Supplementary Information

Crosslinked Metallo-Polyelectrolytes with Enhanced Flexibility and Dimensional Stability for Anion-Exchange Membranes

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1. General Information

Materials

1,5-Cyclooctadiene, hydrobromic acid solution (33% in acetic acid), 2,2'-(ethylenedioxy) diethanethiol, *p*-toluenesulfonyl hydrazide, ethyl vinyl ether and Grubbs 2nd catalyst were purchased from Sigma-Aldrich and used as received. Sodium azide, dicyclopentadiene, anhydrous cobalt bromide, anhydrous *cis*-cyclooctene, *N,N*-dimethylacetamide, standardized hydrochloric acid (0.1 N) and potassium hydroxide solutions (0.1 N) were purchased from VWR.

5-Bromocyclooct-1-ene (**1**) and (trimethylsilyl)ethynyl cobaltocenium hexafluorophosphate (**2**) were synthesized and characterized according to the literature procedures.[1, 2] The synthesis of cobaltocenium cyclooctene monomer (**3**) was modified according to a reported procedure.[3]

Characterization

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained on a Varian Mercury 300 spectrometer using $CDCl_3$ or DMSO-d_6 as solvents and all chemical shifts were compared to tetramethylsilane (TMS) as the reference. For Fourier transform infrared spectrometry (FT-IR) spectra, a PerkinElmer spectrum 100 FTIR spectrometer was applied using attenuated total reflection method. The UV-Vis spectra were recorded by Shimadzu UV-2450 spectrophotometer. The images and elemental analysis of polyelectrolyte membranes were acquired by Zeiss Ultraplus thermal field emission scanning electron microscope (SEM) and Philips Tecnai G2 F20 transmission electron microscopes (TEM). Thermal stability of membranes was studied by thermogravimetric analysis (TGA) using a TGA Q5000 system (TA Instruments), ramping from 50 to 800 °C at 10 °C min^{-1} under N_2 atmosphere. The decomposition temperature (T_d) was determined at 5% weight loss. Differential scanning calorimetry (DSC) for homopolymers and copolymers was conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −60 to 120 °C at a rate of 10 °C min^{-1}. After cooling to −60 °C at the same rate, the data were collected from the second heating scan.

Ion exchange capacity (IEC) was measured by a back-titration method. A hydroxide membrane was dried under vacuum at 80 °C for 24 h and then immediately immersed in 30 mL of 0.1 M HCl standard solution for 48 h. Subsequently, 10 mL of the solution was taken and neutralized with a 0.1 M KOH solution using phenolphthalein as an indicator. The IEC of membranes can be calculated based on equation (**Eq. 1**), where *c* and *V* represent concentration and volume of standard solution, m_{dry} is the weight of dry membranes. The titration step was repeated for three times to obtain accurate IEC value.

$$IEC = \frac{c_{HCl} \times V_{HCl} - c_{KOH} \times V_{KOH}}{m_{dry}} \ \textbf{(Eq. 1)}$$

Water uptake and swelling ratios of polyelectrolyte membranes were measured at 20, 40, 60, 80 °C. Dry samples were weighed first to obtain dry weight (m_{dry}) and dry length (X_{dry}). Then, the membranes were immersed in a water bath at different temperature and waited 20 min for equilibrium. The samples were wiped dry with paper towel and quickly measured the wet weight (m_{wet}) and the wet length (X_{wet}). In the end, the water uptake, swelling ratio and hydration number were calculated respectively according to equations (**Eq. 2-4**):

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \ \textbf{(Eq. 2)}$$

$$SW = \frac{X_{wet} - X_{dry}}{X_{dry}} \times 100\% \ \textbf{(Eq. 3)}$$

$$\lambda = \frac{WU \times 1000}{100 \times 18 \times IEC_{titr}} \ \textbf{(Eq. 4)}$$

Tensile tests of crosslinked membranes were carried out with an Instron 5543A testing instrument. The hydroxide form membranes were first dried under vacuum for 24h before test. Dog-bone shaped specimens were cut from membranes with a length of 20 mm, a width of 5 mm, and a thickness of around 150 μm. Then, the samples were tested with a crosshead speed of 20 mm min^{-1}. The toughness of different samples was calculated from the area under the stress-strain curve.

