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Structure of dioctadecyl L-glutamide-derived lipid self-assembled monolayers on Au(1 1 1) surface

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Abstract

An L-glutamic acid-derived lipid with a terminal thiol has been synthesized and its corresponding self-assembled structure on Au(1 1 1) surfaces described. The surface morphology of the lipid self-assembled monolayer (SAM) exhibits nano-order patterning, where the height of the monolayer (approximately 1.5 nm) could be interpreted as due to the monolayer structure estimated from molecular models. The molecular orientation in the monolayer is almost perpendicular to the Au(1 1 1) surface depending on the three-point hydrogen-bonding sites in the molecule.

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Keywords: Self-assembled monolayer; AFM; Nanofiber; FT-IR/RAS; Molecular orientation

1. Introduction

Two-dimensional integration with low molecular weight self-assembling compounds has been widely used as a method for the formation of functional interfaces for various applications, including sensing and surface modification [1,2]. In order to construct a nano-scaled structure, the formation of thiol-terminated self-assembled monolayers (SAM) has been reported to be a convenient method [3–6]. In these SAMs, it was shown that the intermolecular interaction and the molecule–substrate interactions act cooperatively and/or interactively to form highly ordered monolayer structures. It shows that we can control the SAM structure by a molecular chemical structure.

Here, we introduce the L-glutamic unit as a self-assembling molecular tool for nano-structure creation. This tool is very attractive because nano-fibrillar structures such as nanohelices and nanotubes can be spontaneously produced in aqueous and/or organic media simply by slightly modifying the chemical structure of the functional group [7–10]. Interestingly, the fibrillar aggregation often induces a sol-to-gel transition of the organic medium through the development of three-dimensional network formations driven by hydrogen bonding. Therefore, these compounds are known as ‘‘organogelators’’ [11,12].

In this paper, we synthesized an L-glutamide-derived organogelator (**1**), which is characterized by the fact that self-assembling can be induced via a three-point hydrogen-bonding site on the L-glutamide moiety, and the surface interaction between a terminal thiol group (Scheme 1) and a Au surface. We also describe the self-assembled structure of the L-glutamide-derived lipid (**1**) on a Au(1 1 1) surface, and discuss the molecular orientation of the formed structure as a potential platform to construct biofunctional interfaces.

2. Experimental

2.1. Materials

A thiol group-introduced didodecylamide **1** (Scheme 1) was prepared by coupling of *N*,*N*-didodecyl L-glutamide with γ-thiobutyrolactone according to the method reported previously

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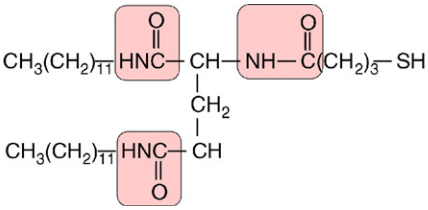

Scheme 1. Chemical structure of lipid **1**.

[13]. Introduction of the terminal thiol group was confirmed by the 2,2′-dithiopyridine (DTP) method [14]. Thiol groups are known to react easily with 2,2′-dithiopyridine, producing equimolar amounts of pyridine 2-thione (2TP) with respect to the number of thiol groups. The concentration of 2TP was calculated from the absorption at 360 nm using the molar extinction coefficient in methanol solution ($\varepsilon = 1.1 \times 10^4$).

The Au(1 1 1) substrate was prepared by evaporation of gold (99.999%) onto a freshly cleaved mica surface in a homemade vacuum chamber. Evaporation was carried out under previously described conditions where the substrate temperature was kept constant at 300 °C and the pressure in the vacuum chamber was kept at 10^{-6} to 10^{-7} Torr during evaporation [10–12]. After evaporation, the substrate was annealed at 350 °C for 3 h.

2.2. *Preparation of SAM on Au(1 1 1) surface*

After cooling the Au(1 1 1) substrate to room temperature, it was treated by flame annealing and immersed into 1.0 and 0.01 mM lipid **1**/MeOH solutions for 24 h at 50 °C. The substrate was quickly removed from the solution and immediately rinsed with enough MeOH and dried with N_2 gas.

