Supporting Information for

A facile synthesis of (PIM-polyimide)-(6FDA-durene-polyimide) copolymer as novel polymer membranes for CO_2 separation

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S-1. Materials

4,4'-(Hexafluoroisopropylidene) di-phthalic anhydride (6FDA), 2,3,5,6-tetramethyl benzene-1,4-diamine (durene), and 4,5-dichloro phthalonitrile (98%), were purchased from Tokyo Chemical Industry (TCI) Co. Ltd. (Tokyo, Japan) and were used as obtained. 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,10-spirobisindane (97%) was obtained from Alfa Aesar. Acetic anhydride, toluene, and triethylamine were obtained from Sigma Aldrich. Methanol, ethanol, dimethylformamide, dimethylacetamide, potassium carbonate, and potassium hydroxide were purchased from DaeJung Chemicals & Metals Co. Ltd. in South Korea. 6FDA, durene, and K_2CO_3 were dried under a vacuum at 60 °C for 24 h prior to use. Anhydride monomer of PIM (**An**) was synthesized following the literature method [00]. All chemicals, unless otherwise noted, were obtained from commercial sources and were used as received.

S-2. Characterization and measurements

The **^{1}H NMR** spectra were obtained on an Agilent 400-MR (400 MHz) instrument using d_6-DMSO or $CDCl_3$ as a reference or an internal deuterium lock.

The attenuated total reflection Fourier transform infrared (**ATR-FTIR**) spectra were recorded using a Bruker Vertex 80v Hyperion 2000 ATR-FTIR spectrometer.

Molar masses were determined by gel permeation chromatography (GPC) using two PL Gel 30 cm × 5 µm mixed C columns at 30 ^{o}C running in DMF and calibrated against polystyrene (M_n = 600×10^6 gmol^{-1}) standards using a Knauer refractive index detector.

The thermal stability of the membranes was analyzed by thermogravimetric analysis (**TGA**) measurements conducted on a Shimadzu TGA-2950 instrument at a heating rate of 10 °C min^{-1} under a nitrogen flow.

The tensile properties were measured on a Shimadzu EZ-TEST E2-L instrument benchtop tensile tester using a crosshead speed of 5 $mm.min^{-1}$ at 25 ^{o}C under 50% relative humidity. The engineering stress was calculated from the initial cross-sectional area of the sample and Young's modulus (E) was determined from the initial slope of the stress-strain curve. The membrane samples were cut into rectangular shapes 40 mm × 10 mm (total) and 20 mm × 10 mm (test area) in size.

The densities of the membranes (g.cm-3) were determined experimentally using a top-loading electronic Mettler Toledo balance (XP205, Mettler-Toledo, Switzerland) coupled with a density kit based on the Archimedes principle. The samples were weighed in air and in a known-density liquid, high-purity heptane. The measurements were performed at room temperature using the buoyancy method, and the density was calculated as follows,

$$\rho_{polymer} = \frac{W_o}{W_o - W_l} \rho_{liquid}$$

where W_0 and W_1 are the membrane weights in air and in heptane respectively. Heptane sorption of the membranes was not considered due to their extremely low absorption properties.

The **X-ray** diffraction patterns of the membranes were measured using a Rigaku DMAX-2200H diffractometer operated at a scanning rate of 4^{o} min^{-1} in a 2θ range from 5^{o} to 30^{o} with Cu Kα1 X-ray radiation (λ = 0.1540598). The *d*-spacings were calculated using Bragg's law ($d = \lambda/2\sin\theta$).

Tapping-mode **AFM** was conducted using a Bruker MultiMode instrument. A silicone cantilever with an end radius of <10 nm and a force constant of 40 Nm^{-1} (NCHR, nanosensors, f=300 kHz) was used to image the samples at an ambient temperature.

S-3. Gas permeation procedure

Permeation measurements of pure gas were taken using a high-vacuum time-lag measurement unit based on a constant-volume/variable-pressure method. All of the experiments were performed at a feed pressure of 2 bar (except for the pressure effect experiments which were carried out in the range of 100 mbar to 2 bar feed pressure) and a feed temperature of 30 °C. Before taking these measurements, both the feed and the permeate sides were thoroughly evacuated to below 10^{-5} Torr (1.33×10^{-8} bar) until the readout showed zero values for the removal of any residual gases. The downstream volume was calibrated using a Kapton membrane and was found to be 50 cm^3. The upstream and downstream pressures were measured using a Baraton transducer (MKS; Model No. 626B02TBE) with a full scale of 10,000 and 2 Torr (13.3 and 2.7×10^{-3} bar), respectively. The pressure on the permeate side was recorded as a function of time using a pressure transducer and passed to a desktop computer through a shielded data cable. The permeability coefficient was determined from the linear slope of the downstream pressure versus a time plot (dp/dt) according to the following equation,

$$\boldsymbol{P = \frac{273}{76} \times \frac{Vl}{ATp_0} \times \frac{dp}{dt}} \qquad (\mathbf{2})$$

