Infrared Spectroscopic Study on the Alkylammonium-Au(dmit)$_2$ LB Films

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The infrared (IR) spectra of the 2C$_n$-Au(dmit)$_2$ LB systems with various chain lengths (n=8, 10, 12, 14, 16, 18) were measured and discussed focusing on the region of 2800-3000 cm^{-1}, where the CH$_2$ symmetric stretching band (CH$_2$ ν_s) and CH$_2$ antisymmetric one (CH$_2$ ν_{as}) exist. The absorbance of the CH$_2$ ν_s and CH$_2$ ν_{as} bands per CH$_2$ moiety tends to increase associated with the appreciable narrowing with increasing the chain length, n. It has been revealed that the longer the chain length is, the more upright the principal axis stands with fewer amounts of gauche C-C bonds. Furthermore, the room-temperature conductivity strongly depends on the chain length, as well. It has been suggested that the difference in conductivity can be interpreted not only by the charge-transfer (CT) ratio but also by the order of the hydrocarbon chains in the 2C$_n$-Au(dmit)$_2$ LB systems.

Key words: Langmuir-Blodgett films, Infrared spectroscopy, Au(dmit)$_2$ complexes, Electrochemical oxidation,
CH$_2$ symmetric stretching band (ν_s), CH$_2$ antisymmetric stretching band (ν_{as})

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 variety of electrical properties ranging from semiconductors to superconductors [1]. We have already reported that the LB film of ditetradecyldimethylammonium-Au(dmit)$_2$ (2C$_n$-Au(dmit)$_2$, Fig. 1, n=14) salt shows a high in-plane conductivity of 40-100 S/cm with a metallic temperature dependence of the conductivity in the range of 230-300 K after the electrochemical oxidation [2]. Furthermore, the ac magnetic susceptibility and resistance suggest the existence of a superconducting phase below 4 K [3-5].
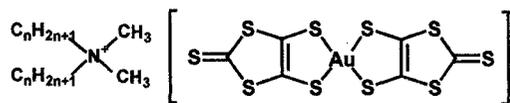

Fig. 1. Molecular structure of the 2C$_n$-Au(dmit)$_2$ salt.

We have also reported on structural characterization of the 2C$_{14}$-Au(dmit)$_2$ LB system by infrared (IR) spectroscopy [6, 7]. A band observed at around 1055 cm^{-1}, which is assigned as C=S stretching band of the edge of Au(dmit)$_2$ moiety, broadened by the post treatment [6, 8]. The broadening is considered to be due to the oxidation of the moiety and the change can be utilized to estimate the formal charge in the following electrochemical process:

$$D^+[Au(dmit)_2]^- + (1-\delta)ClO_4^- \rightarrow D^+{}_\delta[Au(dmit)_2]^{-\delta} + (1-\delta)D^+ ClO_4^- + (1-\delta)e^-,$$
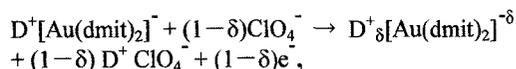
where D$^+$=ditetradecyldimethylammonium and δ= charge transfer ratio (0<δ<1) [6, 7].

In general, macroscopic conductivity of LB systems is sensitive to order of the hydrocarbon chains and we consider that the order of the alkyl chains also plays a crucial role for the microscopic and 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 one of our previous papers, we focused on the order of the alkyl chains and reported the correlation between the room-temperature conductivity and the CH$_2$ symmetric stretching mode (ν_s) and CH$_2$ antisymmetric one (ν_{as}), which are located at around 2850 cm^{-1} and 2920 cm^{-1}, respectively, and concluded that the order of the hydrocarbon chains in the 2C$_{14}$-Au(dmit)$_2$ LB system increases remarkably in the first 30 min of the electrochemical oxidation but it turns to be constant or increase modestly later [7]. Therefore, it has been suggested that the order of the alkyl chains plays a crucial role for realizing higher conductivity in the LB systems as well as the charge-transfer (CT) ratio. Here it should be also noted that the room-temperature conductivity of the dialkyldimethyl-ammonium-Au(dmit)$_2$ (2C$_n$-Au(dmit)$_2$, Fig. 1) LB films strongly depends on the chain length, n. For instance, the room-temperature conductivity of the 2C$_{18}$-

Au(dmit)₂ is 2 S/cm, while that of 2C₁₄-Au(dmit)₂ reaches 40-100 S/cm.

In this paper, as the first step for characterizing the order of the hydrocarbon chains in the series of 2C$_n$-Au(dmit)₂ LB systems, we report on the IR spectra of the as-deposited LB films of the 2C$_n$-Au(dmit)₂ salts with various chain lengths (chain length n=8, 10, 12, 14, 16 and 18), focusing on the region of 2800-3000 cm^{-1} where the CH₂ symmetric stretching band (CH₂ v_s) and CH₂ antisymmetric one (CH₂ v_{as}) exist.

