DOI: 10.1002/anie.200702794

Silicon Surface Chemistry

A Stable Room-Temperature Molecular Assembly of Zwitterionic Organic Dipoles Guided by a Si(111)-7×7 Template Effect[**]

*Younes Makoudi, Madjid Arab, Frank Palmino, Eric Duverger, Christophe Ramseyer, Fabien Picaud, and Frédéric Chérioux**

The adsorption of functional molecules on surfaces plays a vital role in the emerging field of nanoelectronics.[1] In this context, molecular and supramolecular ordering, which are key steps in the development of complexes architectures, are controlled by a balance between intermolecular forces and molecule–substrate interactions.[2] This restructuring is often driven by cooperative molecule–substrate interactions involving many molecules and is not directly related to the shape of the individual molecules.

The deposition of organic molecules and preservation of their entire skeleton, especially on semiconductor surfaces, is still a challenge, although much progress has been made in the development of metallic surface-based devices with organic molecules at low temperature, where the molecule–surface interactions are weak and diffusion remains low.[3] However, the use of metallic substrates is less attractive for potential applications as semiconductors, especially in the field of nanoelectronics.

The deposition of molecules on a semiconductor surface at room temperature with complete control of the adsorption site and without altering their aromatic behavior is still a challenge in view of the development of complex architectures.[4] Polanyi and co-workers, for example, have shown that the adsorption of chlorododecane on Si(111)-7×7 at room temperature leads to the formation of a bistable dimeric corral of self-assembled molecules and have demonstrated on/off electronic switching of a single silicon adatom using molecular field effects.[5] These authors have also described a new strategy for preventing the dissociation of haloalkanes on Si(111)-7×7 up to 373 K. This stability is ensured thanks to the formation of dimeric circular corrals that override the molecule–substrate interactions.[5] Herein, we propose a new concept for the room-temperature deposition of π-conjugated organic molecules, without any modification of their electronic structure, at specific adsorption sites on the surface of the semiconductor Si(111)-7×7 by adsorbing π-conjugated zwitterionic molecules on this semiconductor surface. The presence of a negative charge on the target molecules offsets the electrophilic character of the Si(111)-7×7 adatoms and preserves the π skeleton of the organic molecules after deposition. The half-cells of Si(111)-7×7 act as a template that guides the molecular assembly of achiral molecules, as shown by the induction of chirality in the modified areas. Experimental STM images as well as theoretical calculations are in perfect agreement with the proposed concept.

The electronic properties of molecules are often modified during their adsorption on a Si(111)-7×7 surface. Indeed, Si−C σ bonds are usually formed by reaction of the electron-deficient silicon adatoms of Si(111)-7×7 with the electron-rich carbon atoms of the organic molecules.[6] We propose an original concept to prevent these cycloadditions by using the negative site of a zwitterionic molecule as a shield (by electrostatic interactions) for the molecule on the electrophilic adatoms of Si(111)-7×7. Zwitterionic molecules are ideal candidates since they are neutral but carry formal positive and negative charges on different atoms. In principle, the surface should offset its electron deficit with the negative charge of the molecules instead of its extended electron-rich π-conjugated system. To prove our concept, we synthesized 4-methoxy-4′-(3-sulfonatopropyl)stilbazolium (MSPS), which is terminated by a negatively charged sulfonato (SO_3^-) group (Figure 1a), as a model zwitterionic organic molecule. All experiments were carried out in an ultra-high vacuum chamber with a pressure lower than 2×10^{-10} mbar. The molecules were sublimed from a Knudsen cell at 390 K onto the Si(111)-7×7 surface at room temperature. STM images were acquired in the usual constant-current mode at room temperature.

Figure 1b,c shows STM images taken with two opposite polarities, with atomic resolution, of both the Si(111)-7×7 reconstruction and the adsorbed molecules. One half-cell exhibits a novel threefold star at the center of the image for both filled and empty states. Each arm of the star consists of two matching protrusions, one of which is more intense than the other. The distance between the centers of the two paired protrusions (0.67 nm) is much shorter than the length of a free MSPS molecule (1.3 nm). This difference can be explained by a conformational change caused by MSPS–substrate interactions (see below). Three protrusions are located exactly on top of corner adatoms and the other three are found between a rest-atom and an adjacent center adatom. In the filled states (Figure 1b), the brighter protrusions are situated exactly on top of corner adatoms, whereas in the empty states (Fig-