Hydroxide conductivity of crosslinked membranes (3 cm × 0.5 cm) were measured by a four-probe method in deionized water and under various temperatures using TrueData-EIS (Fuel

Con) RE232 potentiostat. Membranes in hydroxide form were freshly prepared, thoroughly rinsed with deionized water and stored under nitrogen before the measurement. The membrane was then immersed in deionized water and placed between two Teflon plates, ensuring film flat with minimal changes in geometry during heating. The impedance was measured from 200 μHz to 50 kHz, providing the total resistance of the membrane R (Ω) under different conditions. The conductivity was calculated based on the geometry (L, A) and resistance (R) as shown in equation (**Eq. 5**): where R refers to the ohmic resistance measured by impedance instrument (Ω). L (cm) refers to the space between two reference electrodes. A (cm^2) means the electrode area of the membrane.

$$\sigma = \frac{L}{RA} \text{ (Eq. 5)}$$

Temperature-dependent conductivity of membranes was measured with multiple samples and by heating and cooling in deionized water media for several cycles (20 to 80 ˚C). For the time-dependent stability test, the membranes (smoothly placed in a dialysis bag) were stored in a 3M KOH solution at 60 ˚C under nitrogen over time. Before the conductivity test, these samples were cooled to room temperature and thoroughly washed with deionized water. The KOH solution was replaced with fresh ones after each measurement.

2. Experimental Details

Synthesis of cobaltocenium cyclooctene monomer **(3)**.
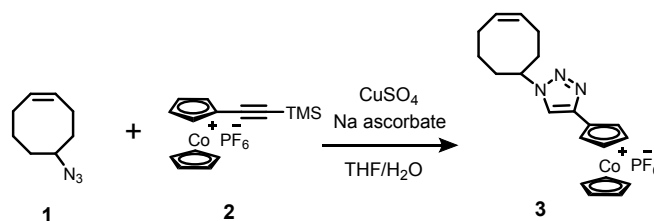
5-Azidocyclooct-1-ene **3** (1 g, 6.61 mmol) and (trimethylsilyl)ethynyl cobaltocenium hexafluorophosphate (2.84 g, 6.61 mmol) were dissolved in a round bottom flask containing 150 mL of solvent THF/water (volume ratio 3:2). Then, an aqueous solution of 1 M CuSO4 (6.61 mmol) was added under N2 atmosphere. At 0 ˚C, a freshly prepared aqueous solution of 1 M sodium ascorbate (13.2 mmol) was added dropwisely and then the solution was allowed to react at room temperature overnight. The mixture was extracted with dichloromethane

(200 mL×2). The organic phase was collected, dried with anhydrous MgSO$_4$ and evaporated. The crude product was dissolved in dichloromethane and precipitated with cold diethyl ether. Purified cobaltocenium cyclooctene monomer **3** could be obtained as yellow solid in a yield of 88%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.87 (m, 10H, -C*H$_2$*- in cyclooctene), 4.81 (m, 1H, -C*H*- in cyclooctene), 5.75 (m, 2H, C*H*=C*H* in cyclooctene), 5.62 (m, 5H, *Cp*), 5.85 (t, *J* = 3.0 Hz, 2H, *Cp*), 6.38 (t, *J* = 3.0 Hz, 2H, *Cp*), 8.30 (s, 1H, -C*H*- in triazole). ^{13}C NMR (CDCl$_3$, ppm): 130.76, 128.88, 95.47, 85.98, 84.36, 80.61, 62.27, 34.90, 25.90 22.79. ^{19}F NMR (CDCl$_3$, ppm): δ=−70.83,−72.72.

Synthesis of cobaltocenium copolymer (**4**).
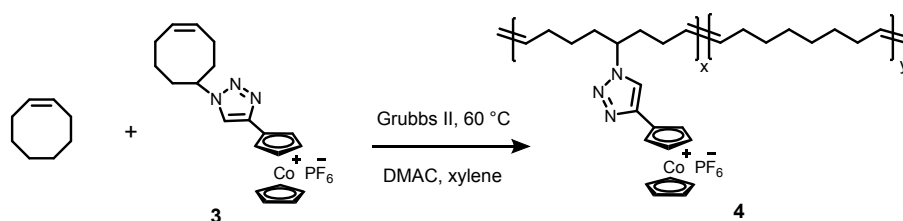
Cobaltocenium copolymers **4** were synthesized by ROMP. Monomer **4** (200 mg, 0.39 mmol), cyclooctene (65 mg, 0.59 mmol) were dissolved in 0.8 mL dimethylacetamide/xylenes (volume ratio 1:1) under nitrogen atmosphere. The reaction temperature was slowly increased to 60 °C and then Grubbs second generation catalyst dissolved in 0.2 mL xylenes was transferred into the reaction solution. Several drops of ethyl vinyl ether were added to quench the polymerization after 60 min and stirred for another 10 min. The copolymer **4** was obtained by precipitation in cold ether/methanol and dried under vacuum overnight (yield: 91%). Copolymers with other molar ratios were prepared in the same way. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ = 1.22 (broad, backbone -C*H$_2$*-), 1.90 (broad, backbone -C*H$_2$*-), 4.55, 4.73 (broad, backbone -C*H*-), 5.29 (broad, backbone -C*H*=C*H*-), 5.69 (m, *Cp*), 5.95 (broad, Cp), 6.33 (broad, *Cp*), 8.72 (broad, -C*H*- in triazole).

