

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667552>

STM Observation of Open- and Closed-Ring Forms of Functionalized Diarylethene Molecules Self-Assembled on a Au(111) Surface

ARTICLE in JOURNAL OF PHYSICAL CHEMISTRY LETTERS · SEPTEMBER 2011

Impact Factor: 7.46 · DOI: 10.1021/jz200875c

CITATIONS

11

READS

55

9 AUTHORS, INCLUDING:



S. V. Snegir

National Academy of Sciences of Ukraine

16 PUBLICATIONS 64 CITATIONS

SEE PROFILE



Pei Yu

Université Paris-Sud 11

40 PUBLICATIONS 1,103 CITATIONS

SEE PROFILE



Oleksiy Kapitanchuk

M.M.Bogolyubov Institute for Theoretical Ph...

24 PUBLICATIONS 72 CITATIONS

SEE PROFILE



Anne Léaustic

Université Paris-Sud 11

34 PUBLICATIONS 736 CITATIONS

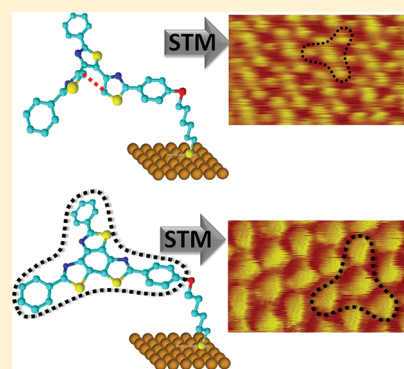
SEE PROFILE

STM Observation of Open- and Closed-Ring Forms of Functionalized Diarylethene Molecules Self-Assembled on a Au(111) Surface

Sergii V. Snegir,^{†,‡,||} Alexandr A. Marchenko,[§] Pei Yu,[⊥] Francois Maurel,[#] Oleksiy L. Kapitanchuk,[∇] Sandra Mazerat,[⊥] Marc Lepeltier,[⊥] Anne Léaustic,[⊥] and Emmanuelle Lacaze^{*,†,||}[†]Institut des NanoSciences de Paris (INSP), CNRS, 4 place Jussieu, 75251 Paris, France^{||}Institut des NanoSciences de Paris (INSP), UPMC Université Paris 6, 4 place Jussieu, 75251 Paris, France[‡]Chuiko Institute of Surface Chemistry, [§]Institute of Physics, and [∇]Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine[⊥]Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, Université Paris Sud 11, 91405 Orsay, France[#]Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR CNRS 7086, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France Supporting Information

ABSTRACT: Ordered self-assembled monolayers (SAMs) of thiolated diarylethene photochromic molecules have been built on a Au(111) surface and characterized by mean of scanning tunneling microscopy (STM) for the first time. It has been revealed that molecules deposited from UV-illuminated (closed-ring isomer) and initial solutions (open-ring isomer) both occupy $4 \times 2\sqrt{3}$ adsorption sites on Au(111) and present a conformation where conjugated parts are parallel to the surface, forming “umbrella-like” structure. On the basis of the distances measured from STM images with intramolecular resolution and on quantum chemical DFT calculations of electronic structure for single molecules, an identical model of molecular packing with a $4 \times 4\sqrt{3}$ unit cell is proposed for both isomers. The variation of internal orbitals between open- and closed-ring isomers leads to significant change of STM contrast, allowing direct identification of each diarylethene isomer using STM images.

SECTION: Surfaces, Interfaces, Catalysis



A promising pathway for the development of recording media stems from a combination of active organic materials grafted on a conductive surface. For this purpose, organic layers have to satisfy two main requirements; a first one is to present light- or field-induced reversible transformation properties; a second one is to be thermally stable with a strong fatigue resistance. Among various organic molecules (rotaxanes, naphthalocyanines, azobenzenes, etc.), diarylethenes with the properties of light-induced reversible transformation are particularly appropriate because of their outstanding thermal stability, good fatigue resistance, high light response, and small structural changes between the open- and closed-ring isomers.^{1–5} On the way of implantation of these molecules into storage devices, two conditions must be fulfilled, a large density of photochromic molecules adsorbed on the substrate and a preservation of their photochromic properties when adsorbed onto the substrate. One solution to avoid quenching of the photochromic reaction is to add an insulating spacer between the photoactive part of molecule and the substrate. This has been achieved with homogeneous SAMs of functionalized azobenzenes^{6–8} on gold substrate, but to the best of our knowledge, only single diarylethene molecules embedded into *n*-alkanethiol monolayers have been characterized on gold substrates up to now.^{9–12} This challenged us to focus on the synthesis of thiolated diarylethene capable of forming ordered domains. We have thus synthesized a

star-shaped diarylethene (Figure 1). Terphenylthiazole-based photochrome is known to show thermally irreversible and photochromic reaction with high fatigue resistance.¹³ To insulate the photoactive site from the gold surface impact and allow, meanwhile, its grafting, one side phenylthiazolyl group was functionalized with a hexyl thiol moiety. Using this functionalized diarylethene, we have demonstrated by STM, for the first time, that homogeneous ordered SAMs can be formed with the two isomers, and we analyzed the corresponding structures.

