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Increased CO_2/N_2 Selectivity of PTMSP By Surface Crosslinking

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Sayali V. Shaligram and Steven L. Regen*

The surface crosslinking of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes by dithiothreitol under thiol-ene click reaction conditions has yielded membranes having CO_2/N_2 selectivities in excess of 30 with CO_2 permeances in excess of 300 GPU (gas permeation units). The simplicity of this surface crosslinking strategy together with these permeation results suggests that PTMSP that is modified in such ways could lead to useful materials for the separation of CO_2/N_2 from flue gas and for certain other gaseous mixtures.

The need for stabilizing the earth's greenhouse gases is considered as urgent if further changes in climate are to be avoided.[1] Of major concern is the CO_2 that is being produced from the combustion of fossil fuels at power plants.[2,3] Due to the climate crisis, efforts aimed at creating cost-effective ways of separating CO_2 from N_2 in flue gas have intensified.[4] One strategy that is being pursued is to create materials that can absorb CO_2, selectively.[5,6] A second strategy involves the creation of polymer membranes that show high permeability towards CO_2 relative to N_2.[7-14] Of these two approaches, membrane-based separations appears to be more feasible due to lower energy and capital requirements.[7,11]

A cost analysis for a real-world capture of CO_2 from flue gas that is based on polymer membranes has shown that the minimum requirements that need to be met are polymers having (i) CO_2/N_2 selectivities that are $\geq$ 30 and (ii) CO_2 permeances that are as high as possible.[7,8] This analysis has further revealed that membranes having CO_2/N_2 selectivities that are much greater than ca. 30 do not help, significantly; i.e., they would have little impact on the economics of the separation. When comparing the gas permeation properties of polymers, in general, permeance values (P/l) are often used instead of permeabilities because they take a membrane thickness into account. More specifically, permeances are permeabilities that have been normalized with respect to a membrane's thickness. In practice, permeances are calculated by dividing the observed flux (J) by the pressure gradient (Δp) that is applied across the membrane (eq. 1).[11] Here, P is a permeability coefficient that is characteristic of a given membrane/permeant combination and l is the thickness of the membrane. To date poly(ethylene glycol)-based polymers appear to be the most promising materials for a real-world capture of CO_2 from flue gas where CO_2/N_2 selectivities of ca. 50 and CO_2 permeances of ca. 1000-2000 GPU have been reported.[7,12,13]

$$P/l = J/\Delta \mathrm{p} \qquad (1)$$

One unique polymer that has attracted broad attention in the gas separation area is poly[1-(trimethylsilyl)-1-propyne] (PTMSP). Owing to its high free volume and glassy state, PTMSP exhibits exceptionally high gas permeances.[14] However, these high permeances are usually accompanied by low permeation selectivities; i.e., there's a "trade-off" between permeance and selectivity.[15] In past studies, we and others have taken advantage of PTMSP's high permeability by using it as support material for extremely thin, permeation-selective Langmuir-Blodgett, Langmuir-Schafer and polyelectrolyte multilayers.[16-18] Other researchers have found that the grafting of poly(ethylene glycol)s to the surface of PTMSP results in a CO_2/N_2 selectivity of ca. 80 with a CO_2 permeance as high as ca. 170 GPU.[19] A detailed comparison of a variety of other polymeric membranes with respect to CO_2 permeances and CO_2/N_2 selectivities has previously been reported.[12]

Recently, we reported that the surface of PTMSP membranes can be modified using aqueous solutions of 3-mercapto-1-propanesulfonate under thiol-ene click reaction conditions to give membranes having a CO_2/N_2 selectivity of ca. 20 with a CO_2 permeance of 530 GPU.[20] In an effort to reach the targeted CO_2/N_2 selectivity of 30, we hypothesized that analogous *surface crosslinking* of PTMSP could result in a beneficial trade-off. Specifically, we reasoned that surface crosslinking would result in smaller pores at the surface of the membrane and an increase in

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Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015, USA.
E-mail: slr0@lehigh.edu.

