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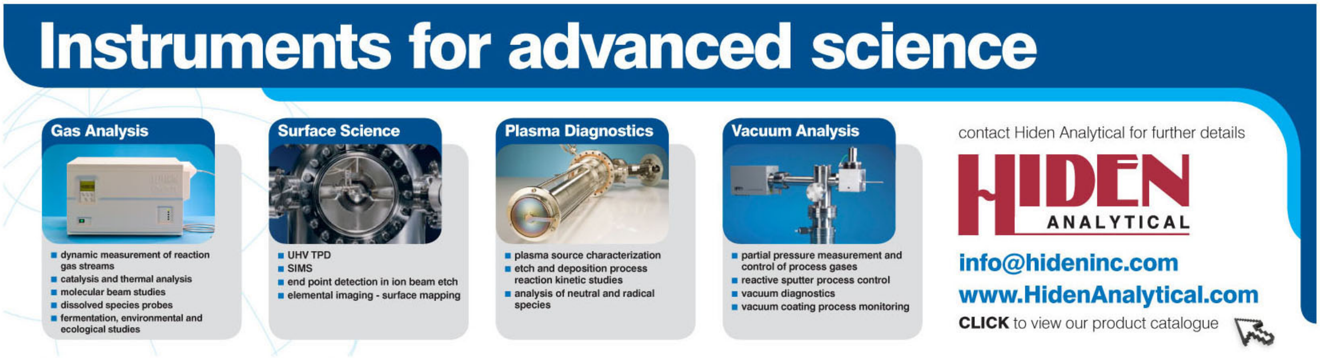

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Conformation, packing, defects, and molecular dynamics in monolayers of dialkyl-substituted benzenes

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Monolayers of the two homologues dihexadecylbenzene and didodecylbenzene were adsorbed at the interface between highly oriented pyrolytic graphite (HOPG) and an organic solution. The derivatization of a small molecule, in this case benzene, with long alkyl sidechains is shown to be a method to immobilize various molecular entities at the interface between HOPG and an organic solution. *In situ* STM studies at the internal interface revealed that the first adsorbed monolayer of the dialkyl-substituted benzenes exhibits a lamellar phase with the molecules extended and oriented parallel to the basal plane of graphite. Bias-dependent experiments allowed to either image preferentially the underlying substrate (at low bias) or the molecular adsorbate (at higher bias), without disrupting the adsorbate layer. From such experiments it was concluded that the alkane sidechains tend to orient parallel to a graphite lattice axis. High resolution images revealed different types of packing within a lamella, which were separated by sharp domain boundaries. Also packing defects involving individual molecules were observed. Most interesting, fast image recording on video tape allowed to directly follow the dynamics of such individual defects on the time scale between 100 ms and several minutes, i.e. the relevant timescale for the slow dynamics in crystalline organic phases.

I. INTRODUCTION

Early attempts to image an organic monolayer by STM, undertaken on Langmuir–Blodgett (LB) films of a fatty acid salt on graphite,[1] indicated that it is possible to obtain high resolution images of ultrathin organic films by STM. However, images compatible with the anticipated film structure with the molecules standing upright on the substrate were found only on small parts of the sample. The problem was that monolayers of fatty acid salts cannot be transferred well onto HOPG. This lack of reproducibility in sample preparation made it difficult to address the issue of electron transport through these layers experimentally. Subsequently it was realized that the molecules in the transferred monolayer on HOPG were generally packing very differently than on the water surface before transfer.[2] Even polymerized fatty acid salt layers did not retain their structure during transfer. In fact, grazing incidence infrared spectroscopy indicated that the hydrocarbon chains were oriented rather parallel to the substrate instead of perpendicular.[2] This, together with the fact that electron transport through any saturated hydrocarbon considerably thicker than 1 nm is difficult to understand theoretically, lead to the idea to prepare monolayers from extended polymers lying flat on the substrate surface. An example is an STM study of an alkyl-substituted cellulose on HOPG.[3] However, also in this case the LB-transfer ratio for the first monolayer onto HOPG was poor, resulting in a patchy film.

A different approach to prepare a monolayer is adsorption, either from gas or liquid phase. Under ultrahigh vacuum conditions monolayer domains of benzene coadsorbed with carbon monoxide were imaged at high resolution[4] and even isolated molecules, phthalocyanines on copper,[5] could be imaged. Another way to investigate organic monolayers by STM is the operation at the internal interface between a conducting solid and a fluid. It could be demonstrated that liquid crystalline materials form highly ordered monolayers on HOPG, which can be imaged by STM, indicating that the molecules are orientied parallel to the surface.[6] An advantage of this preparation is its ease and reproducibility. Moreover, the monolayers are thin enough not to cause any difficulty for an electron to tunnel through. Recently it was shown by STM that highly ordered phases of flat lying molecules do not require liquid crystalline materials, since highly ordered monolayers have also been found for long chain alkanes,[7] in good agreement with the models derived before from more macroscopic experiments.[8,9]

