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Jan Patrick Dela Cruz Calupitan, Olivier Galangau, Takuya Nakashima, Tsuyoshi Kawai, Gwénaél Rapenne. Photochromic Diarylethenes Designed for Surface Deposition: From Self-Assembled Monolayers to Single Molecules. ChemPlusChem, 2019, 84 (6), pp.564-577. <10.1002/cplu.201800640>. <hal-04636404>

HAL Id: hal-04636404

<https://hal.science/hal-04636404v1>

Submitted on 5 Jul 2024

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Photochromic Diarylethenes Designed for Surface Deposition: From Self-Assembled Monolayers to Single Molecules

Jan Patrick Dela Cruz Calupitan,^[a,b,c] Olivier Galangau,^[a,b] Takuya Nakashima,^[a] Tsuyoshi Kawai,^{[a,b]*} Gwénaél Rapenne^{[a,b,c]*}

Abstract: The efficient switching that can occur between two stable isomers of diarylethenes makes them particularly promising targets for opto- and molecular electronics. To examine these classes of molecules for electronics applications, they have been subjected to a series of scanning tunneling microscopy (STM) experiments which are the focus of this Review. A brief introduction to the chemical design of diarylethenes in terms of their switching capabilities along with the basics of STM are presented. Next, initial STM studies on these compounds under ambient conditions are discussed. An overview of how molecular design affects the isomerization and self-assembly of diarylethenes on the solid-liquid interface as investigated by STM is then presented as well as single-molecule studies under ultra-high vacuum. The last section presents further prospects for molecular designs in the field.

1. Introduction

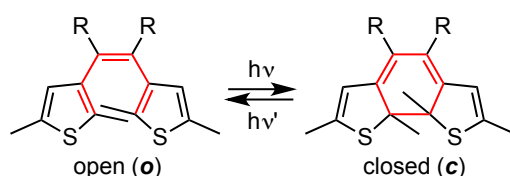
Bistable molecules are prototypical materials for miniaturized nanodevices.^[1,2] In this context, the switching properties of photoresponsive compounds such as azobenzenes,^[3] spiropyrans,^[4] fulgides,^[5] and diarylethenes between their available isomers have been studied in bulk 3D phases such as crystalline and amorphous solids, liquid mixtures, and polymer matrices. They are especially promising for molecular electronics, switches as their nanometer scale can outperform current transistor-based technologies in terms of memory density and switching speed.^[6,7] Among these compounds, diarylethenes and their derivatives have been explored because of their excellent switching properties, high bistability, and large differences in electronic structure between their isomers.^[1,2,8–10]

For such applications, bulk bistability must be translated to single molecular binary switching: each single molecule can be assigned to one bit of information. This provides a way to “write” (by switching) and “read” (by measuring changes in properties) data.^[6,7] These switching molecules have therefore been the subjects of studies from the nanoscale down to the single molecular level in recent years. Studies using scanning tunneling microscopy (STM) have gathered a great deal of attention due to its power to probe molecules and supramolecular assemblies at the scale such nanodevices demand.^[11–13]

This review surveys studies on diarylethenes with respect to how their molecular design affects STM images. A brief introduction to the chemistry and switching properties of diarylethenes are first presented together with a basic overview of the capabilities of STM. The main body of the review delves into STM under ambient and under ultrahigh vacuum at low temperature (LT-UHV) conditions. A more general review on STM of photoresponsive systems at the solid-liquid interface has been recently released^[14] so here we focus on diarylethenes studied by STM under ambient and ultrahigh vacuum (UHV) conditions. We intend to show how techniques in both regimes complement each other. Under ambient conditions, surface assemblies give insight into surface-molecule and molecule-molecule interactions. Meanwhile, UHV conditions give more details about geometric and electronic structures on the 2D plane. This will be put in the context of how switching is different in both regimes with the goal of drawing general molecular design principles, not limited to diarylethenes, that may aid future studies. Perspectives for further STM investigations of this class of compounds are also envisioned.

1.1. Designing diarylethene derivatives as photoswitches

The name diarylethene is due to its structure having two aromatic rings connected by an ethene bridge (Scheme 1, open form). The label open (**o**) is due to the central hexatriene (Scheme 1, **o**, red) moiety. In solution under ambient conditions, the single bonds of this hexatriene moiety may rotate which partly restricts the expansion of π -conjugation among the rings. The electronic structure of the **o** form is therefore determined mostly by the electronic structure of these aromatic rings. Most diarylethenes absorb light in the UV but not in the visible region of the spectrum resulting in colorless solutions. Upon photoexcitation with UV, the **o** form undergoes cyclization to the closed (**c**) form, referring to the cyclohexadiene moiety (Scheme 1, **c**, red) of the compound, characterized by a loss of aromaticity of the side groups. This central moiety holds the conjugated double bonds in a planar configuration so the electronic structure is mainly influenced by π -conjugation expanding over both side groups. An optical band appears in the visible region, presenting a strong visible color. The **c** form was found to be thermally stable, with lifetimes in the scale of months or more and only visible irradiation reversing it back to the **o** form.^[2,8–10]

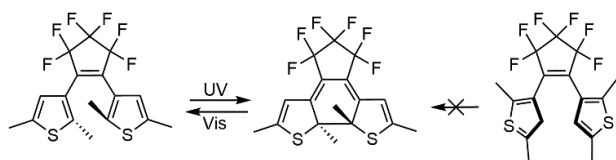


Scheme 1. Typical photocyclization and cycloreversion of diarylethenes. The hexatriene moiety is highlighted in red in the open (**o**) form while the cyclohexadiene is highlighted likewise in the closed (**c**) form.

Since their discovery in 1988,^[15] the synthesis and photochromism of these compounds has expanded and molecular design principles have been developed to improve switching properties and open them to various functionalizations.^[9,10] For example, the modification of the central ethene bridge^[16] using various C=C bond containing groups such as aromatic rings (terarylenes)^[16,17] has led to new functions and fine-tuning of properties. For a more detailed review on the chemistry and photophysics of these compounds, the reader is referred to other books^[2,8] and reviews^[9,10,18,19]. Instead, here we focus on molecular design of diarylethenes in the context of molecular electro-switches.

Prof. Irie listed five main requirements that candidate molecules must fulfil for switching applications: (1) thermal bistability; (2) fast response time; (3) sensitivity to stimuli; (4) fatigue resistance; and (5) solid state reactivity.^[10] Diarylethenes not only satisfy all these requirements but further molecular variations to tune these requirements have also been well-explored.

First, the stability of the **c** form is attributed to the low aromatic stabilization energy present in the **o** form so that there is less driving force towards spontaneous cycloreversion.^[20] Derivatives with rings having high aromatic stabilization energies such as phenyls and indoles simultaneously revert back to their **o** forms.^[10,20] Second, the fast switching responses have been well studied by experimental and theoretical measurements and found to be completed in picoseconds.^[10] Third, photosensitivity is evaluated by the quantum yield (i.e. ratio of molecules converted vs absorbed photons) and was found to depend mainly on the population of anti-parallel conformers in the **o** form. In solution at room temperature, this form equilibrates between the reactive anti-parallel and unreactive parallel conformations (Scheme 2). Only the former results in successful cyclization^[10] so different



Scheme 2. The anti-parallel and parallel conformation of diarylethenes showing that only the former proceeds to successful cyclization.

derivatives have been engineered to push this equilibrium towards the reactive conformation. Designs have included introducing bulky groups to sterically hinder the adaptation of the parallel conformation^[21–23] or using intramolecular attractive forces to hinder rotation^[24]. The latter was found to result to quantum yields near 100 %. However, the high photocyclization quantum yield comes at a cost of low cycloreversion. Nevertheless, other strategies for cycloreversion are also available: heating^[25], multi-photon absorption^[26], triplet sensitization,^[27] and photo/electrocatalytic chain reactions^[28–36]. Fourth, Irie and Uchida reported a diarylethene based on a benzothiophene where the aromatic groups have high fatigue resistance.^[37] Hecht and co-workers found that electron withdrawing groups also increase fatigue resistance.^[38] Lastly, the switching between **o** and **c** forms were also found to be possible in the solid state both in amorphous^[39] and crystalline^[40,41] phases.

