Two-dimensional Molecular Patterning through Molecular Recognition

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Molecular images for the mixed monolayers composed of guanidinium (**G**) and orotate (**O**) amphiphiles on pure water and on aqueous flavin adenine dinucleotide (FAD) solution were taken with an atomic force microscope (AFM). The AFM image of **G/O** mixed monolayer on FAD showed a periodic pattern composed of two kinds of peaks with different heights, whereas that on pure water showed a periodic peak. The molecular pattern is apparently induced by rearrangement of monolayer components based on specific recognition by FAD template molecule.

Designed formation of nanometer-scale molecular patterns should provide exciting possibilities in fundamental supramolecular chemistry and in molecular scale electronic devices.[1] Several techniques that have been recently developed for two-dimensional patterning such as photolithography,[2] laser manipulation[3] and cantilever techniques[4,5] do not supply a molecular resolution. Self assembly of molecules may be utilized for this purpose, if the assembly process is properly controlled. It has been demonstrated in previous studies that molecular monolayers can bind polar guest molecules dissolved in the aqueous subphase through complementary hydrogen bonding.[6,7] These results were extended to multi-site molecular recognition, in which a guest molecule was specifically bound at two functional sites to two monolayer components.[8,9] The subsequent study implied that flavin adenine dinucleotide (FAD) was bound simultaneously to three kinds of monolayer components at three recognition sites.[10] This result suggests that we can produce molecular patterns from monolayer components by using multi-site guest molecules. As a first step for this purpose, we employed two-component monolayers of a guanidinium amphiphile and an orotate amphiphile against complementarily functionalized nucleotide derivatives. The required molecular resolution was achieved by atomic force microscopic observation of transferred films.

Syntheses of guanidinium (**G**) and orotate (**O**) amphiphiles were reported elsewhere.[11] The surface pressure-area curve and x-ray photoelectron spectroscopic measurements of the **G/O** mixed monolayer revealed that the 2:1 molar ratio was suitable for the complexation.[12] A plausible interaction mechanism of FAD and the mixed monolayer is illustrated in Figure 1. The guanidinium unit interacts with the phosphate group in FAD through hydrogen bonding and electrostatic interaction. The orotate unit forms complementary hydrogen bonds with the adenine group in FAD.[7] However, the mixed monolayer became mechanically unstable when the **G** content was increased. Therefore, we spread equimolar **G/O** mixtures in chloroform with the combined concentration of 1×10^{-3} M on pure water and on 0.01 mM aqueous solution of FAD at a subphase temperature of 293 K. The monolayer was compressed up to a surface pressure of 25 mN·m^{-1} and was maintained as such for one hour, in order to prepare mechanically stable monolayers sufficient for

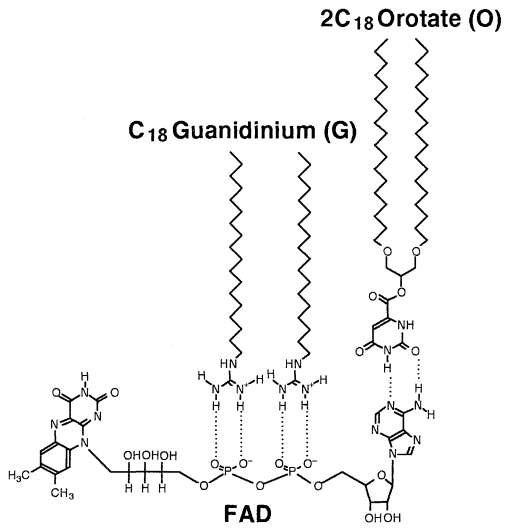

Figure 1. A scheme of multi-site molecular recognition between FAD and a **G/O** mixed monolayer at the air-water interface (FAD: flavin adenine dinucleotide). The flavin unit in FAD may be buried under the phosphate group.

obtaining the molecular-resolution AFM image.[13,14] Each monolayer was transferred onto a freshly cleaved mica by the horizontal drawing-up method.[15] The transfer ratio for each monolayer was unity, indicating that a mica substrate is completely covered with each monolayer. The AFM images of the monolayers were obtained with a SFA300 (Seiko Instruments) in air at 293 K. A 0.8 mm x 0.8 mm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.022 N·m^{-1} were used. Images were recorded in the "constant-height" mode; that is, feedback electronics and software were used to measure the cantilever deflection by keeping the sample height. The applied force on scanning was about 10^{-10} N. In order to reduce the noise component in raw AFM images, only a low-pass filter treatment was carried out.

