Supplementary information

Constructing unique carboxylic proton transport channels via phosphoric acid etching metal organic frameworks in crosslinked branched polybenzimidazoles

Peng Wang [a,b], Yingnan Wu[b], Wenjie Lin[*a,b] and Lei Wang[*a,b]

a School of Chemistry and Environment Engineering, Hanshan Normal University, Chaozhou, Guangdong, 521041, China

b Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, China

Corresponding author: Lei Wang, E-mail: wl@szu.edu.cn；Wenjie Lin, E-mail: lwjzwc@hstc.edu.cn

Section S1. Materials

Zirconium tetrachloride ($ZrCl_4$, 98%), 2-aminoterephthalic acid (99%), 3,3'-diaminobenzidine (DAB, 98%), 4,4'-oxybisbenzonic acid (OBBA, 98%), 1,3,5-tris(4-carboxyphenyl)benzene (B3, 98%), 3-glycidoxypropyltrimethoxysilane (KH-560, 98%), N,N-dimethylformamide (DMF, 99.9%), N-methyl-2-pyrrolidone (NMP, 99.5%), and polyphosphoric acid (PPA) were obtained from Energy Chemical Co. Hydrochloric acid (HCl, 36%), PA (85%), acetone, absolute ethyl alcohol (EtOH), and sodium bicarbonate were purchased from YiXin Technology Company (Shenzhen, China).

Section S2. Instrumentation

Inherent viscosity determined from a polymer solution in H_2SO_4 (98 %) at 30 °C using Ubbelohde viscometer. Five different concentrations of viscosity were tested separately using

Ubbelohde viscometer. And then the intrinsic viscosity [η] was extrapolated by using Huggins Equation:

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \quad (1)$$

Fourier-transform infrared (FT-IR) spectra of the membranes were recorded using a Nicolet 6700 FT-IR spectrometer. The microscopic morphologies of the membranes were observed using a scanning electron microscope (SEM, Zeiss Supra 55). The thermal stabilities of the membranes were measured using thermogravimetric analysis (TGA, TA-Q50) over a temperature range of 100°C–800°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. The mechanical properties of the membranes were measured on a SANS-CMT4204 instrument at room temperature at a strain rate of 2 mm min^{-1}. The oxidative stability of the membranes was investigated by conducting Fenton tests, wherein rectangular samples were immersed in Fenton reagent (3 wt.% H_2O_2, 4 ppm Fe^{2+}) at 80°C for 24 h, and the weights of the membranes were recorded after washing sequentially with deionized water and ethanol several times and subsequent drying at 120°C in a vacuum oven for 24 h. The PA uptake of PBI membranes in wt.% were calculated using Equation (2), and the swelling ratio was calculated according to Equation (3):

$$PA\ uptake = \frac{W_{doped} - W_{dry}}{W_{dry}} \times 100\% \quad (2)$$

$$Swelling\ ratio = \frac{V_{doped} - V_{dry}}{V_{dry}} \times 100\% \quad (3)$$

where W_u and W_d are the weights of the undoped and doped PBI membranes, respectively; and V_{dry} and V_{doped} are the volume of the membranes before and after doping with PA, respectively.

The PA-retention properties were measured using a previously reported procedure. All samples were treated in a constant temperature (80°C) and humidity (40% relative humidity)

incubator. Every 24 h, the samples were removed and dried in an 80°C convection oven for 1 h, and their weights recorded.

The proton conductivities (80°C–200°C, without humidification) of the PA-doped membranes were measured from $1-10^5$ Hz without humidification on a Zahner IM6ex electrochemical workstation via an alternating current (AC) impedance method. Rectangular samples (4 cm × 1 cm) were heated at 120°C for 3 h prior to any measurements being conducted to remove any residual water in their structures, before being assembled into a device with two gold electrodes. The proton conductivity (σ) was calculated according to Equation (4).

$$\sigma = L/RA \quad (4)$$

where L (cm), R (Ω), and A (cm^2) are the distance between the two electrodes, the AC resistance, and the cross-sectional area of the samples, respectively.

