

# Triggering Chemical Reactions by Scanning Tunneling Microscopy

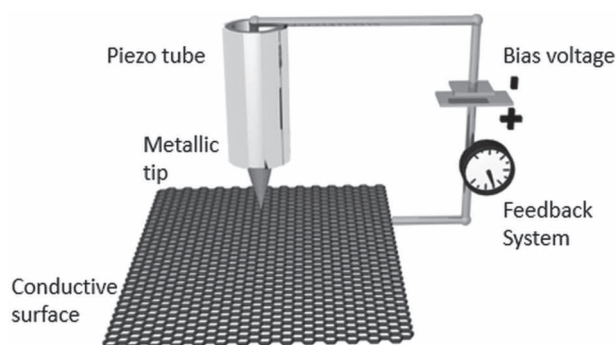
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## 4.1 Introduction

For more than three decades, the scanning tunneling microscope (STM) has proven itself as an indispensable tool to image solid surfaces at the highest detail possible, as well as atoms and molecules adsorbed on them. Since its invention in 1981 (Binnig & Rohrer 1982), the STM has had a huge impact on scientific research, because of its ability to image matter at sub-nanometer resolution. While in its early days, STM was mainly used by physicists to investigate the atomic structure of metals and alloys, often under extreme conditions of ultrahigh vacuum (UHV) and ultralow temperatures; nowadays, the technique is much more widely applied. It is suitable to image large molecules adsorbed to a surface, and it is no longer restricted to extreme environments: it has become fairly straightforward to obtain atomic scale images of matter at room temperature, in air, under high gas pressures, or in liquids (Elemans & De Feyter 2009).

The principle of operation of an STM is relatively simple (Figure 4.1). It consists of an atomically sharp, conductive tip, which is brought at nanometer distance from an atomically flat conductive surface. At sufficiently close distance of these electrodes, electrons are able to tunnel from the tip to the sample, or vice versa. When a bias voltage (typically between 0 and 1 V) is applied between tip and sample, a net tunneling current (typically between 1 pA and 1 nA) will start flowing, which can be measured. This current is highly dependent on the distance between the electrodes, making it also very sensitive to height differences between the tip and the sample. When the tip is mounted into a piezo tube, this height can be very accurately controlled, even at sub-Ångstrom range. When subsequently the surface is scanned while keeping the tip at a constant height, height differences on the surface as small as atoms will cause changes



**FIGURE 4.1** Schematic representation of an STM setup. (Reprinted with permission from den Boer et al., 2016. *Eur. Polymer J.* 83: 390–406. Copyright (2016) by Elsevier.)

in tunneling current, and thus, a topography map at atomic resolution can be obtained, at least in principle. As an alternative to constant height scanning, often a scanning mode is applied that keeps the current constant instead of the height. This means that during scanning, the distance between the tip and sample is continuously adjusted, a process that is controlled by a feedback mechanism. What results is a map of apparent heights, which is equally detailed as that obtained by scanning in the constant height mode, but generally safer, since tip crashes due to direct contact between tip and sample are prevented.

The interpretation of STM images is not always straightforward. Apparent height images are a convolution of ‘real height’ but also of the conductive properties of a surface and adsorbents on top of it. This means that when the tunneling current is also used as a feedback, a more conductive part of a surface may appear higher in an STM image than it is topographically. Despite this duality, it also enables the additional use of STM as a tool to analyze the local

density of states (LDOS) of a sample. Or, in case molecules are adsorbed, STM can image different orbitals or detect variations in oxidation state of metal centers.

In the first decades of its existence, STM was mainly used to investigate surfaces, atoms, and molecules in a static state. Later on, it turned out that it can also serve as an excellent tool to study dynamic phenomena in real time. In this regard, the imaging of chemical reactivity with STM has become a very popular topic, in particular, in the chemistry community (Elemans et al. 2009; Münnighoff & Elemans 2017). The ability to image starting materials, products and intermediates of a reaction, all at the submolecular scale, is highly appealing. In addition, it may provide highly detailed information about a reaction mechanism at a single-molecule level, which may be hidden at the ensemble level. The importance of such research was highlighted in 2007 by the awarding of the Nobel Prize to Gerhard Ertl “for his studies of chemical processes on solid surfaces”.

In addition to just observing and imaging a chemical reaction at a surface, an STM device can also be used to control or trigger a reaction. With an STM tip, atoms and molecules can be moved mechanically along a surface, bringing them in close proximity for a reaction to occur. It can also be used to inject electrons into chemical bonds, which then can break or form. Finally, applying simply a voltage difference between tip and sample may induce reactivity, since an STM can be considered as a (very nonstandard) electrochemical device.

