

## LB Molecule Orientation by DC Electric Field between Line Electrodes

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We have previously succeeded in preparation of high-density Langmuir-Blodgett (LB) molecular film at room temperature by application of ultra sonic vibration and an even DC electric field to the pure LB film comprising a merocyanine dye [1]. Based on this method, we have developed a new orientation treatment using spiropyran dye molecule. Langmuir film of the dye molecule under lateral compression was passed through a DC field generated by a pair of line electrodes set in the water phase and above the water surface. A dense solid LB film prepared by this treatment showed an intense absorbance peak of J aggregates which had formed by the effect of molecular orientation. This orientation procedure is considered highly useful for manufacture of dense LB films with superior photo-chromic and -electronic functionalities.

Keywords: Langmuir-Blodgett film, Orientation control, Electric field, Line electrodes, J-aggregate

### 1. INTRODUCTION

We have recently showed that a highly dense Langmuir film can be manufactured under room temperature through molecular orientation control by means of simultaneous application of electric DC field and ultra sonic vibration to the pure monolayer film of a merocyanine dye [1].

For the purpose to confirm the above phenomenon and to advance our method, we have conducted a similar experiment for the LB film preparation of spiropyran Dye, a typical sample of photochromic and photoelectronic functionalities. The dye molecule forms J-aggregates which has been applied to photochromic devices [2,3]. In this study we examined a new DC orientation treatment in addition to the above DC field and vibration procedure. Here, a local DC field was applied to a supernatant Langmuir (L) film in the course of lateral molecular compression. To prepare a mechanical setup to realize the experiment, a pair of parallel line electrodes was set in the water phase and above the surface of the water and L films were built up on the solid substrate as a solid LB film by the horizontal lifting method. Simultaneously on the DC field application, we altered the direction of field across the L film by changing the angle of straight line combining both electrodes with respect to the water surface from 10° to 90°. The formation of spiropyran J aggregate was investigated as an effect of this orientation control through absorption measurement for the solid LB film. We will show usefulness of the present technique for preparation of a high-density, well-oriented LB films.

### 2. EXPERIMENTAL

#### 2.1 Formation of dense L films

Fig. 1 shows the setup for the field-oriented L film preparation. LB trough (Langmuir MINI trough, Joyce Loebel) was equipped with a pair of flat sheet electrodes for DC field generation, where lower electrode was attached with an electrode box with ultra vibration cell (resonance frequency: 50.6 kHz, manufactured by Tokin Co., Ltd.) and upper electrode, parallel to the

lower, was set above the surface of the water (area of both electrodes, 280 × 160 mm). An amplifier (AMP) was connected with a function generator (FG) for output to an ultrasonic vibration (US) cell [1].

Amphiphilic spiropyran, SP1822, was used as a spiropyran dye. A dilute dye solution in chloroform was spread on the trough water surface and the gas-like L film formed was kept at a surface pressure of approx. 3 m/Nm for 60 s. The film was then subjected to compression and  $\pi$ -A characteristic measurement. Here, electric field of the parallel electrodes was regulated as constant at 5.0 kV/m and US output voltage was set to be 0.5 V as a main parameter.

