

Inducing Single-Molecule Chemical Reactions with a UHV-STM: A New Dimension for Nano-Science and Technology

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Atomic and molecular manipulations with the scanning tunnelling microscope (STM) lead to many fascinating advances during the last decade. Recent achievements in inducing all of the basic steps of a chemical reaction with the STM at a single-molecule level open up entirely new opportunities in chemistry on the nanoscale. In this article, we review various STM-based molecular manipulation techniques and their application in inducing all elementary

chemical reaction steps on surfaces. Prospects for future opportunities of single-molecule chemical engineering and their possible implications to nanoscale science and technology are discussed.

KEYWORDS:

manipulation · molecular devices · nanotechnology · scanning probe microscopy · surface chemistry

In Primo Levi's novel *The Monkey's Wrench*, a chemist explains to a construction engineer the ultimate chemical fantasies about building molecules:

We don't have those tweezers we often dream of at night, the way a thirsty man dreams of springs, that would allow us to pick up a segment, hold it firm and straight, and paste it in the right direction on the segment that has already assembled. If we had those tweezers (and it's possible that one day, we will), we would have managed to create some lovely things that so far only the Almighty has made.^[1]

The dream of constructing individual molecules from various basic building blocks has recently come close to reality, at least on a substrate surface, by using the scanning tunnelling microscope (STM) tip as an engineering tool. Since this Nobel-prize winning invention of Binnig and Rohrer was developed in the early 1980s, the STM has been a celebrated tool of surface science due to its ability to image atomic-scale surface structures. But often experimenters experienced perturbations during STM imaging, caused by interactions between the STM tip and adsorbates. It did not take a long time for these unwanted perturbations to become one of the most fascinating tools to be pursued by scientists: Manipulation of individual atoms and molecules on surfaces. During the last decade, 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 atomic forces or with the electric field between the STM tip and the sample or with the tunnelling electrons. With the advances in manipulation procedures, the fundamental surface reaction steps, such as dissociation, diffusion, desorption, readsorption and association processes,^[2] became inducible at the single-molecule level. In many (metal) catalysed reactions—where the initial reactants are transformed into new molecular species with

the help of a substrate catalyst—one or more of these phenomena are involved as elementary steps.^[2] By choosing a suitable combination of manipulation techniques with an STM tip, a sequence of processes constituting a complete chemical reaction could be recently induced by employing single molecules in a controlled step-by-step manner, which lead to the synthesis of product molecules on an individual basis.^[3] In the following, we describe the induction of four basic reaction steps (lateral manipulation, molecule dissociation, vertical manipulation and bond formation) with the STM tip and provide an illustrative example, a single-molecule Ullmann reaction.

Lateral Manipulation: Controlled Molecular Diffusion on Surfaces

Diffusion of atoms or molecules on surfaces naturally occurs by thermal excitation causing adsorbates to move across the surface in a random fashion. The STM manipulation procedure close to this phenomenon, but at temperatures low enough that the molecules are immobile, is known as "lateral" manipulation. It applies tip–molecule interactions to laterally move the molecule across a surface. This procedure involves moving the tip towards the target molecule at its initial location to increase the tip–molecule interaction force, and then to move the tip along a desired path until it reaches a predetermined destination (Figure 1 a). The molecule moves along with the tip and when

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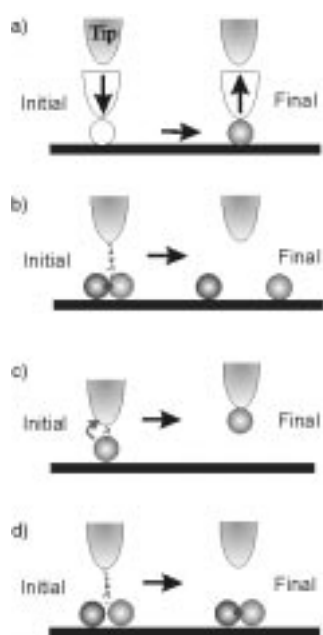


Figure 1. Manipulation procedures used in single-molecule engineering processes. a) Lateral manipulation, b) molecule dissociation, c) vertical manipulation and d) bond formation.

