Invited Review
Engineering of single molecules with a scanning tunneling microscope tip

SAW-WAI HLA

Nanoscale and Quantum Phenomena Institute and CMSS, Department of Physics and Astronomy, Ohio University, Athens, OH 45701, U.S.A.

KARL-HEINZ RIEDER

Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin, Germany

The rapid progress in molecular manipulation with a scanning tunneling microscope (STM) tip opens up entirely new opportunities in nanoscience and technology. With these advances, the ultimate chemical reaction steps such as dissociation, diffusion, adsorption, re-adsorption and bond formation processes become possible to be performed by using the STM tip at the single molecule level with an atomic scale precision. By using a variety of manipulation techniques in a systematic and step-by-step manner, a complete chemical reaction sequence has been induced with the STM tip leading to the synthesis of molecules on an individual basis. In this paper, various STM manipulation techniques useful in the single molecule engineering process are reviewed, and their impact on the future of nanoscience and technology is discussed.

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1. Introduction

The scanning tunneling microscope (STM) is one of the most celebrated instruments of surface science due to its ability to image hills and valleys of the surface landscapes with atomic scale resolution. For about a decade now, the STM has been used in another 'dimension': manipulation of atoms and molecules on crystal surfaces. Various STM tip induced manipulation techniques have been developed based on a variety of tip–adsorbate/surface interactions. Single atoms or molecules can be manipulated with the STM tip by controlling tip–adsorbate interaction forces, by applying an electric field, or by using tunneling electrons [1–9, 11–39]. In combination with complementary tunneling spectroscopy measurements, the STM manipulation becomes one of the most robust and exciting research fields of nanoscience. In most of the early experiments, only one type of manipulation procedure has been used. However, recent examples have demonstrated that effective and fascinating experiments can be performed if several STM manipulation techniques are integrated into a single experiment. One example of such an integrated application is the induction of a complete sequence of chemical reactions with an STM tip [1]. Based on this achievement, a long time chemist's dream of
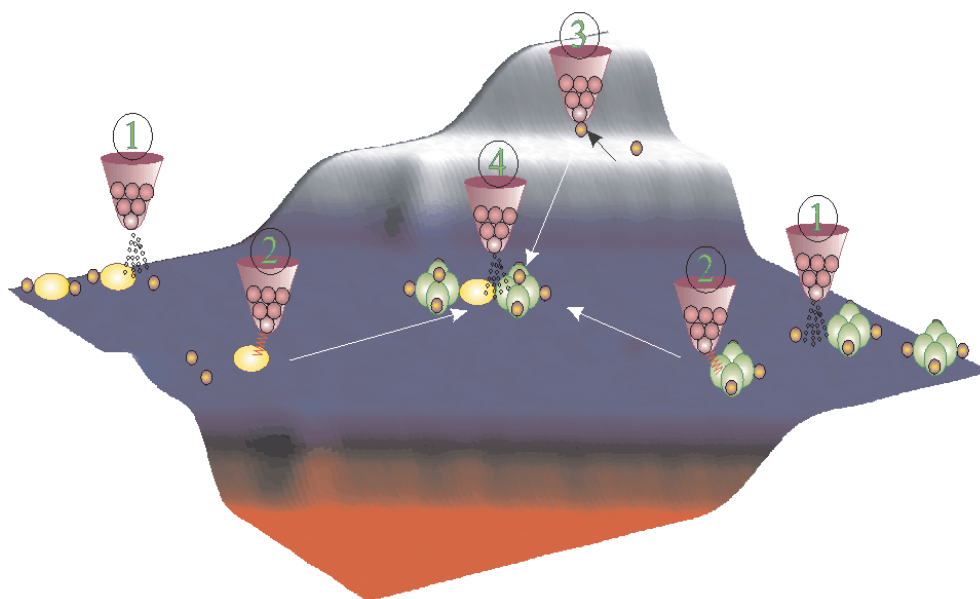
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Fig. 1. Schematic illustration of an STM tip induced single molecule engineering process. Preparation of molecular building blocks by dissociation of larger molecules with the STM tip (1), relocation of molecular building blocks to the assembling site by lateral manipulation (2) and by vertical manipulation (3), assembling of new molecules with the STM tip (4).

construction of individual molecules from the basic building blocks has now become a reality. The concept of single molecule construction using an STM tip is illustrated in Fig. 1.

