Electronic Supplementary Information (ESI):

Multi-cation crosslinked anion exchange membranes from microporous Tröger's base copolymers

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Scheme S2 Synthesis of the Br-TQA.

Scheme S3 Synthesis of the BQB.
Scheme S4 The reaction route of the crosslinked DPM/DMBP-QTB AEMS.
Fig. S1 The $^1$H NMR spectrum and digital photo of the DPM/DMBP-TB copolymer.

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.16 (s, 2H, Ar H), 7.05 (d, $J = 7.6$ Hz, 2H, Ar H), 6.95 (s, 2H, Ar H), 6.85 (d, 2H, $J = 7.6$ Hz, Ar H), 6.70 (s, 2H, Ar H), 4.62 (m, 4H, CH$_2$), 4.28 (s, 4H, CH$_2$), 4.06 (m, 4H, CH$_2$), 3.71 (m, 2H, CH$_2$), 2.42 (d, 6H, CH$_3$).

The peak emerging from $\delta = 6.70 - 7.16$ is in response to the characteristic aromatic protons on the benzene ring. The signal at $\delta = 2.42$ is associated with the protons of methyl on the benzene rings (Ar–CH$_3$) that comes from monomer 4,4’-diamine-3,3’-dimethyl-biphenyl (DMBP). The signal at $\delta = 3.71$ is attributed to the methylene group between two benzene rings (Ar–CH$_2$–Ar) which is associated with monomer 4,4’-Diaminodiphenylmethane (DPM).
Fig. S2 The $^1$H NMR spectrum and digital photo of the Br-QA.

$^1$H NMR (400 MHz, D$_2$O, δ): 1.37 (h, $J = 7.2$, 6.5 Hz, 2H, CH$_2$), 1.47 (m, 2H, CH$_2$), 1.60 (m, 2H, CH$_2$), 1.76 (m, 2H, CH$_2$), 1.85 (p, $J = 6.8$ Hz, 2H, CH$_2$), 3.07 (s, 9H, CH$_3$), 3.28 (m, 2H, CH$_2$), 3.48 (t, $J = 6.7$ Hz, 2H, CH$_2$).

The peak at δ = 3.07 (s, 9H, CH$_3$) is associated with the quaternary ammonium groups from trimethylamine. The single at δ = 1.37 − 1.85 ppm is attributed to alkyl chain from DHB.
Fig. S3 The $^{13}$C NMR spectrum of the Br-QA.

$^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 65.40, 52.48, 35.57, 32.35, 27.44, 25.29, 22.39.
Fig. S4 The $^{15}$N NMR spectrum of Br-QA.

$^{15}$N NMR (600 MHz, D$_2$O): $\delta$ (ppm) 48.77
Fig. S5 FT-IR spectrum of the Br-QA at 25 °C (KBr).

FT-IR (KBr): \( \nu \text{ (cm}^{-1}\text{)} \) 3494, 3446, 3006, 2952, 2859, 1632, 1484, 1457, 1417, 1401, 1362, 1301, 1285, 1255, 1223, 1077, 1052, 1033, 972, 951, 916, 866, 823, 812, 751, 737, 639, 551, 533, 517, 492, 453.
**Fig. S6** The \(^{1}\text{H} \text{NMR} \) spectrum in \( \text{D}_2\text{O} \) and digital photo of the N, N-DQA.

\(^{1}\text{H} \text{NMR} (400 \text{ MHz, D}_2\text{O }\delta):\) 1.30 (m, 2H, CH\(_2\)), 1.40 (m, 8H, CH\(_2\)), 1.72 (m, 6H, CH\(_2\)), 2.12 (s, 6H, CH\(_3\)), 2.27 (m, 2H, CH\(_2\)), 2.98 (s, 6H, CH\(_3\)), 3.05 (s, 9H, CH\(_3\)), 3.25 (m, 6H, CH\(_2\)).

