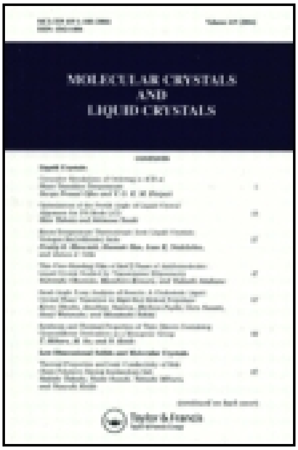

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Highly Conductive Langmuir-Blodgett Films Based on Dialkyldimethylammonium-Metal(DMIT)$_2$

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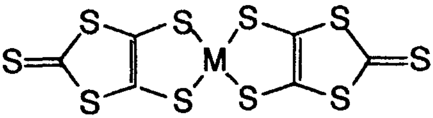
Structure and electrical conductivities of the mixed LB films of dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) and arachidic acid (C20) are studied with various mixing ratios. The in-plane conductivity at room temperature decreases with increasing the molar mixing ratio of C20. Both the as-deposited and electrochemically-oxidized LB films give sharp X-ray diffraction peaks at $2\theta = 3.15°$ indicating a d-spacing of 2.8 nm which is identical to that of pure 2C18-Au system. It is suggested that the 2C18-Au complex forms an identical layered structure both in the pure and the mixed systems.

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)

As a film-forming material for constructing conductive LB films, a great deal of attention has been paid to the sulfur-rich anion metal(dmit)$_2$ because the bulk salts exhibit wide varieties of electronic properties ranging from semiconducting to superconducting[1]. In fact, various conductive LB systems have been fabricated introducing amphiphilic counter cations such as alkylammoniums or alkylpyridiniums[2]. Among them, the LB film of a 1:1 mixture of arachidic acid (C20) and tridecylmethylammonium-Au(dmit)$_2$

(3C10-Au) exhibits the in-plane conductivity as high as 10^1 S/cm at room temperature after an electrochemical oxidation [3]. However, it has been found that the mixed system of C20 and 3C10-Au is heterogeneous and the macroscopic transport is limited by ill-conductive regions[4-7]. In such a system, it is difficult to assign the limiting regions since both the matrix and the ill-oxidized regions can be the limiting regime.

We consider that the studies on the effect of the matrix molecules in the mixed systems can yield crucial information for understanding the systems. We have already reported that dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) forms films of good quality at the air/water interface without the use of matrix molecules and that the in-plane conductivity of the electrochemically-oxidized film reaches 2 S/cm, which is 1-3 orders of magnitude higher than those of the corresponding system when arachidic acid is used as the matrix with a 1:1 molar ratio[8]. Here we report the in-plane conductivities of the mixed LB films of 2C18-Au and C20 with various molar mixing ratios and compare the mixed systems with the pure 2C18-Au system.

EXPERIMENTAL

The dioctadecyldimethylammonium-Au(dmit)$_2$ (2C18-Au) is synthesized following the procedure of Steimecke *et al.*[9] The pure 2C18-Au or the mixtures of 2C18-Au and arachidic acid (C20) were spread on the air/water interface using the 1:1 mixture of acetonitrile and benzene as the solvent. In the binary system, the C20 ratio, [C20] / ([C20]+[2C18-Au]), was 0.14, 0.25, 0.33, 0.40, 0.44 or 0.50. The floating films were transferred onto solid substrates by the horizontal lifting method at 25 mN/m. The as-deposited films were electrochemically oxidized in an aqueous solution of $LiClO_4$ following the procedures of Nakamura *et al.*[10] The details of the sample preparation are given in a previous paper.[8]

X-ray powder diffraction measurements were performed using a Shimadzu XD610 X-ray diffractometer using Cu K_α source. The in-plane conductivities of the pure 2C18-Au system and the binary systems of 2C18-

Au and C20 were measured by a dc 4-probe method using a Keithley model 2001 digital multimeter with a Keithley model 220 programmable current source at room temperature. Gold electrodes beneath the LB layers were used for the measurements. Twenty-layered LB films were used unless otherwise stated.

RESULTS AND DISCUSSION

The as-deposited films of the pure 2C18-Au gave a sharp diffraction peak at $2\theta = 3.15°$ which corresponds to a d-spacing of 2.8 nm assuming that the angle is of 1st-order diffraction; diffraction peaks up to 4th order have been observed. The electrochemically-oxidized films of the pure 2C18-Au also gave a sharp diffraction at $2\theta = 3.15°$, however, the intensity tends to be lower than that of the as-deposited films suggesting a structural disorder created during the oxidation.

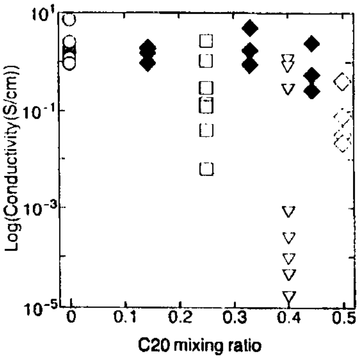


FIGURE 1. Logarithms of the conductivity of the mixed systems of 2C18-Au and C20, where the molar C20 ratio, [C20] / ([C20]+[2C18-Au]) = 0, 0.14, 0.25, 0.33, 0.40, 0.44 or 0.50.

The mixed systems of 2C18-Au and C20 with various C20 ratios (the C20 ratio, [C20] / ([C20]+[2C18-Au]) = 0.14, 0.25, 0.33, 0.40, 0.44 or 0.50) also gave diffraction peaks at $2\theta = 3.15°$ which is in good agreement with the d-spacing of the pure 2C18-Au system (2.8 nm). The intensity of each diffraction peak decreases with increasing the C20 ratio. We have already reported that the π-A isotherms of the pure 2C18-Au system and the 1:1 mixture of 2C18-Au and C20 suggest that 2C18-Au and C20 are phase-separated and that 2C18-Au complex forms an bilayer-like structure both in the pure and the mixed films at the air/water interface[8]. The observed X-ray diffractions are consistent with the above postulation.

Figure 1 shows logarithms of the conductivity of the mixed systems of 2C18-Au and C20 at room temperature plotted against the C20 ratio, [C20] / ([C20]+[2C18-Au]). The conductivity decreases with increasing the molar mixing ratio of C20, however, the conductivity data at a C20 ratio of 0.40 are scattered, as shown in Fig. 1. Further studies are now in progress concerning the correlation between the conductivities and the structures of the mixed systems of 2C18-Au and C20.

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