Cotton effect in the $A_{1g} \rightarrow T_{1g}$ (O_h) region with λ_{max} at 584 nm indicating that 2 has a Λ absolute configuration.[22~24] In this work the optically active L-cysteine has shown a remarkable stereospecificity in its coordination to the racemic compound 2 to yield a Λ optical isomer.

Upon coordination of L-cysteine to 1 *via* the N, S chelation, the symmetry of the compound is reduced from C_2 (1) to C_1 (2), which is shown in the pmr spectrum of 2. The methyl protons on the ethyl group are shown as double triplets at 1.5 ppm for 2 vs a triplet at 1.3 ppm for 1, while the N-methyl protons are resonated as two singlets between 2.7 and 3.1 ppm for 2 *vs* a singlet at 3.1 ppm for 1.

Oxidation of 2 with stoichiometric amount of H_2O_2 has yielded a sulfenato complex of 3 as a reddish purple solid, while oxidation of 2 with H_2O_2 in a $1:3$ (H_2O_2) mole ratio has given a sulfinato complex of 4 as a violet solid. The S-O stretching vibration is shown at 1047 cm^{-1}. The visible spectrum of 3 (Figure 2) shows the λ_{max} at 560 nm, which is shifted toward the shorter wavelength side by about 18 nm upon oxidation of 2 by H_2O_2 to 3. Such shift is due to the electron withdrawing effect of SO as a result of the oxidation of the sulfur atom. It is interesting to note that the H_2O_2 oxidation of 2 has occured without disruption of the primary coordination sphere of the cobalt center. The CD curve of 3 (Figure 2) shows the dominant positive Cotton effect in the T_{1g} transition region (λ_{max} near 550 nm) as expected for the Λ absolute configuration, in which the $\Delta\varepsilon$ has been diminished considerably because of the contribution from the sulfur atom which becomes a racemic(R, S) chiral center upon oxidation. In the pmr spectrum of 3, the methyl protons of the ethyl group are shown as two triplets at near 1.1 ppm more clearly than those in 2, while the N-methly protons are exhibited as two singlets between 2.5 and 2.9 ppm.

Oxidation of 2 by H_2O_2 with $1:3$ mole ratio for a prolonged period of time (12 hrs) has yielded the sulfinato complex of 4. The ir spectrum of 3 shows the S-O stretching vibrations at 1100 and 1250 cm^{-1}. The visible spectrum of 4 (Figure 2) shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}$ (O_h) transition region at 552 nm, which shifted further toward the shorter wavelength side than 3. As expected for the Λ absolute configuration, the CD curve of 4 (Figure 2) shows the positive Cotton effect in the T_{1g} transition region with λ_{max} at near 540 nm in which $\Delta\varepsilon$ are diminished much more considerably than 3 and the effect of the racemic sulfur atom on $\Delta\varepsilon$ is more pronounced here than 3. It is interesing to observe in this work that the L-cysteine has shown the significant stereospecificity in its coordination to the racemic complex of 1.

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Adsorption of Stearic Acid on Hydrophobic Surface : FT-IR Spectroscopic Study

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In the last decade, much attention has been paid to the ultrathin organic films due to their potential application to molecular electronics, optoelectronics, and artificial membranes, etc.[1] In line with this, herein we hope to present the infrared spectroscopic observation made on the consecutive adsorption of octadecyl mercaptan and stearic acid on gold and silver surfaces. The objective of this work is to see how much the orientation of second layer is susceptible to the structure of the first layer and to get information on the adsorption behavior of organic molecules on non-metallic hydrophobic surface.