Compared with the spectrum of the Br-QA, the peak at \( \delta = 3.48 \text{ (t, } J = 6.7 \text{ Hz, } 2\text{H, CH}_2)\) disappeared. Subsequently, there were two new peaks emerged at \( \delta = 2.12 \text{ (s, 6H, CH}_3\text{)} \) and \( \delta = 2.27 \text{ (m, 2H, CH}_2\text{)}.\)
Fig. S7 The $^{13}$C NMR spectrum of the N, N-DQA.

$^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 65.42, 63.46, 63.23, 59.34, 52.61, 50.37, 45.58, 27.19, 26.78, 26.18, 25.59, 22.24, 21.94.
Fig. S8 The $^{15}\text{N}$ NMR spectrum of the N, N-DQA.

$^{15}\text{N}$ NMR (600 MHz, $\text{D}_2\text{O}$): $\delta$ (ppm) 52.27, 48.61, 29.45
**Fig. S9** FT-IR spectrum of the N, N-DQA at 25 °C (KBr).

FT-IR (KBr): $\nu$ (cm$^{-1}$) 3440, 3001, 2936, 2852, 2817, 2781, 2764, 1782, 1629, 1485, 1467, 1422, 1402, 1379, 1354, 1300, 1258, 1223, 1209, 1172, 1158, 1103, 1062, 1042, 974, 951, 918, 850, 803, 730, 530, 453.
**Fig. S10** The $^1$H NMR spectrum and digital photo of the Br-TQA.

$^1$H NMR (400 MHz, DMSO-$d_6$ $\delta$): 1.30 (m, 10H, CH$_2$), 1.45 (m, 2H, CH$_2$), 1.72 (m, 10H, CH$_2$), 1.80 (m, 2H, CH$_2$), 3.04 (s, 6H, CH$_3$), 3.06 (s, 6H, CH$_3$), 3.10 (s, 9H, CH$_3$), 3.3 (m, 10H, CH$_2$), 3.57 (t, $J=6.7$ Hz, 2H, CH$_2$).

Compared with the spectrum of the N, N-DQA, the single at $\delta = 2.27$ (t, 2H, CH$_2$) disappeared. Subsequently, the peak at $\delta = 3.57$ (t, $J=6.7$ Hz, 2H, CH$_2$) appeared again. Furthermore, the three peaks located at $\delta = 3.04 - 3.10$ (s, 21H, CH$_3$) corresponded to three quaternary ammonium groups which indicated that the target product was successfully synthesized.
**Fig. S11** The $^{13}$C NMR spectrum of the Br-TQA.

$^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 65.36, 63.23, 52.54, 50.42, 35.63, 32.37, 27.47, 25.59, 25.53, 22.21, 21.94.
**Fig. S12** The $^{15}$N NMR spectrum of the Br-TQA.

$^{15}$N NMR (600 MHz, D$_2$O): $\delta$ (ppm) 54.17, 50.01, 48.44
Fig. S13 FT-IR spectrum of Br-TQA at 25 °C (KBr).

FT-IR (KBr): ν (cm\(^{-1}\)) 3454, 3009, 2947, 2857, 2694, 2067, 1726, 1620, 1487, 1467, 1419, 1402, 1353, 1315, 1277, 1254, 1133, 1062, 1010, 967, 950, 914, 803, 731, 637, 554, 510, 453.
Fig. S14 The $^1$H NMR spectrum and digital photo of the DPM/DMBP-QTB copolymer.

Apparently, compared with the spectrum of the DPM/DMBP-QTB, the signal at $\delta = 3.04 - 3.10$ (m, 21H, CH$_3$) are attributed to the quaternary ammonium groups from Br-TQA. The peaks located at $\delta = 1.33 - 1.70$ (m, 24H, CH$_2$) were associated with the alkyl chain.
Fig. S15 The $^1$H NMR spectrum and digital photo of the BQB.

$^1$H NMR (400 MHz, DMSO-d$_6$, $\delta$): 1.30 (m, 8H, CH$_2$), 1.45 (dq, $J$ = 9.0, 7.2 Hz 4H, CH$_2$), 1.69 (m, 8H, CH$_2$), 1.83 (dt, $J$ = 14.8, 6.8 Hz 4H, CH$_2$), 3.03 (s, 12H, CH$_3$), 3.28 (dt, $J$ = 12.8, 4.6 Hz, 8H, CH$_2$), 3.55 (t, $J$ = 6.7 Hz, 4H, CH$_2$)
Fig. S16 The $^{13}$C NMR spectrum of the BQB.

