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Adsorption of an organic zwitterion on a Si(1 1 1)-7 × 7 surface at room temperature

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ABSTRACT

The couple sulfonato/Si(1 1 1)-7 × 7 leads to remarkable 2D chiral molecular assembly with a stability improved at room temperature. The voltage-dependency of the STM images has been experimentally investigated and the correlation between STM images and PDOS has been studied. The proposed empirical model of the adsorption of molecules on Si(1 1 1)-7 × 7 has been justified by the experimental and theoretical data.

1. Introduction

To miniaturize the electronic devices, a promising alternative route to small scale functional systems with nanometer dimensions is the self-ordering and self-assembly of atoms and molecules on atomically well-defined surfaces [1]. A rich variety of molecular nanostructures has been successfully assembled on metallic or HOPG surfaces and directly characterized by local probes like scanning tunneling microscopy (STM) [2–14]. The deposition of molecules on a semiconductor surface at room temperature and without alteration of their aromatic behaviour is the most intricating challenge because the use of semi-conductive interfaces remains one of the best choices for the development of operational post-CMOS devices. Difficulties come essentially from the strong molecule–substrate interactions (for example the formation of Si–C σ bonds), which can impede the growth of the supramolecular edifice [15–17]. To prevent the formation of covalent bonds with silicon surfaces, two great strategies have emerged: (i) passivation of the surface by inserting doping elements (for example B or C atoms) [18–22] or (ii) formation of strong supramolecular dimers [23,24]. In a previous paper, we have shown that the adsorbate–substrate interactions can be overridden by shielding the π-skeleton of molecules with the insertion of charged atoms, such as zwitterions [25]. Here, we investigated the voltage-dependency of experimental STM images of the zwitterion adsorbed on the surface. These images have been explained by the analysis of the density of states of the self-assembly calculated with density functional theory (DFT). All experimental data are in very good agreement with the theoretical calculations.

2. Experimental and computational details

2.1. Synthesis

MSPS molecules have been synthesized in accordance with the method previously described by Nicoud and coworkers [26]. The procedure is based on two steps:

2.1.1. Formation on the zwitterion

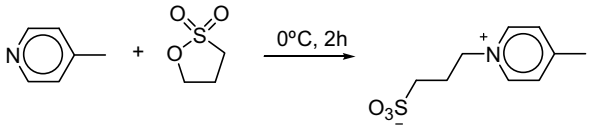
See Scheme 1.

2.1.2. Building of the large dipole

See Scheme 2.

2.1.3. Experimental set-up

4-Picoline was treated at 0 °C with one equivalent of propylsultone, leading to crystalline 4-methyl-(*n*-sulfonatopropyl)pyridinium, which was used for the subsequent reaction without further purification. To a solution of 4-methyl-(*n*-sulfonatopropyl)pyridi-



Scheme 1. Synthesis of 4-methyl-(*n*-sulfonatopropyl)pyridinium.

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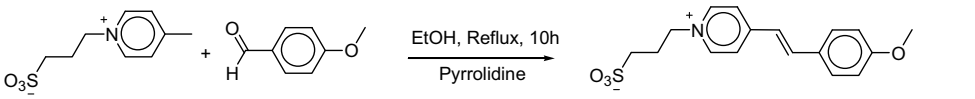

Scheme 2. Synthesis of 4-methoxy-4'-(3-*n*-sulfonatopropyl)stilbazolium (MSPS).

nium in 15 mL of anhydrous ethanol was added one equivalent of the 4-methoxybenzaldehyde and a catalytic amount of pyrrolidine. The mixture was heated under reflux for 10 h and then cooled to 0 °C. The precipitated product was filtered and washed with ether. The pale yellow solid was purified by column chromatography (Silica gel, acetone, R_f close to 0.5). The pure 4-methoxy-4′-(3-*n*-sulfonatopropyl)stilbazolium (MSPS) was isolated as an intense yellow powder after evaporation of the solvent. All spectroscopic data are in agreement with the proposed structure.

2.2. STM experiments

The Si(1 1 1) substrate was heated under ultra-high vacuum by direct current. Clean Si(1 1 1)-7 × 7 surface reconstruction was obtained by repeated cycles of heating at 1200 °C and slow cooling to room temperature. The molecules were sublimed from a Knudsen cell at 390 K onto the Si(1 1 1)-7 × 7 surface at room temperature and a pressure lower than 10^{-9} mbar. STM images were acquired in the usual constant-current mode at room temperature.

