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Communication

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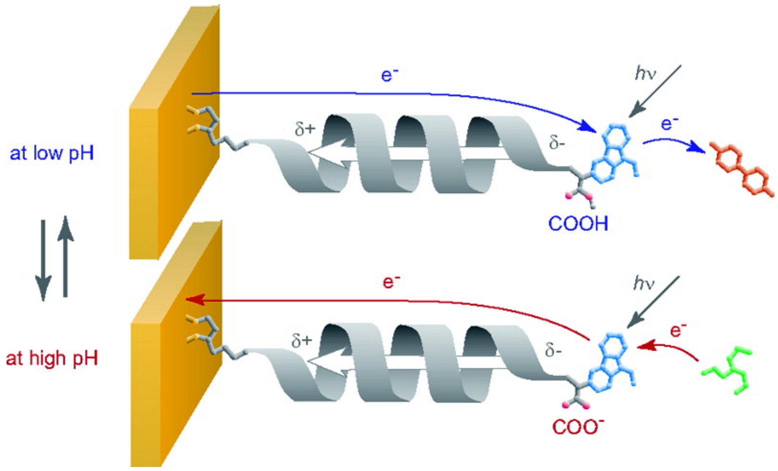

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pH-Controlled Switching of Photocurrent Direction by Self-Assembled Monolayer of Helical Peptides

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For realization of molecular electronics, the first task is to develop individual molecular electric modules;[1−4] the second task is to control the operation of molecular modules in response to external stimuli;[5−8] and the final task is to integrate multiple molecular components into an ordered structure where each component works independently or cooperatively. Self-assembled monolayers (SAMs), formed by a covalent linkage between a molecule and a metal surface, have attracted much attention as highly ordered molecular systems with specific functions,[9,10] and electron-transfer reactions through SAMs have been well established.[11,12] As a representative function of SAMs, photocurrent generation has been extensively investigated.[13,14] In a previous study, we succeeded in reversibly switching the photocurrent direction between anodic and cathodic by choosing the wavelength of irradiation on a SAM composed of two kinds of helical peptides carrying different sensitizers with opposite directions of dipole moment.[15] In the present study, we report another novel molecular system where photocurrent direction can be reversibly switched between anodic and cathodic by changing the pH of the solution.

A 16mer helical peptide composed of an alternating sequence of L-leucine and α-aminoisobutyric acid,[16] with a disulfide group at the N-terminal and L-3-(3-*N*-ethylcarbazolyl)alanine at the C-terminal, is used in this study (ECzCOOH; Figure 1). When the peptide is immobilized on gold at the N-terminal by a gold−sulfur linkage, it forms a highly ordered SAM with vertical orientation,[17,18] locating the C-terminal *N*-ethylcarbazolyl (ECz) group and a carboxyl group at the monolayer surface. Upon immersion of the monolayer into an aqueous solution, the carboxyl group exists as a protonated or carboxylate form, depending on the pH of the solution. It has been reported that the dipole moment of a helical peptide accelerates electron transfer in the same direction by the electric field generated by the dipole moment.[19,20] Therefore, with photoexcitation of the ECz group in an aqueous solution containing an electron donor at low pH, anodic photocurrent generation will be promoted due to photoinduced electron transfer from the donor to gold according to its dipole direction. At high pH, the terminal carboxyl group will dissociate into anionic carboxylate and the anodic photocurrent generation should be further promoted, because the extra negative charge at the C-terminal should enhance the electric field by the original peptide dipole moment. Meanwhile, when negative potentials are applied on gold in the presence of an electron acceptor in solution, the opposite cathodic photocurrent generation should be observed. The cathodic photocurrent generation obtained using this peptide will be more easily attained at low pH than at high pH because the direction of electron transfer is opposite to that of the dipole moment. Under suitable conditions, therefore, the peptide monolayer is expected to hold anodic photocurrent generation due to its carboxylate-enhanced electric field at high pH, while it generates a cathodic photocurrent at low pH; that is, the photocurrent direction can be switched by changing the pH of the solution (Figure 1).

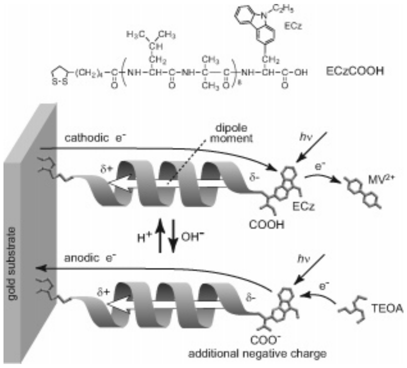

Figure 1. Chemical structure of ECzCOOH and schematic illustration for switching of photocurrent direction by pH change of solution in the self-assembled monolayer composed of the ECzCOOH molecules.

