

## Scanning Probe Studies of Porphyrin Assemblies and Their Supramolecular Manipulation at a Solid–Liquid Interface

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The controlled organization of functional molecules into self-assembled arrays is an area of research with great potential application in material sciences.<sup>[1]</sup> Numerous surfaces have been covered with self-assembled monolayers of molecules and subsequently studied with a variety of scanning probe techniques. In spite of this great interest, a complete control over the specific adsorption of molecules at surfaces, a prerequisite for the construction of predictable and well-defined assemblies, remains difficult to achieve. One route toward obtaining well-defined surface arrays is to use the principles of supramolecular chemistry in tandem with interfacial chemistry. An ideal building block for such an approach is that of a porphyrin, derivatives of which are particularly attractive for the construction of functional surfaces, because of their (photo)catalytic, electronic, and magnetic properties.<sup>[2]</sup> There are many examples of well-defined (metallo)porphyrin arrays that have been constructed via covalent multistep synthesis<sup>[3]</sup> or by using principles of supramolecular self-assembly, e.g., highly predictable metal–ligand coordination,<sup>[4]</sup> hydrogen bonding,<sup>[5]</sup> and  $\pi$ – $\pi$  stacking interactions.<sup>[4b]</sup> The supramolecular approach is less demanding synthetically than the covalent approach, however, the exact control over the positioning of the constituting components into a desired assembly is not trivial. One of the greatest challenges is to obtain detailed understanding of the factors that play a role in these complex and dynamic self-assembly processes.<sup>[6]</sup> In this context, the study of dynamic processes at a solid–liquid interface is of great interest, since it allows the use of scanning probe techniques to visualize the self-assembled architectures down to the molecular level as a function of time. A variety of scanning tunneling microscopy (STM) studies of porphyrin assemblies on a surface have been carried out both in ultra-high vacuum<sup>[7]</sup> and at the solid–liquid interface,<sup>[8]</sup> and in several cases these arrays could be manipulated chemically,<sup>[9]</sup> or mechanically by the STM tip.<sup>[7a,10]</sup> Here, we report studies of dynamic supramolecular self-assembly processes in porphyrin arrays at a solid–liquid interface, and show for the first time that the manipulation of such arrays by metal–ligand coordination can be visualized by STM.

Recently, we have described the synthesis and self-assembly properties of hexakis(porphyrinato) benzenes **H<sub>2</sub>1** and **Zn1** (Fig. 1a).<sup>[11]</sup> From NMR studies it was concluded that in solu-

tion these molecules adopt a disk-like shape, in which the six porphyrins are arranged in three pairs around the central benzene core (Fig. 1b).

Compounds **H<sub>2</sub>1** and **Zn1** form stable Langmuir monolayers on water<sup>[12]</sup> and micrometer-sized rings on solid substrates.<sup>[11,12]</sup> Optical techniques indicated that in both types of assemblies,  $\pi$ – $\pi$  interactions between the extended  $\pi$ -surfaces of the hexamers are the primary driving force for the molecules to self-assemble into columnar stacks.<sup>[12]</sup> In order to study the assembly of these disks on a surface, a drop of a concentrated 1-phenyloctane solution of **H<sub>2</sub>1** was deposited onto a sample of highly oriented pyrolytic graphite (HOPG). Immediately, STM images showed the evolution of a monolayer of the hexamers at the solid–liquid interface (Fig. 2a). Apart from these domains, disordered regions were present in which, apparently, molecules of **H<sub>2</sub>1** had not yet been aggregated and/or exchanged too rapidly with the molecules in the solution to be resolved at the scanning speed applied. In the ordered domains, the well-defined pattern of comparably sized bright and dark spots, respectively, corresponds to the extended aromatic cores of the porphyrins and the aliphatic parts of the molecules of **H<sub>2</sub>1**.<sup>[13]</sup> The size of each of the bright spots (14 Å × 16 Å) is in good agreement with the modeled size of one dimer of porphyrins within a single hexamer. We therefore can readily propose that three of these bright spots comprise one porphyrin hexamer, which is oriented to the surface in a “face-on” manner (see Fig. 2a).

