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Self-Assembled Monolayers on Electroless Gold Impart pH-Responsive Transport of Ions in Porous Membranes

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Introduction

Martin and co-workers reported electroless deposition of gold onto the pore walls in polycarbonate track-etched (PCTE) filtration membranes to achieve electrically tunable charge selectivity.[1−3] Propanethiol chemisorbed to gold was used to protect the surface of gold from adsorption of anions (such as Cl^-) that could result in excess negative charges on the pore walls and cause irreversible changes in charge selectivity.[2] The charge selectivity of the membrane could be reversibly altered by manipulation of the electrical potential applied to the gold. Martin and co-workers also recently reported introduction of permselectivity using such gold-coated PCTE membranes based on the hydrophilicity of the tail groups (-CH_3 and -OH) of chemisorbed thiols onto gold.[4]

The goal of our work is to demonstrate modification of surface properties of the gold-coated PCTE membranes using self-assembled monolayers (SAMs) formed from ω-functionalized thiols that respond to changes in the solution conditions. In an earlier report we have characterized SAMs formed from alkanethiols on the surface of electroless gold.[5] We have shown that close-packed monolayers can be formed onto electroless gold provided that the electroless gold is appropriately treated after deposition. Those results allowed us to form SAMs from functionalized thiols onto electroless gold deposited on silica gel.[6] In this paper, we describe the use of electroless deposition of gold on PCTE membranes followed by self-assembly of carboxylic acid-functionalized thiols onto gold to prepare pH-responsive membranes. Such membranes are useful for controlled delivery systems[7,8] and selective separation of proteins.[9]

Experimental Section

Commercial PCTE membranes (Poretics, Inc.)[10] with hydraulic pore radii (R) of 12 and 28 nm (determined by water flux experiment),[11−13] a pore density[14] of 6 pores/μm^2, and a thickness of 6 μm were used as templates. The PCTE membrane contains parallel cylindrical pores with a narrow distribution of the pore size.[10] We deposited electroless gold on the pore walls and both faces of the membrane using a procedure reported by Menon and Martin.[1] The temperature of the deposition solution was ~1 °C. The gold-coated membrane was immersed in 25% nitric acid for 12 h (so that the surface of the deposited gold was cleaned),[1,5] rinsed thoroughly with water, and dried in air. Milli-Q water (18 MΩ) was used for rinsing and preparation of all solutions. After deposition of gold for 3−5 h using the PCTE membrane with R = 28 nm followed by treatment in 25% nitric acid, the amount of deposited gold was 0.2−0.3 mg/cm^2 of membrane and the hydraulic pore radius of the membrane was reduced to 10−15 nm.[11] The thickness of the gold film may not be uniform throughout the pore. Martin and co-workers have reported a bottleneck structure formed near the ends of the pore.[3] Thus the pore radii reported in this paper are apparent values. To form thiol monolayers on the surface of the deposited gold, the gold-coated membrane was thoroughly rinsed with ethanol and then immersed in an ethanolic solution of ~1 mM thiol for at least 24 h. All thiols used in this paper were from Aldrich. After formation of the monolayers, the membrane was rinsed again with ethanol and dried in flowing nitrogen prior to use in diffusion experiments.

Diffusion experiments were carried out in a diffusion cell shown in Figure 1. A membrane separated the diffusion cell into two compartments (reservoir and sink). The reservoir contained an aqueous solution (45 mL) of a permeant and the sink contained a blank aqueous solution (45 mL) initially without the permeant. The effective area of the membrane was 3 cm^2. Vigorous stirring (at the same speed setting) was applied in both compartments in all diffusion experiments by using two magnetic stirrers and a Corning stirring plate (see Figure 1). Fluxes of permeants across the membrane were measured in a manner as described below. A small amount of solution (~1 mL) was periodically sampled from the sink and the concentration of the permeant was determined by peak absorbance measured with a Varian Cary-3 UV−vis spectrophotometer. Each sample solution was returned to the sink immediately after the measurement (which took 1−2 min). The total diffusion time was controlled so that the concentration of the permeant in the reservoir decreased by less than 2% for all diffusion experiments and thus the gradient of the concentration of the permeant across the membrane was nearly constant. The flux of the permeant across the membrane was obtained from the slope when the measured permeant concentration in the sink was plotted versus the diffusion time.[15]

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(1) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920−8.

