

## Molecular p-n Junction of Chlorophyll *a* and Crystal Violet Fabricated by Langmuir-Blodgett Technique

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The electrical and photoelectrical characteristics in Langmuir-Blodgett films with a heterojunction between chlorophyll *a* (Chl-*a*) and crystal violet (CV) have been studied. First, Chl-*a* were spread on the water surface and transferred onto an ITO-coated glass substrate. Then, a mixed system of CV and arachidic acid (C20) with a molar mixing ratio of 1:5 was transferred onto the Chl-*a* coated surface, and finally, aluminum (Al) top electrode was vacuum-deposited onto the multi-layered system forming a layered structure of ITO/Chl-*a*/CV-C20/Al. Both under dark and photo illumination, the heterogeneous LB system shows rectifying properties, which are forward when a positive potential is applied to the ITO electrode. Furthermore, the action spectra of the photovoltaic current show distinct absorption peaks at 440 nm, 620 nm and 680 nm, which are in agreement with the superposition of the visible absorption spectra of the Chl-*a* and CV-C20 LB films. The polarity of the current and the action spectra indicate that the Chl-*a* and CV act as p-type and n-type molecular semiconductors, respectively forming a molecular p-n heterojunction.

Key words: Langmuir-Blodgett Films, chlorophyll *a* (Chl-*a*), crystal violet (CV), action spectra, rectifying properties, molecular p-n heterojunction

### 1. INTRODUCTION

Chlorophyll *a* (Chl-*a*, Fig. 1), which is one of the principal photoreceptors in the chloroplast of green plants, has long been studied as a building block in the Langmuir-Blodgett (LB) films both from the technological and scientific viewpoints [1-4]. Earlier works reported that the photoconduction in solid Chl-*a* films is of p-type semiconductor [5, 6]. Later, Jones and co-workers reported that the LB system of Chl-*a* molecules acts as p-type semiconductor in the photocell with a layered structure of Au/Chl-*a*/Al because of the polarity of the rectifying properties and the correspondence of the action spectra of the photocurrent to the visible absorption spectra [7].

Saito and co-workers reported that Schottky and p-n junction diodes can be fabricated by the LB technique using various surfactant derivatives of dye molecules [8] and that the diodes exhibit essentially the same photoelectric behavior as the corresponding evaporated dye film diodes, although the LB systems have inert hydrocarbon chains [9, 10]. Since then, the appropriate combination of p- and n-type molecular systems have been explored, and among them, the crystal violet (CV, Fig. 1) derivative forms a relatively good n-type layer to construct the heterogeneous p-n junctions using various p-type molecular systems such as paraquat (PQ) and merocyanine (MO) derivatives [8-10]. For instance, the

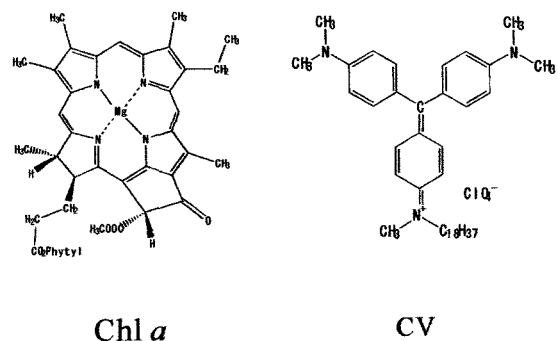


Fig. 1. Molecular structures of chlorophyll *a* (Chl-*a*) and crystal violet (CV) derivative.

open-circuit photovoltage of the Al/CV-C20/MO-C20/Ag LB cell reaches 0.7 V [8].

Although Chl-*a* is known to act as a p-type semiconductor and the Schottky-type photodiodes have been actually fabricated [7, 11], the appropriate combination to form the p-n diodes has not yet come to our knowledge. Lei and co-workers reported that the fluorescence of the Chl-*a* monomer in the Chl-*a*-bialkyne acid mixed LB system is quenched by

CV molecules\* adsorbed on the surface and that the quenching is due to electron transfer rather than energy transfer between Chl-*a* and CV molecules [12].

Here we report that the interface between Chl-*a* and CV molecules in the heterogeneous LB system acts as molecular p-n junction.

## 2. EXPERIMENTAL

### 2.1 Sample preparations

The film-forming materials used in this work are shown in Fig. 1. Chlorophyll *a* (Chl-*a*), purified from *Spirulina*, and the amphiphilic derivative of crystal violet (CV) were purchased from Wako Pure Chemicals (Japan) and Hayashibara Biomedical Laboratories Inc. (Japan), respectively, and used without further purification.

Chl-*a* molecules were spread on the water surface using a mixture of *n*-hexane and acetone, where acetone is 5-10% in volume. The subphase contained 0.5 mM CaCl<sub>2</sub> and 0.5-2.0 mM Tris/HCl buffer to keep the pH in the range 7.5-8.5 for the Chl-*a* monolayer operations. All the operations treating Chl-*a* monolayers were performed under dim green light. The surface pressure( $\pi$ )-area per molecule (*A*) isotherm was in good agreement with earlier works[3, 4, 7, 13-15].

