

Supporting Information

Preparation of novel membranes with multiple hydrogen bonding sites and π -conjugated structure for high temperature proton exchange membrane fuel cells

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1. Experiment

1.1 Materials

Dibenzofuran, isatin, trifluoromethanesulfonic acid (TFSA) and 2,3-Epoxypropyltrimethylammonium chloride were procured from Adamas Reagent Ltd. 3-Chloropropyl(trimethoxy)silane was obtained from Energy Ltd. Anhydrous ether and sodium bicarbonate (NaHCO_3) were purchased from Sinopharm Chemical Reagent Co. Ltd and Dimethyl sulfoxide (DMSO) were obtained from Damao Chemical Reagent Factory. Dichloromethane (DCM) was supplied by Fuyu Chemical Reagent Factory. Notably, all chemicals utilized in this study were used without further purification.

1.2 Synthesis of PBFI and PBFI-*x*%GTA

Fig. 1 illustrates the synthesis of the PBFI polymer through a super electrophilic reaction catalyzed by TFSA. Initially, dibenzofuran (2.00 g, 11.8 mmol) was dissolved in DCM (15 mL) in a two-necked flask under mechanical agitation until completely dissolved. Subsequently, isatin (2.62 g, 17.8 mmol) was added to obtain an orange-red color solution. Continuous mechanical stirring was maintained while slowly adding TFSA (9.5 mL) into the reaction mixture under an ice bath. 30 min later, the ice bath was taken out, and the reaction was able to proceed at room temperature (RT) with stirring for an additional 4 hours. Noting that the viscosity of the solution has increased to a suitable

range, the solution was poured into a 1 M NaHCO₃ solution to precipitate the final yellow fibrous polymer. Afterwards, the product was crushed into powder form using a grinder, followed by thoroughly washed in deionized water to remove excess acid. At last, the yielded polymer was dried in an oven at 80 °C for 24 h, yielding the yellow polymer.

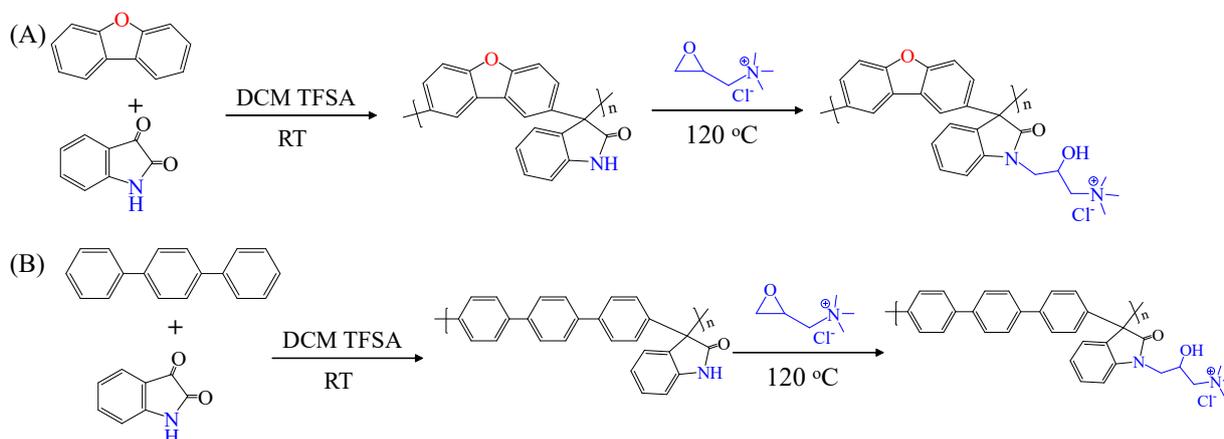


Fig. 1 Synthesis of PBFI (A) and PTI (B), and fabrication of GTA grafted membranes

