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Abstract	The development of nanomachines is a key challenge for the future electronics, energy conversion, biology, and medicine. Semiconductor surfaces have been one of the basic elements of many technologies for 40 years. However, despite their promising interest, semiconductor-based nanomachines are almost unstudied. In this work, a panel of single nanomachines-based semiconductor surfaces is described. The role of molecule–surface interaction for the development of nanomachines is highlighted.	
Keywords (separated by '-')	Molecular machines - STM - Semiconductors - Activation - Molecular interaction - Switch	

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Single Molecular Machines on Semiconductor Surfaces

Younes Makoudi, Frank Palmino and Frédéric Chérioux

Abstract The development of nanomachines is a key challenge for the future electronics, energy conversion, biology, and medicine. Semiconductor surfaces have been one of the basic elements of many technologies for 40 years. However, despite their promising interest, semiconductor-based nanomachines are almost unstudied. In this work, a panel of single nanomachines-based semiconductor surfaces is described. The role of molecule–surface interaction for the development of nanomachines is highlighted.

Keywords Molecular machines · STM · Semiconductors · Activation · Molecular interaction · Switch

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1 Introduction

The formation and control of artificial molecular nanomachines adsorbed onto a surface are two of the most promising challenges in nanotechnology [1–6]. Most of the studies on surface-mounted nanomachines by STM have been achieved on noble metal substrates. Nevertheless, from the viewpoint of future hybrid organic/inorganic molecular devices, while molecular interaction with metallic substrates is better understood, semiconducting interfaces are natural choices due to their wide-range acceptability by the industry. In this chapter, we propose to review some proof of concept of single molecular machines on semiconductor surfaces. The development and fabrication as well as the activation of nanomachines are described. The role of molecule–surface interaction is described in detail due to its important role for the achievement of molecular machines on semiconductors.

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2 Molecular Motions

2.1 1D Molecular Rotation

Semiconductor surfaces in ultra-high vacuum are well known to interact strongly with organic molecules. For example, on Si surfaces, several dangling bonds can lock the molecules adsorbed onto the surface. To circumvent this problem, we need to use a less reactive surface. In the case of molecular rotation, one of the possibilities is to anchor the molecule to only one dangling bond acting as a rotation axis. This idea has been developed on Si(100)-2 × 1 surface with metal phthalocyanine molecules (MPc) [7, 8]. The authors have shown by STM that on the Si(100)-2 × 1 reconstruction, CoPc and CuPc are bound to the surface via their central metal atom. In these conditions, the molecules, parallel to the surface, are in a stationary position (Fig. 1a). To induce a rotation via a single dangling bond, the surface must be, in a first step, passivated. The Si(100)-2 × 1 H-passivated surface is achieved by the exposure of the initial substrate to 1 × 10^{-6} Torr of hydrogen for 10 min with a hot tungsten filament. Subsequently, isolated dangling bonds are created by feedback control lithography (FCL) using the STM tip to induce the desorption of one hydrogen atom (Fig. 1b).

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After evaporation of MPc onto this surface, the 4-lobe structures previously observed were not detected but circular depression with a double diameter of CoPc is observed. This is assigned to one MPc molecule bound to the surface through its outer benzene ring and rotating as depicted in Fig. 1c. A molecular modeling study confirmed that bonding between the benzene ring and the surface induces the lowest adsorption energy. Due to the hydrogen-passivated surface, the adsorption energy difference for different angles around the rotation axis is negligible compared to kT. In these conditions, the CoPc molecule rotates easily around the benzene ring.

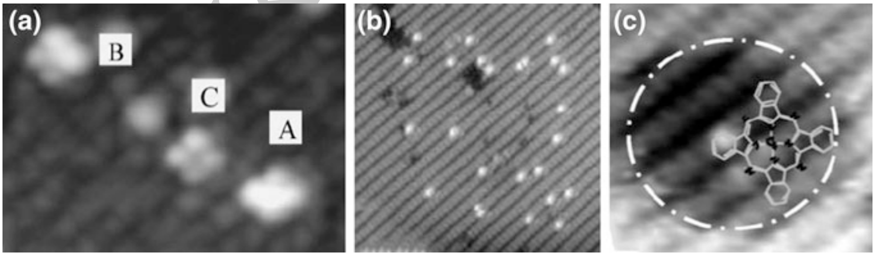

Fig. 1 **a** STM CoPc image on Si(100)-2 × 1 surface ($Vs = -2.5$ V, $It = 0.2$ nA) showing three different configurations. No rotation is observed. **b** Si(100)-2 × 1:H surface where the *bright* protrusions correspond to dangling bonds made by FCL ($Vs = -3$ V, $It = 0.2$ nA). **c** Schematic view of CoPc anchored to a dangling bond via one of its benzene rings and rotated around this benzene ring ($Vs = -2$ V, $It = 0.2$ nA). Reprinted with permission from [8]

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2.2 1D Molecular Sliding on InSb

Thermally activated motion often leads to a molecular Brownian motion [4]. To control the direction of the motion, the use of 1D periodic surfaces or step edges is a good choice to induce a linear movement. Contrary to metallic surfaces, which offer few possibilities to obtain 1D periodic surfaces (Cu–O/Cu [9] or Au(111) [10]), semiconductor or metal–semiconductor interfaces possess a high number of 1D surface reconstructions [11–14]. Few of them have been tested for molecular motion; nevertheless, the results obtained on InSb or SmSi are very convincing. In each case, we can note that the adsorption site as well as the matching between the surface unit-cell dimension and the molecular dimensions is a crucial factors to obtain good conditions for the achievement of matter transport.

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The InSb(001) c(8 × 2) reconstructed surface is strongly anisotropic and constituted by In chains in the top adlayer. Molecular diffusion along the chains has been observed with PbPc [15, 16], a non-planar phthalocyanine, as well as CuPc [17], a planar molecule. On the CuPc/InSb(001) interface, CuPc molecules are adsorbed along the step edges and on the terraces (Fig. 2).