It is at the nanoscale if not the single molecular level that these compounds are promising for electronics and switching applications (i.e. molecular electro-switching) so one must also consider additional requirements: the switching between **o** and **c** forms must be addressable – inducible (writable) and observable (readable) – at such scales. For this, STM provides a well-established technique.

1.2. 'Seeing' through the STM

Binnig and Rohrer demonstrated electron tunneling in vacuum in 1982.^[42] They showed that, due to the exponential dependence of electron tunneling current on the distance between tip and surface, the phenomenon can be used to probe clean surfaces with lateral resolution of 1 nm and vertical resolution down to 0.2 Å.^[43] The technique captured the attention of the scientific community when it resolved the surface reconstruction structure of Si(111), which hitherto had been investigated by indirect diffraction and theoretical methods only.^[44] Subsequent developments demonstrated that the tunneling current is dependent on the electronic structure, the local density of states, of the surface being probed^[45] so the technique of scanning tunneling spectroscopy (STS) was also developed. High currents due to occupied and unoccupied states led to the elucidation of electronic structures of adsorbed atoms^[46] surfaces^[47]. In 1986, the power of the technique dubbed scanning tunneling microscopy (STM) was asserted, when Rohrer and Binnig were awarded the Nobel Prize in Physics for their work which was developed only five years prior. For a more detailed historical background, the reader is referred to their Nobel lecture.^[48]

STM then became an indispensable tool for studying surfaces. In 1988 Ohtani and co-workers imaged the first molecules, a benzene monolayer on Rh(111), under UHV. For the first time, the hexagonal shape of benzene was observed in real space.^[49] With these, calculation techniques were also developed to predict the tunneling current traversing the tip, organic molecule, and the surface to facilitate theoretical STM image calculations in a technique called electronic scattering quantum chemistry (ESQC).^[50] This was then followed by manipulation of single molecules: Foster, Frommer, and Arnett showed direct evidence of the STM tip being able to move, pin, and effect chemical transformations on individual molecules.^[51] In the same year, Foster and Frommer showed that an interface between a solid substrate and a liquid crystal, could also support electron tunneling and thus imaging of molecular assemblies.^[52] This was followed by imaging not under UHV but at the so-called solid-liquid interface of other liquid crystals^[53,54] and assemblies of hydrocarbons^[55,56]. STM was hailed as one of the most important tools for nanotechnology when, in 1990, Eigler showed the incredible power of STM to manipulate the most fundamental units of matter. Equipped with an STM in the IBM labs in California, he showed that individual xenon atoms could be picked up and moved on top of a nickel surface, spelling their company acronym on the scale of nanometers, to produce one of the most iconic images of nanotechnology.^[57]

To sum up, STM is a powerful tool for probing not only surfaces but atoms and molecules at the nanoscale. The STM tip could be useful for mechanical (pushing, stretching, etc.) and chemical (bond breaking/making) manipulations. For a more general review on the said capabilities of STM, the reader is referred to a recent review by Morgenstein *et al.*^[58] STM therefore is now a tool beyond the field of surface science reaching out to solid state chemistry and nanotechnology so much that the first nanocar race was held in 2017 not only to promote the field to the general public but to advance it as well.^[59]

2. STM of diarylethenes

The difference in electronic structure between **o** and **c** forms of diarylethenes causes a difference in conductance between these two isomers. They are thus promising as molecular transistors and switches and initial studies focused on investigating whether each form can be identified at the molecular level. Diarylethenes were first observed to undergo uncontrolled switching by STM under ambient conditions.^[60] Thereafter, the difference in conductance between **o** and **c** forms led to studies on using these molecules in conductance switching experiments.^[61–63] These studies cemented the promise of diarylethenes in molecular electronics and memories as it was shown that they could be addressed, i.e. "written" and "read", at the single molecular level.

STM is carried out either under ambient or UHV conditions. Under ambient conditions, molecules may be imaged as self-assembled monolayers (SAMs) after removal of solvent or at the interface of the solid substrate and a liquid solution containing the molecules (i.e. the solid-liquid interface). For the former, characterization of adsorption properties such as packing direction, coverage, and others may be achieved. For the latter, because the sample is a solution of the molecule in a non-polar solvent deposited on a conducting surface, molecules are either suspended in solution (surrounded by solvent molecules) or deposited on the surface. Thus, there are competing dynamics between molecule adsorption on the surface and desorption from the surface. These are governed by molecule-molecule, surface-molecule, and solvent-molecule interactions. Meanwhile, under UHV conditions, the absence of solvent allows for surface-solution equilibrium of molecules. Therefore, most studies would focus on molecule-surface interactions and how such interactions modify the inherent properties of molecules. A more detailed picture of molecular geometry and interactions on the surface can be obtained. Further, the clean conditions allow for precise single molecular studies and even scanning tunneling microscopy (STS).

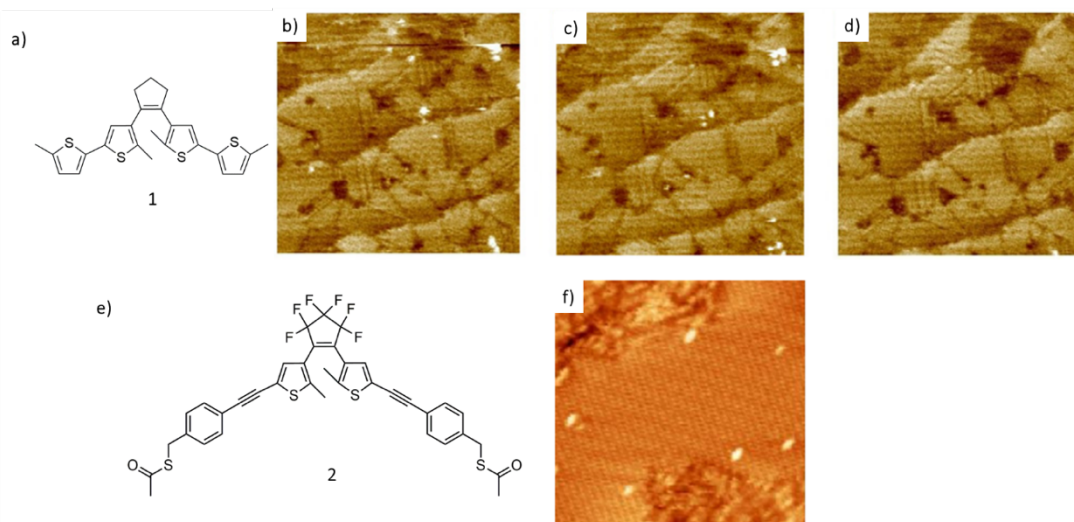


Figure 1. (a) Structure of **1**. (b-d) Consecutive images of the same region showing the uncontrolled disappearance of bright spots after illumination with visible light. 77 nm x 74 nm, 2pA, 0.75 V. Adapted from ref 60. (e) Structure of **2**. (f) Image of **9** embedded in octanethiol SAMs. 25 nm x 26 nm, 0.6 V, 3 pA. Adapted from reference [64] with permission from Elsevier.