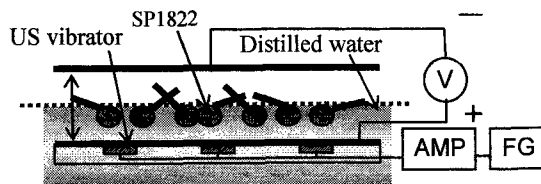


Fig. 1 DC Field control setup in the LB trough

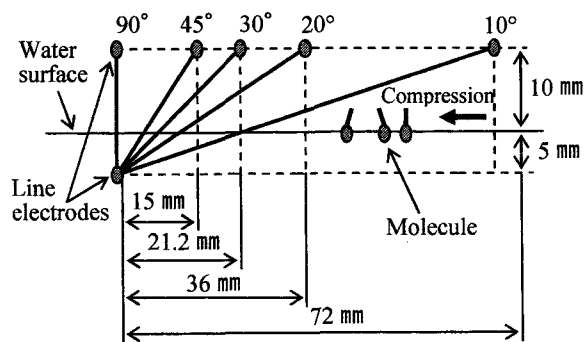


Fig. 2 Vertical sectional view for the line electrodes

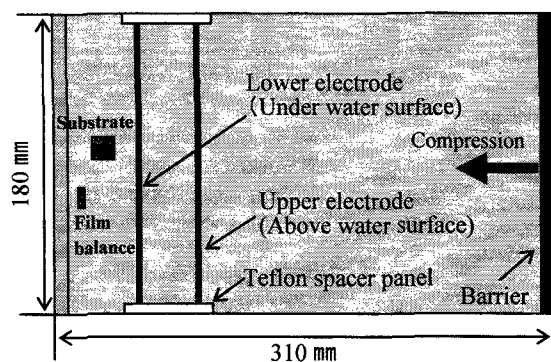


Fig. 3 Position of line electrodes in the trough

## 2.2. Operation of line electrodes and measurement of J aggregate absorption peak

The reason why we used a pair of line electrodes is that it creates unidirectional and vectorial DC electric field that can affect the molecular orientation.

Fig. 2 and 3 show relative position of the line electrodes in the trough. Both line electrodes consisted of piano wires with 180 mm in length and 1 mm in diameter, both ends being fixed with Teflon spacers. This line electrodes unit was set on the lower electrode as described earlier. The lower line electrode of the unit was placed at 5 mm from the surface of the water while the upper one above 10 mm from the surface of the water. Here,  $\theta$  represents the angle of straight line combining both electrodes with respect to the surface of the water. Other than the condition of  $\theta=90^\circ$ , we transferred the upper electrode in direction of the compression bar to set it at  $45^\circ$ ,  $30^\circ$ ,  $20^\circ$  and  $10^\circ$ . Both electrodes were applied with DC voltage to generate an electric field so that the upper electrode became negative.

Following the L film preparation as described in 2.1, we compressed the film under DC electric field applied to the both line electrodes. And we accumulated three layers of solid LB film on a glass surface which had passed through the field of line electrodes by the horizontal lifting method

## 3. RESULTS AND DISCUSSION

### 3.1 Formation of dense L films

Figure 4 shows the  $\pi$ -A characteristics of SP1822 films prepared with and without the DC electric field and US treatments. Here,  $\pi$ -A data with the treatment shows a film of highest density (packing) obtained as a result of changing each parameter of applied voltage and FG output. It is shown that molecular occupation area in the L film at the collapse point was  $A \approx 9.5 \text{ \AA}^2$  for treated film and  $A \approx 23 \text{ \AA}^2$  for non-treated film. The former showed 40% reduction from the latter, indicating that highly dense L film was formed similar to the case of the merocyanine dye [1]. To make this phenomenon clearer for the molecular level, we attempted the structure model simulation. Figure 5 shows the chemical structure of SP1822 molecule. The simulation was made to calculate the projection area on the surface of the water assuming that the hydrophilic group is the major portion to determine the mean area occupied by molecule "A" in the L film. Here, molecular area occupied by the hydrophilic group is represented as "As" in our model.

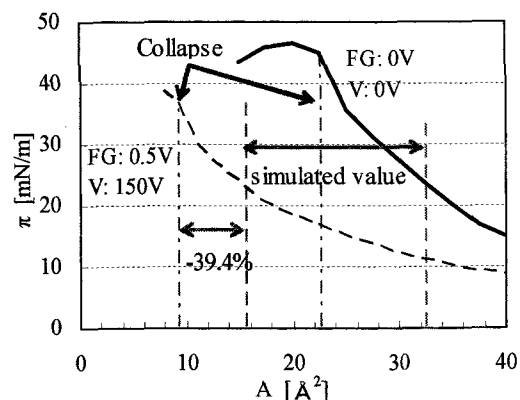
Fig. 4. Comparison of  $\pi$ -A curves by 3D simulation

Fig. 6 (a) and (b) show hydrophilic group models depicted by using 3D simulation software (developed by CS chem Co., Ltd.). Fig. 6 (a) and (b) show maximum and minimum projection area, respectively, of the hydrophilic group floating on the water surface.

The L film as a solid film is in state of the highly packed molecular assembly contacting their hydrophilic groups each other. The "As" area must become maximum when molecules are condensed at random in Fig. 4 (a), and minimum when they are regularly aligned in Fig. 4 (b). Our simulation results show "As" max. =  $32.4 \text{ \AA}^2$  and "As" min. =  $15.5 \text{ \AA}^2$ . These values are based on the assumption that hydrophilic group SP1822 is rigid body and no pin-holes exist in the L film.

