Two-Dimensional DNA-Mimetic Molecular Organizations at the Air−Water Interface

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Received August 14, 1996

Tailoring of molecular organization is one of final goals of supramolecular chemistry[1] and essential for designing molecular devices.[2,3] Weak intermolecular interactions (e.g., hydrogen bonds, van der Waals forces, and hydrophobic interactions) are indispensable architectural tools for assembling molecular organizations.[4,5] Double-helical DNA, one of natural products of molecular organization based on the specific intermolecular interaction, comprises one-dimensionally-stacked base pairs, adenine−thymine and guanine−cytosine, formed by complementary multiple hydrogen bonds. In addition to transferring molecular information as genetic signals, DNA has recently been discovered to transfer an electron through the stacked base pairs.[6,7] Toward the functional application of the stacked base pairs as molecular devices, we report here the tailoring of two-dimensional DNA-mimetic molecular organizations with the specific intermolecular interaction at the air−water interface.

A hydrophobic interface of a monolayer assembly formed on a water surface has been reported to be a sufficient environment for hydrogen bonding even though the chemical substances are surrounded by a large number of water molecules.[8,9] Monolayer-forming amphiphilic nucleobases have already been prepared to demonstrate complementary hydrogen bonding with water-soluble bases at the air−water interface.[10−12] Base pairing at the air−water interface might be a driving force of molecular organization termed "molecular-recognition-directed self-assembly".[1] We are interested in how nucleobase amphiphiles are organized to two-dimensional (2-D) molecular assemblies by the complementary base-pairing at the base pair interface. In this paper, we have used microscopic fluorescence imaging of the base pair interface for the morphological observation of 2-D molecular assemblies.

The singly-alkylated nucleobase derivative 1-octadecylcytosine (C_{18}Cyt) was prepared by a nucleophilic substitution reaction of cytosine with octadecyl iodide in the presence of sodium hydride.[13] As shown in Figure 1, the pressure-area(π−*A*) isotherm of C_{18}Cyt spread from chloroform solution onto a water surface is drastically changed when a small amount (5×10^{-4} M) of guanine nucleosides (guanosine and deoxyguanosine) is dissolved in the neutral water subphase, whereas other nucleosides show little effect on the isotherm (Figure 1).[14] Since the isotherm on the acidic subphase (pH 3.0), on which the cytosine moiety was fully protonated, was not affected by addition of guanine nucleosides, the Watson−Crick base pair of C_{18}Cyt and guanine base is assumed to be formed on the neutral water subphase. The monolayer on the guanosine subphase can be transferred on the freshly deposited gold surface by the ordinary Langmuir−Blodgett technique under the constant surface−pressure condition (20 mN m^{-1}). The C═O stretching bands (1715 and 1666 cm^{-1}) in the FT-IR reflection absorption spectrum of C_{18}Cyt monolayer deposited from the guanosine subphase strongly suggest complementary hydrogen