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Along the step edges, in the [1-10] direction, the molecules are very weakly bound to the surface and appear like two protrusions, while in the [110] direction, the molecules are strongly bound to the surface and no change is observed after several scans. On terraces, some noisy horizontal lines indicate mobile molecules while CuPc molecules appear as eight separated protrusions centered over the bright substrate rows, which correspond to the topmost In atoms. CuPc molecules form chains constituted by a few molecules, which diffuse between two frames. These room temperature STM observations show the high mobility of the molecules along the [110] direction. Based on symmetry considerations, an adsorption model is proposed in Fig. 3.

Two interactions are suggested between molecules and the surface: one between the Cu atom and the In adlayer atom, and the second one between the nitrogen atoms and the In adlayer atom.

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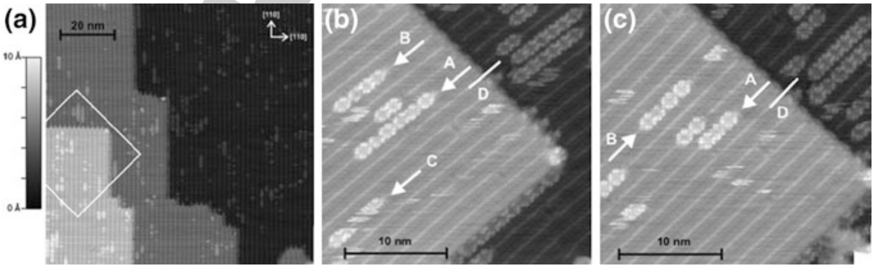

Fig. 2 **a** Large-scale STM image of CuPc/InSb(001) interface(100)c(8 × 2)(100 × 100 nm^2, *Vs* = −1 V, *It* = 0.3 nA). The *white frame* indicates the area scanned and shown in **b** and **c**. **b** and **c** show CuPc molecular diffusion between two STM frames (30 × 30 nm^2, *Vs* = −1 V, *It* = 0.15 nA). Reprinted with permission from [17]

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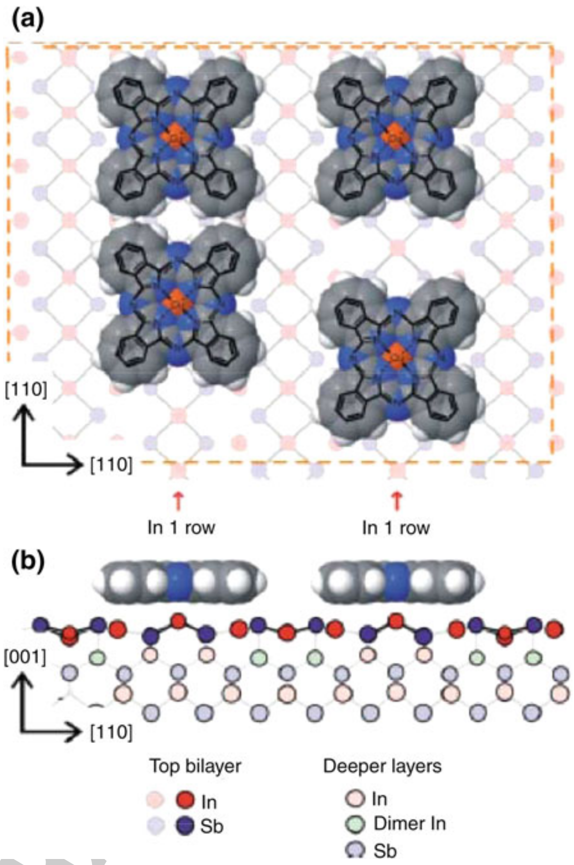

Fig. 3 Adsorption model **a** *top view* and **b** *side view* of CuPc on InSb(001)c(8 × [illegible] reconstruction. The copper atom is always positioned over the In adlayer atom. A major interaction is possible between In and nitrogen atoms. Reprinted with permission from [17]

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2.3 1D Molecular Sliding on Rare Earth Silicides

Due to their low lattice mismatch and their valence changes, rare earth silicides on Si(111) induce a high number of reconstructions depending on rare earth coverage and annealing temperature. In particular, the SmSi(111) interface possesses a complex surface phase diagram with four different 1D reconstructions in the sub-monolayer range (Fig. 4) [18]. These reconstructions are based on a combination of Si honeycomb chain channels (HCCs), Si Seiwatz chains, and Sm rows. They appear like large stripes on the STM images (Fig. 5 b, c). The main interest of these reconstructions with similar electronic properties is the possibility to adapt the periodicity of the unit cell (×3, ×5, ×7, or ×8) to the molecular dimensions.

The 1,4-di(9-ethynyltriptycene)benzene molecule (DETB) (Fig. 5a) has been used to study the directional molecular sliding on the (8 × 2), the (5 × 1), and the (7 × 1) reconstructions described in Fig. 5 b–e [13, 19]. This molecule has been chosen because the distance of 1.64 nm between two Sm rows of SmSi interface corresponds to the length of the molecule.

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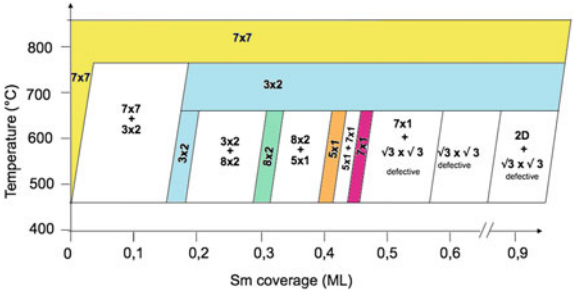
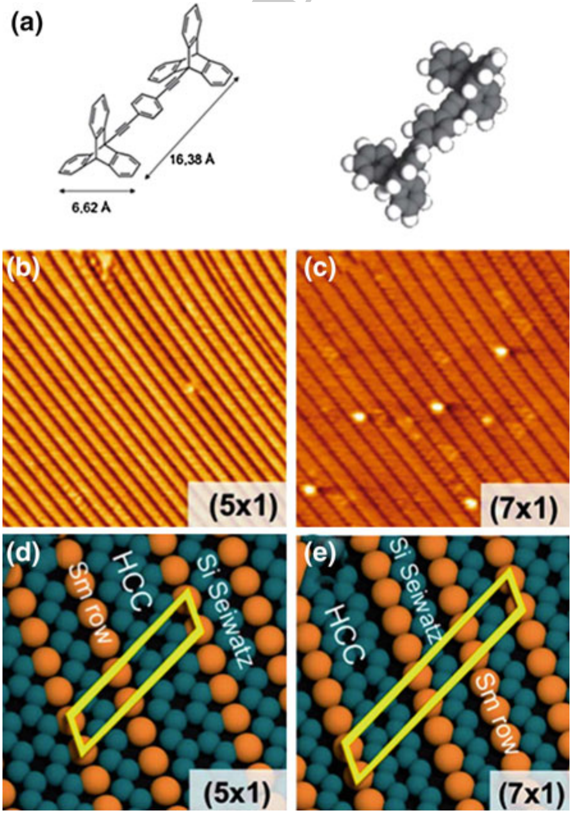