---

[*] Y. Makoudi, Dr. M. Arab, Dr. F. Palmino, Dr. E. Duverger, Dr. F. Chérioux
Institut FEMTO-ST/LPMO, UMR CNRS 6174
32, Avenue de l'Observatoire, 25044 Besancon cedex (France)
Fax: (+33) 8185-3998
E-mail: frederic.cherioux@femto-st.fr
Homepage: http://www.femto-st.fr

Prof. Dr. C. Ramseyer, Dr. F. Picaud
Laboratoire de Physique Moléculaire, UMR CNRS 6624
16 Route de Gray, 25030 Besancon cedex (France)

[**] The authors thank Dr. C. Joachim (CEMES, Toulouse, France) for fruitful discussions. This work was supported financially by the Communauté d'Agglomération du Pays de Montbéliard.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

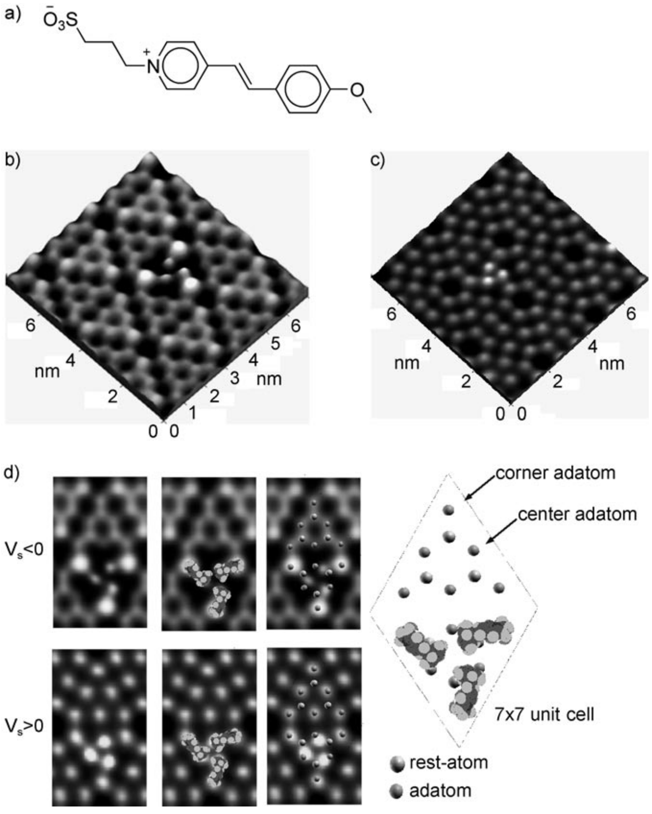

Figure 1. a) Molecular structure of MSPS. b,c) High-resolution, room-temperature STM images ($7\times7\,nm^2$) of MSPS deposited on Si(111)-7×7 in the filled state (sample negative bias voltage: $V_s=-1.6$ V) and in the empty state (sample positive bias voltage: $V_s=+1.9$ V), respectively. d) Both the above STM images with superimposed ball and structural models showing the assembly of three MSPS molecules. The structural model of Si(111)-7×7 (right) with a superimposed ball model of the self-assembly of three MSPS molecules summarizes the STM images in the two polarities.

ure 1 c) the brighter protrusions appear between a rest-atom and a center adatom. The sulfonato moiety in MSPS possesses a negative charge, and the methoxy group is electron-poor owing to conjugation with the pyridinium ring. Therefore, the intense protrusions observed in the filled states on top of corner adatoms can be attributed to the sulfonato groups (Figure 1 b) and the intense protrusions observed in the empty states between a rest-atom and an adjacent center adatom to the methoxy groups (Figure 1 c).

The position of the MSPS molecules in this assembly can be determined unequivocally thanks to the use of two different polarities when recording the STM images. The star shape in each 7×7 half-cell can be attributed to the assembly of three MSPS molecules by molecule–substrate interactions, which change the conformation of the three molecules from *trans* to *cis*. The proposed structural model of the 7×7 assembly is superimposed on the STM images in Figure 1 d.

At very low molecule coverage this adsorption and formation of star shapes occurs preferentially on the faulted half-cell, which is known to be more reactive (Figure 1 b).[7] The occupied half-cells only contain three MSPS molecules, as described above, which means that this assembly process implies high molecular diffusion onto the surface at room temperature.

