Molecular Flexure and Atom Trapping with Sexiphenyl Molecules by Scanning Tunneling Microscope Manipulation

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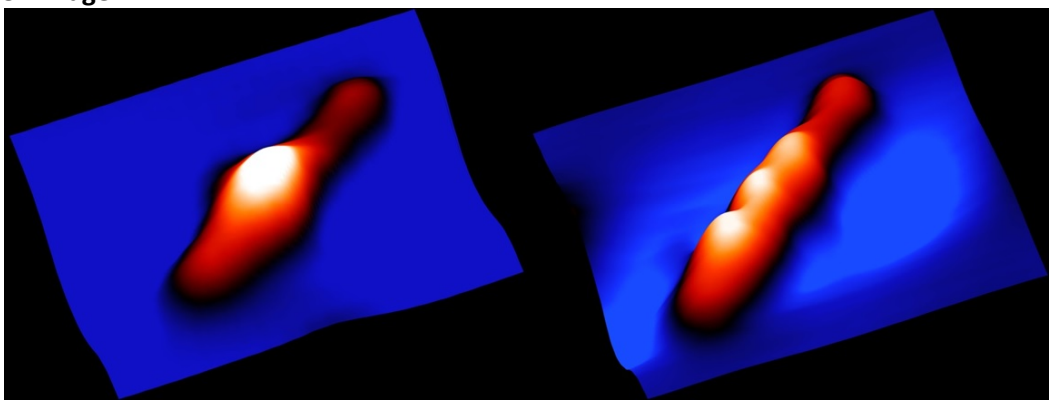
ABSTRACT: Molecular flexure, and molecule-metal contact of para-sexiphenyl molecules on a Ag(111) surface are investigated by using low temperature scanning tunneling microscopy, and molecular manipulations. Atom trapping with sexiphenyl molecules is realized by laterally manipulating the molecules onto individual silver atoms and up to three silver atoms have been trapped. We also demonstrate breaking of a silver dimer into individual silver atoms by atom trapping. STM manipulation experiments show that the molecule-metal complexes formed by the atom trapping are mechanically stable. Moreover, Lateral manipulation of a single sexiphenyl across a Ag(111) atomic step highlights how the molecule moves across step-edges; the molecule can easily conform across the step and it recovers original configuration after the manipulation.

ABSTRACT Image



STM images of a single silver atom (Left) and three silver atoms (right) trapped by a para-sexiphenyl molecule on Ag(111).

Oligomers exhibit semiconducting characteristic and they are useful in electronic and optoelectronic applications such as light emission devices and flexible lasers [1-6]. The tantalizing aspects of oligomers in using electronic devices are their plasticity, easy to fabricate large area devices, and cheap production cost. Para-sexiphenyl, an oligomer molecule, is thermally stable for a relatively high temperature (300°C to 400°C), and they are useful for blue light emitting devices [4,7]. For operation of oligomer based optoelectronic devices, quality of the molecular films and molecule-metal electrode contact are vital for the performance, and therefore, both electronic and growth properties of para-sexiphenyl films on material substrates are intensely studied [8-14]. Although oligomers are already used in industry, their mechanical properties and electrical contact at the single molecule level have yet to be explored. Unlike inorganic materials where the basic growth processes such as diffusion and cluster formation are based on individual atoms, the growth of organic molecular films involves a rich variety of additional processes including molecular conformational changes [10]. Here we investigate how single sexiphenyl molecules can make a strong contact with a metal electrode by trapping individual silver atoms on a Ag(111) surface by using atom/molecule manipulation and scanning tunneling spectroscopy. Moreover, how a single molecule would behave during the diffusion process across the substrate steps is demonstrated by scanning tunnelling microscope manipulations.

For the experiments, a Ag(111) sample was prepared by repeated cycles of sputtering with Ne ions followed by annealing. Different sub-monolayer coverages of para-sexiphenyl (6P) molecules were deposited onto an atomically clean Ag(111) surface held at room temperature using a custom-built Knudson cell under an ultrahigh vacuum environment. The sample was then transferred to a Createc low temperature scanning tunneling microscope (STM) directly attached to the preparation chamber. The measurements were conducted at the sample temperatures between 5 and 10 K. A lock-in amplifier

with an ac modulation of 5 to 20 meV and a frequency range of 750 to 860 Hz were used for all of the tunneling spectroscopy experiments described here.

