

Photocurrent Generation by the Self-Assembled Monolayers Integrating a Photoenergy-Harvesting System and an Electron-Transport System of Helical Peptide

Tomoyuki Morita, Shunsaku Kimura,* Shiro Kobayashi, and Yukio Imanishi†

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501

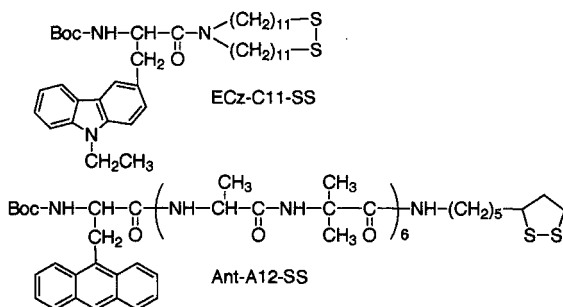
†Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0101

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A self-assembled monolayer (SAM) composed of a dialkyl compound carrying an *N*-ethylcarbazolyl (ECz) group and a helical peptide carrying an anthryl (Ant) group was prepared on gold. The photocurrent magnitude of the bicomponent SAM in the presence of an electron acceptor was larger than that of the unicomponent SAMs. The efficient photocurrent generation of the bicomponent SAM is due to the integration of the photoenergy-harvesting and electron-transport systems.

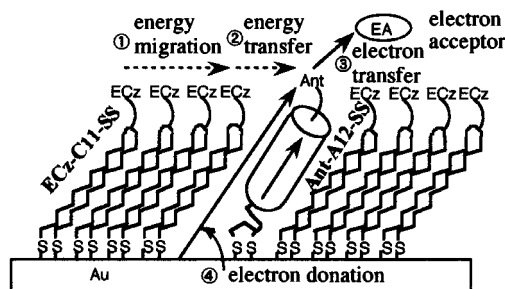
In the first stage of natural photosynthesis, facile energy transfer among highly ordered chlorophyll arrays to a reaction center at interior of the thylakoid membrane is the key factor for the efficient photoenergy harvest.¹ In the previous study, we have prepared monolayer² and bilayer membranes³ of dialkyl-type amphiphiles carrying an *N*-ethylcarbazolyl (ECz) group, and showed that the membranes harvest photoenergy efficiently due to energy migration among ECz groups at high density. The membrane composed of the ECz containing dialkyl-type amphiphile is therefore a good model for the artificial photoenergy-harvesting system due to the regular chromophore arrangement in the membrane.

The helical peptide is considered to be a good mediator for the electron-transfer with providing the pathway via through-bond, through-hydrogen-bond, and through-space processes.⁴⁻⁷ In addition, the electrostatic field generated by the dipole moment of the helices may accelerate the electron transfer.⁸ We have previously reported that in the self-assembled monolayer (SAM) composed of α -helical peptides, the photocurrent generation was actually accelerated by the dipole moment of helical peptide.⁹ We report here a novel molecular assembly system for photocurrent generation by integrating a photoenergy-harvesting system composed of a dialkyl-type compound carrying an ECz group and an electron-transport system composed of a helical peptide carrying an anthryl (Ant) group.



ECz-C11-SS is a dialkyl-type compound carrying an ECz group and a disulfide group at the each terminal of the molecule. A sequence of alternating *L*-alanine (Ala) and α -amino-

isobutyric acid (Aib) was designed because of its high preference for adopting a helical structure.¹⁰ Ant-A12-SS is a tridecapeptide carrying an Ant group at the *N*-terminal and a disulfide group at the *C*-terminal. The synthesis of ECz-C11-SS was described in the literature and Ant-A12-SS was synthesized by the method similarly to the formerly reported compound, ECz-A12-SS.⁹ In the bicomponent SAM of ECz-C11-SS and Ant-A12-SS, photoexcitation of an ECz group will initiate energy migration among ECz groups, and energy transfer from the excited ECz group to the neighboring Ant group. The tilt angles of molecular axis



from the surface normal are considered to be 30° for ECz-C11-SS from the literature¹¹ and about 45° for Ant-A12-SS from the FTIR reflection-absorption spectroscopy measurement of the Ant-A12-SS SAM. The excited anthryl group, then, reduces an electron acceptor in an aqueous phase, followed by electron donation from gold to the oxidized Ant group. The electron donation from gold is expected to be accelerated by the dipole moment directing toward an aqueous phase.

The SAM preparation and the characterization of the surfaces of the SAMs were carried out by the methods reported previously.⁹ The surface coverages of the SAMs of ECz-C11-SS and Ant-A12-SS were estimated by quartz crystal microbalance measurements to be 0.345 and 0.090 nmol/cm², respectively. The corresponding molecular areas were 48.1 and 184 Å²/molecule, respectively. The molecular area of ECz-C11-SS on gold is nearly twice the molecular area of a single-chain *n*-alkanethiol (22 Å²/molecule).¹¹ The high density of the ECz group in the ECz-C11-SS SAM is suitable for an efficient photoenergy-harvesting system. On the other hand, the molecular area of the Ant-A12-SS SAM is much larger than the expected value from the calculation under assumption of hexagonal packing of helical peptide (146 Å²/molecule). This fact may arise from unfavorable repulsion between the dipole moment of the helical peptide and the dipole moment of an AS-Au linkage (S⁻-Au⁺) opposing the helix dipole moment.¹² The Ant-A12-SS SAM is thus considered to possess some defects.

