

Correlation between the Conductance and Infrared Spectra of the Alkylammonium-Au(dmit)₂ LB Films

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We have studied the correlation between the conductance and Fourier transform-infrared (FT-IR) spectra of the Langmuir-Blodgett (LB) film based on ditetradecyldimethylammonium-Au(dmit)₂ [2C₁₄-Au(dmit)₂] salt. The 2C₁₄-Au(dmit)₂ salt was transferred onto a CaF₂ substrate and was electrochemically oxidized using a constant current of 0.8 μA in an aqueous solution of LiClO₄. The conductance and the FT-IR spectra were measured using a slit between the electrodes by taking out the samples from the electrolyte and dried by nitrogen gas every thirty minutes. We have already reported that the conductance gradually increases with time of the oxidation up to 150 min but it turns to decrease modestly later. Accompanied by the oxidation, a broad band appears in a wide range of 850-7000 cm⁻¹ and the peak shifts from 2000 cm⁻¹ down to 1630 cm⁻¹ in the first 120 min and it turns to be constant later. The area change of the IR spectra, which is proportional to the oscillator strength, is in close agreement with the conductance behavior. These results strongly indicate that the broad absorption is of charge transfer (CT) band and the conducting properties can be controlled precisely by monitoring the CT band together with the CH₂ symmetric, CH₂ antisymmetric and C=S stretching bands located at around 2850 cm⁻¹, 2920 cm⁻¹ and 1055 cm⁻¹, respectively.

Key words: Langmuir-Blodgett films, Infrared (IR) spectroscopy, Au(dmit)₂ salts, Electrochemical oxidation, Charge-transfer (CT) band

1. INTRODUCTION

The Langmuir-Blodgett (LB) technique is a powerful tool that allows us to assemble molecules with electronic and opto-electronic functions into tailored two-dimensional (2D) molecular sheets with fairly low energy cost [1]. Among various trials for fabricating LB films with those functions, realization of highly conductive LB systems is one of the important subjects [2]. We have already reported that the LB films based on ditetradecyldimethylammonium-Au(dmit)₂ salt (Fig. 1, n=14) exhibit a high room temperature conductivity

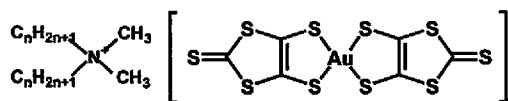


Fig. 1. Molecular structure of the 2C_n-Au(dmit)₂ salt.

of 73 ± 26 S/cm with a metallic temperature dependence in the range of 230-300 K after electrochemical oxidation [3, 4]. Furthermore, we have also pointed out the possible superconductivity below 4 K from the *ac* magnetic susceptibility and resistance data [5-7].

So far, the resistance drop on cooling of the 2C₁₄-Au(dmit)₂ LB film has not been seen for the sample batches of majority and the zero resistance has not yet been observed. This is possibly because the electrochemical oxidation process, which is necessary to render the film conductive, has not been characterized

well. In one of our previous papers, we reported the changes in Fourier transform-infrared (FT-IR) spectra during the electrochemical oxidation, where we focused on the correlation between the room-temperature conductivity and the CH₂ symmetric stretching mode (*v_s*) and CH₂ antisymmetric one (*v_{as}*), which are located at around 2850 cm⁻¹ and 2920 cm⁻¹, respectively, and concluded that the order of the hydrocarbon chains also plays a crucial role for realizing the high room-temperature conductivity [4]. We have also reported the FT-IR spectra of the as-deposited 2C_n-Au(dmit)₂ LB films with various chain lengths (n=8, 10, 12, 14, 16, 18) and pointed out that the longer the chain length is, the more upright the principal axis stands with less amounts of gauche C-C bonds [8].

In the previous two papers [4, 8], however, the spectral change in the fingerprint region cannot be discussed because of the insufficient signal to noise ratios.[†] Then, in order to measure the FT-IR spectra with better signal to noise ratios, we modified the sample structure in which a rectangular aperture of 5 × 10 mm² is set in the middle of the 1-mm gap of the gold electrode, as shown in Fig. 2. Here we report the correlation between the conductance and the FT-IR

[†] In our previous papers, the IR spectra of the as-deposited films were measured by a surface-normal incident, but those during the electrochemical oxidation were measured by an incident, which is tilted 12 degrees from the surface normal, utilizing the interface between the LB film and the gold electrode.

spectra in the wide region of 850-7000 cm⁻¹.

