Hourglass-Shaped Dendrimers on Surfaces: A Comparison of Different Scanning-Tunneling-Microscopy Approaches

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Large molecules adsorbed on surfaces can be analyzed by scanning tunneling microscopy (STM) under various environmental conditions: on a dry surface in air or vacuum, and at the solid-liquid interface. However, can measurements under dissimilar conditions be compared, *e.g.*, when sample *A* was studied at the solid-liquid interface and sample *B* in a dry environment? Only rarely can the same substance be examined with more than one approach, since completely different set-up and preparations are necessary. Furthermore, few substances are suitable for several methods of sample preparation and characterization. We have chosen a large, flexible, nonplanar molecule, namely an alkoxy-substituted second-generation dendritic compound with a chiral core unit, which is peculiar for its 'hourglass' conformation. The assembly properties have been explored by STM both in solution-cast self-organized monolayers (SOMs) and multilayer films, as well as at the solid-liquid interface. The complexity and limits of the three approaches applied to our hourglass-shaped dendritic compound are discussed. Depending on the approach and environmental conditions, several quality levels of image resolution could be achieved; measurements carried out at low temperatures led to highest resolution on the aromatic parts of the molecule. A comparison of equally sized images obtained under these varying conditions reveals not only different packing arrangements, but also spots of unlike shape. Therefore, when the approach, preparation, and/or environmental conditions are not the same, STM measurements of different compounds have to be compared with greatest care.

Introduction. – Since the invention of scanning tunneling microscopy (STM) [1] [2], atomic-force microscopy (AFM) [3], and scanning near-field optical microscopy (SNOM) [4–6], increasing interest has been directed towards real-space imaging of single molecules and (supra)molecular assemblies on surfaces. Even though scanning

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probe microscopy (SPM) techniques are not yet standard analytical methods in chemistry, a growing number of elaborate studies have included SPM measurements in the last years [7–10].

AFM probes the interaction forces between tip and molecules supported by insulating or conducting substrates. Various types of forces, including *Van der Waals*, chemical, electrostatic, friction, or magnetic forces, can contribute when mapping a surface (for a review, see [11]) [12] or acquiring force-distance curves (for a review, see [13]). SNOM investigates structural aspects as well as spectral and dynamic processes, when light is interacting with molecules adsorbed on surfaces [14][15]. STM directly probes the electronic structure of molecules in close vicinity to a conducting substrate. Exploiting the spectroscopic capabilities of the STM, one can study local current-voltage characteristics [16], the local density of states close to the *Fermi* surface (with the first derivative of the signal) [16], and, under advantageous conditions, vibrational properties of molecules (with the second derivative of the signal) [17].

Various large molecules have been investigated by SNOM [18], AFM [13][19], and STM [20] (for a review, see [21]) according to different approaches: SPM in a dry environment (under ambient conditions or in vacuum) (for a review, see [22]) and in a wet environment (at the solid-liquid interface (for a review, see [23]) or with electrochemical methods [24]). All methods can be performed at various temperatures. STM on a dry surface in vacuum can even be operated at very low temperatures, allowing extremely high spatial resolution (due to improved thermal stability and lower noise).

We focus our attention to a chiral dendritic compound synthesized in the group of Prof. *Seebach* in 1995. Since the synthesis of the first dendrimers independently by *Tomalia et al.* [25] and *Newkome et al.* [26] in 1985, a variety of dendritic compounds and dendrimers have been investigated by SPM (for a review, see [27]).

STM Analysis at the solid-liquid interface is performed with the tip immersed in a droplet of a nearly saturated solution of, *e.g.*, dendrimers [28][29].

Samples of dendrimers[6]) for SPM measurements in a dry environment can be prepared according to manifold coating procedures: *a*) with wet-chemistry by spin-coating [29][30], by solution-casting [31], by building metal complexes on the surface [32], by techniques related to the *Langmuir-Blodgett* principle [33], or by electrostatic layer-by-layer deposition [34] and in *b*) high vacuum (HV) by electrospray [35]. Deposition by sublimation in *c*) ultra-high vacuum (UHV) with organic molecular-beam epitaxy is often not applicable to large molecules (in particular dendrimers) due to the thermal instability of the compounds.