$^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 63.29, 50.37, 35.58, 32.38, 27.48, 25.59, 25.35, 22.10, 21.94.
Fig. S17 The $^{15}\text{N}$ NMR spectrum of the BQB.

$^{15}\text{N}$ NMR (600 MHz, $\text{D}_2\text{O}$): $\delta$ (ppm) 51.92.
Fig. S18 FT-IR spectrum of the BQB at 25 °C (KBr).

FT-IR (KBr): $\nu$ (cm$^{-1}$) 3454, 3009, 2947, 2857, 2694, 2067, 1726, 1620, 1487, 1467, 1419, 1402, 1353, 1315, 1277, 1254, 1133, 1062, 1010, 967, 950, 914, 803, 731, 637, 554, 510, 453.

Fig. S19 The preparation process of the crosslinked DPM/DMBP-QTB AEMs.
The broad vibration bands at 3420 cm\(^{-1}\) is contributed to \(-\text{OH}\) groups that comes from the bound water.\(^{[1]}\) The strong single peak near 2950 cm\(^{-1}\) is associated with the Stretching vibration of \(-\text{CH}_2-\) group.\(^{[2]}\) The peaks at 1662 cm\(^{-1}\) is the bending vibration of benzene ring. In addition, the peaks at 1329 cm\(^{-1}\) and 1101 cm\(^{-1}\) are assigned to the C–N and C–N\(^+\) groups, respectively.\(^{[3-5]}\)

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**Fig. S20** FT-IR spectra of the crosslinked DPM/DMBP-QTB AEMs.
Fig. S21 FT-IR spectra of the crosslinked DPM/DMBP-QTB AEMs and BQB.
**Fig. S22** The water contact angles of the crosslinked DPM/DMBP-QTB AEMs at 25 °C.

**Fig. S23** 3D AFM surface topographic of the DPM/DMBP-QTB-1.0 (a) / 2.0 (b) membranes.
Fig. S24 AFM phase images of the membrane DPM/DMBP-QTB-1.0 (a) /2.0 (b).

Fig. S25 The activation energy ($E_a$) of the crosslinked DPM/DMBP-QTB AEMs.

The relationship between the conductivity and temperature can be measured by $E_a$. The $E_a$ for ionic transport can be calculated by Arrhenius equation ($\ln\sigma = \ln\sigma_0 - \frac{E_a}{RT}$), where $\sigma$ is the conductivity of membrane, $\sigma_0$ is the frequency factor which is independent of temperature, $R$
is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and T is the absolute temperature.\(^6\)

**Fig. S26** The solid state \(^{13}\)C NMR spectra for the DPM/DMBP-QTB-1.5 membrane before and after alkaline ability test.

The \(^{13}\)C Cross polarization/magic angle spinning (\(^{13}\)C CP/MAS) solid state spectra were recorded on a Bruker Advance III 400 spectrometer. The signals around 128 ppm correspond to carbon of benzene. The peak at 75 ppm is ascribed to \(=\text{N}^+\text{CH}_2\text{N}−\) in the backbone. The peaks around 63 ppm are associated with the \(=\text{N}^+\text{CH}_2\) groups in the side chain. The peak located at 55 ppm is contribute to the \(=\text{N}−\text{CH}_2−\text{Ar}\) groups. The peak at 52 ppm is ascribed to \((\text{CH}_3)_2\text{N}^+−\) groups.
Fig. S27 The mechanical properties of the DPM/DMBP-QTB-1.5 membrane before and after alkali resistance test.
Fig. S28 The water uptake and swelling ratio of the DPM/DMBP-QTB-1.5 membrane before and after alkali resistance test.
**Fig. S29** The conductivity, stability factor and IEC of DPM/DMBP-QTB-1.5 and other cross-linked AEMs reported recently.7-16 The hollow symbols and solid symbols represent the stability factor and conductivity, respectively.

**References**