2.1 STM of diarylethenes as SAMs

2.1.1 Ambient conditions

Initial STM studies on uncontrolled switching of diarylethenes were done on self-assembled monolayers under ambient conditions. Van Wees et al. studied a diarylethene derivative (**1**, Figure 1a) embedded in SAMs of dodecanethiol.^[60] The appearance of bright spots in otherwise flat images of the alkane thiols were interpreted as diarylethenes embedded in the SAMs. (Figure 1b) It was not clear whether these spots were due to single molecules or aggregates. Subsequent imaging of the same spots under the same conditions lead to stochastic, i.e. unpredictable, switching of the intensity of the bright spots whose origin was not clear. Upon illumination of the substrate with visible light and subsequent STM imaging these bright spots turned dark due to conversion from the conductive **c** to the non-conductive **o** form. (Figure 1c,d) Isomerization from the **o** to **c** form however was not achieved and this was attributed to the covalent bond between thiols groups being and gold atoms on the surface.^[60] In a later report, they followed reversible photochromic switching between **o** and **c** forms.^[63]

Dumas and co-workers on the other hand noted some diarylethenes (**2**, Figure 1e) “flickering” (i.e. displaying uncontrolled switching) under STM.^[64] The compound was a diarylethene functionalized with thioacetyl groups which anchor the molecule onto Au(111); these were embedded in a SAM of octanethiols. STM contrasts of molecules were observed to evolve relative to the contrast of surrounding SAMs. (Figure 1f) They measured these uncontrolled reversible changes over time and proposed three possible sources of these fluctuations: conformational changes by the molecule, changes in the geometry of Au-S bond, or diffusion of species from the environment which can change the electronic properties of the compound. They did not include isomerization between **o** and **c** forms, but proposed hot tunneling electrons with energy of a “few hundreds of meV” as the cause of these fluctuations.^[64]

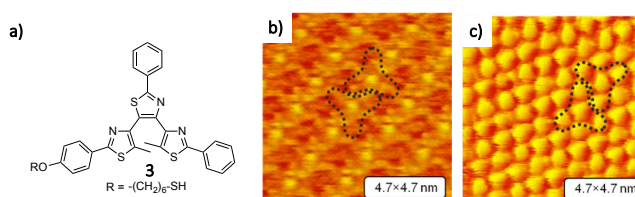


Figure 2. Structure of **3** and the assembly of its b) **o** and c) **c** forms on Au(111). Figures adapted from ref 66. Adapted with permission from reference [66]. Copyright 2014 American Chemical Society.

For terarylenes, two studies on STM of SAMs of **3** (Figure 2a) were reported. The switching unit was a terthiazole derivative functionalized with a long alkyl chain spacer group terminated by a thiol to anchor the molecule on an Au(111) surface.^[65,66] In a preliminary letter, Lacaze and co-workers deposited ethanol solutions of **o** forms and a mixture of **o** and **c** forms on a metallic surface. Upon evaporation of solvent and STM imaging, they showed that the two isomers could be distinguished on the Au surface by a subtle difference in contrast of the STM images and differences in packing parameters. (Figure 2b,c)^[65] This was followed by a full report on the switching between the two isomers by the STM tip and by light. They found that exposing a monolayer of **o** to UV light resulted in conversion to **c** forms. This illustrates that the spacer group was effective enough so as to prevent the electronic structure of Au from modifying that of the switching unit. Scanning a layer of **o** forms with high bias voltages (-1 V) led to formation of quasi-hexagonal structures characteristic of the **c** forms which led them to claim bias-induced switching. The observed surface structures corresponding to the **c**

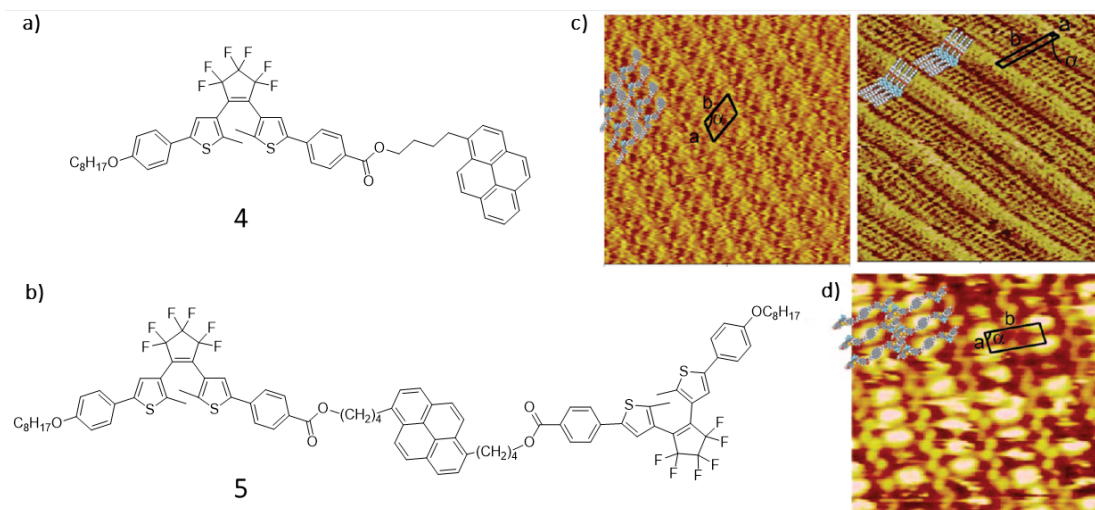


Figure 3. Structures of a) **4** and b) **5**. c) STM images of **o** and **c** forms of **4** respectively. For **4o**, the stacking parameters are: $a = 1.4 \pm 0.1$ nm, $b = 2.6 \pm 0.1$ nm, $\alpha = 115 \pm 2^\circ$. For **11c**, the stacking parameters are: $a = 0.5 \pm 0.04$ nm, $b = 4.9 \pm 0.1$ nm, $\alpha = 109 \pm 6^\circ$. Both images have sizes 50×50 nm². d) 25×25 nm² image of assemblies of **5o-o**, $a = 2.4 \pm 0.2$ nm, $b = 6.3 \pm 0.2$ nm, $\alpha = 87 \pm 2^\circ$. Data and images adapted from reference [67]. Copyright 2008 American Chemical Society.

forms however were unstable and switched back to **o** upon scanning at lower voltages. Intriguingly, they found that if a single **o** form is embedded in a SAM of **c** forms, conversion of the former to the latter is induced by lower bias voltages and found to be stable. These results indicate strong environmental effects on the switching process.^[66]

These studies showed that the differences between the two isomers of diarylethenes can be significant enough to be “read” at the single molecular level by STM. This is due to the immense difference electronic structure of the two isomers which in turn influence the tunneling current. However, a better control of the switching process, either by light or by STM tip stimulation, is sought so that data may be “written” as well. This also necessitated a better understanding of surface-molecule interaction, which could be probed on the solid-liquid interface.