Engineering of single molecules may require preparation of basic building blocks—which can be individual atoms or molecular fragments—, bringing them together to an assembling place and then joining them to form a desired molecule on a surface. This entire procedure is somewhat similar to the assembling process of automobiles or electronic commodities in a factory production line. From the basic science point of view, such molecular construction can reveal intimate details of the underlying chemical processes during a chemical synthesis. From a technology point of view, individual construction of molecules to be used in nanoelectronic and nanomechanical applications becomes closer to reality.

2. Preparation of the molecular building blocks

Organic molecules consist mostly of hydrocarbon components. Hence, various hydrocarbon fragments can be chosen as molecular building blocks to construct an organic molecule. One way to prepare the building blocks for molecular construction is by selective bond breaking of larger molecules with an STM tip. In this way, unnecessary parts of a molecule can be cleaved off and thereby active sites can be created; such molecular fragments can be used as building blocks to join with other deliberately prepared species to build up a new molecule.

Tunneling electrons from the STM tip are mainly used in tip induced molecular bond-breaking processes [1–9]. The possibility to dissociate single molecules with an STM tip was first demonstrated by Avouris and coworkers [2, 3]. They dissociated $B_{10}H_{14}$ and O_2 molecules on Si(111) surface by applying 6 and 4 V voltage pulses, respectively. When electron energies higher than the work function of the tip (roughly >3 eV) are applied to the molecule, the STM tip acts as an electron emission gun and the dissociation process is then in the field emission regime.

The dissociation involving an inelastic tunneling process—in which lower STM biases are used—is easier to control. Stipe *et al*. [4] have demonstrated this process by dissociating diatomic O_2 molecules on Pt(111). However, controlled dissociation of poly-atomic molecules is more complex because more than one bond is involved. Selective bond breaking inside the poly-atomic molecules were later successful in the cases of HCCH, C_6H_6, C_6H_5I and $C_6H_4I_2$ dissociations [1, 8, 9]. To break a molecular bond, the tip is positioned above the molecule or at the location of the bond at a fixed height and then the tunneling electrons are injected into the molecule (Fig. 2A). The electron energy can be transferred to the molecule through resonant states [10]. When the transferred energy exceeds the specific bond-dissociation energy, the respective bond is broken. The corresponding tunneling current can be monitored and current changes can be associated with the dissociation event. The number of tunneling electrons involved in a bond-breaking process can be determined from the dissociation rate versus tunneling current relationship [1, 7].

As an example, a series of STM images acquired during a tip induced dissociation of an iodobenzene (C_6H_5I) molecule adsorbed at a Cu(111) step-edge are illustrated in Fig. 2B–D. In this experiment, the lone C–I bond of the molecule is selectively broken by injecting 1.5 eV tunneling electrons from the STM tip to the molecule. After the C–I bond breaking, the whole π-ring is left intact. This can be achieved due to the inherent differences in bond energies inside the molecule, where the C–I bond is weaker than those of C–C and C–H. The linear dependence of the dissociation rate on the tunneling current in this dissociation process reveals that the energy transfer from a single tunneling electron causes the C–I bond breaking [1]. The resultant phenyl (C_6H_5) is then used as a molecular building block to construct a biphenyl $(C_{12}H_{10})$ molecule. The lesson of this example is that, by choosing a proper molecular system, specific bond breaking can be performed. Ho and coworkers [8, 9] used similar techniques to selectively break the C–H bonds of HCCH and benzene (C_6H_6) producing stable HCC, CC and C_6H_4 fragments on a Cu surface. This is because the C–H bond is weaker than C–C bonds. These achievements allow one to design and produce various hydrocarbon fragments to be used as molecular building blocks to construct new molecules on surfaces.