Initially, the vacuum evaporated silver or gold substrate[2,3] was dipped into 10^{-3} M octadecyl mercaptan (ODM) in ethanol. The substrate was subsequently rinsed with neat ethanol to remove unbound ODM. The Langmuir-Blodgett (LB) stearic acid monolayers were then deposited onto the substrate with a computerized home-made LB trough.[2] After spreading 5×10^{-3} M stearic acid (STA) in chloroform onto the water subphase containing 10^{-2} M $CdCl_2$, chloroform was allowed

to evaporate for 1 hour. Holding the surface pressure at 30 mN/m, the solid-like condensed film was transferred to the ODM layer by moving the substrate vertically into and out of the water subphase at a rate of 1.0 mm/min. The method of recording the infrared reflection-absorption (IRA) spectra of the transferred films has been reported previously.[2~5] The angle of incidence for the p-polarized light was 85°. Besides the IRA spectra, the static contact angles of prepared films toward 2 μL water droplet were determined with a home-made goniometer[2] by averaging 5 separate readings. All chemicals were reagent grade and used as received. Triply distilled water, of resistivity greater than 17.5 MΩ·cm, was used throughout in the preparation of the LB monolayers.

As already reported,[6~9] ODM was adsorbed on gold and silver surfaces very favorably by the self-assembly method. The IRA spectra for the films deposited on gold were nearly independent of the immersion time. Namely, over a period of 30 min to 8 days of self-assembling, the positions and intensities of IRA peaks were observed to barely change. This suggests that complete monolayers can be formed readily by contacting the gold substrate with the ODM solution. On the other hand, the nature of adsorbate on silver seemed, however, to be very susceptible to the preparative condition. This could be evidenced from the observation of quite different IRA spectral pattern depending on the details of the sample preparation. The variance of IRA spectral pattern for mercaptans adsorbed on silver was observed already by Laibinis *et al.*[9] Such a phenomenon was supposed by them to occur due to the formation of silver oxide and silver sulfide. We observed that the most important preparative variable was the length of exposure time to air. The kind of solvent and the self-assembly time were far less important as far as the adsorbate solution was continuously deaerated. Usually noticeable spectral change was observed after a few days of exposure to air. Within a day, however, the spectral cha-

nge was not serious even after the self-assembled film was soaked in water for 3 hours (*vide infra*).

Figure 1a and b represent the typical IRA spectra in the 2800-3000 cm⁻¹ region for ODM monolayers residing, respectively, on the gold and silver surfaces. The spectrum shown in Figure 1b corresponds to what has been taken immediately after the self-assembly on silver. In fact, no peak was seen in the spectral region other than that shown in Figure 1. The S-H stretching peak which appeared at 2550 cm⁻¹ in the transmission spectrum of a neat sample was completely absent in the IRA spectra. This indicates that adsorption occurs by forming metal-sulfur bonds after losing thiol protons.

The peak positions of C-H stretching bands in Figure 1a are hardly different from those in Figure 1b. Nonetheless, the intensity difference between the two spectra dictates the two monolayers to possess quite different structures. For monolayers on gold, the asymmetric stretching band of CH_2 group[9] at 2917 cm⁻¹ is stronger than others. For monolayers on silver, the out-of-plane asymmetric stretching band of CH_3 group[9] at 2964 cm⁻¹ is the most intense one. Invoking the infrared selection rule,[10,11] this indicates the octadecyl chain to be more perpendicularly oriented on silver than on gold. For a more quantitative estimation, we have simulated the IRA spectra in the C-H stretching region based on a single-chain model[23] assuming also that the alkyl chain is fully extended with a trans zigzag structure. The simulated IRA spectrum best fit to the experimental one was found when the tilt and twist angles of octadecyl group were set, respectively, at 15° and 40° for the monolayers on silver and at 25° and 50° for the monolayers on gold (see Figure 2a for the definition of chain tilt and twist angles). The present theoretical result is in good agreement with that of Laibinis *et al.*[9]
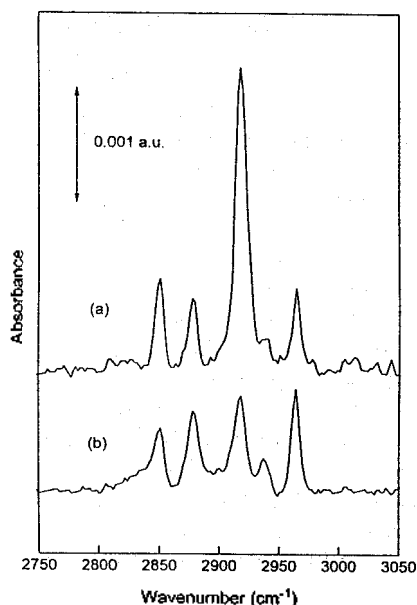