2. Experimental

2.1 Sample Preparation

The 2C₁₄-Au(dmit)₂ salts (Fig. 1, n=14) was synthesized following the procedure of Steimecke *et al.* [9] and spread on the surface of pure water (17°C) using a 1:1 mixture of acetonitrile and benzene. After keeping the salts on the water surface for five minutes, they were compressed up to 25 mN/m and transferred onto a 1-mm-thick CaF₂ substrate by the horizontal lifting method. Twenty layers were deposited unless otherwise stated. Prior to the deposition of the 2C₁₄-Au(dmit)₂ films, the surface of the CaF₂ substrate was hydrophobized by a coating of five layers of Cd-arachidate and then, gold electrode strips were vacuum-deposited forming an aperture of 5 × 10 mm² in the middle of a gap of 1 mm, as shown in Fig. 2. The as-deposited films were immersed in an aqueous solution of LiClO₄ (0.1 M) and electrochemically oxidized by a constant current of 0.8 μA. The gold

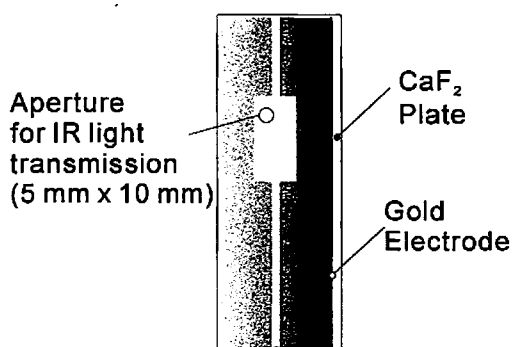


Fig. 2. Top view of the electrode-coated substrate: the CaF₂ surface was coated by five layers of Cd-arachidate, and, then gold electrode strips were vacuum-deposited forming an aperture of 5 × 10 mm² in the middle of a gap of 1 mm.

electrode underneath the 2C₁₄-Au(dmit)₂ layer was used as the working electrode. The counter electrode was of a platinum rod. The details of the sample preparation are in our previous papers [3-8].

2.2 Measurements of infrared spectra and conductance

For the measurements of the transmission Fourier transform-infrared (FT-IR) spectra and electrical conductance, the sample was taken out from the electrolyte and dried by N₂ flow every thirty minutes. The transmission FT-IR absorption spectra were measured at a resolution of 4 cm⁻¹ using a JASCO FT/IR 300 spectrometer under dry N₂ flow. A non-polarized incident, which is surface normal, was irradiated through the rectangular aperture of 5 × 10 mm², as shown in Fig. 2. In order to obtain spectra with a high signal-to-noise ratio, 128 interferograms were co-added.

The electrical conductance was measured by a *dc* two-probe method at room temperature using the gold electrode strips vacuum-deposited underneath the LB films. A Keithley Type 2001 digital multimeter was used.

3. RESULTS AND DISCUSSION

Figure 3(a) shows a typical change in IR absorption spectra of the 2C₁₄-Au(dmit)₂ LB films during the electrochemical oxidation. A broad band appears in the first 30 min of the oxidation and the absorbance increases with increasing the time of the electrochemical oxidation (T_{ox}). Figure 3(b) shows the area changes in the FT-IR spectra (■) and the conductance (□) plotted against T_{ox} . Figure 3(c) also shows the peak positions of the broad band plotted against T_{ox} (●) together with the conductance (◇). In

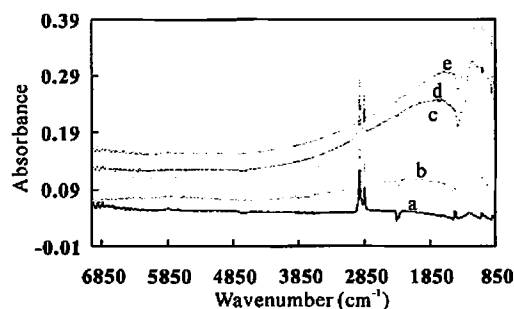


Fig. 3(a). The FT-IR spectra of the 2C₁₄-Au(dmit)₂ LB films with various degrees of electrochemical oxidation: (a) as-deposited, (b) electrochemically-oxidized for 30 min, (c) 60 min, (d) 90 min, and (e) 240 min.

