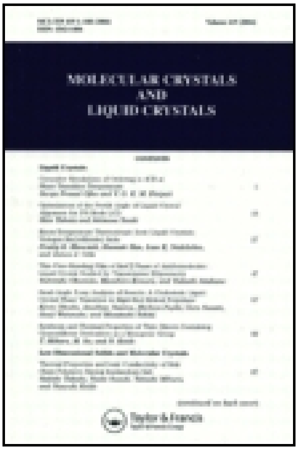

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Photopolymerization of the Diacetylene Nucleobase Monolayers Controlled by Triplex Formation

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Photopolymerization of the Diacetylene Nucleobase Monolayers Controlled by Triplex Formation

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Pressure-area isotherms of ternary component monolayers of nucleobase amphiphiles, octadecylcytosine (C_{18}-Cyt) and diacetylene-containing adenine and thymine amphiphiles (DA-Ade, DA-Thy), were changed by addition of oligonucleotides, $d(GT)_{15}$ or $d(GGT)_{10}$, in the water subphase. Photopolymerization of diacetylene in the monolayer was strongly suppressed on the oligonucleotide subphase. This suggests that the oligonucleotide can act as a template for the diacetylene monomer arrangement via complementary hydrogen bonding at the air-water interface.

Keywords: nucleobase monolayer; diacetylene; photopolymerization; template polymerization; base trimer formation; molecular recognition

INTRODUCTION

DNA has a double helical supramolecular structure composed of Watson-Crick type base pairs between adenine-thymine (A-T) and guanine-cytosine (G-C). A triple helix is another supramolecular structure of DNA composed by the combination of Watson-Crick and Hoogsteen type base-pairing, A-T and T, and G-C and protonated C. In order to mimic the base pairing and the triplex formation at the air-water interface, the monolayers of nucleobase amphiphiles have been prepared. The monolayer of C_{18}-Cyt forms base pair with guanosine dissolved in the water subphase[1,2]. The mixture of octadecyladenine (C_{18}-Ade) and octadecylthymine (C_{18}-Thy) forms A-T base pair at the air-water interface of the pure water subphase[3]. Triplex was formed when the A-T pair monolayer was spread on a thymine or an uridine subphase[4]. If the ternary mixture of C_{18}-Ade, C_{18}-Cyt, and C_{18}-Thy is spread on the subphase containing oligonucleotides of deoxyguanosine and deoxythymidine, both Watson-Crick and Hoogsteen type hydrogen bonds are expected to be formed at the air-water interface.

To confirm the sequenced molecular arrangement transcribed by the template oligonucleotides added in the subphase, a polymerizable group is introduced into the alkyl chain of the adenine and thymine amphiphiles. Diacetylene group is chosen as a polymerizable spectral probe because of its photopolymerization with remarkable color change. Ternary mixtures of DA-Ade, DA-Thy, and C_{18}-Cyt were spread on aqueous subphases containing oligonucleotide, $d(GT)_{15}$ or $d(GGT)_{10}$. The non-polymerizable cytosine amphiphile is expected to be squeezed into the one-dimensional diacetylene arrays to suppress the polymerization.

EXPERIMENTAL

The synthesis of nucleobase amphiphiles were described elsewhere. The 1:1:1 or 1:1:2 mixtures of DA-Ade, DA-Thy, and C_{18}-Cyt was spread from the chloroform/ethanol (8/2, v/v) solution on the surface of 10mM Tris-HCl buffer solution (pH 7.8) containing 25nM of $d(GT)_{15}$ or $d(GGT)_{10}$, respectively. The buffer solution containing 25nM of dT_{30} was also used as the water subphase. The mixed monolayers compressed at 15mN/m were irradiated with UV light (254nm) on the water subphase and spectral changes due to the photopolymerization were followed by a fiber-optics reflection spectrophotometer (LB-100, JASCO).

RESULTS AND DISCUSSION

Figure 1 shows the pressure-area isotherms of DA-Ade/DA-Thy/C_{18}-Cyt monolayer on the buffer solution with and without oligonucleotides. On the buffer solution without oligonucleotide, only the A-T pair contributes to the pressure-area isotherm because C_{18}-Cyt can not form stable monolayer. The isotherm was changed when dT_{30} was added to the buffer subphase. Base trimers of A-T and T were formed at the air-water interface. Difference between two isotherms on dT_{30} and $d(GT)_{15}$ or $d(GGT)_{10}$ indicates that C_{18}-Cyt is mixed with the DA-Ade/DA-Thy pair.

Figure 2 shows the reflection spectra of the mixed monolayers on various oligonucleotide subphases after 20min UV irradiation. These spectra are normalized by the contents of the diacetylene amphiphiles at the molecular area of 15mN/m. The monolayer formed on dT_{30} solution shows "blue form" of polydiacetylene with absorption maximum at 638nm, which is identical with that of the polymerized DA-Ade/DA-Thy monolayer without C_{18}-Cyt. The A-T base pair

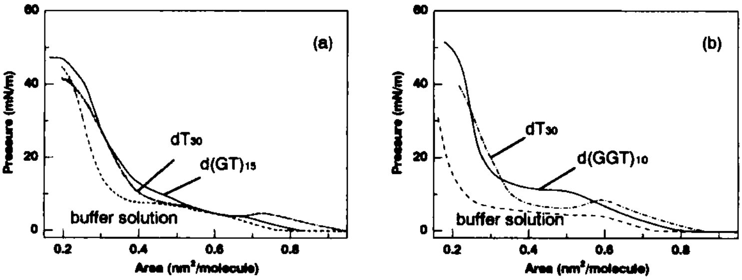

FIGURE 1 Pressure-area isotherms of the 1:1:1 (a) and 1:1:2 (b) mixed monolayer on various nucleotides solutions at 20°C.

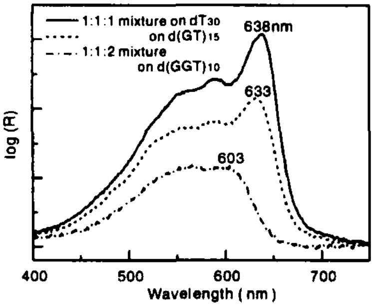

FIGURE 2 Reflection spectra of the mixed monolayer on various oligonucleotide subphases after UV irradiation for 20min.

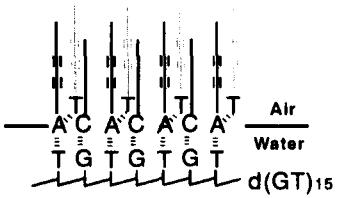

FIGURE 3 Plausible model of molecular arrangement in the 1:1:1 mixed monolayer on the $d(GT)_{15}$ subphase.

interacted with dT_{30} in the subphase and isolated C_{18}-Cyt amphiphiles from the mixed monolayer. On the contrary the photopolymerization of the 1:1:1 mixture spread on the $d(GT)_{15}$ subphase was suppressed and the spectral shift to 633nm was observed. Drastic suppression of polymerization was found when the 1:1:2 mixture was spread on the $d(GGT)_{10}$ subphase. It is suggested that the DA-Ade/DA-Thy base pair and C_{18}-Cyt can recognize dT and dG in the oligonucleotides, respectively. Owing to the inter-chain polymerization the complete suppression of the diacetylene photopolymerization was not achieved in this study. Complete isolation of the single oligonucleotide chain complexed with the ternary mixed monolayer is required to the complete suppression of the polymerization.

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