Fig. 4 Surface phase diagram of SmSi(111) interfaces. The (3 × 2), (8 × 2), (5 × 1), and (7 × 1) are 1D reconstructions in the submonolayer Sm coverage

5 **a** The 1,4-di ynyltriptycene)benzene molecule (DETB). **b–e** STM images (32 × 32 nm^2, $Vs = 2$ V, $It = 0.18$ nA) and structural models of both (5 × 1) and (7 × 1) reconstructions. Reprinted with permission from [19]



On the SmSi(111)-5 × 1 reconstruction at room temperature, the DETB appears on STM images like two paired protrusions attributed to the two triptycene wheels. All the DETB molecules are adsorbed onto the large stripes and are self-aligned along the [1-10] direction with the triptycene wheels above two Sm chains as described in Fig. 6b. Some noisy lines, corresponding to molecular diffusion, are

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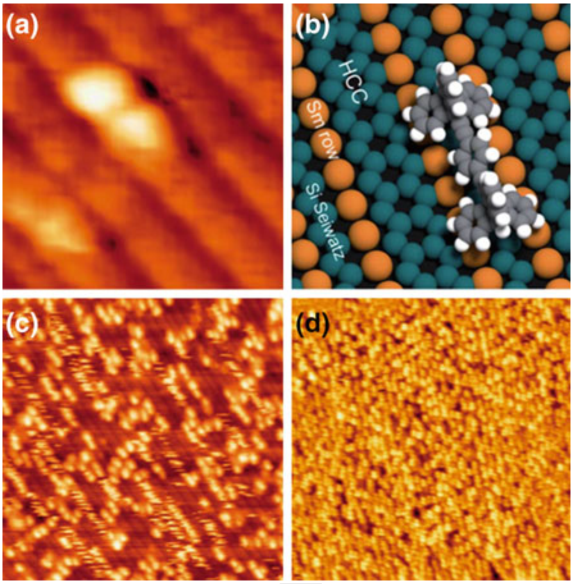

Fig. 6 **a** Isolated DETB molecule on SmSi-(5 × 1) [illegible] 7 × 7 nm^2, $Vs = 1.8$ V, $It = 0.7$ nA). **b** DETB adsorption model on (5 × 1) reconstruction. **c** Interface for 0.3 monolayer molecule coverage. Noisy stripes correspond to DETB diffusion along Sm rows. **d** Interface for 0.9 monolayer molecule coverage showing the self-alignment after the surface diffusion. Reprinted with permission from [19]

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observed along the stripes and prove that the movement is guided by a strong template effect of the surface.

The study of the template effect of the surface on the adsorption and the diffusion of DETB molecules has been done by Bouju et al. [19]. By using a larger unit cell, the SmSi-(7 × 1) instead of a the SmSi-(5 × 1), they shown that the DETB molecules can be adsorbed with a new orientation where their main axis is now perpendicular to the Sm rows (Fig. 7a, b). In these conditions, the molecular motions induce dual frizzled bands on the STM images (black arrows in Fig. 7) corresponding to the two-triptycene wheels. A semiempirical calculation (ASED-MO) confirms that in this orientation, the energy barrier is the most favorable to a sliding onto the surface and that the DETB molecules are confined between two HCC channels.

3 Tools to Induce Molecular Motion at a Semiconductor Surfaces

Self-assembly is an important tool in nanotechnology [20, 21]. In order to achieve self-assembly growth, molecules must be free to move across a surface. However, because of the dangling bonds, this movement is not often possible without an

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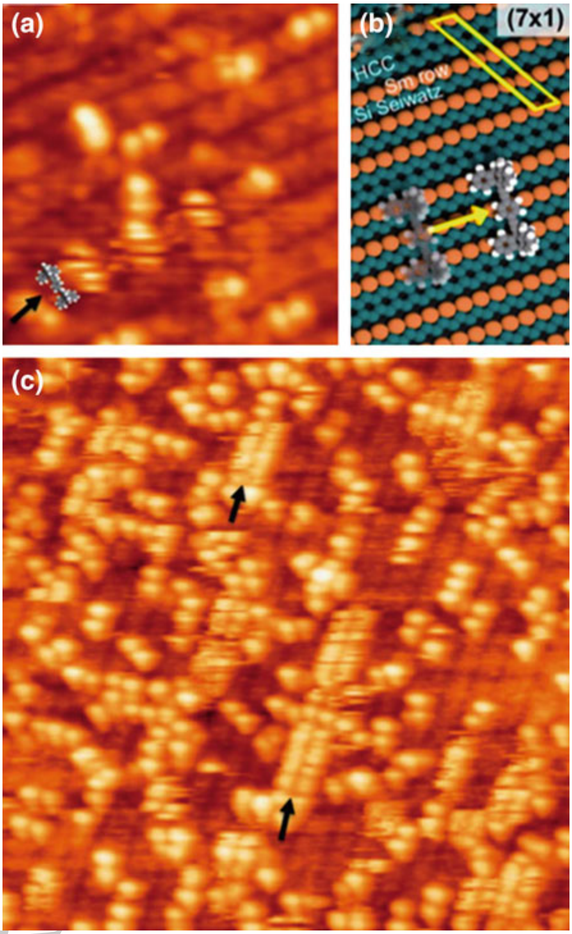

Fig. 7 **a** STM image of DETB molecules on SmSi-(7 × 1) (15 × 15 nm^2, Vs = 1.8 V, It = 0.02 nA). **b** DETB adsorption model which induces the sliding perpendicular to the Sm rows. **c** STM image showing the DETB sliding and the formation of dual bands (*black arrows*). Reprinted with permission from [19]

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external intervention. The idea is to provide some energy to the system (molecule/surface) in order to overcome molecule–surface interactions and diffusion barriers. Three sources of energy (heat, light, or electrons) can be available in a STM chamber and can be used to induce molecular motions on semiconductor surfaces.