The assembly of three molecules into this particular star shape can be explained by the template effect of the surface, which possesses threefold symmetry. This assembly process is probably guided by the template effect of the substrate. Moreover, the intensities of the protrusions at each polarity are not particularly affected by a change of the bias voltage, which means that they are not likely to be due to the well-known formation of C–Si σ bonds between adsorbed molecules and a substrate.[6,8]

The nature of MSPS adsorption on a Si(111)-7×7 surface has been investigated by ab initio calculations at the extended density functional theory (DFT) level using the Vienna Ab Initio Simulation Package (VASP).[9] To simulate the entire system (MSPS + Si(111)-7×7) we first optimized the geometry of one free MSPS molecule in vacuo in the *cis* conformation using Gaussian 03 at the Hartree–Fock 6-31G(d) level of theory.[10] Three of these optimized molecules were then positioned in the *cis* conformation thanks to the help of the high-resolution STM images discussed above. The adsorption energy was then varied at room temperature for different assemblies of molecules and surface distances (d), which correspond to the separation between the Si adatoms and sulfur atom of the sulfonato group. Finally, the local densities of states (LDOS) were determined at each point for a constant current and at bias voltages of -2 and $+2$ V, respectively, with the Tersoff–Hamann scheme.[11]

The adsorption energy for the entire system is depicted in Figure 2 a as a function of the distance d. The equilibrium distance, which corresponds to the energy minimum of -2.66 eV (-0.887 eV per molecule) is close to 0.26 nm, in agreement with a physisorbed state. The LDOS images calculated at the equilibrium distance compare well with the experimental STM images (Figures 2 b and 2 c). Figure 2 d shows the DOS of the whole stable system at $d=0.26$ nm. The two weak interactions observed correspond to a very small electronic transfer from the sulfonato groups to the corner adatoms and from methoxy moieties to Si atoms, respectively, which means that there is no bond formation between any single oxygen atom and a silicon adatom. An interaction between the molecular assembly and the substrate nevertheless exists, but it depends only on the distance, in agreement with a weak electrostatic interaction between the oxygen atoms of the sulfonato moieties and the electrophilic Si adatoms. These results confirm that we have developed a new strategy for stabilizing zwitterionic π-conjugated molecules on a Si(111)-7×7 surface by taking advantage of the electrostatic interactions between silicon adatoms and the anionic groups of these molecules. These interactions are strong enough to stabilize the molecular assembly at room temperature and produce a template effect whereby the Si(111)-7×7 surface imposes a *cis* conformation on the MSPS molecules in the Si(111)-7×7 half-cells.

Figure 3 shows two half-cells, each of which contains an assembly of three MSPS molecules that is a mirror image of the other reflected in a mirror plane. This means that the threefold stars are chiral even though free MSPS is achiral.

