

Hexacene Generated on Passivated Silicon

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Description of the preparation of Si(001)-(2x1):H

Experiments were performed using a LT-STM (Createc) at 5 K under ultrahigh vacuum (UHV) conditions. The Si(001) samples are Sb-doped (n-type), with a conductivity of 8 m Ω ·cm. The samples were first degassed for at least 6 h at 1050 K and flashed several times at 1420 K to remove the oxide layer. After preparing a clean Si(001)-(2 \times 1) reconstructed surface under UHV (base pressure below 1 \times 10⁻¹⁰ mbar), the hydrogenation of the Si(001) surface is performed at a sample temperature of 640 K. Atomic hydrogen was created by cracking molecular hydrogen (p_{H2} = 5 \times 10⁻⁷ mbar) with a W-filament heated to 2170 K and placed 10 cm away from the surface. This preparation enables us to have a 2 \times 1 reconstruction of the hydrogenated Si(001) surface with a certain density of defects on the surface as it can be seen in Figure S1(a). No DB-dimers were observed.

Additional STM data

Figure S1(b) is an overview image after sublimating molecules onto the surface and direct annealing to 250 °C for five minutes. A certain amount of larger agglomerates is present on the surface. Additionally, precursor and partially reacted molecules can be seen (these molecules are encircled in purple). We observe in this image one molecule with the appearance of hexacene that is attached to several defects (surrounded by a red circle).

After a further annealing step to 300 °C we see a reduced molecular coverage and no enlarged agglomerates, but a higher concentration of DB-defects on the surface. Now, we only find molecules that have the appearance of hexacene and are attached to dangling bond defects.

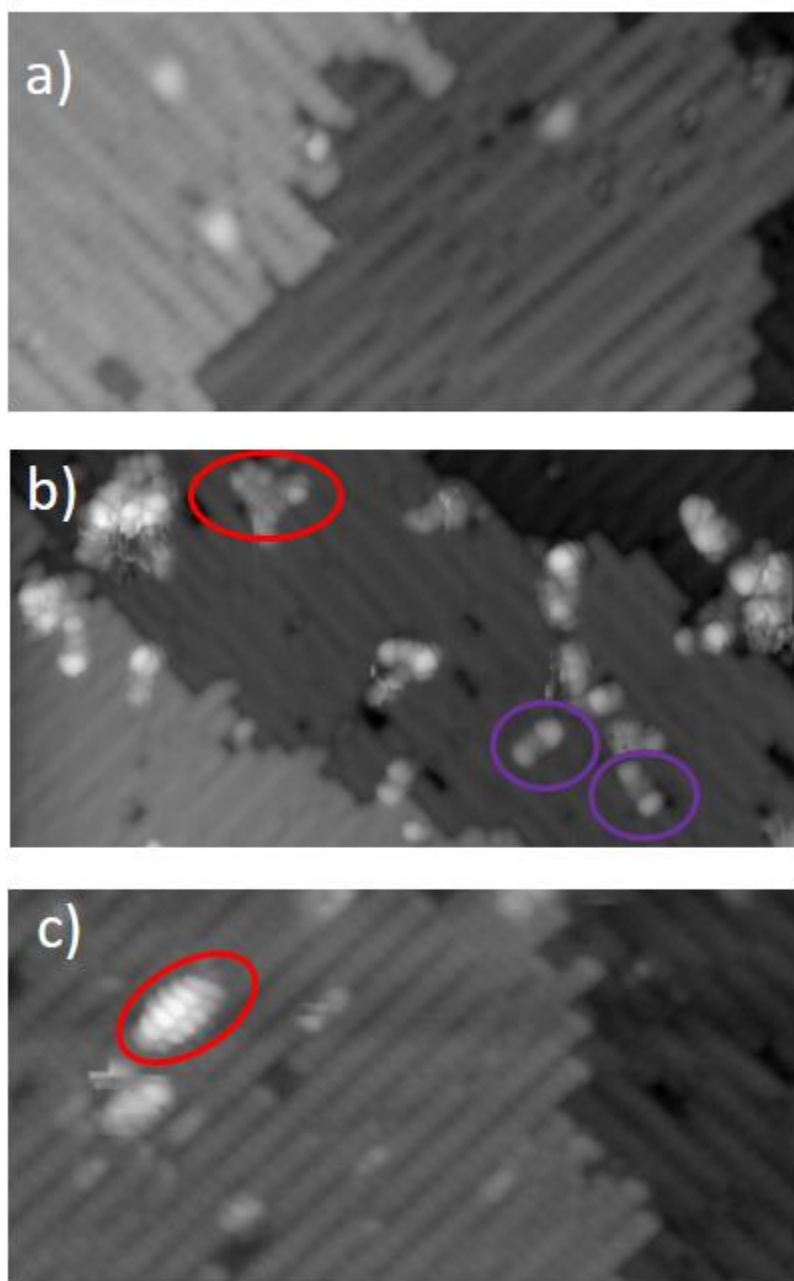


Figure S1. Overview image of the surface after the different preparation steps. (a) Si(001)-(2x1):H before the sublimation of the precursor triepoxyhexacene (Hn3O) onto the surface ($V = -2.0$ V; $I = 50$ pA; image size: 20 nm x 10 nm). (b) A typical overview image after the deposition of Hn3O and subsequently heating of the surface to 250 °C for 5 min. The purple circles show precursor or partially deoxygenated molecules. The red circle presents a completely reacted molecule. In addition, larger adsorbates are present on the surface ($V = -3.0$ V; $I = 15$ pA; image size: 30 nm x 15 nm). (c) Overview image after further annealing to 300 °C for 5 min. The red circle presents a completely reacted molecule ($V = -2.5$ V; $I = 15$ pA; image size: 20 nm x 10 nm).

