6. Benchmark validation of the ReaxFF force field using an aqueous H2SO4 model system. Radial distribution functions obtained from AIMD and ReaxFF MD simulations are compared for (a) O–O pairs and (b) O–S pairs. The O–O RDF reflects the local structure of water, while the O–S RDF characterizes the hydration environment around the sulfonic acid group. The agreement between AIMD and ReaxFF supports the reliability of ReaxFF in describing water structure and acid-group hydration environments.



(a) TpBd-SO_3H (b) TpBd-C_1-SO_3H (c) TpBd-C_2-SO_3H



(d) TpBd-C_3-SO_3H (e) TpBd-C_4-SO_3H

Figure S7. Snapshot projections of the five systems in a hydrated state onto the XY-plane.

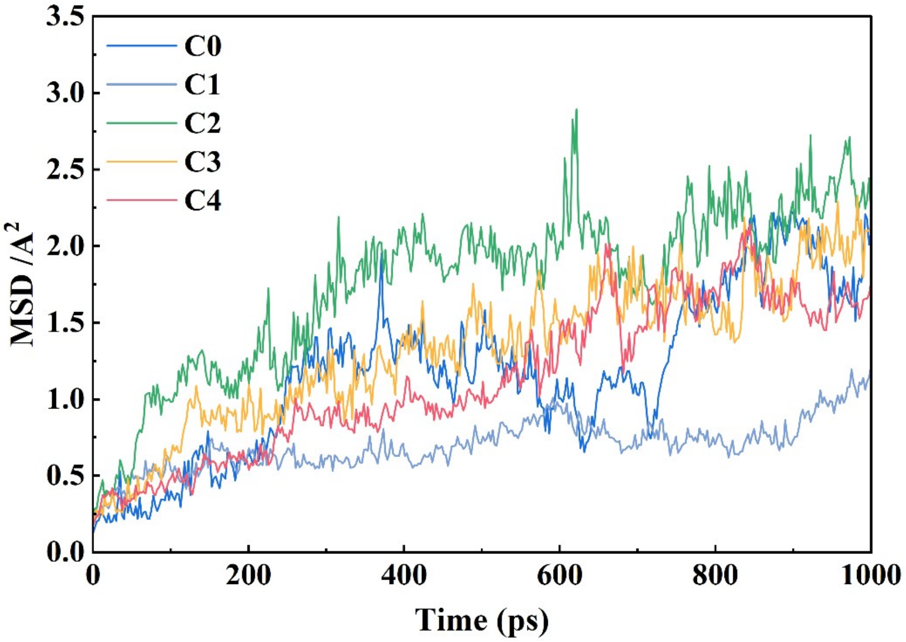


Figure S8. Three-dimensional mean square displacement (MSD) of terminal sulfur atoms in the five hydrated COF systems. The MSD was calculated from the final 1 ns of equilibrated ReaxFF MD trajectories. The limited displacement of sulfur atoms indicates that the sulfonic acid groups remain spatially confined during the simulations.