Figure 1. IRA spectra of octadecyl mercaptan monolayers self-assembled, respectively, on (a) gold and (b) silver surfaces.
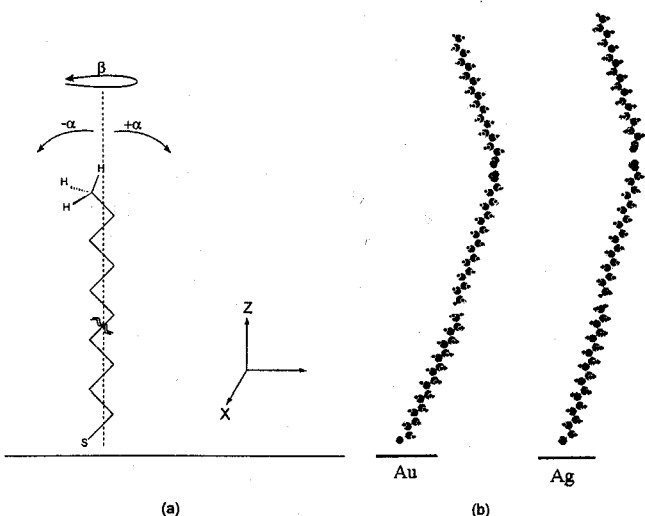

Figure 2. (a) Model used in calculation of the stretching band intensities of CH_3 and CH_2 groups as functions of chain orientation relative to the substrate surface. The labels, α and β, correspond, respectively, to the angle of chain tilt and the angle of chain twist. (b) Plausible orientation of alkyl chains of three-layer films consisting of octadecyl mercaptan and stearic acid on gold and silver surfaces.

The fact that the monolayers formed on silver and gold have different orientation even though the lattice constants[12] of two metals are very comparable to each other suggests that the metal-to-sulfur interaction should control the adsorbate orientation. Invoking that the strength of Au-S bond is greater than that of Ag-S bond,[13] the adsorbate is supposed to take a more tilted orientation as a function of strength of metal-sulfur bond. Difference in the tilt angle implies further that the interchain spacing on silver should be greater than that on gold. Besides, the extent of exposure of the methyl group in the air-monolayer interface should be somewhat larger for the film on silver than that on gold. This seems consistent with the contact angle measurement; the static contact angles of water are 115° and 113° for the films on silver and gold, respectively. The two films can be regarded accordingly as hydrophobic substrates, but possessing slightly different surface characteristics.

After confirming that the quality of mercaptan monolayers prepared in this work was comparable to that of earlier workers, it has been intended to know how much a subtle surface structural difference could affect the structure of other molecules anchoring on them by a hydrophobic interaction. For that purpose, Y-type double layers[14] of STA were deposited on the films of ODM by the LB method. Prior to presenting the IRA spectra of resulting three layered films, it would be worth to remind that the IRA spectra of ODM monolayers were hardly to change even after the ODM films on gold and silver were soaked in an aqueous medium for a period of time needed for the LB transfer of STA onto them (*vide supra*). This implies that the ODM films once formed are structurally very rigid. It may then be supposed that the orientation of ODM monolayers on gold and silver is not affected also by the LB deposition of STA overlayers onto them. Figure 3a and 3b show, respectively, the IRA spectra of the resulting three layer systems on gold and silver surfaces. As one may expect, their IRA spectral

