Electronic Supplementary Information for

Novel PA-doped polybenzimidazole membranes with high doping level, high proton conductivity and high stability for HT-PEMFCs

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Content

1 Experimental

1.1 Materials

Phenylhydroquinone (97%) from Sigma-Aldrich Ltd., 4-fluorobenzonitrile (99%) from Energy Chemical Co., 3,3'-diaminobenzidine (DAB) (97%) from Aladdin Reagent and 4, 4'-oxybis(benzoic acid) (98%) from Alfa Aesar Reagen were used without any purification. Phosphorus pentoxide-methanesulfonic acid (PPMA) solution[1] was prepared by dissolving phosphorus pentoxide (Beijing Chemical Reagent, China) into methane sulfonic acid (Aladdin Reagent) in accordance with the mass ratio of 1:10. N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Tianjin Tiantai Fine Chemicals Co. Ltd. Sodium bicarbonate (NaHCO$_3$), potassium hydroxide (KOH), potassium carbonate (K$_2$CO$_3$), ethanol, acetone and toluene were obtained from Beijing Chemical Reagent, China.

1.2 Synthesis of Ph-PBI and OPBI

As shown in Fig. S1, Ph-COOH, Ph-PBI and OPBI were prepared according to our previous work.[2] A typical synthesis procedure of Ph-PBI is as follows: into a 50 mL three-necked flask with a mechanical stirrer, a nitrogen inlet and a drying tube, 2.1321 g (0.005 mol) of Ph-COOH, 1.0714 g (0.005 mol) of DAB and 10 mL PPMA were added. The mixture was kept at room temperature for a few minutes and then heated at 100 °C for 2 h in nitrogen atmosphere under mechanical stirring. The temperature of the system was raised to180-190 °C, and maintained for 3-4 h. The high viscosity mixture was poured into a large excess of deionized water with stirring. After washing the obtained product for several times with deionized water, the precipitated polymer was soaked into 10 wt% NaHCO$_3$ solution at 40 °C for 48 h. Ph-PBI was washed with deionized water until the pH reached 7.0, and then dried at 100 °C for 24 h under vacuum. Me-PBI and OPBI were prepared using a similar procedure.
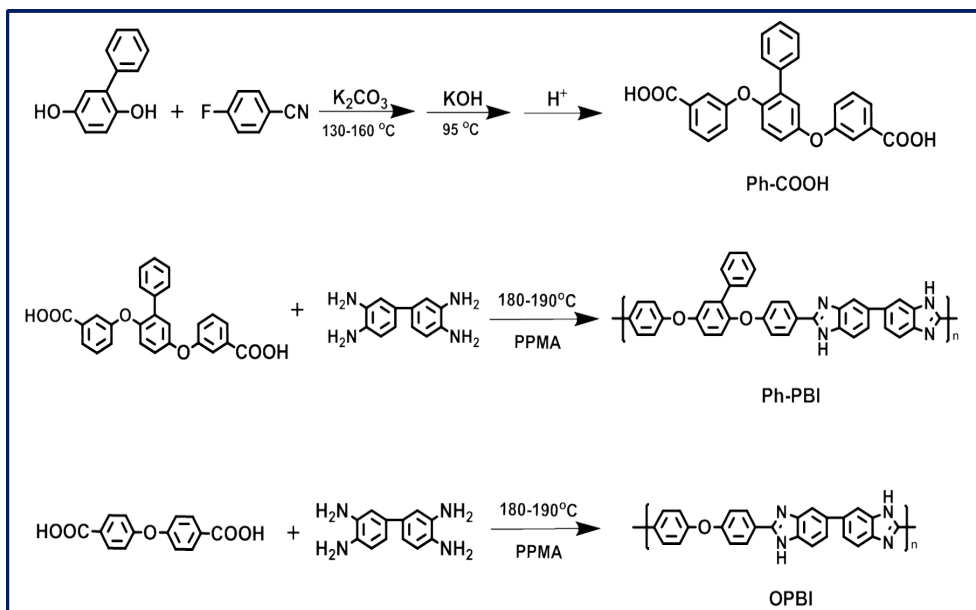
Fig.S1 Synthesis of Ph-COOH, Ph-PBI and OPBI.