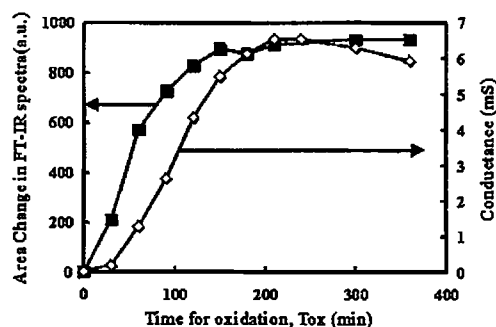


Fig. 3(b). The area changes in the FT-IR spectra (■) and the conductance (□) plotted against time for oxidation, T_{ox} .

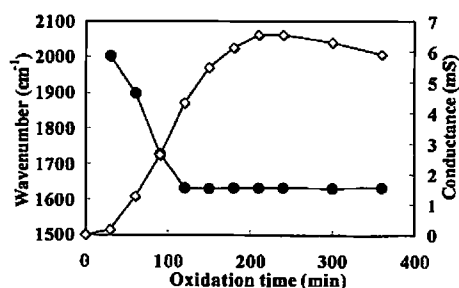


Fig. 3(c). The peak positions of the broad band plotted against T_{ox} (●) together with the conductance (◇).

case $T_{ox}=30$ min, the peak position is located at around 2000 cm^{-1} , but it gradually shifts down to 1633 cm^{-1} up to $T_{ox}=120$ min associated with the electrochemical oxidation. After $T_{ox}=120$ min, however, no appreciable change is seen as for the peak position. The area change of the IR spectra, which is proportional to the oscillator strength, and the peak shift of the band toward the lower-energy region strongly indicate that the broad absorption peak is of charge-transfer (CT) band.

In our previous papers, we have already reported that the order of the alkyl chains in the $2C_{14}\text{-Au(dmit)}_2$ LB film changes remarkably during the electrochemical oxidation [4, 8]. We further pointed out that the amount of the gauche forms decreases in the hydrocarbon chains and the principal axis of the hydrocarbon is getting closer to the surface normal accompanied by the post treatment. So far, we have also pointed out that the oxidation state of the Au(dmit)_2 anion moiety can be monitored by the broadening of a band at around 1055 cm^{-1} , which is assigned as the C=S stretching mode located at the edges of the Au(dmit)_2 moiety [10].

So far, the conditions of the electrochemical oxidation have been set empirically, i.e. a constant current of $0.8\text{ }\mu\text{A}$ was applied for 90-150 min in the aqueous electrolyte of LiClO_4 (0.1 M). We currently consider that conducting properties of the $2C_{14}\text{-Au(dmit)}_2$ LB film can be precisely controlled by monitoring the C-T band together with the CH_2 symmetric stretching ($\text{CH}_2\text{ } \nu_s$), CH_2 antisymmetric stretching ($\text{CH}_2\text{ } \nu_{as}$) and C=S stretching bands.

4. CONCLUSION

We have discussed the correlation between the conductance and FT-IR spectra of the Langmuir-Blodgett (LB) film based on ditetradecyldimethylammonium- Au(dmit)_2 [$2C_{14}\text{-Au(dmit)}_2$] salt. The $2C_{14}\text{-Au(dmit)}_2$ salt was transferred onto a CaF_2 substrate and was electrochemically oxidized using a constant current of $0.8\text{ }\mu\text{A}$ in an aqueous solution of LiClO_4 . The conductance and transmission FT-IR spectra were measured using the slit between the electrodes by taking out the samples from the electrolyte and dried by nitrogen gas every thirty minutes. We have already reported that the conductance gradually increases with time of the oxidation up to 150 min but it turns to decrease modestly later. Accompanied by the oxidation, a broad band appears in a wide range of $850\text{-}7000\text{ cm}^{-1}$ and the peak shifts from 2000 cm^{-1} down to 1630 cm^{-1} in the first 120 min and it turns to be constant later. The area change of the IR spectra, which is proportional to the oscillator strength, is in close agreement with the conductance behavior. These results strongly indicate that the broad absorption is of charge transfer (CT) band and the conducting properties can be controlled precisely by monitoring the CT band together with the CH_2 symmetric, CH_2 antisymmetric and C=S stretching bands located at around 2850 cm^{-1} , 2920 cm^{-1} and 1055 cm^{-1} , respectively.

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