

Amino Acid Ionic Liquid-based Tough Ion Gel Membrane for CO₂ Capture

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SUPPLEMENTARY INFORMATION

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(1) Materials and general procedure for AAILs-based DN gel membrane preparation

Reagents

Tetrabutylphosphonium hydroxide ($[P_{4444}][OH]$, 40 wt% in water), triethylphosphine (99%), 1-bromopentane (98%), triethylphosphine (1 mol/dm³ in THF) and anion exchange resin (OH type) were purchased from Sigma-Aldrich Co. (St Louis, MO, USA). Proline (>99.0%) was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Hexane (>95%) was purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). All reagents were used as received.

AAIL synthesize

A 100 cm³ of triethylphosphine (1 mol/dm³ in THF) was mixed with 15 g of 1-bromopentane and stirred for 6 h at 353 K. Subsequently, 200 cm³ of hexane was added to the prepared solution and stirred for at least 12 h. Finally, the solution was evaporated at 313 K in vacuum for 3 h and $[P_{2225}][Br]$ was obtained (the chemical structure was confirmed by ¹H NMR spectroscopy (Bruker Advance 500, Bruker BioSpin)). $[P_{2225}][Br]$ (40.0 g) was dissolved in water (80.0 g), and the resulting solution was treated with a basic anion exchange resin (142.0 g) to form $[P_{2225}][OH]$.

$[P_{4444}][Pro]$ and $[P_{2225}][Pro]$ were synthesized according to a neutralization procedure written in elsewhere.¹ An aqueous solution of $[P_{xxy}][OH]$ (x, y: carbon number of the alkyl groups, x = 4 or 2, y = 4 or 5) was added to an equimolar proline aqueous solution to prepare the $[P_{xxy}][Pro]$ salts, with water formed as a byproduct. The product was dried in vacuum for more than 8 h at 313 K. The chemical structures of the resulting $[P_{xxy}][Pro]$ were confirmed by ¹H NMR spectroscopy and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics) measurements.

DN hydrogel membrane preparation

Double network (DN) hydrogel film was prepared via multi-step UV polymerization procedure.² The thickness of hydrogel film was controlled by PTFE spacer used between two quartz plates. 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) and dimethylacrylamide (DMAAm) were chosen as monomers for the first and second networks, respectively. In the first step, poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS) gel film was prepared via UV-light initiated polymerization of aqueous solution containing AMPS (1 mol/dm³), N,N'-methylenebisacrylamide (MBAA) as a crosslinker (0.04 mol/dm³), and 2-oxoglutaric acid (OA) (0.001 mol/dm³) as an initiator. The weak hydrogel film was immersed in a pre-DN solution consisting of DMAAm (4 mol/dm³), OA (0.001 mol/dm³) and NaCl (0.08 mol/dm³) for at least 24 h. Here, NaCl was added to the pre-DN solution in order to control the swelling ratio of PAMPS network for easy manipulation of the hydrogel film.^{2b} Subsequently, the swelled hydrogel film was put under UV for 8 h to fabricate a pre-reinforced DN

hydrogel film. Because the mechanical strength of the pre-reinforced DN hydrogel was relatively improved by partially introducing of poly(dimethylacrylamide) (PDMAAm) chain into the first network, it can be easily manipulated by hand. In the next step, the pre-reinforced DN hydrogel film was immersed in distilled water for at least 24 h in order to remove NaCl. The washed hydrogel film was immersed in an aqueous solution dissolving DMAAm (2 mol/dm^3) and OA (0.001 mol/dm^3) for 24 h, and finally put under UV for 8 h to prepare a tough complete double network hydrogel film. The DN hydrogel films were washed by distilled water for more than 4 days before using them for the AAIL-based DN ion gel membranes fabrication.

AAIL-based DN ion gel membrane preparation

To prepare the AAIL-based DN ion gel membranes, the DN hydrogel film was immersed in an AAIL/water mixture for 24 h. The obtained DN gel film containing AAIL/water mixture was dried at room temperature for 24 h and finally put into the vacuum oven at 373 K for 10 h to remove the water and any possible non-reacted monomers. Impregnation of AAILs in the DN hydrogel matrix was confirmed by measuring the AAIL content in the DN gel (the detailed procedure for the measurement of AAIL content is written in the next section).