1.3 Preparation of the PA-PBI membranes

The OPBI and Ph-PBI membranes were prepared by dissolving 1.0 g of polymer powder in dimethyl sulfoxide (DMSO, 10 wt%). Then the homogeneous solution was casted on glass plates and dried at 80 °C for 12 h, 100 °C for 12 h and 120 °C for 12 h. The membranes were obtained after drying at 120 °C for 24 h in a vacuum oven. The PA-PBI samples were obtained by immersing the membranes (OPBI and Ph-PBI) in a dish with 85 wt% PA solution at 160 °C for 3, 12, 36, 72, 108 h, respectively. After acid doping, the membranes were taken out from PA, wiped dry with tissue, and dried under vacuum at 100 °C for 5 h.

1.4 Measurements

^{1}H NMR experiments were carried out on a Bruker 510 spectrometer (300 MHz for 1H) using DMSO-d_6 as solvent. The gel permeation chromatographic (GPC) analysis was carried out with a PL-GPC220 instrument with N,N-dimethylformamide (DMF) as eluent and polystyrene as standard. Thermo gravimetric analysis (TGA) was performed on a Netzch Sta 449c thermal analyzer system thermogravimetric analysis instrument under nitrogen atmosphere at a heating rate of 10 °C·min^{-1} from 100 to 800 °C.

The acid doping level (ADL) was defined as the mole number of PA molecules per molar repeat unit of the PBI. The mechanical properties of membranes were measured at room temperature on SHIMADZU AG-I 1KN at a strain rate of 2 mm·min^{-1}. The size of samples was 15 mm×5 mm. The dimensional swellings were calculated as follows:

$$\triangle A(\%) = [(A_d - A_u)/A_u] \times 100\ \%,$$

$$\triangle T(\%) = [(T_d - T_u)/T_u] \times 100\ \%,$$

$$\triangle V(\%) = [(V_d - V_u)/V_u] \times 100\ \%,$$

Where A_d, A_u, T_d, T_u, V_d and V_u are the area, thickness, volume of doped and undoped samples, respectively.

The wide angle X-ray diffraction (WAXD) spectra of polymers in film form were recorded using a Rigaku X-ray diffractometer (R-AXIS RAPID) with Cu Kα radiation in 2θ range of 5-40°. The average d-spacing (d_{sp}) for the amorphous peak maxima was calculated using Bragg's equation as following:

$$d_{sp} = \lambda/2\sin\theta$$

where n is an integral number (1, 2, 3), λ denotes the X-ray wavelength, d_{sp} stands for the intersegmental spacing between two polymer chains and θ indicates the diffraction angle.

The densities of PBIs were measured by an Electronic Densimeter SD-200L using pre-dried PBI membranes. Water was employed as a solvent for initial measurements but the results were found to be unreliable due to the strong water absorption of PBIs. Therefore, cyclohexane was chosen as a suitable solvent since it is not absorbed by PBIs.[3] Based on density determination, fractional free volume (FFV) was calculated by Bondi's group contribution approach as following [4]:

$$FFV = (V - 1.3\ V_w)/V$$

where V is total molar volume of the repeating unit of polymers (cm^3/mol) derived from the molecular weight of repeating unit by density, and Vw is the van der Waals molar volume.

The molecular simulation of *m*-PBI, OPBI and Ph-PBI of 30 repeating units was made using the UFF method (Universal Force Field) on Gaussian 09 Version D01. The conductivities were measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiost at (Model 5210 frequency response detector, EG&GPARC, Princeton, NJ). The membranes were of 1 cm wide and 5 cm long and were fixed in a temperature-controlled cell with two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops.

Fuel cell tests of PBI membranes were made. The catalyst inks were prepared and the membrane-electrode assemblies (MEAs) were fabricated according to a previously reported method.[5] The active electrode area of the MEAs was 10 cm^2. The fuel cell was operated at 160 °C, atmospheric pressure and dry hydrogen and air were supplied to the fuel cell without pre-humidification. Polarization curves were obtained by a current step potentiometry with the steady state potential recorded 2 min after each current was set.

