Supporting Information

Cationic metal-organic frameworks porous membranes with high hydroxide conductivity and alkaline resistance for fuel cells

Bin Wu‡, Liang Ge‡, Dongbo Yu, Linxiao Hou, Qiuhua Li, Zhengjin Yang and Tongwen Xu*

CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, P.R. China.

1. Reactants and general methods

Bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was kindly supplied by Tianwei Membrane Co. Ltd., Shandong of China. Bromination degree of BPPO was 52%. Polyvinyl alcohol (PVA, average degree of polymerization: 1750±50) was purchased from Shanghai Yuanli Chemical Co. Ltd. (China). 2-Aminoterephthalic acid (99%) is acquired from Alfa Aesar. The other reagents, including ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), N-methyl-2-pyrrolidone (NMP), N, N-thdimethyl formamide (DMF), ethanol (EtOH), glutaraldehyde (GA), isopropanol (IPA), aluminum chloride ($AlCl_3$)，sodium hydroxide (NaOH) and Hydrofluoric acid (HF) are all of analytical grade and commercially obtained from domestic chemical reagents companies. Deionized water was used throughout.

The Fourier transform infrared/attenuated total reflection (FT-IR/ATR) spectra were obtained using a Nicolet iS10 spectrometer. The morphology and semi-quantitative elemental analyses of different samples were characterized by using a FEI-Sirion200 field emission scanning electron microscope (FESEM) equipped with PGT-IMIX PTS energy dispersive spectroscopy (EDS) detector. The Brunauer-Emmett-Teller (BET) and Langmuir surface areas were determined using Tristar II 3020M. The Powder X-ray diffraction(PXRD) data were collected using a D/max-TTR III Advance powder diffractometer operating at 40 kV, 40mA with Cu Kα (λ =1.54178 Å) radiation (2θ range, 1~10°). The X-ray photoelectron spectroscopy (XPS) characterization was determined by a Physical Electronics Escalab250 multi-technique system using monochromatic X-ray at a power of 350 W. The mechanical property test of the membranes was performed using a universal testing machine (INSTRON 5900 Testing System) at room temperature and crosshead speed of 10mm min^{-1}.

2. Materials Preparation

2.1 Synthesis and Purification of Fe-MIL-101-NH$_2$-F

Fe-MIL-101-NH$_2$-F was prepared by solvothermal reactions following the procedures reported by Ferey et al.[S1] 2-aminoterephthalic acid (225mg, 1.2 mmol) and FeCl$_3$·6H$_2$O (675mg, 4.2 mmol) were added place in 7.5mL of DMF, respectively. The mixture of included 1 mmol HF acid was transferred to the Teflon line in a autoclave which was heated for 24 h at 110°C and cooled afterwards slowly to room temperature over a time period. The solid separated from the solution through filtration, was washed three times with DMF. After drying under vacuum oven at 60 °C overnight, the powder of Fe- MIL-101-NH$_2$-F was obtained. To eliminate unreacted organic or inorganic impurities, the product was washed in hot DMF(100°C，immersing 8h，2 times) and in hot EtOH(80°C, immersing 8h, 2 times), filtered off , and dried overnight in an vacuum oven at 60 °C before further treatment.

2.2 Preparation of (Fe-MIL-101-NH$_2$)$^+$ Cl$^-$

The stripping of F ion was followed the procedure reported by Feng et al.[S2] To 15 mg Fe-MIL-101-NH$_2$-F in the 20mL vial were added 15 mL 0.02 M AlCl$_3$ solution. The vial was moved into the 80 °C vacuum oven and kept for 18h before being taken out. The (Fe-MIL-101-NH$_2$)$^+$ Cl$^-$ was obtained by filtration and washed with deionized H$_2$O several times.

2.3 Preparation of the membranes

(1) Preparation of porous matrix

BPPO was dissolved in NMP to yield 35 wt% solution. A quality of 6 % of Fe-MIL-101-NH$_2$-F or (Fe-MIL-101-NH$_2$)$^+$ Cl$^-$ respect to BPPO was added in the BPPO solution. To achieve a homogeneous dispersion of the MOFs particles and sufficient reaction of -NH$_2$ with -CH$_2$Br, the solution was treated for 1h in ultrasonic bath and stirred 24 h to obtain a uniform membrane solution. Then the solution was cast onto a clean glass plate and immediately immersed into isopropanol solution at room temperature for 24 hours to form a porous matrix.

