Infrared Spectroscopic Study on LB Films Based on Ditetradecyldimethylammonium-Au(dmit)₂ Salt

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The infrared spectra of the $2C_{14}$-Au(dmit)$_2$ LB system were measured in the region of 2800-3000 cm^{-1}. It has been revealed that the order of the hydrocarbon chain increases drastically in the first 30 min of the electrochemical oxidation but it turns to be constant or increase modestly later. We have already reported that the band at around 1055 cm^{-1} is broadened by the post treatment. The band is of C=S stretching of the Au(dmit)$_2$ moiety, and the broadening is due to the oxidation of the moiety. We hypothesize that the oxidation of the Au(dmit)$_2$ moiety is accompanied by the incorporation of ClO_4^- anions for the charge compensation and that the order of the alkyl chains of the ammonium moiety increases. Therefore, it is suggested that not only the charge-transfer ratio but also the order of the alkyl chains plays a crucial role for realizing higher conductivity of the LB system.

Key words: Langmuir-Blodgett films, Infrared spectroscopy, Metal(dmit)$_2$ complexes, Electrochemical oxidation, Superconductivity

1. INTRODUCTION

The metal(dmit)$_2$ complexes, where metal=Au, Ni, Cu, Zn, Pt or Pd and H$_2$dmit=4,5-dimercapto-1,3-dithiole-2-thione, have attracted much attention because the bulk salts exhibit a wide variety of electrical properties ranging from semiconductors to superconductors [1]. We have already reported that the LB film of ditetradecyldimethylammonium-Au(dmit)$_2$ ($2C_{14}$-Au(dmit)$_2$, Figure 1) salt shows a high in-plane conductivity of 40 S/cm with a metallic temperature dependence of the conductivity in the range of 230-300
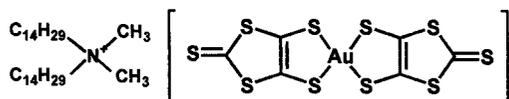
Fig.1   Molecular Structure of the $2C_{14}$-Au(dmit)$_2$ salt.

K [2] after the electrochemical oxidation. Furthermore, the ac magnetic susceptibility and resistance suggest the existence of a supercoundcting phase below 4 K [3-5].

So far, the conditions of the electrochemical oxidation, such as the magnitude and time of the constant current, have been chosen empirically. Recently, we have reported that the C=S stretching mode of the Au(dmit)$_2$ anion is broadened by the oxidation and that the mode can be used as an index of the oxidation state [6]. We consider that the order of the alkyl chains also plays a crucial role for the microscopic and/or macroscopic conduction as well as the oxidation states of the Au(dmit)$_2$ moiety, although the closed-shell alkylammonium layer itself is electrically insulating. In this paper, we focus on the order of the alkyl chains and report the correlation

between the room-temperature conductivity and the CH$_2$ symmetric stretching mode (v_s) and CH$_2$ antisymmetric one (v_{as}) measured in the range of 2800-3000 cm^{-1}.

2. Experimental

2.1 Sample Preparation

The $2C_{14}$-Au(dmit)$_2$ salt (Figure 1) was synthesized following the procedure of Steimecke *et al.* [7] 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 poly(ethylene terephthalate) (PET) substrate by horizontal lifting method. Twenty layers were deposited unless otherwise stated. Prior to the deposition of the $2C_{14}$-Au(dmit)$_2$ salt, both sides of the PET substrate was pre-coated by five layers of cadmium arachidate and four gold electrode strips with a gap of 0.5 mm were vacuum-deposited on it subsequently.

The as-deposited films were immersed in an aqueous solution of LiClO$_4$ and electrochemically oxidized by a constant current method. The gold electrode underneath the $2C_{14}$-Au(dmit)$_2$ layer was used as the working electrode. The counter electrode was platinum. The details of the sample preparation are in our previous papers [2,3].

2.2 Measurements of infrared spectra and conductivity

Infrared absorption spectra were measured at 4 cm^{-1} resolution using a JASCO FT-IR Spectrometer. In order to generate spectra with a high signal-to-noise ratio, 256 interferograms were coded. The as-deposited film or the electrochemically-oxidized film

taken out from the electrolyte and dried by nitrogen gas was set in the spectrometer equipped with a reflection attachment, JASCO RF-81S. The reflection absorption spectra were measured utilizing the interface of the LB films of $2C_{14}$-Au(dmit)$_2$ salt and gold. A non-polarized incident, which is tilted 12 degrees from the surface normal, was used.

The electrical conductivity was measured by a dc two-probe method at room temperature using the gold electrode strips vacuum-deposited underneath the LB films.

