

## Absorption Spectrum of Phthalocyanine Derivatives LB Films

Kuori Katayama, Souki Yamaguchi, Takuya Hashimoto, Nobuyuki Iwata  
and Hiroshi Yamamoto\*

College of Science and Technology, Nihon University, 7-24-1

Narashinodai, Funabashi-shi, Chiba 274-8501, Japan

\*E-mail address : hyama@ecs.cst.nihon-u.ac.jp

The L-film of the Pc derivative, the Aluminum 1, 4, 8, 11, 15, 18, 22, 25, -octabutoxy-29H, 31H-phthalocyanine triethyl siloxide (AlPcTr) was stabilized with arachidic acid (AA). Ca ions were added in the subphase to stabilize AA molecules. The accumulation of the L-film of AlPcTr/AA had the Y-type of structure and resulted in comparatively disordered layers. On the other hand, the Hetero films were prepared by the alternated accumulation of the AlPcTr/AA film and the pure AA one. The surface of the Hetero film was very smooth and constituent molecules were highly oriented. The absorption peak at *ca.* 760nm which was attributed from a  $\pi$ - $\pi^*$  transition in the Pc derivative was distinctly broadened in the Hetero film. The absorption spectra of ionized AlPcTr were investigated by a semi-empirical MO simulation. From the comparison with the experimental and simulated results it was concluded that the change of the absorption spectra was caused by accompanied anions surrounding AlPcTr molecules.

Key words: Phthalocyanine derivative, arachidic acid, LB film, MO simulation, absorption spectrum

### 1. Introduction

Many researchers have been studying about several transition metal oxides and also some organic materials in an electrochromic (EC) system.<sup>1), 2)</sup> The conventional EC phenomena have issues in slow response or a short life of color changes because of chemical redox reactions. Bucher and Kuhn discussed a novel EC phenomenon induced by electric field applied to single dye LB films.<sup>3)</sup> The EC response speed was very high although the color change was little. We have proposed another mechanism of EC color changes induced by electric field without redox reactions. A Phthalocyanine (Pc) has a large  $\pi$ -electrons ring and its color is sensitive to the change of intra-molecular electrons' distribution. We have investigated the Pc derivative, aluminum 1, 4, 8, 11, 15, 18, 22, 25, -octabutoxy-29H, 31H-phthalocyanine triethyl siloxide (AlPcTr) (Fig.1 (a)) as the candidate of the novel EC materials.<sup>4)</sup> The AlPcTr has a large  $\pi$ -electrons ring

and a comparatively large radical. We expect that the absorption spectrum of the AlPcTr is changed by applying electric field perpendicular to the molecular plane.

In order to investigate our EC model the alignment of the molecules was very important.<sup>5)</sup> In this work we paid attentions to obtain a highly orientation of AlPcTr molecules. We prepared the two types of LB films: the Y-type film and the Hetero one. The obtained films were investigated with respect to layered structures and optical absorption spectra. The accumulation of the mixture of AlPcTr/AA resulted in the Y-type structure. As the Hetero films we alternatively accumulated the AlPcTr/AA film and the pure AA one. The Hetero film revealed a superior layered structure. The prepared two types of LB films revealed quite different absorption spectra. We simulated the absorption spectra of ionized AlPcTr by a semi-empirical MO simulation and compared with the experimental results. From the results it was suggested that the characteristic absorption