2. Experimental

2.1 Sample Preparation

The 2C$_n$-Au(dmit)₂ salts with various chain lengths (Fig. 1, n=8, 10, 12, 14, 16 and 18) were 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 quartz substrate by horizontal lifting method. Twenty layers were deposited unless otherwise stated. Prior to the deposition of the 2C$_n$-Au(dmit)₂ salts, the substrates were hydrophobized by keeping them in a container filled with the vapor of 1,1,1,3,3,3-hexamethyldisilazane for more than a day.

2.2 Measurements of infrared spectra and conductivity

Transmission infrared (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 used. In order to obtain spectra with a high signal-to-noise ratio, 128 interferograms were co-added.

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. A SANWA AU-32 multitester or a Keithley Type 2001 digital multimeter was used.

3. RESULTS AND DISCUSSION

Figure 2 shows typical absorption spectra of the 2C$_n$-Au(dmit)₂ LB films (n=8, 10, 12, 14, 16, 18) in the region of 2800-3000 cm^{-1}. Distinct absorption bands at around 2850 cm^{-1} and 2920 cm^{-1} are due to the CH₂ symmetric stretching band (CH₂ v_s) and CH₂ antisymmetric one (CH₂ v_{as}), respectively. As shown in Fig. 3(a), the both bands, CH₂ v_s and CH₂ v_{as}, tend to increase with increasing the chain length. Furthermore, in Fig. 3(b), the absorbance of the CH₂ v_s and CH₂ v_{as} bands shown in Fig. 3(a) are re-plotted as the values per CH₂ moiety. The both bands tend to increase with increasing the chain length, although the intensities of the 2C₁₂-Au(dmit)₂ system and 2C₁₄-Au(dmit)₂ one are almost the same. Since the incident beam is surface normal, the signals from transition moments aligned along the film plane can be detected stronger than those from other alignments. We assume that the longer the chain length is, the more upright the principal axis stands in such a way that the transition moments of the CH₂ v_s and CH₂ v_{as} bands tend to be aligned more parallel to the film plane.
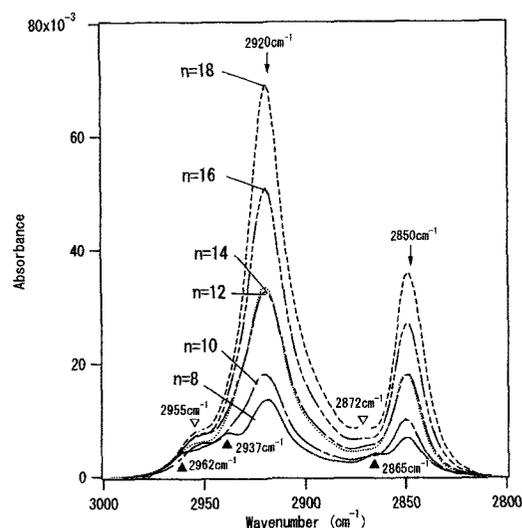
Figure 4 shows the values of the

Fig. 2. Typical transmission infrared (IR) absorption spectra of the as-deposited 2C$_n$-Au(dmit)₂ LB films (n=8,10,12,14,16,18) in the region of 2800-3000 cm^{-1}.
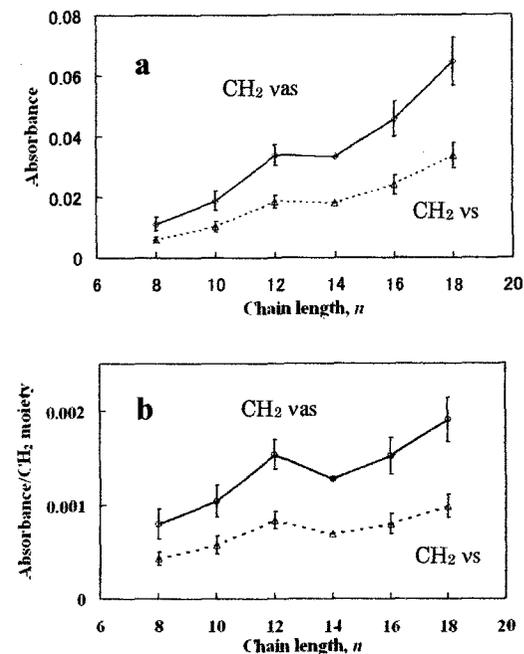

Fig. 3. Absorbance of the CH₂ symmetric stretching band (dotted lines, CH₂ v_s, 2850 cm^{-1}) and CH₂ antisymmetric one (solid lines, CH₂ v_{as}, 2920 cm^{-1}) plotted against the length of alkyl chains, n (a) and the values per CH₂ moiety re-plotted (b). The data are of the averages of at least three data.

