Supplementary Information

Continuous Porous Aromatic Framework Membrane with Acid/Base-induced Reversible Isomerization for Switchable Ion Conductivity

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Experimental Section

Materials

All starting materials and organic solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. All reactions were performed in ovendried glassware under nitrogen or argon atmosphere using standard Schlenk and glovebox techniques.

General instrumentation and methods

¹H NMR spectra were recorded on Varian Inova 500 MHz NMR spectrometer. ¹³C CP/MAS solid-state NMR spectra were obtained using a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. FT-IR measurements were performed on the Nicolet IS50 Fourier transforms infrared spectrometer. The Elemental analyses (for C, H, and N) were measured using a Perkin Elmer 2400 Series II CHNS/O Analyzer. TGA were measured on the METTLER-TOLEDO TGA/DSC 3+ analyzer at the 10°C min⁻¹ heating rate in air atmosphere. N₂-adsorption isotherms and pore size distribution were obtained at 77 K using an Autosorb iQ2 adsorptometer, Quantachrome Instrument. H₂O-adsorption isotherms were obtained at 298 K using an Anton-Paar VSTARTM fully automatic steam adsorption analyzer. The scanning electron microscopy (SEM) images were acquired by the field emission scanning electron microscopy (FE-SEM, SU-8010, Hitachi). The powder X-ray diffraction (PXRD) measurements were carried out on the Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation (40 kV, 30 mA, $\lambda = 1.5418$ Å) and a scanning step of 0.01°. X-ray photoelectron

K α (1200 eV). Atomic force microscopy (AFM) was performed by using Oxford Instruments (Cypher ES). UV-Vis spectra (200-800 nm) were recorded on a Cary 7000 UV-Vis-NIR spectrophotometer.

The ion conductivity of PAFs materials was studied by AC impedance method. Firstly, the activated PAFs materials were fully ground into uniform powder, and then an appropriate amount of the powder materials was put into a die with a radius of 0.25 cm and kept for 2 min curing time under the pressure of 15 MPa. The sample wafers were assembled with the gold electrode and the electrochemical impedances were tested in the frequency range of 1 Hz to 1 MHz and input voltage amplitude of 50 mV by using the IviumStat electrochemical workstation. The equilibrium temperature and humidity were controlled by BPHS-060A chamber. By simulating the equivalent circuit, software ZSimpWin was used to further simulate the Nyquist plots and infer the resistance value of the material. Then the ion conductivity of PAFs materials could be calculated using the Pouillet's equation:

$$\sigma = \frac{L}{AR}$$

wherein σ is the ion conductivity (S·cm⁻¹), *L* is the thickness of the measured sample (cm), *A* is the sectional area (cm²) and *R* is the resistance (Ω).

The ion conductivity of continuous PAF membrane was also obtained using the above method, after the membrane was transferred to an inter-digitated gold electrode. The calculation formula was referenced from the previous literature.^[1]

$$\sigma = \frac{1}{R} \cdot \frac{d}{l(N-1)t}$$

where d is the spacing between the electrode teeth (0.2 mm), t is the thickness of the membrane (nm), l is the length of the electrode teeth (0.41 cm) and N is the number of electrodes (14).

The activation energy corresponding to ion conductivity at different temperatures was determined by Arrhenius equation:

$$\sigma T = \sigma_0 \exp\left(\frac{-E_{\rm a}}{k_{\rm B}T}\right)$$

where σ and σ_0 denote ion conductivity and pre-exponential factor, respectively, *T* indicates the absolute temperature in kelvin, E_a indicates the activation energy and k_B denotes the Boltzmann constant.

Synthetic Procedure

Synthesis of PAF-125 and PAF-126 (powder). To synthesize PAF-125, bromophenol blue (670 1.0 1,2,4,5-tetraethynylbenzene (175)mg, mmol), mg, 1.0 mmol), tetrakis(triphenylphosphine)palladium (120 mg, 0.1 mmol) and copper(I) iodide (40 mg, 0.2 mmol) were added to an oven-dried round-bottom flask. Anhydrous DMF (30 mL) and anhydrous triethylamine (30 mL) were added through a syringe. The reaction mixture was heated to 100°C under N₂ atmosphere and reacted for 36 h. After cooling to room temperature, the product was filtered and washed with excess DMF and methanol, and then Soxhlet extracted with tetrahydrofuran overnight to remove any unreacted monomers and metal catalyst residues. The final products were dried in vacuum for 24 h at 80°C to give PAF-125 (394 mg, 75% yield). PAF-126 (725 mg, 85% yield) was synthesized similar to PAF-125, replacing 1,2,4,5tetraethynylbenzene with 1,3,5-tris(4-ethynylphenyl)benzene (542 mg, 1.4 mmol).

