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Chapter \$

Cooperative Self-Assembly of Photochromic Diarylethenes at Liquid/Solid Interface and Highly Sensitive Photoinduced Transformation of the Ordering

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Abstract: In this Chapter, self-assembly of photochromic diarylethene at liquid/solid interface and photoinduced transformation of the ordering are described. By the use of scanning tunneling microscopy, the process of assembly can be studied at the molecular resolution. By the measurement of concentration dependence of surface coverage and the introduction of cooperative adsorption model, the degree of cooperativity in the self-assembly process can be evaluated and the guiding principle for highly sensitive photoresponsive system can be obtained. It is demonstrated that the precise control of the self-assembly process on 2D surface becomes possible by the careful design of the molecular structure.

Key words: Photochromism; Diarylethene; Scanning Tunneling Microscopy; Self-Assembly; Cooperativity

\$1 Introduction

By the advances of technologies in fabrication and manipulation of nano-scale structure, handling of organic molecule has become possible recently. By making the devices from organic molecule, electroconductive and photophysical properties of single molecule can be utilized in the fields of molecular-scale electronics and photonics.[1-3] By the way, photochromic molecules, which show reversible photoinduced structural change, are considered as a promising candidate for molecular-scale switching device.[4] Among several photochromic molecules, diarylethene derivative show reversible photoinduced change of electronic structure

from the viewpoint of π -conjugation. Therefore, they are considered to work as a molecular-scale switch in molecular electronics.[5]

However, in order to use photochromic molecules practically in molecular electronics, assembly and arrangement of the molecules are very important. Therefore, it is very important to develop methodologies to align molecules on a two-dimensional surface. This chapter describes our recent achievements on the photo-control of the self-assembled ordering composed of photochromic diarylethenes at liquid/solid interface investigated by scanning tunneling microscopy (STM). This technique, originally developed by Rabe et al.,[6] is attracting interests because it can visualize the process of molecular assembly at the molecular resolution.

Two-dimensional crystal engineering at liquid/solid interfaces has attracted growing attention in the last decade.[7–11] To efficiently design and predict the formation of thermodynamically stable molecular ordering formed through self-assembly processes, interplays of various interactions, such as molecule–substrate interactions, intermolecular interaction,[12–15] solvent effects,[16–19] and the balance of enthalpy and entropy terms,[20–23] must be taken into account. The stimuli-responsive interface and the control of the phase transition is also attracting interest.[24,25] In this Chapter we will focus on the use of the cooperative self-assembly to design highly sensitive stimuli-responsive assembly.

§.2 Self-Assembly and Photoinduced Transformation of Molecular Ordering of Photochromic Diarylethenes at Liquid/Highly Oriented Pyrolytic Graphite (HOPG) Interface [26]

Diarylethene-pyrene diad **1** and diarylethene-pyrene-diarylethene triad **2** were synthesized to investigate the photoinduced two-dimensional ordering change at a solution/highly oriented pyrolytic graphite (HOPG) interface by STM. The long alkyl chain and pyrene were introduced into the diarylethene in order to stabilize the 2D structure. Pyrene interacts with HOPG due to extended planar π -conjugation. The alkyl chains are also effective at interacting with the HOPG substrate.

The different photochromic isomers showed different orderings reflecting the differences in their molecular structures. For the diarylethene-pyrene-diarylethene triad **2**, a new ordering appeared upon irradiation with UV light to the ordering of open-open isomer **2(o-o)** and returned to the original ordering upon subsequent irradiation with visible light at octanoic acid/HOPG interface (Fig. §.1). The new ordering was assigned to the ordering of the closed-closed isomer **2(c-c)** by comparing the image with the images of the isolated open-closed isomer **2(o-c)** and the closed-closed isomer **2(c-c)**.