(2) Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700−2.

(3) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655−8.

(4) Hulteen, J. C.; Jirage, K. B.; Martin, C. R. *J. Am. Chem. Soc.* **1998**, *120*, 6603−4.

(5) Hou, Z.; Abbott, N. L.; Stroeve, P. *Langmuir* **1998**, *14*, 3287−97.

(6) Dubrovsky, T. B.; Hou, Z.; Stroeve, P.; Abbott, N. L. *Anal. Chem.* **1999**, *71*, 327−32.

(7) Kono, K.; Tabata, F.; Takagishi, T. *J. Membr. Sci.* **1993**, *76*, 233−43.

(8) Saito, K.; Ishizuka, S.; Mitsura, H.; Tanioka, A. *Polymer* **1996**, *37*, 2493−8.

(9) Li, Y.; Spencer, H. G. *ACS Symp. Ser.* **1994**, *540*, 297−305.

(10) Poretics Products Catalog 1997−1998 Edition, pp 18−23.

(11) The pore radii reported in this work were measured by flux of deionized water across the membrane under a pressure drop of ~2 kPa. The equation used to calculate the pore radius R was obtained from the Hagen-Poiseuille law of capillary flow, $R = (8Q\mu L/\pi\Delta PA\sigma)^{1/4}$ (eq 1), where Q is the flow rate of water across the membrane, μ is the viscosity of water, L is the length of the pores (thickness of the membrane was used, since the pores are nearly perpendicular to the surface of the membrane[10]), ΔP is the pressure drop across the membrane, A is the effective area of the membrane, and σ is the pore density (number of pores per unit area of membrane).

(12) These values of pore radii (12 and 28 nm), however, are not consistent with the nominal pore radii (5 and 15 nm, respectively) provided by the manufacturer. A similar discrepancy has been revealed by a recent report where the pore radius measured by water flux under a pressure drop of 100 kPa is more than 4 times the nominal value.[13] Such a discrepancy was attributed to the expansion of pores under stress (due to pressure drop across the membrane) in that report. However, the pressure drop used in our experiments (~2 kPa) is much smaller.

(13) Kim, K. J.; Stevens, P. V. *J. Membr. Sci.* **1997**, *123*, 303−14.

(14) The pore density of such membranes determined by SEM images[13] is 7.7 ± 2.4 pores/μm^2. Since image analysis usually induces systematic errors, we use the nominal pore density (6 pores/μm^2) provided by the manufacturer.

(15) The flux (J) of the permeant was determined by $J = (1/\pi R^2 VA\sigma)\cdot(\mathrm{d}C_S/\mathrm{d}t)$ (eq 2), where C_S is the concentration of the permeant in the sink measured at time t and V is the volume of solution in the sink. The value of $(\mathrm{d}C_S/\mathrm{d}t)$ was obtained from the plot of C_S against t. The other parameters are the same as in eq 1.[11]

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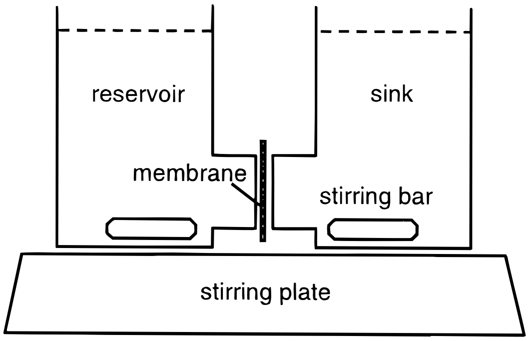

Figure 1. Diagram of the diffusion cell.

