

## Electronic Supplementary Information

### Increased CO<sub>2</sub>/N<sub>2</sub> Selectivity of PTMSP by Surface Crosslinking

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## 1. Materials and Methods

Dithiothreitol and 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) were purchased from Sigma-Aldrich Co. and used as received. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) was purchased from BOC Science, New York and used as received. House-deionized water was purified by using a Millipore Milli-Q-filtering system containing one carbon and two ion-exchange stages. Experimental methods that were used for measuring advancing contact angles and gas permeabilities, and for analyzing surfaces by AFM, were similar to those previously reported.<sup>1-6</sup> Gas permeabilities were measured using a home-built constant volume-variable pressure apparatus.<sup>2</sup> A Ramé-hart (model 100-00) contact angle goniometer (Ramé-hart Instrument Co., Succasunna, NJ) was used to measure contact angles. All AFM measurements were carried out using a tapping mode atomic force microscopy (NanoScope IIIA, Dimension 3000, Veeco, Santa Barbara, CA) and were examined at a minimum of three different locations along the surface. For each sample,  $5 \times 5 \mu\text{m}^2$  size images were obtained.

## 2. PTMSP membranes

The PTMSP membranes were prepared using a casting technique.<sup>3,5</sup> A typical casting apparatus consisted of a Pyrex glass square (8 in  $\times$  8 in  $\times$  1/8 in), an aluminum centering ring seal, 160 ISO flange size (Kurt J. Lesker Co., Allentown, PA), and five (2.10 in o.d.  $\times$  1.64 in i.d.  $\times$  0.010 in) stainless steel washers (Boker's, Inc., Allentown, PA). The Pyrex glass square, ring seal, and five washers were cleaned with chloroform, methanol, and acetone, with the aid of Kimwipes. The ring seal was then adhered to the glass square using a 5% toluene solution (HPLC grade) of PTMSP which acted as a "glue". The steel washers were then placed, symmetrically, within the ring seal/glass square casting unit. A PTMSP/toluene casting solution (ca. 480 mg/30 mL) was then poured into the ring seal and covered with 15 large pieces of filter paper (Whatman qualitative circles, 18.5 cm) in order to keep the casting unit dust-free and to avoid the solvent from evaporating too fast. The toluene was allowed to evaporate for at least 24 h in a clean room, leaving a PTMSP film across the steel washers

and glass square. A surgical blade (S/P Surgical Blades, Baxter Diagnostics) was then used to cut out the individual washers. Deionized water (ca. 30 mL) was poured into the ring seal to help separate the washers. The PTMSP cast films were then dried by placing them between several large filter papers for at least 24 h in the laboratory ambient temperature. The resulting membranes, having a typical thickness of ca. 20-25  $\mu\text{m}$ , were placed in antistatic bags for at least 15 min prior to use for modification.

### 3. Gas Permeation Measurements

Gas permeation measurements were done using a home-built stainless steel permeation apparatus.<sup>2</sup> The gases studied were  $\text{H}_2$  (Ultra High Purity, water < 3 ppm, Messer Griesheim Industries, Inc., Malvern, PA),  $\text{CO}_2$  (Ultra Pure, water < 3 ppm, Praxair, Inc., Danbury, CT) and  $\text{N}_2$  (Prepurified grade, water < 3 ppm, Praxair, Inc., Danbury, CT). Prior to gas permeation measurements, all membranes were allowed to dry in a desiccator for 72 h. During such time, the approximate room temperature was  $22 \pm 2$  °C. Typically, a membrane to be measured was placed in the permeation cell between two Viton rubber O-rings (3.45 cm i.d., Scientific Instrument Services, Inc.) with a support screen (4.70 cm, Millipore Corp.) and held securely with a quick flange clamp (Scientific Instrument Services, Inc.). Membranes were always placed in the cell in such way that the modified surface faced the high pressure side of the pressure gradient. The pressure gradient that was applied across each membrane was 40 psi. Before each measurement, the pressure on the permeate side was reduced to less than 1.5 Torr, while the feed side (upstream) pressure was maintained constant (40 psi). The increase of pressure on the permeate side (downstream) was monitored using a pressure transducer (626C Baratron Capacitance Manometer, MKS Instrument, Inc., MA) under steady state and isothermal conditions. The following equations was used to calculate the permeance values

