

# Photocurrent Generation by Self-assembled Monolayers of Helical Peptides Carrying Naphthyl Groups and Ferrocene Unit as Hopping Sites

Shinpei Okamoto, Tomoyuki Morita, and Shunsaku Kimura\*

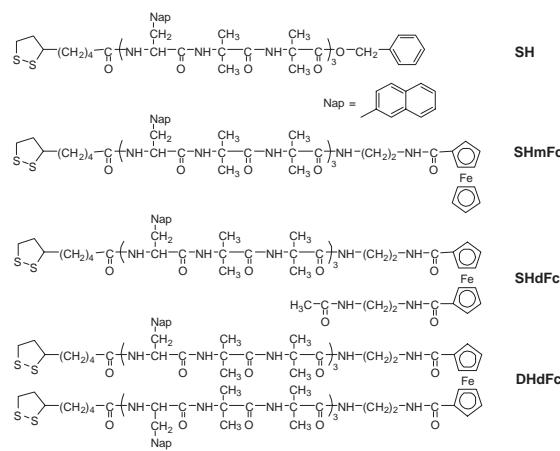
*Department of Material Chemistry, Graduate School of Engineering, Kyoto University,  
Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510*

(Received November 21, 2008; CL-081103; E-mail: shun@scl.kyoto-u.ac.jp)

Helical peptides carrying naphthyl groups at the side chains and a ferrocene unit at the C terminal were self-assembled on gold, and photocurrent generation upon photoexcitation of the naphthyl groups was studied in an aqueous solution containing an electron donor. The ferrocene unit is found to promote photocurrent generation when it has an appropriate oxidation potential to act as an electron hopping site between the naphthyl group and the aqueous donor.

Creation of organic molecules of electronic functions and integration of the molecules into a device are essential for development of molecular electronics, and helpful for understanding of biological electron-transport phenomena at a molecular level.<sup>1,2</sup> Helical peptides are promising candidates for the purpose because they have a regular periodical structure, excellent self-assembling properties, and unique electric features. We have shown that helical peptides can work as a molecular wire,<sup>3</sup> rectifying diode,<sup>4</sup> photodiode,<sup>5-7</sup> and switch<sup>8</sup> on a metal surface. In particular, we have focused our attention on photocurrent generation by self-assembled monolayers (SAMs)<sup>9,10</sup> on gold composed of helical peptides with chromophores as a prototypical molecular electronics device and a compact model of natural photosynthetic systems. We have demonstrated that the helix dipole controls the direction of the photoinduced electron transfer through the monolayer.<sup>7-9</sup> Further, photocurrent generation was effectively promoted by a regular arrangement of multiple chromophores along the helix.<sup>5-7,11</sup> In this study, ferrocene units were introduced to the monolayer surface as a hopping site to facilitate the electron transfer between a chromophore embedded in the monolayer and a donor in the aqueous phase. The effects of the substitution number and the surface density of the ferrocene unit are discussed.

The molecular structures of the peptides are shown in Figure 1. All the peptides have a disulfide group at the N-terminal as a connecting linker to a gold surface. The helical peptide segment is a 9mer of three repeating units of L-2-naphthylalanine- $\alpha$ -aminoisobutyric acid (Aib)-Aib, which forms a  $3_{10}$ -helical structure due to the high content of the Aib residues to result in an arrangement of the side-chain naphthyl groups (Naps) in a linear manner.<sup>6,7</sup> SH is a benzyl-terminated single helix (SH) without a ferrocene unit, SHmFc is a similar single helix but carrying ferrocene monocarboxylic acid (mFc) at the C-terminal, while SHdFc has ferrocene dicarboxylic acid (dFc), and DHdFc is a double-helix (DH) structure in which two helices are connected to dFc. The surface density of the dFc unit in the DHdFc SAM is designed to be half of that in the SHdFc SAM. The peptides were synthesized according to the literature.<sup>6,12</sup> Absorption and fluorescence spectroscopy showed that the Naps exist as a monomer state both in the ground state and excited state. Circu-

