Electronic Supplementary Information

Performance and Stability of Ether-free High Temperature Proton Exchange Membranes with Tunable Pendent Imidazolium Group

Qing Ju[a,b], Hongying Tang[c*], Ge Chao[a,b], Tiegen Guo[d], Kang Geng [a*], Nanwen Li[a,b*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China.

[b] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China.

[c] Tianjin Key Laboratory of Water Resources and Environment, Tianjin Normal University, Tianjin 300387, China.

[d] College of Chemical Engineering and Technology, Taiyuan University of Technology, Taiyuan 030024, China.

*Corresponding author E-mail: hytang@tjnu.edu.cn; gengkang@sxicc.ac.cn; linanwen@sxicc.ac.cn

Synthesis of poly (biphenyl imidazole)

To a 100 ml three-necked round-bottom flask equipped with a mechanical stirrer was added biphenyl (1.54 g, 10 mmol), 4-imidazolecarboxaldehyde (0.96 g, 10 mmol), and 10 mL dichloromethane. Then, the mixture was added dropwise 10 mL TFSA under mechanical stirring with a temperature of 0 ℃. After another 3-5 h of continuous stirring, the mixture turned into a blue-green viscous solution and then it was precipitated in deionized water, white fiber polymer was obtained. The product was washed several times with hot DI water to remove residual acid. Finally, the resulting product was filtered and dried in a vacuum oven at 100 ℃ for 24 hours.

Synthesis of poly (biphenyl isatin)

To a 100 ml three-necked round-bottom flask equipped with a mechanical stirrer was added biphenyl (1.54 g, 10 mmol), isatin (1.47 g, 10 mmol) and 10 mL dichloromethane. Then, the mixture was added dropwise 10 mL TFSA under mechanical stirring with a temperature of 0 ℃. After another 3-5 h of continuous stirring, the mixture turned into a blue-green viscous solution and then it was precipitated in deionized water, white fiber polymer was obtained. The product was washed several times with hot DI water to remove residual acid. Finally, the resulting product was filtered and dried in a vacuum oven at 100 ℃ for 24 hours.

Synthesis of poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (*m*PBI)

In a 100 mL three-neck-round-bottomed flask equipped with a mechanical stirrer and N_2 inlet and an outlet, isophthalic acid (1.6613 g, 10 mmol), DAB (2.1427 g, 10 mmol), and PPA (72 g) were added in sequence. The reaction mixture was stirred at 80 ^{o}C for 2 h until the monomers completely dissolved in PPA solution and then stirred at 120 ^{o}C for 2 h, 140 ^{o}C for 3 h, 180 ^{o}C over 8 h. As the reaction proceeded, the system became a golden yellow viscous solution, which was poured into 500 mL DI water and fibrous polymer was formed, washed with DI water several times, neutralized in $NaHCO_3$ solution overnight, rinsed several times with water and then dried at 120 ^{o}C in vacuum oven till constant weight.