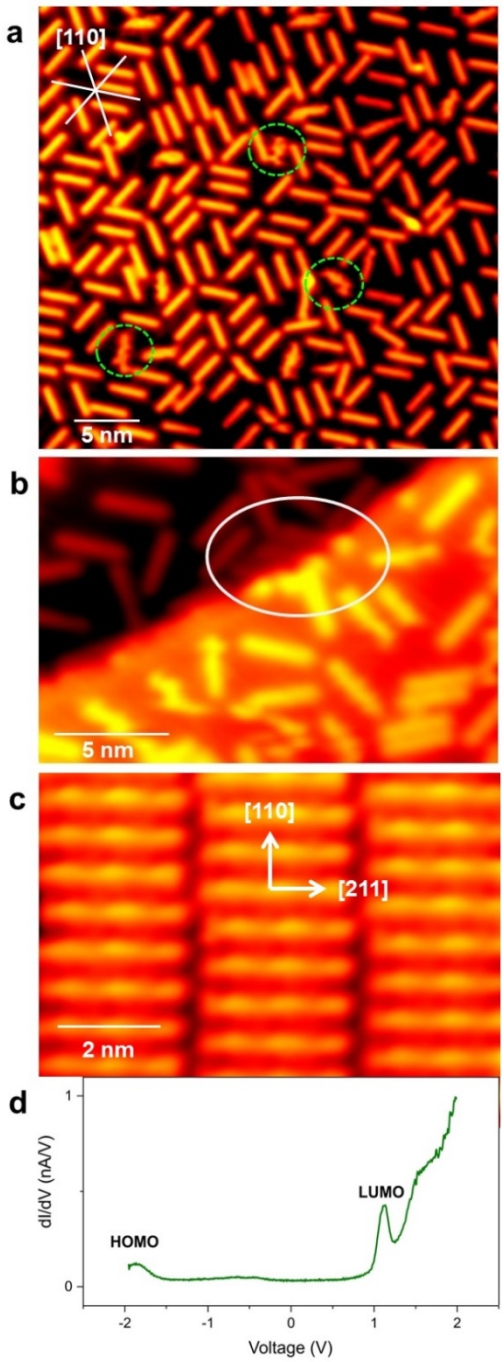


Figure 1. Adsorption of 6P on Ag(111). **(a)** An STM image shows preferential orientation of 6P on Ag(111) surface. The dashed ovals indicate mobile molecules during scanning. [Imaging parameters: -2 V, 2.5 10^{-11} A]. **(b)** 6P molecules adsorbed at a step-edge with bent chain structures. [Imaging parameters: -2 V, 2.0 x 10^{-11} A]. **(c)** STM image of an ordered 6P monolayer layer on Ag(111). [Imaging parameters: 0.8 V, 8.4 x 10^{-10} A]. **(d)** A dI/dV curve of 6P monolayer on Ag(111) reveals the HOMO and LUMO gap. [STM tip set point: -2 V, 1.4 x 10^{-10} A].

Figure 1 presents STM images of 6P adsorbed on a Ag(111) surface. For a sub-monolayer coverage, 6P molecules do not form ordered structures and most molecules preferentially orient their long molecular axes along the surface close-packed directions, i.e. [110] surface directions (Fig. 1a). The length of the 6P is measured as 2.7 Å. Due to a weak molecule-surface binding, the molecules can be easily displaced during scanning with the STM tip even at the low tunnelling (pA) current regime, which can be evident in STM images as distorted bright structures (marked with ovals in Fig. 1a). Interestingly, at the surface step edges, the molecules can be adsorbed across the step by bending its long molecular axis (Fig. 1b) indicating that 6P can easily adapt the substrate morphology underneath depending on the molecule-surface interaction strength. By increasing the coverage, 6P forms an ordered molecular structure (Fig. 1c) where the long molecular axis of 6P orients parallel to each other. Here, the stacking of the molecules is along [110] surface directions and therefore the long molecular axis of 6P is rotated by 30° to the [211] surface direction from the initial single molecule orientation. The dI/dV tunnelling spectroscopy data of the ordered 6P monolayer (Fig. 1d) reveals the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) at -1.9V and +1.1V, respectively, which provides the HOMO-LUMO gap of 6P as 3 eV on this surface.

6P is composed of six π-rings connected as a linear chain (Fig. 2a), and in the gas phase, the adjacent π-rings of 6P are alternately twisted. The twisting (torsional) angle between the alternate π-rings in the gas phase is between 20° and 40° [15] (Fig. 2b). When 6P is adsorbed on Ag(111) surface, its alternate π-rings are still twisted although the torsional angle is reduced due to the interactions between the π-rings and the underlying metal surface. Fig. 2c shows an STM image of a 6P molecule adsorbs on Ag(111) surface where the six π-rings of the molecule appear as six lobes. A line profile measured at the edge of the molecule clearly reveals the height variation between the lobes as expected for the alternately twisted π-rings [16]. Previous STM measurements give the torsional angle of the isolated 6Ps on Ag(111)

