

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 HClO₄ 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 6.3×10^{-11} , 6.2×10^{-11} , and 4.4×10^{-11} mol/cm², 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 experiment¹³ 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.¹³ 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 work¹² that the double-helix structure formed a tighter-packed monolayer due to the two-site immobilization on gold, and thus

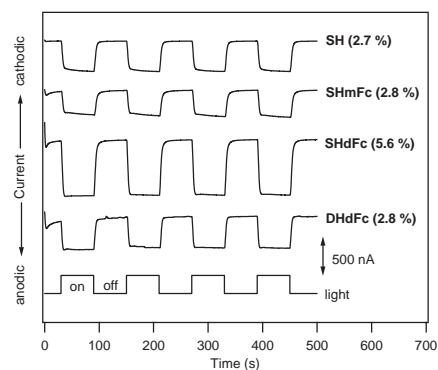


Figure 3. Time courses of the currents in the SAMs upon repetitive photoexcitation with a 280-nm UV light at a gold substrate potential of 0 V vs. Ag/AgCl with 0.05 M TEOA.

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

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- 13 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.htm>.