Polarization Modulation Fourier Transform Infrared Studies of the Effects of Self-Assembly Time on the Order and Orientation of 11-Ferrocenyl-1-undecanethiol Monolayers on Gold

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The effects of self-assembly time on the order and orientation of 11-ferrocenyl-1-undecanethiol ($FcC_{11}SH$) molecular layers on gold were studied with polarization modulation Fourier transform infrared spectroscopy. A comparison between the intensity of the asymmetric methylene stretching mode of a 1-octadecanethiol monolayer and that of the $FcC_{11}SH$ molecular layer confirmed that the $FcC_{11}SH$ molecules formed a self-assembled monolayer on the gold surface. The conformational order of the monolayer increased with longer self-assembly time as evidenced by a decrease in the vibrational frequencies of the methylene stretching modes and a decrease in the full width at half maximum of these bands. The peak area of the asymmetric methylene stretch also decreased with longer self-assembly time, implying that the $FcC_{11}SH$ molecules stood more erect with respect to the gold surface as the monolayer self-assembled.

The chemical modification of metal and semiconductor surfaces by the adsorption of molecular layers with special functionality has been the subject of extensive study.[1] For example, the Langmuir–Blodgett (LB) method has been used frequently to form mono- and multi-molecular layers on solid surfaces.[2—6] Unfortunately, monolayers formed by the LB method only physically adsorb on the solid surface and, therefore, have some stability problems. Recently, molecular layers with better stability have been formed using a self-assembly method, in which the solid substrate is dipped into a solution containing adsorbing molecules that usually have a long hydrocarbon chain.[7—13] The molecules chemisorb onto the solid surface by forming covalent bonds with surface atoms, and then self-assemble through chain–chain interactions. The chemical bonding to the surface leads to more stable molecular layers than those formed by the LB method. Self-assembled monolayers of *n*-alkanethiol derivatives have been studied by a variety of techniques.[11,14] In particular, the effects of chain length and terminal groups on the structure and properties of the monolayers have been investigated thoroughly.[15—17]

One application of self-assembled monolayers has been for the study of electron transfer through molecular layers. We and many other groups have reported the electrochemical characteristics of ferrocenylalkanethiol molecular layers on gold.[18—25] It was found that the position and shape of the redox waves are strongly affected by the mutual interactions between the ferrocene groups and the interaction between the ferrocene groups and anions in solution. To understand the effects of these interactions, additional structural information on the molecular layer is essential, and this structure is a function of self-assembly time.

In previous studies, we have examined the electrochemical properties of the self-assembled monolayers of 11-ferrocenyl-1-undecanethiol ($FcC_{11}SH$) and 6-ferrocenyl-1-hexanethiol (FcC_6SH) prepared with various adsorption times and have also monitored the self-assembly process by an in-situ quartz crystal microbalance technique.[26] These studies revealed that although more than 80% of the total adsorbate adsorbs within 30 s and the adsorption process is almost complete within 1000 s, it takes a much longer time for the molecular layer to reach its final structure and orientation. Thus, additional structural information on the monolayer is needed to understand the self-assembly process. Fourier transform infrared (FTIR) spectroscopy is a technique that has successfully provided structural information on a wide variety of molecular monolayers adsorbed to solid surfaces.[17,27] For ferrocene containing surfaces, Popenoe and Porter recently studied the structure of a monolayer of 11-mercaptoundecyl ferrocenecarboxylate ($FcCOOC_{11}SH$) by FTIR measurement in air.[28] They also investigated the potential dependent structural change of the monolayer on gold by in-situ FTIR measurement. Duevel and Corn monitored the surface reaction of (hydroxymethyl)ferrocene ($FcCH_2OH$) with an adsorbed monolayer of 11-mercaptoundecanoic acid ($HSC_{11}COOH$) using polarization modulation FTIR (PM-FTIR) measurements.[29] In these studies, the structures of the monolayers were identified only for the steady state.

