STM Studies on Nanosized Porphyrin Wheels at the Solid-Liquid Interface

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Abstract. Monolayers of nanometer-sized porphyrin 'wheels' composed of circular hexameric and dodecameric porphyrin macromolecules, can be visualized at the 1-phenyloctane-HOPG interface with the help of ambient STM. By applying a very low tunneling current (1 pA), it is possible to tunnel through layers of molecules of more than 4 nm thick.

INTRODUCTION

The organization of molecules into highly organized functional arrays is an area of research with great potential application in material sciences.[1] Porphyrins are interesting building blocks for the construction of *functional* arrays, because of their (photo)catalytic, electronic and magnetic properties.[2] The construction of nanosized porphyrin assemblies by spontaneous self-assembly of the molecules is an attractive alternative for the construction of porphyrin arrays by multistep and time-consuming covalent synthesis. However, organization of molecules by self-assembly generally involves a complex interplay between kinetics and thermodynamics, and the exact control over the positioning of the constituting components into a desired self-assembled architecture is often far from trivial. One of the greatest challenges, therefore, is to obtain detailed understanding of the factors that play a role in such dynamic processes by translating them to a solid-liquid interface, since this approach allows the use of scanning probe techniques to visualize the self-assembled architectures down to the molecular level. Several scanning tunneling microscopy (STM) studies of porphyrin assemblies on a surface have been carried out, both under ultra-high vacuum conditions[3] and at a solid-liquid interface,[4] and in several cases the surface arrays could be manipulated chemically,[5] or mechanically by the STM tip.[3a,6] Here we report STM studies on self-assembled monolayers of large 'porphyrin wheels' **1** and **2** (Figure 1), which contain 6 and 12 porphyrins, respectively, at a solid-liquid interface. These molecules are macrocycles with a size of several nanometers that have a disk-like structure and which, because of their extended π-surface, were specifically designed to self-assemble into columnar arrays.
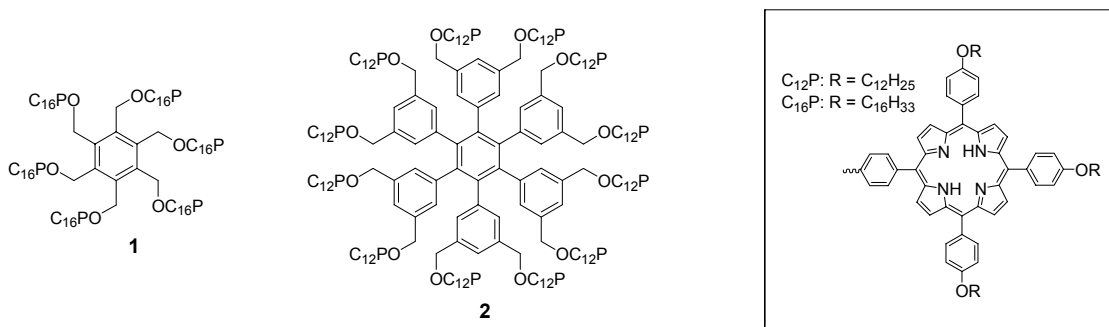
FIGURE 1. Molecular structures of porphyrin wheels **1** and **2**.

