Chapter 5

Reversible Light-Induced Single Molecule Conductance Switching on Gold

In this chapter it is demonstrated that light-controlled reversible switching between two conductive states can be achieved for individual photochromic molecules bound chemically to a gold surface. Controlled opto-electronic switching which results in modulation of conductivity of single molecules linked to gold and inserted in an insulating matrix of alkanethiols is demonstrated by using Scanning Tunneling Microscopy (STM). Furthermore, optical spectroscopy of self-assembled monolayers of diarylethene photoswitches on a semi-transparent Au(111) surface shows the on-off states of the switch. The chemical analysis of the composition of monolayers using X-ray Photoelectron Spectroscopy (XPS) and the stability of monolayers upon irradiation is discussed.¹

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5.1 Introduction

In Chapter 4 reversible light-induced switching was demonstrated for monolayers of diarylethenes assembled on gold nanoparticles and macroscopic gold electrodes. However, one of the most important features of molecules that have potential applications in molecular electronics is to make use of single molecules that function as switches on metal surfaces. This requires the development of molecules, which can switch reversibly between two conductive states in response to an external trigger. Light is a attractive external stimulus for such switches because of ease of addressability, fast response times and compatibility with a wide range of condensed phases. Opto-electronic switches offer a new functionality to molecular electronics provided that their switching properties are preserved when bound to a metal surface. Indeed interactions between molecules and substrate can considerably decrease the lifetime of the excited state of the molecules. These aspects of hybrid metal-molecular systems were also addressed in Chapters 2 and 4.

Diarylethenes are promising synthetic photoswitchable molecules because of the outstanding fatigue-resistant light-induced reversible transformation between two isomers having different absorption spectra. The difference in geometry and electronic structure between the two isomers, which is at the origin of the photochromism in various media, has been exploited successfully to control reversibly other properties such as fluorescence intensity and wavelength, electrochemical properties, acid-base equilibriums, magnetic and self-assembly properties. However, only a few attempts have been made to switch the conductance of surface-bound molecules by light. Light-induced switching of conductance has been studied for individual diarylethenes linked to gold through a thiophene spacer but only one-way switching was observed (Chapter 2). Theoretical studies predicted that the possibility to switch reversibly depends critically on the linker used and the experiments with gold nanoparticles and gold macroscopic electrodes described in Chapter 4 confirm those predictions. Recently, photoisomerization was reported for diarylethenes with a benzyl linker connecting the central switching unit with the anchoring thiol group chemisorbed on gold. It was also shown that a phenyl spacer can preserve the photochromic reactivity of a dimer in solution. In this chapter, we present direct evidence of reversible switching of a diarylethene grafted on Au(111), with the linker based on a meta-substituted phenyl group. Both ring closure and ring opening processes are observed for single molecules and a statistical analysis of numerous switching events confirms reversible behavior.

The two isomers of compound which correspond to a closed and an open form of the molecule are shown in Figure 1. The π-conjugation extends over the entire molecule in the
closed form whereas it is restricted to each half in the open form. As a consequence, the closed form is expected to exhibit better electrical conductance than the open form. We will thus refer to them as the “ON” and the “OFF” states of the switch, respectively. The UV-Vis spectra (see Chapter 3 and 4) of this molecule in toluene show that the wavelengths that can be used for “ON” to “OFF” switching are $420 < \lambda < 650$ nm and $300 < \lambda < 350$ nm for the reverse operation.

Figure 1 Diarylethene switch 23 bound through a thiol bond to Au(111). The ring-closed form corresponds to the more conductive (conjugated) “ON” state (left) and the ring-open form corresponds to the less conductive (non-conjugated) “OFF” state (right). The “ON” state of this molecule is converted into the “OFF” state by UV light, and the “OFF” state returns to the “ON” state under visible light.

