

Probing the Conformation of Physisorbed Molecules at the Atomic Scale Using STM Manipulation

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ABSTRACT

We use scanning tunneling microscope (STM) manipulation and density functional theory calculation to investigate the structural properties of individual sexiphenyl molecules physisorbed on a Ag(111) surface at 6 K. The molecule–surface atomic registry is precisely determined by using atomic markers and a sexiphenyl functionalized tip. The calculations confirm the alternating twist of the sexiphenyl π -rings on Ag(111). The π -ring torsional angle, 11.4° , is directly determined from the geometry of STM manipulation. This innovative experiment opens up a novel application of STM manipulation to probe the properties of “physisorbed” species on surfaces at the atomic level.

The rapid progress in nanoscience creates the possibility of building molecular electronic devices at the single-molecule level.^{1–8} Sexiphenyl, an oligomer group molecule, is intensely studied by many research groups^{9–20} due to its potential application in light emission device fabrication. Sexiphenyl is 2.7 nm long and composed of a linear chain of six π -rings connected via C–C σ -bonds.⁹ The alternate π -rings of sexiphenyl are twisted with a torsional angle between 20° and 40° in the gas phase, and in molecular solids¹⁹ due to the steric repulsion between hydrogen atoms. A recent STM investigation of sexiphenyl on oxygen-passivated Ni(110)²⁰ shows that the π -rings of sexiphenyl do not always lie flat on the surface but occasionally appear tilted. Here, we use several STM manipulation schemes to determine the molecule–surface atomic registry, molecular conformation, and the π -ring torsional angle of individual sexiphenyls *physisorbed* on a Ag(111) surface at 6 K. Since the molecule–metal interface is crucial in controlling the quality of electronic devices, this experiment sets an example for the future investigation of physisorbed species at the atomic level.

The experiments were performed at 6 K substrate temperature by using a home-built ultrahigh vacuum, low-temperature STM system with a Besoke–Beetle type STM scanner, similar to the one described in ref 21. The Ag(111) sample was cleaned by repeated cycles of sputtering and annealing up to 1000 K. An electrochemically etched polycrystalline tungsten wire was used for the STM tip. The tip apex is prepared by using a controlled tip-crash proce-

dure.²² Sexiphenyl was deposited onto the cleaned Ag(111) surface at ~ 70 K substrate temperature from a Knudsen cell. The sample was then cooled to 6 K inside the STM system for the experiment.

STM images show an elongated shape of sexiphenyl with a zigzag-like appearance on Ag(111) (Figure 1). Due to weak molecule–substrate binding, sexiphenyls are easily displaced during STM imaging. Therefore, atomic resolution images of the surface together with the molecule are difficult to obtain. We use two alternative procedures to determine the sexiphenyl–surface atomic registry precisely, by creating atomic position markers and by imaging with a sexiphenyl-functionalized tip.

Creation of silver atomic position markers requires individual atoms on the surface coexisting with the molecules. Conventional silver deposition onto the Ag(111) surface, which already has physisorbed sexiphenyls on it, results in formation of sexiphenyl–silver atom complexes. This hinders the creation of silver atomic position markers. Therefore, instead of using conventional atom deposition, we extract individual atoms locally from the native surface by means of a tip-crash procedure.²² The extracted silver atoms are then repositioned along a surface close packed direction of the Ag(111) using the STM tip^{2,22,23,25} (Figure 1a). Since the silver adatoms are usually located at the 3-fold hollow sites on Ag(111), an atomic-scale net can be drawn to identify their exact positions (Figure 1a, and Supporting Information). Thus, the location of sexiphenyl with respect to the surface can be precisely determined. The measured data show that sexiphenyl is oriented with its long molecular axis parallel to a surface close-packed direction.

