# Self-Organized Monolayer of *meso*-Tetradodecylporphyrin Coordinated to Au(111)

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***Abstract:*** The structure of molecular monolayers formed at the interface between atomically flat surfaces and a solution of free-base *meso*-tetradodecylporphyrins ($H_2Ps$) was examined by scanning tunneling microscopy (STM) at the liquid/solid interface. On the surface of graphite (HOPG), $H_2Ps$ form a well-ordered monolayer characterized by an oblique unit cell. On Au(111), $H_2Ps$ form a self-organized monolayer comprised of two distinct domain types. In both types of domains, the density of the porphyrin cores is increased in comparison to the arrangement observed on HOPG. Also, high-resolution STM images reveal that, in contrast to what is observed on HOPG, physisorption on Au(111) induces a distortion of the porphyrin macrocycle out of planarity. By using X-ray photoelectron spectroscopy, we demonstrate that this is likely to be due to the coordination of the lone pairs of the iminic ($-C=N-$) nitrogen atoms of the porphyrin macrocycle to Au(111).

## Introduction

In many biological systems, the porphyrin macrocycle adopts nonplanar conformations, thus giving nature a powerful method for the subtle alteration of their physicochemical properties.[1] Controlling these distortions from planarity and their resulting changes of physical properties in self-assembled systems constitutes a key step toward building functional porphyrin-based supramolecular architectures.[2] On surfaces, porphyrins have recently been used to form porous networks capable of templating the surface complexation of fullerenes.[3] The conformational flexibility of the porphyrin is proposed to play a key role in the interaction between the fullerene guest molecules in this 2D network.[4] Scanning tunneling microscopy (STM) has allowed for the study of self-assembled monolayers of porphyrins in ultrahigh vacuum (UHV),[5] under electrochemical conditions[6] or under ambient conditions, that is, at the liquid/solid interface.[7] Earlier STM investigations at the liquid/solid interface have focused on the study of *meso*-tetraphenylporphyrins (TPPs) on highly oriented pyrolytic graphite (HOPG).[8−11] In TPP, the phenyl groups adopt an average angle of 36° with respect to the plane of the porphyrin ring, thus forcing the central ring to lie ~0.34 nm above the surface.[12] Alternatively, *meso*-tetraalkylporphyrins (TAPs) such as 5,10,15,20-*meso*-tetradodecylporphyrin (H_2P, Scheme 1) suffer no such steric constraints and can lie in direct contact with the surface. The imaging of porphyrins on Au(111) in a liquid medium is challenging, as is highlighted by a recent investigation, which describes attempts to characterize monolayers of free-base *meso*-undecadecylporphyrins at the Au(111)/*n*-tetradecane interface.[13] To the best of our knowledge, this is the only report on the self-assembling properties of TAPs on a surface. Here, we present our investigation on the self-assembly of free-base TAPs from *n*-tetradecane onto HOPG and Au(111). High-resolution STM images reveal that $H_2P$ porphyrins form very stable arrays on Au(111), not only under the effect of the expected intermolecular interactions, but also because of interfacial interactions dominated by a previously unknown surface coordination of the porphyrin nitrogen atoms. These measurements indicate that free-base porphyrins are coordinated onto the Au(111) surface. The surface coordination of the porphyrin core nitrogens was confirmed at the macroscopic scale by X-ray photoelectron spectroscopy (XPS).

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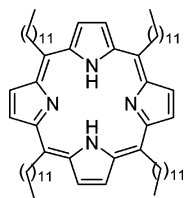
## Results and Discussion

A highly ordered monolayer is formed by deposition of H$_2$P from *n*-tetradecane onto HOPG (Figure 1a). It exhibits a regular pattern of bright features with a diameter of ~0.60 nm assigned to the porphyrin core adsorbing flat on the surface. Interestingly, in Figure 1a, the center of the porphyrin core appears as a bright spot, whereas an earlier report describes the STM contrast of free-base TAP molecules on HOPG as having a dark spot at the center.[13] However, this contrast is dependent on the scanning conditions used. The bright contrast observed in the center of the molecule could be due to the interference of different (parallel) current paths that connect the tip with the substrate through the nitrogen atoms of the porphyrin molecule. Such interference phenomena have been observed in STM images of self-assembled monolayers of alkanes at the Au(111)/*n*-tetradecane interface and have been proven to be very sensitive to the modification of the length of the tunneling paths involved.[14] The average area occupied by each porphyrin in the 2D lattice was determined as $(2.2 \pm 0.1)$ nm$^2$. Considering that each dodecyl chain requires ~0.7 nm$^2$ to physisorb on HOPG[15] and that the area of the H$_2$P heterocycle is ~0.8 nm$^2$, we conclude that only two alkyl chains are physisorbed on the surface of HOPG. Indeed, high-resolution STM pictures show that only two alkyl chains per H$_2$P molecule are observable on HOPG (Figure 1a). The absence of some of the alkyl chains in the STM images has been observed in other monolayers and was interpreted as a nonadsorption of these alkyl chains, which instead point away from the surface into the solution.[16] By modifying the parameters of scan, it is possible to image the HOPG surface beneath the molecules (see Figure S1 in the Supporting Information). From this, we can conclude that the physisorbed alkyl chains lie along one of the main $\langle 100 \rangle$ axes of the HOPG surface. A model based on these observations is schematically drawn in Figure 1b, together with the unit cell characterized by the following parameters: $a = (1.4 \pm 0.1)$ nm, $b = (1.7 \pm 0.1)$ nm, $\gamma = (108 \pm 1)°$.