Because the adlayer is a monomolecular layer, most of the molecules exist in the solution rather than at the interface. Therefore, most of the photochromic reac-

tions take place in the solution not at the interface. When the contents of the solution phase are thereby changed, adsorption and desorption processes exchange molecules between the interface and the solution. The UV irradiation should give both the open-closed isomer **2(o-c)** and the closed-closed isomer **2(c-c)**, but the ordering of **2(o-c)** was not observed. In order to examine the relative magnitudes of the adsorption process, we measured the STM image of the mixture with the ratio of o-o:o-c:c-c = 45:33:22. The image predominantly consisted of the closed-closed isomer **2(c-c)** ordering. This implies that **2(o-o)** and **2(o-c)** are less likely to be physisorbed on the HOPG surface than **2(c-c)**. The difference in the affinity to the substrate is thought to regulate the ordering behavior.

Fig. S.1. Sequence of STM images at the interface of octanoic acid-HOPG upon UV and visible irradiation of compound **1(o-o)** ($100 \times 100 \text{ nm}^2$, the same areas of the sample): (a) before UV irradiation, $I_{\text{set}} = 10 \text{ pA}$, $V_{\text{bias}} = -2.0 \text{ V}$; (b) after UV irradiation for 5 s ($I_{\text{set}} = 10 \text{ pA}$, $V_{\text{bias}} = -2.5 \text{ V}$); (c) after successive visible irradiation ($I_{\text{set}} = 10 \text{ pA}$, $V_{\text{bias}} = -2.5 \text{ V}$). Adapted with permission from [26]. Copyright 2008 American Chemical Society.

S.3 Self-Assembly and Photoinduced Transformation of Molecular Ordering of Diarylethenes Carrying Amide Group [27]

As a next step, we investigated diarylethene **3** carrying amide group that forms hydrogen bond. Diarylethene **3** having two amide groups formed characteristic stripe structures at the 1-octanoic acid/HOPG interface as expected (Fig. S.2), while no ordering was observed with compounds having ester group instead of amide group under the same condition. The result clearly suggests that amide

group acts as an interacting group to stabilize molecular ordering via intermolecular H-bonding network.

The width of the bright rows was 3.5 nm for **3o** (ordering α) and 1.5 nm for **3c** (ordering β), suggesting different ordering patterns for the two isomers. The difference in the arrangement would be attributed to the rigid core framework of the closed-ring isomer whose delocalized π -conjugation system prefers to form face-to-face π - π stacking assembly. Although the structural transformation from the ordering β to the ordering α was reasonably induced by in situ visible light irradiation, in situ UV irradiation resulted in an entirely different third ordering γ no matter whether initial ordering was α or β .

In order to reveal the origin of ordering γ , the annulated isomer **3a** was photochemically synthesized on a milligram scale by UV irradiation to a solution of **3o** overnight and subsequently isolated by HPLC. The ordering of **3a** was confirmed to be identical to the ordering γ that was observed after in situ UV irradiation. From these results, we concluded that the ordering γ is composed of the annulated isomer **3a**. The reason why the ordering β was not observed upon in situ UV irradiation is the strong preferential formation of ordering γ , which may be attributed to the rigid and highly symmetric structure of the annulated isomer. The control over three states was possible in this photochromic molecule.

Fig. S2. STM images of (a) the open-ring isomer **3o** (the ordering α , $I_{\text{set}} = 60$ pA, $V_{\text{bias}} = -1.0$ V, $a = 5.71$ nm, $b = 0.89$ nm, $\alpha = 88^\circ$), (b) the closed-ring isomer **3c** (the ordering β , $I_{\text{set}} = 20$ pA, $V_{\text{bias}} = -0.9$ V, $a = 4.82$ nm, $b = 0.56$ nm, $\alpha = 85^\circ$) at the 1-octanoic acid-HOPG interface. (c) The ordering after UV irradiation for 15 min (the ordering γ , $I_{\text{set}} = 30$ pA, $V_{\text{bias}} = -1.0$ V, $a = 10.2$ nm, $b = 0.48$ nm, $\alpha = 87^\circ$). (d) Enlarged molecular model of the open-ring isomer **3o** and (e) that of the closed-ring isomer **3c**. Hydrogen-bond network of amide groups is highlighted in green. Adapted with permission from [27]. Copyright 2013 The Chemical Society of Japan.

