

Electronic Supplementary Information (ESI)

An anion-conductive microporous membrane composed of a rigid ladder polymer with a spirobiindane backbone

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Materials and Methods

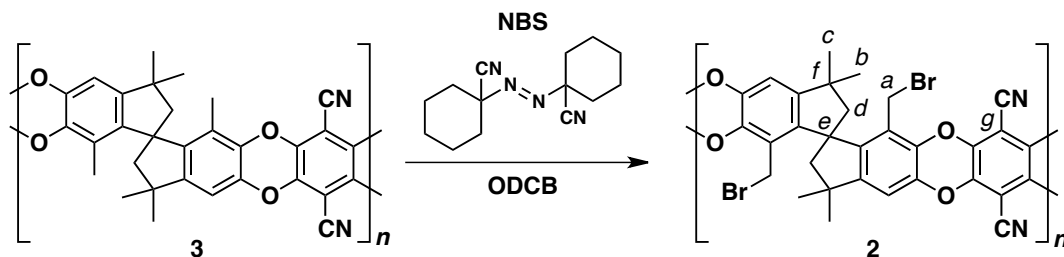
1. Materials. All commercial reagents were used as received. PIM-1 with benzylic methyl functionality (**3**)^{1,2} was prepared according to previously reported procedures and unambiguously characterized by nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC).

2. General. Analytical GPC was performed at 40 °C regulated by column oven on a TOSOH GPC-8020 system equipped with a refraction index (RI) detector and a UV detector (UV-8020), using chloroform (CHCl₃) as an eluent at a flow rate of 0.40 mL/min on a column (Shodex LF-804). The molecular weight calibration curve was obtained by using standard polystyrenes (TSKstandard polystyrene, TOSOH). NMR spectroscopy measurements were carried out at 25 °C on a Bruker AVANCE-500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ¹H [CDCl₃: ¹H(δ) = 7.26 ppm] and ¹³C [CDCl₃: ¹³C(δ) = 78.0 ppm]. Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), and broad (br). ¹³C cross polarization magic angle spinning (CP-MAS) NMR spectroscopy measurements were carried out at 25 °C on a JEOL ECA-600 spectrometer (150 MHz). Infrared (IR) spectra were recorded at 25 °C on a JASCO FT/IR-660_{Plus} Fourier-transform infrared spectrometer. Thermogravimetric analysis-mass spectrometry (TGA-MS) was carried out using a RIGAKU Thermo Plus TG8120 coupled with a RIGAKU Thermo Mass mass spectrometer. N₂ adsorption measurements were performed at 77 K after pretreatment at 150 °C under a reduced pressure for 3 h on a BEL Japan Belsorp-mini II apparatus. The Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P_0) range of 0.05–0.20. Gas chromatography was performed at 90 °C regulated by column oven on a SHIMADZU GC-14B system equipped with SHIMADZU chromatopac C-R8A using a porapak Q 80/100 column (2 mm × 2 m).

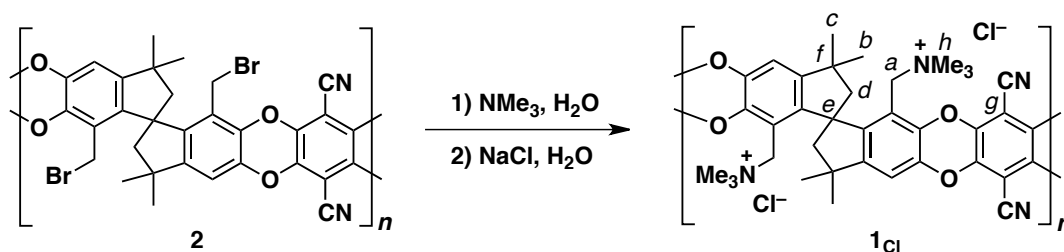
3. Anion-Conductivity Measurement. Anion conductivities were measured by an alternating current impedance method with a Solartron 1260 impedance/gain phase analyzer in the frequency range of 1–10⁶ Hz and at signal amplitude of 50 mV. Temperature and humidity were controlled by an ESPEC Corp. SH-221 benchtop-type temperature and humidity chamber. For OH⁻ conductivity measurement, a membrane of **1**_{Cl} was immersed in an aqueous NaOH solution (0.1 mol/L) for 24 h, washed with deionized water, and then immersed in deionized water for 2 h to remove residual NaOH. Four platinum probes were attached to the resulting membrane of **1**_{OH}, which was then placed in a closed chamber.³ All the sample preparation processes for OH⁻ conductivity measurement were conducted in a glove box filled with N₂ (CO₂ < 1 ppm) to avoid the conversion of OH⁻ into HCO₃⁻ by atmospheric CO₂, and the resistance measurements of **1**_{OH} were conducted under N₂.