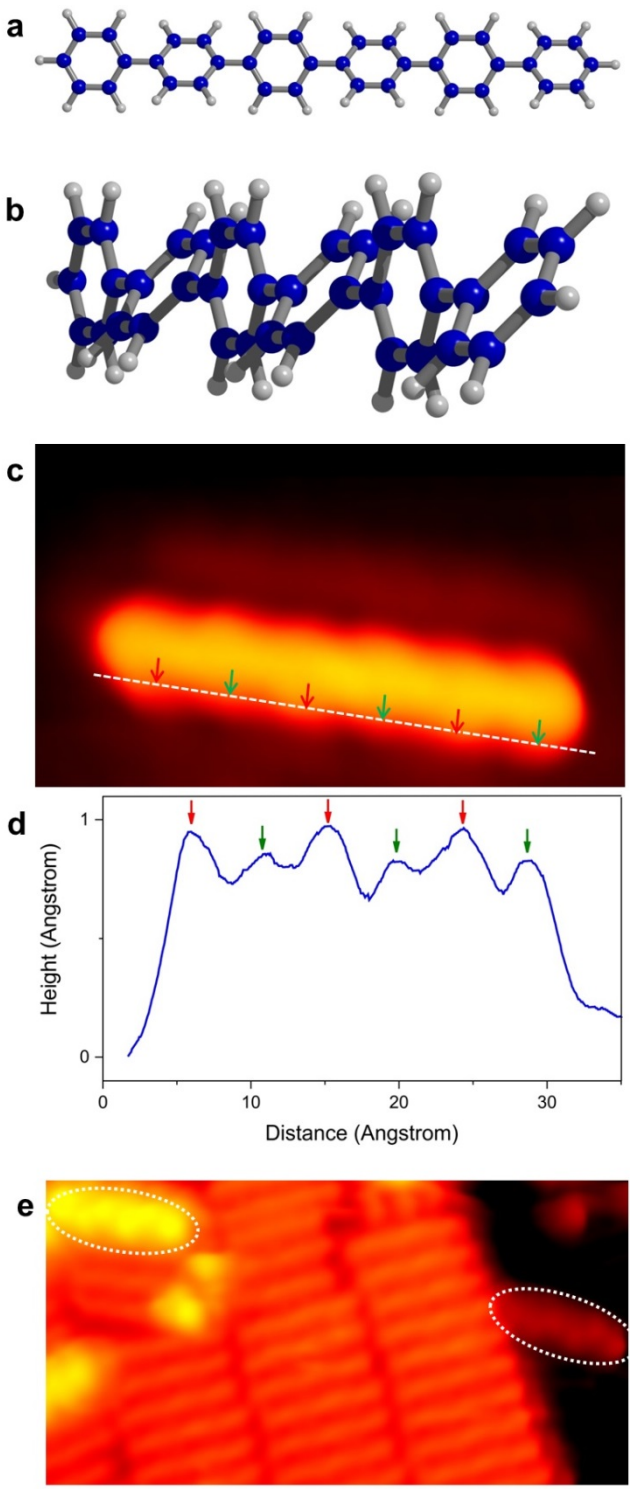


Figure 2. Molecular structure. **(a)** Chemical structure of 6P. **(b)** A model showing twisting of π-rings. **(c)** An STM image of a 6P on Ag(111) [Imaging parameters: 3.8 nm x 2.4 nm, 0.1V, 9.2 x 10^{-11} A]. **(d)** A line profile measured on **(c)** at an edge of the 6P reveals the height difference between the adjacent π-rings due to the twisting. **(e)** An STM image showing individual 6P on top of a self-assembled 6P layer (indicated with ovals). [Imaging parameters: 15 nm x 8 nm, 0.8 V, 8.4 x 10^{-10} A].

as 11.4°[16]. In the ordered molecular layer structure on Ag(111), 6P molecules also appear to be buckled (Fig. 1c) and therefore, the alternate π-rings are also slightly twisted here. At a slightly larger coverage, the added 6P molecules on top of the ordered 6P mono-layer can be observed (Fig. 2e), and they are more mobile than the ones directly adsorbed on Ag(111) surface. Moreover, they appear with a strong zig-zag pattern formed by alternate lobes along the long molecular axis (Fig. 2e) due to a larger torsional angle between the adjacent π-rings (Fig. 2e). This indicates a weaker binding of 6P on the ordered molecular layer than the one directly adsorbs on Ag(111) as expected.