After 2–3 h 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 more favorable lamellar phase evolved (Fig. 2b), which appeared as bright and dark stripes. The measured inter-lamellar distance of  $43 \pm 2$  Å and width of  $35 \pm 1$  Å of the bright stripes is in accordance with the diameter of the aromatic surface of the model of **H<sub>2</sub>1**. Close examination of a magnification of the lamellae revealed that they contain a segmented fine structure (Fig. 2b, magnification). 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 and is the result of two  $\pi$ – $\pi$  stacking interactions ( $2 \times 3.4$  Å, see Fig. 3c). The distance is fully in agreement with a proposed lamellar arrangement of the molecules of **H<sub>2</sub>1**, which are orthogonal to the surface in an “edge-on” orientation.<sup>[14]</sup> The ability of electron tunneling to occur through a layer, which is more than 4 nm in thickness, highlights the remarkable conductivity of the molecules.<sup>[15]</sup>

Earlier ultraviolet (UV) and fluorescence studies indicated that in solution the molecules of **H<sub>2</sub>1** tend to aggregate into columnar structures stabilized by  $\pi$ – $\pi$  interactions between the large aromatic surfaces.<sup>[11,12]</sup> This process, in combination with the dynamic nature of the adsorption and desorption equilibria of the molecules at the solid–liquid interface, can explain the observed change in surface organization. Whereas it can be expected that the adsorption of one single molecule

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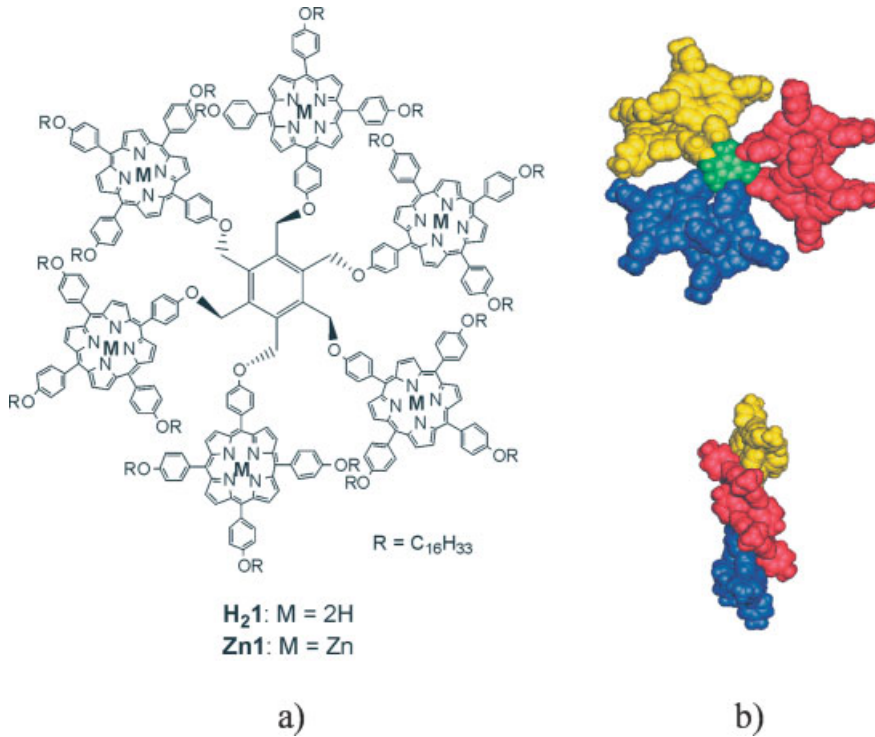


Fig. 1. a) Porphyrin hexamers **H<sub>2</sub>1** and **Zn1**. b) Computer modeled structure of the aromatic core of **1** revealing the propeller-like architecture (front and side view), based on NMR and UV experiments.

