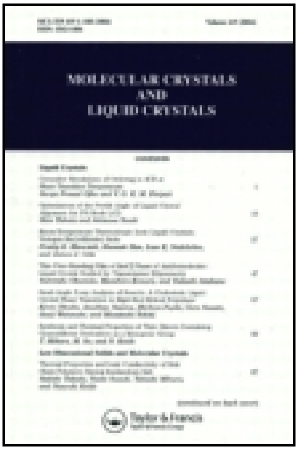

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Structure and Properties of Highly Conductive Langmuir-Blodgett Films Based on Dialkyldimethylammonium-metal(dmit)$_2$

Yasuhiro F. Miura [a] , Takumi Kawasaki [a] , Hideaki Ohnishi [a] , Yoshihito Okuma [a] & Michio Sugi [a]

[a] Toin University of Yokohama, Department of Materials Science, 1614 Kurogane-cho, Aoba, Yokohama, 225, Japan

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YASUHIRO F. MIURA, TAKUMI KAWASAKI, HIDEAKI OHNISHI,
YOSHIHITO OKUMA, and MICHIO SUGI
Toin University of Yokohama, Department of Materials Science
1614 Kurogane-cho, Aoba, Yokohama 225, Japan

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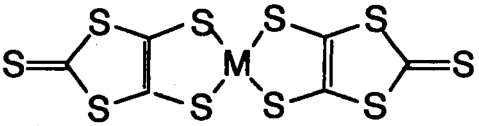
Structure and electrical properties of conductive LB films based on dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) are studied. UV/visible polarized absorption spectra suggest that the longer axis of Au(dmit)$_2$ is appreciably tilted against the film plane. Both of the as-deposited and electrochemically oxidized LB films give sharp X-ray diffraction peaks at $2\theta = 3.15°$ indicating a d-spacing of 2.8 nm. The in-plane conductivity of the film is semiconductor-like with an activation energy of 0.05 eV.

Keywords: Metal(dmit)$_2$; Conductive LB films; Electrochemical oxidation; In-plane conductivity.

INTRODUCTION



Chemical Structure of Metal(dmit)$_2$ (where M = Ni, Au, Pd, Pt, Zn, Cu)

The sulfur-rich anion, metal(dmit)$_2$, is one of the intriguing candidates for constructing conductive LB films because of the wide varieties of electronic properties ranging from semiconductive to superconductive[1]. The initial reports on conductive LB films based on alkylammonium-metal(dmit)$_2$[2,3] attracted much attention and a great deal of progress has been made since then[4]. In particular, the LB system based on tridecylmethylammonium-Au(dmit)$_2$ (3C10-Au) exhibits the in-plane conductivity as high as 10^1 S/cm at room temperature showing a metallic temperature dependence[5]. However, careful efforts revealed that the metal(dmit)$_2$ LB systems are heterogeneous and the macroscopic transport properties are limited by ill-conductive regions[6-9]. The assignments of the limiting regions are controversial because the most metal(dmit)$_2$ LB systems utilize arachidic acid as the matrix and there should be ill-doped regions after the post-treatments.

We consider that studies on metal(dmit)$_2$ LB systems without matrices will give us more straightforward information which helps establish proper models to understand the systems. We have fabricated the LB films based on dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) without matrices and reported that the in-plane conductivities are 1-3 orders of magnitude higher than those of the corresponding systems when arachidic acid is used as the matrix with 1:1 molar ratio[10]. Here we report the measurements of polarized UV/visible absorption spectra, X-ray powder diffraction and the in-plane electrical conductivity in the temperature range 93-283 K and discuss the structure and electrical properties.

EXPERIMENTAL

The dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) is synthesized following the procedure of Steimecke et al[11]. 2C18-Au was spread on the air/water interface using the 1:1 mixture of acetonitrile and benzene as the solvent. The floating films were transferred onto solid substrates by horizontal lifting method at 25 mN/m. Then the as-deposited films were electrochemically oxidized following the procedures of Nakamura et al.[12] The details of the sample preparation are described elsewhere.[10]

Polarized UV/visible absorption spectra of the LB films deposited on quartz substrates were measured using a Shimadzu UV-2100 spectrophotometer. X-ray powder diffraction measurements were performed using a Shimadzu XD610 X-ray diffractometer; Cu-K_α was used. The in-plane conductivity was measured by a dc 4-probe method using a Keithley model 2001 digital multimeter with a Keithley model 220 programmable current source in the temperature range 93-283 K; gold electrodes underneath the LB layers were used for the measurements.

RESULTS AND DISCUSSION

The as-deposited films have absorption peaks at 300 nm, 369 nm and 489 nm.[10] The polarized UV/visible absorption measurements revealed that all the three absorption bands are isotropic in the film plane. For estimating the tilting angle of Au(dmit)$_2$ against the film plane, the substrate plane was rotated against the axis of the incident beam (the inclination angle = α), as shown in Figure 1. The polar angle of the transition dipole moment μ is defined by θ and ϕ. The polarized incident beam is along Z axis with its