Solution UV–vis studies show the expected photochromic properties: (i) reversible interconversion between open-ring (**1o**) and closed-ring (**1c**) isomers occurs under light excitations of appropriate wavelengths; (ii) conversion of **1o** to **1c** at the photostationary state (~ 1 min at 320 nm) is estimated to be $\sim 90\%$ by ¹H NMR spectroscopy; (iii) **1c** is found to be thermally stable at room temperature. Using these solutions (the non-illuminated and UV-illuminated one during 1 min with a concentration of 1.1×10^{-7} M), we were able to form SAMs composed either of molecules in their **1o** form or of molecules in their **1c** form.

Received: June 29, 2011

Accepted: August 24, 2011

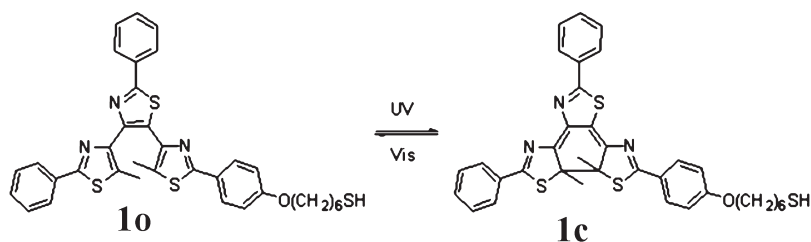


Figure 1. Schematic representation of two isomers of diarylethene photochromic molecules. (Left) open-ring (**1o**) and (right) closed-ring (**1c**) forms. Exposure of the solution to UV ($300 < \lambda_{UV} < 400$ nm) leads to formation of closed-ring isomers, whereas visible light exposure ($480 < \lambda_v < 720$ nm) leads to open-ring isomers.

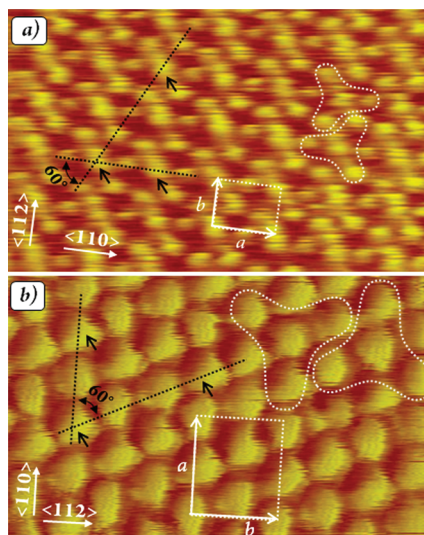


Figure 2. Intramolecular resolution of monolayers on a Au(111) surface. (a) Deposition from nonilluminated solution (**1o**). Scanning parameters: $I_t = 1.74$ pA, $U_t = -716$ mV, 7×4.7 nm². (b) Deposition from UV-illuminated solution (**1c**). Scanning parameters: $I_t = 1.68$ pA; $U_t = -700$ mV, 4.7×3 nm². Equivalent spots are shown by arrows. Star-like dashed lines mark two neighboring molecules.

Quantum chemical calculation of electron density (HOMO level) was performed on the isolated single **1c** molecule because the conjugated part of the molecule is separated from the metallic system of the substrate by a nonconductive alkyl chain. Because negative voltage in STM experiments was used, only HOMO levels of the molecules were taken into account in the discussion. Calculation of conformational changes was done for molecules grafted onto Au₁₉ gold cluster. These calculations were carried out at the density functional theory (DFT) level using the hybrid B3LYP functional with the split valence basis set 6-31G(d).^{14,15} For the gold atoms, the Lanl2dz basis set were used for all calculations carried by the Gaussian 03w program suite.¹⁶

As a first step, we deposited a nonilluminated solution of the molecules onto a reconstructed Au(111) surface (5 min after annealing of the substrate). We expected that the molecules would be adsorbed in the **1o** form. Highly ordered islands were observed, displaying rows oriented along preferential directions. The ordered structure of some islands was interrupted by missing molecular rows or by single vacancies (Supporting Information). The estimated apparent depth of the vacancies was around 25 Å. This value is smaller than the length of an elongated

molecule (~ 30 Å), suggesting that the molecules within the ordered monolayer are tilted with respect to the surface normal.

