Use of Specific Functionalised Tips with STM: A New Identification Method of Ester Groups and Their Molecular Structure in Self-Assembled Overlayers

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Abstract: The influence of chemical modification of scanning tunnelling microscopy tips on image contrast is studied. This technique is applied to the identification of an ester functional group, hardly visible otherwise. Self-assembled overlayers of wax esters [CH_3-$(CH_2)_{14}$-CO-O-$(CH_2)_{15}$-CH_3], adsorbed at the interface between highly oriented pyrolitic graphite and a solution of phenyloctane, are imaged. The gold tips used are chemically modified by 4-mercaptobenzoic acid and 4-mercaptotoluene. The stability of the ordered overlayers formed facilitates the reproducible set of images with submolecular resolution. This allows the identification of the layer regular structure and of other features within molecules, which can be unambiguously related to the fingerprints of the COO bond. Moreover, we are interested in finding evidence of molecular motions observed at domain boundaries.

Keywords: interfaces • scanning probe microscopy • self-assembly

Introduction

The interface between a solid and an organic solution has drawn considerable interest during the past decades.[1–3] Indeed, the investigation of the organic monolayers properties is very important for the fundamental understanding of two-dimensional ordering processes as well as for technological applications as adhesion, lubrification, or manufacturing of new materials designed at molecular scale.[4] In this context, scanning tunnelling microscopy (STM) proves to be an efficient tool for the study of clean and covered surface structures, in air, ultrahigh-vacuum, as well as in liquids.[5–7] Some in situ scanning tunnelling microscopy studies were already successful in investigating the molecular arrangement (such as amphiphilic molecules,[8,9] liquid crystals[10,11] and biomolecules[12–14]) at the liquid/solid interface since molecular and even sometimes atomic resolution is performed. These investigations revealed that the formed layers possess a high degree of two-dimensional ordering. For example, alkanes and alkanols adsorbed on graphite tend to adopt in most cases an all-*trans* conformation with their molecular axes parallel to each other in order to optimise the intermolecular and molecule-substrate interactions.[15–17] Self-assembly was also studied with a number of substituted alkanes,[18–19] long-chain ethers,[20] fatty acids,[21] or benzene derivatives.[22–24]

Moreover, the STM has a wider application field rather than just providing images of surface structures. Another important aspect of the organic layers investigation with STM is its ability to distinguish some functional groups from the methylene groups of the molecule backbone. However, while functional groups such as amines, thiols or halides can be easily distinguished from the molecule skeleton,[25] others such as ester or carboxyl groups are not identified in STM images.[26] Remembering the fact that, in STM configuration, if the tip and the sample are separated by a few angstroms, their electronic wave functions overlap. By applying a bias voltage, a tunnelling current flows between them. This suggests that chemical modification of STM tip could allow discriminating chemical species through rational use of chemical interactions. In our experiments described hereafter, we

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functionalised STM tips in order to study their effect on the tunnelling current, and hence, the different image contrasts observed on specific functional groups. By comparing the image contrast over functional groups obtained with different modified tips, we are able to identify the functional groups chemical specificity and to locate at the atomic scale their positions within a molecule.

Beyond functional group identification, STM has the potential to provide insight into a broad field of topics such as chirality, reactivity and dynamics at liquid/solid interfaces.[27–29] Particularly, it should allow the motion of individual features on the surface to be followed as a function of time. Unfortunately, the range of dynamical phenomena that can be investigated by STM is limited by the nature of the STM experiment itself. Indeed, STM experiments are performed generally at a longer time scale than the single molecule dynamics. Thus, the molecular motion can only be followed provided the phenomena occur on the millisecond time scale, or longer.[22] Such spontaneous dynamic phenomena are imaged and studied in pure monolayer systems at the liquid/solid interface.

More precisely, we compared in this paper, the STM images of a wax ester [palmitoyl palmitate: CH_3-$(CH_2)_{14}$-COO-$(CH_2)_{15}$-CH_3] layer at the phenyloctane/graphite interface. The effect of chemically modified tips on the image contrast is studied. In this case, tips are functionalised with self-assembled monolayers of 4-mercaptobenzoic acid (4-MBA) and 4-mercaptotoluene (4-MT). We also consider molecular motions at domain boundaries, describing their evolution in time.