In this paper we investigate the self-assembly time dependence of the order and orientation of ferrocenylalkanethiol monolayers on gold using PM-FTIR spectroscopy. The structure of these monolayers and the effects of self-assembly time on the structure were analyzed by comparison of the PM-FTIR spectra to those of 1-octadecanethiol ($C_{18}SH$) monolayers on gold.

Experimental

11-Ferrocenyl-1-undecanethiol ($FcC_{11}SH$) was synthesized by the method reported previously.[18] 1-Octadecane-

thiol ($C_{18}SH$), hexane, and ethanol were purchased and used without further purification. Gold substrates were prepared by vacuum deposition of 120 nm of Au onto a slide glass treated with (3-mercaptopropyl)trimethoxysilane.[30]

The thiol monolayers were self-assembled from 1 mM solutions of $FcC_{11}SH$ or $C_{18}SH$ in hexane (1 M=1 mol dm^{-3}). Immersion times varied as described in the results. After immersion, the samples were rinsed thoroughly with pure hexane.

For the electrochemistry, a single-compartment Teflon cell with a standard three-electrode arrangement (Pt counter electrode, sodium chloride saturated calomel reference electrode (SSCE)) was used in conjunction with an IBM EC 225 potentiostat interfaced to an IBM-XT computer. All electrochemical measurements were carried out at room temperature after the solution was deaerated by purging with N_2 gas for at least 20 min. Reagent grade chemicals and water obtained from a Millipore purification system were used to prepare electrolyte solutions.

Infrared differential reflectance spectra were obtained with a Mattson RS-1 spectrometer which had been modified to perform the PM-FTIR spectroscopic experiments. Spectra were obtained at a resolution of 2 cm^{-1}, and at an angle of incidence of 76° from the surface normal. The details of PM-FTIR experiments have been described previously.[31—33]

Results and Discussion

Figure 1 shows the cyclic voltammogram (CV) of a gold electrode modified with $FcC_{11}SH$ by immersing the gold substrate into a 1 mM $FcC_{11}SH$ hexane solution for 10 min. The oxidation–reduction of the surface attached ferrocene/ferricinium ion is confirmed by the symmetrical reversible redox wave with an additional spike, as observed previously.[18] The integrated charge density of the anodic peak is 45.5 $\mu C\,cm^{-2}$, which is equivalent to surface coverage of 2.83×10^{14} molecules cm^{-2}. This is similar to those reported in our previous papers and by other groups,[18,20,24] and suggests that a monolayer of $FcC_{11}SH$ is adsorbed onto the gold surface.

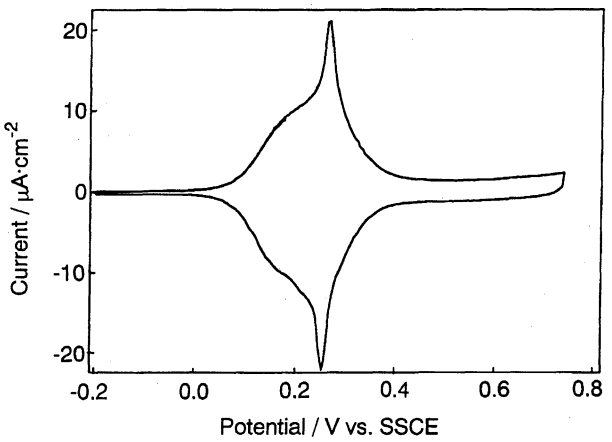

Fig. 1. Cyclic voltammogram of a vapor-deposited gold electrode modified with $FcC_{11}SH$ by immersion into a 1 mM $FcC_{11}SH$/hexane solution for 10 min. The electrolyte solution was 1 M $HClO_4$ and the sweep rate was 50 mV s^{-1}.

