

Regulating the Interactions of Adsorbates on Surfaces by Scanning Tunneling Microscopy Manipulation

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Scanning tunneling microscopy (STM) manipulation has received wide attention in the surface science community since the pioneering work of Eigler to construct surface nanostructures in an atom by atom fashion. Lots of scientists have been inspired and devoted to study the surface issues with the help of STM manipulations and great achievements have been obtained. In this Minireview, we mainly describe the recent prog-

ress in applying STM manipulations to regulate the inter-adsorbate and adsorbate–substrate interactions on solid surfaces. It was shown that this technique could not only differentiate intermolecular interactions but also construct molecular nanostructures by regulating different kinds of inter-adsorbate interactions or adsorbate–substrate interactions.

1. Introduction

The invention of the scanning tunneling microscope in the early 1980s has offered the scientific community an invaluable toolbox for uncovering surface science issues down to the molecular and atomic scale because of its high-resolution real-space imaging and precise in situ manipulation of adsorbates on surfaces. The capability of high-resolution imaging solved the longstanding controversy of the 7×7 reconstruction on Si(111) soon after the advent of scanning tunneling microscopy (STM),^[1] whereas it was not until the pioneering work of Eigler several years later that STM manipulation was first applied to realize the vision of direct manipulation of individual atoms,^[2] as proposed by Richard Feynman in his famous talk “There’s plenty of room at the bottom”.

Later on, the mechanism of STM manipulation was also well discussed accompanied by the continued prosperity of this technology in the surface science community,^[3–7] and could be basically divided into lateral, vertical, inelastic tunneling-induced, and electric field-induced manipulation on the basis of different interactions between the STM instrument tip and the adsorbates.^[4] A great number of efforts have been inspired and devoted to precise fabrication of desired nanostructures based on STM manipulations, and the remarkable achievements include quantum corral,^[8] quantum mirages,^[9] molecule cascades,^[10] linear electron resonators,^[11] molecular holograms,^[12] molecular gears,^[13] molecular ball bearings,^[14] and so on.

With the persistent and rapid development of STM manipulation, its application has been greatly extended from arranging the adsorbates in a desired manner to managing single-molecule chemistry, such as inducing 1) intramolecular confor-

mational changes,^[15–20] 2) intermolecular covalent interactions by coupling two molecules in a controlled step-by-step way,^[21] 3) single-molecule isomerization including *cis–trans* transition of azobenzene,^[22–24] tautomerization of melamine,^[25] isomerization of single chlorobenzene and its analogues,^[26,27] and tautomerization of single free-base naphthalocyanine and porphyrine molecules,^[28,29] and 4) metal–organic complexes including metal–aromatic binding on single-crystal surfaces,^[30–32] K atoms attaching to C_{60} molecules,^[33] hybrid magnetic complexes of V atoms and tetracyanoethylene ligands,^[34] and metal–ligand interactions on insulating films.^[35–37] Moreover, the dynamic behaviors of the adsorbates on surfaces could also be controlled by STM manipulations. It is most common to move the intact adsorbates laterally on surfaces, such as the manipulation of single molecular molds by lateral STM manipulations.^[38,39] The mobility of single diferrocene molecules could be altered by partial decomposition of the molecules by the tunneling current.^[40] The upper porphyrin of the cerium porphyrinato sandwich complexes can be rotated by STM manipulation.^[41] Furthermore, by vertical STM manipulation scientists have achieved the unprecedented possibility of measuring the conductance of single conjugated molecular chains, for example, polyfluorene and graphene nanoribbon, by pulling them up from the surface while the STM tip and surface serve as two electrodes.^[42,43] Also, by picking up a molecule or atom one could sharpen the tip and get a higher resolution or even chemical contrasts.^[44–48]

With the great achievements from STM manipulations, the boundaries of human knowledge on controlling matter at the atomic scale have been greatly advanced and the capability of STM manipulation has been continuously extended. In this Minireview, we mainly describe the capability of STM manipulations in regulating different interactions of adsorbates on surfaces, including adsorbate–adsorbate and adsorbate–substrate interactions. In Section 2 we discuss using STM manipulation to distinguish the weak and strong intermolecular interactions.

