

Supporting information

Novel proton exchange membrane with long-range acid-base-pair proton transfer pathway based on functionalized polyethyleneimine

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Number of pages: 11

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Chemical Structure Characterization of PEIMPA

The Raman spectra were used to characterize the structure of PEIMPA. Fig. S1 show the Raman spectra of PEI, PEIMPA with 50% and 100% replacement rate, the peaks around 960cm^{-1} and 2940cm^{-1} (assigned to $\nu(\text{-NH-}$ and $\text{-NH}_2)$), the PEIMPA have a obviously weaker peak strength, indicating that part of -NH_2 groups had been reacted and replaced. The peaks at 657cm^{-1} and 820cm^{-1} (assigned to P-O) and the peak around 1060cm^{-1} (assigned to P=O) were appeared in PEIMPA molecular, indicating that $\text{-PO}_3\text{H}_2$ groups were introduced into PEI. Therefore, part of the -NH- and -NH_2 groups were functionalized as methylphosphonic acid ($\text{-CH}_2\text{PO}_3\text{H}_2$).

Fig. S2 (a- d) illustrates ^1H and ^{13}C NMR spectrum of PEI and PEIMPA. Compared with the ^1H NMR spectrum of PEI, the peaks at 3.5-4.0 ppm (assigned to $\text{N-CH}_2\text{-PO}_3\text{H}_2$) appeared, and the peak at 2.5 ppm (assigned to $\text{-CH}_2\text{-CH}_2\text{-NH-}$) were moved to around 2.9 ppm, implying that the -NH_2 groups have been reacted with the HCHO and H_3PO_3 , and new N-C bonds were generated. Moreover, the peaks at 57.1 and 58.7 ppm (assigned to $\text{-CH}_2\text{-PO}_3\text{H}_2$) has appeared in ^{13}C NMR spectrum of obtained PEIMPA, indicating that the $\text{-PO}_3\text{H}_2$ were introduced. Therefore, the ^1H NMR, ^{13}C NMR and Raman spectra demonstrated the reaction between -NH_2 , HCHO and H_3PO_3 is successful and the prepared PEIMPA was obtained.