2.3. DFT calculations

The nature of MSPS adsorption on a Si(1 1 1)-7 × 7 surface has been investigated by DFT calculations using the Vienna Ab Initio Simulation Package (VASP) [27,28]. Electron–ion interactions were described using the projector augmented wave (PAW) method, which was expanded within a planewave basis-set up to a cut-off energy of 400 eV. Electron exchange and correlation effects were described by the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE GGA) exchange-correlation functional. 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).

3. Results and discussions

3.1. STM images

Fig. 1 shows the atomic resolution STM filled states image on both Si(1 1 1)-7 × 7 reconstruction and adsorbed molecules. A few faulted half-cells exhibit an original threefold star, each arms consisting of two matching protrusions.

A close examination of a STM image corresponding to a complete covered unit cell is done in Fig. 2 where the structural model of the Si(1 1 1)-7 × 7 is also superimposed. In order to assign each spot to a given part of the molecule, it is necessary to recall that the sulfonato moiety in MSPS possesses a negative charge, and the methoxy group is electron-poor owing to conjugation with the pyridinium ring. We found that, in the filled states (Fig. 2, $V_s < 0$), the most intense protrusions are located exactly on top of corner adatoms and the others are found between a rest-atom and an adjacent center adatom. On the contrary, in the empty states (Fig. 2, $V_s > 0$), the brighter protrusions are situated exactly between a rest-atom and a center adatom.

Therefore, the intense protrusions observed in the filled states can be attributed to the sulfonato groups and the intense protrusions observed in the empty states to the methoxy groups. The structural model of the 7 × 7 assembly derived from these observations is superimposed on the STM images in Fig. 2 [25].

3.2. Chirality of the self-assembly

One consequence of the proposed structural model consists in the chirality of the assembly of three MSPS molecules. This is due to the specific locations of the methoxy groups between a rest-atom and an adjacent center adatom (Fig. 2).

Fig. 3 shows a high resolution STM image of three adjacent complete half-cells, in which each half-cell contains an assembly of three MSPS molecules. In these images, each molecular assembly is the mirror image of the other reflected through the two mirror planes (1) and (2) quoted in Fig. 3. This means that the threefold stars are chiral even though free MSPS are achiral. Moreover, the two possible enantiomers (i.e. *M*- and *P*-enantiomers) can be observed in the same complete cell of the Si(1 1 1)-7 × 7 surface. In our case, the formation of the chiral assembly is not selective. The *M*- or *P*-enantiomers are equiprobably adsorbed on the faulted or unfaulted half-cell of the Si(1 1 1)-7 × 7 surface, leading to the racemic mixture. Aforementionned results show, to the best of our knowledge, the first example of chiral assembly of achiral molecules on Si(1 1 1)-7 × 7 surface. All previous studies regarding chiral structures on semiconductor surfaces have been reported in the case of the formation of at least one stereogenic center, for example after cycloaddition of molecules with silicon or germanium atoms [29–31]. In the case of metal surfaces, the formation of chiral structure by deposition of achiral molecules have been reported [32–35].

3.3. Voltage-dependency of STM images

The equilibrium distance, 0.26 nm, between Si adatoms of the substrate and the S atoms of the MSPS has been calculated by using VASP on the entire system (molecules + surface, Fig. 4). The corresponding energy minimum is −2.66 eV for three MSPS in a half-cell

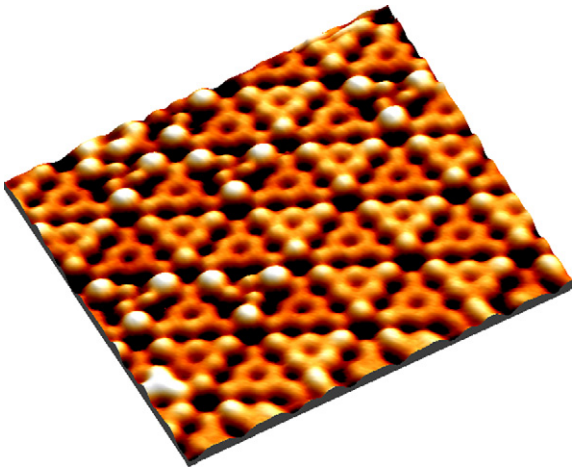

Fig. 1. High resolution STM images (12 × 12 nm^2) at room temperature of MSPS deposited on Si(1 1 1)-7 × 7 (V_s = −1.7 V and I = 0.16 nA).