Supporting Information for

Hydrogen bond-dominated polybenzimidazole semi-interpenetrating network membranes for alkaline water electrolysis

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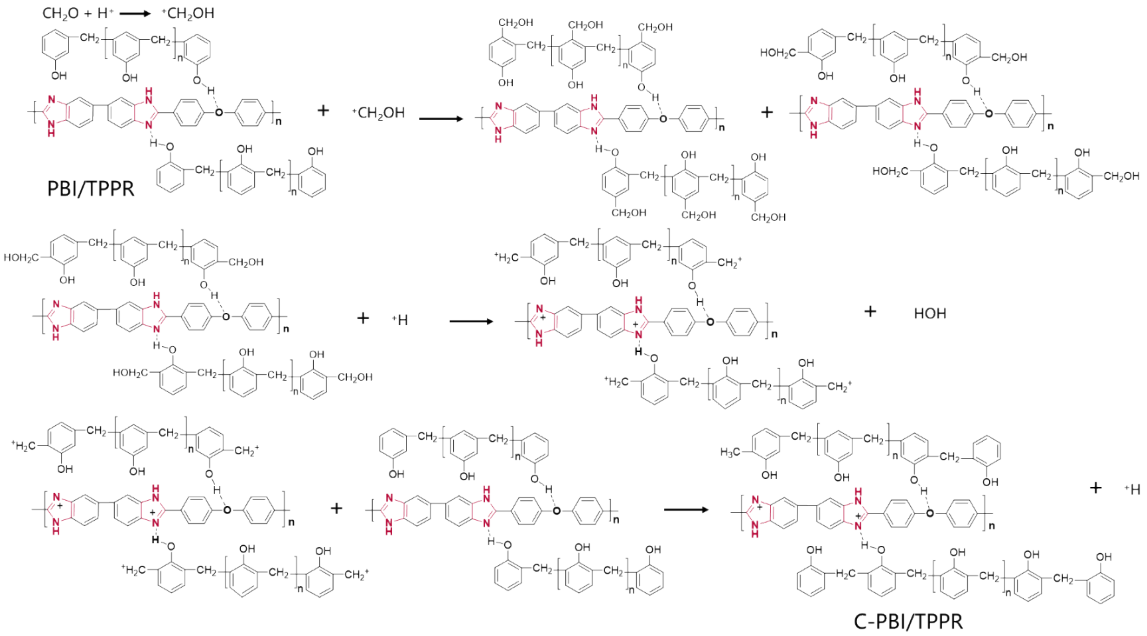
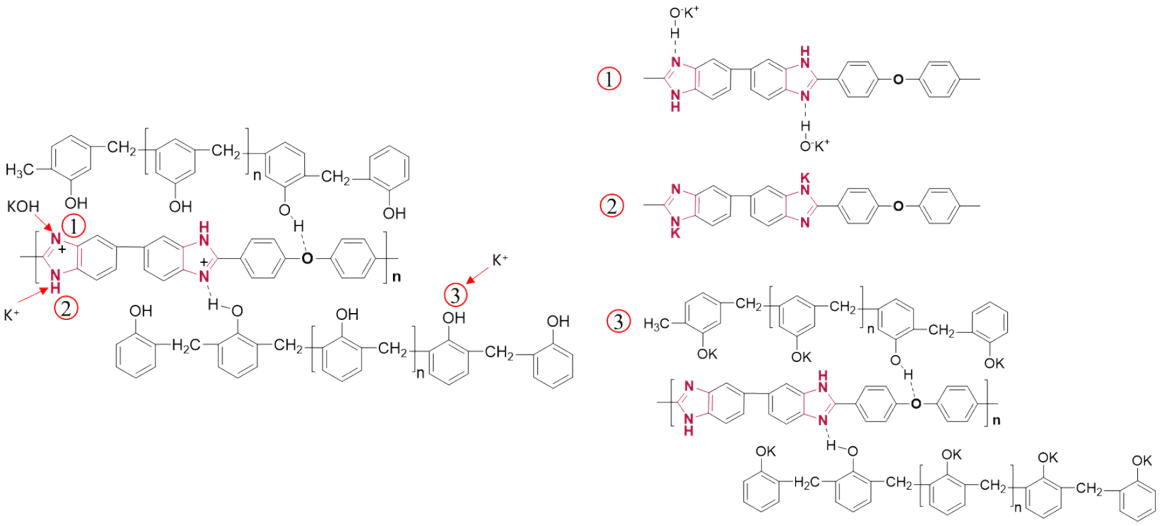


Scheme S1. the route of preparing C-PBI/TPPR membrane



Scheme S2. Three possible combinations between C-PBI/TPPR and KOH.

