Photoelectron Transfer

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Plugging a Molecular Wire into Photosystem I: Reconstitution of the Photoelectric Conversion System on a Gold Electrode**

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It is well known that the quantum yield of the electron transfer process that occurs during photosynthesis is almost unity.[1] The development of photoelectric conversion devices such as those comprising a photosynthetic protein on a Langmuir–Blodgett film,[2,3] or self-assembled monolayers (SAMs),[4] has been attempted. In these cases, however, the photosynthetic protein complexes were just simply placed on the electrodes with which it had a passive electrical interaction.

The high performance of the biosystem is attained because of the well-designed spatial configuration and the environmental control of the functional molecules. Thus, in order to employ a biocomponent as the core part in our artificial high-performance system that functions by transducing a signal between the biosystem and the artificial system, the use of a connector designed in a specific molecular order is a requisite.[5] In previous work, we used a molecular wire consisting of gold nanoparticles to visualize the connection to photosystem I protein complex (PSI).[5a] In this case, however, we had not offered critical evidence that the connector plays an indispensable role during signal transduction. Herein, we describe a novel molecular connector system in which an artificial molecular wire assembled on a gold electrode is plugged into the PSI by reconstitution. We have succeeded both in terms of obtaining the desired output of electrons from PSI and in proving the effectiveness of the molecular wire connector by analyzing the photoelectron transfer kinetics.

PSI, which was isolated and purified from *Thermosynechococcus elongatus*, was chosen for this study as there exist many reports on the structural analysis,[6,7] electron transfer reactions,[8] and extraction and reconstitution of its specific components, for example Vitamin K_1 (VK_1), and iron–sulfur clusters (F_X, F_A, and F_B).[9,10] The photoexcitation of P700 (chlorophyll heterodimer) and the resulting steps of electron transfer reactions along the relay system of PSI are illustrated in Figure 1. The first and second electron transfer reactions

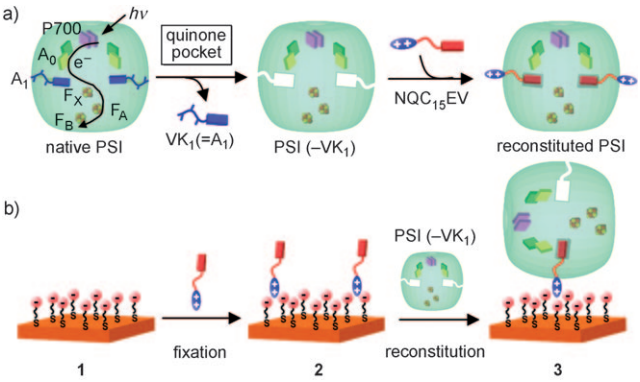

Figure 1. Schematic illustration of the procedures for extraction of VK_1 used to prepare a) a quinone pocket and b) reconstitution with a molecular wire adsorbed on a gold electrode.

(from P700 to $A_1 = VK_1$) occur very rapidly (on a picosecond time scale), whereas the third step occurs at a much slower rate (in the order greater than approximately 10 ns). Thus, the direct connection of an efficient molecular wire to the relay system at the A_1 site will guide the electrons in the direction of the wire. By considering these points, a naphthoquinone–viologen linked compound ($NQC_{15}EV$) was designed and synthesized as the molecular wire (Scheme 1). The three main features of this design are as follows. Firstly, the naphthoquinone unit functions as the binding site for PSI. Secondly, the lengths of the molecular wire and VK_1 are kept identical to ensure that the end of the chain (viologen) remains outside

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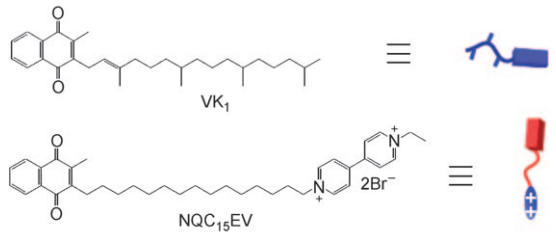

Scheme 1. Structures of VK_1 and molecular wire $NQC_{15}EV$.

the PSI system. Thirdly, the electron-accepting viologen has the appropriate potential to relay electrons through the molecular wire.

The procedures used for the connection and immobilization of PSI by reconstitution are illustrated in Figure 1. Firstly, VK_1 was extracted from PSI to obtain PSI(−VK1), which has a quinone pocket.[9] Secondly, $NQC_{15}EV$ was fixed on a SAM of 3-mercapto-1-propanesulfonic acid sodium salt (MPS), which was prepared on a gold electrode (**1**) by electrostatic interaction, to obtain **2**. To avoid steric hindrance during the reconstitution from neighboring $NQC_{15}EV$, the packing density of $NQC_{15}EV$ was kept low (6.0×10^{-11} mol cm^{-2}) by controlling the concentration (25 nM) and immersion time (10 s) during the fixation process (see the Supporting Information). Lastly, the reconstitution was carried out by immersing **2** into a solution of PSI(−VK1) in MES–NaOH buffer (MES = β-morpholinoethanesulfonic acid)for 24 hours to obtain **3**.

To confirm the photoelectron relay from PSI along the molecular wire, we performed transient absorption measurements of reconstituted PSI with $NQC_{15}EV$ by using an ultrafast laser system.[11] The viologen in $NQC_{15}EV$ also acts as a marker of electron transfer by showing a broad absorption band around 600 nm for the reduced viologen.[12] After photoexcitation at 440 nm (the Soret band of chlorophyll a in PSI), the absorption band appeared at around 600 nm for the reconstituted PSI. The band was not observed in the case of the native PSI.