4. MeOH-Permeability Measurement.⁴ The MeOH permeability of a membrane of **1_{CI}** was measured at 25 °C using a special H-type diffusion cell, where two chambers were connected through the membrane (Fig. S9).⁵ Chambers I and II were filled with pure water (200 mL) and 10 wt% aqueous MeOH solution (200 mL), respectively, under continuous stirring. The water/MeOH composition in each chamber was determined using gas chromatography. The time lag (θ) and permeability constant ($\text{cm}^2 \text{s}^{-1}$) were evaluated from the time dependence of the MeOH concentration in chamber I. The diffusion coefficient (D) of MeOH in the membrane was determined using an equation: $D = L^2/6\theta$ (L : membrane thickness).

5. Synthesis.



Polymer 2. An *o*-dichlorobenzene solution (6 mL) of a mixture of **3** (6.00 g, 12.3 mmol for the monomer unit), *N*-bromosuccinimide (NBS, 6.57 g, 36.9 mmol), and 1,1'-azobis(cyclohexanecarbonitrile) (V-40, 600 mg, 2.46 mmol) was stirred at 85 °C for 36 h. After cooling to 25 °C, isopropanol was added to the reaction mixture, and a yellow precipitate formed was collected by filtration. Repeated reprecipitations of the resultant solid, using CHCl₃ (good solvent) and MeOH (poor solvent), afforded **2** as a yellow powder (5.94 g, 9.23 mmol for the monomer unit) in 75% yield: ¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.91 (s, 2H), 4.21 (br, 2H), 3.93 (br, 2H), 2.60 (br, 2H), 2.38 (br, 2H), 1.47 (s, 3H), 1.37 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 149.5, 143.0, 140.3, 139.3, 138.5, 123.0, 111.7, 109.0, 106.7, 94.7 (g), 58.1 (f), 56.3 (e), 43.7 (d), 32.4 (c), 29.7 (b), 21.9 (a). FT-IR (KBr): ν (cm⁻¹) 2959, 2871, 2365, 1614, 1443, 1326, 1268, 1224, 1043, 617.



Polymer 1_{Cl}. A free-standing membrane of **2** (60 mg, 5 cm diameter, 28.5 μ m thick) was immersed in an aqueous trimethylamine (NMe₃) solution (30 wt%, 100 mL) and allowed to stand for 7 days at 80 °C in an autoclave. After cooling to 25 °C, the resultant membrane was washed with water, immersed in a saturated aqueous NaCl solution for 24 h, and then dried under a reduced pressure, to afford **1_{Cl}** as a yellow free-standing membrane. ¹³C CP-MAS NMR (150 MHz, CDCl₃) δ (ppm) 155.1–136.2, 128.5–122.0, 120.1–108.4, 95.5 (g), 59.6 (h), 57.5 (e, f, a), 43.9 (d), 30.8 (b, c). FT-IR (KBr): ν (cm⁻¹) 3423, 2958, 2218, 1677, 1616, 1440, 1387, 1364, 1329, 1274, 1230, 1164, 1054, 1014.

Supporting Figures.