This overview will focus on the triggering of chemical reactions with STM. It is divided in three sections, each describing a different environment in which such manipulations can be carried out: (i) in UHV, an ultraclean environment in which all possible contaminations can be eliminated, and the dynamics of atoms and molecules can be slowed down tremendously because of the possibility to work at ultralow temperatures (4 K or lower); (ii) under electrochemical control in polar liquids and electrolytes, in which additional electrodes in the STM setup allow full control over the electrochemical potential between tip and surface; and (iii) in apolar liquids or air, in which typically close-packed monolayers of molecules are subjected to chemical reactions under relatively mild conditions that are also encountered in a laboratory environment.

## 4.2 Triggering Reactions with STM in Ultrahigh Vacuum

A chemical reaction generally starts with the making or the breaking of a chemical bond. Pioneering work in which an STM tip was used to break chemical bonds of molecules adsorbed to a surface was carried out by Avouris and coworkers in 1992 (Dujardin et al. 1992). They scanned a silicon surface, onto which decaborane molecules were adsorbed, while applying a large voltage of  $\sim 8$  V between the STM tip and the surface. As a result, a large current density is delivered to the sample, corresponding to about

$10^6$  electrons per second passing to each atomic site of the silicon lattice. When these high-energy electrons passed through adsorbed decaborane molecules, many of these were observed to split into smaller fragments. The concept of breaking chemical bonds by the STM tip has subsequently been applied in a wide variety of dissociation reactions of molecules in UHV, such as acetylene (Gaudioso et al. 1999), pyridine and benzene (Lauhon & Ho 2000b), and molecular oxygen (Martel et al. 1996; Stipe et al. 1997). Also dehydrogenation (the dissociation of hydrogen atoms) of molecules has been accomplished at the single-molecule level by STM, for example of ammonia (Maier et al. 2015) and *trans*-2-butene (Kim et al. 2002).

Dissociation and dehydrogenation reactions on a surface can be performed with an extreme level of control, as has been demonstrated by the groundbreaking work of the group of Ho. They were able to trigger chemical reactions at the same, single molecule, by applying highly local voltage pulses by the STM tip. In this way, an ethylene molecule on a Ni(110) surface was converted by a first voltage pulse to acetylene and then by a second pulse to single carbon atoms (Gaudioso et al. 1999). In follow-up work, single hydrogen or deuterium atoms could be removed stepwise from an acetylene molecule adsorbed to Cu(100), via the injection of low-energy electrons, to first yield ethynyl and then dicarbon (Figure 4.2) (Lauhon & Ho 2000a).

Compared to bond breaking, bond formation using an STM tip has been described much less frequently. Ho and coworkers deposited CO molecules that were connected to an STM tip on top of an iron atom on a Ag(110) surface and formed Fe(CO) and, subsequently, Fe(CO)<sub>2</sub> (Lee & Ho 1999). Similarly, they were able to oxidize CO to CO<sub>2</sub> on the same surface, by depositing a CO molecule from the tip onto an adsorbed oxygen atom (Hahn & Ho 2001).

Chemical bond dissociation and formation does not have to be limited to isolated single molecules but may have an effect on neighboring molecules. Yates and coworkers positioned dimethyldisulfide molecules into close-packed linear chains on an Au(111) surface and triggered the dissociation of an S–S bond of the first molecule in the chain by means of a voltage pulse by the STM tip (Maksymovych et al. 2008). As a consequence, a domino-type cascade of chemical reactions occurred, involving S–S bond recombinations and dissociations along the chain of molecules.

In addition to triggering chemical reactions very locally, the injection of ‘hot electrons’ by the STM tip into a

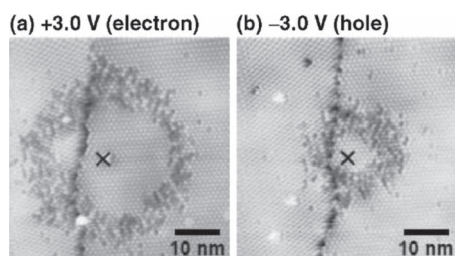


**FIGURE 4.2** STM images and corresponding schematic representations of (a) bis-deuteroacetylene, (b) deuterioethynyl and (c) dicarbon. (Reprinted with permission from Lauhon et al., 2000. *Phys. Rev. Lett.* 84: 1527–30. Copyright (2000) by the American Physical Society.)