The SAMs were investigated by cyclic voltammetry in an aqueous K₃[Fe(CN)₆] solution. With the exception of the Ant-

A12-SS SAM, the voltammograms of the ECz-C11-SS SAM and all the bicomponent SAMs (ECz-C11-SS and 4.3, 7.3, and 12.2 mol% of Ant-A12-SS) showed no redox activity, indicating that these SAMs formed a well-packed structure to exhibit an insulating property. It was thus considered that the alkyl-type compound forms a good matrix for the helical peptide being incorporated regularly to produce no structural defects with respect to the cyclic voltammetry. On the other hand, redox peaks of the ferricyanide ion observed in the Ant-A12-SS SAM indicated that this monolayer possesses defects where the electrolyte can diffuse in. This result agrees with the QCM observation. Even though phase separation might be occurred in the bicomponent SAMs, the degree should not be significant, because they showed a good insulating property as described above.

Photocurrent generation by the single component SAMs was investigated in an aqueous nicotinamide adenine dinucleotide phosphate (NADP) solution. The experimental procedure for photocurrent generation is described in the literature.⁹ NADP was chosen as an acceptor of large size to prevent the diffusion of acceptor through the defects in the Ant-A12-SS SAM. Upon photoexcitation of the ECz or Ant group, electron transfer from the excited chromophore to the electron acceptor NADP, followed by electron donation from gold to the oxidized chromophore (the radical cation of an ECz or Ant group). The reduced NADP diffuses to the auxiliary electrode and transfers an electron, resulting in the generation of a cathodic photocurrent. The photocurrents were 0.091 ± 0.002 and 0.054 ± 0.002 nA for the ECz-C11-SS and Ant-A12-SS SAM, respectively. The large photocurrent was observed in the ECz-C11-SS SAM because of the high density of the ECz group. Since the density of the chromophore (ECz or Ant group) is not the same in the two SAMs, the quantum efficiencies of the photocurrent generation (the number of electron flowed upon photoirradiation / the number of photon absorbed by the chromophores) were calculated for comparison. The quantum efficiencies are 0.25% and 0.38% for the ECz-C11-SS and Ant-A12-SS SAM, respectively. The higher efficiency in the Ant-A12-SS SAM may arise from the dipole effect or the mediation of the electron transfer by the helical peptide.

The bicomponent SAMs integrating the photoenergy-harvesting system (ECz-C11-SS) and the electron-transport system (Ant-A12-SS) were investigated. The mole percentages of Ant-A12-SS in the bicomponent SAMs were determined from the action spectra of the photocurrent generation (Figure 1) as follows. The action spectra of the bicomponent SAMs showed both contributions of the ECz group around 335–350 nm and the Ant group around 350–390 nm. Under assumption that the photocurrents are proportional to the product of the surface density of the chromophores (ECz or Ant group) and the molar absorptivities of the chromophores, the mole percentages of Ant-A12-SS against ECz-C11-SS on gold can be calculated from the magnitudes of photocurrents at 351 nm in the ECz-C11-SS SAM and those at 391 nm in the bicomponent SAMs. The percentages of Ant-A12-SS in the bicomponent SAMs are 4.3, 7.3, and 12.2 mol%, respectively, but these values are at most because of the assumption of equal quantum efficiency between the Ant and ECz groups and the real percentages should be lower. All the photocurrents in the bicomponent SAMs are larger than that in the unicomponent SAM of ECz-C11-SS or Ant-A12-SS. Especially, the bicomponent SAM containing 7.3 mol% Ant-A12-SS showed 1.5 fold larger photocurrent than the

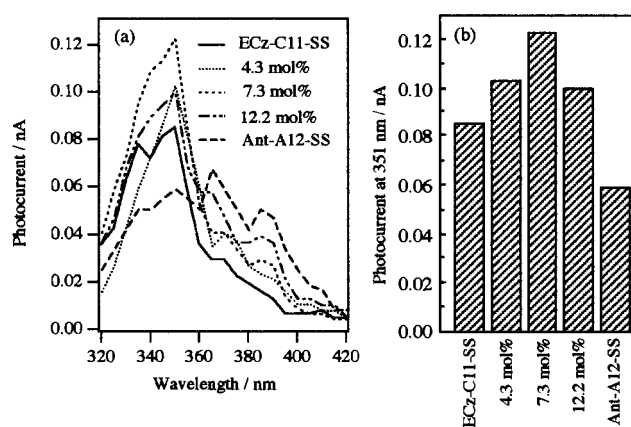


Figure 1. Photocurrent action spectra (a) and photocurrent at 351 nm (b) of the ECz-C11-SS and Ant-A12-SS SAMs and their bicomponent SAMs. The mol% of Ant-A12-SS with respect to ECz C11-SS are indicated.

ECz-C11-SS SAM. Without energy transfer from the ECz group to the anthryl group and the mediation of electron transfer by the helical peptides, the photocurrents of the bicomponent SAMs would be less than that of the ECz-C11-SS SAM. Therefore, the enhanced photocurrents in the bicomponent SAMs should be due to the integrated effect of the photoenergy-harvesting and electron-transport systems described above. The decreased photocurrents with more than 7.3 mol% Ant-A12-SS may be due to the increase of some defects which hinder energy migration among the ECz groups. We have previously reported that via efficient energy migration among ECz groups, about 70% of photoenergy of the ECz group was transferred to the Ant group in the bilayer membrane composed of an ECz-containing amphiphile and an Ant-containing amphiphile (3 mol%), where the distance between the neighboring ECz groups was 9.2 Å.³ The distance between the neighboring ECz groups in the present SAM is calculated to be 7.5 Å, which is shorter than that in the bilayer membrane. Therefore, the photoenergy of the ECz group should be transferred quantitatively to the Ant group. The 1.5-fold enlargement of the photocurrent observed in the bicomponent SAM with 7.3 mol% Ant-A12-SS is explainable in consideration of the quantitative energy transfer and the quantum yields of the photocurrent generation in the unicomponent SAMs (0.25% for ECz-C11-SS, 0.38% for Ant-A12-SS).

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