According to the above simulation, Fig. 4 shows that "A" at the film collapsing point exists between "As" maximum and "As" minimum when no electric field and no US are applied. While "As" of regularly aligned molecular film for the molecular form of Fig. 6 (a) becomes  $28.5 \text{ \AA}^2$ , experimentally obtained "A" at the collapse point in the  $\pi$ -A curve is  $23 \text{ \AA}^2$  (Fig. 4), indicating approx. 19% reduction in area. If the L film contained pin-holes or it orients irregularly, e.g., causing a twisted hydrophobic chain, the area should be increased. However, the present result implies the possibility that molecules are elastically compressed or the hydrophilic group of the molecule took an orientation interaction to give a smaller projection area per molecule.

In the condition of electric field of 5 kV/m and FG output of 0.5 V, the film collapsed at the area  $A = 9.4 \text{ \AA}^2$  that is approx. 40% smaller than the minimum value in the simulated result. For this dense L film, each SP1822 molecule is assumed to stand on the surface of the water taking the projection area of Fig. 6(b) and, since molecules are organic body, they can be elastically compressed resulting in a smaller mean molecular occupation area. The above result demonstrates that electric field and US provisions greatly influence the molecular packing and orientation.

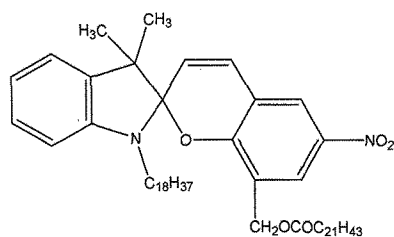


Fig. 5. Structure of SP1822

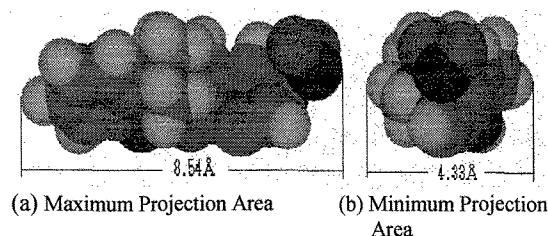


Fig. 6. 3D Molecule models for SP1822

### 3.2. Enhanced J aggregate formation with the line electrodes

Fig. 7 shows absorbance spectra of the spirocyan SP1822 film under application of constant 150 V to the line electrodes as a function of electrode angle  $\theta$  from  $10^\circ$  to  $90^\circ$  according to the procedure described in 2.2. Each curve in this chart has peak value of  $\lambda \approx 620$  nm, which shows formation of J aggregate. Since a major change occurred in peak absorbance, dependence of peak absorbance value on the angle  $\theta$  was plotted in Fig. 8. It should be first noted that the absorption peak of J aggregate appears at  $\theta = 90^\circ$ . Theoretically, in this situation, line of electric force forming in the vicinity of the surface of the water should be incident vertically and is hard to cause J aggregate formation. For this, the following reasons are considered: The SP1822 molecule in Fig. 5 have  $C_{18}H_{37}$  and  $C_{21}H_{43}$  with different lengths of hydrophobic chain,  $28.6 \text{ \AA}^2$  and  $24.5 \text{ \AA}^2$ , respectively. Therefore, electric moment  $\mu$  should be different each other. When these molecules are exposed to electric field, they can be compressed in the condition that the hydrophilic group is tilted against the surface of the water since their revolution torque generated are different each other. On compression in this situation, hydrophilic group and hydrophobic chain are oriented linearly and this can satisfy the condition of J aggregate formation.

Fig. 8 shows that peak absorbance increases with decreasing  $\theta$  from  $90^\circ$  to  $20^\circ$ . In this duration,  $\theta$  reduction is accompanied by an increase in the distance between electrodes and, when molecules under compression pass through both electrodes, electric field intensity that contributes to the orientation torque for hydrophobic chain should decrease. The above result shows that although field intensity decreases, hydrophobic chain may be driven toward  $\theta$  direction receiving an orientation torque.

It is generally considered that, in parallel with reduction of orientation angle, formation of J aggregate tends to be promoted. The above result backs up this. Namely, in our experiment, the hydrophobic chain of the molecule is considered to tilt ultimately by the

influence of directivity electric field toward the direction of both electrodes when molecules under compression are passing through the both electrodes.

On the contrary, absorbance peak decreases at  $\theta = 10^\circ$  compared with  $\theta = 20^\circ$ . For further investigation for this phenomenon, we calculated electric field intensity ( $E_0$ ) at the point of  $10 \text{ \AA}$  above the surface of the water, a crossing point of straight line combined both line electrodes and the surface of the water by means of the magnetic field analysis software (Elec Net: Advance Technology Co., Ltd.).

