



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

Publication details, including instructions for authors and subscription information:

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Version of record first published: 24 Sep 2006

To cite this article: Kyung Sang Cho, Jeong-Woo Choi, Won Hong Lee, Nam Woong Song & Dongho Kim (1999): Photocurrent Characteristics of Ferrocene/Flavin/Viologen/TCNQ Heterojunction, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 275-278

To link to this article: <http://dx.doi.org/10.1080/10587259908026831>

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Photocurrent Characteristics of Ferrocene/Flavin/Viologen/TCNQ Heterojunction

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(Received June 30, 1998; In final form July 15, 1998)

A molecular photodiode was fabricated with the hetero-Langmuir-Blodgett (LB) film consisting of an electron donor (D), sensitizer (S), relay (R) and acceptor (A). Ferrocene, flavin, viologen and TCNQ were used as D, S, R and A units, respectively. By aligning hetero-LB film of D/S/R/A 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 photoswitching function was observed. And action spectrum of MIM device was measured. To investigate the photoswitching time and charge transport rate, transient photocurrent of MIM device was measured. Result shows that efficient charge transport from D to A in the heterojunction was occurred due to the existence of R and less recombination.

Keywords: molecular photodiode; MIM device; action spectrum; transient photocurrent

INTRODUCTION

Various artificial molecular devices have been fabricated by mimicking the electron transport function of biological photosynthesis^[1,2]. One of the characteristics of photosynthesis applicable to the artificial molecular electronic device is the photoswitching effect induced by exciting electrons under light illumination, which initiates electron transfer and enables photodiode effect by transferring electrons unidirectional from electron donors to acceptors due to their redox potential differences. Charge transport with MIM (metal-insulator-metal) structured molecular photodiode consisted of electron sensitizer

(S)/acceptor (A) have been investigated^[3]. But the charge transport in the photodiode consisted of electron donor (D)/sensitizer /relay (R)/acceptor have not been investigated. By using relay molecules, charge recombination from R to ground state S can be reduced and directional flow of one way electron transport from D to A can occur. To investigate the photoinduced charge transport of photodiode, the transient photocurrent study is needed. In this work, to investigate the dynamic process of electron transfer and to observe the performance of molecular photodiode consisted of D/S/R/A MIM device as a photoswitching device, the transient photocurrent of the device are measured.

EXPERIMENTAL DETAILS

Four kinds of functional materials were used. Ferrocene octadecyl amine (Ferrocene), 7,8-dimethyl-10-dodecyl isoalloxazine (flavin), N-Allyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4, 4'-bipyridium dibromide (viologen), N-docosilquinolinium TCNQ (TCNQ) were used as D, S, R and A, respectively. The deposition of LB films was carried out using a circular Langmuir trough (Type 2022, Nima Tech., England). The substrate (bottom electrode) is ITO glass. 11 layers A, 10 layer R, S, D were deposited onto the substrate, sequentially. Top electrode was vacuum evaporated aluminum, so MIM device was constructed.

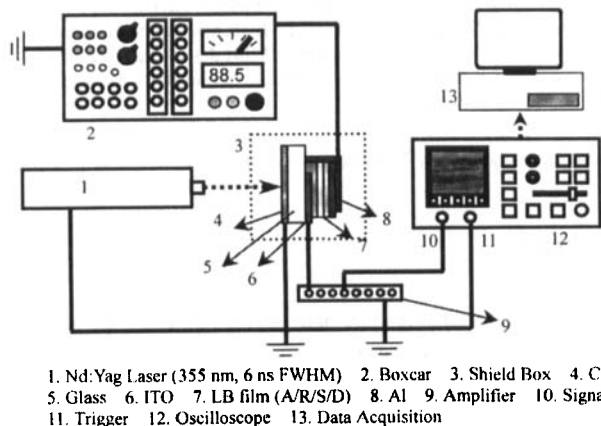


FIGURE 1. Experimental setup for transient photocurrent measurement.

