Photoelectrochemical Responses of Polymer Langmuir-Blodgett Films Containing Tris(2,2'-bipyridine)ruthenium(II) Complex

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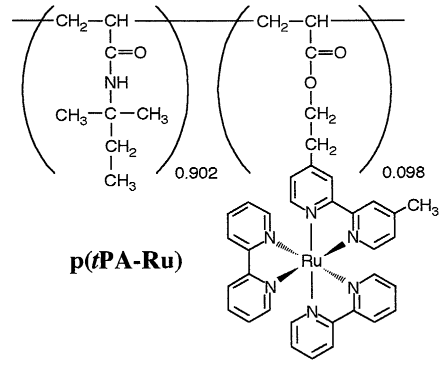
Polymer Langmuir-Blodgett monolayer containing tris(2,2′-bipyridine)ruthenium(II) complex was prepared on an ITO electrode. In the presence of thiosalicylic acid as an electron donor, a large anodic photocurrent was observed by light irradiation on the polymer monolayer. The action spectrum of the photocurrent indicates that the generation of photocurrent is based on the excitation of the ruthenium(II) complex.

Tris(2,2′-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, is markedly attracting as a sensitizer for transformation of solar energy into a storable form of energy,[1-3] and a number of attempts have been made to utilize $Ru(bpy)_3^{2+}$ for design of photoresponsive electrode.[4,5] The arrangement of $Ru(bpy)_3^{2+}$ in thin molecular assemblies on an electrode is a crucial point to accomplish highly efficient energy conversion. Langmuir-Blodgett (LB) technique is one of the useful methods to fabricate highly ordered molecular structure.[6] We have proposed a method where a photofunctional group is introduced into polymer LB films by copolymerization with LB film forming amphiphilic monomer.[7,8]

Electron transfer and energy transfer processes in LB films are known to depend on a distance between donor and acceptor molecules in layered structure, wherein long alkyl chains often constitute a disadvantage in acting as a barrier to electron transport.[9-11] Recently, we have found that *N-tert*-pentylacrylamide (*t*PA) polymer forms a stable condensed monolayer on water surface, and be successively transferred onto solid supports with a film thickness of 10Å.[12] In this paper, we prepared *t*PA copolymer containing $Ru(bpy)_3^{2+}$, and photoresponse of the copolymer monolayer (p(*t*PA-Ru)) deposited onto the ITO electrode was investigated.



p(*t*PA-Ru)

p(*t*PA-Ru) was prepared from a copolymer of *t*PA and 2,2′-bipyridine derivative monomer, 2-(4-(4′-methyl-2,2′-bipyridyl))ethylacrylate. This copolymer was refluxed with $Ru(bpy)_2Cl_2$ in ethanol for 72 h. The composition of p(*t*PA-Ru) was determined from the absorption spectrum. The copolymer was spread on pure water surface from a chloroform-ethanol (9:1) solution at 15 °C in Langmuir trough, and compressed at a rate of 14 cm²/min. The surface pressure - area isotherm of the polymer monolayer indicates the formation of condensed stable monolayer. The condensed monolayer was transferred onto ITO electrode at 20 mN/m by a vertical dipping method.

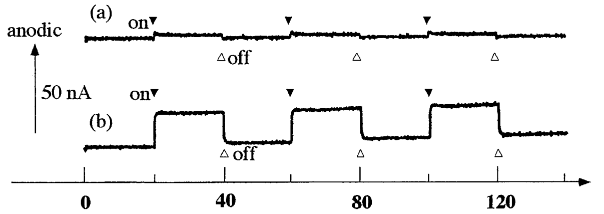


Figure 1. Current changes induced by on-off irradiation cycle on p(*t*PA-Ru) deposited onto ITO electrode in 0.2 M $NaClO_4$ and 0.05 M Borax (pH ≈ 10) in the absence (a), and presence (b) of ArSH (10 mM). 0.0 V vs SCE, 80 mW/cm².