Preparation of polyelectrolyte membranes

To prepare crosslinked cobaltocenium-containing polymer membranes, 150 mg copolymer (**4**) and certain amount of dithiol crosslinker were first dissolved in 2.5 mL dimethylacetamide

(DMAc) followed by purging N_2 for 30 min. The reaction solution was stirred overnight before dropcasting into Teflon molds. The solvent was slowly evaporated at 50 ºC for 12 h. The membrane was then transferred into a vacuum oven and heated at 100 ºC for 24 h to remove the remaining traces of solvents and enhance the film quality by thermal annealing. The resulting transparent and flexible membrane was cooled down to room temperature, and directly peeled off from the Teflon mold for counterion exchange.

Ion exchange procedure

Membranes with PF_6^- counterion were placed smoothly in a dialysis bag and stirred in 2M NH_4Cl aqueous solution with excess IRA-400(Cl) ion exchange resins at 60 °C for 24h. Full conversion of PF_6^- to Cl^- could be confirmed with disappearance of PF_6 absorbance in FT-IR spectra. Then, hydroxide ion exchange with chloride ions was accomplished by immersing the membranes in 1M NaOH aqueous solution for 6 h and under nitrogen atmosphere, and the solution was replaced with fresh basic solutions every two hours.

Tables and Figures

Table S1. Mechanical property of AEM samples.

Samples	Stress (MPa)	Young's Modulus (MPa)	Strain (%)	Toughness (MJ/m^3)
CL-AEM20-OH	5.90	32	352	9.91
CL-AEM25-OH	12.5	210	266	18.9
CL-AEM30-OH	11.9	413	156	15.5

Table S2. Comparison of mechanical properties, conductivity, water uptake and swelling ratios of AEMs.

Stress (MPa)	Strain (%)	Conductivity ^{a} (mS/cm)	Water uptake ^{b} (%)	Swelling Ratios ^{c} (%)	References
5.9-12.5	**156-352**	**5.6-18.6**	**11.2-20.4**	**1.5-4.5**	**This Work**
6-9	130-170	40-48	97-132	*NA*	4
10-25	*NA*	68.7	100-225	*NA*	5
23-29	71-276	100	104-149	22-27	6
35	283	121	155	38	7
2.3-16	7.2-26	14-18	*NA*	1.7 (MeOH)	8
12.5-15	3-10	30.2-64.8	13.25-31.52	9.28-12.45	9
5-7	>80	133-177 (80 °C)	48-82	40 (80 °C)	10
0.6-27	53-87	14.1-28.6 (30 °C)	30-432	28	11
17.3-24.7	17.1-23.2	12-20	9.7-19.5	9.7-16.8	12
15-28	10-15	31.5-58.7	30.3-42.1	8.4-18.9	13
23.9-30.5	16.7-29.4	179 (80 °C)	63.7-185.6	16.5-29.0	14
14-16	18.4-21.7	176 (80 °C)	57-123	15-29	15

