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Photoresponsive supramolecular self-assemblies at the liquid/solid interface

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Abstract: Control over molecular nanostructure is of the utmost importance in bottom-up strategies to create functionalized surfaces for electronic devices and advanced materials. In this context, the study of two-dimensional self-assembled structures consisting of organic molecules on surfaces using scanning tunneling microscopy (STM) has been the subject of intensive research. The formation of stimuli-responsive assemblies, especially photoresponsive ones, on surfaces is attracting interest. Meanwhile, assemblies formed at the liquid/solid interface have been extensively studied using STM from a supramolecular chemistry perspective in order to understand the assembly process of the molecules from the solution phase to the substrate interface. In this review, an overview of advances in photoresponsive supramolecular self-assemblies formed at the liquid/solid interface is given. Recent progress in the analysis of the adsorption process using the nucleation–elongation model of two-dimensional self-assembly will be featured and discussed in the context of photochemical control of the assembly.

1. Introduction

Surface-adsorbed molecular layers can be constructed by self-assembly. Scanning tunneling microscopy (STM), which was developed by Binnig, Rohrer, and co-workers, provides useful insights into the structure, properties, and dynamics of the assembly with submolecular resolution [1]. STM measurements can be performed on metal surfaces under ultra-high vacuum conditions, at the solid/gas interface, or at the liquid/solid interface. In assemblies formed at the liquid/solid interface, molecules are constantly exchanged between the substrate interface and the supernatant solution phase. Therefore, STM measurements at the liquid/solid interface, which were first developed by Rabe and co-workers, can provide information on the process of two-dimensional (2D) self-assembly, or in other words, 2D crystallization [2]. Thus, supramolecular chemistry at the liquid/solid interface has been extensively studied by using STM. The main fields of interest are chirality, polymorphism, guest inclusion, as well as responsiveness to stimuli, such as light, electric fields/pulses, and temperature [3-30]. In particular, the photochemical control of the assembly of structures at liquid/solid interfaces has recently attracted interest. In this review, we will provide an overview of photochemically controlled surface-adsorbed molecular layers that have been studied using STM, focusing on photoresponsive supramolecular self-assemblies at the liquid/solid interface.

2. Photochemical modification of molecular assemblies studied by STM

Light is a typical stimulus that can be used in a non-invasive manner, without requiring additives that could disturb the system. The photochemical reaction of the molecules constituting the assembly can manipulate the whole assembly. By controlling the wavelength and polarization of the irradiation light, it is possible to selectively excite specific molecules. In particular, the use of photochromic compounds, which undergo reversible isomerization, enables reversible control of the assembly. Photoswitching of the properties of photochromic molecules or molecular assemblies has attracted great interest [31-34].

The photopolymerization of diacetylene on surfaces has been studied extensively since the 1990s [35-39]. De Schryver and co-workers reported the photopolymerization of diacetylene molecules assembled at the undecanol/HOPG interface [35]. The molecular packing at the interface was favorable for the photopolymerization of diacetylene. Recently, Zimmt and co-workers reported the polymerization reaction of tetra-diacetylenes with careful control of the molecular packing at the phenyloctane/HOPG interface [38]. It is also worth mentioning that tip-induced polymerization of diacetylenes using STM was reported by Aono and co-workers [40-42].

The photoresponse of photochromic molecules has been studied under ultra-high vacuum conditions [43-49]. The group of Hecht and Grill and the group of Crommie reported the switching of individual molecules of azobenzene derivatives [45-47]. Moreover, Hecht, Grill, and co-workers reported the switching behavior of (4-methoxy-3,3',5,5'-tetra-*tert*-butylazobenzene) on Au(111) under ultra-high vacuum conditions. The formation of a periodic pattern of *cis* isomers was observed after applying a voltage pulse (Fig. 1) [47].

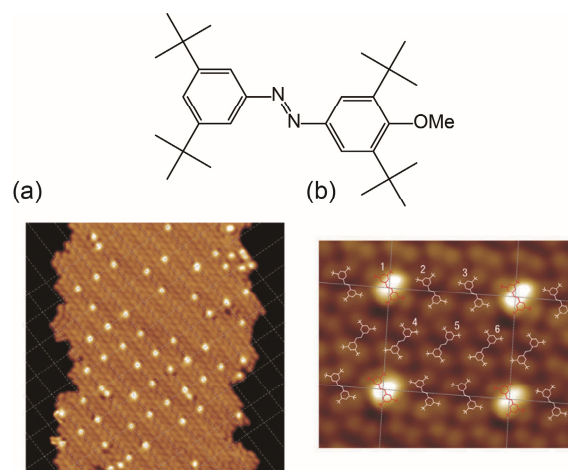


Fig. 1. Structure of an azobenzene derivative, and STM images after switching many molecules to the *cis* state by scanning at a sufficiently elevated bias voltage. The *cis* isomers are arranged in a periodic pattern, forming a lattice. (a) STM image and (b) unit cell of the *cis* isomers. Reprinted with permission from reference 47. Copyright 2008 Macmillan Publishers Ltd.

Several groups have reported the observation of different appearance in the STM image for

the different isomers of photochromic compounds [50-62]. The apparent height in the STM image provides information on both molecular length and conductance; therefore, data regarding the photoswitching of molecular conductance can be obtained. Conductivity characteristics have also been investigated by the measurement of I - V curves. Feringa and co-workers reported the observation of photoswitching in STM images associated with the photochromic reaction of a diarylethene molecule. The closed-ring isomer of diarylethene was demonstrated to have higher conductance than the open-ring isomer [53,60].

Samori and co-workers reported surface modification using photoresponsive azobenzene [56,57,59]. The molecules of the azobenzene derivative 4'-(biphenyl-4-ylazo)-biphenyl-4-thiol were grafted on a Au surface, and its photochemical response was studied [56]. Switching of the entire 2D crystal domain was observed, suggesting a cooperative process (Fig. 2). Additionally, not only light-induced switching, but also tip-induced switching, is possible. The tip-induced switching of thiolated diarylethene assembled on a Au(111) surface was reported by Snegir and co-workers [61,62].

