

Aldehyde-Terminated Self-Assembled Monolayers on Gold: Immobilization of Amines onto Gold Surfaces

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Self-assembled monolayers (SAMs) of thiols on gold have been studied extensively.¹ Much of the interest in these materials arises from their many potential applications, perhaps most intriguing in biological sensors.² Future developments in this area would be greatly facilitated by a simple and rapid means of anchoring different sensor molecules onto existing monolayers. We present here a novel aldehyde-terminated SAM that can covalently bind amine-containing molecules from solution without using other reagents. The aldehyde-terminated monolayers may be used to anchor diverse molecules, including enzymes and antibodies, to electrode surfaces. The formation of the aldehyde-terminated monolayer and its derivatization have been monitored by grazing angle Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and contact angle measurements.

The aldehyde-terminated monolayer was formed by exploiting the equilibrium between 2-hydroxypentamethylene sulfide (HPMS) and its open chain aldehyde isomer in solution (Figure 1). Adsorption of the ring-opened, aldehyde-terminated thiol on gold generates an aldehyde-terminated monolayer.³ The proton NMR spectra of HPMS in CD₃OD showed an equilibrium mixture of open and closed forms of the compound, as well as dimeric or oligomeric materials. Since the formation of hemithioacetal-linked oligomers is highly reversible, we were confident adsorption of HPMS from ethanol followed by rinsing with ethanol would not lead to the formation of hemithioacetal-linked multilayers.

HPMS was easily synthesized in two steps. Commercially available pentamethylene sulfide⁴ was oxidized to the corresponding sulfoxide using sodium periodate.⁵ Pummerer rearrangement of the sulfoxide with trifluoroacetic anhydride, followed by hydrolysis, gave HPMS.⁶ Monolayers were formed

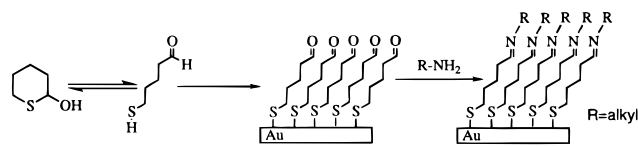


Figure 1. Formation of the aldehyde-terminated SAM on Au.

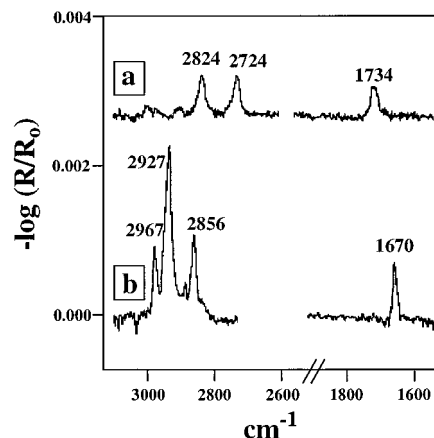


Figure 2. Grazing angle FTIR spectra of (a) an aldehyde-terminated monolayer and (b) an aldehyde-terminated monolayer derivatized with C₁₂NH₂.

by exposing clean gold surfaces⁷ to a 0.01 M ethanolic solution of HPMS under argon for 3–12 h. After adsorption, the surfaces were rinsed thoroughly with ethanol and dried under a stream of dry argon.

Grazing angle (FTIR) spectroscopy^{8,9} confirmed the formation of the aldehyde-terminated monolayer. The FTIR spectrum is shown in Figure 2a. The two strong bands at 2724 and 2824 cm⁻¹ arise from the Fermi resonance between the aldehyde C–H stretching vibration and the first overtone of the C–H rocking vibration.¹⁰ The band observed at 1734 cm⁻¹ is assigned to the C=O stretching mode.¹¹ These three peaks clearly indicate the presence of the aldehyde group on the surface. The FTIR spectra of layers formed by exposure of gold surfaces to solutions of HPMS in ethanol for varying lengths of time (3–12 h) are identical, suggesting that the monolayer is fully formed after 3 h.

These aldehyde-terminated SAMs on Au react rapidly with alkylamines from solution. The chemical reaction between the aldehyde-terminated SAMs and alkylamines was also monitored using FTIR spectroscopy. Shown in Figure 2b are the C–H and C=X stretching spectral regions of an aldehyde-terminated monolayer that has been exposed to a 0.1 M solution of

(6) Konno, K.; Hashimoto, K.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1986**, 27, 3865.

(7) Gold surfaces were prepared by evaporating 200 Å of Cr and then 2000 Å of Au at 4 × 10⁻⁶ Torr onto a polished silicon wafer that had been cleaned with piranha etch solution (3:1 concentrated H₂SO₄/30% H₂O₂). CAUTION: This solution reacts violently with organic compounds and should be used with extreme caution.

(8) FTIR spectra were obtained using an ATI-Matteson Research Series FTIR equipped with a narrow band, liquid nitrogen cooled mercury cadmium telluride (MCT) detector and a Harrick grazing angle accessory. The angle of incidence of the p-polarized light is 74°; 1000 scans at 4 cm⁻¹ resolution were collected.

