

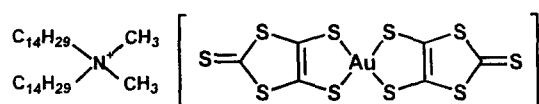
## Structure of the Conductive Langmuir-Blodgett (LB) Films Based on Metal-Dithiolene Complexes

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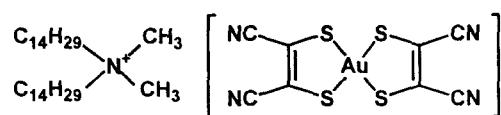
The conductive Langmuir-Blodgett (LB) films based on ditetradecyldimethylammonium-Au(mnt)<sub>2</sub> (2C<sub>14</sub>-Au(mnt)<sub>2</sub>) complex are studied mainly focusing on the improvement of the film quality using matrices. It is suggested that the 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex is well-spread using the matrix of ditetradecyldimethylammonium-bromine (2C<sub>14</sub>-Br) than using arachidic acid (C<sub>20</sub>). Although the reproducible film depositions have been realized for both of the pure and mixed systems, all the LB systems of three types based on the 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex are insulative ( $\sigma_{//R.T.} < 10^{-6}$  S/cm) except a sample batch of the pure 2C<sub>14</sub>-Au(mnt)<sub>2</sub> LB system that has the in-plane conductivity of 10<sup>-3</sup> S/cm. The phase separation seems to limit the macroscopic conductivity.  
 Keywords: Au(mnt)<sub>2</sub> complex, conductive Langmuir-Blodgett (LB) film,  $\pi$ -A isotherm, in-plane conductivity

### INTRODUCTION

There have been a great deal of attention to fabricate molecular ultra-thin films of high electrical conductivity for possible electronic device applications in the future [1]. As the technique to construct the organized ultra-thin systems whose thickness is less than 0.1  $\mu$ m, Langmuir-Blodgett (LB) technique is interesting because it allows us to perform layer-by-layer transfer of monomolecular films from the water surface to solid supports [1]. One great advantage of the LB technique over other methods is that all the film-forming processes are performed at room temperature. In fact, the vacuum deposition technique is applicable to limited numbers of molecular systems because of the thermal decomposition.



Ditetradecyldimethylammonium-Au(dmit)<sub>2</sub>  
 (2C<sub>14</sub>-Au(dmit)<sub>2</sub>)



Ditetradecyldimethylammonium-Au(mnt)<sub>2</sub>  
 (2C<sub>14</sub>-Au(mnt)<sub>2</sub>)

As the film-forming material, metal-dithiolene complexes, such as metal(dmit)<sub>2</sub> and metal(mnt)<sub>2</sub>, are intriguing because of the variety of the electronic properties ranging from semiconducting to superconducting [2]. We have already reported that the LB systems of dialkyldimethylammonium-Au(dmit)<sub>2</sub> (2C<sub>n</sub>-Au(dmit)<sub>2</sub>), where H<sub>2</sub>dmit stands for 4,5-dimercapto-1,3-dithiole-2-thione, exhibit high in-plane conductivities in the range 10<sup>0</sup>-10<sup>1</sup> S/cm after electrochemical oxidation [3,4]. In particular, the LB system of ditetradecyldimethylammonium-Au(dmit)<sub>2</sub> (2C<sub>14</sub>-Au(dmit)<sub>2</sub>) exhibits a metallic temperature dependence of the conductivity in the range 200-300 K [4]. Furthermore, a possible superconducting phase is suggested in the 2C<sub>14</sub>-Au(dmit)<sub>2</sub> system below 3.9 K, which is evidenced by the ac complex magnetic susceptibility [5].

We consider that the 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex is one of the interesting film-forming constituents because of the relevance to 2C<sub>14</sub>-Au(dmit)<sub>2</sub> complex. There are several reports on metal(mnt)<sub>2</sub> LB systems [6], however, no report has come to our knowledge as for the LB systems based on Au(mnt)<sub>2</sub>

complexes. In this paper, we report on the conductive LB film fabricated with ditetradecyldimethylammonium-Au(mnt)<sub>2</sub> (2C<sub>14</sub>-Au(mnt)<sub>2</sub>) mainly focusing on the effect of matrix molecules to improve the film quality.

