

Supporting Information

Click mediated novel high-performance anion exchange membranes with improved water uptake

Abhishek N. Mondal, Yubin He, Liang Wu, Muhammad Imran Khan, Kamana Emmanuel, Md. Masem Hossain, Liang Ge*, and Tongwen Xu*

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

Experimental Section

Materials

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) [BPPO] was obtained from Tianwei Membrane Co. Ltd. (Shandong, PR China). ¹H NMR spectroscopy was employed to determine the degree of benzyl bromination (52%). Before using commercially obtained BPPO was purified in a similar way reported elsewhere.¹ 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and Vinylimidazole (VI) with 98% purity were purchased from Energy Chemical Co. Ltd. (Shanghai, PR China). 1-Hexanethiol was supplied by Shanghai Macklin Biochemical Co. Ltd. (Shanghai, PR China). Other used reagents like silver nitrate (AgNO₃), sodium sulfate (Na₂SO₄), sodium chloride (NaCl), sodium hydroxide (NaOH), N-Methyl-2-pyrrolidone (NMP), potassium chromate (K₂CrO₄), tetrahydrofuran (THF) etc. were purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, PR China). All of these used reagents are of

analytical grade and no further purification was made before use. Here, deionized water (DI water) was used throughout the experiment.

Synthesis of HLTEI

The Thiol-ene click based monomer (HLTEI) was synthesized according to the following procedure. The typical synthetic process involved UV assisted click reaction between vinylimidazole, 1-hexanethiol and 2,2-Dimethoxy-2-phenylacetophenone inside a nitrogen filled glove box. Firstly, a desired quantity of vinylimidazole (1 g, 0.0106 mol) and 1-hexanethiol (1.256 g, 0.0106 mol) were charged in a 10 mL vacuum dried round bottom flask. 2 mL of dry THF was further added to the reaction mixture. Afterwards, a known amount of photo initiator DMPA (0.055 g, 0.000212 mol) was dissolved in 3 mL THF and carefully added to the solution. To initiate the thiol-ene click reaction, round bottom flask containing the reaction mixture was taken out from the glove box and exposed to UV curing for 24 hours at room temperature. With the progress of time colour of the reaction mixture slowly changed from colourless transparent to light brown. After the completion of the reaction, excess amount of solvent (THF) was removed in *vacuo* and the anticipated product HLTEI appeared as a light brown oil with 97% (2.185 g) yield (with respect to vinylimidazole). HLTEI chemical structure was confirmed by ¹H NMR and FTIR spectroscopy. ¹H NMR (CDCl₃, 400 MHz): δ 7.48 (d, 1H), δ 7.00 d, 1H), δ 6.90 (d, 1H), δ 4.06 (t, 2H), δ 2.77 (t, 2H), δ 2.34 (t, 2H), δ 1.52 (m, 2H), δ 1.22 (m, 6H), δ 0.82 (t, 3H) ppm.

General fabrication procedure of the HLTEI based side-chain type AEMs

HLTEI based side-chain type AEMs are prepared via sequential steps, which includes menshutkin reaction between BPPO and HLTEI. A detailed typical procedure is demonstrated below: firstly, a 25 mL round bottom flask was taken with a known amount of BPPO (0.500 g). To ensure the complete dissolution of BPPO, a desired quantity of NMP was carefully added

to the flask at room temperature. In the follow up step, a suitable amount of HLTEI was dissolved in a small volume of NMP (1 mL). Finally, HLTEI solution was dropwise added to the previously stirred BPPO solution. After the complete addition of HLTEI solution, temperature of the reaction was raised to 40 °C and stirring was further continued till 24 h. Finally, the solution was casted on a clean glass plate and dried at ambient temperature (60 °C) for 24 h to obtain a transparent light yellow thin film. Fabricated membranes are designated as ANM-22-30, ANM-22-40, ANM-22-50 and ANM-22-100 respectively. The detailed summary of membrane fabrication is provided in Table S1. Prepared membranes are finally converted into the OH⁻ form by dipping inside aqueous NaOH (1 M) solution at room temperature. After 24 hours, membranes were taken out of the alkali solution and washed further very carefully by DI water to remove traces of NaOH.

Characterization Methods

Nuclear Magnetic Resonance (NMR)

Synthesized clicked monomer HLTEI and membrane ANM-22-100 were isolated by ¹H NMR spectra via an AV III 400 NMR spectrometer (400 MHz, Bruker) using CDCl₃ and MeOD-*d*₄ (with tetramethylsilane used as an internal reference) respectively as solvent.

