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COMMUNICATION

Phototriggered Formation and Disappearance of Surface-Confined Self-assembly Composed of Photochromic 2-Thienyl-Type Diarylethene: A Cooperative Model at the Liquid/Solid interface

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A photoresponsive self-assembly on 2-D surface was investigated by scanning tunnelling microscopy (STM). The open-ring isomer of a diarylethene derivative showed an abrupt ordering formation at a critical concentration, which was successfully reproduced by a cooperative model based on Langmuir-type adsorption.

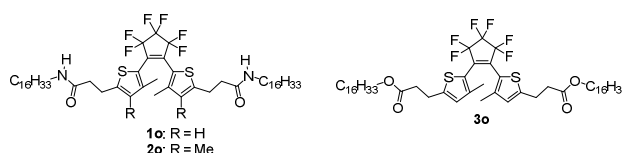
Self-assembly of surface-confined molecules is a powerful approach to construct a functional 2-dimensional (2-D) surface because the ordering pattern and molecular component are fine-tunable at the single-molecule level by rational molecular design.^{1,2} Molecular ordering of photochromic compounds has been attracting much attention because photoisomerization reaction switches molecular properties of the building blocks without adding any chemical additives, which is a potential candidate for photoresponsive functional surface.³⁻⁵

Here, we report STM images of 2-thienyl-type diarylethene derivative at the liquid/highly oriented pyrolytic graphite (HOPG) interface. In addition, we developed a cooperative self-assembly model on 2-D surface on the basis of the Langmuir adsorption model incorporating two different equilibrium constants, nucleation constant K_n and elongation constant K_e . This model successfully reproduced experimentally-observed abrupt change of surface coverage over concentration in a supernatant solution.

The noncovalent interactions, such as hydrogen bonding, dipole-dipole, and van der Waals interactions, play a determining role in self-assembly process on a substrate. From this viewpoint, molecular design is of importance to regulate the ordering formation of functional molecules on 2-D surface. Diarylethenes are a widely used photochromic compound that has excellent properties of fatigue resistance and thermal stability.^{6,7} In this study, we focused on 2-thienyl-type diarylethene (Scheme 1).

Long alkyl side chain have been widely used to make an interfacial interaction with graphite substrate by means of van der Waals

interaction. Furthermore we introduced amide group that stabilizes molecular ordering by means of hydrogen bonding network on



Scheme 1. Chemical structure of 2-thienyl-type diarylethene derivatives.

surface.⁸⁻¹⁰ To give flexibility, ethylene spacer was introduced as a bridge between photochromic core and amide groups. In order to investigate the effect of the amide group which was introduced in compounds **1** and **2**, the ester derivative **3** was also investigated.

2-thienyl-type diarylethene derivatives **1-3** were synthesized and the structure was confirmed by NMR spectroscopy and MS spectrometry.¹¹ Compound **1** showed a good photochromic property in dichloromethane and octanoic acid which was used as a solvent for STM measurements (Fig. S1). Compound **1a** having amide group formed uniform stripe-patterned molecular ordering at the octanoic acid/HOPG interface (Fig. 1). In contrast, either **2a** or **3a** showed no ordering under the same condition with **1a**, suggesting that (i) methyl group on the bottom of diarylethene core disturbs ordering formation on surface and (ii) hydrogen bonding network of amide groups is important to stabilize molecular ordering as described in our previous report.¹² The average domain size of the ordering of **1a** was larger than $1 \mu\text{m}^2$ which was measurement limit of used STM scanner. Since the domain size is determined by the ratio of the growth rate to the nucleation rate, the large domain size of **1a** implies a rapid growing process with respect to the slow nucleation rate.¹³

By a careful inspection of STM image of the ordering of **1a**, the molecular arrangement was clearly determined. Fig. 1b reveals that a bright spot which corresponds to diarylethene core¹⁴ has two alkyl chains extending in the same direction, which indicates the parallel conformation⁷ of **1a** at the octanoic acid/HOPG interface. The ordering

pattern were well reproduced by a molecular modeling study with molecular mechanics/molecular dynamics (MM/MD) approach. It is