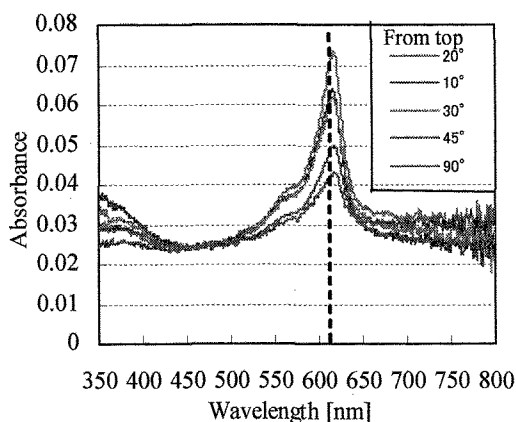


Fig. 7 Absorbance spectra of spirocyan SP1822 as a function of the electric-field incident angle

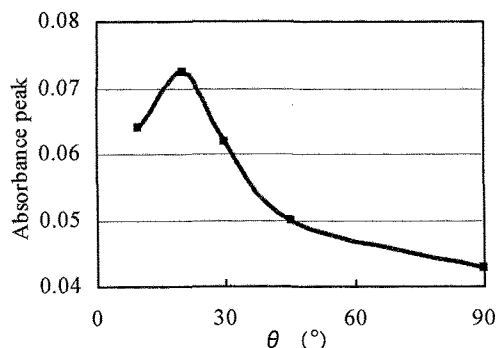


Fig. 8 Dependence of absorbance peak on the electric field angle

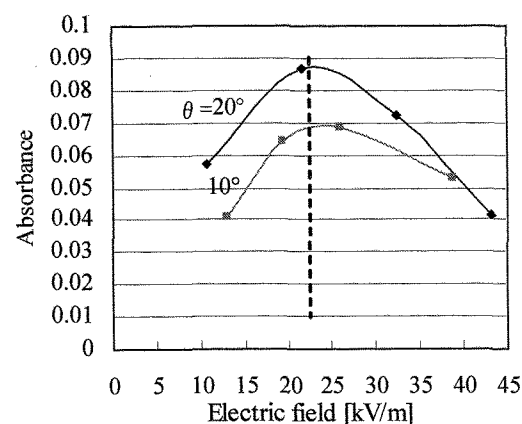


Fig. 9 Electric field dependence of the peak absorbance

Fig. 9 shows  $E_0$  dependence of the absorbance peaks at  $\theta = 10^\circ$  and  $\theta = 20^\circ$  measured for LB films of 3 layers. The electric field that gives maximum absorbance for two curves was equally  $E_0 = 23$  kV/m at both  $\theta$ . However, maximum absorbance shows 20% reduction for  $\theta = 10^\circ$  compared to  $\theta = 20^\circ$ . Furthermore, since the experimental condition was set at constant 150 V of applied voltage between line electrodes,  $E_0$  at  $\theta = 10^\circ$  should be lowered from that of  $\theta = 20^\circ$ . Therefore, insufficient electric field torque could not orient molecules sufficiently toward  $\theta$  direction, or disorder of molecules orientation can be considered because of occurrence of random slippage of place toward  $\theta$  direction among neighboring molecules during the process of molecular compression.

### 3.3 Pressure dependence of the J aggregate formation

Knowing that applying electric field by the line electrodes greatly influences the LB molecule orientation, we next investigated how the film compression pressure  $\pi$  during LB film deposition influences on the molecular orientation.

Fig. 10 shows absorbance peak of the three layer LB film prepared at  $\theta = 20^\circ$  as a function of the surface pressure in the range of  $\pi = 20$  to 35 mN/m, which may be effective to form a solid LB film. Here, maximum peak is shown at  $\pi = 30$  mN/m, where the best desirable form for J aggregate absorption can be seen. In this pressure condition, hydrophilic group and hydrophobic chain may presumably be placed linearly. At  $\pi$  equal or more than 30 mN/m, whole molecule orientation is supposed to change to a right angle direction against the surface of the water. When  $\pi$  comes up to the collapse pressure, disorder in molecules orientation will occur. At lower pressures,  $<30$  mN/m, increase in molecular occupation area leads to reduction of absorbance. Accordingly, it has been clarified that there exists an optimum film compression pressure which generates the desirable J aggregate absorption.