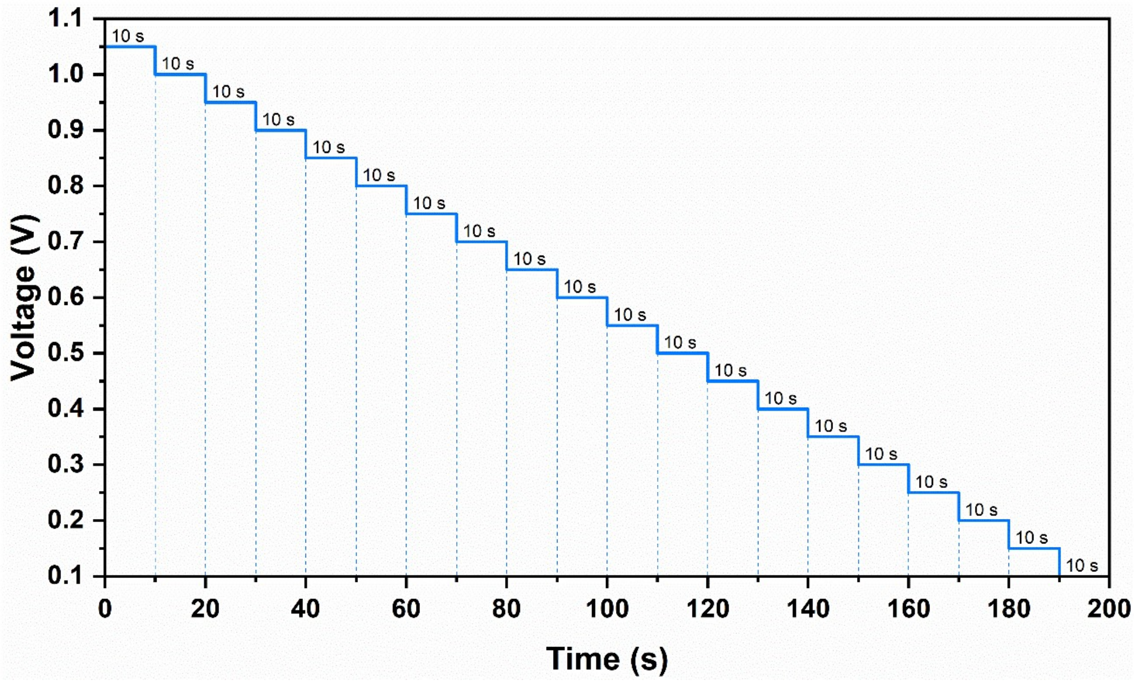

Fig. S1 Polarization curve test protocol.

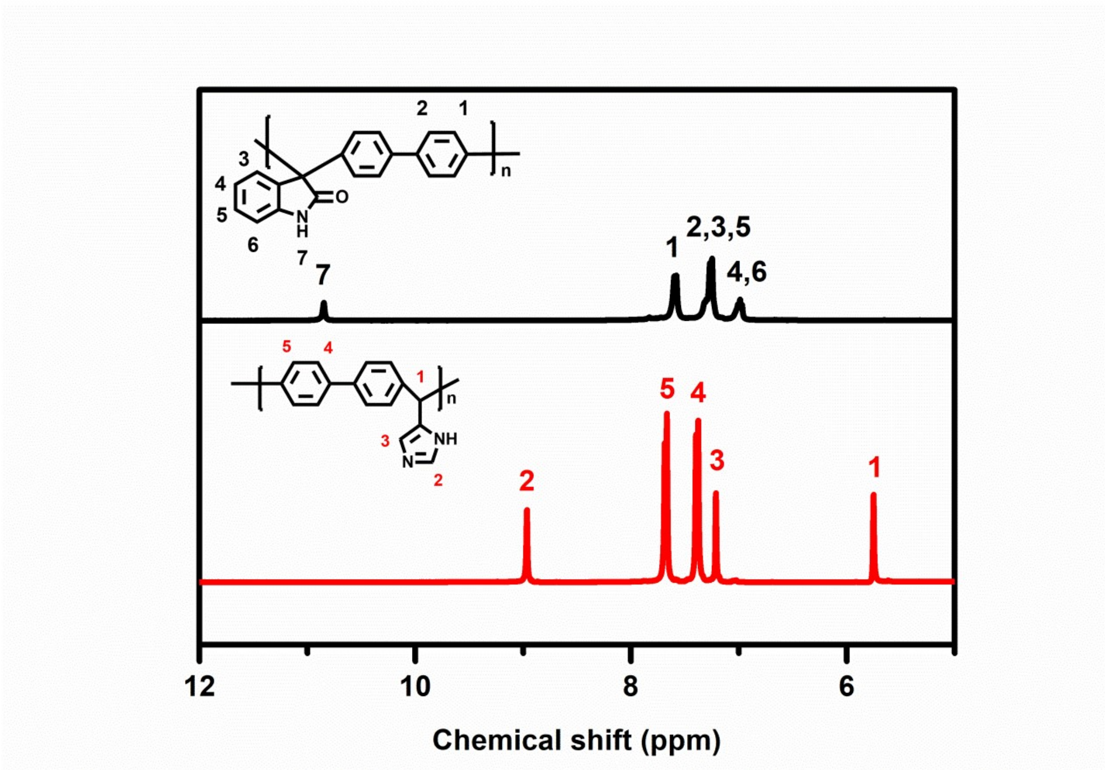

Fig. S2 ^{1}H NMR of poly (biphenyl imidazole) and poly (biphenyl isatin) (solution in DMSO-d_6).