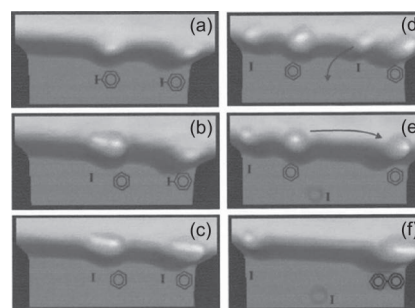
substrate can lead to a lateral travelling of these electrons through the substrate, which can subsequently give rise to chemical reactions in molecules that are adsorbed at remote sites (Macleod et al. 2009). Following this approach, the S-S bonds of thousands of the same dimethyldisulfide molecules as described above, but adsorbed at an Au(111) surface at a distance of up to 100 nm from the STM tip, could be dissociated by a single 2.5 V pulse into the bare metal substrate (Maksymovych et al. 2007).

Not unexpectedly, the nature of the substrate can play an important role in such nonlocal triggering of reactions. For example, the nonlocal dissociation of C-F bonds in copper hexadecafluorophthalocyanine molecules triggered by the injection of high-energy electrons into the substrate was two orders of magnitude more efficient on Ag(111) than on Au(111) (Chen et al. 2009). The difference was explained by a larger overlap of the orbitals of the benzene rings of the phthalocyanines with gold, when compared to silver. As a result, when a hot electron is injected into the benzene  $\pi^*$ -orbital to form an excited anion state, its lifetime is shorter on gold than on silver, which lowers the chance of a dissociation reaction in the former case.

Also chemical bond formation reactions can be triggered nonlocally. When very long voltage pulses of about 30 s were applied to a double layer of  $C_{60}$  molecules on a silicon surface, ring-like features composed of polymerized  $C_{60}$  were formed around the pulse position (Figure 4.3) (Nouchi et al. 2006). The ring shape was explained by assuming that charge carriers can induce both polymerization and depolymerization reactions between the  $C_{60}$  molecules, in which the depolymerizations require a higher energy. After the voltage pulse, the charge carriers start travelling through the substrate, away from the tip in a radial fashion. Initially, they have a high energy and the breaking of bonds dominates the making of bonds. But along their path they lose energy, and after a while, polymerization becomes more favorable than depolymerization. When they travel even further, their energy eventually becomes so low that they can no longer induce either of the reactions. A second voltage pulse, of higher energy, turned out to increase the



**FIGURE 4.3** STM images of the formation of rings of polymerized  $C_{60}$  molecules upon application of (a) positive (injection of electrons) or (b) negative (injection of holes) voltage pulses to a double layer of  $C_{60}$  molecules adsorbed onto a Si(111)  $-7 \times 7$  surface. (Reprinted with permission from Nouchi et al., 2006. *Phys. Rev. Lett.* 97: 196101. Copyright (2006) by the American Physical Society.)



**FIGURE 4.4** All steps of the Ullmann reaction induced and imaged by STM. (a) STM image of two iodobenzene molecules adsorbed at a step edge of Cu(111) (molecular structures are drawn in the image). (b-c) Dissociation of the iodobenzene molecules into phenyl radicals and iodine atoms. (d) Picking up and moving away an iodine atom with the tip. (e) Lateral movement of the phenyl radicals along the step edge. (f) Injection of tunneling electrons via a voltage pulse, making a covalent bond between the phenyl fragments. (Reprinted with permission from Hla et al., 2000. *Phys. Rev. Lett.* 85: 2777-80. Copyright (2000) by the American Physical Society.)

inner diameter of the ring, which supported this hypothesis. When holes were injected instead of electrons, smaller rings were formed, which was explained by the fact that holes dissipate their energy faster when travelling through the substrate.

The group of Rieder was the first who was able to trigger and image all individual steps of a multistep chemical reaction with the STM tip (Hla et al. 2000, 2001). They investigated an Ullmann reaction, in which two iodobenzene molecules are coupled to biphenyl at the step edge of a Cu(111) surface in UHV at 20 K (Figure 4.4). First, the two iodobenzene molecules were dissociated into iodine atoms and benzene radicals, by injecting tunneling electrons into the molecules via highly local voltage pulses with the tip. Next, the fragments were moved along the step edge in a controlled fashion by the same tip, and in the final step, two adjacently positioned benzene radicals were covalently connected, again by applying a voltage pulse via the tip. The success of the coupling reaction was proven by the ability to laterally move the biphenyl molecules along the surface with the tip.

