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Nondestructive Room-Temperature Adsorption of 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine on a Si-B Interface: High-Resolution STM Imaging and Molecular Modeling

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Organic nanostructures on semiconductors are currently investigated but the surfaces are known to interact strongly with molecules. To reduce the molecule-surface interaction, we used the Si(111)-B $\sqrt{3} \times \sqrt{3}R30^\circ$. Deposition of isolated 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine, was achieved at room temperature without modification of their π skeleton. This fascinating arrangement, observed by STM, has been validated by full density functional theory computations onto the entire system. The theoretical results give a clear explanation for the specific adsorption sites of molecules on the substrate.

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The deposition of molecules on substrates is a topical area of current research in view of their promising electronic properties [1–9]. Much progress has been made in the development of new silicon-based devices that combine silicon technology with organic molecules; however, the fabrication of such devices requires low-temperature processes (below 77 K) [10,11]. In all cases, the control and the prediction of the adsorption sites at the interface and the thermal stability of the products remain the main limitations in the development of this promising technology. Moreover, the electronic properties of aromatic molecules are strongly modified when deposited on a silicon surface due to the affinity of the surface for π electrons, which can lead to the formation of Si-C σ bonds between molecules and substrate [12–14]. In contrast to the results of all aforementioned papers, we have now been able to perform the deposition of isolated molecules on a modified silicon surface at room temperature on a specific adsorption site without alteration of their aromatic behavior, which is a key step in view of the development of complex architectures; the position of the first building block being crucial in the ordered growth of a complex system [15]. In this Letter, we report the synthesis, the molecular structure, and the adsorption of 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine molecules on Si(111)-B $\sqrt{3} \times \sqrt{3}R30^\circ$ surface (Si-B). High-resolution STM (scanning tunneling microscopy) images of isolated molecules are obtained at room temperature and investigated by molecular modeling. These results allowed us to determine the specific adsorption site of individual molecules at the Si-B surface.

2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine (compound 1) is chosen for its extended electronic delocalization within the entire molecule. Compound 1 is synthesized at

room temperature by cyclotrimerization of 2-thiophene carbonitrile in dichloromethane with an equivalent amount of trifluorosulfonic acid (see Fig. 1). The reaction gives only the expected trisubstituted triazine in high yield (on a gram scale). The single-crystal x-ray structure analysis of compound 1 reveals the presence of two molecules per asymmetric unit with disordered thienyl groups. The triazine core and the thienyl moieties are almost coplanar, the maximum rotation of a thienyl moiety being 4° (see Fig. 2).

In order to circumvent the problem of traditional silicon surface reactivity with π -conjugated molecules, the Si(111)-B $\sqrt{3} \times \sqrt{3}R30^\circ$ surface is used [19]. This surface has the unique particularity to exhibit depopulated dangling bonds due to the presence of boron atoms under the top silicon layer [20,21]. Consequently, π -conjugated organic molecules could interact weakly with the p_z depopulated dangling orbitals of the surface [22]. Experiments are carried out in an ultrahigh vacuum chamber with a pressure lower than 2×10^{-10} mbar and STM images acquired in constant-current mode at room temperature. The Si-B surface exhibits a $\sqrt{3} \times \sqrt{3}R30^\circ$ reconstruction with a lack of

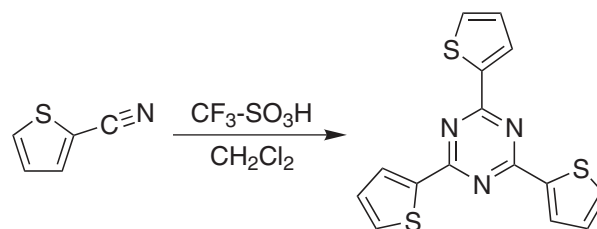


FIG. 1. Synthesis of 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine (compound 1).

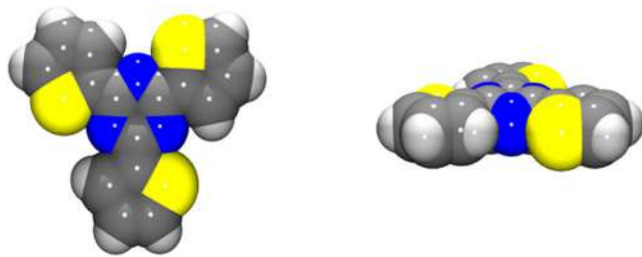


FIG. 2 (color online). Molecular structure of compound 1, view from the top (left) and from the side (right).

boron atoms close to 3 per 200 nm² (white arrows, Fig. 3, top). To determine the adsorption site on the Si-B surface of 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine, these molecules are deposited at a large covering rate (close to 33%, Fig. 3, bottom).