Fourier transform infrared (FTIR)

FTIR spectra of the synthesized clicked product (HLTEI) and the dried membranes (BPPO and ANM-22-100) were recorded by using the attenuated total reflectance (ATR) technique with a FTIR spectrometer (Vector 22, Bruker) having a resolution of 2 cm⁻¹ and a wide spectral range of 4000–400 cm⁻¹.

Thermogravimetric Analysis (TGA)

Thermal stability of the membrane was tested by a Shimadzu TGA-50H analyzer under persistent nitrogen flow, at a constant heating rate of 10 °C/min within the temperature range of 40-700 °C.

Atomic force microscopy (AFM)

Tapping mode atomic force microscopy was performed with a veeco diInnova SPM, using microfabricated Cantilevers with a force constant of approximately 20 N/m.

X-ray photoelectron spectroscopy (XPS)

To assess the surface elemental composition of BPPO and HLTEI modified BPPO, X-ray photoelectron spectroscopy (XPS) was done with ESCALAB 250 instrument fortified with a monochromated Al_{Kα} source (pass energy 30 eV).

Ion exchange capacity (IEC)

IEC was measured through the conventional Mohr method. In a typical standard procedure, firstly membrane sample was converted into the Cl⁻ form by dipping inside 1 M NaCl solution for 24 hours. Afterwards, sample was taken out of the NaCl solution and washed thoroughly with DI water to remove traces of NaCl. The sample was then dried to obtain a constant mass and denoted as W_{dry} . Finally, the membrane sample was dipped in 0.5 M Na₂SO₄ solution for 24 hours to exchange the counter ions from Cl⁻ to SO₄²⁻. The liberated Cl⁻ ions were finally titrated with 0.01 M AgNO₃ solution with K₂CrO₄ used as an indicator. Membrane IEC was calculated according to the following equation, $IEC = ab/w_{dry}$ where w_{dry} , a and b represents the dry weight of the membrane, titre value during titration and the concentration of AgNO₃ solution respectively.

Water Uptake (W_R)

Water uptake (W_R) measurement was done exactly in a same way according to our previously published research article.²

Ionic Conductivity (σ)

Hydroxide conductivity of the membrane was measured by a standard four-point probe technique. The additional details related to membrane ionic conductivity determination procedure remains exactly same as reported previously by our research group.² Ionic conductivity (σ) was determined by the following equation:

$$\sigma = \frac{L}{RWd} \quad (1)$$

Here, L denotes the distance between potential sensing electrodes (1 cm in our case), R known as the membrane resistance, W is the width (1 cm in our case) and d refers to the thickness of the monitored membrane sample.

Alkaline Stability

Alkaline stability of the membrane was determined by the following procedure. Membrane samples were firstly cut into appropriate size of (4*1) cm² and immersed into the aqueous 1 M NaOH solution at 60 °C for a scale of 14 days. Every second day one piece of membrane sample was taken out from the NaOH solution and washed thoroughly with DI water to remove the last traces of NaOH. Lastly, hydroxide conductivity of the each membrane was re-measured at 30 °C and compared with the initial value.

