# Contacting a Conjugated Molecule with a Surface Dangling Bond Dimer on a Hydrogenated Ge(001) Surface Allows Imaging of the Hidden Ground Electronic State

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ABSTRACT Fabrication of single-molecule logic devices requires controlled manipulation of molecular states with atomic-scale precision. Tuning molecule—substrate coupling is achieved here by the reversible attachment of a prototypical planar conjugated organic molecule to dangling bonds on the surface of a hydrogenated semiconductor. We show that the ground electronic state resonance of a Y-shaped polyaromatic molecule physisorbed on a defect-free area of a fully hydrogenated surface cannot be observed by scanning tunneling microscopy (STM) measurements because it is decoupled from the Ge bulk states by the hydrogen-passivated surface. The state can be accessed by STM only if the molecule is contacted with the substrate by a dangling bond dimer. The reversibility of the attachment processes will be advantageous in the construction of surface atomic-scale circuits composed of single-molecule devices interconnected by the surface dangling bond wires.
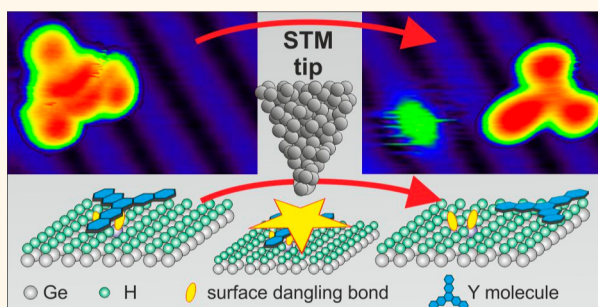
○ Ge   ○ H   ▬ surface dangling bond   ⦙ Y molecule

Detailed knowledge of the electronic structure of individual molecules and the ability to manipulate their electronic states are the key ingredients for the construction of single-molecule logic circuits. One of the most powerful tools to visualize individual atoms and molecules, to probe their electronic properties, and to manipulate them with atomic-scale precision is the scanning tunneling microscope (STM).[1−15] However, the use of an STM requires metallic or semiconducting substrates. As a result, originally designed electronic properties of free molecules are in general not retained after adsorption, due to electronic coupling of the molecular

electronic states with the surface. To overcome this problem, a passivating layer must be inserted between the molecules and the surface of the substrate to minimize those interactions. In recent years, several examples of molecules electronically decoupled by an ultrathin insulating layer on metals[7,16] and on semiconductors[17] have been reported, showing that even a monolayer of insulating material efficiently minimizes the electronic coupling. For example, Bellec et al. have shown that pentacene molecules are decoupled from the semiconductor bulk states by surface hydrogenation.[18] The transport properties of molecules on the hydrogenated surface, however, can

be influenced by the surface dangling bonds (DBs), as demonstrated by Piva et al.[19] Moreover, the ability to create[20] surface DBs on demand by extracting specific hydrogen atoms from the semiconductor surface allows in principle to create a planar atomic-scale contact between a physisorbed molecule and a DB.

In this paper, we demonstrate that a single tri-naphthylene (Y) molecule physisorbed on a hydrogenated semiconductor surface can be reversibly contacted with a single surface DB dimer. This molecule was selected because it was demonstrated to function as a NOR logic gate on a Au(111) surface.[4] On a fully passivated Ge(001):H surface, its ground electronic state resonance cannot be recorded in the corresponding scanning tunneling spectroscopy (STS) dI/dV spectrum because it is very well decoupled from the semiconductor bulk states. However, when this molecule is manipulated to a native or specifically constructed DB dimer to increase its interaction with the Ge bulk electronic states through the DB states, the ground state tunneling resonance becomes observable. This leads to large differences in the recorded STM intramolecular contrast of this molecule when it is positioned on a surface DB dimer compared to the same molecule positioned on a fully hydrogenated surface.