SPM Studies in a dry environment explored, among others, self-assembled monolayers [8], assembled layer-by-layer films [34], mono- or multilayer films [31], molecular stacks [36], or single molecules [37][38]. Contrary to SOMs, the number of layers[7]) in molecular films is difficult to control, and the packing arrangement is hard to characterize.

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[6]) Here, we concentrate only on the work on dendritic compounds and dendrimers. However, the methods can generally be applied for many molecular systems ranging from CO to proteins.

[7]) To measure a larger film thickness, other techniques exist, *e.g.*, steppers also called profilometers.

Measurements of similar molecular systems are frequently compared, even though the results were accomplished by different methods. SPM permits research on the same molecular system under different experimental approaches or environmental conditions.

We report here for the first time a STM study conducted at a solid-liquid interface and in a dry environment (prepared by solution-casting) of the same compound: an hourglass-shaped dendritic compound (see *Fig. 1*). The (*S*,*S*)-enantiomer of the second generation octyl-substituted dendritic compound has a chiral core moiety to which two *Fréchet*-type poly(benzyl ether) branches are attached. For the sake of simplicity, we will refer to it as (hourglass) dendrimer[8]). Self-organized monolayers of the hourglass dendrimers were studied on dry surfaces and at the solid-liquid interface. Both studies were carried out on highly oriented pyrolytic graphite (HOPG) surfaces at room temperature. The measurements on multilayer films of the molecules were carried out on Pt surfaces at room temperature in air as well as at 77 K in high vacuum.

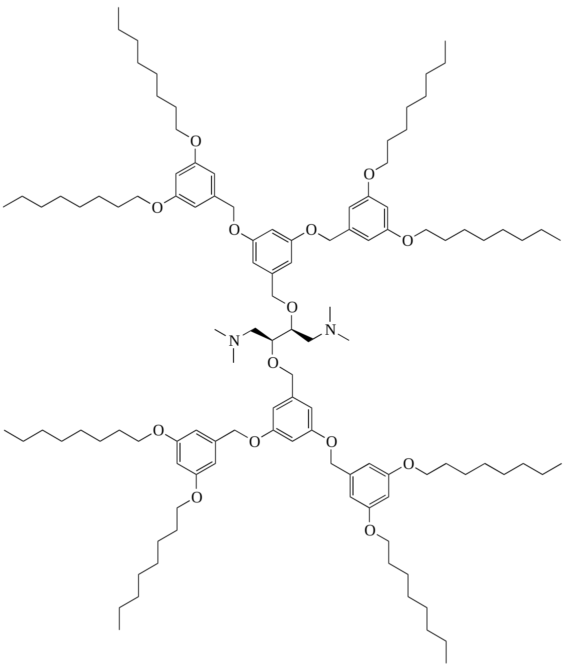

Fig. 1. *Structural formula of the investigated (*S,S*)-enantiomer of the hourglass-shaped dendrimer: a second-generation dendritic compound with a chiral core moiety and two achiral branches*

Results and Discussion. – *Dry Multilayer Films.* The STM images in *Fig. 2,a* and *b*, obtained on Pt(100) at room temperature, display a multilayer film of hourglass

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[8]) Strictly speaking, only dendritic compound having at least three branches and a defined structure is a true dendrimer.

dendrimers and a monolayer of pure benzene, respectively. They both reveal similar hexagonal packing with lattice constants of 0.6 and 0.48 nm for hourglass dendrimers (*Fig. 2,b*) and pure benzene (*Fig. 2,a*), respectively. This different spacing can be explained with the addition of a CH_2O moiety (C–O) between two adjacent phenyl rings in the dendrimer structure[9]).