An important issue in molecular electronics is the contact between the molecule and the metal electrode, which controls the device performance [17-19]. The simplest form of a molecule-metal contact can be established by attaching a single metal atom to a molecule [20-23]. Such atom attachment can be realized by trapping the atom under the molecule [24,25], and the process is dubbed as the atom trapping chemistry [26]. Here, we explore how 6P would behave when it contacts to a metal atom by atom trapping experiments using STM manipulation. To make a molecule-metal contact, individual Ag atoms are extracted from the native Ag(111) surface using an STM atom extraction procedure [27]. Here, the Ag clusters are initially produced by slightly dipping the STM tip into a Ag(111) surface area. Then individual Ag atoms are extracted one at-a-time basis with the same STM tip [28]. The extracted Ag atoms are then repositioned on the surface with six atomic distances apart along a [110] surface direction to form an atomic array for the demonstration purpose (Fig. 3a). To trap a Ag atom, a 6P molecule is laterally moved with the STM tip until the molecule is positions above the atom, which forms a 6P-Ag complex (Fig. 3b). In order to check the complex formation, the molecule is then moved along the surface by STM lateral manipulation (Fig. 3c and 3d). The Ag atom remains trapped under the 6P molecule throughout the lateral manipulation process although its position relative to the molecule is occasionally altered (Fig. 3c, and 3d). An I-V tunnelling spectroscopy data is measured by

positioning the STM tip static above the trapped Ag atom location (Fig. 3e) in 6P-Ag complex. The measured I-V spectrum is presented in Fig. 3f together with an I-V spectrum of 6P measured on an ordered 6P layer for a comparison. The dI-dV spectra of 6P-Ag complex and Ag(111) surface are provided in supplementary information.