2.1.2 Solid-liquid interface

Matsuda *et al.* recently published a general review on photoresponsive molecules investigated by STM at the solid-liquid interface.^[14] Asserting that “the central point in the design of an efficient photoresponsive monolayer at the liquid/solid interface lies in the choice of the photochromic units,”^[14] the said article surveyed STM studies of several photoresponsive compounds such as diazoanthrone, thioindigo diacetylene, azobenzene, stilbene, diarylethene, and their respective derivatives (if any). In this particular section of our present review, we focus on diarylethenes and how functionalities attached to their switching units affect the assembly/disassembly process in the solid/liquid interface. This section therefore aims to draw molecular design principles for surface assembly formation based on the particular geometry and photochemistry of diarylethenes on the solid/liquid interface, as such processes can give insight to surface-molecule interactions.^{49,69}

Diarylethenes are promising for molecular electronics due to their bistable isomerization. For such applications, the effects of such interconversion on molecule-molecule and surface-molecule interactions on a 2D solid surface are important. Diarylethene derivatives were first self-assembled and imaged by STM on the interface between highly-oriented pyrolytic graphite (HOPG) and 1-phenyloctane.^[67] Compounds **4** and **5**, (Figure 3a,b) having one and two photoswitching units respectively, were designed for such studies. The pyrene moiety was expected to interact with HOPG by π - π interactions while the long alkyl chains could interact with the octanoic acid solvent. Therefore, there were competing forces for the equilibrium between molecules in solution (stabilized by van der Waals interactions) and those adsorbed on the surface (stabilized by π - π interactions). Both **o** and **c** forms of compound **4** assembled neatly on the 2D surface. Those of the **o** form displayed unit cell parameters similar to those in the 3D crystalline phase. In the **o** form, the pyrene unit was found to be parallel to the surface, confirming the hypothesis that these are instrumental in stabilizing the surface assemblies. Meanwhile in the **c** form, the pyrene unit was found to be perpendicular to the surface and parallel to the photoswitching unit (Figure 3c). The destabilization from loss of the pyrene-HOPG interaction seemed to be offset by molecule-molecule π - π interactions in the denser core of the **c** form. The assembly of **o** forms disappeared upon UV illumination *in situ* inferring: (1) photocyclization occurs only in molecules suspended in solution and (2) the existence of **c** forms disrupts the assembly of **o** forms by interfering with its adsorption-desorption equilibrium.^[67]

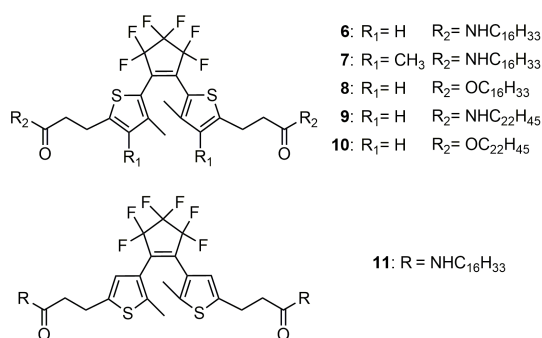
Meanwhile, the assembly of **o-o** and **c-c** forms (in which both of the two diarylethene moieties are in the **o** and **c** forms respectively) of **5** also showed long-range ordering. In this case, the images and molecular mechanics calculations showed

that in both forms, the pyrene moieties are always parallel to the surface with the alkyl chain allowing for rotation (Figure 3d). The π - π stacking between pyrene and HOPG seemed to be the stronger interaction that stabilizing 2D assemblies. It is noteworthy that the *in situ* illumination of the **o-o** assemblies did not lead to its disappearance as in **4**; instead, the **c-c** assembly was formed. Subsequent illumination of the **c-c** assemblies for about ten minutes reformed the **o-o** assemblies.^[67]

It is noteworthy that Matsuda and his team also showed that alkyl chains have a contribution in the stabilization of the 2D networks as a derivative without such groups did not result in formation of assemblies.^[67]

They further studied other diarylethene derivatives. (**6-11**, Scheme 3)^[68-71] From a survey of these studies, general molecular design principles could be drawn to come up with an idea of what functional groups aid in the formation of assemblies. Compound **6** has amide groups capable of hydrogen bonding; **7** has extra methyl groups; **8** has no amide groups. Among these three compounds, only **6** formed 2D assemblies. Interestingly, assemblies showed the **o** forms in a parallel conformation. This implies that the arrangement of alkyl chains in such a way aids in the formation of assemblies.

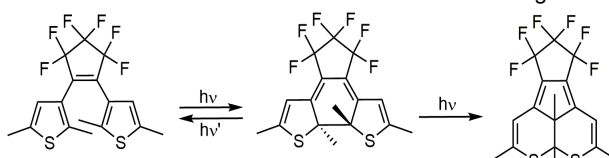
The methyl groups in **7** disrupted effective tethering on the surface by steric effects. The absence of the amide groups in **8** results in insufficient hydrogen bonding interactions to stabilize the 2D assembly. This indicates that both H-bonding and van der Waals interactions contributed to the formation of the assembly of **6**. Upon *in situ* UV irradiation, the assembly disappeared which implied that conversion happens in the solution phase and not on the surface: photocyclization leads



Scheme 3. Structures of compounds **6** to **11**.

to a decrease in the concentration of the **o** form in solution, causing surface-bound molecules to dissolve. It is not surprising that photoconversion happened in the solution phase where the molecules have freedom to adopt the reactive anti-parallel conformation, which is not the case for surface-bound molecules trapped in the parallel conformation due to steric effects. Then, the assembly could be reversibly formed upon subsequent visible light irradiation on the same time scale.^[68] Another implication of photocyclization/cyclo-reversion happening in the liquid phase is that illumination to produce either **o** or **c** isomer was on the timescale of minutes similar to standard photochemical measurements in solutions.

These findings were further expanded to derivatives of **6** and **8** having various alkyl chain lengths on HOPG-octanoic acid interface.^[69] By showing that the critical concentration to achieve maximum surface coverage decreases as alkyl chain length increases, Matsuda's team illustrated that these alkyl chains contribute well to the stabilization of the 2D assemblies, albeit not as strongly as through hydrogen bonding. On Scheme 3 is shown the derivatives having twenty two carbon chains **9** and **10**. The maximum surface coverage was reached when equilibrium between molecules in solution and those adsorbed on the surface has been reached within the timescale of STM experiments (5 mins) as similarly assumed for other studies. Alkyl chain lengths of up to twenty two carbon atoms were necessary for the derivative without amide groups, **10**, to form assemblies, and even then, a critical concentration of twenty five times higher than that of **9** was necessary for full surface coverage. The **c** form of **9** also formed an assembly in which the alkyl chains are pointing in the opposite direction in contrast to the **o** form. By looking at the concentration dependence of surface coverage, Matsuda *et al.* remarked that the nucleation process for **9c** assemblies was more thermodynamically favorable than that of the **o** form.^[69]



Scheme 4. General degradation scheme of diarylethenes to the annulated form.

In **c** forms which force the alkyl chains into an anti-parallel direction, the photochromic core seems to be the dominant structure for stabilizing the 2D networks. This was demonstrated in a subsequent work by comparison between compounds **11** and **6**. STM showed that UV irradiation of the **o** form of **11** induced the formation of new assemblies upon UV irradiation unlike that of the case of **6**^[68]. Molecular mechanics simulations showed that in **11**, the thiophene rings have more contact with the surface than those of **6c**. With the large sulfur atoms available to the surface, the planar photochromic core was seen to also interact with the surface more and contribute to the stabilization of the assembly.^[70]

Once Matsuda's team established which functional groups aid in assembly formation and stabilization, switching applications were explored. These depend on reliable isomerization between **o** and **c** forms and as such fatigue resistance, the ability to undergo consecutive switching without significant loss of function due to side reactions, is an important consideration. The general degradation reaction for diarylethenes is shown in Scheme 4. Prolonged exposure of the **c** form leads to the irreversible formation of the annulated form.^[9,10] This was first observed by STM for compound **12** (Figure 4a).^[71] STM imaging of the **o** form of **12** showed ordering labelled as α (Figure 4b). This was stabilized by van der Waals and hydrogen bonding interaction similar to previous reports.^[68,70,72] Deposition of the **c** form resulted in a different ordering labelled β (Figure 4c). In-situ irradiation of **o** or **c** on the surface revealed a different ordering labelled γ (Figure 4d), which

was confirmed to be the annulated isomer. In a surprising result, a ratio of only 5 % of the annulated isomer relative to the **o** or **c** forms was enough for the γ ordering to dominate the surface.^[71]

