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Supporting Information

Tuning proton dissociation energy in proton carriers doped 2D covalent organic frameworks for anhydrous proton conduction at elevated temperature

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Content

1. Experimental Section

1.1 General

2,4,6-triformylphloroglucinol (TP) was synthesized from Phloroglucinol according to the literature. All other reagents and solvents were received from commercial sources and used without further purification.

Fourier transform infrared (FT-IR) spectra were performed using a Nicolet iS50 ATR-FTIR instruments. **Powder X-ray diffraction (PXRD)** measurements were recorded on a Bruker D8 ADVANCE diffractometer with Cu-K a radiation operating at a voltage of 50 kV and a current of 200 mA. **Scanning electronic microscopy (SEM)** images and EDS mapping were recorded by a MAIA3 LMH scanning electron microscope. **The Nitrogen adsorption/desorption isotherms** were measured on a Micromeritics ASAP 2046. N_2 adsorption/desorption measurements were carried out at 77 K. **Thermo gravimetric analyses (TGA)** were carried out on a STA449F5 analyzer under air atmosphere within a temperature range of 30-800 °C. **Elemental analyses** were recorded on a vario EL cube analyzer. **Impedance spectroscopy** and **Dielectric properties** were measured using Novocontrol Concept 80 broadband dielectric spectrometer in the frequency range of 10^{-1} Hz-10 MHz.

1.2 Synthesis of COFs, PA@COFs and tra@COFs

Synthesis of TAP-COF. Synthesis of TAP-COF was done by reacting 2,4,6-triformylphloroglucinol (TP, 1.0 mmol) and 2,4,6-triaminopyrimidine (TAP, 1.0 mmol), along with 20 mL solvent mixture of 1,4-dioxane and mesitylene (v/v, 1:1), with 4 mL of 6M aqueous acetic acid. After sonication for 30 min, the reactor was sealed off and then heated at 120 °C for 6 days. After filtration, a brown precipitate was collected, washed with dimethylformamide(DMF) thrice, and then subjected to Soxhlet extraction with methanol as the solvent for one day. The powder collected dried at 100°C under vacuum overnight to get corresponding COFs in ~90% isolated yield.

Synthesis of PD-COF. Synthesis of PD-COF was done by reacting 2,4,6-triformylphloroglucinol (TP, 1.0 mmol) and P-Phenylenediamine (PD, 1.5 mmol), along with 20 mL solvent mixture of 1,4-dioxane and mesitylene (v/v, 1:1), with 4 mL of 6M aqueous acetic acid. After sonication for 30 min, the reactor was sealed off and then heated at 120 °C for 6 days. After filtration, a deep red precipitate was collected, washed with dimethylformamide(DMF) thrice, and then subjected to Soxhlet extraction with methanol as the solvent for one day. The powder collected dried at 100°C under vacuum overnight to get corresponding COFs in ~80% isolated yield.

Synthesis of DAAQ-COF. Synthesis of DAAQ-COF was done by reacting 2,4,6-triformylphloroglucinol (TP, 1.0 mmol) and 2,6-diaminoanthraquinone (DAAQ, 1.5 mmol), along with 20 mL solvent mixture of 1,4-dioxane and mesitylene (v/v, 1:1), with 4 mL of 6M aqueous acetic acid. After sonication for 30 min, the reactor was sealed off and then heated at 120 °C for 6 days. After filtration, a red precipitate was collected, washed with dimethylformamide(DMF) thrice, and then subjected to Soxhlet extraction with methanol as the solvent for one day. The powder collected dried at 100°C under vacuum overnight to get corresponding COFs in ~80% isolated yield.

Synthesis of EB-COF. Synthesis of EB-COF was done by reacting 2,4,6-

triformylphloroglucinol (TP, 1.0 mmol) and ethidium bromide (EB, 1.5 mmol), along with 20 mL solvent mixture of 1,4-dioxane and mesitylene (v/v, 1:1), with 4 mL of 6M aqueous acetic acid. After sonication for 30 min, the reactor was sealed off and then heated at 120 °C for 6 days. After filtration, a dark red precipitate was collected, washed with dimethylformamide(DMF) thrice, and then subjected to Soxhlet extraction with methanol as the solvent for one day. The powder collected dried at 100°C under vacuum overnight to get corresponding COFs in ~85% isolated yield.

Synthesis of phosphoric acid loading inside COFs (PA@COFs). The activated COF powders were mixed with the specified amount of crystalline, anhydrous phosphoric acid. The mixture was dried at 100 °C for 24h.

Synthesis of 1,2,4-Triazole loading inside COFs (tra@COFs). The guest molecules in the COF channels were excluded under reduced pressure. 1,2,4-Triazole was vaporized into the COF at 150℃ for 24 h to yield tra@COFs.