Preparation of continuous PAF-126 membrane by surface-initiated polymerization (SIP). The surface functionalization of silicon wafers was prepared as previously reported.^[2] Following a typical procedure, The functionalized silicon wafers were put into the mixture of anhydrous toluene and triethylamine 20 mL (1:1)vol). The catalyst tetrakis(triphenylphosphine)palladium (12 mg, 0.01 mmol) and CuI (4 mg, 0.01 mmol) were added into the mixture and stirred at room temperature for 1 h. The monomers bromophenol blue (67 mg, 0.1 mmol) and 1,3,5-tris(4-ethynylphenyl)benzene (54.2 mg, 0.14 mmol) were added into the mixture, and reacted at 100°C for 72 h. After that, the formed precipitate was collected by filtration, washed with DMF and methanol to remove residual monomers and dried at 100°C under vacuum for 12 h. The PAF membrane was grown on silicon wafer substrates following a brief ultrasound and similar procedure described above.

The PAF-126 membrane polymerized on Si/SiO₂ substrate surface was evenly coated with PMMA chlorobenzene solution to protect the membrane. Then Si/SiO2 wafer is etched off with 2% hydrofluoric acid, and transfer the PMMA/PAF membrane to an inter-digitated gold electrode. Finally, the PMMA was washed by acetone.



Figures S1. IR spectra of PAF-125, BPB, and TEB.



Figures S2. IR spectra of PAF-126, BPB, and TEPB.



Figures S3. Pore-size distribution profiles of PAF-125.



Figures S4. Pore-size distribution profiles of PAF-126.



Figures S5. PXRD patterns of PAF-125.



Figures S6. PXRD patterns of PAF-126.



Figures S7. The scanning electron microscopy (SEM) images of PAFs.

Sample	% C	% H	% S
PAF-125	71.272	3.634	0.464
PAF-126	75.363	4.379	1.778



Figures S8. TGA plot of PAF-125.



Figures S9. TGA plot of PAF-126.



Figures S10. UV-vis spectra and color contrast images of PAF-125 after acidic and alkali treatment.



Figures S11. The impedance Nyquist plots of PAF-126-OH at 25°C and under different humidity conditions.



Figures S12. Nyquist plots of PAF-125-OH at different temperatures under 98% RH.



Figures S13. Temperature-dependent ion conductivities of PAF-125-H and PAF-125-OH under 98% RH.

	Ion conductivity σ / S cm ⁻¹			
	PAF-125-H	PAF-125-OH	PAF-126-H	PAF-126-OH
25 °C	3.87×10 ⁻⁶	1.1×10 ⁻²	3.36×10 ⁻⁷	4.59×10 ⁻³
30 °C	2.76×10 ⁻⁵	4×10 ⁻²	2.93×10 ⁻⁶	7.42×10 ⁻³
35 °C	8.18×10 ⁻⁵	4.35×10 ⁻²	3.87×10 ⁻⁶	1.06×10 ⁻²
45 °C	3.75×10 ⁻⁴	5.88×10-2	1.3×10 ⁻⁵	2.25×10 ⁻²
55 °C	1.26×10 ⁻³	7.7×10 ⁻²	3.64×10 ⁻⁵	3.24×10 ⁻²
65 °C	2.83×10 ⁻³	1.02×10 ⁻¹	1.74×10 ⁻⁴	5.89×10 ⁻²
75 °C	3.12×10 ⁻³	1.20×10 ⁻¹	9.51×10 ⁻⁴	7.58×10 ⁻²
85 °C	3.42×10 ⁻³	1.38×10 ⁻¹	2.87×10-3	9.85×10 ⁻²
95 °C			8.89×10 ⁻³	1.4×10 ⁻¹

Table S2 The detailed results of ion conductivity of PAFs-H and PAFs-OH under 98% RH.



Figures S14. Arrhenius plots of PAF-125-H and PAF-125-OH under 98% RH.



