

Preparation of Phthalocyanine Derivative Ultrathin Films by Langmuir-Blodgett Method

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A phthalocyanine derivative has been focussed as a noble chromogenic material. For the first time LB films of mixture of aluminium 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine triethyl siloxide and arachidic acid were deposited on glasses under the conditions of the surface pressure of 30 mN / m, the stroke speed of 12mm / min on the water subphase of pH = 10.3. The obtained films have a Y-type of accumulated layers with the lattice spacing of about 5.3 nm. The surfaces of the films were very smooth with the cohesive structures of about 300 nm and 15 nm thick. The films revealed the characteristic optical absorption peaks of the phthalocyanine derivative.

Key words: chromogenic materials, phthalocyanine derivative, LB films, absorption spectrum

1. INTRODUCTION

A Langmuir-Blodgett (LB) technique¹⁾ has been widely adopted to prepare functional organic molecular ultrathin films with characteristic accumulation structures. Especially the assembly structure with an alignment of molecules is a determinant to make clear a substantial function of the molecule. In this work, we have paid attentions the phthalocyanine derivative as a noble chromogenic material.

As chromogenic materials several transition metal oxides²⁾ and also some organic materials³⁾ have been studied in an electrochromic system. The conventional electro chromic phenomena have, however, several drawbacks, for example, slow responses or a short life of color changes because of chemical redox reactions. So applications of the electrochromic materials for a flat panel display have not widely been developed. Then we have proposed a new mechanism of color changes by electric fields without redox reactions in the system of aligned organic dye molecules.

In Fig. 1., we show the chemical structure of

aluminium 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine triethyl siloxide (AlPcTr). Since the AlPcTr is not an amphiphilic molecule, an arachidic acid (AA, $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$) was used in order to stabilize the Langmuir film on the subphase. The purposes of this work are to prepare the AlPcTr / AA mixed LB films and to investigate the fundamental materials properties of the films. LB-film preparations of the phthalocyanine derivative with a very complex molecular structure are reported for the first time.

