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Photo-induced vectorial electron transfer through oriented metal-coordinated peptide assembly on a self-assembled monolayer

Masahiro Higuchi *

Department of Materials Science and Technology, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-5888, Japan

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Abstract

A vertically and unidirectionally oriented metal-coordinated α-helical peptide assembly having an amino acid sequence of $Leu_2His(Co(II))$-$Leu_6His(Co(II))Leu_6$-C_{60} was fabricated on a mixed self-assembled monolayer (SAM) surface consisting of amino-alkanethiol, dialkyl disulfide, and ferrocenyl alkanethiol by a stepwise polymerization of the amino acids using the modified conventional solid-phase peptide synthesis. We have demonstrated that vectorial electron transfer through the peptide assemblies on the mixed SAM. The Co(II)-His complexes in the peptide assembly on the SAM accelerated the electron transfer coupled with the macro-dipole moment of the peptides through the assembly. Furthermore, upon photo-irradiation to the peptide assembly, electron transfer occurred from the excited ferrocenyl group on the SAM surface to the electron acceptor, C_{60}, at the terminal through the metal-coordinated α-helical peptide assembly. This method has the advantage of permitting simple fabrication of oriented peptide assemblies consisting of sequential peptides having functional groups such as electron donors and acceptors at the desired positions. This system may be useful for signal transduction devices.

Keywords: Vertically and unidirectionally orientation; Metal-coordinated peptide assembly; Mixed self-assembled monolayer; Stepwise polymerization; Photocurrent; Electrochemical properties

1. Introduction

The spatially specific arrangement of functional groups in membrane proteins is closely related to the vectorial signal transfer through a biological membrane. For example, in a photosynthesis system, the specific location of a special pair chlorophylls, two pherophytins, and two quinines bound to an α-helical peptide bundle in a lipid membrane yields the photo-induced vectorial electron transfer through the membrane [1,2]. Further, a vertically oriented α-helical peptide assemblies whose molecular dipole moment aligns unidirectionally provide optical switches based on second-order non-linear effects [3,4]. Studies on vertically and unidirectionally oriented peptide assembly systems may be important not only to the understanding of a simple and/or essential mechanism for the signal transduction through biological membrane but also may provide the basis for a molecular device capable of transferring information. The fabrication of vertically oriented α-helical peptide assemblies such as Langmuir–Blodgett (LB) films [5–7] and self-assembled monolayers (SAMs) [8–12] and grafted polypeptide layers prepared by the ring opening polymerization of *N*-carboxyanhydride of amino acids (NCA) on the initiator immobilized substrate surfaces [13–16] has been reported. However, the LB films are practically insufficient because of the lack of physical stability due to the fact that the individual peptide chain remains unfixed. For SAMs, the antiparallel α-helix packing is significantly preferable to a parallel one because of the dipole–dipole interaction between the α-helices. On the other hand, in the grafted polypeptide layers on the substrate, the individual α-helical rod has unidirectional alignment, through the sequential polypeptide whose functional groups locate specifically in the rod cannot be obtained by NCA polymerization on the substrate. Recently, we have reported that fabrication of vertically and unidirectionally oriented peptide assemblies on

* Tel./fax: +81 52 735 7156.
E-mail address: higuchi.masahiro@nitech.ac.jp.

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self-assembled monolayers by the stepwise polymerization [17]. This method has the advantage of permitting simple fabrication of oriented peptide assemblies consisting of sequential peptides having functional groups such as electron donors and acceptors at the specific positions.

In this paper, we have reported that the fabrication of a vertically and unidirectionally oriented metal-coordinated peptide assembly by the stepwise polymerization on a substrate. We demonstrated the vectorial electron transfer through the peptide assembly coupled with macro-dipole moment of the peptides. Furthermore, we demonstrated photo-induced vectorial electron transfer through the metal-coordinated peptide assembly having electron acceptor, C_{60}, at the *N*-terminal from ferrocenyl group, which was fixed at the SAM surface by UV light irradiation. This system may be useful for organic signal transduction devices such as supra-integrated photo-diode.