RESULTS AND DISCUSSION

The synthesis of **1** has been reported in the literature[7] and the synthesis of **2** will be described elsewhere.[8] Hexamer **1** consists of a benzene core to which six porphyrins are attached via benzyl ether linkers. Dodecamer **2** has an extended core of which the central benzene ring is functionalized with six additional benzene rings. To each of these benzene rings two porphyrins are connected. The porphyrins in **1** and **2** are all functionalized with three aliphatic tails ($C_{16}H_{33}$ tails in the case of **1** and $C_{12}H_{25}$ tails in the case of **2**). The 3-dimensional structures of **1** and **2** in chloroform and toluene solution were determined by molecular modeling, taking into account spectroscopic data of the molecules which were obtained from UV-vis, 1D and 2D proton NMR experiments. It appeared that as a result of favorable intramolecular $\pi-\pi$ interactions between the porphyrins, both molecules adopt a disk-like shape. The six porphyrins of hexamer **1** are organized in three pairs, arranged in a propeller-like fashion around the central benzene ring (Figure 2a). In dodecamer **2**, the twelve porphyrins are arranged in two six-membered flat disks, which are sitting on top of each other with the porphyrins oriented in an offset geometry (Figure 2b).
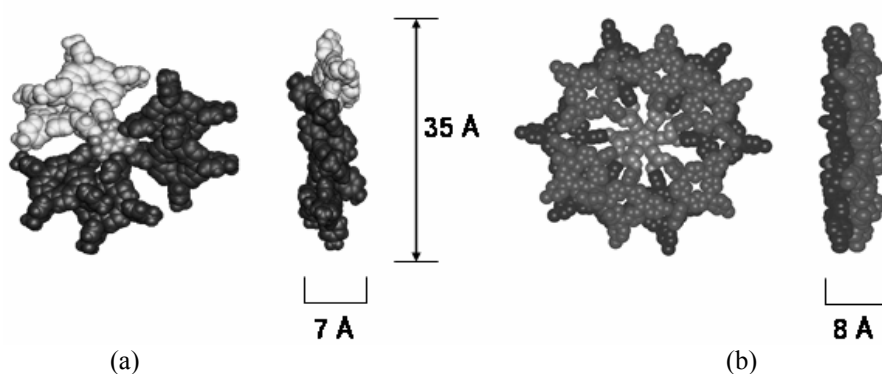

(a)   (b)

FIGURE 2. Computer modelled 3D structures (top and side-view) of porphyrin hexamer **1** (a) and porphyrin dodecamer **2** (b). Alkyl chains have been omitted for clarity.

In solution, porphyrin hexamer **1** and dodecamer **2** are both prone to aggregate into columnar arrays, as was evidenced by proton NMR and fluorescence spectroscopy. To

investigate whether **1** and **2** would also adsorb to a surface in a self-assembled monolayer, STM studies were carried out at a solid-liquid interface.[9] In a typical experiment, a drop of a concentrated solution of **1** or **2** in 1-phenyloctane was deposited onto a freshly cleaved 0001 basal plane of highly oriented pyrolytic graphite (HOPG). The tip (Pt/Ir) was immersed into the drop, and STM images were recorded in the constant current mode applying very low (1 pA or lower) tunneling currents.

