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Tailored Molecular Design for Supramolecular Network Engineering on a Silicon Surface

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The formation of large-scale and periodic supramolecular networks on a surface is of primary interest for the development of smart nanocomponents.[1] Such objectives require the synthesis of organic molecules with appropriate functions in order to obtain supported organic nanostructures with a geometry of atomic precision on a surface.[2] Supramolecular networks, which are based on non-covalent interactions such as van der Waals (vdW) forces, hydrogen bonding and metal coordination, have been widely investigated on noble metal or HOPG surfaces.[3–18] More recently, supramolecular self-assembly on graphene has been reported.[19] On insulating surfaces, some examples of supramolecular networks have been investigated by AFM.[20–23] In contrast, the adsorption of molecules on semiconductor surfaces is generally governed by the reactivity of the surface dangling bonds. Avoiding covalent bonding of the molecules is thus achieved either by choosing an appropriate molecular architecture or by passivating the surface dangling bonds.[24–32] To succeed in the formation of a supramolecular assembly over a macroscopic area ($>1\ \mu m^2$) on semiconductor surfaces, we have chosen the second solution, through the use of a passivated Si(111)-B surface.[31–33] This surface is inert to π-conjugated molecules due to the boron atoms present underneath the silicon adatoms, which depopulates all the dangling bonds of the silicon adatoms. Based on the observation of supramolecular networks with scanning tunneling microscopy, we propose to investigate the role of a few substituents in molecules on the geometry of the molecular arrangements. We demonstrate that the formation of an open or a close-packed network can be achieved by choosing an adequate molecule termination. As non-covalent bonds are weak, we also examine the robustness of the supramolecular networks at different temperatures.

Deposition of 1,3,5-tri(4′-bromophenyl)benzene (TBB, Figure 1 a) molecules on Si(111)-B leads to the formation of a large-scale 2D open supramolecular network with a thermal stability up to 400 K.[31] This network is commensurable with the surface, with an unique adsorption site. Therefore, the supramolecular network growth results from both attractive molecule–substrate interactions and attractive molecule–molecule interactions. In order to highlight the role of the end-groups that saturate the molecule termination, two new molecules based on the same 1,3,5-triphenylbenzene molecular backbone were synthesized. They consist of different end-groups, bearing either iodine or hydrogen atoms. These novel molecules, 1,3,5-tri(4-iodophenyl)benzene and 1,3,5-triphenylbenzene are labeled TIB and THB in Figures 1 b and 1 c respectively. In each case, the distance between the center of the phenyl groups of each arm is equal to 0.68 nm. The separation between two end-groups for TBB and TIB are similar (~ 1.30 nm), while it is slightly shorter for THB (1.17 nm).

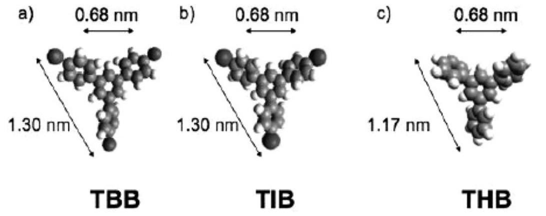

Figure 1. CPK (Corey–Pauling–Koltun) model of the gas-phase minimum-energy conformation of a) 1,3,5-tri(4′-bromophenyl)benzene (TBB), b) 1,3,5-tri(4-iodophenyl)benzene (TIB) and c) 1,3,5-triphenylbenzene (THB).

Figure 2 a shows a STM image of the TIB/Si(111)-B interface for a monolayer coverage. Two types of protrusions are visible. The brightest ones are attributed to the features of the molecular network, whereas the dim ones are located below the molecular layer and correspond to the Si adatoms.[33] From the atomic lattice of the Si(111)-B $\sqrt{3}\times\sqrt{3}R30^\circ$, we find that the supramolecular network adopts a $3\sqrt{3}\times 3\sqrt{3}$ periodicity, commensurable with the underlying atomic lattice. The molecular network consists of pores that are surrounded by six bright protrusions. Given the dimensions of a molecule and assuming that the symmetry of the molecules in the gas phase is not strongly altered after adsorption of the molecule, we are able to identify individual molecules in the network. Each molecule connects three adjacent pores. Interestingly, two types of domains are found. Comparison of Figures 2 a and 2 b obtained on two different molecular islands shows the existence of chiral networks. The formation of two enantiomers is due to the location of the center of all TIB molecules between three silicon adatoms and the rotation of the I–I axes of the TIB molecules by $+30^\circ$ (Figure 2 c) or by -30° (Figure 2 d) with respect to the rows of Si adatoms. Therefore, the 2D nanoporous network shows a similar geometry as that found for the TBB/