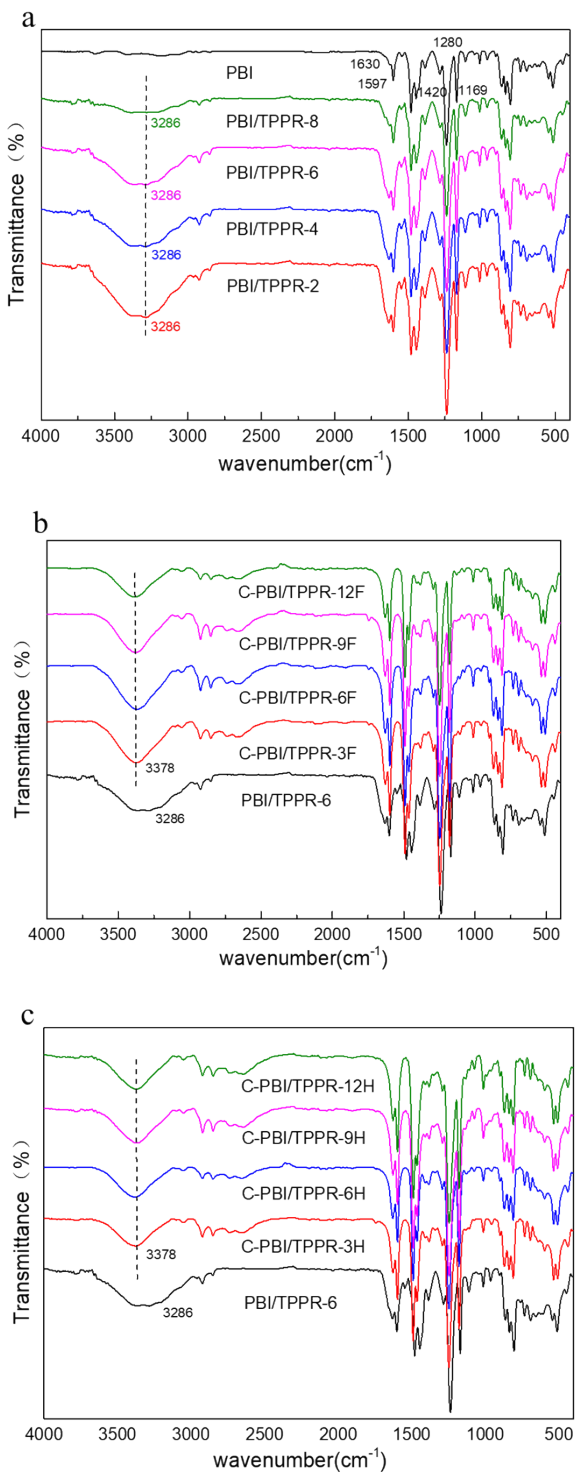


Fig. S1. FTIR spectra of (a) PBI/TPPR-X, (b) C-PBI/TPPR-YF and (c) C- PBI/TPPR-ZH membranes.