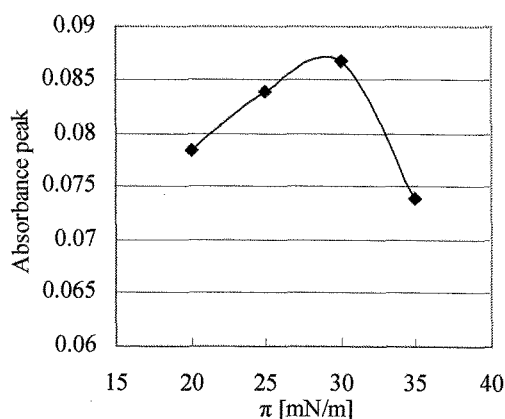


Fig. 10 Film pressure dependence of absorbance peak

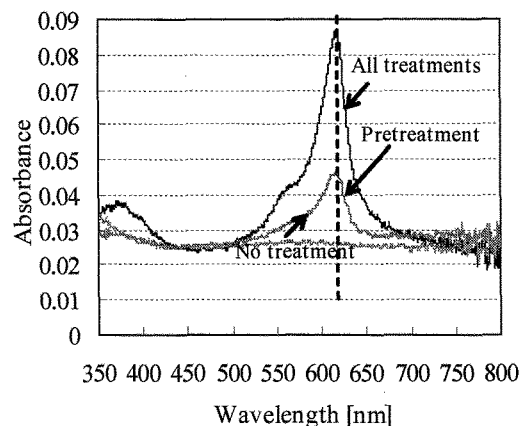


Fig. 11 Effect of film treatments on the film absorbance peak of spiropyran SP1822

### 3.4 Effect of treatment on absorbance enhancement

The above series of experiments concern three types of major treatment for L film orientation, namely,

- (1) None of orientation treatment
- (2) Pre-treatment by application of even DC electric field and US provision after spreading L molecules on the surface of the water.
- (3) Following (2), conducting film compression at  $\theta = 20^\circ$  that promotes molecular orientation to one direction between the line electrodes.

Fig. 11 compares absorbance spectra of SP1822 LB films (three layers) prepared under the above three treatment conditions. The spectrum for (1) of no treatment, despite a flat-looking pattern, proved to contain a weak absorption assigned to H aggregate. The spectrum for (2) of pretreatment shows retreat of the H aggregate absorption and development of a sharp peak of J aggregate absorption. In curve (3) for all treatments, a peak value is doubled, showing an obvious effect of the additional treatment by the line electrodes.

Fig. 12 depicts molecular orientations of SP1822 as models which we consider for the three cases (1)-(3). Fig. 12 (1) shows a disordered orientation. Fig. 12 (2) shows an ordered orientation in which hydrophilic group takes an approx.  $20^\circ$  tilting angle against the surface of the water. In Fig. 12 (3), hydrophilic group and hydrophobic chain are aligned linearly and whole molecules are tilting at angle of  $20^\circ$  to the surface of the water.

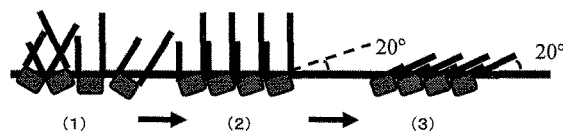


Fig. 12. Molecular orientation models for spiropyran SP1822 under the three treatment conditions

#### 4. CONCLUSION

We have clarified the following points for molecular orientation and J aggregate formation of spiropyran SP1822 through the DC field and US treatments at the air-water interface:

- 1) Preparation of high-density L film by application of even DC electric field and US provisions (pretreatment) showed 40% reduction at maximum of molecular occupation area and gave higher packing density compared with the result obtained from a simulation model that assumes a rigid body of hydrophilic group.
- 2) The LB film which underwent the above pretreatment leads to formation of J aggregate as shown by absorption peak.
- 3) Formation of J aggregate is proved to be highly enhanced by applying DC electric field to the L film under compression using a pair of line electrodes.

For further investigation, confirmation of orientation for LB solid film through X-ray diffraction method or observation by AFM is required

The method of LB molecule packing and orientation presented in this study is a powerful tool for manufacturing functional organic films in thin film technology. It will be useful for construction of photochromic system involving spiropyran LB films [2,3], nonlinear optical devices [4], and thin-layer photoelectronic devices using functional organic molecules [5].

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