RESULTS AND DISCUSSION

Physisorbed Molecules. Filtering the Ground Electronic State Resonance by a Hydrogenated Surface. Low-temperature STM measurements performed after molecule deposition show that all molecules are located either at the surface step edges or on defect-like native DBs (see Figure 1, molecule 2). This indicates that the interaction between the Y molecules and the Ge(001):H surface is very weak. The Y molecules are physisorbed on the surface and are highly mobile, as observed previously for pentacene molecules on Si(001):H.[18] However, on Si(001):H the molecules were found only at step edges, while on Ge(001):H Y molecules can also be trapped by native DB defects. This is because a DB on Ge(001):H protrudes further into the vacuum than on Si(001):H. Therefore, a flat aromatic molecule can interact more strongly with a surface DB on Ge(001):H without any significant distortion of its planar structure. Still, Y molecules can be easily detached from DBs by STM lateral molecular manipulation. This procedure facilitates the identification of the native Ge(001):H surface defects that trap the Y molecule after adsorption (see Figure 1). The atomic structure of these surface defects is determined by a comparison between the appearance of a defect in an STM image, its STS characteristics, and the results of our recent studies of DB nanostructures constructed by STM tip-induced hydrogen desorption.[20]

The characterization of the uncovered DB defect is indeed consistent with results obtained for an intentionally created DB dimer on Ge(001):H, demonstrating that, during deposition, Y molecules are stabilized by
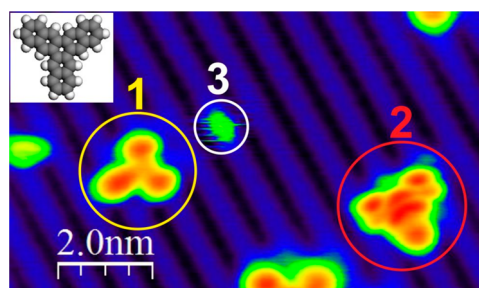

Figure 1. Filled state STM image of Y molecules on a hydrogenated Ge(001) surface. (1) Y molecule physisorbed on a defect-free Ge(001):H surface. The molecule was intentionally detached from a DB dimer (3) and placed on a defect-free area by STM tip-induced manipulation. (2) Y molecule in an initial geometry immobilized by a surface DB dimer. Inset: Atomic structure of the Y molecule. STM imaging conditions: bias voltage −2.0 V, tunneling current 2 pA. The image is acquired at liquid helium temperature (4.5 K).
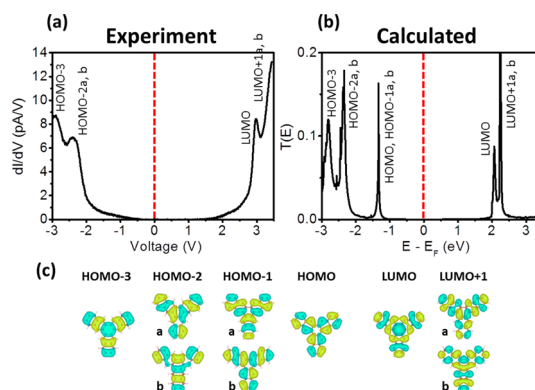

Figure 2. (a) STS spectra recorded over a physisorbed Y molecule on a defect-free Ge(001):H surface with indicated filled (−2.9 V; −2.4 V) and empty states (+3.0 V). (b) Transmission coefficient spectra, T(E), calculated for a physisorbed Y molecule on Ge(001):H. (c) Extended Hückel molecular orbitals for the gas-phase Y molecule.

native DB dimers on Ge(001):H.[20] It is worth emphasizing that our ability to remove a Y molecule from a DB dimer and to place it on the defect-free part of the Ge(001):H surface is extremely advantageous. This allows for a detailed characterization of the electronic properties of a molecule without any perturbation of its electronic structure by substrate defects. Our measurements show that Y molecules placed on the hydrogenated surface by the STM tip are stable enough to perform both STM imaging and STS characterization at liquid helium temperature. Although initially all molecules are trapped by surface defects, we will first discuss the electronic states and STM image of a Y molecule physisorbed on a fully hydrogenated Ge(001) surface, followed by a discussion of the electronic states and STM image of a Y molecule on a DB dimer.

