

## Supplementary Information

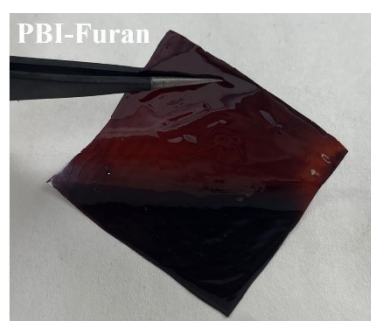
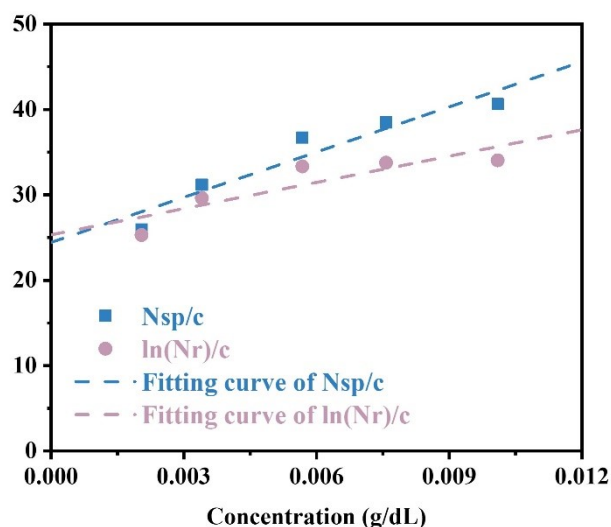
### Robust and self-Healable Polybenzimidazole Membranes via Diels-Alder Chain Extension

Minjun Yin <sup>a,b</sup>, Hongting Pu <sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory of Advanced Civil Engineering Materials (Ministry of Education),  
School of Materials Science & Engineering, Tongji University, Shanghai, 201804,  
China

<sup>b</sup> Department of Polymer Materials, School of Materials Science & Engineering,  
Tongji University, Shanghai, 201804, China

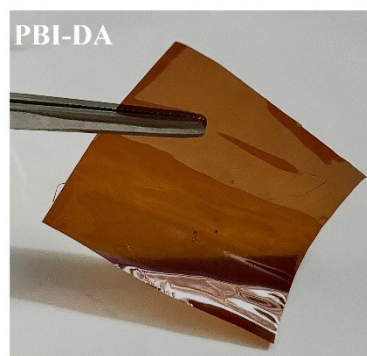
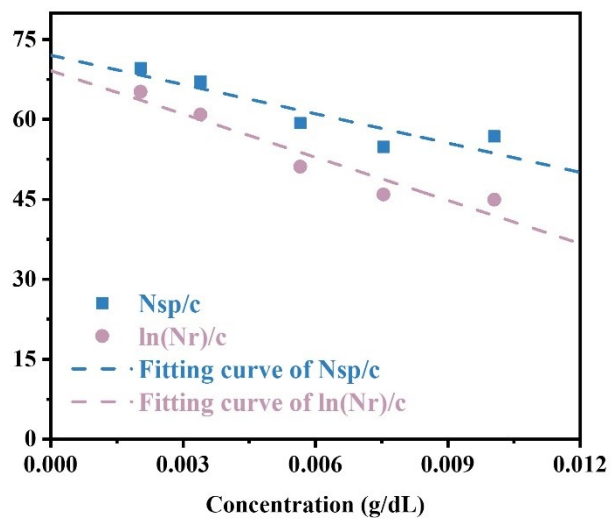
Corresponding author: [puhongting@tongji.edu.cn](mailto:puhongting@tongji.edu.cn)



