Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Photodiode Consisting of Flavin-Viologen Hetero-Langmuir-Blodgett Films

Jeong-Woo Choi [a], Min Jin Kim [a], Sung Wook Chung [a], Se Yong Oh [a], Won Hong Lee [a] & Dong Myung Shin [b]

[a] Department of Chemical Engineering, Sogang University, Seoul, 121-742, Korea

[b] Department of Chemical Engineering, Hong Ik University, Seoul, 121-791, Korea

Version of record first published: 04 Oct 2006.

To cite this article: Jeong-Woo Choi , Min Jin Kim , Sung Wook Chung , Se Yong Oh , Won Hong Lee & Dong Myung Shin (1996): Molecular Photodiode Consisting of Flavin-Viologen Hetero-Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 367-372

To link to this article: http://dx.doi.org/10.1080/10587259608040357

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 367–372
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR PHOTODIODE CONSISTING OF FLAVIN-VIOLOGEN HETERO-LANGMUIR-BLODGETT FILMS

JEONG-WOO CHOI, MIN JIN KIM, SUNG WOOK CHUNG, SE YONG OH, WON HONG LEE
Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea
DONG MYUNG SHIN
Department of Chemical Engineering, Hong Ik University, Seoul 121-791, Korea

Abstract A molecular photodiode was fabricated with the hetero-Langmuir-Blodgett(LB) film consisting of an electron acceptor(A) and sensitizer(S). N-Allyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4,4'-bipyridium Dibromide and 7,8-dimethyl-10-dodecyl isoalloxazine were used as A and S units, respectively. By aligning hetero-LB film of A/S units on ITO glass with an aluminum thin film, a molecular photodiode with the structure of Metal/Insulator/Metal(MIM) was constructed. Due to excitation by irradiation with a 460 nm monochromatic light source, the photo-induced unidirectional flow of electrons in the MIM device could be achieved and was detected as photocurrents. The direction of energy flow was in accordance with the energy level profile across the LB films. The photoswitching function was achieved and the rectifying characteristic was observed in the molecular device.

INTRODUCTION

In the initial process of photosynthesis, a biological electron transfer system, photoelectronic conversion occurs and then long-range electron transfer takes place very efficiently in one direction through the biomolecules.[1,2] The specific energy and electron transfer takes place on a molecular scale due to the redox potential difference as well as the electron transfer property of functional molecules, especially the electron-acceptor and sensitizer.[3,4]

Various artificial molecular devices have been fabricated by mimicking the electron transport function of biological photosynthesis.[3-8] The electrochemical photodiode consisting of Langmuir-Blodgett(LB) films of three functional molecules or an aligned triad on the electrode which worked in electrolyte solution have been made.[4-5] Studies of electron transfer between electrode and excited dye molecules were carried out. The Metal/Insulator/Metal(MIM) structured device consisting of hetero-LB film of a sensitizer(flavin) and an electron acceptor(phorphyrin) was fabricated and photo-induced electron transfer was investigated.[3,6-8]

In the present paper, the MIM structured device was fabricated with the hetero-Langmuir-Blodgett(LB) film consisting of viologen and flavin derivatives, which are an electron acceptor(A) and a sensitizer(S), respectively. Molecules of two functional materials were arranged on ITO glass regularly in space normal to the electrode surface, e.g. S/A, by the LB method. Finally by depositing aluminum on the hetero-LB film, a molecular device with MIM structure was constructed. Photocurrent properties of the MIM structured device were investigated to evaluate the direction of electron transfer and photoswitching function.

EXPERIMENTAL DETAILS

Materials and Deposition of LB Films

Two kinds of functional materials were used. N-Allyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4,4'-bipyridium Dibromide (viologen) and 7,8-dimethyl-10-dodecyl isoalloxazine (flavin) were used as A and S unit, respectively. Two materials were synthesized according to the methods in reference 3, 9 and 10. The measurement of surface pressure-area isotherms and the deposition of LB films were carried out with a circular Langmuir trough (Nima Tech., England).

Cyclic Voltammetry

Cyclic voltammetry was carried out at 25°C with a CV-75 potentiostat (BAS, Germany). A three-electrode system composed of the working (Pt plate), reference (Ag/AgCl) and counter (Pt plate) electrode was used. The deionized water containing KCl for the cyclic voltammetry of A was used as the electrolyte. The working electrode was a Pt plate deposited with LB film of A for the measurement of redox potential.

Photocurrent Measurement

The molecular photodiode was fabricated with the hetero-Langmuir-Blodgett(LB) film consisting of A and S units, respectively. A and S materials were arranged on ITO glass regularly in space normal to the electrode surface by the LB method. By depositing aluminum on the hetero-LB film, a molecular device with the structure of Metal/Insulator/Metal(MIM) was constructed. A schematic diagram of the apparatus for photocurrent measurement is shown in Figure 1. An input exciting light of wavelength 460nm was generated with xenon lamp system. The photocurrent was detected through a current-voltage amplifier, A/D converter and personal computer. I-V measurement was carried out using Hewlett Packard 4145B parameter analyzer.