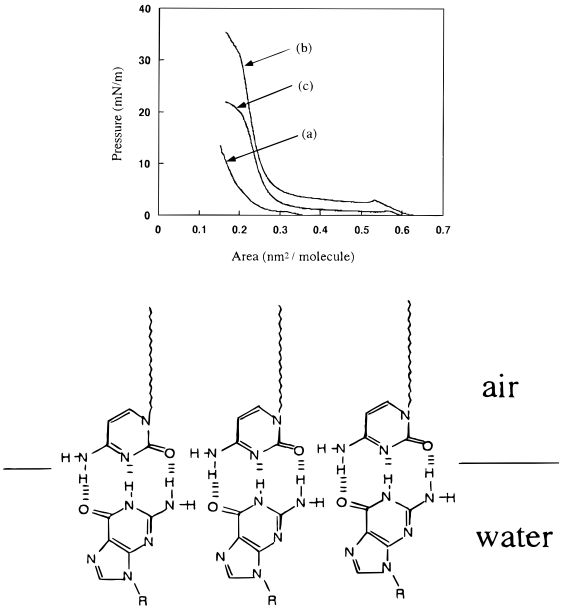
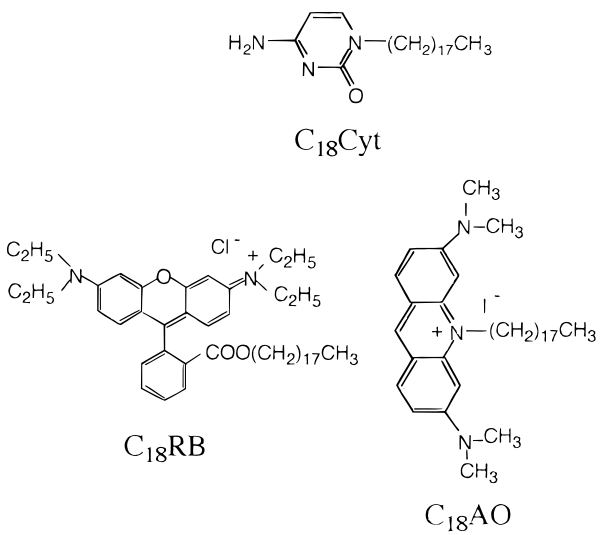


Figure 1. Pressure−area isotherm of C_{18}Cyt on (a) pure water, (b) guanosine, and (c) deoxyguanosine subphase at 20 °C and schematic illustration of Watson−Crick base-pairing at the air−water interface.



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S0002-7863(96)02847-8 CCC: $14.00

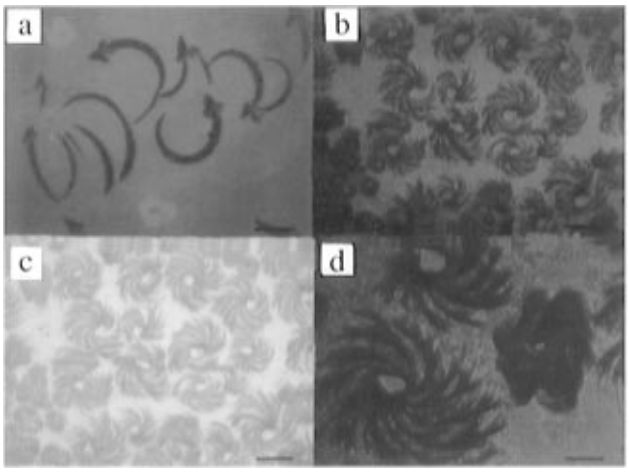

Figure 2. Fluorescence images of the C_{18}Cyt monolayer at 3 mN m^{-1} (a) on pure water subphase observed with a G-filter (546 nm) for C_{18}-RB excitation, scale bar = 200 μm, (b) on guanosine subphase observed with a G-filter, scale bar = 100 μm, (c) on guanosine subphase observed with a B-filter (410 nm) for C_{18}AO excitation, scale bar = 100 μm, and (d) a close-up image on guanosine subphase, scale bar = 25 μm.

bonding, since the spectrum is very similar to that of the double-stranded DNA, poly(dC)·poly(dG) (1711, 1664 cm^{-1}, KBr), but not the simple addition of guanosine (1694 cm^{-1}, KBr) and C18Cyt (1665 cm^{-1}, deposited monolayer from a pure water subphase).