3. Relocation of the molecular building blocks

After preparation of the molecular building blocks, they need to be collected at a specific place on the surface in order to assemble a desired molecule. Thus, the ability to bring the atoms or molecular fragments to an assembling place on the surface with atomic scale precision is an important and integral part of the single molecule engineering process. An STM manipulation technique to relocate single atoms or molecules across a surface is known as 'lateral' manipulation [11–29]. It applies tip–adsorbate interactions to laterally move the atom or molecule. This procedure involves approaching the tip towards a target particle at its initial location, this increases the tip–adsorbate interaction force, and then scanning the tip along a desired path until it reaches a predetermined destination (Fig. 3A). The adsorbate moves along with the tip and when the tip retracts back to the normal imaging height, it is left behind on the surface. This kind of controlled manipulation was first demonstrated by Eigler and Schweizer [11] in 1990 by writing the 'IBM' letters with Xe atoms on a Ni(110) surface. An extremely fine control of the tip–adsorbate–surface interactions is a necessary ingredient to achieve atomic scale precision in this procedure.

A fascinating aspect of this technique is that one can extract further information—such as how the atom or molecule moves and what kind of interactions are involved during manipulation—from the corresponding STM feed-back or tunneling current signals. Based on the nature of the tip–adsorbate interactions, three basic manipulation modes, pushing, pulling and sliding, can be distinguished [20, 23, 24]. Attractive interactions lead the atom/molecule to follow the tip in the pulling mode while repulsive interactions cause pushing. The atom/molecule is either trapped under the tip or bound to the tip during a 'sliding' mode operation. Figure 3B and C demonstrate a lateral movement of a di-iodobenzene molecule along a Cu(111) step-edge at 12 K. Figure 3D shows a typical pulling curve which was recorded during a lateral manipulation of a di-iodobenzene molecule on Cu(111) [24].