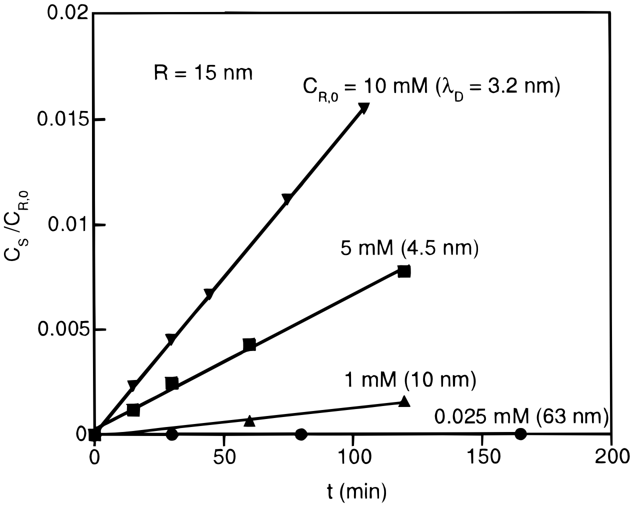

Figure 2. Diffusion of permanganate (MnO_4^-) anions across a PCTE/Au/Cl^- membrane: concentration of MnO_4^- in the sink (C_S) as a function of diffusion time (t) with different initial concentrations of MnO_4^- in the reservoir ($C_{R,0}$). The Debye length (λ_D) corresponding to each value of $C_{R,0}$ is also shown.

Results and Discussion

We first investigated the dependence of ionic diffusion through charged pores on the thickness of the electrical double layer. A gold-coated PCTE membrane with chloride ions adsorbed on the surface of gold was used for this purpose. The hydraulic pore radius (R) of this membrane was 15 nm and that of the template PCTE membrane was 28 nm. The gold-coated membrane was immersed in an aqueous solution of 1 mM KCl for 1 h and then rinsed thoroughly with water prior to each diffusion experiment. Permanganate anion (MnO_4^-) was used as the permeant. Before diffusion started, the reservoir contained an aqueous solution of $KMnO_4$ and the sink contained water. Figure 2 shows the concentration of MnO_4^- in the sink, C_S (normalized by the initial concentration of MnO_4^- in the reservoir, $C_{R,0}$) as a function of diffusion time (t). Each line corresponds to a value of $C_{R,0}$ and the associated Debye length (λ_D)[16] that is used to represent the thickness of the electrical double layer. The slope of the line is proportional to the flux of MnO_4^- across the membrane.[15] It is seen from Figure 2 that the flux of MnO_4^- decreases as the concentration of the feeding solution decreases (or as the Debye length increases). When the concentration is so low that the Debye length is large compared to the pore radius (15 nm), the double layer interactions between MnO_4^- anions in the solution and the negatively charged pore walls dominate the partitioning of MnO_4^- into the pores. In that case, the PCTE/Au/Cl^- membrane effectively blocks the diffusion of MnO_4^-.

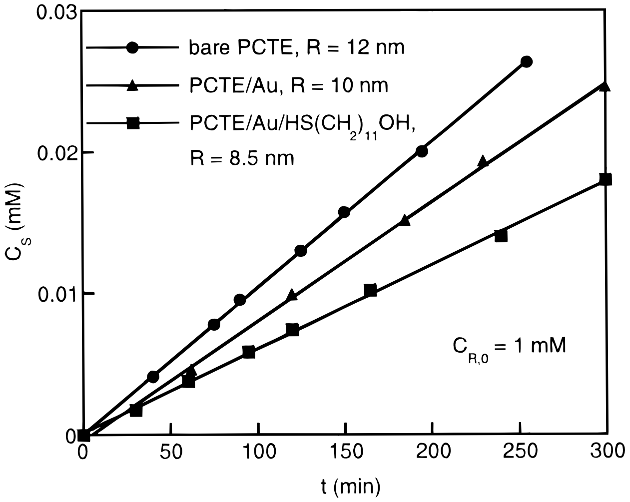

Figure 3. Diffusion of pyridine across bare PCTE, PCTE/Au, and PCTE/Au/$HS(CH_2)_{11}OH$ membranes. The pore radius of the bare PCTE membrane was determined by water flux. The pore radii of PCTE/Au and PCTE/Au/$HS(CH_2)_{11}OH$ membranes were obtained from comparison of the fluxes of pyridine across these membranes to that measured with the bare PCTE membrane.