Despite the importance of this step for the development of molecular electronics, only very few examples dealing with the subject are available in the literature.

3.1 Heat

The usual and easiest method to provide energy in a STM is based on the heating of the investigated system. Our work in this domain illustrates well the effect of temperature in self-assembly formation [22–24]. Although molecular deposition

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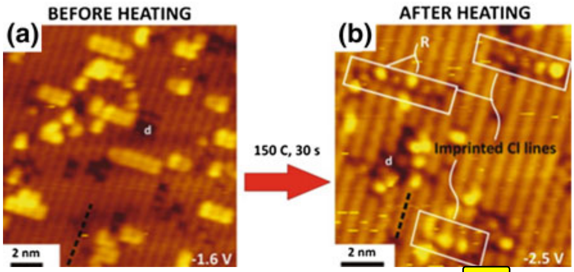

Fig. 8 STM images recorded at room temperature of a Si(100)-2 × 1 surface exposed to 0.04 L dose of chloropentane. **a** *Before heating* the surface at 150 °C during 30 s (*Vs* = −1.6 V, *It* = 0.2 nA, 15 nm²). **b** *After heating* (*Vs* = −2.5 V, *It* = 0.2 nA, 11 nm²). Physisorbed lines of CP are imprinted as chemisorbed lines of Cl pairs. Reprinted with permission from [25]

was performed at room temperature, this thermal energy was sufficient for molecules to overcome diffusion barriers and then form different self-assemblies.

Heat can also be used to activate a local atomic reaction (LAR) as reported by Harikumar et al. Indeed, LAR of the physisorbed lines of 1-chloropentane (CP) pairs was induced by heat. Figure 8 shows representative images of physisorbed lines of CP pairs after dosing at room temperature and after heating to 150 °C for 30 s. Some lines have completely reacted after heating and producing new lines of pairs of Si–Cl covalent bonds.

This result shows that we can transform a weakly attached physisorbed pattern, by using heat as source of energy, in order to induce chemical reaction with semiconductor surface and so rendering the pattern permanent.

3.2 *Electrons*

Excitation of molecules at a surface can be achieved by the STM tip and can induce molecular motions in four possible directions: (1) toward the surface (transition from a physisorbed interaction to chemisorbed one) [26]; (2) away from the surface (desorption) [27]; (3) parallel to the surface (migration, diffusion) [28]; or (4) rotating around a point of the surface (molecular switch) [29]. The third case is the direction favoring the self-assembly.

Harikumar et al. [30], for example, showed that electron excitation of chemisorbed benzene at Si(100) causes long-range (around 48–35 Å in Fig. 9a) molecular recoil in the plane of the surface as illustrated in Fig. 9. This movement is induced by an electron pulse (−2 V, 0.2 nA, 1 s) with the STM tip and is followed by a chemisorptive reattachment of the molecule. The migration is due to molecular cartwheeling rotation. It is directed along the dimer rows and over a missing dimer defect, carrying the molecules over raised surface obstacles.

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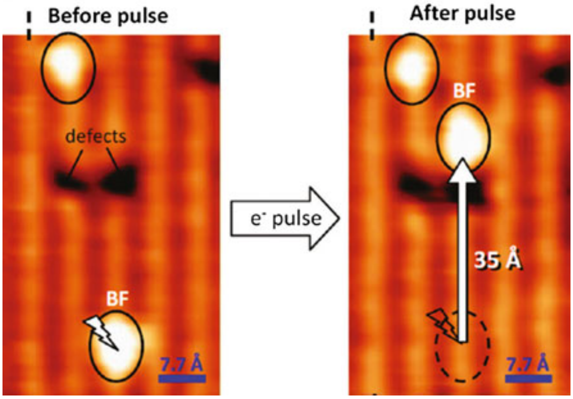

Fig. 9 Benzene migration over Si(100)-2 × 1 surface at room temperature. STM images (V_s = −1.5 V, I_t = 0.2 nA) of the same area *before* and *after* an electron pulse (V_s = −2 V, I_t = 0.2 nA, 1 s). Reprinted with permission from [30]

3.3 Light

Although this excitation source is widely used in air and in liquid environments [31], to our knowledge, only one example has been reported for its use in UHV and on semiconductor surfaces. This example concerns, once again, the Harikumar et al. [25] work concerning 1-chloropentane on Si(100) surface. Like in the case of heat as energy source of excitation, LAR of the physisorbed lines of CP pairs can also be induced by light. Indeed, Fig. 10 shows photo-imprinted Cl lines after 2 h of laser irradiation of physisorbed CP on Si(100)-2 × 1 surface. The photo-induced reaction is due to electrons ejected from the substrate rather than direct excitation of the molecule.

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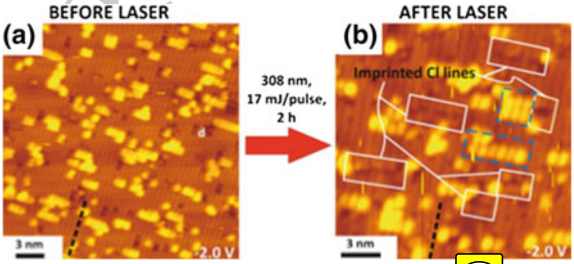

Fig. 10 STM images recorded at room temperature of a Si(100)-2 × 1 surface exposed to 0.04 L dose of chloropentane. **a** *Before laser* irradiation (V_s = −2 V, I_t = 0.2 nA, 25 nm^2). **b** *After* 2 h of laser irradiation (V_s = −2 V, I_t = 0.2 nA, 18 nm^2). Physisorbed lines of CP are photo-imprinted as chemisorbed lines of Cl pairs (*white rectangles*). Non-reacted physisorbed CP lines are highlighted by *blue broken rectangles*. Reprinted with permission from [25]

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4 Bistable Molecules as Model Systems of Molecular Machines

4.1 Adsorption of Bistable Azobenzene Molecules on Semiconductors

The most basic approach to study molecular bistability on a surface consists in the deposition of a molecule that is intrinsically bistable. Then, in a second step, one checks whether the molecular bistability is maintained or altered by the presence of the surface. Azobenzene derivatives have been deeply investigated as model system of bistable molecules in gas phase or in solution [32–37]. The presence of a $N=N$ double bond located between two phenyl groups allows a reversible isomerization between *trans* and *cis* structural isomers (i.e., diastereoisomers). The adsorption of azobenzene derivatives has also been investigated on noble metal surfaces at low temperature (<100 K) [38–48]. The switching processes are based on the isomerization of molecules induced by an external stimulus, such as light or temperature (which are also used in gas phase or in solution experiments), inelastic tunneling electrons (IET), tip-induced molecular deformation, and electric field due to the presence of the STM junction. Semiconductor surfaces are fascinating for surface photo- or tip-induced switching due to their tunable optical and electronic properties.