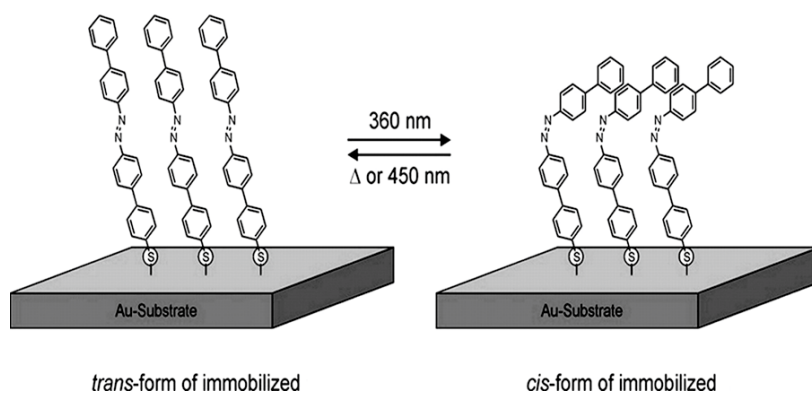


Fig. 2. Schematic drawing of the cooperative switching of a small domain of 4'-(biphenyl-4-ylazo)-biphenyl-4-thiol immobilized on a Au surface. Intermolecular interactions between adjacent molecules stabilize the packing of domains consisting exclusively of *trans* isomers, as well as the packing of domains consisting exclusively of *cis* isomers. Reprinted with permission from reference 56. Copyright 2007 National Academy of Sciences of the USA.

In systems under ultra-high vacuum and at air/solid interfaces, the molecules are immobilized on the surface, and therefore the stability of these materials is high. On the other hand, in the case of liquid/solid interfaces, molecules are exchanged between the substrate interface and the supernatant solution phase. Therefore, STM at the liquid/solid interface provides a suitable platform to investigate their 2D self-assembly processes.

3. Supramolecular control of molecular assemblies formed at the liquid/solid interface

Among several platforms for measuring STM, liquid/solid interface is particularly interesting because exchange occurs between the molecules at the interface and in solution. Therefore, the 2D self-assembly process can be studied quantitatively from a supramolecular chemistry perspective [63-82]. Molecular assemblies at the liquid/solid interface have been studied in terms of chirality, polymorphism, guest inclusion, etc.

Responses to various stimuli, including not only light, but also electric fields/pulses, temperature, etc., have also been studied at the liquid/solid interface. The reorganization induced by an external stimulus can lead to dramatic changes in the adsorbed monolayer.

Tobe, De Feyter, Tahara, and co-workers demonstrated that the 2D chiral honeycomb arrangement of alkoxyated dehydrobenzo[12]annulene derivatives can be controlled by molecular recognition and thermodynamic control. Chiral induction by dehydrobenzoannulene with a chiral side chain was demonstrated [72]. Moreover, careful investigation of the assembly process revealed the effects of temperature and concentration in inducing the reversal of the chirality upon heating [82].

Wan and co-workers reported that the structure of an assembly of bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine) was converted from lamellar to hexagonal by the thermal-annealing process [63]. Additionally, they reported that the application of a mild electric field induced the formation of bilayer structure of

1,3,6,8-tetrakis(1-butyl-1*H*-1,2,3-triazol-4-yl)pyrene molecules on top of a trimesic acid network [76].

4. Photoresponsive molecular assemblies formed at the liquid/solid interface

4.1. Design of photoresponsive molecular assemblies

Because the liquid/solid interface is an ideal platform to study 2D supramolecular chemistry, the photoresponsive behavior of molecular assemblies composed of photochromic compounds at the liquid/solid interface has recently attracted interest. Although strong quenching of photoreactions is usually observed on metal surfaces [83], some photoreactions have been reported to occur on HOPG [95].

Upon irradiation, photochemical reactions can change the concentration of the solute in the solution and induce changes in the assembly formed at the liquid/solid interface. The ordering transformation occurs by the exchange of molecules between the interface and the solution; thus, understanding of the process of 2D self-assembly is important to control the photoinduced ordering transformation (Fig. 3). The adsorbabilities of different molecules on a substrate are different, and quantitative characterization of the adsorption process is important. A large variety of patterns have been reported: single rows, double rows, rosettes, porous networks, honeycombs, etc. The ordering formation at the interface can be regarded as 2D crystallization; thus, the pattern is determined by the molecular structure of the components.

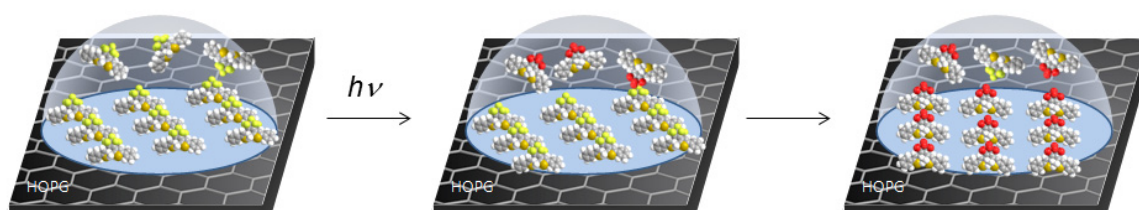


Fig. 3. Schematic drawing of a phototriggered ordering transformation at the liquid/solid interface.

The central point in the design of an efficient photoresponsive monolayer at the liquid/solid

interface lies in the choice of the photochromic units. To date, existing systems have been based on the photodecomposition of diazoanthrone [84] or the photoisomerization of thioindigo [85], anthracene dimer [86], azobenzene [87–95], stilbene [94,96], diarylethene [97–104], or terthiophene [105] (Fig. 4).

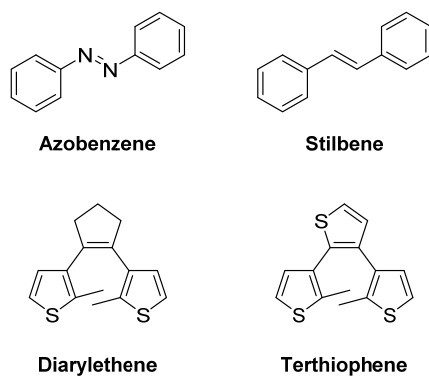


Fig. 4. General chemical structures of photochromic units used in the design of photoresponsive monolayers.

The majority of the systems that have been studied to date have been based on the azobenzene photochromic unit. Azobenzene compounds are well known to undergo photoisomerization between *cis* and *trans* isomers. The same behavior is observed for stilbene derivatives. However, stilbene can also undergo a [2+2] photodimerization that leads to the formation of a substituted cyclobutane [96]. The isomerization from the *trans* to the *cis* form can be induced by UV light irradiation. The opposite isomerization occurs via visible light irradiation. Thermal treatment also induces *cis* to *trans* isomerization. The major drawback of azobenzene and stilbene is the small difference between the absorption spectra of their two isomers, which makes selective irradiation difficult. Consequently, *trans*-to-*cis* and *cis*-to-*trans* isomerization usually occur concomitantly upon irradiation.