In the following subsections two different experimental techniques demonstrating reversible light induced switching for molecule 23 bound to gold are discussed. First, optical spectroscopy is used to observe optical changes for a homogenous monolayer of compound 23. This is followed by STM studies in order to demonstrate conductive changes upon light induced switching (for a short description of the STM technique see Chapter 6). Mixed monolayers are used to demonstrate switching events at the level of a single molecule.
5.2 Optical Switching of Homogeneous Monolayer on Gold

Coupling spectroscopic techniques to scanning probe microscopy requires the preparation of atomically flat and conductive, but also semi-transparent gold surfaces. Earlier work has reported the use of semi-transparent Au(111) substrates, but to our knowledge preparative conditions employed did not allow formation of conductive layers. In such case it is therefore difficult to compare directly the observed spectroscopic and scanning probe results, since such gold substrates are composed of small clusters of gold which possess discrete energy levels unlike bulk gold. Therefore, we prepared a conductive semi-transparent layer of 20 nm of Au(111) on mica (for details, see experimental section). Our substrates present flat terraces of Au(111) as shown by STM (Figure 2). The possibility of recording of STM pictures itself confirms that the semi-transparent gold substrate is conductive. Such gold substrate then allows to some extent transmission of light and can be used for spectroscopic characterization of adsorbed molecules.

![STM picture](image)

**Figure 2** STM picture (218 x 218 nm²) of a semi-transparent Au(111) surface of 20 nm thickness on mica in air. The cross-section, corresponding to the blue stripe on the STM picture, highlights the presence of atomically flat terraces.

Homogeneous monolayers of the closed form of compound 23 were formed on semi-transparent gold surfaces by self-assembly (for the synthesis of 23, see Chapter 3). The anchoring of the molecule to the gold surface is ensured by a thiol anchor group. For
reasons of stability, the thiol group is protected by a thioacetate function which splits off spontaneously upon chemisorption. In order to confirm attachment of a thiol anchoring group to gold, X-ray Photoelectron Spectroscopy was used.

5.2.1 XPS Characterization of Monolayers

Figure 3 shows the S 2p core level region for a self-assembled monolayer of the closed form of compound 23 on Au(111). For analysis of the data, each experimental spectrum is mathematically reconstructed with a minimum number of peaks consistent with the raw data and the molecular structure of 23. Following this procedure, the analysis of the S 2p core level region reveals two contributions. The first peak for which S 2p$_{3/2}$ is found at 161.8 eV is attributed to XPS spectra of thiols chemisorbed on the Au surface, indicating thiolate formation. The main peak with the S 2p$_{3/2}$ at 163.4 eV corresponds to the thiophene sulfur atoms. In order to check the stability of the monolayer towards UV irradiation the same samples were exposed for 10 min to UV light (λ=313 nm). After irradiation oxidized sulfur species were not detected at binding energies in between 168.5 eV and 170 eV. Therefore, we can conclude that the self-assembled monolayer is stable, that gold-sulfur bond is preserved and that the layer has consequently not been destroyed upon UV irradiation.

![S2p XPS spectrum](image)

**Figure 3** Photoemission spectrum and fit of the S 2p core-level region for a homogeneous self-assembled monolayer of switches on Au(111).
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5.2.2 Optical Switching of Monolayer Monitored by UV-Vis Spectroscopy