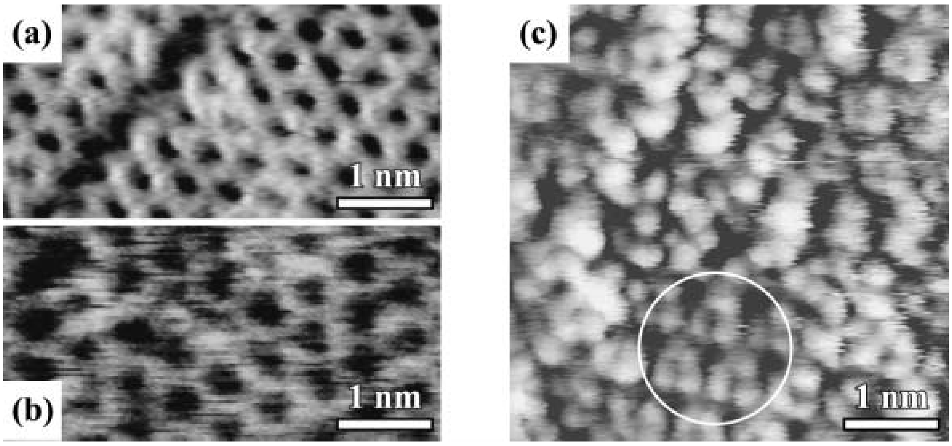

Fig. 2. *STM Image of* a) *pure benzene on Pt(100) measured at ambient conditions* ($U_{bias} = 85$ mV, $I_t = 300$ pA) *and a multilayer film of hourglass dendrimers on Pt(100) measured* b) *under ambient conditions* ($U_{bias} = 60$ mV, $I_t = 700$ pA) *and* c) *at 77 K and* 10^{-6} *mbar* ($U_{bias} = 30$ mV, $I_t = 500$ pA)

The same multilayer film investigated at 77 K (*Fig. 2,c* and *Fig. 3,a*) shows protrusions sometimes exhibiting a three-lobed substructure. Especially in *Fig. 2,c*, the three lobes are clearly visible (encircled), and a dense packing with only short-range order is observed. *Fig. 3,a* shows a larger area of the same sample, which also provides evidence for long-range ordering.

Dry Self-Organized Monolayers. On HOPG, solution-cast hourglass dendrimers adsorb in a 2D lattice, as seen in *Fig. 3,b*[10]) and *d*, extended over an area much larger than 100 × 100 nm^2 (not shown). The regularly arranged protrusions have a 'triangular' shape, and their size suggests that one molecule is represented by two triangular protrusions in a butterfly-like shape. This supports the interpretation that the contrast in the STM image is caused by interference effects between frontier orbitals (as well as other orbitals close to the *Fermi* level) of the particular part of the molecule, and the through-space electronic current between the tip and the underlying metallic surface [39]. Aromatic moieties, such as phenyl rings, appear brighter because of their π orbitals. Additionally, if the phenyl rings are arranged flat on the HOPG surface, π stacks could be formed due to strong electron–electron correlation effects [40]. Noteworthy, our molecules bear six phenyl rings: each branch of the dendrimer holds three phenyl rings arranged in a triangle. At room temperature, one protrusion

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[9]) Although Pt is known to act as a catalyst, we believe that the molecules do not decompose because the STM images were time-stable during repeated scans.

[10]) *Fig. 3,b* shows the same picture as *Fig. 3,d,* enlarged by a factor of two to allow easy comparison with *Fig. 3,a.*

