Supporting information for

Poly(binaphthyl-co-terphenyl quinuclidinium) Anion Exchange Membrane with Excellent Alkaline Stability and Enhanced Anion Conductivity

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Materials

With the exception of 1,1'-Binaphthyl obtained from Sia Reagent, all other chemicals were procured from Labgogo and underwent no additional purification steps before the reaction.

Synthesis of Poly(binaphthyl-co-terphenyl quinoline)

Synthesis Protocol for Poly(binaphthyl-co-terphenyl quinoline) (PBTQ-10): A mixture comprising 1.037 g of triphenylene, 0.907 g of 3-quinuclidinone hydrochloride, 0.130 g of 1,1'-Binaphtyl, and 12 mL of dichloromethane was introduced into a round-bottom flask at 0 °C. Then trifluoromethanesulfonic acid and trifluoroacetic acid were added from a pressure-equalizing dropping funnel. After stirring overnight, pure water was added into the resulting solution to stop the polymerization. The precipitate was thoroughly washed with pure water until neutral, then dried at 120 °C for 2 hours, yielding PBTQ-10 (1.7 g) in the form of a pink solid.

Quaternization

In a flask with a single neck, 1 g of PBTQ-10 was dissolved in DMSO, and 1.6 g of potassium carbonate, along with 0.6 mL of iodomethane, were added. The mixture was stirred at 50°C. Upon completion of the reaction, a precipitate was obtained by addition of ethyl acetate. The precipitate was washed multiple times with water. Following drying at 100°C for 12 hours, a pink solid, denoted as PBTQ-I-10 (0.92 g), was successfully obtained.

Membrane preparation and ion exchange

The solution for PBTQ-I in DMSO, was cast onto a PET sheet and subsequently dried at 50 °C. Subsequent to immersion in pure water, the membrane can be peeled off and designated as the PBTQ-I membrane. This membrane can be ion exchanged in a 1M NaOH solution at 80 °C for 10 hours to give PBTQ-OH.

IEC determination

The ion exchange capacity (IEC) of the membrane was determined through molar titration, employing the $AgNO_3 + Br$ ——AgBr (precipitate) reaction. The IEC value of Br- was determined through titration, and subsequently, the IEC value of OH- was computed. The dry weight (W_{dry}) was recorded using PBTQ-Br-10 subjected to Br- ion exchange. The ion exchange process involved three consecutive exchanges using a 0.1M NaNO₃ solution, with each exchange lasting for 12 hours. After three exchanges, the solution was collected and titrated with a 0.01M AgNO₃ solution, employing K₂CrO₄ as an indicator. The IEC was calculated utilizing the following equation.

$$IEC(Br^{-}) = \frac{0.01 * V_{AgNO_3}}{W_{dry}}$$
$$IEC(OH^{-}) = \frac{0.01 * V_{AgNO_3}}{W_{dry} - 0.629 * V_{AgNO_3}}$$

Water uptake (WU) and swelling ratio (SR)

To assess the WU and SR of the membrane, a membrane sample of $3.0 \times 3.0 \text{ cm}^2$ is prepared and subjected to drying at 120 °C for 4 hours. At this stage, the dry weight (W_{dry}) and dry length (L_{dry}) of the membrane are documented. The experimentation involves immersing the membrane in deionized water at various temperatures (20 °C, 40 °C, 60 °C, 80 °C) for 12 hours. The determination of the wet state weight (W_{wet}) and wet state length (L_{wet}) of the membrane necessitates the removal of surface moisture. The specific WU and SR were calculated using the following formulas:

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

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

The hydration number (λ) is the number of water molecules adsorbed by the quinuclidinium group and is calculated as follows:

$$\lambda = \frac{10 * WU}{IEC(OH^{-}) * 18}$$

Electrochemical impedance spectroscopy (EIS) and conductivity measurement

The electrochemical impedance spectra were acquired using a CHI760E electrochemical workstation within the frequency range of 1 Hz to 1 MHz. A membrane sample of $1.0 * 3.0 \text{ cm}^2$ was utilized, and the measurements were conducted under fully hydrated conditions. The conductivity (σ) was determined using the following formula:

$$\sigma = \frac{L}{AR}$$

Where R is the resistance measured by ESI, L is the distance between the electrodes (L=1 cm), A is the effective cross-sectional area during the test.

$$A = HW$$

H is the thickness of the membrane, W is the width of the membrane

Intrinsic viscosity

The intrinsic viscosity of PBTQ-OH-X in DMSO solution at 31°C was performed by an Ubbelohde viscometer. The polymer solution was gradually diluted into three different concentrations, and the efflux time was recorded. The reduced (η_{red}), inherent (η_{inh}), and intrinsic viscosities can be calculated using the following equations:

$$\eta_{red} = (\frac{t_1}{t_0} - 1)/c$$
$$\eta_{inh} = (\ln \frac{t_1}{t_0})/c$$

 t_1 is the efflux time of a polymer solution, t_0 is the efflux time for a DMSO solution, and c is the concentration of the polymer solution. In a plot of η versus c, the y-intercept was obtained by extrapolating the η_{red} and η_{inh} to c = 0. The intrinsic viscosity was obtained by calculating the average of the obtained y-intercept values.