(2) Preparation of the sandwiched-porous membranes

PVA (1 g) was dissoved in 90 °C deionized water under stirring for at least 3 hours to prepare a 2 wt.% PVA solution. After cooling down to room temperature, 1M HCl solution was added to adjust the pH to 1. Then a glutaraldehyde (GA) aqueous solution (27%wt) which was quarter of -OH concentration was added dropwise to initiate the crosslink reaction in PVA solution. The

various porous membranes were dipped into PVA-GA solution in 3 min and dried at 60 °C in 6 h. Then the porous matrix was sandwiched respectively between two pieces of glass plate and dried from 60 °C to 130 °C at the rate of 100 °C/h, and kept at 130 °C for 3 h. The resulting membranes were treated with 1M NaOH aqueous solution for 24 h at room temperature and then washed with deionized water and stored therein before use. The membrane was denoted as pc-MBPPO.

For comparisons, the porous membrane from BPPO (denoted as p-MBPPO) and that from BPPO and neutral MIL-101-Fe-NH$_2$-F (denoted as pn-MBPPO) were also prepared. The dense PVA layer is coated on both sides of all membranes.

3. Hydroxide conductivity (κ) measurement

The hydroxide conductivity of the membranes were measured using the normal four-point probe technique. The samples were in the hydroxide form and fully hydrated. The impedance was determined using an Autolab PGSTAT 30 (Eco Chemie, Netherlands) set at potentiostatic mode over the frequency range from 1MHz to 50 Hz. Using a Bode plot, the frequency region over which the impedance had a constant value was recognized, and the resistance was then obtained from a Nyquist plot. The hydroxide conductivity is calculated according to the following equation:

$$\kappa = L/(R \cdot W \cdot d)$$

where R is the obtained membrane resistance, L is the distance between potential-sensing electrodes, and W and d is the width and thickness of the membrane, respectively.

4. Methanol permeability

Methanol permeability measurement was carried out following the procedures reported previously.[S3] A two compartment diffusion cell was separated by a vertical membrane sample which has an effective area of 4.52 cm^2. The feed compartment of the cell was filled with 100 mL methanol solution (20%), and an equal volume of deionized water was added in the receiving compartment. The compartments were stirred continuously during the permeability measurement. Methanol permeates across the membrane by the concentration difference between the two compartments. The methanol concentration value in compartment was detected with time by using a Differential Refractive Index Detector (DRID). The detected refractive values were converted to the digital signal and transferred for a programmed computer. Finally, the methanol permeability (P$_M$) was determined by the following equation:

$$P_M = (d \cdot c_B/(dt)) \times (V_B \cdot d/S \cdot c_A)$$

where d is the thickness as above, S is the active area of the membrane, c_A is the initial concentration in compartment, V_B is the volume of the receiving compartment, dt is the measuring time and c_B is the methanol concentration in compartment. ($d \cdot c_B/(dt)$) can be obtained from the slope of the straight line recorded on the computer.

5. Water uptake (WU) and linear expansion ratio (LER) measurement

All kinds of membranes in OH⁻ form (4 cm in length and 1 cm in width) were immersed in deionized water for 24 h. To investigate the impact of temperature on water uptake and swelling ratio of the membrane, the samples were immersed in hot water with different temperatures and equilibrated. The wet samples were taken out and the surface of samples was quickly wiped with tissue paper and then weighed and length measured immediately. The membranes were subsequently dried at 60 °C until a constant weigh. The weight and length of the dry membranes were obtained as well.

Water uptake (WU) of membranes was calculated as follows.

$$WU = (W_{wet} - W_{dry})/W_{dry} \times 100\%$$

where W_{wet} is the weight of wet membrane samples and W_{dry} is the weight of dry membrane samples.