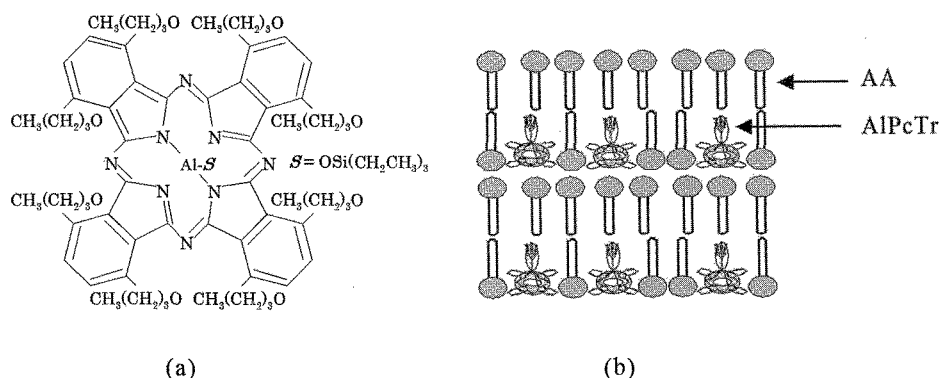


Fig.1. (a)The molecular structure of the phthalocyanine derivative (AlPcTr).  
(b)The schematic layered structure of the Hetero film.

spectrum observed in the Hetero film was caused by the positively charged AlPcTr.

## 2. Experimental

### 2-1. Accumulation of LB film

The LB films were fabricated by a Kuhn type of apparatus.<sup>6)</sup> 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 (L-film) on a subphase. A mixture chloroform solution was prepared with AlPcTr at the concentration of 0.64 mmol / l and AA at 3.2 mmol / l. The AlPcTr and AA were commercial products of Aldrich-Chemical Co., Ltd. and Wako Pure Chemical Industries, Ltd., respectively.

After spreading the solution, the L-film of AlPcTr / AA was kept on the water subphase at pH = 10.3 containing 2 mmol / l  $\text{CaCl}_2$  and 0.1 mmol / l NaOH. The subphase temperature was maintained at 290 K. The films were transferred onto substrates at the constant surface pressure (24 mN / m) through vertical dipping / lifting strokes of which speed was 12 mm / min.

The substrates were indium tin oxide (ITO) glasses (Sumitomo Heavy Industries, Ltd) cut to the size of 1.0  $\text{cm}^2$ . The sheet resistance of the ITO glasses was 20  $\square / \text{cm}^2$ . The two kinds of LB films were prepared. The first type was the simple accumulation of AlPcTr / AA, namely the Y-type film. The other was the alternated accumulation of AlPcTr / AA and a pure AA, namely the Hetero film as schematically shown in Fig.1 (b). The effect of a buffer layer was also studied by the accumulation of 4 layered AA films prior to the accumulation of the AlPcTr / AA films.

The surface morphology of the obtained films was observed by an atomic force microscopy (AFM) (Seiko

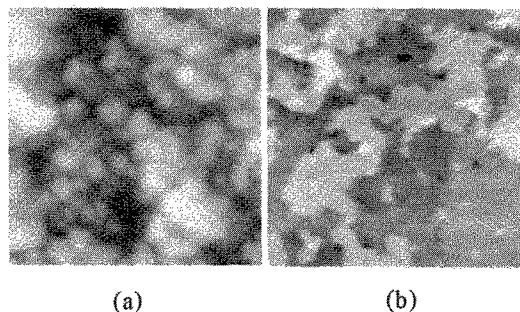


Fig.2. (a) The AFM images of the Y-type film (a) and the Hetero film (b). The scanning area is 2 $\mu\text{m}^2$ .

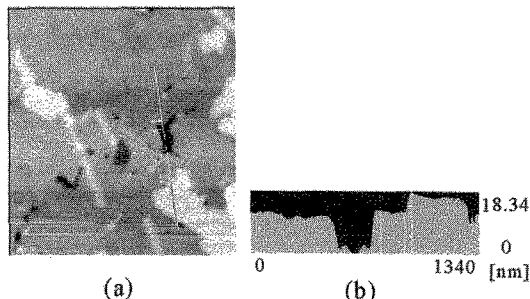


Fig.3. The AFM image of Hetero film/AA buffer//ITO (a) and the line profile (b). The scanning area is 2 $\mu\text{m}^2$ .