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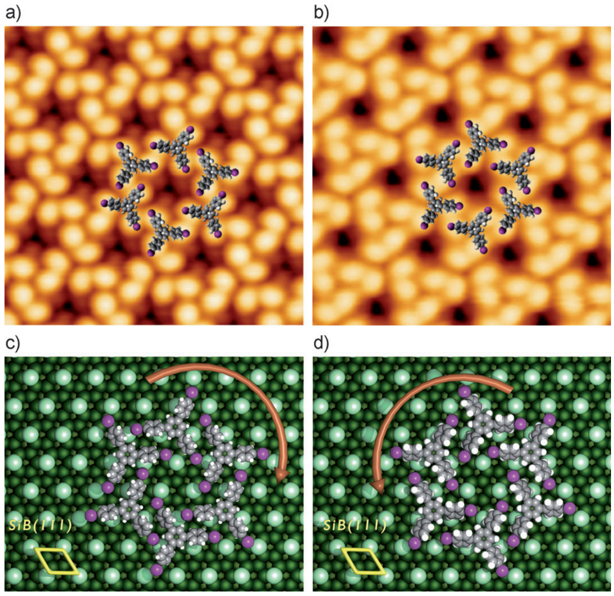

Figure 2. STM images, obtained for monolayer coverage, of the two enantiomeric, a) clockwise, b) anti-clockwise, TIB networks on a Si(111)-B surface with six superimposed TIB molecules (Vs = +2.4 V, I_t = 0.06 nA, 7×7 nm^2, 77 K). Adsorption model of the two enantiomeric, c) clockwise, d) anti-clockwise, TIB/Si(111)-B, where the Si adatoms are shown by light balls and Si bulk atoms are shown by dark balls.

Si(111)-B interface,[31] and the substitution of bromine atoms by iodine atoms does not affect the supramolecular assembly of the molecules. We also note that the network is stable in the 100–300 K temperature range. Moreover, within this temperature range, we were not able to see isolated molecules adsorbed on the surface.

In order to check if the halogen atoms play a key role in the formation of the TIB network on Si(111)-B surface, the adsorption of a molecule with the same molecular backbone and terminated with hydrogen atoms was also investigated for temperatures of 100 and 300 K. 1,3,5-triphenylbenzene molecules (THB, Figure 1 c) were deposited onto the Si(111)-B surface. At low coverage, the THB molecules self-assemble into small islands. From the comparison of STM images acquired over a period of times of several minutes at the same position on the substrate, we find that the island morphology changes. For example, Figure 3 b was recorded ten minutes after Figure 3 a at 100 K and it is clear that the shape and size of the islands are different. Such a result indicates that the molecules diffuse at 100 K. At 300 K, the molecular network is no longer visible, indicating that the molecules return to their gas phase or that they cannot be imaged due to their fast diffusion.

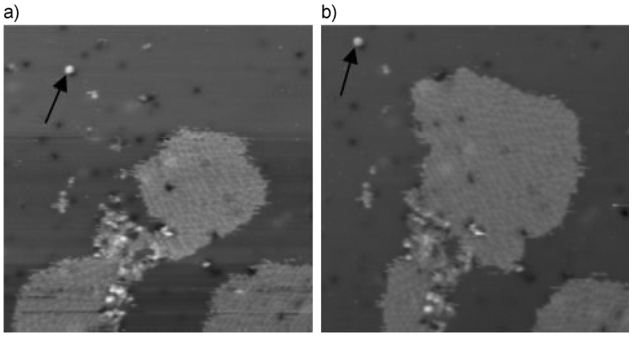

Figure 3. a) STM image of the THB/Si(111)-B interface (Vs = +2.0 V, I_t = 0.01 nA, 60×60 nm^2, 100 K). b) STM image of the same area recorded 10 min after (a). The black arrow, corresponding to a surface defect, is used as a static reference.