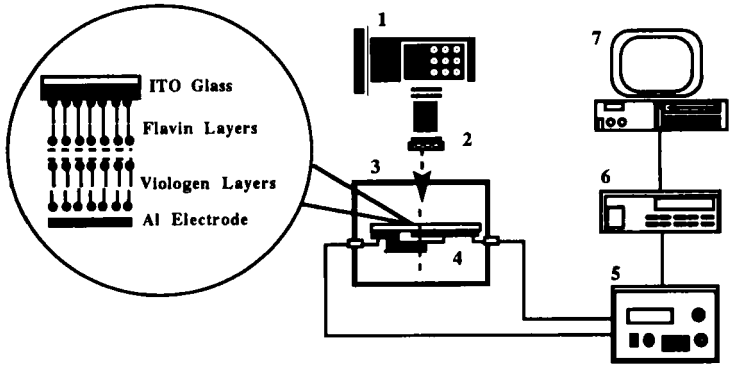

FIGURE 1 Schematic illustration of a hetero-type cell and experimental setup: 1, 150W Xe lamp; 2, 460nm filter; 3, shield box; 4, MIM device; 5, current-voltage converter; 6, A/D converter; 7, personal computer.

RESULTS AND DISCUSSION

Surface-pressure Area Isotherm

The π-A isotherm of each materials are shown in Figure 2..The isotherm of the monolayer of S has two condensed regions at 20mN/m and 40mN/m. At 40mN/m, the monolayer is more stable and the limiting area per molecule is 24Å^2. By contrast, the expanded and condensed regions are clearly observed for the monolayer of A. At a surface area less than 60Å^2/molecule, there is an abrupt increase of slope. This is clearly also due to a phase change and represents a transition to ordered solidlike arrangement of the two-dimensional array of molecules. The limiting area per molecule is 60Å^2.

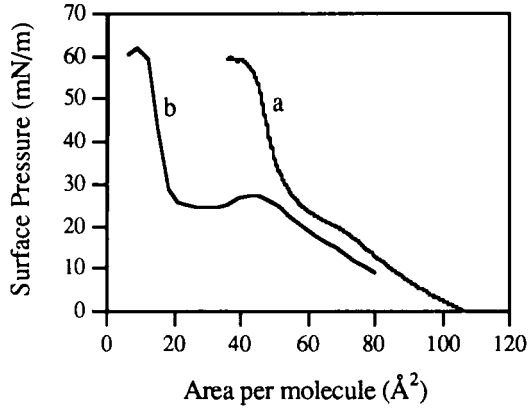

FIGURE 2 Surface pressure-area isotherm of functional materials: a, A; b, S.

Analysis of Cyclic Voltammograms

The cyclic voltammogram of A is shown in Figure 3. During positive potential sweep, the anode current reaches a maximum at -0.15V (vs. Ag/AgCl electrode). This indicates that the concentration of oxidized A is maximized at -0.15V. When the cyclic direction is reversed, the oxidized form of A is reduced back to the original starting material at -0.44V. Thus the redox potential of A is -0.36V. The redox potential of S is about -0.3V.[6]

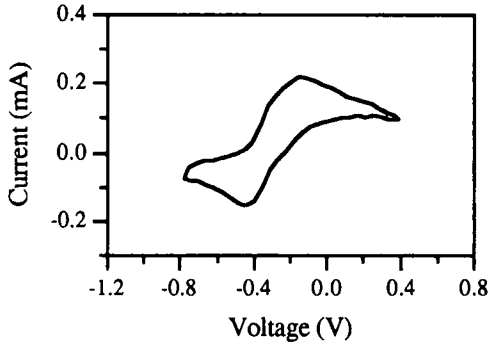

FIGURE 3 Cyclic voltammogram of A.

Photocurrent Response

Figure 4. shows the photocurrent-time response with the irradiation of a 460nm monochromatic light by a xenon lamp system. The photocurrent of the MIM device consisting of A/S is generated by light excitation. When a forward bias is applied in accordance with the energy level profile in the MIM device, a stable photocurrent is

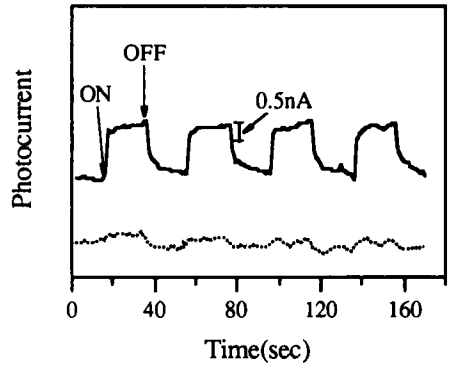

FIGURE 4 Photocurrent-time curve of MIM device at 2.5(V) bias voltage: line, forward bias voltage; broken line, reverse bias voltage.

generated. With repeated step illumination, the reproducible photocurrent is generated accordingly. The photocurrents are very stable and level of responses is consistent during the repeated cycle over 30 minutes. The results indicate that the photoswitching function of the MIM device is achieved. When reverse bias is applied, photocurrent is much smaller than that of forward case. In the proposed molecular device, the photo-induced unidirectional flow of electrons could be achieved due to the redox potential difference as well as electronic coupling between the functional molecules.