Figure 2 shows a three-dimensional AFM image of the **G/O** mixed monolayer on aqueous FAD with a scan area of 1.8 x 2.1 nm^2. The AFM image revealed that the higher portions of the **G/O** mixed monolayer on aqueous FAD[16] are regularly aligned with a distorted hexagonal array. Furthermore, the AFM image displays a periodic wave-like structure composed of two different peaks. The height difference between the two peaks is several angstrom. The binding of FAD with the mixed monolayer as illustrated in Figure 1 would cause a height difference between the two terminal CH_3 groups. Hence, the higher and lower peaks in the AFM image may be assigned to the **O** and **G** molecules, respectively. Thus, a regular arrangement of the methyl terminals

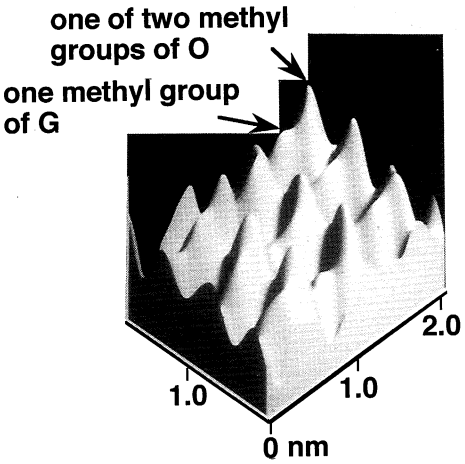

Figure 2. Three-dimensional AFM image (1.8 x 2.1 nm^2) of the monolayer prepared from an equimolar mixture of **G** and **O** on the aqueous FAD subphase.

of **O** molecule is seen as a molecular pattern in the mixed monolayer. On the other hand, the AFM image on pure water revealed a periodic wave-like pattern composed of only one kind of peak corresponding to individual methyl terminals of **G** or **O** molecule, as shown in Figure 3. They are regularly arranged in a hexagonal array, indicating that the height of the terminal CH_3 group of the **G** and **O** component is the same. These results are derived from regular spatial alignment of the same C_{18} chains of the two components above the water surface. The longer polar region of the **O** component would then be buried in the aqueous subphase deeper than the shorter guanidinium unit. It is clear that the alkyl chain packing is altered by FAD binding.

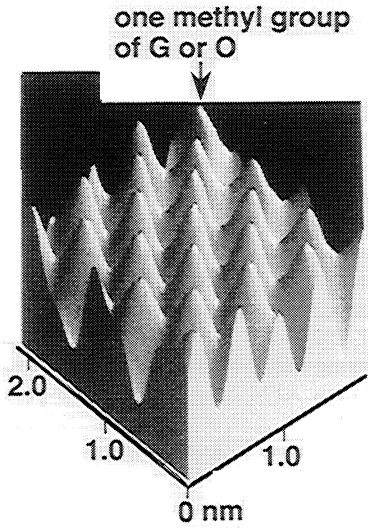

Figure 3. Three-dimensional AFM image (1.9 x 2.1 nm^2) of the monolayer prepared from an equimolar mixture of **G** and **O** on the pure water subphase.

In conclusion, two-dimensional molecular patterning has been achieved by rearrangement of monolayer components as directed by specific recognition by an aqueous template molecule. Regularly repeating patterns are readily prepared by this approach. The two-dimensional arrangement of interacting groups in a template molecule is transformed into height patterns of alkyl chains. Proper molecular design of templates and mixed monolayers would yield a number of novel molecular patterns and the consequent functionalities.

References and Notes

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12 The molecular area was calculated from π-A isotherms for mixed **G/O** monolayers with different compositions. The area deviation from the ideal mixture was largest at the 2:1 molar ratio. Furthermore, the ratio of N over P evaluated by x-ray photoelectron spectroscopy of the transferred films indicated that the **G/O** molar ratio of 2:1 was suitable for the complexation.
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16 Figure 2 is a representative AFM image of regular molecular arrangement for the 2:1 **G/O** composition. An AFM image in a larger area showed dislocation-like molecular arrangements probably due to introduction of extra **G** components. The overall **G/O** composition of the mixed monolayer was set at 1:1 because of the monolayer stability. This composition does not agree with the 2:1 composition that would produce stoichiometric interaction with FAD.