2. Proton dissociation energy

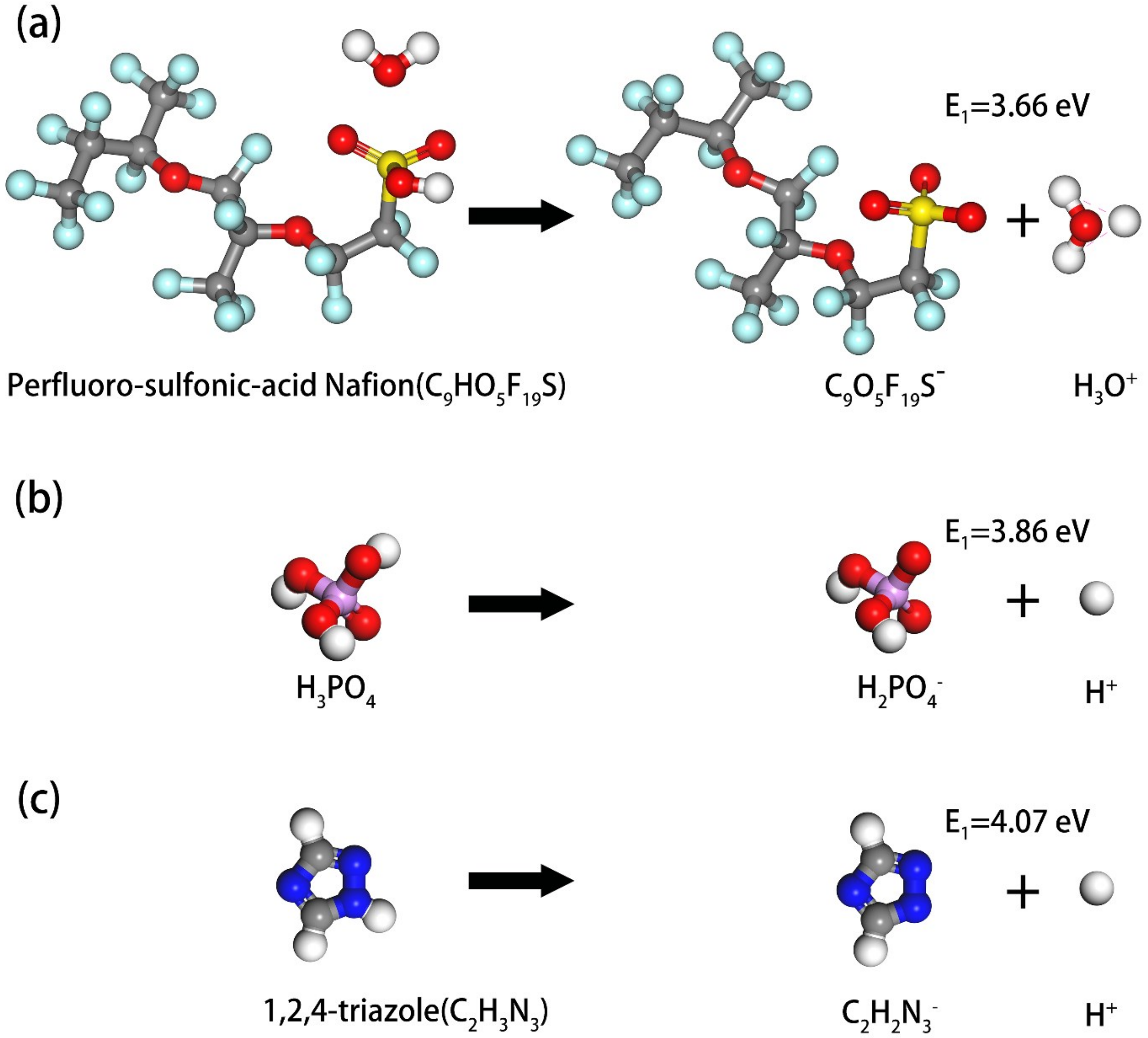

Figure S1. Proton dissociation energy of water in perfluoro-sulfonic-acid polymers **(a)**, PA **(b)** and 1,2,4-Triazole **(c)**. The proton dissociation energy was calculated by density functional theory (DFT). (H, white; P, purple; O, red; N, blue; C, gray; F, green.)

3. FT-IR Spectra

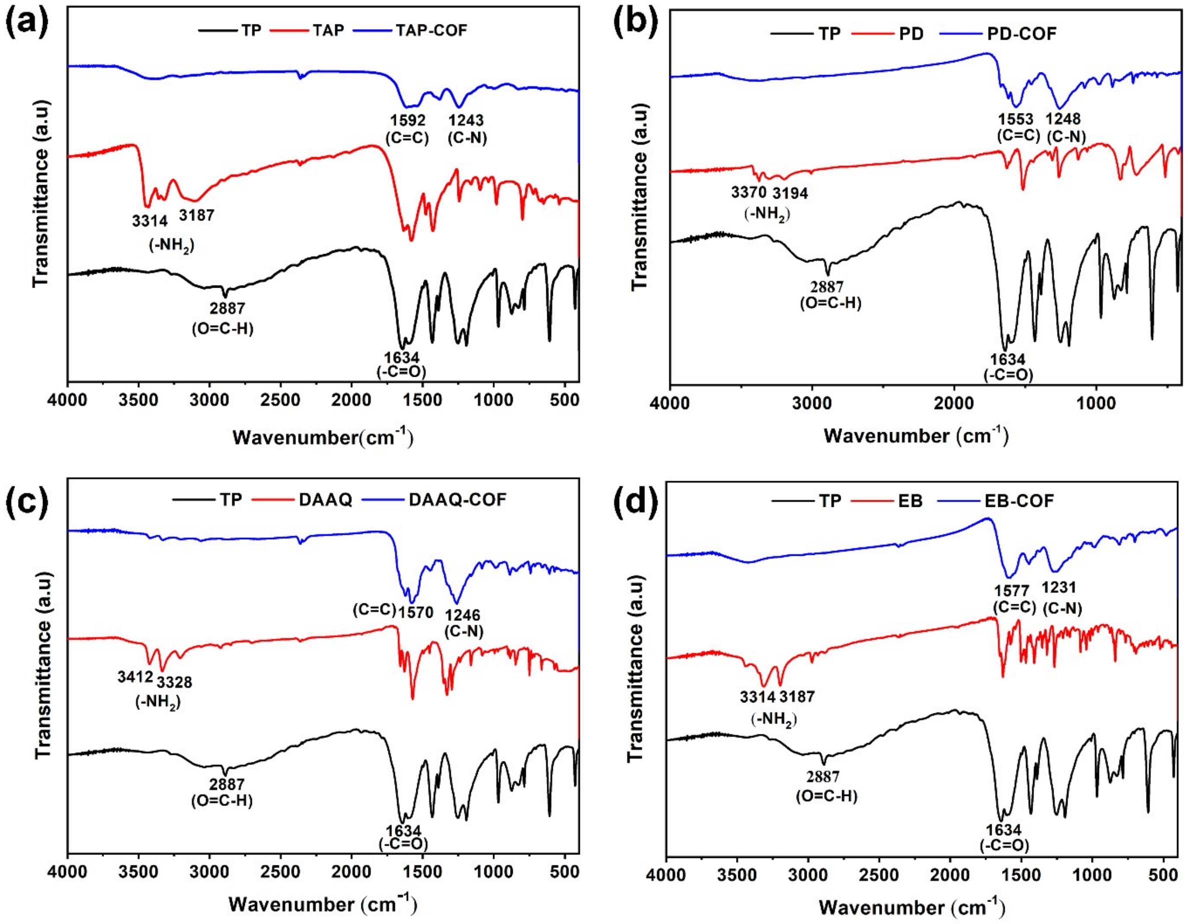

Figure S2. Fourier transform infrared spectra (FT-IR) of the COFs compared with reactants TAP-COF **(a)**, PD-COF **(b)**, DAAQ-COF **(c)** and EB-COF **(d)**.