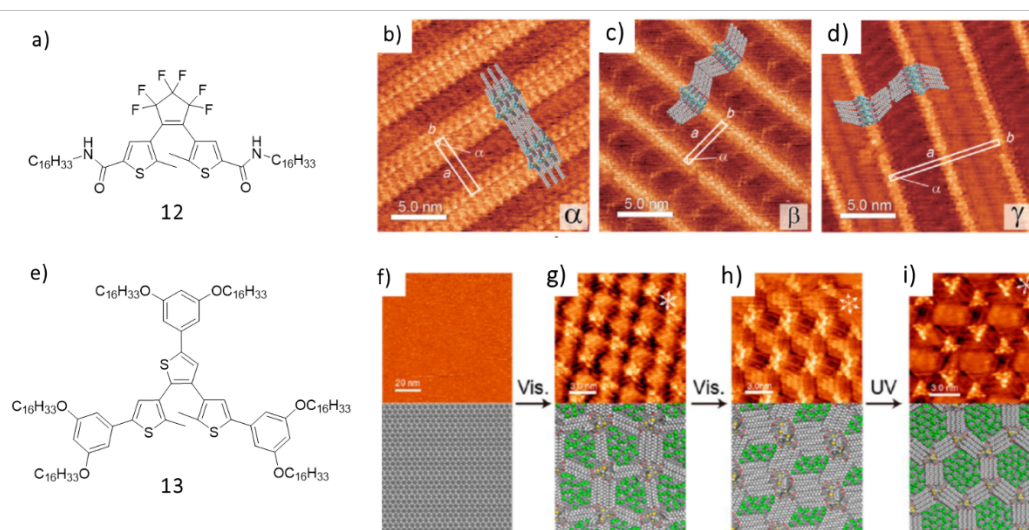
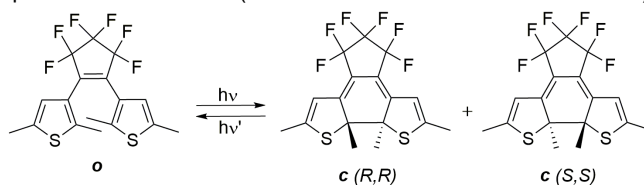


Figure 4. (a) Structure of **12**. (b-d) assemblies of the **o**, **c**, and annulated form of **12**. Packing parameters for b) $a = 5.71$ nm, $b = 0.89$ nm, $\alpha = 88^\circ$; c) $a = 4.82$ nm, $b = 0.56$ nm, $\alpha = 85^\circ$; d) $a = 10.2$ nm, $b = 0.48$ nm, $\alpha = 87^\circ$. Adapted with permission from ref 68. Copyright 2015 American Chemical Society. (e) Structure of **13**. (f-i) Four-state transformation of the **c**, **o**, and annulated isomer. Adapted from ref [75].

A subsequent report showed that the annulated isomer has a high affinity to the surface, so it disproportionately dominates STM images even when produced in small quantities. In addition, by a careful examination of the effect of **c** concentration on the assembly formation of **o**, they showed that the former could increase the cooperativity for the assembly of the latter.^[72] A report from Hecht, Samori and co-workers showed by molecular mechanics calculations that the annulated isomer has a denser packing than that of the **c** form. This explains its strong surface adsorption and disproportionate dominance on STM images.^[73] These studies explained well the strong surface adsorption and disproportionate dominance of the annulated isomer on STM images even at 5 % ratio.^[71]

The irreversibility of the annulated form could make it an unwanted side-reaction from the viewpoints of rewritable optical memories or switches but it could be useful for permanent memories (non-rewritable or write-once memories) similar to applications sought for diarylethenes with very low cycloreversion quantum yields.^[74]

Subsequently, Matsuda *et al.* found that the **o** form of **13** (Figure 4e) can have two packing patterns depending on the concentration of the solution. Together with the **c** form and the annulated compound formed by UV-illumination in a timescale of 10-30 minutes, a total of four possible orderings were developed with four states observed using STM as shown in Figure 4f-i.^[75]



Scheme 5. Photochromic reaction showing the isomers of the **c** form.

Finally, the solid-liquid interface also afforded a medium to resolve the chiral isomers of the **c** forms (Scheme 5). Whereas in bulk solution, these isomers are indistinguishable as they both have the same photophysical and switching properties, STM affords molecular-level separation and a 2D plane that could resolve these two isomers. The 2D plane has less symmetry elements than the 3D space so that molecules which are achiral in solution, crystal, or gas phase could be chiral on the metallic surface allowing the resolution of the enantiomeric forms.^[76,77] This was shown for the closed form of **11**. STM imaging of the previously synthesized and separated **c** forms of **11** showed domains which have bright lines tilted either $+7^\circ$ or -7° relative to the main axis of the graphitic surface. This is a clear indication of the chirality of the assemblies (Figure 5).^[78]

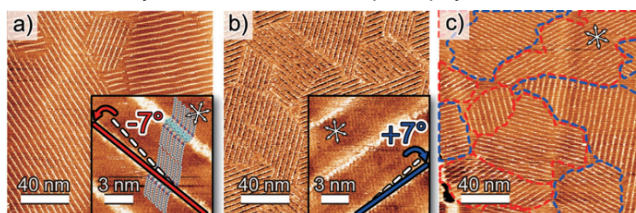


Figure 5. STM images of the (a) (R,R) isomer, (b) (S,S) isomer, and (c) racemic mixture of **11**. Adapted with permission from reference [78]. Copyright John Wiley and Sons 2017.

From these studies, some general principles can be gathered regarding assembly formation of diarylethenes. First, one may attach photo-inactive groups to modulate intermolecular forces of attraction. For example, alkyl chain lengths may be functionalized onto the compound to illustrate the effect of van der Waals interactions. These should of course be considered in relation to the nature of solvent and surface. Flat aromatic polycycles would preferentially adsorb parallel to an HOPG surface. Molecules may thus be oriented on HOPG in a rigid manner; otherwise alkyl chains allowing for flexibility must be attached as well. Second, for compounds having different conformational isomers, a surface that induces additional steric hindrance may favor one conformational isomer over another. This is especially true if groups that orient themselves towards the surface are large enough to disrupt assembly formation of one isomer over another. Third, other than conformational isomers, stereoisomers of the same conformation may be observed; this is due to the low degree of symmetry on the 2D plane. Understanding of the surface structure of the surface is therefore necessary to identify opposite in-plane orientations around different crystallographic directions. Lastly, in multi-state systems, the preferential formation of one isomer over others may lead one to think that only such an isomer is present or its concentration is high relative to others. One must note that in the solid-liquid interface, there is a dynamic exchange of molecules between surface and solvent so that the observation of assemblies also attest to the strength of surface-molecule interactions; one isomer may dominate the surface because it preferentially adsorbs on it, even if in lower concentrations.

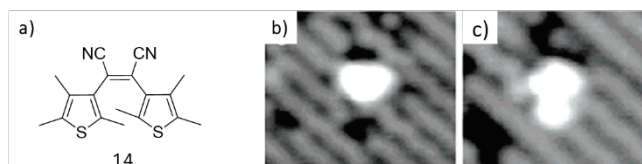


Figure 6. (a) Structure of **14**. STM of **o** and **c** forms of **14**. Adapted with permission from reference [80]. Copyright 2007 American Chemical Society.

It must be noted that these general principles are not exhaustive, they were derived only from those observed for diarylethenes. However, such design principles may be modified to be applied to other classes of molecules as well. These rather specialized studies on which design principles allow the formation of diarylethene assemblies therefore opens other molecules, photoactive or not, to be studied as 2D architectures on the solid-liquid interface.

2.2 STM of diarylethenes in SAMs

2.2.1 Diarylethenes under UHV

To focus on single-molecular properties, studies under UHV conditions are necessary (although assembly formation may also be observed under UHV for strongly-interacting systems.) Since there are no solvent molecules surrounding the sample, interactions between the surface and the molecule or between interacting molecules can be isolated. Further insights about molecular absorption geometry and electronic structure may be realized.

