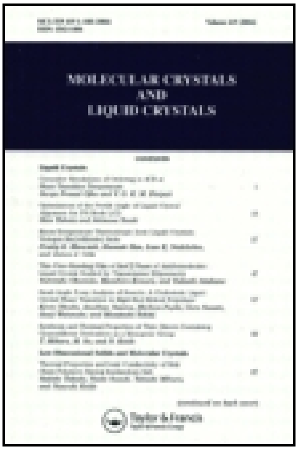

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# Fabrication of Photoresponsive Nano-Organized Polymer Assemblies

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# Fabrication of Photoresponsive Nano-Organized Polymer Assemblies

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We describe here fabrication of organized polymer assemblies where the vectrial photoinduced electron transfer can be controlled by the spatial molecular arrangement by LB technique. The hetero-deposited redox polymer Langmuir-Blodgett (LB) films consisting of poly(*N*-dodecylacrylamide-*co*-ferrocenylmethylacrylate)(Fc copolymer) and poly(*N*-dodecylacrylamide-*co*-(4-(acryloylmethyl)-4'-methyl-2,2'-bipyridine)-bis(2,2'-bipyridine) ruthenium diperchlorate)) (Ru copolymer) were investigated by cyclic voltammetry and the steady state photocurrent measurement. Two kinds of the hetero-deposited structures are constructed by varying with the deposition order of these redox polymer monolayers using the LB technique. The cyclic voltammograms of the hetero-deposited redox polymer LB films show current rectifying and charge storage properties. On light irradiation, the anodic photocurrent is observed at the hetero-deposited redox polymer LB films consisting of Ru copolymer LB film as an inner layer and Fc copolymer LB film as an outer layer on the ITO (Fc/Ru/ITO) electrodes, whereas cathodic one is observed at the reverse layered structure (Ru/Fc/ITO) electrodes. The direction of photocurrent flow is controlled by the deposition order of the redox polymer LB films on ITO electrode. The magnitude of photocurrent depends on electrode potential, light intensity, sacrifier concentration, and irradiation wavelength. The mechanism for photocurrent generation is discussed.

*Keywords:* polymer LB film; photoredox; electron transfer; electrochemistry

## INTRODUCTION

Langmuir-Blodgett (LB) technique is one of methods to fabricate highly ordered molecular assemblies and ultrathin films on solid substrates[1]. The organized molecular assemblies similar to biomenbrane where each components are spatially arranged for functional performance can be fabricated by a layer by layer hetero-depositon of functional monolayers taking a part of role. The hetero-deposited LB films have been expected to develop a novel molecular function because various spatial arrangements of different functional molecules are possible. We have continued to investigate the preparation of polymer LB films. Recently, various functional polymer LB films can be fabricated from the copolymers with *N*-dodecylacrylamide (DDA) which is found to have an excellent ability to form a stable monolayer on a water surface and LB film [2]. In this study, we have prepared polymer monolayers containing redox species such as ferrocene (Fc) and tris(bipyridine)ruthenium(II) (Ru) derivatives (Fig. 1). The hetero-deposited polymer LB films with Fc and Ru monolayers on ITO electrodes were found to show rapid and effective current generation on light irradiation.

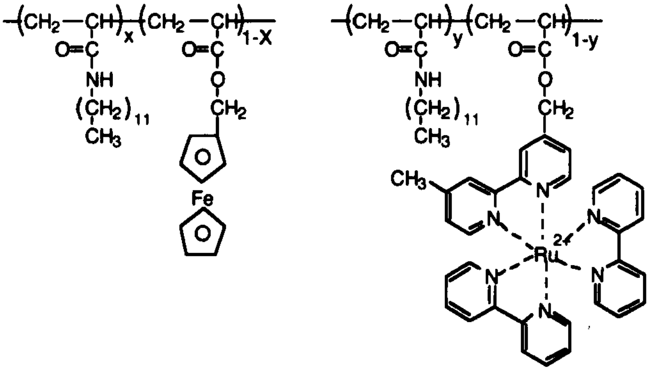

FIGURE 1 Chemical structure of redox copolymers investgated

## EXPERIMENTAL SECTION

**Materials.** The Fc copolymer and Ru copolymer were prepared as described previously [3]. Briefly, the Fc copolymer was prepared by free radical copolymerization of DDA with Fc. The Ru copolymer was prepared as follows; 4-hydroxymethyl-4'-methyl-2,2'-bipyridine was reacted with acryloyl chloride in the presence of triethylamine in chloroform at room temperature to obtain 4-(acryloylmethyl)-4'-methyl-2,2'-bipyridine as a ligand monomer. The copolymer of DDA with the ligand monomer was copolymerized, as well as the Fc copolymer. The resulting copolymer was refluxed with *cis*-bis(2,2'-bipyridine)dichlororuthenium(II) in ethanol.