The adsorption of *trans*-azobenzene (TAB) and *cis*-azobenzene (CAB) was investigated on Ag/Ge(111)-$\sqrt{3} \times \sqrt{3}$ R30° by Wu et al. [49] at 100 K. Single TAB molecules were observed as two paired lobes on the surface. The formation of large, well-organized, and closely packed domains was achieved by increasing the coverage rate. From in situ observation of the substrate lattice, the TAB adsorption site was determined. TAB monolayer is commensurable with the substrate and forms a 2 × 1 structure (Fig. 11). The driving forces of TAB monolayer growth are hydrogen bonds between TAB molecules and molecule–substrate interactions. CAB molecules have been deposited on the same surface. However, it is quite difficult to obtain pure CAB molecules because of their unstability (spontaneous isomerization). Therefore, a mixture of TAB and CAB, containing 10 % of CAB, was adsorbed on the surface. CAB molecules are adsorbed on TAB domain boundaries. CAB molecules appear as two paired lobes, one spot being brighter than the other due to one out-of-plane phenyl group. Despite many attempts, TAB photoisomerization is unsuccessful on Ag/Ge(111)-$\sqrt{3} \times \sqrt{3}$ R30°. The absence of TAB photo-isomerization is explained by the strong TAB–surface interaction that leads to a surface energy relaxation instead of the desired isomerization process.

Decreasing the molecule–surface interactions seems to be a key point for the successful achievement of azobenzene isomerization on semiconductors. Molecule–surface interaction can be tuned by using:

- Passivated semiconductors
- Tailored molecules

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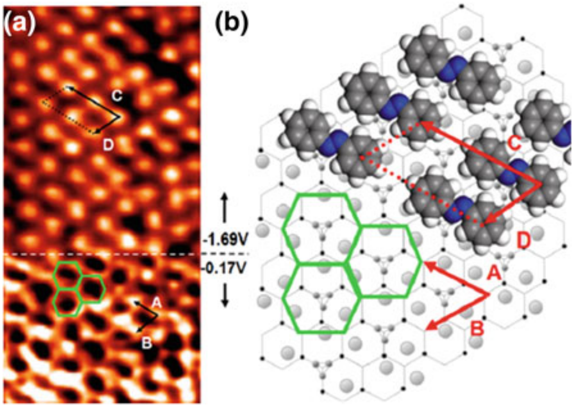

Fig. 11 **a** STM image (5 × 10 nm²) of a TAB monolayer on Ag/Ge(111)-√3 × √3-R30°. The tip bias is altered during the scan to image simultaneously the TAB molecules (*upper part* with *Vs* = −1.69 V and *It* = 80 pA) and the hexagonal pattern of the substrate atoms (*lower part* with *Vs* = −1.69 V and *It* = 80 pA). **b** Structural model of image shown in **a**. Reprinted with permission from [49]

When π-conjugated molecules, such as azobenzene derivatives, are deposited on a semiconductor, the main contribution to the molecule–surface interactions is the interaction of the molecule's π-electrons and electrons of surface dangling bonds. Recently, we have demonstrated that the molecule–surface interactions can be controlled by using the Si(111)-B, √3 × √3-R30° surface, noted Si(111)-B. The silicon adatoms dangling bonds are depopulated because of the presence of a boron atom underneath each silicon adatom, leading to a weak π-conjugated molecule–surface interaction [22, 24, 50–52]. In all these cases, molecule–surface interaction is weak enough to achieve the formation of large-scale supramolecular networks. In order to check the feasibility of azobenzene isomerization on a Si(111)-B surface, we tried to deposit TAB molecules on this surface. However, the observation of single or self-assembled TAB molecules was impossible in the 100–300 K temperature range. Another azobenzene derivative, 4-pyridylazobenzene (PAB) molecule, has been synthetized (Fig. 12). Due to the presence of a pyridyl group, PAB-Si(111)-B interactions should be stronger than TAB-Si(111)-B. A single PAB molecule has indeed been observed on a Si(111)-B surface at room temperature. PAB molecules appear as two paired lobes, one being longer than the other. In empty states STM images, the interaction between the nitrogen atom lone pair and the silicon adatom is highlighted by a bright protrusion (Fig. 12b, c) [53].

PAB manipulation at room temperature was successfully achieved by applying a STM tip pulse bias voltage of 3 V during 300 ms after positioning the STM tip above a PAB molecule (Fig. 13a).

In these conditions, PAB molecules switch reversibly from one state to the other, which are mirror images of each other by a plane mirror; therefore, they are enantiomers. No *cis–trans* PAB isomerization occurs on a Si(111)-B surface, and it

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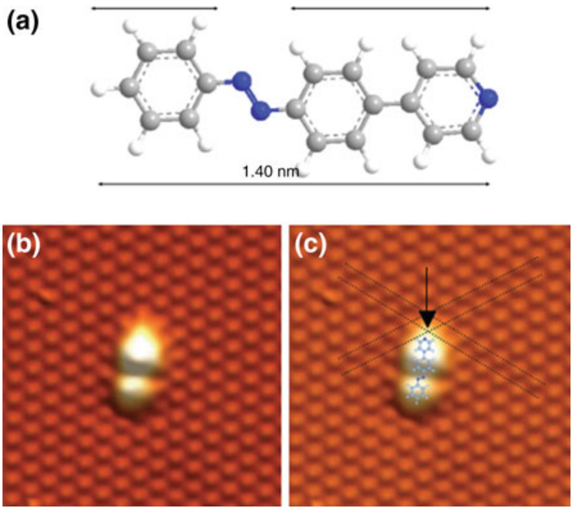