^{a} hydroxide conductivity under room temperature unless stated otherwise; ^{b} water uptake under room temperature; ^{c} swelling ratios under room temperature unless stated otherwise; *NA*: data not available.
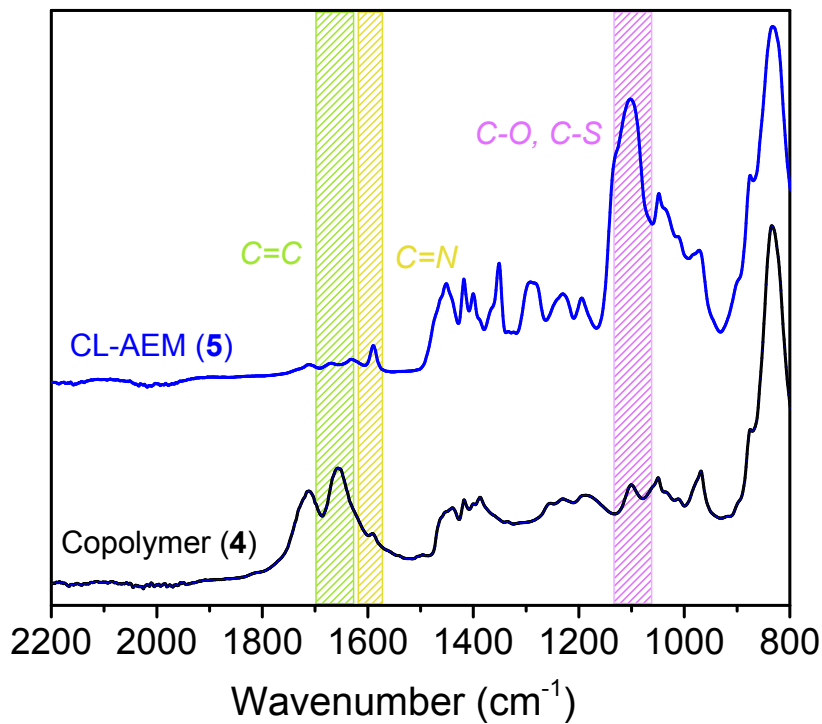
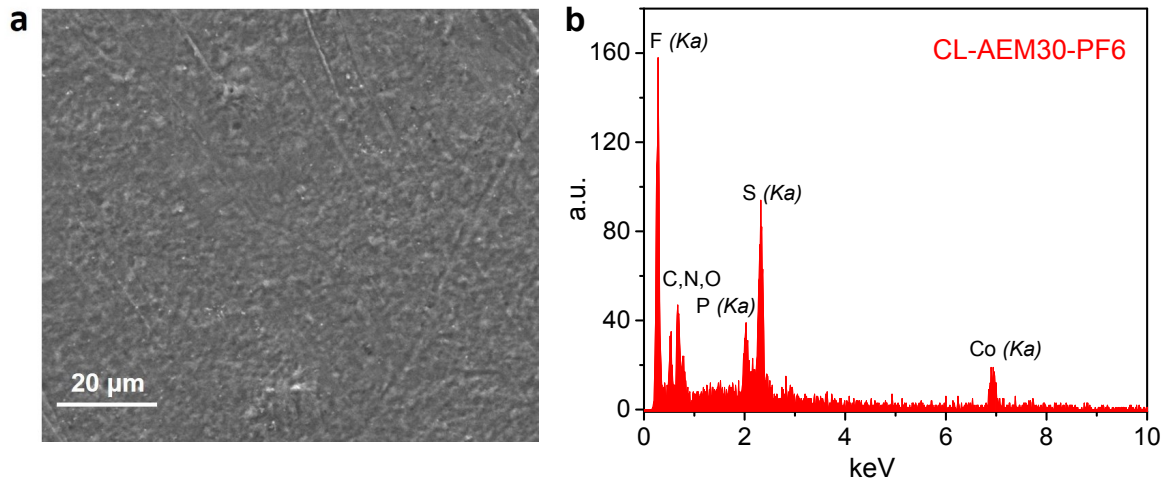**Figure S1.** FT-IR spectra of crosslinked membrane and copolymer **4**.