STS measurements are performed on Y molecules positioned on a defect-free area of the Ge(001):H surface. As shown in Figure 2a, two distinct peaks are recorded at approximately −2.4 and −2.9 V below the Ge bulk Fermi level. A single resonance is also recorded

at +3.0 V in the conduction band of bulk Ge. Contrary to previous experiments with conjugated molecules on hydrogenated semiconductor surfaces,[18,21] the lowest excited state of the Y molecule can be probed with tunneling electrons on Ge(001):H. However, the apparent electronic gap between the first peak below and the first peak above the Fermi energy as measured by STS is approximately 5.4 eV, considerably larger than the HOMO−LUMO gap of 3.5 eV calculated for a gas-phase Y molecule. The electronic structure of a Y molecule physisorbed on defect-free Ge(001):H does not differ from a free molecule. In order to understand the large apparent gap between the STS peaks, the electronic transmission spectrum, T(E), for a Y molecule physisorbed on Ge(001):H is calculated with the STM tip apex located above the Y molecule (Figure 2b). The T(E) spectrum below the bulk Ge Fermi level comprises three peaks. The first resonance involves three molecular orbitals (MOs), HOMO, HOMO−1a, and HOMO−1b, which have nearly the same energy (separated by less than 0.05 eV). Note that these MOs are not located in the band gap of the Ge substrate. The second resonance originates from HOMO−2a and HOMO−2b, and the third resonance, which is the last peak within the energy window shown, is attributed to HOMO−3. The first resonance above the Fermi level corresponds to the LUMO and the second one to LUMO+1a and LUMO+1b (see Figure 2c for the spatial expansion and symmetry of those MOs for the isolated Y molecule). The calculated tunneling resonance gap of 3.5 eV is consistent with the HOMO−LUMO gap of a free Y molecule.

Interestingly, the first peak corresponding to HOMO, HOMO−1a, and HOMO−1b is calculated to be a very sharp Lorentzian resonance, implying that its contribution to the tunneling current intensity is very small. This is because the Y molecule is very well decoupled from the Ge bulk states by the hydrogen surface layer, and this decoupling is enhanced by the very small number of Ge bulk channels near the top of the valence band edge. Both effects limit the tunneling current in this energy range. Therefore, in this energy range, the tunneling current intensity is dominated by the tails of the HOMO−2a, HOMO−2b, and HOMO−3 resonances. Furthermore, for bias voltages down to −2.0 V, the STM images recorded for a Y molecule on a defect-free Ge(001):H do not exhibit any intramolecular contrast that would correspond to the HOMO/HOMO−1ab peak (see Figure 3a,b). The absence of the intramolecular contrast is apparent when these images are compared with the STM image of a Y molecule on a Au(111) surface measured at the ground state (HOMO) energy, which clearly shows the characteristic HOMO intramolecular features.[4] These images rather reflect the Ge-(001):H surface corrugation recorded through a planar Y molecule. The first HOMO/HOMO−1ab resonance is hence filtered by the tunneling junction, indicating that the interaction of those MOs with the Ge bulk states is
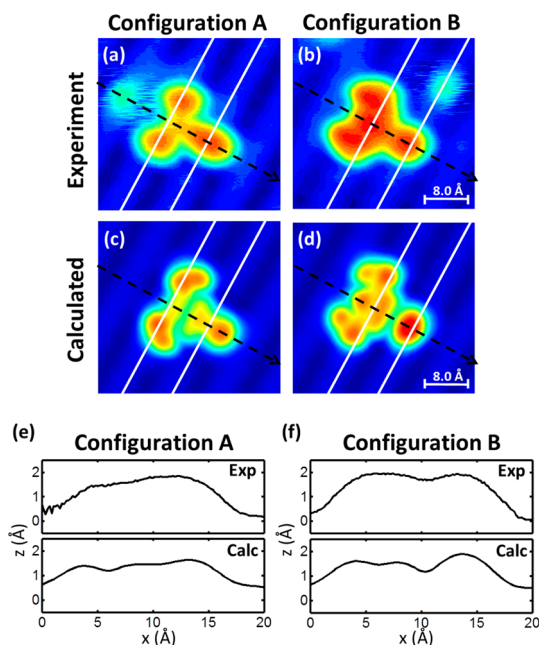