the tip retracts back to the normal imaging height, the molecule is left behind on the surface. A nice example for this kind of controlled manipulation was first demonstrated by Eigler and Schweizer in 1990.^[4] They wrote “IBM” with 35 xenon atoms on a Ni(110) surface. Because extremely fine control of the tip–molecule interactions is a necessary ingredient to achieve atomic-scale precision, cryogenic substrate temperatures are favoured in most experiments^[3–10] in order to reduce thermal excitation and drift. However, room temperature manipulation is also possible for larger molecules such as copper tetra-(3,5-di-*tert*-butylphenyl)porphyrin (CuTBPP)^[11] or fullerene (C₆₀) molecules.^[12–14]

A fascinating aspect of this technique is that one can extract further information—such as how the molecule moves and what kind of interactions are involved during manipulation—from the corresponding STM feedback or tunnelling current signals. Based on the strength of the tip–molecule interactions, three basic manipulation modes, pushing, pulling and sliding, can be distinguished.^[8] Attractive tip–molecule interactions force the molecule to follow the tip in the pulling mode while repulsive interactions cause pushing. The molecule is strongly bound to the tip during a “sliding” mode operation. Molecular “pulling” is dominant for small- and medium-sized molecules such as diiodobenzene (C₆H₄I₂)^[10] and biphenyl (C₁₂H₁₀)^[3] on copper surfaces. However for large molecules, such as porphyrin-based systems, “pushing” is the main manipulation mode.^[11] A typical pulling operation of a single diiodobenzene molecule on Cu(111) is illustrated in Figure 2. A molecular artwork, demonstrating the abilities for precise positioning of molecules, is presented in Figure 3 where the millennium year number 2000 is written with 47 CO molecules on Cu(211). Further detailed experimental and theoretical investigations of the manipulation signals of single

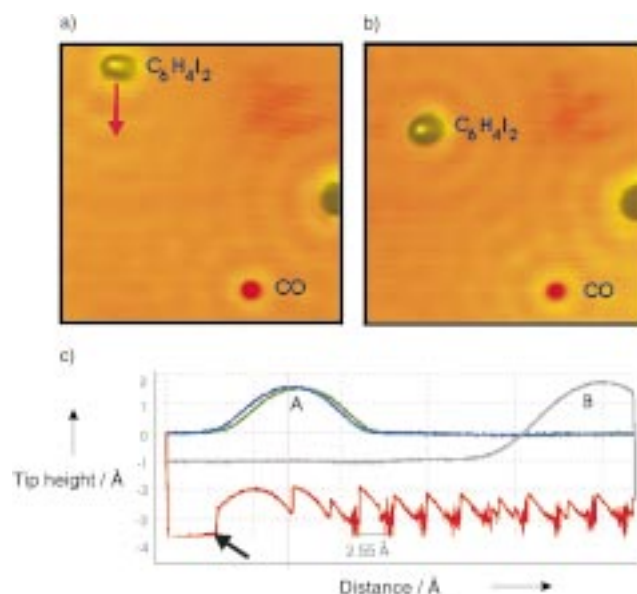


Figure 2. a, b) A diiodobenzene molecule on Cu(111)—upper left corner in (a)—is laterally moved to a new position in (b). The CO molecule (red circle) is used as a landmark. c) During the manipulation operation the tip first makes a trial scan at a height of about 6 Å along the manipulation path and records the initial molecule position (A), then the actual manipulation was performed by reducing the tip height by 3.5 Å. A sudden increase in tip height (shown by the arrow) occurs due to molecule hopping towards the tip. The vertical line is drawn to show the initial molecule position. The molecule follows the tip in the pulling mode with mostly single hops (2.55 Å). The tip is retracted at the final position and rescanned along the manipulation path to check the successful manipulation of the molecule to location (B).

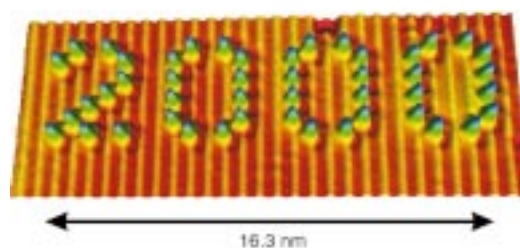


Figure 3. The new millennium is celebrated in our group by writing 2000 with single CO molecules on Cu(211). Each protrusion represents an individual CO molecule; the background vertical lines are the intrinsic Cu surface step edges. The image was acquired with a CO-functionalised tip.^[17]

molecules can even reveal how the molecules behave during their movements such as internal conformational changes^[15] or movement of the molecules relative to the tip.^[16]

Molecular Dissociation

Tunnelling electrons from the STM tip can be used to break the bonds inside a molecule. Based on the electron energy, two regimes, field emission and inelastic tunnelling, can be distinguished. High electron energies (roughly > 3 eV) are involved in field emission regime where the tip acts as emission gun. The dissociation process in this regime is less controllable. Early examples include dissociation of adsorbed B₁₀H₁₄^[18] and O₂^[19] on Si(111) with voltages ≥ 4 and ≥ 6 V, respectively.