Results and Discussion

The probed molecules are symmetrical esters, as shown in Figure 1. In this figure, grey balls represent methylene groups, except those marked by a black arrow, which represent oxygen atoms. Previous results, from single crystal XRD experiments,[30] allowed us establishing their crystalline structure and their molecular characteristics, in particular the molecular length (about 4 nm).

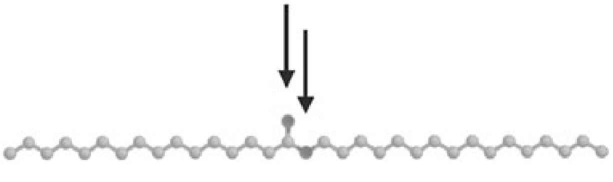

Figure 1. Chemical structure of the Palmitoyl Palmitate (PP). Arrows indicate oxygen atoms. All other balls represent methylene groups.

In those previous studies, STM experiments of wax esters (PP) assemblies at the phenyloctane/graphite interface are also reported. The STM images shown therein (obtained with Pt/Ir tips) revealed different kinds of two-dimensional assemblies. In all cases, during experiments, the difficulties of obtaining interpretable and reproducible images are recorded and submolecular resolution is not achieved despite a considerable number of trials. Moreover, the position of the functional group is not revealed by the STM data.

The use of chemically modified gold tips with 4-MBA and 4-MT facilitates molecular imaging at the liquid/solid interface. Moreover, comparison between monolayer images obtained with 4-MBA and 4-MT modified gold tips reveals the ester group position within the molecule. Measures obtained with unmodified bare gold tips are exposed as a reference.

Modified tips and ester group position: Figure 2 shows a typical image of wax ester's overlayer observed with an unmodified gold tip. Side-to-side packing of lamellae forms this overlayer. These lamellae, which are separated by troughs (less than 2 Å deep), are found to be repeated at a distance of about 5 nm. Each lamella appears to be formed by a closed-packing arrangement of parallel sticks, oriented at about 60° with respect to the troughs. Those sticks are about 3.9 nm long.

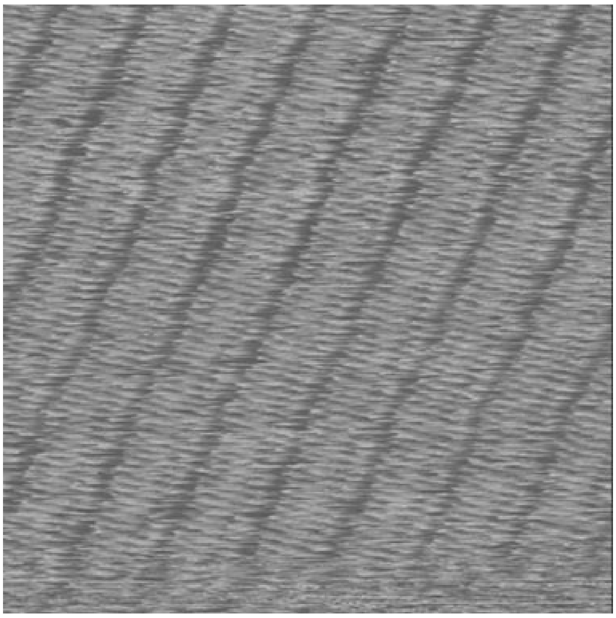

Figure 2. STM image of PP at the phenyloctane/graphite interface obtained with unmodified gold tip (30 nm × 30 nm, 710 pA, −480 mV).