(2) AAIL content measurement of prepared DN gel membranes

The AAIL content of fabricated DN gel films was measured by the following procedure. Firstly, the AAIL-based DN ion gel samples with different AAIL content were prepared. Small pieces of DN hydrogel were immersed in aqueous solutions containing 10, 30, 40, 50, 60, 70, and 80 wt% of AAIL for 24 h. Then, the DN gel sample containing AAIL/water mixture was removed from the aqueous solution and the equilibrium AAIL concentration in the aqueous solutions was measured for every sample. The removed DN gel samples were dried at room temperature for at least 10 h followed by complete drying in the vacuum oven at 373 K for 5 h. The weight of the prepared samples, m_1 , were immediately measured.

Subsequently, the AAIL in the samples were completely extracted to obtain the only polymer based-skeleton of PAMPS/PDMAAm double-network. The DN ion gel samples were immersed in large amount of distilled water (500 cm³) for 48 h in order to remove the AAILs. The distilled water was changed with fresh water every 10 h to make sure all AAIL being removed from the gel. After complete AAIL extraction, the obtained DN hydrogels were put into the vacuum oven at 373 K for 5 h in order to evaporate all water, and finally the weights of the dried DN skeletons, m_2 , were measured.

The AAIL content in each sample was calculated by the following equation.

$$\text{AAIL content (wt\%)} = \frac{m_1 - m_2}{m_1} \times 100$$

The relationship between the AAIL content and the equilibrium concentration of the AAIL in the aqueous solution used for the preparation of the AAIL-based DN ion gel samples are presented in Fig. S1.

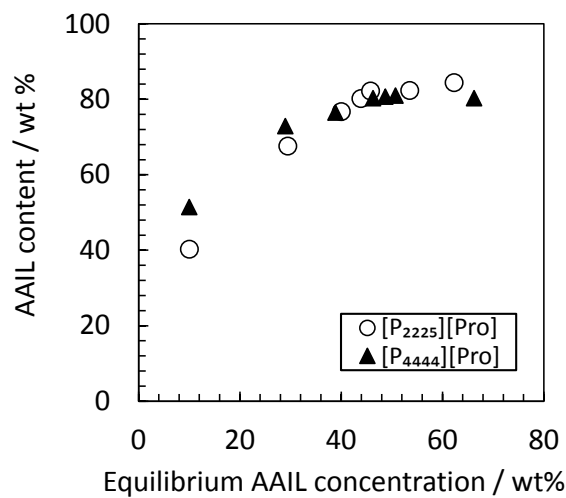


Fig. S1 Relationship between AAIL content in the DN ion gel and the equilibrium AAIL concentration in the AAIL/water mixture used for DN ion gel preparation

(3) General procedures of gas permeability test

CO₂ and N₂ gases with 99.9% purity were used for gas permeation tests. A schematic of the experimental set-up of gas permeation test is shown in Fig. S2(a). The gas transport properties of the membrane were measured by using a flat-type permeation cell (Fig. S2(b)) that was placed in a thermostat oven (YAMATO Scientific Co. Ltd., Japan) adjusted to the desired temperature. The permeation cell (GTR TEC Co., Japan) is made of stainless steel with an effective permeation area of 9.51 cm².

A model feed gas was prepared by mixing of the CO₂ and N₂ under dry condition. The flow rates of CO₂ and N₂ were controlled by mass flow controllers (Hemmi Slide Rule Co. Ltd., Japan) to adjust the mole fraction of each gas. The total flow rate of the feed gas was adjusted to 1.49×10^{-4} mol/s at 298 K and 101.3 kPa. The flow rates of the feed streams were measured by soap-film flow meters (HORIBA STEC Ltd., Japan). The feed gas was pre-heated by a coiled heat exchanger and introduced into the cell. The permeability tests were carried out at 373 K.

Helium was supplied to the permeate side of the cell through a coiled heat exchanger as a sweep gas with the flow rate of 2.98×10^{-5} mol/s at 298 K and 101.3 kPa. The flow rate of the sweep gas was measured by soap-film flow meters (HORIBA STEC Ltd.). The pressure on the sweep side was maintained at atmospheric pressure.

The sweep gas containing the permeated CO₂ and N₂ through the AAIL-gel membranes was introduced to a gas chromatograph (Shimadzu GC-8A, column: activated carbon, 1 m) to determine the composition of permeate.