In case of inelastic tunnelling, low-energy tunnelling electrons are usually involved in bond breaking. To break a bond, the tip is positioned above the molecule or at the location of the bond at a fixed height (Figure 1 b) and then the tunnelling electrons are injected into the molecule. The tunnelling electron energy can be transferred to the molecule through resonance states^[20] and, when the transferred energy exceeds the specific bond-dissociation energy, the respective bond is broken. The corresponding tunnelling current can be monitored and current changes can be associated with the dissociation event. This process was demonstrated in the dissociation of O₂ on Pt(111).^[21] However, controlled dissociation of polyatomic molecules is more complex because more than one bond is involved. In case of benzene and acetylene (HCCH) dissociation on Cu(100),^[22, 23] the C–H bonds of the molecule can be broken while leaving the C–C bonds intact. The selective breaking of a specific single bond inside a polyatomic molecule was demonstrated in case of the C–I bond scission of C₆H₅I on Cu(111).^[3] This can be achieved due to the inherent differences in bond energies inside the molecule as the C–I bond is the weakest. The lesson of this example is that, by choosing a proper molecular system, specific bond breaking can be performed. An example for molecular dissociation is shown in Figure 4, where the two C–I bonds of a C₆H₄I₂ molecule on Cu(111) have been broken by using an inelastic tunnelling process.^[24]

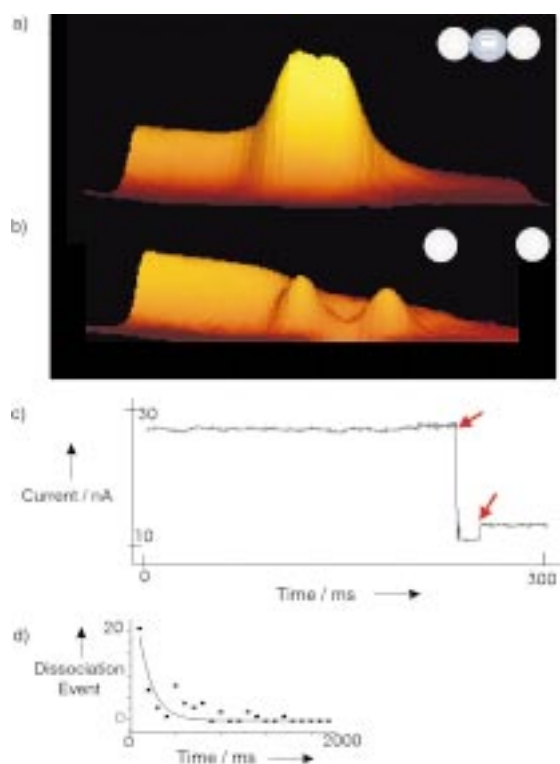


Figure 4. Iodine abstraction via molecular bond breaking. a) A p-diiodobenzene (C₆H₄I₂) molecule adsorbed at a screw dislocation on Cu(111). b) After breaking the two C–I bonds of the molecule using inelastic tunnelling electrons, the two iodine atoms remain adsorbed. The other fragment of the parent molecule, C₆H₄, diffused away after breaking the second C–I bond. c) The two abrupt changes in the tunnelling current signals (shown with arrows) correspond to the each bond-breaking event. d) The C–I bond dissociation probability collected from 70 dissociation events.

Vertical Manipulation

Vertical manipulation involves transfer of molecules between the tip and substrate, and vice versa. Closely related surface phenomena for this case are the desorption and readsorption processes. An “atomic switch” operated by repeatedly transferring a xenon atom between the STM tip and a Ni(110) substrate^[25] and improvement of the STM resolution using a xenon tip^[7] were the first examples to demonstrate this kind of manipulation. Further work on vertical molecular manipulation includes C₆H₆,^[5] CO^[26–28] and C₃H₆.^[29] During manipulation, the STM tip is positioned exactly above the molecule and voltage pulses are applied. The excitation with tunnelling electrons and/or the electric field causes cleavage of the molecule–substrate bond. The molecule then desorbs and is readsorbed at or near the tip apex (Figure 1 c).