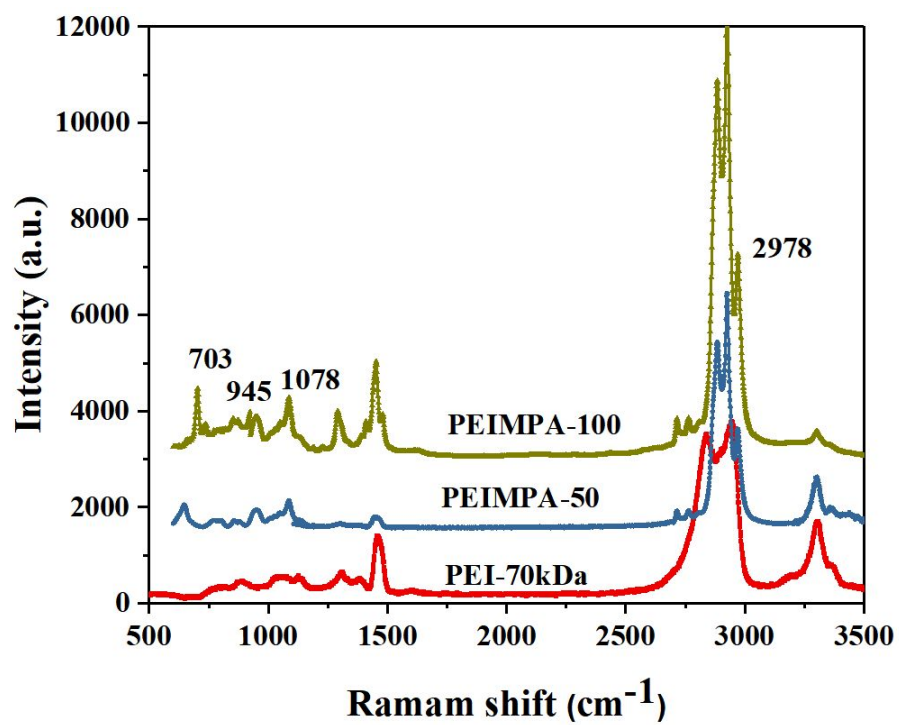
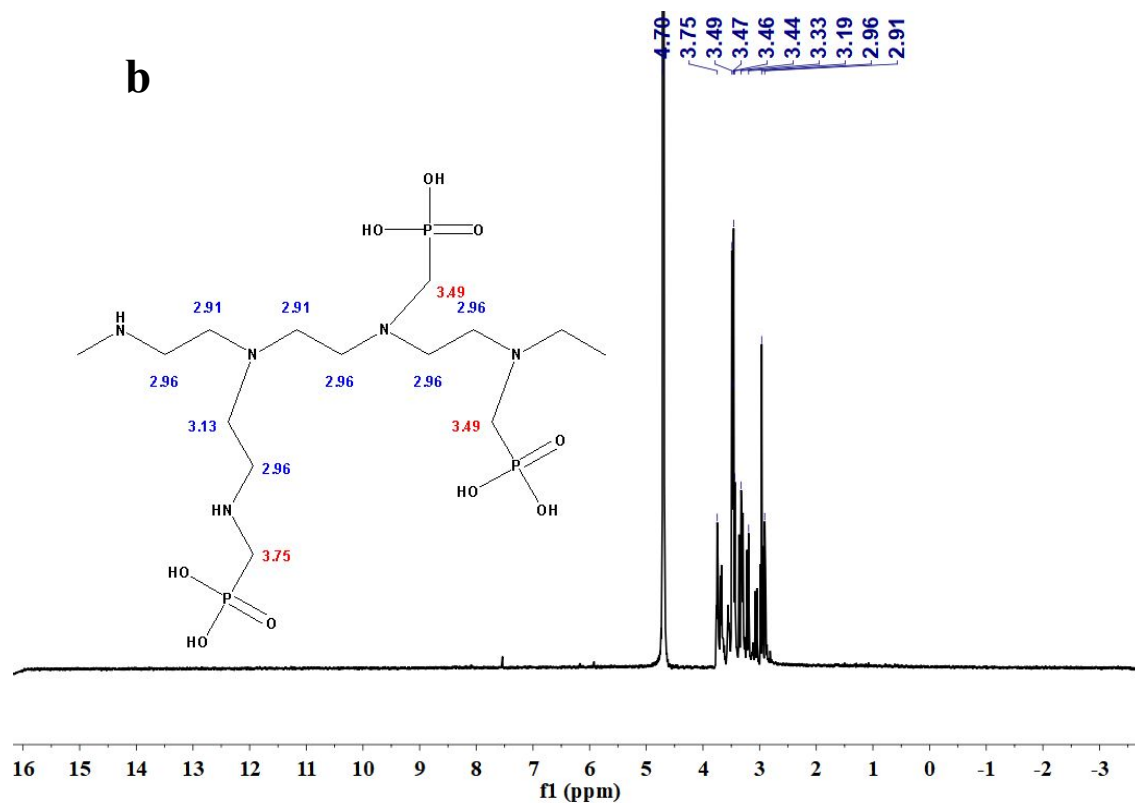
