Supplementary Materials

pH-gated ion transport in covalent organic framework membranes functionalized with oxygen-containing groups

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Cation transference number (t_+) calculation

The ionic transference number of cations (t_+) in the TpPa-based COF membranes was determined from diffusion potential measurements under a KCl concentration gradient. The transference number was calculated using the following equation:[1]

$$t_+ = \frac{1}{2}\left\{\frac{E_{diff}}{\frac{RT}{zF} ln\left(\frac{\gamma_{c_H} c_H}{\gamma_{c_L} c_L}\right)} + 1\right\}$$

where, E_{diff} is the diffusion potential (mV) measured under the concentration gradient; R is the ideal gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature (K); z is the charge number of the ion (z=1 for K^+); F is the Faraday constant (96485 C mol^{-1}). γ_{cH} and γ_{cL} are the activity coefficients of KCl in the high- and low-concentration compartments, respectively. c_H and c_L are the KCl concentrations in the high- and low-concentration compartments (M). In practice, because the measurements were performed in dilute KCl solutions (10^{-3} and 10^{-2} M), the activity coefficients were approximated as unity, reducing the logarithmic term to $\ln(c_H/c_L)$. The diffusion potential E_{diff} was recorded as the open-circuit potential between the two Ag/AgCl

electrodes under a concentration gradient of c_H = 10^{-2} M and c_L = 10^{-3} M at pH 7. The resulting t_+ values were averaged from five independent measurements for each membrane.

Membrane surface charge density calculation

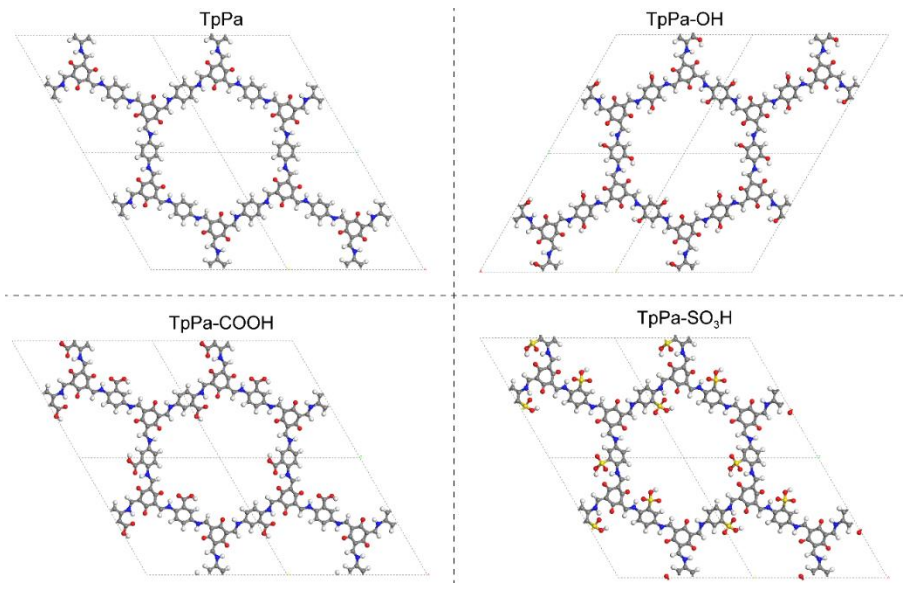
The membrane charge density (σ, C·m^{-2}) can be calculated using an Gouy-Chapman equation[2]:

$$\sigma = \sqrt{8\varepsilon RTC_0} \cdot \sinh\left(\frac{F\zeta}{2RT}\right)$$