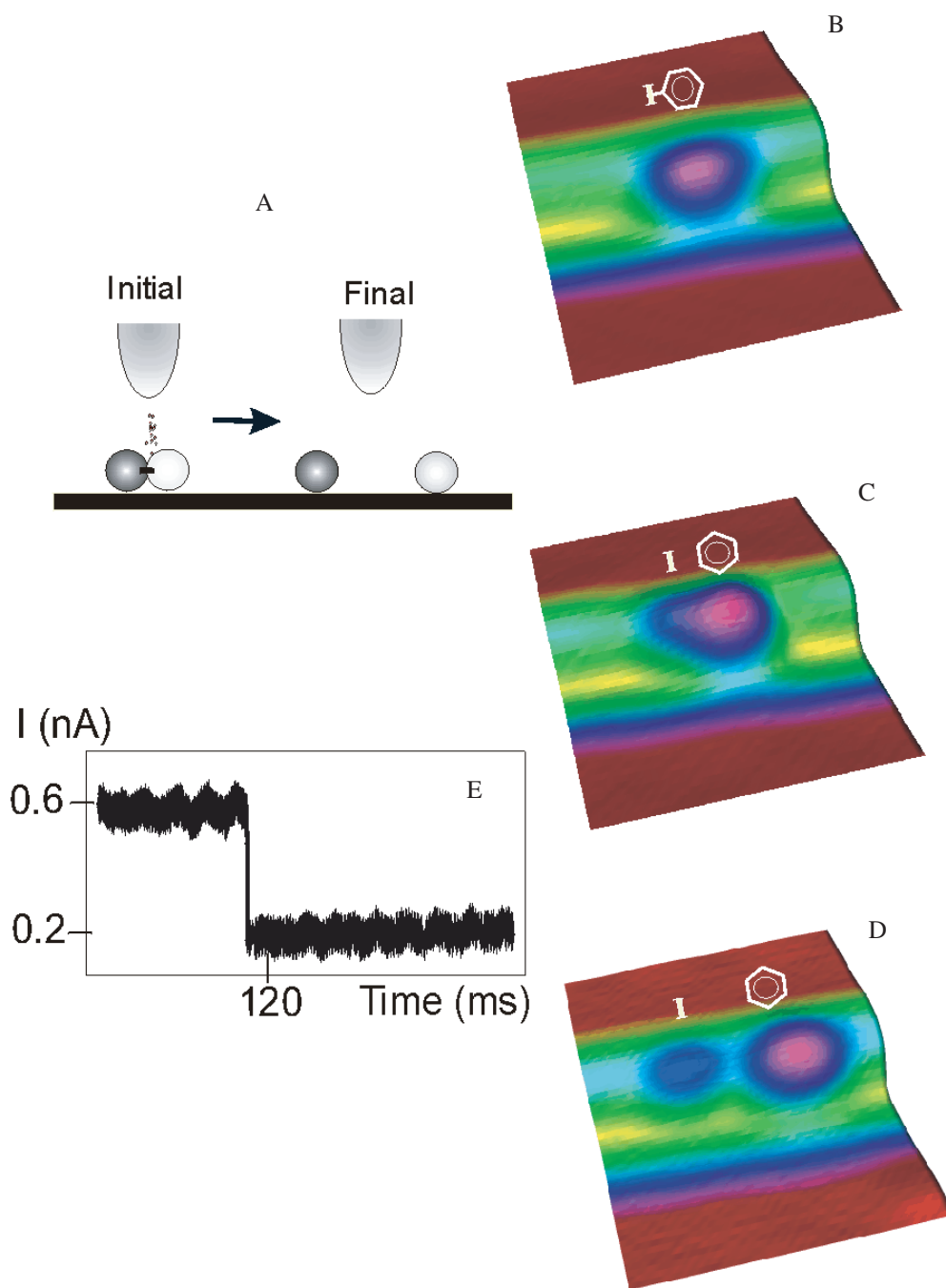
Fig. 2. Selective molecular bond breaking process. Schematic drawing illustrating the tip induced bond breaking procedure (A). An iodobenzene (C_6H_5I) molecule adsorbed at a Cu(111) step-edge (B). After breaking the C–I bond, both the iodine atom (smaller bump) and the phenyl fragment are adsorbed at the Cu step (C) and they are further separated by lateral manipulation (D). A sudden drop in tunneling current, which was recorded during this dissociation process, reveals the dissociation event (E).
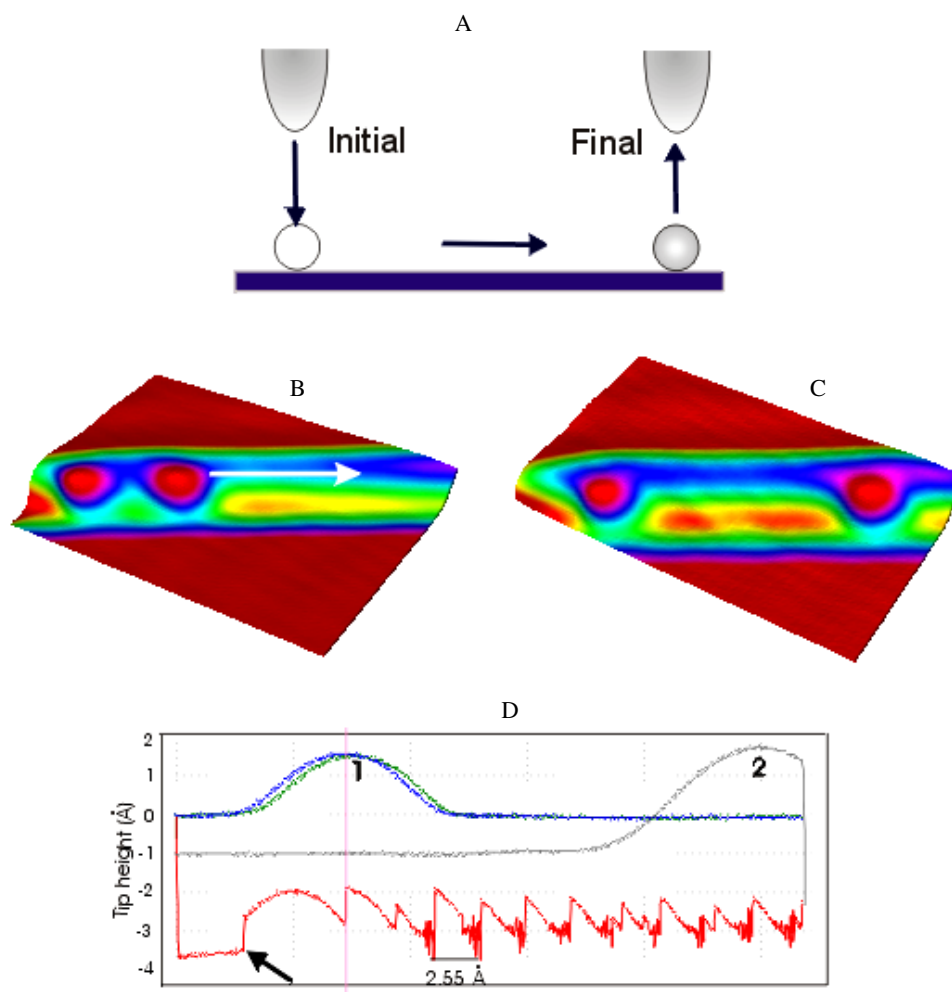
Fig. 3. Lateral manipulation process. Schematic drawing illustrates the lateral manipulation procedure (A). A di-iodobenzene molecule adsorbed at a Cu(111) step-edge (B) has been moved to the right side using the lateral manipulation technique with the STM tip (C). The STM tip height curves (D) demonstrate a lateral manipulation operation. First, a trial scan was performed along the manipulation path with a normal imaging height. This scan recorded the initial molecule position (1). Then the actual manipulation was accomplished by reducing the tip height by 3.5 Å from its original location. A sudden increase in tip height (indicated by an arrow) occurs due to a jump of the molecule toward the tip. The vertical line is drawn to show the initial molecule position. The manipulation curve reveals a typical pulling behavior in which the molecule followed the tip mostly by hopping across single Cu atomic sites (2.55 Å). The tip was then retracted at the final position and re-scanned along the manipulation path to assess the success of the operation. During this, the final position of the molecule was recorded at (2).