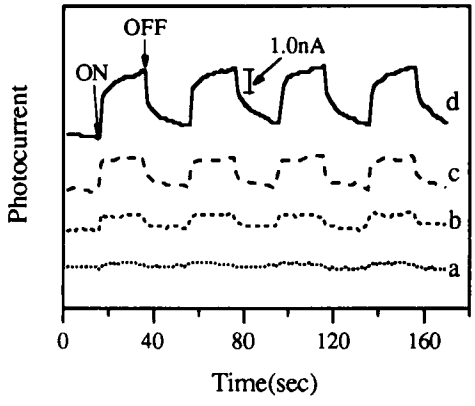

FIGURE 5 Photocurrent-time curves of MIM device to the various forward bias voltage: curve a, 0.5V; curve b, 1.5V; curve c, 2.5V; curve d, 3.3V.

In Figure 5., it is also observed that the intensity of the photocurrent is dependent on the external bias voltage. As the external bias voltage is increased, higher photocurrents are generated. As shown in Figure 6., the rectifying characteristic is observed from the measurement of photocurrent(I)-voltage(V).

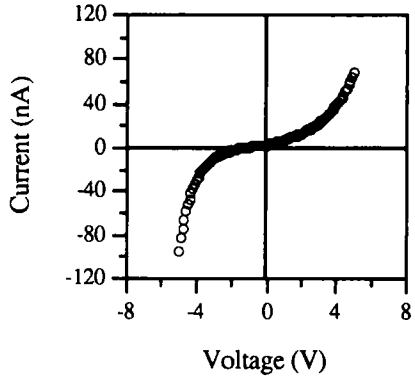

FIGURE 6 I-V characteristics of the MIM device.

CONCLUSIONS

It has been demonstrated that a molecular photodiode with metal/insulator/metal(MIM) structure is fabricated by the formation of LB multilayers consisting of an electron acceptor(A) and a sensitizer(S). By depositing aluminum on the hetero-LB film, a molecular device with the structure of Metal/Insulator/Metal(MIM) is constructed. When the forward bias voltage is applied in accordance with the energy level profile in the MIM device, stable photocurrents are generated. With repeated step illumination, the photoswitching function of the MIM device is achieved. Photocurrent flows in the direction of the energy profile of constituted LB films on illumination by light which can be absorbed by the sensitizer. Since the rectifying characteristic is observed in the I-V curve, a molecular device fabricated has the feasibility to be used as an photodiode.

ACKNOWLEDGEMENT

This work was supported by Research Fund, Korea Ministry of Education (Biochemical Engineering) 1995. Acknowledgement is also made to Dr. S. Isoda and Mr. M. Miyamoto at the Mitsubishi Electronic Corporation for their helpful discussion.

REFERENCES

1. J.Deisenhofer, Nature, 318, 618 (1985).
2. H. Kuhn, in F.T.Hong (ed.) Molecular Electronics: Biosensors and Biocomputers (Plenum Press, New York, 1993), p. 3.
3. S. Isoda, S. Nishikawa, S. Ueyama, Y. Hanazato, H. Kawakube and M. Maeda, Thin Solid Films, 210/211, 290 (1992).
4. M. Fujihira, K. Nishiyama and H. Yamada, Thin Solid Films, 132, 77 (1985).
5. M. Fujihira, K. Nishiyama and K. Aoki, Thin Solid Films, 160, 317 (1988).
6. S. Isoda, FED Journal, 2, 59 (1992).
7. M. Miyamoto, S. Isoda, K. Akiyama, S. Ueyama, S. Nishikawa, H. Kawakubo, Y. Hanazato, O. Wada and M. Maeda, Proc. 13th Symp. Future Electron Devices (Tokyo, October, 1994, FED, Japan), p. 192.
8. J.W.Choi, G.Y. Jung, S.Y. Oh, W.H. Lee and D.M. Shin, Thin Solid Films, accepted (1995).
9. F. Yoneda, Y. Sakuma, M. Ichiba and K. Shinomura, Chem. Pharm. Bull., 20, 1832 (1972).
10. P. Tundo, D. Kippenberger, M. Politi, P. Klahn and J. Fendler, J. Am. Chem. Soc., 104, 5352 (1982).