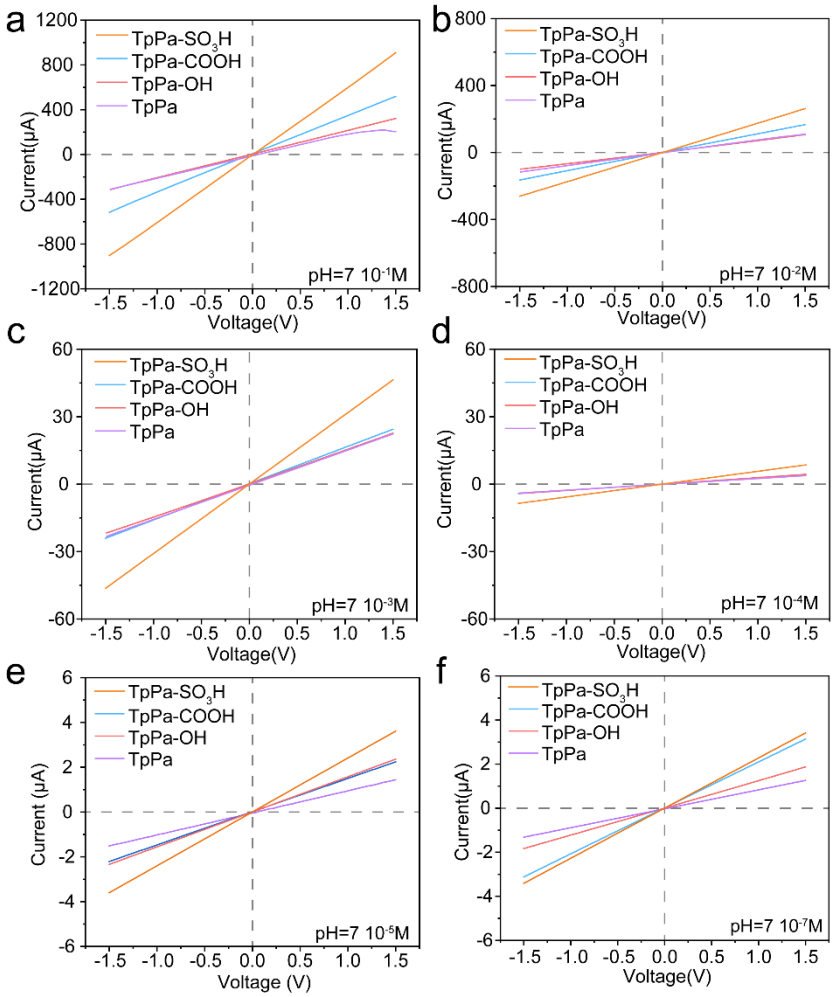
where ε (6.933×10^{-10} F·m^{-1}) is the absolute permittivity, ζ (V) is the membrane zeta potential, F (96485 C·mol^{-1}) is the Faraday constant, R (8.3145 J·mol^{-1}·K^{-1}) is the gas constant, C_0 (mol·m^{-3}) is the concentration of the electrolyte, and T (K) is the temperature.