In case of CO vertical manipulation, the CO/Cu bond is broken by attachment of an electron to the CO 2π* state.^[27] The resultant excited CO molecule can either jump to nearby copper surface sites or toward the tip. One useful application of this technique is the “functionalisation” of the STM tip with a molecule. The tip plays a crucial role in STM imaging and usually it is difficult to know what kind of chemical element exists at the tip apex. By deliberate transfer of a molecule to the tip apex, the tip becomes sharper and thereby yields good image contrast. Additionally, the tip becomes well defined with respect to its chemical constitution. The application of functionalised tips has proven useful in molecular recognition imaging. For example, CO and O₂ can be distinguished when CO functionalised tips are used.^[26] An application is shown in Figure 5.

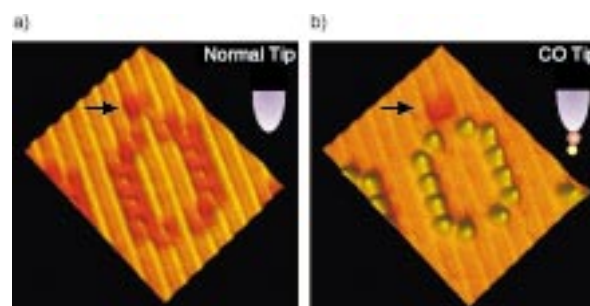


Figure 5. Imaging with CO-functionalised tip: STM images showing the number “0” formed with eight CO molecules on Cu(211). CO molecules appear as an indentation (a) when imaged with a normal tip and protrusions (b) when imaged with a CO-functionalised tip. An unknown adsorbate (indicated with the arrow) is still remains as indentation in both images, thus chemical contrast can be achieved.^[30]

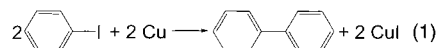
The molecule can be transferred back to the surface by applying a reverse-polarity voltage pulse.^[26, 28] Therefore this manipulation technique is also useful in repositioning the molecules across substrate obstacles. For example, CO molecules have been repositioned by picking them up with the STM tip and putting them back at the other side of a substrate trough which could not be surmounted by lateral manipulation.^[26] In this case, the vertical manipulation process is similar as the loading and unloading operation of a crane at a construction site in our macroscopic world.

Bond Formation

The STM tip can also be used for molecular bond formation processes. In fact, the transfer and redeposition 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^[28] by forming $[\text{Fe}(\text{CO})_2]$ on Cu(100). They used vertical manipulation to deposit a CO molecule over an adsorbed iron atom on a copper surface. Then, another CO molecule was brought with the tip and the process repeated. Because the adsorbed iron atom can accommodate more than a single 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).^[3] This process is mediated by excitation with tunnelling electrons on two closely located phenyl molecules (Figure 1 d). It involves breaking of the two phenyl–substrate bonds so that the two phenyl components are free to form a stable biphenyl molecule.

Single-Molecule Ullmann Reaction

Almost all chemical reactions we know today are studied in bulk-scale experiments where enormous numbers of molecules are involved. The corresponding chemical equations are based on these experiments. Studying a chemical reaction at the single-molecule level will have a great impact on the basic understanding of chemistry on atomic scale. The Ullmann reaction is a basic textbook-chemistry case and an important aromatic-ring coupling reaction widely used in synthetic chemistry. Almost a century ago, Ullmann and co-workers discovered that heating a mixture of $\text{C}_6\text{H}_5\text{I}$ liquid and copper powder to $\sim 400\text{ K}$ resulted in formation of $\text{C}_{12}\text{H}_{10}$.^[31] From this experiment, they derived Equation (1).



There are three elementary steps involved in this reaction after adsorption of $\text{C}_6\text{H}_5\text{I}$ onto copper: Dissociation of $\text{C}_6\text{H}_5\text{I}$ into phenyl ($\text{C}_6\text{H}_5\cdot$) and iodine ($\text{I}\cdot$) radicals, diffusion of the phenyl radical to its reaction partner, another radical, and then association to form biphenyl. Copper acts as a catalyst in this reaction. Naturally, the Ullmann reaction is triggered by thermal

excitation. Dissociation of $\text{C}_6\text{H}_5\text{I}$ occurs at $\sim 180\text{ K}$ and biphenyl is formed at $\sim 400\text{ K}$.^[32–34] Thus it is necessary to conduct single-molecule experiments at low temperatures to avoid thermal influences. Figure 6 demonstrates an example for the single-molecule Ullmann reaction sequence induced at 20 K by using the STM tip. This sequence is different from the case published previously^[3] because here we used an iodine-functionalised tip to induced most of the basic reaction steps. The use of an iodinated tip does not effect the detailed tunnelling parameters, such as tunnelling voltage or current for the reaction steps, but has the advantage that the image contrast is enhanced, thus allowing more precise tip positioning.