A template PCTE membrane with $R = 12$ nm was used to investigate the effects of deposition of electroless gold and formation of self-assembled monolayers (SAMs) of long-chain thiols on the pore size of the membrane. The average pore radius was determined from diffusion of pyridine across the membrane (see Figure 3). The slope of each line in Figure 3 is proportional to R^2. By comparison of the slopes, the average pore radii after gold deposition and formation of SAMs were obtained. Figure 3 shows that gold deposition (at ~1 °C for 0.5 h) reduces the pore radius by 2 nm and formation of SAMs from $HS(CH_2)_{11}$-OH onto gold further reduces the pore radius by 1.5 nm. The latter value reflects the thickness of the thiol monolayer and is in agreement with the thickness of the monolayer of $HS(CH_2)_{11}CH_3$ on gold determined by ellipsometry[17] or surface plasmon resonance spectroscopy.[18]

We then proceeded with thiol monolayers formed on the gold-coated pore walls containing pH-dependent ionizable surface groups. The membrane should have pH-responsive properties of ionic transport, which are useful in delivery and separation applications.[7-9] For this purpose, we investigated ionic diffusion across gold-coated PCTE membranes with SAMs of $HS(CH_2)_{10}COOH$ formed onto gold. Benzenesulfonate (BS)[19] was used as the permeant, and the pH of the solutions in both the reservoir and the sink was variable. Before each diffusion experiment started, the reservoir contained an aqueous solution of 1 mM sodium benzenesulfonate (SBS), x mM HCl (or NaOH), and $(1 - x)$ mM NaCl while the sink contained an aqueous solution of 0 mM SBS, x mM HCl (or NaOH), and $(2 - x)$ mM NaCl, where x was varied between 0 and

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[16] The Debye lengths (λ_D) reported in Figure 2 were evaluated on the basis of the initial concentration of permeant in the reservoir ($C_{R,0}$), or simply: $\lambda_D = (\epsilon RT/2F^2z^2C_{R,0})^{1/2}$ (eq 3), where ϵ is the dielectric constant of the solution, R is the thermodynamic gas constant, T is temperature, F is the Faraday constant, and z is ionic valence.

[17] Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321−35.

[18] Lingler, S.; Rubinstein, I.; Knoll, W.; Offenhausser, A. *Langmuir* **1997**, *13*, 7085−91.

[19] We did not use permanganate as the permeant when using membranes with thiol monolayers because our contact angle measurements showed that permanganate could damage the monolayers.

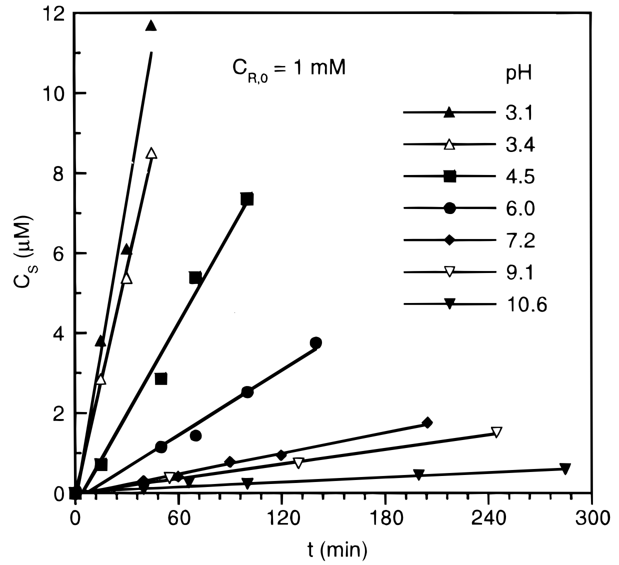

Figure 4. Diffusion of benzenesulfonate (BS) anions across a PCTE/Au/HS$(CH_2)_{10}$COOH membrane: effect of external pH. See text for details. (R = 8 nm, λ_D = 7 nm.)