Fig. 12 **a** Molecular structure of 4-pyridylazobenzene (*PAB*). **b** Room temperature STM image (7×6 nm^2, $V_s = 1.5$ V and $I_t = 76$ pA) of a single PAB molecule deposited on Si(111)-B. **c** Superimposed structural model of PAB/Si(111)-B. PAB-Si(111)-B interaction is highlighted by a *black arrow*. Reprinted with permission from [53]

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is a chiral switching between two enantiomers. PAB is not a chiral molecule but a prochiral molecule. The presence of the surface induces the formation of chiral adsorbates. From a mechanistic point of view, the PAB chiral switching is based on the tunneling electron transfer to PAB LUMO, located around 3 V (Fig. 13b), leading to a negatively charged transient state. Then, energy transfer to molecular vibrations leads to chiral switching by molecular rotation of the azophenyl group around the C–N bond (Fig. 13c) instead of *cis–trans* isomerization. This chiral switching is of interest in order to store information at the molecular level on a semiconductor surface because this switching occurs reversibly at room temperature and in a controlled manner.

In order to observe the *cis–trans* isomerization of azobenzene derivatives, Crommie et al. [54] proposed to use GaAs(110) as semiconductor surface and 3,3′,5,5′-tetra-*tert*-butylazobenzene (TTB-AB) as molecules at low temperature (<20 K). The (110) surface of GaAs was chosen due to the absence of surface states within its direct band gap (1.43 eV) [55], and TTB-AB was chosen because the TTB-AB aromatic molecular plane is held away from the surface by *tert*-butyl groups. Formation of TTB-AB large-scale monolayer islands on GaAs(110) was achieved in (Fig. 14a). The supramolecular network is commensurable with the surface, and TTB-AB shows the same shape (four-lobed structure) as the one observed on noble metals, corresponding to the *trans*-isomer [47]. TTB-AB photoswitching on GaAs (110) was investigated by STM with UV light illumination (375 nm) during 18 h. UV light exposure leads to morphological modifications of the TTB-AB monolayer islands. Several bright protrusions, forming some stripes, have appeared along

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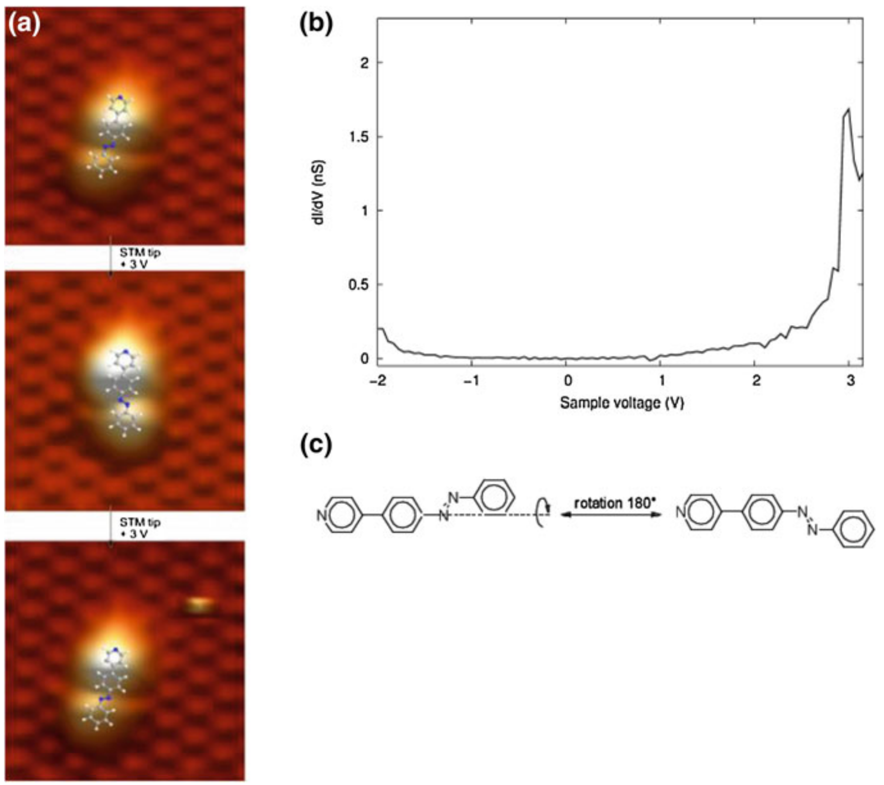

Fig. 13 **a** Sequence of PAB manipulation by STM tip bias voltage pulse on a Si(111)-B surface with superimposed structural model on STM images. **b** Spectrum of the differential conductance, dI/dV, recorded on a PAB molecule adsorbed on a Si(111)-B surface. **c** Two PAB conformers rotated by 180° of an azophenyl group around a C–N bond. Reprinted with permission from [53]

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preferential directions of the GaAs(110) surface (Fig. 14b). Bright protrusions have been assigned to TTB-AB *cis*-isomers, as previously observed on noble metal surface, due to the out-of-plane configuration of the *cis*-isomer [46].

On Au(111) surface, TTB-AB photoswitching is a random process because the bright protrusions are randomly distributed on the surface [46]. In the case of GaAs (110), formation of *cis*-isomer stripes is in favor of a cascade-like process. This very interesting process can be explained by the reduced steric hindrance after TTB-AB photo-isomerization. When a first *trans*-TTB-AB molecule is photo-isomerized, the *cis*-isomer occupies a smaller area than the *trans*-isomer because *cis*-TTB-AB is out of plane. But, as molecule surface is stronger on GaAs(110) than on Au(111), TTB-AB cannot diffuse on the surface and the network can no longer be re-organized to become once again compact. Therefore, after a first TTB-AB photo-isomerization, TTB-AB neighboring molecules can be more easily isomerized because local steric hindrance has decreased.