Figure 3. Two slightly different configurations (denoted as A and B) of physisorbed Y molecules on a defect-free Ge(001):H surface. (a and b) Filled state STM images. (c and d) STM images calculated when the HOMO/HOMO−1ab resonance is excluded. The presence of the Ge(001):H surface rows underneath the molecule, marked by white solid lines, results in the contrast variation over the molecule. The variation is different for configurations A and B, reflecting the positions of the hydrogenated surface rows. All images are acquired at −2.0 V bias voltage and 2 pA tunneling current. The bright green noisy features clearly visible in the experimental images correspond to the DB dimer. (e and f) Comparison of experimental and calculated corrugations of the Y molecule obtained along the black dashed lines shown in panels a−d.

so small that this resonance cannot be captured in the dI/dV spectra. The decoupling of these MO states from the Ge bulk states is also shown by the calculated MO structure, where almost no extension of Y MOs to the Ge bulk is observed (Figure 5g). This explains the very large apparent gap recorded for the Y molecule physisorbed on a defect-free Ge(001):H surface, even though those MOs are located neither in the intrinsic band gap of the Ge bulk nor in the surface band gap of the Ge(001):H surface.

Experimental STM images show that a Y molecule can physisorb in two slightly different configurations denoted as configurations A and B, respectively (Figure 3a,b). In both configurations, the Y molecule lies flat on the Ge(001):H surface with one Y arm perpendicular to the surface hydrogen dimer rows. The difference in the STM images arises from the slight displacement of the molecule perpendicular to those rows. In both cases, the structure of the Y molecule is not affected by the presence of the surface, and the resulting geometry resembles the gas-phase geometry. The results are in good agreement with previous theoretical calculations for polyacene molecules physisorbed on a fully hydrogenated Si(001) surface.[22,23]

The calculated STM images for configurations A and B are presented in Figure 3c,d. The slight differences in
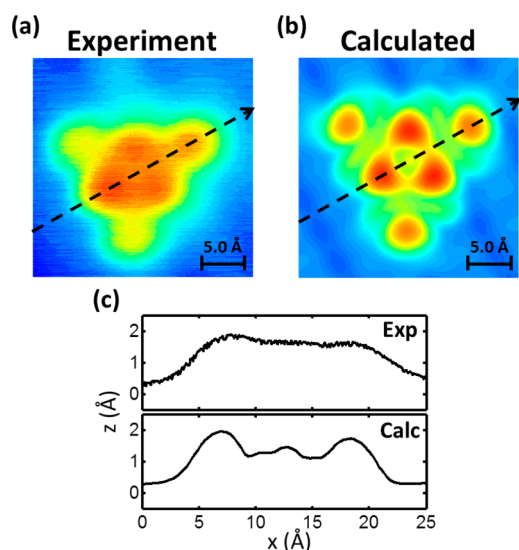
Figure 4. Excited state imaging. (a) Experimental empty state STM image of a Y molecule on defect-free Ge(001):H acquired at +3.5 V bias voltage and 2 pA tunneling current. **(b)** Calculated empty state STM image acquired at +2.1 V bias voltage and 2 pA tunneling current. **(c)** Comparison of experimental and calculated corrugation obtained along the black dashed lines in panels a and b.

the STM contrast between A and B originate from imaging of the Ge(001):H surface corrugation through the tails of the HOMO−2a, HOMO−2b, and HOMO−3 electronic state resonances. For example, the STM image of configuration A exhibits a higher contrast (conductance) for the arm perpendicular to hydrogenated surface rows (Figure 3c). The STM image of configuration B, where the central phenyl ring is located closer to the hydrogenated surface row, displays higher contrast (conductance) for the other arms and significantly lower conductance between these arms and the third arm (Figure 3d). The experimental and calculated surface corrugations of the physisorbed Y molecule are shown in Figure 3e,f.

The very weak coupling between the states of the Y molecule and the Ge bulk states is confirmed by STM imaging at a positive bias voltage (Figure 4). The STM image of a Y molecule on a Ge(001):H surface at +3.5 V resembles the images of a Y molecule physisorbed on Au(111) and on NaCl/Cu(111) surfaces, where three characteristic central lobes corresponding to a large conductance are observed near the LUMO resonance.[4,24] These lobes correspond to the spatial expansion of the LUMO of the Y molecule. The similarity of the first excited state image on Ge(001):H and on Au(111) indicates that the Y molecule is physisorbed and not chemisorbed on a Ge(001):H surface, and therefore the coupling between the states of the Y molecule and the Ge bulk states is weak. The calculated image agrees reasonably well with the experimental image (Figure 4). The difference in bias voltages is due to the difference in the position of the LUMO in the experimental dI/dV and in calculated T(E) spectra.

