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Jeong-Woo Choi [a] , Byung Shik Seok [a] , Junhong Min [a] , Won Hong Lee [a] & Dong Myung Shin [b]

[a] Dept. of Chem. Eng., Sogang Univ., Seoul, 121-742, Korea

[b] Dept of Chem. Eng., Hong Ik Univ., Seoul, 121-791, Korea

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[a]Dept. of Chem. Eng., Sogang Univ., Seoul 121-742, Korea
[b]Dept of Chem. Eng., Hong Ik Univ., Seoul 121-791, Korea

A molecular photodiode with Metal/Insulator/Metal (MIM) structure was fabricated using the hetero-Langmuir-Blodgett (LB) films consisted of an electron acceptor (A) and a sensitizer (S). N-Docosylquinolium-TCNQ and 7,8-dimethyl-10-dodecyl isoalloxazine were used as A and S units, respectively. Due to excitation by irradiation with a 460 nm monochromatic light source, the photoinduced unidirectional electron flow in the MIM device could be achieved and was detected as photocurrent. The photoswitching function was achieved and the rectifying characteristics was observed in the proposed molecular device.

Keywords : Molecular Photodiode; Hetero-LB Films; Photocurrent; TCNQ; Flavin

INTRODUCTION

In the initial process of biological photosynthesis, an electron transfer system, the photoelectronic conversion occurs and then a long-range electron transfer takes place very efficiently in one direction through the biomolecules[1]. 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 an electron-acceptor and a sensitizer[2]. Various artificial molecular devices have been fabricated by mimicking the electron transport function of biological system[3-6]. In the present paper, a MIM structured device was fabricated with the hetero-LB

film consisting of TCNQ and flavin derivatives used as an electron acceptor (A) and a sensitizer (S), respectively. Photocurrent properties of the proposed device were investigated to evaluate the direction of electron transfer and photoswitching function.

EXPERIMENTAL DETAILS

TCNQ and flavin were synthesized according to the methods, [2,6-7] and used as A and S units, respectively. 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 was carried out at 25°C with a CV-75 potentiostat (BAS, Germany). The photoinduced electron transfer between the excited flavin LB films and the TCNQ LB films was investigated by steady-state fluorescence quenching experiments. An input exciting light of 460nm wavelength was generated with xenon lamp system, and the photocurrent of the MIM structured device was detected through a current-voltage amplifier, A/D converter and personal computer.

RESULTS AND DISCUSSION

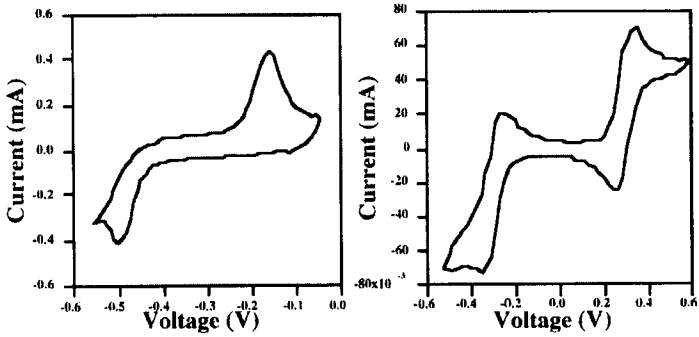


FIGURE 1. Cyclic voltammogram : (a) sensitizer, flavin; (b) acceptor, TCNQ

Based on the π-A isotherms of flavin and TCNQ, the target surface pressures for dipping were determined as 39 mN/m and 45 mN/m, respectively. The cyclic voltammograms of S and A were shown in Figure 1. During the positive potential sweep, the anode currents reached a maximum value at -0.16V and 0.33V (vs. Ag/AgCl electrode), respectively. When the cyclic direction was reversed, the oxidized form of S and A was reduced back to the original starting materials at -0.5V and 0.28V. Thus the redox potential of S and A were determined as -0.33V and 0.3V, respectively.

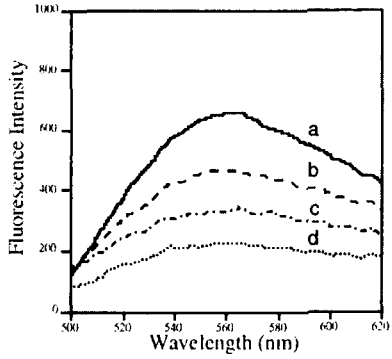
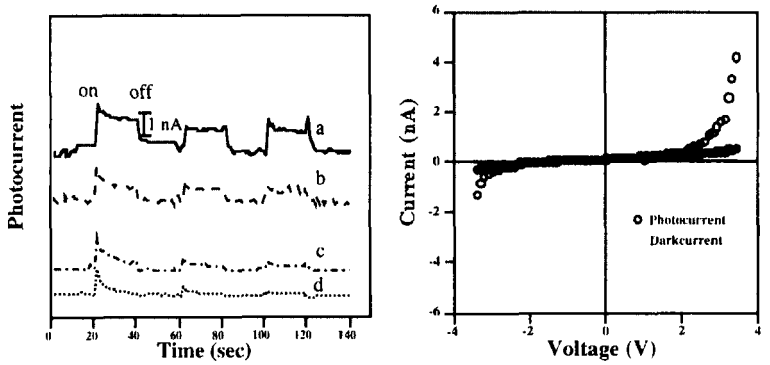


FIGURE 2. Fluorescence spectra of hetero-LB films of S(flavin)/A(TCNQ): a, S(12layers); b, S(12layers)/A(6layers); c, S(12layers)/A(12layers); d, S(12layers)/A(18layers).

In Figure 2, the monomer fluorescence peak of flavin LB films at 560nm decreased as the number of TCNQ LB film was increased. So that, the photo-excited electrons in flavin molecules were transferred to the TCNQ molecules and successive charge separation could be achieved.

The photocurrent of the MIM device consisted of A/S was detected with the irradiation of 460nm monochromatic light by a xenon lamp system. When a forward bias was applied in accordance with the energy level profile in MIM device, stable and reproducible photocurrent was generated accordingly with repeated step illumination. When reverse bias was applied, the photocurrent was much smaller than that of forward case. In the 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.



(a) (b)

FIGURE 3. (a) Photocurrent-time curves of the MIM device for the various forward bias voltage : a, 3.5V; b, 2.5V; c, 1.5V; d, 0.5V (b) I-V characteristics of the MIM device.

The dependence of photocurrent intensity on the external bias voltage and the rectifying characteristics of the MIM device based on the I-V measurement were also investigated as shown in Figure 3 (a) and (b), respectively.

Acknowledgments
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