Several minutes after the deposition of a drop of a solution of **1** onto the HOPG surface, STM images showed the evolution of a monolayer of the molecules as a well-defined pattern of bright and dark spots (Figure 3a,b), corresponding to the extended aromatic cores of the porphyrins and the aliphatic parts of the molecules of **1**, respectively.[10] The size of each of the bright spots (14 × 15 Å) is in good agreement with the computer-modeled size of one dimer of porphyrins within a single hexamer. It is therefore proposed that three of these bright spots comprise the porphyrins of one hexamer, which is oriented to the surface in a 'face-on' manner (see the schematic molecules superimposed on Figure 3b). In the dark spots the aliphatic tails of the molecules are situated, however, the restricted space that is available requires that only parts of them are adsorbed to the surface whereas other parts are coiled into the supernatant.
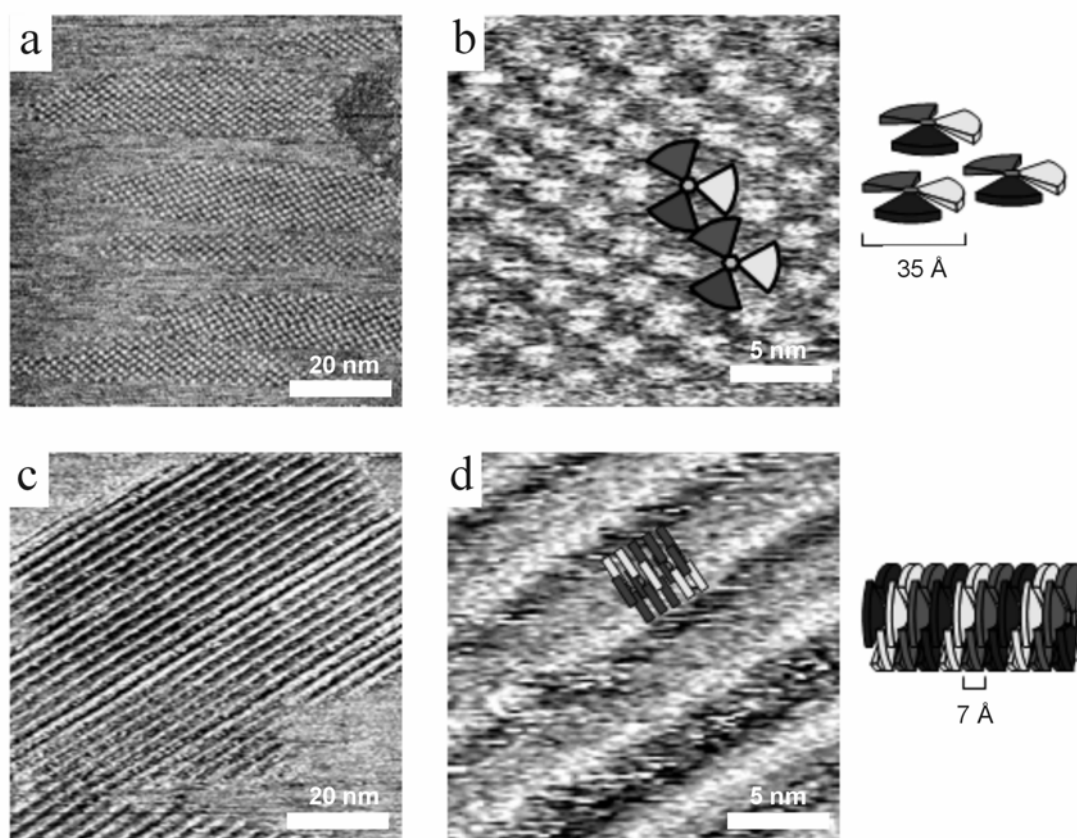

FIGURE 3. STM topograpic images of monolayers of porphyrin hexamer **1** at the interface of HOPG and 1-phenyloctane (V_{bias} = −0.25 V, i_{set} = 1 pA). (a,b) Kinetically formed 'face-on' structures. (c,d) Thermodynamically stable 'edge-on' structures. Schematic molecules of **1** are superimposed onto the magnifications, and next to the images the schematic molecular organization is shown.

After 2-3 hours, the kinetically favored, 'face-on' oriented structures were observed to gradually disappear, and the formation of a completely different molecular organization became evident. Large domains (up to several hundreds of nanometers in size) of a thermodynamically stable lamellar phase evolved (Figure 3c,d). The lamellar distance amounted to 44±1 Å, and the width of 35±1 Å of the bright stripes within the lamellar pattern is in accordance with the diameter of the aromatic surface of the model of **1** (see Figure 2a). Close examination of a magnification of the lamellae revealed that they contain a segmented fine structure (Figure 3d). The periodicity of the segments, as determined from the STM profiles, was 7 Å, which is compatible with the predicted distance between two hexamer centers in a columnar array. The distance is fully in agreement with a proposed columnar arrangement of the molecules of **H$_2$1**, which are oriented orthogonally to the surface in an 'edge-on' orientation.