Fig. 1 shows the experimental setup for the transient photocurrent. A light pulse from a Q-switched Nd:YAG-dye laser (FWHM: 6 ns, wavelength: 355 nm, repetition rate: 10 Hz) was introduced to excite the Flavin molecules. With fast electronics using a V/V amplifier of 300 MHz frequency (Model SR445, stanford research) and a storage oscilloscope of 500 ps resolution (2Gs/s, model 54616B, Hewlett-Packard), the interlayer photocarrier movement was detected as voltage built up between electrodes which form a 50 Ω strip line geometry in order to acquire signals with high time resolution.

RESULTS AND DISCUSSION

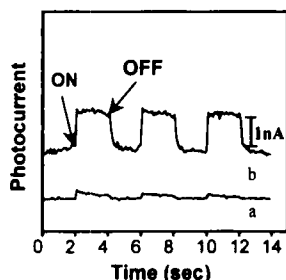


FIGURE 2 Photocurrent-time response of MIM device : a, 1.5 V; b, 3.5 V.

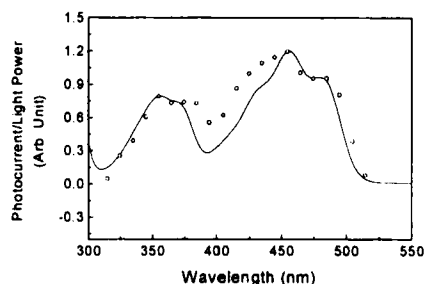


FIGURE 3 Action sepctrum of A/S/R/D MIM device (O); uv-vis absorption of flavin LB film (—).

In the photocurrent-time response were shown in Fig. 2. With repeated step illumination, the reproducible photocurrent was generated accordingly. The photocurrents were very stable and level of responses was consistent during the repeated cycle over 30 minutes. Photocurrent increased as applied voltage increased. The results indicated that the photoswitching function of the MIM device was achieved. In the proposed molecular device, the photo-induced unidirectional flow of electron could be achieved due to the redox potential difference as well as electronic coupling between the functional molecules. Fig. 3 shows the action spectrum of the molecular heterojunction and absorption spectrum of the flavin homo LB film. These results are well correlate each other which indicates that initial photocarrier generation of MIM device is the photoexcitation of flavin.

Fig. 4 shows the transient photocurrent of S homojunction and D/S/R/A

heterojunction. Time constants for the initial of the transient photocurrent were found to be virtually identical to that of the rise of the excitation pulse (nanosecond order). The initial increase of the photocurrents has concerned with the charge separation rate. The charge separation rate can not be differentiated since the intrinsic time constant of charge separation rate is sub-nanosecond order. But the charge transfer rate can be calculated due to the nanosecond order of time constant. The decay time constant of photocurrent was about 7500 ns for homojunction and 1200 ns for heterojunction, respectively, which indicates the charge-shift and -transport rate in the MIM device. Efficient charge transport of hetero LB film might be due to the directional flow of charge in the hetero LB film through their redox potential difference and less recombination due to the existence of R molecules.

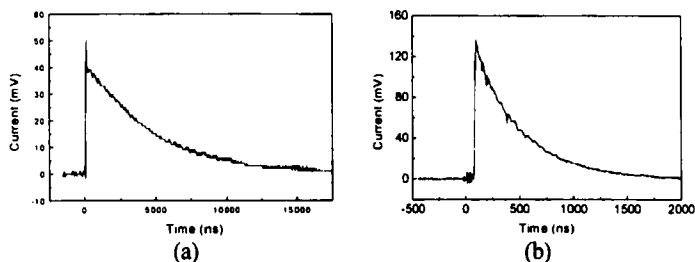


FIGURE 4. Transient photocurrent of MIM device : a, homojunction; b, heterojunction.

Acknowledgement

This work is supported by the Research Fund on Optical Technology (F-15, 1997) of Korean Ministry of Science and Technology, and supported by Creative Research Initiatives of the Korean Ministry of Science and Technology.

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