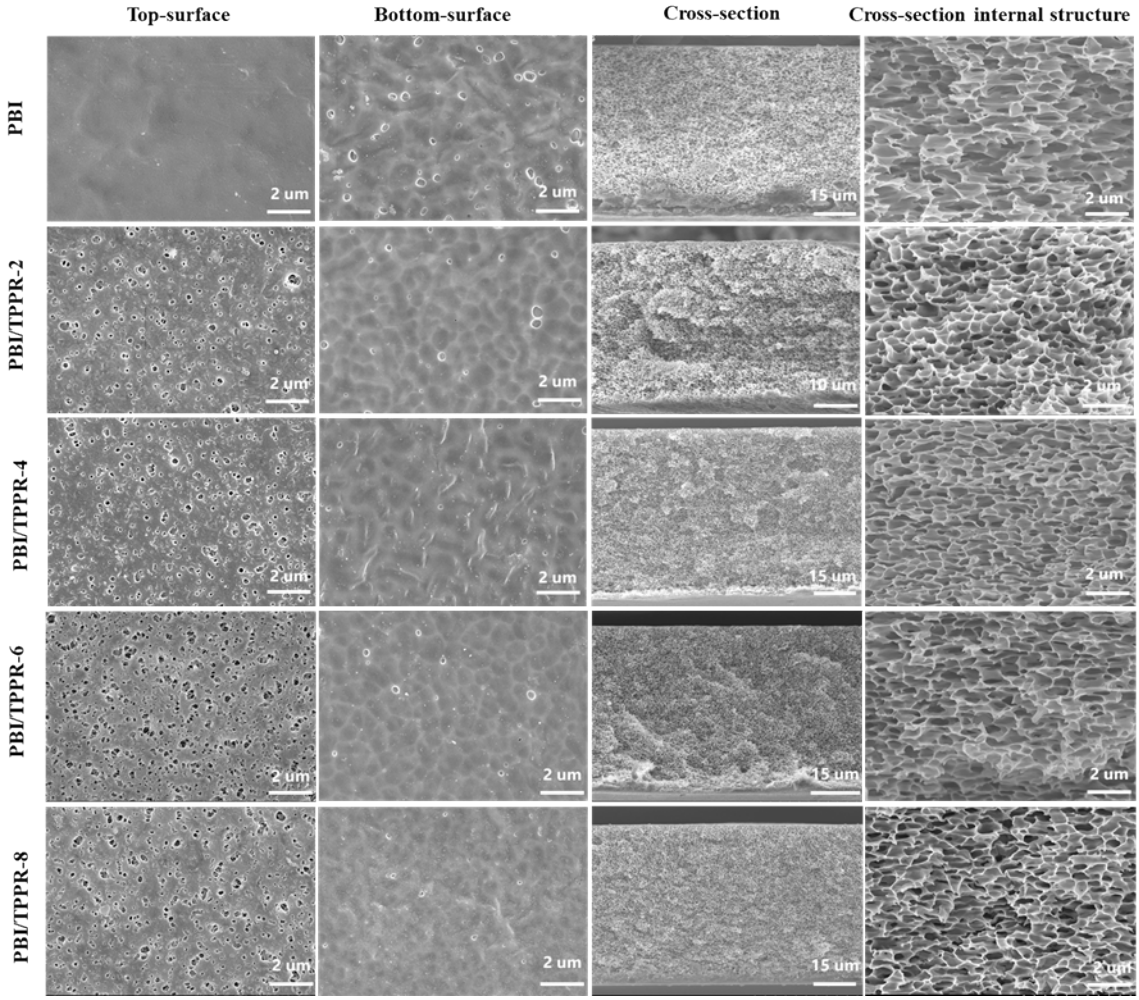


Fig.S2. SEM morphology of PBI, PBI/TPPR-2, PBI/TPPR-4, PBI/TPPR-6, PBI/TPPR-8 membranes