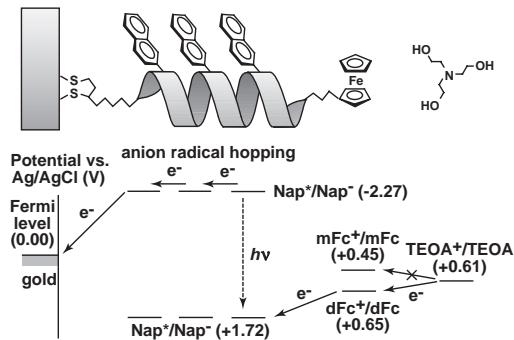


**Figure 1.** Chemical structures of the peptides.

lar dichroism spectra of the peptides in solution showed a strong splitting peak centered at 225 nm, indicating that the Naps are arranged closely and counterclockwise by  $3_{10}$ -helical conformation.<sup>6,7</sup> A gold substrate was immersed in ethanol solutions of the peptides to prepare SAMs and the monolayer defects were filled in with dodecanethiol in a gas phase.<sup>12</sup>

The molecular orientation of the helical peptides on surfaces was studied by infrared reflection-absorption spectroscopy.<sup>3,5,6</sup> The tilt angles of the helix from the surface normal were determined to be 48, 49, 45, and 42°, for the SH, SHmFc, SHdFc, and DHdFc SAMs, respectively, showing that they have upright orientation on the surface. Theoretical monolayer thicknesses are estimated from the molecular lengths (27 Å for SH and 33 Å for the others) and the tilt angles to be 18, 22, 23, and 25 Å in the above order, which agree well with those (20, 22, 18, and 26 Å) measured by ellipsometry, indicating monolayer formation. The monolayer packing was checked by cyclic voltammetry in an aqueous solution containing redox hexacyanoferrate(II) ions. The SAMs did not show redox peaks of hexacyanoferrate(III)/hexacyanoferrate(II), showing that the monolayers are free from defects which allow diffusion of the ions into the monolayer.

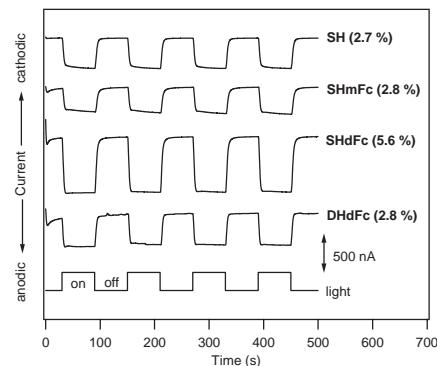
Photocurrent generation by photoexcitation of the Naps was investigated in an aqueous solution containing triethanolamine (TEOA) as an electron donor. The mechanism of the anodic photocurrent generation is schematically shown in Figure 2. In the absence of a ferrocene unit, when the Nap at the C-terminal (nearest to the aqueous phase) is photoexcited, photoinduced electron transfer from TEOA to the excited Nap occurs to generate the Nap anion radical, which hops among the Naps to reach the gold surface to complete the overall electron transfer from TEOA to gold. The electron transfer from TEOA to the other



**Figure 2.** Energy diagram for anodic photocurrent generation by the SAMs upon photoexcitation of the Nap.

Naps is negligibly slow. Our idea is that if the oxidation potential of the ferrocene unit is located between the TEOA oxidation potential (+0.61 V vs. Ag/AgCl reference) and the excited Nap reduction potential (+1.72 V), the ferrocene unit will act as a hopping site between TEOA and the Nap to promote the electron transfer between them and will also suppress the subsequent back electron transfer from the Nap anion radical to the oxidized TEOA, leading to more efficient photocurrent generation. The oxidation potentials of the ferrocene units were determined by cyclic voltammetry of the SAMs in an aqueous  $\text{HClO}_4$  solution to be +0.45 V for mFc and +0.65 V for dFc, respectively. Therefore, it is thus expected that the dFc unit will act as the hopping site to promote photocurrent generation. The surface coverages of the SHmFc, SHdFc, and DHdFc SAMs were determined to be  $6.3 \times 10^{-11}$ ,  $6.2 \times 10^{-11}$ , and  $4.4 \times 10^{-11}$  mol/cm<sup>2</sup>, respectively, by integration of the anodic peaks in the cyclic voltammograms. A similar coverage is expected for the SH SAM.

