Controlled Templating of Porphyrins by a Molecular Command Layer

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Supporting Information

ABSTRACT: The copper porphyrin (5,10,15,20-tetraundecylporphyrinato)copper(II) can be templated in a well-defined arrangement using p-(hexadecyloxy carbonyl)phenylacetylene as a command layer on graphite. The bicomponent system was characterized at the submolecular level at a solid/liquid interface by scanning tunneling microscopy (STM). It is proposed that the layer of copper porphyrins is templated on top of the command layer in a hierarchical fashion, via a combination of intermolecular π−π stacking and van der Waals interactions. A very subtle effect, i.e., a superstructure in the alkyl chain region of the phenylacetylene monolayers, was identified as a decisive factor for the templating process.

INTRODUCTION

The application of single molecules as the smallest building blocks for functional nanodevices continues to be a topic of intensive research.1–4 For their characterization by microscopic techniques and their implementation in a working device it is essential to immobilize these molecules on a surface and to get their adsorption geometry under full control.5 Detailed scanning tunneling microscopy (STM) studies have revealed that in the fields of molecular electronics6–9 and single molecule catalysis,10–17 a specific surface monolayer structure can be closely related to its function.18 For the expression of single molecule function, the organization of molecules in large aggregates at a surface should be prevented, but this is still a challenge. At a solid/vacuum interface it is possible to deposit submonolayers of molecules by using evaporation or spraying techniques, but not all molecules are suitable for such a treatment. At this interface, however, the possibilities to obtain specific two-dimensional (2D) patterns of molecules are rapidly increasing by combining modeling studies with a careful molecular design.19 Alternatively, molecular layers can be created by means of self-assembly at solid/liquid interfaces, but with this approach molecules tend to arrange themselves into closely packed 2D crystals, fully covering the available surface. Most approaches to achieve a high level of control over 2D molecular self-assembly at a solid/liquid interface make use of a careful chemical design of the building blocks, to force them to interact with each other via well-defined and directional supramolecular interactions.20 In recent years, however, atomic force microscopy (AFM) and STM studies have revealed that also physical parameters, such as dewetting,21–24 flow,25 the concentration of solutes in the liquid phase,26–30 and variations in the temperature,31,32 can play a decisive role in the outcome of a molecular self-assembly process.

When it comes to the self-assembly of ordered multicomponent systems at a solid/liquid interface, the use of 2D porous surfaces, in which guest molecules can be captured and thereby isolated from each other, has proven to be highly successful.33 As guests, molecules are often used that are not easily immobilized in an unaggregated form at a surface, such as bucky balls34,35 and graphene-like derivatives.36–39 A different, less frequently reported approach to the positioning and isolating of molecules at well-defined locations on a surface is by making use of a templating monolayer of molecules for the target molecules adsorbing on top of them. In this way, for example, monolayers of fatty acids have been used to template urea,40,41 nitrobenzene derivatives,42 and gold particles,43 monolayers of alkylamines to template benzoic acid,44 phthalocyanines,45,46 and DNA,47 monolayers of shape-persistent macrocycles to template metallacycles,48 monolayers of oligo(phenylene-ethynylene) molecules to template sandwich lanthanide phthalocyanine complexes,49 and monolayers of Zn-porphyrins to template 3-nitropyridine molecules.50 Recently, a combination of templating by a porous network and by a molecular template was reported, where heterocirculenes were captured in self-assembled networks of trimesic acid, and templated in multilayers.51

Here we present the templating behavior of p-(hexadecyloxy carbonyl)phenylacetylene (1) (Scheme 1) at a solid/liquid interface. STM studies reveal that layers of 1 are capable of templating a second layer of the copper porphyrin (5,10,15,20-tetraundecylporphyrinato) copper(II).
20-tetradecylporphyrinato)copper(II) (2, CuTUP) in highly distinct 2D patterns, and that subtle structural features in the templating layers, such as the presence of a superstructure, have a profound influence on the templating process.