Initial STM studies of diarylethenes under UHV involved the deposition either of the as-synthesized **o** forms or a pre-irradiated mixture of contains **o** and **c** forms. Deposition of a solution of **14o** and **c** (Figure 6a) led to the observation of two shapes of molecules on Si(001) (Figure 6b,c). With the aid of calculations, these were assigned to their **o** and **c** forms. A possible scenario in which the adsorption configuration is heavily influenced by the surface through the formation of a Si-S bond that forces the two thiophene rings in different configurations has been proposed.^[79]

Meanwhile, in a separate study, Coudret and co-workers observed standing waves when a diarylethene derivative was adsorbed on Cu(111) surface.^[80] This pointed to interactions with the Cu surface. Due to the small size of the scattering zone with respect to the molecule, it was suggested that these waves are due to chemisorption of the cyclopentene moiety with the surface. This was supported by calculations. Electrochemical measurements also suggested a possible charge transfer scenario from the metallic surface to the compound.^[80]

The charge transfer between surface and molecules is also important in the context of bistable compounds because the properties of the **o** and **c** forms in their charged radical states are different from their neutral ones.^[28-36] Kim's group clearly demonstrated this when they showed that the **c** form is more stable than the **o** form in STM studies of **15** (Figure 7a) on metallic surfaces. Deposition and subsequent imaging of the as-synthesized **o** forms resulted in the observation of both **o** and **c** forms, seen as extended and triangular lobes respectively, on Cu(111) at room temperature (Figure 7b). Annealing at 80°C converted the remaining **o** forms to the **c** forms, indicating a rather low kinetic barrier separates the two; with some of the **o** having already been converted due to surface interactions. Upon thermal activation the more stable **c** isomer is formed (Figure 7b,c). Although evidence pointed to strong charge transfer interactions on the reactive Cu(111), similar observation of stability reversal was also found in the more inert Au(111).^[81]

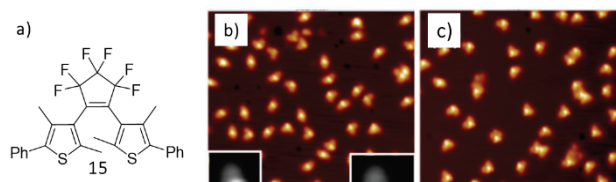


Figure 7. (a) Structure of **15**. (b) Deposition of **15** on Cu(111) showed two shapes corresponding to **o** and **c** forms which (c) transformed to 100 % **c** forms upon heating. Adapted from reference [81]. Reproduced by permission of the Royal Society of Chemistry.

Kim's group also reported ion-dipole interactions led to the assembly of diarylethenes on the surface even under UHV. As there are no solvents involved, deposition of molecules on the substrates usually proceeds by sublimating them from a Knudsen cell directly on a path to the substrate and no condensed phase could serve as the medium for molecules to interact by intermolecular forces. Kim's group however showed that NaCl could easily nucleate on the surface with a diarylethene having a perfluorocyclopentene core on a substrate held at 5 K. In consequence, the surface ions interact with the perfluorocyclopentene moiety to form assemblies. The molecule was calculated to have a high dipole moment (5.83 D) capable of interacting with NaCl by ion-dipole interactions with the latter aiding in assembly on Cu(111).^[82]

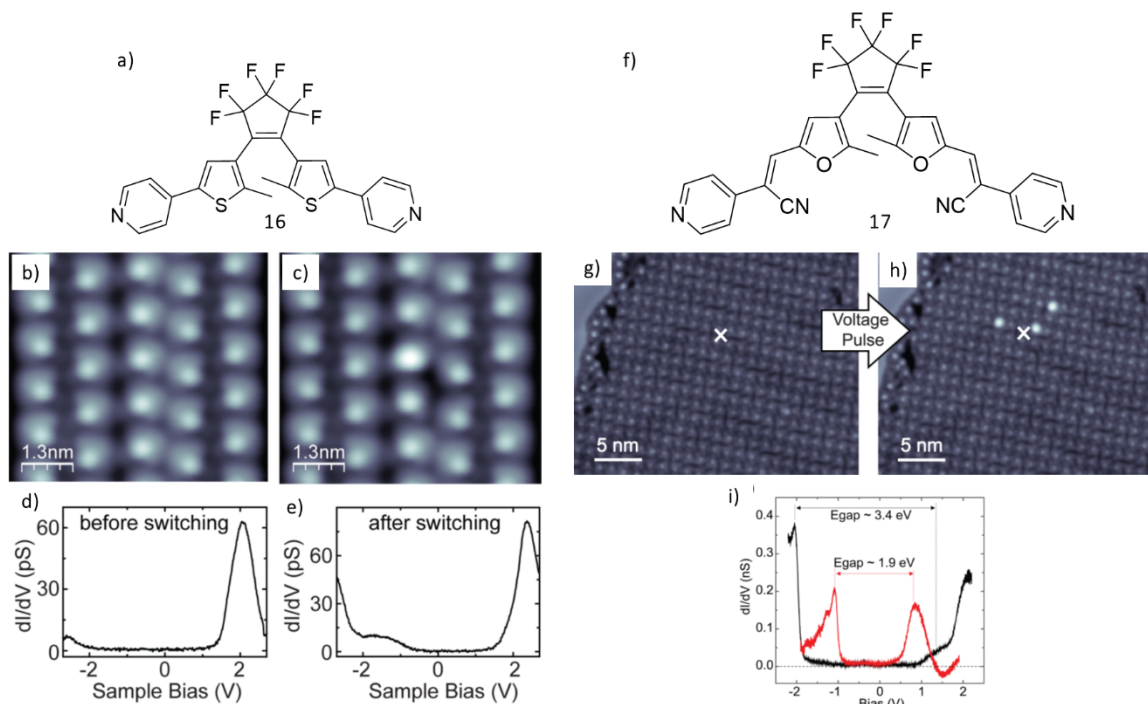
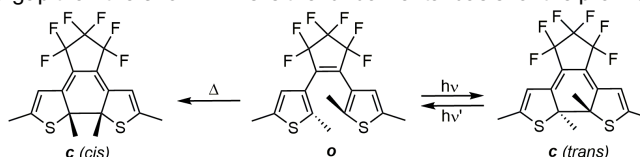


Figure 8. (a) Structure of **16**. (b) and (c) the same area before and after a switch-inducing bias pulse was applied. (d) and (e) show STS spectra before and after the switching event. Adapted with permission from reference 83. Copyright 2015 American Chemical Society. (f) Structure of **17**. The change in contrast is more remarkable for this compound (g-h) than that for **16**. (i) STS spectrum of the unswitched (dark) and switched (red) molecules. Adapted with reference from reference [86].

Only one group has so far succeeded to use the STM tip in switching diarylethenes between **o** and **c** isomers while adsorbed on a surface tip under UHV. In a 2015 report, Franke and co-workers investigated compound **16** (Figure 8a) which was found to form assemblies on surfaces due to strong hydrogen bonds between aryl protons and F atoms on the cyclopentadienyl bridge of neighboring molecules.^[83] These were performed on the more inert Ag(111) surface. They observed switching upon application of bias pulses higher than 1.5 V, as evidenced by a subtle change in contrast in one of the spots (Figure 8b-c). There is only a small difference in geometry between the **o** form in the reactive conformation and **c** form so no considerable change in the shape of spots was seen. However, it is well-known that in diarylethenes, the **c** form is more conductive than the **o** forms so the former may show brighter contrasts under the same bias voltages. Also, in solution, the **c** forms have a lower HOMO-LUMO gap than the **o** form. This is the fundamental basis for the promise of diarylethenes for molecular electronics applications. These were observed as the shift in contrast is evidence of a change in the electronic structure.