The self-assembled monolayer (SAM) of the switches in the “ON” state (closed form) formed on semi-transparent Au(111) was subsequently used for UV-Vis spectroscopy experiment. The UV-Vis spectra of these SAMs were not directly informative because of the relatively low concentration of the molecules and the absorption due to the gold plasmon band. Hence, the following procedure was adopted: after self-assembly of the switches in the “ON” state, measurement of an initial spectrum ($I_{ON}$) is followed by 10 min irradiation using visible light to allow a photochemical ring opening. A second spectrum is recorded ($I_{OFF}$) and the cycle is completed by 5 min of UV irradiation. The differential spectrum $I_{ON}-I_{OFF}$ reveals a broad absorption feature at $\lambda_{\text{max}} = 540$ nm (Figure 4). The position of the band corresponds to the $\lambda_{\text{max}}$ of the differential absorption for the same switch 23 in solution. Consequently, we attribute the observed feature to the differential absorption signal of the “ON” to “OFF” for the switches on Au(111). A key factor that allows its assignment to the light-triggered molecular switching process is its reproducibility and reversibility through several switching cycles. Also, control experiments on self-assembled monolayers of $n$-dodecanethiol never produced any significant absorption in the UV-Vis spectrum. Over the three cycles presented in Figure 4, the system shows reversible switching without evidence of significant degradation or change in the switching properties. This experiment shows that collective structure-property relationships are preserved upon self-assembly of the switch on Au(111). The photochemical reaction of such switches in self-assembled monolayers is apparently not hampered by molecule-molecule interactions in accordance with the minor conformational change taking place during ring opening or ring closing of diarylethenes. These results are in agreement with the results that were discussed for SAMs of molecule 23 formed on gold nanoparticles and gold electrodes used in electrochemical experiments (Chapter 4).
5.3 Conductance Switching of Single Molecules

A requirement for the development of molecular electronics is the ability to obtain precise atomic scale data under ambient conditions. Next, we show at the level of a single molecule that our molecular design avoids quenching from the gold surface and can be used as a prototype model for light-triggered single molecule electronic devices. Pioneering work has shown how two-dimensional isolation of molecules in host SAMs in combination with STM can be used to study the electronic properties of individual molecules. We use an \(n\)-dodecanethiol monolayer as a matrix to isolate the switch molecules \(23\) (the same approach as in Chapter 2). STM measures a so-called apparent height which is a convolution of electronic and topographic characteristics. Consequently, it allows in-situ studies of conductance modification on isolated switches within a matrix of \(n\)-dodecanethiol.
5.3.1 STM Characterization of Mixed Monolayer

An STM image of the \( n \)-alkanethiol monolayer with switches inserted in the “on” state is shown in Figure 5. The switches appear as bright spots surrounded by domains of close-packed \( n \)-dodecanethiol molecules. The switches chemisorb preferentially on the etch-pits (dark circles) which are characteristic of these self-assembled monolayers, \(^{21}\) on Au(111) step edges and boundaries between ordered domains of dodecanethiol. Though Figure 5 shows a large scale picture, molecular resolution of the alkanethiol lattice is already distinguishable under the aspect of preferential alignments (see also inset of Figure 5).

![Figure 5](image.png)

**Figure 5** Scanning tunneling microscopy characterization of a mixed monolayer of the switches and dodecanethiol. (Upper part) The switches have been inserted by a replacement reaction with an \( n \)-dodecanethiol SAM on Au(111). Molecular resolution of the \( n \)-dodecanethiol matrix is distinguishable under the aspect of alignments. The bright spots correspond to inserted switches in the closed form. \( V_T = -0.811 \) V, \( i_T = 8.7 \) pA. Insert: 30x30 \( \text{nm}^2 \) (Bottom part) cross-sectional profile of the STM picture along the double arrow.

Figure 5 (bottom part) also shows the cross-sectional profile along the arrow depicted in Figure 5 (upper part). The etch pits have a depth of \( \sim 0.3 \) nm, consistent with the theoretical value 0.28 nm. \(^{21}\) The apparent height of dodecanethiol is \( \sim 0.1 \) nm, which is consistent with previous reports. \(^{22}\) Under typical scanning conditions \( V_T = -800 \text{mV} \) and \( i_T = 10 \text{pA} \) the apparent height of switches in the “on” state is (0.60 ± 0.15) nm. The deviation from the mean value is relatively large but consistent with reported apparent heights of conductive nanowires. \(^{23}\)
5.3.2 Observation and Switching of Single Molecule