where, P is the permeability expressed in Barrer (1 Barrer = 10^{-10} [cm^3 (STP) $cm.cm^{-2}.s^{-1}.cm^{-1}.Hg^{-1}$], V (cm^3) is the downstream volume, l (cm) is the membrane thickness, A (cm^2) is the effective area of the membrane, T (K) is the measurement temperature, p_o (Torr) is the pressure of the feed gas in the upstream chamber, and dp/dt is the rate of the pressure change under a steady state. For each gas, the permeation tests were repeated more than three times, and the standard deviation from the mean values of the permeabilities was within ca. ± 3%. Sample-to-sample reproducibility was high and within ± 3%. The effective membrane areas were 15.9 cm^2. The ideal permselectivity, $\alpha_{A/B}$, of the membrane for a pair of gases (A and B) is defined as the ratio of the individual gas permeability coefficients:

$$\boldsymbol{\alpha_{A/B} = \frac{P_A}{P_B}} \qquad (\mathbf{3})$$

The diffusivity and solubility were obtained from the time-lag (θ) value according to the equations

$$\boldsymbol{D = \frac{l^2}{6\theta}} \qquad (\mathbf{4})$$

$$\boldsymbol{S = \frac{P}{D}} \qquad (\mathbf{5})$$

where, D ($cm^2\ s^{-1}$) is the diffusivity coefficient, l is the membrane thickness (cm) and θ is the time lag (s), as obtained from the intercept of the linear steady-state part of the downstream pressure versus a time plot. The solubility, S, was calculated from Eqn. (**5**) with the permeability and diffusivity obtained from Eqns. (**3**) and (**4**).

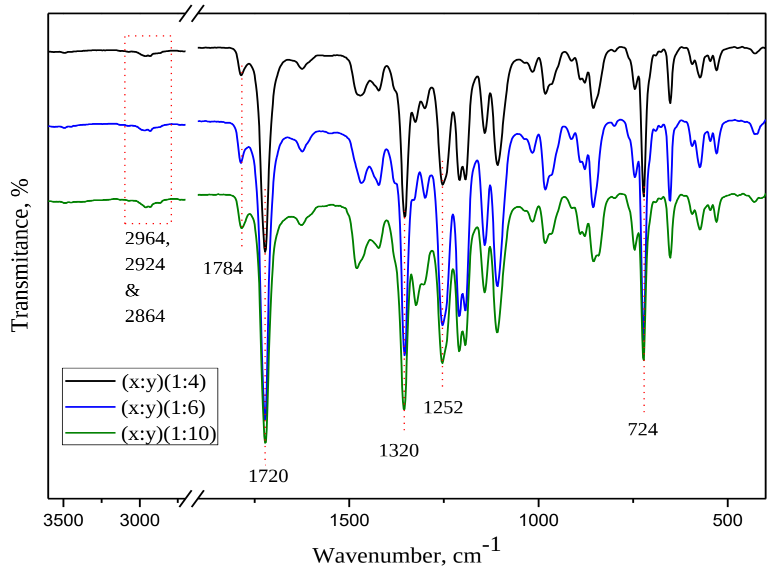

Figure S1. ATR-FTIR spectra of the [(PIM-PI)$_x$-(6FDA-durene-PI)$_y$] copolymers with two different compositions (x:y = 1:4, 1:6 and 1:10)

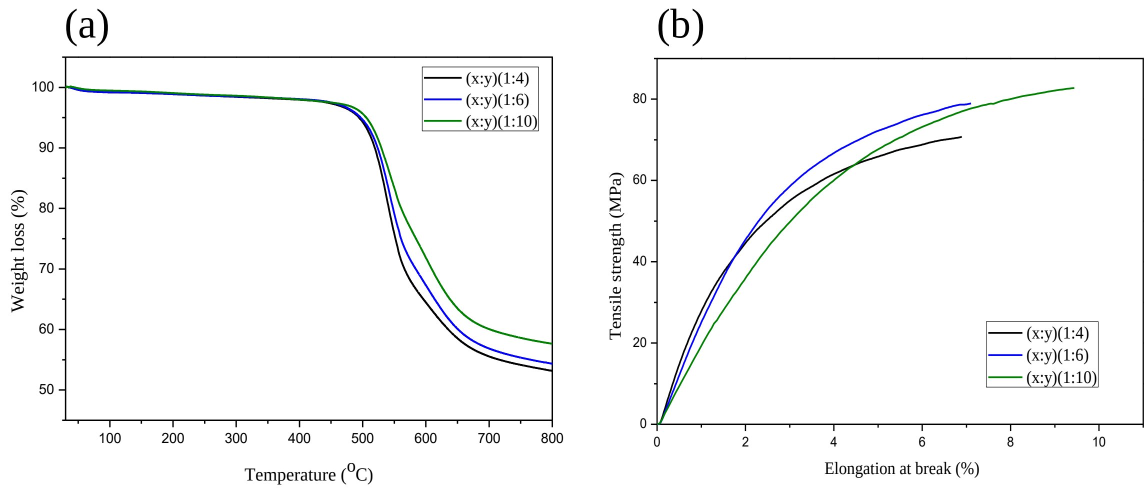

Figure S2. TGA graph (a) and S-S curve (b) of the copolymer [(PIM-PI)$_x$-(6FDA-durene-PI)$_y$] membranes