Diarylethene and terthiophene are a different type of photochromic unit, which usually undergo an electrocyclic reaction between the open- and closed-ring isomers. Selective irradiation of each isomer is usually possible due to the greater differences in their absorption compared to *trans*-

cis photochromophores. Another advantage is the higher thermal stability of the open- and closed-ring isomers, which can usually be isolated and studied independently. Sometimes, a side reaction leads to the formation of a by-product known as an annulated-ring isomer, which can form an ordering of its own (vide infra).

4.2. Photoresponsive molecular assemblies based on *trans*–*cis* isomerization

Upon irradiation of a solution containing the azobenzene *trans* isomer with UV light, a photostationary state containing both the *cis* and *trans* isomers is obtained. A solution of pure *cis* isomer is never obtained due to the lack of selectivity in the irradiation.

De Schryver and co-workers reported that after the deposition of a photostationary state mixture, domains of both *trans* and *cis* isomers were observed simultaneously and characterized by the differences in their lattice parameters and the orientation of their respective 2D crystal phases [87]. Another study by Jiang and co-workers reported that in-situ irradiation led to a monolayer composed solely of the *cis* isomer [88]. In that case, no thermal *cis*-to-*trans* back reaction was observed at the interface. This can be explained by the energetically favored ordering of the *cis* isomer compared to that of the *trans* isomer. Indeed, the *cis* isomer geometry facilitates the formation of a hydrogen bond network, and the denser packing increases van der Waals interactions.

A strategy to control the inclusion of a coronene guest into a nanoporous network was developed by Wang and co-workers [89]. The shape and size of the pores could be tuned by appropriate light irradiation of the bi-component monolayers composed of TCBD and 4NN-Macrocycle **1** (1,2,17,18,33,34,48,49-octaaza-[2₈](4,4')cyclophane-1,17,33,48-tetraene), which contains four azobenzene groups. Reversible control of the adsorption/exclusion of the coronenes inside/outside the pores was also achieved (Fig. 5) [92]. Modellization based on molecular mechanics/molecular dynamics (MM/MD) calculations was used to simulate the orderings obtained for the corresponding multi-component assemblies.

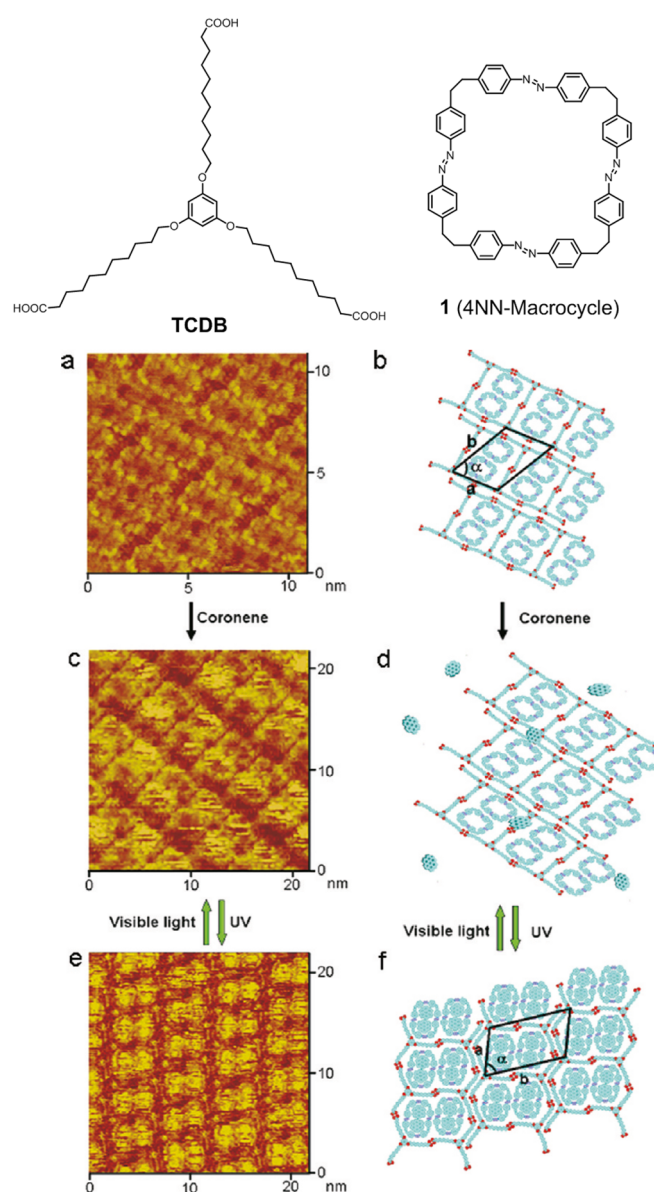


Fig. 5. (a) High-resolution STM image of the TCDB₁/1(t,t,t,t) network structure. (b) The molecular model of the TCDB₁/1(t,t,t,t) structure. (c) STM image of the ternary adlayer of TCDB₁/1(t,t,t,t)/coronene before UV irradiation. (d) The molecular model of the TCDB₁/1(t,t,t,t)/coronene adlayer. (e) STM image of the TCDB₂/1(t,c,t,c)/coronene architecture after UV irradiation. (f) The molecular model of the ternary TCDB₂/1(t,c,t,c)/coronene network. In all the molecular models, the red balls represent oxygen atoms; blue, carbon; and purple, nitrogen. The hydrogen atoms are omitted for clarity. Reprinted with permission from reference 92. Copyright 2011 American Chemical Society.

The same group developed a monolayer, based on azobenzene-diacetylene derivative **2**, in which two types of photocontrol are possible by changing the wavelength of the irradiation light (Fig. 6) [93]. By irradiation with 254 nm light, a polymerization of the diacetylene units on the lateral chains could be initiated. Reversible switching between the *trans* and *cis* isomers was controlled by alternate irradiation with 365 nm and 435 nm light at the phenyloctane/HOPG interface.