**Measurements.** The measurement of surface pressure (π) - area (A) isotherms and deposition of the monolayers were carried out with a computer-controlled Langmuir trough FSD-11 (USI) at 20 °C. Chloroform was used as a solvent for spreading the monolayer on the water surface. The ITO electrode was cleaned by sonication in a chemical detergent solution, water, acetone and chloroform, successively. The monolayers of the Fc and Ru copolymers were transferred onto these substrates by vertical dipping method at a dipping speed of 10 mm $min^{-1}$ under a surface pressure of 20 and 30 mN $m^{-1}$, respectively at 20 °C.

Cyclic voltammetry and photocurrent measurement were performed using a potentiostat (HA-501, Hokuto) and a function generator (HB-104, Hokuto). A 500 W xenon lamp equipped with IR-cut off filter (IRA-2S, Toshiba) and UV-cut off filter (VY43, Toshiba) was used as a light source. The ITO electrode is mounted at the cell window using a silicon rubber O-ring (14 mmϕ). An electrode area of 1.54 $cm^2$ is exposed to the electrolyte solutions.

## RESULTS AND DISCUSSION

The Fc and Ru copolymers are spread onto the water surface to measure surface pressure -area (π-A) isotherms. The π - A isotherms indicate that the stable condensed monolayers are formed with a high collapse pressure. The limiting molecular occupied surface areas of the Fc and Ru copolymers are 0.26 and 0.25 $nm^2$ repeat $unit^{-1}$, respectively from the extrapolation of the linear part of the π-A curve to zero surface pressure. Assuming that the limiting area of the DDA homopolymer is 0.28 $nm^2$ repeat $unit^{-1}$, the limiting areas of ferrocene and ruthenium moiety in the copolymers are estimated to be 0.24 and 0.01 $nm^2$ $molecule^{-1}$, respectively. On the other hand, the cross-sectional areas of ferrocene and rutheniumtris(bipyridine) derivative are reported to be ca. 0.50 and 1.0 $nm^2$ /molecule[4,5]. From these results, the monolayer structures of Fc and Ru copolymers on the water surface would be supposed to be that alkyl side chains of amphiphilic DDA stood up from the water surface and that the ferrocene and ruthenium complex moieties placed in the water subphase. These Fc and Ru copolymer monolayers can be transferred on ITO electrodes as a Y-type film with a transfer ratio of unity.

Photocurrent of the hetero-deposited redox polymer LB films was measured at an applied voltage, 0.0 V vs SCE under nitrogen atmosphere on a light irradiation above 430 nm wavelength from a 500 W xenon lamp (Fig. 2). Cathodic photocurrent appeared at the Ru/Fc/ITOelectrode on a light irradiation(Fig. 3, top). *Anodic photocurrent was also observed at the reversed structure, Fc/Ru/*