This structure can be interpreted as a two-dimensional array of ester's molecules at the liquid/graphite interface. The length of an ester C-C-C zigzag is almost the same as the 0.246 nm spacing between hollows in the graphite lattice. This lattice match promotes adsorption and is the origin of ester's affinity for graphite.[2] The length of the lamella is in good agreement with the length of ester's molecules measured from XRD experiments.[30]

4-MBA functionalised gold tips were used for the STM observation of PP structured layers. This kind of tips enhances the contrast between ester and methylene groups in esters' molecules. Indeed, recent studies shown that chemically modified tips can be applied for the identification of several functional groups hardly visible otherwise.[31–35] This was explained as a consequence of the ease of electron tunnelling through the overlap of the electronic wave functions by the interaction between tip and sample.[32–35] While some functional groups (such as hydroxyl, carboxyl and ether oxygen) appeared as dark spots (under identical conditions) with unmodified tips, they are observed as bright spots when using 4-MBA modified gold tips, due to hydrogen bond making easier electron tunnelling. It was also found that a stronger hydrogen-bond interaction causes a more enhanced contrast for the functional groups. The difference in the strength of the hydrogen-bond interaction between the tip and sample allows discrimination of the differently oriented ether oxygens.[32]

Figure 3 shows typical STM image of ester's layers at the phenyloctane/graphite interface obtained with 4-MBA modified gold tips. Self-assembled layers organise themselves in a lamellar structure. The troughs separating these lamellae are found to be repeated at a distance of about 4.3 nm.

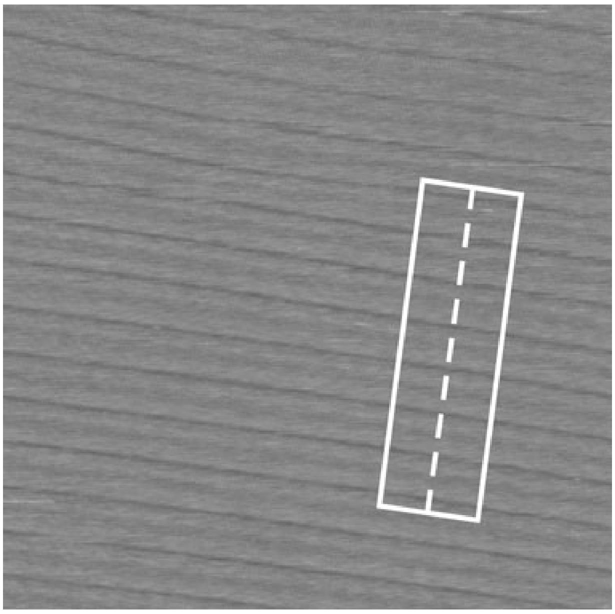

Figure 3. STM image of PP at the phenyloctane/graphite interface obtained with 4-MBA modified gold tip (60 nm × 60 nm, 740 pA, −485 mV).

Moreover, lamellae appear to be formed by a close-packing arrangement of parallel sticks, oriented at 60° compared with the troughs, as depicted in Figure 4. This Figure is a high-resolution image of one ester lamella. In this lamella individual sticks can be distinguished. They are approximately 3.9 nm long. It is also possible to evaluate the number of bright spots forming the sticks: between fifteen and seventeen (as highlighted in the Figure 4). The width of the trough and the space between two adjacent sticks can also be evaluated at 2 and 4 Å, respectively. Figure 5 represents a line profile (dash line in Figure 3), perpendicularly oriented to the trough direction. The transversal curve shown in this Figure is averaged on all the line profiles laying in the white rectangle of Figure 3. Troughs are approximately 0.8 Å deep. Between each adjacent trough, small depressions are clearly visible. They are 0.4–0.5 Å deep and positioned at the lamella centre.

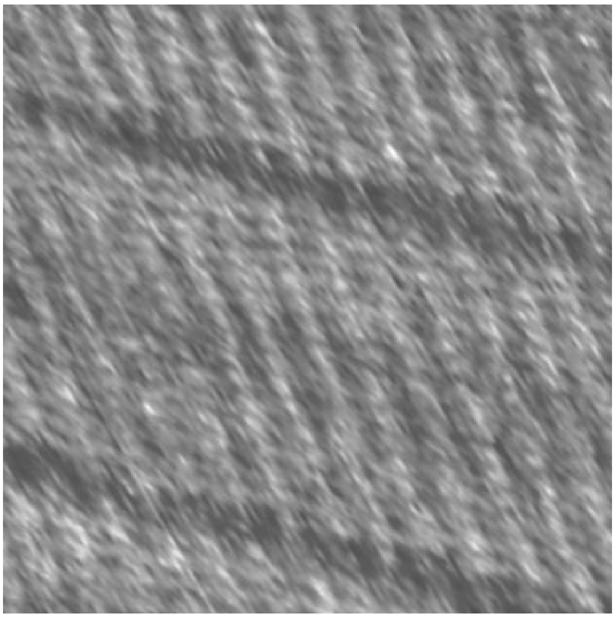

Figure 4. High-resolution STM image of PP lamellae at the phenyloctane/graphite interface obtained with 4-MBA modified gold tip (6 nm × 6 nm, 740 pA, −485 mV).