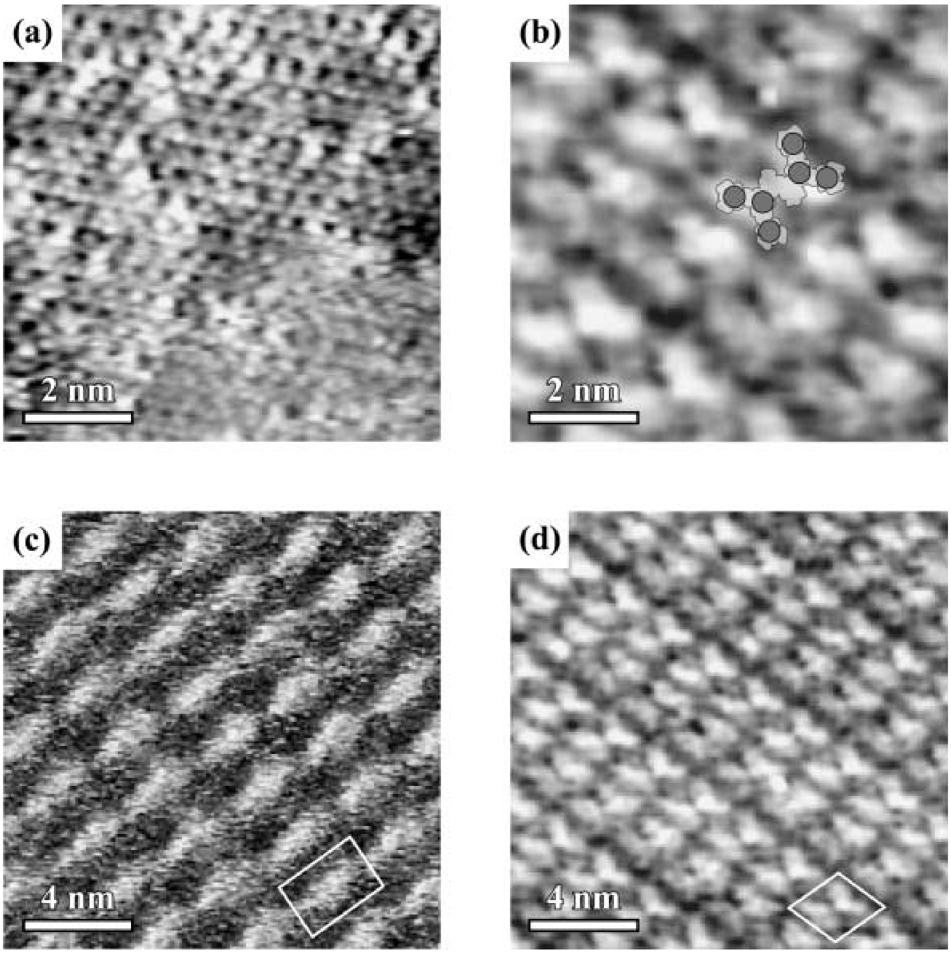

Fig. 3. a) *STM Image of a multilayer film of hourglass dendrimers on Pt(100) measured at 77 K and* 10^{-6} *mbar* ($U_{\text{bias}} = 30$ mV, $I_t = 500$ pA). b) *An enlargement of* Fig. 3,d, *displaying a SOM of these dendrimers on a dry HOPG surface.* A cartoon of an hourglass dendrimer (without alkyl chains) is superimposed. c) *STM Image of a SOM of hourglass dendrimers at the solid-liquid interface on HOPG with a unit-cell of the molecular lattice drawn in white* (room temperature, $U_{\text{bias}} = +1$ V, $I_t = 1$ nA). d) *STM Image of a SOM of hourglass dendrimers on HOPG on a dry surface also with a unit-cell drawn in* (ambient conditions, $U_{\text{bias}} = +700$ mV, $I_t = 1$ pA). A convolution filter was applied.

probably contains three phenyl rings blurred by thermal motion. The 'butterflies' form regular rows with a rhombic unit-cell of size 1.45 nm × 2.25 nm containing one molecule.

Self-Organized Monolayers at the Solid-Liquid Interface. The hourglass dendrimers adsorb at the HOPG-solution interface in a crystalline architecture[11]), appearing in the

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[11]) As the self-organization process probably takes place in a thermal equilibrium, one could also speak of a self-assembled monolayer.

STM image as a 2D lattice of elliptic spots (*Fig. 3,c*). The distances between the centers of two bright spots are 3.2 and 2.1 nm. If each spot represents one molecule, the distance between two molecules would then be larger than in the SOM on the dry surface. This discrepancy will be discussed below.

Comparison between Multilayer Films and SOMs in a Dry Environment. Fig. 3,b shows an enlarged section of *Fig. 3,d*, to allow easy comparison of the multilayer films (*Fig. 3,a*) measured at low temperature and the SOMs (*Fig. 3,b*) measured at room temperature. It is reasonable to compare SOMs and multilayer films of the same compound: the films are cast from a highly diluted solution, and the STM tip is located very near to the substrate, hence, only a few molecular layers can be present. From a comparison between the images *Fig. 3,a* and *b*, two main issues are noted for the multilayer films: *a*) a substructure *within* a phenyl ring at low temperature, and *b*) a rather close-packed arrangement, where the molecular perimeter cannot be discerned.