Figure S2. (a) SEM image and (b) SEM-EDX (in an area of ~50×50 μm) analysis of as-prepared crosslinked membrane with PF$_6$ counterion.
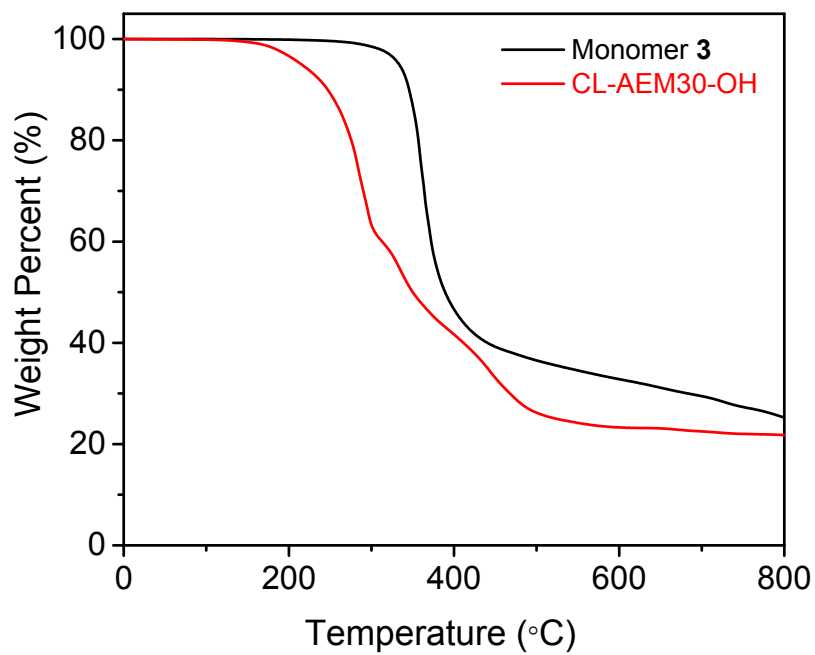
Figure S3. TGA curves of cobaltocenium monomer **3** and crosslinked membrane CL-AEM30-OH under N_2 atmosphere.
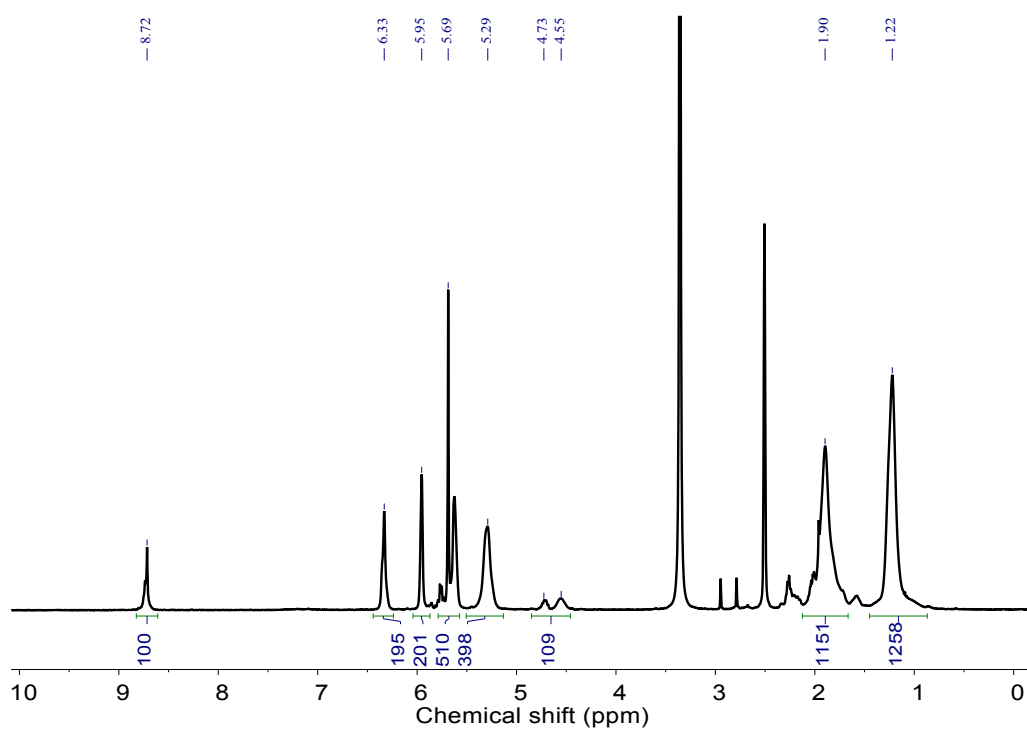

