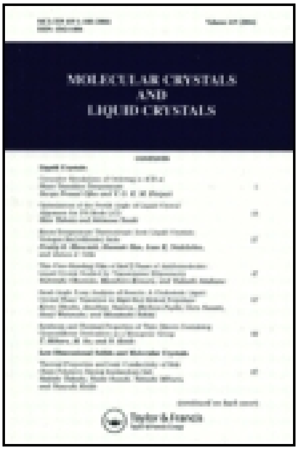

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IMAGING OF SURFACE POTENTIAL DISTRIBUTION IN CYANINE DYE MONOLAYER BY SCANNING MAXWELL STRESS MICROSCOPY (SMM)

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abstract Scanning Maxwell stress Microscopy (SMM), which is a type of scanning probe microscopy designed to image microscopic electrical properties, has been applied to cyanine dye Langmuir-Blodgett (LB) monolayers. In combination of epi-fluorescence microscope technique with SMM, the cyanine J-aggregate formation way was clearly observed. Further the light induced electron transfer between cyanine and viologen in LB film system could be detected as a surface potential change by SMM technique.

INTRODUCTION

Recent development of scanning probe microscope techniques has made it possible to investigate, not only microscopic surface topography, but also physical and chemical properties on the sub-micron scale. The scanning Maxwell stress microscopy (SMM) is surface characterization tool capable of mapping both the surface topography and electrical properties, such as surface potential, surface charge, dielectric constant of thin films with a sub-micron resolution by means of the AC voltage driven oscillation of a metal coated cantilever[1-4]. In this study we observed the surface potential distribution and molecular ordering of a cyanine dye in Langmuir-Blodgett (LB) films.

EXPERIMENTS

3-Octadecyl-2-[3-(3-octadecyl-2(3H)-benzoxazolylidene)-1-propenyl]benzoxazolium perchlorate (cyanine) was used as a donor, and 1,1'-dioctadecyl-4,4'-bipyridinium dibromide (viologen) as an acceptor molecule. Each dye compound was mixed with arachidic acid at a molar ratio of 1 : 10 and spread onto a water subphase. The monolayer was formed at the air-water interface of a rectangular Teflon made trough. For topographic and surface potential measurements in the dark, the monolayer was deposited onto a silicon (111) surface with LB technique.

The microscope basically consists of a commercial AFM (Nanoscope III), two lock-in amplifiers and a function generator. Cobalt metal coated cantilevers are used after the ozone cleaning process. An AC voltage with a frequency of 7.66 kHz and a peak to peak

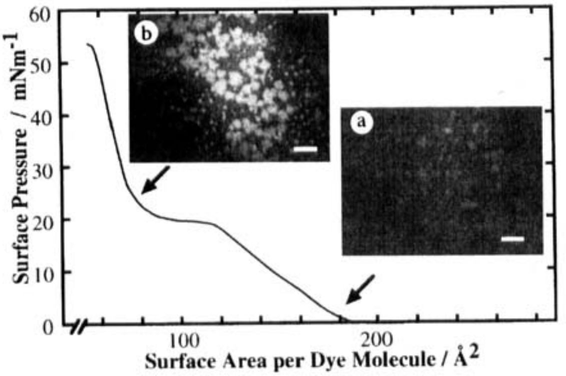

Fig. 1 The molecular area- surface pressure isotherm of a mixed monolayer of cyanine dye and arachidic acid (molar ratio = 1:10). Fluorescence micrographs are taken at a surface pressure of (a) 5 mNm^{-1} and (b) 25 mNm^{-1}.

voltage of 4 V is applied between tip and sample surface for all the SMM measurements. To measure the light induced surface potential changes, 488 nm light from a CW argon ion laser was used.

SURFACE POTENTIAL IMAGING OF CYANINE MONOLAYER

Figure 1 shows the molecular area - surface pressure isotherm of a mixed monolayer of cyanine dye and arachidic acid. The isotherm exhibits a plateau around a surface pressure 20 mNm^{-1}. In the simple case, a plateau or a kink in isotherms means that the monolayer undergoes a fluid to solid phase transition from the expanded state. To confirm phase transition od this monolayer, microscopic surface morphologies of deposited films on silicon substrate were observed at a surface pressure of 5 and 25 mNm^{-1}.

Figures 2 (a) and 2 (b) show topographic images of mixed monolayer of cyanine and arachidic acid deposited onto silicon substrate at a surface pressure of 5 mN m^{-1} and 25 mNm^{-1}, respectively. At a surface pressure of 5 mNm^{-1}, many small clusters of which height is about 3.0-3.5 nm, are formed. The increase of the surface pressure brings about an increase in the number of small clusters and the formation of big circular domains whose diameters range from 2 μm to 40 μm are formed. In accordance with the fluorescence micrograph images shown in Fig. 1 (b), circular domains were observed together with relatively surrounding region. The size and shape of circular domains coincides well with those obtained from the fluorescence microscope image. To evaluate feature of these domains, the absorption and fluorescence spectra of 6 layers of this monolayers deposited at a surface pressure 5 mNm^{-1} and 25 mNm^{-1} on the glass substrate are measured. The two absorption peaks are observed at 465 nm and 490 nm. These absorption peaks have been assigned to those of cyanine monomer and J-aggregate respectively. The intensity of J-aggregate peak increase with increasing surface pressure.