1.3 Fabrication of PBFI-*x*%GTA membranes

PBFI (1.00 g 3.36 mmol) was dissolved in DMSO (30 ml) in a round-bottomed flask, and the temperature was raised to 120 °C. After the polymer was completely dissolved, 2, 3-epoxy-propyl trimethylammonium chloride (0.765 g 5.05 mmol) was added, and the mixture was stirred at 120 °C for 12 h. During this period, the color of the mixed solution changed from yellow to deep red, and then the grafted product was dropped into anhydrous ether for precipitation for 12 h, filtered and dried, and the obtained polymer showed deep red. The polymer with different grafting degree was obtained by controlling the molar amount of 2, 3-epoxy-propyl trimethyl ammonium chloride added. Similarly, the resulting polymer was dissolved using DMSO, then coated on a glass plate with a diameter of 60mm and placed in a vacuum oven at 80°C for 12 h. The resulting film is rinsed with deionized water to remove residual solvents. The resulting film was uniformly transparent and named PBFI - *x*%GTA, where *x*% represented different grafting degrees, and finally PBFI-86%GTA, PBFI-48%GTA and PBFI-26%GTA was obtained. The preparation procedure is depicted in Fig. 1.

1.4 Acid doping and swellings

PBFI along with its grafted PBFI- $x\%$ GTA membranes were soaked in 85 wt% PA solutions at 30 °C for 24 h till the quality of each membrane remained unchanged value. The mass, area and volume of each membrane was recorded before and after PA doping as previously reported [1,2]. Then used filter paper to wipe off the acidic liquid on the surface of membrane, and placed the membrane in a vacuum oven at 80 °C for a period of time to remove adsorbed water. According to Equation (1), the acid doping content (ADC%) of the membrane could be calculated, while the area and volume swellings were also calculated according to Equations (2) and (3).

$$ADC\% = \frac{(m_{PA} - m_{dry})}{m_{dry}} \times 100\% \quad (1)$$

$$S\% = \frac{S_1 - S_0}{S_0} \times 100\% \quad (2)$$

$$V\% = \frac{V_1 - V_0}{V_0} \times 100\% \quad (3)$$

1.5 Characterization

Using tetramethyl silane as the internal standard, the chemical structure of PBFI and PBFI - $x\%$ GTA were determined by ^1H NMR spectroscopy on Bruker Avance NEO (400 MHz). Fourier transform infrared (FT-IR) spectra were collected on a Bruker Vertex 70 spectrometer within the scope of 4000 to 400 cm^{-1} . The surface morphology of the membrane which had been sputtered platinum plated was characterized using SU-8010 scanning electron microscopy (SEM). For mechanical properties measurement, cut the membrane into a dumbbell shape using a mold. Its specific dimension was 4 mm in width and 25 mm in length. The mechanical stress-strain curve was collected using a CMT2000 tensile strength meter at a tensile speed of 20 mm min^{-1} at room temperature (RT). The tensile strength (ε) and elongation at break (η) of one membrane were determined according to Equations (4) and (5).

$$\varepsilon = \frac{F}{A} \quad (4)$$

$$\eta = \frac{L_1 - L_0}{L_0} \times 100\% \quad (5)$$

Similar to our previous work, the proton conductivity of different membranes was determined by the four-probe method [ii]. The membranes was dried at 100 °C for 2 h to avoid the influence of water. The proton conductivity of the membrane was calculated by Equation (6):

$$\sigma = \frac{L}{RS} \quad (6)$$

To study the HT-PEMFC performance of the membranes, the evaluation of the polarization curve and cell durability was performed according to our previous work [3]. Membrane electrode assemblies (MEAs) were produced through hot-pressing the PA-doped membrane and two gas diffusion electrodes together at 25 kg cm⁻² and 110 °C for 1.5 min. The active area of the electrode was 1.0 cm², while the loadings of Pt/C catalyst and PBI binder were 0.9 mg cm⁻² and 0.07 mg cm⁻². Single cells were assembled and operated at ambient pressure within the temperature range 120 - 180 °C, flowing dry H₂ and O₂ into the anode and cathode at flow rates of 60 mL min⁻¹ and 30 mL min⁻¹, respectively.