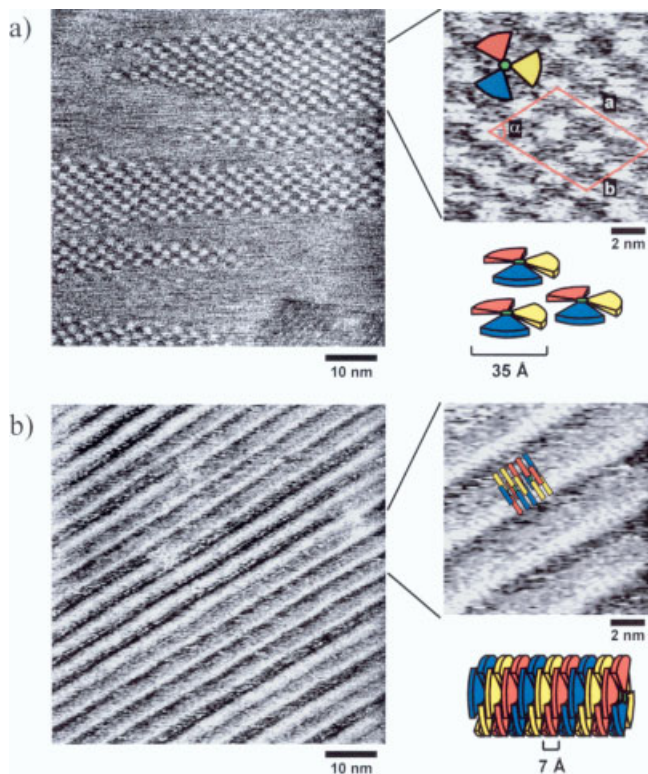


Fig. 2. a) STM topography of a domain of “face-on” oriented molecules of **H<sub>2</sub>1** on HOPG ( $V_{\text{bias}} = -250$  mV,  $i_{\text{set}} = 1$  pA); one schematic molecule of **H<sub>2</sub>1**, in which each of the triangular lobes represents one dimer of porphyrins, is superimposed onto the high-resolution image; unit cell (containing two molecules of **H<sub>2</sub>1**):  $a = 72 \pm 2$  Å,  $b = 49 \pm 2$  Å,  $\alpha = 61 \pm 2^\circ$ . b) STM topography of a domain of columnar arrays of “edge-on” oriented molecules of **H<sub>2</sub>1** on HOPG ( $V_{\text{bias}} = -250$  mV,  $i_{\text{set}} = 1$  pA); five schematic molecules of **H<sub>2</sub>1** are superimposed onto the high-resolution image.

