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## Switching at the Nanoscale: Light- and STM-Tip-Induced Switch of a Thiolated Diarylethene Self-Assembly on Au(111)

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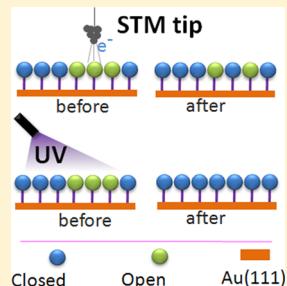
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**ABSTRACT:** The light-induced and STM-tip-induced switching of photochromic thiol functionalized terphenylthiazole-based diarylethene self-assembly on Au(111) has been investigated in ambient conditions. For such a purpose, we took advantage of the formation of highly ordered domains of opened-ring (**1o**) or closed-ring (**1c**) diarylethene isomers. We evidenced a STM-tip-induced switching for the **1o** isomer characterized by a tip bias threshold of 1000 mV above which switching of all molecules of the ordered **1o** domains occurs into the **1c** isomer. In contrast, switching from **1c** form into **1o** form is not observed at the same tunnelling conditions within a domain formed by ordered **1c** molecules. We compared tip-induced switching of ordered **1o** domains and switching of single **1o** isomers embedded in **1c** domains. This led to the demonstration that the process of switching of the **1o** isomer is determined by geometry of the molecules but also that the stability of the switched **1c** isomer depends on the nature of the surrounding isomers. We also compare tip-induced switching and switching under the action of external UV light irradiation of ordered **1o** domains. In contrast with STM tip-induced switching, the UV light induces switching of **1o** domains into their stable **1c** form, in agreement with a collective switching under irradiation, which cannot occur under the action of STM tip.



### INTRODUCTION

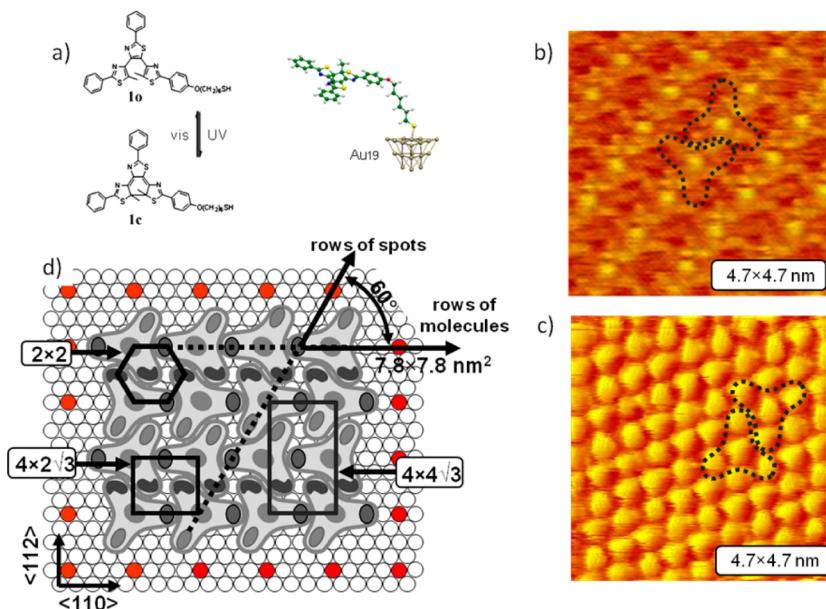
There is a growing interest for molecular switches that can be reversely triggered between at least two states by external optical and/or electrical stimuli due to their potential application in various molecular electronics elements and sensors with control at the nanometric scale.<sup>1–5</sup> Monolayers of molecular switches adsorbed on metallic substrates are thus particularly interesting because a large density of switches, necessary for the development of ultracompact devices, can be achieved. However, compared to reversible isomerization reactions which occur in solution, the switching properties can be partially or completely quenched in the vicinity of metallic substrate.<sup>6,7</sup> This arises due to one of the following reasons: (i) Hybridization of electronic states of adsorbed molecules under the influence of the surface. This changes the optical absorption spectrum (and subsequent photoswitching properties) of molecules.<sup>8–10</sup> (ii) Electronic lifetime effect which appears when surface-modified lifetime of photoexcited state is shorter than the time taken by a molecule to complete a conformational change.<sup>11,12</sup> (iii) Steric hindrance: lack of free space for conformation changes when molecular motion is restricted by neighboring molecules within a self-assembled monolayer (SAM). This last restriction occurs mainly for azobenzene molecules since a large mechanical motion is associated with the switching reaction in these systems.<sup>8,9,13,14</sup>