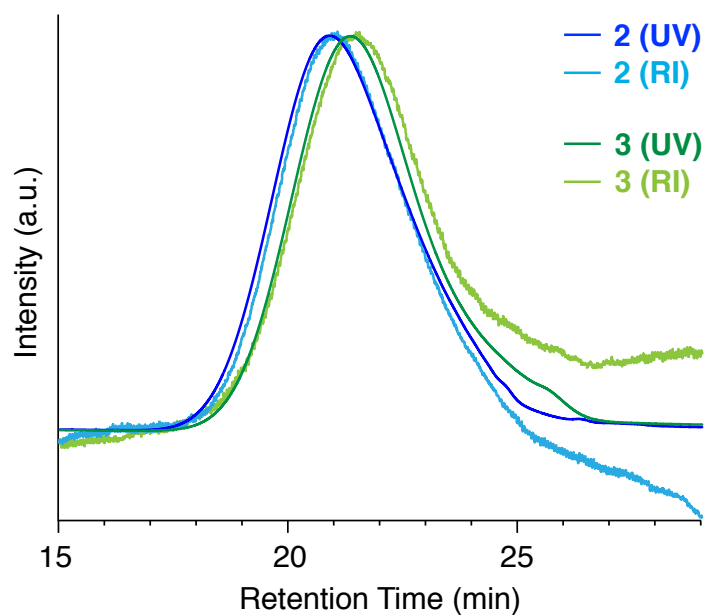


Fig. S1. GPC profiles of **2** ($M_n = 29,300$ Da, PDI = 2.42) and **3** ($M_n = 28,000$ Da, PDI = 2.30) (eluent: CHCl_3 , polystyrene standards).

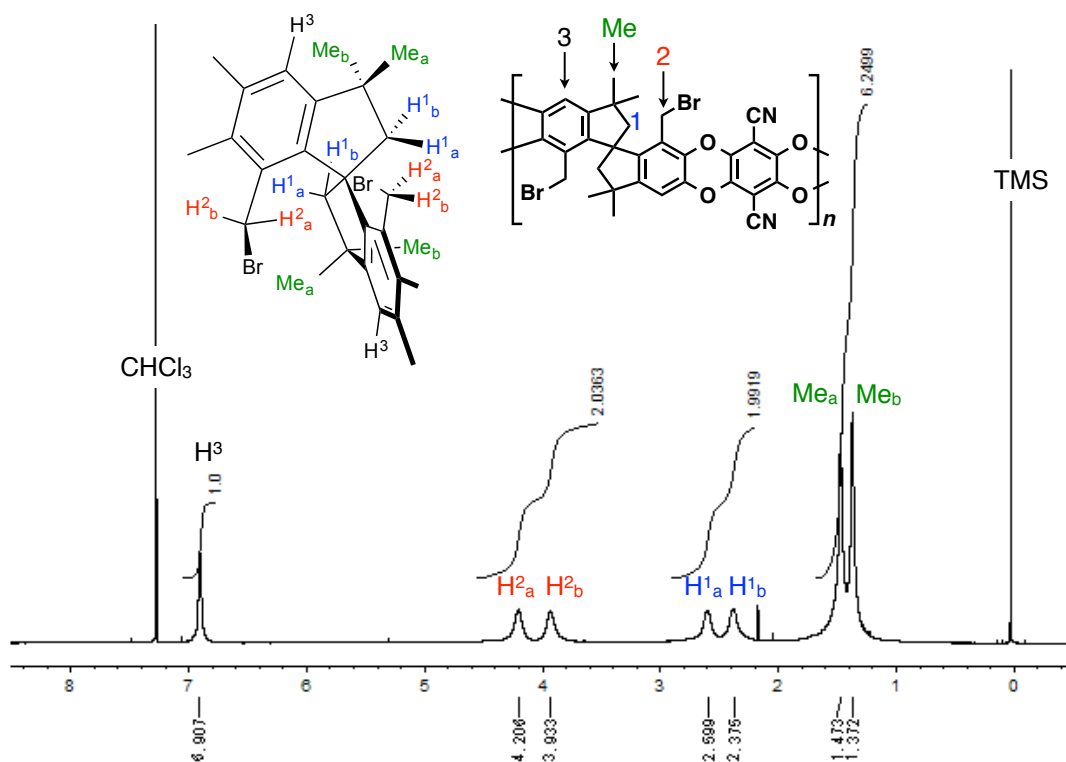


Fig. S2. ^1H NMR spectrum of **2** (500 MHz) in CDCl_3 at 25 °C.

