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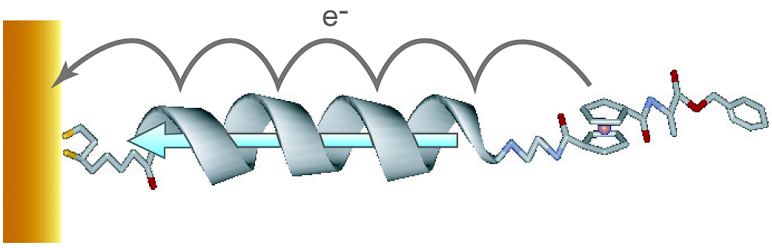

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Long-Range Electron Transfer over 4 nm Governed by an Inelastic Hopping Mechanism in Self-Assembled Monolayers of Helical Peptides

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In biological systems such as chloroplasts or mitochondria, electron-transfer (ET) reactions along a sequential redox chain occur very efficiently over a long distance.[1] Uncovering the full scope of such efficient long-range ET reactions in biological systems should lead to the development of molecular electronics. The redox centers comprising the electron relay systems are surrounded by polypeptide matrixes composed of α-helices or β-sheets, that are generally supposed to fix the three-dimensional locations of the redox entities and decide the direction and paths of ET reactions.[2] Moreover, the electric field generated by a dipole moment of an α-helix will influence the direction and rate of the ET.[3]

Two distinct mechanisms are involved in long-range ET reactions in biological systems.[4] One is an elastic superexchange mechanism, where a direct molecule-mediated tunneling takes place as an elastic tunnel process. In this mechanism, the ET rate decreases exponentially with a distance between a pair of redox entities, that is confirmed by several self-assembled monolayers (SAMs) composed of alkane thiols with a redox entity at the terminal end.[5] The other is an inelastic hopping mechanism, where electron tunneling is accompanied by energy dephasing at the boundary sites of the molecular terminals as well as in the internal molecular units.[6] The latter mechanism becomes more efficient due to the ohmic behavior if the molecular length is increased.[7]

To gain further insight into the ET reaction in biological systems, we prepared SAMs from helical peptides carrying a redox-active group at the terminal, which are the simplest model for the polypeptide matrixes seen in biological systems, and investigated the ET reactions occurring therein by electrochemical techniques. Two kinds of helical peptides, one carrying a ferrocene (Fc) moiety at the N-terminal end and a disulfide group at the C-terminal end (FcL16SS, Figure 1) and the other, respectively, at the opposite terminal ends (SSL16Fc, Figure 1), and their reference compounds without a Fc moiety were synthesized.

Previous studies have shown that similar disulfide-terminated helical peptides formed ordered SAMs on a gold surface with a parallel arrangement and vertical orientation.[8] One noticeable point with these peptides is that the large dipole moment of the helix directs in an opposite way on gold. For the Fc-containing peptides, the kind and number of atoms between the disulfide group and the Fc moiety were designed to be the same. Because other molecular aspects of the helical peptides except the direction of the dipole moment are the same, the dipole effect on the ET reaction through a peptide monolayer can be examined clearly.

A gold substrate was immersed in an ethanol solution of the helical peptide to prepare SAM-modified substrates. The molecular orientation of the peptide SAMs was investigated by Fourier transform infrared reflection−absorption spectroscopy (FTIR-RAS). Calculations based on the amide I/amide II absorbance ratios gave the tilt angles of the helix axis from the surface normal (35°, 28°, 39°, and 28°, respectively, for the FcL16SS, SSL16Fc, BL16SS, and SSL16B SAMs). These results indicate that the helix axis in each SAM oriented vertically to the surface.

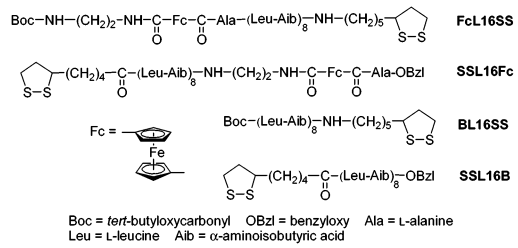

Figure 1. Chemical structures of ferrocene-containing helical peptides and reference peptides without a ferrocene moiety.

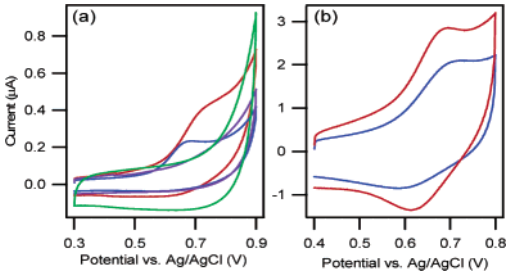

Figure 2. Cyclic voltammograms of the helical peptide SAMs in a 1 M $HClO_4$ aqueous solution at a sweep rate of 2 mV/s (a) and 10 mV/s (b): FcL16SS (red), SSL16Fc (blue), BL16SS (green), and SSL16B (purple), respectively.