CV molecules were mixed with arachidic acid (C20) with molar mixing ratio [CV]:[C20]=1:5 in chloroform and spread on the water surface. The subphase contained 0.5 mM CaCl<sub>2</sub> and the pH was kept in the range 6.0-6.5 by adding appropriate amount of NaHCO<sub>3</sub> and HCl for CV-C20 monolayer operations.

The Chl-*a* molecules were compressed to 18 mN/m and transferred onto a clean ITO (indium-tin-oxide)-coated glass plate by the vertical dipping technique. First, the substrate was immersed in the subphase, and then, Chl-*a* monolayer was formed and the transfer was initiated by the upward movement of the substrate beneath the water surface. The dipping speed was 5.4 mm/min. Forty layers were deposited on the substrate unless otherwise stated. The deposition ratio was 1.0 for upward strokes but systematically lower for downward ones (ca. 0.8), which were in good agreement with the earlier works [16].

Subsequently, the mixed films of CV-C20 were transferred on the Chl-*a* coated surface by the vertical dipping method at 25 mN/m with the dipping speed of 5.4 mm/min. Forty layers were also deposited on the Chl-*a* coated surface in order to fabricate the heterojunction between Chl-*a* and CV dyes, and finally, circular aluminum (Al) top electrodes of 0.3 cm<sup>2</sup> were vacuum-evaporated onto the heterogeneous LB system to fabricate the layered structure of ITO/Chl-*a*/CV-C20/Al, as shown in Fig. 2.

Temperature of the subphase was kept in the range 18-22°C both for Chl-*a* and CV operations.

### 2.1 Optical, electrical and photoelectrical measurement

\*The mixed LB system of Chl-*a* and bialkyne was immersed in an aqueous solution of CV for 5 min and the sample was dried [12].

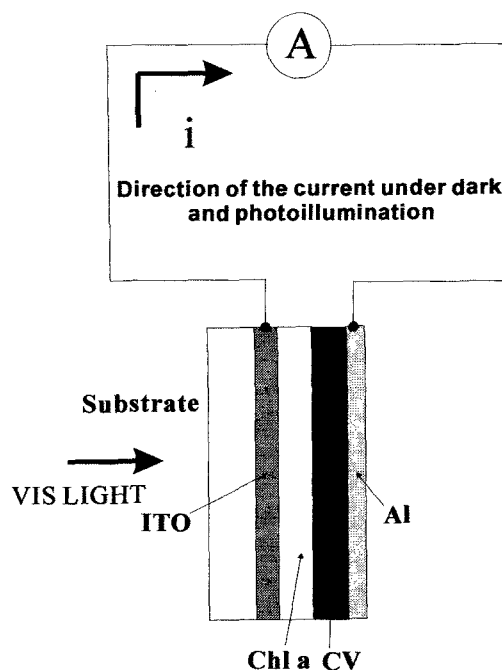


Fig.2. The layered structure of ITO/Chl-*a*/CV-C20/Al fabricated by LB technique and the direction of the short-circuit current under dark and photo illumination.

Visible absorption spectra of the LB films were measured by a Hitachi Model 320 spectrophotometer.

The samples were set in an aluminum box through which dried nitrogen gas of 20-22°C was flowed and the electrical and photoelectrical measurements were performed using a Keithley Model 617 programmable electrometer. A 75 W xenon lamp was used as the light source, which was monochromatized by a Ritsu-Oyokogaku Model MC-10N monochromator. The light power was monitored by an Advantest Model TQ8210 optical power meter during the whole photoelectrical measurement.

## 3. RESULTS AND DISCUSSION

An appreciable short circuit current of the order of pA was observed under dark and the direction of the current is of Al to ITO in the photocell, as shown by the arrow in Fig. 2.

The direction of the short-circuit photocurrent was also the same as that under dark. Figure 3 shows the short-circuit photocurrent of an ITO/Chl-*a*(40 layers)/CV-C20(40 layers)/Al cell under the illumination of 440-nm monochromatic light. The photocurrent increases linearly with increasing the light intensity up to 0.2 W/m<sup>2</sup> but it shows sublinear behavior when illuminated by the greater power.

Figure 4 shows the I-V characteristics of the ITO/Chl-*a*(40 layers)/CV-C20(40 layers)/Al cell under dark and 440-nm illumination, which were obtained by measuring the steady-current of the photoresponse. The cell shows a weak rectifying property, which is forward when a positive potential is applied to the ITO electrode both under dark and photo illumination. The quantum

efficiency, the maximum power conversion efficiency and the fill factor were  $10^{-5}$  (0.01%),  $10^{-6}$  (0.0001%) and 0.33, respectively.

