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Molecular logic devices using mixed self-assembled monolayers

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Abstract

We have developed a photoelectric conversion device which functioned as molecular logic gates. It consisted of a mixed self-assembled monolayer (SAM) of tris(2,2′-bipyridine)ruthenium(II)–viologen linked thiol and phthalocyanine thiol compounds. Photocurrents from the SAM could be controlled by an excitation wavelength as well as an applied potential. As molecular logic devices, two kinds of light emitting diodes (LEDs) were used as light sources. Photocurrents at $E = 0$ V clearly responded as the XOR logic gate whereas those at -0.2 V as the OR logic gate.

Keywords: Photodiode; Molecular logic device; Self-assembled monolayer; Photocurrents

1. Introduction

Design and fabrication of high-performance molecular systems on conductive supports are basically important to create high-density information processing devices or artificial sense organs. In order to achieve the goal, it is essentially important to fabricate various molecular devices such as wires, switches, logic gates, and so on. The self-assembling method is one of promising approaches to obtain well-ordered molecular films. Particularly, the self-assembling method using thiol derivatives is very useful for the fixation or implantation of plural photofunctional molecules on the electrode at once. Especially, the gold–sulfur self-assembled monolayer (SAM) of an electron donor (D)–acceptor (A) pair has been successfully applied for molecular photoelectric conversion devices since 1995 [1]. Later, similar SAMs with various kinds of D–A pairs have been fabricated for photoelectric conversion [2–9].

As described before, one of the noteworthy advantages of the self-assembling method is that plural molecules can be implanted on the electrode at once [10–12]. Recently, we preliminarily reported, for the first time, a photoelectric conversion SAM, consisting of a ruthenium complex-viologen linked compound and a phthalocyanine and found that the SAM functioned as a bi-directional (cathodic and anodic directions) photoelectric conversion device depending on the irradiation wavelength [10]. We also investigated the bi-directional photocurrent mechanism and found to be able to function as a molecular XOR logic gate [13].

In the present study, we have extensively used two photodiodes (blue and red) to selectively photoexcite the ruthenium complex-viologen linked compound or the phthalocyanine dye in the mixed SAM, and have optimized the intensities of bi-directional photocurrents by changing the sacrificial reagent and the applied potentials. The system could function as XOR and OR logic gates.

2. Experimental

Synthetic procedures of tris(2,2′-bipyridine)ruthenium (II)–viologen linked disulfide $[RuVS]_2$ [14] and a phthalocyanine disulfide $[PcS]_2$ [15] have been described previously. The gold electrode was prepared by vacuum deposition of titanium as an adhesive layer and then gold

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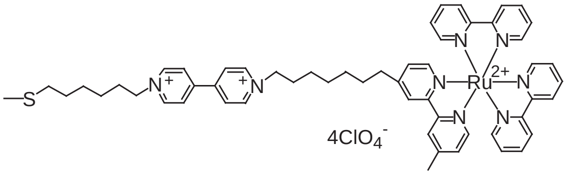
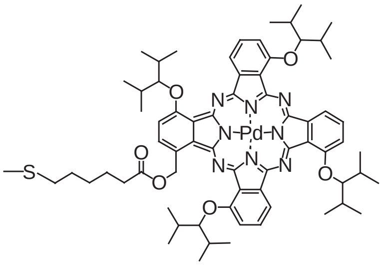
onto a glass plate at 300 °C. Next, the gold electrode was immersed into a mixed solution of CH_3CN and CH_2Cl_2 (1:1 v/v) containing **RuVS** (1×10^{-3} M as monomer unit) and/or **PcS** (1×10^{-3} M as monomer unit) for 4 days to obtain the modified electrode with **RuVS**, **PcS**, or **RuVS** and **PcS** as: **RuVS/Au**, **PcS/Au**, or (**RuVS**+**PcS**)/**Au**, respectively.