Figure 6a (left panel) shows a zoomed in area of an STM picture where individual dodecanethiol molecules from the dodecanethiol lattice are distinguishable. On Figure 6a (right panel), the same domains of close-packed dodecanethiol molecules are visible. On this picture, a photochromic switch appears as a bright protrusion with the height of 0.5 nm. The picture on right panel is obtained after irradiation of the sample shown in the left panel with UV light. This means that, as expected, the photochromic molecule switched from “OFF” to “ON” (or open to closed form). There is no distinctive difference between the apparent heights of dodecanethiol and switches in the “OFF” state (0.1 nm). The switch has the same apparent height as dodecanethiol, but the diameter of the corresponding spot is larger (~2.0 nm). This is the expected diameter for an inserted molecule and it is in accordance with previous observations on single molecules.\textsuperscript{20} In the “ON” state, the apparent height of the bright spot is increased from 0.1 nm to 0.5 nm (similar results were obtained for compound 6, Chapter 2). This is consistent with previous reports showing that the resistance of the “ON” isomer is in the MΩ range, whereas it is more than two orders of magnitude higher for the “OFF” form.\textsuperscript{10,12} It can be concluded that the “ON” state of compound 23 is easily detectable whereas the “OFF” state cannot be directly distinguished from the n-dodecanethiol matrix.

\textbf{Figure 6} In-situ evidence of light-controlled switching of single molecules. (a) STM pictures registered in a time interval of ~3 min on the same area under UV (λ=313 nm) irradiation. The molecular resolution of the alkanethiol lattice is evidenced by the classical
\( \sqrt[3]{3x\sqrt{3R30}} \) structure on top left part of the picture and the \( c(4x2) \) superstructure on the bottom down part of the picture. The conductance modulation of the switches resulting from “OFF” to “ON” transition is visible (12x12 nm\(^2\), \( V_T = -0.853 \) V, \( i_T = 12 \) pA). The cross-sections show that the “OFF” form slightly protrudes from the monolayer with an apparent height of ~0.1 nm, whereas the “ON” form has an apparent height of ~0.5 nm. (b) Extracted frames displaying single molecules (8x8 nm\(^2\)). The time interval between frames is 3 min. “ON” to “OFF” switching is observed during irradiation by visible light and the reverse process happens during UV irradiation.

In Figure 6b, switching in both directions for single molecules is demonstrated. Low contrast spots corresponding to “OFF” switches transform into bright spots under UV light, and reversibly, bright spots corresponding to “ON” forms become less conductive under irradiation by visible light.\(^{24}\) The observed modifications in apparent heights could be due to an attenuation of the conductance of the molecules or a change in their physical height or a combination of both. However, the difference in molecular length between the open and closed forms is very small (0.1 nm). Consequently, we attribute the two different STM contrasts to two different conductive states of the switches. The apparent height difference is thus a signature for the two distinctive states of a single molecule.

5.3.3 Statistical Analysis of Multiple Single Molecule Switching Events

Using STM, we have established that many molecules switch back and forth under proper irradiation. This constitutes a strong indication that we succeeded in reversibly switching a photochromic molecule on gold. However, this does not constitute a sufficient proof to assign conductance switching to a light-induced phenomenon. Random conductance switching of individual thiol-derivatized conjugated wires surrounded by alkanethiols has been previously reported\(^{20b}\) and attributed to fluctuations of the Au-S bond\(^{25}\) or to tip-induced conformational modifications of the molecules.\(^{23c}\) All these aspects of stochastic switching have been addressed in Chapter 2. In order to unequivocally demonstrate light-controlled switching, it is essential to use statistical analysis. In the following, this is demonstrated for a small number of isolated molecules.