One solution to preserve isomerization reactions of molecular switches grafted on a metallic surface is to functionalize molecules by tailored insulating spacer which can separate the photoactive part of the molecule from the substrate. Several attempts have been focused on photo- and electron-induced isomerization of various photochromic molecules functionalized by alkanethiol and covalently bound onto Au(111) through chemical sulfur–gold interactions. Most of the studies are related to azobenzene derivatives. Even if the switching reaction can be prevented by steric hindrance within molecular self-assembly, azobenzene was found to undergo reversible trans/cis isomerization under UV/vis light illumination<sup>8,15–18</sup> as well as under applied electric field in the tunneling gap<sup>19–22</sup> of the scanning tunneling microscope (STM). These latter observations are particularly exciting, since they demonstrate the possibility of writing a molecular state at the molecular scale. For azobenzene, they have been interpreted on one hand as inelastic tunneling, associated with different mechanisms: tunneling electrons can induce switching by resonance with molecular vibrations<sup>2,22</sup> or with molecular rotation,<sup>23</sup> or by resonance in the HOMO level<sup>24</sup> and in the

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**Figure 1.** (a) Schematic representation of two isomers of hexanethiol functionalized TPT-DE molecules: **1o** and **1c** forms (on the left); theoretical model of **1c** molecule grafted onto a  $\text{Au}_{19}$  gold cluster “umbrella-like” conformation (on the right).<sup>32</sup> (b) STM images of **1o** SAMs.  $I_t = 1.7 \text{ pA}$ ,  $U_t = -680 \text{ mV}$ . (c) STM images of **1c** SAMs.  $I_t = 1.68 \text{ pA}$ ,  $U_t = -700 \text{ mV}$ . (d) Packing model of diarylethene molecules in **1o** and **1c** states on  $\text{Au}(111)$ . Panel (d) reprinted with permission from ref 32. Copyright 2011 American Chemical Society.

LUMO one.<sup>25</sup> The switching for molecules not in contact but still close to the substrate has been shown to be active but strongly influenced by the substrate,<sup>25</sup> similarly to the case of switching under irradiation.<sup>26</sup> On the other hand, switching can be induced by electric field in the tunneling gap of the STM, which modifies electronic orbitals of the molecules.<sup>2,19,22</sup> In the majority of cases, only a limited fraction of the molecules are being switched by the STM tip. The bias of the tip necessary to switch appears often quite high, of the order of a few volts.<sup>19,22–25</sup> Moreover, easy thermal back (*cis/trans*) reaction<sup>27</sup> limits the use of azobenzene as a molecular device. In such a context, diarylethene molecules appear promising due to their outstanding thermal stability of both states, good fatigue resistance, and fast light response.<sup>7</sup> For the development of ultracompact data storage devices with large density of data units, the switching phenomenon in diarylethene SAMs is promising. However, to the best of our knowledge, few works have been focused on STM study of diarylethene molecules. Only switching of single diarylethene molecules under UV/vis light modulation<sup>27,28,31</sup> together with molecular conductance flickering induced by of STM tip<sup>29–31</sup> have been demonstrated so far.

The SAMs of thiol functionalized terphenylthiazole-based diarylenes (hereafter named TPT-DE) on  $\text{Au}(111)$  surface have been formed and characterized by STM already in our previous study.<sup>32</sup> We have shown that deposition from nonilluminated solution (**1o** isomer) and from illuminated solution (**1c** isomer) led to the formation of an equivalent two-dimensional molecular network for both forms. Due to a strong modification of molecular orbitals of photochromic unit when irradiated using UV and visible light, a large evolution in the STM images is observed between **1o** and **1c** states. This difference leads to a possibility of STM identification of switching phenomenon induced by electric field or by UV/vis light irradiation.

In the present contribution, we extend our previous study to the light- and the tip-induced switching of self-assembled TPT-

DE on  $\text{Au}(111)$ . The SAMs were formed by deposition of solutions containing **1o** or **1c** molecules, as well as their mixture. We demonstrate tip-induced switching of **1o** into **1c** form. The stability of the **1c** form appears to depend on the geometry of the surrounding molecules. These results constitute one of the rare examples of switching induced by STM tip or UV light, obtained at ambient temperature at air and identified at the molecular scale.

## EXPERIMENTAL METHODS

**Sample Preparations.** The synthesis of the TPT-DE photochrome (Figure 1) has already been reported elsewhere.<sup>32</sup> To avoid quenching of excited states induced by the gold surface and allow, meanwhile, its grafting, one side phenylthiazole group was functionalized with a hexanethiol moiety.<sup>32</sup> It is known to show thermally irreversible and photochromic reaction with high fatigue resistance.<sup>33</sup>