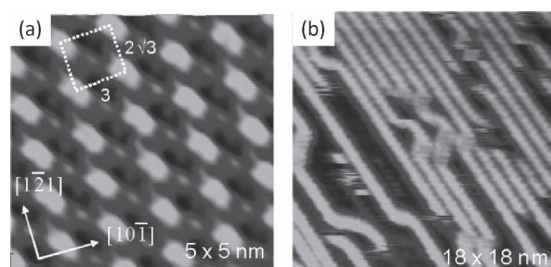
### 4.3 Triggering Reactions with STM under Electrochemical Control in Polar Liquids

In the previous section, it was demonstrated that by means of voltage pulses that are applied via the STM tip, chemical reactions can be triggered in single molecules or groups of molecules very locally. However, when it is desired to induce reactions in larger groups, or even complete monolayers of molecules, the relatively local nature of a voltage pulse is inefficient. An alternative approach, which can address layers of adsorbed molecules on a much larger scale, is to

use an electrochemical STM (EC-STM, also referred to as *in situ* STM). It typically operates in aqueous solutions or in organic solvents containing an electrolyte. The STM tip needs to be isolated in order to prevent leakage current effects, which is usually accomplished by coating it with an insulating polymer film. The STM bias voltage is not directly applied between tip and sample, but their potentials are set relative to a so-called reference electrode, which has a known redox potential. The electrochemical potentials of sample and tip can then be deduced by comparing them to the known potential of the reference electrode. Furthermore, a counter electrode is present, which supplies the electrons that are required to drive a chemical reaction that takes place at the sample (or sometimes at the tip). With the setup, ultimate control can be obtained over the potential of the surface. Thus, an EC-STM can be used as an electrochemical cell equipped with a microscope, which can trigger processes that occur at the electrode/liquid interface and image these processes at molecular or atomic scale. An EC-STM is therefore also an ideal tool to detect, identify, and manipulate molecules that can change their oxidation state.

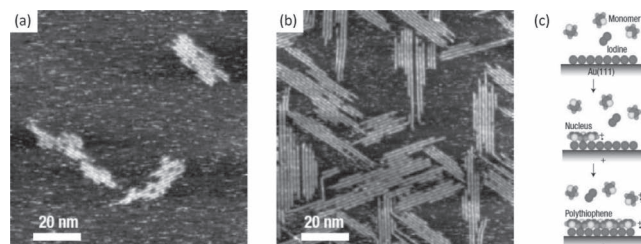
With EC-STM, chemical reactions can be triggered in adsorbed molecules across an entire surface, by setting its electrochemical potential at a certain, desired value. In this way, for example, aniline molecules adsorbed at the interface of an Au(111) surface and an aqueous 0.1 M sulfuric acid solution could be oxidatively polymerized by increasing the electrochemical potential of the surface (Figure 4.5) (Yang et al. 2007). The polymerization process was evident from the STM images, in which regular patterns of aniline monomers were gradually converted to extended wire-like structures, corresponding to the polyaniline chains. Within these chains, the monomeric components, which were oriented in a zig-zag pattern, could still be resolved (Figure 4.5b).

In contrast to the local nature of bias voltage pulsing via the STM tip, in an EC-STM also nonlocal voltage pulses of the electrochemical potential can be applied,



**FIGURE 4.5** (a) STM image of aniline molecules adsorbed at the interface of Au(111) and aqueous 0.1 M  $\text{H}_2\text{SO}_4$  at an electrochemical potential of 0.9 V (versus a reversible hydrogen electrode). (b) Appearance of polyaniline chains when the electrochemical potential is raised to 1.05 V. (Reprinted with permission from Yang et al., 2007. *J. Am. Chem. Soc.* 129: 8076–7. Copyright (2007) by the American Chemical Society.)

which can influence large parts of a surface, the molecules adsorbed thereon, and molecules dissolved in the supernatant solution. Following this approach, 3-butoxy-4-methylthiophene (**BuOMT**) could be electropolymerized at the interface of Au(111) and an electrolyte consisting of a dichloromethane solution containing molecular iodine and  $\text{NBu}_4\text{PF}_6$  (Sakaguchi et al. 2004). When electrochemical voltage pulses of 1.4 V were applied to the system, STM images showed the formation of well-defined linear polythiophene wires, which were organized epitaxially along the three-symmetry axes of the underlying gold substrate (Figure 4.6a). Both the surface coverage and the lengths of the polymeric wires increased when more pulses were applied (Figure 4.6b). Polymers with lengths up to 75 nm, corresponding to a polymerization degree of  $\sim 200$ , were observed. A mechanistic study of the consecutive reaction steps (Figure 4.6c) revealed that the presence of iodine in the solution was essential for both the formation and the adsorption of the polythiophenes. After the **BuOMT** monomers had been dissolved in the electrolyte solution, UV-vis spectroscopy revealed the formation of trimeric thiophene species, presumably via an oxidation reaction mediated by the co-dissolved  $\text{I}_2$ . A subsequent voltage pulse of 0.77 V oxidized these trimers to radical cations, which were proposed to act as polymerization nuclei. These adsorbed at the Au(111) surface, aided by an adsorbed adlayer of hexagonally organized iodine atoms. Subsequently, propagation occurred from the nuclei and thiophene chains grew along the solid/liquid interface. In follow-up work, thiophene-based block copolymers could be synthesized by following a similar approach (Sakaguchi et al. 2005). First, voltage pulses induced the polymerization of 3-octyl-4-methylthiophene (**C8MT**) at the  $\text{I}_2$ -covered Au(111) surface. Next, this surface was placed in another electrolyte solution, containing the structurally related monomer 3-octyloxy-4-methylthiophene (**C8OMT**) and again voltage pulses were applied. These activated both the **C8OMT** in solution, and the termini of the **C8MT** polymers at the surface. As a result, heteropolymeric