4. Elemental Analysis

Table S1: Elemental analysis of the COFs

Sample	**Element**			**C/N Ratio**	
	C	**N**	**H**	**Elemental analysis**	**Theoretical**
TAP-COF	21.29	50.59	3.837	2.376	2.23
PD-COF	10.8	56.16	4.603	5.2014	5.14
DAAQ-COF	6.76	63.55	3.502	9.3988	8.57
EB-COF	9	68.49	4.713	7.6089	7.71

5. SEM and EDS Mapping

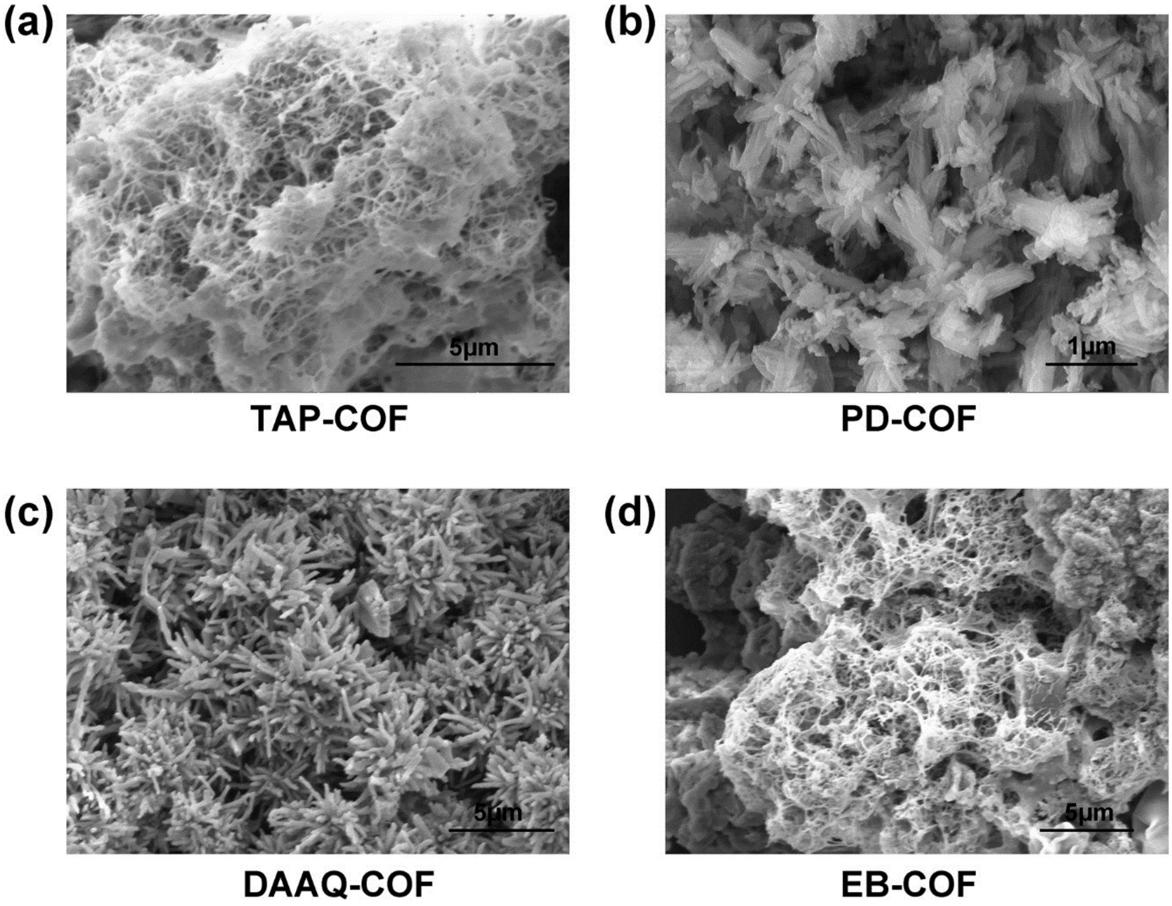

Figure S3. **(a)** SEM image of TAP-COF. **(b)** SEM image of PD-COF. **(c)** SEM image of DAAQ-COF. **(d)** SEM image of EB-COF.