For a sequence of measured STM pictures of a mixed monolayer of \( n \)-dodecanethiol and switches in the “ON” state, we use a routine to determine the number of molecules in the “ON” state, which present an apparent height over a fixed threshold of 0.40 nm (see experimental section). A curve displaying the number of molecules in the “ON” state as detected by STM during in-situ irradiation is given in Figure 7. After 30 min of scanning, irradiation of the switches with visible light is started (\( \lambda > 420 \) nm). The number of molecules in the “ON” state drops immediately and reaches a lower level after typically 20
min, with some fluctuations. After stabilization of this part of the curve, UV irradiation is started ($\lambda = 313 \text{ nm}$) and the number of molecules in the “ON” state increases. While UV irradiation continues, a plateau is reached after the same characteristic time constant of 20 min. The correspondence between changes of irradiation and changes of the number of molecules in the “ON” state are strong indications of the occurrence of light-induced processes. The reversibility of the phenomenon indicates that the switch is not degraded. The establishment of plateaus is a characteristic of photoinduced isomerisation mechanisms for which equilibrium between two isomers is obtained. The time needed to reach such a photostationary state for the same switches in solution is 2 min. This difference of one order of magnitude between switching times in solution and on the surface is probably due to shortening of the lifetime of the excited state of the photochromic molecule by interaction with the metallic surface. The results of the experiments described in Chapter 2 and 4 as well as other studies of the photochemistry of monolayers on metal surfaces have shown that the excited states are partially quenched by the metal, and that the observed quantum yields of the photochemical reactions are lower than either in solution or in the solid state.\textsuperscript{26} Also, a relatively low intensity reaches the sample in the STM setup. After repopulation of the “ON” state, the number of “ON” molecules is decreased by 10\% compared to the initial situation. Presumably, this is due to the fact that the photostationary state for switches on Au(111) is modified by the presence of the metal surface. The fluctuations observed within each plateau may have different origins. The first one is the well-known random switching.\textsuperscript{20b,25} Second, we do not exclude a possible influence of tip-induced switching between the “ON” and “OFF” states promoted by electrochemical changes in the molecule.\textsuperscript{6,27} Nevertheless, the plateaus corresponding to “ON” and “OFF” states are clearly recognizable and show an “ON” to “OFF” ratio of 2.5. This ratio is comparable with electrochemically activated molecular switching systems on surfaces.\textsuperscript{28} The fact that some “ON” state molecules cannot be switched to the “OFF” state is attributed to tilting of these molecules towards the surface, which quenches their excited state and thus prohibits light-induced switching. This indicates that the insertion matrix plays a critical role in the switching of the guest molecules.
Figure 7 Number of “ON” switches as a function of time for 60x60 nm\(^2\) pictures. The pictures correspond to the series displayed in Figure 5. The plain horizontal lines correspond to mean values of the plateaus of the data. The dotted lines are guides to the eye.

5.3.4 Comment on Possible Temperature Effects

Heating accompanies all other possible effects arising from absorption of light. In STM the most dramatic consequence of heating is thermal expansion of the tip, which affects the width of the tunneling gap. This effect is not important in the steady state with constant illumination, in which the STM feedback loop simply settles to a new equilibrium tip height.\(^{29}\) We consequently exclude that the statistical phenomenon we observe could be a consequence of temperature. The broadening of the height distribution for the mixed switch-dodecanethiol monolayers during irradiation is illustrated by Figure 8. The broadening is more important when turning from the dark to visible irradiation. Nevertheless, this tendency is overcome by the light induced effects as the decrease of the number of molecules in the “ON” state was observed (Figure 8, right part). Therefore it can be concluded that the broadening does not affect the light-induced effects and for high apparent heights this tendency is overcome by the light-induced effects. The broadening of the height distribution is weaker when turning from visible to UV irradiation. This is consistent with the irradiation power provided by the lamp through the different filters.
Figure 8 Mean number of pixels for each apparent height of the STM pictures for three different sequences: in the dark, and during visible and UV irradiation. (Left) Global distribution of apparent heights. (Right) Zoom for apparent heights higher then 0.4 nm. Plain line: before irradiation. Dashed line: during UV irradiation. Dotted line: during irradiation by visible light.

5.4 Conclusions

In summary, two independent experiments were used to demonstrate light-controlled reversible switching for meta-phenyl linked diarylethene molecule 23 on gold. This is drastically different from the behavior of the switch 6 described in Chapter 2, which has a thiophene linker. The UV-Vis spectroscopy experiments show that dynamic changes of molecules are detectable for as tiny amount as one monolayer. The structural stability of the molecular monolayer on gold and retention of the thiolate-gold bonding upon irradiation was confirmed by XPS.