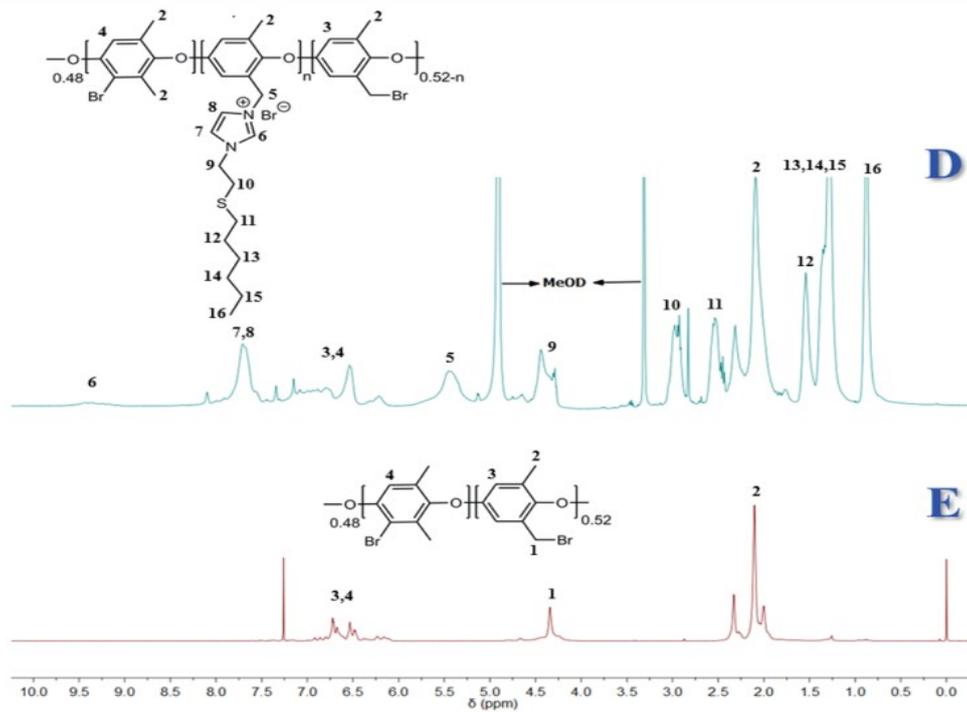
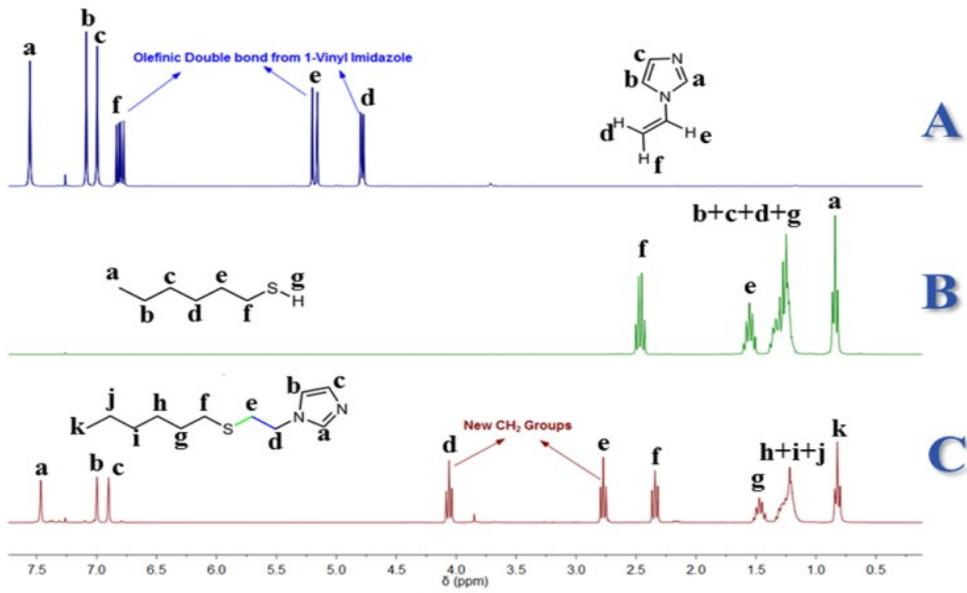


Figure S1. (TOP) NMR spectrum of (A) vinylimidazole, (B) 1-hexanethiol, (C) HLTEI;
(Bottom) Comparison of NMR spectrum between (D) ANM-22-100 and (E) BPPO.

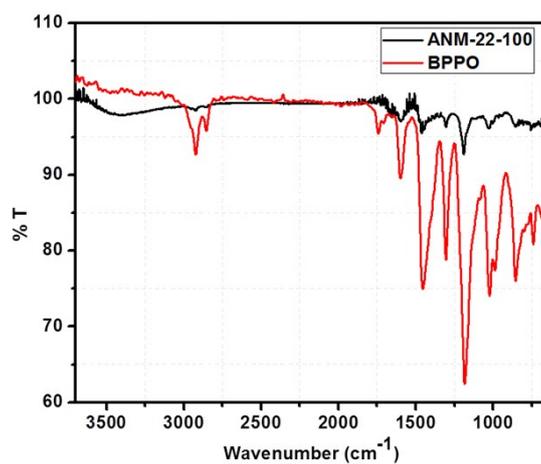


Figure S2. Comparison of IR spectrum of ANM-22-100 and BPPO.