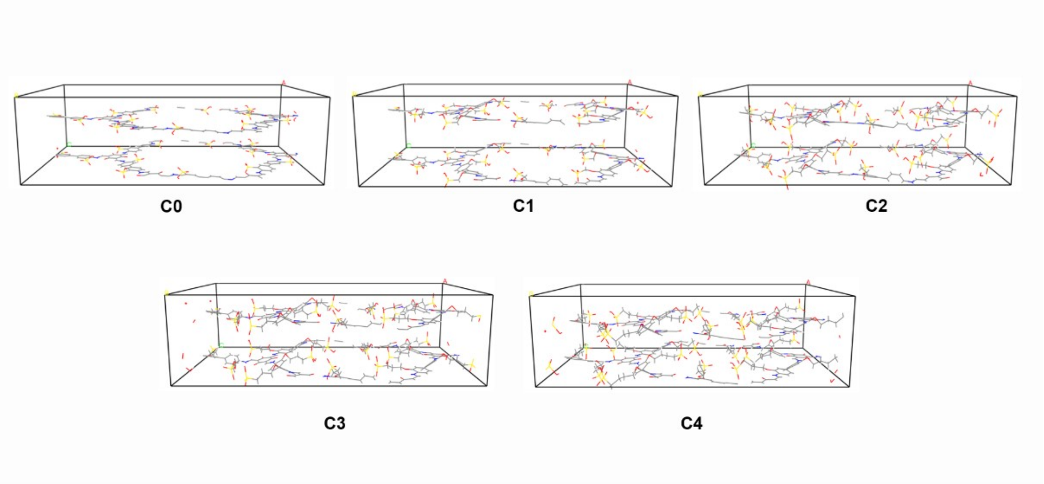


Figure S9. Atomic configuration of the unit cell in the YZ direction

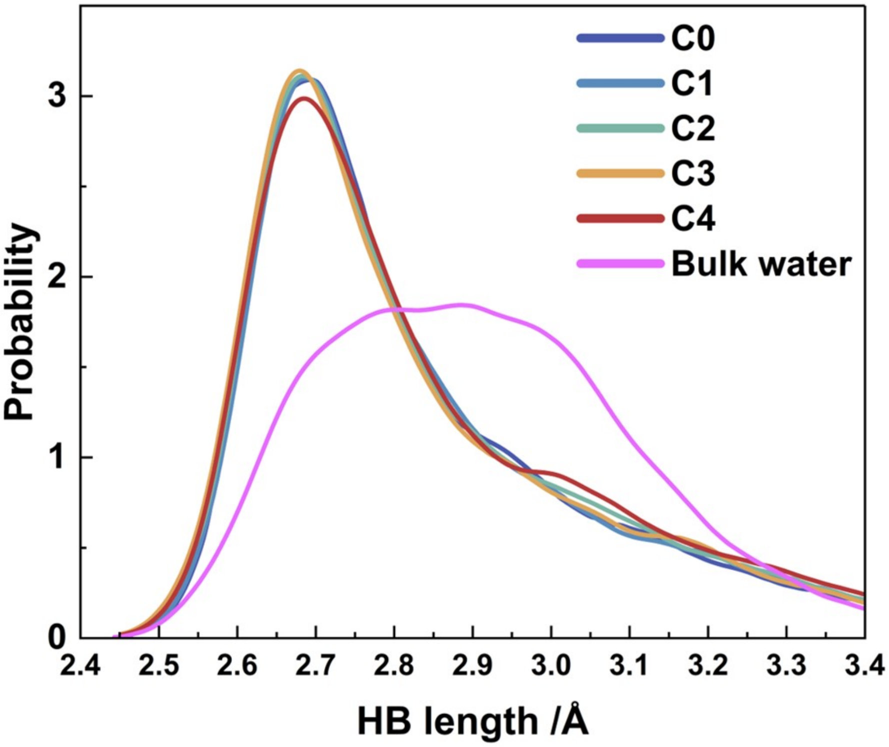


Figure S10. Probability distribution of hydrogen-bond lengths in different systems.

Table S1. Model system sizes of the five systems after equilibrium under AIMD and ReaxFF MD

	x(AIMD)	y(AIMD)	z(AIMD)	x(ReaxFF)	y(ReaxFF)	z(ReaxFF)
TpBd-SO_3H（unit:Å）	30.002	25.9825	10.5699	30.002	51.965	14.4059
TpBd-C1-SO_3H（unit:Å）	30.002	25.9825	11.4462	30.002	51.965	15.2524
TpBd-C2-SO_3H（unit:Å）	30.002	25.9825	10.3529	30.002	51.965	13.9492
TpBd-C3-SO_3H（unit:Å）	30.002	25.9825	10.464	30.002	51.965	13.8655
TpBd-C4-SO_3H（unit:Å）	30.002	25.9825	10.1267	30.002	51.965	13.4218

Table S2. Permeation test results of five systems

The water content under saturated humidity was determined through a permeation-based ReaxFF MD protocol. A large simulation box was first filled with bulk water at a density of 1.0 g cm^{-3}, into which four COF nanosheets were inserted. The system was equilibrated for 5 ns at 300 K and 1 atm, allowing water molecules to spontaneously permeate into the COF pores and reach thermodynamic equilibrium. The average number of water molecules residing within each COF layer was then calculated by spatial analysis of the final 1 ns of the trajectory and used as the equilibrium water content for subsequent AIMD simulations.

	TpBd-SO3H	TpBd-C_1-SO_3H	TpBd-C_2-SO_3H	TpBd-C_3-SO_3H	TpBd-C_4-SO_3H
Number of water per layer (Permeation experiment)	99	92	80	76.5	60
Water number (AIMD)	144	135	120	112	93
Water number (ReaxFF MD)	396	377	320	306	240

REFERENCES

[1] Shi L, Xu A, Pan D, Zhao T. Aqueous proton-selective conduction across two-dimensional graphyne[J]. Nature Communications, 2019, 10(1): 1165.

[2] Al-Salih, H.; Abu-Lebdeh, Y. Investigating the phase diagram-ionic conductivity isotherm relationship in aqueous solutions of common acids: hydrochloric, nitric, sulfuric and phosphoric acid. Scientific Reports 2024, 14, 7894.