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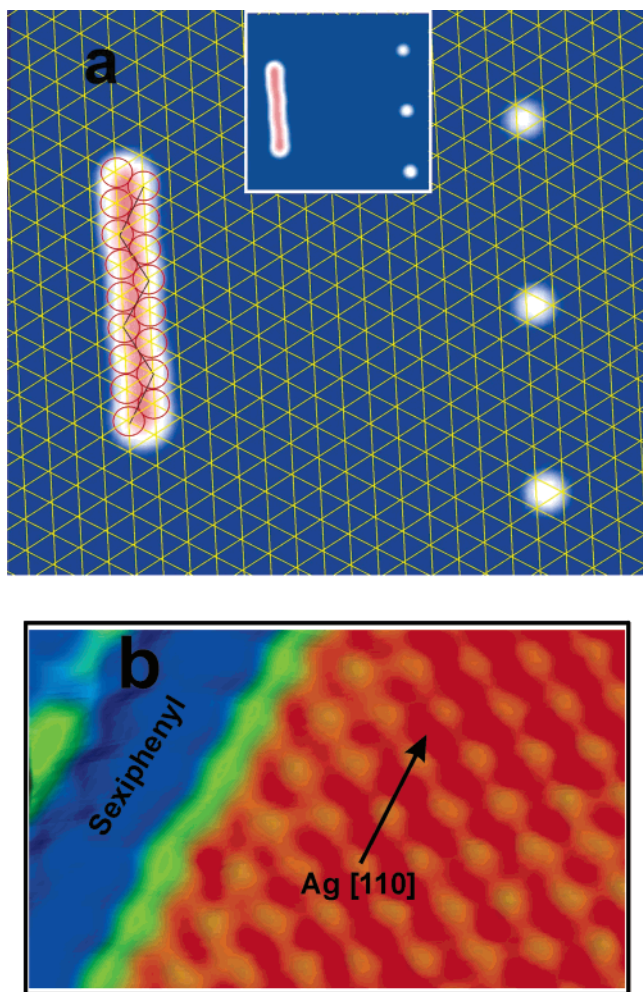


Figure 1. Sexiphenyl-surface atomic registry. (a) The individual silver atoms (white circles) are positioned by using the STM lateral manipulation^{2,22,23} along a surface close-packed direction with a six nearest-neighbor atom distance apart. The surface atom locations under the molecule (red circles) are resolved from the atomic net. The zigzag structure of sexiphenyl as determined from the molecule shape (inset) is indicated with a dashed line. [Imaging parameters: $V_t = 50$ mV, $I_t = 1.1$ nA, scan area = 6×5 nm²]. (b) An atomic resolution STM image of Ag(111) with a part of a sexiphenyl at left is acquired by using a sexiphenyl-functionalized tip. [Imaging parameters: $V_t = 50$ mV, $I_t = 1$ nA, scan area = 2.8×1.8 nm²].

In the second procedure, the sexiphenyl-surface atomic registry is determined by using a sexiphenyl-functionalized tip.^{2,24} Here, a sexiphenyl molecule is transferred to the tip-apex by a tip-molecule contact.² Imaging with a sexiphenyl tip allows to resolve silver atoms from the surface together with physisorbed sexiphenyls. Figure 1b shows an STM image of a part of sexiphenyl together with surface atomic structure, which confirms the previously measured location of sexiphenyl on Ag(111).

Figure 2a presents a close-up STM image of a single sexiphenyl molecule on Ag(111). Here, the zigzag appearance of sexiphenyl is more pronounced. We attribute this sexiphenyl appearance in the STM image as due to the π -ring twist, which can be explained as follows. The STM records the higher edge of the π -ring as a protrusion because it is closer to the tip. Since the π -rings are twisted in an alternating fashion, the protruding parts of the molecule

