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Two-Dimensional Nucleobase Self-Organization Supported by Base-Pairing and Stacking at the Air-Water Interface

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Octadecyl substituted amphiphiles of the four nucleobases, adenine, cytosine, guaine, and thymine (C_{18}-Ade, C_{18}-Cyt, C_{18}-Gua, and C_{18}-Thy, respectively), were prepared. Binary mixtures of these amphiphiles were spread on water surface as monolayer assemblies. Pressure-area isotherms of all pairwise combination of the nucleobase amphiphiles indicate that the Watson-Crick type base-pairings and base-stacking can stabilize monolayers at the air-water interface. Unexpected stabilization was observed in the combination of C_{18}-Gua and C_{18}-Thy, which resembles a "wobble" pair in RNA. Langmuir-Blodgett films were prepared on gold substrates for FT-IR measurement of the complementary hydrogen bonding between the nucleobase amphiphiles.

Keywords: Watson-Crick type base-pair; "wobble" base-pair; hydrogen bond, base-stacking; molecular recognition; monolayer

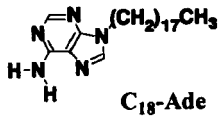
INTRODUCTION

DNA is a supramolecular assembly composed of one-dimensional stacking of complementary base-pairs formed by specific hydrogen bonds between adenine

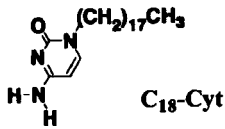
and thymine, guanine and cytosine, respectively. We have already reported that C_{18}-Cyt spread on the air-water interface can selectively interact with guanine bases dissolved in the subphase.[1] Two-dimensional nucleobase assemblies, so-called DNA-mimetics, were formed when the Watson-Crick combination of C_{18}-Ade and C_{18}-Thy was spread on a pure water subphase.[2] The DNA-mimetics is another supramolecular base-pair stacking of two-dimension. In this report, 9-octadecylguanine (C_{18}-Gua) is newly synthesized to investigate binary combination of four nucleobase amphiphiles for stable organization of DNA-mimetics at the air-water interface.

EXPERIMENTAL

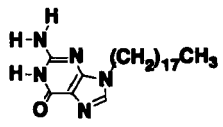
Preparation of C_{18}-Cyt, C_{18}-Ade, and C_{18}-Thy were described elsewhere.[1,2] According to Mullah, *et al.*[3], C_{18}-Gua was prepared. 2-Amino-6-chloro-9-octadecylpurine was prepared by alkylation of 2-amino-6-chloropurine. After alkylation chlorine was eliminated by acid hydrolysis to form carbonyl group. Chloroform/ethanol (9/1 *v/v*) solutions of binary mixtures of nucleobase amphiphiles were spread on a pure water subphase. Monolayer experiments were carried out by a computer-controlled Langmuir film balance (USI, FSD-50). Y-type double layers were prepared on gold-coated ITO glass at 30 mN/m by Langmuir-Blodgett technique and characterized by FT-IR reflection absorption spectroscopy (RAS) (JASCO, FT/IR-300) to confirm complementary hydrogen bonding.



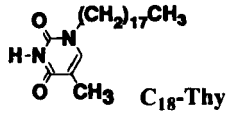
C_{18}-Ade



C_{18}-Cyt



C_{18}-Gua



C_{18}-Thy

RESULTS AND DISCUSSION

Mixing experiments of the pressure-area isotherm of the C_{18}-Ade/C_{18}-Thy mixture indicate that the equimolar mixture forms a stable monolayer, while single component of each amphiphile can not form a stable monolayer, respectively (Fig. 1a). Steep pressure rise in the isotherm of 1:1 mixture suggests densely packing of the stacked Watson-Crick base-pairs at the air-water interface. Guanine-cytosine pair is another Watson-Crick base-pair of DNA. Surface pressure-area isotherms (Fig. 1b) show that mixing of two components can stabilize monolayer as well as another Watson-Crick combination. As was expected, the non-complementary mixing, C_{18}-Ade/C_{18}-Gua, C_{18}-Ade/C_{18}-Cyt, and C_{18}-Cyt/C_{18}-Thy, could not stabilize monolayer (Fig. 2a).