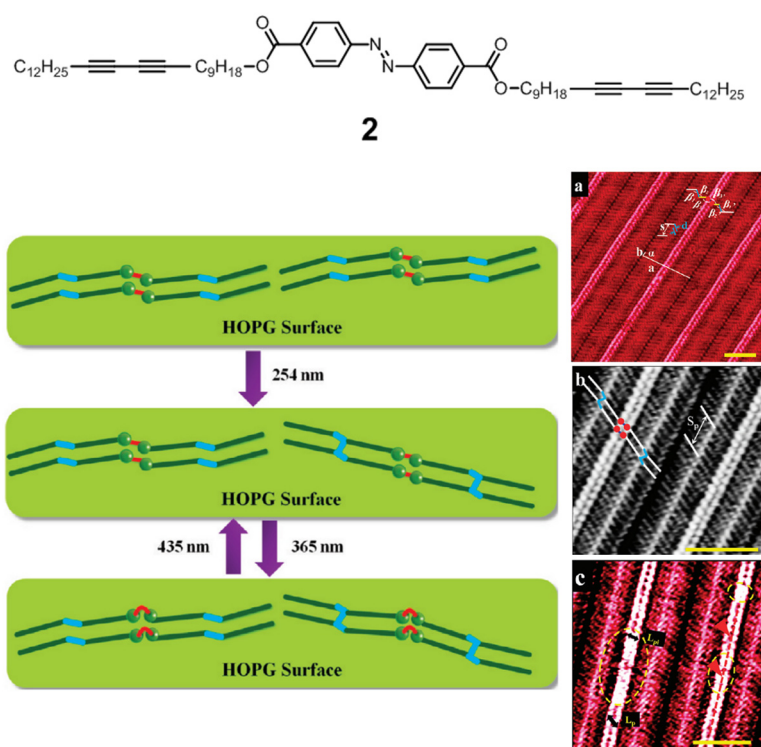


Fig. 6. STM images (scale bar = 5 nm) of (a) **2** (before irradiation), (b) **2** upon UV irradiation at 254 nm, and (c) **2** upon UV irradiation at 365 nm for 30 min. Adapted with permission from reference 93. Copyright 2012 American Chemical Society.

The same group reported a bi-component system fabricated with tetraacidic azobenzene and dipyrindylethene that could be reversibly regulated by irradiation with UV and visible light [94]. An example consisting of pure stilbene monolayers was also reported (Fig. 7) [94]. The ordering transformation induced by the *trans*–*cis* isomerization of stilbenes **3** and **4** upon in-situ irradiation at

the phenyloctane/HOPG interface was analyzed by STM. Brief irradiation of the compound **4** monolayer also led to the formation of the *cis* isomer molecular ordering. A longer irradiation time induced a [2+2] photodimerization reaction that formed cyclobutane, and led to additional changes in the molecular ordering.

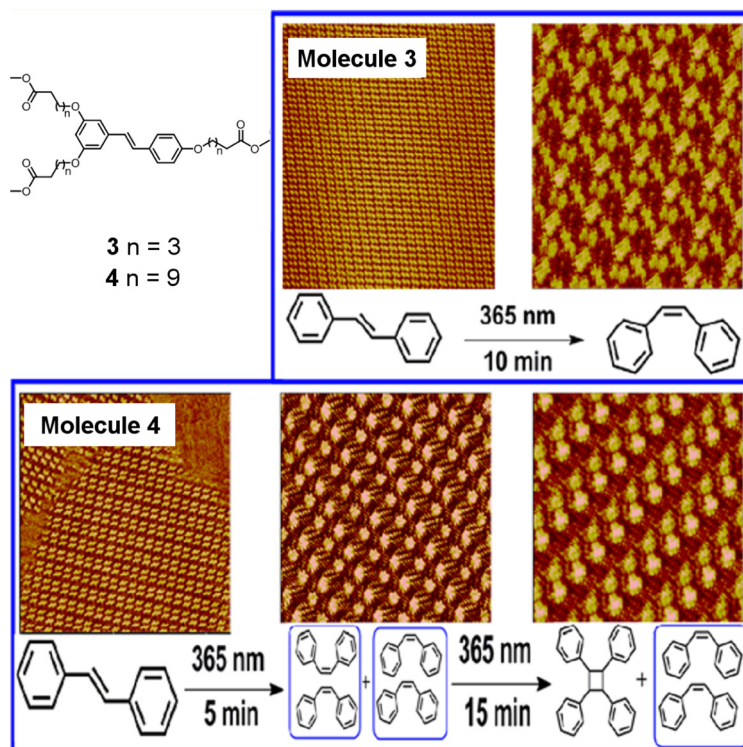


Fig. 7. Photoresponsive monolayers based on stilbenes **3** and **4**. Adapted with permission from reference 96. Copyright 2014 American Chemical Society.

The groups of Tobe and De Feyter collaborated on a study of nanoporous monolayers obtained from dehydrobenzo[12]annulene (DBA) **5**, which bears three azobenzene units that form a central hexagonal pore (Fig. 8) [95]. In that case, no significant transition between different molecular orderings was observed upon irradiation. However, the inclusion of a guest coronene molecule inside the central pore was controlled by light. Prior to irradiation, most pores were occupied by only one coronene guest molecule. In-situ UV irradiation induced a *trans*–*cis* isomerization that increased the size of the central pores, allowing them to host two (16.3% of occurrence), three (2.9%), and up to four (0.2%) coronene molecules. Reversible control was

possible, and the original state was regenerated by visible light irradiation.