For deposition of the molecules on  $\text{Au}(111)$  surface, a freshly saturated solution of **1o** molecules in ethanol ( $1.1 \times 10^{-7} \text{ M}$ ) was prepared and then divided in two equal portions. In order to convert **1o** molecules into **1c**, one portion of solution was subjected to UV irradiation ( $\lambda = 320 \text{ nm}$ ) for 1 min, a time required to attain the photostationary state (the conversion of **1o** to **1c** is estimated to be 90%). Preparation of SAMs with **1o** or **1c** isomers was performed by deposition of the corresponding solutions onto the gold substrate. SAMs containing both **1o** and **1c** molecules were prepared by deposition of 50:50 mixture of solutions with **1o** and **1c** isomers. For *in situ* UV irradiation of the molecules grafted on  $\text{Au}(111)$ , under the STM tip, irradiation was performed during 45 s at  $\lambda = 365 \text{ nm}$ . The  $\text{Au}(111)$  substrates are Neyco gold films (thickness  $\sim 150 \text{ nm}$ ), carefully annealed in a gas flame (propane + air) in order to obtain a reconstructed surface. STM analysis was started 10–15 min after evaporation of the solvent at ambient conditions.

**STM Measurements.** The monolayers were investigated using a commercial STM equipped with a low current head (Bruker, Nanoscope 3A). The STM tip was prepared by mechanical cutting of Pt/Ir (80:20) wire. For each kind of monolayer, several STM images recorded in constant current mode with current ranging from 1 to 60 pA and tip bias from  $\pm 500$  to  $\pm 1200 \text{ mV}$  were obtained with different samples and tips to check reproducibility and to ensure that

the results are free from artifacts. All STM images presented here were recorded under ambient conditions.

Basic values of the tunneling current and bias were equal to 10 pA and  $\pm 500$  mV. No switching from one isomer into another was observed using these parameters and absolute value of switching bias threshold was determined by gradual increasing from 500 to 1200 mV by steps of 100 mV. For each value of the applied bias, one full scan was recorded. Systematically, if a modification of contrast was detected, the bias was lowered/increased back by 100 mV in order to compare with the initial contrast and to identify eventual variations of STM tip. The threshold value was established when reproducible change of STM contrast occurred, accompanied by change of symmetry, without any tip variation. If no change of STM contrast was observed, the bias increasing/decreasing was continued.

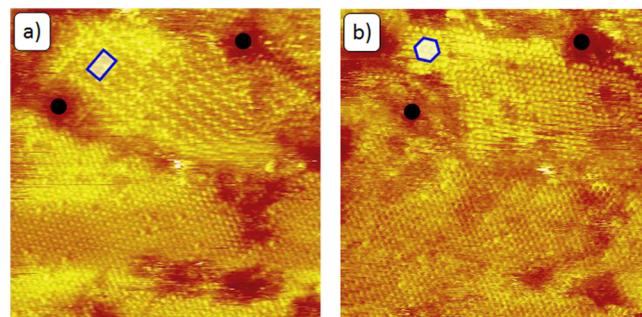
To gain more insight on the switching properties of the TPT-DE molecule, DFT calculations were undertaken to determine the ground state reaction pathway from **1o** to **1c**. Density functional theory calculations were performed using the Gaussian03 program package.<sup>34</sup> The geometries of the different **1o**, **1c** and transition state (TS) for ring closure reaction have been optimized using the Berny algorithm (energy convergences parameter of  $10^{-4}$  eV), in the gas phase and without symmetry constraint, using the B3LYP functional<sup>35</sup> and the 6-311+G(2d,p) basis set. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima and transition state on the potential energy surface.

## RESULTS

The STM study of tip-induced switching of diarylethene molecules between **1o** and **1c** isomers requires precise analysis of the STM images, associated with each state of the molecules. As demonstrated in our previous study, TPT-DE molecules, with a star shape, substituted by hexanethiol chain, can be ordered on the Au(111) surface. In such SAMs, the alkyl chains of each molecule are oriented almost perpendicular to the substrate plane, while the conjugated parts are oriented parallel to the substrate plane (so-called “umbrella-like” structure shown in Figure 1a). In this geometry, upon scanning, the STM tip is in direct tunneling contact with the conjugated moiety of the molecule. Thus, the STM images only reveals the aromatic parts while alkylthiol chains remain invisible and remain unmodified by the STM tip.<sup>32</sup>

The monolayers formed by **1o** and **1c** molecules present the same crystallographic network, displayed in Figure 1d. However, the STM images recorded with intramolecular resolution reveal a major difference in STM contrast of each form, due to strong differences of molecular orbital shapes: the **1o** molecules display rowlike STM contrast (Figure 1b), and the **1c** molecules are characterized by hexagonal-like STM contrast (Figure 1c). Consequently, the differences in STM contrast of **1o** and **1c** monolayers give us the possibility to probe the **1c** and **1o** molecules in switching experiments, whereas the identical molecular network of the two isomers may facilitate switching of the SAM.