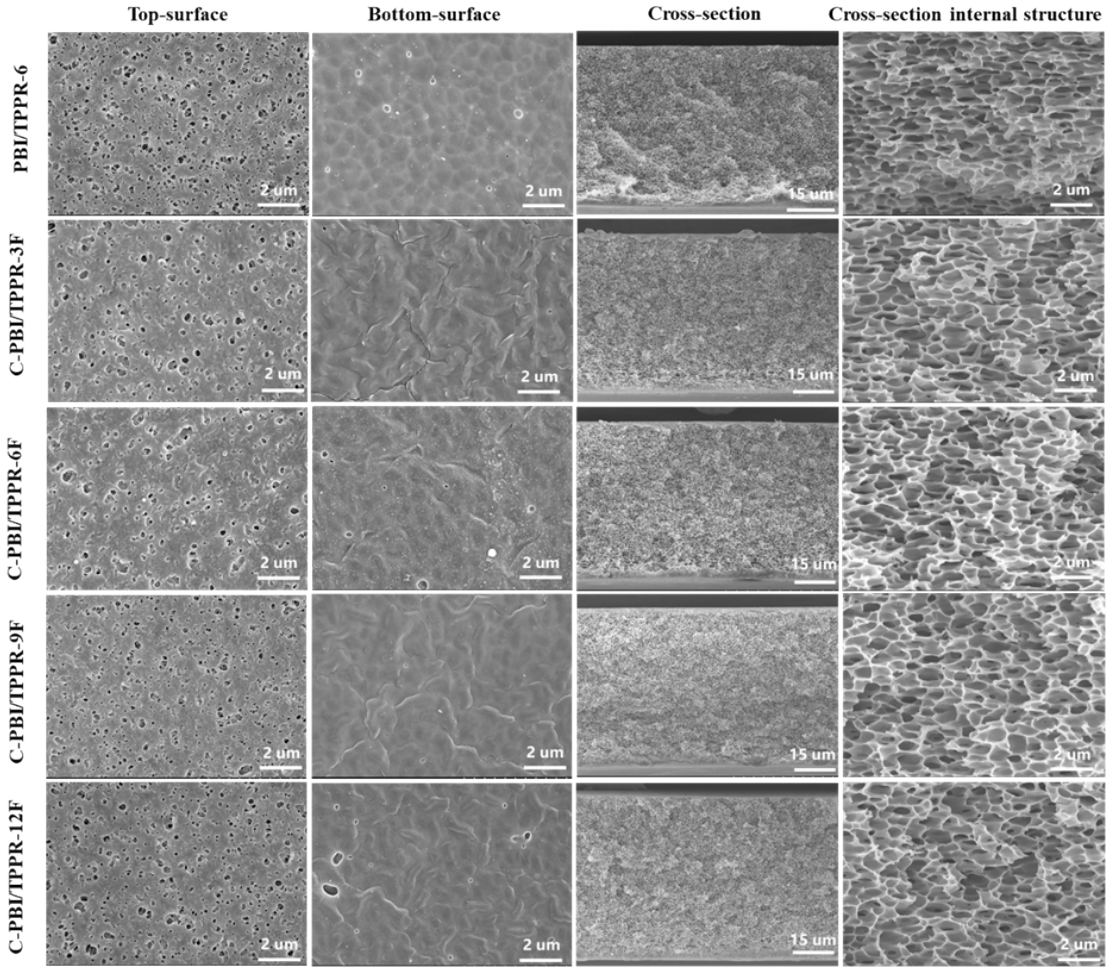


Fig.S3. SEM morphology of PBI/TPPR-6, C-PBI/TPPR-3F, C-PBI/TPPR-6F, C-PBI/TPPR-9F, C-PBI/TPPR-12F membranes

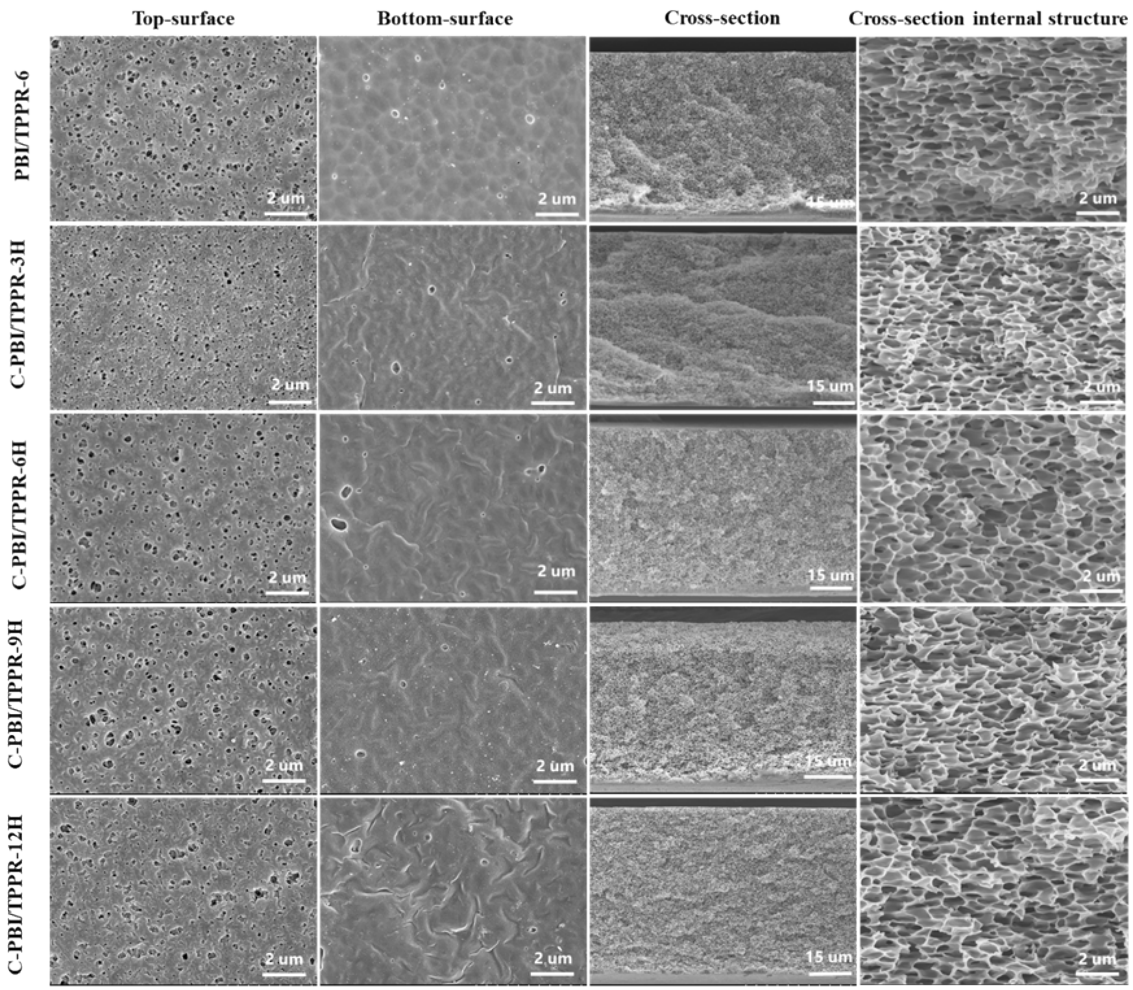


Fig.S4. SEM morphology of PBI/TPPR-6, C-PBI/TPPR-3H, C-PBI/TPPR-6H, C-PBI/TPPR-9H, C-PBI/TPPR-12H membranes

