Very Efficient Visible-Light-Induced Uphill Electron Transfer at a Self-Assembled Monolayer with a Porphyrin−Ferrocene−Thiol Linked Molecule

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Construction of a very efficient artificial photosynthesis system is one of the most important goals of modern chemistry. In natural photosynthesis systems, molecules of various functionalities such as a photon absorber and electron donors and acceptors are organized with molecular dimensions so that very efficient photoinduced charge separation is achieved with minimum reverse electron transfer.[1] Thus, it is of great interest to mimic the elaborate molecular machinery of natural systems for the realization of a highly efficient artificial photosynthetic system. Various attempts have been made to construct artificial photosynthetic systems by arranging molecules in order using lipid bilayer membranes[2] and the Langmuir−Blodgett (LB) method.[3] Unfortunately, however, the quantum efficiencies of these systems are still very low (0.4−1.5%)[2,3] compared with that of the natural systems.

A self-assembly (SA) technique has been very widely used to construct ordered molecular layers of various functionalities, and self-assembled monolayers (SAMs) of alkanethiols on gold have been the most well studied system.[4] Thus, the SAM with a photoactive group (S) and an electron relay group (R) formed on a metal electrode (M) in a solution containing an electron acceptor (A) whose redox potential is much more negative than that of R (Figure 1a) should be a good candidate for a stable, efficient photoconversion device where uphill photoinduced electron transfer, i.e., photocurrent generation, takes place. The energetics of the system are described schematically in Figure 1b. Although few attempts have been made to construct this type of system using thiol molecules containing S and R,[5,6] the quantum efficiencies of these systems are relatively low (0.3−3.0%),[5,6] maybe because these molecules have no alkyl chains and/or the adsorbed amount of the molecules are low and, therefore, the orders of the molecular layers were low.

We have now achieved a very efficient visible-light-induced photocurrent generation at a gold electrode modified with a SAM of a novel molecule (Figure 1c), which has porphyrin, ferrocene, and thiol groups as photoactive, electron transport or relay, and surface binding groups, respectively, separated from each other by alkyl chains ($PC_8FcC_{11}SH$). Ferrocene was chosen as the electron relay group because the electron transfer of this group is known to be very fast[7] and the alkyl chains were introduced to form a well-ordered SAM so that the reverse
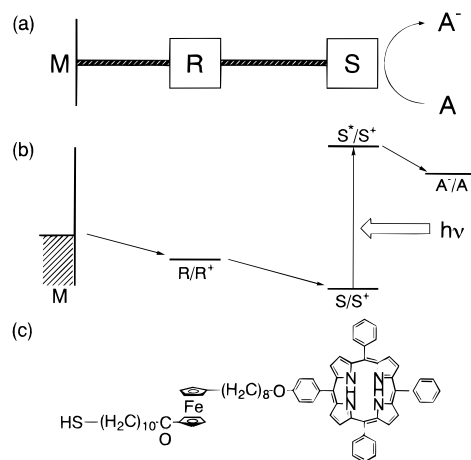

Figure 1. Schematic diagram (a) with energetics (b) showing a metal electrode (M)/SAM/electrolyte solution interface. SAM contains a photoactive (S) and an electron relay (R) groups. Electrolyte solution contains an electron acceptor (A). (c) Molecular structure of $PC_8FcC_{11}SH$.

electron transfer and energy transfer from the excited porphyrin to the gold electrode can be reduced.

The cyclic voltammogram of the $PC_8FcC_{11}SH$ SAM modified gold electrode in a phosphate buffered 0.1 M $NaClO_4$ solution (pH = 4.5) showed a redox potential of the ferrocene group at +640 mV (vs Ag/AgCl). An adsorbed amount of PC_8FcC_{11}-SH on the gold electrode calculated from the charge of the anodic peak of the ferrocene moiety was 1.2×10^{14} molecule cm^{-2}.[8] This is very high compared with previously reported coverages of the LB and SAM containing porphyrin group ($3-7 \times 10^{13}$ molecule cm^{-2}).[5,6,9,10] This number corresponds to an 83 Å^2 molecule^{-1}. Considering the areas of the perpendicular and flat porphyrin group orientations to be ca. 50 and 250 Å^2 molecule^{-1}, respectively,[10] one can conclude that the monolayer was relatively well packed with almost a perpendicularly oriented porphyrin group. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) of the $PC_8FcC_{11}SH$ SAM modified gold electrode showed that the thiol, the ferrocene, and the porphyrin groups were aligned in this order, as shown in Figure 1.[11]

