

Chromogenic Properties of Phthalocyanine Derivatives Langmuir-Blodgett Films

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A phthalocyanine derivative has been focused as a noble chromogenic material. For the first time we grew mixtured LB films, which consist of aluminium 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine triethyl siloxide (AlPcTr) and arachidic acid (AA). These were deposited on glasses under the conditions of the surface pressure of 24 mN / m, and the stroke speed of 12mm / min on the water subphase of pH = 10.3. The obtained films had a Y-type of accumulated layers with the lattice spacing of about 5.3 nm. Changes of absorption spectra were observed by applying voltages to the sample ITO / AlPcTr / Al₂O₃ / Al.

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 assembled structure with an alignment of molecules is a determinant to make clear a substantial function of the molecule film. In this work, we have paid attention to 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 (EC) system. The conventional EC 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 been developed.

Bucher and Kuhn have reported EC phenomenon produced by the electric field application to the single molecule film of coloring matter.⁴⁾ According to the report, response speed was very quick although the amount of color change was small. 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 this study, we prepared the AlPcTr / AA mixtured LB films and studied the fundamental materials properties of the films. Furthermore the chromogenic properties of the films induced by applying electric fields were discussed.

2. EXPERIMENTAL PROCEDURES

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, CH₃(CH₂)₁₈COOH) was used in order to stabilize the Langmuir film on the subphase. We prepared a 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 is obtained from Kanto-Chemical Co., Ltd.

We fabricated LB films by a Kuhn type of apparatus⁵⁾ with a moving barrier and a vertical dipping / lifting handler. The details of the apparatus are described

elsewhere⁶⁾. 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 NaOH⁷⁾.

The film was transferred onto the substrates at a constant surface pressure (24 mN / m) through vertical dipping / lifting strokes. The stroke speed was 12 mm / min. The substrates used were ITO glasses (Kinoene-Kogaku-Kougyou Co., Ltd) cut to the size of 1.5 cm². The sheet resistance of the ITO glass was 10 Ω / cm². The accumulated structures of the obtained films were investigated by a X-ray diffraction (XRD) (Rigaku Co., Ltd). The EC cell was prepared to measure the absorption spectra of the reflection. The solid cell has a configuration of glass / ITO / Al₂O₃ / Al as is schematically shown in Fig. 2 (a). The thickness of the LB film was

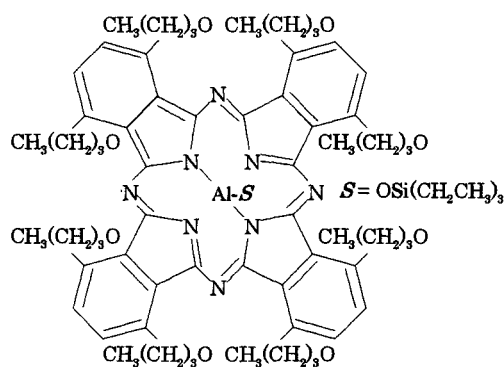


Fig. 1. Chemical structure of AlPcTr

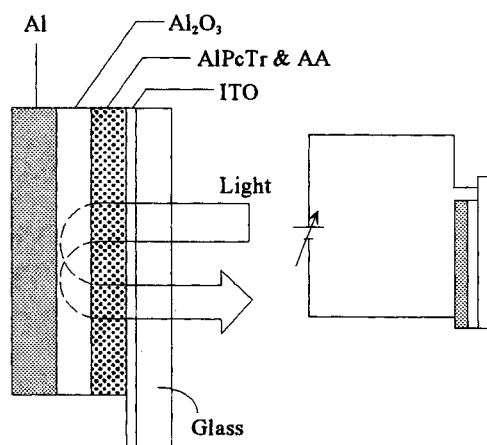
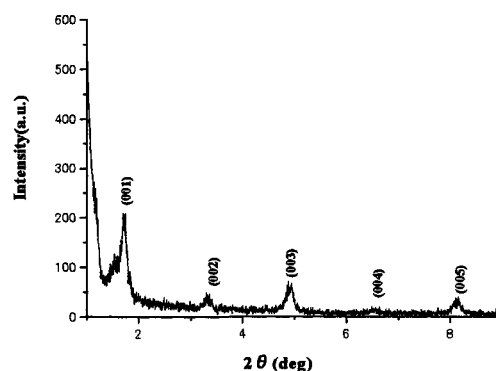