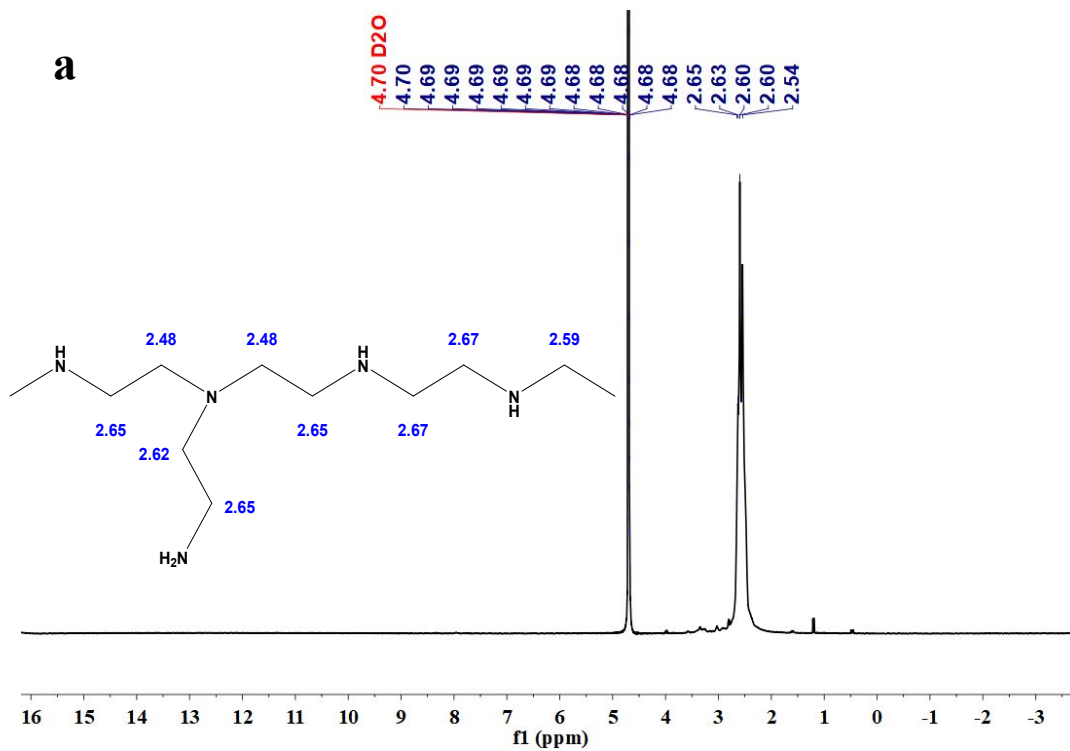