#### EXPERIMENTAL

The 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex was synthesized following the procedure of Davison and Holm [7]. Three LB systems have been prepared: (a) the pure 2C<sub>14</sub>-Au(mnt)<sub>2</sub> system, (b) 1/1 mixture of Au(mnt)<sub>2</sub> and ditetradecyldimethylammonium-bromide (2C<sub>14</sub>-Br) and (c) 1/1 mixture of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> and arachidic acid (C<sub>20</sub>). The systems were spread on the water surface using the 1/1 mixture of benzene and acetonitrile (0.25 mM). The subphase water with the resistivity larger than  $1.8 \times 10^7 \Omega \cdot \text{cm}$  was prepared using a Milli-Q SP reagent water system (Millipore Co., Ltd.). The surface pressure ( $\pi$ ) vs. area per molecule (A) isotherms were measured at a compression speed of  $0.067 \text{ \AA}^2/(\text{molecule} \cdot \text{s})$  at 17 °C using a home-made trough. The floating salts were compressed to 20–25 mN/m and transferred onto solid substrates by the horizontal lifting method. The surface pressure was measured by a Wilhelmy-type surface balance.

As for the samples for measuring the in-plane electrical conductivity ( $\sigma_{//}$ ), gold was first vacuum-deposited onto the glass substrates through a mask to form electrodes with gaps of 0.5 mm, and then the floating films were transferred onto the electrode-coated substrates. The as-deposited LB films were electrochemically oxidized in an aqueous solution of LiClO<sub>4</sub> following the procedure of Nakamura *et al* [8]. A positive potential was applied to the gold electrodes underneath the LB films and a constant current of 0.8  $\mu\text{A}$  was applied for 150 min using a counter electrode of platinum. The lateral conductivities of the 20-layered LB films were measured by a dc two-probe method utilizing gold electrodes deposited underneath the LB films.

The UV/visible absorption spectra of the LB films deposited onto the quartz glass substrates were recorded by a Shimadzu UV-2100 spectrometer. The FT-IR absorption spectra of the LB films were recorded by a Perkin-Elmer System-2000 spectrometer using CaF<sub>2</sub> plates as

the substrates.

The quartz glass substrates were hydrophobized by keeping them in a container filled with the vapor of 1,1,1,3,3,3-hexamethyldisilazane for more than one day. The CaF<sub>2</sub> plates were hydrophobized by the deposition of five layers of cadmium arachidate on both sides.

#### RESULTS AND DISCUSSION

Figure 1 shows the  $\pi$ -A isotherms obtained for the pure system (2C<sub>14</sub>-Au(mnt)<sub>2</sub>, curve A), the 1/1 mixture of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> and 2C<sub>14</sub>-Br (2C<sub>14</sub>-Au(mnt)<sub>2</sub>/2C<sub>14</sub>-Br, curve B) and the 1/1 mixture of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> and C<sub>20</sub> (2C<sub>14</sub>-Au(mnt)<sub>2</sub>/C<sub>20</sub>, curve C). As for the mixed systems, the abscissa shows the averaged areas occupied by the two components.

The 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex occupies 7  $\text{\AA}^2$  at 20 mN/m in the pure system, as shown by curve A in Fig. 1. The occupied area of 7  $\text{\AA}^2$  is too small considering that the dialkyldimethylammonium moiety typically occupies 40  $\text{\AA}^2$  in the monomolecular system. This suggests that the 2C<sub>14</sub>-Au(mnt)<sub>2</sub> complex forms a quasi-three dimensional (Q-3D) structure which has the thickness of several molecular layers.

The averaged area per molecule of the mixed system of 2C<sub>14</sub>-Au(mnt)<sub>2</sub>/2C<sub>14</sub>-Br is 32  $\text{\AA}^2$  at 20 mN/m, as shown by curve B in Fig. 1. Then the occupied area of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> moiety in the mixed system is estimated to be 24  $\text{\AA}^2$ ,

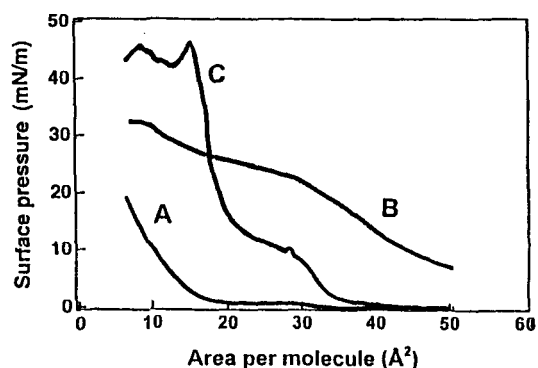


Fig. 1 The  $\pi$ -A isotherms of the (A) pure 2C<sub>14</sub>-Au(mnt)<sub>2</sub>, (B) 1/1 mixture of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> and 2C<sub>14</sub>-Br, and (C) 1/1 mixture of 2C<sub>14</sub>-Au(mnt)<sub>2</sub> and C<sub>20</sub>. The abscissa is the averaged value of two components as for the mixed systems.

assuming that the occupied area of the  $2C_{14}$ -Br matrix is  $40 \text{ \AA}^2$  at 20 mN/m. The occupied area of  $2C_{14}$ -Au(mnt)<sub>2</sub> moiety ( $24 \text{ \AA}^2$ ) corresponds to one half of the typical cross section of the dialkyldimethylammonium moiety, which suggests the formation of a quasi-two dimensional (Q-2D) structure, e.g. a bilayer-like one, on the water surface.