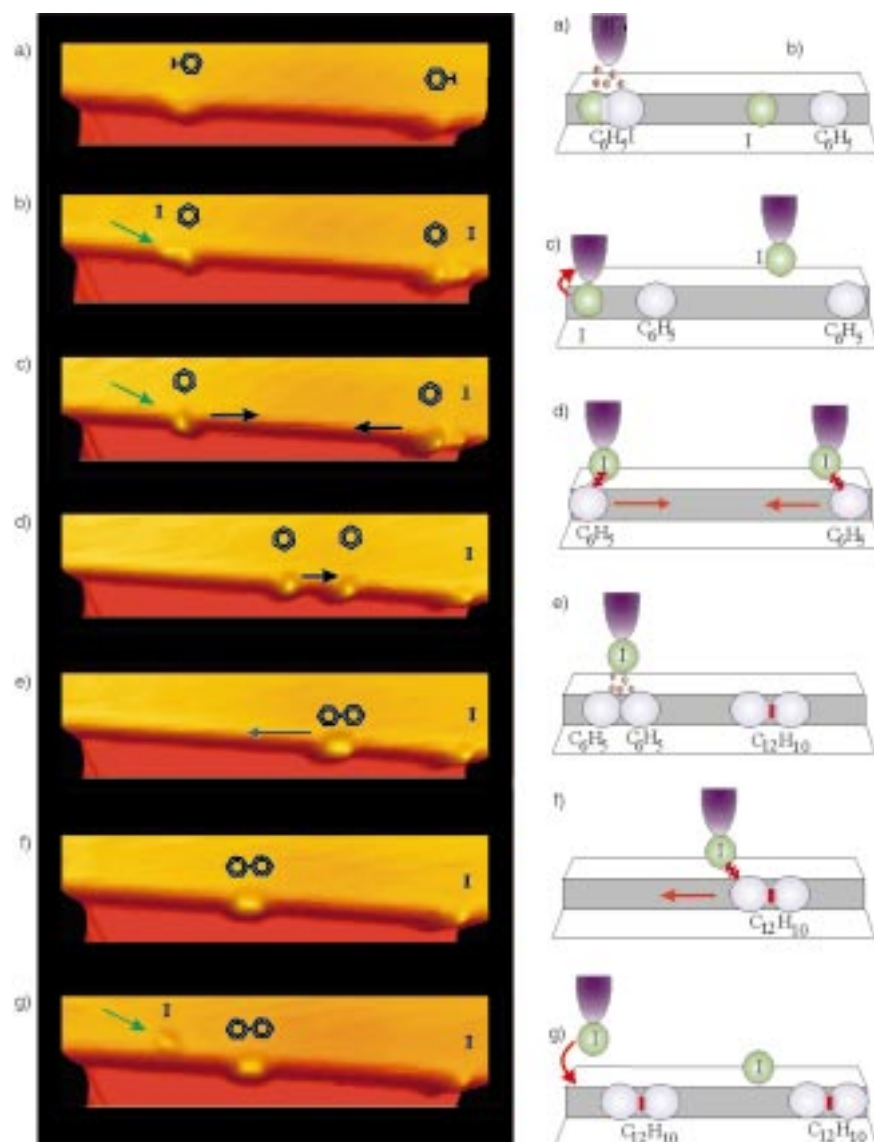


Figure 6. Single-molecule Ullmann reaction, shown both as the STM images and schematically. a) Two iodobenzene molecules are adsorbed at a Cu(111). b) After dissociation with tunnelling electrons, two phenyl (larger bumps) and two iodine radicals are adsorbed at the copper step-edge. c) After the iodine at the far left (indicated by a green arrow) has been transferred to the tip apex via vertical manipulation, the image contrast improves. d) The two phenyl radicals are moved via lateral manipulation towards each other. e) When the two radicals are in close proximity, a splash of electrons at 500 meV is supplied to excite them to biphenyl formation. f) The newly synthesised biphenyl is then pulled by the tip to the left side of the image proving successful chemical association. g) Finally, the iodine from the tip apex is transferred back to the substrate (indicated by a green arrow).