(9) Certain commercial products and instruments are identified to adequately specify the experimental procedure. In no case does such identification imply endorsement by the National Institute of Standards and Technology.

(10) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G., Eds. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: New York, 1991; p 122.

(11) A general procedure for the derivatization of aldehyde-terminated SAMs by alkylamines is as follows: the aldehyde SAM was placed in a 0.1 M ethanolic solution of the alkylamine under Ar for at least 3 h. After exposure, the layer was rinsed thoroughly with ethanol and dried under a stream of Ar.

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(1) (a) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly*; Academic Press: New York, 1991. (b) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, 5, 1147. (c) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, 8, 1330. (d) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* **1991**, 113, 1499. (e) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, 109, 733. (f) Zhang, L.; Lu, T.; Gokel, G. W.; Kaifer, A. E. *Langmuir* **1993**, 9, 786. (g) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, 6, 87.

(2) See inter alia: (a) Motesharey, K.; Myles, D. C. *J. Am. Chem. Soc.* **1994**, 116, 7413. (b) Leggett, G. J.; Roberts, C. J.; Williams, P. M.; Davies, M. C.; Jackson, D. E.; Terndler, S. J. *B. Langmuir* **1993**, 9, 2356. (c) Mrksich, M.; Whitesides, G. M. *Tibtech* **1995**, 13, 228. (d) Singvi, R.; Kumar, A.; Lopez, G. P.; Bhatia, S. K.; Hickman, J. J.; Ligler, F. S. *J. Am. Chem. Soc.* **1992**, 114, 4432. (e) Ebara, Y.; Okahata, Y. *Langmuir* **1993**, 9, 574. (f) Miyasaka, T.; Koichi, K.; Watanabe, T. *Chem. Lett.* **1990**, 627. (g) Willner, I.; Riklin, A.; Shoham, B.; Rivenzon, D.; Katz, E. *Adv. Mater.* **1993**, 5, 912. (h) Willner, I.; Riklin, A. *Anal. Chem.* **1994**, 66, 1535. (i) Collinson, M.; Bowden, E. F. *Langmuir* **1992**, 8, 1247. (j) Prime, K. I.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, 115, 10714.

(3) Prof. Marc Porter (Ames, Iowa) has reported a similar aldehyde-terminated monolayer. Personal communication and Electrochemical Society Meeting, Chicago, IL, October, 1995.

(4) Pentamethylene sulfide is available from Aldrich Chemical Co., 1001 W. Saint Paul Ave., Milwaukee, WI 53233.

(5) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, 27, 282

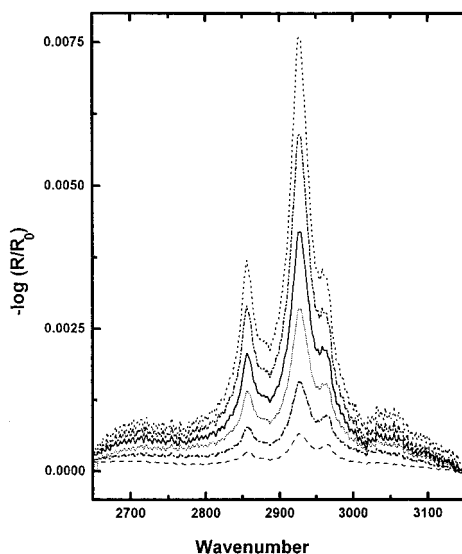


Figure 3. Grazing angle FTIR spectra of the aldehyde terminated monolayer exposed to (---) $C_{10}NH_2$; (- - -) $C_{11}NH_2$; (···) $C_{12}NH_2$; (—) $C_{13}NH_2$; (- - -) $C_{15}NH_2$; and (- - -) $C_{16}NH_2$. The spectra are stacked in the plot for clarity.

dodecylamine in ethanol.¹¹ The aldehyde Fermi doublet at 2724 and 2824 cm^{-1} and the C=O stretch at 1734 cm^{-1} have been replaced by strong C-H stretching absorbances at 2856, 2927, and 2967 cm^{-1} assigned to the symmetric CH_2 stretch, the asymmetric CH_2 stretch, and the asymmetric CH_3 stretch, respectively. A strong C=N stretching band is observed at 1670 cm^{-1} , indicating that the condensation has gone to completion.¹² Examination of the IR spectra of derivatized monolayers shows little or no absorbance in the range of 3200 cm^{-1} where the amino group of unreacted alkylamine would be expected; thus there appears to be no residual amine associated with the derivatized monolayer.

