

Cooperativity Analysis of the Open-, Closed- and Annulated-Isomers of Diarylethene that form 2-D Ordering at the Liquid/Solid Interface and their Photochemical Interchanges

(Kyoto Univ.) FRATH, Denis; SAKANO, Takeshi; IMAIZUMI, Yohei, YOKOYAMA, Soichi; HIROSE, Takeshi; MATSUDA, Kenji;

[Introduction] The controlled formation of self-assembled monolayer (SAM) by a strategic molecular design is a powerful approach to construct functional two dimensional (2-D) surfaces.^[1,2] We recently reported 2-D orderings of photochromic diarylethenes stabilized by hydrogen bond networks at the 1-octanoic acid/Highly Oriented Pyrolytic Graphite (HOPG) interface.^[3,4] A specific ordering was observed by Scanning Tunneling Microscopy (STM) for each of the Open-, Closed- and Annulated-Isomers of diarylethene **1** (Figure 1). Changes that occur when irradiating light on these photoresponsive monolayers were also investigated.^[4] Surprisingly, only ordering γ , formed by compound **1a**, was observed even if the annulated-isomer is supposed to be a byproduct of the photoreaction induced by irradiation with UV light.^[5,6] Ordering β , formed by the main photoproduct **1c**, was never observed after irradiating the surface.

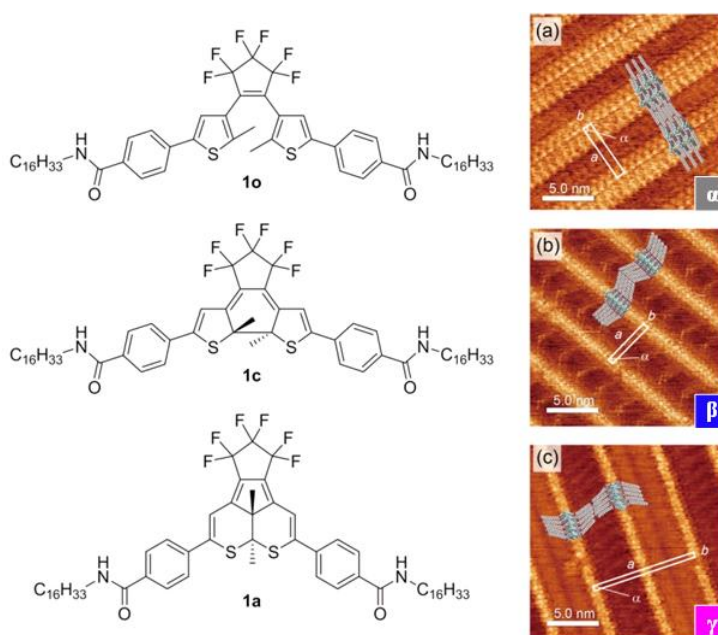


Figure 1. Open-, Closed-, and Annulated-isomers of diarylethene **1**: STM images of (a) open-isomer **1o** (b) closed-isomer **1c** (c) annulated-isomer **1a** at the 1-octanoic acid/HOPG interface

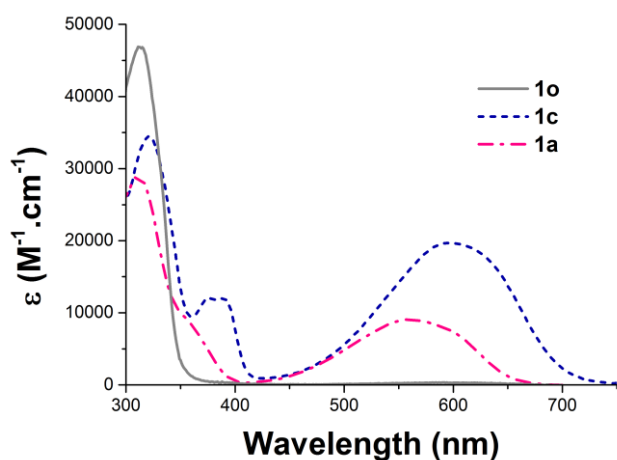


Figure 2. Absorption spectra for compounds **1o**, **1c** and **1a**

[Experimental] In order to understand the mechanisms controlling the photochemical interchanges between the different orderings, as well as the favorable appearance of ordering γ , several experiments were conducted. UV-vis. spectroscopy was used to determine the molar absorption coefficients of each isomer (Figure 2) and to monitor the evolution of a solution of open-isomer **1o** upon irradiation with UV light (Figure 3). The concentration dependence of the ordering-covered fraction of the surface was probed by STM (Figure 4).