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Drs. S. V. Shaligram and Prof. S. L. Regen*
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania 18015 (USA)

Email:slr0@lehigh.edu

Supporting information for this article (experimental procedures and characterization) can be found given under http://

the CO_2/N_2 selectivity due to a greater reduction in diffusivity for the larger N_2 molecule relative to that of the smaller CO_2 molecule. We further reasoned that the CO2 permeance should remain high as compared to most polymers that have been reported to date since surface crosslinking would involve only a thin outer layer of PTMSP. Although there have been other reports describing the crosslinking of PTMSP, to the best of our knowledge, none have been specifically designed to crosslink its surface with the goal of improved selectivity.[21,22]

To test our hypothesis, we chose dithiothreitol (DTT) as a surface crosslinking agent. Previous studies have shown that DTT is effective in crosslinking alkene-containing polymers *via* thiol-ene click reactions.**[23,24]** Because of its limited solubility in water (ca. 50 mg/mL), we envisioned that DTT would readily adsorb onto the hydrophobic surface of PTMSP and undergo thiol-ene crosslinking. We also reasoned that successful surface modification of PTMSP with DTT would be apparent by a significant increase in the membrane's hydrophilicity as its surface becomes hydroxylated.

With these ideas in mind, cast films of PTMSP (ca. 30 µm in thickness) were immersed in aqueous solutions containing varying concentrations of DTT plus 8 mg/mL of the free radical initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH, Fig. 1).[20] Surface modifications were then carried out by simply heating each solution for 5 h at 70°C under an argon atmosphere, followed by rinsing each film with deionized water. The advancing contact angle for water on untreated PTMSP was 90° ± 3°. The PTMSP surfaces that were treated with aqueous solutions that were 0.5, 5.0, 25 and 50 mg/mL in DTT showed contact angles of 85°± 2°, 78°± 3°, 58° ± 3° and 55° ± 2°, respectively. Examination of these films by ATR-FTIR analysis further revealed a steady increase in DTT content that accompanied this increase in hydrophilicity as evidenced by small but detectable increases in the O-H and C-S stretching regions (Figure 2).[25,26]

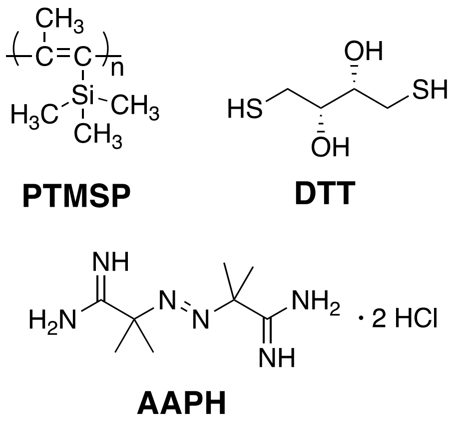

Fig.1. Structures of PTMSP, DTT and AAPH used in this work.

Gas permeation measurements were made using a home-built constant volume-variable pressure apparatus.**[27]** The order that was used for gas measurements was H_2 followed by CO_2 and then N_2. To ensure that no damage occurred during these analyses, H_2 measurements were repeated and found to be essentially unchanged. Table 1 lists the permeance values for each gas along with H_2/N_2 and CO_2/N_2 selectivities. Although elevated temperatures are known to produce thiyl radicals for thiol-ene reactions even without radical initiators, maximum CO_2/N_2 and H_2/N_2 selectivities were obtained when the free radical initiator, AAPH, was included in the reaction (Table 1).**[28,29]** Thus, the production of thiyl radicals, and the resulting thiol-ene reaction, appear to be more efficient when a free radical initiator is employed.