At higher coverage, the islands are more stable and high-resolution STM images are readily obtained. In contrast to the TIB network, the images clearly show the existence of a compact layer (Figure 4 a). In order to attribute the protrusions corresponding to a single THB molecule, the first point is to consider the C_3 symmetry of THB molecule. From the expected size of a single molecule, a THB molecule would consist of three protrusions that are located at the vertices of an equilat-

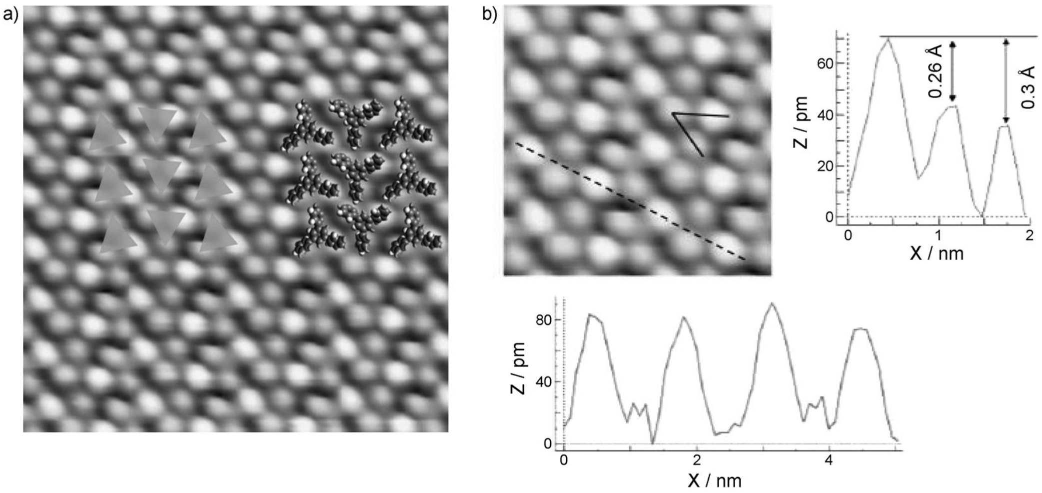

Figure 4. a) STM image of a commensurable monolayer of THB on a Si(111)-B surface with superimposed THB molecules (Vs = +2.0 V, I_t = 0.06 nA, 10×10 nm^2, 100 K). b) *Z*-profiles along dashed and black lines of STM image.

eral triangle, as shown in Figure 4. Then, if we consider the central molecule of the cluster, which is superimposed to the STM image in Figure 4a, we see that the adjacent molecules positioned above and below are pointing both downward, toward the same direction, whereas the left and right neighbours have the opposite orientation. Therefore, the molecular network consists of alternating rows of molecules pointing either upward or downward. Such an arrangement leads to a tiling that maximizes the molecular interactions, because each molecule has two arms interdigitated with the arm of two molecules in adjacent rows.

Surprisingly, whatever the configuration is, each molecule shows a protrusion that is much brighter than the two others the (see the height profile along the black solid line shown in Figure 4b). Based on the commensurability of the molecular network with the Si(111) surface (with a periodicity of ×2, see the height profile along the dashed line in Figure 4b and the Supporting Information), we do not expect a variation in the contrast for a planar molecule. Indeed, if we consider that the central phenyl is located in the middle of a triangle formed by three adjacent adatoms, as shown in Figure 2, the symmetry imposes an equal distance between those adatoms and the phenyl group of each arm. As a result, the three different phenyl end-groups do not have the same tilt and the transmission probability through each arm will be different due different electronic coupling between the arm and the surface. Such rotation of the arms might be favored by an increase of molecular interaction or by steric hindrance.

Based on the identification of the lobes obtained for the THB molecules, we now return to the TIB molecules. While superimposing the structural model on the STM image does not allow us to conclude whether a bright lobe is caused by the phenyl group or the halogen atom of each arm, additional information can be provided by imaging the molecular features with different sample voltages. Figure 5 compares two STM images obtained at two opposite voltages. The empty-state image acquired at +2.3 V (Figure 5a) shows a similar contrast as the one seen in Figure 2 and measured at +2.0 V. Conversely, at a voltage of −2.3 V, the contrast changes. First, the features surrounding a pore are alternatively bright and dim, indicating that adjacent molecules have two different adsorption states. Then, from the arrangement of the molecules determined in Figure 2, we can see that the end-groups appear bright. They are connected by a dark thread, which features the molecular backbone. Therefore, we attribute the protrusions seen at positive and negative sample voltages in the STM images to the iodine atoms. Finally, we note that an additional faint contrast is seen between each end-group and the center of an adjacent molecule, suggesting the existence of a chemical linkage between molecules.