1. The HCl and NaOH solutions were used to adjust the pH of the solutions to be equal in both compartments. The actual pH values were measured with a Fisher Accumet pH meter (Model 815MP). NaCl was used as a balance species to maintain the ionic strengths of the solutions in both compartments the same and constant (2 mM) at pH values between 3 and 11. The above design minimizes the effect of any change of ionic strength due to adjustment of pH on electrical double layer forces and eliminates reverse osmosis. In addition, the pK_a value (0.7)[20] of the BS anion ensures that the diffusing species is completely dissociated within the investigated range of pH.[21] Therefore, the change of the flux of BS with variation of pH can be attributed to the change of surface properties of the membrane. For each membrane, the diffusion experiment was performed with the pH varied between higher and lower values alternatively and repeatable results were obtained. For each pH value, the membrane had been conditioned in a solution that was the same as the solution in the sink for at least 0.5 h before the diffusion experiment started.

Figure 4 shows the changes of concentrations of BS in the sink (C_S) with diffusion time (t) measured at different external pH values with a PCTE/Au/HS$(CH_2)_{10}$COOH membrane. The hydraulic pore radius of this membrane was 8 nm (the initial pore radius of the template PCTE membrane was 28 nm). The initial concentration of BS in the reservoir ($C_{R,0}$) in all cases was 1 mM. The flux of BS passing through the membrane was determined from the slope of the C_S-t plot[15] shown in Figure 4 and plotted in Figure 5a as a function of the external pH. It is seen that the flux of BS dramatically drops as the external pH increases. The flux of BS varies by a factor of 110 between pH 3.1 and 10.6. This variation factor of flux is about 10 times higher than that obtained with a pH-responsive poly(acrylic acid)−poly(ethylenimine) complex membrane.[7]

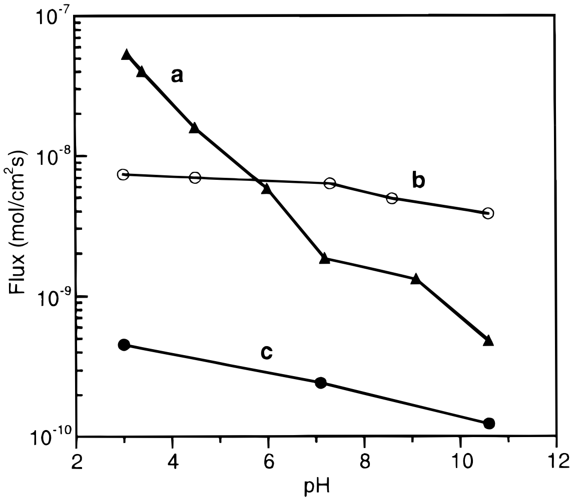

Figure 5. Flux of benzenesulfonate anion as a function of external pH obtained with (a) PCTE/Au/HS$(CH_2)_{10}$COOH; (b) bare PCTE; and (c) PCTE/Au membranes.