2.3. *FT-IR RAS measurement*

The FT-IR reflection–absorption spectroscopy (FT-IR RAS) measurements of lipid **1** on Au(1 1 1) were recorded on a Bio-Rad FTS-6000 Fourier transform infrared spectrometer, using a p-polarized beam obtained through a polarizer. The spectrometer was purged with N_2, and a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used for the reflection measurement. The spectra were recorded at a 4 cm^{-1} resolution with 256 scans. A Au(1 1 1) surface was used for background measurements in order to minimize experimental error.

2.4. *AFM measurement*

The AFM system used in this study was a NanoScope IIIa (Digital Instruments, Inc.). The measurements were performed in the tapping and contact modes (15 μm scanner) in air at room temperature. For the tapping mode measurement, Si cantilevers (Nanoprobe NCH-10T, Digital Instruments) with a length of 125 μm were used, while for contact mode measurements, Si_3N_4 cantilevers with a spring constant of 0.12 N/m (Nanoprobe NP-S, Digital Instruments) for molecular resolution imaging were used. All the images were collected in the "height mode" while maintaining a constant force. In order to minimize drift effect, the system was calibrated for 6–8 h using a standard mica sample. Images shown in this paper are flattened and plane-fitted, without

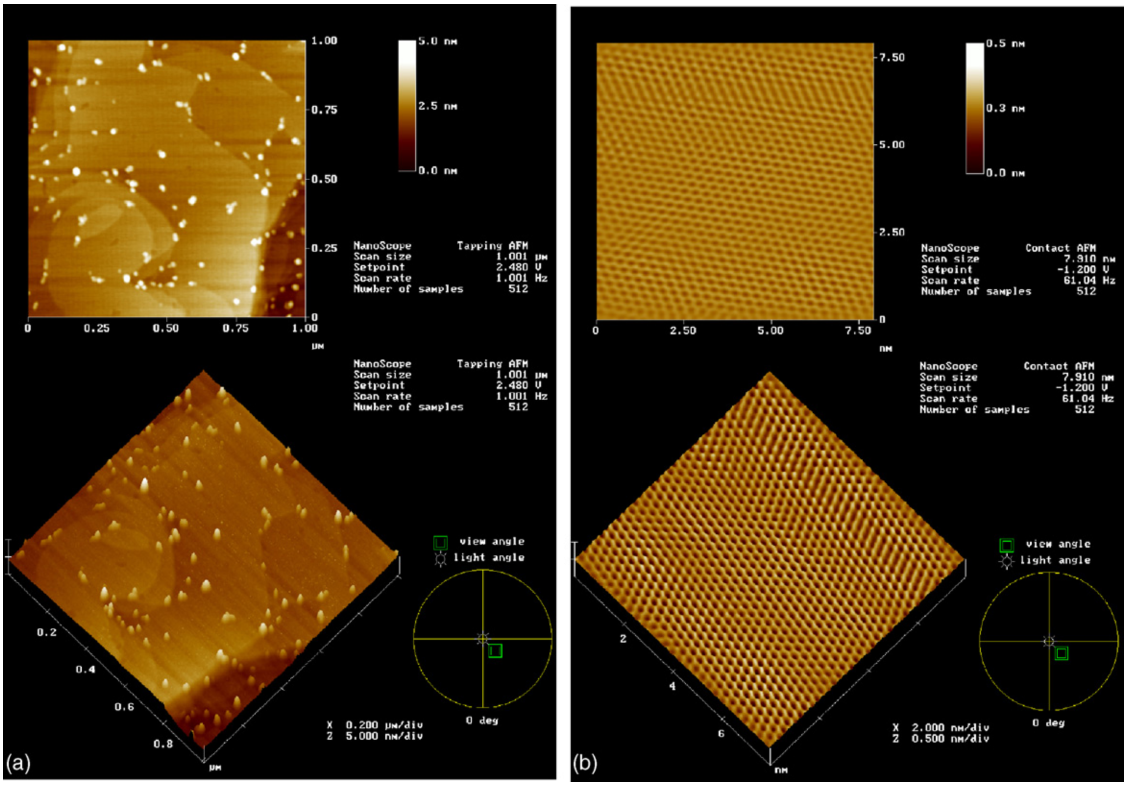

Fig. 1. AFM images of Au(1 1 1) crystal surface deposited on cleaved mica surface: (a) 1 μm × 1 μm and (b) 8 nm × 8 nm. In the images, the bright regions correspond to the high region and the dark regions correspond to the low region.