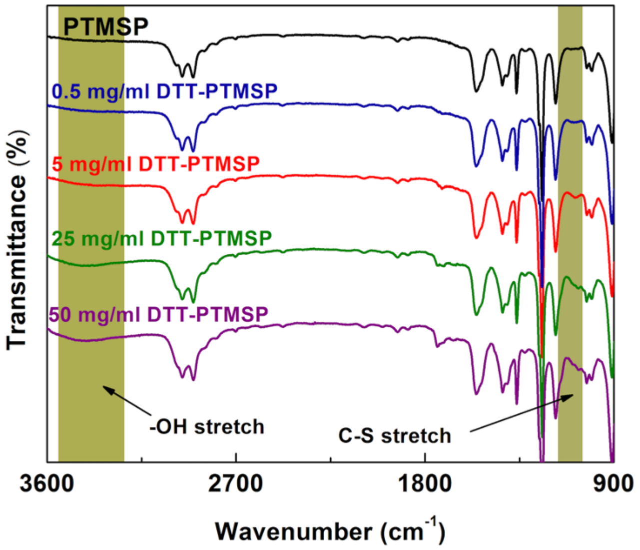

Fig.2. ATR-FTIR spectra of PTMSP that has been treated with increasing concentrations of DTT under thiol-ene click reaction conditions..

Table 1. Permeances and Permeation Selectivities[a]

DTT (mg/mL)	H_2	CO_2	N_2	H_2/N_2	CO_2/N_2
0.0[b]	940	1900	420	2.2	4.5
0.5[b]	350	820	120	2.9	6.8
	360	850	130	2.8	6,5
5.0[b]	300	580	46	6.5	13
	310	600	47	6.6	13
25[c]	280	480	25	11	19
	280	490	27	10	18
50[c]	190	430	12	16	36
	190	430	13	15	33
50[c,d]	180	410	11	16	37
	180	400	11	16	36
50[c,e]	230	550	46	5.0	12
	250	560	47	5.3	12
50[c,f]	180	320	8	23	40
	180	320	8	23	40
50[c,g]	160	380	11	15	35
	160	370	11	15	34

[a] Permeance values are given in GPU units, where 1 GPU = 1 x 10^{-6} ($cm^3/cm^2 \cdot s \cdot cm$ Hg). All permeances are ideal (single gas) values obtained at ambient temperatures using a pressure gradient of 2069 Torr. Unless noted otherwise, all surface modifications were carried out at 70°C for 5 h in the presence of 8 mg/mL AAPH. [b] Average values (± 5%) obtained from two independent measurements of the same sample. [c] Average values (± 5%) obtained from five independent measurements of the same sample. [d] 24 h reaction time. [e] AAPH was absent in this surface treatment. [f] The membranes were aged for 30 days. [g] Water-saturated gases were employed

Examination of the surface of PTMSP by atomic force microscopy, before and after surface crosslinking under conditions that produced the maximum CO_2/N_2 selectivity, revealed root mean-squared surface roughnesses (RMS) of 2.13 nm and 8.23 nm, respectively (Figure 3). Although we believe that crosslinking by DTT is the primary mode of surface modification of PTMSP, since H_2S is known to be released from DTT under free radical conditions, it is possible that H_2S may also be contributing to this surface crosslinking.[30]

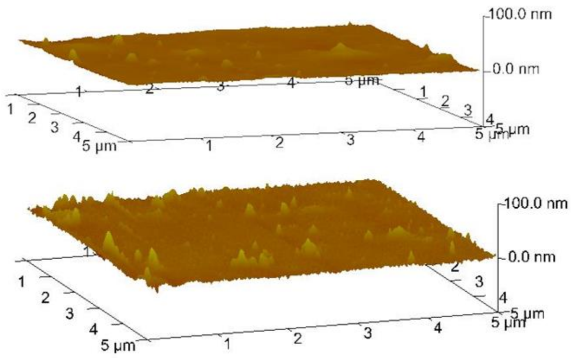

Fig.3. AFM image of PTMSP before (top) and after DTT-modification using 50 mg/mL DTT, 8 mg/mL AAPH and 70°C for 5 h (bottom).