Photoresponsive behavior of the monolayer electrode was investigated with an assembled apparatus consisting of potentiostat and function generator (Hokuto HA-504, HB104). Photocurrent observed at 0.0 V vs SCE was measured under nitrogen atmosphere using a three electrode cell consisting of the monolayer modified electrode, SCE electrode, and counter platinum electrode. Light irradiation was made by a xenon lamp (500 W) through cut-off filters (Toshiba VY-45 and IRA-25S). Monochromatic light was obtained by using interference filters. On light irradiation on the p(*t*PA-Ru) monolayer deposited ITO electrode, a photocurrent generation was observed in the presence of 10 mM ArSH as a sacrificial electron donor in 0.1 M $NaClO_4$ / Borax($Na_2B_4O_7$) electrolyte solution (pH≈10). A steady and rapid anodic photocurrent response (20 nA/cm²) was induced repeatedly to switching on and off of the irradiation (Figure 1). It is very interesting that a large photocurrent is produced from the monolayer of only 10 Å thickness, suggesting efficient electron transfer process occurs in the monolayer. Anodic photocurrent action spectra of the monolayer deposited ITO electrode in the presence of ArSH are shown in Figure 2. The action spectra shows a characteristic band around 450 nm, which corresponds to the charge transfer band from metal to ligand (MLCT) of $Ru(bpy)_3^{2+}$ in the absorption spectrum. The fact that these two spectra are similar in shape to each other implied that the generation of photocurrent is attributable to the excitation of $Ru(bpy)_3^{2+}$ incorporated in p(*t*PA-Ru) monolayer.

As the mechanism for photocurrent generation, we consider the following scheme (Scheme 1). First, $Ru(bpy)_3^{2+}$ is excited by light irradiation and the excited state is effectively quenched by thiolate anion forming Ru^+ species. An anodic current is produced by electron transport from Ru^+ to the ITO elec-

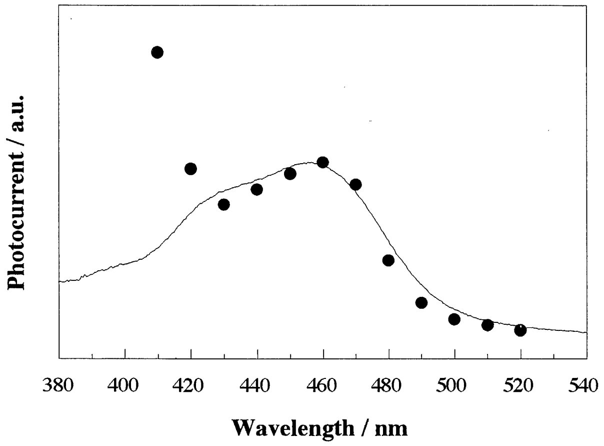
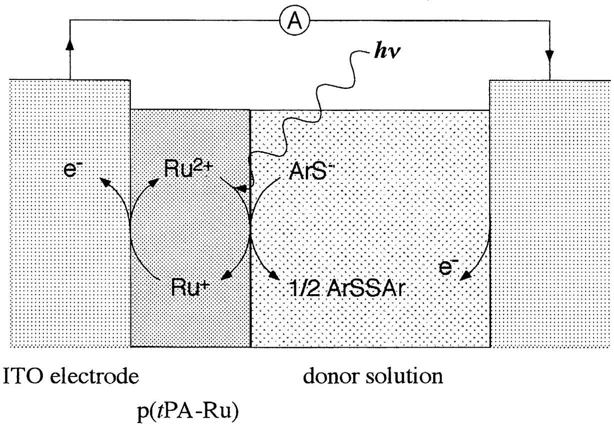


Figure 2. Anodic photocurrent action spectra (●) and absorption spectra (—) of p(*t*PA-Ru) deposited onto ITO electrode. 0.0 V vs SCE, [$NaClO_4$] = 0.2 M, [Borax] = 0.05 M, [ArSH] = 10 mM.

Scheme 1.



trode. The electron transport process is expected to be very efficient, because the process is essentially one molecule process in the monolayer. Further detailed study is necessary to make the mechanism clear.

In conclusion, p(*t*PA-Ru) LB monolayer deposited onto ITO electrode is working as a photoresponsive polymer ultrathin film to convert photoenergy to electric energy. The works is in progress to realize more efficient photoenergy conversion system using organized polymer assemblies.

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References and Notes

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