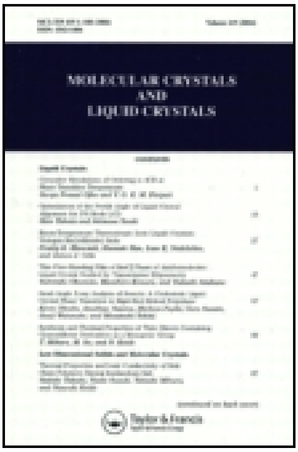

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High Resolution Imaging of Physisorbed Organic Monolayers by Scanning Tunneling Microscopy

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HIGH RESOLUTION IMAGING OF PHYSISORBED ORGANIC MONOLAYERS BY SCANNING TUNNELING MICROSCOPY

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Abstract Scanning Tunneling Microscopy (STM) reveals details down to the molecular and submolecular scale. This paper presents STM images taken under solution of three well known organic compounds deposited on highly oriented pyrolitic graphite. Dotriacontane, stearic acid and tetracosanoic acid showed to form highly organized monolayers that have a characteristic two-dimensional structure. Conditions for high resolution and optimal contrast are discussed. Different monolayer packing for stearic acid in correspondence of two concentration values are also reported.

INTRODUCTION

In recent years increasing attention has been devoted to the study of organic low dimensional systems in order to determine their molecular organization and charge transport properties keeping in view possible applications in information technology.[1]

For such investigations Scanning Tunneling Microscopy (STM)[2] is a very appealing technique as it can be applied also to ultrathin organic films deposited on conductive substrates revealing details down to the molecular and submolecular scale.[3]

The most suitable organic systems for STM investigations are those in which molecules organize themselves lying flat on the substrate giving rise to layers thin enough to permit electron tunneling with bias parameters in the range usually employed in air.[4]

Microcalorimetric studies[5] have established that alkanes adsorb on graphite and on other ordered substrates forming monolayers at the interface: in the following, high resolution images of such monolayers physisorbed under solution on highly oriented pyrolitic graphite (HOPG) are presented.

RESULTS AND DISCUSSION

Dotriacontane ($C_{32}H_{66}$), stearic acid ($C_{18}H_{36}O_2$) and tetracosanoic acid ($C_{24}H_{48}O_2$) (Fluka Chemie) were dissolved in phenyloctane at room temperature. The concentrations for dotriacontane (4 mg/ml), stearic acid (15 mg/ml and 13 mg/ml) and tetracosanoic acid (19 mg/ml) were all near the saturation values.

Experiments were performed in the following way. Freshly cleaved HOPG was at first imaged with a new tip (mechanically formed from Pt-Ir 90/10 wire), in order to assess tip quality and overall STM (Nanotec STM 100) performance. Then a droplet of the solution was transferred on HOPG and images of the organic layers were taken keeping the tip immersed in the solution. STM was operated at quasi-constant height in the variable current mode.

As illustrated by the figures, all organic compounds showed to organize themselves onto the surface of HOPG, each having a characteristic two-dimensional structure.

The STM image contrast was sensitive to bias voltage: for low voltage values the images were dominated by the graphite lattice structure, while for high voltage values the two-dimensional array structure become more evident. The threshold value for good adsorbate resolution varied from session to session, but in general good resolution was obtained with bias values near 1 Volt (tip positive). Dependence on current setting was less evident and similar images have been obtained for values between 0.3 nA and 1 nA.

Tip condition was also important. Occasionally we have found necessary to apply voltage pulses (amplitude between 3 Volt and 4.5 Volt, duration between 100 ns and 100 μs) in order to improve the image contrast through tip conditioning; in any case the appearance of adsorbate structure was not dependent on them, as we have often imaged adsorbates without applying voltage pulses. It was possible to obtain images of adsorbates also in the constant current operation mode of the STM, but image contrast was poor and imaging not easily obtained.

Figure 1 shows two images of dotriacontane taken with different scan sizes. The width of each high contrast region separated by dark bands, a lamella, is comparable with the length of one molecule, while the number of enhanced sites in one row perpendicular to the lamella boundary is 16, half the number of carbon atoms in the molecule. Moreover, the distance between the enhanced sites is the same as for carbons

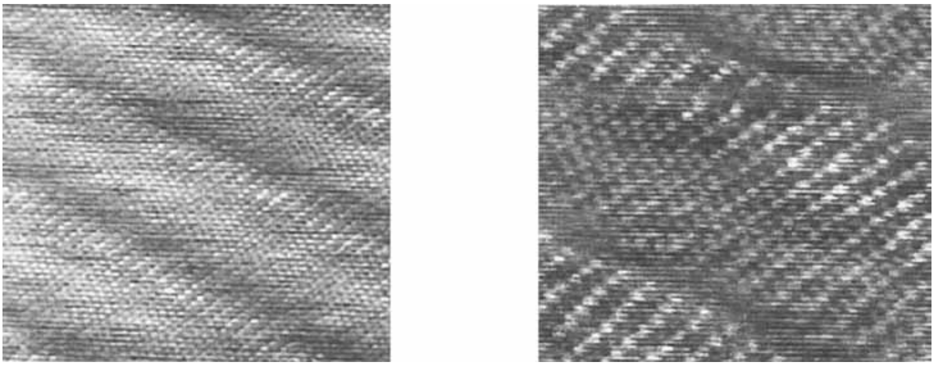

FIGURE 1 STM images of a monolayer of dotriacontane ($C_{32}H_{66}$) adsorbed on graphite. On the left the field of view is approximately 15 x 15 nm, tip bias 1 V and 1.2 nA. On the right the field of view is approximately 7 x 7 nm, tip bias 0.6 V and 0.6 nA. See Color Plate I.

in the graphite lattice, while the spacing between adiacent rows is comparable to that between second next carbon rows of the graphite substrate. One can ideally separate each lamella in two regions parallel to the boundaries: one shows contributions of all rows of graphite carbon site, while in the other one can observe an enhancement of the firts sites in alternating rows. Such rows are shifted of one graphite lattice constant between two adiacent lamellae.