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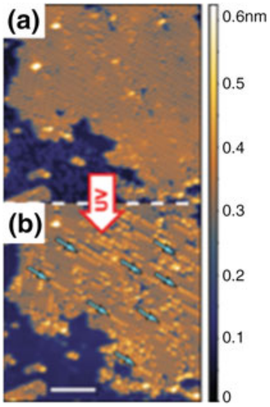

Fig. 14 TTB-AB photo-isomerization on GaAs(110) surface. The same TTB-AB molecular island is shown **a** *before* and **b** *after* an 18 h exposure to UV irradiation at 375 nm and 92 mW/cm^2 ($Vs = -2.0$ V, $It = 25$ pA). Molecules in the *cis* configuration appear to have one brighter lobe and occur in 1D stripes, as indicated by *blue arrows*. *White scale bar*, 10 nm. Reprinted with permission from [54]

To conclude, azobenzene derivatives switching on semiconductors are strongly dependent on the molecule–substrate interactions. The switching can be quenched, like on Ag/Ge(111)-$\sqrt{3} \times \sqrt{3}$-R30° or used to form stripes, like on GaAs(110) or to form enantiomers, and like on Si(111)-B.

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4.2 *Molecular Bistability Induced by Adsorption on Semiconductors*

In the previous paragraph, we described changes in the photomechanical properties of intrinsic bistable molecules after their adsorption on a semiconductor. Here, we propose to discuss the design of molecular bistability induced by the presence of the surface.

Dujardin et al. [56, 57] have investigated the induced bistability of biphenyl molecules on a Si(100) surface. Biphenyl is based on two phenyl groups linked by a single C–C bond. This molecule has no intrinsic bistability in solution, in solid state, or in gas phase. However, when biphenyl molecules are deposited at room temperature on a Si(100)-2 × 1 surface and observed by STM at 5 K, they can be adsorbed with one of the two phenyl ring covalently linked with a silicon adatom of the surface, the second phenyl ring being covalently linked with two silicon adatoms (i.e., a butterfly configuration, Fig. 15a, d for the corresponding structural model). This strongly chemisorbed configuration is stable because no motion is observed from 5 to 300 K.

In the case of p-type boron-doped silicon surface, biphenyl molecules can be switched with tunneling electrons by applying a negative surface pulse voltage of

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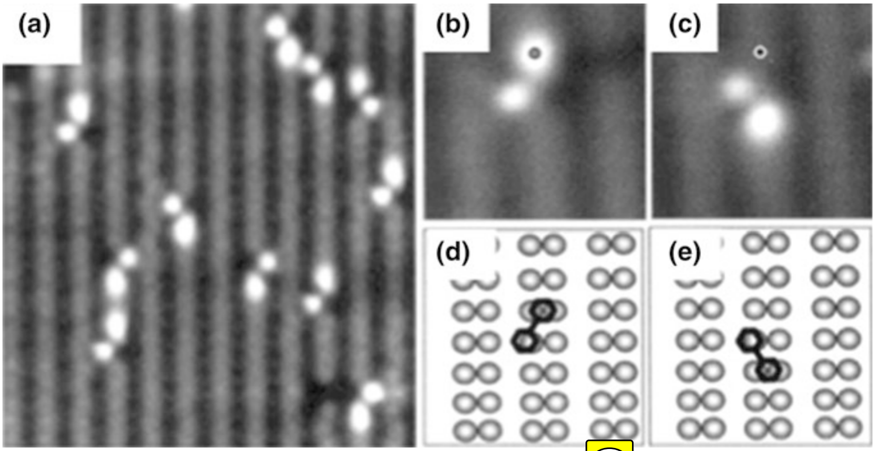

Fig. 15 **a** STM image of biphenyl molecules on a Si(100)-2 × 1 surface at 5 K (9 × 9 nm^2, *Vs* = −2.0 V, *It* = 200 pA). **b** Zoom (2.1 × 2.1 nm^2) of STM image shown in **a** showing a single biphenyl molecule in a stable configuration. The STM position for surface voltage pulse is indicated by a *dot*. **c** STM image of the same zone showing in **b** recorded after the surface voltage pulse. **d** and **e** Superimposed structural model of, respectively, **b** and **c**. Reprinted with permission from [56]

−3 V on adsorbed molecules (Fig. 15b–e). The mechanism of this switching has been deeply investigated [56]. For the first time, an electronic excitation process, based on the resonant transfer of one electron from the biphenyl HOMO to the STM tip, has been fully demonstrated [56]. As the process implies a charged transient oxidative state of biphenyl molecule (i.e., due to the loss of one electron), the nature of the doped, p or n, silicon substrate is relevant. The electronic excitation and relaxation processes are not modified by changing p-doping to n-doping. Nevertheless, the dynamics of switching is strongly altered. Indeed, the transient state is negatively charged (due to charge delocalization on molecule), leading to a strong repulsive interaction with n-doped silicon surface instead of attractive interaction with p-doped silicon surface [57]. This example proves the role of the molecule–surface interaction for the development of nanomachines on semiconductor surfaces. Biphenyl molecules adsorption on Si(100)-2 × 1 leads to other exotic bistable configurations which can be thermally activated [58].

Adsorption of 1,5-cyclooctadiene (COD) on a Si(001)-2 × 1 surface at 7 K was investigated by STM experiments [59–61]. Free COD molecules are prochiral; therefore, COD adsorption on a Si(001) surface leads prevalently to the formation of two degenerate configurations, corresponding to a bridge structure, where the two C=C bonds are involved in a [2 + 2] cycloaddition reaction with two silicon dimers of the surface, as supported by DFT calculations [62] (Fig. 16a).

Time spectroscopy of the tunnel current under standard experimental setup (feedback loop turned off and STM tip at a fixed distance over adsorbed COD molecule) shows a random telegraph signal with an on–off ratio of 1.2:1 in (Fig. 17). Additional experiments were performed to determine the switching process.