2 Results and discussion

2.1 Characterization of PBIs

In the ^{1}H NMR spectra of PBIs, the peaks at 12.93-12.99 ppm were assigned to the amine protons on the benzimidazole moieties and signals at 6.88-8.29 ppm represented the proton on the aromatic groups. All signals were well in agreement with their suggested polymeric structure. The ^{1}H NMR spectra (Fig. S2) suggested that PBIs were successfully synthesized. The PBIs had relative high molecular weights, and the number-average molecular weights of Ph-PBI and OPBI were 55100 and 99300 g·mol^{-1}, respectively (Table S1).
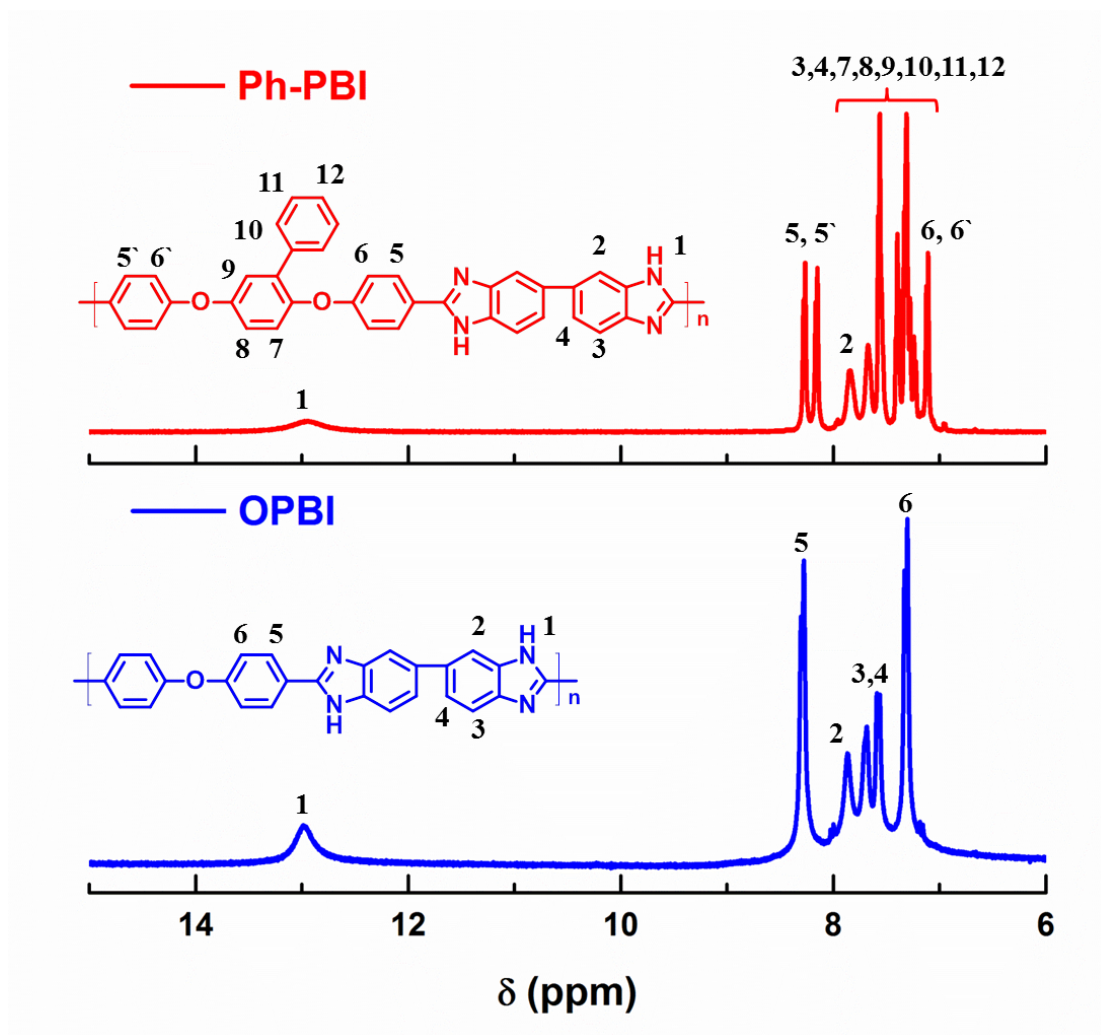

Fig. S2 ^{1}H NMR spectra of Ph-PBI and OPBI.