Based on the above-mentioned results, one may conclude that it is not the liquid crystalline character of the bulk material, which is responsible for the ordering at the HOPG interface, but that alkyl derivatives quite generally tend to form lamellae with the molecules oriented parallel to the HOPG surface. A systematic investigation of alkyl derivatives would offer a possibility to better understand the current through different molecular entities, or in other words the contrast mechanism for STM on organics. Moreover, the role of epitaxy versus monolayer crystallization is a long standing problem in the case of alkane derivatives on HOPG.[8,9] We have investigated a number of different alkyl derivatized atoms or small molecules by STM, all of which exhibited lamellar phases. In the present paper we present a more detailed STM study of two dialkyl-substituted benzenes, dihexadecylbenzene (DHB), and didodecylbenzene (DDB).

II. EXPERIMENT

DHB and DDB were a donation of F. Helmer-Metzmann. They were synthesized according to Rehahn *et al.*[10] Concentrated solutions were prepared from three different solvents, for comparison: Diphenylsulfide (Merck), phenyloctane (Aldrich), and 1,3,5-trimethyl-1,1,3,5,5-pentaphenyltrisiloxane (ABCR GmbH). Highly oriented pyrolytic graphite (HOPG, quality ZYB) was obtained from Union Carbide. The STM has been described before.[2] It was operated at the internal interface between an organic solution and HOPG. Electrochemically etched Pt/Ir tips were employed and the tunneling current was 2 nA at a tip bias up to 1.5 V. The images were video recorded in the variable current mode at a scanning frequency in x direction of 1 kHz, implying a time resolution of 200 ms for 200 line images.

III. RESULTS AND DISCUSSION

In situ STM studies at the internal interface between HOPG and organic solutions of both dialkyl-substituted benzenes, DHB and DDB, in various solvents revealed lamellar phases with the molecules parallel to the basal plane of graphite. Figure 1 shows the image of a little more than one lamella of DDB. The lamellae are identified by their periodicity. Their width is of the order of the length of the molecule. The spacing within the lamellae of about 0.45 nm indicates that individual molecules, extended and inclined to the lamellae boundaries are imaged. More difficult is the question, where the end of a molecule and where the benzenes are located, respectively. In this context it is helpful to compare the image to what is obtained for long chain n-alkanes. In all the cases we studied, in particular the corresponding n-dotriacontane (C_{32}) and n-tetracosane (C_{24}), we found a displacement of the molecules from lamella to lamella by half a molecular spacing. Therefore, we assign in Fig. 1 the end of the molecules to the position where they appear diplaced by half a molecular spacing. Consequently, the position of highest contrast in the middle of a lamella is attributed to the benzene. Noteworthy, at low bias (a few 100 mV) the images show preferentially the underlying graphite substrate with only a hint of the molecular images, just enough to be convinced that the monolayer has not been destroyed by this procedure. From such experiments it can be concluded that the molecular chain is oriented preferentially parallel to a graphite lattice axis. The relative contrast as a function of bias, together with a more detailed discussion of the role of epitaxy will be discussed in a forthcoming paper.[11]

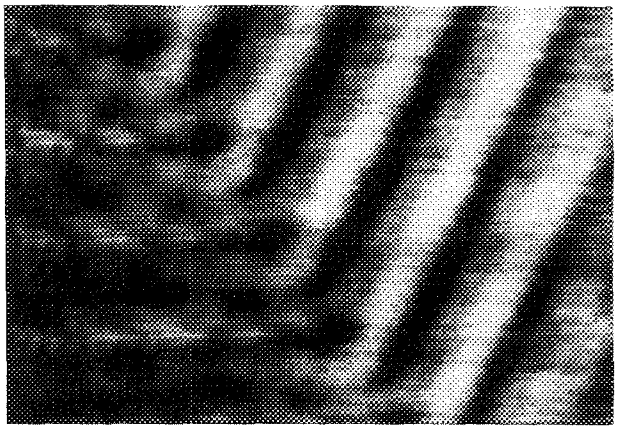

FIG. 2. Domain boundary of a DDB monolayer on HOPG, with two adjacent domains. Sample bias: 1 V. STM image size: 18 × 13 nm.

