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Kyung Sang Cho [a], Jeong-Woo Choi [a], Won Hong Lee [a], Nam Woong Song [b] & Dongho Kim [b]

[a] Dept. of Chem. Eng., Sogang Univ., C.P.O. BOX 1142, Seoul, 100-611, Korea

[b] Spectroscopy Lab., Korea Research Institute of Standards and Science, C.P.O. BOX 102, Yusong, Taejeon, 305-600, Korea

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Time-Resolved Fluorescence of Ferrocene/Flavin/Viologen/TCNQ Hetero LB Film

KYUNG SANG CHO[a], JEONG-WOO CHOI[a], WON HONG LEE[a], NAM WOONG SONG[b] and DONGHO KIM[b]

[a]*Dept. of Chem. Eng., Sogang Univ., C.P.O. BOX 1142, Seoul 100–611, Korea; and* [b]*Spectroscopy Lab., Korea Research Institute of Standards and Science, C.P.O. BOX 102, Yusong, Taejeon 305–600, Korea*

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Time-resolved fluorescence was measured with hetero Langmuir-Blodgett (LB) films consisting of ferrocene/flavin/viologen/TCNQ on quartz substrate. Ferrocene, flavin, viologen and TCNQ were used as a electron donor (D), sensitizer (S), relay (R) and acceptor (A) units, respectively. Power dependence on charge separation rate was investigated to examine the local heating problem or the excited state annihilation. Based on the decay of fluorescence, charge separation from excited S to R (or A) was calculated. Result showed that long-range electron transfer from S to A occurred in the D/S/R/A hetero LB film in addition to the electron transfer from S to R.

Keywords: Langmuir Blodgett film; time-resolved fluorescence; charge separation; power dependence

INTRODUCTION

In the biological photosynthesis, photoelectric conversion and long-range electron transfer occur not only efficiently but also unidirectional through the functional groups of biomolecules. Various artificial molecular devices have been fabricated by mimicking the biological electron transfer. The photoinduced electron transfer with electron sensitizer (S)/acceptor (A) hetero LB film[1] and photocurrent measurement with S/A, D (donor)/S/A and S/R (relay)/A heterojunction have been done[2]. But the charge separation rate with D/S/R/A hetero LB films have not been investigated. D/S/R/A structure hetero LB films have the similar structure with the photoinduced electron transfer in the natural system[3]. In this work, time-resolved fluorescence of D/S/R/A hetero LB film was measured to investigate the charge separation rate and transport mechanism.

EXPERIMENTAL DETAILS

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) and N-docosilquinolinium TCNQ (TCNQ) were used as D, S, R and A, respectively. The deposition of LB films on quartz substrate was carried out using a circular Langmuir trough (Type 2022, Nima Tech., England).

Fluorescence decay profiles were recorded by using a TCSPC technique with a femtosecond Ti:Sapphire laser pulse excitation (Fig. 1). The laser pulse width was 150 fs, and the average power was 500 mW at 82 MHz operation. The observed instrumental response function (IRF) for the excitation pulse was about 52 ps (FWHM) at 420 nm.

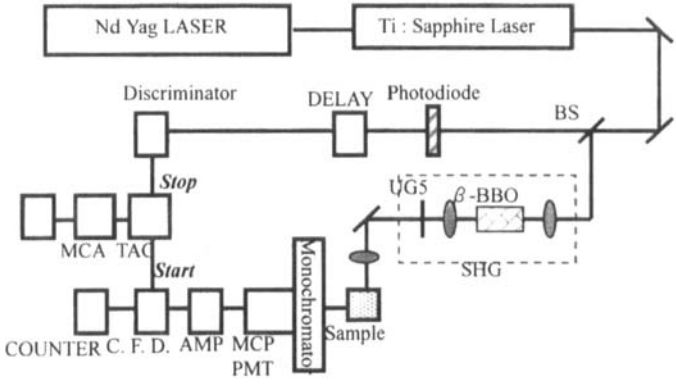

FIGURE 1 Experimental setup for time-resolved fluorescence measurement.