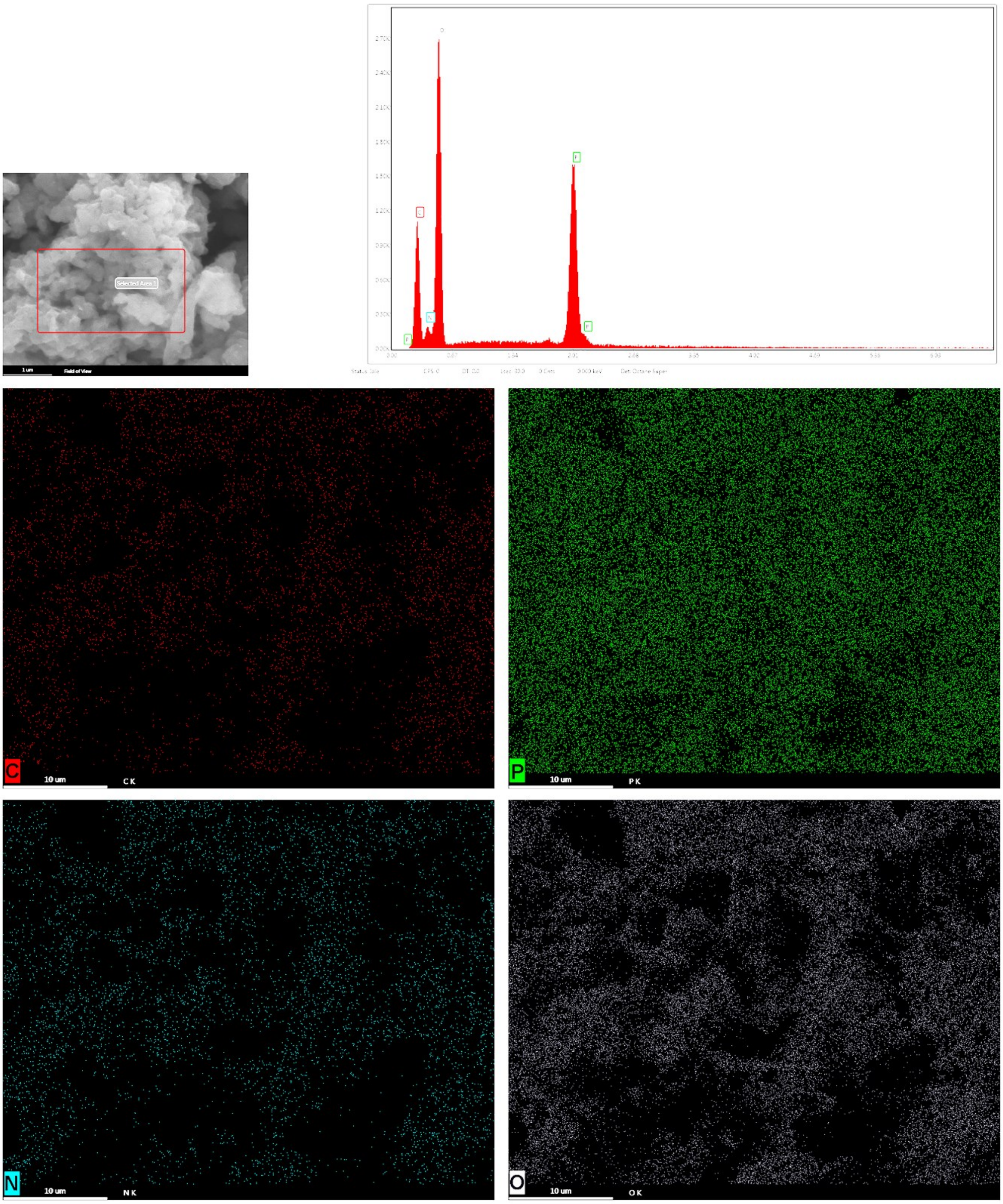

Figure S4. EDS patterns of PA@EB-COF

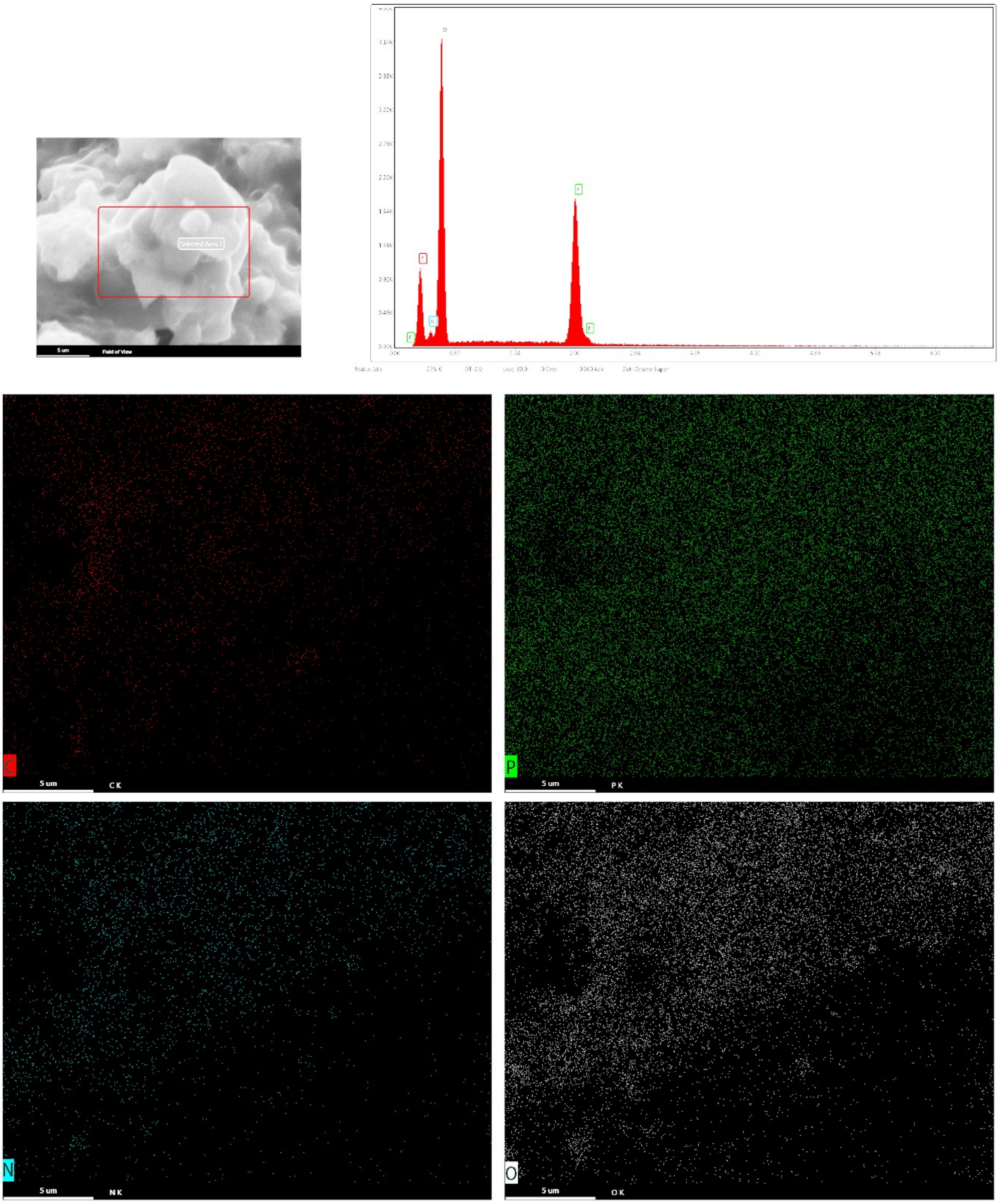

Figure S5. EDS patterns of PA@DAAQ-COF

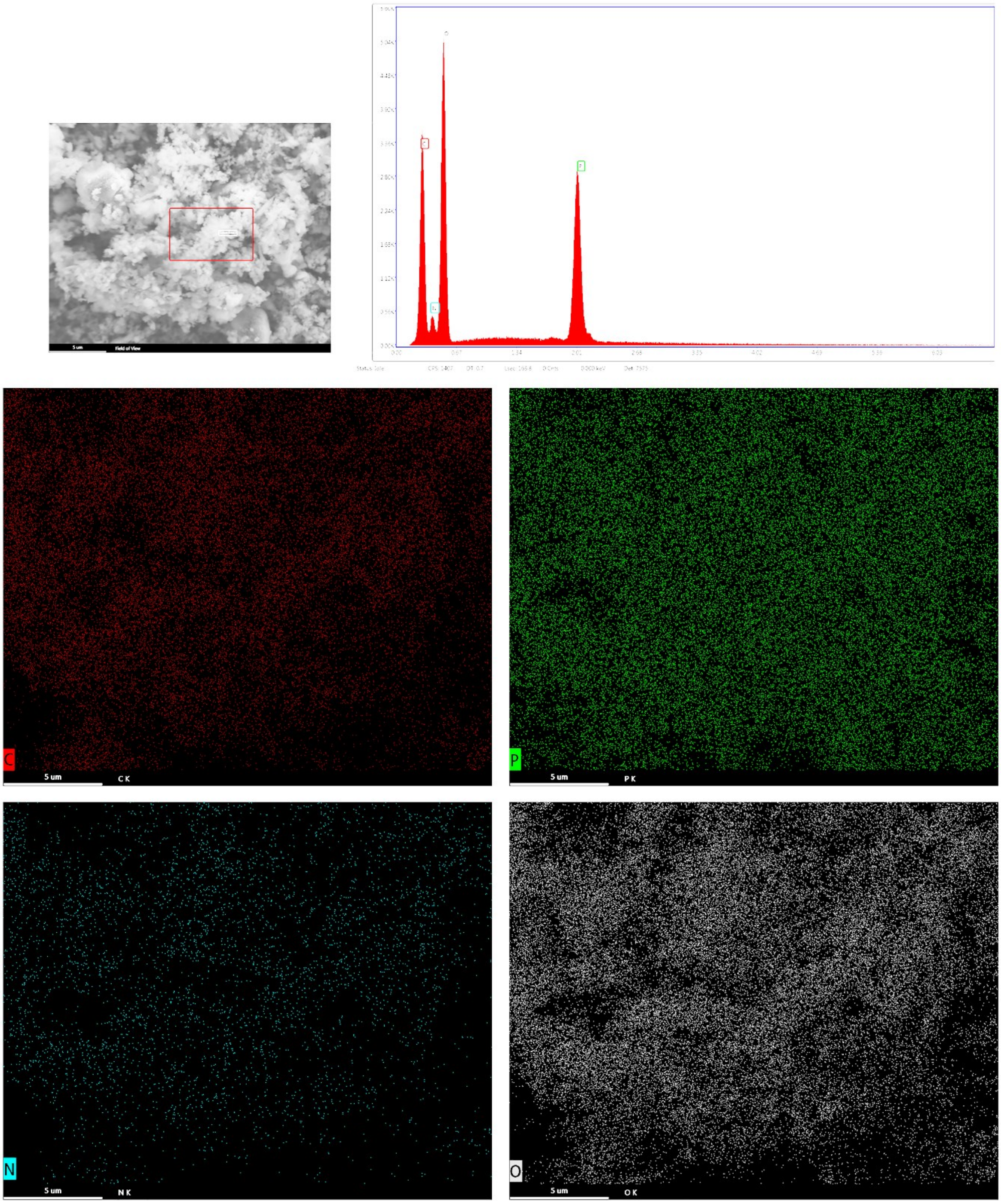

Figure S6. EDS patterns of PA@PD-COF

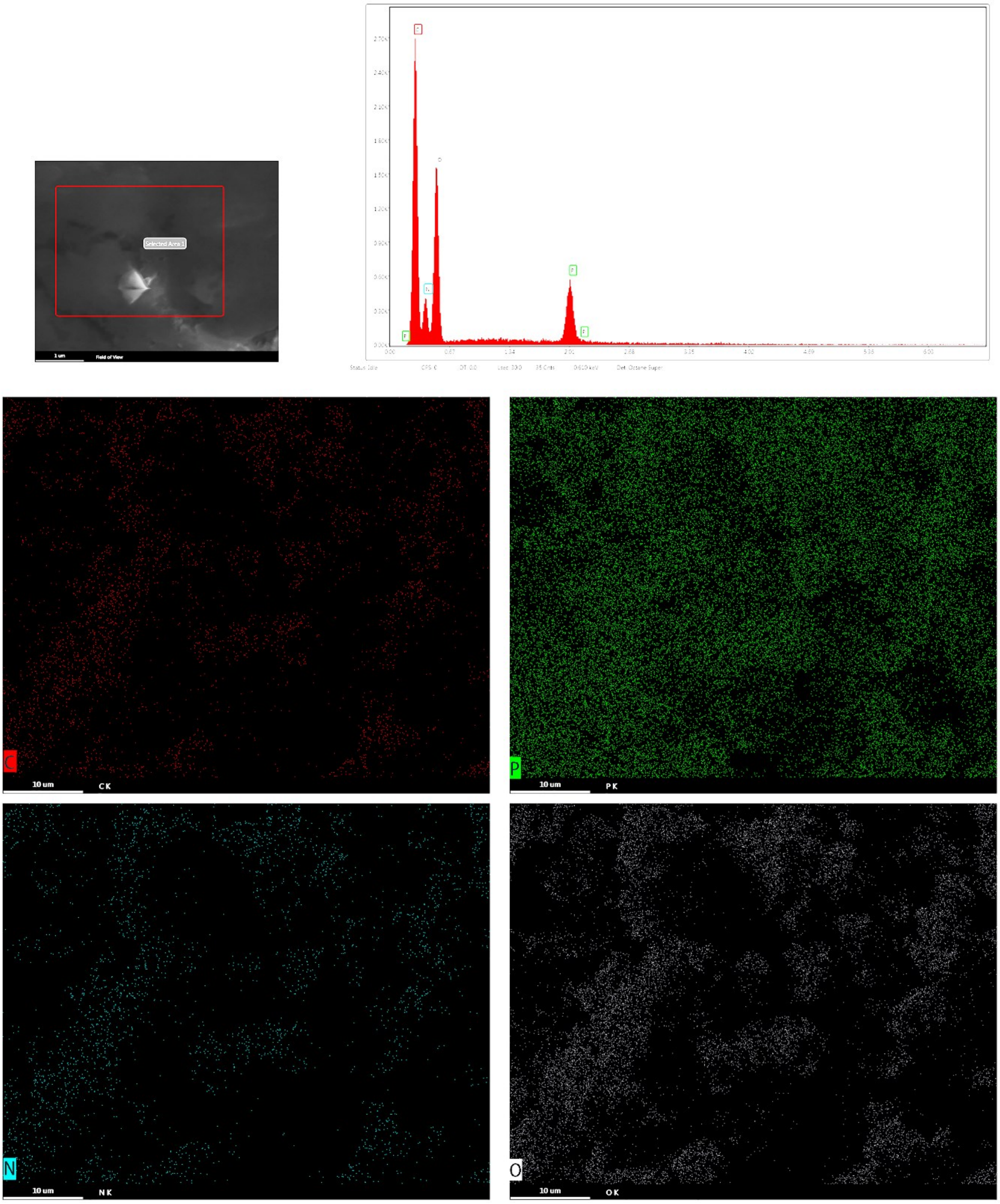

Figure S7. EDS patterns of PA@TAP-COF

6. Thermo gravimetric Analysis (TGA)

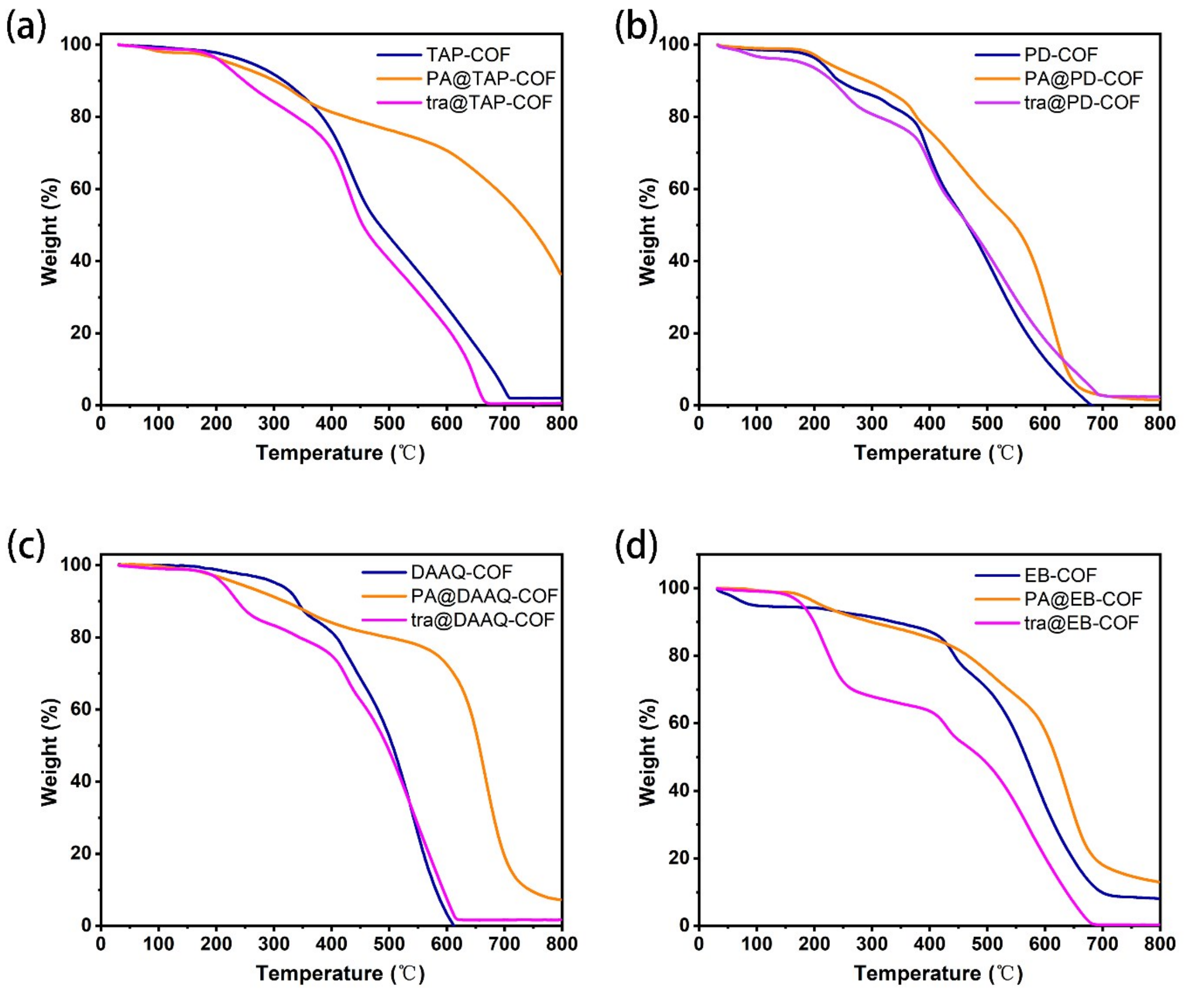

Figure S8. TGA of four pristine COFs(blue), PA@COFs (orange) and tra@COF (carmine): TAP-COF **(a)**, PD-COF **(b)**, DAAQ-COF **(c)** and EB-COF **(d)**.

7. Dielectric Constant and Proton Conductivity Studies of COFs

Impedance spectroscopy and Dielectric properties were measured using Novocontrol Concept 80 broadband dielectric spectrometer in the frequency range of 10^{-1} Hz-10 MHz. About 70-80mg samples were pressed into pellets(13mm in diameter, 0.2～0.6cm in thickness) under 30 MPa for 1 min, which was then placed in an anhydrous chamber and measured the dielectric constants and conductivities under different temperatures.

The proton conductivity can be calculated using the equation:

$$\sigma = L/(R \times A)$$

Here, $\boldsymbol{\sigma}$ is the conductivity (S cm^{-1}), **L** is the thickness of the measured sample (cm), **A** is the electrode area (cm^2) and R is the resistance (Ω) measured from the semicircles in the Nyquist plots.

The activation energy (**Ea**) values for the proton conduction process were obtained from Arrhenius equation:

$$\ln(\sigma)=\ln(A_0)-Ea/RT$$

Here, $\boldsymbol{\sigma}$ is the conductivity (S cm^{-1}), $\mathbf{A_0}$ is a constant, **T** is the absolute temperature(K), **R** is the Boltzmann constant and **Ea** is activation energy value.