Y Molecule Contacted with a DB Dimer: Recoupling the Ground Electronic State Resonance to the Substrate. The intramolecular STM corrugation changes significantly when one end of the Y molecule is placed intentionally over a DB dimer. The electronic coupling between the electronic states of the Y molecule and the Ge substrate states is enhanced due to coupling through the DB dimer states. These states protrude into the vacuum and are located close to the energy range of the HOMO, HOMO−1a, and HOMO−1b molecular states around 1.0 eV below the Fermi level. The difference in the spatial expansion and hybridization of the states of the Y molecule on Ge(001):H with and without DB dimer is shown in Figure 5f,g, respectively. Notice that initially all Y molecules are trapped by surface DB dimers and other surface defects. By manipulating a Y molecule away from the surface defect using the STM tip, one can confirm that the molecule was on a DB dimer. The Y molecule can then be manipulated back to the DB dimer to investigate how the DB dimer states are coupled to the states of the Y molecule. Through such precise contacting, the interaction between the states of the Y molecule and the DB dimer states recouples the HOMO/HOMO−1ab states of the Y molecule to the Ge(001) states and therefore to the Ge bulk states, allowing for STM imaging of this hidden ground electronic state. This is evident from the difference in contrast between the experimental STM images of a Y molecule on a defect-free Ge(001):H surface (Figure 3a,b) and of a Y molecule contacted by a DB dimer (Figure 5a). The experimental and calculated images of a Y molecule contacted by a DB dimer are compared in Figure 5a,b, with the corresponding corrugations in Figure 5d,e. The DB dimer is located at the intersection of the dashed lines A and B. The images agree reasonably well. The differences in the amplitudes can be attributed to details of tip apex electronic structure. Notice that when the Y molecule is contacted by a DB dimer, one arm of the molecule is parallel to the Ge(001):H dimer rows, whereas for the Y molecule on a defect-free Ge(001):H surface, one arm of the molecule is perpendicular to the Ge(001):H dimer rows.

We first compare the calculated images and corrugations of the Y molecule contacted with a DB dimer with the corrugation for a Y molecule on defect-free Ge(001):H (Figure 5b,c,e) for an identical configuration. When the Y molecule contacts the DB dimer, a higher conductance is expected because this structure resembles the structure where one end of a conjugated molecular wire contacts a metallic step edge. For such a structure, a high conductance at contact was indeed observed experimentally.[25−27] The line scans across the Y molecule in contact with a DB dimer (solid lines in Figure 5e) clearly show a larger corrugation compared to the line scans without the DB dimer (dashed lines in Figure 5e). This higher conductance results from the
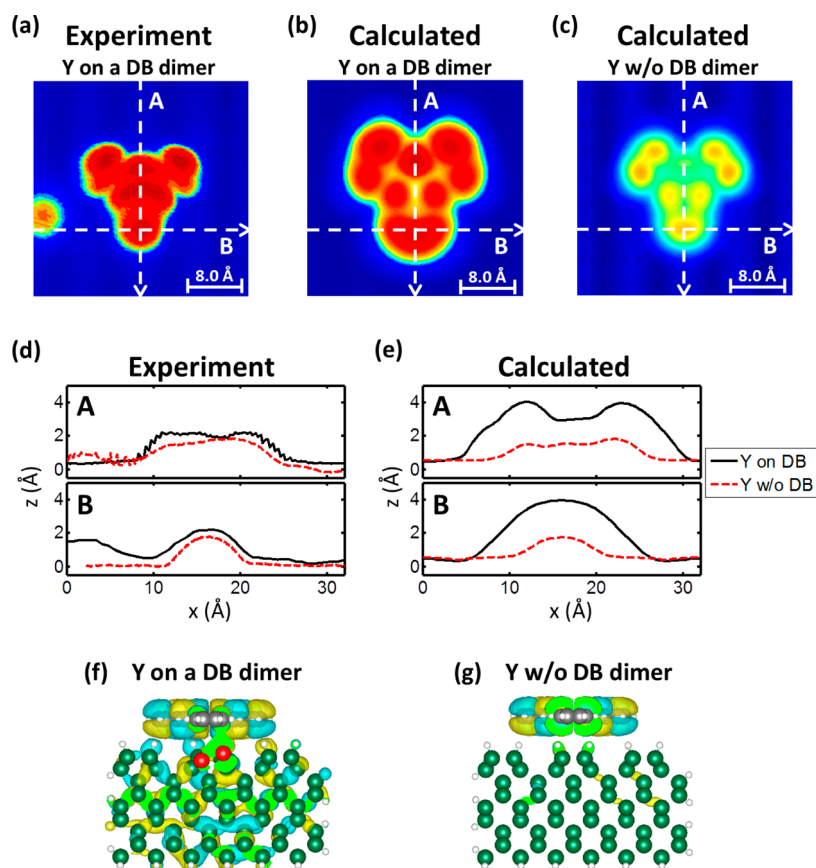
(a) Experiment Y on a DB dimer