Fig.S1 Raman spectra of the PEI and PEIMPA with 50% and 100% replacement rate



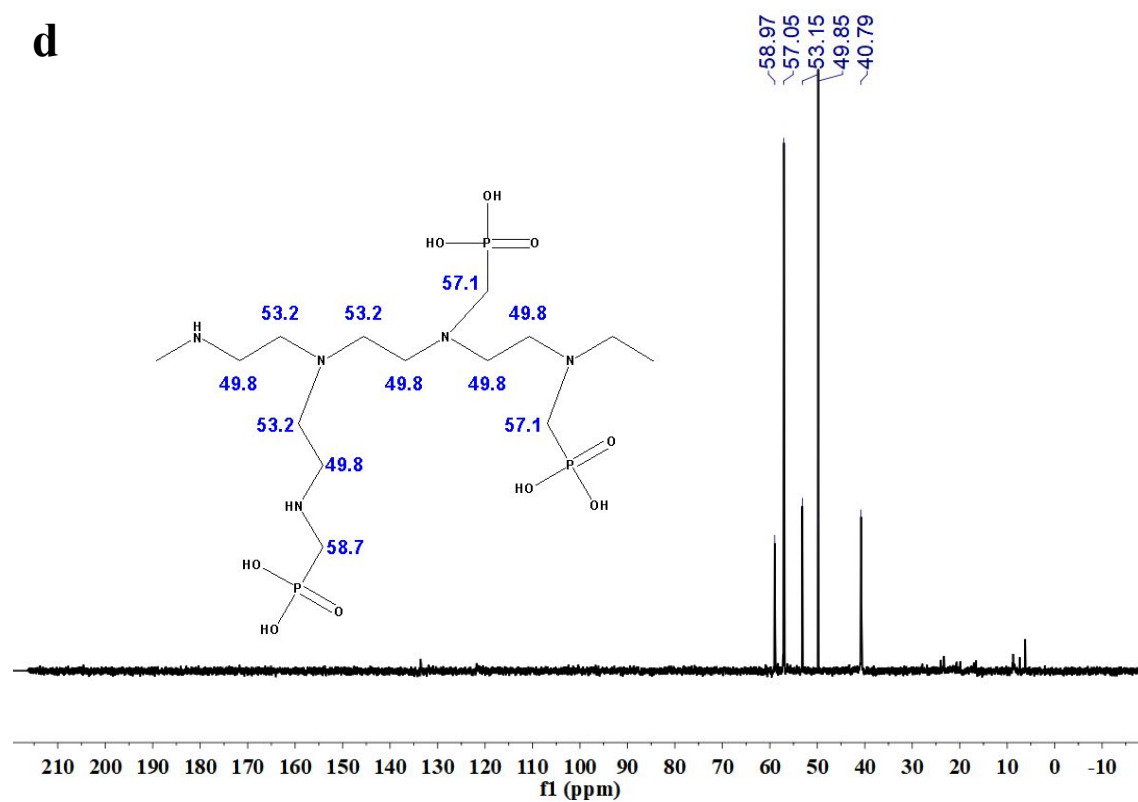
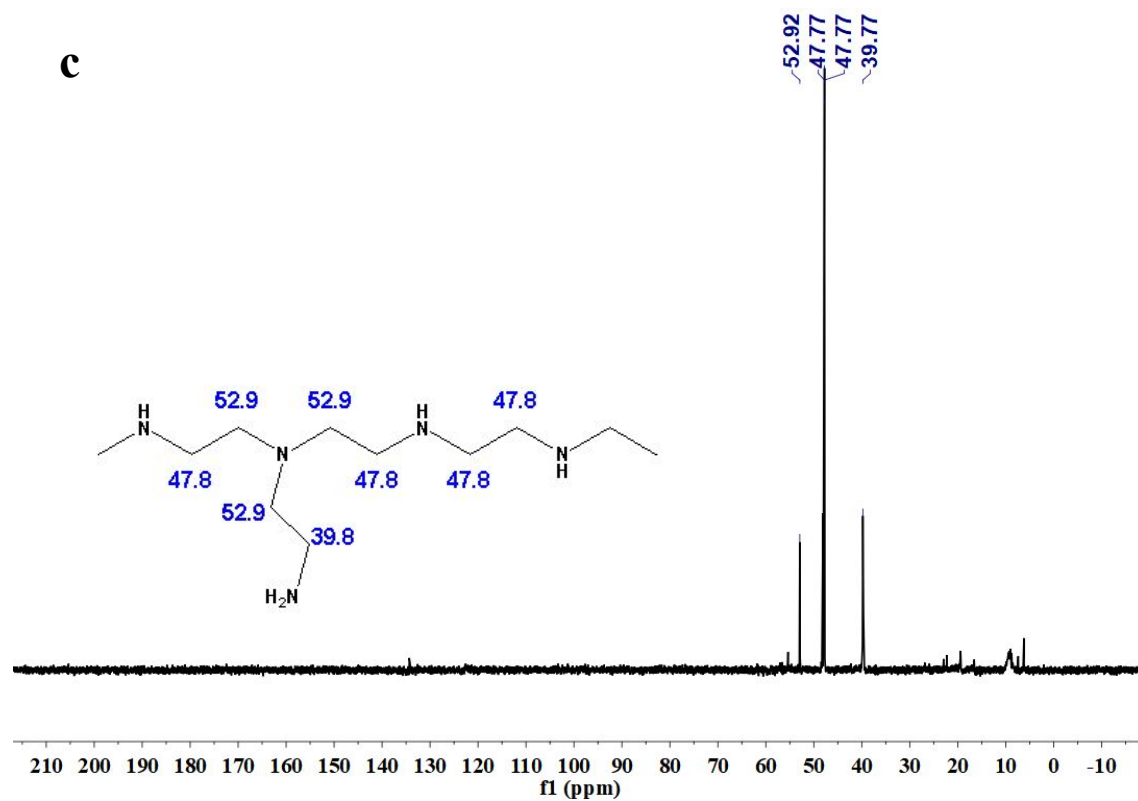