Water electrolysis measurement

The AEM was sandwiched between the NiFe and NiMo electrodes. Consequently, an electrolyzer was assembled in a clamp, and a KOH alkaline solution was introduced and circulated through the electrolyzer. Pertinent current and voltage data were meticulously recorded utilizing a stabilizing voltage source. Stability studies were performed at a consistent current of 0.5 A cm⁻² and 1A cm⁻², respectively.



Figure S1. Total energy and Torsion angle of 1,1'-Binaphthyl



Figure S2. Total energy and Torsion angle of p-terphenyl



Figure S3. Phase images of PBTQ-I measured by AFM (the dark region represents ionic domains while the bright region represents hydrophobic domain.) (a) PBTQ-I-5 (b) PBTQ-I-10 and (c) PBTQ-I=15; (d) PBTQ-I-10 section taken with SEM

Table S1. Mechanical Properties of Membranes Treated with 1, 5, and 10 M NaOH at 80 $^{\circ}\mathrm{C}$ for 2556 h.

Lye	YM/MPa	TS/MPa	EB/%
concentration			
pristine	1160.11	35.56	22.66
1M	108.92	1.99	2.75
5M	427.84	19.63	7.26
10M	1178.60	41.97	11.66



Figure S4. SEM of (a)PBTQ-I-5, (b)PBTQ-I-10 and (c)PBTQ-I-15



Figure S5. TGA of PBTQ-OH-x membranes

Table S2.	Performance	of recently	reported	AEMs
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Name	IEC	SR%80	Conductivity
PBTQ-OH-10	2.85	7.13	167
PDTP-25	2.8	33.3	166
b-PTP-2.5	2.84	25.9	146
PFPE-P	2.49	9.4	80.4
PBP-TPEG	3.07	115.8	56.1
P2PA-73	1.85	14.5	27
qPBN-CA10	2.02	33	41.1
PAP	2.84	33.2	138
PTP-90	2.52	15.4	128.9
PBC3/QPPO	1.42	14.59	62.58
HQCS/QPVDF	2.53	53.21	66.18
PDPF-bisPip2.8	2.65	34	150
PEP80	4.52	350	85

PB1Pip-1C	2.55	42.5	165
QPTFP-25	2.88	25	155
PTTPQ4-40	3	19.4	155.3

1 X. Wu, N. Chen, C. Hu, H.-A. Klok, Y. M. Lee and X. Hu, Adv. Mater., 2023, 35, 2210432.

2 Y. Ou, T. Qu, F. Cheng, H. Yang, F. Hu, J. Wang, H. Liu, G. Liu, S. Wen and C. Gong, Carbohydr. Polym., 2023, 322, 121363.

X. Hu, Y. Huang, L. Liu, Q. Ju, X. Zhou, X. Qiao, Z. Zheng and N. Li, Journal of Membrane Science, 2021, 621, 3 118964.

T. Jiang, C. Wu, Y. Zhou, S. Cheng, S. Yang, H. Wei, Y. Ding and Y. Wu, J. Membr. Sci., 2022, 647, 120342. L. Yang, Z. Wang, F. Wang, Z. Wang and H. Zhu, J. Membr. Sci., 2022, 653, 120448. 4

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F. Wang, T. Qu, H. Yang, H. Yang, Y. Ou, Q. Zhang, F. Cheng, F. Hu, H. Liu, Z. Xu and C. Gong, ACS Appl. 6 Mater. Interfaces, 2024, 16, 2751-2762.

N. Chen, C. Hu, H. H. Wang, S. P. Kim, H. M. Kim, W. H. Lee, J. Y. Bae, J. H. Park and Y. M. Lee, Angew 7 Chem Int Ed Engl, 2021, 60, 7710-7718.

L. Ma, L. Li, M. Yuan, L. Bai, A. Zhang, X. Yan, G. He and F. Zhang, ACS Sustainable Chem. Eng., 2022, 10, 8 5748-5757.

9 F. Xu, Y. Chen, B. Lin, J. Li, K. Qiu and J. Ding, ACS Macro Lett., 2021, 10, 1180-1185.

10 A. Shirole, P. M. Bakvand and P. Jannasch, ACS Appl. Energy Mater., 2023, 6, 7240-7249.



Figure S6. Impedance diagram of PBTQ-OH-10 and PBTQ-Cl-10 during conductivity measurement.



Figure S7. PBTQ-OH-10 (a) ¹H NMR spectra of the AEM at different periods after alkaline treatment in 1M at 80 °C (b) and 5M NaOH 80 °C.



Figure S8. The WU and SR of PPTQ-OH-10 membranes at different periods after alkaline treatment.



Figure S9. Polarization curves of PBTQ-OH-10 AEMWE at different temperatures (1 M KOH).