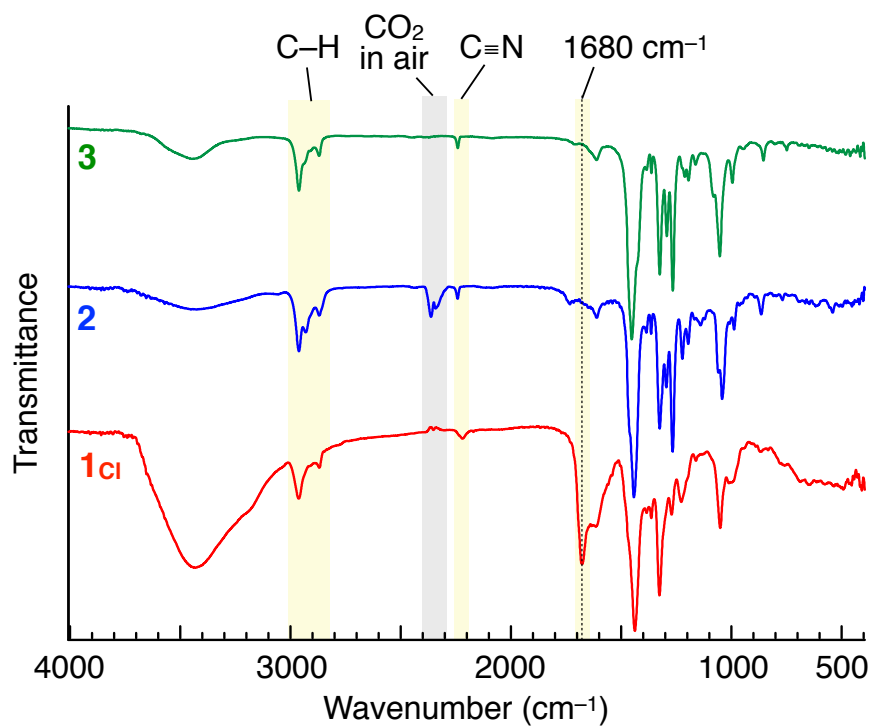


Fig. S3. IR spectra of **1_{Cl}**, **2** and **3** at 25 °C (KBr).

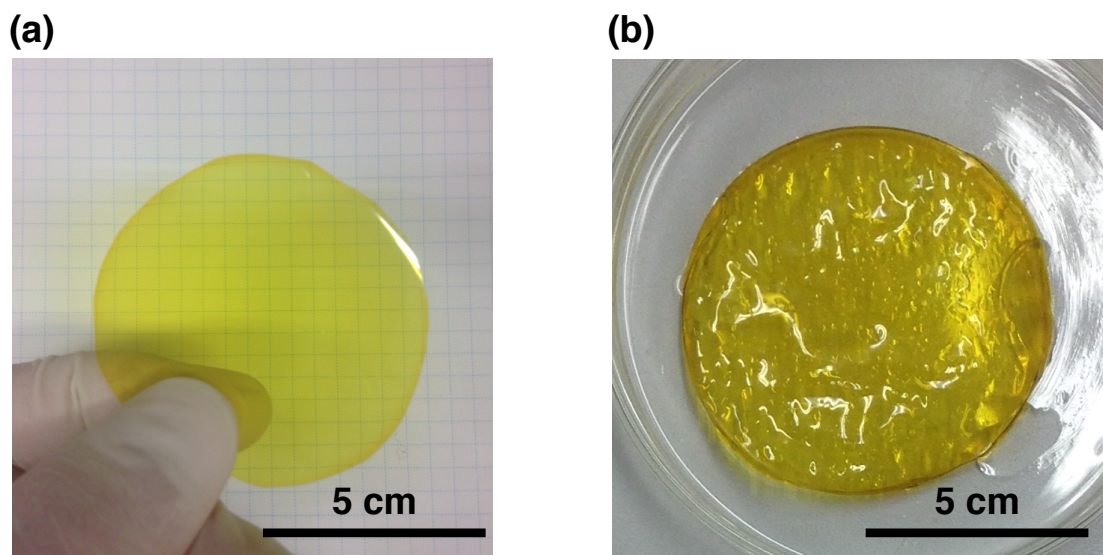


Fig. S4. Photographs of the membranes of (a) **2** and (b) **1_{Cl}**.

