

## **Electrostatic attraction induces cationic covalent-organic framework to pack inorganic acid ions for promoting proton conduction**

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## EXPERIMENTAL SECTION

**Materials and instrumentation.** The commercial reagents were directly used without further purification.

### Synthesis of Tp

Tp was synthesized according to the procedures described in the literature.<sup>31</sup> Hexamethylenetetramine (15.098 g, 108 mmol) and 1,3,5-Trihydroxybenzene (6.014 g, 49 mmol) were added into trifluoroacetic acid (90 mL) under N<sub>2</sub>. The solution was heated to 100 °C and maintained for ca. 2.5 h. With adding 150 mL of 3 M HCl, the mixture was kept at 100 °C for another 1 h. After cooling to room temperature, the solution was filtered, followed by extraction with dichloromethane (4×100 mL). Then, the organic phase was dried over anhydrous MgSO<sub>4</sub> for 12 hours and filtered to obtain a settled solution. Rotary evaporation of the solvent afforded the orange powder. The solid was repeatedly washed with hot ethanol to get a light pink powder.

### Synthesis of Br@CCOF

The process of preparing Br@CCOF by hydrothermal method is as follows:<sup>27</sup> 0.1 mmol 1,3,5-triformylphloroglucinol (TP) and 0.15 mmol ethidium bromide (EB) were mixed in a small glass bottle, followed by addition of 1 mL mesitylene and 1 mL 1,4-dioxane, and then 0.2 ml glacial acetic acid (catalyst) was added into the vial with a pipette. The mixture was ultrasonicated for 30 min and held at 120 °C in an oven for three days. The dark red precipitate was collected by filtration and washed with THF (tetrahydrofuran) through Soxhlet extraction method, and then the dark red substance was taken out of the extractor and dried in vacuum to afford Br@CCOF.

### Synthesis of SO<sub>4</sub><sup>2-</sup>@CCOF and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>@CCOF.

The ion exchange processes are as follows: 100 mg Br@CCOF was dispersed in 100 ml 0.1 mol L<sup>-1</sup> potassium bisulfate or potassium dihydrogen phosphate solution. The mixture was stirred continuously and the solution was renewed daily until the exchange is sufficient. The precipitate was washed with deionized water five times after separation, and dried to obtain SO<sub>4</sub><sup>2-</sup>@CCOF and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>@CCOF.

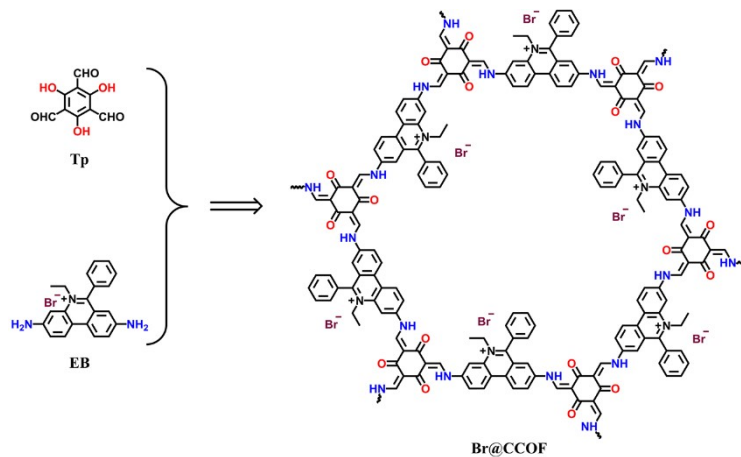
**Characterization of Br@CCOF, SO<sub>4</sub><sup>2-</sup>@CCOF and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>@CCOF.** Powder X-ray diffraction (PXRD) was performed on the Rigaku D/max-3B diffractometer. Fourier-transform infrared (FT-IR) spectra were collected on PE spectrum 200 at room temperature. Thermogravimetric analysis (TGA) were tested on SDT-2960 type thermal analyzer under nitrogen atmosphere. The cross-sectional morphology and other morphological features of the hybrid film were obtained by a field emission scanning electron microscope (FESEM, NanoSEM430).