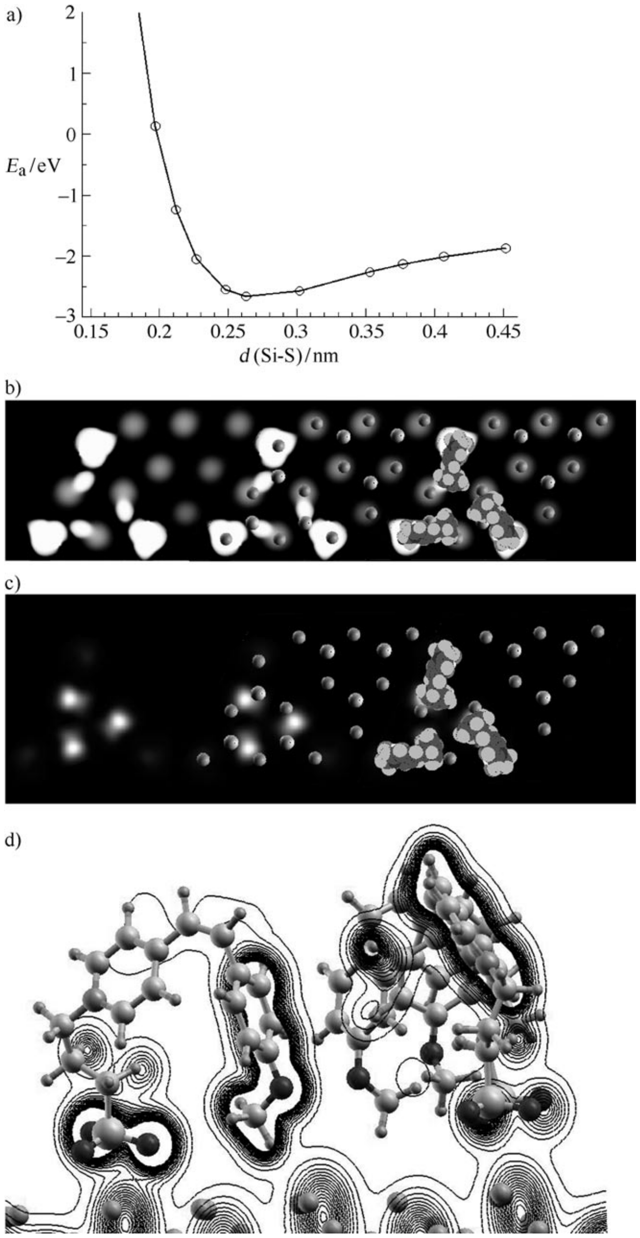

Figure 2. a) Adsorption energy as a function of distance. b, c) Integrated LDOS images of three MSPS molecules on Si(111)-7×7 (left) and with a superimposed ball model (right) with a negative bias voltage (−2 V, b) and a positive bias voltage (+2 V, c). d) A side view of the density of states of MSPS adsorbed on Si(111)-7×7 showing weak molecule–substrate interactions.

The chirality of these molecular assemblies can be explained by the template effect of the Si(111)-7×7 surface. The sulfonato group can swivel upon the corner adatom, whereas the surface forces the methoxy moieties to be fixed between a rest-atom and a center adatom (Figure 3). The two possible enantiomers in this case, which are formed by a clockwise or anticlockwise folding, are termed the (*P*)-enantiomer and the (*M*)-enantiomer, respectively. Most previous studies regarding chiral structures have been concerned with metal surfaces,[12] and relatively little work has been reported for semiconductor surfaces.[13] However, the chirality induced in these previous studies on semiconductors is due to the formation of at least one stereogenic center after the chemisorption, for example by cycloaddition, of molecules on silicon or germanium atoms. The results reported here show, to the best of our knowledge, the first example of chiral assembly of achiral molecules on Si(111)-7×7.

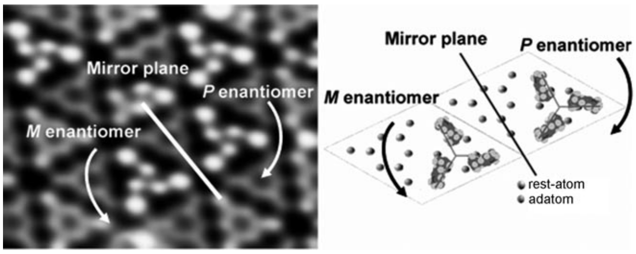

Figure 3. A room-temperature STM image ($V_s = -2.1$ V, 7×9 nm^2) showing the two enantiomers of the chiral supramolecular self-assembly of MSPS deposited on Si(111)-7×7 (left) and a schematic model of these two enantiomers on Si(111)-7×7 (right).

In conclusion, the results reported herein are remarkable from several different points of view, especially the molecular assembly of organic dipoles at room temperature, the chirality of the assembly, and the stability and conservation of the π-conjugated skeleton on the semiconductor surface at room temperature. This zwitterionic strategy, where the sulfonato group acts as an electrostatic shield that protects the π skeleton of organic molecules against the dangling bonds of the semiconductor surface, may become an important method for the deposition of π-conjugated molecules.

Experimental Section

The Si(111) substrate was heated under ultra-high vacuum by direct current. Clean Si(111)-7×7 surface reconstruction was obtained by repeated cycles of heating at 1200 °C and slow cooling to room temperature. Deposition of the MSPS molecules from an Mo crucible onto the sample at room temperature was performed at 120 °C and a pressure lower than 10^{-10} mbar.

Electron–ion interactions were described using the projector-augmented wave (PAW) method, which was expanded within a plane-wave basis-set up to a cut-off energy of 400 eV.[14] Electron exchange and correlation effects were described by the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE GGA) exchange-correlation functional.[15] The Brillouin zone was sampled using the gamma point only. Simulations were performed using a volume box (21.67 nm^3) containing one 7×7 unit cell (DAS model with four silicon layers).[16] The adsorption energy was calculated from the difference between the total energy of the entire system (substrate + molecules) when interacting and the sum of the total energies of each free component.