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In Section 3 we review using STM manipulation to switch intermolecular hydrogen-bonding interactions. In Section 4 we discuss the recent progress in constructing covalently bonded structures with STM manipulation. In Section 5 we review the progress in metal–organic interactions induced by STM manipulation. Finally, in Section 6 we review the progress in regulating the interactions between the adsorbates and substrates.

2. Probing the Hierarchical Intermolecular Interactions by STM Manipulation

The construction of various molecular nanostructures on surfaces has been investigated intensely over the last few decades due to its wide applications in nanoscience and nanotechnology. By delicately designing molecular precursors with different functional groups, a large number of molecular nanostructures have been fabricated on different surfaces, which were linked by the intermolecular interactions from relatively weak noncovalent (van der Waals (vdW) force, hydrogen bonding, dipole–dipole interaction, electrostatic interaction, metal–ligand interaction, etc.) to

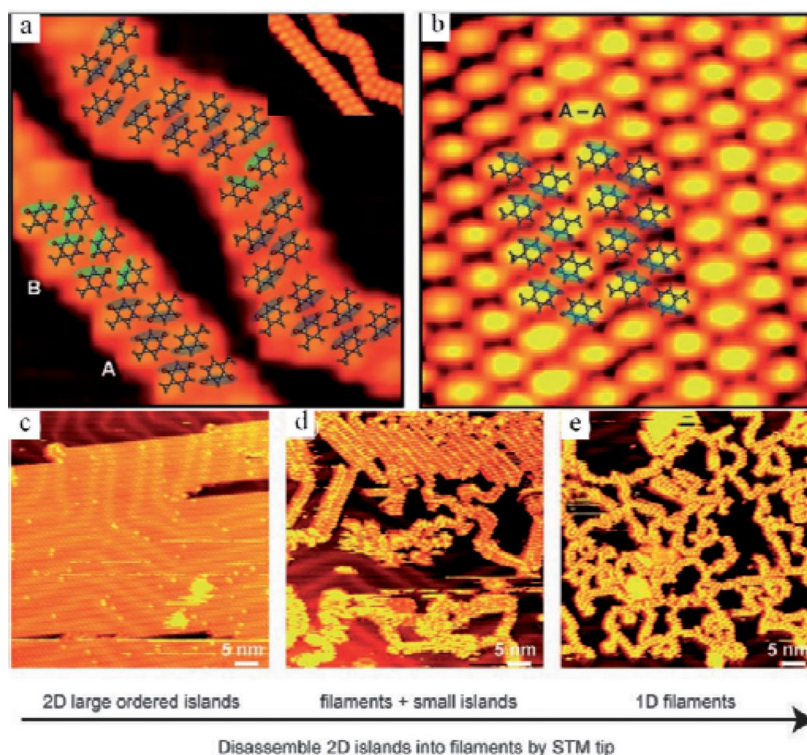
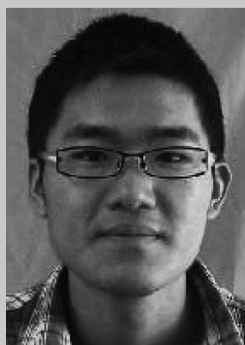


Figure 1. a) STM image of 1D T filaments after deposition of T molecules on Au(111) at low surface coverage. The filamentary structures are linked together by intermolecular hydrogen bonding. A and B denote two calculated most stable filament structures. b) STM image of extended 2D T islands after deposition of T molecules on Au(111) at relatively high coverage. The 2D structures are hierarchically built up by the T filamentary structures. c–e) Sequential STM images showing that the 2D T islands could be decomposed into 1D T filaments by in situ STM manipulation. Adapted with permission from ref. [50].

robust covalent interactions.^[49] However, one major concern lies in how to identify different intermolecular interactions within self-assembled nanostructures with a relatively simple and general method. STM manipulation has proven to be a fea-