$P/l$ .<sup>7</sup>

$$p_t = p_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A}{V_p \cdot V_m} \cdot \frac{p_f \cdot P}{l} \left( t - \frac{l^2}{6D} \right) \quad (1)$$

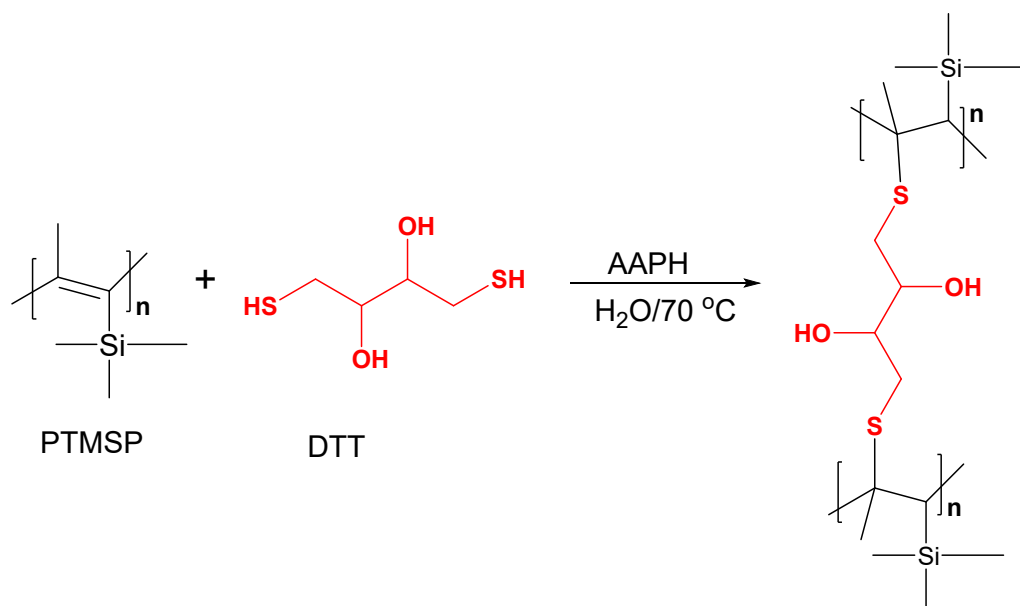
$$\frac{P}{l} = \frac{V_p \cdot V_m}{RT \cdot A \cdot p_f} \left( \frac{dp}{dt} \right) \quad (2)$$

Here  $P$  is the permeability coefficient,  $l$  is the membrane thickness,  $p_t$  is the permeate pressure at time  $t$ ,  $p_0$  is the starting pressure,  $(dp/dt)_0$  is the baseline slope,  $p_f$  is the feed pressure,  $R$  is the universal gas constant ( $8.314 \times 10^{-5}$  in  $\text{m}^3 \cdot \text{bar} / \text{mol} \cdot \text{K}$ ),  $T$  is the absolute temperature (298 K),  $A$  is the exposed membrane area ( $9.62 \text{ cm}^2$ ),  $V_p$  is the permeate volume,  $V_m$  is the molar volume of the permeating gas ( $22.41 \times 10^{-3}$  in  $\text{m}^3 / \text{mol}$ ) at standard temperature and pressure ( $0^\circ \text{C}$  and  $1 \text{ atm}$ ). The term  $p_0 + (dp/dt)_0 \cdot t$  in eq. 1 refers to the starting pressure and the baseline slope is negligible in a well evacuated and sealed system. Rearrangement of the slope  $dp/dt$  in eq. 1 gives the eq. 2, where  $dp/dt$  is the increase in pressure over time that was measured experimentally.

In general, the permeation properties were first measured for  $\text{H}_2$ ,  $\text{CO}_2$  and then for  $\text{N}_2$ . To ensure that no damage to the membrane had occurred while these measurements were being made, after the last permeant was investigated, the  $\text{H}_2$  permeances were measured again and found to be unchanged.