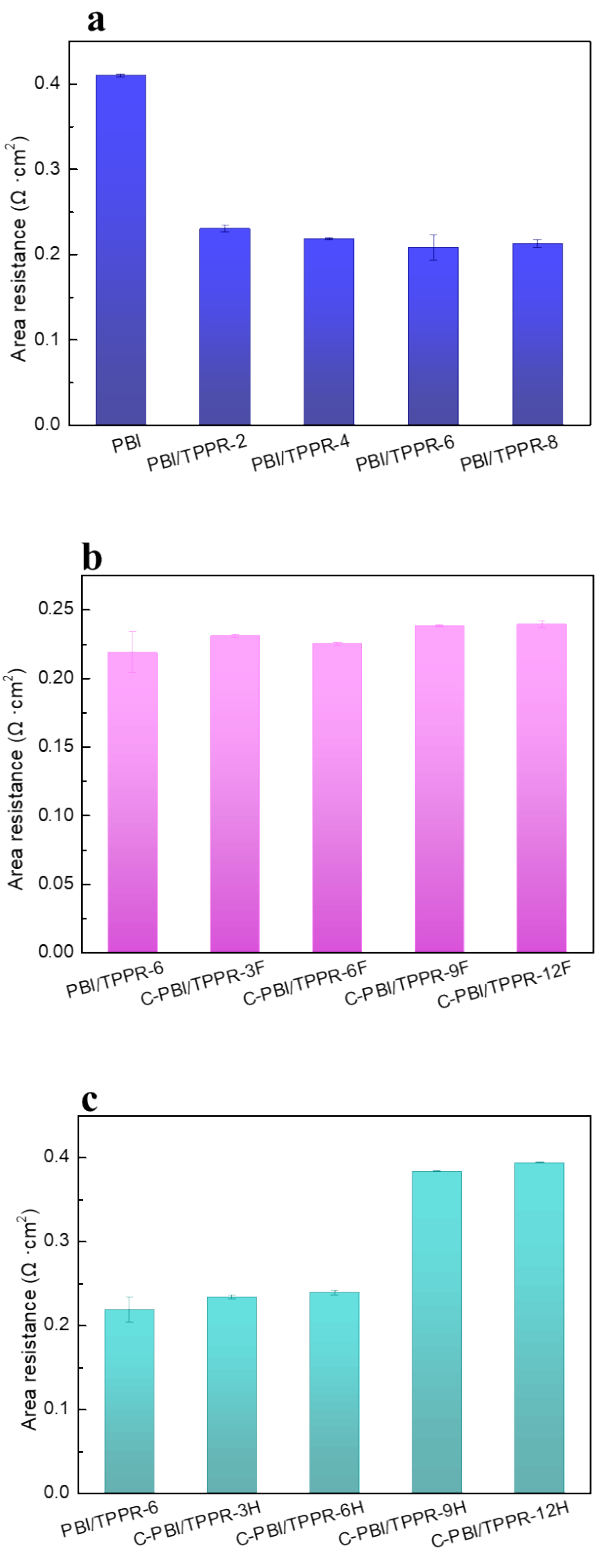


Fig. S5. Area resistance of pristine PBI, PBI/TPPR-X and C- PBI/TPPR-YF membranes in 1M KOH solution

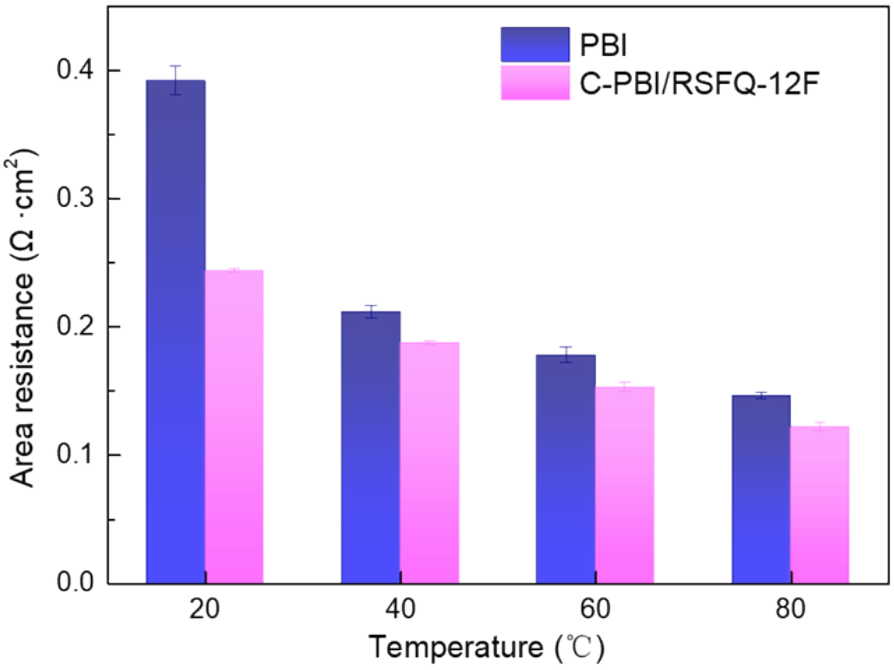
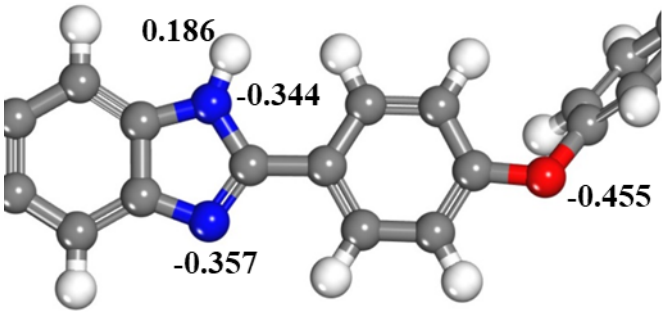