High-resolution imaging on multilayer films is very challenging, as it drives the instrument to its resolution limit. Stable images can be obtained only in absence of external disturbances. On the other hand, measurements on SOMs are possible for many hours, if the concentration of molecules on the surface is finally optimal. This indicates that, in the case of SOMs on HOPG, the molecule–substrate interaction is stronger than the molecule–molecule interaction, stabilizing the molecular packing.

Comparison between SOMs in Liquid and on a Dry Surface. In both self-organized monolayers (*Fig 3,c* and *d*) the molecules are ordered in 2D crystalline architectures, but exhibit a different packing arrangement. A comparison of the two images suggests that one elliptic spot at the solid-liquid interface represents one molecule, and that the packing is more loose. At the solid-liquid interface, the molecules can be partially solvatated in the phenyloctane[12]), extending in the half-space of the liquid. The 'swimming' of the aliphatic chains of the dendrimers in the phenyloctane solvent could cause a lack of constriction. Furthermore, co-adsorption of solvent molecules[13]) could lead to a larger spacing between the dendrimers. With the additional blurring by thermal motion[14]), it is conceivable that one elliptic spot per molecule is observed at the solid-liquid interface.

On the dry surface, the energy minimization of the self-organization process takes place during the fast evaporation or even in the absence of the solvent (in this case CH_2Cl_2). One could think of a metastable state, where the molecules randomly collapse, inducing high disorder. However, the high degree of order over large areas and domain formation (not shown) rather speaks for another conformation of the molecules. The flexible core moiety would allow a narrow distance between the poly(benzyl ether) branches (see cartoon of molecule in *Fig. 3,b*). This could be a more energetically favored conformation to build a nearly commensurate molecular lattice on a dry HOPG surface.

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[12]) Both the molecules and the solvent contain octyl chains.

[13]) Alkane chains (depending on the tunneling parameters) often do not contribute to the contrast observed by STM.

[14]) Even without thermal motion an overlap of molecular orbitals can effect that only one protrusion is visible. Furthermore, the tip-sample interaction has to be taken into account.

While the solution-casting process requires tedious optimization of the concentration, this is not necessary for STM at the solid-liquid interface working in nearly saturated solutions. On the other hand, the operation time is limited by the evaporation of the solvent (if not sealed in a fluid cell), and the samples can be cooled only to a temperature close to the solidification temperature of the solution. A stimulus by voltage pulse can help to initiate the ordering. It is challenging to distinguish spontaneous ordering of the molecules under the scanning tip from a substantially ordered architecture, which could also, in rare cases, include defects. The probability of finding spontaneous ordering under the tip is much reduced on a dry surface, and, thus, also the possibility of finding ordering at all. The SOM of hourglass dendrimers in a dry environment is not induced by the tip – pictures close to the quality of *Fig. 3,d* could be obtained directly after the tip approached the surface, and, furthermore, defects were visible in exceptional cases (not shown).

Discussion. STM can provide a map of the electronic structure of the accessible orbitals of the molecules interfering with the electronic states of the substrate surface, which inherently depends on the packing of the molecules. As already mentioned, in our case, the contrast in the STM image is caused mainly by the π-orbitals (of the phenyl rings) perpendicular to the basal plane of the substrate [41]. The three-lobed substructure, clearly visible in the low-temperature high-resolution image (*Fig. 2,c*), is in agreement with one of the models[15]) of *Sautet* and *Bocquet* for benzene on Pt surfaces [39]. Comparison of the equally sized *Fig. 3,a* and *b* allows us to count how many phenyl rings approximately fit into a triangular protrusion of the SOM: one triangular protrusion seems to consist of three phenyl rings belonging to one dendrimer arm, blurred due to thermal motion. Thus, one molecule is, indeed, represented by two triangular protrusions, resulting in a butterfly-like shape. This agrees with the interpretation of the SOM image (*Fig. 3,c*) at the solid-liquid interface, where a large spot of about the size of two 'butterfly' wings represents one molecule.