In Figure 4 are shown plots of CO_2 and N_2 permeances, and CO_2/N_2 selectivities as a function of degree of surface modification as judged by contact angle measurements. Thus, significant increases in surface modification (i.e., increased hydrophilicity) were accompanied by lower permeances and higher CO_2/N_2 selectivities.**[15]** The fact that the surface modification of PTMSP by 3-mercapto-1-propanesulfonate (an agent that is incapable of crosslinking) produces a surface that is even more hydrophilic than that produced with DTT but with significantly reduced CO_2/N_2 and H_2/N_2 selectivities, indicates that surface hydrophilicity plays a minor role in influencing the membrane's permeation and selectivity properties.[20] At the same time, this comparison provides inferential evidence for surface crosslinking by DTT. The fact that the H_2 permeances were always found to be greater than those of N_2 is a likely result of its smaller size and permeability coefficients that are dominated by diffusivity; i.e., the kinetic diameters for H_2 and N_2 are 0.289 and 0.364 nm, respectively.**[31]** This implies that changes in diffusivity are major contributors to the enhanced selectivity of this surface modified PTMSP. Since CO_2 has a kinetic diameter of 0.330 nm, which is significantly larger than that of H_2, the fact that all of the CO_2 permeances were greater than those of H_2 is the likely result of a greater solubility contribution to the permeability coefficient for CO_2; i.e., $P = S \times D$ where and S and D are the solubility and diffusivity coefficients, respectively.**[15]** Whether specific interactions between CO_2 and surface-bound DTT contribute significantly to the increased CO_2/N_2 selectivity of PTMSP remains to be established.

In preliminary studies, PTMSP membranes that were modified using 50 mg/mL of DTT and stored in a desiccator for 30 days at ambient temperature showed a ca. 25% decrease in their CO_2 permeances to 320 GPU with a ca. 10% increase in CO_2/N_2 selectivity of 40.**[32]** In separate experiments, when freshly prepared membranes were exposed to water-saturated CO_2 and N_2 gases, the CO_2 permeances were reduced by ca. 10% to 380 GPU along with a negligible change in their CO_2/N_2 selectivity (Table 1).

The significant improvement in the CO_2/N_2 selectivity that we have observed for PTMSP through surface crosslinking may extend to other gaseous mixtures of interest. For example, surface crosslinked PTMSP might exhibit significant selectivity for H_2O/C_2H_5OH separations where an ideal selectivity of 0.9 was observed for pure PTMSP.**[33,34]** In principle, an increased selectivity should be possible by taking advantage of the difference in the kinetic diameters for water (0.296 nm) and ethanol (0.430 nm).

Whether surface crosslinked PTMSP membranes in flat form, or in hollow fiber form (having surface areas 5 to 10 times greater per unit volume) can function, effectively, under real-world operating conditions for a given separation is a question that remains to be answered.[35,36] In a broader context, these results should encourage other investigators to consider related surface crosslinking strategies for improving the permeation properties of other high free volume polymers. Studies that are continuing in our laboratories are aimed at creating other surface crosslinked PTMSP membranes that may exhibit even higher CO_2 permeances with CO_2/N_2 selectivities that are in excess of 30. Studies in progress are also being aimed at minimizing aging effects.[37]