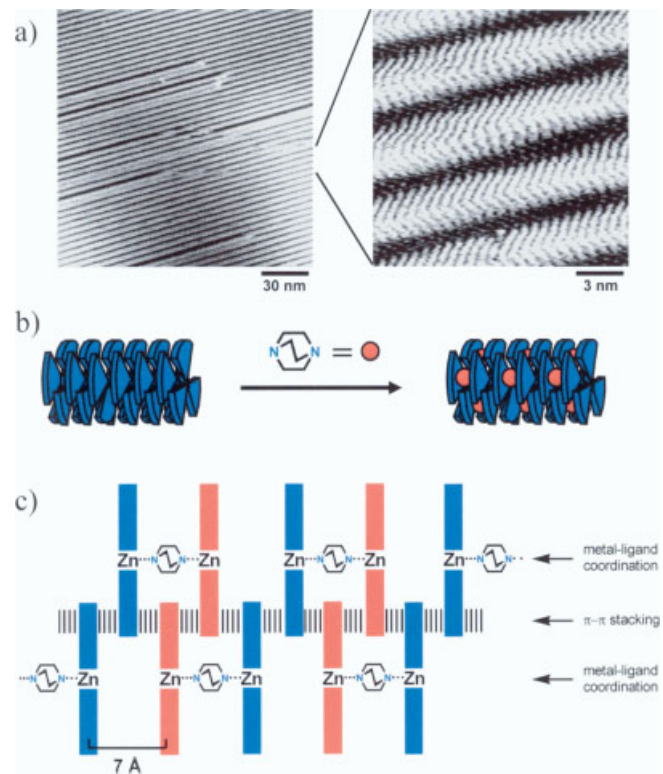


Fig. 3. a) STM topography and a high-resolution image of a domain of “edge-on” oriented complexes of **Zn1** and DABCO on HOPG ( $V_{\text{bias}} = -220$  mV,  $i_{\text{set}} = 1$  pA). b) Proposed consequences of the addition of DABCO, which connects the molecules of **Zn1** intermolecularly resulting in a better defined columnar structure. c) Schematic side-view of this interconnection; the red and blue bars represent zinc porphyrin pairs of adjacent hexamers, which interact via both DABCO ligand coordination and  $\pi$ - $\pi$  interactions (dashed lines) between the aromatic surfaces (for clarity only one porphyrin pair per molecule of **Zn1** is shown).

of **H<sub>2</sub>1** on HOPG in an “edge-on” manner is relatively unfavorable, the “edge-on” adsorption of small columnar oligomers of molecules of **H<sub>2</sub>1**, which are pre-assembled in solution only after a period of time, can become more favorable than adsorption of the molecules in a “face-on” orientation. These “edge-on” positioned oligomers act as a seed, from which the lamellar arrays grow.

To develop this hypothesis more fully, the surface self-assembly properties of **Zn1** were also investigated with STM, since the aggregation of this molecule can be manipulated by the addition of coordinating axial ligands. For **Zn1** only “edge-on” oriented assemblies (inter-lamellar distance  $42 \pm 2$  Å) were observed, which are very similar to those formed by **H<sub>2</sub>1** (image not shown). The lack of a kinetically favored “face-on” orientation is thought to be the result of the potential of zinc porphyrins to bind an axial ligand, which would inhibit a “face-on” orientation (e.g., a trace of water present in the solution), and the increased  $\pi$ - $\pi$  interactions between the molecules.<sup>[16]</sup>

The fact that **Zn<sup>II</sup>** porphyrins have one vacant coordination site to which nitrogen containing ligands can strongly coordinate opens up the possibility to manipulate the assemblies of **Zn1** by metal-ligand coordination. Upon the addition of the bidentate ligand diaza[2.2.2]bicyclooctane (DABCO) to a solution of **Zn1** in 1-phenyloctane, the porphyrin Soret band in the UV-visible (UV-vis) spectrum displayed a bathochromic shift of 3 nm, indicating coordination of an axial ligand. A UV-vis titration revealed that even in the presence of a 10-fold excess of DABCO only three molecules of the ligand are strongly bound to one molecule of **Zn1** ( $K_a = 8.4 \times 10^6$  M<sup>-1</sup>). To investigate the consequences of such a molecular recognition process on the surface ordering of the hexamers, a concentrated sample of **Zn1** containing a 10-fold excess of DABCO in 1-phenyloctane was studied by STM. Instantaneously, large domains (>400 nm × 400 nm) of lamellar assemblies of “edge-on” positioned molecules of **Zn1** were observed, which were stable for many hours (Fig. 3a). Within the lamellae, the molecules can be clearly distinguished and the fine structure present in the arrays is more defined than in the “edge-on” assemblies formed by **H<sub>2</sub>1** and uncomplexed **Zn1**. The mutual distance between the molecules of **Zn1** in the presence of DABCO remained 7 Å, identical to that observed for uncomplexed **Zn1**. This distance is fully compatible with a columnar array on the surface in which the molecules of DABCO bind to **Zn1** in an intermolecular fashion, interconnecting the porphyrin hexamers (Figs. 3b,c). The increase in definition and size of the domains formed can be directly correlated to the increase in strength of the intermolecular interactions. This intermolecular complexation was also confirmed by <sup>1</sup>H NMR spectroscopy of the complex in [D8]-toluene solution. The DABCO molecules could not be observed directly in the STM images, but the increase in stability and definition of the lamellae must be a direct result of their supramolecular coordination. Molecular modeling revealed that in the case of intermolecular complexation of DABCO (N-N distance 3.8 Å) the strong  $\pi$ - $\pi$  interactions between adjacent zinc porphyrin