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Prof. Dr. Wei Xu was born in 1981 and studied physics at Aarhus University where he received his Ph.D. on “Adsorption of organic molecules on solid surfaces—A scanning tunneling microscopy study” with Prof. Flemming Besenbacher in 2008. Thereafter he was a postdoctoral fellow at the Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark and at the Departments of Chemistry and Physics (with Prof. Paul S. Weiss), Penn State University, USA. Since 2009 he has been a full professor at Tongji University. He was also appointed as the deputy director of Tongji–Aarhus joint research center for nanostructures and functional nanomaterials. Currently, his research interests are focused on the investigation of surface physical chemistry, including molecular self-assembly, chemical reactions, and atomic-scale manipulations, under ultrahigh vacuum conditions by the interplay of high-resolution STM imaging and DFT calculations.



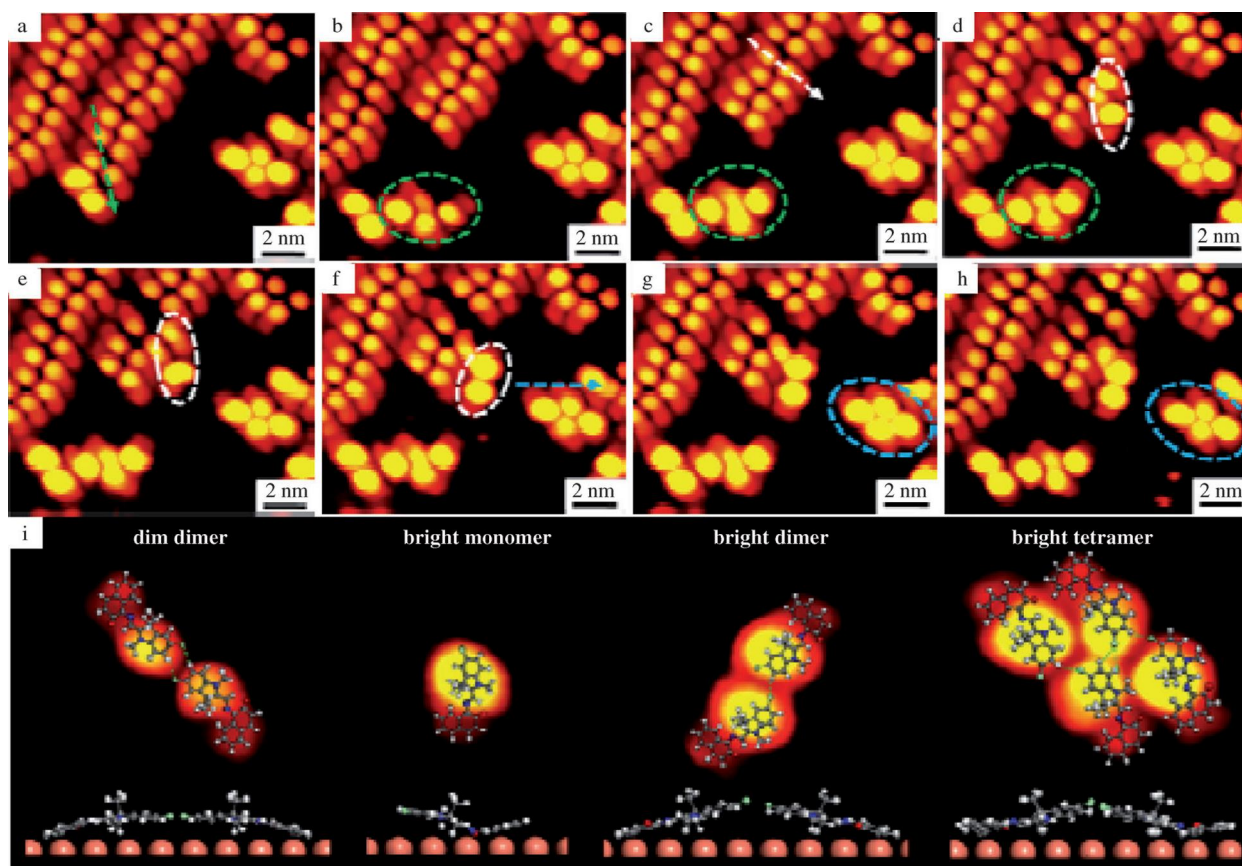


Figure 2. Controllable switches among the hydrogen-bonded structural motifs by lateral STM manipulations. a–d) Two adjacent dim dimers are converted into a bright tetramer as indicated by the green arrow and ellipses. c–f) One dim dimer is converted into a bright dimer as indicated by the white arrow and ellipses. f–h) The variation and spontaneous recovery of the STM feature of the two molecules along the short diagonal within a bright tetramer as indicated by the blue arrow and ellipses. i) High-resolution STM images and the calculated models of the three structural motifs and the single molecule on Cu(110). Adapted with permission from ref. [57].

sible strategy in probing the intermolecular interactions within the nanostructures by in situ perturbation of the formed nanostructures into their components, which may also give further information for analyzing the structures from an experimental point of view.