Instruments Inc.). The layered structures of the obtained films were investigated by a reflected X-ray diffraction (XRD) (Rigaku Co., Ltd). Absorption spectra were measured by a double beam spectrometer (Shimadzu Co., Ltd) in the reflection mode with a configuration of Glass/ITO/ LB films /Counter Electrode of Al film. The chemical bonding states of AlPcTr in the LB films were investigated by X-ray photoelectron spectroscopy (XPS) with a Mg X-ray source (Shimadzu Co., Ltd).

### 2-2. Simulation of Absorption Spectrum

WinMOPAC 3.9 Professional (Fujitsu) was used for the simulation of the absorption spectrum of AlPcTr. It is Semi-empirical Molecular Orbital program. For the first step, we optimized the molecular structure by using PM5 method of MOPAC2000. Optical absorption spectra were calculated by using a CNDO/S method of MOS-F.

It is expected that the intra-molecular electrons distribution and the optical absorption spectrum of AlPcTr are changed by applying electric field. It was, however, difficult to evaluate the electric field effect directly using MOPAC. Here we ionized the AlPcTr molecule and evaluated the absorption spectra indirectly. In the experiment  $\text{CH}_3(\text{CH}_2)_3\text{O}$  radical were added to AlPcTr in order to increase solubility to an organic solvent. But the calculation was done without the side chain, since the electronic influence of the side chain on

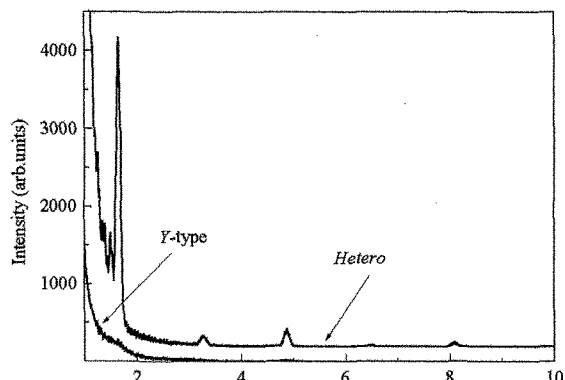


Fig.4. The XRD patterns of the Y-type and the Hetero film.

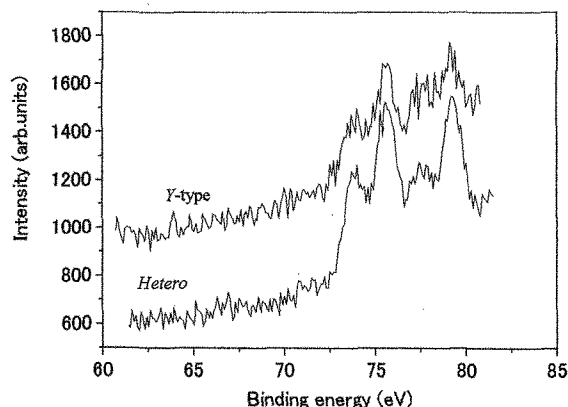


Fig.5. The XPS spectra of the Al 2p<sub>1/2</sub> 2p<sub>3/2</sub> in the Y-type film and the Hetero film.

the  $\pi$ -electrons ring was little.

### 3. Results and Discussion

Figure 2 shows the AFM images of the Y-type film with 60 layers (a) and the Hetero film with 40 layers (b) on ITO. The surface roughness  $R_a$  of the films was (a) 10.5 nm and (b) 2.4 nm, respectively. The Y-type film revealed a cohesive structure and comparatively disordered layers. On the other hand, the Hetero film was stratified well. It was thought that the difference of molecular length in AA, 2.7 nm and AlPcTr, 1.0 nm resulted in the cohesive structure of the Y-type film. The fluctuation of the layered structure was, however, reduced by introducing the pure AA layer in the Hetero film. Furthermore Fig. 3 shows AFM image and the line profile of the Hetero film (20 layers) / AA buffer // ITO. Since the substrate surface became hydrophobic by introducing the AA buffer layers, the laminar and smooth film was obtained. The surface flatness has improved to  $R_a$  of 1.6 nm. Then the surface flatness did not change even the number of layers was increased. The step height evaluated was *ca.* 5.8 nm or 11 nm, of which the value was well consistent with the length of one or two couples of AA molecules.