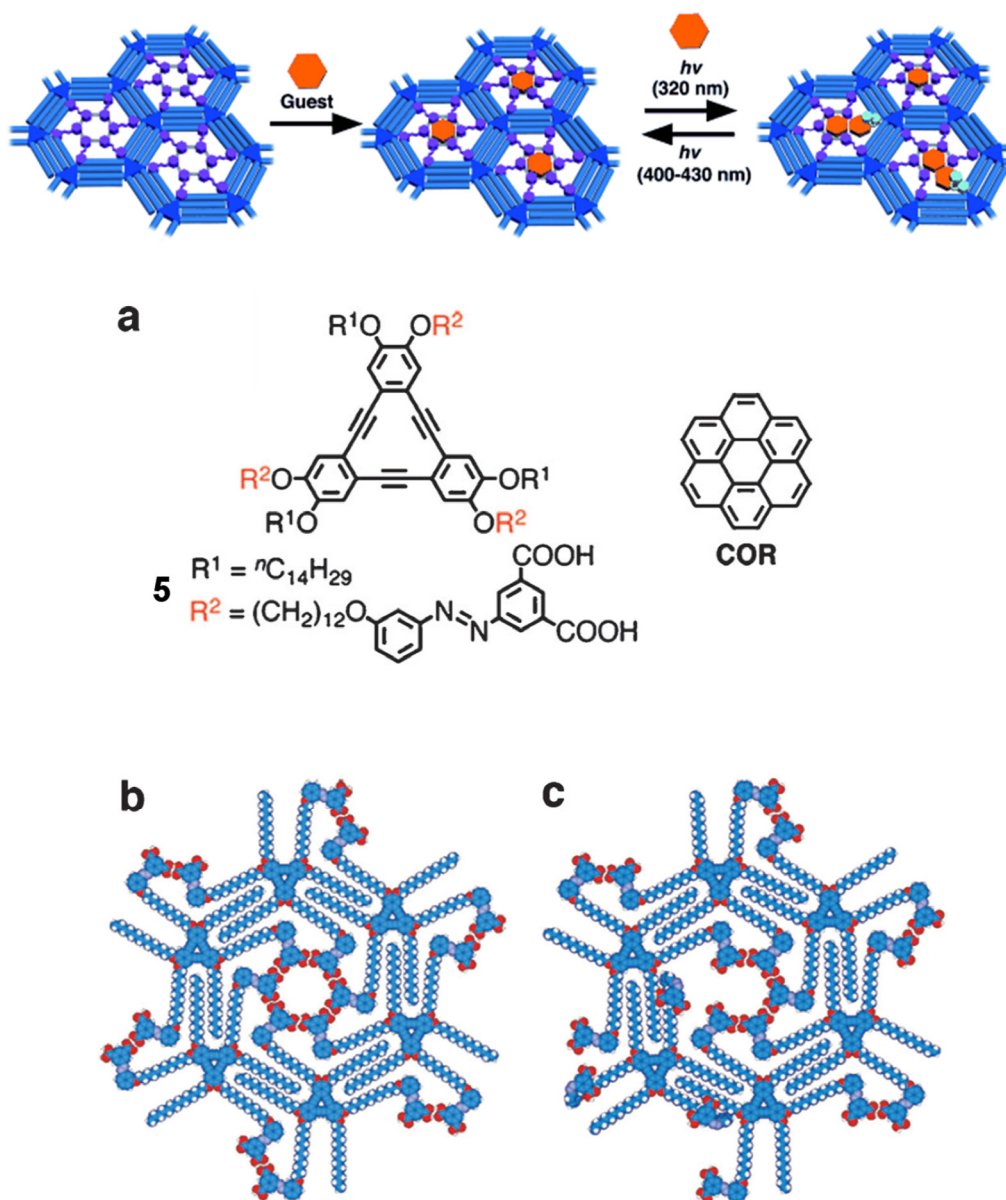


Fig. 8. a) Structural formula of the DBA *trans*-**5**, coronene (COR), and hexakis(phenylethynyl)benzene. b) Molecular models of the honeycomb structure formed by the self-assembly of *trans*-**5** with all-*trans*-azobenzene units in which a hydrogen-bonded hexamer of dicarboxyazobenzene units creates a size- and shape-confined space. c) The same pore as (b) with one of the dicarboxyazobenzene units adopting a *cis* configuration. Adapted with permission from reference 95. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA.

4.3. Photoresponsive molecular assemblies based on electrocyclic reactions

Generally, the individual isomers of diarylethenes and terthiophenes can be isolated and studied independently due to their high stabilities. Moreover, irradiation usually leads to photostationary states containing predominantly the open- or closed-ring isomer, due to the high conversion ratio of the electrocyclic reactions. Occasionally, side photoreactions can form the annulated-ring isomer and lead to multiple ordering transformations.

The first example of the use of diarylethene in reversible switching between two stable orderings was achieved by our group, in which a diarylethene-pyrene dyad and a diarylethene-pyrene-diarylethene triad were analyzed on phenyloctane/HOPG and octanoic acid/HOPG interfaces, respectively (Fig. 9) [97]. Preferential adsorption of the closed-closed isomer of the triad **6c-c** over the open-open isomer **6o-o** or the open-closed isomer **6o-c** was observed.

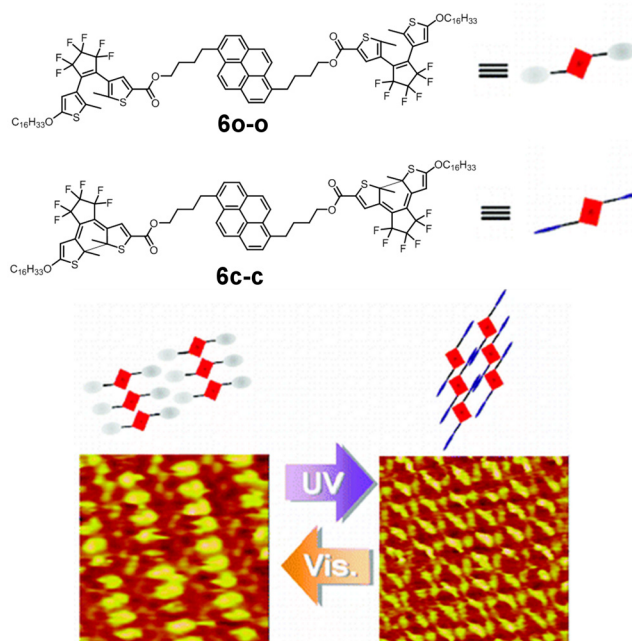


Fig. 9. Reversible ordering transformation between the orderings of the diarylethene derivatives **6o-o** and **6c-c**. Adapted with permission from reference 97. Copyright 2008 American Chemical Society.

The in-situ formation of the annulated-ring isomer molecular ordering was also reported for the first time by our group for diarylethene **7** (Fig. 10) [98]. A two-step transition between three

molecular orderings was possible due to the formation of this third isomer. The amide groups were reported to stabilize the molecular orderings through the creation of a hydrogen bond network. No molecular orderings of the open-ring isomer were observed to form for diarylethene substituted with ester groups.

