

Electronic supplementary information

Highly conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross-linking

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**Sodium salt of 3-hydroxyphenylacetylene
(End-group cross-linker)**

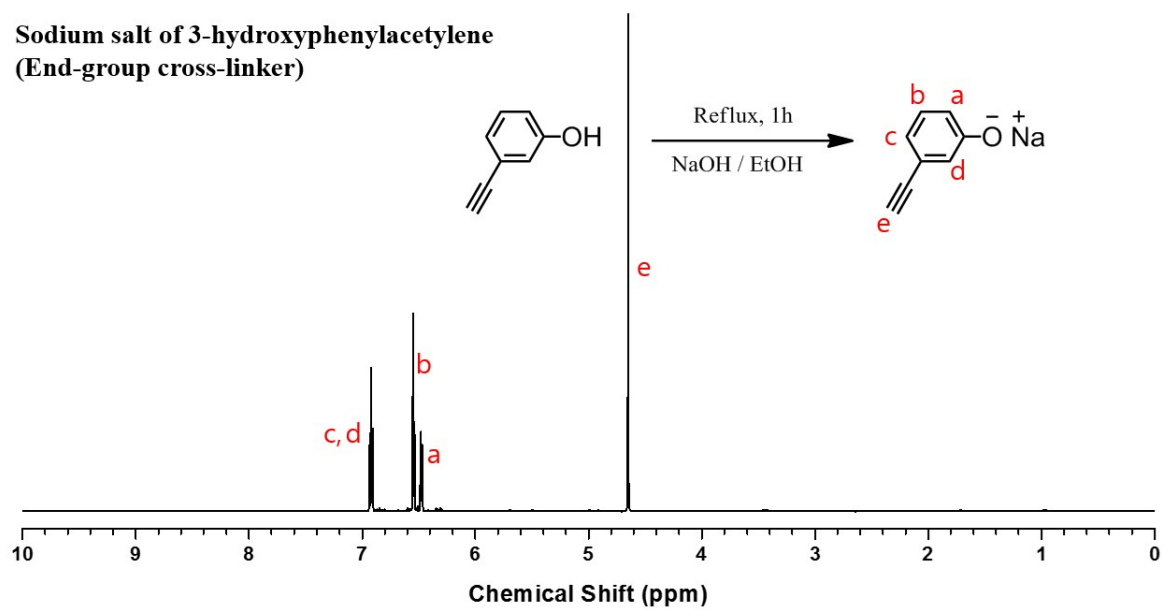


Fig. S1 ¹H-NMR spectra in D₂O of synthesized sodium salt of 3-hydroxyphenylacetylene as end-group cross-linker