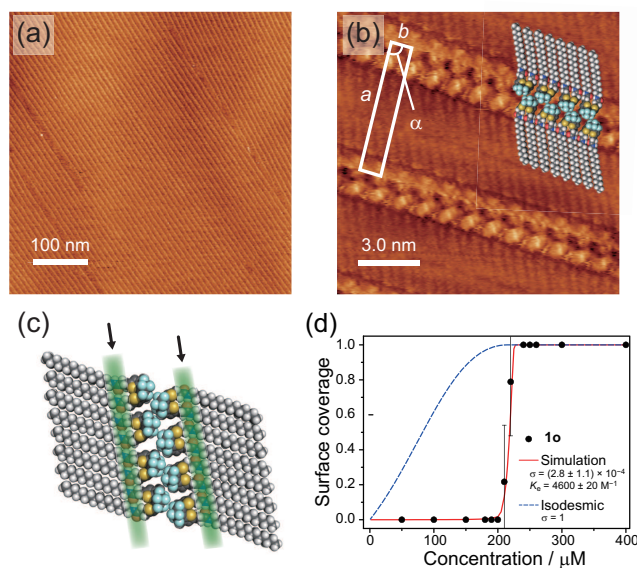


Fig. 1 (a) STM image of the ordering of **1o** at the octanoic acid/HOPG interface ($c = 250 \mu\text{M}$, $I_{\text{set}} = 30 \text{ pA}$, $V_{\text{bias}} = 800 \text{ mV}$). (b) High resolution image and molecular model of **1o** ($a = 6.3 \pm 0.2 \text{ nm}$, $b = 1.04 \pm 0.04 \text{ nm}$, $\alpha = 88.6 \pm 0.9^\circ$). (c) Enlarged molecular model of **1o**. Hydrogen-bond network of amide groups is highlighted in green. (d) Concentration dependence of the fractional coverage of **1o**. Solid red line denotes the best-fit curve by the model simulation ($K_e = 4600 \pm 20 \text{ M}^{-1}$, $\sigma = (2.8 \pm 1.1) \times 10^{-4}$) and dashed blue line denotes the simulated curve with isodesmic model ($\sigma = 1$). Histogram of the surface coverage at 220 μM and 230 μM was shown in Fig. S4.

revealed that a parallel conformer of the open-ring isomer is stabilized by intramolecular hydrogen bonding between the embedded two amide groups. Furthermore, two of the parallel conformers of **1o** arranged in head-to-head orientation that forms striped lamella arrangement linked via two intermolecular hydrogen bonding networks (Fig. 1c). Both width of lamella layers ($a = 6.3 \pm 0.2 \text{ nm}$) and intermolecular distance ($b = 1.04 \pm 0.04 \text{ nm}$) observed from lattice parameters were well reproduced by the molecular model.

No ordering was observed when the concentration was less than 200 μM , while the complete coverage was observed at the concentration larger than 240 μM (Fig. 1d). The stripe-patterned ordering was thermodynamically stable and no polymorph, such as a porous ordering or an ordering composed of anti-parallel conformation of **1o**, was observed at the all concentration conditions.^{15,16} In the concentration range from 200 to 240 μM , large distribution in fractional coverage was observed at different areas of substrate as manifested by the long error bars in Fig. 1d. It was usually observed that one graphite terrace was completely covered by the ordering but there is no ordering in another terrace in a STM scan, which is consistent with the large domain size of the ordering of **1o** (Fig. S3). Another important finding is that the average domain size significantly decreased when the concentration became larger than 700 μM (Fig. S5–7). It is noteworthy that there is a linear relationship between the sample concentration and the reciprocal of the average domain size. This result insists that the average domain size would be strongly related to the number of nucleus on surface at the beginning of ordering formation; the rate of nucleation

should be proportional to the sample concentration hence large number of domains generate at a high concentration.

Simulation of the ordering formation process is of great importance to understand the mechanism, which gives a rational strategy for crystal engineering on 2-D surface.¹⁷ To obtain more detailed insight into the concentration dependence of fractional coverage, an equilibrium model at the liquid/solid interface was developed in this study. The model is based on Langmuir-type adsorption which considers active sites on surface where adsorbate can interact. Although conventional Langmuir model takes into account no interaction between adsorbates, the model developed in this study considers intermolecular interaction between neighboring molecules on substrate by introduced two ordering formation processes having different equilibrium constants of nucleation, K_n , and elongation, K_e , which was inspired from the cooperative self-assembly in solution.^{18–20} The mass balance at a liquid/substrate interface and fractional coverage on substrate θ are given by

$$c_t = c_{\text{sol}} + \frac{(1 - \theta) A_{\text{sub}}}{LN_A} \frac{\sigma K_e [A^{\text{sol}}]}{(1 - K_e [A^{\text{sol}}])^2} \quad (1)$$

$$\theta = (1 - \theta) \frac{\sigma K_e c_{\text{sol}}}{(1 - K_e c_{\text{sol}})^2} \quad (2)$$

where c_t and c_{sol} are total concentration and concentration in supernatant solution, A_{sub} is total area of substrate, L is volume of supernatant solution, N_A is the Avogadro constant, S is the unit area occupied by one molecule on substrate, and σ is degree of cooperativity defined as the ratio of K_n/K_e which is smaller than unity for a cooperative process.¹¹ Combining eqns (1) and (2) yields eqn (3):

$$\theta = (1 - \theta) \frac{\sigma K_e (c_t - \alpha \theta)}{\{1 - K_e (c_t - \alpha \theta)\}^2}, \quad \text{where } \alpha = \frac{A_{\text{sub}}}{L \cdot N_A \cdot S} \quad (3)$$