RuVS



PcS

These electrodes were then removed from the solution, rinsed with CH_3CN and CH_2Cl_2 in sequence, and dried in air. Photocurrent measurements were carried out using a three-electrode photoelectrochemical cell, consisting of the as-described modified electrode (working), an Ag/AgCl (sat. KCl) electrode (reference), and a platinum wire (counter) in a 0.1 M $NaClO_4$ aqueous solution under aerated condition, as described previously [10]. In addition, triethanolamine (TEOA: 50 mM) and methylviologen (MV^{2+}: 5 mM) were added as sacrificial electron donor and an electron acceptor, respectively. Photocurrent action spectra were measured by using the monochromatic light from a Xenon lamp (300 W). In the case of logic operation experiments, two kinds of light emitting diodes (LEDs) having peaks at 470 (blue LED) and 640 nm (red LED), respectively, were used as excitation light sources. The LEDs were fixed in front of the photoelectrochemical cell to irradiate the almost same region of the modified electrode, simultaneously or independently. Schematic illustration of photocurrent measurement systems is shown in Fig. 1.

3. Results and discussion

3.1. Effects of sacrificial reagents on photocurrents

As reported previously, photocurrents from the mixed monolayer assembly, (**RuVS**+**PcS**)/**Au**, are ascribed from the competition of electron-transfer reactions among **RuVS**, **PcS**, and sacrificial reagents. Thus, it is important to investigate the effects of sacrificial reagents on the photocurrent generation.

Fig. 2 shows photocurrent action spectra of **RuVS/Au** and **PcS/Au** under aerobic condition, where the applied potential (E) is 0 V vs. Ag/AgCl. The photocurrent action spectrum for **RuVS/Au** showed a broad band around 460 nm, corresponding well with the absorption band of **RuVS** in CH_3CN, and its direction was anodic. As reported previously, the oxidized *Ru (Ru^{3+}) is effectively reduced by TEOA; the higher the concentration of TEOA, the larger the anodic photocurrents [16,17]. In the presence of 5 mM *N*,*N*′-dipropyl viologen sulfonic acid (denoted as 4ZV) that was analogue with MV^{2+} in the electrolyte solution, the anodic photocurrent from **RuVS/Au** decreased to nearly the half value of that in the absence of 4ZV [18], but the anodic photocurrent was still observed. This was also the case in this case, because the photocurrent was observed in the anodic direction even in the presence of 5 mM MV^{2+}. This suggests that the intramolecular electron-transfer from the photoexcited state of ruthenium complex moiety (*Ru) to the viologen (V^{2+}) moiety is quite faster than that to MV^{2+} and/or the oxygen in the bulk. However, MV^{2+} as well as oxygen was necessary to obtain appreciable cathodic photocurrents from **PcS/Au**, as described below.

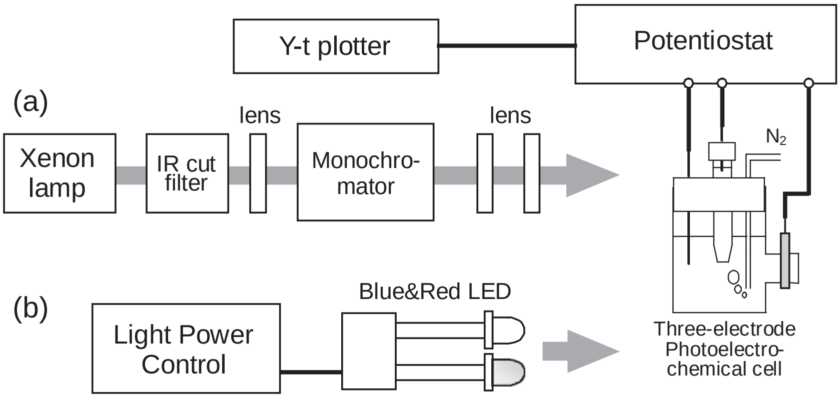


Fig. 1. Schematic illustration of the experimental apparatus: (a) for the measurements of photocurrent action spectra; (b) for the operation as molecular logic gates using two LEDs.