The activation energies (E_a) of the PA-doped membranes were calculated according to the Arrhenius equation:

$$\sigma = \sigma^0 \exp\left(\frac{-E_a}{RT}\right) = \frac{A}{T} exp(\frac{-E_a}{RT}) \quad （5）$$

where the σ^0 and A are pre-exponential factors, and σ is the proton conductivity of the membranes.

The active area of the membrane electrode assembly (MEA) was 5 cm^2. To fabricate MEA, a PA-doped membrane was sandwiched between two carbon paper electrodes (HeSen Company) with a Pt/C catalyst loading of 1.0 mg cm^{-2}. Non-humidified hydrogen and oxygen were supplied to the single cell at flow rates of 80 and 160 mL min^{-1}, respectively. A multiple independent channel test station (Arbin® MITS PRO 7.0) was used to collect the data.

Section S3. Method and Characterization

Preparation of UIO-66-NH$_2$

UiO-66-NH$_2$ was synthesized via a method previously reported by Rao et al[1]. ZrCl$_4$ (0.629 g, 2.7 mmol) and 2-aminoterephthalic acid (1.925 g, 10 mmol) were fully dissolved in a mixed solution of DMF (75 mL) and HCl (5 mL) to obtain a homogeneous yellow solution. This solution was then added to a polytetrafluoroethylene (PTFE) autoclave and heated in an oven at 120°C for 24 h. After being allowed to cool naturally to room temperature, the yellow crude product was poured into a beaker together with the solution, and was then washed with DMF and anhydrous methanol several times, before being soaked in anhydrous methanol for 3 days to replace the involatile solvent in the pores of UiO-66-NH$_2$. Finally, the mixture was dispersed in deionized water and freeze dried for 3 days to obtain UiO-66-NH$_2$ as a light-yellow powder.

Characterization of the BOPBI polymer

The chemical structure of BOPBI was confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, as shown in Fig. S1, the results of which are consistent with our previous reports. Typically, peaks attributable to the branched structure were observed at 7.18, 8.04, and 8.07 ppm, assigned to H6, H7, and H8 in the structure, respectively, see Fig. S1. The peak at 13.09 ppm corresponds to the N–H group in the imidazole ring. Overall, these results indicate that BOPBI was synthesized successfully.