The most important finding is that controlled single molecule switching of conductance has been achieved. Using STM it was possible to visualize single molecules and the molecular matrix. The subsequent statistical analysis of numerous single molecule switching events proves the light-induced origin of the switching phenomenon. Our results suggest that a single molecule could substitute bulk devices that are normally used to control conductance. To the best of our knowledge this is the first example of light-triggered fully reversible conductance switching for isolated molecules at ambient conditions. This is an important milestone in the field of molecular electronics. Potential future single-molecular
devices will be performing their actions at ambient conditions and not under ultra-high vacuum and at low temperatures for the sake of high cost requirements.

A few more challenges are about to be faced before a fully operating molecular device based on diarylethenes can be realized. It is essential to assemble large number of molecules in a controlled fashion in order to create large-scale, high-density circuits. Well-defined stable and reliable molecular junctions must be formed and each element of the device must be independently addressable. The so-called “crossbar” geometry, a periodic array of crossed wires with molecules sandwiched between electrodes, provides a promising architecture for molecular electronic circuitry and might be a promising alternative to “wire up” diarylethene switches into a “real” molecular device.

5.5 Experimental Section

General Remarks
For general remarks see Chapter 2.

Preparation of substrates
Mica sheets were purchased from Pelco and heated for 16h at $T = 375\,^{\circ}\mathrm{C}$ under a typical pressure of $P = 3.3 \times 10^{-7}$ mbar in a home-made vacuum deposition system. Gold was deposited on the hot substrate at a constant rate of 0.01 nms$^{-1}$ to form semi-transparent (20 nm) Au(111) layers, and at a rate varying between 0.01 nms$^{-1}$ and 0.1 nms$^{-1}$ for 150 nm Au(111) layers. After deposition the substrates were kept at $T = 375\,^{\circ}\mathrm{C}$ for 1h and subsequently the temperature was decreased to reach room temperature in approximately 5h.

Preparation of a solution of the “ON” form
A closed form of compound 23 (23c or “ON” state) was prepared by irradiation of a 4 mmoL$^{-1}$ solution of an open form (23o) (for the synthesis and full characterization of 23 see Chapter 3) in toluene with ultraviolet light (313 nm). Photoisomerization was controlled by UV-Visible spectroscopy. The mixture obtained in the photostationary state was subjected to flash chromatography ($n$-hexane/dichloromethane 7:2) to give a pure closed form of 23. All subsequent operations were handled in the dark to prevent back isomerization. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.86-1.96 (m, 2H), 2.03 (s, 6H), 2.45 (s, 3H), 2.43-2.53 (m, 4H), 6.42 (s, 1H), 6.43 (s, 1H), 7.29-7.43 (m, 5H), 7.52-7.58 (m, 4H) ppm.
Preparation of the monolayers

For optical spectroscopy and XPS, the substrates were immersed 12 h at room temperature in a 1 mmolL\(^{-1}\) solution of compound 23c in ethanol. The sample were rinsed 3 times in ethanol and dried under argon flow to remove the solvent. For STM, the samples were prepared following a replacement procedure adapted from Donhauser et al.\(^{23b}\) After 30 s flame-annealing in a hydrogen flame, Au(111) samples were placed in a 0.5 mmolL\(^{-1}\) solution of \(n\)-dodecanethiol (Acros, 98.5+%) in ethanol for 12 h at room temperature. The solution was then heated for 5 h at 333 K (60°C). After removal of the sample from the dodecanethiol solution it was rinsed 3 times with ethanol and immersed for 12 h at room temperature in a 0.5 mmol L\(^{-1}\) solution of compound 23c ("ON" state) in ethanol. The acetyl-protecting group is spontaneously removed to allow grafting on gold, as confirmed by XPS spectra. Before the experiments the samples were rinsed three times in ethanol and dried under an argon flow to remove the solvent.