The results of the photocurrent generation experiment<sup>13</sup> are presented in Figure 3. All the SAMs generated an anodic photocurrent in response to photoirradiation with a 280-nm UV light. The action spectra confirmed the excitation of Naps is responsible for the photocurrent.<sup>13</sup> The quantum yields of the photocurrent generation (percentage of the number of generated electrons out of the number of photons absorbed by the SAM) are shown in Figure 3 in parentheses. There is no difference in the quantum yields between the SH and SHmFc SAMs, clearly showing that the mFc unit whose oxidation potential is above the TEOA oxidation potential does not work as the hopping site and thus does not affect the photocurrent generation. In contrast, the quantum yield of the SHdFc SAM is twice that of the SH and SHmFc SAMs. This result indicates that the dFc unit acts as a hopping site between TEOA and the excited Nap as expected and effectively promotes the photocurrent generation. On the other hand, the quantum yield of the DHdFc SAM is substantially lower than that of the SHdFc. This can be rationally explained by the reduced surface density of the dFc units, which in turn confirms that the dFc unit is responsible for the increased quantum yield of the SHdFc SAM on the basis of the similar Nap densities between the SAMs. However, this reason alone is not enough to explain the quantum yield of the DHdFc SAM decreased as low as those of the SH and SHmFc SAMs. It was shown in previous work<sup>12</sup> that the double-helix structure formed a tighter-packed monolayer due to the two-site immobilization on gold, and thus



**Figure 3.** Time courses of the currents in the SAMs upon repetitive photoexcitation with a 280-nm UV light at a gold substrate potential of 0 V vs. Ag/AgCl with 0.05 M TEOA.

the molecular motions in the monolayer were suppressed, leading to deceleration of electron transfer through the monolayer. This effect might have cancelled out the acceleration effect of the dFc unit, incidentally resulting in the comparable quantum yield with the SAMs lacking the dFc unit.

In conclusion, we have studied photocurrent generation by self-assembled monolayers of helical peptides carrying linearly-arranged naphthyl groups at the side chains and a ferrocene unit at the terminal, and have demonstrated that a ferrocene unit of an appropriate oxidation potential acts as a hopping site between the monolayer interior and the aqueous phase to effectively promote the photocurrent generation. A double-helix structure was found to be less beneficial to photocurrent generation compared to a single-helix structure probably owing to reduction of the ferrocene surface density and deceleration of the electron transfer by suppression of molecular motions.

## References and Notes

- 1 C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
- 2 M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435.
- 3 T. Morita, S. Kimura, *J. Am. Chem. Soc.* **2003**, *125*, 8732.
- 4 K. Kitagawa, T. Morita, S. Kimura, *J. Phys. Chem. B* **2005**, *109*, 13906.
- 5 S. Yasutomi, T. Morita, Y. Imanishi, S. Kimura, *Science* **2004**, *304*, 1944.
- 6 K. Yanagisawa, T. Morita, S. Kimura, *J. Am. Chem. Soc.* **2004**, *126*, 12780.
- 7 T. Morita, K. Yanagisawa, S. Kimura, *Polym. J.* **2008**, *40*, 700.
- 8 K. Kitagawa, T. Morita, S. Kimura, *Angew. Chem.* **2005**, *117*, 6488.
- 9 H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, *J. Phys. Chem. B* **2000**, *104*, 2099.
- 10 J. J. Wei, C. Schafmeister, G. Bird, A. Paul, R. Naaman, D. H. Waldeck, *J. Phys. Chem. B* **2006**, *110*, 1301.
- 11 T. Morita, S. Kimura, S. Kobayashi, Y. Imanishi, *J. Am. Chem. Soc.* **2000**, *122*, 2850.
- 12 S. Okamoto, T. Morita, S. Kimura, in submission.
- 13 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.htm>.