It was found by Xu et al. that the hierarchical interactions (vdW force and hydrogen bonding) within the self-assembled nanostructures formed by thymine (T) molecules could be distinguished by in situ STM manipulation.^[50] One-dimensional (1D) filamentary structures linked by hydrogen bonds through the carbonyl and imino groups were initially formed at low coverage on the surface (see Figure 1). At higher coverages, the 1D filaments self-assembled into two-dimensional (2D) islands through vdW interactions of methyl groups. The 2D islands could be disassembled into 1D filaments by applying voltage pulses during scanning accompanied by perturbation of relatively weak vdW interactions in between the filaments, while the filamentary structures were kept intact indicating that the relatively strong hydrogen bonds remain undisturbed. This study has demonstrated a simple and general method for distinguishing the hierarchical intermolecular interactions with different strengths. Likewise, the STM manipulation has also been adopted to distinguish the covalent and noncovalent in-

teractions by disturbing the weaker noncovalent intermolecular interactions.^[51]

Furthermore, based on the “disturbing ability” of this strategy one could separate an intact single molecule out of the assembled structures on surfaces and identify the structure of the single molecules.^[52–54] Normally, the “unbroken behavior” of targeting structures could be regarded as the characteristic of a relatively strong interaction.^[55,56]

However, a quantitative analysis of the strength of such STM manipulations still needs to be further explored. As the intermolecular forces are highly sensitive and dependent on the functional groups of the molecules, we hope that this technique would be further developed to gain chemical information on the adsorbates on surfaces.

3. Probing Intermolecular Hydrogen-Bonding Interactions by STM Manipulation

It has been a popular and well-developed method to build up various kinds of supramolecular nanostructures on surfaces by intermolecular hydrogen bonds. The hydrogen-bonded structures are normally formed in a self-assembled manner. However, in a recent study it was shown that the hydrogen-bonded