RESULTS AND DISCUSSION

2D Self-Assembly Behavior of Pure 1 and Pure 2. Self-assembled monolayers of the phenylacetylene 1 were studied by STM at the graphite/1-phenyloctane interface. A 3−5 μL droplet of a solution of the compound was applied to the surface. In the concentration range 5 × 10^{-3} to 1 × 10^{-2} M, a monolayer structure as shown in Figure 1a was observed. Lamellar arrays are visible, with bright areas corresponding to the phenyl head groups lying flat ("face-on") on the surface. Within the lamellae these head groups are arranged in a zigzag configuration, while the alkyl chains are interdigitated and appear oriented nearly perpendicular to the lamellar troughs. The lamellar periodicity is 3.4 ± 0.1 nm and the distance between the centers of two adjacent phenyl rings corresponds to 0.71 ± 0.06 nm. Overall, the molecular density is 0.83 ± 0.09 molecules/nm². By changing the tunneling resistance while scanning, the monolayers could be imaged alternatingly with the underlying graphite lattice, which revealed that the alkyl chains are preferentially aligned in the direction of one of the graphite main symmetry axes (see figure in Supporting Information).

For some of the alkyl chains visible in the STM image in Figure 1a their topography shows two dots per carbon atom, an effect that has been attributed to alkyl chains oriented perpendicular to the graphite surface. On average, the alkyl chains of 1 are 0.36 ± 0.03 nm apart, which is a somewhat smaller distance than observed for n-alkanes perpendicular to a graphite surface (0.41−0.42 nm). The often observed presence of a superstructure in the alkyl chain region of 1 along the lamellar direction (Figure 1c) suggests that the alkyl chains are not commensurate with the underlying graphite, which corroborates the fact that the distance between these chains is smaller than expected. The periodicity of the superstructure, a_s = 2.1 ± 0.1 nm, corresponding to 6 molecules of 1, and it has an angle, γ_s of 83 ± 7° with respect to the lamellar troughs. The value of 2.1 nm also corresponds to a value that would be expected for an array of 5 alkyl chains that are commensurate with the graphite lattice. A cross-section through the alkyl chains shows an apparent height difference in the alkyl

Scheme 1. Molecular Structure of Phenylacetylene Derivative 1 and CuTUP 2

Figure 1. (a) STM topography of a molecular layer of 1 on the graphite/1-phenyloctane interface. The unit cell is drawn: a = 0.71 ± 0.05 nm, b = 3.4 ± 0.1 nm, γ = 83 ± 7°. Main directions of the underlying graphite are indicated by the white lines. Concentration: 1 × 10^{-2} M. V_{bias} = 860 mV, I_{set} = 575 pA. (b) Proposed corresponding molecular model, the unit cell is drawn. (c) STM topography of a molecular layer of 1 on the graphite/1-phenyloctane interface showing the superstructure in the alkyl chains. Its unit cell is drawn: a_s = 2.1 ± 0.1 nm, b_s = 3.4 ± 0.1 nm, γ_s = 83 ± 7°. An angle α is indicated, defining the direction with respect to the lamellae of 1. Concentration: 1 × 10^{-4} M. V_{bias} = 450 mV, I_{set} = 10 pA. (d) Cross-section, corresponding to the red trace in (c).
chains of about 0.05 nm (Figure 1d). Similar values were found for measurements carried out at other bias voltages (i.e., at −600, −450, +300, and +400 mV). While such a superstructure can be an electronic effect, it is also possible that its cause is geometric in nature, due to the observed “buckling” of the alkyl chains. The reason for the incommensurability of the alkyl chains with the graphite lattice might be a misfit with the adsorption of the phenyl groups of 1 and the surface.

The self-assembly behavior of porphyrin CuTUP 2 on a surface was also studied by STM. A 5 μL droplet of 1-phenyloctane containing 2 in a concentration of $1 \times 10^{-4}$ M was applied to a graphite surface, and in the resulting monolayer the molecules, which are arranged in lamellar arrays, could be clearly resolved (Figure 2). The unit cell was determined to be $a = 1.26 \pm 0.05$ nm, $b = 2.05 \pm 0.05$ nm, and $\gamma = 79 \pm 4^\circ$. Each molecule occupies about 2.5 ± 0.3 nm$^2$. Taking into account that the porphyrin core occupies an area of about 0.8 nm$^2$, an area of 1.7 ± 0.3 nm$^2$ is left for the alkyl chains, which are poorly resolved. Since one undecyl chain occupies about 0.6 nm$^2$, this suggests that per molecule of 2 three of the four alkyl chains are adsorbed on the surface, leaving the fourth probably dissolved in the supernatant solution.