Since the values of A_{sub} , L , and S were experimentally determined, the α was treated as a constant in the model simulation. The experimental data was well reproduced by a non-linear regression analysis in which c_t and θ were predictor variables, and K_e and σ were response variables (Fig. 1d).²¹ The characteristic two values were observed from the model simulation; the elongation constant $K_e = 4600 \pm 20 \text{ M}^{-1}$ and the degree of cooperativity $\sigma = (2.8 \pm 1.1) \times 10^{-4}$ for the ordering formation of **1o**. The large degree of cooperativity characterized by the observed small σ value would be attributed to the formation of hydrogen bonding network via amide groups in the molecular ordering of **1o**.²²

In situ photoirradiation enables external control over concentration of molecular components by means of photoisomerization between two isomers. In order to observe the molecular ordering of the photogenerated isomer upon UV irradiation, STM measurement was carried out with the closed-ring isomer **1c** after isolation by column chromatography. In contrast to the open-ring isomer, no ordering of **1c** was observed at various concentrations ranging from 100 to 1000 μM (Fig. S8), which is plausibly due to the large geometrical change between the parallel conformation of **1o** and **1c**. This result suggests that reversible formation/disappearance of molecular ordering is possible by means of photoisomerization between **1o** and **1c**, which was indeed observed by in situ photoirradiation cycles (Fig. 2a, Fig. S10).

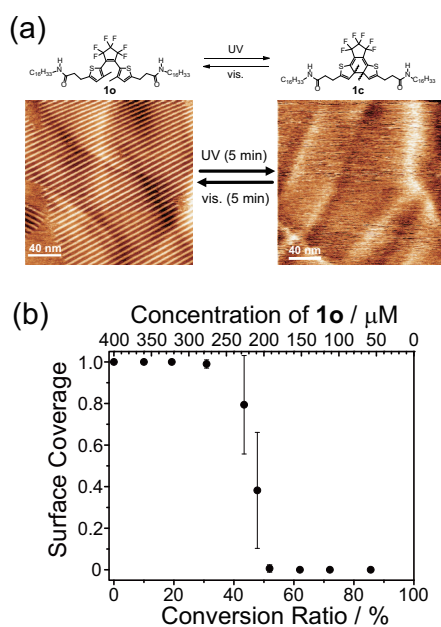


Fig. 2 (a) Reversible ordering formation/disappearance of **1** upon in situ photoirradiation at the octanoic acid/HOPG interface ($c = 500 \mu\text{M}$, $I_{\text{set}} = 30 \text{ pA}$, $V_{\text{bias}} = 800 \text{ mV}$). (b) The plot of surface coverage over the conversion ratio of sample solution ($c = 400 \mu\text{M}$). Photoirradiation was performed ex situ. The upper axis shows concentration of **1o** obtained from the conversion ratio.

To validate this concept more clearly, we evaluated the relationship between surface coverage and conversion ratio of **1** at the octanoic acid/HOPG interface (Fig. 2b). The sample concentration was set at $400 \mu\text{M}$. As expected, surface coverage showed rapid decrease when the conversion ratio was $\sim 50\%$ at which the concentration of **1o** in supernatant solution became the critical concentration ($\sim 200 \mu\text{M}$). Interestingly, the critical concentration of **1o** observed from the photoirradiation experiment was well corresponds to the simple dilution experiment shown in Fig. 1d, suggesting that the presence of the closed-ring isomer **1c** did not influence on the ordering formation of **1o**. As a consequence, the fine photocontrol over the cooperative 2-D ordering formation/disappearance process on surface is possible.

In conclusion, our STM results revealed that a 2-thienyl-type diarylethene derivative forms uniform stripe-patterned ordering at the octanoic acid/HOPG interface, which is photoresponsive due to preferable ordering formation of the open-ring isomer and no ordering formation of the closed-ring isomer. Concentration dependence of fractional coverage suggests a cooperative aggregation on surface, which was well reproduced by the 2-D ordering formation model based on Langmuir-type adsorption that was developed in this study. This modeling approach enables quantitative evaluation of critical concentration at which molecular ordering start to be observed and the degree of cooperativity in the ordering formation process on surface. The relationship between chemical structure of molecular component and cooperative parameter is now under investigation in our group.

This work was supported by NEXT program (no. GR062) from JSPS, Japan. This work was also supported by a Grant-in-Aid for Young Scientists (B) (no. 25810048).

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†Electronic Supplementary Information (ESI) available: Experimental procedures, additional STM images, details of the model simulation. See DOI: 10.1039/c000000x/

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