On the other hand, the averaged area per molecule of the mixed system of  $2C_{14}$ -Au(mnt)<sub>2</sub>/ $C_{20}$  is  $17 \text{ \AA}^2$ , as shown by curve C in Fig. 2. Then the occupied area of the  $2C_{14}$ -Au(mnt)<sub>2</sub> moiety in the mixed system is estimated to be  $14 \text{ \AA}^2$ , assuming the typical area per molecule of  $20 \text{ \AA}^2$  for  $C_{20}$  at 20 mN/m. The value of  $14 \text{ \AA}^2$  is still too small considering the existence of two alkyl chains of the dialkyldimethylammonium moiety, suggesting the formation of the Q-3D structure on the water

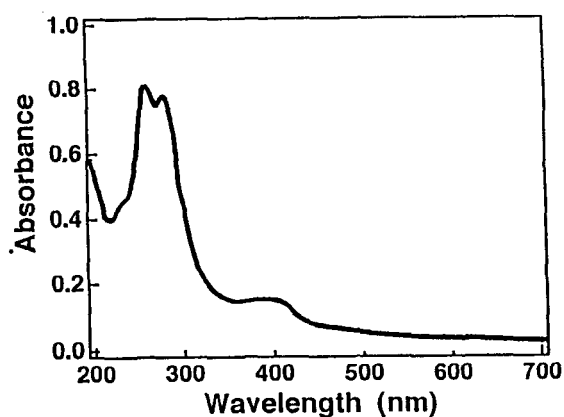


Fig. 2(a) The UV/visible absorption spectrum of the 15-layered LB system of  $2C_{14}$ -Au(mnt)<sub>2</sub> complex.

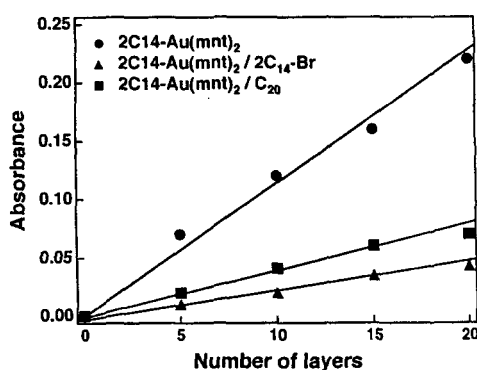


Fig. 2(b) The absorbance at 400 nm of the pure and the mixed LB systems; (●):  $2C_{14}$ -Au(mnt)<sub>2</sub>, (▲): 1/1 mixture of  $2C_{14}$ -Au(mnt)<sub>2</sub>/ $2C_{14}$ -Br, and (■): 1/1 mixture of  $2C_{14}$ -Au(mnt)<sub>2</sub>/ $C_{20}$ .

surface, although the average thickness of the Q-3D aggregates seems to be one half than those in the pure  $2C_{14}$ -Au(mnt)<sub>2</sub> system.

Figure 2(a) shows the typical UV/visible absorption spectrum of the as-deposited LB film of the pure  $2C_{14}$ -Au(mnt)<sub>2</sub> complex. The absorbance of the distinct peaks at 400 nm are plotted against number of deposited layers, as shown in Fig 2(b). As shown in Fig 2(b), the absorbance of the distinct peaks at 400 nm increases linearly with the number of layers for the pure and the mixed systems, indicating the reproducible film deposition up to 20 layers.