2.2 Thermal stability

Elevated temperatures enhance the reaction kinetics and reduce the thermodynamic voltage losses of AEMFCs. Therefore, it is important to prepare membrane materials having good thermal stability, capable of operating at elevated temperatures. Thermal stability of the undoped polymers was examined by TGA under nitrogen atmosphere to determine their degradation temperatures up to 800 °C (Fig. S3). The PBI membranes exhibited excellent thermal stability, which had only a one-step degradation pattern attributed to the decomposition of the polymer main chain. As listed in Table S1, the 5% weight loss temperatures of OPBI and Ph-PBI were 629 and 523 °C, respectively. The corresponding residuals at 800 °C were 85, and 71 %, respectively. The results indicated the good thermal stability of PBIs.
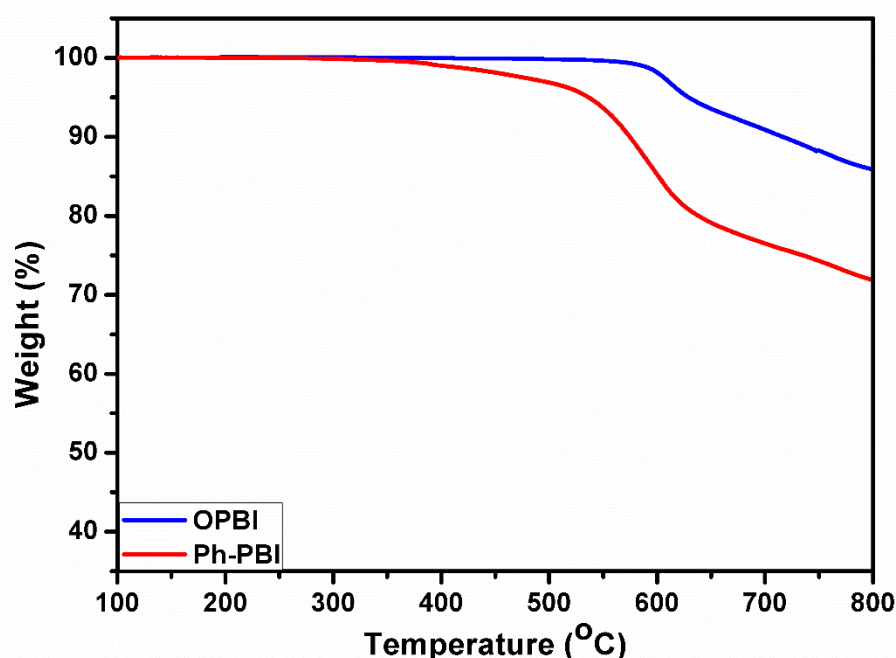

Fig. S3 The TGA curves of OPBI and Ph-PBI.