patterns are different from each other. It is intriguing, however, that the spectra obtained by spectral subtraction between the digitized files of Figure 3a and 1a as well as between those of Figure 3b and 1b were barely different, as can be seen from Figure 3c and 3d. This should imply that the structure of STA double layers is rather insensitive to that of underneath hydrophobic layer. The simulated IRA spectra best fit to the C-H stretching region of Figure 3c and 3d are found when the two consecutive stearic acid layers assume a symmetrical structures as shown in Figure 2b, with tilt and twist angles on gold at *ca.* 17 and 50° and on silver at *ca.* 15 and 40°, respectively. Their structural difference seems to be minimal. The static contact angles of water are measured to be 114 and 113° for the 3-layered films on gold and silver, respectively. This may indicate that the structure of STA is governed very weakly by the structure of its underneath hydrophobic layer.

It can be noted that the peak positions of CH_2 group stretching bands are barely different between the spectra in Figure 1a and 3a (or Figure 1b and 3b). As being assumed for the ODM monolayers, this may suggest that the alkyl chains of STA double layers possess also a fully extended trans zigzag structure (*vide infra*). There exist, however, some frequency differences between the C-H stretching bands of CH_3 group. The asymmetric stretching band[2,15] which appears at 2964 cm^{-1} in Figure 1a (or 1b) is observed at 2962 cm^{-1} in Figure 3a (or 3b). The symmetric stretching bands[2,15] appearing at 2939 and 2877 cm^{-1} in Figure 1a (or 1b) are observed at 2931 and 2874 cm^{-1} in Figure 3a (or 3b). The CH_3 symmetric stretching band at 2939 cm^{-1} which is in Fermi resonance[15] with the overtone of CH_3 asymmetric deformation is shifted considerably more than others. Such a frequency shift can be attributed to the interaction of two methyl groups between stearate and octadecyl mercaptide caused by the Y-type LB transfer of STA. Similar spectral shifts are seen also in the IRA spectra of 1- and 3-layers of STA deposited on fresh silver substrates by the Y-type LB deposition.

Several distinct peaks appear in the 1100-1800 cm^{-1} region upon the transfer of STA on the monolayers of ODM. The so-called progressional bands[16] appear distinctly in the 1150-1350 cm^{-1} region. Those bands are known to indicate that the alkyl chains are fully extended in the solid state with a trans zigzag structure as we have assumed previously. Both the symmetric and asymmetric stretching bands of COO^- group appear also at *ca.* 1432 and 1550 cm^{-1}, respectively, in the two spectra. The symmetric stretching band is several times more intense than the asymmetric stretching band. Invoking the infrared selection rule,[10,11] this reflects that the two oxygen atoms of carboxylate group should lie nearly parallel to the metal substrates.

In summary, the present work reveals that although the structure of the first layer depends on the properties of underneath solid substrate, the structure of succeeding organic layers is not susceptible greatly to that of the first layer as far as two organic layers interact with each other via the relatively weak hydrophobic interaction. This information is expected useful when one investigates the structure-function relationship for biomimetic bilayered membranes.
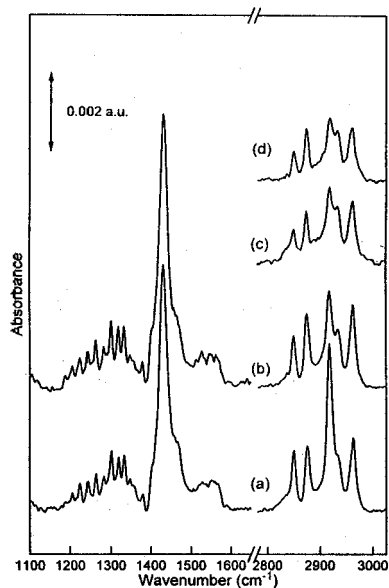
Figure 3. IRA spectra of three-layer films on (a) gold and (b) silver surfaces. Difference spectra between Figure 1a and 3a (c) and between Figure 1b and 3b (d).