Recent investigations of detailed single atom movement behaviors duringlateral manipulation operations highlight not only the complex atom movement mechanisms but also the energetic behavior of different adsorption sites on the surface [28]. When the lateral manipulation technique is applied to large molecules, the recorded manipulation signal can even reveal intramolecular conformational changes and the nature of different tip–molecule interactions at various parts of the molecule with atomic level precision [26, 29]. Thus, the lateral manipulation is also useful to probe mechanical stability and conformational changes of the molecules. Such information is valuable for future nanomechanical applications.

Another STM manipulation procedure, known as 'vertical' manipulation, can also be used to relocate the molecular building blocks on a surface. It involves transfer of single atoms or molecules between the tip and substrate and vice versa. This transfer process is realized by using an electric field, or by applying voltage pulses, or by making mechanical contact between the tip and atom/molecule [30–39]. An 'atomic switch' operated by repeatedly transferring a 'Xe' atom between the STM tip and a Ni(110) substrate has been the first demonstration for this kind of manipulation [30]. Further work on vertical molecular manipulation includes transfer of C_6H_6, CO and C_3H_6 between the tip and surface [12, 35–37, 39].

One useful application of vertical manipulation is to modify the STM tip. The sharpness of the tip and the chemical element that forms the tip apex are extremely critical for STM applications. A single atom/molecule tip can be formed by deliberately transferring an atom/molecule to the tip apex. This will improve the tip sharpness and thus the image contrast will be enhanced. Additionally, the tip will be better defined with respect to its chemical constitution. Such kinds of functionalized tips are useful in molecular recognition imaging. For example, CO and oxygen can be distinguished when CO functionalized tips are used [36]. This technique is also particularly useful in transporting the atoms/molecules across substrate obstacles. For example, CO molecules have been repositioned by picking them up with the STM tip and putting them back at the other side of a substrate trough which could not be surmounted by lateral manipulation [36]. In this case the vertical manipulation process is similar to the loading and unloading operation of a crane at a construction site in our macroscopic world. Because of this, vertical manipulation may be useful in three-dimensional molecular assemblies.