The density of Si adatoms which do not possess a B atom underneath is systematically checked before and after the deposition of molecules. In all experiments, we observe that the density of these defaults is constant. Therefore, on the basis of this experimental observation, we conclude that the molecules are not adsorbed on the Si adatoms without B atom underneath. In order to investigate the nature of the molecule-substrate interactions and to avoid possible molecule-molecule interactions, STM images at a lower covering rate of compound 1 on the Si-B surface (below 10%) were obtained (Fig. 4).

The STM image presented in Fig. 4, acquired from a positive bias voltage (empty states), shows a remarkable atomic resolution of the Si-B surface, the white protrusions being characteristic of the absence of a boron atom underneath a Si adatom [20–22]. Moreover, in the left part of the STM image, two isolated 2, 4, 6-tri(2'-thienyl)-

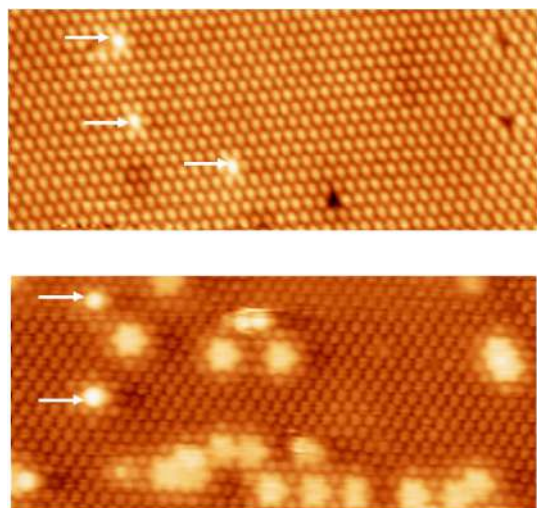


FIG. 3 (color online). High-resolution STM images of the Si-B surface before (top) and after (bottom) deposition of 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine molecules ($V_s = +1.0$ V, $I_t = 0.4$ nA, 20 nm \times 20 nm).

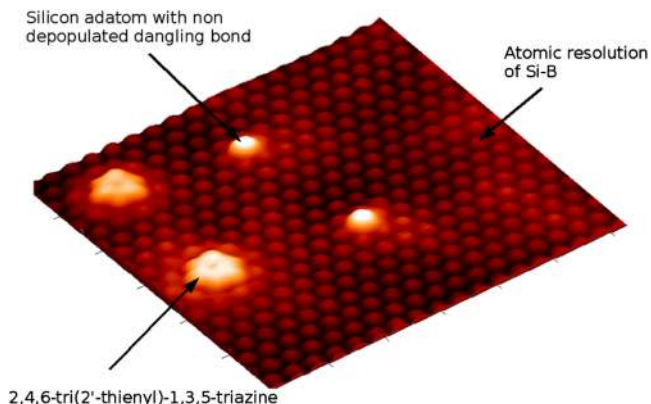


FIG. 4 (color online). STM image (empty states) showing two 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine molecules adsorbed on the Si-B substrate ($V_s = +1.2$ V, $I_t = 0.3$ nA, 14 nm \times 9 nm).

1, 3, 5-triazine molecules are observed at an exceptional resolution. Enlargement (Fig. 5) of any isolated molecule clearly shows that the center of the triazine core of compound 1 (noted c) is precisely on top of a Si adatom and that two series of three distinguishable spots surround this triazine core. The three protrusions with lower intensities (noted 1, 2, and 3, Fig. 5) correspond exactly to the Si adatoms network of the surface, while the three brighter protrusions (noted x, y, and z) do not match with this network. The distance measured between two lobes of equivalent intensities (0.70 nm) is in agreement with the average centroid-centroid distance observed between two adjacent thienyl moieties (x-ray data, 0.69 nm). Moreover, the length of the molecule, longest H:H separation between thienyl moieties (x-ray data, 1.13 nm), is close to the length of the main diagonal of the reconstructed Si-B surface (1.16 nm). On the basis of these experimental results, we cannot definitively attribute the series of three protrusions which corresponds to the thienyl moieties of compound 1. In view to rationalize the presence of six lobes in the STM images, *ab initio* calculations with extended density functional theory, and plane wave basis set, using the Vienna *ab initio* simulation package (VASP) were performed

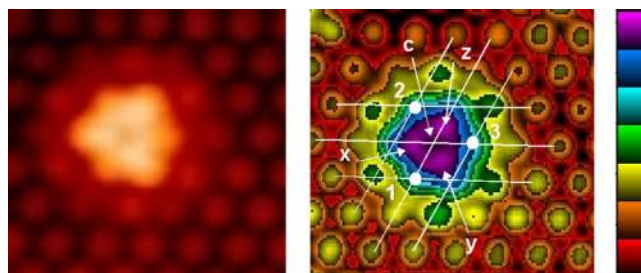


FIG. 5 (color online). Same STM image (empty states) with two linear (left) and high contrasted multicolor (right) look-up tables showing one 2, 4, 6-tri(2'-thienyl)-1, 3, 5-triazine molecule adsorbed on the Si-B surface. ($V_s = +1.2$ V, $I_t = 0.3$ nA, 7 nm \times 6 nm).