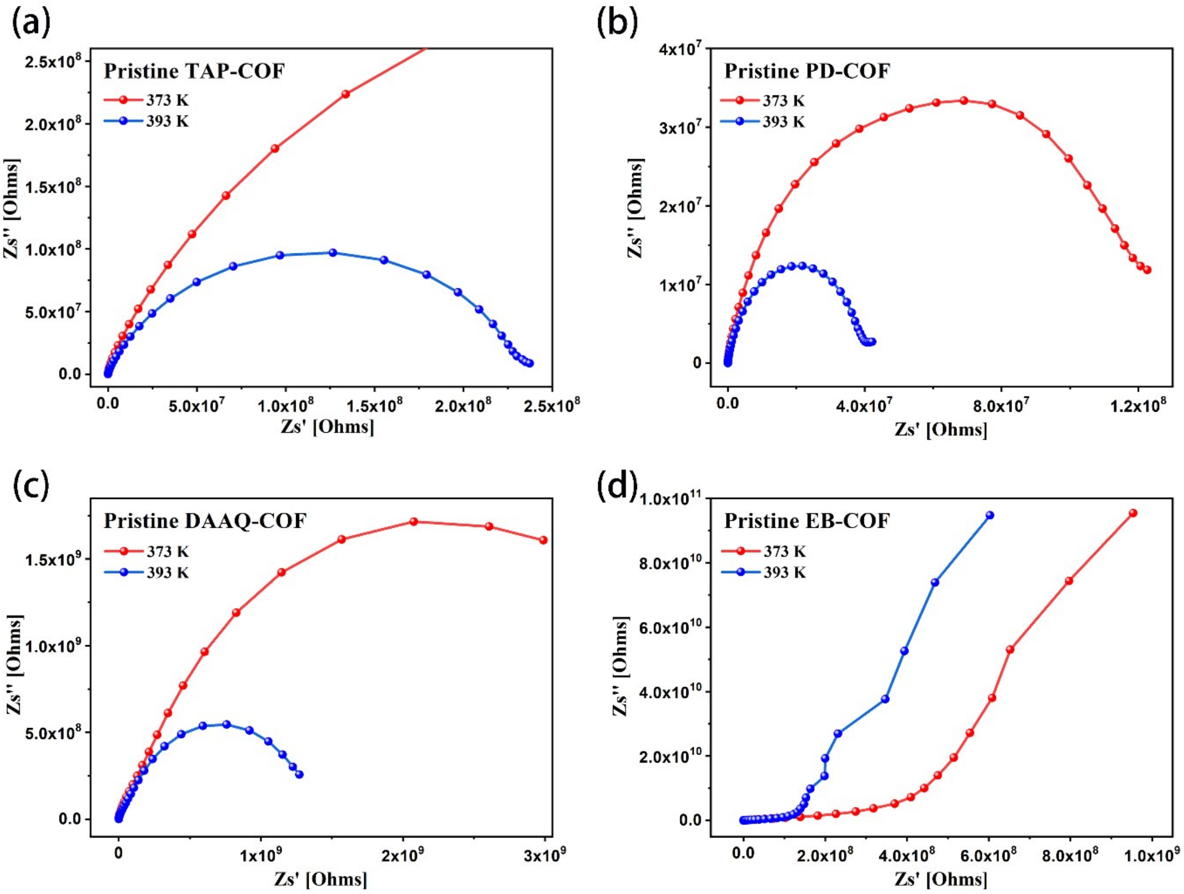

Figure S9. Nyquist plots of pristine COFs at 100 ℃ and 120 ℃ under anhydrous condition **(a)** TAP-COF, **(b)** PD-COF, **(c)** DAAQ-COF, **(d)** EB-COF.

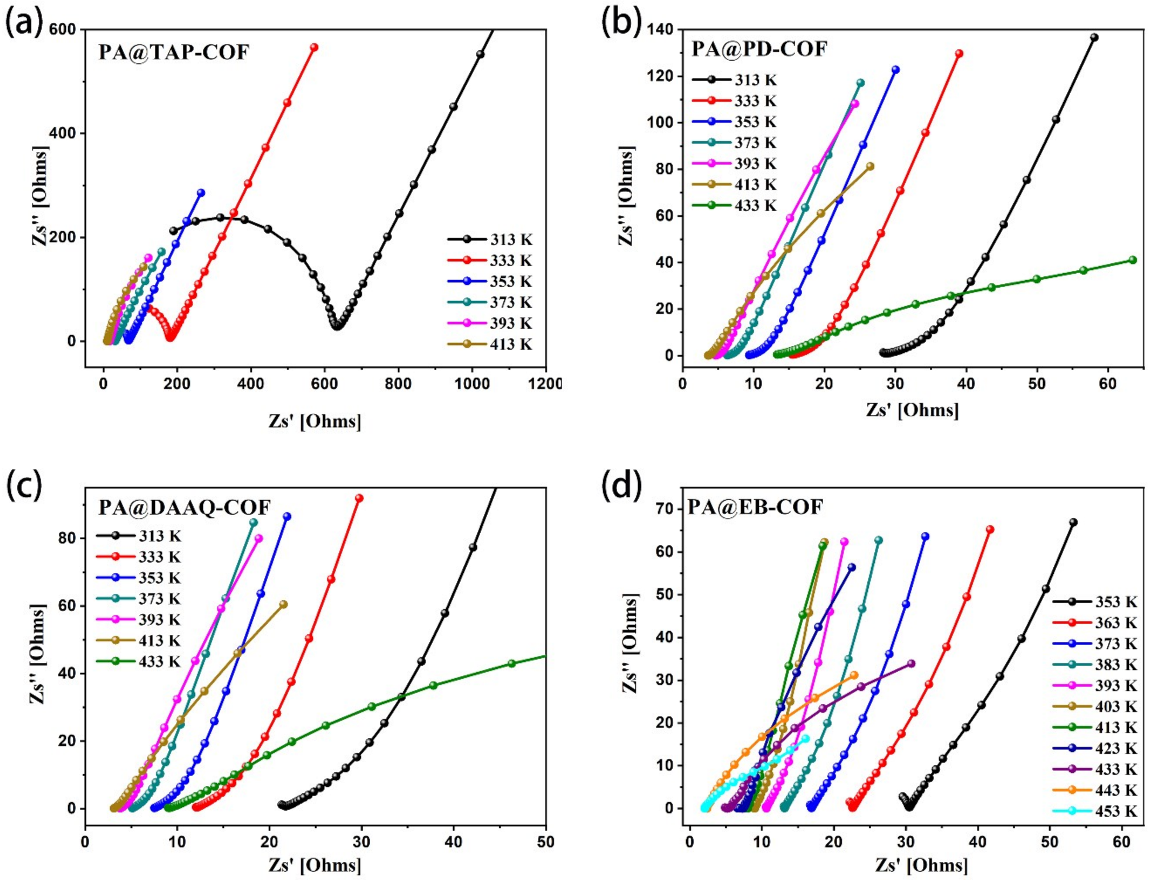

Figure S10. Nyquist plots of PA@COFs at different temperatures under anhydrous condition **(a)** PA@TAP-COF, **(b)** PA@PD-COF, **(c)** PA@ DAAQ-COF, **(d)** PA@EB-COF.