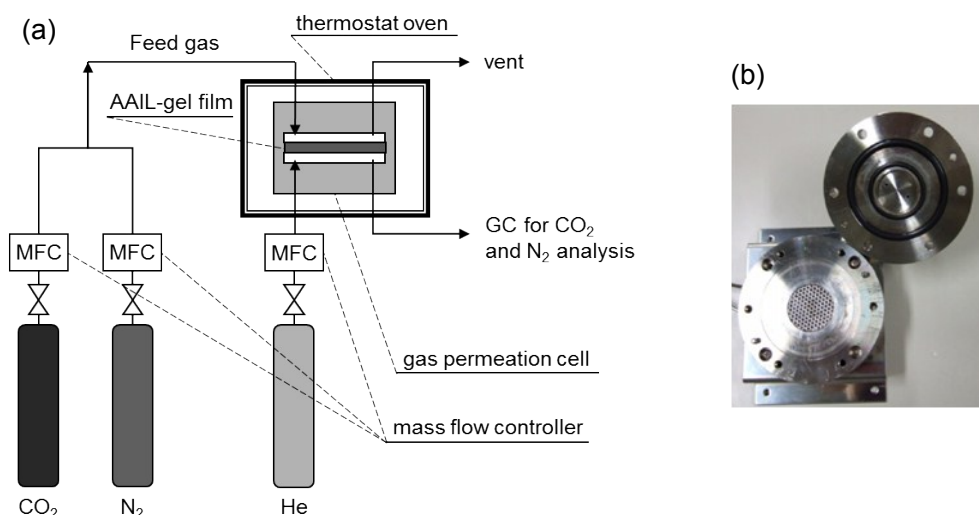


Fig. S2 Schematic of gas permeation measurement set-up (a) and the stainless steel flat-type permeation cell (b)

(4) Relationship between AAIL content in the AAIL-based DN gel membranes and gas permeabilities

The CO₂ and N₂ permeabilities were measured by using the AAIL-based DN gel membranes containing different amount of [P₄₄₄₄][Pro] and [P₂₂₂₅][Pro] (Figs. S3). It was found for both AAIL-based DN gel membranes that N₂ permeability increased with increasing AAIL content because of the increase of solute diffusivity resulted from the decrease of polymer network content in the DN ion gels. In the case of CO₂, AAIL content dependency of the CO₂ permeability was much stronger than N₂ and thus, CO₂/N₂ selectivity increased with the increase of AAIL content. The drastic increase of the CO₂ permeabilities is the combined effects of the decrease of the above mentioned diffusion resistance and the increase of the CO₂ absorption amount, caused by increase of available carriers forming selective complex reaction with CO₂.

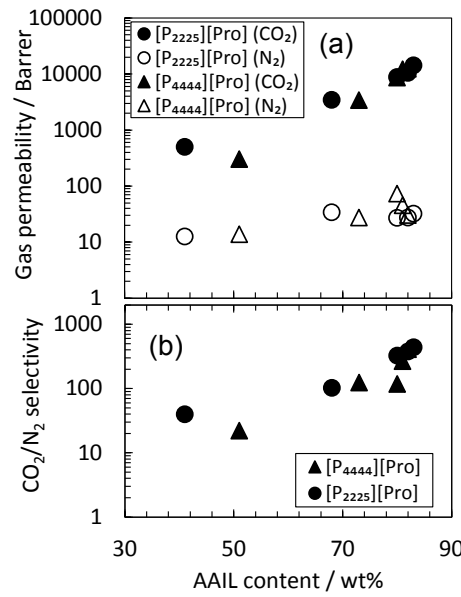


Fig. S3 Relationship between (a) CO₂ and N₂ permeabilities and (b) CO₂/N₂ selectivity and the AAIL content in the AAIL-based DN ion gel membranes containing [P₂₂₂₅][Pro] and [P₄₄₄₄][Pro] with ca. 600 μ m of their thickness (Experimental conditions: $T = 373$ K, $P_{\text{feed}} = P_{\text{sweep}} = \text{atmospheric pressure}$, $P_{\text{CO}_2, \text{feed}} = 2.5$ kPa, and relative humidity = 0%)

(5) CO₂ partial pressure dependency of AAIL-based DN gel membranes

To confirm the CO₂ and N₂ permeation mechanisms through AAILs-impregnated DN gel membranes, CO₂ and N₂ permeabilities were measured at different CO₂ partial pressures (Figs. S4 and S5). It was found that CO₂ permeability decreased with increasing CO₂ partial pressure. This behavior is a well-known trend of facilitated transport membranes resulting from the saturation of carriers via CO₂ absorption.³ In the case of N₂, permeability remains relatively constant with increasing CO₂ partial pressure; i.e. decreasing N₂ partial pressure. In conclusion, it was confirmed that CO₂ and N₂ permeation mechanisms are the facilitated transport and solution–diffusion mechanisms, respectively.