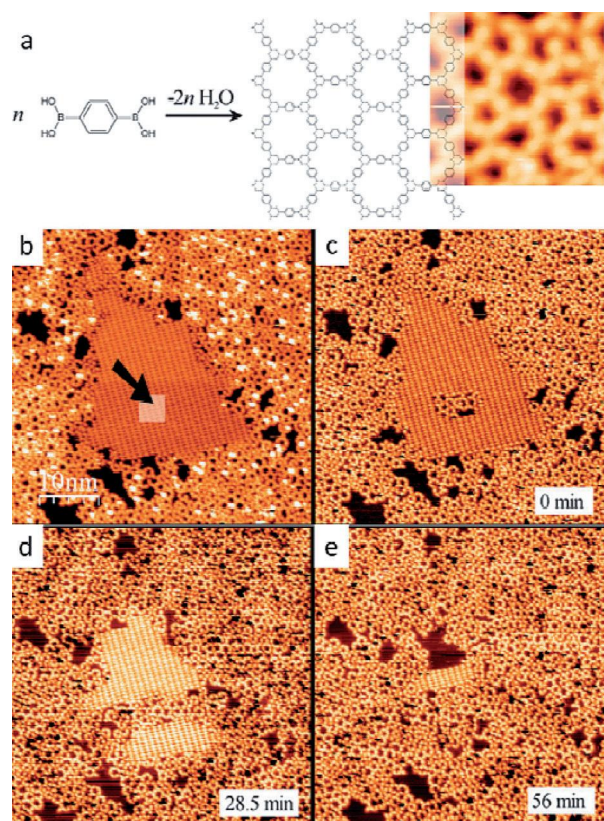


Figure 3. a) Reaction scheme of the polymerization of BDDBA molecules and the corresponding STM image of the nanoporous structure. b) STM tip scanning over a small area of hydrogen-bonded phase with a rather low tunneling resistance. c–e) STM images showing the initiation and propagation of disappearance of hydrogen-bonded phase and emergence of polymerized phase. Adapted with permission from ref. [62].

structural motif could be switched by in situ STM manipulation to another with a different hydrogen-bonding configuration.^[57]

As shown in Figure 2, there are three hydrogen-bonded structural motifs formed on the surface and their corresponding close-up STM images and DFT optimized models are shown in Figure 2i. Figure 2a–d shows that after lateral STM manipulation of the two adjacent dim dimers, the four molecules are disturbed and subsequently evolve into a bright tetramer structure (see the green arrow and ellipses). After another STM manipulation performed on an individual dim dimer (see Figure 2c–f), the dim dimer is separated from the stripe and evolves spontaneously into the bright dimer (see the white arrow and ellipses). The bright tetramer has also been manipulated (see Figure 2f–h), and after a transient relaxation of the structure the bright tetramer is recovered to its original feature (see the blue arrow and ellipses). Another example is selective control of internal hydrogen-bonding rearrangement of ice nanoclusters by injecting electrons from the STM tip into the ice clusters.^[58] The findings demonstrate that STM manipulation could be extended from distinguishing different intermolecular interactions (e.g. hydrogen bonding versus vdW forces) to probing the small difference within intrinsically the same intermolecular interaction (e.g. different hydrogen-bonding schemes) in self-assembled nanostructures.

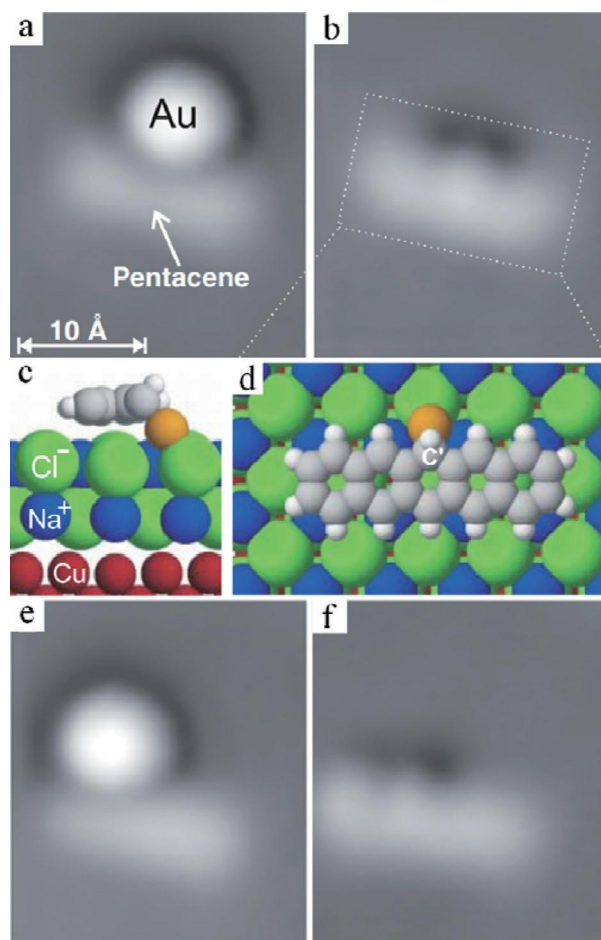


Figure 4. a) STM image of isolated pentacene molecule and gold atom before bond formation between them on a Cu(100)-supported NaCl bilayer. b) STM image showing the Au-pentacene complex after the STM tunneling through the pentacene and the corresponding calculated geometry: c) side view of a cut perpendicular to the long molecular axis and d) top view of the adsorbed complex in which the interacting carbon is denoted by C'. e) STM image showing that the Au atom was detached from the complex and f) rebonded to the pentacene forming another structural isomer of the Au-pentacene complex. Adapted with permission from ref. [35].