full-width-half-height (FWHH) of the CH₂ v_s and CH₂ v_{as} bands plotted against the chain length, n. The data are of the averages of at least three data. The FWHH values of the both bands tend to decrease with increasing the chain length, n, indicating that the relative amount of
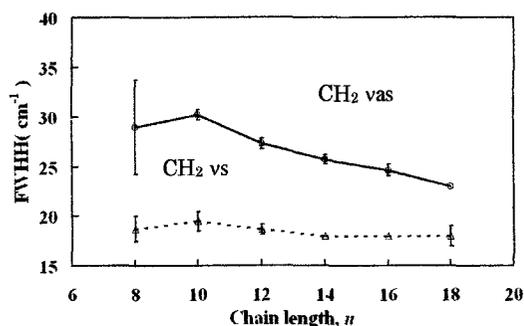
Fig. 4. The full-width half height (FWHH) of the CH_2 symmetric stretching band (dotted lines, CH_2 v_s, 2850 cm^{-1}) and CH_2 antisymmetric one (solid lines, CH_2 v_{as}, 2920 cm^{-1}) plotted against the number of chain length, n.

gauche forms decreases in the hydrocarbon chains with increasing n. It should be noted here that the chain length dependence of the CH_2 v_s band is not noticeable as that of the CH_2 v_{as} band is. Since the $2C_n$-Au(dmit)$_2$ systems have two alkyl chains, both of the intra- and inter-molecular interactions should be taken into account in order to interpret the stretching modes.

Furthermore, as shown in Fig. 2, in the spectra of the $2C_n$-Au(dmit)$_2$ LB systems, when n=10, 12, 14, 16 and 18, a common peak and a shoulder are seen at around 2872 cm^{-1} and 2955 cm^{-1}, respectively. The peak at 2872 cm^{-1} and the shoulder at 2955 cm^{-1} are assigned as CH_3 symmetric stretching band and CH_3 asymmetric stretching one, respectively [10, 11]. The spectrum of the $2C_8$-Au(dmit)$_2$ LB system, however, has three pronounced peaks at around 2865 cm^{-1}, 2937 cm^{-1} and 2962 cm^{-1}, which are ascribed as CH_3 symmetric stretching, CH_3 symmetric stretching (Fermi resonance) and CH_3 asymmetric bands, respectively [10, 11]. Among the series of the $2C_n$-Au(dmit)$_2$ LB systems (n=8, 10, 12, 14, 16 and 18), the $2C_8$-Au(dmit)$_2$ LB has unique electrical properties; for instance, conductivity as high as 10^0-10^1 S/cm can be often obtained without any post treatment [12].

Table 1. The room-temperature conductivity of the 2C$_n$-Au(dmit)$_2$ LB systems

Chain length, n	Conductivity at room temperature
8	46±20 S/cm
10	54±28 S/cm
12	70±21 S/cm
14	73±26 S/cm
16	10±5 S/cm
18	2.2±0.6 S/cm

The room-temperature conductivities of the 2C$_n$-Au(dmit)$_2$ LB systems with various chain lengths (n=8, 10, 12, 14, 16 and 18) are summarized in Table 1. The values are of maximal ones obtained during the electrochemical oxidation process and are the averages of 6-57 different sample batches. The thickness is assumed to be 3 nm per layer. We consider that the difference in conductivity can be interpreted by

analyzing the order of the alkyl chains together with the estimation of the charge-transfer (CT) degrees. Further studies for analyzing the structure of the hydrocarbon chains in the 2C$_n$-Au(dmit)$_2$ LB films with various chain lengths may reveal the correlation between the structure and electrical conductivity of the 2C$_n$-Au(dmit)$_2$ LB systems.

4. CONCLUSION

The infrared (IR) spectra of the 2C$_n$-Au(dmit)$_2$ LB systems with various chain lengths (n=8, 10, 12, 14, 16, 18) were measured and discussed focusing on the region of 2800-3000 cm^{-1}, where the CH_2 symmetric stretching band (CH_2 v_s) and CH_2 antisymmetric one (CH_2 v_{as}) exist. The absorbance of the CH_2 v_s and CH_2 v_{as} bands per CH_2 moiety tends to increase associated with the appreciable narrowing with increasing the chain length. It has been revealed that the longer the chain length is, the more upright the principal axis stands with less amounts of gauche C-C bonds. Furthermore, it has been revealed that the room-temperature conductivity strongly depends on the chain length. The difference in conductivity can be interpreted not only by the charge-transfer ratio but also by the order of the hydrocarbon chains in the 2C$_n$-Au(dmit)$_2$ LB systems.

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