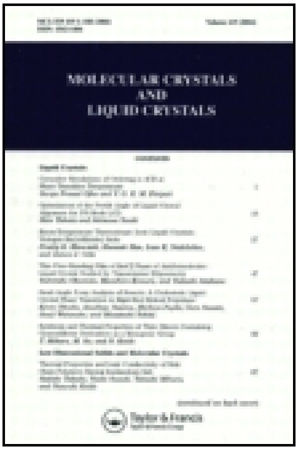

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SPM Analysis for Nanodomain Structure Composed of Hydrocarbons and Fluorocarbons

Jeong-Woo Choi [a], Young-Jae Choi [a], Hyun-Goo Choi [a] & Won Hong Lee [a]

[a] Dept. of Chem. Eng., Sogang Univ, Seoul, 121-742, Korea

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JEONG-WOO CHOI, YOUNG-JAE CHOI, HYUN-GOO CHOI, and
WON HONG LEE
Dept. of Chem. Eng., Sogang Univ., Seoul 121-742, Korea

Nanodomain structure of the complex thin films consisted of HC (Hydrocarbons) and FC (Fluorocarbons) was investigated using AFM (Atomic Force Microscope) and the current flowing through the electron transfer molecules subsequently deposited on the HC-FC nanodomain was detected by STM (Scanning Tunneling Microscope). The complex thin films consisted of arachidic acid and perfluorodecanoic acid were fabricated by LB (Langmuir-Blodgett) technique with the various conditions (i.e. pH, molar ratio, and counterion). The molecular array composed of viologen (electron acceptor), flavin (sensitizer), and ferrocene (electron donor) was aligned by LB technique onto HC-FC mixed thin films deposited under the optimal condition. The molecular array deposited onto nanodomain structure was investigated to provide the possibility of molecular device design.

<u>Keywords</u> : Nanodomain; Complex LB Films; AFM; STM

INTRODUCTION

Recently, molecular nanotechnology has been one of the most interesting fields, which can provide a breakthough for nanomachining, manipulation, and fabrication of advanced materials and devices[1]. Scanning probe microscope (SPM) is considered as a powerful tool that can be used in characterization and manipulation of molecules in nanometer scale[1,2].

Electron transfer through the functional molecules has been investigated by mimicking the biological photosynthetic reaction center[3-5]. The specific energy and electron transfer take place on a molecular scale due to the redox potential difference as well as the electron transfer property of the functional molecules, especially the electron donor, sensitizer, and electron acceptor.

In the present paper, nanodomain structure of the thin films consisted of HC (Hydrocarbons) and FC (Fluorocarbons) was investigated using AFM (Atomic Force Microscope) and the current flowing through the electron transfer molecules subsequently deposited on the HC-FC nanodomain was detected by STM (Scanning Tunneling Microscope).

EXPERIMENTAL DETAILS

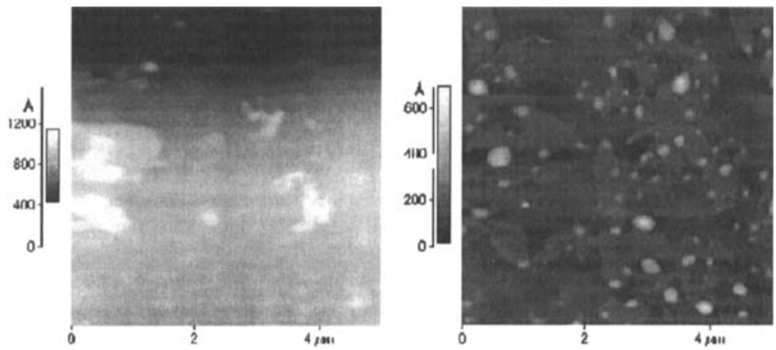
Arachidic acid($C_{19}H_{39}COOH$), eicosenoic acid, and nonadecafluorodecanoic acid($C_9F_{19}COOH$) were used as HC and FC, respectively. The electron transfer molecules, viologen (electron acceptor, A), flavin, (sensitizer, S), and ferrocene (electron donor, D), were synthesized[3,4]. Thin films of HC and FC were formed onto mica substrate using LB technique (Circular type, Model 2022, Nima Tech, UK) at the target surface pressure of 38 mN/m and 25 mN/m, respectively. The series of experiments for fabrication of complex thin films of HC-FC were performed with the variation of operating conditions, such as pH, molar ratio, and counterion ($CdCl_2$) contents. The electron transfer molecules, A, S, and D, were deposited onto HC/FC complex thin films aligned on the mica and ITO glass substrate. Phase separation and electron transfer properties of A/S/D deposited HC/FC complex films were investigated with AFM and STM (Autoprobe CP, Park Scientific Instruments, USA).