Figure 2 shows the PM-FTIR absorption spectrum of the CH stretching region of the $FcC_{11}SH$ molecular layer on gold obtained before the electrochemical measurement shown in Fig. 1. Three vibrational bands are observed at 3100, 2923, and 2851 cm^{-1} and are assigned as the CH stretching mode of the ferrocene ring ($\nu(CH)_{Fc}$), the asymmetric methylene stretching mode ($\nu_{as}(CH_2)$), and the symmetric methylene stretching mode ($\nu_s(CH_2)$), respectively. The positions of these bands are essentially the same as those reported by Popenoe et al., for a 11-mercaptoundecyl ferrocenecarboxylate ($FcCOOC_{11}SH$) monolayer.[28] They observed $\nu(CH)_{Fc}$ at 3105 cm^{-1}, $\nu_{as}(CH_2)$ at 2923 cm^{-1}, and $\nu_s(CH_2)$ at 2853 cm^{-1}. The bulk liquid FTIR spectrum of $FcC_{11}SH$ dispersed in fluorolube gave three bands in the CH stretching region at 3097, 2930, and 2856 cm^{-1}.

$C_{18}SH$ monolayers on gold are known to be well-ordered, and the PM-FTIR spectrum in the CH stretching region is shown in Fig. 3. This spectrum differs slightly from those reported previously[34] due to differences in the incident angle of the FTIR measurements. The $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ bands appear at 2919 and 2851 cm^{-1}, respectively. Also, three stretching bands of the CH_3 group are observed: 2964 cm^{-1} (asymm.), 2938 cm^{-1} (shoulder; symm. Fermi resonance), and 2879 cm^{-1} (symm. Fermi resonance). These positions agree with those reported by other research groups.[12] By comparing the spectra of $FcC_{11}SH$ and $C_{18}SH$ molecular layers, one can detect differences in peak intensity, peak position, and the full width at half maximum (FWHM).

The peak intensity of the CH_2 bands depends upon the surface concentration, orientation, and conformation of the adsorbed molecules. The absorbance observed for the CH_2 asymmetric stretching modes is 9.5×10^{-4} for $FcC_{11}SH$ and 2.0×10^{-3} for $C_{18}SH$. The

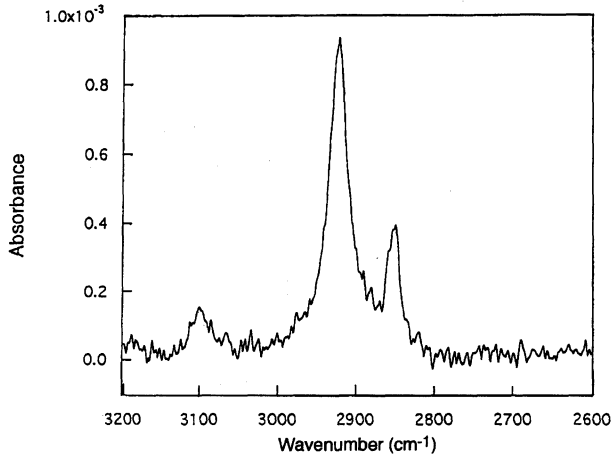

Fig. 2. The CH stretching region of the PM-FTIR absorption spectrum for a $FcC_{11}SH$ monolayer self-assembled onto a gold electrode for 10 min.

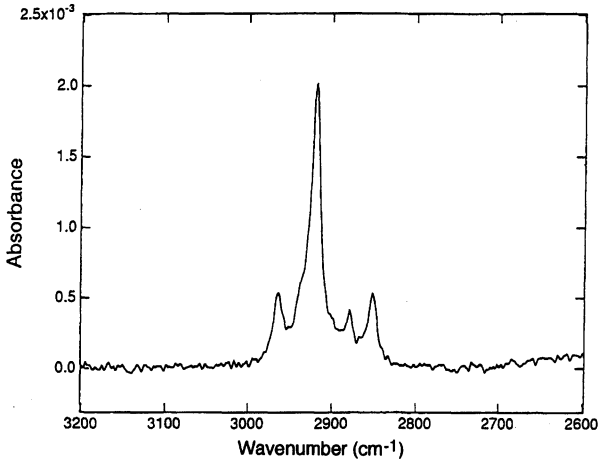

Fig. 3. The CH stretching region of the PM-FTIR spectrum of a $C_{18}SH$ monolayer self-assembled onto a gold substrate.