3. Results and Discussion

Figure 2(a) shows a typical room-temperature conductivity plotted against the time of the electrochemical oxidation (T_{ox}). The conductivity gradually increases with the oxidation until T_{ox}=180 min and it turns to decrease with further oxidation, as shown in Fig. 2(a). Figure 2(b) shows the infrared (IR)

spectra in the region of 2800-3000 cm^{-1} measured for the samples electrochemically-oxidized with T_{ox}=0 min, 30 min and 300 min, whose room-temperature conductivities correspond to the values indicated by the arrows I, X and F in Fig. 2(a), respectively. The distinct absorption bands located at around 2850 cm^{-1} and 2921 cm^{-1} are due to the CH$_2$ symmetric stretching mode (v_s) and CH$_2$ antisymmetric one (v_{as}), respectively. For each band, the absorbance increases remarkably in the first 30 min. For instance, the peak values of the v_s and v_{as} modes increase 4.0 and 2.3 times larger in the first 30 min, respectively. Further oxidation also gives appreciable but moderate increase of the absorbance as well; for instance, in the range of T_{ox}=30-300 min, the peak values of the v_s and v_{as} modes increase 1.3 and 1.2 times, respectively. Moreover, the enhancement of the absorbance is accompanied by the appreciable narrowing, as shown in Fig. 2(b).

Fig.2 (a) The room-temperature conductivity of the $2C_{14}$-Au(dmit)$_2$ LB film plotted against time of the electrochemical oxidation (T_{ox}). (b) Infra-red spectra of the $2C_{14}$-Au(dmit)$_2$ LB film; the spectra I, X, F were measured for the LB samples fabricated by the cases T_{ox}=0 min, 30 min and 300 min, respectively.
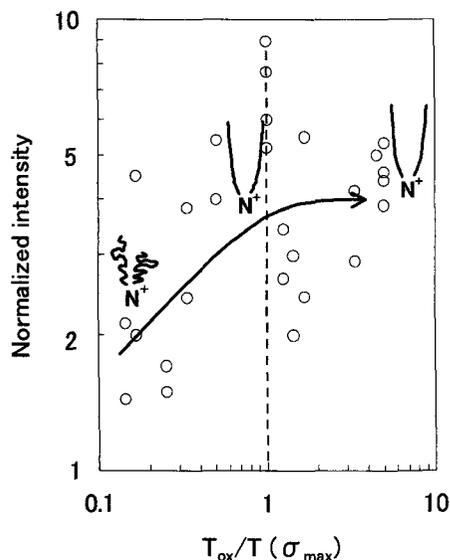
Fig.3 The normalized absorbance plotted against $T_{ox}/T_{ox}(\sigma_{max})$. The data points are both of CH$_2$ symmetric stretching (v_s) and CH$_2$ antisymmetric (v_{as}) modes, located at 2850 cm^{-1} and 2921 cm^{-1}, respectively, normalized using the absorbance of the as-deposited film.

Figure 3 shows the intensity of the absorption bands, v_s and v_{as}, plotted against T_{ox}; the vertical and horizontal axes are normalized using the peaks of the absorption bands in case T_{ox}=0 min and the T_{ox} values that exhibits maximum conductivity ($T(\sigma_{max})$), respectively. As shown by the arrow in Fig. 3, the intensity increases remarkably at the earlier stage of the oxidation but it turns to be constant or increase modestly later.

During the electrochemical oxidation, we postulate that the ClO_4^- anions are incorporated in the film for the compensation of the charge as follows:

$$D^+[Au(dmit)_2]^- + (1-\delta)ClO_4^- \rightarrow D^+{}_\delta[Au(dmit)_2]^{-\delta}$$
$$+ (1-\delta)D^+ ClO_4^- + (1-\delta)e^-,$$
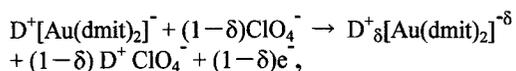
where D^+=ditetradecyldimethylammonium and δ= charge transfer ratio ($0<\delta<1$). The narrowing of the two bands indicates an improvement of the order of the hydrocarbon chains. Furthermore, remarkable increase of the absorbance suggests that the orientation of the hydrocarbon chain changes so that the transition
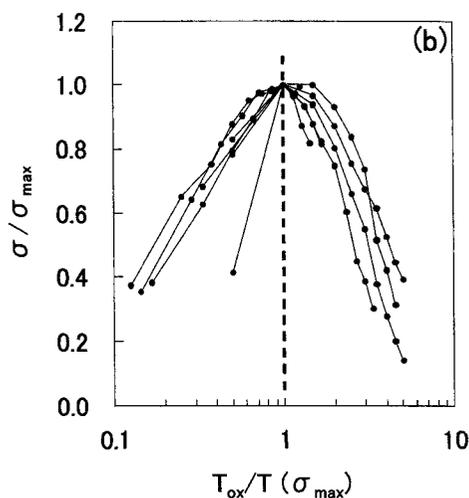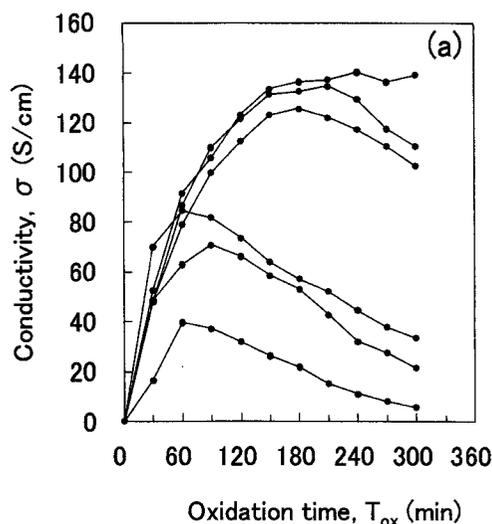
Fig.4   (a) The room-temperature conductivity (σ) of the $2C_{14}$-Au(dmit)$_2$ LB film plotted against time of the electrochemical oxidation (T_{ox}) for various sample batches.