**UV-Irradiation Switching.** We have first studied the switching behavior of SAM of TPT-DE grafted on Au(111) under UV-irradiation at ambient conditions. For this purpose, we prepared a mixture of **1c** and **1o** solutions, with 50% of each solution. STM images of the SAMs resulting from the mixtures of **1c** and **1o** molecules are presented in Figure 2a. They indicate a segregation process between **1o** and **1c** isomers as shown by the presence of domains with a rowlike structure of the STM spots (suggesting **1o** domains) together with domains of quasi-hexagonal organization of the STM spots (suggesting **1c** domains). Figure 2b shows the STM image of the same

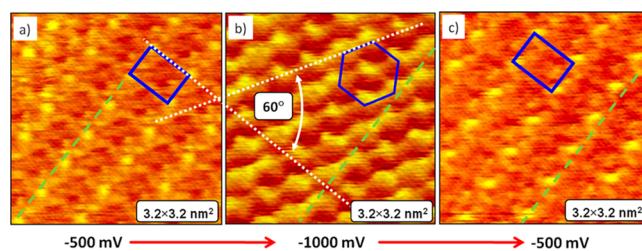


**Figure 2.** Two STM images ( $25 \times 25$  nm) obtained at  $I_t = 12$  pA,  $U_t = 700$  mV. (a) Ordered domains obtained after deposition of a mixed solution of **1c** and **1o** molecules revealing formation of **1c** (indicated by hexagon) and **1o** (indicated by rectangle) domains. (b) Same region imaged after UV ( $\lambda = 365$  nm) irradiation during 45 s.

surface as in Figure 2a, obtained after UV irradiation (45 s at  $\lambda = 365$  nm). Figure 2b shows a surface only covered by STM spots with a quasi-hexagonal organization. It reveals that the surface initially covered by coexisting **1c** and **1o** domains became entirely covered by **1c** domains.

Remarkably, a complete switching occurs. This confirms an efficient decoupling with the substrate, thanks to the hexanethiol moiety as a spacer. It could suggest that the yield for the phototransformation is close to the one in solution. It shows that the ability of light-induced switching of the closed-packed molecules within a SAM does not suffer from neither intermolecular interactions nor specific “umbrella-like” adsorption geometry on Au(111). This is in contrast to several of the ordered systems composed of azobenzene with similar spacers,<sup>14,22,24</sup> in agreement with the strong geometric changes related to azobenzene switching which may inhibit switching in the presence of neighboring molecules. For a successful switching, they require specific spacers<sup>17,18</sup> in contrast with diarylethene. The question is now: can we also locally switch these diarylethene monolayers under an STM tip? With azobenzene functional groups, such a local switching has been demonstrated, but with a low efficiency, and still never with diarylethene groups. The fact that, in those star-shaped diarylethenes, the crystallographic network is the same for the two molecular forms may be favorable for a local switching.

**Bias-Induced Switching of SAM.** A one-component solution of TPT-DE issued from a non-UV-irradiated solution was deposited onto Au(111), leading to formation of **1o** monolayers with typical rowlike contrast (Figure 3a). In order



**Figure 3.** Three consecutive STM images obtained at  $I_t = 1.2$  pA, for a SAM originally built by **1o** molecules. The rectangle corresponds to the rowlike STM contrast of the **1o** molecules. The rows are indicated by a green line. The hexagon corresponds to the hexagonal-like STM contrast of the **1c** molecules, revealing a switching of the corresponding SAM induced by the variation of the bias in tunneling gap.

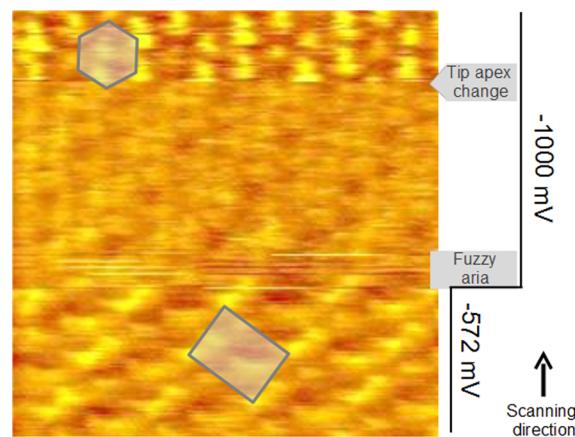
to investigate tip-induced switching properties of TPT-DE monolayers, we varied the tip bias from  $\pm 500$  to  $\pm 1200$  mV. Figure 3 shows that the jump of the bias from  $-500$  mV to  $-1000$  mV led to a change in the contrast and symmetry of the STM images. Three consecutive images are presented. The image in Figure 3b corresponds to a change of bias from  $-500$  to  $-1000$  mV with respect to Figure 3a. Figure 3c is obtained after reverse changing of bias from  $-1000$  to  $-500$  mV. Two main peculiarities should be noted.