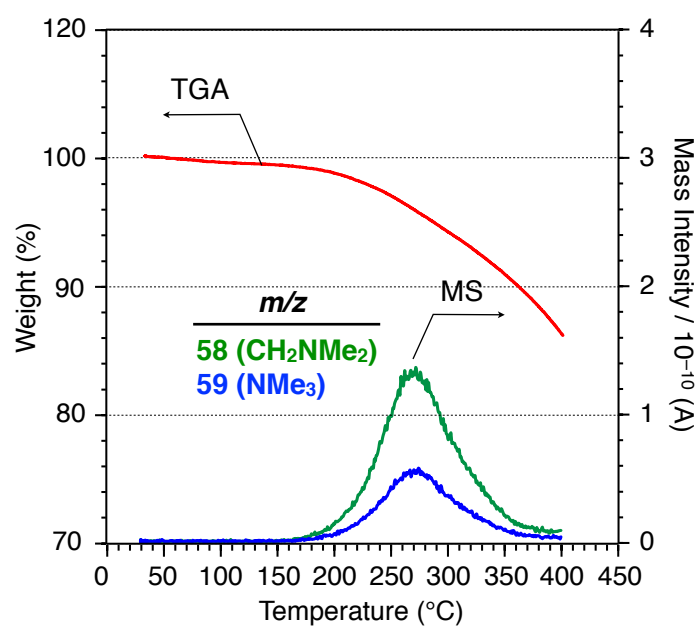


Fig. S5. TGA-MS profile of **1_{Cl}** measured upon heating at a rate of 10 °C/min.

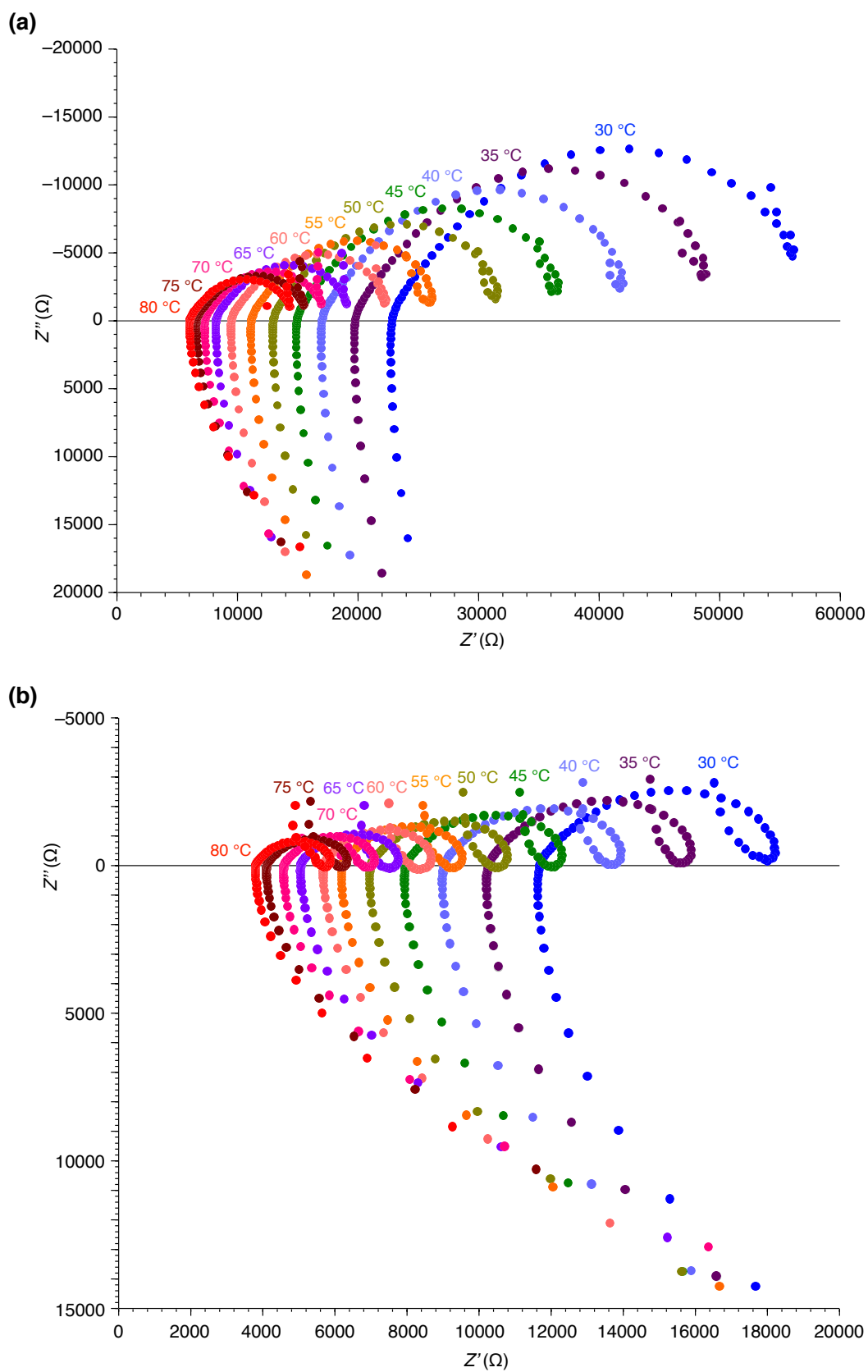


Fig. S6. Typical Nyquist plots observed for membranes of (a) 1_{Cl} and (b) 1_{OH} under 100% RH.