(b) Calculated Y on a DB dimer

(c) Calculated Y w/o DB dimer

(d) Experiment

(e) Calculated

— Y on DB
--- Y w/o DB

(f) Y on a DB dimer

(g) Y w/o DB dimer

Figure 5. Y molecules on a DB dimer. (a) Filled state STM image of a Y molecule contacted by a DB dimer at −2.0 V and 2 pA. **(b)** Calculated STM image of a Y molecule contacted by a DB dimer. **(c)** Calculated STM image of a Y molecule on a Ge(001):H surface without a DB dimer. **(d and e)** Corrugation along the dashed lines A and B in panels a−c for calculated and experimental images. The black solid lines and red dashed lines correspond to the corrugation of a Y molecule on a DB dimer and on a fully hydrogenated Ge(001) surface, respectively. Note that the dashed lines in panel d show the corrugation of a Y molecule in configuration A shown in Figure 3a. **(f)** MO expansion, illustrating the coupling of the HOMO/HOMO−1ab states with the Ge bulk states *via* the DB dimer state. **(g)** MO expansion of a Y molecule on a fully hydrogenated Ge(001) surface, showing the decoupling of the HOMO/HOMO−1ab state from the Ge bulk states.

overlap between the DB dimer states and the MO states of the Y molecule, as shown in Figure 5f. The experimental STM image and line scan of the Y molecule on a fully hydrogenated Ge(001) surface and with one of the arms parallel to the surface H dimer rows could not be obtained due to the structural instability of this configuration. However, the experimental line scans of a Y molecule contacted by a DB dimer (solid lines in Figure 5d) have larger corrugations compared to the line scans of a Y molecule on a defect-free Ge(001):H in configuration A (dashed lines in Figure 5d), showing the same trend as the calculated results. Notice that the experimental line scan of configuration B (Figure 3f) cannot be used for comparison since the internal contrast of the Y molecule in configuration B is increased by the corrugation of the hydrogenated Ge (001) surface rows underneath the molecule.

To determine which state (HOMO, HOMO−1a, or HOMO−1b) contributes most to this contact conductance and therefore to the STM images, we have analyzed the symmetry of these states and of the experimentally recorded images. From the symmetry,

it is clear that the appearance of a single lobe at the Y-DB dimer contact point corresponds to the HOMO−1a (see Figure 2c). In addition, the lobes at the two other arms also resemble the symmetry of the HOMO−1a. Calculations also show that when the Y molecule contacts the DB dimer, the maximum of the transmission peak contains a dominant contribution from the HOMO−1a state. Notice that experimentally, the precise recording of the d*I*/d*V* spectra in the energy range of the HOMO/HOMO−1ab states is very delicate due to the instability of the Y molecule positioned on a DB dimer against higher currents and bias voltages, resulting in the uncontrolled detachment of Y molecules from the DB dimers during the acquisition of the STS spectrum. The STM images are recorded with an extremely small current, but this current is insufficient for STS measurements.