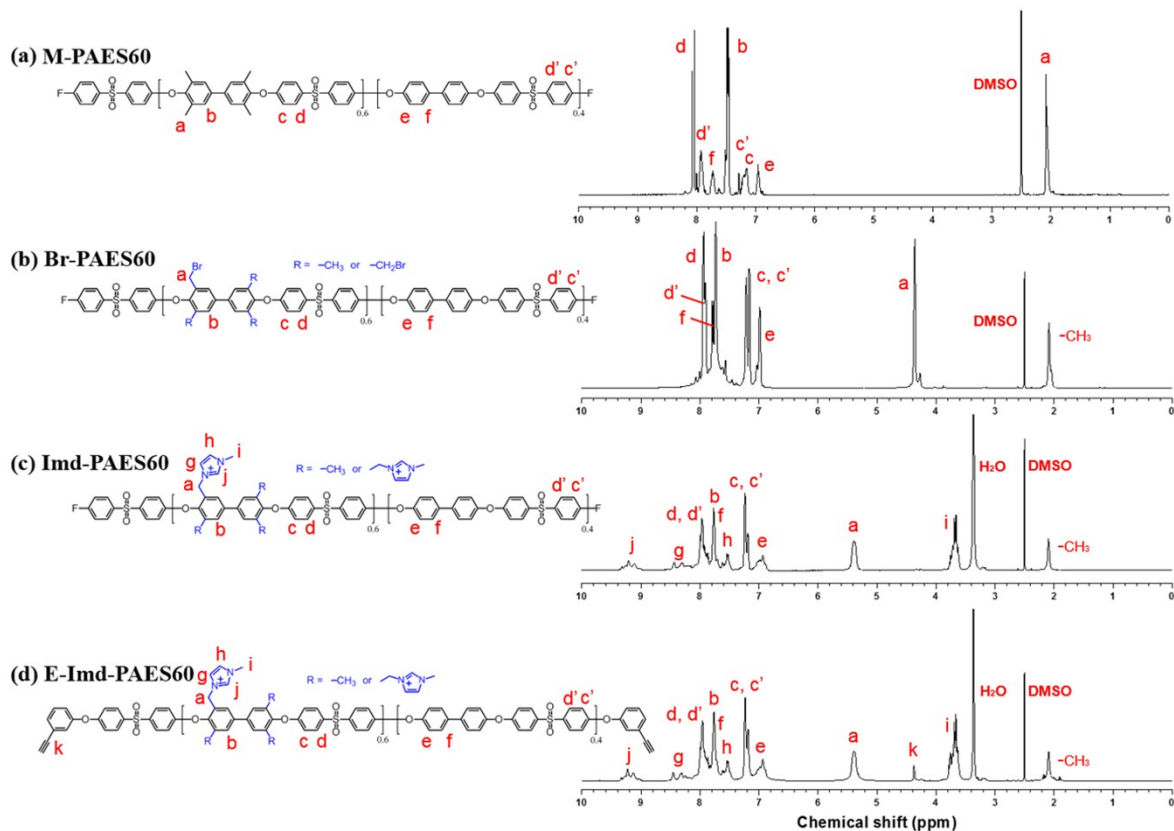


Fig. S2 $^1\text{H-NMR}$ of synthesized copolymer E-Imd60 as a representative sample in $\text{DMSO-}d_6$. (a) M-PAES: first synthetic step having tetra methyl moiety. (b) Br-PAES60: after radical benzylic bromination. (c) Imd-PAES60: 1-methyl imidazolium functionalized state. (d) E-Imd-PES60: After termination of end-group from $-\text{F}$ to phenylacetylene cross-linker.

Table S1. Molecular weight, thermal and mechanical properties of Imd60 and 70 series. Cross-linking time and gel fraction of XE-Imd60 and 70.

Samples	M _w ^a (kDa)	PDI	T _g ^b (°C)	T _{d 5%} ^c (°C)	Cross-linking Time ^d (min)	Gel fraction ^e (%)
E-Imd60	186	2.5	260.5	234.5	-	-
E-Imd70	175	2.3	265.3	270.1	-	-
XE-Imd60	186	2.5	260.5	256.7	40	62
XE-Imd70	175	2.3	265.3	279.6	40	65

^a Weight-based molecular weight measured by gel permeation chromatography (GPC). ^b Measured by differential scanning calorimetry (DSC). ^c The 5% weight loss temperature. ^d Thermal end-group alkyne trimerization at 180 °C. ^e Gel fraction test in NMP at 100 °C for 12h.