The pH-dependent flux of the BS anion across the PCTE/Au/HS$(CH_2)_{10}$COOH membrane can be interpreted by pH-dependent ionization of the surface carboxylic groups in the SAMs and electrostatic interactions between the negative charge on the pore walls and the BS anion in the solution. The Debye length associated with the ionic strength (2 mM in both reservoir and sink) is 7 nm, comparable to the hydraulic pore radius (8 nm). The electrostatic interactions have the dominant effect on the fluxes of the BS anion at high pH values when the carboxylic groups of the thiol are ionized. The design of the diffusion experiments ensures that the effects of changes in double layer forces due to adjustment of pH and reverse osmosis are negligible. The apparent pK_a values of the surface carboxylic acid groups in the SAMs formed from thiols on flat gold surfaces have been reported to be 6−8, dependent on the chain length of the thiols and method of measurement.[22−27] We cannot identify an apparent pK_a based on our results shown in Figure 5a. Note that the apparent diffusivity of BS at pH 3.1 estimated from the corresponding flux shown in Figure 5a is 3.2×10^{-5} cm^2/s.[28,29] This value is larger than the diffusivity of BS measured in bulk solutions (1.0×10^{-5} cm^2/s).[30] This result suggests that the flux of BS at low pH (when most of the surface carboxylic acid groups are not ionized) may be dominated by surface diffusion. Surface diffusion is a surface transport process driven by the gradient of the surface concentration of a species adsorbed on the surface.[31] Surface diffusion likely enhances the

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[20] CRC Handbook of Chemistry and Physics, 73rd ed.; CRC Press: Boca Raton, FL, 1992.

[21] Our measurements of conductivity of the diffusion solutions verify that the dissociation degree of the BS anion is >95% at all investigated pH values in this paper.

[22] Whitesides, G. M.; Biebuyck, H. A.; Folkers, J. P.; Prime, K. L. *J. Adhes. Sci. Technol.* **1991**, *5*, 57−69.

[23] Wang J.; Frostman, L. M.; Ward, M. D. *J. Phys. Chem.* **1992**, *96*, 5224−8.

[24] Lee, T. R.; Carey, R. L.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741−9.

[25] Creager, S. E.; Clarke, J. *Langmuir* **1994**, *10*, 3675−83.

[26] Hu, K.; Bard, A. J. *Langmuir* **1997**, *13*, 5114−9.

[27] Kane, V.; Mulvaney, P. *Langmuir* **1998**, *14*, 3303−11.

[28] Using the Goodman-type integration of the Nernst−Planck flux equation,[29] the diffusion potentials across the membranes under our experimental conditions are estimated to be between −1.2 and −2.5 mV as the external pH varies between 3.1 and 10.6. The drift flux due to diffusion potential with values shown above was only 5−10% of the diffusion flux due to concentration gradient. The drift flux is thus ignored and the total flux J is approximated by $J = DC_R/L$ (eq 4), where D is apparent diffusivity, C_R is approximately constant (1 mM) with changes <2% during diffusion, and C_S is ignored because C_S is small compared to C_R. Equation 4 is used to estimate the apparent diffusivity of BS from the flux of BS determined by eq 2.[15]

[29] Lakshminarayanaiah, N. *Transport Phenomena in Membranes*; Academic Press: New York, 1969; pp 93−99.

[30] Paduano, L.; Sartorio, R.; Vitagliano, V. *J. Phys. Chem. B* **1998**, *102*, 5023−8.

flux of BS at low pH and consequently complicates the identification of pK_a. We are currently investigating the mechanism of surface diffusion of BS in the PCTE/Au/thiol membranes.

The variation factor of the flux of BS across the template PCTE membrane ($R = 28$ nm) shown in Figure 5b is <2, much smaller than that across the PCTE/Au/HS$(CH_2)_{10}$-COOH membrane. This result confirms that the pores in the latter membrane were derivatized by the carboxylic acid group within the SAMs. Past studies suggested that there might be surface charges on the pore walls of PCTE membranes.[32,33] The ζ potential of a PCTE membrane with the same pore size as in Figure 5b was reported to vary from -3 to -6 mV as the external pH changed from 4 to 5 and to become constant at -6 mV when the pH was ≥ 5.[33] The cause of the surface charges on PCTE membranes, however, has not been clarified. Possible causes proposed in past studies include adsorption of Cl^- or OH^- ions on the membrane surface and dissociation of surface acid groups formed during the track-etch process used to fabricate the pores.[32,33]

Figure 5c shows that the fluxes of BS across a gold-coated PCTE membrane ($R = 10$ nm) without thiol monolayers are at least 15 times smaller than those obtained using the bare PCTE membrane at all investigated pH values. This result is attributed to the chemisorption of Cl^- (present in diffusion solutions) to gold that forms negative surface charges on the pore walls. Recent studies have revealed that BS anions can also be adsorbed to gold.[34] The variation of the flux of BS shown in Figure 5c is likely caused by pH-dependent dissociation of the adsorbed Cl^- and/or BS anions. Further investigations on this result may need to be carried out but the fluxes at all pH values are too small for practical interests.