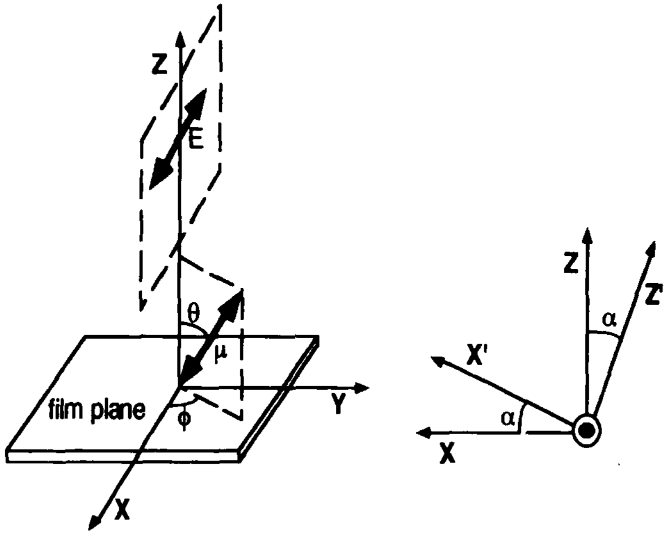


FIGURE 1. Procedure for estimating the inclination angle of Au(dmit)$_2$ against the film plane. The incident beam of the linearly polarized light is along Z axis with its electrical vector in X-Y plane.

electric vector in X-Y plane, as shown in Fig. 1. In such a case, the inclination-angle-dependent peak intensity A(α) due to the transition dipole moment μ is expressed as:

$$A(\alpha) \propto \frac{\frac{1}{2}(1-3\cos^2\theta)\cos^2\alpha+\cos^2\theta}{\cos\alpha}, \qquad (1)$$

assuming the in-plane isotropy.[13]

Figure 2 shows the observed inclination-angle dependence of the peak absorbance at 489 nm. The data are well fitted by eq. (1) assuming that $\theta = 73°$ (curve e). This leads us to a picture that the angle between the longer axis of the $Au(dmit)_2$ anion and the film plane is about 17 ° which is in agreement with the estimated tilting angle of $Au(dmit)_2$ proposed by Matsuzaki et al. for interpreting their X-ray powder diffraction profile of 3C10-Au LB films.[9] In an accurate treatment, the inclination angle α should be corrected using the refractive index of *n*. However, we neglected such a correction this time because of the complexity for determining refractive index of molecular films with a thickness comparable or smaller than the wavelength.[13]

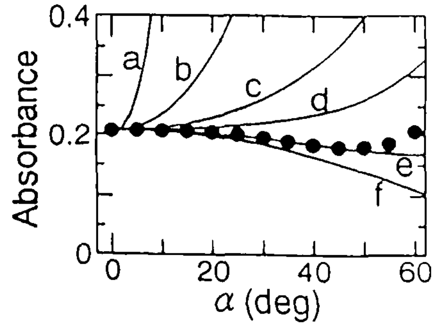


FIGURE 2. Observed inclination-angle dependence of the peak absorbance at 489 nm (closed circles). Solid lines refer to the behaviors calculated using eq. (1) ; (a) θ= 10° , (b) θ=30° , (c) θ=50° , (d) θ=60° , (e) θ=73° and (f) θ=90° .

The as-deposited LB films gave a sharp diffraction peak at $2\theta = 3.15°$ which corresponds to a d-spacing of 2.8 nm if this is the first-order diffraction. Electrochemical oxidation did not change the position of the diffraction peak. However, the peak intensity tended to decrease appreciably suggesting a slight disorder created in the film during the post treatment. We have already reported that 2C18-Au might form a bilayer on the water surface considering the measured occupied area of 22 Å^2.[10] The sharp diffraction at $2\theta = 3.15°$ is possibly the second-order diffraction if the present multilayer is a stacking of the bilayer on the water surface. X-ray powder diffraction at lower 2θ angles are now in progress.

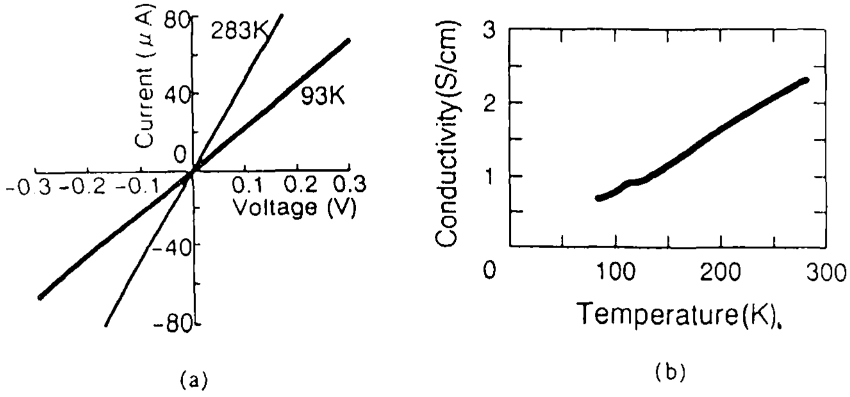


FIGURE 3. (a) Current-voltage(I-V) characteristics of a 20-layered 2C18-Au LB film at 93 K(○) and 283 K(●); (b) Temperature dependence of the in-plane conductivity of the 20-layered 2C18-Au LB film in the temperature range 93-283 K.

Figure 3(a) shows the current-voltage(I-V) characteristics of a 20-layered 2C18-Au LB film at 93 and 283 K. Within the range I-V characteristics was linear over the entire temperature range. Figure 3(b) shows the temperature dependence of the in-plane conductivity of the 20-layered 2C18-Au LB film in the temperature range 93-283 K; a constant current of 10μA was used. An assumed thickness of 3 nm/layer was used for the calculation. The conductivity gradually increases with increasing temperature, exhibiting a semiconductor-like behavior over the whole temperature range. The activation energy estimated from Arrhenius' plot is 0.02 eV.

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