First, the initial row structure, underlined with a green line in Figure 3, is being transformed into a quasi-hexagonal one (Figure 3b), which corresponds to a STM contrast variation equivalent to the one observed after UV irradiation (Figure 2a,b). The experiment presented in Figure 3 has been repeated several times with different tips, always leading to similar jumps of STM contrast under a bias threshold value around  $\pm 1$  V. We believe that the observed contrast changes when bias is varied do not correspond to the detection of new electronic states of the molecules, but correspond to a switching between **1o** form of the molecules and **1c** form. The contrast of the **1o** forms, when submitted to a STM bias around  $-1000$  mV, abruptly varies and becomes very similar to the contrast of the **1c** form, with this latter one remaining mainly unchanged between  $-500$  and  $-1000$  mV. In particular, the drastic variation of symmetry in the STM image is associated with an angle of  $60^\circ$  between the direction perpendicular to the rows and the direction of aligned spots (Figure 3b), in excellent agreement with a variation between **1o** and **1c** forms, as predicted by the packing model presented in Figure 1d. Accordingly, the modifications of Figure 3 also appear very close to the ones observed after switching of ordered **1o** forms submitted to UV illumination (Figure 2).

Second, a switching occurs only for the molecules located below the tip with a bias  $-1000$  mV. When the bias is set back to  $-500$  mV (Figure 3c), the molecules appear to have switched back to their initial **1o** state. This back switching is systematically observed independently of the value of the final tip bias if its absolute value is below the bias threshold. This explains in particular why no switching has ever been evidenced when the STM tip was immobilized with a large bias on top of a given molecule. In the scan performed with a low bias, immediately after the tip immobilization, the molecules that possibly switched into **1c** form in the presence of the STM tip were already switched back in their initial state.

The switching phenomenon in the presence of high bias absolute value is confirmed by the experiment shown on Figure 4. It presents the STM scanning of a **1o** monolayer. The scanning occurs from bottom to top. The bottom of the area is probed with a tip bias of  $-572$  mV. It is associated with a rowlike STM contrast of the **1o** state. A variation of the tip bias to  $-1000$  mV occurs in the middle of the image as shown on the right side of Figure 4. It leads to the appearance of a fuzzy area characterized by horizontal white lines. On the top of this fuzzy area, the STM contrast has changed from a rowlike contrast to a quasi hexagonal-like one. On top of Figure 4, the STM contrast remains quasi-hexagonal but changes in intensity due to a modification of the tip apex.

The fuzzy area is consecutive to the change of tip bias, from  $-512$  to  $-1000$  mV. This change has occurred during the scanning of a number of molecules in a single scanning line. It may have induced the switching of the molecules and thus an abrupt change of their geometry. As a consequence, a tip-molecule interaction may have occurred leading to a motion of



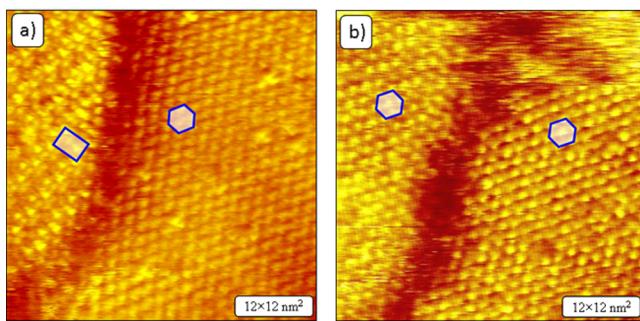
**Figure 4.** STM image ( $7 \times 7 \text{ nm}^2$ ) of an ordered domain of **1o** molecules initially scanned at  $I_t = 12 \text{ pA}$   $U_t = -572 \text{ mV}$  and scanned from the bottom to the top. The bias change of  $-1000 \text{ V}$  in the middle of the image is indicated on the right, together with the specificities of the STM picture.

the molecules under the tip associated with a fuzzy area. Once these molecules are switched and their geometry is optimized under the STM tip, the next molecules may switch at the first moment of interaction with the tip, possibly even at some distance from the tip apex. So no motion of the molecules, directly under the tip, is expected, with the switching being extremely rapid (of the order of 1 ps in solution or in bulk<sup>36,37</sup>). We thus expect a fuzzy area only for the molecules being scanned during the change of bias, as observed. Since we would not expect this kind of fuzzy area for a simple detection of new electronic states of the molecules, Figure 4 confirms the occurrence of switching phenomenon.