The time profiles of the absorbance of the reconstituted PSI and native PSI are shown in Figure 2. Both profiles are almost identical before 5 ps, this similarity is explained by the small absorbance of the chlorophyll a in PSI. For the reconstituted PSI, the absorbance increase in the order of 10 ps overlaps with the decay observed in native PSI. The time scale of the absorption rise is quite reasonable for the electron relay system of the PSI[8] and inadequate for other factors such as intermolecular electron donation from the solvent. Therefore, we conclude that the photoelectron in PSI is transferred to the viologen along the electron relay system of PSI and the $NQC_{15}EV$ molecular wire.

Photocurrent measurements with **3** employed as the working electrode were carried out in the presence of sacrificial electron donors.[4b,c,5a] When the system was irradiated with monochromatic light (0.32 mW at 680 nm), photocurrent responses in the anodic direction were observed at 0 V versus Ag/AgCl in all wavelength regions between 650 and 700 nm (Figure 3 (●), 40 nA cm^{-2} at 680 nm). The action spectrum of **3** shows a clear peak around 680 nm: this peak

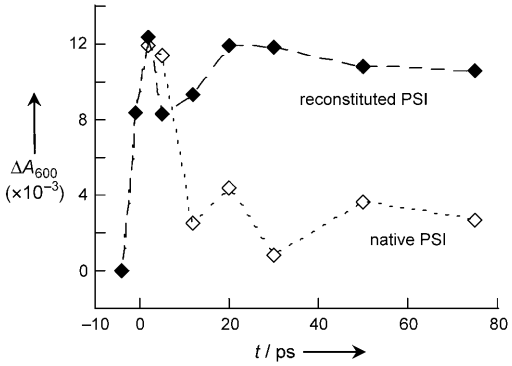

Figure 2. Temporal profiles of the absorbance at 600 nm (ΔA_{600}) of the native PSI (◇) and the reconstituted PSI (◆) at 600 nm after irradiation at 440 nm. The values are relative to that at −4 ps. The absorbance of each of the sample solutions at 680 nm was about 1.25 with a 1 cm path length. The solution composition was 2,6-dichloroindophenol (DCIP, 26 μM), ascorbate (16 mM), NQC15 EV (500 μM), n-dodecyl-β-maltoside (0.02% v/v), and Mes–NaOH buffer (pH 6.4, 20 mM).

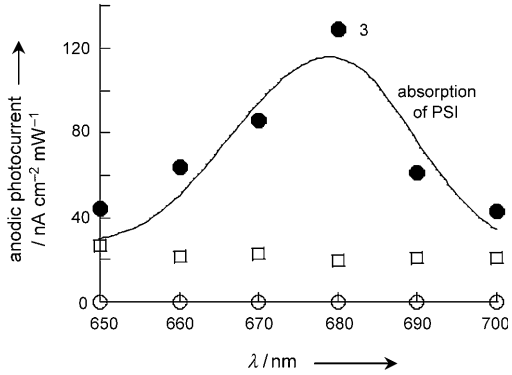

Figure 3. Photocurrent action spectra for the modified gold electrodes and absorption spectrum of PSI (solid line). The working electrodes are **3** (●), PSI(−VK1)-immobilized **1** (control electrode 1; ○), and PSI(−VK1) and MV-immobilized **1** (control electrode 2; □). Conditions: $E = 0$ V versus Ag/AgCl, $\Delta\lambda = \pm 6.5$ nm. The solution composition was sodium ascorbate (NaAsc; 0.25 M), DCIP (2.5×10^{-3} M), $NaClO_4$ (0.1 M), and MES–NaOH buffer (pH 6.4).

overlaps with the absorption spectrum of PSI (solid line). This result clearly indicates that these photocurrent responses are mainly due to the photoexcitation of PSI. To clarify the effectiveness of the molecular wire $NQC_{15}EV$, two control experiments were carried out (see the Supporting Information). In the first experiment, an electrode was prepared by using the same procedure, except that $NQC_{15}EV$ was not fixed, so that there were no binding sites for reconstitution and no electron acceptors on the electrode. However, immobilization of PSI(−VK1) was observed by surface plasmon resonance (SPR) measurements. Under the same conditions described above, photocurrent responses were not observed at all measured points (Figure 3: ○). One of the reasons for this effect is a breakdown of the electron relay system at the VK_1 site in PSI(−VK1), which strongly induces a backward electron transfer from chlorophyll a (A_0) to P700. This result indicates that PSI(−VK1), which is randomly immobilized on the electrode in **3** by electrostatic interactions

has no influence on the photocurrent response. In the second control experiment, methyl viologen (MV) was used instead of $NQC_{15}EV$, so that there were no binding sites available for reconstitution with PSI(−VK1), but there were electron acceptor units present. In this case, weak photocurrent responses were observed under the same conditions; however, the action spectrum shows no peaks around 680 nm (Figure 3 (□); 6 nA cm^{-2} at 680 nm). This indicates that the photocurrent responses are not a result of direct electron transfer from photoexcited P700 and/or other chlorophyll units to the viologen unit. These results and comparisons strongly indicate that the PSI(−VK1) in **3** was reconstituted with $NQC_{15}EV$ fixed on the gold electrode and that the electrons generated from photoexcited P700 inside the PSI were relayed and transferred along the molecular wire to the gold electrode.

In conclusion, we have succeeded in obtaining electrons from the electron relay system within PSI by using a molecular wire as a connector, which was designed for facile electron transfer. This study has confirmed the validity of the new approach and strategy to utilize biocomponents as the core parts of an artificial system, which can be applied to various biofunctions. This work on the optimization of the molecular connecter is key in obtaining an effective performance from a device comprising biocomponents, and further work on this area is in progress.

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