The monolayer structure was determined from the STM images with molecular resolution (Figure 2a). We note that STM contrast of the **1o** molecules is strongly sensitive to the scanning parameters. At certain values of bias voltage and tunneling current, the bright spots have been transformed into two-dimensional objects having irregular shape (Supporting Information). The arrangement of bright spots can be described by a rectangular cell with basic vectors $a = 11.5 \pm 0.2$ Å and $b = 10 \pm 0.2$ Å (Figure 2a). According to the Au period along the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions and taking into account the fact that molecular rows lie parallel to Au step edges, which are known to be parallel to the $\langle 110 \rangle$ direction,¹⁷ we conclude that packing of molecules corresponds to the $4 \times 2\sqrt{3}$ structure. As a result, the monolayer is commensurate with a Au(111) lattice.

Close inspection of the STM image in Figure 2a reveals important peculiarities, namely, the size and arrangement of spots. Some spots are larger and have elongated shape (shown by white arrows in Figure 2a). The spots with a given shape appear to present repeatability along the dashed lines in Figure 2a. Each second and each fourth large spot in the $\langle 110 \rangle$ direction and in the direction rotated by 60° has a similar shape.

Deposition from UV-illuminated solution led to formation of a monolayer with the **1c** isomers. Close inspection of islands revealed significant differences in STM contrast compared to the SAM of the **1o** isomer; a quasi-hexagonal packing of protrusions was observed (Figure 2b) that appeared less sensitive to the scanning parameters as compared with the SAM of the **1o** isomer.

The measured distances between neighboring protrusions (~ 5 Å) are too small to assign each spot to a single molecule. On the other hand, a close inspection of the STM image in Figure 2b reveals two main peculiarities. First, different shapes can be defined for the protrusions. For instance, some protrusions have almost triangular shape with the apex oriented along a particular direction (marked by arrows). Second, a cell with basic vectors $a = 11.5 \pm 0.2$ Å and $b = 10 \pm 0.2$ Å can be defined, as shown in Figure 2b. We note that this unit cell is the same as that obtained from the STM image in Figure 2a.

In order to interpret the STM contrast in Figure 2b and build a model of molecular packing, we used DFT calculations of geometry parameters of **1c** and **1o** isomers grafted onto Au₁₉ (Figure 3a) and of the spatial distribution of the electron density (surface of the wave functions) for the HOMO level of a single **1c** isomer (Figure 3b). In the most stable conformation of **1c**, the alkyl chain was found in a perpendicular plane with respect to the planar conjugated system and largely tilted from the normal to the Au(111) surface with a tilting angle of 23° . The angle

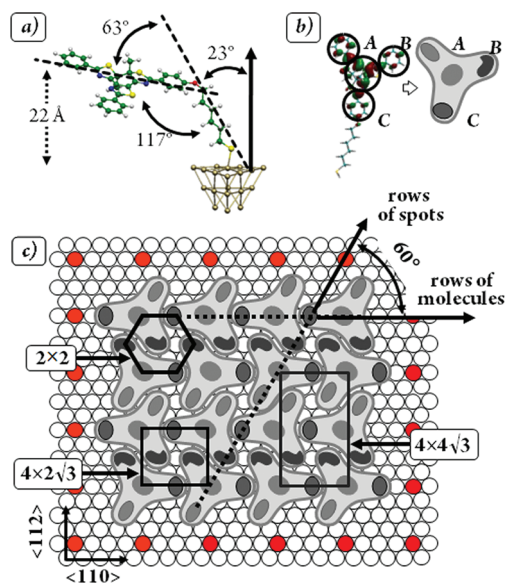


Figure 3. (a) **1c** molecule grafted onto a Au₁₉ gold cluster with denoted angles between the conjugated part, alkyl chain, and surface normal; (b) spatial distribution of the electron density (HOMO level) of a single **1c** molecule with a schematic model of its conjugated part; (c) packing model of the molecules on Au(111).

between the conjugated plane of the molecule and the alkyl chain axis was found to be 117°, so that the conjugated part of a molecule was almost parallel to the Au(111) surface. The geometry of the **1o** molecule grafted onto Au₁₉ is found to be similar. This tilted adsorption geometry appears in good agreement with the measured distance of ~25 Å, associated with the **1o** molecular length, leading us to propose that both **1o** and **1c** isomers adopt an umbrella-like molecular conformation. The HOMO electron density for **1c** is localized on the central part of the molecule and also distributed on the three peripheral lobes (A, B, and C in Figure 3b). It can be schematically depicted with a star-like model (Figure 3b).