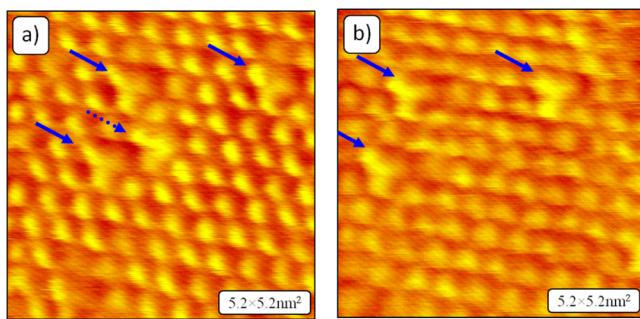
In contrast to **1o** monolayers, it was never possible to switch the domains formed by self-assembled **1c** molecules despite numerous attempts with different tips and bias increasing up to  $\pm 1200$  mV.

**Tip-Induced Switching of Single Molecules.** In addition to the switching of ordered **1o** domains, we performed STM study of tip-induced switching phenomenon of single diarylethene molecules, with these single molecules being embedded in domains of **1c** isomers. The corresponding SAMs were obtained from mixtures of **1c** and **1o** molecules. They contain rowlike domains (**1o** molecules, Figure 2a) coexisting with quasi-hexagonal domains (**1c** molecules, Figure 2a). We first checked that the ordered **1o** and **1c** molecules display different switching behavior under the STM tip as observed already for single component SAMs. Figure 5 shows two different SAM domains: the left part is dominated by the **1o** isomers, while the right presents an organization of **1c** isomers. When the STM tip bias is increased from  $580 \text{ mV}$  (Figure 5a) to  $900 \text{ mV}$  (Figure 5b), some drift is observed, with the bottom of Figure 5a being shifted to the middle of Figure 5b. Nevertheless, it appears clearly that the rowlike STM contrast of the left side of Figure 5a is transformed into a quasi-hexagonal one, visible in the left middle of Figure 5b, with a contrast similar to the one of the right side of Figure 5a and b. Moreover, the vertical tip position of both domains appears identical in Figure 5b, in contrast with Figure 5a. Both features are consistent with a switching of **1o** molecules of the left side into **1c** molecules, with no switching of the **1c** molecules of the right side.

Second, as shown on Figure 6, in each ordered domain of **1c** form, dispersed defects are revealed by the STM images (also



**Figure 5.** STM images of mixed domains of **1o** and **1c** molecules. The rectangle defines the domain of the **1o** molecules with rowlike STM contrast, while the hexagon denotes the domain of the **1c** molecules. (a) Domains imaged at  $I_t = 12\text{ pA}$ ,  $U_t = 580\text{ mV}$ . (b) Domains imaged at  $I_t = 12\text{ pA}$ ,  $U_t = 900\text{ mV}$ .



**Figure 6.** (a) STM image of a **1c** domain formed after deposition of a mixed solution of **1c** and **1o** molecules. Scanning parameters are  $I_t = 12\text{ pA}$ ,  $U_t = 700\text{ mV}$ , scan size  $5.2 \times 5.2\text{ nm}^2$ . The arrows denote single **1o** molecules surrounded by **1c** ones. The dotted arrow is pointing onto a **1o** molecule with different STM contrast compare to the three other ones. (b) STM image of the same **1c** domain (some drift is observed toward the left) at  $I_t = 12\text{ pA}$ ,  $U_t = 700\text{ mV}$  after a preceding increasing of STM bias at  $900\text{ mV}$ . A stable switching of the single molecule from **1o** into **1c** is revealed.

visible in Figure 2a and 5a). Such defects were never observed in domains originating from one component solutions. This

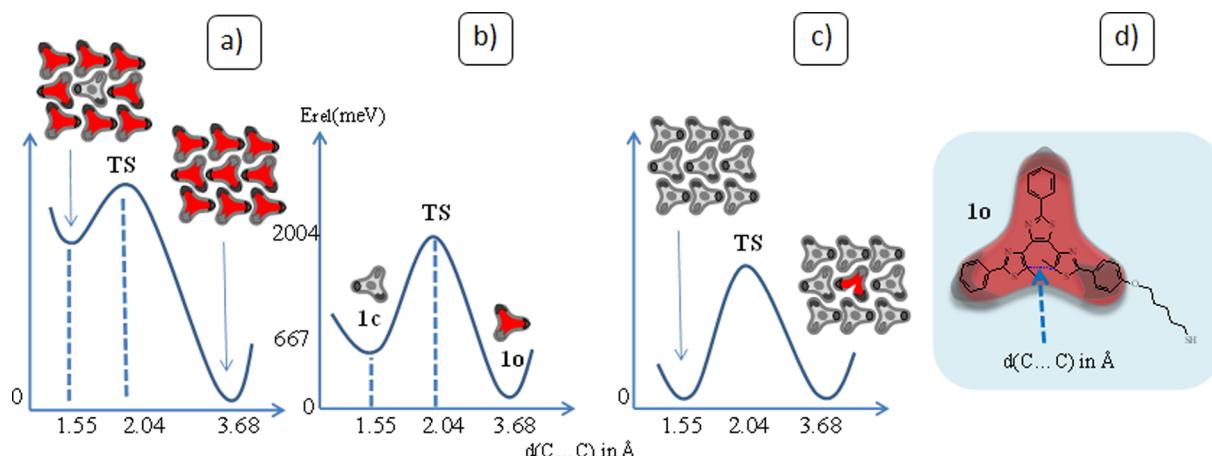
demonstrates that they consist of **1o** molecules dispersed in ordered **1c** domains.