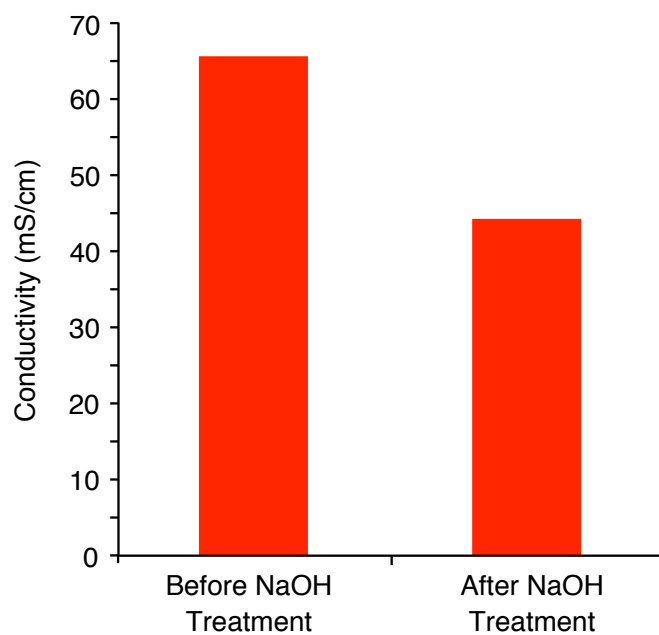


Fig. S7. OH^- conductivities of a membrane of $\mathbf{1}_{\text{OH}}$ (at $80\text{ }^\circ\text{C}$) obtained before (left) and after (right) treating with an aqueous solution of NaOH (1.0 M) at $80\text{ }^\circ\text{C}$ for 24 h.

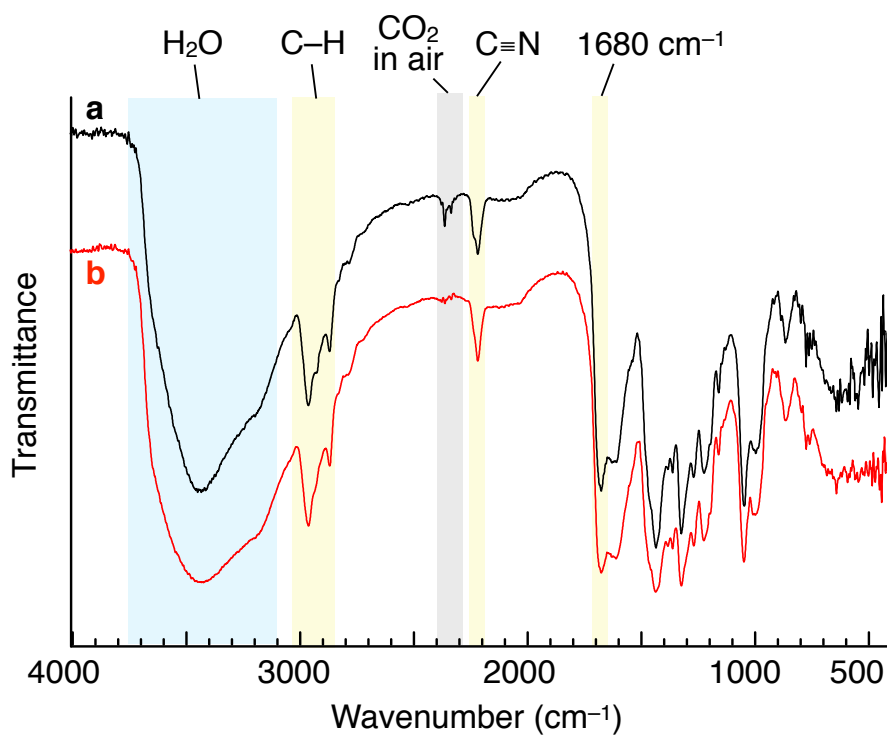


Fig. S8. IR spectra (KBr) of $\mathbf{1}_{\text{OH}}$ measured before (a) and after (b) treating with an aqueous solution of NaOH (1.0 M) at $80\text{ }^\circ\text{C}$ for 24 h.