Cyclic voltammetry (CV) was employed to investigate the oxidation of the Fc moiety on the SAM-modified substrates in a 1 M $HClO_4$ aqueous solution. It was confirmed that an α-helical structure is maintained in this acidic medium and the peptide monolayers are nearly free from defects (see Supporting Information). At normal scan rates (0.1−100 V/s), no peak was observed, suggesting the ET rate from the Fc moiety to gold is extremely slow. However, oxidative peaks were detected with the Fc-containing SAMs at the first scan when the voltammograms were recorded at a scan rate of 2 mV/s (Figure 2a). These peaks are considered to be due to the oxidation of the Fc moiety because their peak-potentials were about the same as that of the ferrocene derivative having two amide groups, BFcB in acetonitrile (see Supporting Information). The lack of the reductive peak is due to decomposition of the ferrocenium ion produced in a strong acidic medium after the first oxidation process,[9] because the scan rate is too slow to reduce electrochemically the ferrocenium in the lifetime. On the other hand, at a little faster scan rate (10 mV/s), a set of oxidative and reductive peaks were observed even though they were slightly indistinct (Figure 2b). The formal potentials obtained from a couple of the redox peaks were 0.643 and 0.633 V for the FcL16SS and SSL16Fc SAMs, respectively. These values were nearly the same, suggesting that the Fc moiety would not experience

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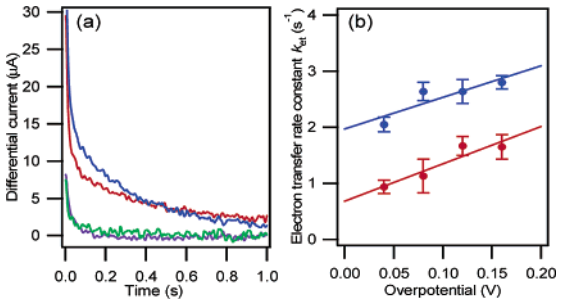

Figure 3. Chronoamperometry of the SAMs: (a) Differential chronoamperometric curves obtained for the FcL16SS (red), SSL16Fc (blue), BL16SS (green), and SSL16B (purple) SAMs. (b) Dependence of electron-transfer rate constants on overpotentials for oxidation of the ferrocene moiety in the FcL16SS (red) and SSL16Fc (blue) SAMs.

the partial charge of the helix terminal, because the Fc moiety is exposed to a water environment to reduce the partial charge effect of the dipole moment. The linear relationship between the peak currents and scan rates was also shown, indicating that the electron transfer occurs through densely packed peptide monolayers but not through defects (see Supporting Information).

The rate constants of ET reactions through the monolayer were examined by chronoamperometry (CA). In the present case, the contribution of the oxidative current of the Fc moieties to cyclic voltammograms is much smaller than capacitic or faradaic background currents (Figure 2), which represents a slow ET rate due to the long-range ET reaction (more than 4 nm). However, the oxidative current was evaluated properly from the $i-t$ curves in CA measurements just by subtracting the $i-t$ curve obtained after a CV scan at 2 mV/s, which abolished the redox ability of the Fc moiety without changing the rest of the molecular system. For example, the differential $i-t$ curves of the four kinds of SAMs at an overpotential of 0.08 V are shown in Figure 3a.

A significant differential current remained for the Fc-containing SAMs, which decayed to zero with time. In contrast, in the case of the SAMs without Fc, the current after subtraction was nearly zero except for at the very beginning of the time course (0.0−0.2 s). Therefore, the differential currents are ascribed to the oxidative current of the Fc moieties. Analyses of the currents by a single-exponential fitting in the time range of 0.2−1 s gave the ET rate constants, which are summarized in Figure 3b as a function of the overpotential. Standard rate constants, k_{et}^0, which were obtained by extrapolation of the data in Figure 3b to zero overpotential, are 0.68 s^{-1} for the FcL16SS SAM and 2.0 s^{-1} for the SSL16Fc SAM. These values are quite large as compared to the calculated value of 0.003 s^{-1}, assuming the exponential decay constants with lengths (the superexchange mechanism) of 1.2 per CH_2[10] and 6.6 nm^{-1},[11] respectively, for the alkyl chain and helical peptide moieties of the present peptides (see Supporting Information). It is thus indicated that the inelastic hopping mechanism should dominate over the superexchange mechanism in the long-range ET reactions in the present SAMs. This interpretation is also supported by the very weak dependency of the ET rates on the overpotential (Figure 3b). It has been pointed out that the electron tunneling rate via the superexchange mechanism is strongly dependent on the overpotential, but that via the inelastic hopping mechanism is not.[12] As hopping sites, amide groups in the peptide chain are the most plausible.

Another noticeable point of the present results is the dipole effect on the ET rate. It was reported that the ET reaction of a redox pair fixed on an α-helical peptide is facilitated or reduced depending on the spatial order of the redox pair against the helix dipole moment, because the redox potentials are influenced by the electrostatic potentials generated by the dipole moment.[13] Consistently, the ET rate in the SSL16Fc was about 3-fold faster than that in the FcL16SS SAM. The reason for the rate acceleration, however, is not likely due to the shift of the redox potential as is shown by the similar formal potentials of the Fc moieties between these peptide SAMs. Another plausible explanation for the acceleration of the ET rate is the positive partial charge of the N-terminal of the helical peptide in the SSL16Fc SAM, which should lower the barrier height at the interface between the gold surface and the peptide layer. Lowering the barrier height will lead to an acceleration of the plausible rate-determining step of electron transfer between gold and the nearest amide group.

In conclusion, we prepared the well-ordered SAMs from helical peptides carrying a Fc group at the N- or C-terminal end, and we observed a long-range ET reaction over 4 nm, which is accompanied by the oxidation of the Fc moiety. Electrochemical measurements revealed that the ET reaction is predominantly governed by the inelastic hopping mechanism. To our knowledge, this is the first example showing that the ET reaction according to the hopping mechanism is actually independent of the driving force, which has been theoretically postulated. Furthermore, the accelerating effect of the helix dipole on the ET rate is also demonstrated. We are now investigating ET reactions in peptide SAMs containing redox entities in the middle of the chain to obtain further insight.

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

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