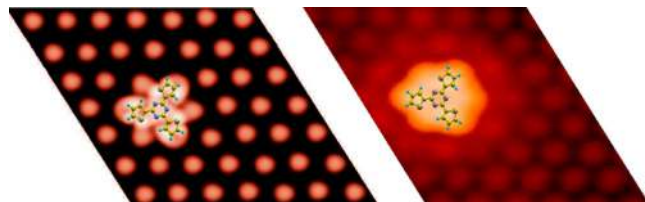


FIG. 6 (color online). Simulated LDOS image (left) and experimental STM image (right) of compound 1 onto Si-B surface with positive bias voltage ($V_s = +1.2$ V).

[23,24]. All pictures were plotted with XCRYSDEN [25,26]. Thanks to the high resolution of the STM images, compound 1 was positioned with atomic precision on the Si-B surface and then, the corresponding integrated local density of states (LDOS) image of molecules on this surface was simulated in positive bias voltage range (Fig. 6). In the empty states, the most intense protrusions are assigned to the π skeleton of the organic molecule and the orbitals of the triazine core are slightly less intense than the orbitals of the thienyl moieties. The p_z depopulated dangling orbitals of the surface are attenuated as compared to the orbitals of compound 1. Therefore, the six lobes observed in the STM images can be fully interpreted: the most intense protrusions are assigned to the thienyl moieties, while the three others correspond to the Si adatoms underneath the nitrogen atoms of the triazine core. Furthermore, the nature of the molecule-substrate interaction was investigated by density of states (DOS) calculation of the entire system (compound 1 and Si-B). The contributions of the adsorbed molecule and the surface were both investigated: The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy positions, around -2.0 and $+1.3$ eV with respect to the Fermi level, were determined by DOS as a function of the energy of the adsorbed molecule on Si-B surface. The corresponding band gap (3.3 eV) is close to the calculated band gap of isolated molecule (3.1 eV). Moreover, the energy positions of HOMO and LUMO of the adsorbed molecule are located near p_z silicon state peaks of the substrate at around -2.3 and $+1.2$ eV, respectively. The representation of the isodensity in the conduction band integrated between the Fermi level and the molecule LUMO energies shows a weak interaction that corresponds to a small transfer of electronic density from the triazine core to a Si adatom of the substrate (Fig. 7). All these results clearly suggest that the molecule-substrate interactions are weak and do not involve any Si-C σ bonds.

In conclusion, we have shown that the weak interactions between rich π -electron molecules with empty p_z depopulated dangling orbitals of the Si-B surface are most likely to be at the origin of the specific adsorption of isolated triazine molecules at the Si-B surface. This structure is stable at room temperature, and the π -conjugated skeleton of compound 1 is preserved even after deposition.

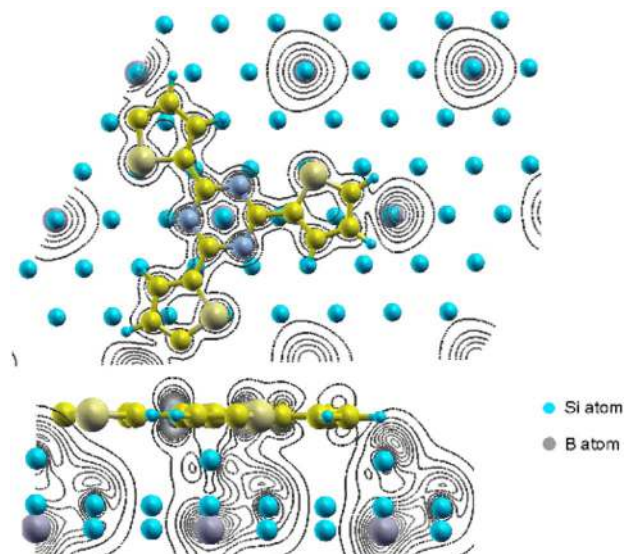


FIG. 7 (color online). Top and side views of the density of states of adsorbed molecules of compound 1 on the Si-B surface integrated in the conduction band until the LUMO molecule band, showing a weak interaction between molecule and substrate. The scale of the contour lines represents the LDOS isolines with a step variation of 0.008.

Molecular modeling supports all experimental data and supramolecular self-assemblies based on this building block are currently under investigation.

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