2. Experimental details

2.1. Materials

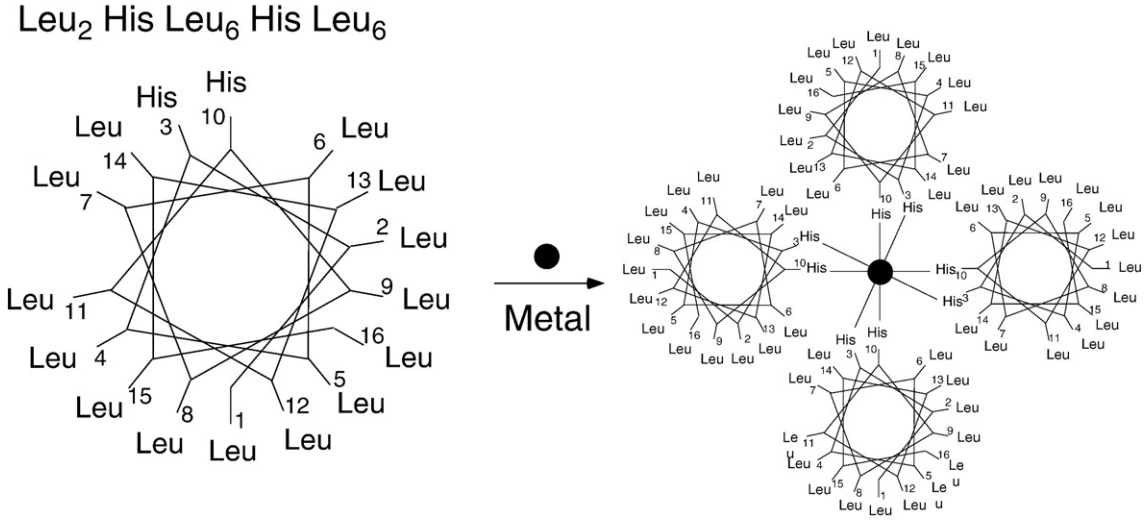
2.1.1. Preparation of a mixed SAM

A gold-deposited glass plate (Nippon Laser & Electronics Lab) was used for substrate. A mixed SAM consisting of 11-amino-1-undecanthiol (C11N) and n-butyl disulfide (C4) on the gold surface was prepared by immersing the substrate in a 0.1 mM ethanol solution containing C11N and C4 for 24 h, and then the substrate was rinsed with ethanol several times. The molar ratio of C11N and C4 was fixed to 1:4.5. Furthermore, a mixed SAM composed of C11N, C4, and 6-ferrocenyl-1-hexanethiol (C6Ferro) was prepared in a manner similar to the above. The molar ratio of C11N, C4 and C6Ferro was fixed to 1:4:1.

2.1.2. Stepwise polymerization of amino acids on SAM surfaces

The amino acid sequence of the peptide was chosen as $Leu_2HisLeu_6HisLeu_6$. Two imidazole groups of the His moieties are located in same direction of the one side surface, when the peptide forms α-helical conformation. The complexation between metal and the imidazole groups of α-helical peptides can be formed stable peptide bundle structure on the SAM surface (Scheme 1).

The metal-coordinated peptide having $Leu_2His(Co(II))Leu_6$-$His(Co(II))Leu_6$ sequence on the mixed SAM surface was obtained by the modified method of conventional solid-phase peptide synthesis method [18] according to the previous paper [17]. Activation of *N*-α-(9-fluorenylmethoxycarbonyl)-amino acid (Fmoc-amino acid) was carried out as follows. Fmoc-amino acid was dissolved in *N,N*-dimethyl formamide (DMF) (1 mM) with benzotriazole-1-yloxytris-(dimethylamino)-phophonium hexafluorophophate (BOP), *N*-methylmorpholine (NMM), and *N*-hydroxy-benzotriazole (HOBt). The molar ratio of Fmoc-amino acid, BOP, NMM, and HOBt was 1:1:1.5:1. This solution was stirred for 5 min at room temperature. First, the substrate was immersed in DMF solution of activated ester for Fmoc-L-Leu for 3 h to attach the Fmoc-L-Leu to the amino group on the surfaces. After the reaction, the surface of the substrate was rinsed by pure DMF and then the substrate was immersed in DMF solution containing 20 vol.% piperidine to remove the amino terminal Fmoc-protecting group for 1 h. After the reaction, the surface of the substrate was rinsed by pure DMF until the pH of the immersed DMF solution was neutral. This reaction cycle was repeated two times to obtain the Leu-Leu layer on the SAM. Next, the Fmoc-L-His(Tri) was coupled to the Leu-Leu layer by the same protocol and then the substrate was immersed in aqueous solution containing 95 vol.% trifluoroacetic acid to remove the Tri-protecting group of the His moiety for 1 h. After the reaction, the surface was rinsed by pure water until the pH of the aqueous solution was neutral and the substrate immersed in a 0.1 M aqueous solution containing Cobalt(II) acetate for 1 day to form complex between Co(II) and His residues in the peptide layer on the SAM. After the complexation between the His residues and Co(II), the substrate was rinsed with deionized water and pure DMF several times to remove free Co ion and to



Scheme 1. Molecular design of the metal-coordinated α-helical peptide.