RESULTS AND DISCUSSION

The π-A isotherm of each material was shown in Fig. 2. The isotherms for the monolayer of S and A has two condensed region. The limiting area of monolayer was 24 $Å^2$ for S and 35 $Å^2$ for A. In contrast, the expanded and condensed region were clearly observed for monolayer of R and A. The limiting area per molecule is 60 $Å^2$ and 50 $Å^2$ for R and A, respectively.

Fig. 3 and 4 show the power dependence on fluorescence decay rate in homo and D/S/R/A hetero LB films when 63 % and 35 % input powers were reduced

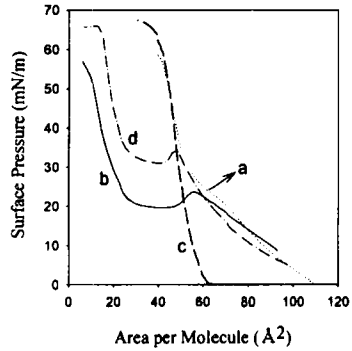

FIGURE 2 Surface pressure-area isotherms: a, D; b, S; c, R; d, A.

by using transparent filters and in the case of no reduction of input power. No power dependence on fluorescence decay rate indicates that charge separation rate did not affected by local heating and excited state annihilation did not occur in the flavin LB film by irradiation of light.

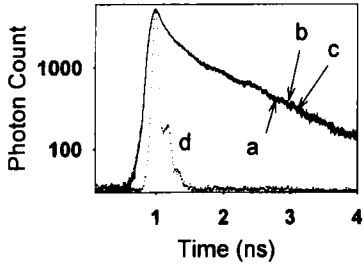

FIGURE 3 Power dependence on fluorescence decay of S homo LB film : a, no filter; b, 63 % filter; c, 35 % filter; d, IRF.

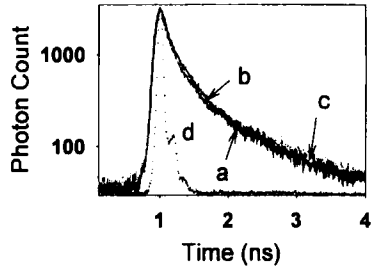

FIGURE 4 Power dependence on fluorescence decay of D/S/R/A hetero LB film : a, no filter; b, 63 % filter; c, 35 % filter ; d, IRF.

Time-resolved fluorescence of LB films are obtained at 520 nm. Fig. 5 shows the decay of fluorescence of S (ll layer), S (2 layer)/R (3 layer), S (2 layer)/R (2 layer)/A (3 layer) and D (2 layer)/S (2 layer)/R (2 layer)/A (3 layer) hetero LB films. In the hetero LB films decay rate becomes faster than that of homo LB film due to the charge separation.

The electron transport rate (k_e) of excited S to R (or A) can be written as

$k_a = 1/\tau_t - k_s = 1/\tau_t - 1/\tau_s$

where k_a is the electron transport rate from excited S to R (or A), τ_t and τ_s is the fluorescence lifetime of flavin in hetero and homo LB films, k_s is the fluorescence decay rate of excited S in homo LB film. Based on the above equation, the charge separation rate can be obtained from the fluorescence lifetime of S in homo and hetero LB films. The lifetime of electron transfer rate in S/R and D/S/R/A are 370 ps and 295 ps, respectively. In the D/S/R/A hetero LB film, decay rate was faster than S/R hetero LB film. This result indicate that long range electron transport from S to A occurred due to the larger redox potential difference between S and A since the redox potential of S, R, A are -0.33 V, -0.30 V, 0.30 V, respectively.

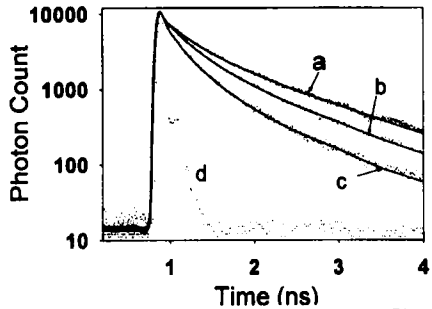

FIGURE 5 Decay of fluorescence in hetero LB films : a, S; b, S/R; c, D/S/R/A; d, IRF (instrumental response function).

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