**FIGURE 4.6** (a) EC-STM image of polymers formed from **BuOMT** at the interface of Au(111) and an electrolyte consisting of a dichloromethane solution containing molecular iodine and  $\text{NBu}_4\text{PF}_6$  after five electrochemical voltage pulses of 1.4 V for a period of 150 ms. (b) Idem, after 13 pulses. (c) Schematic representation of the proposed mechanism. (Reprinted with permission from Sakaguchi et al., 2004. *Nat. Mater.* 3: 551–7. Copyright (2004) by Springer Nature.)



wires were formed, in the sense that, **C8OMT** wire fragments propagated from the **C8MT** wires already present at the surface. The two polymer types could be clearly identified because of their difference in brightness in the STM images. When both the **C8MT** and **C8OMT** monomers were present in solution and voltage pulses were applied, only multiblock heteropolymers were formed and no random copolymers. This observation indicates that preferentially homopolymers are formed, which are occasionally covalently linked via a heterojunction to form a block copolymer.

An EC-STM is also a suitable tool to control the electronic properties of adsorbates with well-defined redox states. In this regard, porphyrins and their related derivatives are interesting molecules. They can complex a large variety of transitional metals, which may exist in a range of oxidation states. In addition, also the free porphyrin ligand displays a rich redox chemistry. Borguet and coworkers investigated the redox behavior of monolayers of *meso*-tetrapyrrolyl porphyrins adsorbed at the interface of Au(111) and aqueous 0.1 M H<sub>2</sub>SO<sub>4</sub> (He & Borguet 2007). When a slightly negative electrochemical potential (−0.1 V versus a saturated calomel electrode) was applied to the surface, these molecules adsorbed to the surface in a reduced state in which two electrons were added to the porphyrin ring (Ye et al. 2006). In the corresponding STM images, all the porphyrins had a similar, bright appearance. When subsequently a short electrochemical voltage pulse of 0.3 V was applied to the system, dark signatures appeared in the STM image. When the pulses had a longer duration or a larger magnitude, the population of these dark signatures increased, and for that reason, they were assigned to oxidized porphyrin species.

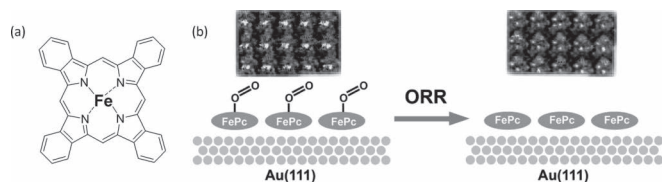
Just like porphyrins, structurally related phthalocyanine molecules often readily self-assemble into well-defined arrays at a surface. When adsorbed at the interface of Au(111) and an aqueous 0.1 M perchloric acid solution in an EC-STM setup, iron phthalocyanines (**FePcs**, Figure 4.7) appeared in two distinct contrasts, dark and bright, in the STM images, when the surface potential exceeded 0.3 V (Gu et al. 2016). The abundance of these contrasts was strongly dependent on the environment: under an inert nitrogen atmosphere, mostly dark signatures were present, whereas under an oxygen atmosphere, the bright signatures were

dominant. Based on these observations and on theoretical calculations, the dark signatures were assigned to native **FePc** molecules, while the bright ones were identified as **FePc**-O<sub>2</sub> complexes. Upon lowering the surface potential under oxygen atmosphere, the bright signatures started to convert to dark ones, which was attributed to the initiation of an oxygen reduction reaction ( $O_2 + 4H^+ + 4e \rightarrow H_2O$ ) and the concomitant dissociation of O<sub>2</sub> from the **FePc**-O<sub>2</sub> complexes. The process was found to be fully reversible: upon increasing the surface potential, the bright signatures returned. As expected, under a nitrogen atmosphere, these signature changes were not observed. Further analysis of the **FePc**-covered electrode surface by cyclic voltammetry revealed a shift in the offset potential for the oxygen reduction reaction, which indicates that the monolayer of **FePc** molecules is catalytic.