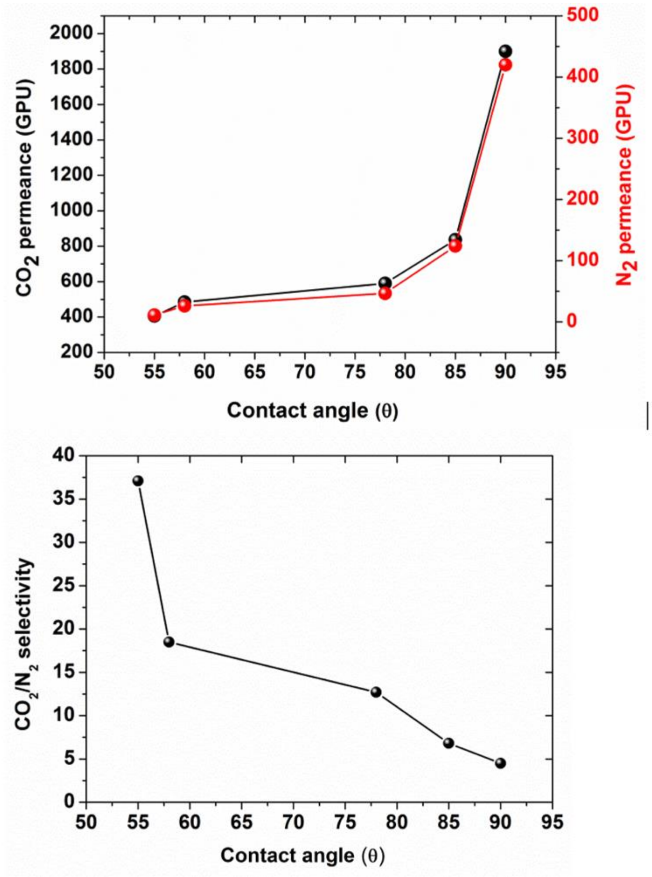

Fig 4. Plot of (top) CO_2 and N_2 permeance and (bottom) CO_2/N_2 selectivity as a function of the advancing contact angle for water.

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Conflicts of interest

There are no conflicts of interest to declare.

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Electronic Supplementary Information

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Sayali V. Shaligram and Steven L. Regen*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015, United States

Table of Contents

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.[1-6] Gas permeabilities were measured using a home-built constant volume-variable pressure apparatus.[2] 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 × 5 μm^2 size images were obtained.

2. PTMSP membranes

The PTMSP membranes were prepared using a casting technique.[3,5] A typical casting apparatus consisted of a Pyrex glass square (8 in × 8 in × 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. × 1.64 in i.d. × 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 μm, 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.[2] The gases studied were H_2 (Ultra High Purity, water < 3 ppm, Messer Griesheim Industries, Inc., Malvern, PA), CO_2 (Ultra Pure, water < 3 ppm, Praxair, Inc., Danbury, CT) and 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 ± 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*.[7]

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

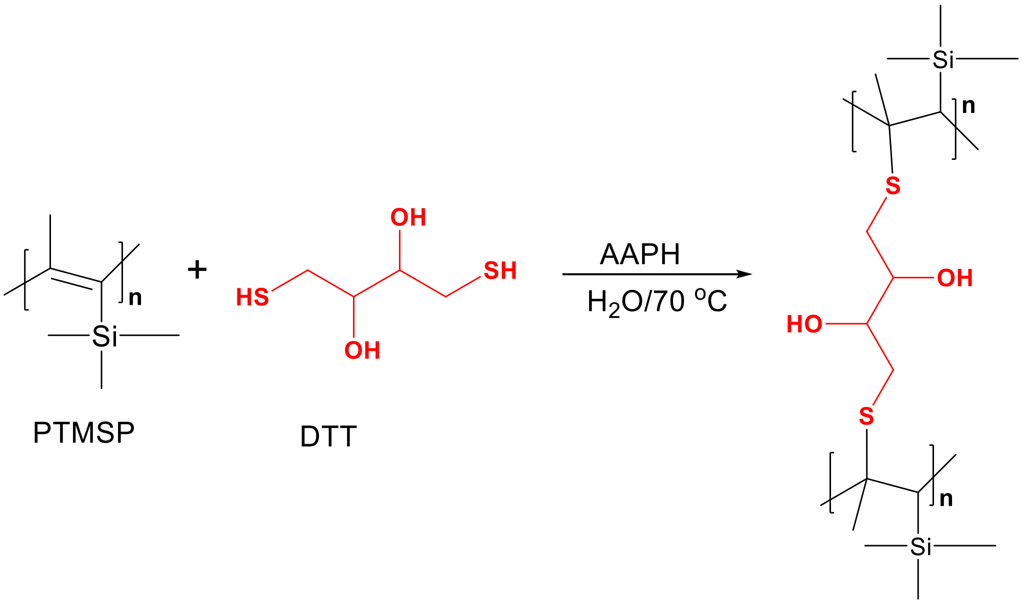
$$\frac{P}{l} = \frac{V_p \cdot V_m}{RT \cdot A \cdot p_f}\left(\frac{dp}{dt}\right) \qquad (2)$$

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 x 10^{-5} in $m^3 \cdot bar/mol \cdot K$), T is the absolute temperature (298 K), A is the exposed membrane area (9.62 cm^3), V_P is the permeate volume, V_m is the molar volume of the permeating gas (22.41 x 10^{-3} in m^3/mol) at standard temperature and pressure (0 °C and 1 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 H_2, CO_2 and then for 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 H_2 permeances were measured again and found to be unchanged.

