Self Organization of Molecular Patterns through Hydrogen Bonding

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Abstract

Hydrogen bonding plays a most important role for creation of well-designed supramolecular assemblies, as typically exemplified by DNA and proteins in the biological world. We recently demonstrated that molecular recognition at the air-water interface can be realized in specific and efficient manners by complementary hydrogen bonding in spite of bulk water. This concept was subsequently extended to multi-site recognition. Mixed monolayers that are composed of three different functional components formed a stoichiometric complex with FAD molecules through hydrogen bonding at three recognition sites. It was possible to observe by atomic force microscopy unique molecular patterns of related multi-component monolayers formed by the simultaneous recognition of the multi-site guest molecules. Designed disposition of individual molecules should be useful for preparation of novel molecular materials.

Design of Molecularly-Precise Patterns

Disposition of individual molecular units in appropriately designed three-dimensional arrangements is an important target of molecular materials research. This is not possible with the current chemical and physical means. An approach toward this goal is to combine designed two-dimensional disposition of unit molecules with adjusted vertical stacking of the resulting 2-D molecular arrangement. Then, we need to develop three different methodologies to achieve the final goal. First, it is necessary to develop ways to arrange small molecular units (or atomic units) in two dimension in desired disposition. Secondly, these 2-D molecular (and atomic) organizates must be accumulated layer-by-layer in predetermined order. Additional

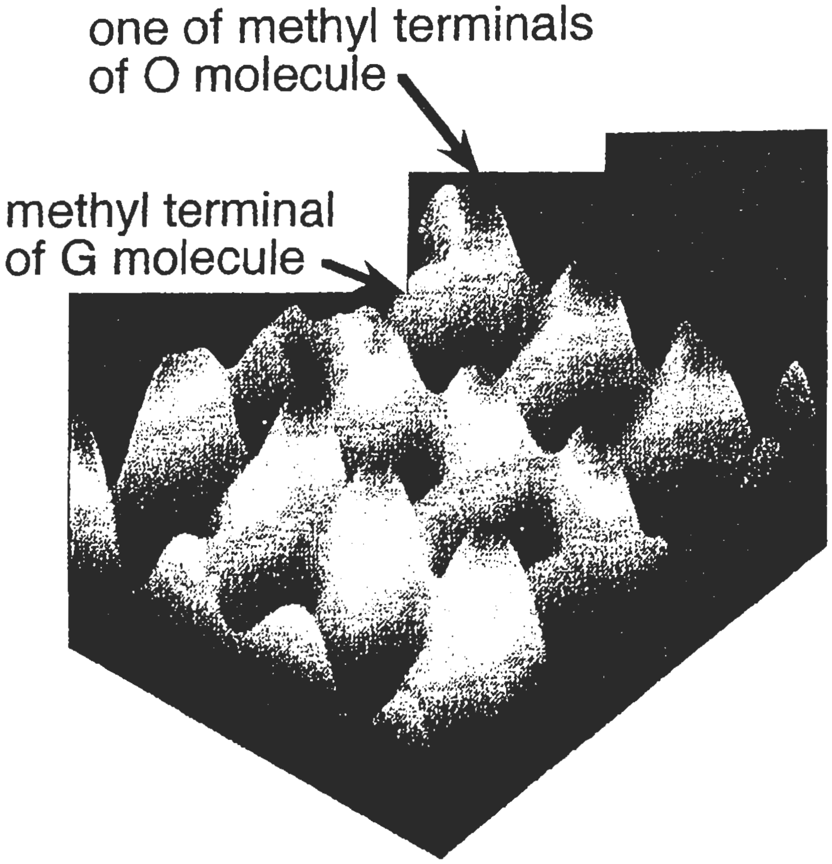

Fig.1 3D AFM image of alkyl chain terminal upon binding of FAD template

requirement is spatial matching of the neighboring molecular layers. We discuss below hydrogen bond-mediated molecular recognition at the air-water interface and its application to molecular patterning via multi-site recognition. The latter technique is a promising starting point to develop means to control arrangements of individual molecules in two dimension.