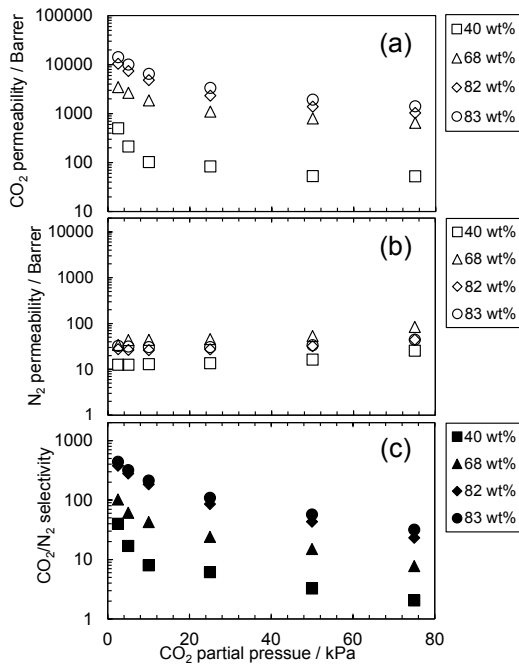


Fig. S4 CO₂ partial pressure dependency of (a) CO₂ permeability, (b) N₂ permeability and (c) CO₂/N₂ selectivity of [P₂₂₂₅][Pro]-based DN ion gel films with different [P₂₂₂₅][Pro] content and similar membrane thickness of ca. 600 μ m (Experimental conditions: $T = 373$ K, $P_{\text{feed}} = P_{\text{sweep}} = \text{atmospheric pressure}$, and relative humidity = 0%)

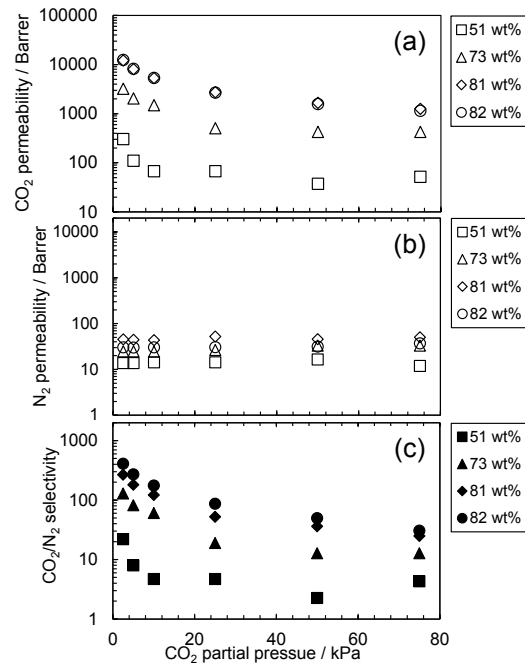


Fig. S5 CO₂ partial pressure dependency of (a) CO₂ permeability, (b) N₂ permeability and (c) CO₂/N₂ selectivity of [P₄₄₄₄][Pro]-based DN ion gel films with different [P₄₄₄₄][Pro] content and similar membrane thickness of ca. 600 μ m (Experimental conditions: $T = 373$ K, $P_{\text{feed}} = P_{\text{sweep}} = \text{atmospheric pressure}$, and relative humidity = 0%)

(6) Mechanical properties of AAIL-based DN ion gel membranes

Compression and tensile stress–strain measurements were performed using an automatic recording universal testing instrument (Autograph AGS-X, Shimadzu Co.). Compression tests were performed by using cylindrical samples. The $[P_{4444}][Pro]$ -based ion gel samples consisted of PAMPS/PDMAAm double-network and PVP single network were set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 10%/min. Tensile tests were carried out using a dumbbell shaped sample. The sample was held between two clamps and the tensile stress was loaded at a strain rate of 100%/min. The typical stress-strain curves for compression and tensile tests are shown in Figs. S6(a) and (b), respectively. The tensile fracture stresses of the AAIL-based DN gels containing various compositions of $[P_{4444}][Pro]$ and $[P_{2225}][Pro]$ are summarized in Figs. S6(c) and S6(d), respectively.