Conclusions. – We have presented a STM study performed on an hourglass-shaped dendrimer according to three different approaches. At low temperatures, single phenyl rings in the dendrimer films could be resolved as three individual protrusions on a Pt(100) surface. In SOMs on the dry surface (under ambient conditions on HOPG), the three phenyl rings of one dendritic arm appear as one triangular protrusion due to thermal motion. Therefore, an individual molecule can be identified as a butterfly. On the other hand, at the solid-liquid interface, one elliptic protrusion corresponds to one molecule.

Thus, the STM results obtained provide evidence that the imaging depends not only on the environmental conditions and the substrate, but also on the chosen approach of STM technique and sample preparation. As the conformation of a molecule is forced to adapt to the given conditions, contrasting images of the same compound can lead to new insights into the adsorption process of molecules on surfaces. This study also proves that a comparison of SPM measurements of different molecular systems should

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[15]) *Sautet* and *Bocquet* modeled benzene rings on various sites of a Pt(111) surface and found cases of hollow-*Kekulé* and hollow regular three-lobed electronic structures.

be undertaken with greatest care, when the chosen approach, preparation, or environment are not the same.

We are very grateful for the collaboration with Prof. *D. Seebach*, who raised questions on structural properties of dendrimers to be answered by SPM and so initiated all the research in the group of *B. A. H.* on large molecules. We would like to acknowledge valuable discussions with *B. Hecht*, *R. Bennewitz* on SNOM and AFM, respectively, and with *H. P. Lang* and *P. Jess* about the multilayer films. This project is supported by the NRP47 *'Supramolecular Functional Materials'*. *B. A. H.* is grateful for a *Liebig* stipend of the *Fonds der Chemischen Industrie* and *BMBF*, Germany, which made the begin of this research much easier.

Experimental Part

Synthesis. The dendrimer was prepared by *P. M.* as part of a study on chiral dendritically modified catalysts within the group of Prof. *D. Seebach* [42][43]. With the chiral dendritic compound presented in this study, (*S*,*S*)-1,4-bis(dimethylamino)-2,3-dimethoxybutane (DDB) was tested as a core moiety for dendritic amine catalysts. The DDB core was synthesized in five steps from (−)-L-diethyl tartrate and coupled with poly(benzyl ether) branches to give the dendritically expanded DDB molecule (molecular weight 1807 Da) [44]. This dendritic compound was fully characterized and shown to be monodisperse and without defects by MALDI-TOF mass spectrometry.

Dry Multilayer Films. For the preparation of the dendrimer films, the molecules were dissolved in CH_2Cl_2 (0.1 mM) and soln.-cast onto mechanically polished and annealed Pt substrates. The measurements were performed in constant-current mode at r.t. with a *DI Nanoscope III* and at 77 K (10^{-6} mbar) with a home-built low-temp. STM. Typical tunneling parameters were a setpoint of 500–800 pA and a bias voltage of 30–70 mV.

Dry Self-Organized Monolayers. The dendrimers (0.24 mM in CH_2Cl_2) were soln.-cast onto freshly cleaved HOPG substrates by spreading 2 to 3 droplets of the soln. onto the substrate. After the solvent evaporation, the measurements were carried out with a *DI Nanoscope III* equipped with a low-current converter operating in constant-current mode at ambient conditions. The tunneling current ranged from 1 to 3 pA at a bias voltage of *ca.* +700 mV. In both approaches on the dry surface mechanically sharpened Pt/Ir (90:10) tips were used.

Self-Organized Monolayers at the Solid-Liquid Interface. The dendrimer molecules were dissolved in phenyloctane, which has a low vapor pressure so that the solvent evaporates slowly. A drop of the nearly saturated soln. was deposited onto a freshly cleaved HOPG substrate. The measurements at the solid-liquid interface were performed with a home-built *Besocke* beetle-type STM running with an *Omicron* controller. The STM was operated in constant-height mode employing electrochemically etched Pt/Ir (80:20) tips. Typical scan parameters were a tunneling current of 1 nA and a bias voltage of 1 V.

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