All synthetic procedures and calculations are fully described in the Supporting Information.

Received: June 25, 2007
Revised: September 13, 2007

Keywords: chirality · scanning probe microscopy · semiconductors · surface chemistry · zwitterions

[1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541–548.

[2] a) J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671–679; b) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, *Nature* **2002**, *417*, 384–387.

[3] a) F. Rosei, M. Schunack, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Science* **2002**, *296*, 328–330; b) J. A. Theobald, N. S. Oxtoby, N. A. Philipps, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029–1031; c) L.-J. Wan, *Acc. Chem. Res.* **2006**, *39*, 334–342.

[4] a) G. Kirczenow, P. G. Piva, R. A. Wolkow, *Phys. Rev. B* **2005**, *72*, 245306; b) I. R. McNab, J. C. Polanyi, *Chem. Rev.* **2006**, *106*, 4321–4354; c) P. G. Piva, G. A. DiLabio, J. L. Pitters, J. Zikovsky, M. Rezeq, S. Dogel, W. A. Hofer, R. A. Wolkow, *Nature* **2005**, *435*, 658–661.

[5] a) K. R. Harikumar, J. C. Polanyi, P. A. Sloan, S. Ayissi, W. A. Hofer, *J. Am. Chem. Soc.* **2006**, *128*, 16791–16797; b) S. Dobrin, K. R. Harikumar, R. V. Jones, N. Li, I. R. McNab, J. C. Polanyi, P. A. Sloan, Z. Waqar, J. Yang, S. Ayissi, W. A. Hofer, *Surf. Sci.* **2006**, *600*, 43–47.

[6] F. Tao, G. Q. Xu, *Acc. Chem. Res.* **2004**, *37*, 882–893.

[7] H. Tomimoto, T. Takehara, K. Fukawa, R. Sumii, T. Sekitani, K. Tanaka, *Surf. Sci.* **2003**, *526*, 341–350.

[8] a) P. A. Sloan, R. E. Palmer, *Nature* **2005**, *434*, 367–371; b) R. J. Hamers, S. K. Coulter, M. D. Ellison, J. S. Hovis, D. F. Padowitz, M. P. Schwartz, C. M. Greenlief, J. N. Russell, Jr., *Acc. Chem. Res.* **2000**, *33*, 617–624.

[9] a) G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558–561; b) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.

[10] a) J. B. Foresman, A. Frisch in *Exploring Chemistry with Electronic Structure Methods* (2nd ed. Gaussian Inc.), Pittsburgh, PA, **1996**; b) M. J. Frisch, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, **2004**.

[11] J. Tersoff, D. R. Hamann, *Phys. Rev. B* **1985**, *31*, 805–813.

[12] a) S. Stepanow, N. Lin, D. Payer, U. Schlickum, F. Klappenberger, G. Zoppellaro, M. Ruben, H. Brune, J. V. Barth, K. Kern, *Angew. Chem.* **2007**, *119*, 724–727; *Angew. Chem. Int. Ed.* **2007**, *46*, 710–713; b) R. Fasel, M. Parshau, K.-H. Ernst, *Angew. Chem.* **2003**, *115*, 5336–5339; *Angew. Chem. Int. Ed.* **2003**, *42*, 5178–5181; c) M. Böhringer, K. Morgentern, R. Car, *Phys. Rev. Lett.* **1999**, *83*, 324–327; d) M.-C. Blüm, E. Cavar, M. Pivetta, F. Pattey, W. D. Schneider, *Angew. Chem.* **2005**, *117*, 5468–5471; *Angew. Chem. Int. Ed.* **2005**, *44*, 5334–5337.

[13] a) G. P. Lopinski, D. J. Moffat, D. D. M. Wayner, R. A. Wolkow, *Nature* **1998**, *392*, 909–911; b) J. W. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 5016–5017; c) J. W. Kim, M. Carbone, J. H. Dil, M. Tallarida, R. Flammini, M. P. Casaletto, K. Horn, M. N. Piancastelli, *Phys. Rev. Lett.* **2005**, *95*, 107601.

[14] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.

[15] J.-P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[16] K. D. Brommer, M. Needels, B. E. Larson, *Phys. Rev. Lett.* **1992**, *68*, 1355–1359.