intensity of $\nu_{as}(CH_2)$ for the $FcC_{11}SH$ molecular layer is about half that of the $C_{18}SH$ monolayer, which is reasonable if one considers that the number of CH_2 groups in $FcC_{11}SH$ is only 65% of that of $C_{18}SH$. Since it is known that $C_{18}SH$ forms a compact self-assembled monolayer, we conclude that $FcC_{11}SH$ is also adsorbed to the gold surface with approximately a monolayer surface coverage. Popenoe et al. reported an absorbance of 1.5×10^{-3} for $\nu_{as}(CH_2)$ of a $FcCOOC_{11}SH$ monolayer.[28] Their value differs by 50% from ours, even though the number of CH_2 groups is the same. This discrepancy may be explained by considering the effects of orientation on the absorbance as discussed later.

The peak positions of the methylene stretching bands differ for the $C_{18}SH$ and $FcC_{11}SH$ monolayers: for example, $\nu_{as}(CH_2)$ of the $FcC_{11}SH$ monolayer is at 2923 cm^{-1}, but at 2919 cm^{-1} for the $C_{18}SH$ monolayer. Furthermore, a large difference was observed between the peak position of $\nu_{as}(CH_2)$ of the $FcC_{11}SH$ monolayer (2923 cm^{-1}) and that of liquid $FcC_{11}SH$ (2930 cm^{-1}). Similar tendencies are observed for the $\nu_s(CH_2)$ band. It is well known that the positions of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ are strongly affected by molecular conformation, and vary significantly from the solid to liquid state.[12] The methylene stretching bands are observed at lower peak frequencies for samples in the solid state where the molecules are in the all trans conformation, than those in the liquid state. For example, 1-docosanethiol ($C_{22}SH$) has bands at 2918 cm^{-1} ($\nu_{as}(CH_2)$) and 2851 cm^{-1} ($\nu_s(CH_2)$) in the solid state but at 2924 cm^{-1} ($\nu_{as}(CH_2)$) and 2855 cm^{-1} ($\nu_s(CH_2)$) in the liquid state. The frequencies of 2919 cm^{-1} ($\nu_{as}(CH_2)$) and 2851 cm^{-1} ($\nu_s(CH_2)$) for the $C_{18}SH$ monolayer suggest that it is well-ordered and close to crystalline. The peak positions of the $FcC_{11}SH$ monolayer appear at higher frequencies (2923 $cm^{-1}:\nu_{as}(CH_2)$, 2851 $cm^{-1}:\nu_s(CH_2)$) than those of the $C_{18}SH$ monolayer, but at lower frequencies than those of the liquid $FcC_{11}SH$ (2930 $cm^{-1}:\nu_{as}(CH_2)$, 2856 $cm^{-1}:\nu_s(CH_2)$). These results suggest that the order of the $FcC_{11}SH$ monolayer lies between the solid and liquid state, but that it is not as ordered as the $C_{18}SH$ monolayers. The monolayer is also not as ordered as a simple alkanethiol monolayer of similar chain length: a monolayer of 1-decanethiol ($C_{10}SH$) on gold has been reported by Chidsey and Loiacono to have nearly crystalline packing with methylene stretches at 2920.5 and 2850.5 cm^{-1}.[35]