Unexpected stabilization was found in the equimolar mixture of C_{18}-Gua/C_{18}-Thy (Fig. 2b). A guanine-uracile pair is known as a "wobble" base-pair in RNA [4a] And "wobble" GT pair in poly[dGdT] provides an isosteric double-helical structure [4b]. Planar structure of the "wobble" GT pair enables their close stacking to stabilize the monolayer.

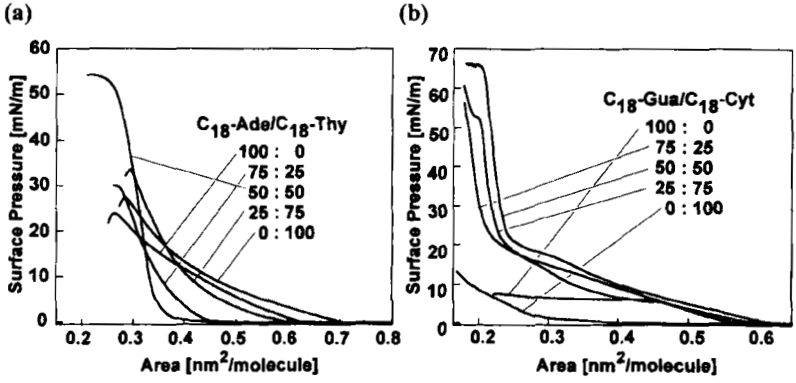


FIGURE 1. Surface pressure-area isotherms of binary mixtures of C_{18}-Ade/C_{18}-Thy (a) and C_{18}-Gua/C_{18}-Cyt (b) on pure water at 20 °C.

In the Watson-Crick monolayers, complementary hydrogen bonding was comfirmed by FT-IR RAS. Absorbance of C=O stretching of guanine base shifted from 1711 cm^{-1} (in pure C_{18}-Gua monolayer) to 1705 cm^{-1} (in C_{18}-Gua/C_{18}-Cyt monolayer). Similar spectral shift to 1706 cm^{-1} was observed in the "wobble" pair of C_{18}-Gua/C_{18}-Thy monolayer.

Molecular recognition-directed supramolecular organization of the DNA-mimetics was investigated by six combination of the four nucleobase amphiphiles at the air-water interface. The "wobble" type GT combination can stabilize monolayer assembly as well as Watson-Crick pairs. Stacking of the planar base-pairs can be utilized as a building block for supramolecular architectures.

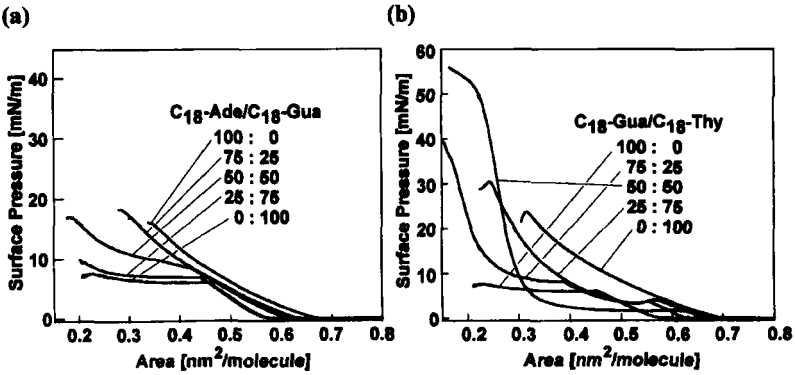


FIGURE 2. Surface pressure-area isotherms of binary mixtures of C_{18}-Ade/C_{18}-Gua (a) and C_{18}-Gua/C_{18}-Thy (b) on pure water at 20 °C.

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