The calculated distance between the central part and each peripheral lobe is about 5 Å, similar to that measured between neighboring spots in the STM image in Figure 2b. This appears in agreement with an umbrella-like structure for the molecules. Each spot in Figure 2b corresponds to one of the four electron density areas defined in Figure 3b, and the alkyl chains are invisible in the STM images. On the basis of this, we propose a schematic packing model where molecules form inversely directed rows along the <110> direction (Figure 3c). As a result, each fourth and each second spot along directions defined as rows of spots and rows of molecules corresponds to the same part of the molecule (Figure 3c). This appears perfectly consistent with the peculiarities observed in STM images in Figure 2a and b. The different shapes of spots for the two forms (Figure 2a and b) reflect the difference between molecular orbitals of **1o** and **1c** isomers. The strong variations of the STM contrast of the conjugated part observed for **1o** isomer with the bias voltage are most probably connected to the deformation of the photochromic group of **1o**.¹⁸ In contrast, the quasi-flat conjugated plane of **1c** leads to a quasi-hexagonal network formed by different fragments of neighboring molecules. The model in fact reveals a $4 \times 2\sqrt{3}$ structure for molecular adsorption sites and a $4 \times 4\sqrt{3}$ crystallographic cell for adsorbed molecules (Figure 3c).

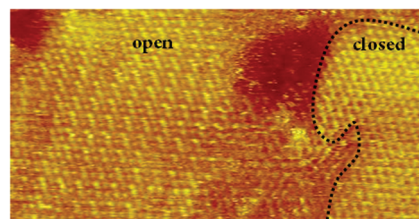


Figure 4. Coexistence of islands formed by photochromic molecules in **1o** (row) and in **1c** (quasi-hexagonal structure) forms. Scanning parameters: $I_t = 1.68$ pA; $U_t = -700$ mV, 25×13 nm².

in both forms. The observed two kinds of contrast are attributed to the two different isomers (**1o/1c**). However, there are several examples of adsorbates that form different metastable structures without conformational (or structural) changes.¹⁹ For example, simple molecules like *n*-alkylthiols being adsorbed on Au(111) form two kind of packing, tilted and rectangular lamella.²⁰ The confirmation of the fact that both structures observed for monolayers correspond to different isomers of the photochromic molecule is presented in Figure 4. The coexistence of two structures shown in Figure 4 was obtained after deposition of UV-illuminated solution. The two structures display the typical STM contrasts of **1o** and **1c** isomers, like the ones shown in Figure 2a and b. Moreover, the scanning axis being parallel to OX, any change of the STM tip can be ruled out in this experiment. We attribute this observation to the coexistence of **1c** and **1o** isomers in the deposited solution. Taking into account the fact that UV–vis light illumination does not lead to 100% phototransformation of diarylethene molecules into the **1c** form, this result is expected. On the other hand, all of our attempts to observe such coexistence in monolayers deposited from initial (nonilluminated) solutions were unsuccessful, in agreement with only **1o** molecules being adsorbed on Au(111) and associated with row-like STM contrast.

In conclusion, use of an all-thiazole-based diarylethene allowed us to prepare and to characterize ordered SAMs of photochromic diarylethenes on Au(111) in both **1o** and **1c** forms. We showed that both isomers form an umbrella-like structure where molecular spacers (hexanethiols) are organized in $4 \times 2\sqrt{3}$ structures. Both isomers present the same structure associated with a $4 \times 4\sqrt{3}$ crystallographic cell.

The STM contrast appears significantly different between both forms due to the variation of molecular orbitals induced by photochromic reaction. This result appears promising for future experiments of SAM switching triggered directly on Au(111). Indeed, in contrast with some alkylthiol-functionalized azobenzene molecules, no steric restriction is expected during the switching of diarylethene molecules²¹ because both molecular forms present the same self-organization on Au(111). Moreover, the STM contrast associated with an internal orbital's variations should allow identification of reversible switching phenomena in SAMs.

■ ASSOCIATED CONTENT

S Supporting Information. NMR and mass spectrometry data of synthesized compounds; details of the monolayer preparation and STM scanning parameters; images of the SAM of the **1o** form under varied STM parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Emmanuelle.lacaze@insp.jussieu.fr.

■ ACKNOWLEDGMENT

We thank Agence Nationale de la Recherche (ANR) for financial support, corresponding to the project ANR-Nanophotoswitch (ANR-07-Nano-025).