#### **4. Surface modification of PTMSP via Thiol-ene reaction**

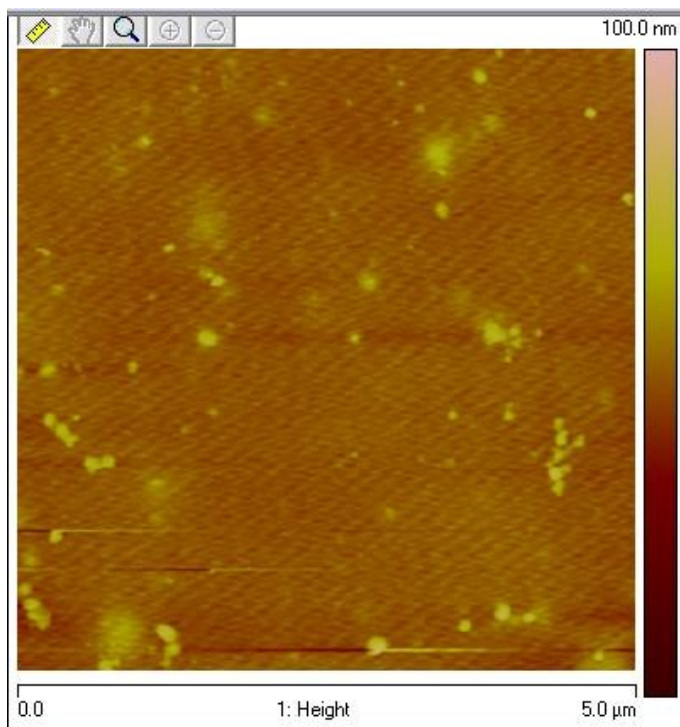
In a typical surface modification of PTMSP, the stainless steel washer containing an attached membrane was fully submerged in a solution of dithiothreitol (50 mg/mL) and 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) (2 mg/mL) in Mili-Q DI water. Prior to heating, this solution was purged with argon at room temperature for 30 min. Then the membrane was heated at  $70^\circ \text{C}$  for 5 h or 24 h under an argon atmosphere. The membrane was then vigorously washed using DI water multiple times, dried overnight in a vacuum oven at  $40^\circ \text{C}$  and the permeability of the membrane recorded with respect to  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{N}_2$ .

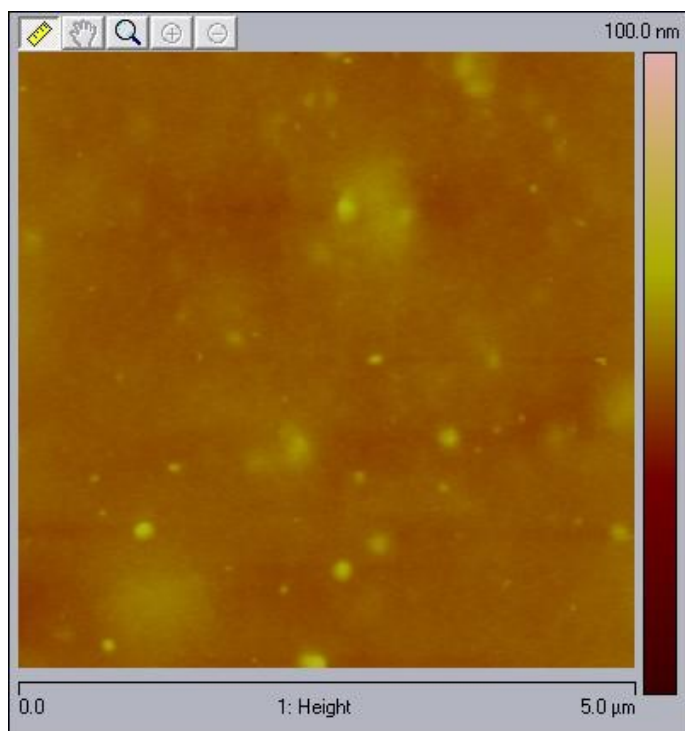


**Scheme S1.** Thiol-ene reaction on PTMSP surface.

### 5. Atomic Force Microscopy (AFM) analysis

Unmodified PTMSP and thiol-modified PTMSP membrane were directly analyzed using AFM to study the morphology of the membranes.





**Fig S2.** AFM height images of thiol-modified PTMSP (top) and unmodified PTMSP (bottom).

## 7. References

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