$\eta=0.243$

$M=8248$

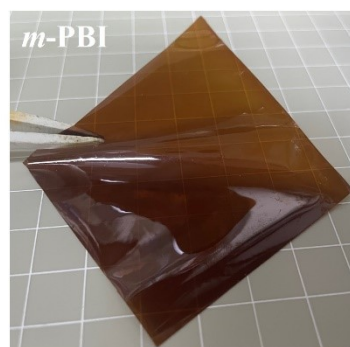
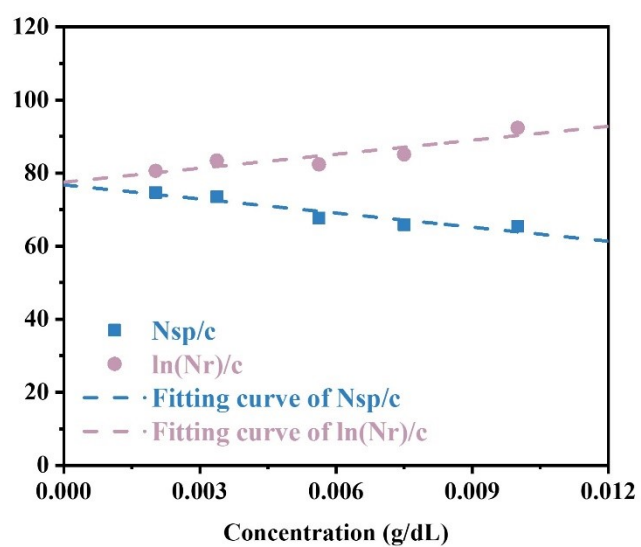
Figure S1. Intrinsic viscosity fitting curve of PBI-Furan



$$\eta=0.727$$

$$M=32974$$

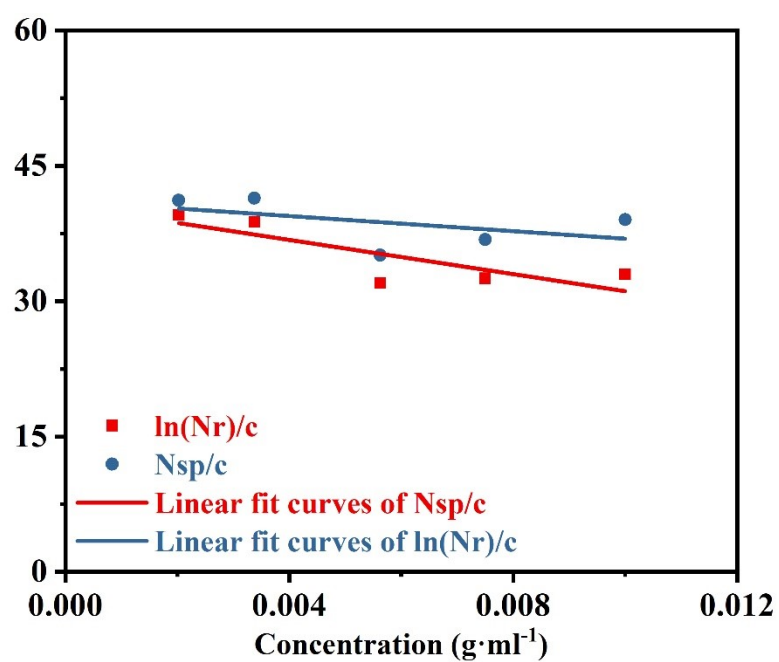
**Figure S2.** Intrinsic viscosity fitting curve of PBI-DA.