Data analysis

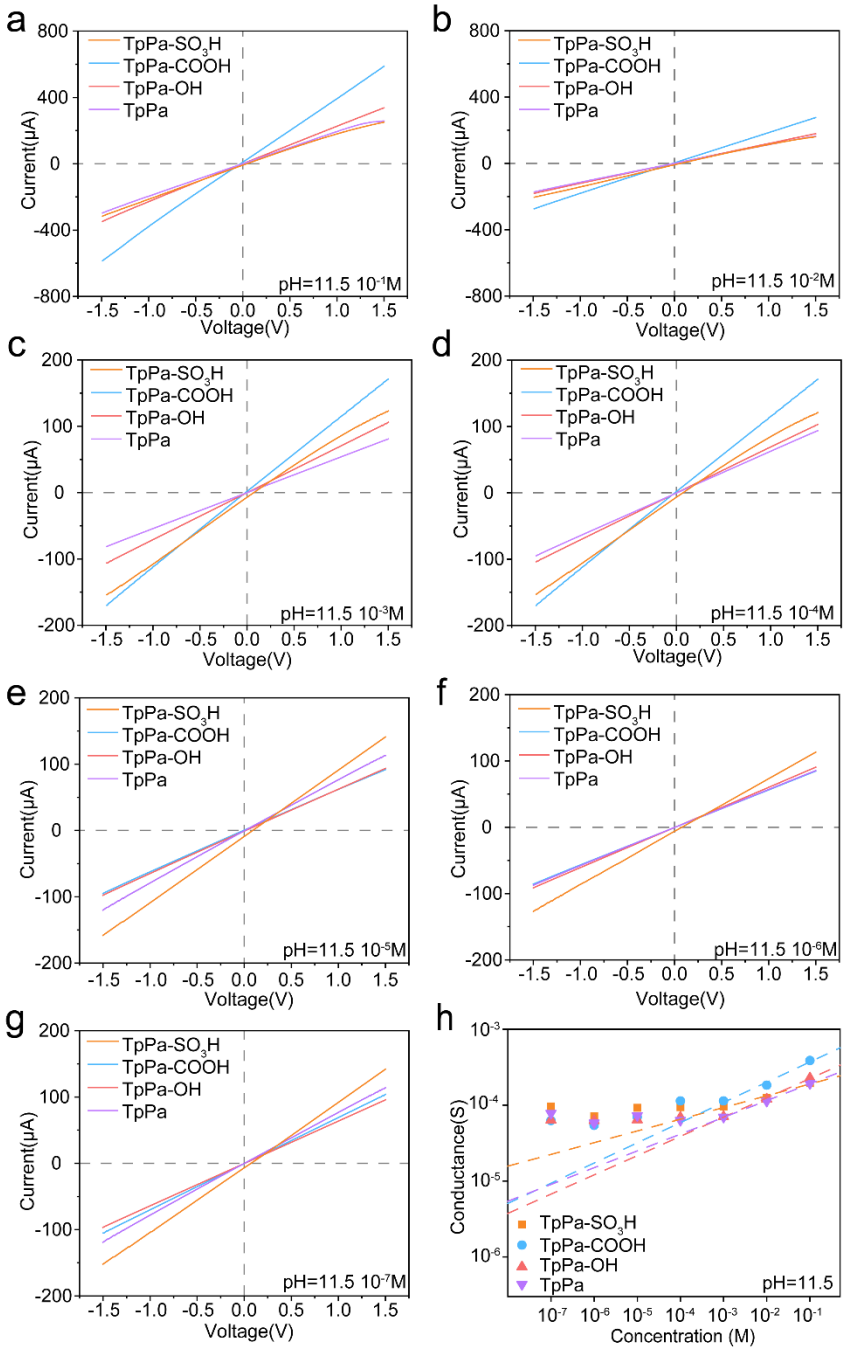
The acquired data were subsequently saved in .xlsx and .dat formats. The obtained electrical measurement data were processed and plotted using Origin. The ionic conductance of COF films was calculated by performing a linear fit on the I-V measurements to obtain the slope. The statistical analysis results of the conductivity of the four COF films are shown in Figures 3, Supplementary Figures 2-6 and Supplementary Tables 3-4.