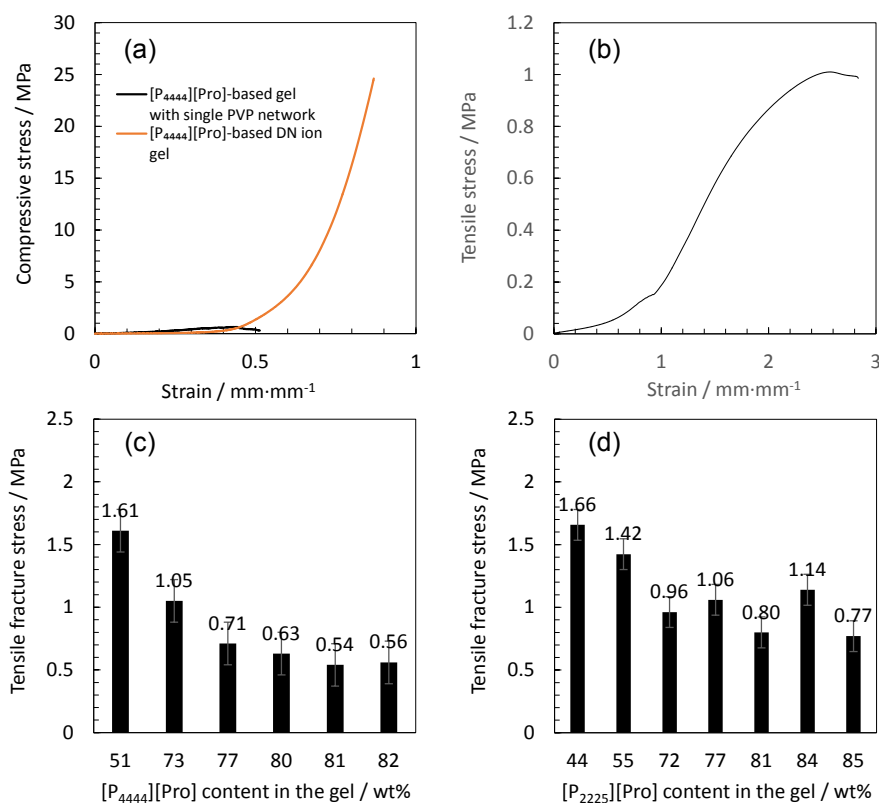


Fig. S6 Typical stress-strain curves of AAIL-based DN ion gels. (a) compression test; black line shows the result for single PVP network gel containing ca. 70 wt% of $[P_{4444}][Pro]$ and red line is that for PAMPS/PDMAAm DN gel containing ca. 80 wt% of $[P_{4444}][Pro]$. It should be noted that the DN ion gel sample was not broken at 25 MPa, which was the maximum loading stress of our universal testing instrument. (b) tensile test for PAMPS/PDMAAm DN gel containing ca. 80 wt% of $[P_{4444}][Pro]$. (c, d) summary of tensile fracture stress of the DN ion gels containing various AAIL contents; (c) $[P_{4444}][Pro]$ and (d) $[P_{2225}][Pro]$. The values in the figures indicate the averages.

The stress-strain curves for cyclic tensile tests are shown in Fig. S7. In both cases, clear hysteresis and softening behavior were observed. This is the evidence of double-network structure formation.⁴

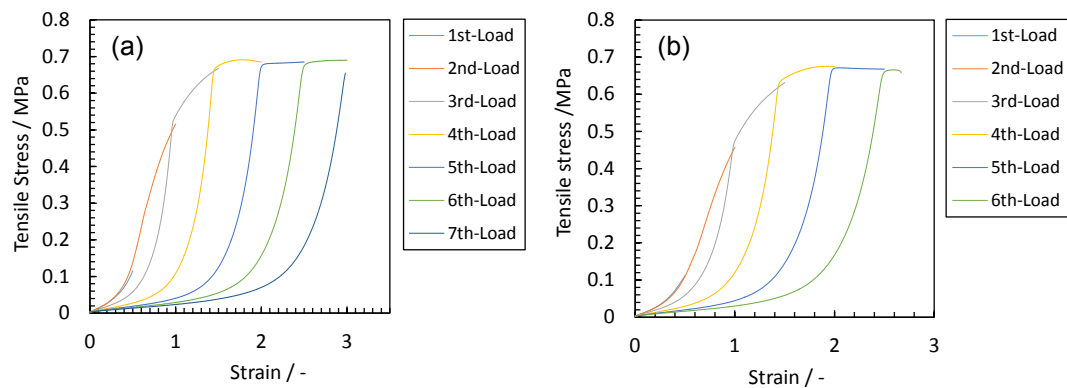


Fig. S7 Stress-strain curves for cyclic stretching tests of PAMPS/PDMAAm DN ion gels containing (a) ca. 80 wt% of $[P_{4444}][Pro]$ and (b) ca. 85 wt% of $[P_{2225}][Pro]$