3.1. Molecular assembling

The final part of the single molecule engineering process is to weld the molecular building blocks, i.e. to join the atoms or molecular fragments, which are already prepared and transported to an assembling place. In scientific terms, this means chemical bonds have to be formed between them. The STM tip can also be used in this process [1, 39]. In fact, the transfer and re-deposition processes in vertical manipulation can be considered as forming a bond between the molecule and the tip or the substrate, respectively. Additional bond formation was demonstrated by Lee and Ho by forming $Fe(CO)_2$ on Cu(100) [39]. They used vertical manipulation to deposit a CO molecule over an adsorbed Fe atom on a Cu surface. Then another CO molecule was brought with the tip and the process repeated. Because the adsorbed Fe atom can accommodate more than a CO molecule, an additional bond could be formed. The bond formation process between two radicals on a surface was first demonstrated by creating a biphenyl molecule out of two phenyl radicals on Cu(111) [1]. In this case, the molecular excitation by inelastic tunneling was accomplished by injecting 500 meV energy tunneling electrons into two closely spaced phenyl fragments at a Cu(111) step-edge.

Figure 4B visualizes the chemical association of two phenyls brought to the closest approach possible by the STM tip. The upper half of this image was acquired before association and the lower half was acquired after association. The distance between the phenyl centers changes upon association to 4.4 ± 0.05 Å (see Fig. 4B inset), which is consistent with the distance of 4.3 Å between the two centers of the π rings in gas-phase biphenyl. This association process involves breaking of phenyl–substrate bonds which results in the formation of a new C–C bond between the two phenyls.

4. Single molecule construction

Figure 5 demonstrates an example for the single molecule construction sequence performed at 20K using an STM tip. In this sequence, all the manipulation techniques described previously are systematically applied to construct a new molecule. This series is a reproduction of a century old aromatic-ring coupling mechanism, known as the 'Ullmann' reaction, in the form of single molecules. In 1901, Ullmann and co-workers [40]
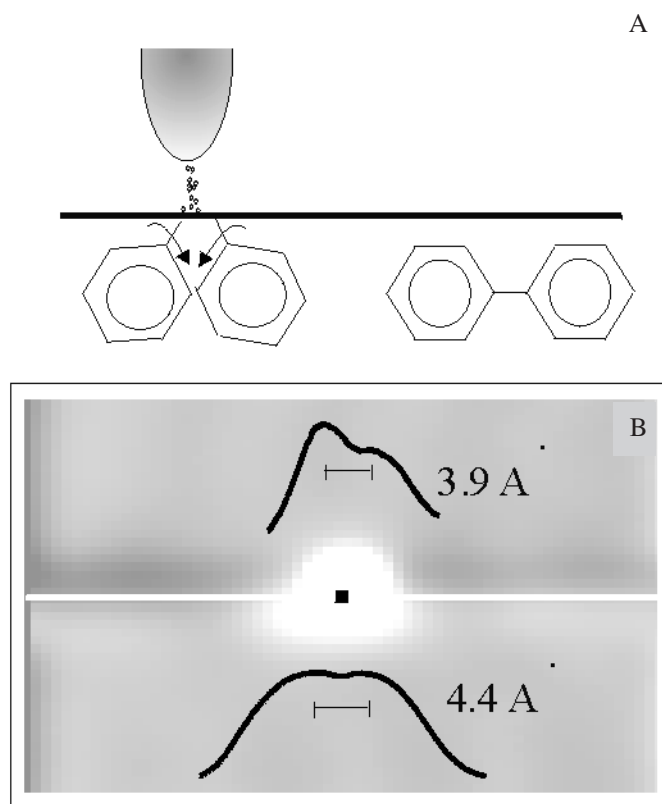
Fig. 4. STM tip induced bond formation process. Bond formation between the two molecular fragments can be realized by exciting them with tunneling electrons (A). A background subtracted STM image with a phenyl couple in its center. The upper and lower parts correspond to the stages before and after the chemical association. The tip height profile across the centers of the synthesized biphenyl molecule is indicated. (Image parameters: $+100$ mV, 1.3 nA; 24×7 Å^2.)