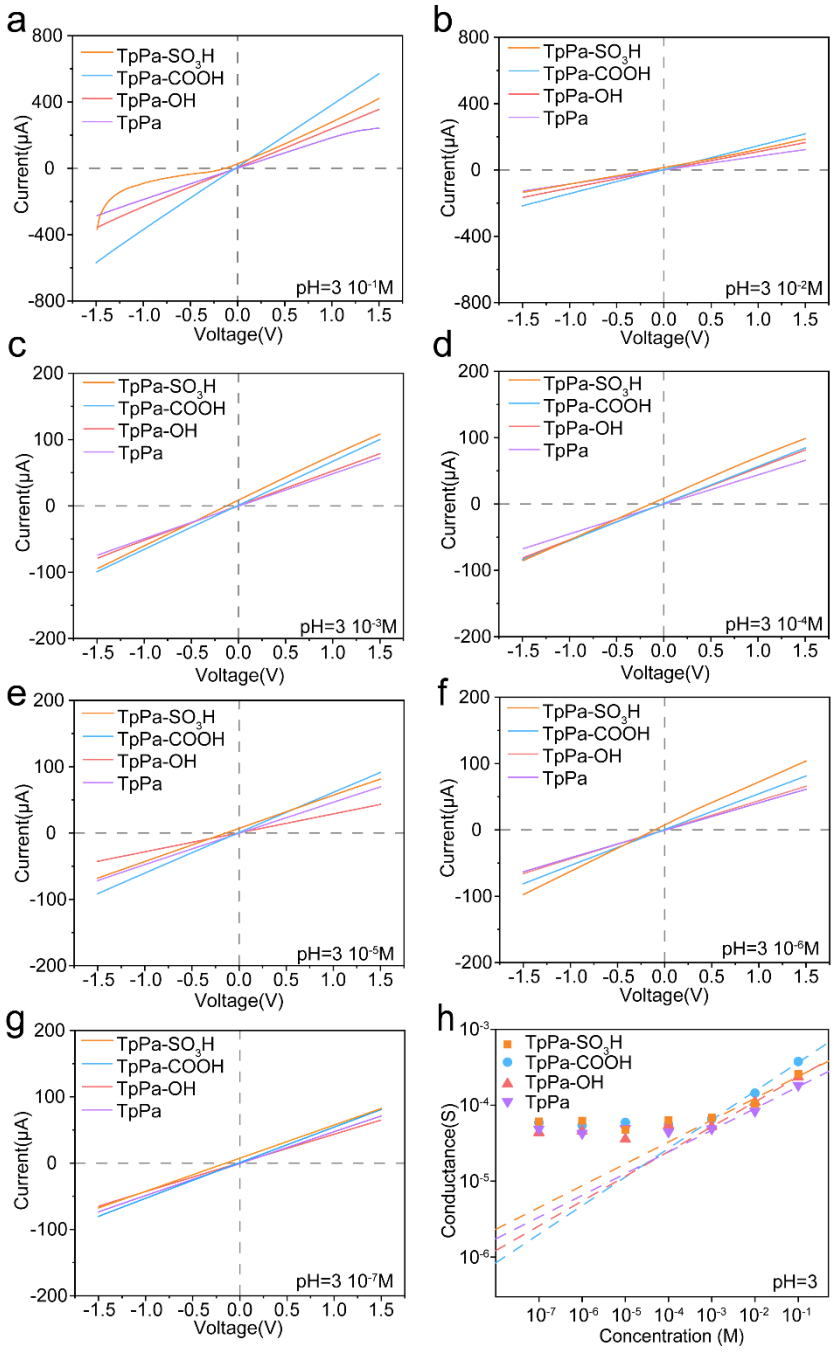
Supplementary Figure 1. Optimized crystal structures for TpPa and TpPa-R. The lattice parameters and atomic positions were optimized under the universal force field.