Linear expansion ratio (LER) was calculated in a similar way.

$$LER = (L_{wet} - L_{dry})/L_{dry} \times 100\%$$

where L_{wet} is the length of wet membrane samples and L_{dry} is the length of dry membrane samples.
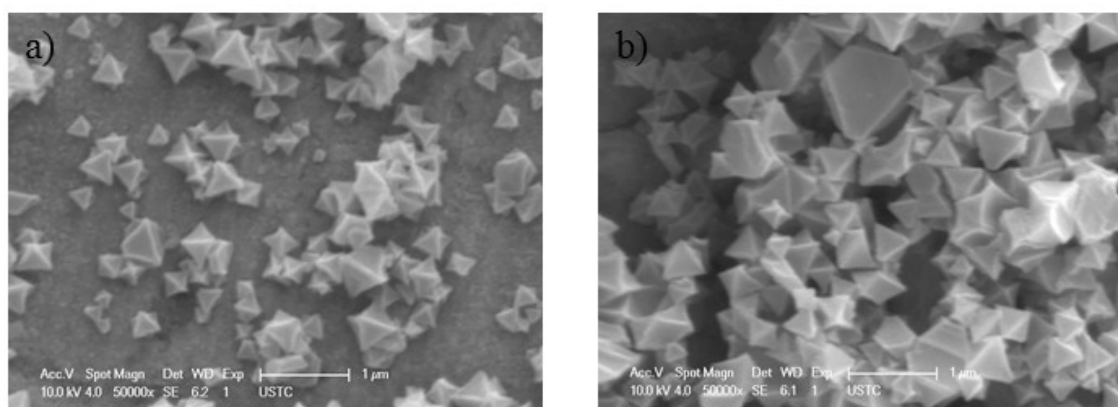
6. Supporting Figures

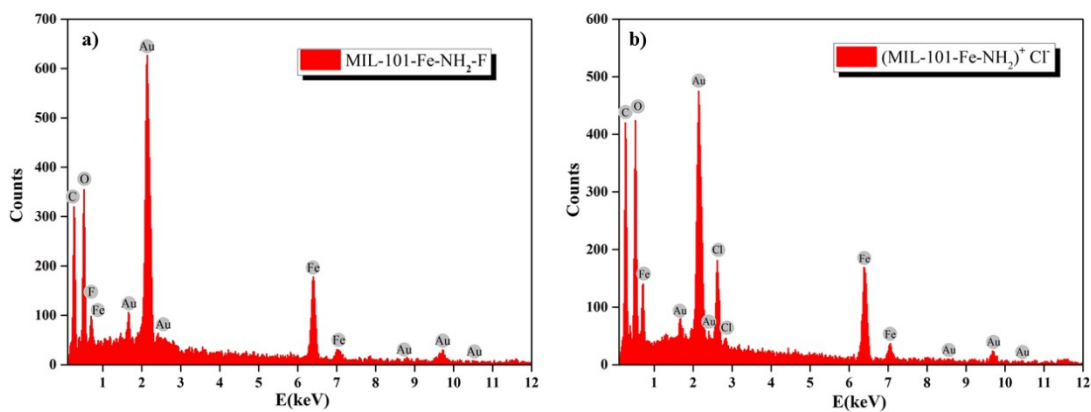**Fig.S1** SEM images (a) of MIL-101-Fe-NH$_2$-F and (b) of (MIL-101-Fe-NH$_2$)$^+$ Cl$^-$

Fig.S2 EDS for as prepared MIL-101-Fe-NH$_2$-F (a) and (MIL-101-Fe-NH$_2$)$^+$ Cl$^-$ (b), The Au

peaks came from the coating materials used in the SEM measurement.
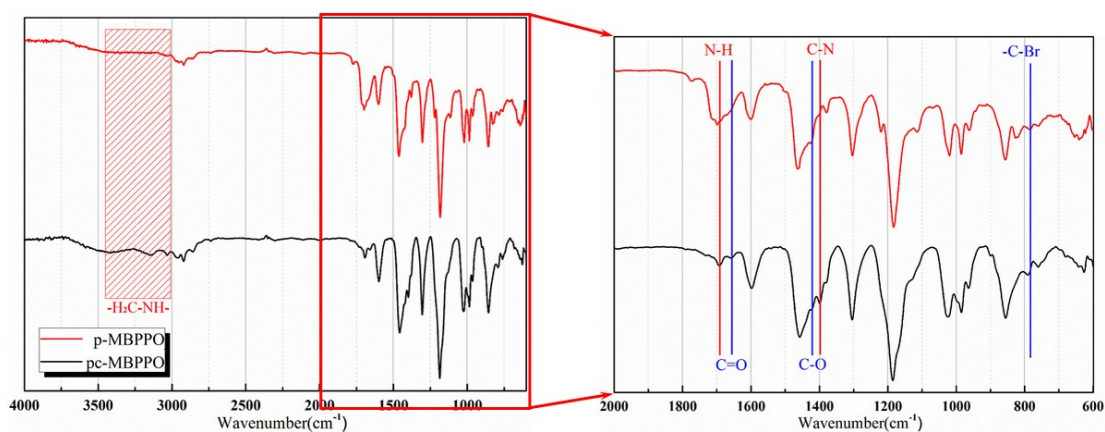