Figures S15. Reversible ion conductivity and color contrast images of PAF-125 after soaking in alkaline (pH=14) and acidic (pH=1) solutions at 25 °C and 98% RH.



Figures S16. Reversible ion conductivity and color contrast images of PAF-126 after soaking in alkaline (pH=14) and acidic (pH=1) solutions at 25 °C and 98% RH.



Figures S17. IR spectra of PAF-126 and PAF-126M.



Figures S18. XPS spectra of PAF-126 and PAF-126M.



Figure S19. The SEM images of PAF-126M.



Figure S20. The EDS elemental mapping images of PAF-126M.



Figure S21. The PXRD patterns of PAF-126M.



Figure S22. The water contact angle images of PAF continuous membrane (a) and powder (b).

Table S3 The detailed results of ion conductivity of PAF-126M-H and PAF-126M-OH.

	Ion conductivity σ / S cm ⁻¹	
	РАҒ-126М-ОН	РАF-126М-Н
30 °C	1.56×10 ⁻¹	3.80×10 ⁻³
35 °C	2.12×10 ⁻¹	4.63×10 ⁻³
40 °C	2.75×10 ⁻¹	5.36×10 ⁻³
45 °C	3.60×10 ⁻¹	6.25×10 ⁻³

50 °C	4.20×10 ⁻¹	7.20×10 ⁻³
55 °C	4.55×10 ⁻¹	8.06×10 ⁻³
60 °C	5.15×10 ⁻¹	9.35×10 ⁻³
65 °C	5.63×10 ⁻¹	1.07×10 ⁻²
70 °C	6.00×10 ⁻¹	1.26×10 ⁻²
75 °C	6.57×10 ⁻¹	1.36×10 ⁻²
80 °C	6.71×10 ⁻¹	1.59×10 ⁻²
85 °C	7.29×10 ⁻¹	1.72×10 ⁻²



Figures S23. Nyquist plots of PAF-126M at different pH under 98% RH at 30 °C.

	System	ion conductivities	Measurement conditions	Ref.
		(S cm ⁻¹)		
Porous powder samples				
1	HOF-GS-10	0.75×10 ⁻²	30 °C 95% RH	3
1	HOF-GS-11	1.8×10-2		5
2	H ₃ PO ₄ @CTF-TF	1.82×10 ⁻¹	150 °C	4
3	CPOS-1	1.0×10-2	60 °C, 98% RH	5

Table S4 Compared ion conductivity for previously reported porous materials and this work.

	CPOS-2	2.2×10-2			
4	H ₃ PO ₄ @USTB-5r	5.3×10 ⁻²	140 °C	6	
	H ₃ PO ₄ @USTB-50	6.3×10 ⁻²	140 C		
	H ₃ PO ₄ @NKCOF-52	1.12×10-3			
5	H ₃ PO ₄ @NKCOF-53	1.24×10-2	160 °C	7	
	H ₃ PO ₄ @NKCOF-54	2.33×10 ⁻²			
6	H ₃ PO ₄ @TPB-DMTP-COF	5.02×10 ⁻²	160 °C	8	
7	H ₃ PO ₄ @TPBDMeTP-COF	3.06×10-1	160 °C	9	
8	[OH [–]]100-TPB-BPTA-COF	1.53×10-2	80 °C	10	
Q	PAF-125-OH	1.38×10 ⁻¹	85 °C, 98% RH	This work	
	РАҒ-126-ОН	1.40×10 ⁻¹	95 °C, 98% RH		
Men	nbranes				
10	TpBD-(SO ₃ H) ₂ iCOFMs	6.2×10 ⁻¹	90 °C, 100% RH	11	
11	COFQA-2	2.12×10 ⁻¹	80 °C, 100% RH	12	
12	SCOF	5.4×10 ⁻¹	80 °C, 100% RH	1	
13	TpPa-SO ₃ H/SPEEK-1%	7.5×10 ⁻²	20 °C, 100% RH	13	
14	PAF-MPIP-6	3.57×10 ⁻¹	80 °C, 98% RH	14	
Opt	Optically switchable porous materials				
15	1''-TfH-10	3.0×10 ⁻⁴	110 °C	15	
16	Cu ₂ (F ₂ AzoBDC) ₂ (dabco)	1.20×10-6	25 °C	16	
Acid/Base responsive membrane					
17	PAF-126M-OH	7.29×10 ⁻¹	85 °C, 98% RH	This work	

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