Figure 4 shows the typical XRD patterns of the Y-type and the Hetero film, respectively. Bragg reflection peaks were clearly observed in the Hetero film, while those were not obvious in the Y-type film. The lattice space of the Hetero film was *ca.* 5.4 nm, of which the value was approximately twice as long as the molecular length of AA. The larger intensity in the odd

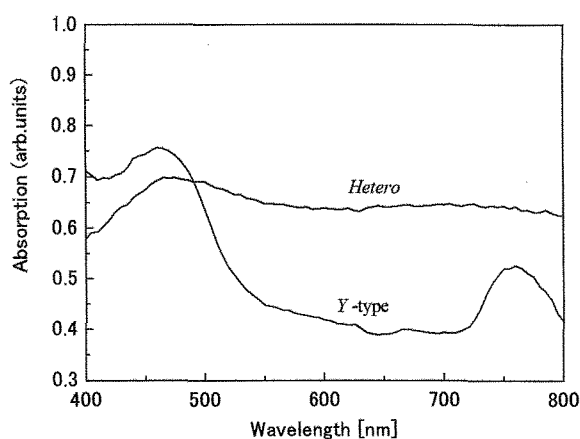


Fig.6. The Absorption spectra of the Y-type film (80 layers) and the Hetero film (60 layers).

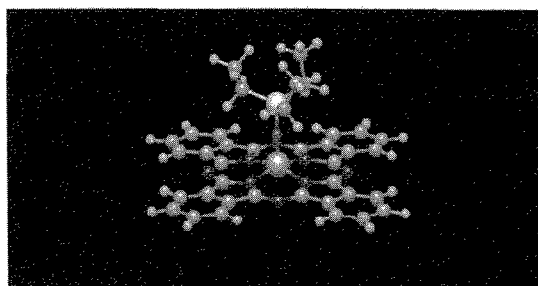


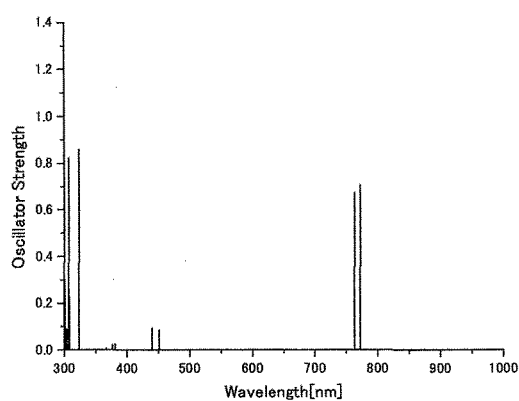
Fig.7. The optimized molecular structure of AlPcTr.

Miller index was caused by Ca ions at interfaces every two layers.

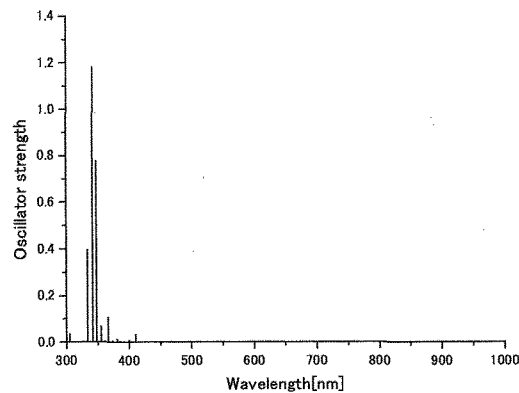
Figure 5 shows the XPS spectra of the Y-type and the Hetero film. The films were etched by Ar ions for 1 min. The XPS spectra were calibrated by the Au 4f<sub>7/2</sub> peak. The concentration ratio of Al 2P<sub>1/2</sub> 2P<sub>3/2</sub> in (Y-type film : Hetero film) was (1.0 : 1.3). It indicated that AlPcTr molecules were similarly accumulated in the both LB film.