As expected, these molecules in **1o** form are associated with elongated spots (Figure 1b). However, STM contrast appears slightly different for the molecule marked by a dotted arrow in Figure 6a, suggesting a different geometry for one of the four **1o** molecules. Whereas the STM contrast remained stable for a tip bias  $U_t < 900\text{ mV}$ , we succeeded to switch this latter molecule by increasing the bias up to  $900\text{ mV}$ . Surprisingly, this molecule remained stable (being in **1c**) even after lowering of the tip bias (Figure 6b). The density of single **1o** forms being not very large, it remains difficult to precisely determine the proportion of successful switching for isolated **1o** forms in ordered **1c** domains. Based on large scale pictures, we can only estimate the proportion of successful switching events to be comprised between 0.25 and 0.4. This observation contrasts with the **1c** molecules originating from the switching of an ordered domain of molecules in **1o** state. As shown on Figure 3, in an ordered domain, all molecules switch in **1c** form at high tip bias, but all molecules switch back in **1o** form when the tip bias is lowered again.

The fact that single **1o** forms can be switched and are still observed in **1c** forms for STM bias below the threshold value appears consistent with our interpretation of Figure 3 results: the STM contrast jump observed for ordered **1o** forms under applied STM tip bias of 1 V (Figure 3) may be associated with switching between **1o** and **1c** forms instead of corresponding to the detection of new electronic states of the molecules.

## DISCUSSION

Our results evidence switching between **1o** and **1c** forms of TPP-DE molecules self-organized in ordered SAMs on Au(111). The switching mechanism is consequently efficiently disconnected from the influence of the substrate allowing direct study of organic molecules interaction with electric field and light in nanoscale. There is no quenching of the switching thanks to the presence of the alkyl spacer, either under UV irradiation or under STM tip. This feature is different from the switching of azobenzene molecules, which switch only poorly under irradiation with similar spacers, because of steric



**Figure 7.** (a) Expected energetic changes when TPT-DE is surrounded by **1o** molecules. (b) Calculated energy levels (B3LYP/6-311+G(2d,p) calculations) of **1o**, **1c**, and ground state transition state (TS) of TPT-DE molecule as a function of a reaction coordinate ( $d(\text{C}\cdots\text{C})$  distance in Å). (c) Expected energetic changes when TPT-DE is surrounded by **1c** molecules. (d) Schematic representation of **1o** isomer of TPP-DE.

hindrance,<sup>13,14</sup> allowing for a large distance between the functional groups.<sup>17,18</sup>

Our results suggest also that the switching behavior of a single molecule strongly depends on the molecular geometry and on the environment. Either all molecules ordered in **1o** domains (Figure 3) or one isolated **1o** isomer in an all-ordered **1c** domain, with the **1o** isomer being associated with some specific geometry (Figure 6), have been successfully switched by the tip for bias between 900 and 1200 mV. This latter result suggests that the geometry of single molecules may influence the switching mechanism. On the other hand, we also demonstrate that, once switched, the single **1o** molecule within a **1c** ordered domain remains in **1c** form when the tip bias is lowered, in contrast with ordered **1o** domains. This result may be related to the presence of ordered **1c** molecules around the single **1o** molecule.

If we assume that the intermolecular attractive van der Waals interactions are the driving forces to organize a well-ordered SAM, it can be anticipated that intermolecular interactions will change the ground state energies of **1o** and **1c** isomers. Molecules with similar geometry may be better packed and may present larger interactions. As a consequence, single **1o** (respectively **1c**) molecules will be better stabilized when it is surrounded with **1o** (respectively **1c**) molecules with respect to single **1o** (respectively **1c**) molecules immersed in the **1c** (respectively **1o**) environment. On the basis of this assumption, we can expect a change in the equilibrium between **1o** and **1c** states. Van der Waals attraction between two closed-packed methyl groups is of the order of 150 meV<sup>38</sup> and decreases rapidly with the distance. We can thus safely estimate the stabilization for one given molecule surrounded by identical ones to be of the order of some hundreds of meV. This would lead to the change in the ground state energetical diagrams, schematically shown in Figure 7 where the lowest energy is taken to be of 0 eV by definition for each diagram.