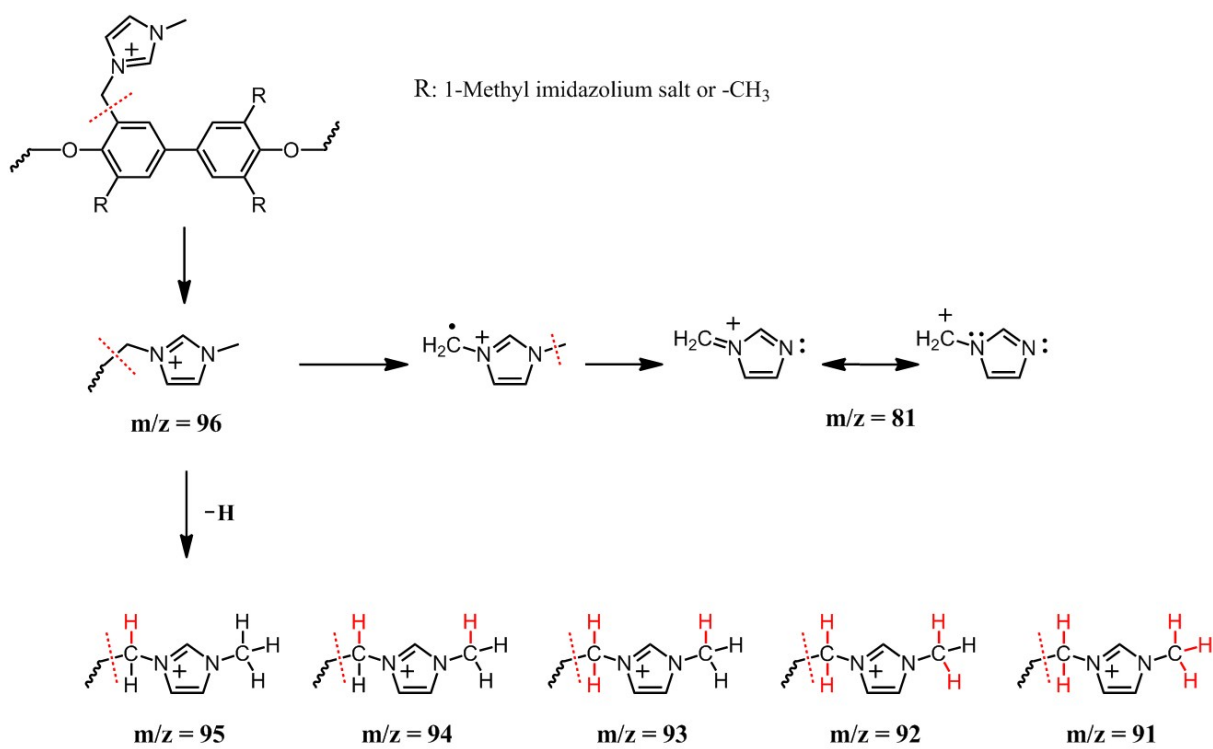


Fig. S3 Thermal decomposition of 1-methylimidazolium groups of E-Imds during TG-MS analysis.

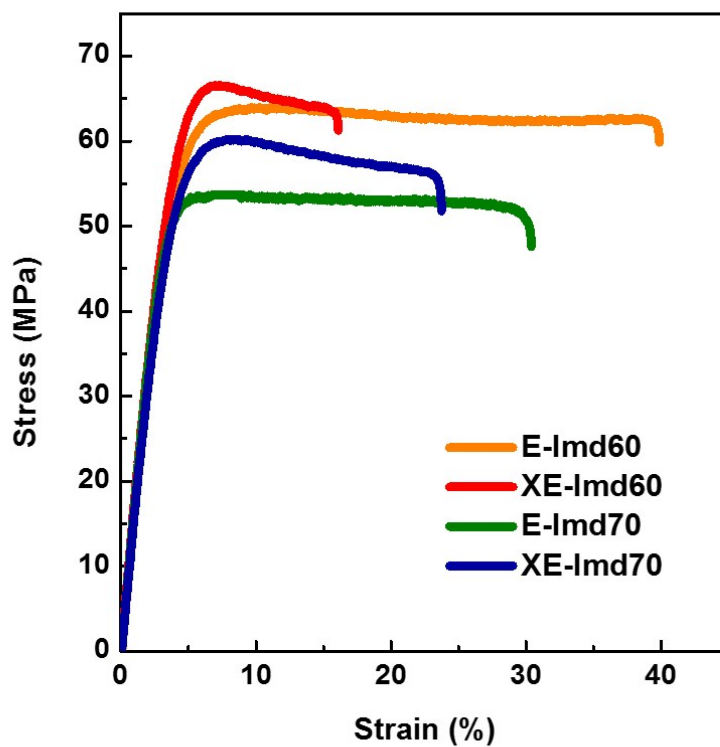


Fig. S4 Stress-strain curves of pristine E-Imds and cross-linked XE-Imds. Measurements were carried out at least ten times for each sample, and the representative samples are shown.