4. Intermolecular Covalent Interactions Induced by STM Manipulation

Normally, after deposition of well-designed molecular precursors on surfaces, external stimuli, such as heat, light, STM manipulation, and so forth, are applied to induce the formation of specific nanostructures. Among these, STM manipulation has gained more and more attention because of its controllable, localized characteristic followed by simultaneous characterization and the multiple choices of different stimulating modes, such as electric field, inelastic electron tunneling, voltage pulse, and so on.

Because of the robust characteristic and good electron-transport property within covalently interlinked nanostructures, fabrication of surface nanostructures through covalent interactions has become one of the intensely studied subjects in recent years.^[59–61] Clair et al. have demonstrated the dehydration reaction of a boronic acid molecule (1,4-benzenediboronic

acid, BDBA) to form an extended 2D covalently bound network on Ag(100), which was locally facilitated by STM manipulation (see Figure 3).^[62] As shown in Figure 3b, a densely packed hydrogen-bonded domain of BDBA molecules was surrounded by the porous network. By scanning over a small area indicated by the black arrow within the densely packed domain with a rather low tunneling resistance (i.e. by decreasing the tip-sample distance), the polymerization reaction was immediately initiated at the scanning area and nucleated to an extended nanoporous structure. Another kind of molecule, a diacetylene compound, has also been used to fabricate single conductive polymer chains by the stimulation of the STM tip.^[63–66]

To get the controllable covalently interlinked surface nanostructures by STM manipulation, one prerequisite is the formation of well-organized domains of the molecular precursors, in which the active sites of the molecular precursors are in proximity to each other to facilitate the pre-designed reactions. Another prerequisite is the relatively low activation energy of the reaction, which may help to avoid side reactions and increase the reaction efficiency.

5. Metal–Organic Interactions Induced by STM Manipulation

The construction of 2D metal–ligand coordination networks on surfaces has been investigated widely in the last decade, mostly by combining transition-metal centers and molecular ligands including pyridyls, carbonitriles, carboxylic acids, and so forth.^[49] Meanwhile, STM manipulation has also demonstrated its versatility in building metal–organic hybrid nanostructures. For example, Repp et al. have shown the bond formation of a pentacene molecule and gold atom on ultrathin insulating films supported by copper substrate triggered by STM manipulation (see Figure 4).^[35] The two reactants are located close to each other before the STM manipulation. After an excitation of inelastic electron tunneling through the pentacene molecule, an Au–pentacene complex was generated involving bond formation between the Au atom and the C atom within the pentacene. The Au–pentacene interaction could also be disturbed by the STM manipulations. Note that this is an addition reaction, which does not involve the de-

hydrogenation of the organic molecule. Similar gold–organic complexes initiated by STM manipulation on surfaces have also been reported elsewhere.^[32,36,44,67] In addition, the alkali metals have been successfully attached to organic molecules with the STM tip.^[31,33] Formation of metal–ligand coordination between transition metals and organic molecules functionalized with cyano groups has also been achieved on surfaces.^[34,37]

6. Modulation of Adsorbate–Substrate Interactions by STM Manipulation

STM manipulation has shown its great applications in modulating intermolecular interactions, as we have reviewed above. As is known, the substrates also play a vital role in the formation of surface nanostructures due to specific adsorbate–substrate interactions. Li et al. have shown an electron-induced self-assembly of phenylacetylene molecules on Au(111) by STM manipulation, which could be reversibly controlled through regulating the sample bias.^[68] As shown in Figure 5, a fuzzy image is yielded after deposition of phenylacetylene molecules on Au(111), which indicates a mobile molecular overlayer composed of physisorbed flat-lying molecules on the surface. The disordered phase could be changed to an ordered structure