We start with two C_6H_5I molecules adsorbed at the lower part of a Cu(111) step-edge (Figure 6a). The first reaction step, dissociation, was performed by injecting tunnelling electrons (energy 1.5 eV) into the molecule. The energy of a single tunnelling electron transferred to the molecule breaks the C–I bond.^[3] The resulting fragments, phenyl and iodine radicals (Figure 6b), are separated by $2.5 a_0$ for the left and $3.5 a_0$ for the right molecule ($a_0 = 2.55 \text{ \AA}$ and denotes the nearest-neighbor distance in copper). Then the abstracted iodine atom at the far left was transferred to the tip apex using vertical manipulation (Figures 6b and 6c). Now the tip becomes sharper and the image contrast is improved (Figure 6c).

The second reaction step, diffusion, was performed by using the lateral manipulation technique. Both phenyl radicals are moved towards each other (Figure 6d) until they are closely located (Figure 6e). To realise the third reaction step, association, the phenyl couple at Figure 6c was excited by applying 500 meV voltage pulses for 10 s. Formation of biphenyl was confirmed by pulling the synthesised molecule from its front end with the STM tip (Figure 6f). Since the entire unit follows the tip from behind in the pulling mode, this verifies the successful chemical association of the two radicals to form a biphenyl molecule.

Finally, the iodine atom from the tip apex was transferred back to the substrate (Figure 6g) by applying reverse voltage pulses. In the sequence of Figure 6, the first image (Figure 6a), showing two adsorbed C_6H_5I molecules on copper, exactly represents the left side of the Ullmann equation while the final image (Figure 6g), a biphenyl molecule and two iodine atoms on copper, exactly represents the right side of the equation. Thus the whole chemical equation can be visualised with individual reactants for the first time.

Additionally, the important role of step edges in catalytic reactions is reflected in this atomic-scale reaction sequence. Although as early as 1929 one-dimensional defects were proposed as the catalytically active sites in the “Adlineation Theory” of Schwab and Pietsch,^[35] only a few detailed studies for metal catalysis at step edges have emerged.^[36, 37] During our experiment, we found that it is much easier to induce the reaction at copper step edges, especially at very low molecule coverages, because of the following four reasons. a) Adsorption: Due to their mobility, most C_6H_5I molecules are adsorbed at the copper step edges even at $\sim 20 \text{ K}$ and therefore they are easy to locate. b) Dissociation: Due to the stronger binding at the step edges than on the terraces, the phenyl radicals attach to the step edges after dissociation. c) Diffusion: Again due to the stronger binding, it is easier to laterally manipulate the phenyl radicals along step edges without losing them. Step edges were therefore also used as navigation aid for the manipulation paths. Moreover, there is a higher probability for a phenyl group to meet its reaction partner, another phenyl, at the step edges. d) Association: Because the step edge locks the closely located phenyl couple, it is easier for them to join.

Future Prospects for Single-Molecule Engineering

Engineering of single molecules may require creation of basic building blocks, bringing them together to an assembling place

and then joining them to form a desired molecule. This entire process is somewhat similar to the assembling process of automobiles or electronic commodities, such as TVs, computers and so forth, in a factory production line.

Basic blocks for construction of a molecule can be atoms, molecules or radicals. By selective bond breaking with an STM tip, unnecessary parts of a molecule can be cleaved and thereby active sites can be created; such molecules can be used as basic blocks to join with other deliberately prepared species to build a new molecule. The individual molecules may also be constructed with the STM tip and collected to use them further as basic blocks to assemble still larger molecules.

The ability to bring these basic blocks to an assembling place with atomic-scale precision is an important and integral part of the process. A crucial step in the bond formation procedure is the proper alignment of molecular blocks so that they can be joined in a correct geometry. For this, reorientation and repositioning of molecules in the desired way with atomic-scale precision is necessary. At sufficiently low temperatures, this can also be achieved by using the STM tip.^[16]

By inducing the chemical reactions with the STM tip, the detailed underlying reaction processes can be studied on 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. But this is exactly the advantage for nanotechnology, since synthesis of individual man-made molecules, never before seen in nature or made in chemical reactors, may eventually become a possibility. Molecules with specific functions, to be used in nanoelectronic and nanomechanical devices, possibly may be constructed and their physical and chemical properties may be studied in situ with STM spectroscopy techniques on an individual basis. Thus, with these achievements in molecular manipulation with the STM, an entire new dimension for future nanoscience and technology is now opened wide.

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