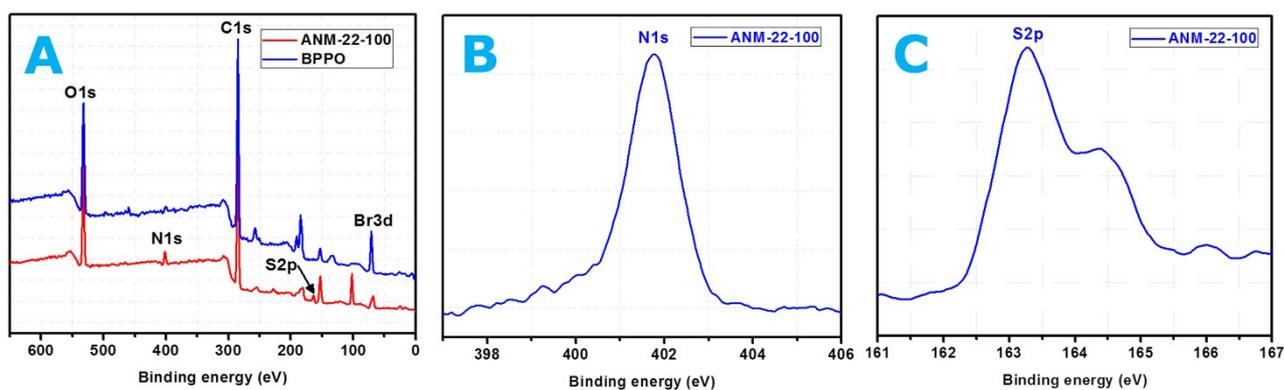


Figure S3. (A) Comparison of XPS spectra of BPPO and ANM-22-100, (B) High-resolution spectrum of N1s region (C) S2p region of ANM-22-100 membrane respectively.

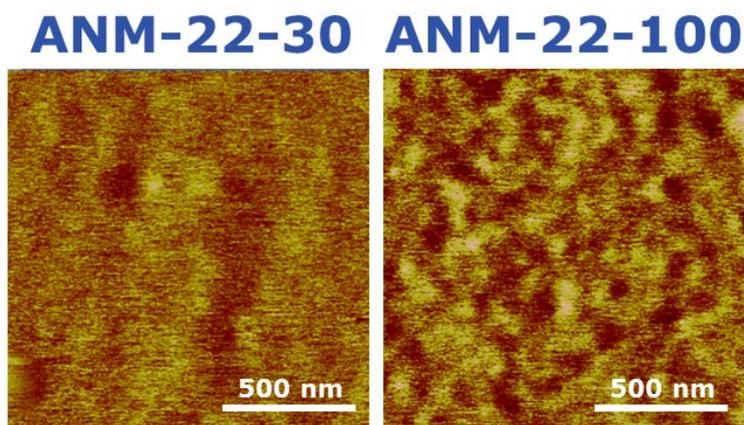


Figure S4. AFM phase image of the membrane ANM-22-30 and ANM-22-100 (scan box is 500 nm × 500 nm).

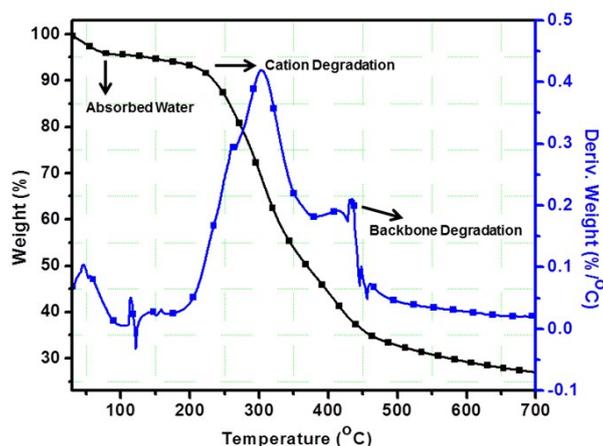


Figure S5. TGA diagram of the membrane ANM-22-100.

Table S1 Detailed membrane compositions

Membrane Code	BPPO (wt%)	Weight ratio of HLTEI/BPPO (g)	Feed molar ratio of -n CH ₂ Br/HLTEI
ANM-22-30	4 wt% in NMP	0.083g/0.500g	1/0.3
ANM-22-40	4 wt% in NMP	0.111g/0.500g	1/0.4
ANM-22-50	4 wt% in NMP	0.140g/0.500g	1/0.5
ANM-22-100	4 wt% in NMP	0.278g/0.500g	1/1

Table S2 Comparison of water uptake and hydroxide conductivity of different literature reported AEMs with ANM-22-100

AEMs	Temperature (°C)	Conductivity (mS/cm)	WU (wt%)	References
ANM-22-100	30 °C	51.30±6.14	22.39±0.37	This work
PPO-DMHDA-55	20 °C	35.00	20.4	3
gQAPPO	30 °C	27.02	53.6	4
C10D60	RT	28	16.0	5
B-g-Q-2	20 °C	39.0	74.7	6
NAPAEK-Q-100	80 °C	49.0	24.3	7
[PUVBIIm][OH]	30 °C	16.0	37.25±2.54	8
[PVMBIm][OH]	30 °C	10.90±0.60	67.62±7.82	9
PAES-Q-90	25 °C	39.2±0.02	60.60±4.10	10
X60Y60	25 °C	18.00	18.0	11
HB-QPVC	20 °C	39.57	35.2	12

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