**Measurements of proton conductivity.** All AC impedance tests were measured with RST5200F electrochemical workstation. The tablets of COFs samples with a radius of 0.25 cm were fabricated under a pressure of 5 Mpa, and then clamped by copper electrodes, which were subject to different temperature and relative humidity conditions for conductivity measurements. The proton conductivity was investigated using alternating current impedance spectroscopy, which were performed through the prepared tablets of COFs with copper sheets as electrodes attached to both sides of the tablets. The AC impedance spectra of COF's tablets and hybrid membranes were collected at 20 mv AC in a frequency range of 0.1 Hz to 1 MHz. The conductivity and activation energy of the samples were calculated from the impedance value according to the two equations:

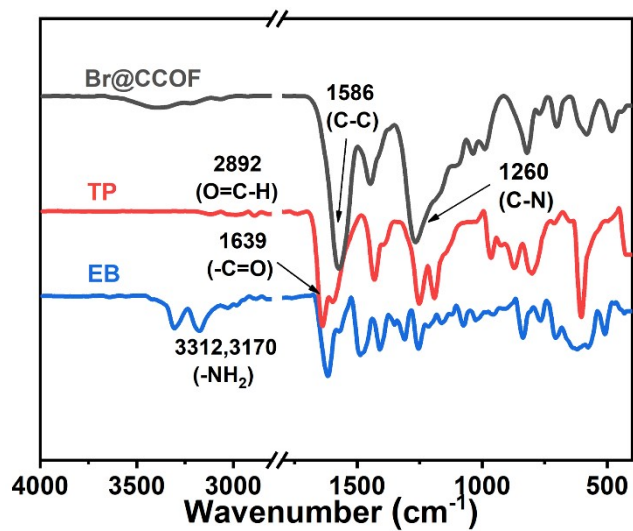
$$\sigma = L / SR$$

$$\sigma_T = \sigma_0 \exp \left( - E_a / k_B T \right)$$

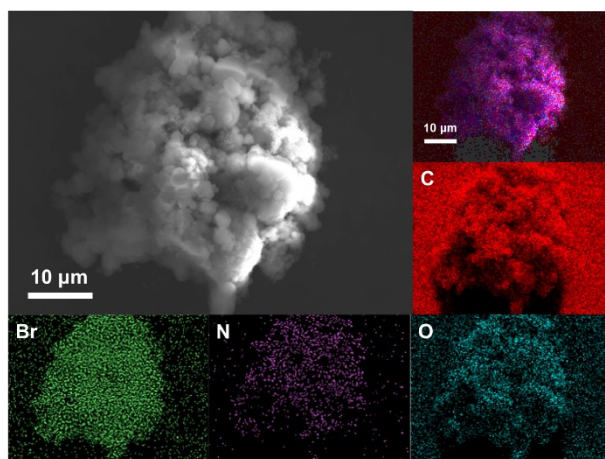
$\sigma$  (S/cm) means the conductivity;  $L$  (cm) is the thickness,  $A$  (cm<sup>2</sup>) is the area; and  $R$  ( $\Omega$ ) is the resistance;  $\sigma_0$  is the pre-exponential factor;  $k_B$  is the Boltzmann constant;  $T$  is temperature.



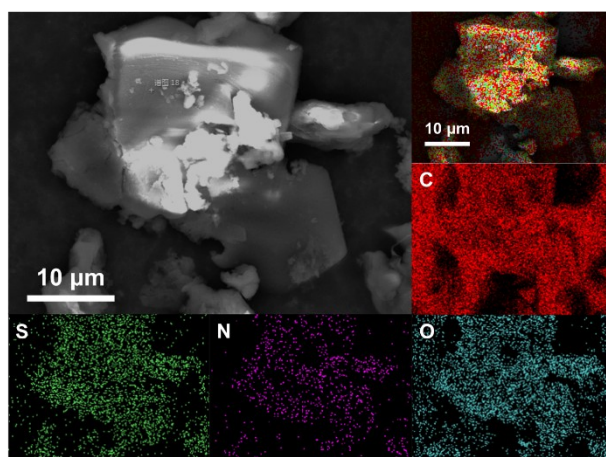
**Fig. S1** Synthesis of Br@CCOF.



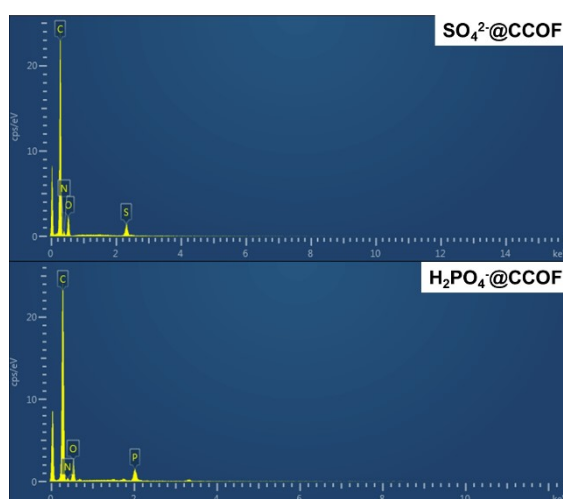
**Fig. S2** FT-IR spectra of Br@CCOF, Tp and EB.