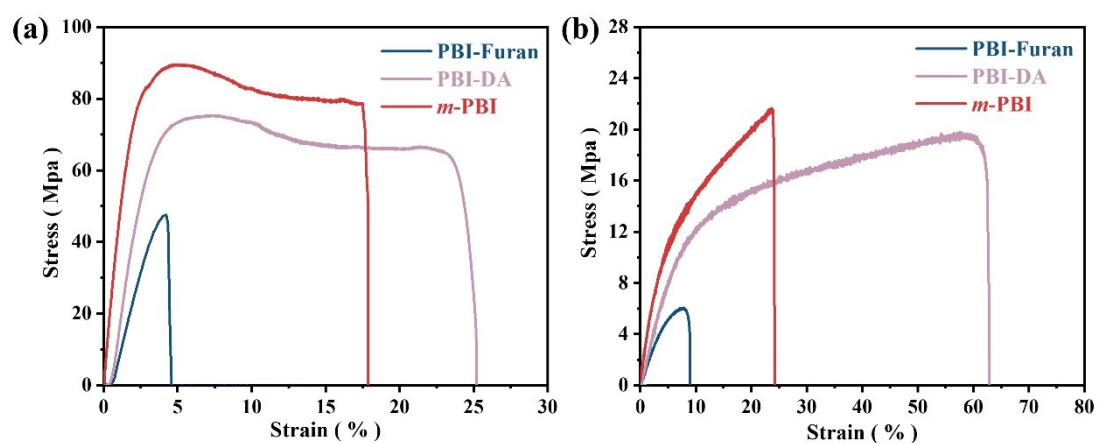
$$\eta=0.767$$

$$M=35273$$

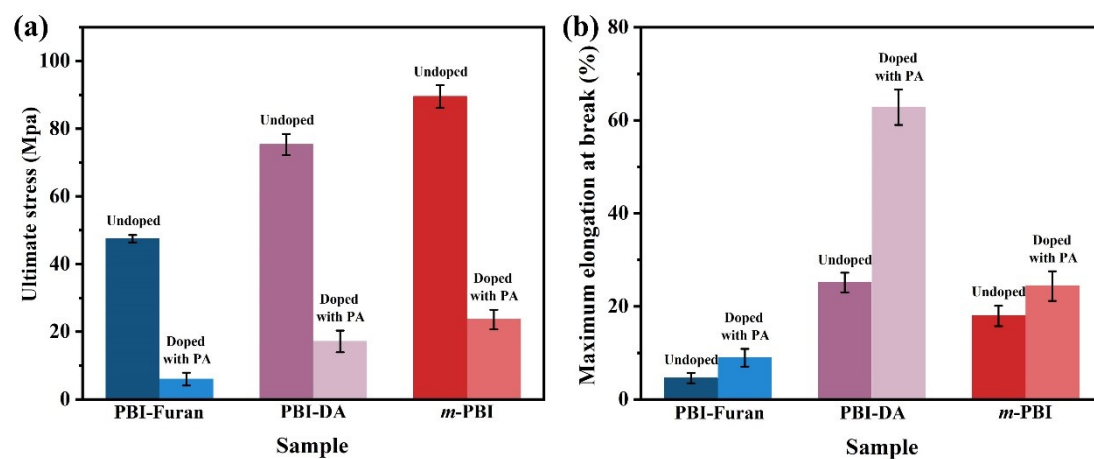
**Figure S3.** Intrinsic viscosity fitting curve of *m*-PBI.



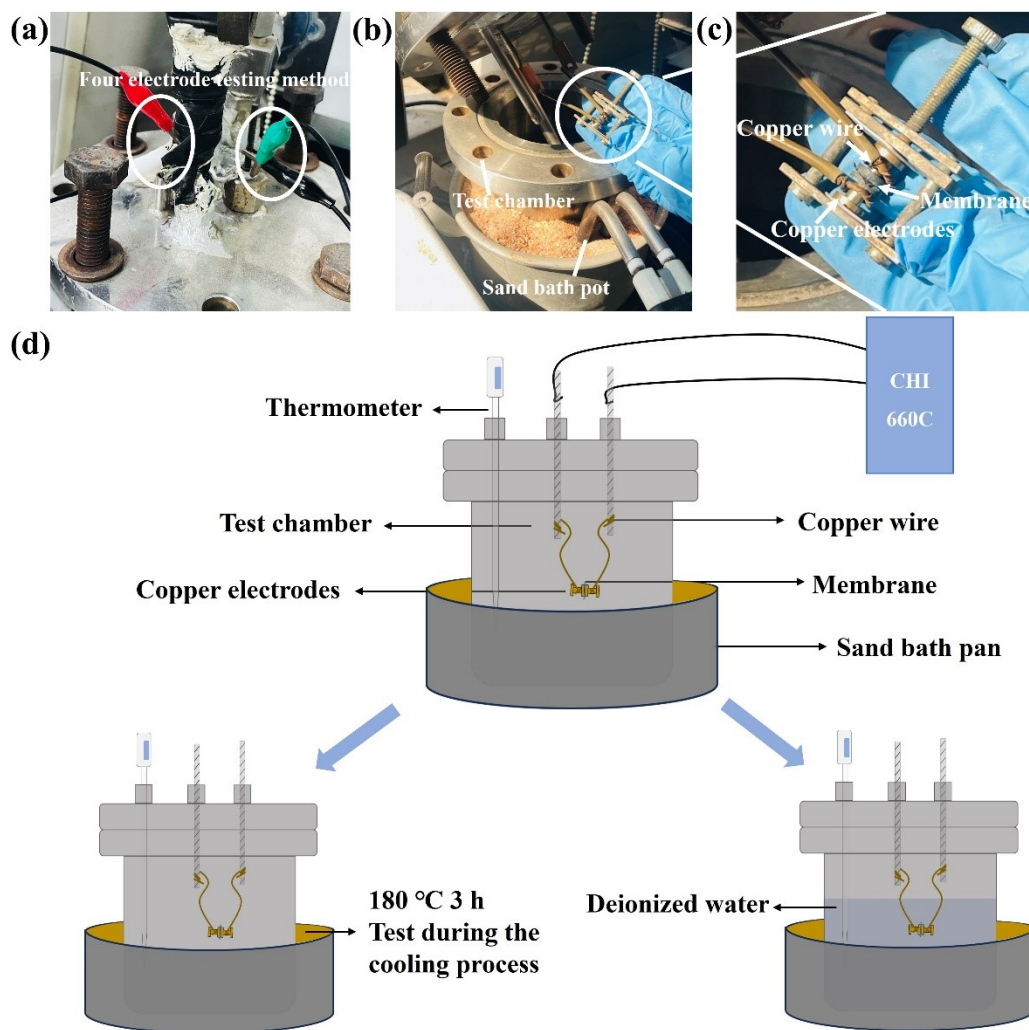
**Figure S4.** Intrinsic viscosity fitting curve of phosphoric acid doped PBI-DA membrane (heat treatment at 170 °C for 3 h).