**Templating Properties of Molecular Layers of 1.** When the molecular layer of the phenylacetylene 1 (Figure 1) was used as a command layer, the molecules of the porphyrin CuTUP 2 appeared to become templated in a highly distinct organization. The bicomponent surface structure was prepared by first bringing a 3 μL droplet of a $1 \times 10^{-3}$ M solution of 1 in 1-phenyloctane on the graphite surface. After confirming with STM that an ordered monolayer structure had been formed, a 3 μL droplet of a $1 \times 10^{-4}$ M solution of 2 in 1-phenyloctane was carefully added and the changes in surface structure were monitored over time. At these concentrations, typically after 11–15 h domains started to form a “dotted” layer of molecules of 2 on top of the layer of 1 (Figure 3a). The rather long time it takes for this bicomponent structure to start forming is attributed to a slow evaporation of the 1-phenyloctane solvent, leading to a gradual increase in the concentrations of 1 and 2. At higher starting concentrations of 1 and 2 the bicomponent structure was found to form faster (e.g., at concentrations of 1 and 2 of $5 \times 10^{-3}$ and $5 \times 10^{-3}$ M, respectively, small domains of the templated structure already appeared within tens of minutes). The bicomponent domains grew steadily over time, until they eventually completely covered the surface 4–7 h after observing the first “dots” (Figure 3b,c; see also movie in Supporting Information). Identical bicomponent structures were formed when the experiment was started with a monolayer of 2 followed by the addition of a solution of 1, or when the two components were premixed in solution. This indicates that the observed final structure is the thermodynamically favorable one. There is, however, a delicate concentration balance; if the concentration of 1 is not at least an order of magnitude higher than the concentration of 2, exclusively a layer of 2 is formed (as observed in Figure 2) instead of the templated bicomponent structure.

The formation of the bicomponent domains is not tip-induced, because STM images at remote locations revealed the same population of “dots”. The molecules of 2 lie on top of the monolayer of 1 and are not integrated with it, which was concluded from the STM images in Figure 4. In Figure 4a,b two consecutively scanned STM images with a 3 min interval are shown. In the second image a whole array of molecules of 2 has shifted position to an adjacent lamella (indicated by the ellipse). This can be either due to a spontaneous reorganization or induced by the STM tip. An incorporation of the molecules of 2 in the underlying layer of 1 appears highly unlikely, since such a collective accommodation would require a number of synchronous movements. Furthermore, the relatively large apparent height difference resulting from a comparison of the cross sections of a templated molecule of 2 (Figure 4b) and a molecule of 2 on bare graphite (Figure 2c) supports the conclusion that the molecules of 2 lie on top of the monolayer of 1.

The STM images clearly show that the molecules of CuTUP 2 are templated by the molecular layer of phenylacetylene 1 in a highly specific geometry. They are centered on top of the bright lines corresponding to the aromatic moieties of 1. Only in very few cases were molecules of 2 observed on top of the alkyl chains, but these never stayed there for longer than ~10 min. Those on top of the aromatic moieties of 1 generally remained immobilized for more than 15 h, although there appeared to be still some lateral dynamics (as can be seen in Figure 4a,b). It was found that isolated templated molecules of 2, which were not part of a templated domain, were less stably bound and usually
disappeared within several minutes. Within a templated domain the molecules of 2 remain strongly immobilized, and the growth of the domains (Figure 3 and movie in Supporting Information) indicates that the molecules of 2 do not return into the solution but stay on the surface. In the case of desorption, it is expected that during measurements at low concentrations vacancies would appear that could not be immediately replaced, but such defects were never observed.

In the immobilization of porphyrin CuTUP 2 by the templating layer of phenylacetylene molecules 1, favorable face-to-face $\pi-\pi$ stacking interactions between the aromatic groups of 1 and the porphyrin plane of 2 are proposed to play an important role: the extended aromatic planes of 2 are almost exclusively situated on top of the phenyl and acetylene groups of 1. By correlation averaging of 50 molecules of 2 templated by a molecular layer of 1, $V_{bias} = -400$ mV, $I_{set} = 1$ pA. Inset: molecular models of the porphyrin center of 2 and half the molecule of 1 are superimposed on the STM image.
submolecular structure of a fully immobilized molecule of 2 could be revealed (Figure 4c). In this image, the “four-leaf clover” shape of 2 and the alkyl and phenyl groups of 1 become recognizable. In Figure 6 schematic computer models of the top and side view of the bicomponent structure are shown, based on the STM images. From the side view it can be seen that besides the proposed favorable \( \pi-\pi \) stacking interactions there might also be a favorable docking effect of the porphyrin ring of 2 in the lamellar troughs of the templating layer of 1.