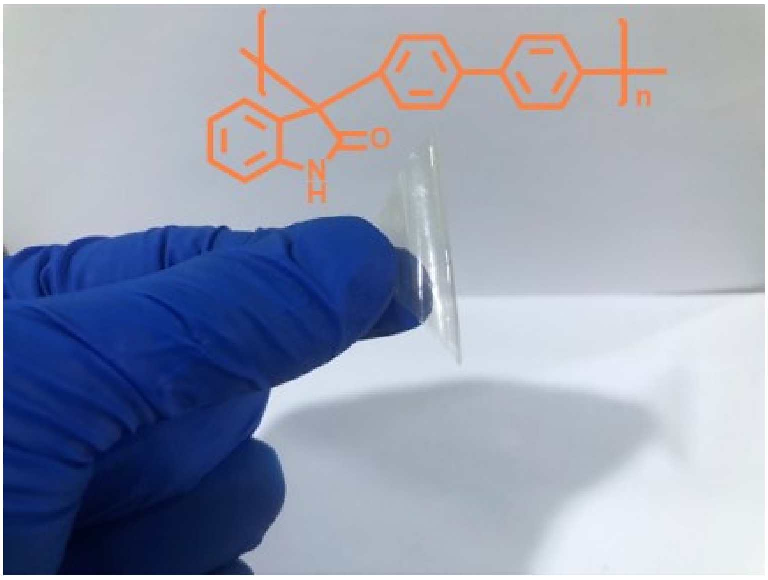

Fig. S3 Poly (biphenyl isatin) membrane solubility in 85 wt% PA solution at 80 ℃ more than 48 h.

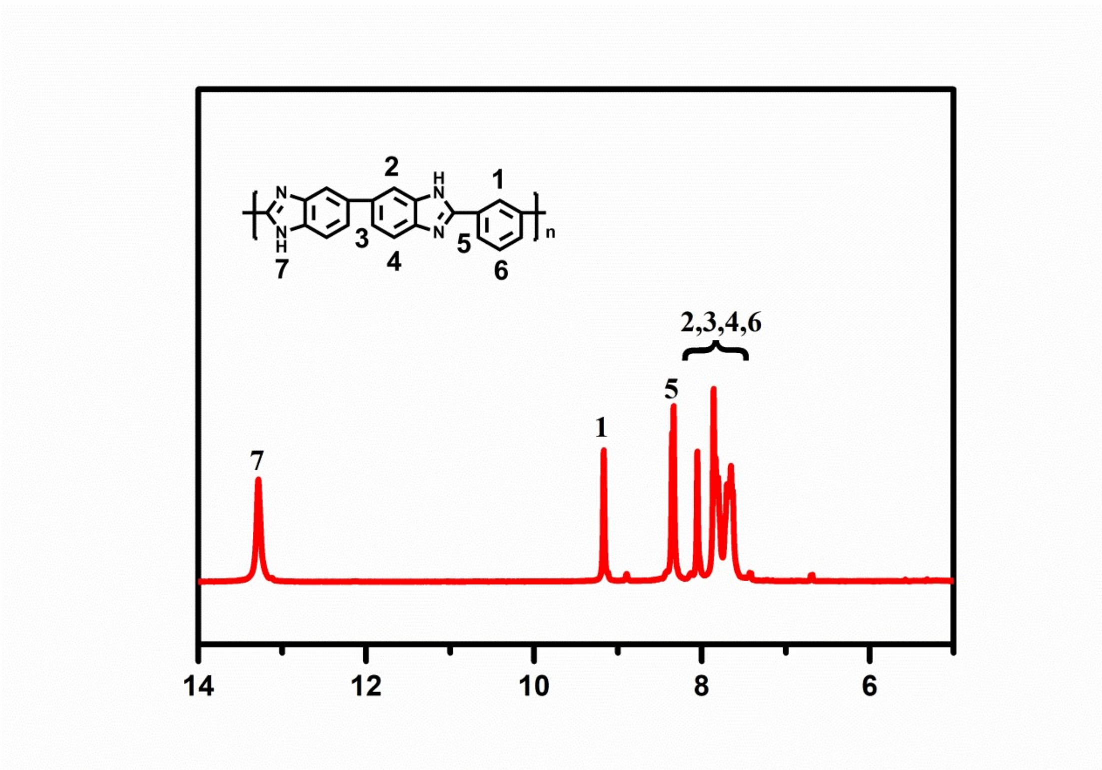

Fig. S4 ^{1}H NMR of *m*PBI polymer used for fuel cell test in this work (solution in DMSO-d_6).