4. Surface modification of PTMSP via Thiol-ene reaction

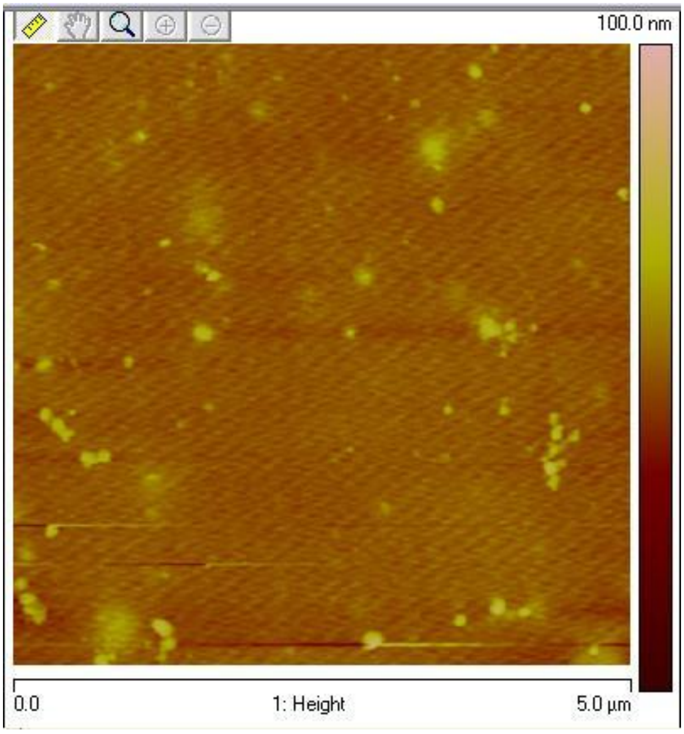
In a typical surface modification of PTMSP, the stainless steel washer containing an attached membrane was fully submerged in a solution of dithiothreitol (50 mg/mL) and 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) (2 mg/mL) in Mili-Q DI water. Prior to heating, this solution was purged with argon at room temperature for 30 min. Then the membrane was heated at 70 ˚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 ˚C and the permeability of the membrane recorded with respect to H_2, CO_2 and 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.



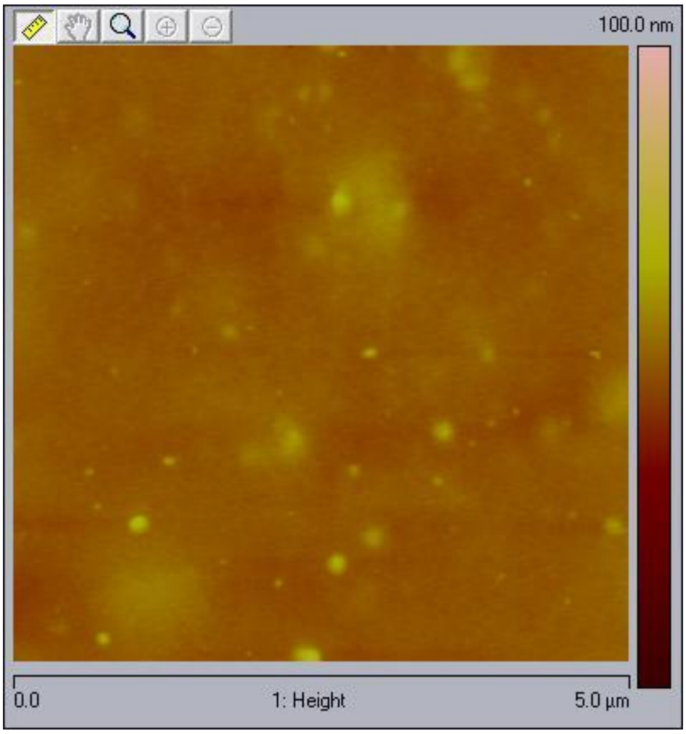


Fig S2. AFM height images of thiol-modified PTMSP (top) and unmodified PTMSP (bottom).

7. References

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