RESULTS AND DISCUSSION

The deposition characteristics of long-chain fatty acids was affected by the operating conditions such as subphase pH and addition of counterion. The counterions are frequently added to the subphase to enhance the monolayer stability and the deposition characteristics[6]. At pH 4 or less, long-chain fatty acids bear no electrical charges, but the ionization of the carboxyl groups is occurred to form hydrogen ions in the subphase and carboxylate ions in the films under the more alkaline subphase. In subphase containing counterions, such as $CdCl_2$, the salt formation takes place as follow.

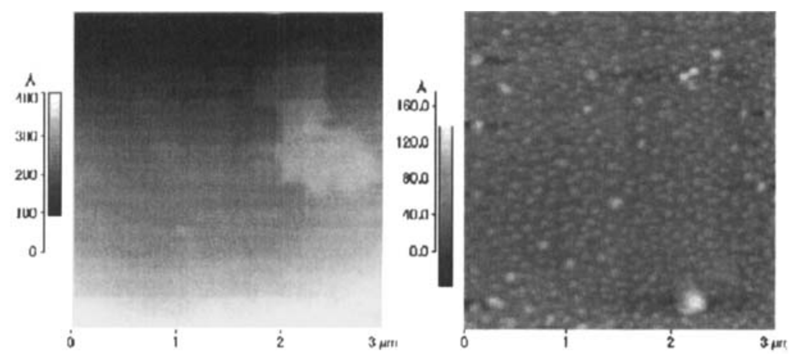
$$2C_nH_{2n+1}COOH + CdCl_2 \rightleftharpoons (C_nH_{2n+1}COO)_2^{-}Cd^{2+} + 2HCl$$

The formation of cadmium arachidate are more favored in high subphase pH, and monolayer stability can be enhanced by the more condensed monolayer state. The phase separations of HC-FC complex LB films formed with the fixed pH (=10) and the different molar ratio were investigated using



(a) (b)

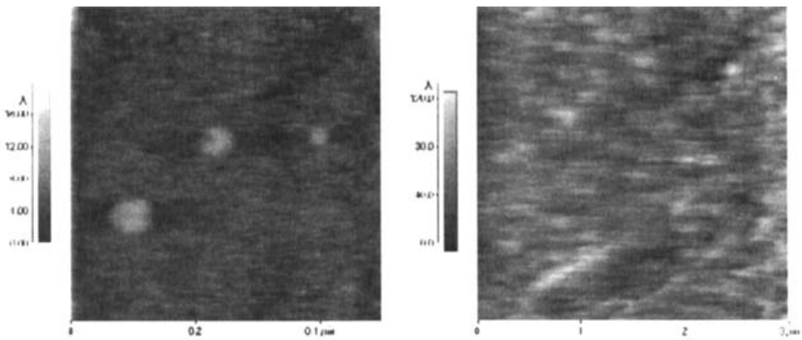
FIGURE 1. AFM image of HC-FC complex thin films (pH=10, HC:FC=1:1)
(a) without counterion; (b) with counterion



(b) (b)

FIGURE 2. AFM image of HC-FC complex thin films (pH=10, HC:FC=1:1)
(a) without counterion; (b) with counterion

AFM. As shown in Figure 1 and 2, the phase separation was more observed in the case of the molar ratio of HC:FC=2:1 with the counterion ($CdCl_2$). The deposition of electron transfer molecules (A, S, and D) onto the HC-FC complex films aligned with the optimal condition for the phase separation was verified with the AFM image as shown in Figure 3 (a).



(a) (b)

FIGURE 3. A/S/D deposited onto HC-FC (2:1) complex thin films
(a) AFM image; (b) STM image

In Figure 3 (b), based on the image contrast, it can be found that the electron transfer through the functional molecules was different depending on whether A/S/D were deposited on HC or FC. It can be concluded that the nanodomain structure with phase separation is usefully applicable to the design and fabrication of functional molecular array in nanoscale.

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