hexamers can still be preserved at the same time as axial ligation (Fig. 3c).<sup>[17]</sup>

To investigate if the relationship between supramolecular architecture and surface array formed is correct, studies were carried out on the self-assembly behavior of **Zn1** in the presence of a bidentate ligand, which according to molecular modeling is too large (7–8 Å) to allow the hexamers, once connected, to retain any intermolecular  $\pi$ - $\pi$  interaction. In the same way as for the **Zn1**-DABCO complex, a concentrated sample of **Zn1** and a 10-fold excess of 4,4'-bipyridine (BIPY, N-N distance 8 Å) in 1-phenyloctane was deposited on HOPG and studied by STM.<sup>[18]</sup> Huge domains (>500 nm × 500 nm) of only “face-on” arranged molecules of **Zn1** became immediately visible (Fig. 4a). In all STM experiments, no “edge-on” arranged molecules were observed. In contrast to the “face-on” structure observed for **H<sub>2</sub>1**, each bright spot

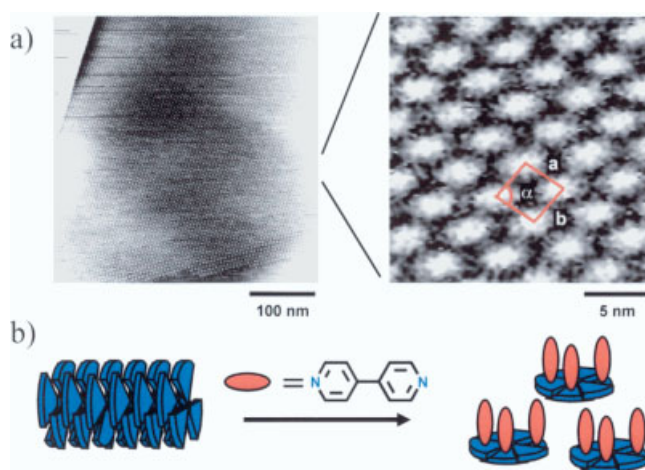


Fig. 4. a) STM topography and a high-resolution image of a domain of “face-on” oriented complexes of **Zn1** and BIPY on HOPG ( $V_{\text{bias}} = -180$  mV,  $i_{\text{set}} = 1$  pA); each white spot represents one molecule of **Zn1**; unit cell:  $a = 61 \pm 2$  Å,  $b = 56 \pm 2$  Å,  $\alpha = 82 \pm 3^\circ$ . b) Proposed model of the structure after the addition of BIPY ligands, which inhibit intermolecular  $\pi$ - $\pi$  interactions between the molecules of **Zn1** within the columnar stack; as a result the hexamers adopt a “face-on” orientation with respect to the HOPG surface. In the scheme, three molecules of BIPY are coordinated to one molecule of **Zn1**, but in principle the coordination of maximally six molecules of BIPY is possible.

now has a diameter of 36 Å, which corresponds exactly to the diameter of the aromatic surface of **Zn1**. The shape and lack of definition of the spots indicates a more dynamic distribution of the porphyrins within one hexamer on the surface. While there is some fine structure present, single porphyrins of **Zn1** within the spots could not be clearly distinguished, and no conclusions could be drawn about the number of coordinated ligand molecules. The complete absence of “edge-on” oriented assemblies indicates that the BIPY ligands indeed act as inhibitors to columnar stacking and direct the molecules of **Zn1** into a “face-on” arrangement to the surface (Fig. 4b).