Figure S2 ^1H and ^{13}C NMR spectrum of the PEI (a,c) and PEIMPA (b,d).

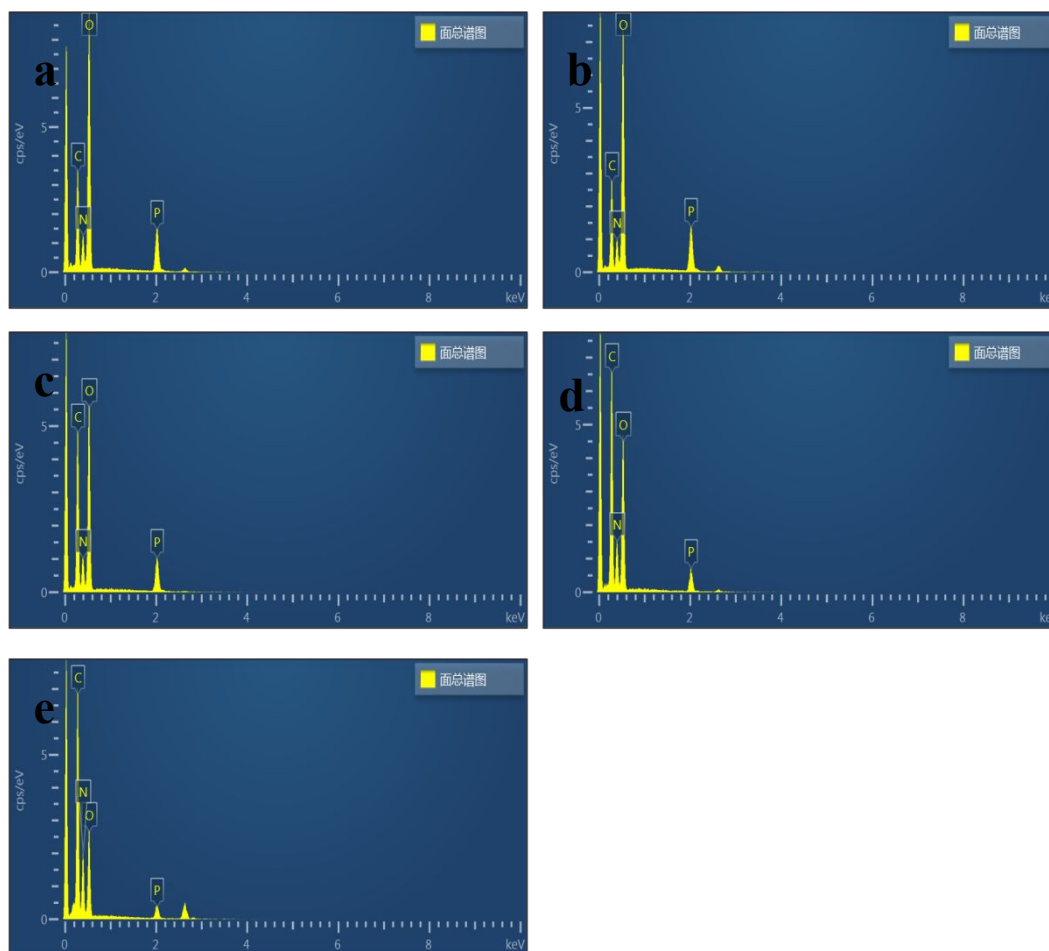


Figure S3 EDS mapping for PEI and PEIMPA with various replacement rates: (a)PEIMPA-4.5kDa-100, (b)PEIMPA-12kDa-100, (c)PEIMPA-70kDa-100, (d) PEIMPA-70kDa-75, (e)PEIMPA-70kDa-50