2. Results

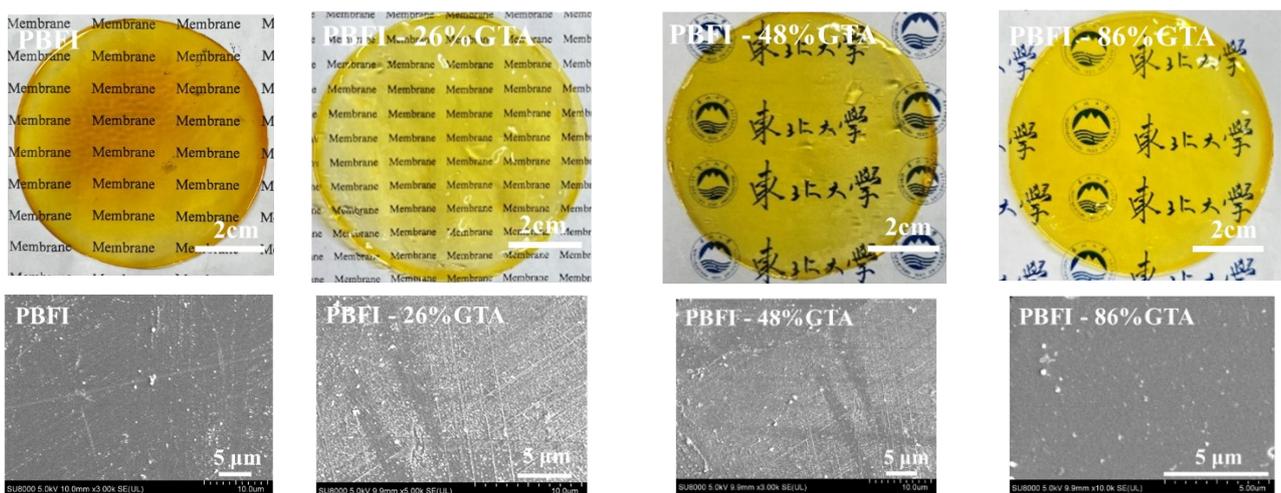


Figure S2 Photographic and SEM images of PBFI-x%GTA membranes with different grafting degrees

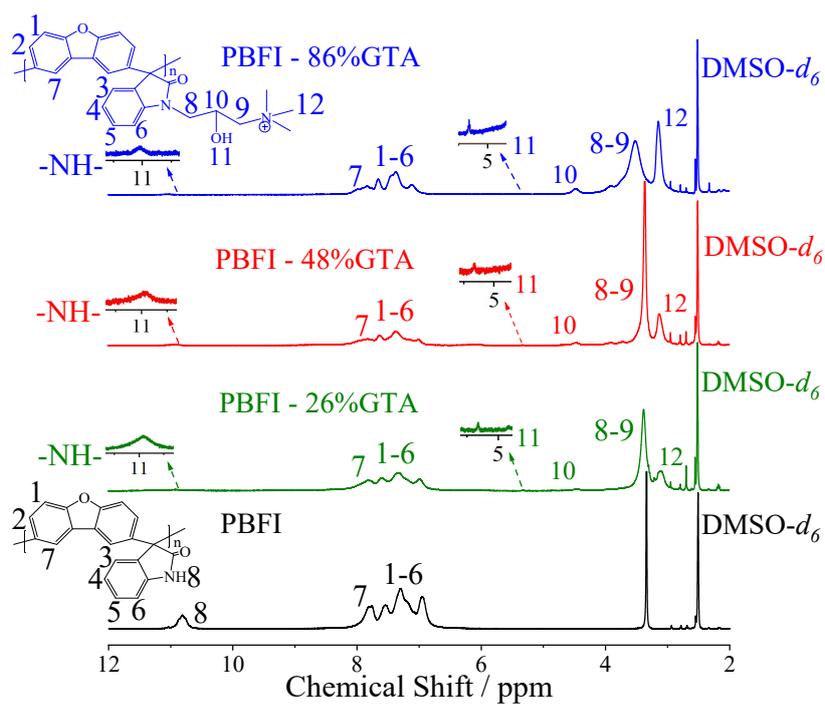


Figure S3 ^1H NMR spectra of PBFI- $x\%$ GTA membranes with different grafting degrees