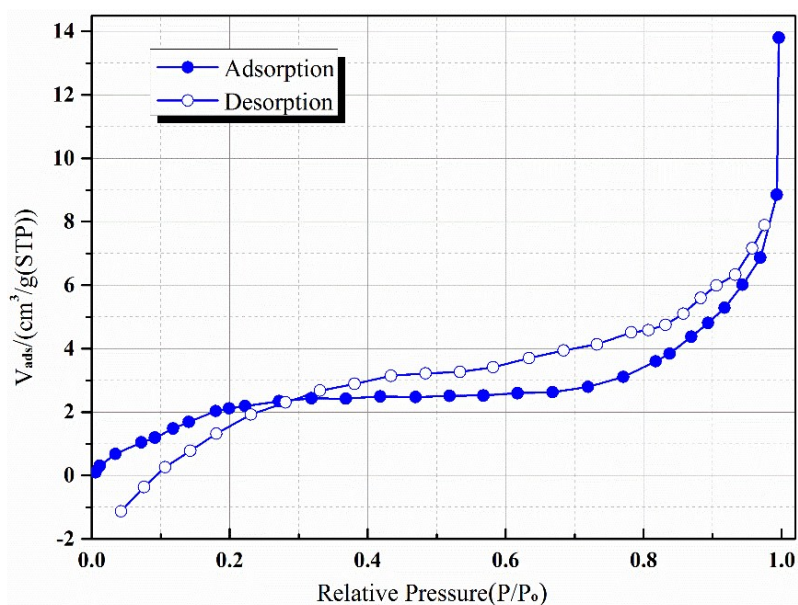**Fig. S3** Comparative FTIR spectra of pc-MBPPO and p-MBPPO.

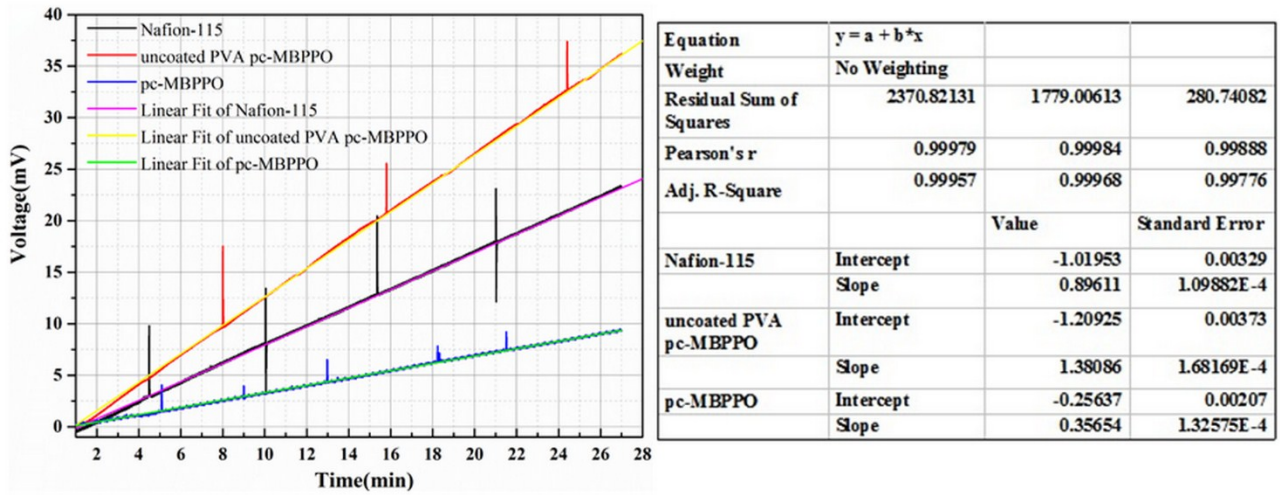**Fig.S4** N$_2$ adsorption isotherm measured on the pc-MBPPO
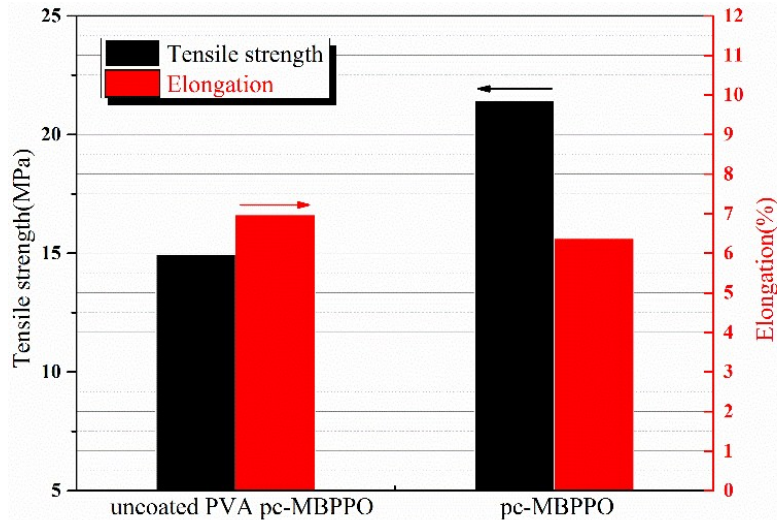
Fig. S5 Methanol permeability of Nafion-115 and pc-MBPPO.