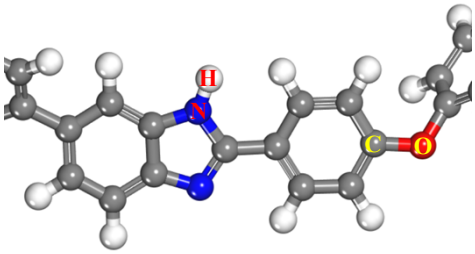
Fig. S6. Area resistance of pristine PBI and C- PBI/TPPR-YF membranes in 1M KOH solution at different temperatures

a

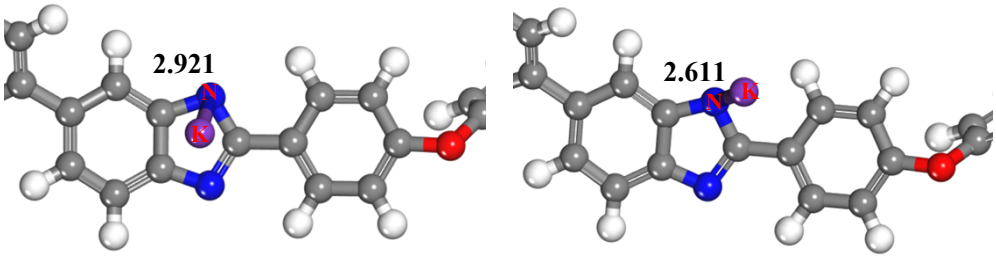


b

PBI

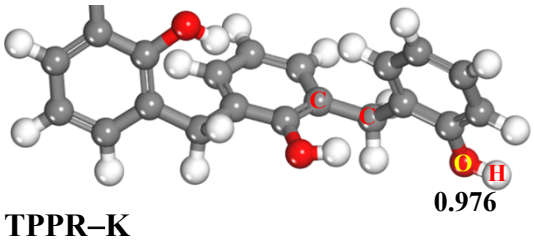


PBI–K



0 kJ/mol **10.98 kJ/mol**

TPPR



TPPR–K

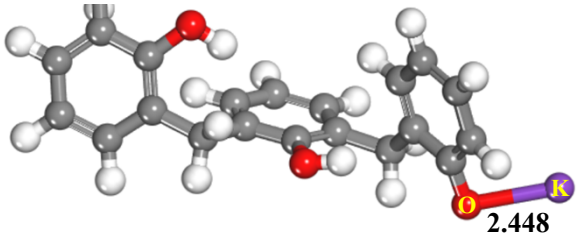


Fig. S7. (a) Mulliken charge distribution and (b) binding energy

Table S1 Binding energy (kJ/mol) and bond length (Å) for PBI, TPPR and related systems

System	Chemical bond	Binding energy	Bond length
PBI	**N–H**	**383.31**	**1.013**
	C–O	314.82	1.393
PBI–K	**N–K**	**301.74**	**2.921**
TPPR	**O–H**	**363.21**	**0.976**
	C–O	460.13	1.387
	C–C	372.68	1.518
TPPR–K	**O–K**	**283.55**	**2.448**
PBI···TPPR	N···H–O	67.05	1.717
	O···H–O	35.66	1.788
	NH··· O	33.72	2.090