Characterization of the UiO-66-NH$_2$ MOF

The X-ray diffraction (XRD) pattern of UiO-66-NH$_2$ is shown in Fig. S3a. The peak positions of UiO-66-NH$_2$ proving that UiO-66-NH$_2$ was successfully synthesized with high purity. The surface area of UiO-66-NH$_2$ was 699.05 m^2 g^{-1}, calculated using the Brunauer–Emmett–Teller (BET) method from the N$_2$ sorption isotherm shown in Fig. S3b. It can be seen from the TEM image shown in Fig. S1c that the synthesized UiO-66-NH$_2$ adopts the form of spherical particles, with a diameter of 60–80 nm.
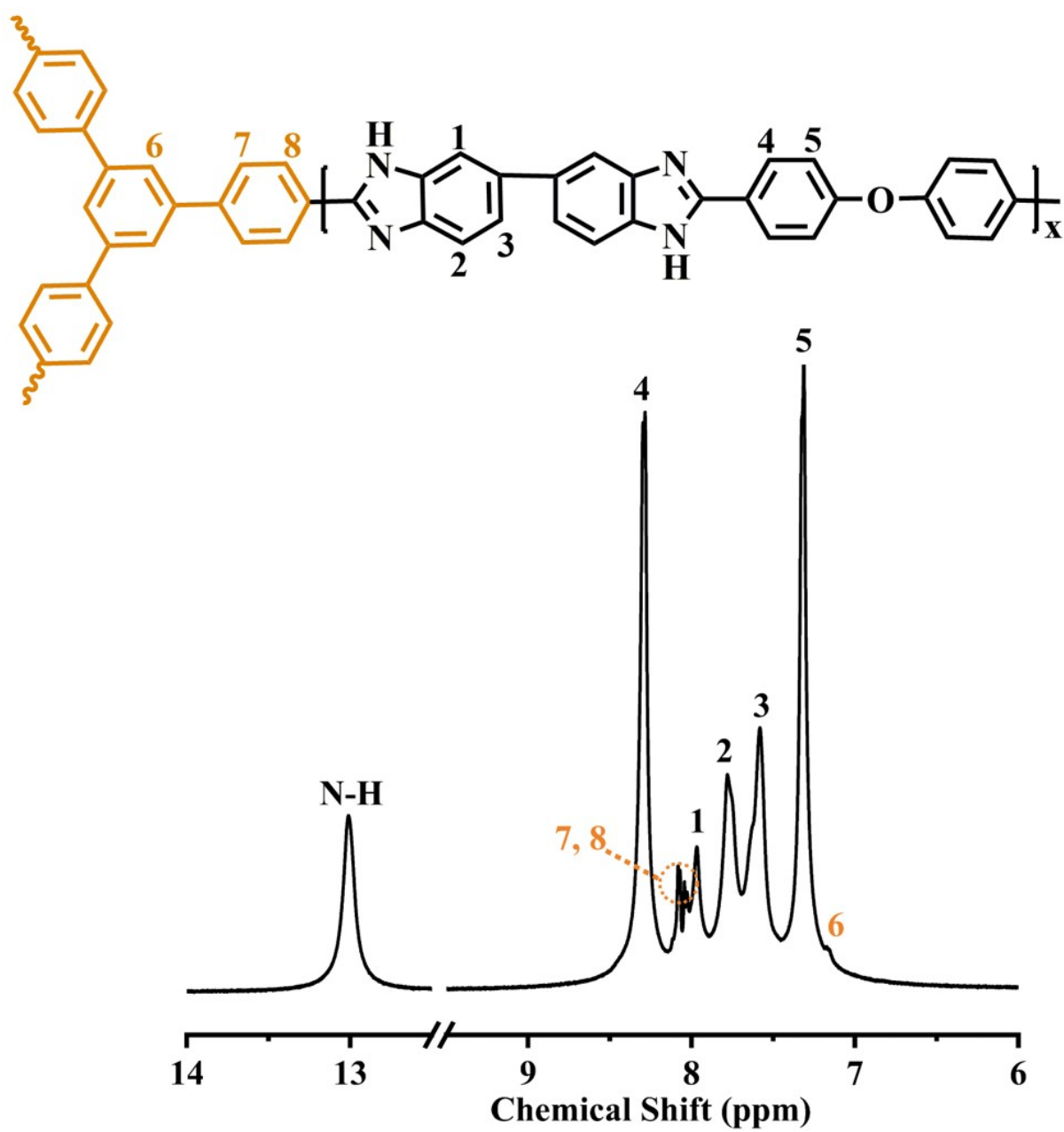
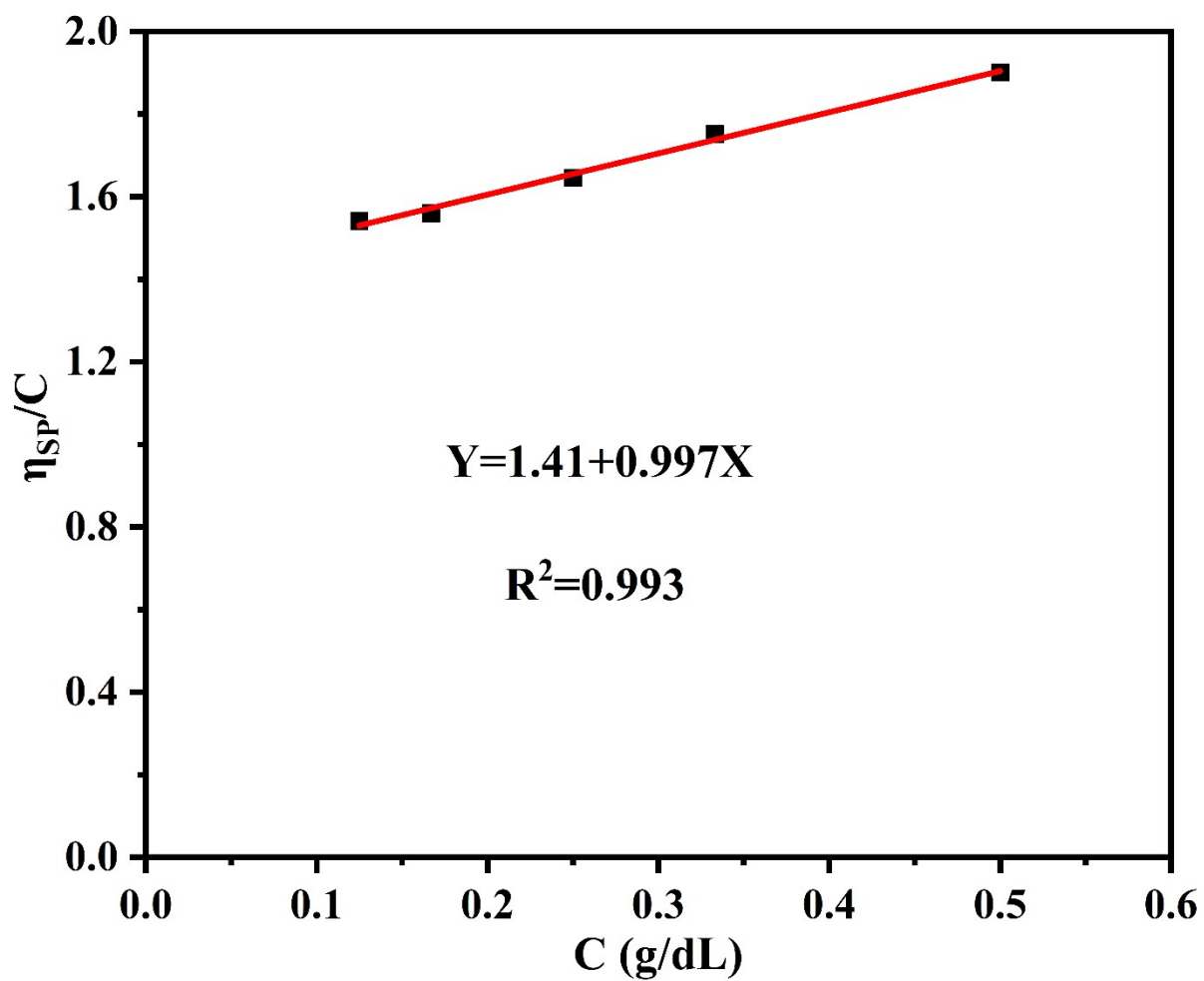**Fig. S1** ^{1}H NMR spectra of the synthesized BOPBI.
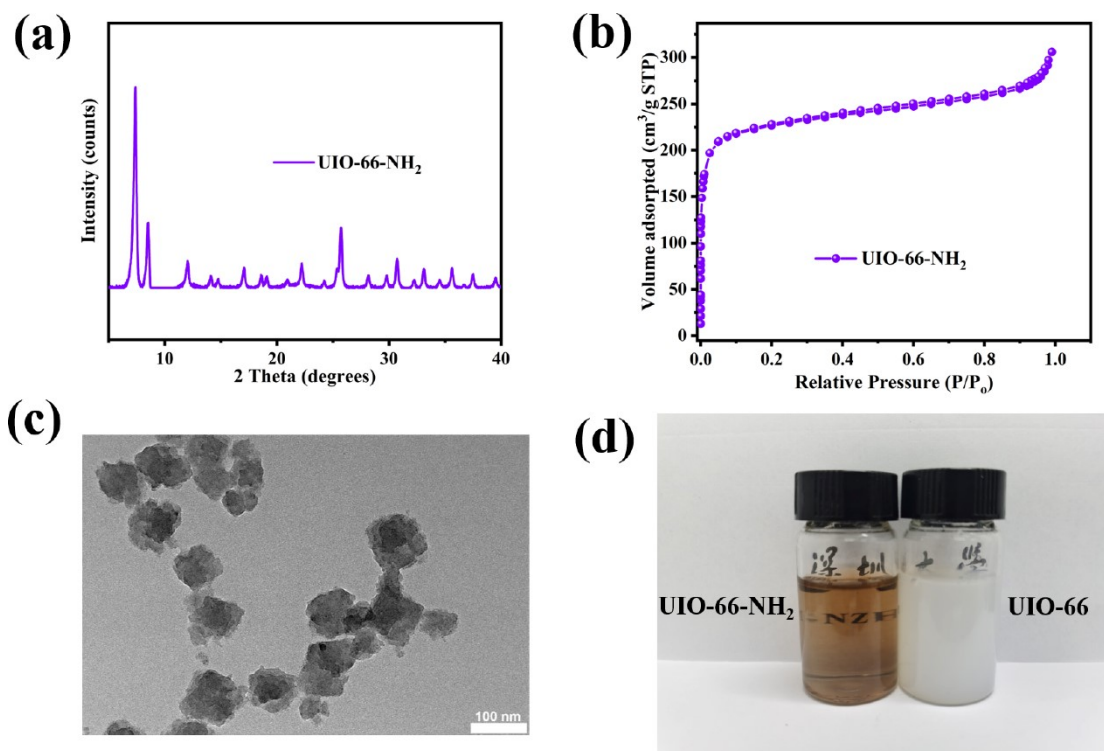
Fig. S2 Inherent viscosity of BOPBI.

