PHOTOCONTROL OF 2-DIMENSIONAL SELF-ASSEMBLY OF PHOTOCHROMIC DIARYLETHENE AT LIQUID/SOLID INTERFACE

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Supramolecular photochemistry at two-dimensional (2-D) surface or interface is attracting interest because surface functionalization becomes possible by assembling molecules with desired orientation at surface. The change of ordering of diarylethene has been studied by scanning tunneling microscopy (STM) upon in situ photoirradiation at a liquid/highly oriented pyrolytic graphite (HOPG) interface. As the first example, a diarylethene-pyrene-diarylethene triad was reported to show the photoinduced two-dimensional ordering change. The new arrangement was found to originate from the closed-closed isomers.[1]

Recently we have introduced cooperative model on 2-D assembly of a 2-thienyl-type diarylethene derivative 1 (Figure 1a). The open-ring isomer 1o, having an amide group, formed uniform stripe-patterned molecular ordering (Figure 1b). The concentration dependence of surface coverage showed abrupt increase at around 200 mM. Meanwhile, no ordering was observed for the closed-ring isomer 1c at various concentrations. We developed a cooperative self-assembly model on a 2-D surface on the basis of the Langmuir adsorption model incorporating two different equilibrium constants, the nucleation constant $K_n$ and the elongation constant $K_e$ (Figure 1c). The high cooperativity was found to be the origin of the experimentally observed abrupt change of surface coverage over concentration in a supernatant solution. By using high cooperative system, high sensitive photochemical control of the assembly becomes possible.[2] Mixed-induced assembly was also investigated.[3]

According to the above analysis, we have investigated the relationship between molecular structure and the mechanism of cooperative ordering formation. The concentration dependence of the fractional coverage of 1o...

Figure 1. (a) Molecular structure of diarylethene 1o and 1c. (b) High resolution STM image and molecular model of 1o ($a = 6.3 \pm 0.2$ nm, $b = 1.04 \pm 0.04$ nm, $\alpha = 88.6 \pm 0.9^\circ$). (c) Concentration dependence of the fractional coverage of 1o.
at which a stable 2D molecular ordering is observed by STM exponentially decreases with increasing length of the alkyl chain. Compounds bearing amide groups have higher degrees of cooperativity in self-assembly on 2D surfaces (i.e., $\sigma$, which is defined as $K_a/K_c$) than compounds with ester groups. The self-assembly process of the open-ring isomer of an ester derivative is close to isodesmic, whereas that of the closed-ring isomer is cooperative.$^{[4]}$

In the case of 2-thienyl-type DAE, ordering was observed only for the open-ring isomer, but no ordering was observed for the closed-ring isomer. However we found that both the open- and the closed-ring isomers of a 3-thienyl-type DAEs formed orderings and that the process of self-assembly on a 2-D surface was highly cooperative for both isomers. The difference in assembling behavior was analyzed by the concentration dependence of surface coverage and computational studies that includes MM/MD calculations.$^{[5]}$

The ordering of two photochromic diarylethenes closed-ring isomers was investigated using scanning tunneling microscopy at the liquid/graphite interface. The racemic mixture of the closed-ring isomer of one of the diarylethenes showed spontaneous separation of its enantiomers upon 2-D crystallization, whereas that of the other diarylene formed a pseudoracemic crystal in which two enantiomers coexist in a 2-D ordering domain. The mixing of enantiomers in 2-D assemblies was analyzed via the dependence of the surface coverage on the concentration of enantiomers at different enantiomeric ratios (Figure 2).$^{[6]}$

![Chemical structures](image)

**Figure 2.** Concentration dependence of the surface coverage of a) 2 and b) 3 at the octanoic acid-HOPG interface. c) Representation of the spontaneous separation of enantiomers observed for 2 and d) representation of the formation of a mixed crystal observed for 3.

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**References:**