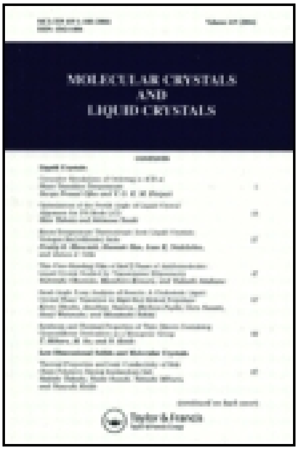

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Molecular Recognition and Monolayer Formation of Azobenzene-Containing Nucleobase Amphiphile Assisted by cis→trans Photoisomerization at the Air-Water Interface

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Molecular Recognition and Monolayer Formation of Azobenzene-Containing Nucleobase Amphiphile Assisted by *cis→trans* Photoisomerization at the Air-Water Interface

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An amphiphilic cytosine derivative containing an azobenzene chromophore was prepared in order to align azobenzene chromophores along single-strand DNA as a template. The *trans*-amphiphile was too coalescent to be spread as a monolayer at the air-water interface. On the other hand, the *cis*-amphiphile formed an expanded monolayer. After photoisomerization of the *cis*-monolayer with the visible light irradiation at the air-water interface, the regenerated *trans*-amphiphile can form a stable monolayer only on the guanosine subphase.

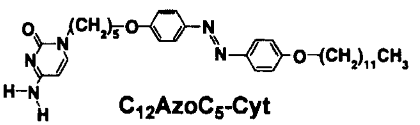
Keywords: azobenzene chromophore; photoisomerization; base-pairing; molecular recognition; monolayer; molecular organization

INTRODUCTION

Complementary hydrogen bonding of nucleobases is indispensable to build up suprastructure of DNA. In the biomimetic chemistry, construction of supramolecular architectures based on molecular recognition at the air-water interface has been studied [1]. We have reported that the nucleobase monolayers can form two-dimensionally stacked base-pairs, so-called DNA mimetics, at the air-water interface [2].

An amphiphilic cytosine derivative containing an azobenzene chromophore, $C_{12}AzoC_5$-Cyt, was newly prepared in order to align azobenzene chromophores along single-strand DNA as a template. Highly stacked π-electron system can be formed in the one-dimensional chromophore array of the DNA-monolayer complex.

Monolayer formation of the nucleobase amphiphile and its interaction with nucleosides dissolved in subphases were investigated by surface pressure-area (π-A) isotherms measurements and atomic force microscopy (AFM).



$C_{12}AzoC_5$-Cyt

EXPERIMENTAL

$C_{12}AzoC_5$-Cyt was newly synthesized according to references [3].

Surface pressure-area isotherms were measured by micro-processor controlled Langmuir film balance (USI System, FSD-50). Nucleosides used in this experiment were commercially available and dissolved in subphases without further purification. Water used for a subphase was purified to 18MΩ·cm by a Milli-Q SP system. The mixture of chloroform and ethanol 10 vol.%, spectroscopic grade, was used for a spreading solvent.

Trans→*cis* photoisomerization of $C_{12}AzoC_5$-Cyt was carried out in the spreading solution by photoirradiation at 365nm by a UV lamp (UVP Co., UVL-56). The molar ratio of *cis*-isomer was estimated to be *ca.*94% from ^{1}H-NMR. The *cis*-isomer solution was spread immediately after UV light irradiation. Photoisomerization from *cis* to *trans* at the air-water interface was accomplished by irradiation of visible light longer than 460nm from a 500W

Xe-lamp (USHIO, UI-501C) equipped with a UV (HOYA, Y46) and an IR cut filter (SIGMA Kouki Co., HAF-50S-50H).

The monolayers at the air-water interface were transferred onto mica substrates and then observed by AFM. AFM measurements were carried out with a vibrating tip mode of AC-AFM (Olympus, NV2500) bearing a cantilever with a spring constant of 3.5N/m (Pointprobs, NV2-CL-SLM).

RESULTS AND DISCUSSION

When the *trans*-C_{12}AzoC$_5$-Cyt molecules were spread on an aqueous guanosine solution, AFM observation revealed that three-dimensional microcrystals were formed (Fig. 1). It is considered the *trans*-C_{12}AzoC$_5$-Cyt molecules are too coalescent to be spread as a monolayer on water surface.

On the other hand, the *cis*-C_{12}AzoC$_5$-Cyt molecules formed a fluid expanded monolayer on water surface (Fig.2a).

The π-A isotherms of *cis*-C_{12}AzoC$_5$-Cyt were drastically changed by visible light irradiation inducing *cis*→*trans* isomerization at the air-water interface. The stable monolayer was formed only on the guanosine subphase (Fig. 2a). Formation of the monolayer after photoirradiation on the guanosine subphase was confirmed by AFM (Fig. 2b). These results indicate that complementary G-C base-pairing at the air-water interface can dramatically stabilize the monolayer.

It is concluded that the stable monolayer of the cytosine amphiphile having a *trans*-azobenzene chromophore can be

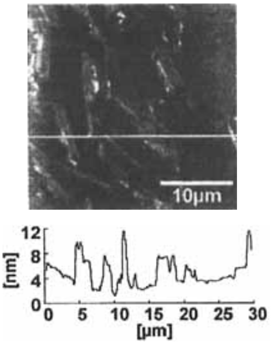


FIGURE 1. Atomic force micrograph and its depth profile of *trans*-C_{12}AzoC$_5$-Cyt transferred on the mica substrate from 0.5mM guanosine subphase at 5mN/m.

See color plate XIV at the back of this issue.

formed after regeneration from the *cis*-isomer on the guanosine subphase. *Trans*-azobenzene chromophores are expected to be aligned in the nucleobase amphiphile monolayer at the air-water interface.

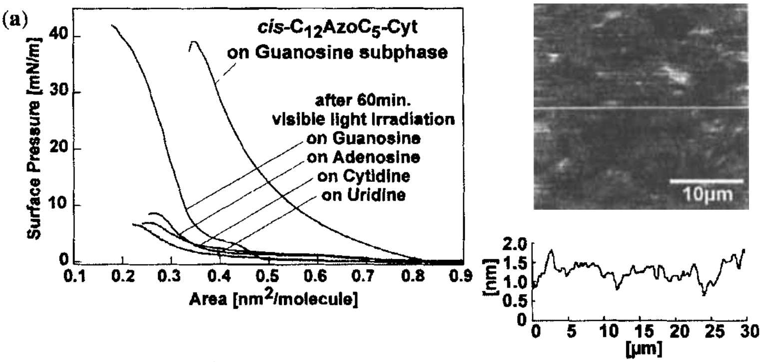


FIGURE 2. (**a**) Surface pressure-area isotherms of *cis*-monolayer and *trans*-monolayer formed after visible light irradiation on 0.5mM nucleoside subphase at 20°C. $C_{12}AzoC_5$-Cyt was spread immediately after UV-light irradiation and then irradiated with visible light (>460nm) for 60 minutes at the air-water interface. (**b**) Atomic force micrograph and its depth profile of the regenerated *trans*-$C_{12}AzoC_5$-Cyt monolayer transferred on the mica substrate from 0.5mM of guanosine subphase at 5mN/m. See color plate XVat the back of this issue.

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