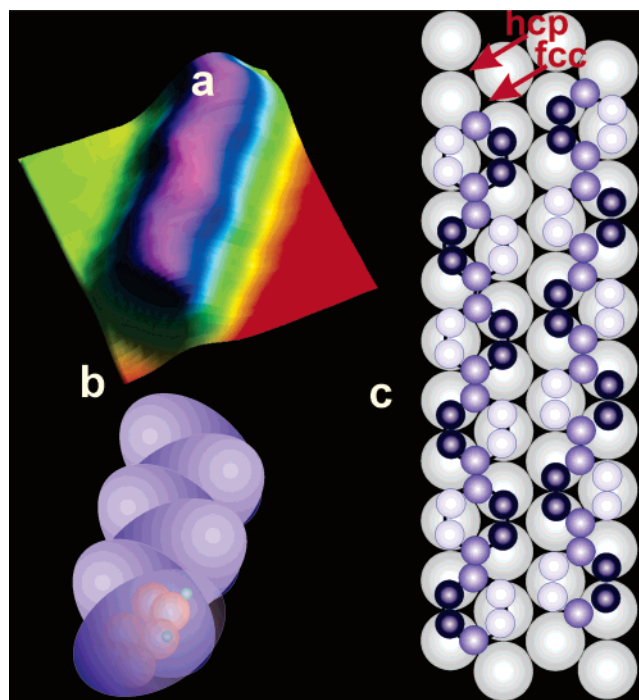


Figure 2. Sexiphenyl π -ring twist. (a) An STM image of sexiphenyl on Ag(111) at 6 K shows a zigzag appearance of the molecule. (b) A ball model demonstrates the π -ring twist (each ball represents a π -ring) producing a zigzag appearance. (c) The molecule-surface atomic registry as measured from Figure 1a. Light and dark balls represent the carbon atoms from upward and downward tilted π -ring edges, respectively. Notice that moving the sexiphenyl for a half silver atom distance along the surface close-packed direction (between hcp and fcc sites) will alter the molecule-surface atomic registry.

appear in a zigzag arrangement as demonstrated in the ball model (Figure 2b). Figure 2c illustrates the position of the molecule relative to the surface atoms as determined from Figure 1a and b. At this location, one side of the π -ring edge (two carbon atoms) is positioned on a single surface atom while the other edge is located above two surface atoms, and this arrangement is repeated. The π -ring edge above the single silver atom appears as a protrusion, indicating that this side is geometrically higher than the other π -ring edge. Therefore, this π -ring edge is tilted upward while the other edge is tilted downward. Because of the Ag(111) surface geometry, the two edges of the next π -ring will be reversed (Figure 2c), allowing the molecule to satisfy its natural tendency, alternating twist of the π -rings.

Let us consider shifting the molecule position along the surface close-packed direction by a half atomic distance, i.e., between an hcp and an fcc site (Figure 2c). From the sexiphenyl-surface atomic registry (Figure 2c), it can be seen that this will reverse the twisting arrangement. The π -ring edge previously located above two surface atoms will now be positioned above a single surface atom. In this case, the higher edge should now become a lower edge and the previously lower edge will now be the higher edge. This means that all the π -rings of sexiphenyl will flip to the opposite torsional angle. Figure 3 provides experimental evidence of such π -ring flipping. Initially, two sexiphenyls located in the upper part of image in Figure 3a appear in an

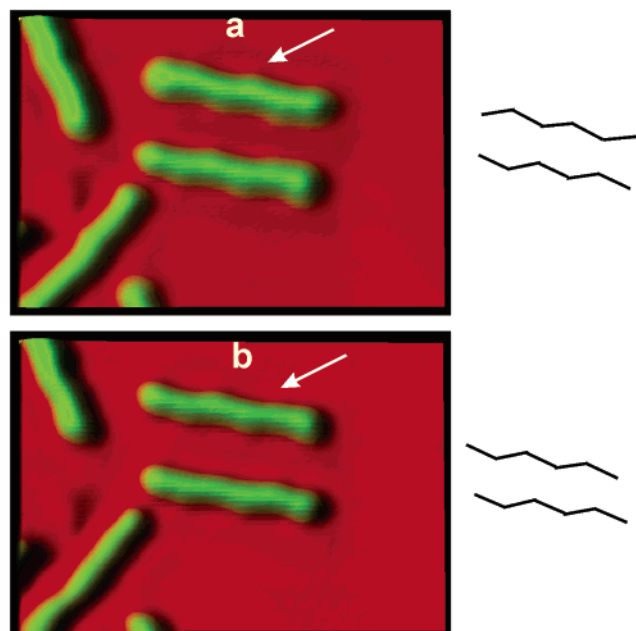


Figure 3. Sexiphenyl π -ring flipping. (a) An STM image of individual sexiphenyls on Ag(111) at 6 K shows an opposite zigzag arrangement of the two molecules located parallel (indicated by line drawings at right). (b) The same zigzag arrangement appears after moving the upper molecule (shown with an arrow) along the long-molecular axis direction. [Imaging parameters: $V_t = 49$ mV, $I_t = 0.16$ nA, scan area = 6.3×4.2 nm²].

opposite zigzag arrangement. The next image, which is acquired after moving the upper molecule forward (Figure 3b), shows a symmetric zigzag arrangement between the two sexiphenyls (Figure 3b), indicating that flipping of the π -ring twist has occurred.