Figure 6 shows the optical absorption spectra of the Y-type and the Hetero film. The absorption peak at *ca.* 760 nm, which was attributed to the  $\pi$ - $\pi^*$  transition of the Pc derivative, was distinctly broadened or vanished in the Hetero film.

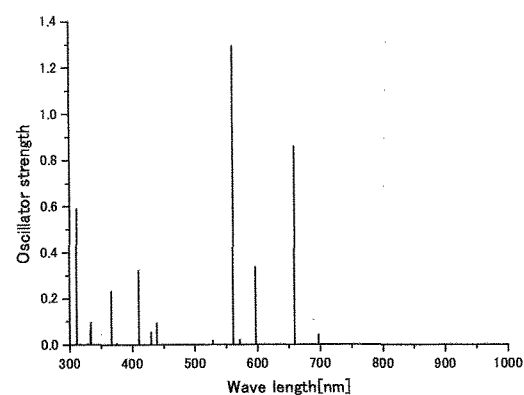
Figure 7 shows the molecular structure of AlPcTr



(a)



(b)



(c)

Fig.8. The simulated absorption spectra of AlPcTr (a), AlPcTr<sup>2+</sup> (b), and AlPcTr<sup>2-</sup> (c).

optimized by PM5 method of MOPAC2000. Without any bonding breaks the calculation converged to the stable AlPcTr structure. Figure 8 shows the absorption spectrum of the AlPcTr (a), AlPcTr+2 (b) and AlPcTr-2 (c) calculated by CNDO/S method of MOS-F. In the simulation the characteristic absorption peak of  $\pi-\pi^*$  transition at *ca.* 760nm appeared. It almost disappeared in the positively charged AlPcTr in contrast with a small blue shift of the negatively charged state. And the absorption spectrum of the positively charged AlPcTr was similar to that of the Hetero film.

From the results of AFM images and XRD patterns it was confirmed that the alignment of the LB films was strictly improved by inserting the AA buffer layers on ITO substrates and by adopting the accumulation of the Hetero structure. However the characteristic absorption peak of the Pc derivative almost vanished. From the comparison with the simulated results it was thought that the change of the absorption spectra was caused by accompanied anions surrounding AlPcTr molecules in the Hetero film.

#### 4. Summary

The LB films of the mixture of AlPcTr and AA were accumulated. From the results of AFM images and XRD patterns it was confirmed that the alignment of the LB films was strictly improved by adopting the accumulation of the Hetero structure and/or by inserting the AA buffer layers on ITO substrates. The absorption peak at *ca.* 760 nm was broadened or vanished in the Hetero film. The results of the MO simulation suggested that the AlPcTr molecules in the Hetero film were positively charged possibly by the effect of anions surrounding the molecules. The obtained results also demonstrate the possibility of the novel EC color changes by applying electric field in the LB films.

#### References

- [1] C. G. Granqvist: Handbook of Inorganic Electrochromic Materials (1995).
- [2] P. N. Moskalev and N. I. Alimova: Russ. J. Inorg. Chem. **20** (1975) 1474
- [3] H. Bucher, and H. Kuhn: Z. Naturforsch **25b** (1971) 1323.
- [4] T. Kato, S. ALSADOON, N. Iwata, H. Yamamoto: Advanced Nanomaterials and Nanodevices (2002) 545-555.
- [5] K. Suzuki, M. Okamoto, S. ALSADOON, H. Yamamoto: Trans. MRS-J **27**[2] (2002) 345
- [6] H. Kuhn, D. Mobius, and H. Bucher, Techniques of Chemistry, edited by A. Weissberger and B. W. Rossiter, Wiley (1973).

(Received December 23, 2004; Accepted January 31, 2005)