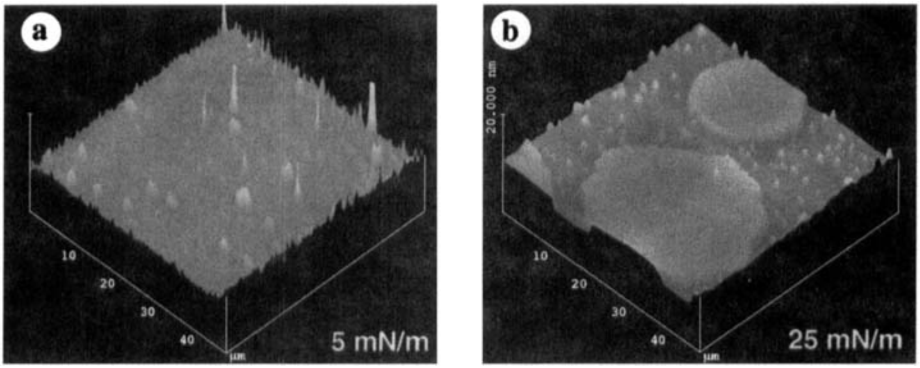

Fig. 2 The topographic images of mixed monolayer of cyanine dye and arachidic acid monolayer deposited at a surface pressure of (a) 5 mNm^{-1} and (b) 25 mNm^{-1} (Scan Area : 50 x 50 µm^2). (See Color Plate III).

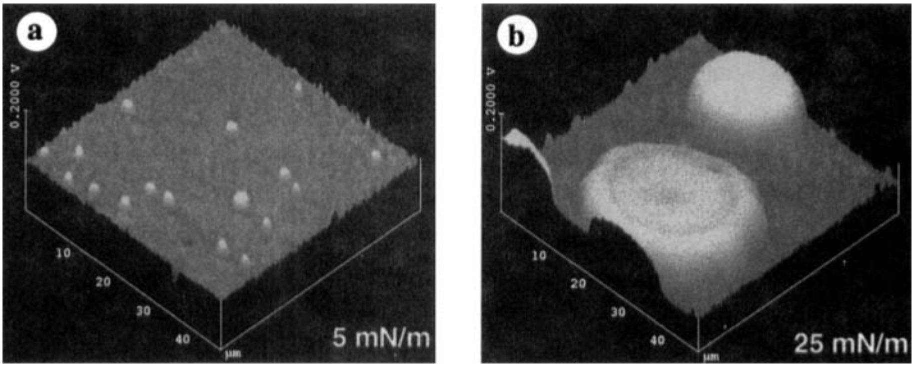

Fig. 3 The surface potential images of mixed monolayer of cyanine dye and arachidic acid monolayer deposited at a surface pressure of (a) 5 mNm^{-1} and (b) 25 mNm^{-1} (Scan Area : 50 x 50 µm^2). (See Color Plate IV).

These results suggest that the circular domains consist mainly of cyanine J-aggregate, whereas the surrounding regions are composed of cyanine monomer and arachidic acid.

Figure 3 (a) and 3 (b) show surface potential images of the same region of Fig. 2 (a) and 2(b), respectively. The surface potential difference between the J-aggregate domain (big, circular) and flat surrounding region is about 60-80 mV. On the other hand, small cluster like domains show 30-40 mV higher surface potential than the surrounding region. In the topographic image, the heights of J-aggregate and small cluster domain are almost same. Since the surface potential of thin film is roughly proportional to the surface concentration and the effective perpendicular component of dipole moment, the cyanine J-aggregate domains achieve higher molecular packing and ordering than that of small cluster domains.

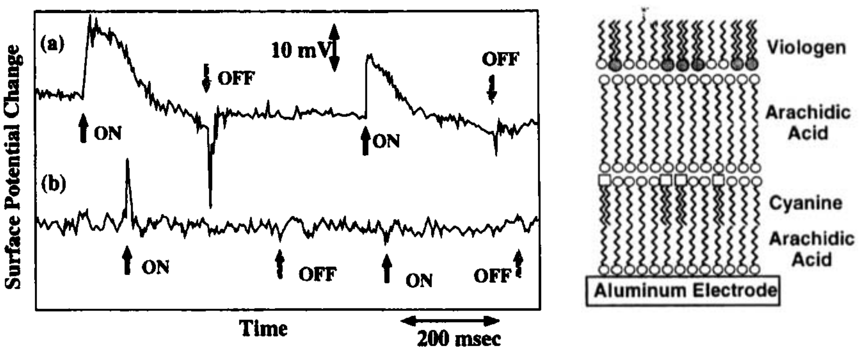

Fig. 4 The light induced surface potential response of the hetero-type LB films together with the reference (response of bare Al electrode).

SURFACE POTENTIAL CHANGES IN DONOR-ACCEPTOR LB FILMS

Figure 4 shows light induced surface potential responses of aluminum electrode | cyanine | arachidic acid | viologen hetero-type LB film (structure is illustrated on the right hand side of Fig. 4). In association with the turning on and off the light, transient surface potential changes were observed. The resulting direction of surface potential changes are almost consistent with the expected directions from the light induced electron transfer[5]. However the direction and amplitude of surface potential changes depended on a position even in the same membrane. These results suggest that the electron transfer process in the hetero-type LB film is rather complicated owing to the microstructure in the film.

CONCLUSION

We have demonstrated that the SMM can be used for imaging surface potential distribution over the dye monolayer surface and also be used for detecting light induced surface potential changes in hetero type LB film. This is the first step towards the understanding of electrical phenomena in organic materials and biological systems with SMM.

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