Formation of Molecular Patterns based on Multi-Site Recognition

Our past experience indicates that specific hydrogen bonding is efficiently formed between a variety of host-guest pairs. When multi-functional components—either host or guest—are used, it is possible to prepare specific supramolecular units in which component molecules—in either host or guest—are aligned in fixed arrangements at the interface.

Strong, specific binding between functional units in host and guest is essential for fixed molecular disposition within a mixed monolayer. Very strong binding constants (10^6-10^7 M^{-1}) were observed between a guanidinium monolayer and phosphate derivatives such as AMP or ATP.1) The interaction between guanidinium and carboxylate was similarly effective. We have demonstrated that multi-functional receptors composed of two monolayer components bind aqueous nucleotides via multi-site interaction. Flavin adenine dinucleotide (FAD) can bind three kinds of monolayer components specifically. This is a convenient system to test formation of molecular patterns. As a first step, we employed two-component monolayers of a guanidinium amphiphile and an orotate amphiphile against complementarily functionalized nucleotide derivatives. The required molecular resolution is achieved by atomic force microscopic observation of transferred films.

Figure 1 shows a three-dimensional AFM image of the G/O mixed monolayer on aqueous FAD.2) Within a scan area of 1.8 x 2.1

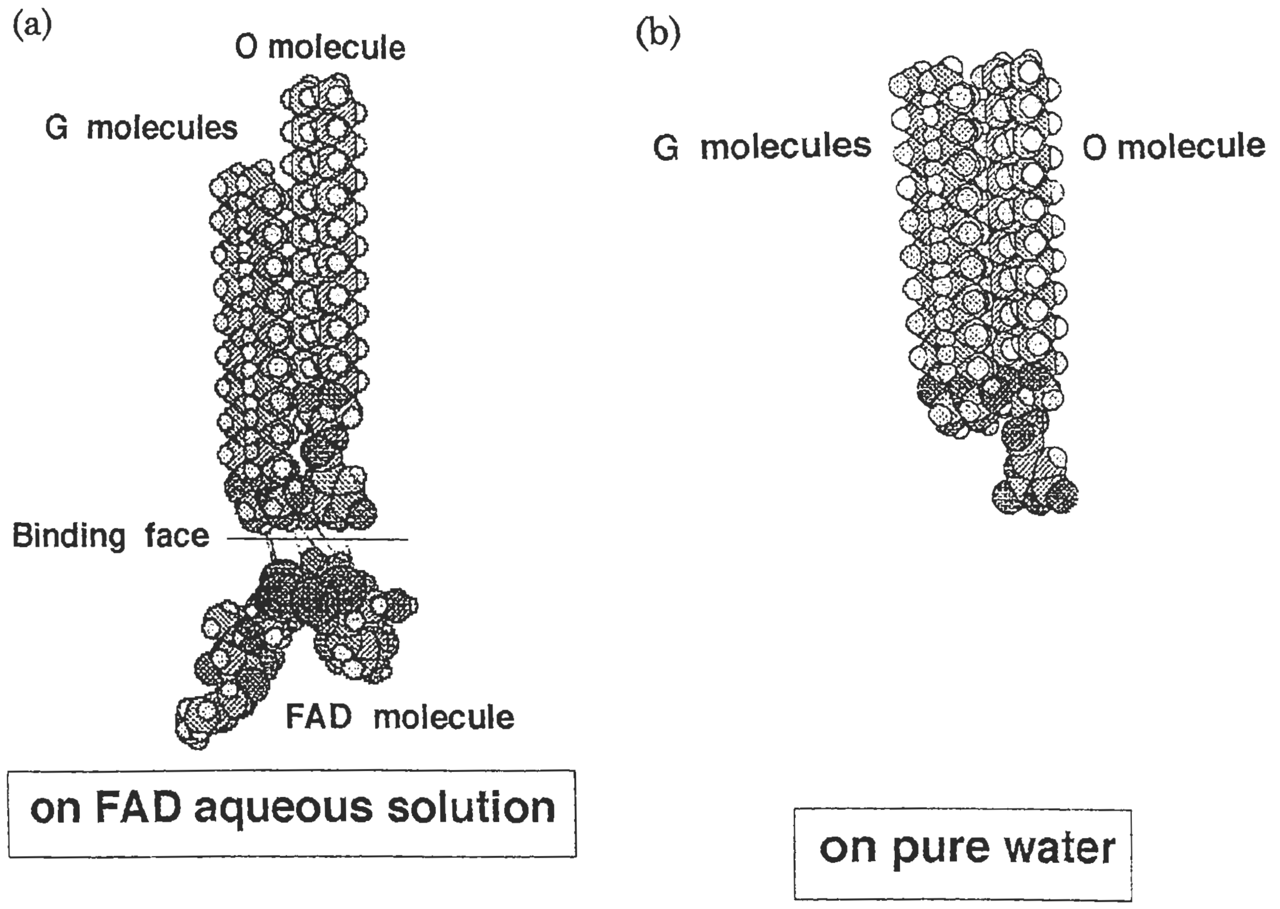

Fig.2 Spatial arrangement of monolayer components with and without FAD binding

nm^2, individual methyl terminals are clearly noticed, revealing that the higher terminal group of the G/O mixed monolayer is regularly aligned with a distorted hexagonal array. The AFM image displays a periodic wave-like structure composed of two different peaks, with height difference between the two peaks of several angstrom. The complementary binding of FAD with the mixed monolayer as illustrated in Figure 2a would cause the observed height difference between the two terminal CH_3 groups. Hence, the higher and lower peaks may be assigned to the O and G molecules, respectively. The regular arrangement of the methyl terminals of O molecule is seen as a molecular pattern in the mixed monolayer. On the other hand, the AFM image on pure water gives a periodic wave-like pattern composed of only one kind of peak corresponding to individual methyl terminals of G and O molecule, as shown in Figure 2b. They are regularly arranged in a hexagonal array, and the height of the terminal CH_3 group of the G and O component is unchanged, due to regular spatial alignment of the same C_{18} chains of the two components. The longer polar region of the O component would then be buried in the aqueous subphase deeper than the shorter guanidinium unit.