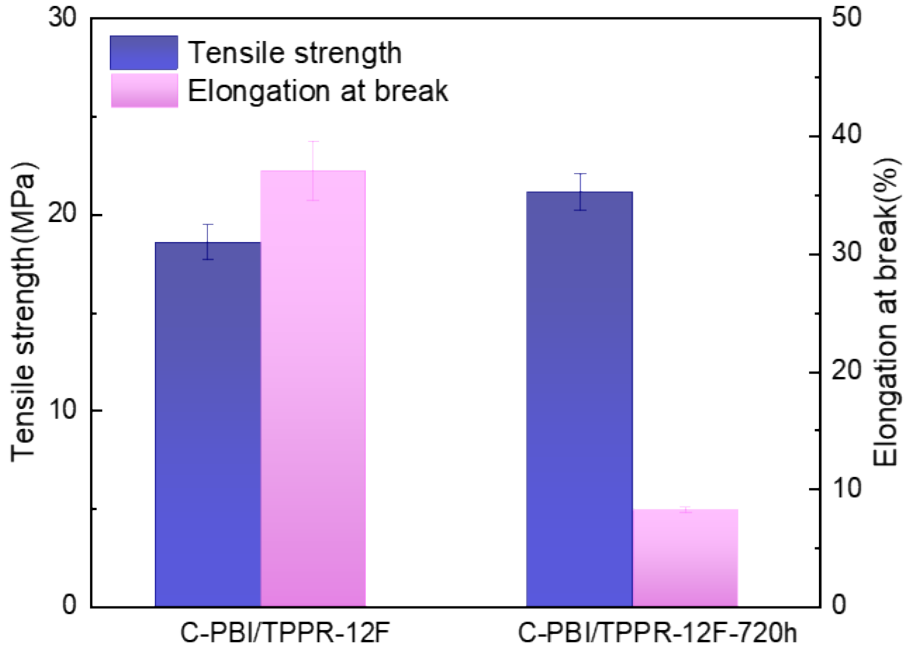
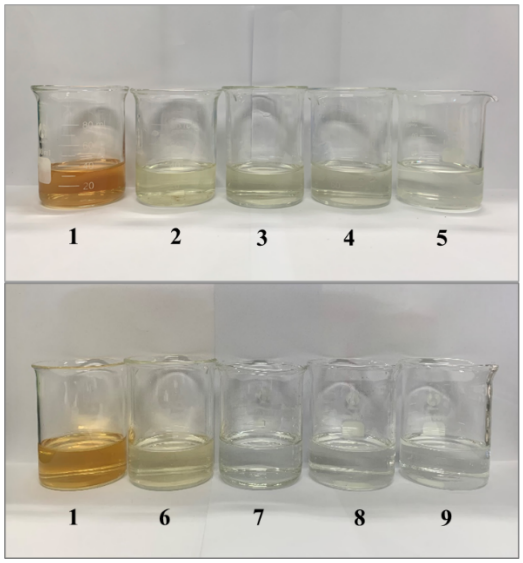


Fig. S8. Stress-strain behavior of C-PBI/TPPR-12F membrane before and after 720 h alkaline treatment



Number	CH_2O	HCl
1	0%	0%
2	3%	6%
3	6%	6%
4	9%	6%
5	12%	6%
6	12%	3%
7	12%	6%
8	12%	9%
9	12%	12%

Fig. S9. Chemical stability of C-PBI/TPPR membranes cross-linked with different concentrations of formaldehyde and hydrochloric acid