(b) The normalized conductivity, σ/σ_{max}, plotted against the normalized oxidation time, $T_{ox}/T_{ox}(\sigma_{max})$, where σ_{max} and $T_{ox}(\sigma_{max})$ are the maximum conductivity and the oxidation time which exhibits the maximum conductivity.

moments of the CH$_2$ bands tend to align parallel to the substrate surface, as schematically shown in Fig. 3, because the non-polarized incident is tilted only 12 degrees from the surface normal.   We assume that the amount of the gauche forms decreases in the hydrocarbon chain and the principal axis of the hydrocarbon is getting closer to the surface normal accompanied by the post treatment.

Figure 4(a) shows the lateral resistance plotted against the time of the oxidation for various sample batches. We have already reported that the surface pressure (π)-area per molecule (A) isotherm of the $2C_{14}$-Au(dmit)$_2$ salt strongly depends on "waiting time", which is defined as the time for keeping the salts at the air/water interface before compression, since an oxidation of the salts is proceeding at the air/water [6].

The atomic force microscopy (AFM) has revealed that the morphology of the film surface changes from sample to sample.   Therefore, the difference of the maximum conductivity and the time for realizing the maximum is probably due to the difference of the oxidation state, thickness and morphology of the as-deposited films.   The room-temperature resistance values, normalized using the maximum conductivity, σ/σ_{max}, are re-plotted against the normalized oxidation time, $T_{ox}/T(\sigma_{max})$, as shown in Fig. 4(b).   It appears that the line $T_{ox}/T=1$ is the axis of symmetry.   The symmetry is possibly related to our hypothesis where ClO_4^- anions are incorporated in the film for the charge compensation, however, investigation of the origin is now in progress.

4. Conclusion

The infrared spectra of the $2C_{14}$-Au(dmit)$_2$ LB system measured in the regions of 2800-3000 cm^{-1} have revealed that the order of the hydrocarbon chain increases drastically in the first 30 min of the post treatment but it turns to be constant or increase modestly later.   We have already reported that the band at around 1055 cm^{-1} is broadened by the post treatment.   The band is of C=S stretching of the Au(dmit)$_2$ moiety, and the broadening is due to the oxidation of the moiety. We hypothesize that the oxidation of the Au(dmit)$_2$ moiety is accompanied by the incorporation of ClO_4^- anions for the charge compensation and that the order of the alkyl chains of the ammonium moiety increases. Therefore, it is suggested that not only the charge-transfer ratio but also the order of the alkyl chains plays a crucial role for realizing higher conductivity of the LB system.

Reference

[1] "Organic Superconductors", Ed. by T. Ishiguro, K. Yamaji and G Saito, Springer Series in Solid-State Sciences, Springer, Berlin (1997).

[2] Y. F. Miura, Y. Okuma, H. Ohnishi, T. Kawasaki and M. Sugi, Jpn. J. Appl. Phys., **37**, L1481 (1998).

[3] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi: Solid State Comm., **113**, 603 (2000).

[4] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi, Synth. Met., **120**, 727 (2001).

[5] Y. F. Miura, M. Horikiri, S. Tajima, T. Wakaita, S.-H. Saito and M. Sugi, Synth. Met., **133-134**, 663 (2003).

[6] M. Horikiri, Y. F. Miura, Y. Ohkuma, K. Ikegami and M. Sugi, Jpn. J. Appl. Phys., **40**, 295-296 (2001).

[7] G. Steimecke, H. J. Sieler, P. Kirmse and E. Hoyer: Phosphorus Sulfur, **7**, 49 (1979).