Figure S4. ^1H NMR spectrum of copolymer **4** in DMSO-d_6.
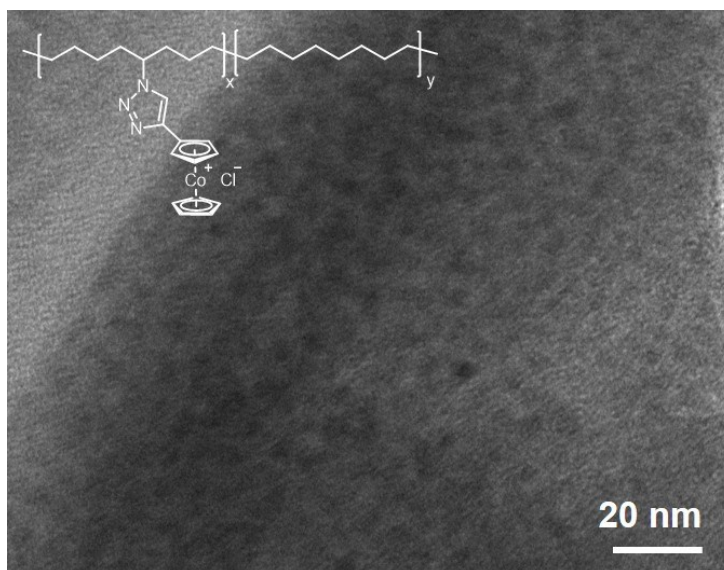
Figure S5. TEM image of polyolefin based copolymer with 40 mol% cobaltocenium units (polymer structure was shown in the figure).
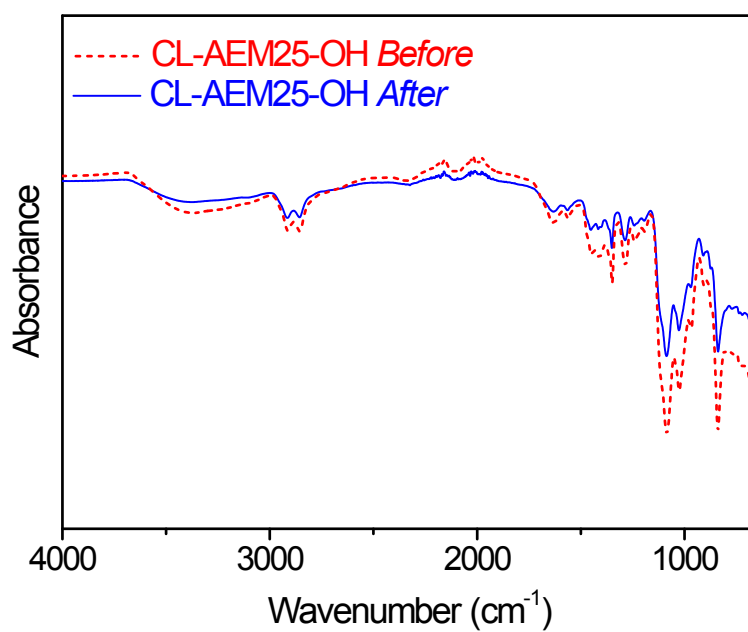

Figure S6. FT-IR spectra of crosslinked membranes before (red dash) and after (blue line) alkaline stability test.
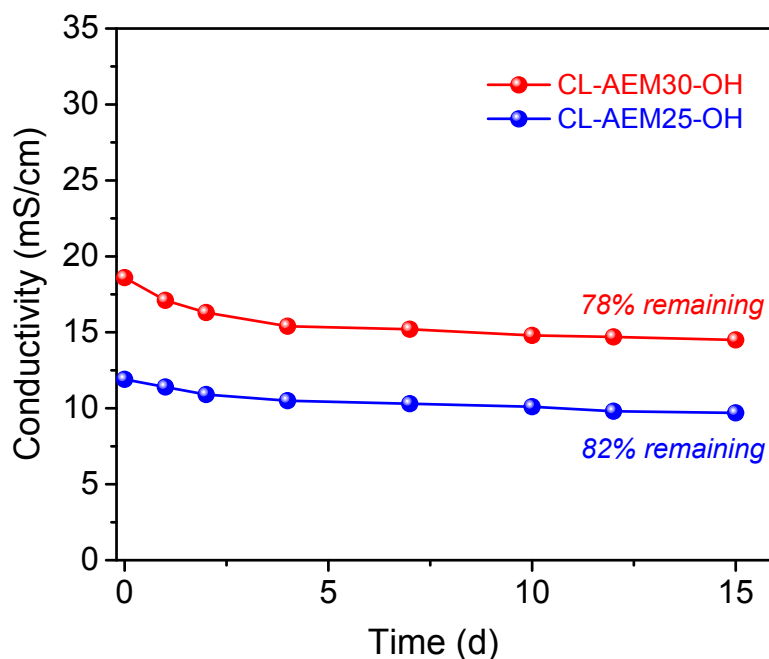
Figure S7. Room temperature conductivity as a function of immersion time of membranes that were soaked in 3 M KOH at 60 °C (the membranes were taken out from the KOH solution for measurement).

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