2.3 Molecular simulation

The molecular simulation of *m*-PBI, OPBI and Ph-PBI of 30 repeating units was made using the Universal Force Field method (UFF) on Gaussian 09 Version D01. Fig. S4 shows that the Ph-PBI had a loose helical polymer chains, which were prone to pack and form a "sponge-like" structure. These is related to the chemical structure of Ph-PBI, which has two flexible ether linkages and one rigid biphenyl moiety per repeat unit. In comparison, conventional *m*-PBI with more rigid molecular chains had a tendency to form a tight structure, and OPBI with more regular and less flexible molecular chains may form a denser structure with fewer tangles.
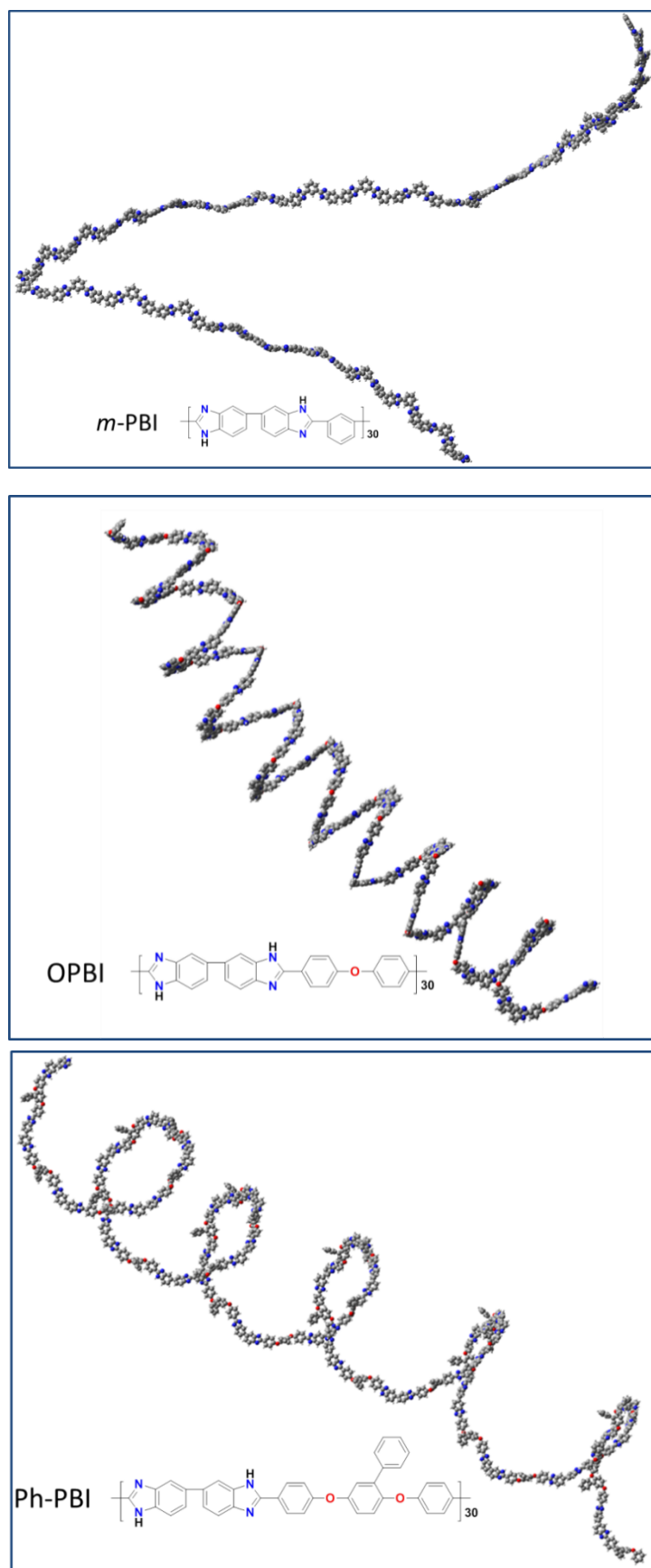
Fig. S4 The results of the molecular simulation of *m*-PBI, OPBI and Ph-PBI.