Equation (7) for calculating grafting degree:

$$GD\% = \frac{10 \times A_{12}}{9 \times A_{(1-7)}} \quad (7)$$

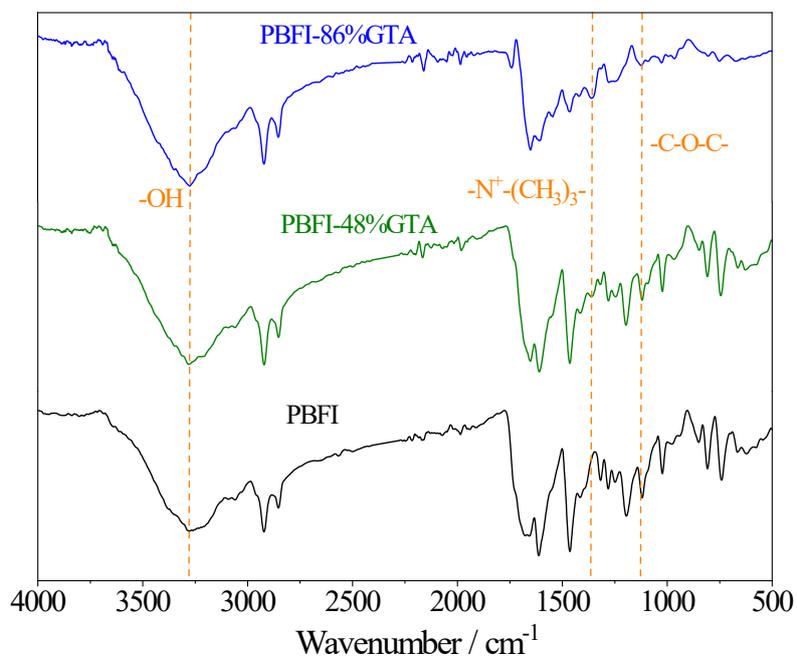


Figure S4 FT-IR spectra of PBFI and PBFI- $x\%$ GTA membranes with different grafting degrees

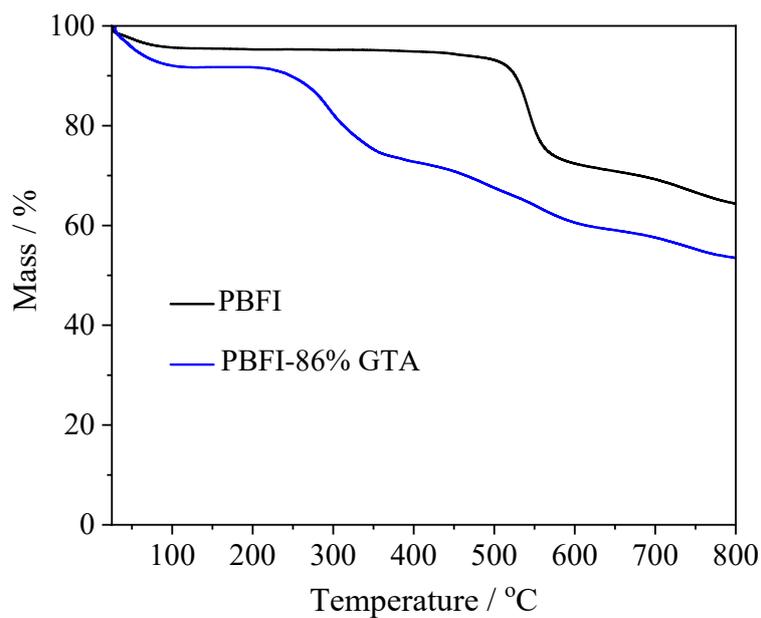


Figure S5 TGA curves of PBFi and PBFi-86%GTA in N₂ at a heating rate of 10 °C min⁻¹.