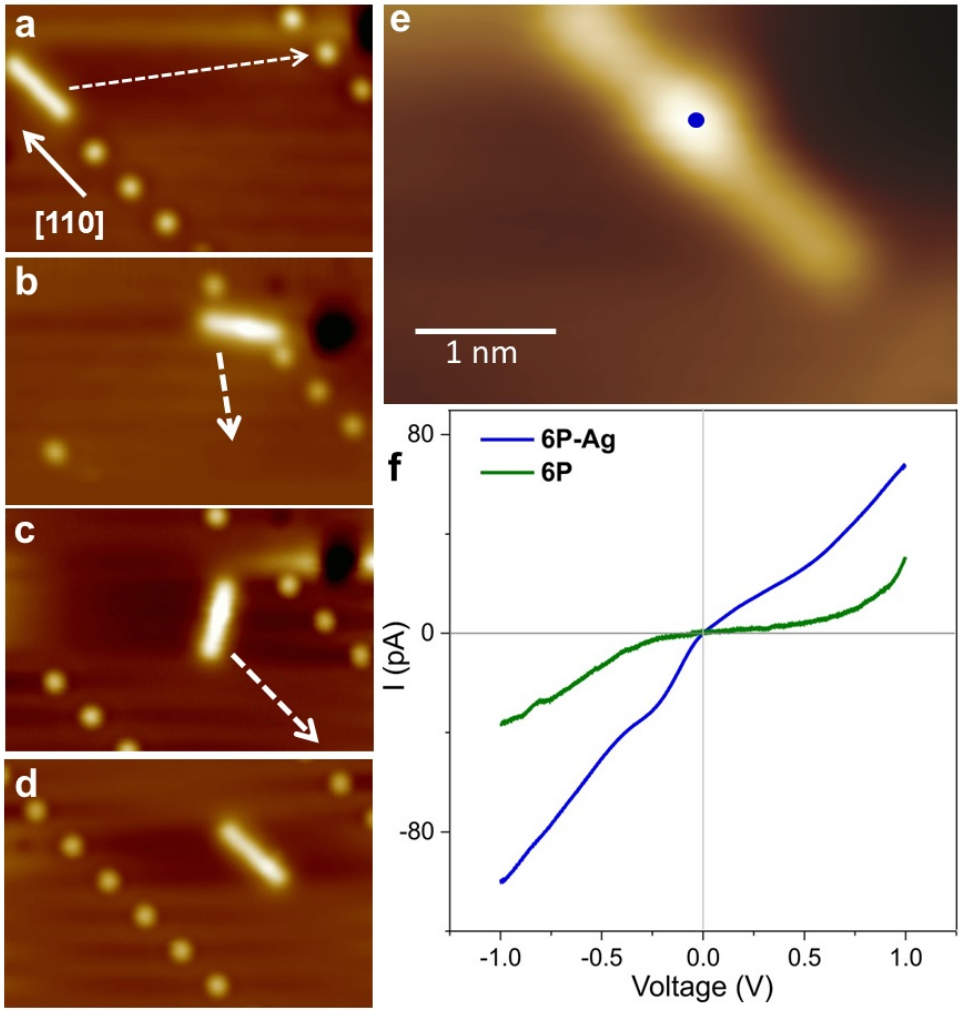


Figure 3. Atom trapping. **(a)** A 6P molecule and individual Ag atoms positioned along [110] direction with six atomic distances apart. The white arrow indicates manipulation direction of 6P, which forms a 6P-Ag complex **(b)**. **(c)** and **(d)**, the 6P-Ag complex is laterally manipulated across the surface. [Imaging parameters: 13 nm x 9 nm, 0.8 V, 4 x 10^{-10} A, STM manipulation parameters: R_t = 1.2 MΩ, V_t = 120 mV]. **(e)** A zoom in STM image of 6P-Ag complex. [Imaging parameters: 0.8 V, 3.8 x 10^{-10} A] **(f)** I-V plots correspond to 6P-Ag complex measured over the blue dot in (e) (blue) and on a 6P ordered layer on Ag(111) (green).

At the next step, we explore trapping of a Ag dimer with a 6P-Ag complex. Figure 4a presents a 6P-Ag complex together with a Ag dimer and a Ag atom, which are positioned by laterally moving them with the STM tip. Although a metal dimer is formed by two atoms bonded together, it normally appears as a single protrusion in STM images, and therefore it is necessary to distinguish from a single atom. For reference, a Ag atom is placed next to a Ag dimer for a comparison, and it is removed from the area before the experiment (Fig. 4b). Then the 6P-Ag complex is brought next to the Ag dimer by laterally moving with the STM tip (Fig. 4c). To trap the dimer, the molecular complex is rotated counter-clockwise from its initial position with the STM tip until it is positioned on top of the dimer (Fig. 4d). This manipulation results in trapping the dimer under the molecular complex, and a 6P-3Ag complex is now formed. The line profiles of 6P-Ag and 6P-3Ag complexes are presented in figure 4e and 4f. The lengths of the 6P molecules in both complexes are measured as ~2.7 nm, which is the same as that of a pristine 6P. If the molecule is bent to accommodate the atom, then the lengths of the molecular complexes should appear shorter than the length of a pristine 6P. Therefore the atom trapping does not alter the length of the molecule. From the line profile (Fig. 4e) measured on the 6P-Ag molecular complex in figure 4a, the location of the trapped Ag atom is determined at the center of the 3rd π-ring. From the line profile of the 6P-3Ag complex (Fig. 4f), the trapped Ag atoms can be identified at the highest protrusion locations, which are ~4.5 Å apart. If the Ag dimer remains intact after trapping under the molecule, the separation between the two Ag atoms should be 2.9 Å. Therefore, the Ag dimer is now split to individual atoms upon trapping. This is surprising because based on our experience [27], a metal dimer cannot be