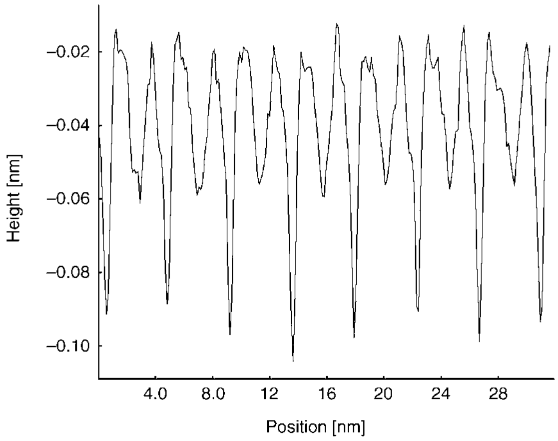

Figure 5. Line profile obtained along white dash line of Figure 3, averaged on the white rectangle.

4-MT modified gold tips allow us to observe a structure such as the one presented in Figure 6. The lamellar structure observed is similar to the structure observed in the previous section. Lamellae have a measured width of about 4.3 nm. These structures seem uniformly visible on large domains on the sample surface. Figure 7 depicts a line profile (dash line in Figure 6), perpendicularly oriented to the trough direction. The transversal curve shown in this Figure is averaged on each line profiles lying inside the white rectangle of

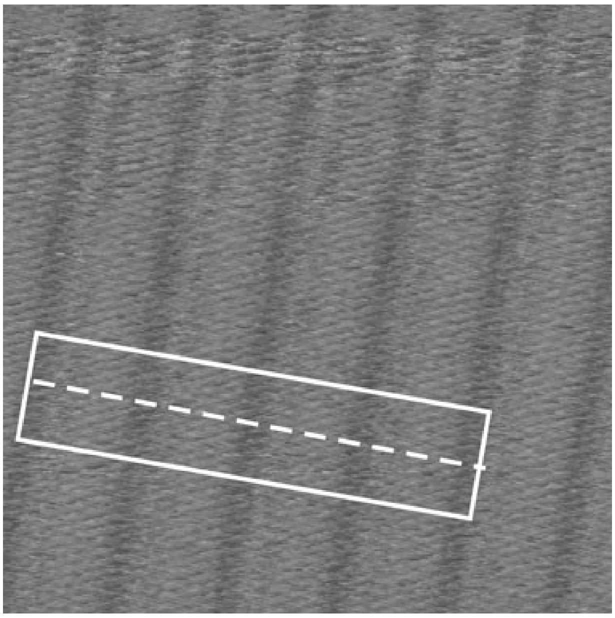

Figure 6. STM image of PP at the phenyloctane/graphite interface obtained with a 4-MT modified gold tip (23.5 nm × 23.5 nm, 490 pA, −500 mV).

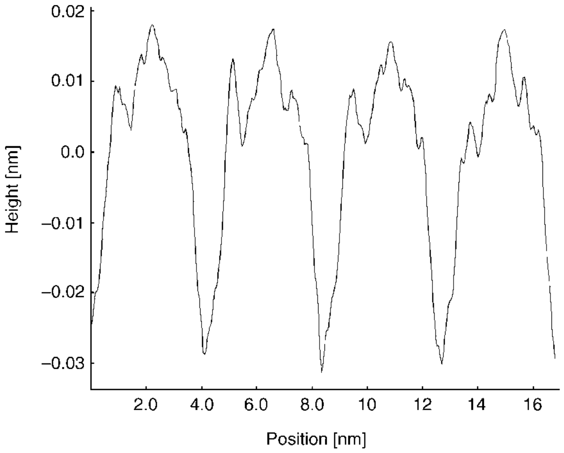

Figure 7. Line profile obtained along white dash line of Figure 6, averaged on the white rectangle.