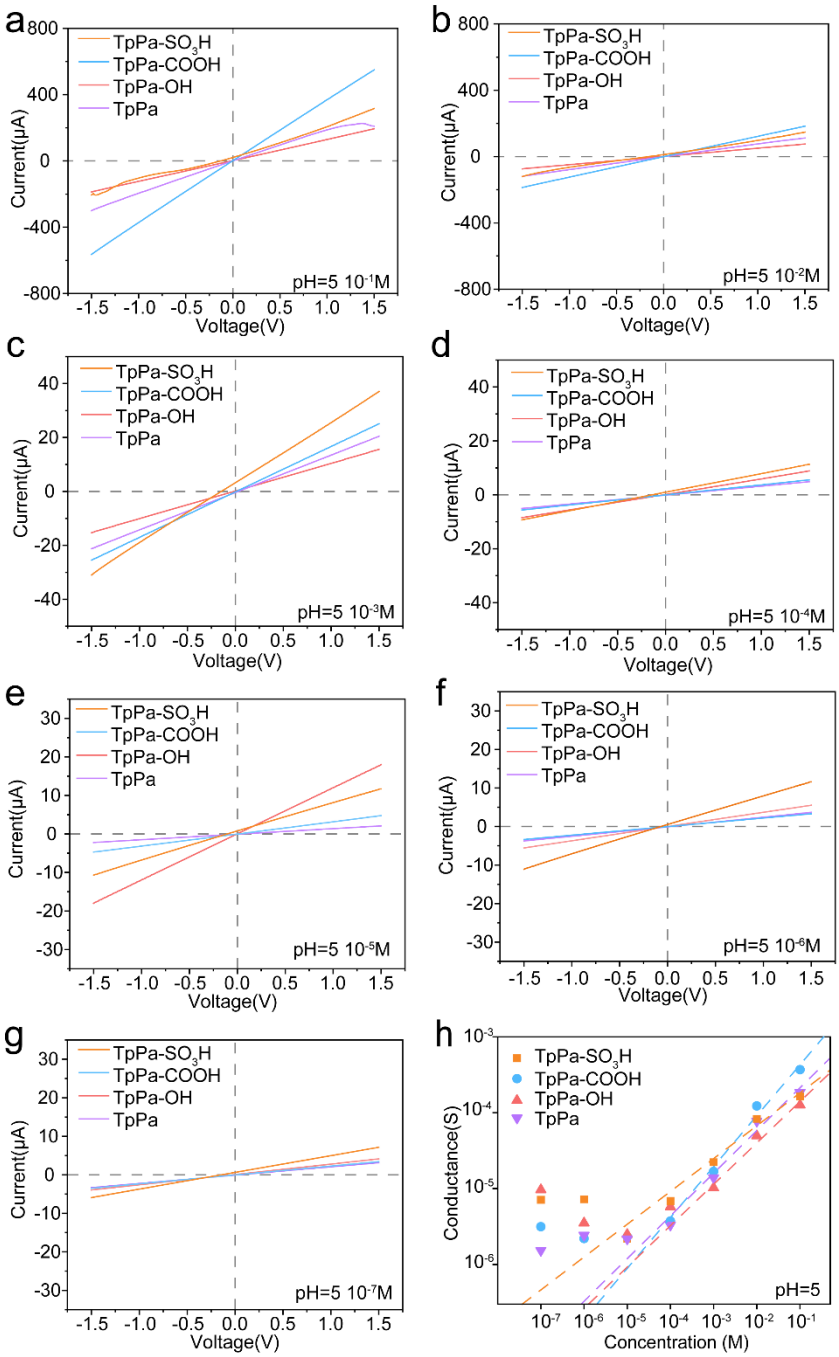
Supplementary Figure 2. I-V curves of TpPa and TpPa-R membranes in KCl (pH 7) at concentrations of (A) 10^{-1} M, (B) 10^{-2} M, (C) 10^{-3} M, (D) 10^{-4} M, (E) 10^{-5} M, and (F) 10^{-7} M.