With all compounds it was necessary to prepare concentrated solutions in order to observe lamellae: for low concentration values only HOPG was imaged. We have found that in the case of stearic acid the image contrast varied for different concentration values.

Figure 2 shows two images obtained using different stearic acid solutions, respectively at a concentration of 13 mg/ml and 15 mg/ml. In the image taken on the sample prepared from the solution at higher concentration (right), the lamellae show a different contrast and are narrower of about 10% than in the other case (left). In this last image one can also perceive a contrast modulation that extends along each lamella.

Figure 3 illustrates results obtained imaging tetracosanoic acid. Again one can count (left) within the lamella a number of enhanced sites, 12, that are half the number of carbon atoms in the molecule. It was possible to obtain larger scans (right) still keeping a good resolution which shows how the two-dimensional order involves a

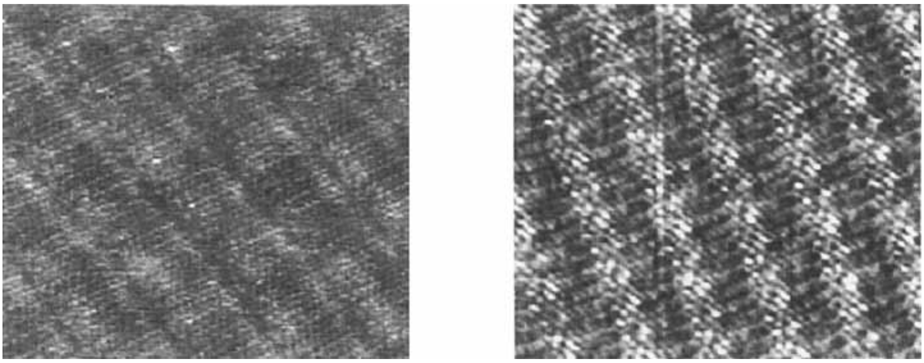

FIGURE 2 STM images of stearic acid adsorbed on graphite. Both pictures show an area of approximately 15 x 15 nm. On the left the concentration of the solution is 13 mg/ml, tip bias 1 V and 0.3 nA. On the right the concentration was 15 mg/ml, tip bias 1 V and 1.2 nA. See Color Plate II.

great number of molecules. In the lower left side of the image one can observe a defect in the molecular packing, with a shift that involves all the lamellae. As in the case of stearic acid, a superstructure can be found along the lamellae.

Imaging of alkanes and fatty acids has been interpreted[6] in terms of a local enhancement of some of the usually observed graphite atomic sites due to the presence of the physisorbed organic monolayer, so that what we observe is a modulation of the underlying graphite and not the real adsorbate's molecular structure. The enhancement of the firts sites in every row next to the edge of the lamellae in the case of dotriacontane has been interpreted as due either to a tilt of the molecules with respect to the graphite lattice, with the alkane's carbon skeletons laying flat on the substrate[7], either to a slight mismatch between the graphite lattice and the alkane's carbon skeletons, with the skeleton plane perpendicular to the graphite surface plane[6]. The absence of a superstructure along the dotriacontane lamellae has been attributed to the commensurability of the adsorbate lattice with the substrate lattice and favours the second explanation.

In the case of fatty acids, a superstructure can be observed along the lamellae, and this can be interpreted by assuming that molecules lie with the plane of the carbon skeleton parallel to the graphite substrate.[6]

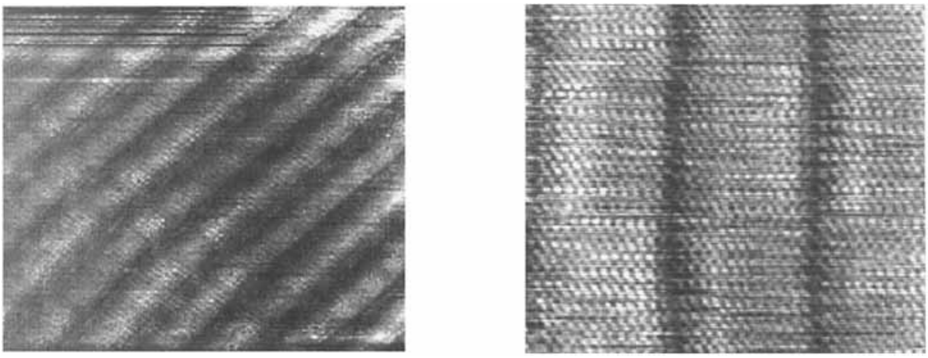

FIGURE 3 STM images of tetracosanoic acid ($C_{24}H_{48}O_2$) adsorbed on graphite. On the left the field of view is approximately 30 x 30 nm, tip bias 0.4 V and 0.4 nA. On the right the field of view is approximately 12 x 12 nm, tip bias 0.8 V and 0.6 nA. See Color Plate III.

CONCLUSIONS

Monolayers of an alkane and of fatty acids adsorbed onto graphite have been imaged with STM under solution at the liquid/graphite interface.

The ordered structures observed can be attributed to the tunneling current flowing from the graphite lattice modulated by the presence of the adsorbed molecules. This modulation depends on the tunneling parameters. Under appropriate voltage and current bias settings, high resolution imaging of the resulting lamellar structures can be achieved.

Adsorbtion depends on the solution concentration value and, in the case of stearic acid, differences in image contrast and molecule arrangement were found.

The ability to obtain high resolution imaging of organized organic low-dimensional systems is a first essential step for any application that involves their exploitation.

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