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Structural Control of Alkylammonium-Au(dmit)$_2$ LB Films

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The structure of conductive LB films based on dioctadecyldimethylammonium-Au(dmit)$_2$ ($2C_{18}$-Au(dmit)$_2$) is studied by introducing into a parameter, "waiting time", which is defined as the time between the application of spreading solvent and the onset of compression. The π-A isotherms and the Brewster angle microscopy suggest that $2C_{18}$-Au(dmit)$_2$ complex forms multi-layered films on the water surface, whereas, the in-plane conductivity of the LB films after anodic oxidation increases with increasing the "waiting time".

Keywords: Au(dmit)$_2$; conductive LB film; in-plane conductivity

INTRODUCTION

Dioctadecyldimethylammonium-Au(dmit)$_2$ ($2C_{18}$-Au(dmit)$_2$) complex, whose structure is indicated in the inset of figure 1, is one of the intriguing candidates for constructing conductive LB films because

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of its high conductivity at room temperature after anodic oxidation [1].

Gupta *et al.* reported that the aggregation state of Metal(dmit)$_2$ complex is sensitive to various subphase conditions[2],[3]. Among them, the "waiting time", which is defined as the time between the application of the spreading solvent and the onset of compression, is an interesting parameter. We have focused on $2C_{18}$-Au(dmit)$_2$ complex and fabricated the LB films with varying the "waiting time". In this paper, we report the "time-domain" control of the structure of $2C_{18}$-Au(dmit)$_2$ LB films utilizing the film-forming parameter, "waiting time".

EXPERIMENTAL

The dioctadecyldimethylammonium-Au(dmit)$_2$ ($2C_{18}$-Au(dmit)$_2$) complex was synthesized following the procedure of Steimecke *et al.*[4] and spread on the water surface using the 1:1 mixture of acetonitrile and benzene as the solvent.

A KSV-5000 trough was used for π -A isotherm measurement. The KSV-5000 trough and a homemade trough whose dimension is the same with that of the KSV-5000 were used for film deposition. The "waiting time" was varied from 5 minutes up to 120 minutes for both of the film deposition and of the π -A isotherm measurements. The morphological studies of the floating films of $2C_{18}$-Au(dmit)$_2$ complex were performed using Brewster angle microscopy (BAM). Then the floating complexes at the water surface were compressed to 25 mN/m and were transferred onto solid supports by horizontal lifting method.

The as-deposited films were electrochemically oxidized in an aqueous solution of $LiClO_4$. The details of the sample preparation are in the previous papers[1],[5].

RESULTS AND DISCUSSION

Figure 1 shows the typical π -A isotherms of $2C_{18}$-Au(dmit)$_2$ complex that are observed with various "waiting times". The area per complex

at 25 mN/m where the film deposition was carried out is 10Å^2 for a π-A isotherm obtained for the "waiting time" of 5 min. The occupied area is too small if the limiting area of dialkyldimethylammonium(40-50 Å^2) is taken into account, suggesting that the complexes form a multi-layered structure on the water surface. The occupied area of the complex increases to 16Å^2 for the "waiting time" of 30 min and it reaches 27Å^2 for the "waiting time" of 120 min.

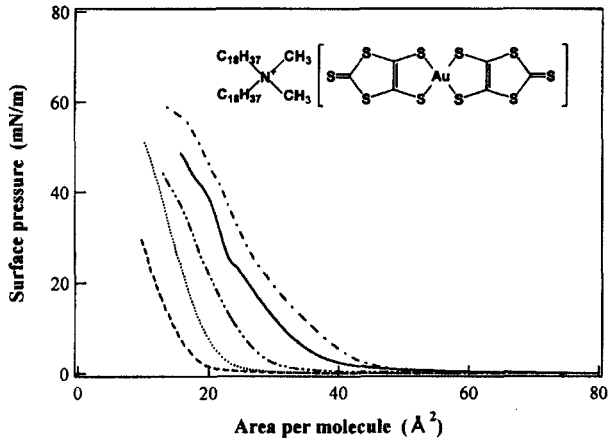

FIG. 1 The π-A isotherms obtained for $2C_{18}$-Au(dmit)$_2$ complex with "waiting times" of 5 min(---), 30 min(····), 60 min(—··—), 90 min(—) and 120 min(—··); subphase tempemperature=17 ℃.

Figure 2 shows the BAM image obtained for $2C_{18}$-Au(dmit)$_2$ complex for the "waiting time" of 5 min during film compression, where the surface pressure was 0 mN/m. The rate of compression was 0.067Å^2 /molecule·min. The bright parts correspond to the cluster of complexes, whereas the dark ones may reflect the absence of the films. The results lead to a picture that the complexes on the water surface are coagulated and the film has a quasi 3D structure such as a multi-layered one, immediately after the application of spreading solvent, and then

FIG. 2 The BAM image of the $2C_{18}$-Au(dmit)$_2$ complex during the compression ; subphase temperature=17 ℃.

the films would relax to a lower-dimensional structure with the "waiting time".

The atomic force microscopy (AFM) revealed that the surface of the LB films tends to have "lower-dimensional structure" with increasing the "waiting time". Our preliminary conductivity measurement indicates that the in-plane conductivity of the films tends to increase with increasing the "waiting time".

References

[1] Y.F. Miura, Y. Kurashige, Y. Hirano, J. Kawata and M. Sugi, *Thin Solid Films,* **327–329,** 443(1998).
[2] S.K. Gupta, D.M. Talor, P. Dynarowicz, E. Barlow, C.E.A. Wainwringht and A.E. Underhills, *Langmuir,* **8,** 3057, 1992.
[3] S.K. Gupta, D.M. Talor, A.E. Underhill and C.E.A. Wainwringht, *Synthetic Metals,* **58,** 373 (1993).
[4] Steimecke, H.J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus and Sulfur,* **7,** 49(1979).
[5] Y.F. Miura, Y. Okuma, H. Ohnishi, T. Kawasaki and M. Sugi, *Jpn. J. Appl. Phys.,* **37,** L1481(1998).