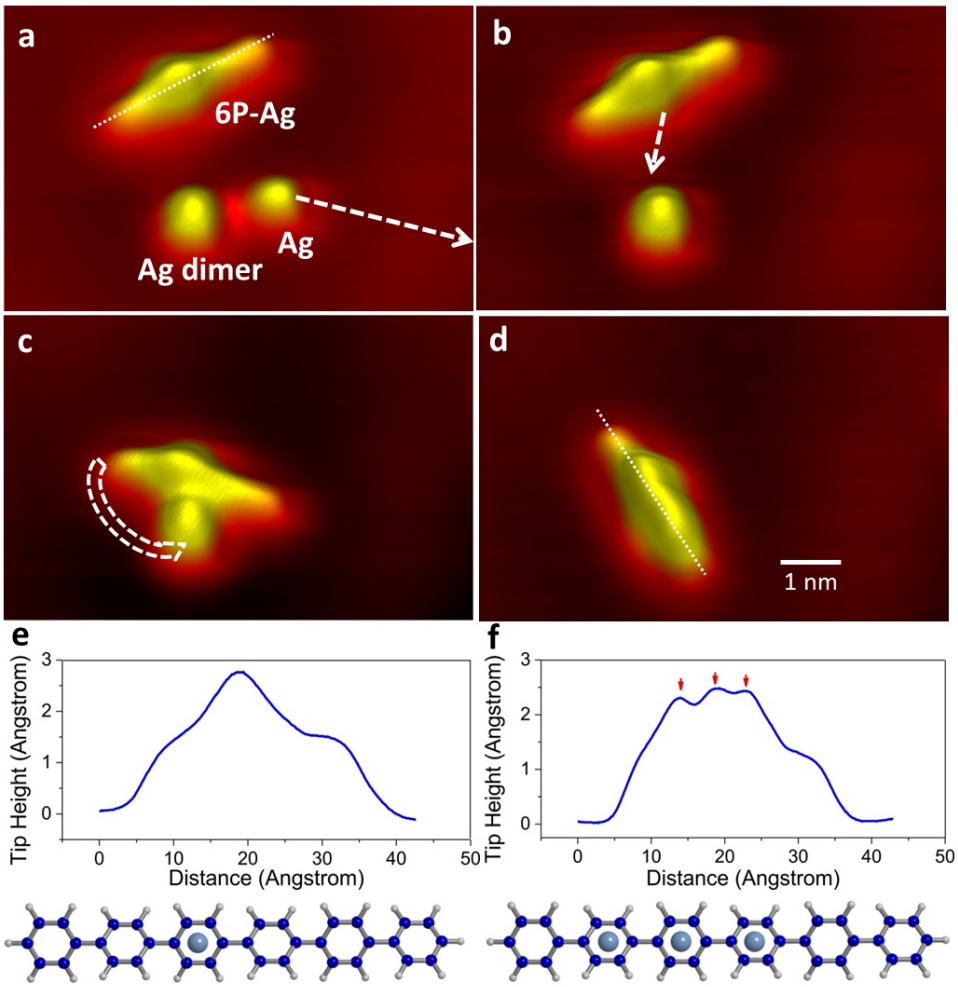


Figure 4. Dimer trapping. **(a)** A 6P-Ag molecule together with a Ag dimer and a Ag atom on Ag(111). **(b)** After removing the Ag atom along the white arrow in **(a)**, the 6P-Ag complex is brought next to the Ag dimer **(c)** by STM manipulation. After turning the 6P-Ag complex counter-clockwise, the dimer is trapped under the molecule **(d)**. **(e)** The line profile of the 6P-Ag complex measured along the dashed line in **(a)**, and corresponding model. **(f)** The line profile of 6P-3Ag complex measured along the dashed line in **(d)** shows three separate protrusions with ~0.5 nm distance apart (indicated with red arrows). The model below presents the trapping sites of three Ag atoms in the 6P molecule. [Imaging parameters: 0.4 V, 9.4 x 10^{-10} A, manipulation parameters: R_t = 150 kΩ for (b) and 300 kΩ for (c), V_t = 30 mV].