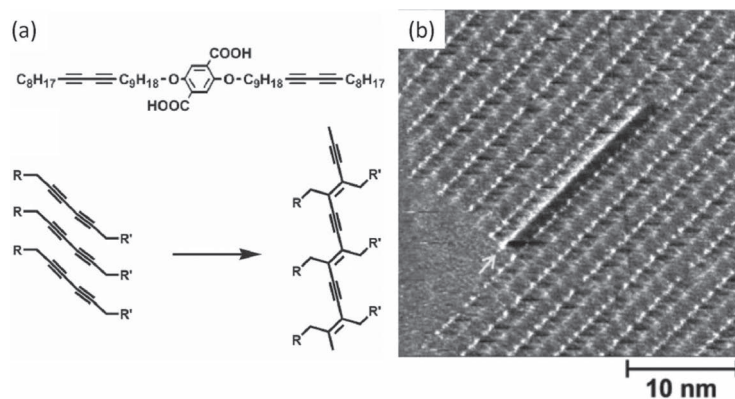
#### 4.4 Triggering Reactions with STM in Nonpolar Liquids or in Air

In addition to UHV or polar liquid environments, nonpolar organic liquids atop solid substrates have become increasingly popular environments to investigate self-assembly and functionality of molecules (Elemans et al. 2009). And also in organic liquids, or even in air, chemical reactions can be triggered locally by the STM tip or more globally by adjusting the bias voltage between tip and surface. Solid/liquid interfaces are generally excellent environments to construct closely packed (2D crystal-like) arrays of organic molecules. Via rational synthetic design, such molecules can express a certain function or reactivity. For example, molecules with polymerizable groups, such as alkenes or alkynes, can be organized within a monolayer such that these groups are in each other's proximity. They can then be subjected to a so-called 'topochemical polymerization', as a result of which covalently connected 2D networks are formed. Such polymerizations can be initiated by irradiating the layer by light of a certain wavelength (Grim et al. 1997; Miura et al. 2003; Okawa 2001a, b) or by applying a local voltage pulse. As an example of the latter method, diacetylene moieties were incorporated in a long alkane chain containing a terephthalic acid group, and these molecules were self-assembled via drop casting into lamellar arrays at a graphite surface (Figure 4.8) (Miura et al. 2003). Within the arrays, the acetylene functions were perfectly aligned, and when during scanning a voltage pulse was applied, their polymerization was initiated. The success of the reaction was apparent from the follow-up STM scan, which clearly showed the presence of a bright line along the lamellar axis, corresponding to a highly electron-conducting polydiacetylene chain. The length of these chains could be controlled elegantly by creating defects, which acted as chain termination points, with the STM tip into the self-assembled monolayer.

At a solid/liquid interface of graphite and 1-phenyloctane, related diacetylene-functionalized molecules did not only



**FIGURE 4.7** (a) Structure of **FePc**. (b) STM images and schematic representation of the oxygen reduction reaction mediated by **FePc** and imaged in the EC-STM setup. (Reprinted with permission from Gu et al., 2016. *ACS Nano* 10: 8746–50. Copyright (2016) by the American Chemical Society.)



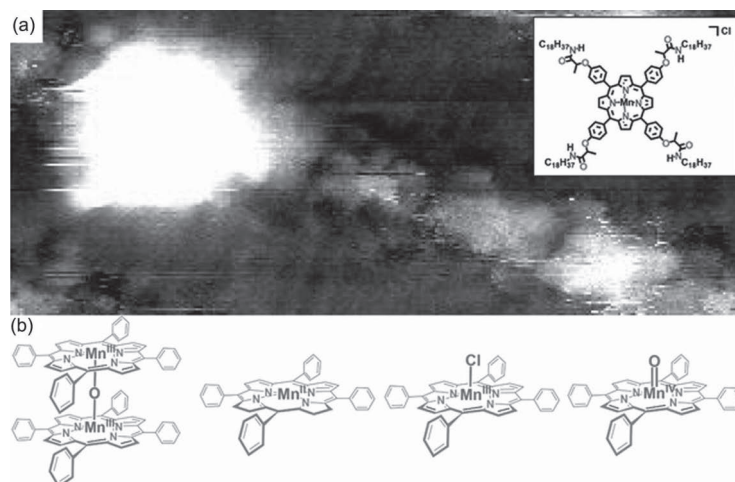
**FIGURE 4.8** (a) Structure of the compound containing diacetylene functions (top) and a representation of the polymerization of the diacetylenes (bottom). (b) STM image of a self-assembled monolayer of these diacetylene compounds at the graphite/air interface. The arrow indicates the location where a voltage pulse was applied and from which a bright polydiacetylene chain has grown. (Reprinted with permission from Miura et al., 2003. *Langmuir* 19: 6474–82. Copyright (2003) by the American Chemical Society.)