Photoelectrochemical characteristics of the $PC_8FcC_{11}SH$ SAM modified gold electrode were investigated in a phosphate-buffered 0.1 M $NaClO_4$ solution (pH = 4.5) containing 5 mM MV^{2+} as an electron acceptor. Figure 2 shows the time course of the current when the electrode was illuminated with 430 nm pulsed light. A stable cathodic photocurrent flowed as soon as the electrode was illuminated and fell instantly when illumination was terminated if the potential was more negative than +650 mV, which coincides with the redox potential of the ferrocene moiety in the $PC_8FcC_{11}SH$ SAM. One should note that, at the porphyrin−mercaptoquinone SAM modified electrode, a cathodic photocurrent was observed in the same solution only when the potential was more negative than +200 mV, which is in agreement with the redox potential of the quinone moiety of the SAM and the photocurrent was much smaller.[5] Furthermore, only a very small photocurrent was observed at the electrode modified with the SAM of the porphyrin−alkanethiol linked molecule. These results confirmed that the photoinduced electron transfer took place through the electron transport group, i.e., ferrocene in this case. The stable photocurrent flowed for more than 3 h without any signs of

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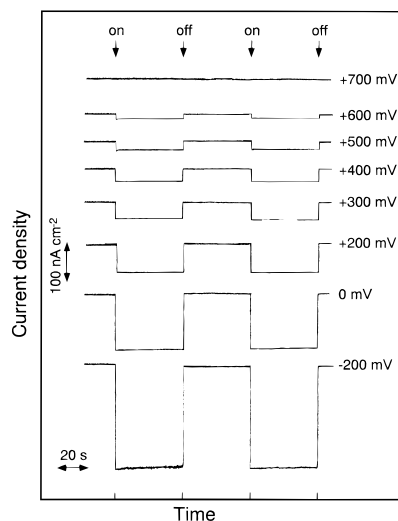(7) Chidsey, C. E. D. *Science* **1991**, *251*, 919−922.

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Figure 2. Time course of the current at the $PC_8FcC_{11}SH$ SAM modified gold electrode held at various potentials when the electrode was illuminated with pulsed light of 430 nm (40 μW cm^{-2}; 8.7×10^{13} photon s^{-1} cm^{-2}).

deterioration when the potential was kept between +650 and −250 mV. After prolonged illumination of the electrode, the color of the solution in front of the electrode changed to blue, showing that MV^{2+} was reduced to the methylviologen cation radical ($MV^{+\bullet}$). Since the redox potential of $MV^{2+}/MV^{+\bullet}$ is −630 mV,[12] we have achieved an uphill transport of electrons of more than 1.2 eV by visible light illumination at this interface. The cathodic photocurrent increased as the potential was made more negative, showing that the rate of electron transfer between the ferrocene moiety and the gold electrode controlled the photocurrent generation. Time course of the photocurrent was strongly dependent on the MV^{2+} concentration. Although the photocurrent just after the illumination was not affected by the MV^{2+} concentration, the stable photocurrent decreased with the decrease in MV^{2+}.

Figure 3 shows an absorption spectrum of the $PC_8FcC_{11}SH$ SAM observed in air[13] and a photocurrent action spectrum of the $PC_8FcC_{11}SH$ SAM modified gold electrode obtained at −200 mV. A strong peak at 430 nm and four small peaks between 500 and 700 nm were observed in the absorption spectrum. This spectrum is similar to the absorption spectra of the same molecule and free-base porphyrin[14] in benzene solution. The strong peak at 430 nm and four small peaks can be assigned to the Soret band and the Q-bands of the porphyrin ring, respectively. The Soret band of the SAM was red-shifted by ca. 10 nm from and was broader than that in solution, suggesting the existence of an interaction between the porphyrin rings in the SAM.[9] The shape of the photocurrent action spectrum is in very good agreement with the absorption spectrum of the SAM, confirming that the porphyrin group in the SAM really acted as a photoactive site.