Fig. 2. (a) The schematic configuration of the solid EC cell. (b) The block diagram of the measurement system for optical and electric properties of the solid cell

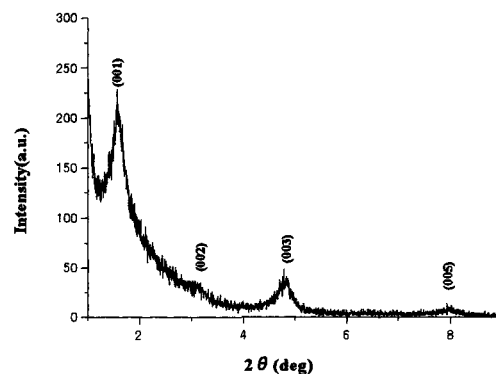
about 850 nm. The absorption spectra of the reflection were measured by a double beam spectrometer (Shimadzu Co., Ltd). The voltage-current (V-I) characteristic were measured by a potentiostat / galvanostat (Hokuto-Denko Co., Ltd.) The triangular voltage was scanned at the rate of 2 V / min.

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 reports⁸⁾.



(a) AA LB films



(b) AlPcTr / AA LB films

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

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.

When the cells had the structure shown in Fig. 2, most of the cells revealed irreversible changes of absorption spectra by applying comparatively high voltage above +2V. Then the cyclic voltammogram (CV) of the cell was studied. Figure 4 shows the typical CV characteristics. The 1st cycle revealed a large hysteresis in the cell of Al electrodes, while no hysteresis in the case of Au electrodes. The ohmic current observed was comparatively large and was caused by the leakage through defects of insulation. The transitional color changes observed may be related to the 1st cycle V-I response.

On the other hand, the successive CV were stable and showed a small hysteresis. These results suggest that stable small redox reactions take place in the cell but no color change is caused by them.

Color changes depending on the applied voltage were seldom observed in some samples. Figure 5 shows the typical changes in the absorption spectra of the film.

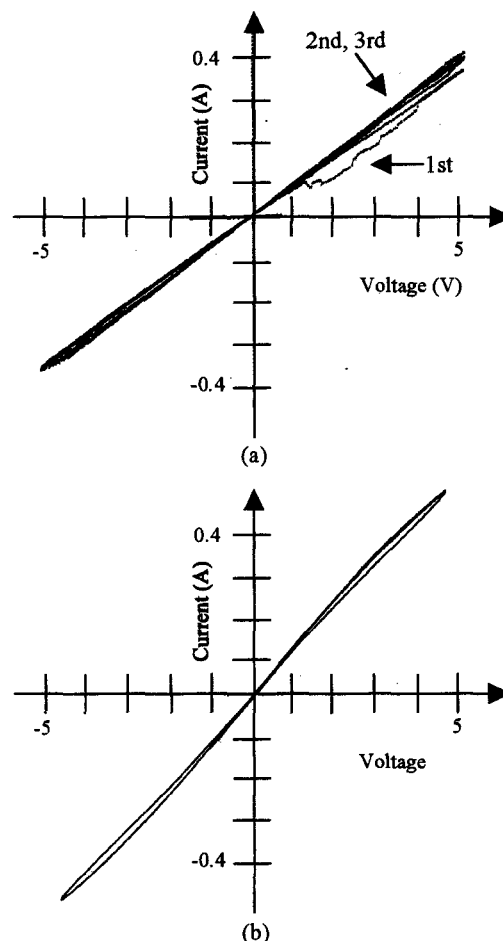


Fig. 4. The V-I characteristics of the EC cell. The triangular voltage was scanned at the rate of 2 V / min in the cell of (a) ITO / LB films / Al and (b) ITO / LB films / Au. The area of the electrode was about 100 mm².