**Fig. S3** SEM and corresponding EDS elemental mapping of Br@CCOF.



**Fig. S4** SEM and corresponding EDS elemental mapping of  $\text{SO}_4^{2-}$ @CCOF.



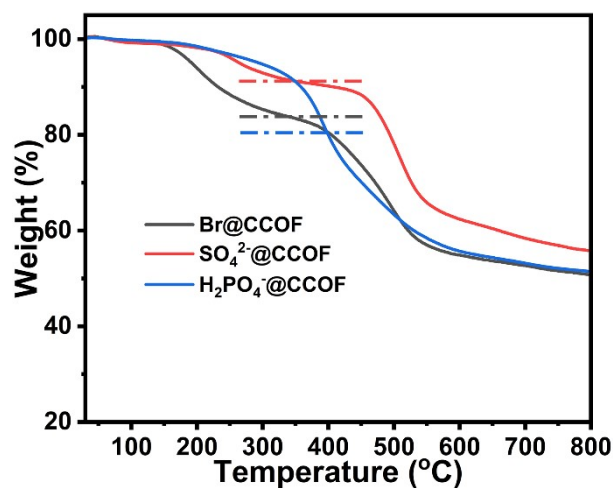
**Fig. S5** EDS energy spectrum of  $\text{SO}_4^{2-}$ @CCOF and  $\text{H}_2\text{PO}_4^-$ @CCOF.

**Table S1:** The elemental analysis of  $\text{Br}$ @CCOF,  $\text{SO}_4^{2-}$ @CCOF and  $\text{H}_2\text{PO}_4^-$ @CCOF.

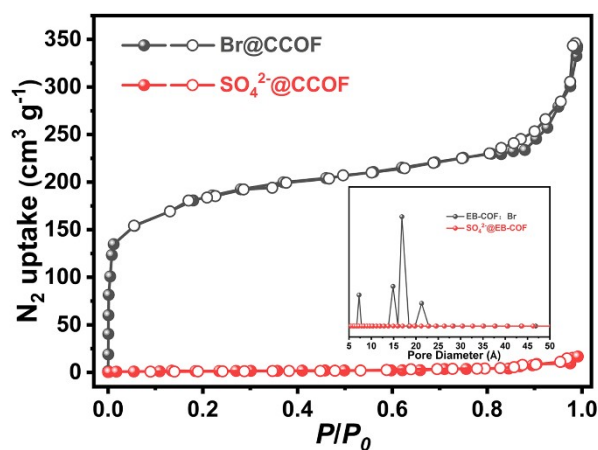
	C [%]	N [%]	H [%]	S [%]	P [%]
theoretical value of $\text{Br}$ @CCOF	65.07	8.43	4.05	—	—
$\text{Br}$ @CCOF	57.56	7.37	4.58	—	—
theoretical value of $\text{SO}_4^{2-}$ @CCOF <sup>1</sup>	69.52	9.01	4.32	3.44	—
$\text{SO}_4^{2-}$ @CCOF	61.12	7.76	4.90	2.96	—
theoretical value of $\text{H}_2\text{PO}_4^-$ @CCOF <sup>1</sup>	62.91	8.15	4.30	—	6.01
$\text{H}_2\text{PO}_4^-$ @CCOF	59.60	7.79	5.05	—	5.72 <sup>2</sup>

<sup>1</sup> Br- was completely exchanged with  $\text{SO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$  anion.

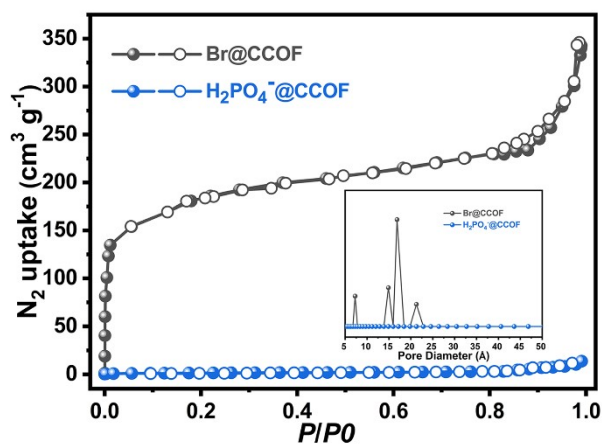
<sup>2</sup> Calculated from C and N elements.