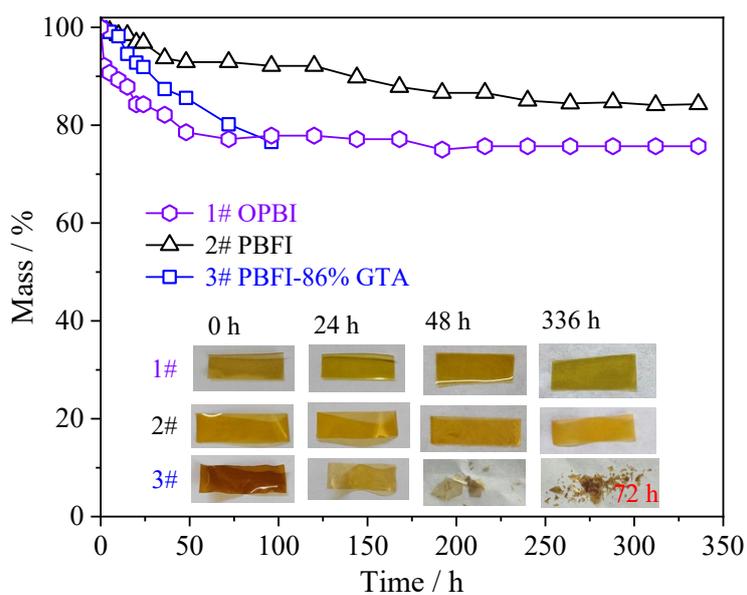


Figure S6 Fenton test of OPBI, PBFi and PBFi-86%GTA in 3 wt% H₂O₂ and 4 ppm Fe²⁺ at 68 °C

and morphological photos of membranes before and after Fenton test.

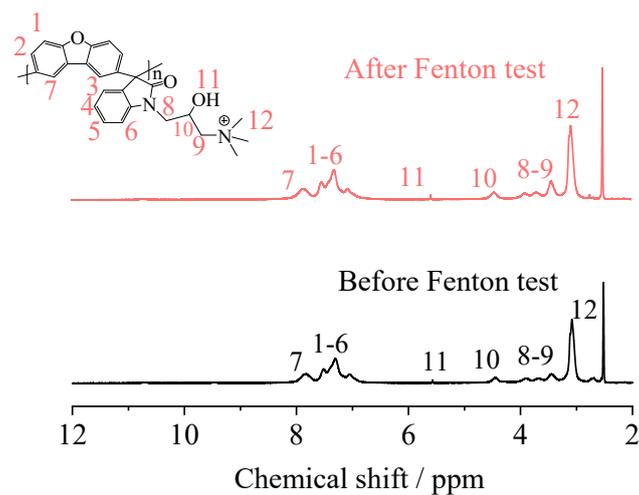


Figure S7 ^1H NMR spectra of PBFI-86%GTA before and after Fenton test for 72 h.