Notes

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Conformational Properties of Potassium 1,3-Dithiolan-2-ylidenemalonate

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A series of ylidenemalonates containing dithioether rings have been elucidated to be fascinating ligands by the au-

thors: the ligands may be coordinated to a platinum atom *via* one of three distinct modes of O,O'-, O,S-, or S,S'-chelation depending on the dithioether ring size.[1,2] The variety of chelation modes could be explained in terms of the basicity of sulfur atoms. In our previous work on dimethyl 1,3-dithiolan-2-ylidenemalonate, an intramolecular sulfur-oxygen interaction was also shown to be governed by the basicity of sulfur atoms.[3] However, the crystal structure of the dimethyl 1,3-dithiolan-2-ylidenemalonate is not sufficient to discern its coordination mode as an anionic ligand. In order to scrutinize a relationship between the structure and the coordination mode of the anionic ligand, it is worthwhile to point out the crystal structure of its metal salt. Here is reported the structural properties of potassium 1,3-dithiolan-2-ylidenemalonate.

Experimental

Dimethyl 1,3-dithiolan-2-ylidenemalonate was prepared by the literature method.[4] Potassium hydroxide (1.68 g, 25 mmol) in 40 mL of 95% ethanol was added dropwise to dimethyl 1,3-dithiolan-2-ylidenemalonate (2.34 g, 10 mmol) in 40 mL of 95% ethanol, and then refluxed for 4 h. The precipitated crystalline potassium salt was obtained in quantitative yield. Elemental analysis: calculated for $C_6H_4O_4S_2K_2 \cdot CH_3OH$: C, 26.74; H, 2.56. Found: C, 26.69; H, 2.49. IR (KBr, cm^{-1}): ν_{as} (C=O): 1587, 1550, ν_s (C=O): 1382. ^1H NMR (D_2O, ppm): 3.49 (s). ^{13}C NMR (D_2O, ppm): 37.82, 125.27, 125.45, 179.90.

Elemental analysis was carried out at the Advaced Chemical Analysis Center, KIST. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer operating at 300 MHz (^1H) and 75.48 MHz (^{13}C) in pulse mode with Fourier transform. IR spectrum was measured as KBr pellet on a MIDAC model 101025 FT-IR spectrophotometer.

A crystal ($0.15 \times 0.30 \times 0.35$ mm) suitable for X-ray analysis obtained by recrystallization in a solvent pair of water/methanol (1:1) was sealed in a Lidemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated molybdenum radiation. The unit-cell parameters were determined by least-squares refinement of 25 intense reflections ($15 < 2\theta < 25$). Data were collected at ambient temperature [296(2) K] in $\omega/2\theta$ scan mode using variable rates, $\theta_{max} = 25°$ for the range $0 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 31$, and three standard reflections measured after every hour did not reveal any systematic variations in intensity. Maximum $\sin\theta/\lambda$ reached in intensity measurement was 0.59 $Å^{-1}$; 2743 measured intensities, 1599 unique, 1589 unique observed [$I > 2\sigma(I)$]. Lorentz-polarization corrections but not absorption corrections were made. The crystal structure was determined by the conventional heavy atom method and Fourier techniques. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. Two carbon atoms (C(5), C(6)) were located in disordered positions; an occupancy factor of 0.5 was assigned according to the height of the Fourier synthesis. The maximum shift-to-e.s.d. in the final cycle of least squares was 0.137 for U_{11} of disordered C(6). All calculations were performed on IBM PC 486 computer using *SHELXS*-5a and *SHELXL*-93[5b] and atomic scattering factors for all nonhydrogen atoms were supplied by the *SHELXS*-86 system. Crystal pa-