UV-visible Spectroscopy

Optical measurements were performed on a Hewlett-Packard HP 8453 diode-array spectrometer. In situ illuminations of the samples were carried out with a 200 W Hg lamp (LOT-Oriel). The samples were irradiated in situ. Illumination times were typically 10 min for visible irradiation (420 nm cut-off filter) and 5 min for UV light (313 nm band-pass filter). Each spectrum is the result of addition of 16 acquisitions.

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were performed using an X-PROBE Surface Science Laboratories photoelectron spectrometer equipped with a monochromatic Al K\(\alpha\) X-ray source (\(h\nu=1486.6\) eV). The energy resolution was set to 1.65 eV and the photoelectron take-off angle was 37°. The base pressure in the measurement chamber was 2x10\(^{-10}\) mbar. All binding energies were referenced to the Au 4f\(_{7/2}\) core level.\(^{31}\) Spectral analysis included a linear background substraction and peak separation using mixed Gaussian-Lorentzian functions in a least squares curve-fitting program (Winspec) developed in the LISE laboratory of the Facultes Universitaires Notre-Dame de la Paix, Namur, Belgium. Three to five different points of each sample were examined. The presented spectrum is the sum of the scans taken at all points. The summing of the spectra was done to increase the spectral signal to noise ratio while minimizing the time the samples were exposed to the X-ray source. This should minimize the possibility of sample degradation by the incident X-rays or exciting photoelectrons.
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Scanning Tunneling Microscopy (STM)

STM images were acquired in the constant current mode under ambient conditions in air. The experiments were performed with a Picoscan scanning tunneling microscope (molecular imaging). Tips were mechanically etched from a Pt-Ir wire (80-20) of 0.25 mm of diameter. The achievement of molecular resolution of the alkanethiol lattice demonstrates the quality of the tip which was used. The setting for tunneling current and voltage range from 10 to 50 pA and from -0.6 to -1.0 V. The presented pictures have been flattened by a routine procedure. No filtering procedure was used. Experiments required minimizing drift (i.e. to use a relatively low power of illumination), molecular resolution and scanning of flat areas (not more than one stepedge). In our setup, the typical drift evaluated by following the position of a stepedge or a defect over time is ~0.5 nm per min. This drift was partially compensated by controlled displacement of the scanning area. In-situ illumination was carried out with a 300 W Xenon lamp (LOT-Oriel) through an optical fiber. For irradiation with visible light, a &lambda;>420 nm cut-off filter was used. For irradiation with ultraviolet light, a &lambda;=313 nm band-pass filter was used.

Octave routine

An octave routine was used to treat the statistics of evolution of proportions of closed and open forms under irradiation (the software is available free of charge at www.octave.org). The image provided by the raw data is flattened by subtraction of the mean plane of the picture (Figure 9) which is calculated for each picture by the least squares method. After subtraction, the “zero” level corresponds to the maximum of the Gaussian peak for n-dodecanethiol apparent height. Then, all pixels under the threshold of 0.40 nm were attributed the value zero, whereas the others were attributed the value 1 (Figure 9).

Figure 9 Illustrations of the data treatment process for a 60x60 nm² STM picture. (a) After flattening of the raw picture (b) After thresholding of the flattened picture.
The number of switches in the “on” state on each picture is then proportional to the sum of remaining pixels. Experimentally, we observe that for the ~1 nm bright spots corresponding to a single switch, the mean number of pixels overpassing the threshold is 3, so the number of pixels is transformed in a number of molecules by division. No other treatment than routine flattening has been applied to STM pictures before analysis. The resulting curve has been submitted to a simple three point smoothing.

5.6 References and Notes

This is confirmed by the S 2p core level X-ray photoelectron spectroscopy (XPS) spectrum. The first peak for which S 2p$_{3/2}$ is found at 161.8 eV indicates chemisorbed thiols. The main peak with the S 2p$_{3/2}$ at 163.4 eV corresponds to the thiophene sulfur atoms.

XPS excludes the possibility of desorption of the molecules, because after irradiation, no oxidized species of sulfur can be detected at binding energies between 168.5 and 170 eV.
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