Table S2. Mechanical properties of E-Imds and XE-Imds. Measurements were carried out at least ten times for each sample.

Samples	Tensile Strength (MPa)	Elongation at break (%)	Young's Modulus (GPa)
E-Imd60	63.9 ± 5.2	39.9 ± 7.8	1.58
E-Imd70	53.7 ± 4.9	30.4 ± 5.2	1.56
XE-Imd60	66.5 ± 3.5	16.1 ± 2.3	1.69
XE-Imd70	60.2 ± 3.3	23.7 ± 3.1	1.67

Table S3. Density, IEC_w and IEC_v measured at 20 °C.

Samples	Density ^a (g cm ⁻³)	IEC _w ^b (meq g ⁻¹)	IEC _{v(dry)} (meq cm ⁻³)	IEC _{v(wet)} (meq cm ⁻³)
E-Imd60	1.42	2.47	3.51	4.72
E-Imd70	1.48	2.77	4.10	5.63
XE-Imd60	1.45	2.43	3.52	4.12
XE-Imd70	1.51	2.72	4.11	4.95

^a Measured at 20 °C. ^b Titration value by Mohr method.

Table S4. Hydration number, water uptake, swelling ratio and hydroxide conductivity of all membranes at 80 °C.

Samples	λ	WU (wt%)	WU (vol%)	$\Delta_{//}$ (%)	Δ_{\perp} (%)	$\sigma_{//}$ (mS cm ⁻¹)	σ_{\perp} (mS cm ⁻¹)
E-Imd60	43	189.6	269.2	149 ± 8	117 ± 5	79 ± 1.5	75 ± 2.5
E-Imd70	45	225.6	333.9	171 ± 11	138 ± 5	82 ± 1.9	87 ± 1.5
XE-Imd60	21	92.4	134.0	48 ± 5	45 ± 2	99 ± 2.5	97 ± 2.7
XE-Imd70	24	115.6	174.6	62 ± 4	57 ± 2	103 ± 1.5	107 ± 1.8

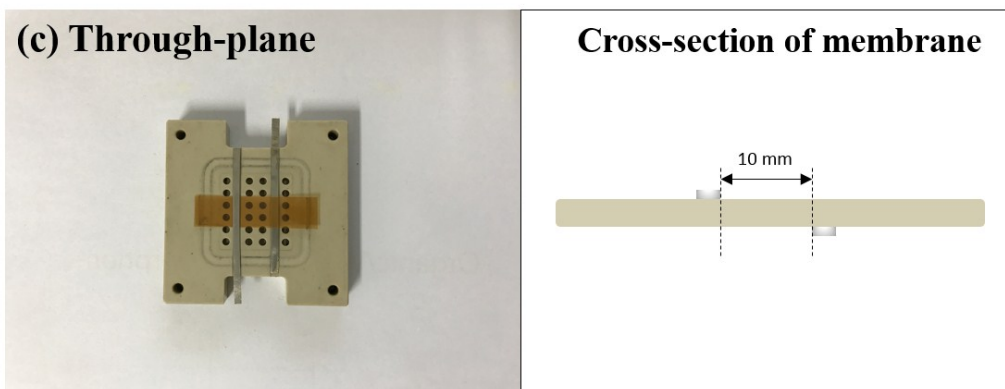
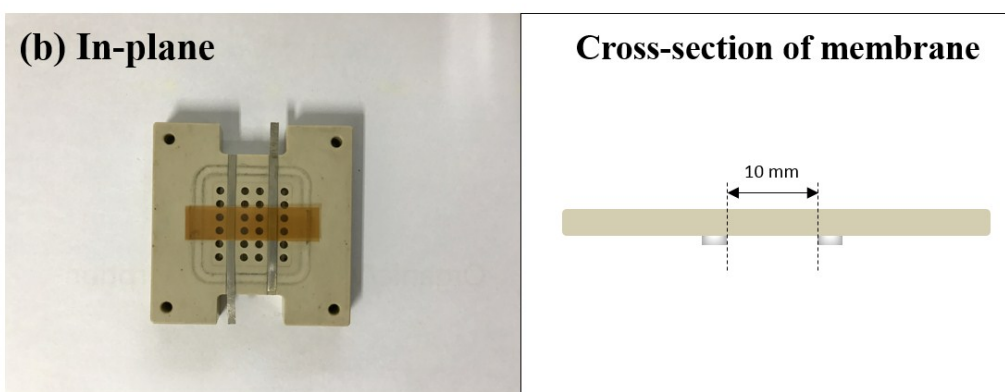


