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Adsorption Behavior of DNA onto Self-assembled Monolayer Containing Intercalator

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We synthesized an unsymmetric disulfide containing an anthryl group, which can form a self-assembled monolayer (SAM) on a gold surface, to immobilize DNA onto the gold surface through the intercalation between DNA and anthryl groups. A surface plasmon resonance (SPR) measurement indicates that the SAM can detect DNA efficiently at a liquid-solid interface.

Key Word: DNA; Intercalation; Self-assembled monolayer; Surface plasmon resonance

INTRODUCTION

It is important to immobilize DNA efficiently onto the surface for the sequencing of DNA because efficiency of DNA attachment to the surface is required for the technique.[1] Here we utilize an intercalation, which is an incorporation phenomenon of chromophore in stacked base-pairs of DNA, to immobilize DNA on a surface. Thiol or disulfide derivatives can form a closely-packed monolayer on a gold surface, called a self-assembled monolayer, when the metal substrate is immersed in a thiol or disulfide derivative solution. [2] To immobilize DNA efficiently, an unsymmetric disulfide containing an anthryl group which has the ability to bind DNA through an intercalation was used because the unsymmetric disulfide is expected to form SAM on which

anthryl groups were distributed. An anthryl group which has the ability to bind DNA through an intercalation, and we investigated the interaction on the surface by SPR. Schematic illustration of for this system is shown in figure 1.

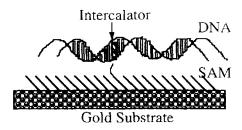


FIGURE 1. Schematic illustration for immobilization of DNA on SAM prepared on a gold substrate.

EXPERIMENTS

Unsymmetric disulfide was synthesized via Bunte salt.[3] The schematic procedure for the synthesis of 11-(2-anthroyloxy)-octhyl disulfide (compound **2**) is shown in Scheme 1. Anthryl group was attached to the terminal OH group of compound **1** by esterification in CH₂Cl₂ using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) as a condensing agent.

HO-
$$C_{11}H_{22}$$
-Br $\frac{Na_2S_{2O_3} \cdot 5H_2O_{(4.6 g)}}{EtOH:H_2O=1:1, reflux}$ HO- $C_{11}H_{22}$ -S-SO₃ Na^+ $(3.7 g, 64 \%)$ HO- $C_{11}H_{22}$ -S $(2.6 g, 61 \%)$ C_8H_{17} -S C_8H_{1

The structure of compound 2 was identified by H¹-NMR and FT-IR.[4] The SAM was prepared by immersing a gold substrate into a 1 mM chloroform solution of compound 1 or 2 for 24 hours at room temperature. DNA was dissolved in a 0.2 N NaCl solution, with a concentration was 50 mg/l.

RESULTS AND DISCUSSION

The interaction between DNA and the SAM which was prepared from the solution of compound 2 was estimated by SPR. The adsorption process occurring at the solid-liquid interface can be followed in-situ by selecting an appropriate angle of incidence θ and monitoring the reflected intensity as a function of time.[5]. This means the DNA was adsorbed onto the SAM because the thickness of the adsorbate on the surface was changed after injection of DNA.

Figure shows adsortion-desorption kinetic curves of SAMs which were prepared from compound 1 or 2 solutions. In the case of a SAM prepared from compound 2 solution, the reflectivity of SAM increased with time and saturated around one hour, while there is little change of reflectivity for SAM prepared from

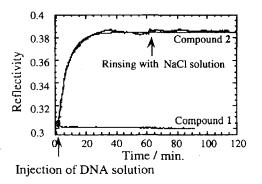


FIGURE 2. Kinetic curves for adsorption of DNA onto SAMs prepared from compound 1 and 2 solutions:

compound 1 solution. This indicated that anthryl moieties on a SAM could interact with DNA at the liquid-solid interface, leading to the increase of the thickness of the SAM. The adsorption of DNA behaves like a formation of monolayer because the kinetic curve agrees with a Langmuir adsorption isotherm. Assuming that the refractive index of the adsorbed DNA is 1.45, the thickness of the adsorbed DNA is estimated to be 2.6 nm.[6]

CONCLUSION

We succeeded in preparing SAM which could immobilize DNA on a gold substrate efficiently. By introducing this functionalized SAM, a new DNA monolayer has been realized without flattening and denaturation, because the interaction between the intercalator and DNA is due to the van der Waals force. The alignment of DNA onto the surface two-dimensionally is possible using this method. Now we are investigating the character of DNA on the SAM.

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