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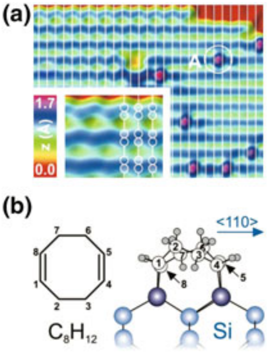
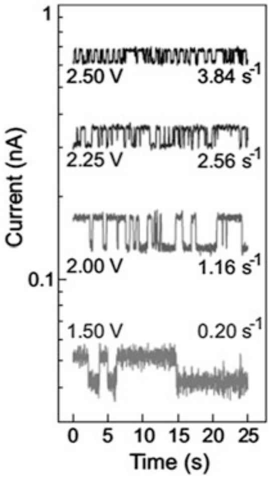


Fig. 16 **a** STM image of a COD molecule on a Si(001) surface at 7 K (10 × 8 nm^2, $Vs = -2.0$ V, $It = 600$ pA). The *inset* (3 × 2 nm^2) shows the Si dimer buckling at the upper step edge serving as a marker for the dimer position within a row. **b** COD molecule and structural model of the bridge structure. Reprinted with permission from [58]

Fig. 17 Binary current fluctuations detected when tunneling through a COD molecule adsorbed in the bridge structure at a constant tip height (set point $It = 150$ pA, $Vs = +2$ V). The switching rate obtained for each current trace is indicated. Reprinted with permission from [59]



On the basis of experimental results, Nacci et al. proposed that COD switching between two degenerate configurations is triggered by an inelastic single electron process. This process is fully reversible and is achieved without any bond breaking or reforming, a case that remains rare in the literature.

4.3 Adatom Bistability Induced by Adsorption of a Molecule

Adsorption of a molecule on a semiconductor surface can induce the modification of molecular properties leading to molecular bistability, as described in the previous

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section. In this last part, we propose to describe the switching of an adatom (of the surface) induced by molecular adsorption. Polanyi et al. [63, 64] have investigated the adsorption of chlorododecane on the Si(111)-7 × 7 surface. These molecules are non-covalently adsorbed on the surface. Pairs of chlorododecane molecules are self-assembled into two types of dimers, forming a corral surrounding a silicon corner hole or a corner adatom (respectively, I and II in Fig. 18).

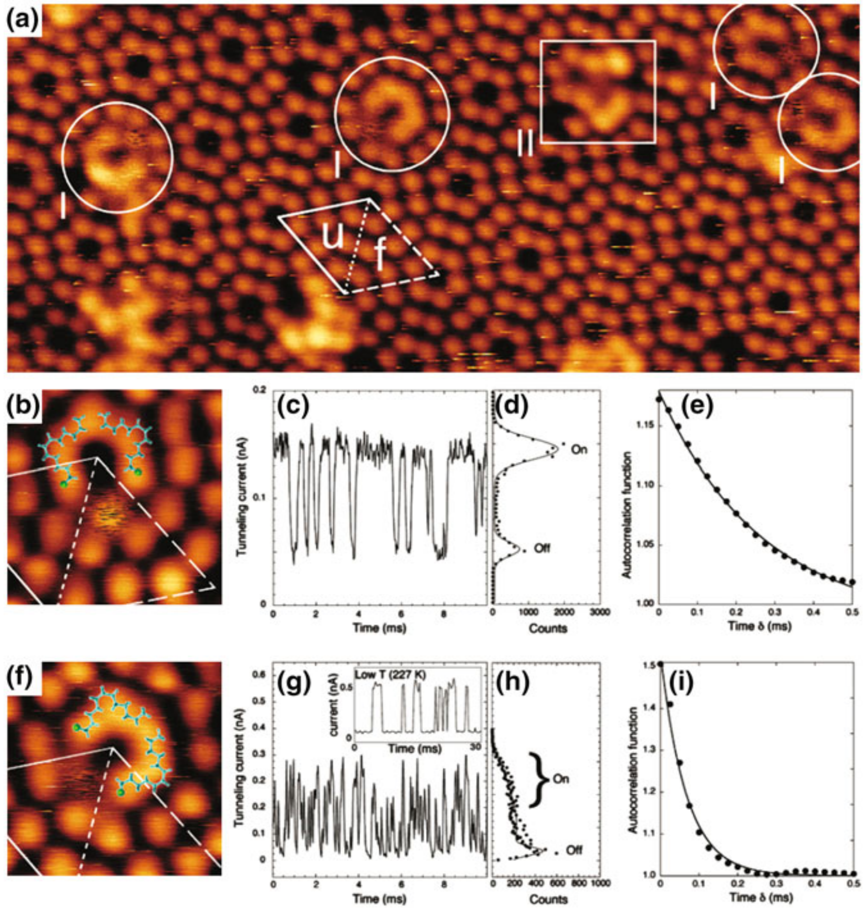

Fig. 18 **a** STM image (room temperature, 23 × 10 nm^2, Vs = 2.0 V, It = 100 pA) of chlorododecane molecules adsorbed on a Si(111)-7 × 7 surface with two types of dimers surrounding a corner hole (*type I*) or corner adatom (*type II*). Faulted (*f*) and unfaulted (*u*) half-cells of Si(111)-7 × 7 are marked. **b** High resolution STM image (3 × 3 nm^2, Vs = 2.5 V, It = 400 pA) of *type I* corral with superimposed structural model. **c** Tunneling current versus time measurements over a faulted corralled adatom (shown in **b**) at Vs = +2.5 V. **d** The corresponding tunneling current distribution with a pair of Gaussian functions fitted. High-current (on) and low-current (off) states are labeled. **e** The autocorrelation of the tunneling current time trace of **c**. Reprinted with permission from [64]

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When a pair of chlorododecane molecules surrounds a corner hole, a corner adatom, located between jaws of the corral, remains uncovered (Fig. 18b). This adatom exhibits a streaky appearance, corresponding to a switching between conductance states. This can be demonstrated by recording the tunneling current versus time (Fig. 18c–e). This switching has been interpreted as a single-atom electronic switch due to molecularly induced field effect. Small changes in the configuration of self-assembled pairs of chlorododecane molecules, which are dipoles, have a large electronic effect leading to high and low conductance. This interpretation is supported by DFT calculations. This is a new route toward molecular nanoelectronics induced by the adsorption of molecules on a silicon surface.

5 Conclusion and Perspectives

The development of single molecular machines on semiconductors is still a challenge. Some proofs of concepts have been successfully achieved. Molecule–surface interactions play a key role in this field because molecular motion is strongly conditioned by the molecule–surface interactions. In terms of perspective, semiconductors could be used as templates to guide molecular motions and to develop devices operating at room temperature.

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