It required several hours of scanning before a stable monolayer of porphyrin dodecamer **2** became visible at the interface of HOPG and 1-phenyloctane. Eventually, lamellar arrays of **2** slowly evolved, which were hundreds of nanometers long and resembled the lamellar arrays observed for hexamer **1** (Figure 4). The lamellar distance of 43±1 Å is somewhat smaller than that observed for **1**, whereas the width of 34±1 Å of the bright stripes within the lamellar pattern is again in accordance with the diameter of the aromatic surface of the computer modeled structure of **2** (see Figure 2b). In Figure 4b it is clearly visible that the lamellae are columnar arrays of disk-like segments. The distance between two segments of 8±1 Å corresponds exactly to the thickness of one molecule of **2**.
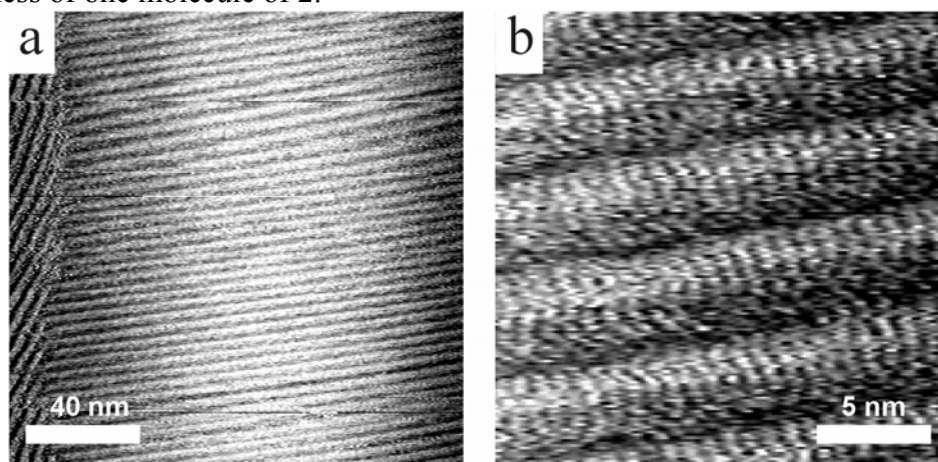

FIGURE 4. STM topograpic images of monolayers of 'edge-on' oriented porphyrin dodecamers **2** at the interface of HOPG and 1-phenyloctane (V_{bias} = –0.25 V, i_{set} = 1 pA).

When the ordering of both porphyrin macrocycles at the solid-liquid interface is compared, it is remarkable that for dodecamer **2** no kinetic structure is observed in which the molecules are oriented 'face-on' to the surface. The reason for this is believed to be the fact that the molecules of **2** self-assemble in solution into a columnar assembly at a much earlier stage than the molecules of **1**, as was also concluded from fluorescence dilution experiments in solution. As a result, the hexamer molecules stay molecularly dissolved for a longer time, which allows them to adsorb 'face-on' to the surface in their monomeric form. After a while they desorb from the

surface again, which allows them to aggregate in solution in small columnar arrays which re-adsorb to the surface to form the thermodynamically stable lamellar structure. It is also clear that the fine structure within the lamellar arrays, *i.e.,* the molecular resolution, is less well-defined in the case of hexamer **1** than in the case of dodecamer **2**. This can be attributed to the fact that the 3-dimensional structure of **2** is more disk-like than that of **1** (see Figure 2), and to the extended π-surface of **2** which is larger than that of **1**; both effects are expected to lead to π–π interactions within the columnar array that are much stronger for the larger porphyrin wheel **2**.

A very important observation is that for both monolayers of columnar arrays of **1** and **2** electron tunneling occurs through a layer of at least 4 nm thick. This might indicate a considerable conductivity of the porphyrin macrocycles in the direction perpendicular to the HOPG surface, however, it should also be noted that visualization of the arrays was possible only if a very low tunneling current of **1** pA was applied. At higher tunneling currents, the images were completely lost, apparently because the tip then contacts the monolayer, resulting in its destruction.

CONCLUSION

It has been demonstrated that it is possible to visualize the organization of porphyrin macrocycles into columnar arrays at the solid-liquid interface of HOPG and 1-phenyloctane. The visualization of these nanometer-sized molecules appeared to be only possible when a very low tunneling current of 1 pA was applied. Current research is focused on the incorporation of metal centers within the centers of the porphyrins. Their organization and visualization at a solid-liquid interface might be an exciting breakthrough in obtaining well-defined surfaces that can exhibit a variety of catalytic and photophysical properties.

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