The procedure described in this work for modification of filtration membranes may be used to prepare porous ion-selective membranes. In conventional ion-selective membranes prepared by polymer chemistry, ion transport operates in the gel phase formed by sorption of water due to the hydrophilic functional groups on the polymer backbone.[35] The pore size of these membranes is a function of water content and is thus poorly controlled, leading to reduced permselectivity. Porous ion-selective membranes have been prepared by etching of polymer ion-exchange membranes,[36] chemical modification of preformed ultrafiltration membranes,[37] and removal of inorganic fillers from a polymer blend.[38] The procedure described in this work, we believe, has several advantages over those techniques. First, self-assembly offers flexibility in tailoring the membrane properties. A variety of functional groups or mixed functional groups[22−27,39−41] can be introduced into the membrane in a relatively convenient way. Second, the template membranes have well-defined structures and uniform pore sizes. The pore size can be adjusted by electroless-deposited gold and the chains of adsorbed thiols. Third, degenerated functional groups can be removed from the membrane by desorption of the old SAMs from the gold surface.[42,43] New functional groups can be introduced into the membrane by reformation of new SAMs. The porosity of the PCTE membranes used in this work is low. It would be more useful to use template membranes with higher porosities (such as the Anopore alumina membranes) for practical applications.

Conclusion

We demonstrate the modification of the surface properties of pore walls in polycarbonate track-etched (PCTE) membranes by formation of self-assembled monolayers (SAMs) from ω-substituted thiols onto electroless gold deposited on the pore walls of the membrane. SAMs formed from a carboxylic acid-functionalized thiol impart to the membrane high pH-dependence of ionic fluxes across the membrane. The surface-modification procedure described in this work may provide an alternative route to prepare porous ion-selective membranes.

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(31) Kapoor, A.; Yang, R. T.; Wong, C. *Catal. Rev. Sci. Eng.* **1989**, *31*, 129−214.

(32) Keesom, W. H.; Zelenka, R. L.; Radke, C. J. *J. Colloid Interface Sci.* **1988**, *125*, 575−85.

(33) Kim, K. J.; Fane, A. G.; Nystrom, M.; Pihlajamaki, A. *J. Membr. Sci.* **1997**, *134*, 199−208.

(34) Dutkiewicz, E.; Skoluda, P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3763−7.

(35) Leddy, J. J. In *Synthetic Membranes*; Chenoweth, M. B., Ed.; MMI Press Symposium Series 5; Harwood Academic Publishers: London, 1986; pp 119−28.

(36) Mizutani, Y.; Kusumoto, K.; Nishimura, M.; Nishimura, T.; Asada, E. *J. Appl. Polym. Sci.* **1990**, *39*, 1087−100.

(37) Breitbach, L.; Hinke, E.; Staude, E. *Angew. Makromol. Chem.* **1991**, *184*, 183−96.

(38) Bryjak, M.; Pozniak, B.; Trochimczuk, W. *Angew. Makromol. Chem.* **1992**, *200*, 93−108.

(39) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87−96.

(40) Stroeve, P.; Nagtegaal, M.; Tremel, W.; Knoll, W. *Polym. Preprints* **1997**, *38* (1), 965−6.

(41) Jong, L. I.; Abbott, N. L. *Langmuir* **1998**, *14*, 2235−7.

(42) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335−59.

(43) Calvente, J. J.; Kovacova, Z.; Sanchez, M. D.; Andreu, R.; Fawcett, W. R. *Langmuir* **1996**, *12*, 5696−703.