In the next step, we directly detect the flipping of a sexiphenyl π -ring during its movement across the surface by laterally manipulating the molecule with the STM tip.²⁵ For this manipulation, the STM tip is initially positioned at an edge of the front π -ring (Figure 4). When the tip is moved along the surface close-packed direction, the sexiphenyl moves together with the tip. Here, we use a constant-current scanning mode where the tip height is maintained by means of the STM feedback loop. The corresponding tip-height signal recorded during this manipulation shows periodic low–high peaks repeating at every fcc–hcp site. From this manipulation signal, the sexiphenyl movement can be explained as follows. When the π -ring edge is down, a low height signal is recorded, and when it is up, a higher height signal appears.^{2,25} The periodic flipping of the π -ring twist when the sexiphenyl is moved along the surface close-packed direction provides the observed low–high manipulation signal. The torsional angle of π -rings is determined as 11.4° from the tip–sexiphenyl geometry and from the height difference between the low–high manipulation signals (Figure 4).

To confirm the observed π -ring twist and the physisorption state of sexiphenyl, density functional theory (DFT) calculations using the local density approximation (LDA) have been performed. Here, we use a quaterphenyl (four π -ring molecule) located on a Ag(111) slab instead of six sexiphenyl

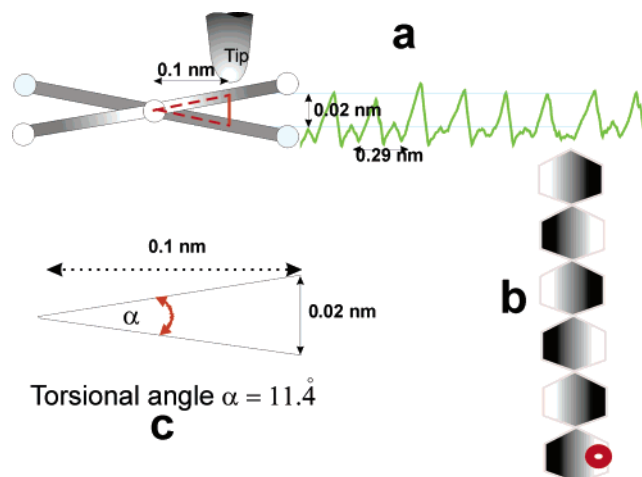


Figure 4. π -Ring torsional angle measurement. (a) A bar drawing demonstrates a cross-sectional view of an alternate twist of two π -rings. The STM tip is located 0.1 nm from the molecule center axis during lateral manipulation in order to record a pronounced flipping signal. The height difference between the low–high manipulation signal²⁵ (green curve) is 0.02 nm, which can be directly related to the flipping height between the up and down sides of the π -ring edge. (b) The top-view drawing illustrates the tip position (red circle) above the sexiphenyl during lateral manipulation. (c) From the determined geometry shown in (a), the π -ring torsional angle of sexiphenyl is determined as 11.4° .

π -rings, due to the computational space limit. The four π -rings can reproduce the π -ring twisting nature of sexiphenyl. For the substrate, three layers of 4×8 silver atoms with (111) surface arrangement are used. Calculations are performed by using a plane wave basis set together with pseudopotentials.²⁶ The π -rings are positioned along a close-packed direction of the Ag(111) slab, as determined from the experiment (Figure 1). Three different sets of molecule–substrate geometries are calculated (Figure 5). The first geometry (Figure 5a) belongs to a chemisorbed flat π -ring conformation. Here, the molecule center axis is positioned 1.5 Å above the surface. At this distance, strong molecule–surface interactions lead to the chemisorption state.²⁷ The second geometry (Figure 5b) is for a chemisorbed twisted π -ring conformation. The molecule is positioned at the same height as in the previous case, i.e., the center axis is 1.5 Å above the surface, but the opposite π -rings are allowed to twist with an 11° torsional angle. The third geometry (Figure 5c) belongs to a physisorbed twisted π -ring conformation. In this case, the molecule center axis is lifted 2.6 Å above the surface to ensure a weak molecule–substrate binding.