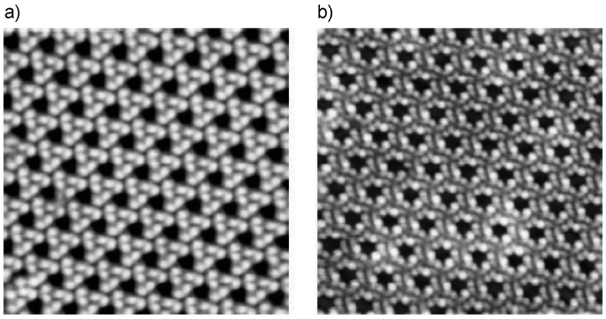

Figure 5. STM images, obtained for monolayer coverage, of TIB/Si(111)-B interface, obtained in the two polarities ($I_t = 0.06$ nA, 15×15 nm^2, 77 K, a) Vs = +2.3 V, b) Vs = −2.3 V).

As described in the previous paragraph, changing the halide atoms does not change the basic pattern of the supramolecular network. However, the substitution of the halide atoms by hydrogen atoms strongly modifies the basic pattern of the network. TIB leads to an open network whereas THB leads to a close-packed network. In the case of THB, the diffusion of the molecules at room temperature rules out any chemical reaction of the phenyl groups with the Si adatoms. The network self-assembles through intermolecular interactions that are of the type of VdW interactions because THB molecules contain only hydrogen and carbon atoms (no charge, no dipole, etc.). The VdW interactions are attractive, not directive, long-range and weak. In the case of the TIB and TBB molecules, we suspect the presence of iodine to overcome the VdW interactions and thus modify the intermolecular interactions.

TIB and TBB molecules are structurally very similar because they differ only in the nature of the halide atoms (iodine versus bromine) linked to the ends of each arm. Thus, it is quite reasonable that the networks obtained after deposition of these molecules on the Si(111)-B surface are identical. Remarkably, the comparison of the empty-state images for both systems reveals the same contrast.[31] The molecules appear with three bright protrusions. Since a faint contrast is seen between the TIB molecules in Figure 5b, which could be indicative of intermolecular interactions, we show enlarged STM images of the TIB and TBB molecular network at negative sample bias in Figure 6.

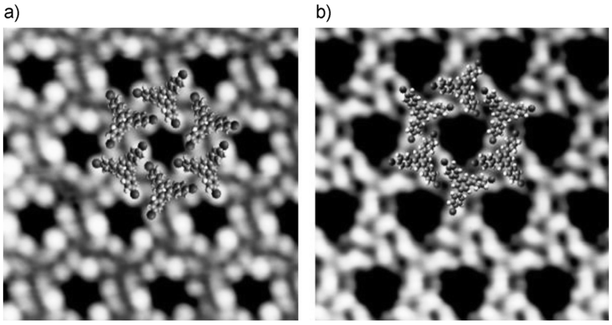

Figure 6. a) STM images, obtained for monolayer coverage, in filled states of TIB/SiB(111) surface with six superimposed TIB molecules (Vs = −2.3 V, $I_t = 0.02$ nA, 7×7 nm^2, 77 K. b) TBB/Si(111)-B interface surface with six superimposed TBB molecules (Vs = −2.3 V, $I_t = 0.06$ nA, 7×7 nm^2,77 K).

In the case of the TBB molecules (Figure 6b), three protrusions are linked by a thin thread, that allows us to distinguish the backbone of each molecule. Similarly to the TIB molecule, such an observation demonstrates that the halide atoms predominantly contribute to the STM contrast in the empty-state images. Knowing the positions of the halide atoms, we notice that the end-groups of adjacent TBB molecules are also linked by a bright thread. Thus, this feature is common to both TIB and TBB molecules and suggests the formation of molecule–molecule interactions of the type aryl—X···H hydrogen bonds, X being a halogen atom.[37–39] In the adsorption model of Figure 7, six aryl—I···H hydrogen bonds per molecule are possible, involving the three hydrogen atoms of the central phenyl ring and the three iodine atoms of each TIB molecules. We find a distance I···H of 0.33 nm, which is in good agreement with literature data.[38]