The aldehyde-terminated SAM was exposed to a series of ethanolic solutions of alkylamines of varying chain length ($C_nH_{2n+2}NH_2$, abbreviated C_nNH_2). The FTIR spectra (Figure 3) of these samples show, qualitatively, an increase in the intensity of the C-H stretching modes with increasing n , as expected. Similar chain length dependent behavior was observed in wetting experiments.¹³ As longer chain alkylamines are chemically bound to the surface, the contact angles of the derivatized layers asymptotically approach those of a pure alkanethiol monolayers (Figure 4). This is consistent with a monolayer structure that has the polar imine functionality buried within the monolayer, where it cannot affect the wetting properties of the layer. Although the amine-derivatized aldehyde SAMs are likely not as well ordered as the corresponding alkanethiolate monolayers, the difference between advancing and receding contact angles (hysteresis) decreases as n increases, suggesting increasing order¹⁴ in the monolayer with increasing n .¹⁵

Further evidence that amines react with the aldehyde SAM is found in the XPS¹⁵ data. Examination of XPS data for the derivatized aldehyde SAMs shows the appearance of a signal corresponding to the N 1s photoelectron, indicating the presence

(12) It is clear that the reaction of amines and aldehydes is nearly complete. The number of unreacted aldehyde groups falls below the detection limit of the grazing angle FTIR experiment. The detection limit of this experiment for measuring the aldehyde group bands is less than 5% of the pure aldehyde-terminated monolayer. The C=N absorbance shows a time dependent reduction in intensity. After the derivatized monolayers are exposed to air at ambient temperature and humidity (ca. 20–40%) for 72 h, the intensity of the C=N stretching absorbance is reduced to less than 20% of its original value. We are currently investigating this process in greater detail.

(13) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155.

(14) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

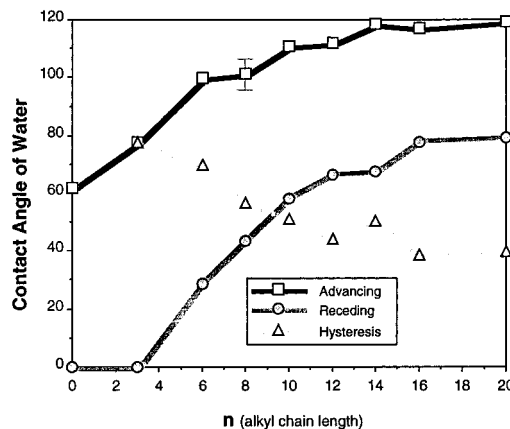


Figure 4. Advancing and receding contact angles for aldehyde-terminated monolayer derivatized with alkylamines [$(CH_3(CH_2)_{n-1}NH_2)$].

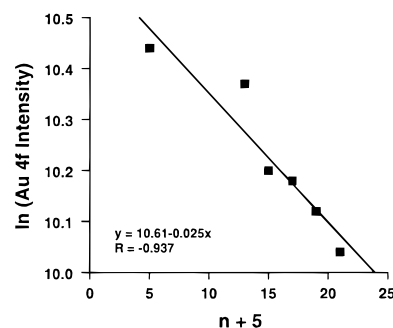


Figure 5. Change in $\ln(Au\ 4f\ intensity)$ vs number of carbon atoms in the monolayer ($n + 5$). The intensity of the Au 4f signal (80–92 eV) at a take-off angle of 90° was determined by measuring the integrated area of the XPS signal.

of nitrogen in the layer.¹⁶ As expected, as the alkylamine chain length increases, the Au 4f signal decreases, due to attenuation by the SAM overlayer (Figure 5). Bain and Whitesides showed that the intensity of the Au 4f signal is inversely proportional to n , the number of carbons in the alkane chain and derived the expression: $\ln(Au_n) = -nd/\lambda(\sin \theta) + \text{constant}$ (where $Au_n = Au\ 4f\ intensity$ for a self-assembled monolayer with n carbons, $d = \text{thickness of a single } CH_2 \text{ [calculated to be } 1.1 \text{ \AA}]$, $\lambda = \text{escape depth of the Au 4f photoelectron}$, and $\theta = \text{takeoff angle}$).¹⁷ Bain and Whitesides report an escape depth of $42 \pm 1 \text{ \AA}$ for alkanethiolate SAMs. Using the expression of Bain and Whitesides and assuming $d = 1.1 \text{ \AA}$, the escape depth λ for the amine-derivatized aldehyde SAMs is $44 \pm 2 \text{ \AA}$. The similarity of the escape depths for the two systems suggests that the coverage of the monolayers is also similar.

The aldehyde-terminated SAM may prove useful for attaching enzymes and other receptor systems onto gold surfaces for sensor applications. The covalent attachment is both rapid and complete. Further work is being carried out to develop applications of this system.

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Supporting Information Available: XPS and FTIR spectra of HPMS and HPMS + dodecylamine (2 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The XPS spectra were obtained using the experimental apparatus described in Tarlov, M. J. *Langmuir* **1992**, *8*, 80. X-rays were generated by an Al anode operated at 240 W. The hemispherical analyzer was operated in the retarding mode at a band-pass energy of 20 eV, with the emitted photons collected at 90° with respect to the surface normal.

(16) See the Supporting Information for a comparison of N 1s region of the XPS for HPMS and HPMS + dodecylamine SAMs.

(17) Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 1670.