Figure 6. Troughs are approximately 0.5 Å deep. Between each adjacent trough, small mounds are clearly visible. They are 0.1–0.2 Å higher and positioned at lamella center.

Previous experiments already demonstrated the difficulty of obtaining reproducible and good-quality STM images on esters with Pt/Ir tips at the liquid/solid interface.[30] By contrast, reproducible results with periodic structures are easily seen with unmodified gold tips. However, the position of the ester group cannot be deduced from these STM images (Figure 2). The use of chemically modified tips reveals identical molecular organisation. However, a different chemical used to functionalise the tip (4-MBA or 4-MT) provides a different image contrast at the ester group position, which is not visible otherwise. Small depressions with 4-MBA gold tips and small mounds with 4-MT gold tips were observed at the centre of the molecule. This can be explained as a consequence of the (un)easiness of electron tunnelling through the overlap of the electronic wave functions by the interaction between tip and sample, as described in the literature.[32–35] Indeed, it was shown theoretically and observed experimentally that adsorption of atoms or molecules on a STM tip changes the tip structure and/or the tip electronic states, and therefore the STM images.[36] For example, a single CO molecule onto STM tip was reported to achieve chemical contrast allowing distinction of CO molecules and oxygen atoms adsorbed on Cu(111). In this case, chemical sensitive imaging is due to contrast inversion of CO molecules adsorbed on Cu(111) caused by CO molecule at the tip apex.[37–39] Evidently, CO decorated tips have a much higher power to resolve the structures on some samples than bare tips. Umezawa et al. explained this contrast modification as a consequence of the hydrogen-bond formation between functional groups on tip and sample, making easier electron tunnelling. We also found that stronger hydrogen-bond interaction causes a more enhanced contrast for the functional groups, and the difference in the strength of the hydrogen-bond interaction between the tip and sample allowed discrimination of the differently oriented ether oxygens.[32]

Line profiles in Figures 5 and 7, obtained with 4-MBA and 4-MT modified gold tips, respectively, clearly indicate the position of the ester group, which is the only reactive part of the molecule. Figures 5 and 7 also indicate that the same functional group on sample is "seen" as a depression and as a mound when imaged with 4-MBA and 4-MT modified tips, respectively. Following the interpretation of Umezawa et al.,[32–35] the interactions between the ester group on the sample and alkyl group "on the tip (4-MT)" facilitates the electron tunnelling through the overlap of the electronic wave functions, which is not the case between the ester group on the sample and the carboxyl "on the tip (4-MBA)". These observations agree well with an ester group pointing "up" away from the graphite surface. Indeed, this organisation can induce hydrogen bonding between sample and tip, leading to an overlap of the sample and tip electronic wave functions.

Domain boundary formation and evolution: STM images developed in this section are aimed at confirming that we can observe with functionalised tips on esters the dynamical processes routinely observed with standard STM tips on different adlayers deposited from a solution. Moreover, the results obtained with modified tips reveal equivalent (or better) contrast and image quality at the boundaries.

Chemically 4-MBA modified STM gold tips allow us to observe the birth and evolution of junctions between two domains, as mentioned above. Figure 8a shows two domains oriented in the same direction and composed of similar lamellae. In this image, solvent molecules are probably co-adsorbed in a non-structured way at the gap (about 4 nm wide) between domains 1 and 2. The gap between domains

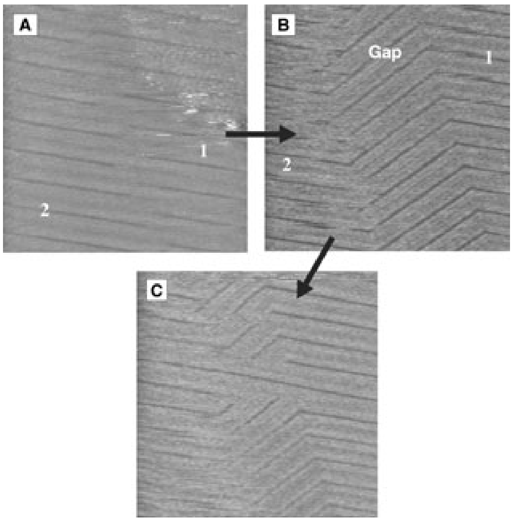

Figure 8. STM images showing the evolution of a domain boundary in self-assembled overlayers of PP at the phenyloctan/graphite interface obtained with 4-MBA-modified gold tip (740 pA, −485 mV). a) Initial state, field of view is 40 nm × 40 nm. b) Intermediate state, field of view is 40 nm × 40 nm. c) Final state, field of view is 50 nm × 50 nm.