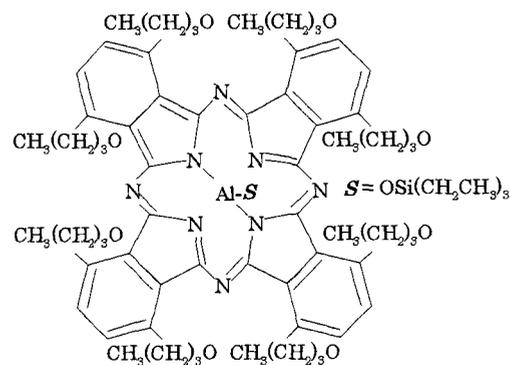


Fig. 1. Chemical structure of AlPcTr

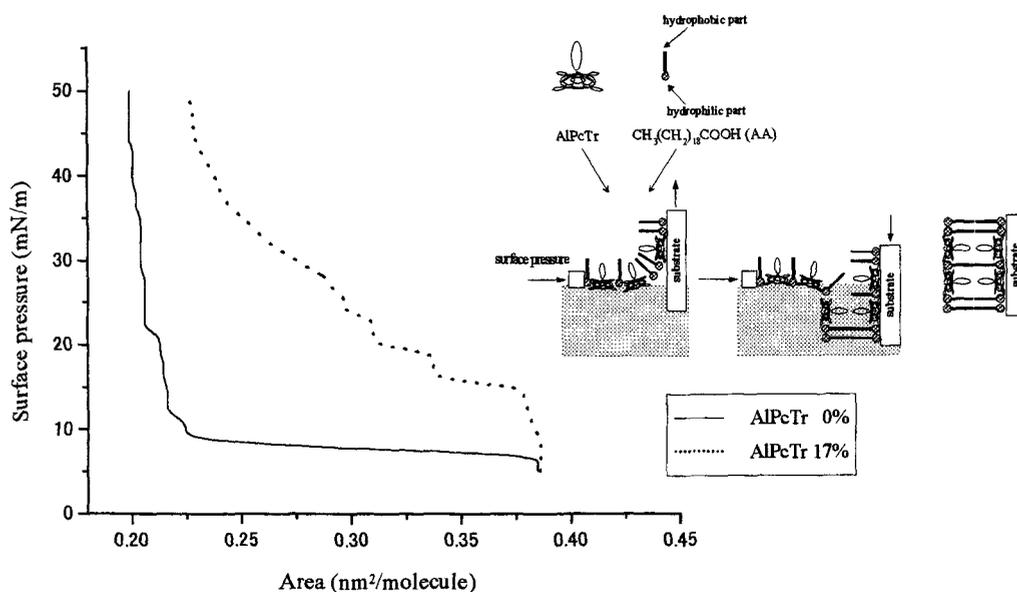


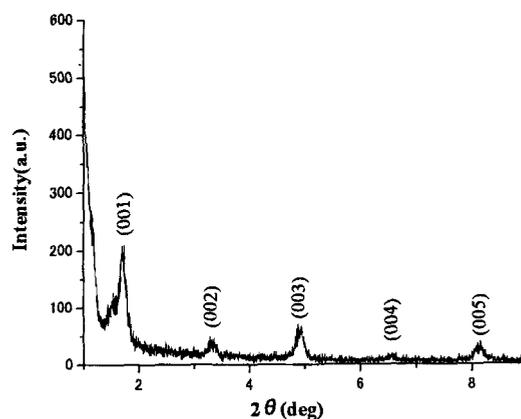
Fig. 2. π -A isotherm curves of the AlPcTr / AA and the AA when the subphase pH was 10.3.

2. EXPERIMENTAL PROCEDURES

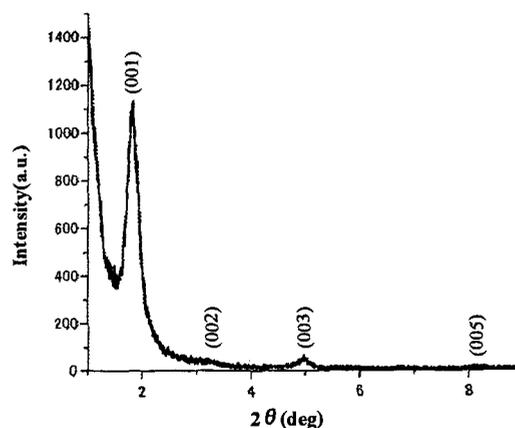
We prepared chloroform solution of AlPcTr at a concentration of 0.64 mmol / l and AA at 3.2 mmol / l. The AlPcTr used in this work is a commercial product of Aldrich-Chemical Co., Ltd., and the AA was obtained from Kanto-Chemical Co., Ltd.

We fabricated LB films by a Kuhn type of apparatus⁴⁾ with a moving barrier and a vertical dipping / lifting handler. The details of the apparatus were described elsewhere⁵⁾. After spreading the solution a L-film of AlPcTr / AA was kept on a water subphase at pH = 10.3 containing 2 mmol / l CaCl₂ and 0.1 mmol / l NaOH. The subphase was maintained at 290 K in a clean room.

In Fig. 2 the typical π -A isotherm curves for AA and AlPcTr / AA are shown together with a schematic LB process. The AlPcTr / AA curve was extrapolated to $\pi = 0$ and the limiting area was obtained. Since the molecular occupation area of pure AA was 0.225 ± 0.025 nm², that of AlPcTr was evaluated to be about 1.43 nm². From this result it was thought that AlPcTr molecules were condensed with AA molecules and the molecular planes are parallel to the subphase surface. The substrates used were slide glasses (Matsunami Ind., Ltd) cut to the size of 1cm².



(a) AA LB film



(b) AlPcTr LB film

Fig. 3. XRD patterns of the AlPcTr / AA and the AA LB films

The film was transferred onto the substrates at a constant surface pressure (30 mN / m) through vertical dipping / lifting strokes. The stroke speed was 12 mm / min. The accumulated structures of the obtained films were investigated by a X-ray diffraction (XRD) (Rigaku Co., Ltd). The absorption spectra were measured by a double beam spectrometer (Shimadzu Co.,Ltd). The surface morphology was observed by an atomic force microscopy (AFM) (Seiko Instruments Inc.).

3. RESULTS AND DISCUSSION

Figure 3 shows XRD patterns of the AlPcTr / AA and the AA LB film. In the AlPcTr / AA film the strong Bragg peaks of (00n) with odd-numbered n appeared. Also, the (00n) peak intensities of the AA film of odd-numbered n were relatively strong compared with those of even-numbered n. The result of the latter case was quite similar to the other reports⁶⁾.