Fig. S5 (a) Conductivity cell fixture set for two-probe measurements. (b) Equipment picture and schematic cross-section figure of in-plane conductivity and (c) through-plane conductivity.

Gas permeability test

Table S5. Fuel (i.e., hydrogen) permeability of E-Imd60 and XE-Imd60 with values for the selected ion exchange membranes and commercial polysulfone membrane (Radel A-100[®]) for comparison.

Samples	E-Imd60	XE-Imd60	Nafion [®] 212 ^b	In0505 _{DMAc} ^{c,1}	Radel A-100 ^{® d,2}
P_{H_2} (Barrer ^a)	1.6	2.5	6.7	8.80	10.8

^a 1 Barrer = 10⁻¹⁰ cm³ (STP) cm / cm² sec cm Hg

^b measured at 20±1 °C and 3.0 X 10⁵ Pa

^c measured at 20±1 °C and 3.0 X 10⁵ Pa, In0505_{DMAc} means partially fluorinated poly(arylene ether sulfone) multiblock copolymers bearing perfluorosulfonic functions obtained by commercial polysulfone (Radel[®])

^d measured at 35 °C and 3 bar

Experimental

To investigate the effect of fuel (i.e., hydrogen) permeability, E-Imd60 and XE-Imd60 were selected. As a representative sample of aliphatic hydrocarbon-based membranes, Nafion 212 was also tested for comparison although it is a cation exchange membrane. Gas permeation experiments were conducted with an in-house instrument using the constant-pressure/variable-volume method (time-lag method).³ Hydrogen permeability coefficients were determined in the steady-state downstream pressure region as a function of time using the following equation:³

$$P = \left(\frac{273.15 \cdot V \cdot l}{76 \cdot T \cdot \Delta p \cdot A} \right) \frac{dp}{dt}$$

where P (Barrer) is the hydrogen permeability, V (cm³) is the volume of downstream chamber, l (cm) is the membrane thickness, T (K) is the operation temperature (35 °C in this study), Δp (cmHg) is the pressure difference between upstream and downstream (76 cmHg), A (cm²) is the effective membrane area, and dp/dt is the rate of pressure increase in the downstream chamber.

Results and discussion

Hydrogen permeability for reference Nafion[®] 212 was 6.7 Barrer (1 Barrer = 10⁻¹⁰ cm³ (STP) cm / cm² sec cm Hg), which is in good agreement with the result from the literature.⁴ E-Imd60 showed a hydrogen permeability of 1.6 Barrer, indicating that it showed an enhancement in hydrogen barrier properties compared to the Nafion[®] 212 due to highly packed aromatic matrix. Upon end-group crosslinking, hydrogen permeability of XE-Imd60 apparently increased to 2.5 Barrer, however, it still represented lower hydrogen permeability than that of Nafion[®] 212. It can be postulated that the end-group cross-linking step induced the resulting membranes with larger tortuosity and fractional free volume.^{3, 4} In comparison to the In0505_{DMAc}, partially

fluorinated sulfonated poly(arylene ether sulfone) multiblock cation exchange membranes, XE-Imd60 still represented enhanced hydrogen barrier properties.

References

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