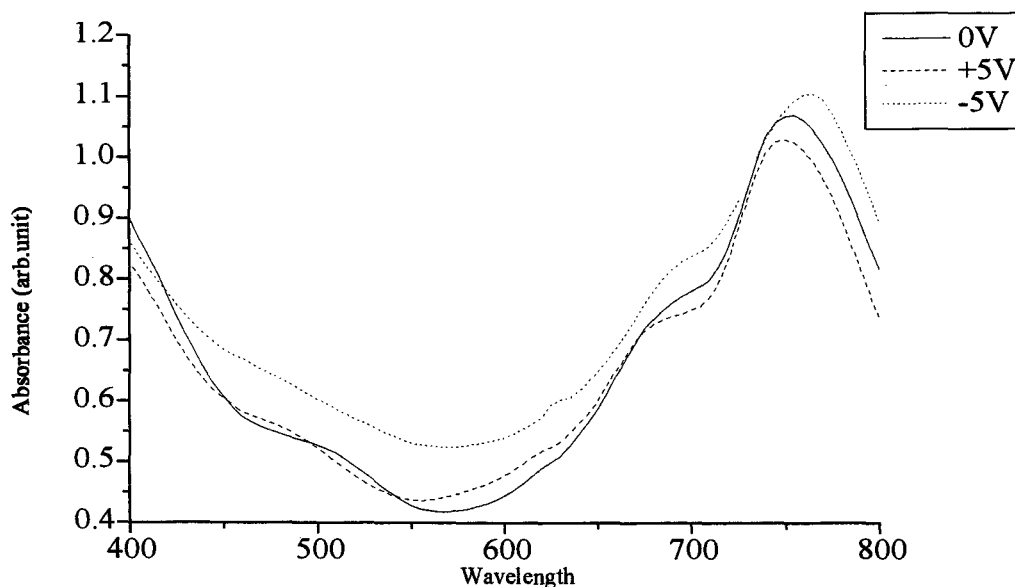


Fig.5. The absorption spectra of the reflection of the AlPcTr / AALB films.

The spectrum of the original green state has a λ_{max} at about 750 nm and a subpeak at about 680 nm. The color of the cell changed slightly, when a voltage above 5 V was applied at the ITO electrode. The spectrum has a large peak at about 740 nm and a subpeak at about 670 nm. On the other hand, the color of the cell changed largely by applying a voltage of -5 V. Then λ_{max} shifted to about 770 nm. There color change was observed clearly only by the 1st applying voltage. This result may indicate the possibility of EC induced by electric field accompanying with the comparatively large leak current.

4. SUMMARY

The chloroform solution of a 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 24 mN / m, and 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 spectrum of the original green state has a λ_{max} at about 750 nm and a subpeak at about 680 nm. In the most of cells irreversible color changes by applying voltages were formed accompanying with a hysteresis V-I characteristic. Seldom transitional color changes corresponds to the polarity of electric field were also found. The leak current of the cells must be suppressed in order to clear the possibility of EC by applying electric fields.

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References

1. K. B. Blodgett, *J. Am. Chem. Soc.*, **57** (1935) 1007.
2. C. G. Granqvist, "Handbook of Inorganic Electrochromic Materials", Elsevier, Amsterdam (1995).
3. P. N. Moskalev and N. I. Alimova, *Russ. J. Inorg. Chem.*, **20** (1975) 1474.
4. H. Bucher, and H. Kuhn, "Z. Naturforsch", **25b** (1971) 1323.
5. H. Kuhn, D. Mobius, and H. Bucher, "Techniques of Chmistry", edited by A. Weissberger and B. W. Rossiter, Wiley (1973), Vol. **I**, Part **IIIB**.
6. H. Yamamoto, T. Sugiyama, and M. Tanaka, *Jpn. J. Appl. Phys.* **24** (1985) L305.
7. K. Suzuki, T. Kato, Y. Nakamura, N. Iwata, H. Yamamoto, *Trans. Mate.Res.Soc.Jpn.*, **26**(2001) 1335.
8. A. Matsuda, M. Sugi, T. Fukui, S. Iizima, M. Miyahara, and Y. Otsubo, *J. Appl. Phys.* **48** (1977) 771.

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