§.4 Cooperative Self-Assembly of 2-Thienyl-Type Diarylethene and Photoinduced Transformation of the Ordering [28]

In order to further develop photocontrollable assembly at liquid/solid interface, we have introduced cooperative model on the analysis of adsorption process of a 2-thienyl-type diarylethene derivative **4** (Fig. §.3). The open-ring isomer **4o**, having an amide group, formed uniform stripe-patterned molecular ordering. The ordering pattern was successfully reproduced by a molecular modeling study with the molecular mechanics/molecular dynamics (MM/MD) approach. It is revealed that a parallel conformer of the open-ring isomer is stabilized by intramolecular hydrogen bonding between the embedded two amide groups.

The concentration dependence of surface coverage showed abrupt increase at around 200 mM. Meanwhile, no ordering was observed for the closed-ring isomer **4c** at various concentrations. Inspired by the cooperative self-assembly in solution, we developed a cooperative self-assembly model on a 2D 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 (Fig. §.4).[29] The elongation constant K_e and the degree of cooperativity $\sigma = K_n/K_e$ were obtained as $4600 \pm 20 \text{ M}^{-1}$ and $(5 \pm 2) \times 10^{-4}$, respectively. The high cooperativity was found to be the origin of the experimentally observed abrupt change of surface coverage over concentration in a supernatant solution.

Fig. §.3. (a) STM image of the ordering of **4o** at the octanoic acid/HOPG interface ($c = 250 \text{ mM}$, $I_{\text{set}} = 30 \text{ pA}$, $V_{\text{bias}} = 800 \text{ mV}$, $a = 6.3 \pm 0.2 \text{ nm}$, $b = 1.04 \pm 0.04 \text{ nm}$, $\alpha = 88.6 \pm 0.91^\circ$). (b) Concentration dependence of the fractional coverage of **4o**. The solid line denotes the best-fit curve by the model simulation ($K_e = 4600 \pm 20 \text{ M}^{-1}$, $\sigma = (5 \pm 2) \times 10^{-4}$) and the dashed line denotes the simulated curve with an isodesmic model ($\sigma = 1$). Adapted with permission from [28]. Copyright 2014 The Royal Society of Chemistry.

This result suggests that reversible formation/disappearance of molecular ordering is possible by means of photoisomerization between **4o** and **4c**. We evalu-

ated the relationship between the surface coverage and conversion ratio of **4**. As expected, the surface coverage showed a rapid decrease at certain conversion ratio, at which the concentration of **4o** in a supernatant solution shows the abrupt change of the surface coverage. Interestingly, the critical concentration of **4o** observed from the photoirradiation experiment corresponds well to the simple dilution experiment, suggesting that the presence of the closed-ring isomer **4c** did not influence the ordering formation of **4o**. As a consequence, highly sensitive photo-control over the cooperative 2D ordering formation/disappearance process on the surface is possible.

Fig. S.4. Schematic drawing of cooperative self-assembly at a liquid/solid interface. K_n denotes nucleation equilibrium constant and K_e denotes elongation equilibrium constant.

S.5 Effects of Alkyl Chain Length and Hydrogen Bonds on the Cooperative Self-Assembly of 2-Thienyl-Type Diarylethene [30]

In the previous section, we have described the cooperative self-assembly of diarylethene molecules at liquid/solid interface. To investigate the relationship between molecular structure and the mechanism of cooperative ordering formation, we synthesized 2-thienyl-type diarylethenes **5o-Cn** (**5o-C16** is equivalent to **4o**) bearing various lengths of alkyl side chains linked via an amide group. The concentration dependence of the surface coverage was analyzed using a cooperative model for a 2D surface based on two characteristic parameters, nucleation equilibrium constant (K_n) and elongation equilibrium constant (K_e) (Fig. S.5).