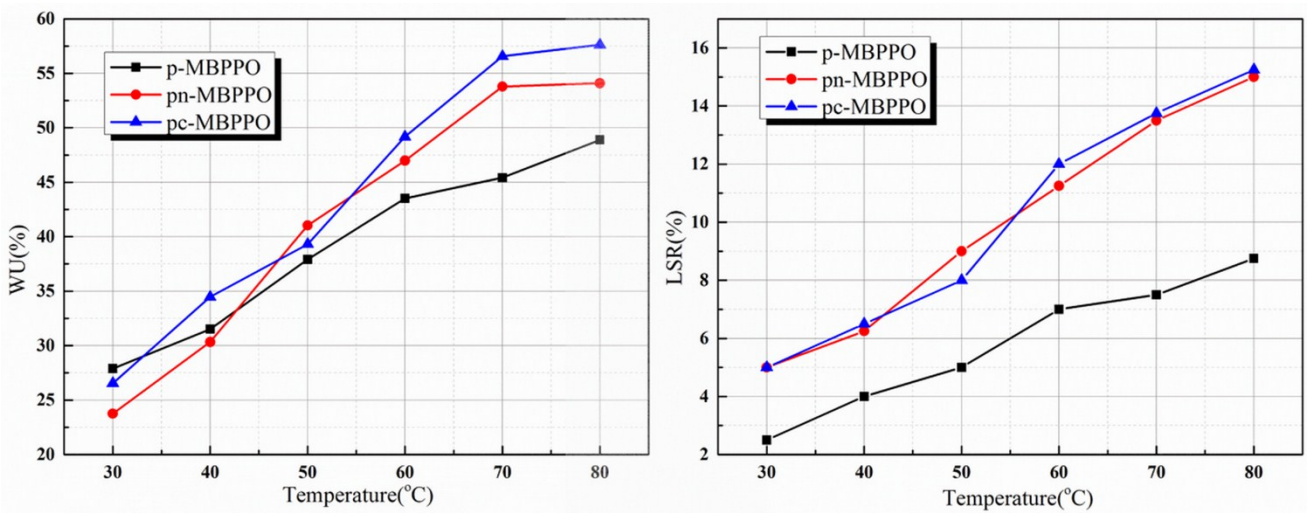**Fig.S6** The histograms of TS and Eb of pc-MBPPO and uncoated PVA pc-MBPPO