Quantum efficiencies based on the number of photons adsorbed by the SAM were calculated by using the photocurrent and the absorbance determined from the absorption spectrum. When the electrode kept at −200 mV was illuminated by monochromated 430 nm light, the photocurrent density was 250 nA cm^{-2} and the calculated quantum efficiency was 11%. The photoenergy conversion efficiency at this condition is calculated to be 1.8% as the input photon energy is 2.9 eV and the energy

Figure 3. Absorption spectrum of the $PC_8FcC_{11}SH$ SAM on a transparent gold substrate observed in air (dotted line) and a photocurrent action spectrum of the $PC_8FcC_{11}SH$ modified gold electrode (solid line). Inset: Energy diagram for the $PC_8FcC_{11}SH$ modified gold electrode/MV^{2+} solution interface when the electrode potential is more negative than the redox potential of the ferrocene moiety. Fc, Fc^+, P, P^+, and P^* are ferrocene, ferricenium cation, porphyrin, oxidized state of porphyrin, and excited state of porphyrin, respectively.

difference between the redox potential of $MV^{2+}/MV^{+\bullet}$ (−630 mV) and the electrode potential (−200 mV) is 0.43 eV. This is the highest quantum efficiency and energy conversion efficiency ever reported for photoinduced electron transfer at a monolayer modified metal electrode.[2,3,5,6]

On the basis of these experimental results, the energy diagram for the photoinduced electron transfer at the $PC_8FcC_{11}SH$ SAM modified gold electrode in a solution containing MV^{2+} is constructed and is shown in the inset of Figure 3. If the electrode potential was more negative than the redox potential of the ferrocene moiety, the photoexcited electron of the porphyrin was transferred to MV^{2+} and electron transfer from the electrode to the vacant HOMO site of the porphyrin took place through the ferrocene group.

At least two possible reasons can be considered to explain why this system showed such a very high efficiency. One is the high electron-transfer rate between the ferrocene moiety and the gold. The rate constant of this system estimated by Laviron's method[15] was much higher than those between the electrodes and other redox moieties such as quinone.[16] The other is the effective inhibition of reverse electron transfer and/or energy transfer from the excited state of the porphyrin moiety to the gold electrode. Very high coverage of this molecule on the gold substrate, 1.2×10^{14} molecule cm^{-2}, means that this monolayer is relatively well packed and ordered. The ordered structure was also confirmed by the ARXPS results. Thus, the alkyl chain connecting the porphyrin and ferrocene groups and that between the ferrocene group and the gold electrode are expected to be extended so that the distance between the porphyrin moiety and the gold electrode is quite large. This is very suitable for the inhibition of electron transfer and energy transfer from the excited state of the porphyrin moiety to the gold electrode. The monolayer should also act as an effective barrier for the oxidation of $MV^{+\bullet}$, i.e., an electron transfer from $MV^{+\bullet}$ to gold.

Supporting Information Available: Text and scheme describing experimental procedures for the synthesis of $PC_8FcC_{11}SH$, preparation of the gold substrate, and photoelectrochemical measurement (5 pages). See any current masthead page for ordering and Internet access instructions.

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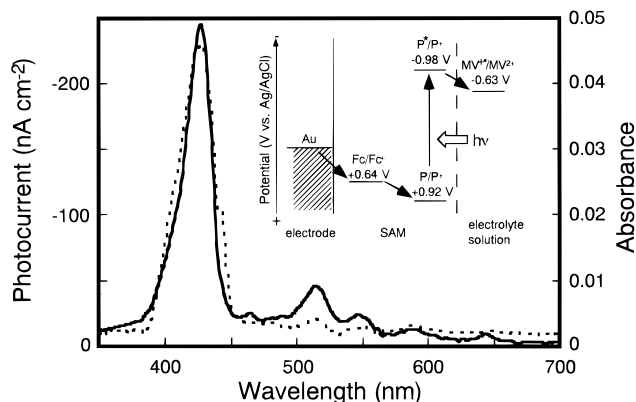
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