form self-assembled monolayers but also bilayers and additional layers on top of that (Takajo et al. 2007). Compared to the domains of the first monolayer, the domains of the additional layers grew very large (up to micrometers) because they interacted much weaker with the first monolayer than the first monolayer with the underlying graphite substrate. When a voltage pulse was applied to the system, remarkably, only the diacetylene molecules in the top layer were topochemically polymerized, while the molecules in the bottom layer remained unaffected. This difference in reactivity was explained by assuming a model in which the formed polydiacetylene backbone is lifted from the alkyl substituents by 0.14 nm. Such a lifting is possible in the top layer but not in the bottom layer(s) due to steric confinement.

By means of topochemical polymerization, also other types of potentially functional molecules could be attached

covalently to a self-assembled monolayer, in a process named ‘chemical soldering’. When, for example, on top of a layer of diacetylene molecules, a small cluster of phthalocyanine molecules was deposited, polymerization of the diacetylenes by a local voltage pulse led to the growth of a polymer chain, which reactive chain terminus linked covalently to a phthalocyanine it encountered at its path of polymerization (Okawa et al. 2012). In a similar way, polydiacetylene chains have been connected to C<sub>60</sub>-molecules (Nakaya et al. 2014).

As was observed at interfaces of solid and aqueous or organic electrolytes in an EC-STM, also at the interface of a solid and an organic liquid, a predefined setting of the bias voltage between sample and tip can induce reactivity in molecules adsorbed at that interface. An example of this approach is the triggering of multistep redox reactions of manganese(III)porphyrins adsorbed at a graphite/1-octanoic acid interface (Figure 4.9) (den Boer et al. 2013).



**FIGURE 4.9** (a) STM image of a self-assembled monolayer of the manganese porphyrin in the inset at a graphite/1-octanoic acid interface. Four different signatures are observed, which correspond to the porphyrin species that are shown directly underneath as the structures in panel (b). (Reprinted with permission from den Boer et al., 2016. *Eur. Polymer J.* 83: 390–406. Copyright (2016) by Elsevier.)

Manganese porphyrins are capable to complex molecular oxygen and subsequently activate and dissociate the strong oxygen–oxygen bond. For that reaction to occur, however, first a reduction of the manganese center from Mn(III) to Mn(II) has to take place. It turned out that if the graphite surface in the STM setup was sufficiently negatively biased (below  $-700$  mV), this reduction spontaneously occurred and the Mn(II)porphyrins appeared as darker signatures than the Mn(III)porphyrins in the STM images. After their reduction, these Mn(II)porphyrins appeared to be highly reactive for oxygen binding and dissociation, resulting in the formation of Mn(IV)=O species that appeared even brighter than the Mn(III)porphyrins. Interestingly, the unique spatial resolution of STM revealed that the Mn(IV)=O species were preferentially generated in pairs of two, at adjacent locations at the surface. From this observation, it was concluded that they were the product of a homolytic dissociation of O<sub>2</sub>, followed by distribution of the two oxygen atoms over neighboring manganese porphyrins. In the absence of molecular oxygen in the system, or at bias voltages less negative than  $-700$  mV, none of these signature changes were observed. Occasionally, also very large, bright signatures were observed, in particular at increased concentrations of manganese porphyrins in the supernatant solution. These signatures were identified as Mn porphyrin  $\mu$ -oxo sandwich-type dimers, formed by coupling of an additional Mn porphyrin from solution to Mn(IV)=O complex at the surface. The formation of these  $\mu$ -oxo-bridged dimers could also be directly triggered, in a highly local fashion, by applying a voltage pulse of several volts via the STM tip to the monolayer (Li et al. 2014). During this pulse, a strong inhomogeneous field is generated that can induce (local) charges in polarizable particles, which make them move to the region of highest field density, i.e., the tunneling gap between tip and surface. This leads to an enhanced local concentration, which is assumed to favor the close by formation of the  $\mu$ -oxo-bridged dimers at the surface. In a radius of approximately 10 nm around the location of the pulse, none of these dimers were present as a result of desorption of part of the monolayer due to pulse and subsequent re-adsorption of non-reacted molecules from the supernatant.