In related work, alkylamines \(^{45,46} \) and oligo(phenylene-ethynylene)s (OPEs) \(^{49} \) were used as templating layers for phthalocyanines. In the case of the template of alkylamines, the phthalocyanine cores were located on the alkyl chains of the templating layer, which is opposite to our findings. In the case of the template of OPEs, the phthalocyanine derivatives were not templated on top of specific parts of this layer, but in a close-packed molecular arrangement.

Besides the observation that the molecules of CuTUP 2 are almost exclusively centered on the aromatic parts of the layer of 1, it is obvious from the STM images that they are distributed nonrandomly on the template. Remarkably, every time a molecule of 2 is on top of the aromatic parts of a lamella of the phenylacetylene 1, the corresponding aromatic parts of the adjacent lamellae remain uncovered. This peculiar distribution cannot straightforwardly be explained by the \( \pi-\pi \) stacking interactions between the aromatic groups of 1 and the porphyrin plane of 2, and it therefore appears that other interactions also play an important role. Since the average molecular density of templated 2 was quite large (3.5 \( \pm \) 0.9 molecules per 100 nm\(^{2} \)), it is possible to quantify the distribution of 2 on the template. For this purpose 2807 templated molecules of 2 from 5 different STM measurements were localized. Figure 5a shows the spatial distribution function, which gives the ratio of the local density and the average density, within a range of 15 nm of a reference porphyrin molecule located in the center of the plot, at \((x = 0, y = 0)\).

In the direction almost perpendicular to the lamella (\( \alpha = 83^\circ \)), the smallest distance observed between two templated molecules of CuTUP 2 is 6.8 \( \pm \) 0.3 nm (peak A in Figure 5a), while the lamellar periodicity of the monolayer of phenylacetylene 1 is only 3.4 nm. Only 0.5% of all 2807 localized molecules of 2 had a close neighbor on an adjacent lamella. Molecules of 2 can be templated on the adjacent lamellar trough, but only when they make an angle \( \alpha \) of at most 56° with that lamellar trough (e.g., peak B in Figure 5a). In that case, the distance between the porphyrins is 4.0 \( \pm \) 0.7 nm.

Taking into account that the underlying template has a superstructure, it was investigated whether this superstructure was a determinative factor for the distribution of the porphyrins. Preferred adsorption sites related to a superstructure have recently been reported for copper phthalocyanines and buckyballs on a molecular command layer, in an ultrahigh vacuum environment.\(^{56} \)

When the superstructure observed in the alkyl chain regions of 1 (\( a_1 = 2.1 \pm 0.1 \) nm, \( b_1 = 3.4 \pm 0.1 \) nm, \( \gamma_1 = 83 \pm 7^\circ \); see Figure 1c) is compared with a grid fitted through peaks A and B (\( a_G = 2.1 \) nm, \( b_G = 3.4 \) nm, \( \gamma_G = 83^\circ \), see Figure 5a), one can see that these values correspond closely. We therefore propose that the preferred locations of 2 on the lamellae of 1 are governed by the superstructure. Since the superstructure was only observed in the alkyl chains of 1, and not in its aromatic parts, the only way that it can influence the templating of 2 is via intermolecular interactions between the alkyl chains. In the STM image in Figure 1d it was shown that parts of the

![Figure 5](dx.doi.org/10.1021/la104724v/figlangmuir2011,27,2644–2651)
superstructure in 1 have an increased apparent height. If this increase is caused by a geometric effect (as opposed to an electronic effect), it can explain why preferred adsorption spots of 2 are governed by the superstructure. In that case, some of the alkyl chains of 1 are geometrically higher than their neighbors and as a result they can interact via van der Waals interactions with the alkyl chains of templated molecules of 2. By assuming such “anchor points”, it can also be explained why the corresponding location on the adjacent lamella next to a templated molecule of 2 on top of the molecular layer of 1.