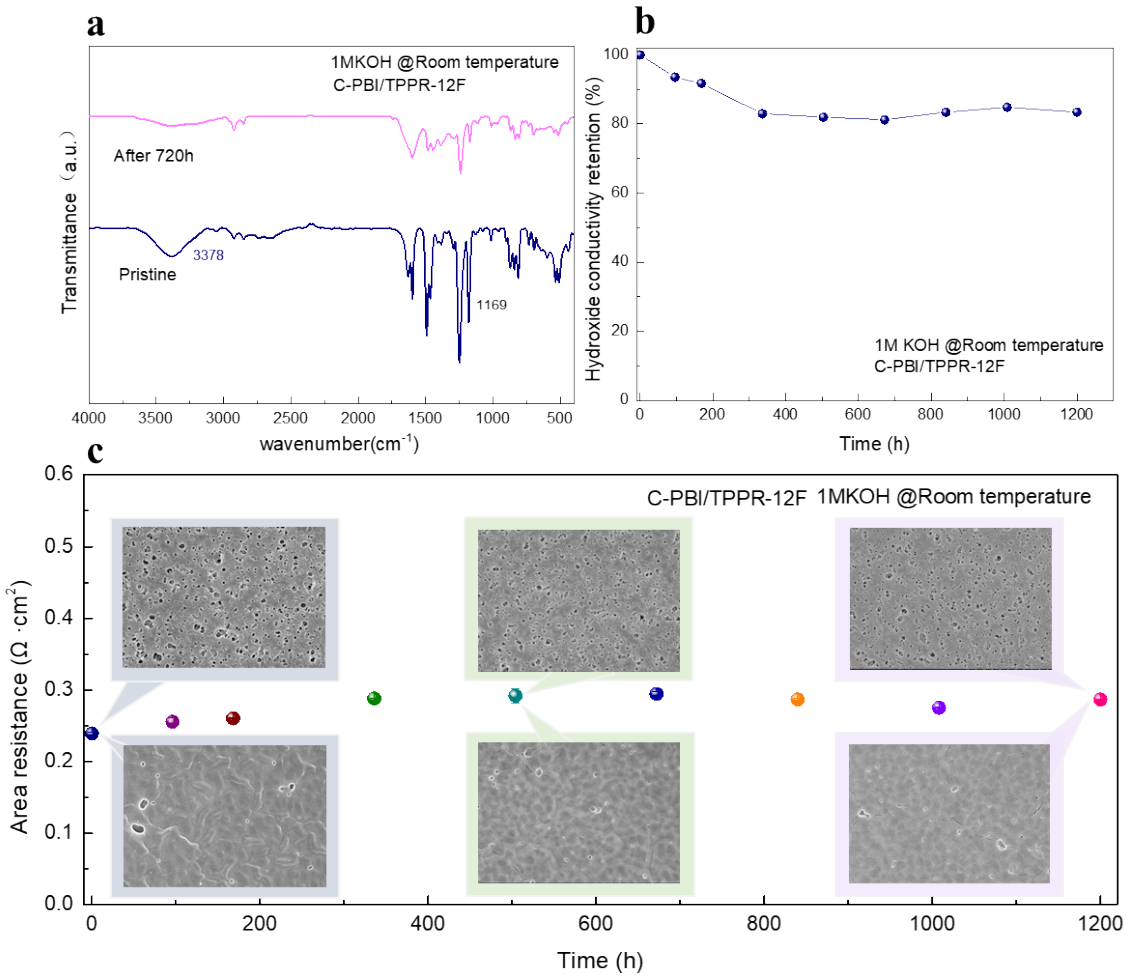


Fig.S10. Alkaline stability of the C-PBI/TPPR-12F membrane in 1 M KOH at Room temperature: (a) ATR-FTIR spectra, (b) hydroxide conductivity remaining; (c) SEM surface morphology before and after 720 h alkaline treatment and change in area resistance during 720h.

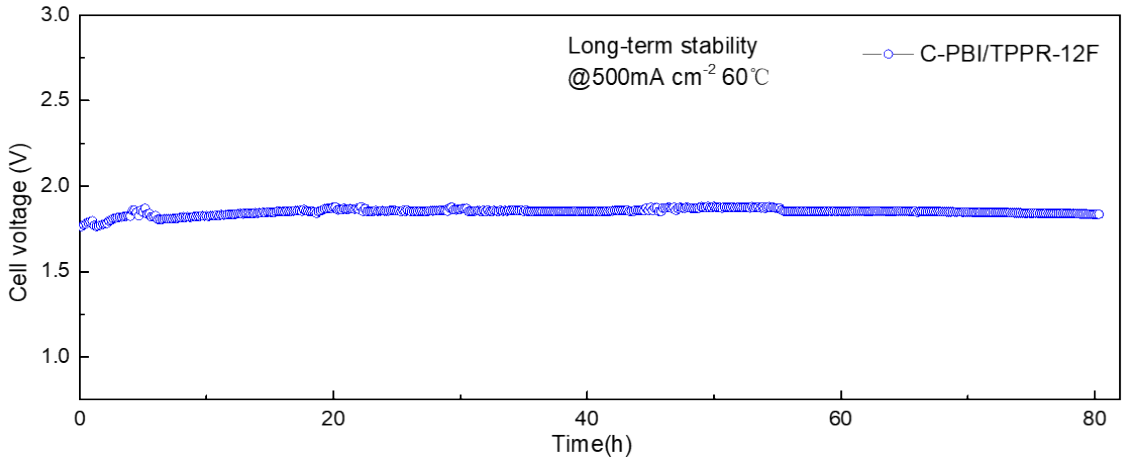


Fig. S11. Chemical stability of C-PBI/TPPR membranes cross-linked with different concentrations of formaldehyde and hydrochloric acid

Table S2 Surface composition of pristine PBI, PBI/TPPR-6 and C- PBI/TPPR-12F membrane determined by XPS analysis.

Name	C1s	N1s	O1s	O1s/ C1s (%)	N1s/ C1s (%)
PBI	74.96	10.09	14.95	19.94	13.46
PBI/TPPR-6	72.52	7.12	20.37	28.09	9.82
C-PBI/TPPR-12F	80.08	3.86	16.05	20.04	4.82

Table S3 Surface composition of C-PBI/TPPR-12F composite membranes before and after alkaline stability test by XPS analysis.

Name	C1s	N1s	O1s	K2p	O1s/ C1s (%)	N1s/ C1s (%)
C-PBI/TPPR-12F- after 720h (1MKOH Room temperature)	75.32	6.01	15.35	3.32	20.38	7.98
C-PBI/TPPR-12F- after 720h (3MKOH 80℃)	76.02	8.53	13.61	1.84	17.90	11.22