1 and 2 gets progressively structured. Lamellae begin to appear in the gap, tending to align along those of domains 1 and 2, forming a continuous lamella as depicted in Figure 8b. Note that the small depressions visible at the center of the lamella are also observed in the lamella constituting the "gap" in Figure 8b. This indicates that the characteristics observed thanks to the functionalised gold tips are independent of the scan direction. The final stage of this process can be deduced from structures in Figure 8c. The progressive disappearance of the gap is observed because of the formation of continuous and linear lamellae between domains 1 and 2.

These images clearly illustrate the dynamical processes, which occur at domain boundaries, within overlayers at the liquid/solid interface. These discontinuities were also reported in STM images (obtained with Pt/Ir tips) of several other molecules such as alkanes or fatty acid derivatives.[42,43] However, to our knowledge, this paper reports on the first STM observation of ester overlayers evolution in time through molecular adsorption–desorption processes between the solution and the overlayer. The process observed in Figure 8 can be summarised as follows: a small domain (the gap) shrinks until it disappears, while the larger domains grow at its expense: domains 1 and 2 are becoming a single one. In this case, the dynamics are strongly directed resulting in a growth of larger domains. This process, that is, particle growth within two-dimensional systems (called Ostwald ripening), has already been intensively studied in previous works.[42,43]

Conclusion

In summary, images of two-dimensional arrays of esters at the phenyloctane/graphite interface using a scanning tunnelling microscope are obtained. Molecules in layers are organised in lamellae separated by troughs. Each lamella is composed of parallel molecules oriented at 60 degrees compared to the troughs. High-quality images obtained with functionalised gold tips indicate that the molecules are lying on the substrate with the plane formed by their carbon chain perpendicular to the substrate. Moreover, the image contrast difference obtained with the modified tips reveals the position and orientation of the ester group, which is the only reactive part of the molecule. We also observed molecular motions at domain boundaries.

Materials and Methods

STM experiments: Experiments were performed with a commercial STM (Nanoscope IIIa, Digital Instruments) under ambient conditions. Highly oriented pyrolitic graphite (HOPG), used as substrate, was obtained from Advanced Ceramics (ZYH grade). Palmitoyl Palmitate (PP) was purchased from Aldrich and used without further treatment. They were dissolved near saturation in phenyloctane (Aldrich).

During a scan, the tip was immersed in several drops of the solution, deposited on the freshly cleaved graphite surface. The liquid/graphite interface was then imaged with the STM operating in the constant current mode with gold, 4-mercaptobenzoic acid (4-MBA) and 4-mercaptotoluene (4-MT) functionalised gold tips, respectively. A zero-order flattening procedure was used to normalize the vertical offset produced. Typical operating conditions were 0.5 to 1.0 nA at −0.5 to −1.0 V bias (sample negative). Experimental results were reproducible, but not predictable. Typically, many trials were required before ordered layers were observed. We found that ordered layers were easily visible when the solution's layer was very thin, during the experiments performed with modified tips.

Tip modification: STM tips were prepared from gold wire (0.20 mm diameter, Goodfellow, England; 99.99 %) by mechanical cutting. Before cutting, tips were washed by sonication in ethanol and further dipping in piranha solution (7:3 concentrated H_2SO_4/H_2O_2. **CAUTION**: piranha solution reacts violently with organic compounds and should not be stored in closed containers). Tips were finally washed again in ethanol. For the formation of self-assembled monolayers on tips, we immersed them for 12 h in a saturated 4-mercaptobenzoic acid (4-MBA; Aldrich, 97 %) or 4-mecaptotoluene (4-MT; Aldrich) solution in ethanol. The tips were then rinsed with ethanol and dried in a stream of nitrogen.

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