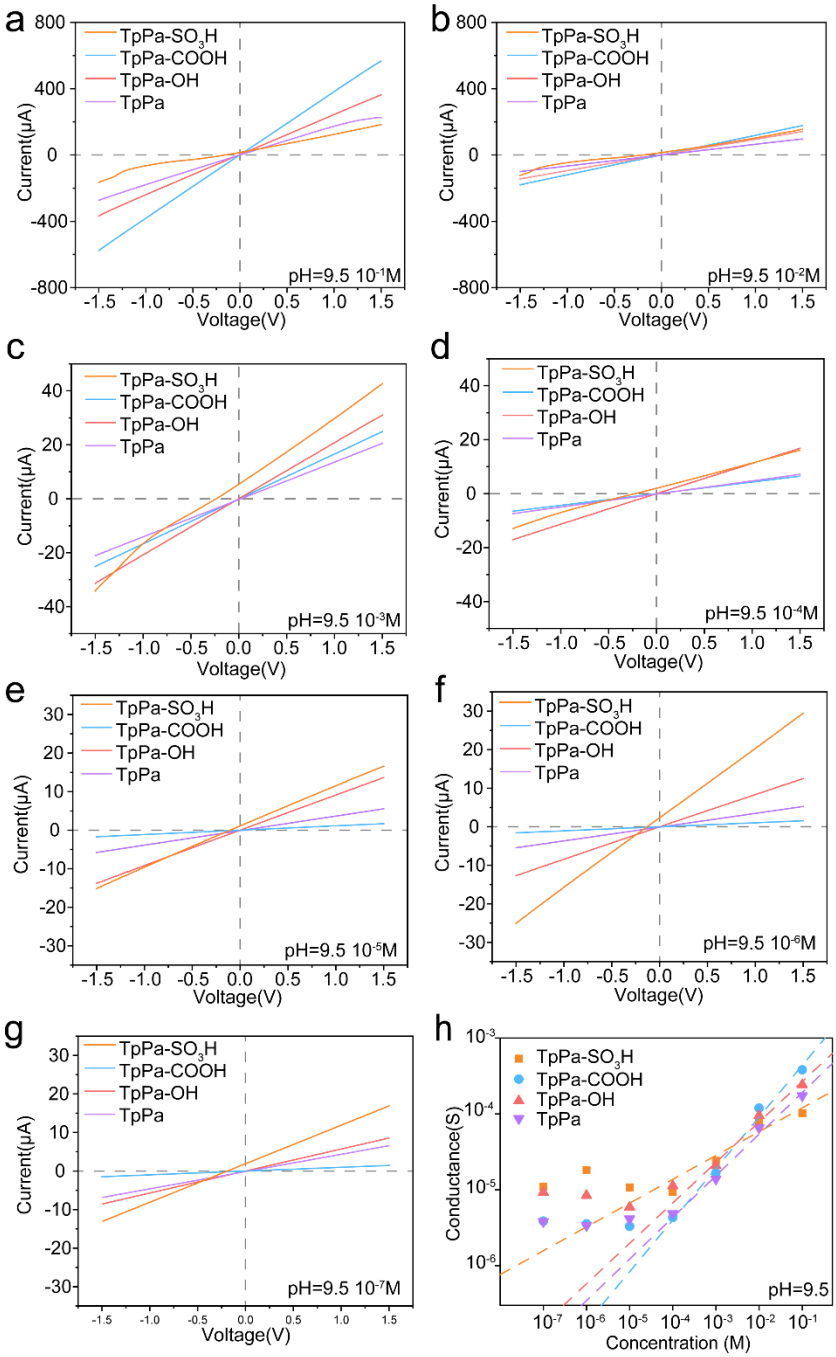
Supplementary Figure 3. I-V curves for TpPa and TpPa-R membranes in KCl (pH 11.5) at concentrations of (a) 10^{-1} M to (g) 10^{-7} M. (h) Ionic conductance as a function of KCl concentration for the four membranes at pH 11.5.



Supplementary Figure 4. I-V curves for TpPa and TpPa-R membranes in KCl (pH 3) at concentrations of (a) 10^{-1} M to (g) 10^{-7} M. (h) Ionic conductance as a function of KCl concentration for the four membranes at pH 3.



Supplementary Figure 5. I-V curves for TpPa and TpPa-R membranes in KCl (pH 5) at concentrations of (a) 10^{-1} M to (g) 10^{-7} M. (h) Ionic conductance as a function of KCl concentration for the four membranes at pH 5.



Supplementary Figure 6. I-V curves for TpPa and TpPa-R membranes in KCl (pH 9.5) at concentrations of (A) 10^{-1} M to (G) 10^{-7} M. (H) Ionic conductance as a function of KCl concentration for the four membranes at pH 9.5.

Supplementary Table 1. Simulated structural parameters for TpPa and TpPa-R in the *P*1 space group

Entry	TpPa	TpPa-OH	TpPa-COOH	TpPa-SO3H

Crystal Parameters	*a*/Å	3.5452	3.6168	3.6898	4.1076
	b/Å	22.9509	22.6370	23.1544	21.5266
	c/Å	22.6994	22.7500	22.2842	22.1467
	α	60°	60°	60°	60°
	β	90°	90°	90°	90°
	γ	90°	90°	90°	90°
Pore size/nm		1.77	1.69	1.65	1.55

Supplementary Table 2. Zeta potential of four TpPa-based COF membranes at different pH values