discovered that heating a mixture of C_6H_5I liquid and Cu powder to ~ 400 K resulted in the formation of biphenyl ($C_{12}H_{10}$). From this experiment, they derived the following formula;
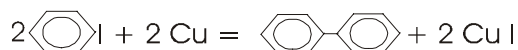
Three elementary steps are involved in this reaction: dissociation of C_6H_5I into phenyl (C_6H_5) and iodine, diffusion of C_6H_5 to meet its reaction partner—another C_6H_5—and finally, joining of two C_6H_5 to form a $C_{12}H_{10}$ molecule. Cu acts as a catalyst in this mechanism. Naturally, the Ullmann reaction is triggered by thermal excitations and no reaction occurs at our working temperature of 20 K.

As an initial stage, two C_6H_5I molecules adsorbed at the lower part of a Cu(111) step-edge (Fig. 5A) are selected. C_6H_5 (phenyl) can be used as the basic building block in this case and two C_6H_5 are needed to construct a $C_{12}H_{10}$ molecule. C_6H_5 can be prepared by breaking the C–I bond of the C_6H_5I molecule (Fig. 5B). After dissociation, the resulting phenyl fragments are bonded to the step-edge Cu atoms. The iodine atom at the left side (indicated by a green arrow) is then transferred to the tip apex by using the vertical manipulation technique. Due to the existence of the iodine atom at the tip apex, the tip becomes sharper which enhances the image contrast (Fig. 5C). Using this iodinated tip, the phenyls are repositioned close to each other with the lateral manipulation technique (Fig. 5D and E). Voltage pulses of 0.5 V are
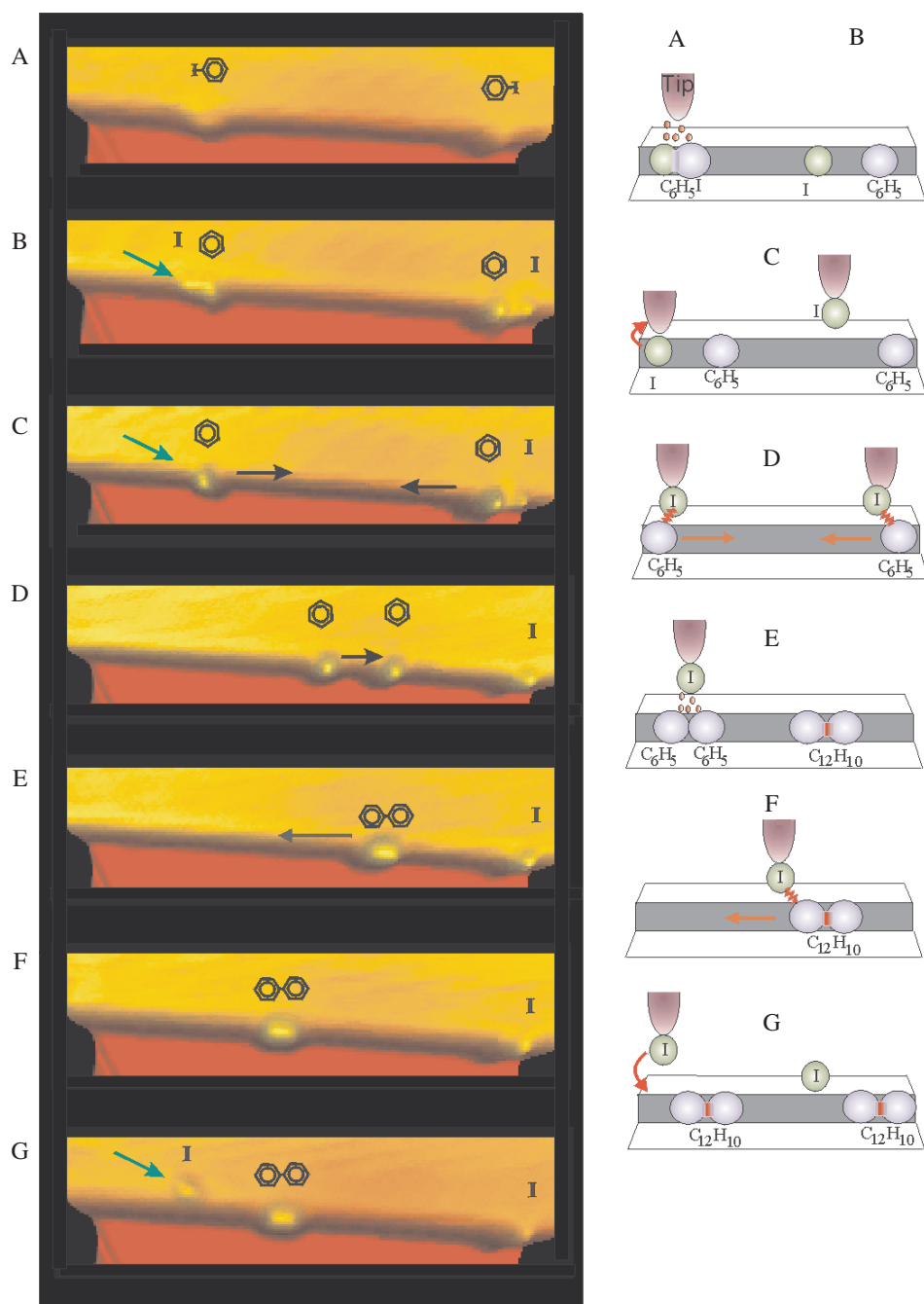
Fig. 5. Single molecule Ullmann reaction: two iodobenzene molecules are adsorbed at a Cu(111) step (A). After dissociation with tunneling electrons, two phenyl radicals (larger bumps) and two iodine atoms are adsorbed at the Cu step-edge (B). After the iodine at the far left (indicated by a green arrow) has been transferred to the tip apex via vertical manipulation, the image contrast improves (C). The two phenyls are moved via lateral manipulation towards each other (D). When the two phenyls are in closest proximity, tunneling electrons having energies up to 500 meV are supplied to induce the biphenyl formation (E). Then, the newly synthesized biphenyl is pulled with the tip to the left side of the image proving successful chemical association (F). Finally, the iodine from the tip apex is transferred back to the substrate (G) (indicated by a green arrow).