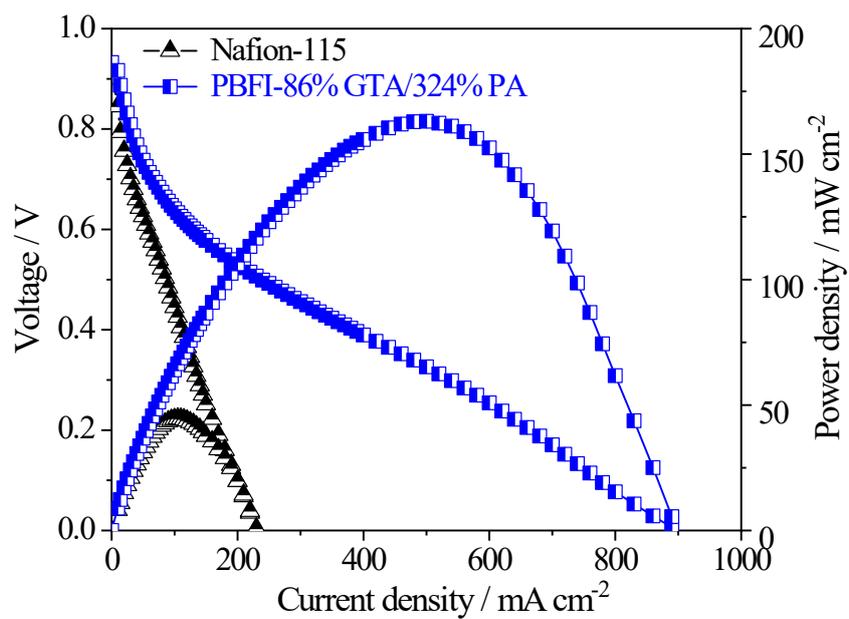


Figure S8 Performance of $\text{H}_2\text{-O}_2$ fuel cells with Nafion 115 and PBFI-86%GTA/324%PA membranes at $80\text{ }^\circ\text{C}$ without any humidification or backpressure.

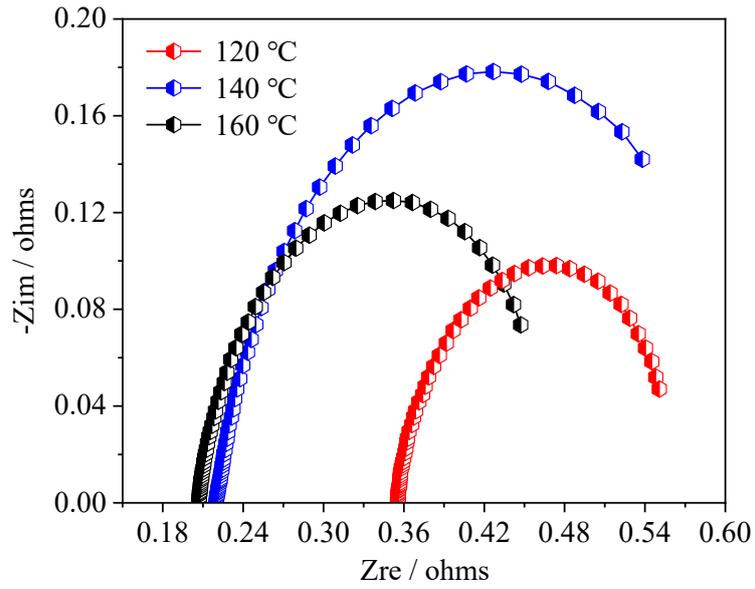


Figure S9 EIS results of the H₂-O₂ cell with PBFI-86%GTA/324%PA at different temperatures.

Table S1 Water uptake, PA doping content and swellings of various membranes

Membrane	85% PA			H ₂ O		
	ADC/%	Area/%	Volume/%	Water/%	Area/%	Volume/%
PBFI	32	9.1	13.9	9.2	0.0	1.5
PBFI-86%GTA	324	64.2	115.4	75	62.2	71.5
PBFI-48%GTA	163	47.6	92.7	-	-	-
PBFI-26%GTA	108	7.3	38.3	-	-	-
PTI	2.6	0.0	3.8	0.0	0.0	0.0
OPBI	162	20.8	76.6	-	-	-

3. References

- [1] Y. Jin, R. Liu, X. Che, T. Wang, J. Yang, New high temperature polymer electrolyte membranes based on poly (ethylene imine) crosslinked poly (ether ketone cardo), *J. Electrochem. Soc.* 168 (2021), 054524.
- [2] Y. Jin, T. Wang, X. Che, J. Dong, Q. Li, J. Yang, Poly (arylene pyridine): new alternative materials for high temperature polymer electrolyte fuel cells, *J. Power Sources* 526 (2022), 231131.
- [3] J. Yang, L. N. Cleemann, T. Steenberg, C. Terkelsen, Q. F. Li, J. O. Jensen, H. A. Hjuler, N. J. Bjerrum, R. H. He, High molecular weight polybenzimidazole membranes for high temperature PEMFC. *Fuel Cells* 14 (2014) 7-15.