The calculated charge density isocontour plots are shown in Figure 5. The chemisorbed flat π -ring conformation shows a uniform charge density across the molecule (Figure 5a), while the two π -ring twist geometries (Figure 5b and 5c) reveal alternate protrusions of charge density resembling the zigzag appearance of sexiphenyl in STM images (Figure 2). In both of these two, the physisorbed twisted conformation produces higher charge density at the upper tilted site of π -ring edges (Figure 5c). The chemisorbed twisted conformation shows small depressions at the silver surface atom locations beneath the molecule, which are not observed in STM images. Furthermore, an enhanced interaction between

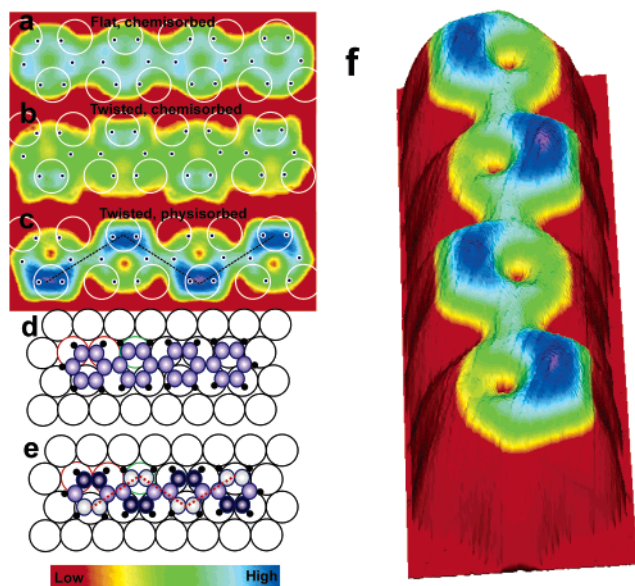


Figure 5. Calculated charge density plots and models. The charge density plots of chemisorbed flat π -rings (a), chemisorbed twisted π -rings (b), and physisorbed twisted π -rings (c). (Circles: surface atoms, dots: π -ring carbon atoms.) The molecule–surface geometries for the flat and twisted π -rings used in the calculation are shown in (d) and (e), respectively. In (e), the π -ring edge on the red silver atoms will be tilted downward (dark balls) while that on the green atom will be lifted upward (light balls). The dashed lines in (c) and (e) are drawn to highlight the zigzag appearance of the molecule. (f) A 3-D image of a calculated molecule with a π -ring twist configuration is illustrated for a direct comparison with Figure 2a.

the surface silver and the π -ring carbon atoms results in a decrease in charge density at the chemisorbed twisted π -ring conformation. For both twisted geometries, the upward tilted site appears brighter in STM images than the downward tilted edge of the π -ring. These calculated results unambiguously reveal the alternating twist of sexiphenyl in the observed STM images (Figure 2).

In summary, we have demonstrated a novel application of STM manipulation in combination with DFT calculation to precisely determine the molecule–surface atomic registry and internal conformation changes of a physisorbed sexiphenyl on a Ag(111) surface. This achievement opens up new way to probe the physical/chemical properties of physisorbed molecules on surfaces at the atomic level and therefore is valuable for a fundamental understanding of the molecule–metal contact, which is a critical issue in the molecular electronic device development.

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Supporting Information Available: An STM image of a sexiphenyl molecule and 10 silver atom position markers. The silver atoms are positioned along a surface close-packed direction of Ag(111) with six nearest neighbor atom distance apart. An atomic scale net is drawn over the image, which reveals the silver atom locations underneath the molecule (red circles). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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