The FWHM of the $\nu_{as}(CH_2)$ band for the $FcC_{11}SH$ monolayer (30 cm^{-1}) is about twice that of the $C_{18}SH$ monolayer (15 cm^{-1}). Band broadening results from greater inhomogeneity in the distribution of the vibrational frequencies being measured—commonly due to a lack of order in the adsorbate overlayer.[36] Thus, the difference between the FWHM's also implies that the $FcC_{11}SH$ monolayer is not as ordered as the $C_{18}SH$ monolayer. The decrease in order may be due to the existence of the large ferrocene head group and/or the shorter adsorption time in the case of the $FcC_{11}SH$ system. The effects of adsorption time were examined by obtaining PM-FTIR spectra for $FcC_{11}SH$ monolayer that were allowed to self-assemble in a hexane solution for 1 min, 10 min, and 15 h.

Figure 4 shows the relationship between the peak positions of the CH stretching modes of the $FcC_{11}SH$ monolayer and self-assembly time. The $\nu_{as}(CH_2)$ band of the $FcC_{11}SH$ monolayer on the gold substrate appeared at lower frequencies as adsorption time increased (2925 cm^{-1} for 1 min, 2923 cm^{-1} for 10 min, and 2920 $cm^{-1}$for 15 h adsorption). Also note that the monolayer

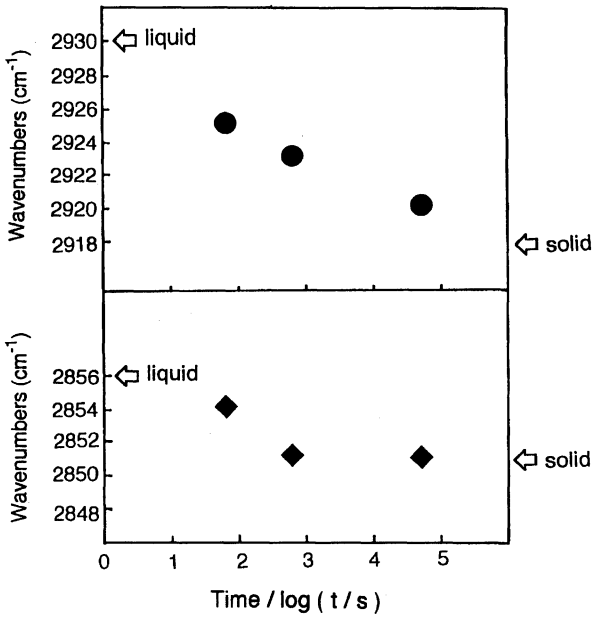

Fig. 4. The relationship between the peak positions of the methylene stretching modes (●: $\nu_{as}(CH_2)$, ◆: $\nu_s(CH_2)$) of the $FcC_{11}SH$ monolayer and self-assembly time. Also denoted are the methylene stretching frequencies for liquid $FcC_{11}SH$ and solid $C_{22}SH$.

Table 1. The FWHM and Peak Area of $\nu_{as}(CH_2)$ for a Monolayer of $FcC_{11}SH$ on Gold along with the Charge Density. All as a Function of Self-Assembly Time.

Self-assembly time	FWHM (cm^{-1})	Peak area (arb. unit)	Charge density ($\mu C\,cm^{-2}$)
1 min	32±2	2.8±0.08	40.4
10 min	30±2	2.8±0.08	45.4
15 h	20±2	1.6±0.10	46.3

that self-assembled in just 1 min had a $\nu_{as}(CH_2)$ at a lower frequency than that of the liquid state $FcC_{11}SH$ (2930 cm^{-1}). Figure 4 also displays a similar tendency for the $\nu_s(CH_2)$ band. These results suggest that even monolayers prepared in only 1 min have some order and that this order increases with longer self-assembly time. The $FcC_{11}SH$ monolayer prepared in 15 h approaches the order of the solid state, as evidenced by $\nu_{as}(CH_2)$ at (2920 cm^{-1})—the same as for the $C_{10}SH$ monolayer,[35] and close to the 2919 cm^{-1} of the $C_{18}SH$ monolayer and the 2918 cm^{-1} of the bulk solid $C_{22}SH$.