Scheme 6. Thermally-induced and photochemically-induced cyclization reactions of diarylethenes result to two isomeric **c** forms.

Under UHV, STS affords a tool to investigate these subtle changes in electronic structure. A lower resonance in the region above the Fermi level (Figure 8d-e) was observed for the **c** forms than the **o** forms which mirrors the change in HOMO-LUMO gap of diarylethenes in solution. By DFT calculations and analyses of switching voltages, they claimed that cyclization proceeded by a mechanism that favors a disrotatory reaction and produced the *cis* isomer of the **c** forms. Traces of the *cis* **c** form were suggested to have been produced in solution but it was not isolated^[84] so that this must be the first time to observe and isolate this isomer. (Photocyclization in solution proceeds via a conrotatory mechanism which always leads to the *trans* isomer in accordance with Woodward-Hoffman rules^[85], Scheme 6). Furthermore, the strong linear dependence of switching voltage to tip-surface distance suggested some electric field effects. The switching process

was proposed to be important to commence by reaction by an electric field-induced erection of the molecule allowing rotation of the methyl groups to the disrotatory conformation.^[83]

This was followed by a second study on compound **17**, (Figure 8f) intentionally devoid of any sulfur heteroatom to prevent strong interactions with the surface. This compound similarly assembled on Au(111). They did observe a larger difference in contrast between **o** and **c** forms upon tip-induced switching. (Figure 8g-h) and also performed conductance switching experiments and imaged dI/dV maps.^[86] In a subsequent report on the same compound, the authors showed that the switching could be induced either by tunneling electrons or the electric field between the tip and surface.^[87]

2.2.2 Terarylenes under UHV

Diarylethenes having novel ethene bridges such as terarylenes^[16,17] promise additional functions beyond the **o-c** switching. To illustrate, compound **16**, a terthiophene derivative has been prepared which developed four-state switching on the surface. Additional aromatic rings or heteroaromatic atoms may also potentially show new interactions on the surface. It is noted that the **c** form of terarylenes has a more extended π electronic structure than that of diarylethenes. This makes them especially interesting in the context of molecular electronics.

In a recent report, compound **18** (Figure 9a) was chosen and studied by deposition on Cu(111) under UHV because of its highly sensitive photocyclization quantum yield in solution.^[24] At 80 K, **18** was seen as random islands with no apparent ordered structure. (Figure 9b) Upon tip retraction and application of a 3 V bias pulse for 100 ms, new ordered islands appeared. (Figure 9c) The adatom (yellow arrow) and step height were used as landmarks to ensure the same regions were imaged even after tip retraction. Islands having two ordered domains separated by a disordered domain were found but larger single-domain islands were also imaged. (Figure 9d) The 3-fold symmetry of the Cu(111) surface seemed to influence assembly formation as all domains are oriented 60° with respect to each other.^[88] The assembly formation was proposed to be due to electric-field induced alignment of molecules. The bias pulse induced an electric field between tip and surface which caused molecules to align in one direction according to their dipole moment. With enough molecules aligning in the same direction, intermolecular forces take over and stabilize the self-assembled monolayer.

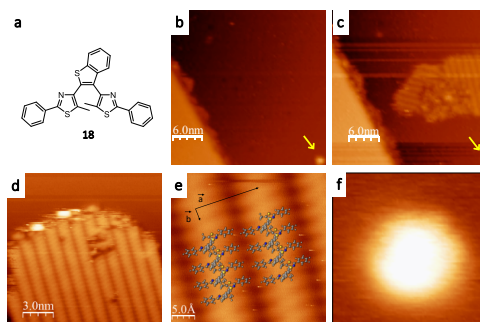


Figure 9. (a) Structure of **18** and its (b-c) tip-induced formation of assemblies. (d) Assemblies show streaking patterns indicative of moving molecules at the periphery. (e) packing of **18**. Adapted with permission from reference 91. Copyright 2017 American Chemical Society. F) Single molecular imaging at 5 K. Adapted with permission from reference [88]. Copyright 2018 American Chemical Society.

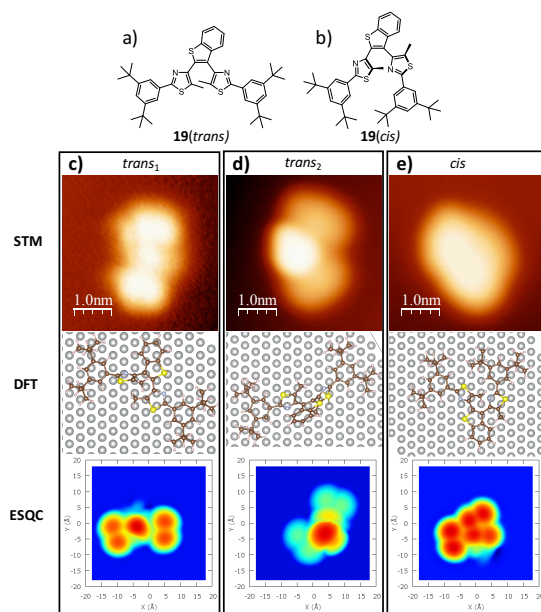


Figure 10. Structure of the (a) *trans* (anti-parallel) conformation and (b) *cis* (parallel) conformation of **19**. (c-e) show the experimental STM, calculated adsorption structure, and predicted ESQC STM images of the three surface conformations. Adapted with permission from reference [93]. Copyright 2018 American Chemical Society.

However, it was seen that molecules in the peripheries diffuse on the surface after several hours proving the dynamic nature of the assembly.^[88]

Imaging at 5 K was therefore performed to lower the kinetic mobility of the molecules. However, imaging (Figure 9f) did not show similar shapes as at 80 K and did not reveal the symmetry of the compound.^[89] **18** was then modified to harbor *tert*-butyl groups (compound **19**, Figure 10a) as they were shown to have high STM contrasts and prevent aggregation.^[90–92] By a combination of DFT calculations, spectroscopic measurements and photophysical properties the *tert*-butyl groups were shown to preserve the excellent photochemical properties of the original compound.^[89]

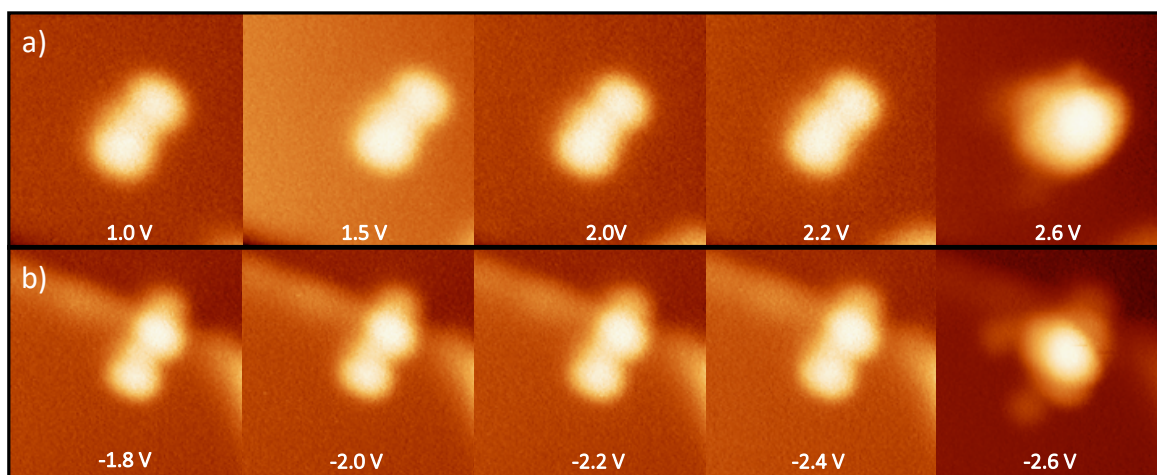


Figure 11. Mapping of (a) unoccupied and (b) occupied states of **19** (structure on Fig. 12) on NaCl(001)/Ag(111) at 5 K. Sizes of each image at (a) 6 nm x 6 nm at (b) 7 nm x 7 nm. Adapted with permission from reference [93]. Copyright 2018 American Chemical Society.