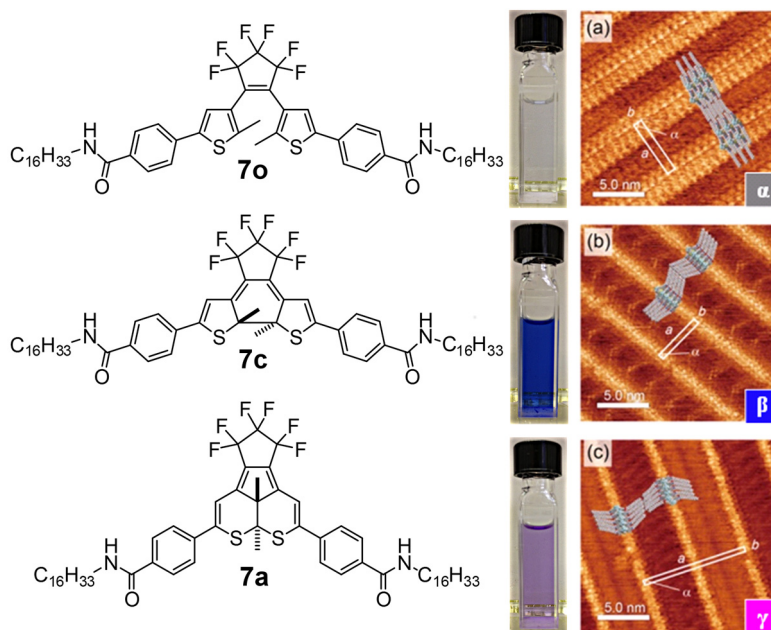


Fig. 10. Chemical structures and STM images of (a) the open-ring isomer **7o** (ordering α), (b) the closed-ring isomer **7c** (ordering β), and (c) the annulated-ring isomer **7a** (ordering γ). See references 45 and 47 for details of the orderings. Adapted with permission from reference 101. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

Lateral ester alkyl chains sufficiently stabilized molecular ordering for a similar diarylethene reported recently by Cechini, Hecht, Samorì, and co-workers [99]. A two-step transition was again observed for diarylethene **8**, and reversible transition between isomers **8o** and **8c** was even possible (Fig. 11). A theoretical model was used to determine the adsorption energy, intermolecular interaction energy, and total energy per molecule per unit cell of the diarylethene monolayers. The annulated-ring isomer **8a** adsorbed most favorably on the surface due to the higher stability of its molecular ordering, which was highlighted by the simulated values (Table 1).

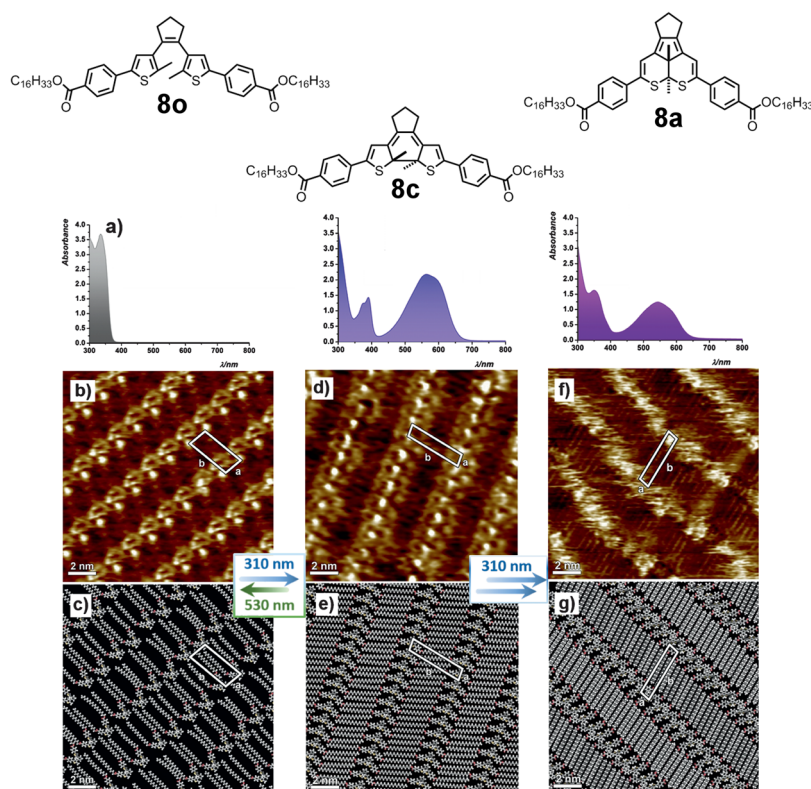


Fig. 11. a) Chemical structures and UV/Vis spectra of the investigated diarylethene in its open (**8o**), closed (**8c**), and the closed form containing 60 % of (irreversible) by-product (**8a**). STM height images of monolayers of b) **8o**, d) **8c**, and f) **8a**. Minimized molecular packing motifs of c) **8o**, e) **8c**, and g) **8a**. Adapted with permission from reference 99. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

Table 1. Estimated thermodynamic quantities for the isomers of diarylethene **8**. E_{ads} is the adsorption energy, E_{inter} the interaction energy with the neighboring molecules, E_{uc}/A the total energy per molecule normalized by the unit cell area, and γ the free energy excess considering both energetic and entropic contributions.

	E_{ads} [kcal mol ⁻¹]	$E_{\text{inter}}/2$ [kcal mol ⁻¹]	E_{uc}/A [kcal mol ⁻¹ nm ⁻²]	γ [kcal mol ⁻¹ nm ⁻²]
8o	-119.1	-15.7	-26.38	-21.04
8c	-112.7	-32.6	-38.14	-30.83
8a	-101.3	-46.1	-42.60	-34.61

Terthiophene **9** was used to achieve a four-state, three-step ordering transformation due to the formation of polymorphs (Fig. 12) [105]. The closed-ring isomer **9c** did not exhibit any ordering, but in-situ irradiation with visible light induced the formation of the open-ring isomer **9o**, which provided two polymorphs (orderings α and β) depending on its concentration. Irradiation with UV light led to the formation of an annulated-ring isomer **9a** that exhibited the characteristic honeycomb molecular ordering γ .