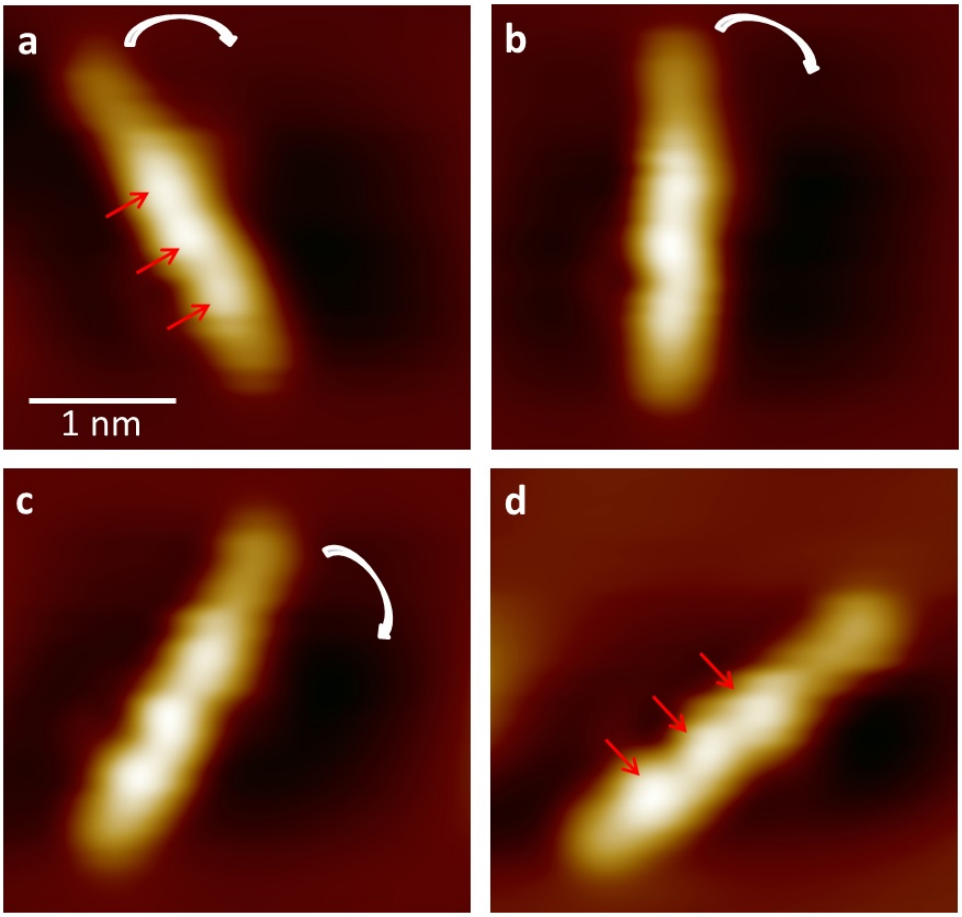


Figure 5. Manipulation of 6P-3Ag. **(a)** STM image of 6P-3Ag molecule. The arrows indicate the location of the trapped Ag atoms. STM images after rotating the molecular complex by 32° **(b)**, 58°**(c)**, and 82°**(d)** show that the trapped Ag atoms remain in their position. [Imaging parameters: 0.037 V, 1.1 x 10^{-9} A, STM manipulation parameters: R_t = 300 kΩ, V_t = 30 mV].

separated with the STM tip manipulation. Moreover, Ag atoms cannot be positioned less than four atomic distances (11.6 Å) apart using the STM tip manipulation on a Ag(111) surface because of their tendency to form a dimer already at this distance. The 4.5 Å separation is the distance between the centers of the nearest π-rings in 6P, and from this line profile, the locations of the three trapped Ag atoms are determined as the centers of the 2^{nd}, 3^{rd}, and 4^{th} π-rings of the 6P, respectively. Indeed, the centers of the π-rings are the ideal locations to trap the atoms because the interactions between the molecule and the atoms can be maximized there. A direct imaging of metal-sexiphenyl bonding and imaging molecular orbitals would be useful to confirm this. The current finding should also valid for the

atomic doping of other phenylenes such as potassium doped p-terphenyl [29,30] where the dopant atoms most likely position at the centers of the π-rings.

On fcc(111) noble metal surfaces, the added metal atom normally adsorbed at the three fold hollow sites on the surface. Thus, the surface symmetry (hexagonal in this case) and adsorption sites of the metal atoms are limiting factors in designing different geometries for atom-by-atom assembled structures with the STM tip such as quantum corrals on the surfaces [27]. Since these atoms are trapped under the molecule, they interact with both the surface and the molecule. Thus how stable is the 6P-3Ag molecular complex on Ag(111) surface is the next question we want to address. Using the STM lateral manipulation scheme, we have rotated the molecular complex as shown in the sequence of images (Fig. 5). Such rotation of the molecular complex is realized by positioning the STM tip at the top end of the molecule and then laterally moving the tip with a close tip-molecule distance towards the desired locations. STM images reveal that the positions of the trapped Ag atoms under the 6P remain the same in all the rotation events indicating that the 6P-3Ag molecular complex is rather stable. If the trapped Ag atoms were to adsorb on three fold hollow sites of Ag(111) surface, then such rotation angles with maintaining integrity of the molecular complex is not possible. Therefore, this rotation experiment also highlights that the binding of the trapped Ag atoms to the molecule is stronger than their binding to the Ag(111) surface.

After investigating the molecule-metal contact by atom trapping, we focus our attention on the mechanical flexure of 6P. An important process for the molecular film growth is the diffusion of molecules on the surface. Unlike single atoms, molecules can alter the conformation depending on the