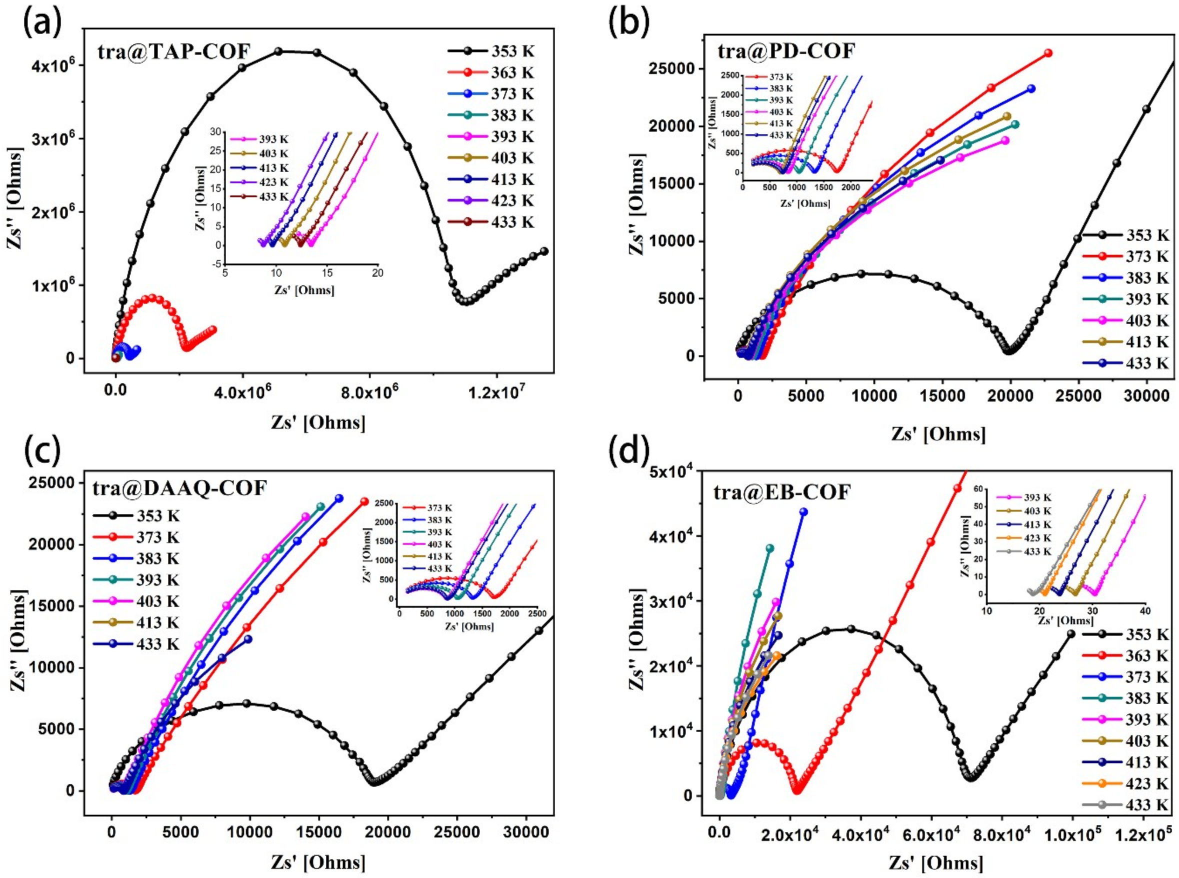

Figure S11. Nyquist plots of tra@COFs at different temperatures under anhydrous condition **(a)** tra @TAP-COF, **(b)** tra @PD-COF, **(c)** tra @ DAAQ-COF, **(d)** tra @EB-COF.

Table S2: The proton conductivity of PA@ COFs at different temperature and their activation energy

Sample	Temperature (K)	Proton Conductivity (S·cm^{-1})	activation energy (eV)
PA@TAP-COF	313	4.52×10^{-5}	0.49
	333	1.15×10^{-4}	
	353	3.76×10^{-4}	
	373	8.35×10^{-4}	
	393	1.48×10^{-3}	
	413	**2.65×10^{-3}**	

Sample	**Temperature (K)**	**Proton Conductivity ($S\cdot cm^{-1}$)**	**activation energy (eV)**
PA@PD-COF	313	6.57×10^{-4}	0.27
	333	1.20×10^{-3}	
	353	2.08×10^{-3}	
	373	3.10×10^{-3}	
	393	4.26×10^{-3}	
	413	$\mathbf{5.51\times10^{-3}}$	
	433	1.66×10^{-3}	
PA@DAAQ-COF	313	1.23×10^{-3}	0.25
	333	2.29×10^{-3}	
	353	3.70×10^{-3}	
	373	5.45×10^{-3}	
	393	7.42×10^{-3}	
	413	$\mathbf{9.20\times10^{-3}}$	
	433	2.64×10^{-3}	
PA@EB-COF	353	1.60×10^{-3}	0.26
	363	2.30×10^{-3}	
	373	3.07×10^{-3}	
	383	3.97×10^{-3}	
	393	4.95×10^{-3}	
	403	5.88×10^{-3}	
	413	6.63×10^{-3}	
	423	6.94×10^{-3}	
	433	9.66×10^{-3}	
	443	2.21×10^{-2}	
	453	$\mathbf{2.77\times10^{-2}}$	

Table S3: The proton conductivity of tra@ COFs at different temperature and their activation energy

Sample	Temperature (K)	Proton Conductivity ($S\cdot cm^{-1}$)	activation energy (eV)
tra@TAP-COF	393	2.37×10^{-3}	0.26
	403	3.08×10^{-3}	
	413	3.47×10^{-3}	
	423	**3.82×10^{-3}**	
	433	2.61×10^{-3}	
tra@PD-COF	373	1.99×10^{-5}	0.34
	383	2.62×10^{-5}	
	393	3.35×10^{-5}	
	403	4.17×10^{-5}	
	413	**4.98×10^{-5}**	
	433	4.67×10^{-5}	
tra@DAAQ-COF	373	1.12×10^{-5}	0.32
	383	1.44×10^{-5}	
	393	1.81×10^{-5}	
	403	2.23×10^{-5}	
	413	**2.62×10^{-5}**	
	433	2.19×10^{-5}	
tra@EB-COF	393	2.02×10^{-3}	0.22
	403	2.31×10^{-3}	
	413	2.61×10^{-3}	
	423	3.05×10^{-3}	
	433	**3.25×10^{-3}**	