Entry		**TpPa-SO_3H**	**TpPa-COOH**	**TpPa-OH**	**TpPa**
Zeta potential (mV)	pH 3	-11.8 ± 0.07	-4.2 ± 0.32	+8.1 ± 0.33	+20.4 ± 0.08
	pH 5	-17.0 ± 0.29	-17.2 ± 0.55	-9.6 ± 0.23	-7.1 ± 0.02
	pH 7	-21.4 ± 0.18	-21.0 ± 0.29	-17.6 ± 0.10	-23.7 ± 0.26
	pH 8.5	-25.8 ± 0.06	-22.8 ± 0.41	-20.2 ± 0.24	-27.5 ± 0.04
	pH 10	-30.2 ± 0.43	-26.8 ± 0.46	-24.7 ± 0.20	-30.0 ± 0.20

Supplementary Table 3. pH-gated ion transport properties of four TpPa-based COF membranes in KCl at 10^{-5} M

C_{KCl}	**Entry**	**TpPa-SO_3H**	**TpPa-COOH**	**TpPa-OH**	**TpPa**
10^{-5} M	Conductance at pH 3 (μS)	47.7 ± 2.18	59.3 ± 2.58	35.8 ± 10.1	49.4 ± 3.33
	Conductance at pH 5 (μS)	4.3 ± 0.54	2.3 ± 0.16	2.5 ± 0.29	2.2 ± 0.08

Conductance at pH 7 (μS)	2.49 ± 0.16	1.35 ± 0.02	1.39 ± 0.24	0.91 ± 0.04
Conductance at pH 9.5 (μS)	10.8 ± 0.51	3.3 ± 0.34	5.9 ± 0.46	4.14 ± 0.49
Conductance at pH 11.5 (μS)	92.2 ± 8.45	69.9 ± 5.24	63.9 ± 7.02	72.6 ± 10.55

Supplementary Table 4. pH-gated ion transport properties of four TpPa-based COF membranes in KCl at 10^{-6} M

Entry	**TpPa-SO_3H**	**TpPa-COOH**	**TpPa-OH**	**TpPa**
pKa	-1	4 ~ 5	9~10	/
Conductance at pH 3 (μS)	62.7 ± 2.19	54.4 ± 3.56	45.5 ± 6.29	42.7 ± 2.40
Conductance at pH 5 (μS)	7.3 ± 0.37	2.2 ± 0.18	3.5 ± 0.52	2.4 ± 0.29
Conductance at pH 7 (μS)	0.89 ± 0.09	0.48 ± 0.04	0.62 ± 0.12	0.60 ± 0.05
Conductance at pH 9.5 (μS)	18.3 ± 3.62	3.6 ± 0.69	8.4 ± 0.41	3.4 ± 0.40
Conductance at pH 11.5 (μS)	71.1 ± 10.17	54.6 ± 4.96	62.5 ± 2.65	58.3 ± 4.61
ON/OFF ratio (Acidic/Neutral)	70	113	74	71
ON/OFF ratio (Alkaline/Neutral)	79	114	101	98
Zero-current potential (mV)	17.4 ± 2.47	12.8 ± 1.34	4.9 ± 2.24	40.7 ± 1.33

Supplementary Table 5. The absolute value of the apparent charge density of four TpPa-based COF membranes at different pH values

Entry	TpPa-SO_3H	TpPa-COOH	TpPa-OH	TpPa
Apparent charge density at pH = 3 (mC/m^2)	0.86	0.30	0.59	1.51
Apparent charge density at pH = 5 (mC/m^2)	1.25	1.27	0.70	0.51
Apparent charge density at pH = 7 (mC/m^2)	1.59	1.56	1.32	1.77
Apparent charge density at pH = 8.5 (mC/m^2)	1.94	1.73	1.50	2.08
Apparent charge density at pH = 10 (mC/m^2)	2.31	2.02	1.85	2.29

REFERENCES

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2. Xu, R.; Kang, Y.; Zhang, W.; Pan, B.; Zhang, X. Two-dimensional MXene membranes with biomimetic sub-nanochannels for enhanced cation sieving. *Nat Commun* 2023, 14 (1), 4907. DOI: 10.1038/s41467-023-40742-8.