A lattice spacing of the AlPcTr / AA film evaluated from the (003) peak was about 5.3 nm, which was approximately twice as long as a molecular length of the AA. These results reveal that a Y-type of accumulated structure was achieved in the LB films. Furthermore since the transfer ratio was almost unity in the both strokes, the accumulated films were also expected to have a Y-type of layers.

AFM images of the AlPcTr / AA and the AA LB film with 30 layers are shown in Fig. 4. The observed surfaces were very smooth. So it was concluded that the accumulation process was well done. In the AA film about 5 nm thick assembled structures with the size of about 400 nm were observed. On the other hand, the morphology of the AlPcTr / AA film revealed cohesive structures of smaller size with the thickness of about 15 nm. The result indicates that the elasticity of the AA L-film was increased by adding AlPcTr molecules. This was consistent with the results of π -A isotherm curves.

The absorption spectra of the AlPcTr / AA mixed LB film and the develop solution are shown in Fig. 4. Two characteristic absorption peaks of the AlPcTr were observed at $\lambda = 770$ and 690 nm in solution, while the films indicated the absorption peaks at $\lambda = 750$ and 670 nm. The blue shift of the peaks took place in the LB film

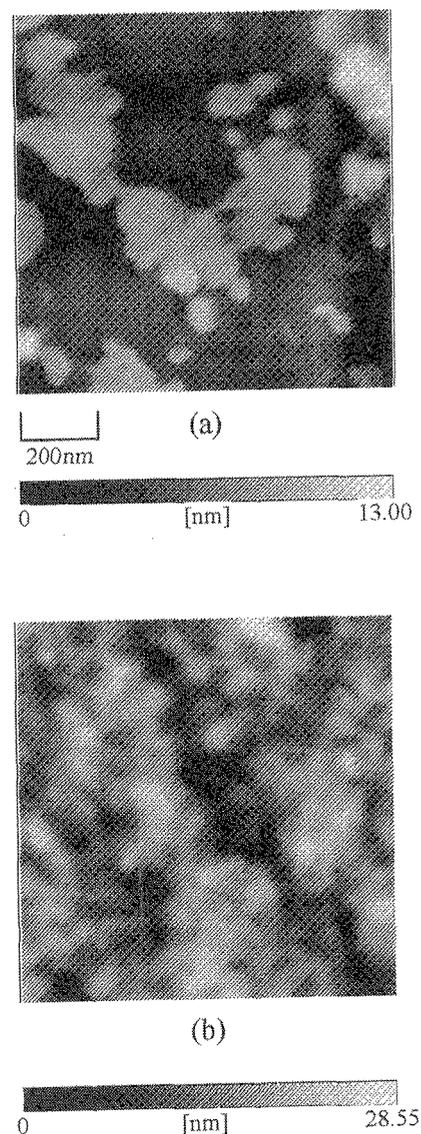


Fig. 4. (a) AFM image of the AA LB film. (b) AFM image of the AlPcTr / AA LB film. The both films were deposited 30 layers on glasses.

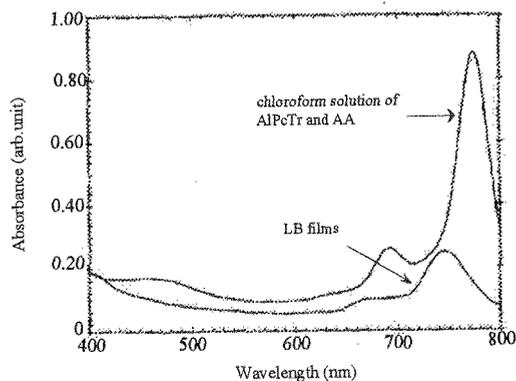


Fig. 5. Absorption spectra of the AlPcTr / AA LB film and the AlPcTr in chloroform solution

4. SUMMARY

The chloroform solution of mixture of AlPcTr and AA was prepared at a molar ratio of 1 : 5. LB films were prepared under the conditions of the surface pressure of 30 mN / m, the stroke speed of 12 mm / min on the water subphase of pH = 10.3. Since the obtained films had the lattice spacing of about 5.3 nm, it was confirmed that a Y-type of structure was obtained. The cohesive structures with the size of about 300 nm were observed on very smooth surfaces. The films revealed the characteristic optical absorption peaks at $\lambda = 750$ and 670 nm. The color changes expected in the film by applying electric fields will be investigated in future.

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