**Figure S5.** Mechanical properties of (a) undoped and (b) phosphate doped membranes.

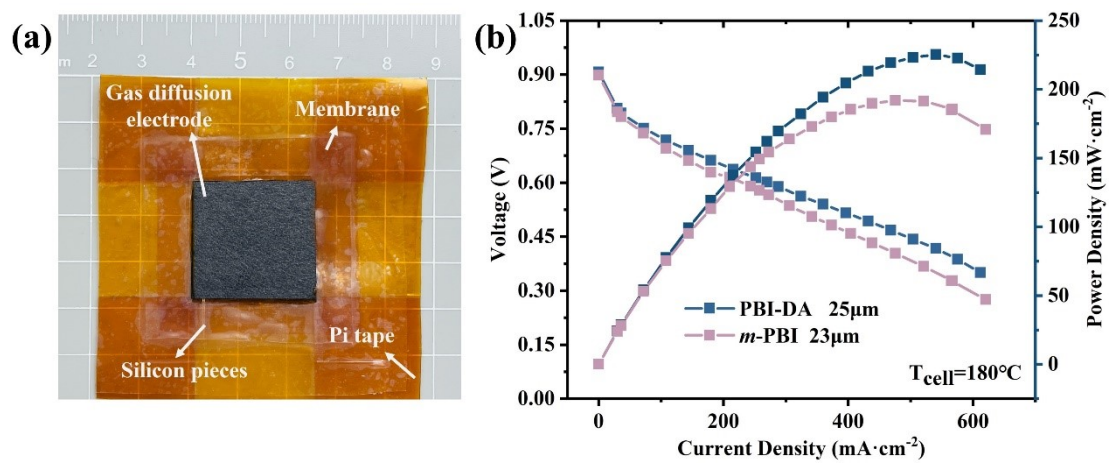


**Figure S6.** (a) Maximum tensile strength and error analysis of phosphate doped and undoped membranes. (b) Maximum elongation at break and error analysis of phosphate doped and undoped membranes.



**Figure S7.** (a) Schematic diagram of ion conduction test; (b-d) Actual device diagram for conductivity test using the four electrodes method.

Conductivity test: When testing the proton conductivity and anion conductivity of the membrane at 0% humidity, desiccant was placed at the bottom of the testing chamber and the testing chamber was first heated to 180 °C for 3 h, the test is conducted during the cooling process to ensure a dry environment; When testing the anion conductivity at 100 % humidity, deionized water was poured into the testing chamber to immerse the test membrane.



**Figure S8.** (a) Schematic diagram of the composition of membrane Electrode (MEA). (b) The variations of battery voltage and power density of PBI-DA with current density.



**Table S1.** Shrinking rate of PBI-Furan, PBI-DA and *m*-PBI (drying treatment for 3 h).

Samples	Temperature (°C)	Cooling time (min)	Shrinking rate (%)
PBI-Furan	120	30	0.24
	180	30	0.27
PBI-DA	120	30	0.66
	180	30	0.61
<i>m</i> -PBI	120	30	0.57
	180	30	0.55