Figure 6. (a) Schematic computer-modeled representation showing the molecular layer of 1, and molecules of 2 lying on top of this layer. The two competing mechanisms for the templating behavior are visible. Two unit cells of the superstructure in the alkyl chains of 1 are drawn, as well as molecules of 2 with interacting alkyl chains along the lamellar trough. The distance of 2.5 nm between these molecules of 2, corresponding to peak C in Figure 5b, is indicated by the arrow. (b) Side view of a single templated molecule of 2 on top of the molecular layer of 1.

CONCLUSIONS

At the solid/liquid interface of graphite and 1-phenyloctane, the phenylacetylene 1 self-assembles in an ordered molecular layer, which templates copper porphyrin CuTUP 2 in a well-defined pattern. In this templating, the superstructure in the alkyl chains of the layers of 1 plays a decisive role, leading to preferred adsorption spots for the molecules of 2. It is proposed that these preferred adsorption spots are the result of geometrically higher alkyl chains in the templating layer of 1, which can have favorable van der Waals interactions with the alkyl chains of the molecules of 2.

The molecular layer of 1 templates the molecules of 2 via face-to-face π–π stacking interactions into individual entities that are centered on the lamellar troughs of the monolayer of 1. The sequence in which 1 and 2 were added to the surface did not influence the final arrangement, indicating that the bicomponent structure is thermodynamically favored. Perpendicular to the lamellar troughs the adsorption site on the adjacent lamellar molecules of 2 with fully stretched, interacting alkyl chains. It is proposed that interacting alkyl chains between two molecules of 2 along the lamellar trough have a stabilizing effect on these templated molecules (Figure 6a).

Apparently, in addition to favorable π–π stacking interactions between the aromatic groups of 1 and the porphyrine plane of 2, two competing interactions are at work in the templating process. On the one hand, the superstructure provides anchor points for adsorption of 2 on top of the template, as a result of van der Waals interactions between the alkyl chains of 2 and specific alkyl chains in the templating layer of 1, and on the other hand, there is a stabilizing effect when molecules of 2 can have interacting alkyl chains along a lamellar trough. These competing mechanisms are illustrated in Figure 5c, in which a superstructure grid with a repeating distance of 2.1 nm (a1) is plotted on the STM topography of templated molecules of 2. Going from top to bottom in the figure, it can be seen that after a few unit cells of the superstructure of 1 the porphyrin molecules 2 do not follow this superstructure anymore. This deviation is the result of two molecules of 2 being present next to each other on the same lamella, stabilized at a distance of 2.5 nm as a result of their interacting alkyl chains. After an additional number of unit cells of the superstructure, however, the superstructure-controlled arrangement of templated molecules of 2 re-establishes itself, i.e., the templated molecules of 2 coincide again with the grid of the unit cells of the superstructure.

In Figure 6, a schematic representation of the bicomponent structure is shown; the geometry is computer-modeled and is based on all the STM observations and proposed intermolecular interactions. The distance between the phenyl rings of the phenylacetylene 1 in the layer fits well with the distances between the pyrrole rings of porphyrin CuTUP 2, maximizing the possibility for favorable face-to-face π–π interactions. In this model, both competing templating mechanisms—anchoring at locations directed by the superstructure in the template and favorable alkane–alkane interactions between the molecules of 2—are presented. Finally, although the STM measurements provide no direct evidence, we propose that the alkyl chains of molecules of 2 that do no interact directly with a neighbor porphyrin are aligned with the alkyl chains of the underlying templating layer of 1 to maximize the van der Waals interactions.
troughs always remains unoccupied due to blocking of the adsorption site by the alkyl chains of 2. Along the lamellae two competing templating mechanisms govern the adsorption spots of the molecules of 2: adsorption of the porphyrins at preferred spots on the superstructure, and a stabilizing effect of interacting porphyrin alkyl chains.

This templating method paves the way to control the positioning of functional porphyrin molecules at well-defined positions, and to investigate their function (e.g., catalytic, electric, optical) in comparison to their properties in closely packed self-assembled monolayers composed of the pure compound. Work along this line is in progress.

**References**