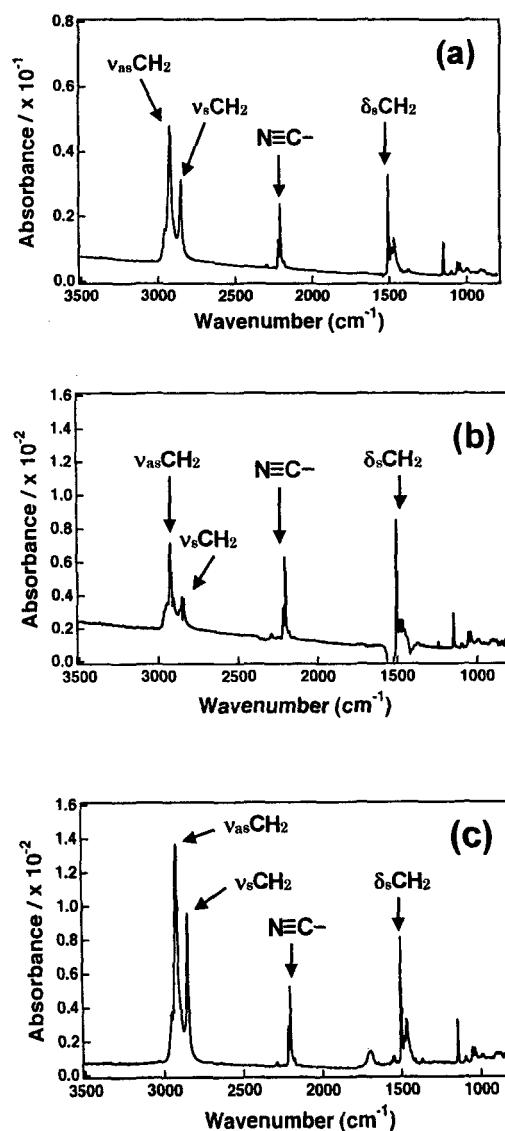


Fig. 3 The IR absorption spectra for the 20-layered LB films of (a)  $2C_{14}$ -Au(mnt)<sub>2</sub>, (b)  $2C_{14}$ -Au(mnt)<sub>2</sub>/ $2C_{14}$ -Br, and (c)  $2C_{14}$ -Au(mnt)<sub>2</sub>/ $C_{20}$

Figure 3 shows the IR spectra of the 20-layered LB films of (a)  $2C_{14}\text{-Au(mnt)}_2$ , (b)  $2C_{14}\text{-Au(mnt)}_2/2C_{14}\text{-Br}$  and (c)  $2C_{14}\text{-Au(mnt)}_2/C_{20}$ .

Some of the key bonds are as follows:  $2918\text{ cm}^{-1}$ ,  $\text{CH}_2$  asymmetric stretching,  $\nu_{\text{as}}\text{CH}_2$ ;  $2850\text{ cm}^{-1}$ ,  $\text{CH}_2$  symmetric stretching,  $\nu_{\text{s}}\text{CH}_2$ ;  $1471\text{ cm}^{-1}$ ,  $\text{CH}_2$  symmetric scissoring,  $\delta_{\text{s}}\text{CH}_2$ ;  $2222\text{ cm}^{-1}$ ,  $\text{N}\equiv\text{C}$  stretching.

The absorbance of the  $\text{N}\equiv\text{C}$  stretching mode for the mixed LB films ( $2C_{14}\text{-Au(mnt)}_2/2C_{14}\text{-Br}$  and  $2C_{14}\text{-Au(mnt)}_2/C_{20}$  LB films) are 25% of that of the pure  $2C_{14}\text{-Au(mnt)}_2$  LB system, indicating the decrease of the complex deposited on the substrates. The absorbance at  $1417\text{ cm}^{-1}$  ( $\delta_{\text{s}}\text{CH}_2$ ) is also 25% compare to the pure system, which coincides well with the decrease of the absorbance of the mode for  $\text{N}\equiv\text{C}$  stretching. However, as for the mixed LB film of  $2C_{14}\text{-Au(mnt)}_2/2C_{14}\text{-Br}$ , the absorbance at  $2850\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{CH}_2$ ) is 13% of that of the pure system, which is incompatible with the decrease for the  $\delta_{\text{s}}\text{CH}_2$  and  $\text{N}\equiv\text{C}$  stretching modes if we assume that the decrease in absorbance is simply due to the decrease of the amount of the substance deposited onto the substrate. The cause of the incompatibility is now under investigation together with that the mode of  $\nu_{\text{s}}\text{CH}_2$  for the mixed LB system of  $2C_{14}\text{-Au(mnt)}_2/2C_{14}\text{-Br}$  is splitting.

It was demonstrated that the structure of the  $2C_{14}\text{-Au(mnt)}_2$  LB films were changed by using the matrix molecules of  $2C_{14}\text{-Br}$  and  $C_{20}$ . The spreading effect of  $2C_{14}\text{-Br}$  is better than that of  $C_{20}$ . Although the reproducible film depositions have been realize for both of the pure and the mixed systems, the electrochemically-oxidized LB systems of the three types are insulative ( $\sigma_{//R.T.} < 10^{-6}\text{ S/cm}$ ) except a sample batch of the pure  $2C_{14}\text{-Au(mnt)}_2$  LB system that has the in-plane conductivity of  $10^{-3}\text{ S/cm}$ . This is probably because the phase separation of the  $2C_{14}\text{-Au(mnt)}_2$  complex and matrix in the LB films and/or insufficient oxidation condition. Further optimization of the film-forming conditions is now in progress.

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