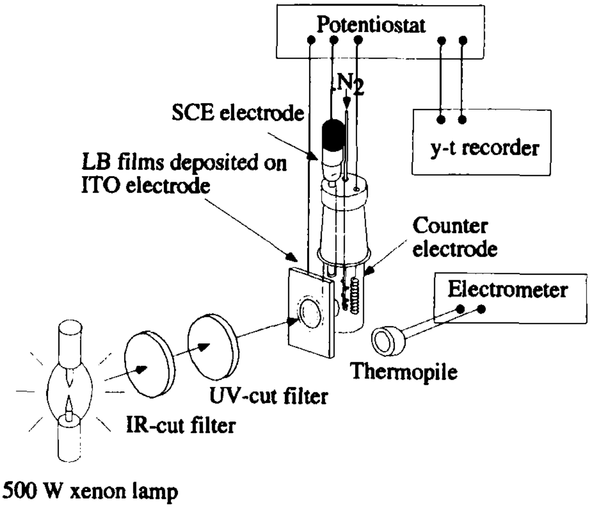

FIGURE 2 Schematic illustration for photochemical measurement

ITO electrode(Fig. 3 bottom). These phenonema did not appear at the homogenoues Ru LB film on ITO electrodes because of rapid reverse electron transfer process after photoinduced electron transfer reaction between Ru LB film and ITO electrode. The results show that the direction of photocurrent flow can be controlled by the deposition order of redox polymer LB films on electrodes. The spatial charge separation between the photo-excited ruthenium complex and ferrocene is significant to control the direction of photocurrent flow in the hetero-deposited redox polymer LB film. The anodic photocurrent increases with the addition of the electron donor triethanolamine (TEOA) into the electrolyte solution at the Fc/Ru/ITO electrode. The maximum steady-state photocurrent was observed above 0.5 M concentratiðn of TEOA. The photocurrent was measured as a function of light wavelength, that is, action spectrumwas obatined. Since the action spectrum of the Fc/Ru/ITO electrode is identical to the absorption spectrum of the Ru LB film on the quartz substrate(Fig. 4), the photocurrent ocurrs caused by metal to ligand charge transfer of photo-excited tris-(bipyridine) ruthenium complex. Based on the results of the anodic photocurrent as functions of various factors, we propose a possible mechanism for photocurrent generation as shown in Figure 5; the excited Ru complex (MLCT) is quenched by Fc monolayer via electron transfer mechanism. The oxidized Fc group is regenerated by electron tranmsfer from a sacrifacial electron donor (TEAO). The cycle consistting of three components is working effectively by the hetero-deposited LB strucutre.

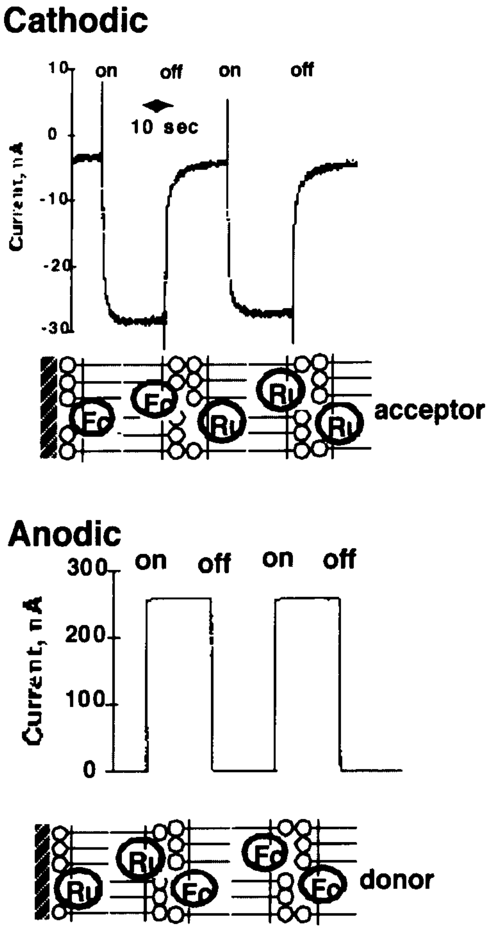

FIGURE 3 Photocurrent response against light irradiation on the hetero-deposited LB films

The quantum efficiency of the Fc/Ru/ITO electrode is determined to be 5.9 % at 468 nm wavelength. This value is higher than 2.7 % of Ru LB film on the ITO electrode. Therefore, the rate of the photo-induced electron transfer is improved by the hetero-deposited redox polymer LB film because of inhibition of the reverse electron transfer process.

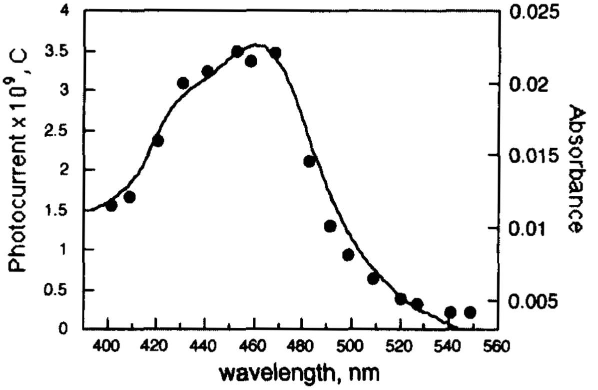

FIGURE 4 Action spectrum of photocurrent and the absorption spectrum

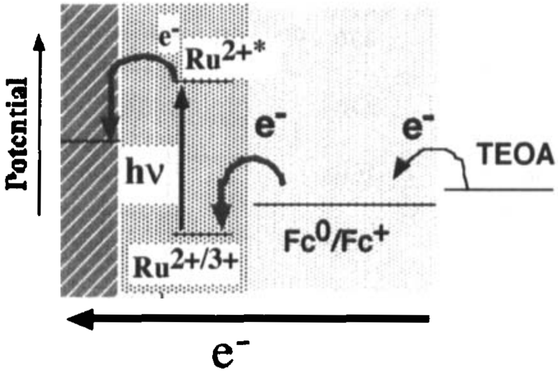

FIGURE 5 A possible mechanism for anodic photocurrent

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