In Figure S2(a) hexacene is imaged once more with the appearance of the HOMO resonance. To evaluate the anchoring point, we try to detach the molecule from this point and are able to

remove hexacene during scanning at + 2.0 V (see Figure S2(b)). Once more measured at the same position, we image a single DB, where hexacene has been imaged before. With the help of a defect close by, the position of the DB below the molecule can be specified. As this is at the position that has been figured out to be lower in the apparent height, we can determine that this is the position of the anchoring.

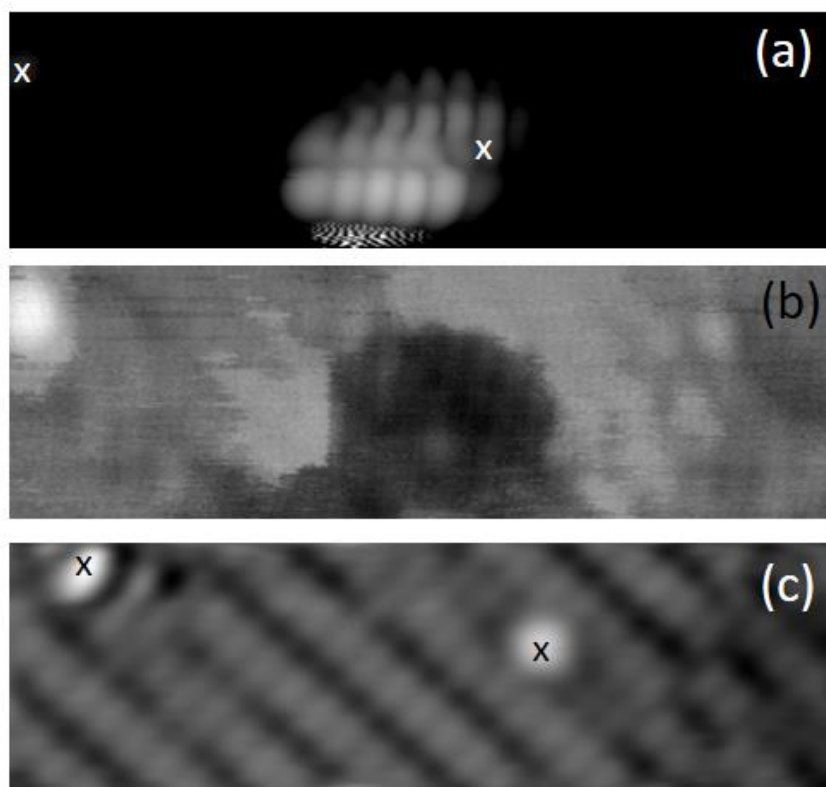


Figure S2. (a) Hexacene molecule above a single DB. The white cross marks the position of a defect on the surface and the other cross marks the position where the DB has been found in c) below the molecule. The color code is chosen to be black and white to focus just on the molecule, as we had a slight double tip (image size: 10 nm x 3 nm; $I = 80$ pA; $V = -3.0$ V). In (b) we show the image during a measurement at positive bias. Clearly the molecule was removed from the DB (image size: 10 nm x 3 nm; $I = 20$ pA; $V = +2.0$ V). In Figure (c) we clearly visualize the DB (image size: 10 nm x 3 nm; $I = 20$ pA; $V = -2.5$ V). With the help of the defect, the position of the DB underneath the molecule can be marked in (a).

Additional DFT data

We optimized triepoxyhexacene above five DB-dimer rows to see, whether a deoxygenation above these defects is possible or not. Furthermore, we want to discuss the ability of the reduction for the different configurations of oxygen (up and down) and assume that a similar behavior can be seen above single DB's. The configuration of the acene-derivative used here is

up-down-up, which describes the direction in that the oxygen of the epoxy-group is pointing. After optimization, the non-planar fashion of the molecule becomes clear (see Figure S3).

For the oxygen pointing towards the surface, it seems to be likely that a chemical reaction between surface and molecule does occur. In this means, the molecule is reduced and the oxygen is cleaved from the molecule. A different situation can be seen for the epoxy groups pointing away from the surface, where no chemical reaction occurs. Furthermore, we observe the intercalation of the oxygen into the silicon substrate.

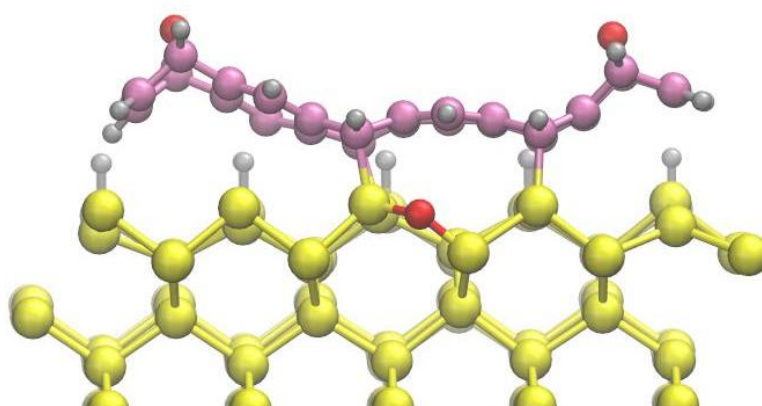


Figure S3. DFT-calculated optimized molecular structure of Hn3O above five dimer rows of dangling bonds on Si(001)-(2x1):H.