2.4 WAXD, Density and FFV

The WAXD spectra in Fig. S5 of OPBI and Ph-PBI show the polymers are amorphous in nature. The introduction of phenyl in Ph-PBI results in a peak shift to lower 2θ compared with OPBI. The d_{sp} results in Table S1 show Ph-PBI (4.91 Å) and Me-PBI (5.07 Å) have larger intersegmental spacing than that of OPBI (4.41 Å).
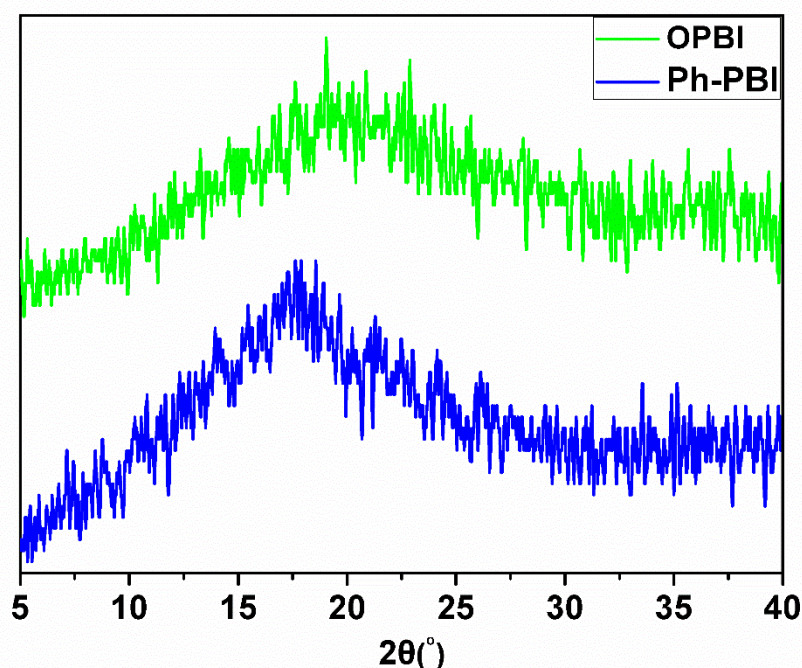

Fig. S5 The WAXD spectra of OPBI and Ph-PBI.

The densities and estimated FFV of O-PBI and Ph-PBI are shown in Table S1. The lower densities and larger FFV of Ph-PBI (1.25 g·cm^{-3}, 0.138) than that of OPBI (1.32 g·cm^{-3}, 0.106) can be ascribed to the presence of phenyl groups which disrupt the close polymer chain packing caused by intermolecular hydrogen bonds. These results provide supporting evidence for a "sponge-like" structure of Ph-PBI.

Table S1 Molecular weight and some physical properties of PBIs

Samples	Mn[a] (g·mol^{-1})	PDI[b]	T_{d5}[c] (°C)	Char yield[d] (%)	Density (g·cm^{-3})	FFV	d_{sp} (Å)
OPBI	99300	1.29	629	85	1.32	0.106	4.41
Ph-PBI	55100	1.88	523	71	1.25	0.138	4.91

[a] Number-average molecular weight obtained by GPC. [b] The polydispersity index.
[c] Temperature at 5% weight loss. [d] Residual weight (%) at 800 °C in nitrogen.

Table S2 The ADLs and corresponding tensile properties, swelling ratios and conductivities of the membranes.

Samples	ADLs	Tensile stress MPa	Tensile strain %	Tensile modulus GPa	Area swelling %	Thickness swelling %	Volume swelling %	Conductivity S·cm^{-1}	
								120 °C	200 °C
OPBI	0	112.1	12.0	2.11	0	0	0	--	--
O-3	15.1	2.8	26.4	0.07	66	79	198	0.054	0.099
O-12	19.4	2.0	27.2	0.05	108	91	297	0.093	0.142
Ph-PBI	0	106.7	18.2	2.39	0	0	0	--	--
Ph-3	10.1	22.3	25.5	0.66	25	50	88	0.037	0.065
Ph-12	13.2	18.5	30.8	0.41	34	56	109	0.052	0.088
Ph-36	16.3	14.6	34.2	0.29	49	76	162	0.069	0.101
Ph-72	19.1	9.7	36.9	0.20	59	81	188	0.079	0.138
Ph-108	24.6	5.5	40.6	0.10	65	97	224	0.119	0.217
Ref.13(a)	9.7	10.2	53.6	0.15	--	--	91	--	0.046[a]
Ref.13(b)	11.5	16.4	98.7	0.12	58	--	171	--	0.033[b]
Ref.13(c)	8.6	4.6	27.9	0.12	--	--	225	--	0.102[c]

[a] 200 °C; [b] 160 °C; [c] 180 °C

3 References

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