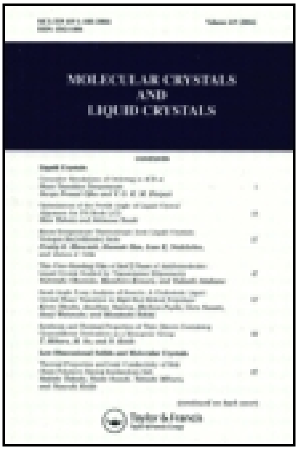

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STM Analysis of Cytochrome *c* Adsorbed Hetero-LB Film using Bridging Molecules

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Ferrocene(1-1'-ferrocene-N-dioctadecyl carboxamide), flavin(7,8-dimethly-10-dodecylisoalloxazine), viologen [N-allyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4,4'bipyridiumdibromide), and cytochrome *c* were used as an electron donor (D), sensitize (S), the first electron acceptor (A_1), and the second electron acceptor (A_2), respectively in fabricating molecular device. Malonic acid or poly-L-aspartic acid were used as a bridging molecule for the adsorption of A_2 molecules onto A_1 layers. In order to confirm the electron transfer, Scanning tunneling microscopy(STM) investigation was performed.

Keywords : Cytochrome *c*; Malonic acid; Poly-L-aspartic acid; Scanning tunneling microscopy

INTRODUCTION

Various artificial molecular devices have been fabricated by mimicking the electron transfer function of biological photosynthesis[1].

Cytochrome *c* is one of the most widely studied proteins due to its stability and solubility in water as well as an electron transport property[2]. The key feature of cytochrome *c*, the capability of electron transfer, is driven from the redox state change and conformational change of heme groups bound covalently via two thioether linkages formed by two cysteine side chains and two axial ligands, histidine and methionine[3]. Since cytochrome *c* acts as an electron transport component in the bacterial photosynthetic reaction center, it is very reasonable approach to use cytochrome *c* as an electron transfer system in an artificial molecular photodiode.

In this paper, the author investigated the characteristics of molecular photodiode consisting of cytochrome *c*-adsorbed hetero-LB films using the molecular organization composed of ferrocene, flavin, viologen and cytochrome *c*. Malonic acid and poly-L-aspartic acid were used as a bridging molecule for the adsorption of cytochrome *c* onto the viologen surface. To investigate the process of electron transfer and to observe the performance of the hetero-LB films, STM experiments were performed.

EXPERIMENTAL DETAILS

Ferrocene(1-1'-ferrocene-N-dioctadecyl carboxamide), flavin(7,8-dimethl-y-10-dodecylisoalloxazine), viologen [N-allyl-N'-[3-pr-opylamido-N",N"-di(n-octadecyl)]-4,4'bipyridiumdibromide), and cytochrome *c* (extracted from horse heart, type VI) were used as an electron donor(D), a sensitizer(S), the first electron acceptor(A_1), and the second electron acceptor(A_2), respectively. Ferrocene, flavin, viologen were synthesized and cytochrome *c* was purchased from Sigma Chemical Company. Malonic acid (Kanto Chemical Co.) and poly-L-aspartic acid (Aldrich chemical Co.) were used as bridging molecules for the adsorption of A_2 onto A_1 layer, the surface of the hetero-LB films.

D, S, A_1 molecules were transferred onto ITO-coated glass by Langmuir-Blodgett technique. The hetero-LB films were dipped into the malonic acid(0.1M) or poly-L-aspartic acid solution(1mM), and then the malonic acid or poly-L-aspartic acid treated-molecular films were immersed into the cytochrome *c* solution for thirty minutes.

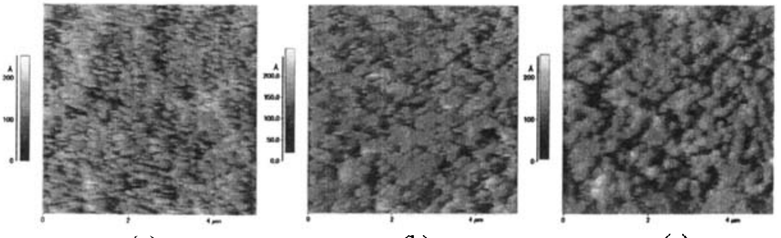
STM experiments were carried out using Autoprobe CP(PSIA, KOREA). Electrochemically etched- tungsten wire(ϕ 0.5mm diameter) was used as STM tip. Tunneling images were obtained in constant-current mode.

Typical tunneling tip bias, set point, and servo gain were 0.84mV, 0.2-0.3nA and 2 respectively.

RESULTS AND DISCUSSION

Fig. 1 shows morphology of viologen LB films and adsorbed bridging molecules, malonic acid and poly-L-aspartic acid, on the viologen surface by STM.

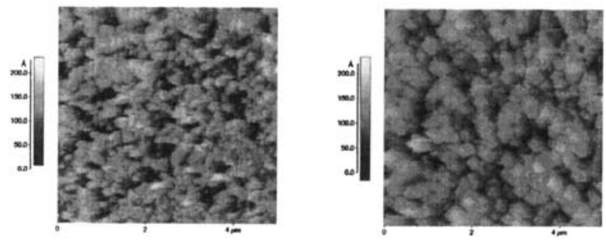
Fig. 1(a) shows STM image of viologen molecules deposited onto flavin LB film. Fig. 1(b) and Fig. 1(c) show STM image of adsorbed malonic acid and poly-L-aspartic acid on the viologen surface. By electrostatic interaction between the viologen layers and the bridging molecules, malonic acid and poly-L-aspartic acid molecules were uniformly adsorbed onto the viologen surface.



(a) (b) (c)

FIGURE 1. STM image of viologen(a), malonic acid(b), and poly-L-aspartic acid(c)

Fig. 2 shows STM images of cytochrome *c* adsorbed onto bridging molecules. Cytochrome *c* molecules were electrostatically adsorbed onto the hetero-LB film with the negatively charged surface using malonic acid or poly-L-aspartic acid. Cytochrome *c* molecules on bridging molecule surface were aggregated with one another. Nevertheless, cytochrome *c* molecules were fairly uniformly adsorbed onto the hetero-LB film surface via bridging molecules. Also, cytochrome *c* was more uniformly adsorbed onto the malonic acid than poly-L-aspartic acid.



(a) (b)

FIGURE 2. STM images of cytochrome *c* surface on malonic acid(a) and poly-L-aspartic acid

The molecular photodiode using malonic acid for cytochrome *c* adsorption is more advantageous than using poly-L-aspartic acid. Also, the STM images of cytochrome *c* surface exhibit that electron transfer takes place from the ferrocene(D) to the cytochrome $c(A^2)$. Hence, electron transfer through the molecular array consisting of $D/S/A^1/A^2$ was verified.

Acknowledgement

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