As another functional combination, we carried out an extensive investigation on the interaction of monolayers of alkyl-substituted melamines and aqueous barbiturates. Melamine monolayers with two active hydrogen bonding faces form linearly extended network of hydrogen bonding, as confirmed by equimolar incorporation of guest barbiturates, by AFM observation and by molecular dynamics calculation.3) The extended length of the hydrogen bond network is determined by size matching between host and guest, and a tetra-alkyl melamine cannot form extended hydrogen bonds. A monolayer of a tris-melamine amphiphile is apparently capable of formation of two-dimensionally extended network of hydrogen bonding. 4)

Towards 3D Molecular Materials with Nanometer Precision

Designed formation of nanometer-scale molecular patterns should provide exciting possibilities in supramolecular chemistry and in molecular-scale electronic devices. Several techniques that have been recently developed for two-dimensional patterning such as photolithography, laser manipulation and cantilever fabrication do not supply a molecular resolution. The molecular patterning technique as discussed above should be an effective tool for this purpose. Unique functional supermolecules may be assembled by using monolayer components that possess both of recognition and functional moieties.

Once designed disposition of molecular components is achieved in two dimension, the individual layer must be accumulated to produce three-dimensional materials. Various techniques have been developed for simple accumulation of molecular layers. The Langmuir-Blodgett method is a well-known method for sequential transfer of monomolecular layers from water surface. A serious disadvantage of this method is that the monolayer component usually contains alkyl chains that are detrimental for layer matching. Other, more recent techniques such as alternate adsorption and chemical overlayer formation may be more useful. For example, alternate adsorption and its modifications could be better qualified approaches for vertical inter-layer matching, since alkyl chains are not required for monolayer formation.5) Physical methods represented by chemical vapor deposition and the surface sol-gel process6) are also useful for preparation of ultrathin layers, but the design of 2-D molecular pattern is still almost impossible. Although we have various means to prepare monomolecular layers and can even control 2-D molecular arrangement in selected examples, functional matching of the neighboring monolayers remains an unsolved problem.

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