In summary, we have been able to visualize dynamic self-assembly and metal-ligand coordination processes of large porphyrin hexamers at a HOPG-1-phenyloctane interface. A subtle balance between interfacial and intermolecular forces dictates the supramolecular organizations formed, which are

oriented either “face-on” or “edge-on” on the surface. The generation of micrometer-sized, stable, and highly organized domains of “edge-on” or “face-on” oriented zinc porphyrin hexamer assemblies can be controlled by the addition of coordinating axial ligands, which control the supramolecular architecture formed. Such a precise and unique control over surface organization, as well as its visualization with STM, is of great interest for future applications of these porphyrin assemblies. Future research will be directed to obtaining even more control over the organization of the porphyrin hexamers by varying conditions such as the temperature and concentration of the self-assembling components. In addition, the effect of other coordinating, e.g., chiral ligands, which can induce chirality into the arrays, and the replacement of the Zn<sup>II</sup> ions by Mn<sup>III</sup> ions, which can provide the molecules with magnetic and catalytic properties, resulting in well-defined functional surfaces, will be studied.

## Experimental

STM measurements were carried out in the constant current mode using a home-built low-current STM. For each experiment the HOPG surface was freshly cleaved and the STM tips were mechanically cut from a Pt:Ir (80:20) wire. A drop of a nearly saturated solution of molecules or complexes in 1-phenyloctane was brought to the surface. Typically, an STM image (1024 lines × 1024 points) was recorded over a period of 10 min. All STM experiments were carried out at least in duplicate, and the raw data were processed only by the application of background flattening. Before and after the experiments the piezo was calibrated in-situ by lowering the bias voltage to 100 mV and raising the tunneling current to 50 pA, which allowed imaging of the HOPG surface underneath the molecules.

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- [16] Experimental data and molecular modeling calculations have shown that  $\pi$ - $\pi$  interactions between zinc porphyrins are stronger than between free base porphyrins. See: C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, 112, 5525.
- [17] The herringbone-like fine structure observed by STM is tentatively attributed to the propeller-like structure of the molecule (see Biemans et al. [11]) and is currently under further investigation.
- [18] UV-vis and <sup>1</sup>H NMR data showed that in solution the BIPY ligands bind to Zn1 orders of magnitude weaker than to DABCO, however, the complicated UV-vis titration curves were inconclusive about the binding stoichiometry.

## Vapor-Liquid-Solid Growth of Silicon-Germanium Nanowires\*\*

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The fabrication of semiconductor nanowires with built-in heterostructures along the radial or longitudinal direction is of interest, both for fundamental studies of carrier confinement effects in these materials as well as nanoscale device development.<sup>[1]</sup> In the group IV semiconductor system, vapor-liquid-solid (VLS) growth is commonly used to fabricate Si and Ge nanowires.<sup>[2-6]</sup> In VLS growth, a metal catalyst, such as gold (Au), is used to catalyze the decomposition of a source gas, such as silane (SiH<sub>4</sub>) or germane (GeH<sub>4</sub>), resulting in the formation of a Au-Si or Au-Ge liquid alloy provided that the temperature is greater than the eutectic temperature of the alloy. A nanowire is precipitated from the liquid alloy when it becomes supersaturated with Si or Ge. Based on the binary phase diagrams, the eutectic temperatures of Au-Si<sup>[7]</sup> and Au-Ge<sup>[8]</sup> are essentially identical (~360 °C), which would suggest that similar growth conditions could be used to form SiGe alloy nanowires and heterostructures. While there have been numerous studies of individual Si and Ge nanowire syn-

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