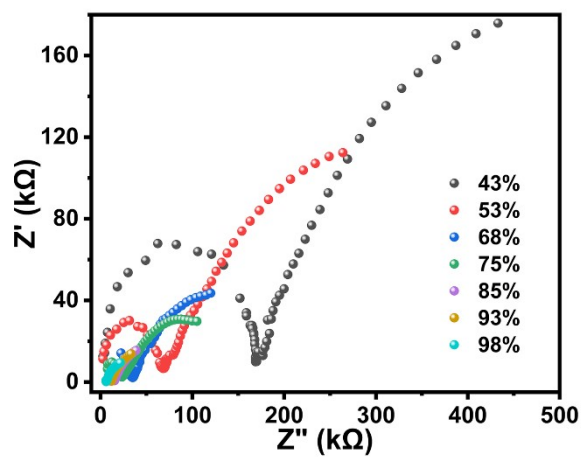
**Fig. S6** Thermogravimetric curves of prepared Br@CCOF and samples after ion-exchange.



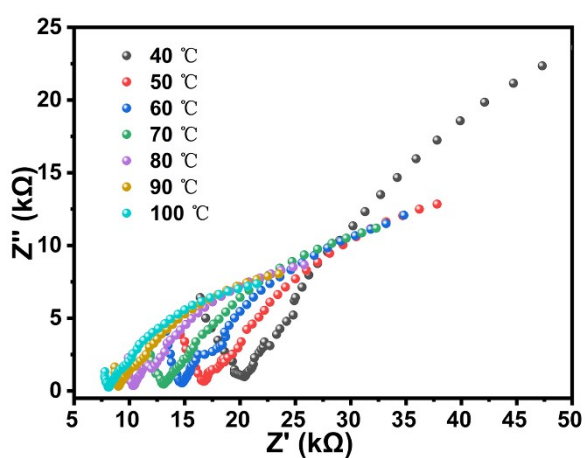
**Fig. S7** Nitrogen adsorption curves of comparison between Br@CCOF and  $\text{SO}_4^{2-}$ @CCOF. Insert: Pore size distribution of comparison between Br@CCOF and  $\text{SO}_4^{2-}$ @CCOF.



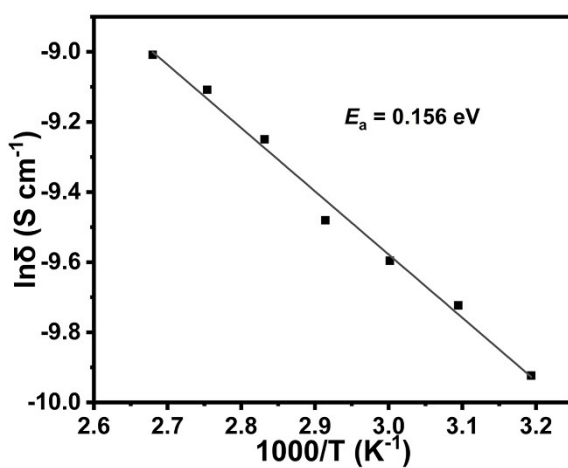
**Fig. S8** Nitrogen adsorption curves comparison of Br@CCOF and  $\text{H}_2\text{PO}_4^-$ @CCOF. Insert: Pore size distribution of comparison between Br@CCOF and  $\text{H}_2\text{PO}_4^-$ @CCOF



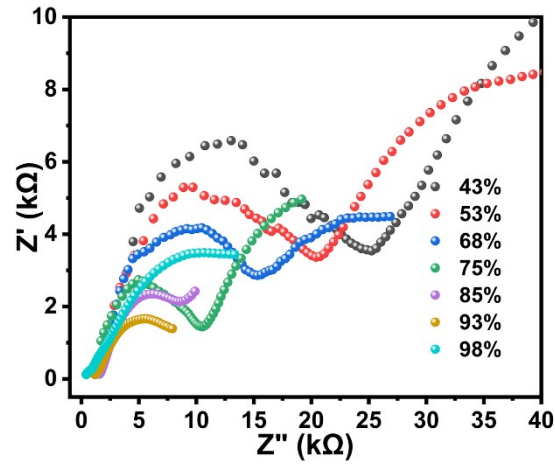
*Fig. S9* AC impedance diagram of Br@CCOF at different relative humidity.