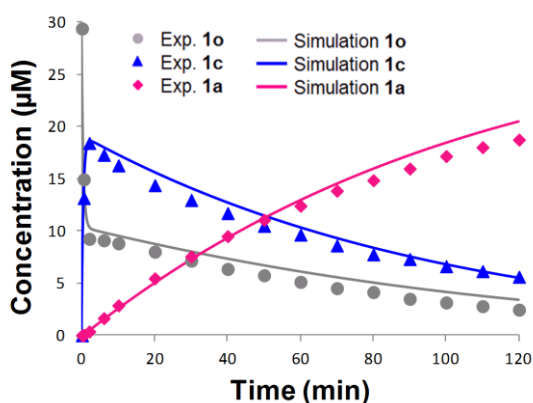


Figure 3. Evolution of the composition of the solution upon irradiation with UV light ($\lambda=365\text{nm}$).

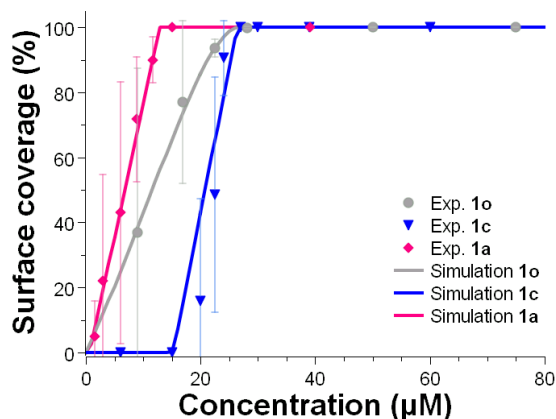


Figure 4. Concentration dependence of the HOPG surface coverage for compound **1o**, **1c** and **1a**

[Results and Discussion] The experimental data obtained for the evolution in solution (Figure 3) were used to estimate the ratio between the photoreaction quantum yields (Φ). The ratio $\Phi_{o \rightarrow c} : \Phi_{c \rightarrow o} : \Phi_{c \rightarrow a}$ was calculated to be 1 : 0.054 : 0.00079. Inspired by the concept of cooperative supramolecular polymerization in solution,^[7,8] a similar process at the liquid/solid interface was considered. A model based on Langmuir-type adsorption has been developed and proved its efficiency to simulate the cooperative formation of diarylethenes SAM.^[3] It was applied to the surface coverage of the Open-, Closed- and Annulated-Isomers (Figure 4). We established that compound **1c** presents a cooperative behavior whereas compound **1o** is not cooperative. The equilibrium constant associated with the growth of **1o** ordering ($K = 6.7 \cdot 10^4 \text{ M}^{-1}$) and **1c** ordering ($K = 6.5 \cdot 10^4 \text{ M}^{-1}$) are higher than values reported previously ($K = 4.6 \cdot 10^3 \text{ M}^{-1}$).^[3] Moreover the equilibrium constant of compound **1a** is even higher by almost two orders of magnitude ($K > 10^6 \text{ M}^{-1}$). The critical **1c** concentration required to observe a full coverage by ordering β is about 27 μM . On the other hand HOPG is completely covered by **1a** at a lower concentration ($\sim 13 \mu\text{M}$) which is probably the main reason for the favorable appearance of ordering γ upon irradiation. By combining the results obtained for photoreaction quantum yields and for surface coverage, we have developed a model that simulates the time-resolved evolution of orderings fractional coverage depending of the initial concentration. We are currently using this tool to optimize the conditions to achieve controlled reversible photochemical interchanges at the liquid/solid interface. To conclude, we have demonstrated that a strategic molecular design, introducing supramolecular interactions, enables the formation of very stable SAM with photoreactive properties. This work highlights the great potential of diarylethenes as efficient organic building blocks for the elaboration of functionalized surfaces.

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