The FWHM of the $\nu_{as}(CH_2)$ band for the $FcC_{11}SH$ monolayer as a function of self-assembly time is listed in Table 1. Longer adsorption time leads to narrower bands—implying a more uniform distribution of conformations of $FcC_{11}SH$ molecules in the monolayer. After 15 h, the conformation of $FcC_{11}SH$ molecules in the monolayer is almost as uniform as the $C_{10}SH$ monolayer prepared by Chidsey (FWHM of 19 cm^{-1}),[35] but not as ordered as the longer chain $C_{18}SH$ monolayer (FWHM of 15 cm^{-1}).

Table 1 also shows the self-assembly time dependence of the peak area of the $\nu_{as}(CH_2)$ band. The peak areas for the $FcC_{11}SH$ monolayers prepared in 1 min and 10 min are nearly equal, but the value decreases significantly for the monolayer formed in 15 h. The p-polarized light used in the PM-FTIR experiments only interacts with vibrational modes perpendicular to the sample surface. Thus, the peak area of a mode such as $\nu_{as}(CH_2)$ depends on both the amount and orientation of adsorbed molecules. The amount of adsorbed molecules can be measured electrochemically from the charge passed during the redox of the attached ferrocenyl group. The charge densities observed for the anodic peak of the monolayers prepared by various self-assembly times are given in Table 1. This electrochemical data suggests that the number of $FcC_{11}SH$ molecules adsorbed on gold reaches almost 100% saturation in 10 min, as reported before.[18] Therefore, the decrease in the absorbance of $\nu_{as}(CH_2)$ is not due to a decrease in the number of adsorbed molecules, but rather a change in molecular orientation and conformation.

What changes in the orientation of the methylene groups relative to the gold surface will lead to a decrease in the intensity of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ stretching modes? If the alkyl backbone stands perpendicular to the surface (a tilt angle of 0°), the C–H bonds would be nearly parallel to the surface and not absorb much p-polarized light. On the other hand, a tilt angle greater than zero would orient the C–H bonds more perpendicular to the surface and thereby increase the absorbance (peak area). Since the peak area of $\nu_{as}(CH_2)$ decreases with the longer self-assembly time, we conclude that the tilt angle of the alkyl chain of the adsorbed $FcC_{11}SH$ molecules becomes smaller, i.e., the molecules stand closer to the surface normal, as the self-assembly time increases.

Similarly, orientation changes of the ferrocene ring can be identified, in principle, based on the peak area of C–H stretching mode of the ferrocene ring, $\nu(CH)_{Fc}$. Unfortunately, the signal-to-noise ratio of the $\nu(CH)_{Fc}$ band at 3100 cm^{-1} was too low to discuss this orientation (cf. Fig. 2).

Conclusion

Using PM-FTIR spectroscopy, we have studied the self-assembly time dependence of the structure and orientation of a $FcC_{11}SH$ molecular layer on a vapor-deposited gold substrate. Comparison between the intensity of $\nu_{as}(CH_2)$ of a $C_{18}SH$ monolayer and that of the $FcC_{11}SH$ molecular layer confirms that the $FcC_{11}SH$ self-assembles into a monolayer on the gold surface within 10 min. The frequencies of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ of the $FcC_{11}SH$ monolayer are lower than those observed in the bulk liquid, suggesting that the molecules are more ordered after forming the monolayer. Longer self-assembly time increases the conformational order of the monolayer, as evidenced by (i) a decrease in the vibrational frequencies of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes, and (ii) a decrease in the FWHM of these bands. Furthermore, the decrease in the absorbance observed for the methylene stretches with longer self-assembly time can be explained by a change in the orientation. Specifically, the average tilt angle from the surface normal of the *n*-alkyl chain in the $FcC_{11}SH$ decreases with longer self-assembly time, i.e., the molecules stand more erect with respect to the gold surface.

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