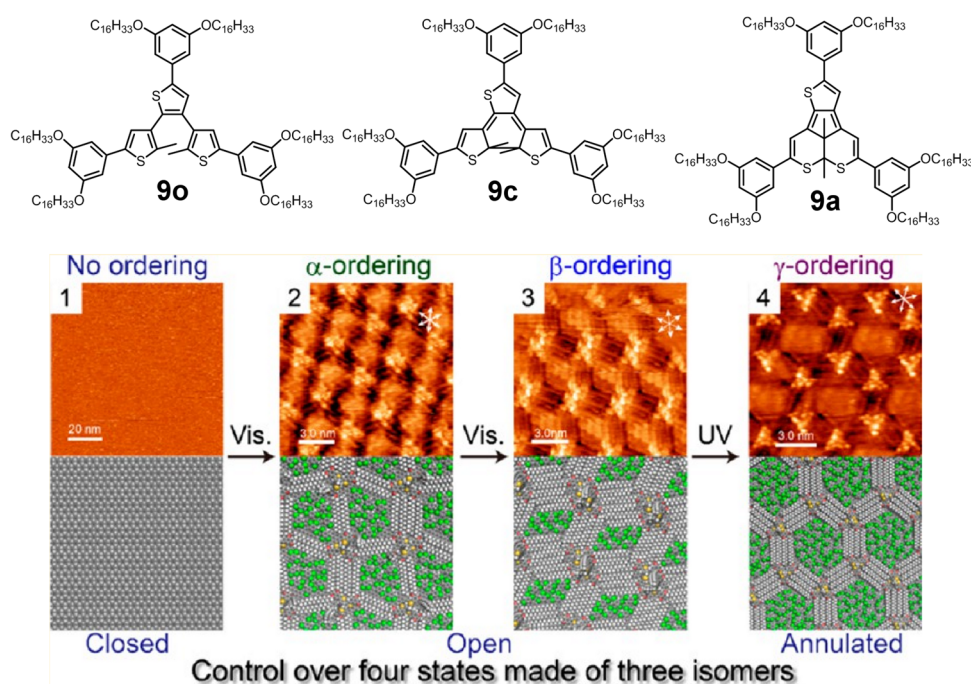
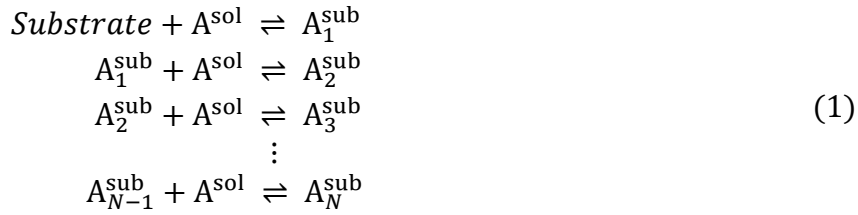


Fig. 12. Four-state, three step ordering transformation observed for terthiophene **9**. Adapted with permission from reference 105. Copyright 2008 American Chemical Society.

In addition to the ability to control the transition between multiple states, sensitivity to the stimulus is another important aspect of an efficient photoresponsive system. A high rate of exchange at the liquid/solid interface and cooperativity in the adsorption process are two parameters that can contribute to the creation of highly stimuli-responsive systems.

Inspired by cooperative supramolecular polymerization in solution [108,109], our group has recently developed a model of the equilibrium at the liquid/solid interface and used this model to

investigate the formation of 2D molecular orderings [100,102,106,107]. The model considers two different equilibrium constants, the nucleation (K_n) and elongation (K_e) constants, for the first nucleation step and the subsequent elongation steps described in equation 1, respectively. σ is the degree of cooperativity, which is defined as the ratio of K_n/K_e . For a cooperative process, this ratio is smaller than unity. This model takes into account the intermolecular interactions between neighboring molecules on the substrate.



The parameters can be obtained by the fitting the concentration dependence of the surface coverage using equation 2,

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

where c_t is the total concentration, A_{sub} is the total area of the substrate, L is the volume of the supernatant solution, N_A is the Avogadro constant, and S is the unit area occupied by one molecule on the substrate.

Diarylethene **10** was used to achieve reversible assembly/disassembly triggered by light at the octanoic acid/HOPG interface (Fig. 13) [100]. This result demonstrated that the use of a cooperative adsorption process can enable highly sensitive photocontrol over 2D ordering. The equilibrium constants for the elongation, nucleation, and degree of cooperativity for diarylethene **10** were found to be $K_e = 4600 \text{ M}^{-1}$, $K_n = 2.1 \text{ M}^{-1}$, and $\sigma = 5 \times 10^{-4}$, respectively [102].

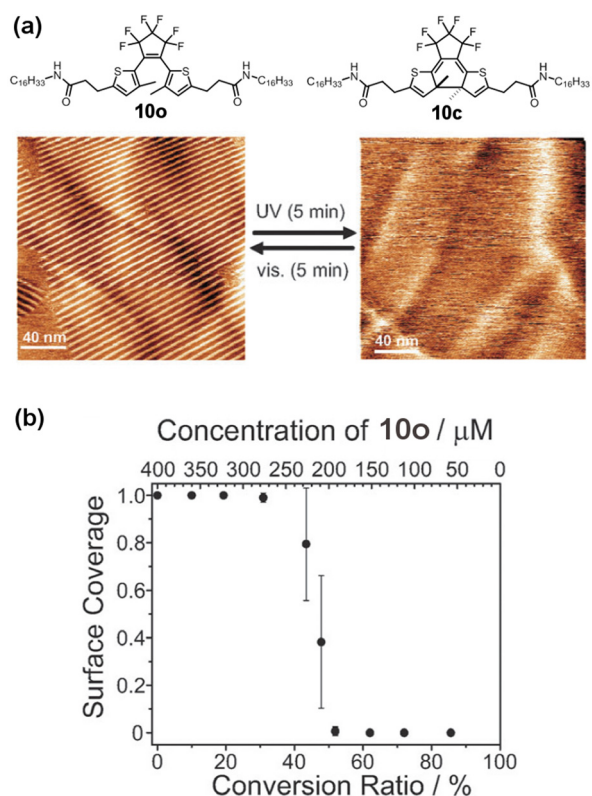


Fig. 13. (a) Formation and disappearance of the reversible ordering of **10** upon in-situ photoirradiation at the octanoic acid/HOPG interface. (b) The plot of surface coverage against the conversion ratio of the sample solution. Adapted with permission from reference 100. Copyright 2014 The Royal Society of Chemistry.

The adsorption parameters for each isomer of diarylethene **7** were determined by fitting the simulated curves from the cooperative model with the experimental STM data at the octanoic acid/HOPG interface (Fig. 14, Table 2) [101]. The high equilibrium constant of elongation observed for the annulated-ring isomer **7a** rationalized the previously reported favorability of the formation of this molecular ordering upon in-situ irradiation with UV light [98]. The cooperative model also revealed co-crystallization and mixing-induced cooperativity in the formation of orderings from mixtures of the isomers **7o** and **7c** [101]. The two isomers **7o** and **7c** influence each other during the formation of molecular orderings, and form mixed crystals. Moreover, mixing-induced cooperativity in the ordering formation process was observed in the STM measurements; the closed-ring isomer **7c**

can induce cooperativity in the formation of orderings that are mainly composed of the open-ring isomer **7o**. It was revealed that mixing of the components influences the formation of 2D orderings at the liquid/solid interface.