Deposition and imaging of **19** on Ag(111) at 5 K led to observation of three surface conformations using the *tert*-butyl groups to identify the differing molecules on the surface. This molecule has been shown to keep its reactive anti-parallel conformation via intramolecular forces of interaction even at room temperature^[93], so finding multiple conformations was surprising. Torsion angle scans (DFT), however, predicted that other stable conformations could be found if the molecule was exposed at higher temperatures, which is exactly the case as the molecule was deposited on the surface by sublimation at high temperature under UHV.^[93] One such conformation is the *cis* conformation which is equivalent to the parallel conformation. (Figure 10b) With the aid of DFT and ESQC calculations^[50], two of these conformations were assigned to the reactive anti-parallel conformation (labelled as *trans*, referring to the direction of the methyl groups with respect to the central benzothiophene ring) while the other was assigned to the unreactive parallel (labelled as *cis*) conformation. (Figure 10) The two *trans* conformations differ by their adsorption geometry, which is expected as the molecule has a low level of symmetry due to the benzothiophene moiety (as opposed to perfluorocyclopentene bridges in classical diarylethenes); different adsorption sites result to unique surface conformations. This was also expected as multiple S atoms on the molecule can adsorb on the Ag(111) surface. Meanwhile, the *cis* conformation is a rotational conformer of the molecule (see Scheme 2). This conformation has been detected by ¹H-NMR in solution¹³ but this was the first time to isolate and visualize at the single molecular level under UHV. However, light or STM induced switching was quenched due to the strong Ag-S bond.

The *tert*-butyl groups allowed for the mapping of occupied and unoccupied states on NaCl(001)/Ag(111). (Figure 11) At very positive and very negative voltages, the *tert*-butyl groups lost their influence on the images of **19** with only the central photoswitching part present. TD-DFT calculations of the molecular orbitals (MOs) of the molecule in the gaseous state did show that such *tert*-butyl groups do not contribute to the highest occupied MOs and the lowest-occupied MOs, leading the authors to conclude that such absence of the *tert*-butyl groups in the STM images was an indication of mapping occupied and unoccupied states. A rough approximation of 5.0 V was found for when the molecule was adsorbed on NaCl(001)/Ag(111), which was higher than that observed in the solution state.^[93] This was the first time that such occupied and unoccupied electronic states of diarylethenes were directly mapped at the single molecular level thanks to the UHV conditions. The understanding of the electronic structure of diarylethenes is fundamental to its switching and thus for its applications so such studies that show how the electronic structure changes upon adsorption on a solid substrate are important in opening diarylethenes to technologies that require a solid substrate.

3. Conclusions and perspectives

STM has greatly advanced the field of photoswitching compounds as it allowed investigations on a solid 2D surface at the single molecular level or at the nanoscale, which are especially important for the promise of next generation molecular electronics.

For such applications, one of the ultimate goals is understanding and controlling the switching process. Between ambient solid-liquid interface and UHV conditions, there seem to be a large difference. In the solid-liquid interface, photocyclization mainly happens in the solution state. That is, *in situ* UV irradiation causes cyclization of **o** forms suspended in solution above the surface. This disturbs their solution-surface equilibria and causes the disappearance of **o** assemblies. The concurrent increase of **c** forms in the supersaturated solution above the surface may push the formation of **c** assemblies for some molecules discussed in section 2.1.1. The same is true for the cycloreversion reaction.

Reversible switching by light or the STM tip has been observed under ambient conditions but remains a challenge for diarylethenes at the single molecular scale under UHV. This is due to strong interactions with the metallic surface that drastically changes the electronic structure of the molecule. Only two derivatives (**16**, **17**) were observed to switch via the STM tip and such switching was not found to be reversible. It seems that some structural requirements that were necessary for switching could be observed. Whereas in bulk states (solution/solid), a structurally diverse family of diarylethenes may be observed to switch, some variety is lost when transferring from the bulk states to 2D on the single molecular level.

For switching under UHV to be observed, it is necessary to prevent strong surface-molecule interactions. There are two possible ways in which this could be accomplished: 1) the side of the choice of the surface and 2) the side of the molecular design. The use of semi-metallic surfaces led to successful switching of spiropyrans^[94] while an insulating surface was used for single-molecular switching of azobenzene^[95]. The surfaces used must also be considered for such studies. On the side of the molecule, it may be necessary to lift the active part from the surface to avoid strong surface interactions. These could be accomplished by double decker designs^[96-99] that put the switching part on top of anchoring groups such as tripodal metal-based ligands^[96,97,100]. We note that it may be possible to extend these design principles to other switching molecules.

Meanwhile, as outlined in 2.1.1, design principles with respect to assembly formation is mostly the concern in the solid-liquid interface since switching happens in the solutions state anyway, in which a structurally diverse set of diarylethenes may already be switched. Intermolecular interactions promoting self-assembly process such as π - π , H-bonding, and van der Waals interactions may be considered in designing new molecules.

In addition, functions beyond this classical **o** to **c** switching afforded by extension of diarylethenes to terarylenes could also be investigated. For example, STM experiments on molecular rerouter derivatives^[101] using the recently developed four-point probe^[102] capable of doing simultaneous STM imaging and conductance measurements.

Some terarylenes that display thermally-induced release of organic species after subsequent cyclization could be used for both rewritable and non-rewritable memories for photopolymer systems.^[103-106] The reversible **o** to **c** isomerization can be used for rewritable memories while the irreversible release of the leaving group could be applied to non-rewritable memory. In addition, the final product in this reaction is an extended planar polyaromatic system important for molecular electronics. Graphene-based systems have recently been popular^[107] although those doped by other non-metals have also been increasingly gaining attention.^[108,109] These actually resemble the polyaromatic heterocyclic side products of organic species-releasing systems. Further, the low symmetry due to the central aromatic ring could give rise to varied surface structures due to surface chirality.^[76,77,110] This was suggested for terarylenes^[93] but was not confirmed so other derivatives having chiroptical switching capabilities^[111-113] may be investigated as well.

In conclusion, the past three decades have seen the combination of photoswitching diarylethenes and STM which come from two seemingly disjunct areas to form a new field in which both sides inform each other. STM was able to uncover new properties of diarylethenes and diarylethenes offer new design principles for other molecules (photoswitching or not) that may be studied by STM. With results from chemical synthesis, photo/electro-chemistry, DFT, and surface science, the field continues to open up new opportunities for nanotechnological applications in the 21st century.

Acknowledgements

This work was supported by the MEXT Program for Promoting the Enhancement of Research Universities in NAIST, the CNRS and the University Paul Sabatier (Toulouse). This research was also partly supported by the JSPS KAKENHI Grant Number JP26107006 in Scientific Research on Innovative Areas "Photosynergetics" and the Programme Investissements d'Avenir ANR-11-IDEX-0002-02, reference ANR-10-LABX-0037-NEX. We also acknowledge Dr Olivier Guillermet, Prof. R. Coratger, Dr Sébastien Gauthier and Dr Xavier Bouju for fruitful discussions and collaborations which resulted to some of the research cited in this review. We warmly thank Dr Colin Martin for his careful reading of the final version of the manuscript.

Keywords: diarylethenes • molecular switches • scanning tunneling microscopy • self-assembly • single-molecule studies

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