(7) Durability test of AAIL-based DN gel membranes

Durability of AAIL-based DN ion gel membranes was investigated under pressurized condition ($P_{\text{feed}} = 500$ kPa and $P_{\text{sweep}} = 100$ kPa) at elevated temperature ($T = 373$ K). The CO_2 and N_2 permeabilities and CO_2/N_2 selectivity are presented in Fig. S8.

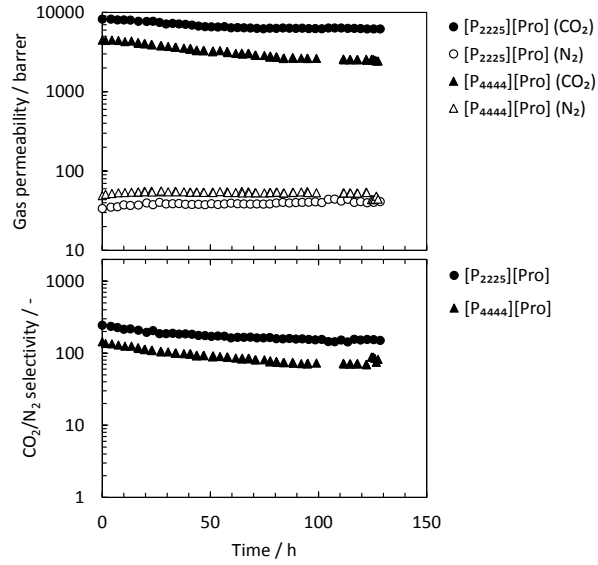


Fig. S8 Time course of (a) CO_2 and N_2 permeabilities and (b) CO_2/N_2 selectivity of AAIL-based DN ion gel membranes containing ca. 80 wt% of $[\text{P}_{2225}][\text{Pro}]$ and $[\text{P}_{4444}][\text{Pro}]$ with ca. $600 \mu\text{m}$ thickness (Experimental conditions: $T = 373$ K, $P_{\text{feed}} = 500$ kPa, $P_{\text{sweep}} = \text{atmospheric pressure}$, $P_{\text{CO}_2, \text{feed}} = 10$ kPa, and relative humidity = 0%)

(8) Effect of membrane thickness on CO₂ and N₂ permeances

Effect of membrane thickness on CO₂ and N₂ permeances were investigated at elevated temperature ($T = 373$ K; P_{feed} and P_{sweep} were atmospheric pressure). The relationships between CO₂ permeances measured under different CO₂ partial pressure conditions and inverted thickness of the DN gel membranes containing ca. 80 wt% of [P₄₄₄₄][Pro] are presented in Fig. S9.

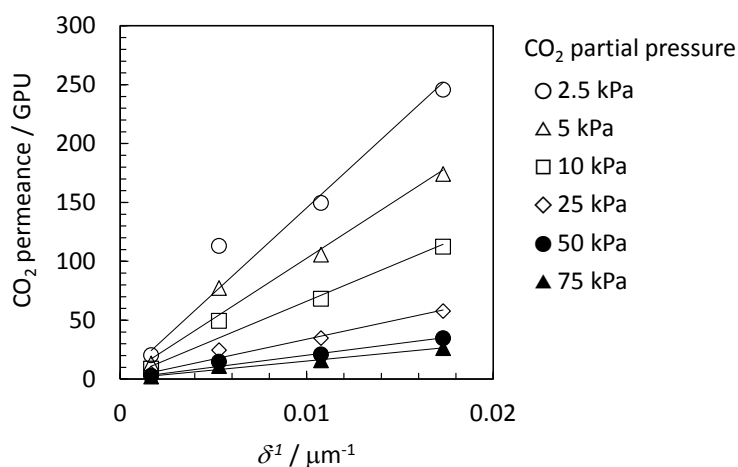


Fig. S9 relationship between CO₂ permeances measured under different CO₂ partial pressure conditions and inverted thickness of the DN gel membranes containing ca. 80 wt% of [P₄₄₄₄][Pro] (Experimental conditions: $T = 373$ K, $P_{\text{feed}} = P_{\text{sweep}} =$ atmospheric pressure, and relative humidity = 0%)

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