Fig. S3 (a) XRD pattern of the synthesized UIO-66-NH$_2$; (b) N$_2$ adsorption isotherms at 77 K for the UIO-66-NH$_2$; (c) TEM morphology of UIO-66-NH$_2$; and (d) solubility testing in PA of the UiO-66-NH$_2$ MOF.
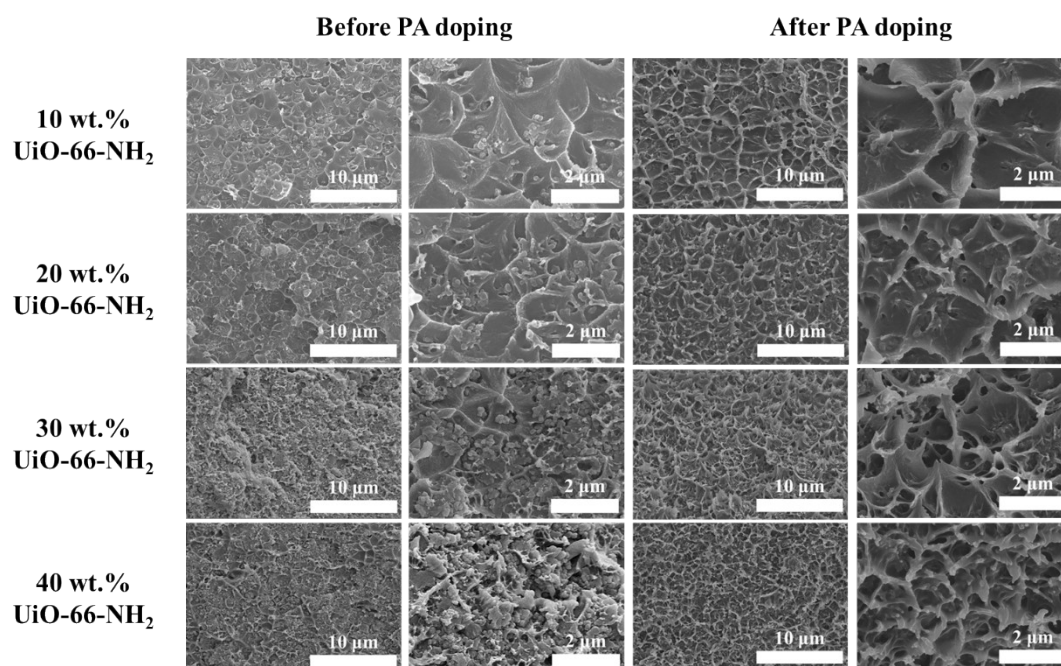

Fig. S4 Cross-sectional morphologies of the UiO-66-NH$_2$/CBOPBI and CBOPBI-P

membranes.

References

1.   Z. Rao, K. Feng, B. Tang and P. Wu, *Journal of Membrane Science*, 2017, **533**, 160-170.