The details of the synthesis are available in the Supporting Information. ECzCOOH was obtained by hydrolysis of ethyl ester-capped ECzCOOEt,[15] which was used as a control peptide, and their α-helical conformation in solution was confirmed by CD spectroscopy. A gold substrate was immersed into the peptide solutions to prepare the respective SAMs. First, to obtain information on molecular orientation, the monolayers were subjected to infrared reflection−absorption spectroscopy. Amide I and II bands appeared at around 1675 and 1545 cm^{-1}, respectively, indicating that α-helical conformation is retained on the substrate.[21] The tilt angles of the helix axis from the surface normal were calculated on the basis of the amide I/amide II absorbance ratios to be 28.6° and 29.1° for the ECzCOOH and ECzCOOEt SAMs, respectively. This indicates that both helical peptides take vertical orientation on the surface. The tilt angle in the ECzCOOH SAM did not change after soaking into a 1 N NaOH solution upon conversion to a carboxylate form. Further, the well-packed nature of both monolayers was confirmed by cyclic voltammetry in an aqueous $K_4[Fe(CN)_6]$ solution, and the packing of the ECzCOOH monolayer was not affected by the solution pH (see Supporting Information).

Photocurrent generation experiments were carried out at an applied potential of 0 V in an aqueous solution containing an electron donor, triethanolamine, at pH 10. All applied potentials are referred to the reference electrode used in this study, Ag/AgCl/3 M NaCl. The supporting electrolyte was a 0.1 M Na_2SO_4 aqueous solution. Both SAMs generated an anodic photocurrent upon irradiation by 351 nm light (see Supporting Information). The action spectra of photocurrent generation agreed well with the absorption spectrum of the peptide in solution, indicating that the ECz group sensitizes photoinduced electron transfer from triethanolamine to gold to generate the anodic photocurrent. Noticeably, the photocurrent generated by the ECzCOOH SAM was about 3 times larger

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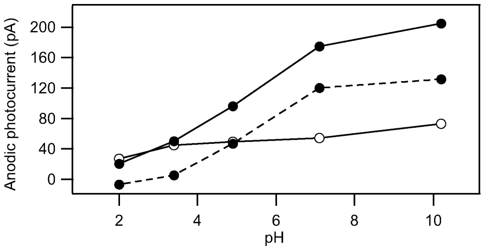

Figure 2. Dependence of anodic photocurrents on the pH of the solution containing triethanolamine, for the ECzCOOH SAM (●, solid line) and the ECzCOOEt SAM (○, solid line), and the difference curve for the ECzCOOH SAM obtained by subtraction of the curve of the ECzCOOEt SAM from that of the ECzCOOH SAM (●, dashed line). The applied potential was 0 V.

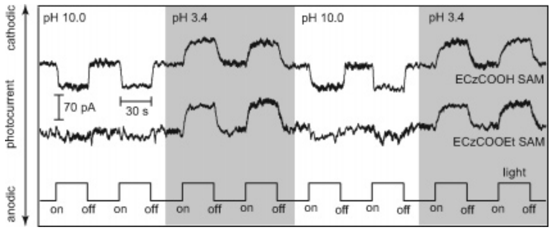

Figure 3. Switching of photocurrent direction by pH change in the peptide SAM in a mixed aqueous solution containing triethanolamine and methyl viologen (50 mM). The respective curves at different pHs were collected separately and the data combined afterward.

than that generated by the ECzCOOEt SAM, and the quantum yields for photocurrent generation were 2.0% and 0.73%, respectively. Next, the pH dependence of the photocurrent generation was examined (Figure 2). At low pH of 2−4, the photocurrent intensities were comparable between the two SAMs, but beyond pH 4 a rapid increase in photocurrent with increasing pH was observed in the ECzCOOH SAM, while the ECzCOOEt SAM showed only a moderate increase up to pH 10 (solid lines). It is thus considered that the C-terminal of ECzCOOH dissociates into anionic carboxylate at high pH, and the photoinduced electron transfer from triethanolamine to gold should be promoted due to the enhanced electric field. In detail, the electrostatically negative potential around the ECz group shifts the redox potential of the ECz group to a more negative value to accelerate the electron transfer from the ECz group to gold, and that should be the rate-determining step due to its long distance. On the other hand, the moderate decrease in the photocurrent observed in the ECzCOOEt SAM as pH deceases is probably due to deactivation of triethanolamine by protonation at low pH. To compensate for these possible effects, we subtracted the photocurrent curve of the ECzCOOEt SAM from that of the ECzCOOH SAM. The subtracted curve (dashed line) clearly shows a change in the region of pH 4−6, which should correspond to dissociation of the carboxyl group because carboxylic acids immobilized on a monolayer surface usually have their pK_a values around this region.[22]