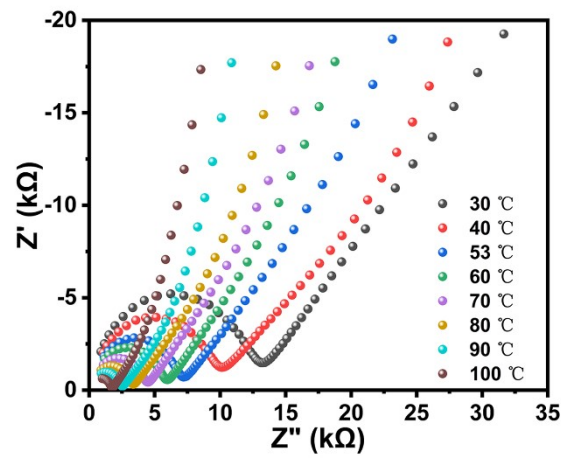
*Fig. S10* AC impedance diagram of Br@CCOF at different temperatures under RH 98% conditions.



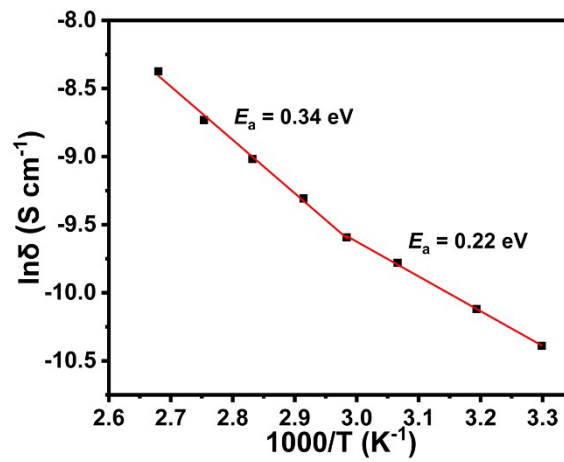
*Fig. S11* Proton conduction activation energy of Br@CCOF at RH 98%.



**Fig. S12** AC impedance diagram  $\text{SO}_4^{2-}$ @CCOF at different relative humidity.

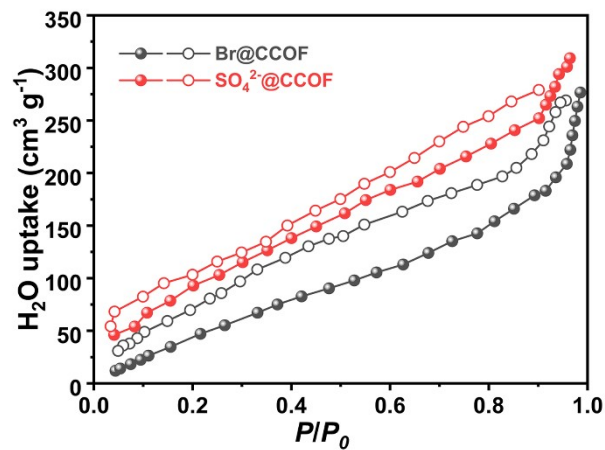


**Fig. S13** AC impedance diagram of  $\text{SO}_4^{2-}$ @CCOF at different temperatures under RH 98% conditions.

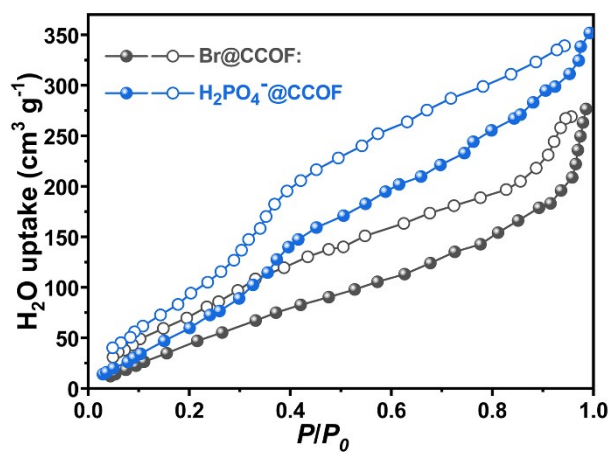


**Fig. S14** Proton conduction activation energy of  $\text{SO}_4^{2-}$ @CCOF at RH 98%.





**Fig. S15** Comparison of water vapour adsorption curves between Br@CCOF and SO<sub>4</sub><sup>2-</sup>@CCOF.



**Fig. S16** Comparison of water vapor adsorption curves between Br@CCOF and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>@CCOF.