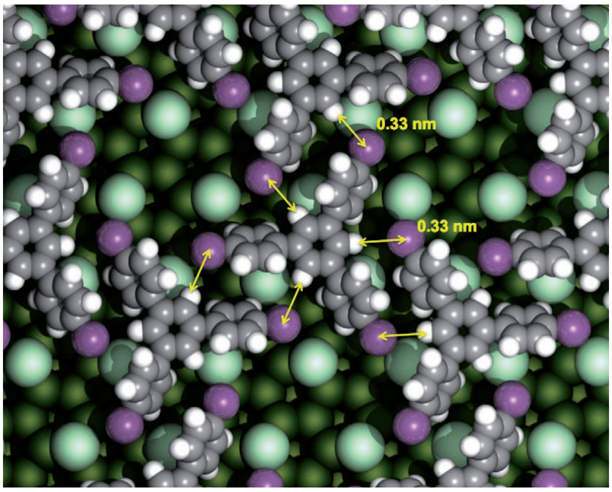

Figure 7. Six aryl—I···H hydrogen bonds per TIB molecule in adsorption model of THB/Si(111)-B.

Therefore, we suspect the six aryl—I···H hydrogen bonds per TIB molecule to stabilize the molecule arrangement in the network and to be at the origin of the pore formation. In the case of THB, the network is only stabilized by VdW interactions, which are weaker than aryl-I···H hydrogen bonds. These hypotheses are also supported by the stability of the TIB network at room temperature whereas the THB network is not observed at this temperature.

We report the formation of supramolecular networks under ultrahigh vacuum on a silicon surface. The role of halogen atom for increasing the thermal stability of supramolecular networks on a Si(111)-B surface is demonstrated. By using tailored molecules with a slight modification of geometrical parameters, molecule–molecule interactions can be tuned in order to obtain close-packed or open frameworks. Substitution of halogen atoms by hydrogen atoms implies a decrease in molecule–molecule interaction, leading to the formation of a close-packed network.

Experimental Section

Molecules

1,3,5-tri(4′-bromophenyl)benzene, 1,3,5-tri(4′-iodophenyl)benzene and 1,3,5-triphenylbenzene were purchased from Aldrich and then purified by column chromatography on silica gel and then sublimated.

STM Experiments

The Si(111) substrate was heated under ultrahigh 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 molecules from a Mo crucible onto the sample at room temperature was performed at 60 °C and a base pressure lower than 10^{-10} mbar. STM experiments were performed with a VT-STM Omicron microscope installed in an ultrahigh vacuum chamber with a base pressure lower than 2×10^{-10} mbar. STM images were acquired in constant-current mode at room temperature (RT), or at low temperature (77–100 K). All STM images were analyzed using WSxM software.[40] The artwork was produced with Blender.[41]

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Supporting Information

Tailored Molecular Design for Supramolecular Network Engineering on a Silicon Surface

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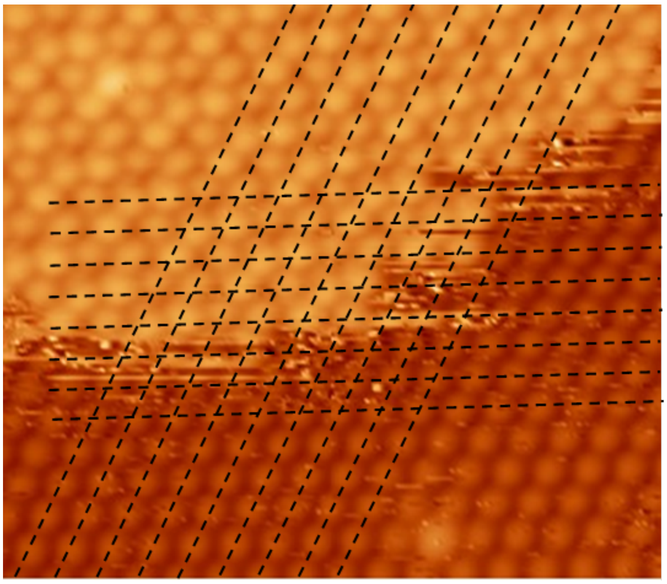

Figure S1. STM image of step edge of THB/Si(111)-B interface Vs = 1.9 V, It = 0.01 nA, 13x13 nm^2, 100K

The top of the STM image shows the molecular network, while the periodic protrusions seen at the bottom of the image correspond to the Si adatoms. The periodicity and the adsorption sites are revealed by drawing lines along the atomic rows of the Si surfaces.