applied to join the phenyl couple at Fig. 5E. The stability of the synthesized biphenyl ($C_{12}H_{10}$) is then checked pulling the molecule from its front end with the STM tip and observing that the entire unit follows the tip (Fig. 5F). The iodine atom at the tip apex is then transferred back to the upper part of the terrace (Fig. 5G).

5. Future prospects for single molecule engineering

By inducing chemical reactions with the STM tip, the detailed underlying reaction processes can be studied on an atomic level. Chemical relationships like the Ullmann equation can be checked and confirmed. However, one should be cautious in making direct relationships between the natural and tip induced reactions. Under the influence of the tip, reactions can be forced to proceed which otherwise may not occur in nature. This, on the other hand, is exactly the advantage of nanotechnology, since synthesis of individual man-made molecules, never before seen in nature or made in chemical reactors, may eventually become a possibility. One of the research goals in development of nanotechnology is to synthesize specially designed single molecules for nanoelectronic applications. It has already been proposed that single molecules with specific unique functions may act as monoelectronic devices [41, 42]. For example, the molecule with donor–spacer–acceptor structure can behave as a rectifier when it is placed between two electrodes [42]. The demonstrated examples include single molecule transistors, single atom and molecule switches and molecular wires [26, 30, 43–47]. It is therefore favorable to find ways for molecular synthesis on an individual basis. This would also allow scientists to probe and understand the intimate details of the underlying mechanisms of the synthesis processes. Even though the goal to engineer individual nanoelectronic and nanomechanic devices is yet to be reached, the progress in construction of simple molecules such as biphenyl is, without a doubt, a step forward in this direction. With STM and scanning tunneling spectroscopy (STS) techniques, physical and chemical properties such as bond strengths, electrical conductivity, mechanical stability and conformational changes of synthesized molecules can be studied locally. This may very well initiate their mass scale production for industrial use. Thus, recent progress in molecular manipulation made possible by STM techniques will open an entire new dimension for future nanoscience and nanotechnology.

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