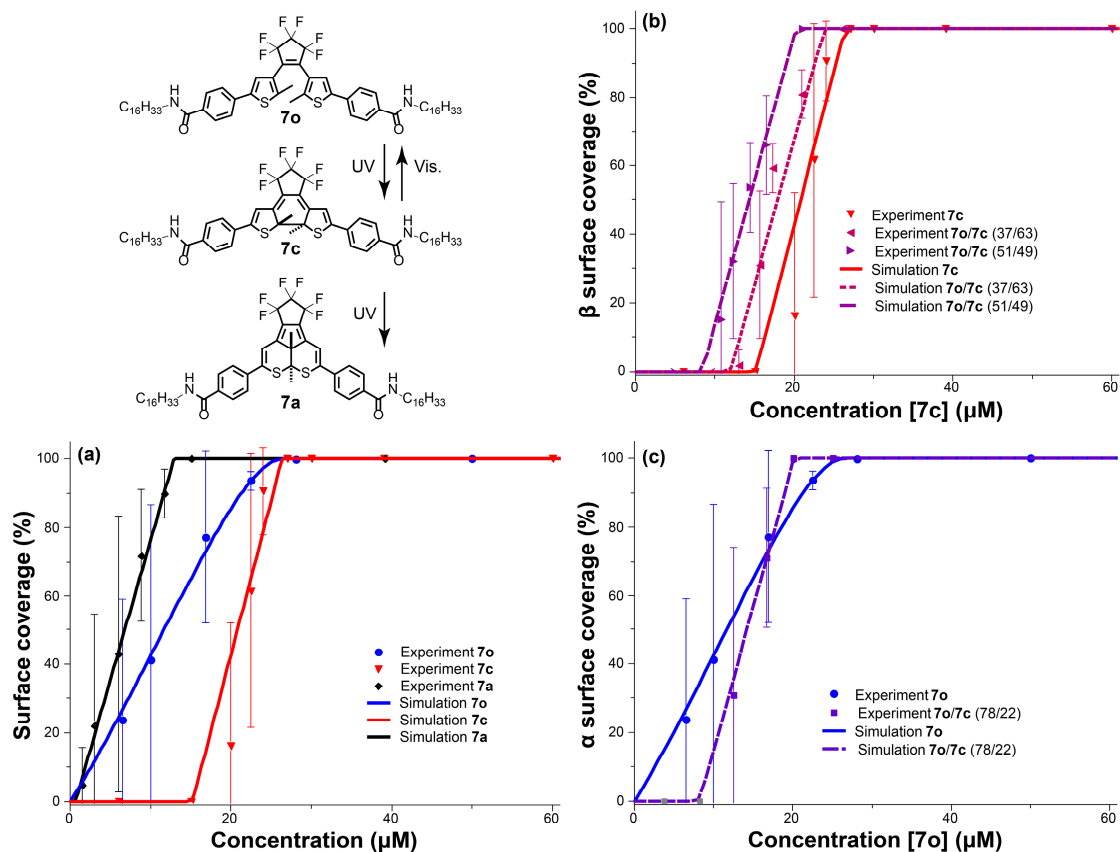


Fig. 14. (a) Concentration dependence of the surface coverage of **7o**, **7c**, and **7a** at the octanoic acid/HOPG interface. Concentration dependence of the surface coverage of (b) ordering β for **7c** and mixtures of **7o/7c** (37:63 and 51:49) and of (c) ordering α for **7o** and a mixture of **7o/7c** (78:22). Adapted with permission from reference 101. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

Table 2. Best-fit adsorption parameters for **7o**, **7c**, and **7a** at the octanoic acid/HOPG interface

	K_e [M^{-1}]	K_n [M^{-1}]	σ
7o	6.8×10^4	6.4×10^4	0.95
7c	6.6×10^4	$\leq 6.6 \times 10^{-2}$	$\leq 10^{-6}$
7a	1.5×10^6	≤ 1.5	$\leq 10^{-6}$

5. Conclusions and perspectives

In the field of photochemical control of surface-adsorbed molecular layers, considerable advances have been recently achieved using STM. In particular, remarkable advances have been made in photoresponsive self-assemblies at the liquid/solid interface using a supramolecular chemistry approach. High-level control of the transition between several stable molecular orderings has become possible by controlling the adsorption process of each photochromic isomer. Moreover, elaborate supramolecular structures can be controlled using molecular recognition. Additionally, a better understanding of their physisorption properties was made possible by the use of various theoretical models.

The packing structures of an assembly at the interface can be reproduced using MM/MD simulations, but it is still difficult to predict the whole packing from only the molecular structure. From our experience, alkyl chains with amide groups contribute to the formation of stable assemblies at the interface. The nucleation and elongation equilibrium constants have been revealed to be related to the molecular structure, but they are also difficult to predict from only the molecular structure. For example, the reason for the very strong adsorption of the annulated-ring isomer **7a** cannot be understood from its molecular structure. However, photochemical modulation of the molecular structure does affect its packing structure and the equilibrium constants, making photocontrol of the assembly possible.

In the case of diarylethene **10**, the open-ring isomer aligns at the interface in a parallel conformation that is not photoreactive, making photoreaction at the interface impossible. The photoisomerization is believed to occur in the supernatant solution phase. However, the photoisomerization of azobenzene **5** is believed to occur at the interface. The excited state of the adsorbate is reported to be effectively quenched by the surface. The detailed dynamics of the photoexcited molecule at the surface or interface are still not completely understood, and have been

attracting interest.

There is still room for improvement and innovation towards sophisticated photoresponsive systems. Adsorption at the liquid/solid interface is a supramolecular process, and thus many strategies that are used in supramolecular chemistry in solution can be applied. The structure–property relationships of the adsorption process are not clear enough. The effect of the solvent and the substrate should also be investigated more systematically to facilitate development toward practical applications. With this knowledge, photoresponsive surfaces with appropriate sensitivity and fast response time could be developed for practical applications in several fields, such as optoelectronic devices, molecular nanomaterials, and even heterogeneous catalytic systems.

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