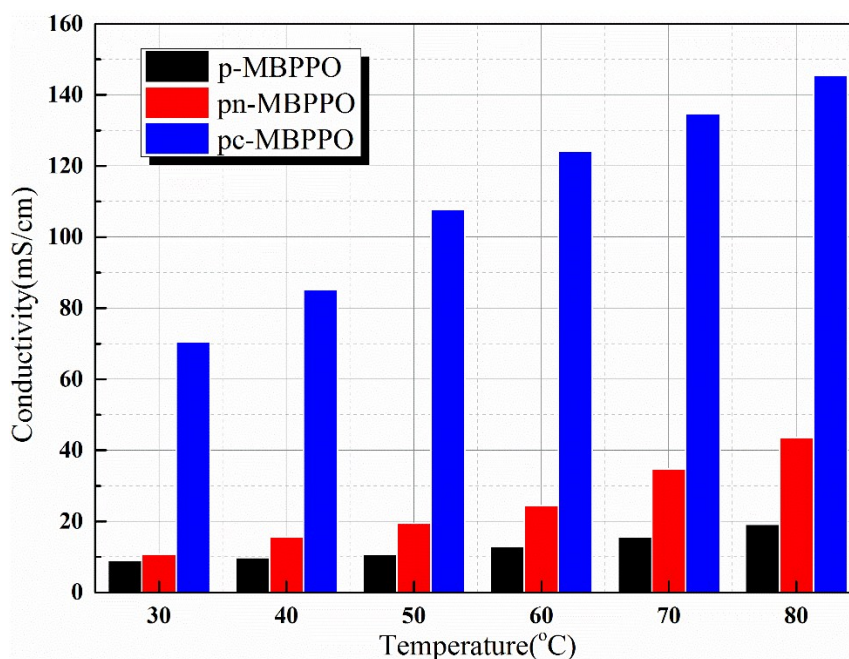**Fig. S7** WU and LSR of p-MBPPO, pn-MBPPO and pc-MBPPO at different temperatures

Fig. S8 Temperature dependence of the hydroxide conductivities of various membranes after immersing NaOH solution.
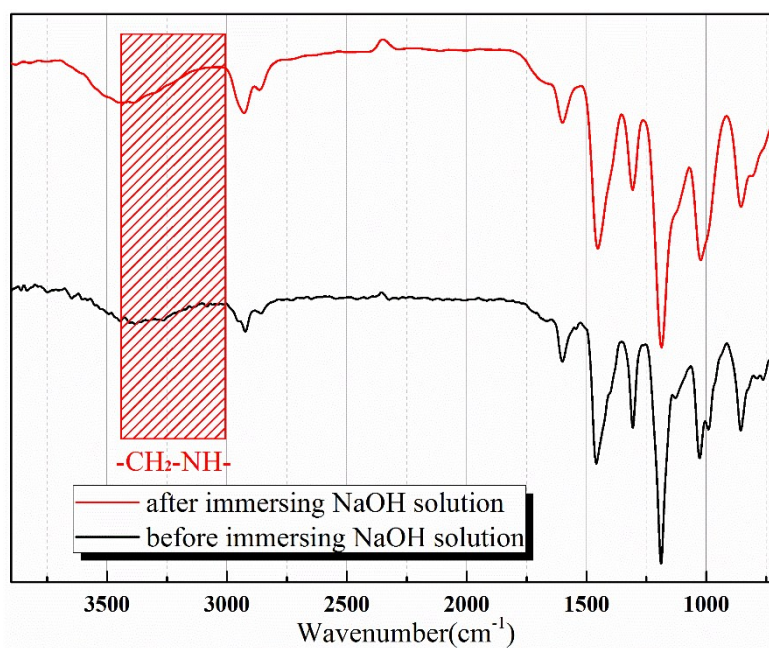

Fig. S9 FTIR of pc-MBPPO during alkaline treatment.

6. References

S1. G. Ferey, C. M. Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science*, 2005, **309**, 2040.

S2. C. Y. Mao, R. A. Kudla, F. Zuo, X. Zhao, L. J. Mueller, X.H. Bu, P. Y. Feng, *J. Am. Chem. Soc.,* 2014, **136**, 7579.

S3. Z. L. Yao, Z. H. Zhang, L. Wu, T. W. Xu, *J. Membr. Sci.*, 2013, **455**, 1.