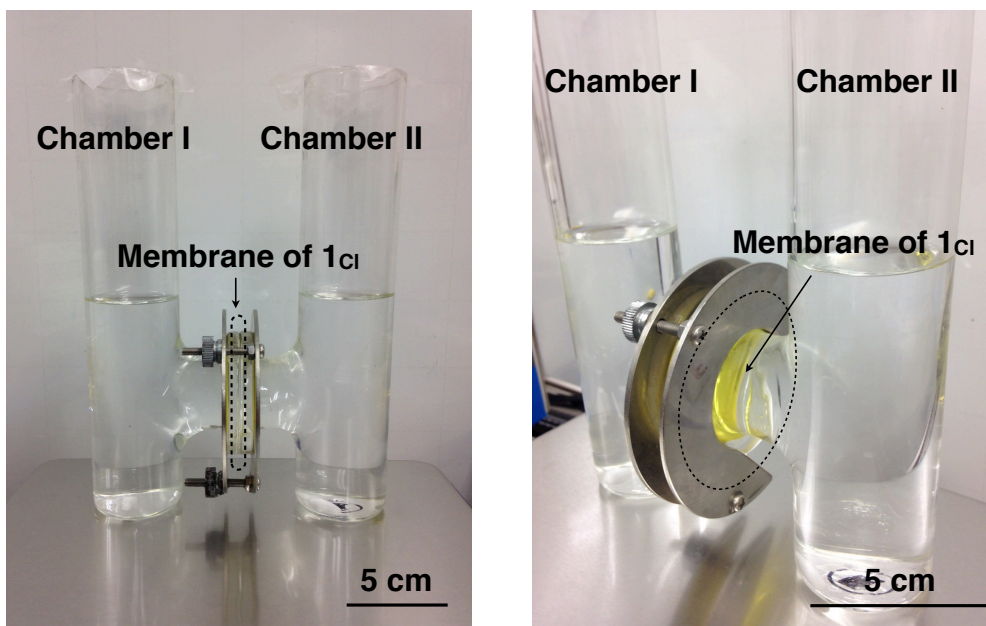


Fig. S9. Experimental setup for the MeOH permeability test of a membrane of 1_{Cl} .

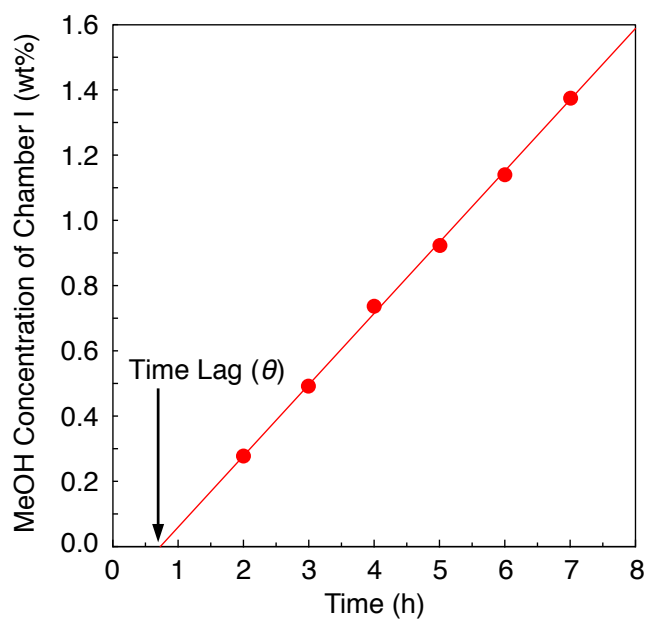


Fig. S10. Time dependence of the MeOH concentration in chamber. From the linear plot, MeOH permeability, time lag and diffusion coefficient of MeOH were determined to be $1.5 \text{ mol}\cdot\text{m}/\text{m}^2\text{s}$, 2610 s and $5.2 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively.

References

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