In the range of applied potentials from −0.2 V up to 0.2 V, the SAMs generated only an anodic photocurrent. However, with the addition of an electron acceptor, methyl viologen, to the solution, cathodic photocurrent generation was observed. In the present systems, any reactions due to excitation of methyl viologen, such as direct electron transfer from gold to methyl viologen, are excluded because methyl viologen does not absorb 351 nm light. Figure 3 shows the photocurrent generation in the presence of equal moles of triethanolamine and methyl viologen at an applied potential of −0.1 V upon repeatedly changing the pH between 10 and 3.4. The dependence of photocurrents on applied potentials is available in the Supporting Information. The ECzCOOH SAM generated an anodic photocurrent at pH 10, while it generated an opposite cathodic photocurrent at pH 3.4. This switching behavior in the direction of photocurrent generation was reversible. On the other hand, the ECzCOOEt SAM did not generate a clear anodic photocurrent at pH 10, even though it generated a cathodic photocurrent comparable to that generated by the ECzCOOH SAM at pH 3.4. This prominent difference at high pH and resemblance at low pH between the two SAMs are consistent with the result obtained without an acceptor (Figure 2). It is thus concluded that the ECzCOOH SAM shows photocurrent switching in response to pH due to the change of the electric field accompanied by a change of the dissociation state of the carboxyl group.

In conclusion, a highly ordered SAM was prepared on gold where an ECz group and a carboxyl group are located at the monolayer surface, and the switching of photocurrent direction by changing the dissociation state of the terminal carboxyl group by changing the pH of the solution was successfully demonstrated.

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Supporting Information Available: Details of the synthesis, sample preparation, and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687−5692.
(2) Metzger, R. M.; Chen, B.; Hopfner, U.; Lakshmikantham, M. V.; Vuillaume, D.; Kawai, T.; Wu, X. L.; Tachibana, H.; Hughes, T. V.; Sakurai, H.; Baldwin, J. W.; Hosch, C.; Cava, M. P.; Brehmer, L.; Ashwell, G. J. *J. Am. Chem. Soc.* **1997**, *119*, 10455−10466.
(3) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705−1707.
(4) Liang, W. J.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, H. *Nature* **2002**, *417*, 725−729.
(5) Hayes, R. T.; Wasielewski, M. R.; Gosztola, D. *J. Am. Chem. Soc.* **2000**, *122*, 5563−5567.
(6) Walter, D. G.; Campbell, D. J.; Mirkin, C. A. *J. Phys. Chem. B* **1999**, *103*, 402−405.
(7) Doron, A.; Portnoy, M.; LionDagan, M.; Katz, E.; Willner, I. *J. Am. Chem. Soc.* **1996**, *118*, 8937−8944.
(8) Campbell, D. J.; Herr, B. R.; Hulteen, J. C.; VanDuyne, R. P.; Mirkin, C. A. *J. Am. Chem.* Soc. **1996**, *118*, 10211−10219.
(9) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.
(10) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1169.
(11) Chidsey, C. E. D. *Science* **1991**, *251*, 919−922.
(12) Finklea, H. O.; Hanshew, D. D. *J. Am. Chem. Soc.* **1992**, *114*, 3173−3181.
(13) Uosaki, K.; Kondo, T.; Zhang, X. Q.; Yanagida, M. *J. Am. Chem. Soc.* **1997**, *119*, 8367−8368.
(14) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099−2108.
(15) Yasutomi, S.; Morita, T.; Imanishi, Y.; Kimura, S. *Science* **2004**, *304*, 1944−1947.
(16) Otoda, K.; Kitagawa, Y.; Kimura, S.; Imanishi, Y. *Biopolymers* **1993**, *33*, 1337−1345.
(17) Miura, Y.; Kimura, S.; Imanishi, Y.; Umemura, J. *Langmuir* **1998**, *14*, 6935−6940.
(18) Morita, T.; Kimura, S. *J. Am. Chem. Soc.* **2003**, *125*, 8732−8733.
(19) Galoppini, E.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 2299−2300.
(20) Morita, T.; Kimura, S.; Kobayashi, S.; Imanishi, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2850−2859.
(21) Kennedy, D. F.; Crisma, M.; Toniolo, C.; Chapman, D. *Biochemistry* **1991**, *30*, 6541−6548.
(22) Sugihara, K.; Teranishi, T.; Shimazu, K.; Uosaki, K. *Electrochemistry* **1999**, *67*, 1172−1174.

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