In a similar approach, the group of Hipps reported the complexation of molecular oxygen to cobalt porphyrins adsorbed at the interface of HOPG and 1-phenyloctane and also showed that once adsorbed at a surface reactive, molecules can behave quite differently compared to when they are in solution (Friesen et al. 2012). Cobalt(II) octaethylporphyrin has been shown to bind O<sub>2</sub> in solution only at low temperatures or when an electron-donating axial ligand is coordinated to the porphyrin metal center. At the solid/liquid interface, the metal porphyrins appeared in two different signatures in the STM images, bright and dark. The bright signatures were identified as the native CoOEP complexes and the darker ones as CoOEP–O<sub>2</sub> adducts. This assignment was based on an STM experiment conducted in argon atmosphere (i.e., oxygen-deficient),

in which the bright structures predominantly covered the surface. Further evidence for the assignment of the dark topographies came from varying the partial pressure of oxygen in the system, which had direct impact on the relative population of the various signatures. In fact, the number of dark signatures at the surface exactly followed the Langmuir absorption isotherm. In a follow-up experiment, the partial oxygen pressure was fixed, the temperature of the system varied, and the relative abundance of CoOEP–O<sub>2</sub> species at each set temperature was analyzed. From these data, the enthalpy and entropy of the oxygen binding reaction could be derived as being  $\Delta H = 68 \pm 10$  kJ/mol and  $\Delta S = 297 \pm 30$  J/mol K. These values indicate that adsorption of the cobalt porphyrins to the (biased) surface triggers strong complexation of O<sub>2</sub>. This unexpected behavior was attributed to the surface acting as an electron-donating reservoir that stabilizes the polarized cobalt-oxygen bond, much alike the stabilization by electron-donating axial ligands that coordinated to the cobalt porphyrins in solution. Similar axial-ligand-like behavior of the biased surface was observed for the coordination behavior of the nickel analogue of CoOEP NiOEP (Nandi et al. 2016). While this metal complex does not axially coordinate nitrogen-based ligands in solution, it readily binds them when it is adsorbed at the 1-phenyloctane/HOPG interface. The coordination of a ligand like imidazole is favored because it behaves as a  $\pi$ -acceptor of charge that is donated, via the nickel porphyrin, from the biased surface.

## 4.5 Conclusion and Outlook

This overview has shown that an STM is not only an excellent tool to image atoms and molecules but also to manipulate them in chemical reactions. By injecting high-energy electrons via a voltage pulse, chemical bonds can be broken or formed in a very local fashion. Following this concept, quite some examples of polymerization reactions between molecules have already been described, in a variety of environments. Alternatively, when high-energy electrons (or holes) are injected into the surface, they can travel over distances of hundreds of nanometers to trigger reactions at a remote location. And when one has the ability to control the electrochemical potential, by using a dedicated EC-STM setup, the reactivity of atoms or molecules of an entire monolayer on a surface can be triggered. In addition to providing insight into reaction mechanisms, at the highest detail possible, STM can also be utilized to manipulate reactivity. This ability may open the way to the bottom-up chemical design of molecular surfaces. Nowadays, nearly every desired molecule can be synthesized, and already to a large extent, the self-assembly of molecules on a surface over large distances can be predicted and controlled (Elemans 2016). By employing relatively weak but directional supramolecular interactions between molecular building blocks, specific and potentially functional patterned surfaces can be obtained. The disadvantage

of such organized layers, however, is often their relatively weak adsorption to the underlying substrate. As a result, they can be easily disrupted by external factors such as increases in temperature or the presence of solvents. To solve these problems, the covalent connection of molecules within self-assembled monolayers, for example, by polymerization triggered by the STM tip may increase their robustness and applicability.

Despite its potential, the use of STM to manipulate reactions still comes with some challenges. In particular, when high-energy voltage pulses are applied as a trigger, undesired side effects may occur: molecules can, for example, decompose or desorb from the surface. This probably implies that for every type of reaction or set of molecules, specific reaction conditions have to be found to provide the desired effect. One must realize that currently the investigation of chemical reactions with STM, including their triggering, is still a research area that is very much in its infancy. However, given the importance of functional surfaces in everyday life, it can be expected that obtaining fundamentally new insights in their structure and reactivity, at the highest detail possible, may lead to the future rational design of new materials and catalysts.

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