Table S1 Mechanical properties of PIBI-70 and PIBI-Qx membranes.

Membranes	PIBI-70	PIBI-Q60	PIBI-Q70	PIBI-Q80

	undoped	doped	undoped	doped	undoped	doped	undoped	doped
Tensile strength (MPa)	99.3	14.1	111.7	12.1	125.2	4.1	107.7	3.9
Elongation at break (%)	14.5	46.0	7.0	25.0	10.8	33.6	6.0	39.0
Young's modulus (MPa)	2175.7	208.5	2505.3	192.6	2727.0	29.0	2411.3	27.0

Table S2 The thickness of all membranes before and after doped with PA for fuel cell test.

Membranes	Thickness (before)	Thickness(after)
PIBI-70	65 μm	105 μm
PIBI-Q60	70 μm	102 μm
PIBI-Q70	64 μm	100 μm
PIBI-Q80	66 μm	104 μm
***m*PBI**[a]	50 μm	102 μm

[a]With thickness swelling of 103.0%

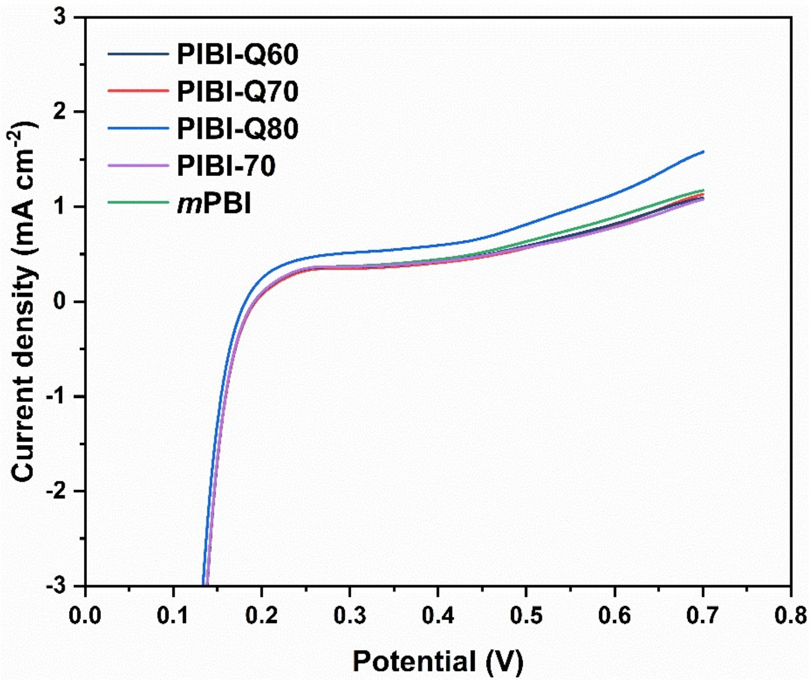

Fig. S5 The crossover current density of the PA doped PIBI-Qx/PIBI-70 and PBI membranes on single cells at 160 °C.

Table S3 Comparison of OCV, peak power density, Pt loading and fuel gas of single cell for PIBI-Qx membrane with PBI-based HT-PEM reported from 2019 to 2021.

Membranes	**OCV (V)**	**Peak power density (mW cm^{-2})**	**Fuel gas**	**Pt loading (mg cm^{-2})**	**Ref.**
PIBI-Q80 (104 μm)	0.92	600.0	H_2/O_2	0.5	This work
*m*PBI-333%PA (102 μm)	1.01	522.5	H_2/O_2	0.5	This work
30%-CTFs-OPBI (about 50 μm)	0.94	534.7	H_2/O_2	1.0	1
NbPBI-TSPDO$_{30}$ (84 μm)	1.01	159	H_2/air	---	2
PBI/SPAEK-SPOSS-1% (not given)	>0.90	300	H_2/O_2	0.6	3
p-PBI@NH_2-POSS-10 (not given)	>0.943	486	H_2/O_2	1.0	4
Ph(CF_3)-pyOPBI (68 μm)	>0.91	240.02	H_2/O_2	0.6	5
OPBI-0.8AM (not given)	0.90	565	H_2/O_2	1.0	6
PA/PBI/1Mus (not given)	~1.00	586	H_2/O_2	1.0	7
1%-OPBI (about 50 μm)	>0.98	597.5	H_2/O_2	0.6	8

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