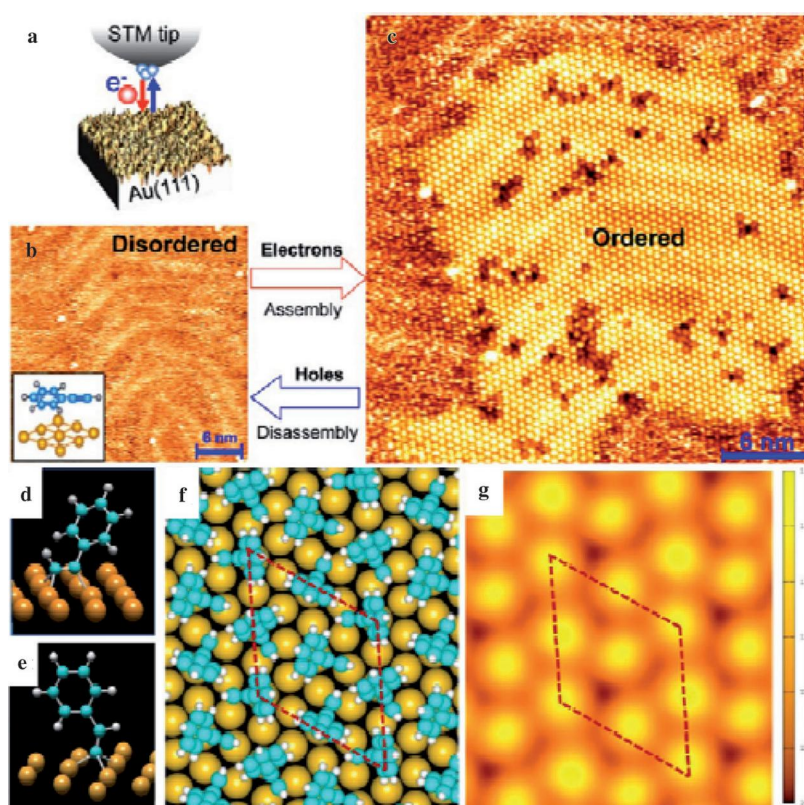


Figure 5. a) Schematic drawing showing the STM tip-induced experiment. b) STM image of a blurred morphology indicating the disordered phase of the phenylacetylene molecules on Au(111). c) STM image showing the clearly resolved and ordered structure after injection of electrons into the substrate. d,e) DFT-relaxed structural models of a single styrene derivative (d) and phenylvinylidene (e) on Au(111). f) Top view of the relaxed model of the self-assembled styrene derivative on Au(111) and g) its corresponding simulated STM image. Adapted with permission from ref. [68]. Copyright (2012) American Chemical Society.

when the surface was scanned with a positive sample bias and a strong chemical interaction between phenylacetylene and substrate was adopted. DFT calculations have also been performed to validate that the ordered phase is attributable to the covalent interaction between the alkynyl groups and the substrate. Such induced strong interaction could be controllably changed back to the weaker interaction on applying a negative bias pulse to the ordered phase.

Besides, it has been shown that the mobility of the iron phthalocyanine molecule on Au(111) could be regulated at a fixed temperature by controlling the electric fields of the STM tip.^[69] By creating molecular anchor points through the STM voltage pulse it is able to stabilize the azobenzene molecule on Au(111), which implies a strong interaction between the molecule and substrate.^[70]

7. Conclusions and Outlook

We have reviewed the recent progress in applying STM manipulations to regulate the inter-adsorbate and adsorbate–substrate interactions on solid surfaces. This technique has demonstrated a versatile and general method to not only differentiate intermolecular interactions but also construct molecular nanostructures by regulating the inter-adsorbate interactions or adsorbate–substrate interactions. It has been illustrated that the strengths of the inter-adsorbate interaction could be regulated ranging from weak vdW forces over hydrogen bonding to strong covalent interaction, which is of particular interest from both a technological and scientific point of view.

It has been more than twenty years since the first attempt at building surface nanostructures in an atom by atom fashion through STM manipulations, and vast efforts have been devoted in this field to the ultimate goal of bottom-up fabrication of nanostructures or nanodevices from atomic or molecular building blocks. The field is still very exciting and we expect to see more and more significant advancements in the near future.

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