Figure 7b displays the energy levels of the **1o**, **1c**, and transition state (TS) for cyclization of a single TPT-DE molecule determined using DFT calculations. Figure 7a shows the expected changes in the energies of the different states of the molecule, when it is surrounded with molecules in **1o** states. The **1c** isomer becomes destabilized with respect to the **1o** one, in agreement with the observed nonstability of **1o** molecules shifted in **1c** ones within ordered **1o** domains (Figure 3). In contrast, for **1o** molecules shifted in **1c** ones in ordered **1c** domains, the equilibrium is expected to be shifted toward the cyclized state. The **1c** state can become stable, in agreement with the experiments (Figure 6). According to the Hammond postulate,<sup>39</sup> it can even be expected that the activation energy for ring closure (**1o** → **1c**) will be lower, if the molecular geometry can be considered as similar, than the one obtained for isolated molecules.

Our results consequently suggest that STM tip-induced switching phenomenon is strongly dependent on the presence of the surrounding molecules. In contrast, the UV irradiation leads to a switching for all the molecules within an ordered **1o** domain, with the induced **1c** isomers remaining stable after irradiation. This observation may be related to a collective switching of all molecules in a same time, which eliminates the destabilizing influence of the neighbors. This is different from the localized switching under STM tip, where **1o** isomers are consecutively switched when the STM tip passes on top. As a consequence, switched **1c** isomers remain localized in **1o**

ordered domains, which leads to a destabilization by the neighbors.

Concerning the switching mechanism, the first observation is that, on these self-organized diarylethene monolayers, no flickering of single molecules under applied bias voltage was observed. Indeed, on both kinds of domains (**1c** and **1o**) scanned at bias less than 900 mV, the STM contrast appears extremely stable. These molecules, being organized in ordered monolayers, do not switch at ambient temperature, in contrast with a number of diarylethene molecules embedded in passive alkylthiol matrices.<sup>29,30</sup> This appears to be in agreement with the calculation of energetic barrier for our single **1o** molecules, equal to 1.3 eV (~50kT), more than 4 times larger than that for the molecule of ref 30 (Figure 7b).

Two main hypotheses can explain the observation of threshold bias for the tip-induced switching, either inelastic tunneling or field induced switching.<sup>2,22</sup> The energy required for over passing the switching barrier for cyclization/cycloreversion can be brought by tunneling electrons if their energy is high enough or molecular switching may be related to molecular modifications due to electric field of the STM tip. The **1o** molecules, in contrast to the **1c** ones, present aromatic moieties which may be associated with local dipoles distributed in the functional group and with a nonzero projection along the STM electric field. This may lead to dielectrophoresis phenomenon in the presence of electric field gradient. A rough calculation with an overestimated dipole of 1D and a gradient of 0.01 V Å<sup>-2</sup> leads to forces of the order of 10<sup>-12</sup> N, too weak to induce significant molecular distortions. However, it is known that the electric field can be highly asymmetric between tip and substrate.<sup>40</sup> This is expected to be the case for our system of diarylethene molecules characterized by a very precise localization of the functional group between tip and substrate, due to the specific umbrella structure (Figure 1). This could lead to particularly high local electric fields in the tunneling gap. The observed stability of **1c** molecules, which do not switch for tip bias as high as 1.2 V, could be associated with the corresponding coplanar geometry of the cores, thus being mainly perpendicular to the electric field, in contrast with **1o** molecules. Flat azobenzene molecules usually also reveal (in UHV and at low temperature) switching occurring for bias largely higher than 1.2 V<sup>19,24</sup> and increasing with the molecule-tip distance.<sup>25</sup>

## CONCLUSION

A light-induced and STM tip-induced switching of photochromic diarylethene molecules self-assembled on Au(111) is demonstrated. It evidences the high efficiency of short spacers consisting of alkyl chains with six carbons, which avoids the quenching of the switching by the metallic substrate. The tip-induced switching occurs for STM bias as low as 1 V and appears to be one of the rare examples of reproducible switching induced by STM tip at air and at ambient temperature. We demonstrate a strong influence of the neighboring molecules for localized switching under the STM tip. If they are composed of ordered **1o** isomers, the switched molecules become unstable in contrast with a surrounding composed of ordered **1c** isomers. This phenomenon is absent for switching under UV irradiation, which evidences collective switching in this latter case. In contrast to the **1o** isomer, the **1c** isomer does not switch at such a low bias. It will be now important to establish if fine control of the scanning conditions, with possibly higher electric field values, can stabilize the

switching phenomenon of **1o** forms and extend it to the **1c** form for a future local “writing/erasing” of these dense adsorbed monolayers.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

SAM, self-assembled monolayer; **1o**, open form of molecule; **1c**, closed form of molecule; TPT-DE, terphenylthiazole-based diarylethenes

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