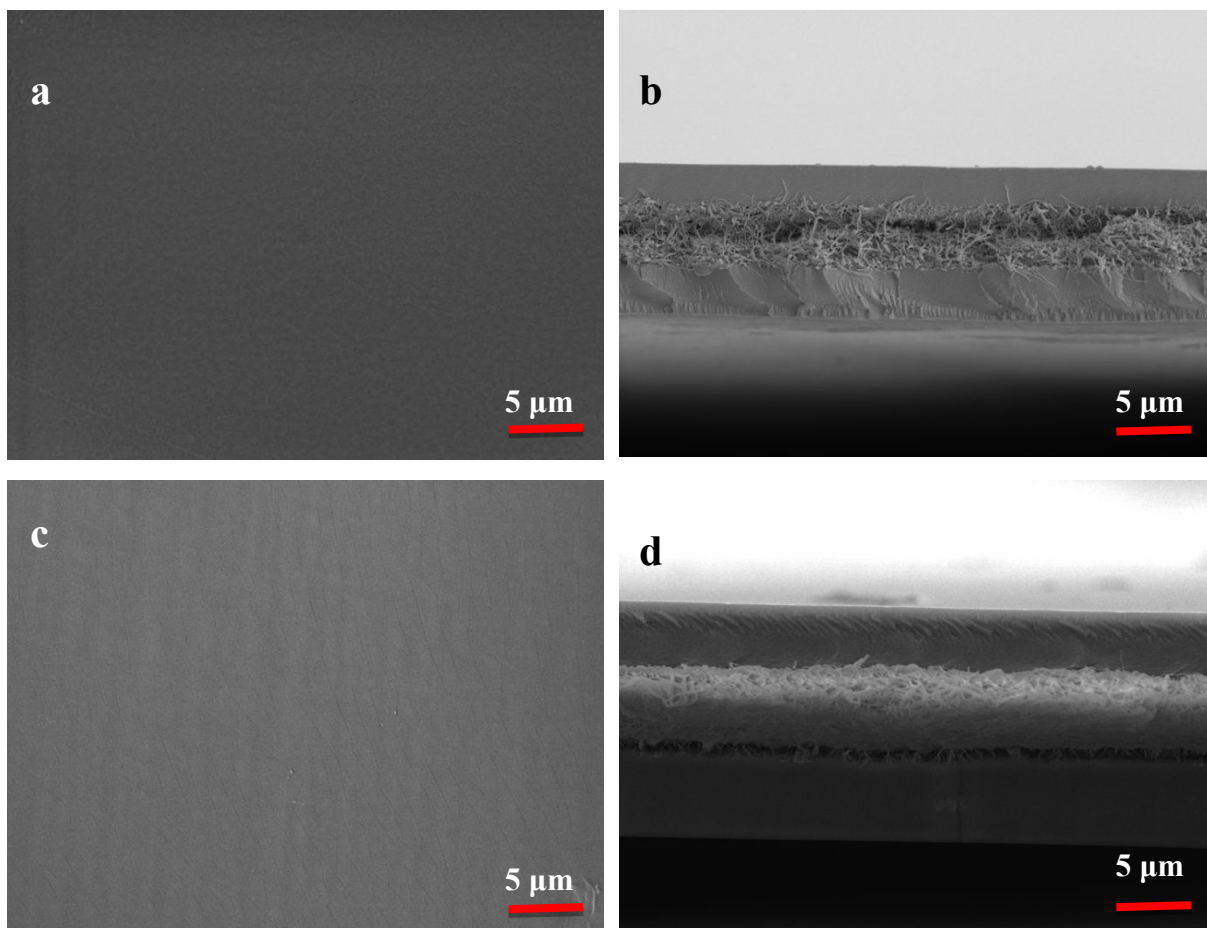


Figure S4 Surface and cross-sectional SEM image of PFSA/PEIMPA-70kDa-50 (a,b) and PFSA/PEIMPA-70kDa-100 (c,d).

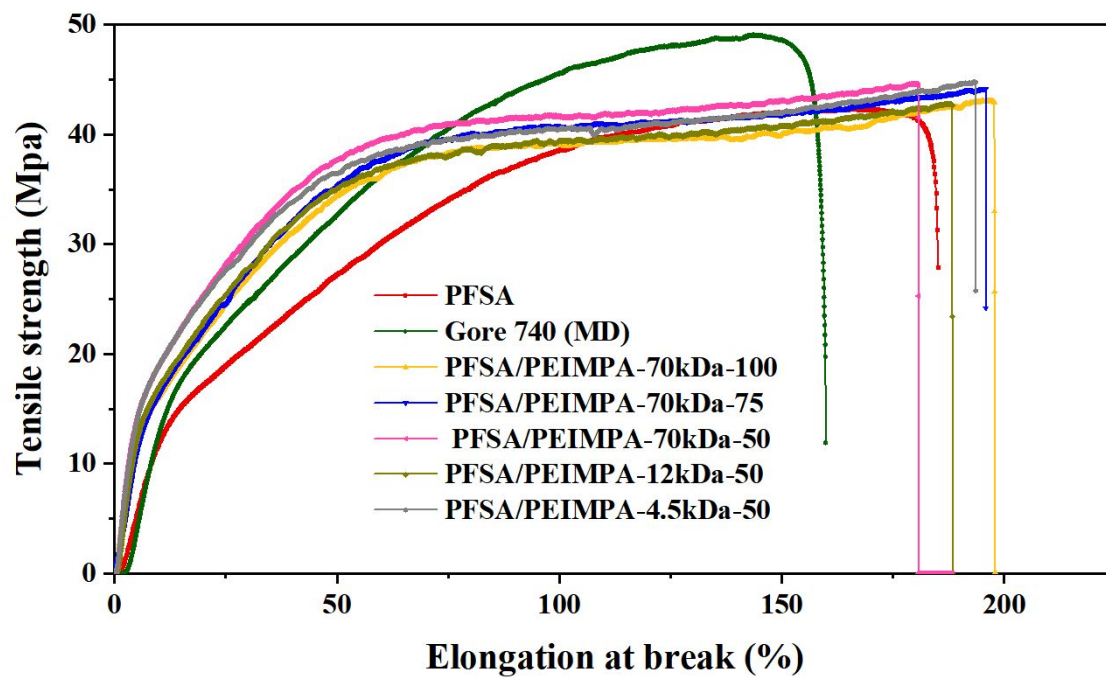
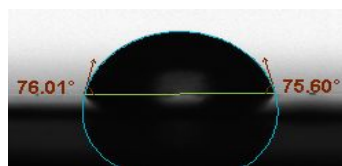
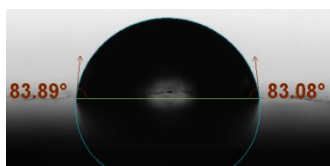


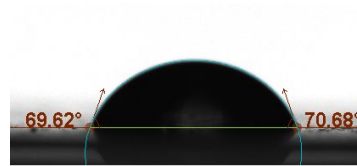
Figure S5 Stress-strain curves of PFSA , Gore 740 and PFSA/PEIMPA composite membranes.