■ REFERENCES

- (1) Chijung, Y.; Jungmok, Y.; Jeonghun, K.; June, H.; Eunyoung, K. Photochromic Fluorescence Switching From Diarylethenes and Its Applications. *J. Photochem. Photobiol., C* **2009**, *10*, 111–129.
- (2) Raymo, F. M.; Tomasulo, M. Electron and Energy Transfer Modulation With Photochromic Switches. *Chem. Soc. Rev.* **2005**, *34*, 327–336.
- (3) Kawata, S.; Kawata, Y. Three-Dimensional Optical Data Storage Using Photochromic Materials. *Chem. Rev.* **2000**, *100*, 1777–1788.
- (4) Xie, N.; Chen, Y.; Yao, B.; Lie, M. Photochromic Diarylethene for Reversible Holographic Recording. *Mater. Sci. Eng. B* **2007**, *138*, 210–213.
- (5) Pu, S.; Yao, B.; Liu, G.; Wang, Y. Polarization Multiplexing Holographic Optical Recording of a New Photochromic Diarylethene. *Opt. Eng.* **2008**, *47*, 030502.
- (6) Pace, G.; Ferri, V.; Grave, C.; Elbing, M.; von Hänisch, C.; Zharnikov, M.; Mayor, M.; Rampi, M. A.; Samori, P. Cooperative Light-Induced Molecular Movements of Highly Ordered Azobenzene Self-Assembled Monolayers. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 9937–9942.
- (7) Smaali, K.; Lenfant Karpe, S.; Oafrain, M.; Blanchard, P.; Deresmes, D.; Godey, S.; Rochefort, A.; Roncali, J.; Vuillaume, D. High On–Off Conductance Switching Ratio in Optically-Driven Self-Assembled Conjugated Molecular Systems. *ACS Nano* **2010**, *4*, 2411–2421.
- (8) Bléger, D.; Ciesielski, A.; Samori, P.; Hecht, S. Photoswitching Vertically Oriented Azobenzene Self-Assembled Monolayers at the Solid-Liquid Interface. *Chem.—Eur. J.* **2010**, *16*, 14256–14260.
- (9) He, J.; Chen, F.; Liddell, P.; Andreasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; et al. Switching of a Photochromic Molecule on Gold Electrodes: Single-Molecule Measurements. *Nanotechnology* **2005**, *16*, 695–702.
- (10) Katsonis, N.; Kudernac, T.; Walko, M.; J. van der Molen, S.; J. van Wees, B.; Feringa, B. L. Reversible Conductance Switching of Single Diarylethenes on a Gold Surface. *Adv. Mater.* **2006**, *18*, 1397–1400.
- (11) J. van der Molen, S.; van der Vegte, H.; Kudernac, T.; Amin, I.; Feringa, B. L.; J. van Wees, B. Stochastic and Photochromic Switching of Diarylethenes Studied by Scanning Tunnelling Microscopy. *Nanotechnology* **2006**, *17*, 310–314.
- (12) Battaglini, N.; Klein, H.; Hortholary, C.; Coudret, C.; Maurel, F.; Dumas, Ph. STM Observation of a Single Diarylethene Flickering. *Ultramicroscopy* **2007**, *107*, 958–962.
- (13) Nakashima, T.; Atsumi, K.; Kawai, S.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. Photochromism of Thiazole-Containing Triangle Terarylenes. *Eur. J. Org. Chem.* **2007**, 3212–3218.
- (14) Becke, A. D. Density Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (15) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.
- (16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- (17) Mäkinen, A. J.; Long, J. P.; Watkins, N. J.; Kafafi, Z. H. Sexithiophene Adlayer Growth on Vicinal Gold Surfaces. *J. Phys. Chem. B* **2005**, *109*, 5790–5795.
- (18) Irie, M. Photochromism of Diarylethene Molecules and Crystals. *Proc. Jpn. Acad., Ser. B* **2010**, *86*, 472–483.
- (19) Anselmetti, D.; Baratoff, A.; Güntherod, H.-J.; Delamarche, E.; Michel, B.; Gerber, Ch.; Kang, H.; Wolf, H.; Ringsdorf, H. Domain and Molecular Superlattice Structure of Dodecanethiol Self-Assembled on Au(111). *Europhys. Lett.* **1994**, *27*, 365–370.
- (20) Vericat, C.; Vela, M. E.; Salvarezza, R. C. Self-Assembled Monolayers of Alkanethiols on Au(111): Surface Structures, Defects and Dynamics. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3258–3268.
- (21) Klajn, R.; Stoddart, J. F.; Grzybowski, B. A. Cheminform Abstract: Nanoparticles Functionalised With Reversible Molecular and Supramolecular Switches. *Chem. Soc. Rev.* **2010**, *39*, 2203–2237.