To resolve whether the Y molecule is adsorbed over a buckled or an unbuckled DB dimer, surface structure optimizations have been performed. Experiments show that a DB dimer is buckled at liquid helium temperature. However, when measured at increasing bias voltages,

the DB dimers flip frequently, as shown already in Figure 1. The stability of the buckled geometry is confirmed by calculations showing that the buckled geometry is 0.5 eV more stable than the unbuckled one. Thus, it is unlikely that the weak interaction with the Y molecule stabilizes the unbuckled geometry. Yet, the asymmetry of the buckled DB dimer under the Y molecule is not reflected in the experimental STM images. The symmetric appearance of the Y molecule positioned over a DB dimer seems to arise from either (1) oscillations of the DB dimer caused by tunneling electrons or (2) the filtering of the DB states by the bulk states of the Ge substrate, which provide an averaged symmetric contribution, similar to the recently reported symmetric appearance of buckled silicon dimers on a Si(001)-$c(4\times2)$ surface, where the buckling of the dimer is not apparent from the image when imaging is performed at a higher voltage.[28] To reproduce these effects in the calculated image, the images of the Y molecule on a DB dimer with two buckling configurations are calculated, and the average of the two images is obtained. This results in a symmetric image (Figure 5b) that agrees reasonably well with the experimental image.

CONCLUSIONS

In conclusion, we have shown that a large polyaromatic molecule physisorbed on a defect-free Ge(001):H surface can be imaged using STM. Because DB states on a Ge(001):H surface extend further into the vacuum compared to Si(001):H surface DBs, such molecules can be contacted with a DB dimer without significant distortion of their planar geometry. The ground electronic state of the physisorbed Y molecule on a defect-free Ge(001):H surface cannot be observed in the STM images due to the very weak electronic coupling of those states with the Ge bulk states through the Ge(001):H surface states. The ground electronic state becomes visible when the molecule is precisely positioned over a DB dimer, resulting in its direct STM observation. The reversibility of the electronic contact formation by LT-STM manipulation allows for a controlled coupling of a single conjugated molecule to a Ge substrate *via* a surface DB dimer, which can be native or precisely constructed using the STM tip. This opens up the possibility of constructing surface atomic-scale circuits using single-molecule devices and DB wires as interconnects.

METHODS

Experimental Details. All experiments are performed using a low-temperature Omicron GmbH STM operated at liquid helium (4.5 K) temperature in ultra-high-vacuum (UHV) conditions with a base pressure at the low 10^{-10} mbar range. The samples are cut from an undoped Ge wafer (TBL Kelpin Crystals, n-type, ~45 Ωcm). After insertion into the UHV chamber, the substrate is prepared by subsequent cycles of Ar$^+$ ion sputtering (600 eV, sputtering time: 10 min). During sputtering, the sample temperature is kept at 1020 K and controlled by an infrared pyrometer. The quality of the surface is checked by LEED and STM measurements. The surface hydrogenation procedure is performed using a home-built hydrogen cracker as described by Kolmer et al.[20] During the passivation procedure, the sample is kept at 485 K and the hydrogen pressure is maintained at 1×10^{-7} mbar. The trinaphthylene (Y) molecules are deposited from a three-cell Kentax effusion cell onto the sample, which is removed from the microscope cryostat just before the evaporation to keep the sample at cryogenic temperature. The molecular powder is purified before evaporation. The deposition is performed with the crucible at 450 K.

Calculation Scheme. To analyze the STM images, the electronic properties of a Y molecule adsorbed on a Ge(001):H surface are studied using theoretical approaches. The tunneling transmission coefficient, T(E), spectra (equivalent to the dI/dV experimental spectra) and the STM images are calculated using the surface Green-function matching (SGFM) method[29] with an extended Hückel molecular orbital (EHMO) Hamiltonian. The structures of Ge(001):H surfaces are optimized using the density functional theory (DFT) with the Perdew—Burke—Ernzerhof (PBE) functional[30] as implemented in the Vienna *ab initio* simulation package (VASP).[31−34] The parameters in the EHMO Hamiltonian are fitted to accurate DFT band structures obtained with the HSE06 functional,[35−37] which provides a more accurate description of the Ge band gap than the PBE functional.[20] The STM junction is modeled as described by Kolmer et al.[20] and takes into account all the electronic couplings inside the STM tunneling junction, including the coupling between the surface and the tip and the native couplings between the surface and the bulk electronic states.

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