Fluorescence imaging of the water surface with an epifluorescence microscope is an *in situ* observation method not only for the liquid-to-crystal phase transition of monolayers[15] but also for the dynamic process of the molecular organization by specific molecular interaction. A small amount (2 mol %) of octadecylrhodamine B (C_{18}RB), which is squeezed out from the crystalline phase to the liquid phase,[16] is added as a fluorescence probe for negative imaging of the molecular assemblies composed of C_{18}Cyt. Fishhook-shaped dark domains were observed on pure water surface (Figure 2a). When the result of the isotherm measurement is taken into consideration, the dark domains on the pure water subphase are assumed to be three-dimensional crystallites of C_{18}Cyt. Fluorescence image was almost identical when the nucleosides, which did not affect the $\pi-A$ isotherm, were added into the water subphase. While the monolayer was spread on the guanosine subphase and compressed to the plateau region of the $\pi-A$ isotherm (see Figure 1), spiral-shaped dark domains were generated in a bright-red field of the fluorescence microscope (Figure 2b). Similar shaped spiral domains were also observed on the deoxyguanosine subphase. This is the first direct finding of the molecular organization by complementary base-pairing in the two-dimensional world.

Acridine derivatives are known to be intercalating agents which insert into the stacked base pairs of double-stranded DNA. An amphiphilic intercalator, octadecylacridine orange (C_{18}AO),[17] was used as a positive imaging probe of the molecular-recognition-directed self-assembly. If the base pairs of C_{18}Cyt and guanosine stack laterally in the spiral-shaped 2-D crystals, the C_{18}AO molecule could be incorporated in the crystalline domains as well as in the stacked base pairs of DNA and the crystalline domains could show an intense green emission of the intercalated acridine fluorophore. Green-colored spiral domains were found when 5 mol % of C_{18}AO was added to the spreading solution of C_{18}Cyt (Figure 2c). A typical monomer emission with 530 nm maximum of the acridine fluorophore was measured by a spectrofluorimeter equipped to the epifluorescence microscope. The monomer emission is a spectral evidence on the intercalation of the acridine fluorophore into stacked base pairs. It can be concluded that the spiral-shaped 2-D crystals consist of lateral-stacked cytosine−guanine pairs. It is noted that the fishhook-shaped domains showed no green emission.

Stacking of the base pairs in double-stranded DNA shows hypochromism (diminution of absorbance) in the UV-vis absorption spectra of the purine and the pirimidine chromophores. To our surprise, the C_{18}Cyt−guanosine monolayer, transferred on a quartz plate, showed a large shift in the absorption maximum. The absorption maximum of the guanine−cytosine pair in DNA, 256 nm in an aqueous poly(dG-dC)·poly(dG-dC) solution, shifted to 284 nm in the monolayer. The $\pi-\pi$ interaction of the stacked base pairs in the 2-D DNA-mimetics is stronger than that in double-stranded DNA.

The chiral feature of the crystal domain is ascribable to the molecular chirality of the carbohydrate moiety of the guanine nucleoside. A peculiar finding is that we found two types of chiral diffusion-limited aggregates (DLA)[18] for 2-D molecular crystals even though we used pure optical isomers of the nucleosides having D-ribose or D-deoxyribose. Figure 2d is a close-up of the two DLAs, a compact DLA with clockwise crystal growth and a widely expanding DLA with an anticlockwise sense. Since these crystals are not mirror images, their crystal structures must be different. Polymorphism of 2-D crystals of the DNA-mimetic monolayer seems to be strongly correlative to the left-handed double-helix Z-DNA, specially formed from polynucleotides composed of dG and dC.

Formation of the chiral 2-D crystals based on the complementary base pairing at the interface is one of the interesting examples of molecular organizations by specific intermolecular interaction. We would like to emphasize that the C_{18}Cyt molecule is endowed with organization ability at the interface by the guanine bases dissolved in the water subphase. In our case, the hydrogen bonding is simultaneously used as a tool of the molecular recognition and the structure formation. The 2-D spiral domain of the stacked base pairs is expected to be an electron π-way,[6,7] which is a suitable medium of long-range electron and/or energy transfer through the highly oriented π-electron array.

Acknowledgment. This work was funded by a Grant-in-Aid on Priority-Area Research "Molecular Superstructure-Design and Creation" from the Ministry of Education, Science, Sports, and Culture, Japan (08231201).

JA962847U

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