In the case of DDB many domain boundaries and different types of packing within the lamellae have been observed. Figure 2 shows such a domain boundary. In Fig. 3 a higher resolution image of the left domain of Fig. 2 is given. The image indicates that the molecules appear tilted relative to the lamella boundary and packed laterally in groups of four. This means that they cannot be in full registry with the graphite substrate. While the structure shown in Fig. 3 is periodic within the domain of in this case a few 10 nm, also defects involving individual molecules have been observed. Figure 4 shows a lamella with such a defect. While the benzenes remain highly ordered in this region, the alkyl sidechains surrounding the defect are more disordered. The lifetime of defects of this sort can be on the time scale of seconds

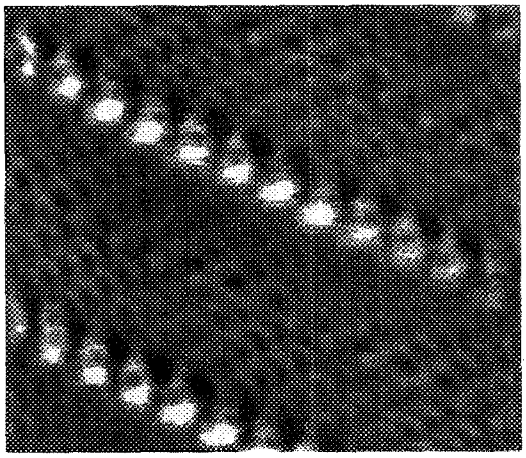

FIG. 1. STM current image of lamellae of DDB adsorbed flat on HOPG. The molecules are extended and tilted relative to the lamellae boundary. From lamella to lamella they are displaced by half a lattice spacing. The current contrast is largest in the middle, i.e., the location of the benzene; it varies along the alkyl parts. Sample bias: 1 V. STM image size: 6 nm × 5 nm.

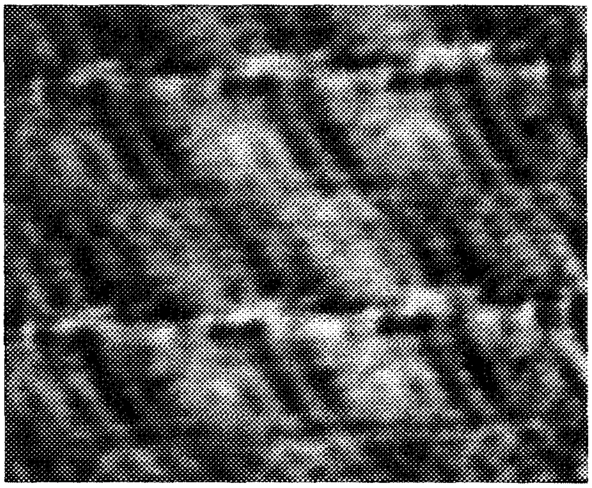

FIG. 3. Higher resolution STM image of the left domain of Fig. 2, indicating that the molecules in this lamellar phase form groups of four. Sample bias: 1 V. STM image size: 7.8 nm × 6.7 nm.

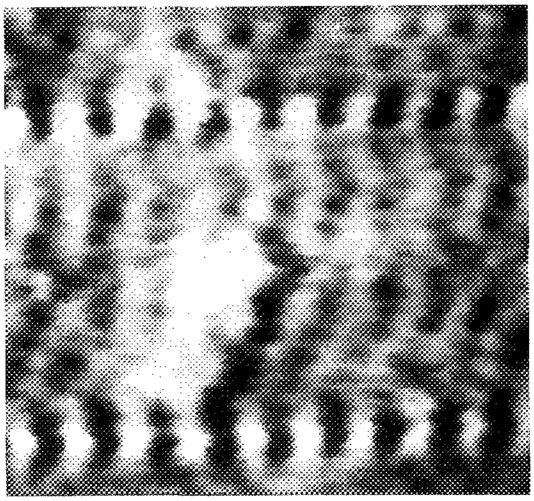

FIG. 4. Metastable defect and disordered sidechains in another lamellar phase of DDB on HOPG. Sample bias: 1 V. STM image size: 5.0 nm × 4.7 nm.

or minutes. Most interesting, with our fast image recording on video tape it was possible to follow directly the slow dynamics of such defects in crystalline monolayer phases, i.e., their appearance, diffusion, and eventual annealing could be observed in many instances, including the case of some long chain alkanes. More details on the dynamics will be discussed elsewhere.[12]

IV. CONCLUSIONS

Alkyl substitution turned out to be a general and most effective method to immobilize small organic molecules on HOPG. It opens the possibility to address various organic entities with the STM tip, a prerequisite for any sort of spectroscopy or modification with the STM. The monolayer structure of two dialkyl-substituted benzenes was investigated at molecular resolution, revealing different types of packing with sharp domain boundaries between them. Moreover, the conformation of the molecules within a lamella was determined and defects involving individual molecules could be resolved. Fast image recording allowed to follow the dynamics, i.e., the creation, diffusion and the annealing of such defects on the time scale between 100 ms and many minutes, i.e., a relevant timescale for the slow dynamics in crystalline organic phases. Voltage-dependent imaging turned out to be suitable to investigate the role of epitaxy for the monolayer structure. It was found that the molecules tend to orient along a graphite lattice axis. The various packings observed for DDB, however, are not compatible with complete epitaxy of the alkyl sidechains.

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