Figure 5 shows a typical action spectrum of the photocurrent of the cell. The spectrum is of

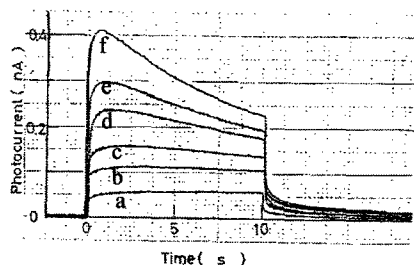


Fig. 3. The short-circuit photocurrent of an ITO/Chl-a/CV-C20/Al cell under photo illumination of 440-nm monochromatic light; a:0.08 W, b:0.14 W, c:0.22 W, d:0.36 W, e:0.50 W, f:0.74 W.

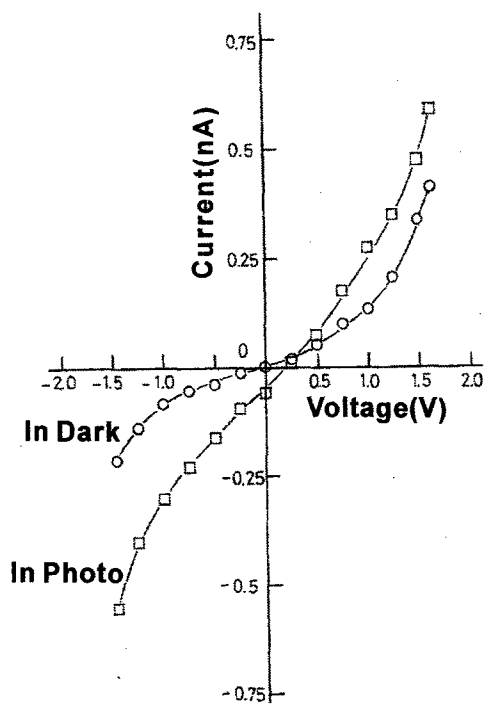


Fig. 4. The I-V characteristics of the ITO/Chl-a(40 layers)/CV-C20(40 layers)/Al cell under dark and 440-nm illumination, which were obtained by measuring the steady-current of the photoresponse.

photocurrent normalized to the incident power of the light source at each wavelength. The action spectra of the photovoltaic current show distinct absorption peaks at 440 nm, 620 nm and 680 nm, which are in good agreement with the superposition of the absorption spectra of the Chl-a and CV-C20 LB films, as shown in Fig. 6. The visible absorption spectra of the Chl-a and CV-C20 LB films are also in good agreement with those reported in the earlier work by Jones *et al.* [7] and Sugi *et al.* [8], respectively. The polarity of the current under dark and photo illumination and the resemblance of the action spectra of the photocurrent to the superposition of the two dyes indicate that the Chl-a and CV are acting as p-type and n-type molecular semiconductors, respectively forming a molecular p-n heterojunction, although the hopping regime should be taking into account because of the inert alkyl-chain moiety [9].

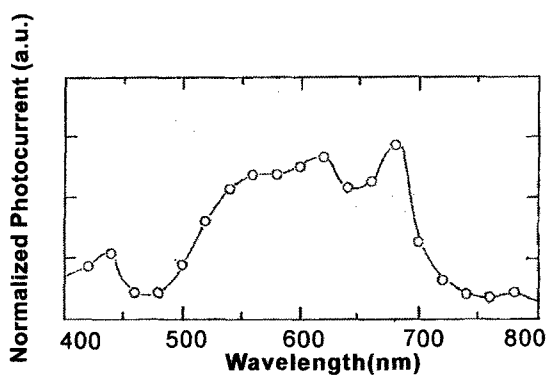


Fig. 5. A typical action spectrum of the photocurrent of the ITO/Chl-a(40 layers)/CV-C20(40 layers)/Al cell. The spectrum is of photocurrent normalized to the incident power of the light source at each wavelength.

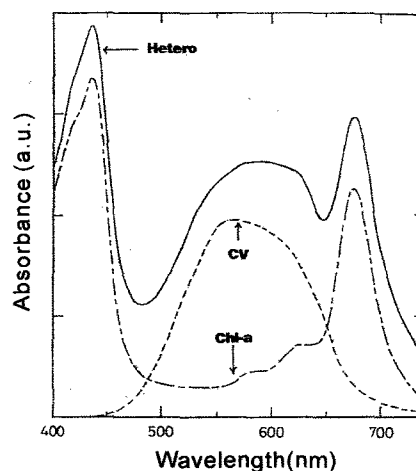


Fig. 6. The visible absorption spectra of the Chl-a, CV and heterogeneous (Hetero) Chl-a/CV-C20 LB films.

#### 4. CONCLUSION

The electrical and photoelectrical characteristics in Langmuir-Blodgett films with a heterojunction between Chl-*a* and CV have been studied. Both under dark and photo illumination, the heterogeneous LB system with the layered structure of ITO/Chl-*a*/CV-C20/Al shows a rectifying property, which is forward when a positive potential is applied to the ITO electrode. Furthermore, the action spectrum of the photovoltaic current has distinct absorption peaks at 440 nm, 620 nm and 680 nm, which are in agreement with the superposition of the visible absorption spectra of the Chl-*a* and CV LB films.

It has been revealed that Chl-*a* and CV form p-type and n-type LB layers, respectively, giving an appropriate combination for constructing molecular photodiode that covers overall visible region.

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