As the length of the alkyl chain of diarylethene increased, the K_e value increased exponentially, although the pattern of molecular ordering did not change. This behavior resulted from enthalpy gain with increasing alkyl chain length, which was associated with the concentration dependence of micelle formation. For diarylethenes **6o-Cn**, in which amide groups at the root of the alkyl chain were replaced by ester groups, the cooperative parameter, σ , approached unity and the mechanism resembled an isodesmic process. This was likely to be due to the absence of hydrogen-bonding interactions for the ester derivative. In terms of the effect of core structure for the ester derivatives of **6o-C22** and **6c-C22**, the σ value of the closed-ring isomer **6c-C22** was significantly smaller than that of the opening isomer **6o-C22**, but the K_e values were similar. This suggests that K_e values of diarylethenes **6o-C22** and **6c-C22** are regulated by dispersion interactions between the alkyl chain and HOPG substrate, irrespective of the core structure; on the other

hand, K_n was significantly affected by the core structure. The energy gain for nucleation on substrates for the closed-ring isomer **6c-C22** was lower than that of the open-ring isomer **6o-C22**, which gave rise to a large difference in cooperative self-assembly on the HOPG surface.

In conclusion of this section, it is demonstrated that the precise control of self-assembly process on 2D surface becomes possible by the careful design of the molecular structure.

Fig. S.5. Concentration dependence of surface coverage of the amide derivatives **5o-C14** (circle), **5o-C16** (square), **5o-C18** (upward-pointing triangle), **5o-C20** (downward-pointing triangle), and **5o-C22** (diamond) at the octanoic acid/HOPG interface. Solid lines denote the curves of best-fit by the cooperative equilibrium model. The dashed line denotes the curve based on theoretical maximum for a monolayer. Adapted with permission from [30]. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

S.6 Cocrystallization and Mixing-Induced Cooperativity [31]

The adsorption behavior of amide-containing diarylethene **3** was revisited by using cooperative adsorption model. The nucleation (K_n) and elongation (K_e) equilibrium constants were determined by the analysis of concentration dependence of surface coverage. It was found that the annulated isomer has a very large equilibrium constant, which explains the predominantly observed ordering of the annulated isomer (Fig. S.6a).

The effect of the presence of **3o** on the formation of ordering β is seen in Fig. S.6b, where surface coverage of ordering β is plotted against the concentration of **3c**. If the formation of ordering β is independent of the presence of the open-ring isomer **3o**, the same concentration dependence is expected for any ratio of isomers (**3o/3c**). However, at a given concentration of **3c**, the surface coverage of ordering β is significantly increased by addition of **3o**. This suggests that the ordering β is likely a mixed crystal composed of the two isomers.

Upon mixing the closed-ring isomer **3c** to ordering α that is mainly composed of the open-ring isomer **3o**, a steep rise emerged in the concentration dependence of surface coverage (Fig. S.6c). The prominent increase of the cooperativity was observed. It is suggested that the presence of **3c** induces cooperativity into the formation process of molecular ordering composed of **3o**. A quantitative analysis of the formation process of ordering using the cooperative model has provided a new view of the formation of 2D multicomponent molecular ordering.

Fig. S.6. (a) Concentration dependence of the surface coverage of **3o**, **3c**, and **3a** at the octanoic acid/HOPG interface. Concentration dependence of the surface coverage of (b) ordering β for **3c** and mixtures of **3o/3c** (37:63 and 51:49) and of (c) ordering α for **3o** and amixture of **3o/3c** (78:22). Adapted with permission from [31]. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

Conclusion

We have demonstrated the quantitative study of self-assembly process of photochromic diarylethene at liquid/solid interface by scanning tunneling microscopy. By the measurement of the concentration dependence of the surface coverage and the introduction of cooperative adsorption model, the degree of cooperativity of self-assembly process can be evaluated and the guiding principle for highly sensitive photoresponsive system can be obtained. These results provided a significant amount of information on the self-assembly of photochromic molecules for the application to molecular-scale electronics and photonics.

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