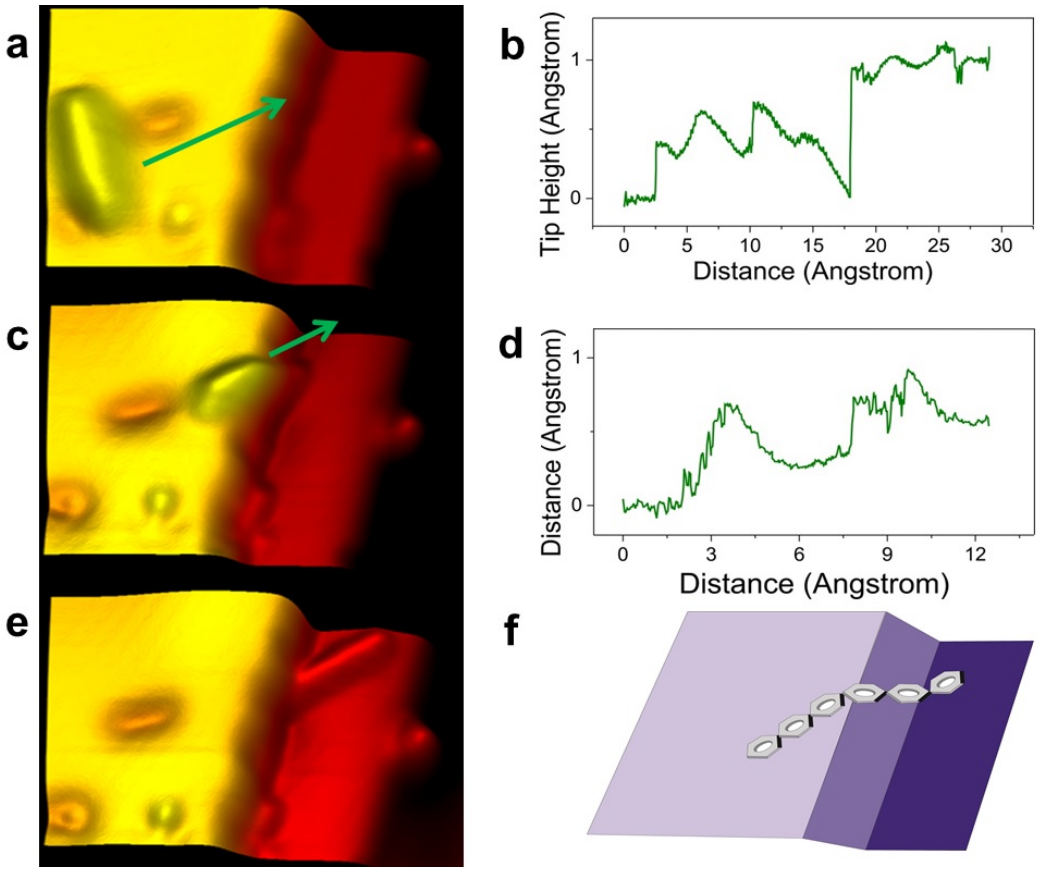


Figure 6. Mechanical flexibility of 6P. **(a)** A 3-D rendered STM image showing 6P molecule at the upper terrace. (**b)** Corresponding manipulation signal. **(c)** The 6P positions across the step after manipulation. **(d)** Manipulation signal corresponds to moving the molecule onto the lower terrace. **(e)** After the manipulation, the molecule is located at the lower terrace. **(f)** A model showing the bent conformation of 6P across the step. [STM imaging parameters: 10 nm x 6 nm, 0.44 V, 1.6 x 10^{-9} A. STM manipulation parameters: R_t = 300 kΩ, V_t = 30 meV]

landscape underneath. Hlawacek et al. [10] proposed that 6P diffuses across the substrate step-edges by bending its π-rings, thereby lowering the Ehrlich–Schwoebel barrier [31] existing at the step-edges. In order to test this we employ the STM lateral manipulation procedure to move a 6P molecule across a surface step-edge. Figure 6a presents an STM image of a 6P molecule located at an upper terrace of the surface. For the controlled lateral movement, the STM tip is lowered over the 6P molecule to increase the tip-molecule interactions, and then the tip is scanned across the surface step along a green arrow shown in figure 6a in a constant scanning mode until the molecule is located right on the step-edge. The corresponding manipulation signal (tip-height signal) is presented in figure 6b. The molecule moves in a

pulling mode [27] due to attractive tip-molecule interactions. The STM image in figure 6c acquired after this manipulation event clearly reveals that the 6P is deformed from its straight axis to a bent axis across the step-edge. In order to check whether the 6P molecule is still intact, another STM manipulation is performed by moving the molecule along a green arrow shown in figure 4c. The resultant manipulation signal is presented in figure 6d. The STM image acquired after this manipulation (Fig. 6e) shows that the molecule has relocated on the lower terrace. Here, the manipulated 6P molecule not only appears as intact but also it regains the original shape. This 6P manipulation sequence directly confirms that the molecule can move across the surface step-edges by bending its π-ring joints as demonstrated in figure 6f, and that it is mechanically stable.

In summary, we have investigated the molecule-metal contact by trapping individual Ag atoms with a sexiphenyl molecule using STM manipulation schemes on a Ag(111) surface, which forms 6P-Ag complexes. Trapping can be realized not only to individual atoms but also to a dimer as well. Surprisingly, the Ag dimer breaks up to individual atoms upon trapping with the sexiphenyl molecule. From the STM line profiles acquired over the molecule-metal complexes, the locations of the trapped silver atoms are identified at the center of the π-rings. The mechanical stability of the 6P-Ag and 6P-3Ag molecular complexes are also tested by STM manipulation on Ag(111) surface, and they show that the atoms remain trapped under the molecule during its movement across the surface or rotations of the molecular complexes. Moreover, the lateral manipulation of 6P across the step-edge of Ag(111) further reveals that the molecule can easily adapt to the substrate land-scape underneath. This work provides fundamental understanding of molecule-metal contact as well as mechanical properties of sexiphenyl and may be useful for the improvement of molecular device performance.

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