PFSA



Gore 740



PFSA/PEIMPA-70kD-50



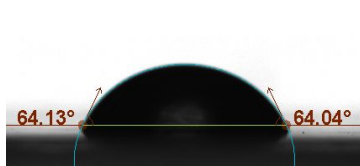
PFSA/PEIMPA-70kDa-75



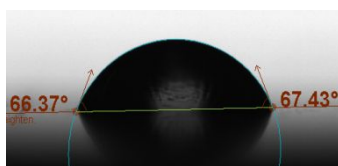
PFSA/PEIMPA-70kDa-100



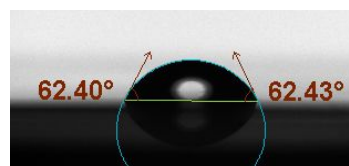
PFSA/PEIMPA-12kDa-50



PFSA/PEIMPA-12kDa-100



PFSA/PEIMPA-4.5kDa-50



PFSA/PEIMPA-4.5kDa-100

Figure S6 the contact angle image of PFSA, Gore 740 and PFSA/PEIMPA composite membranes.

Tab.S1 Element content of PEI and PEIMPA with various replacement rates based on EDS mapping

	C	O	N	P
PEI	45.27	0.03	53.69	0.01
PEIMPA-4.5kDa-100	27.72	36.29	17.62	18.37
PEIMPA-12kDa-100	29.64	34.24	18.44	17.68
PEIMPA-70kDa-100	30.20	26.59	26.24	16.97
PEIMPA-70kD-75	33.07	23.21	31.16	12.56
PEIMPA-70kDa-50	38.14	13.58	39.72	8.65

Table S2 Mechanical properties of PFSA,Gore 740 and PFSA/PEIMPA composite membranes

Membrane	Tensile strength (Mpa)	Elongation at break (%)	Young's modulus (Mpa)
PFSA	36.86±2.01	174.6±12.5	220.4±14.83
Gore740	50.24±1.84	158.4±13.9	296.2±22.3
PFSA/PEIMPA-70kDa-100	39.62±2.15	194.6±23.4	245.5±16.7
PFSA/PEIMPA-70kDa-75	41.34±1.58	184.7±26.4	262.7±19.8
PFSA/PEIMPA-70kDa-50	43.27±2.34	178.6±19.5	281.3±25.4
PFSA/PEIMPA-12kDa-100	39.87±1.43	176.8±21.1	204.3±14.2
PFSA/PEIMPA-4.5kDa-100	38.62±1.57	183.42±16.7	187.6±11.4

Table.S3 The water uptake, swelling ratio and water contact angle of the PFSA, Gore 740 and PFSA/PEIMPA composite membranes.

membrane	replacement	Water uptake	Swelling ratio	Contact angle
	rate (%)	(%)	(%)	(°)
PFSA		38.7 ± 0.48	3.86 ± 0.16	76.2 ± 1.16
Gore 740		36.8 ± 0.16	2.68 ± 0.12	84.23 ± 1.29
PFSA/PEIMPA	50	41.6 ± 0.72	3.12 ± 0.17	69.74 ± 1.56
-70kDa	75	44.8 ± 0.54	3.56 ± 0.24	67.46 ± 0.68
	100	48.9 ± 0.39	4.05 ± 0.20	65.42 ± 0.58
PFSA/PEIMPA	50	42.2 ± 0.87	3.28 ± 0.13	68.12 ± 1.35
-12kDa	75	45.2 ± 0.29	3.74 ± 0.22	66.87 ± 1.89
	100	49.6 ± 0.52	4.26 ± 0.31	64.35 ± 1.74
PFSA/PEIMPA	50	42.7 ± 0.72	3.67 ± 0.29	67.11 ± 0.94
-4.5kDa	75	45.8 ± 0.37	4.12 ± 0.17	66.12 ± 2.05
	100	50.3 ± 0.28	4.65 ± 0.35	62.55 ± 1.50