Figure 2 shows a large-scale STM image of the reconstructed Au(111) surface covered by an ordered array of H$_2$Ps. While submolecular resolution is impossible at this scale, bright pairs of parallel stripes elevated from ~0.02 nm are distinguishable under an array of bright spots corresponding to individual H$_2$P molecules. These stripes are characteristic of the Au(111) surface reconstruction and are aligned in the $\langle 112 \rangle$ direction of Au(111).[17] Reconstruction with a herringbone feature, however, was not observed. The simultaneous imaging of the organic
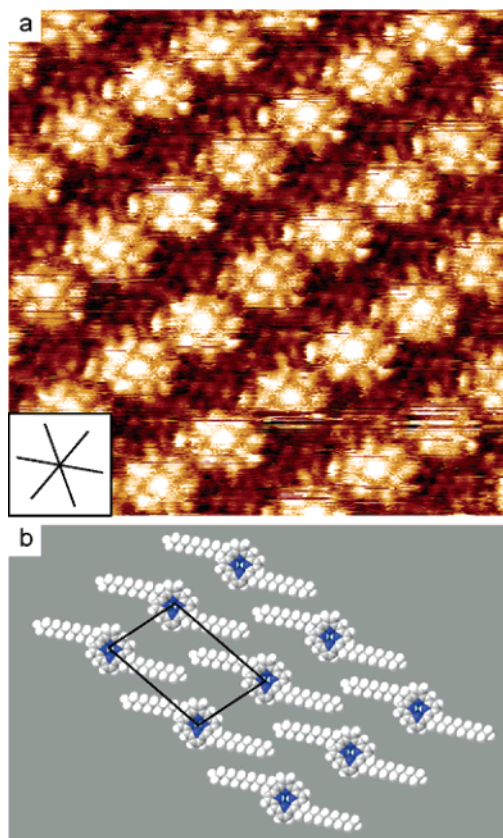
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**Figure 1.** (a) STM image $(8.1 \times 8.1$ nm$^2)$ of the self-assembled monolayer of H$_2$P on HOPG. The orientation of the main axes of HOPG is superimposed in the bottom-left part of the picture. $V_T = 355$ mV, $i_T = 17$ pA. (b) Schematic representation of the model of packing proposed and corresponding unit cell.
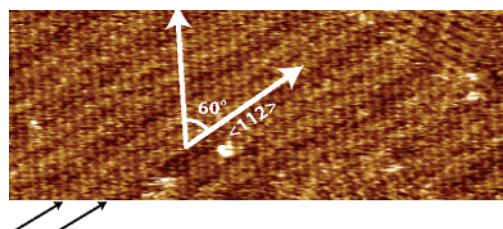


**Figure 2.** STM image (58 nm × 22 nm) of the reconstructed Au(111) surface covered by H$_2$Ps. The scanning conditions used are $V_T = -341$ mV, $i_T = 73$ pA. The reconstruction stripes are distinguishable behind the organic lattice. This allows for determination of the orientation of the monolayer.

overlayer and of the Au(111) reconstruction stripes allows for determination of the orientation of the molecular lattice with respect to Au(111) (white arrows, Figure 2).

High-resolution STM images allowed further investigation of the orientation of the molecules within the monolayer. On such pictures (Figure 3a and b), each bright lobe of the four-leaf clover shape motif has a diameter of ~0.35 nm. Clear bias-dependence was not observed, and the nonsymmetric four-lobes contrast was always a characteristic feature of the STM image. Each lobe corresponds to a pyrrole unit. On Au(111), the self-assembly of dodecane into a compact lattice requires an area per alkyl chain of ~0.8 nm$^2$.[18] Considering that the total area occupied per each H$_2$P molecule on Au(111) is $(1.8 \pm 0.1)$ nm$^2$, we expect that only one alkyl chain per molecule is physisorbed

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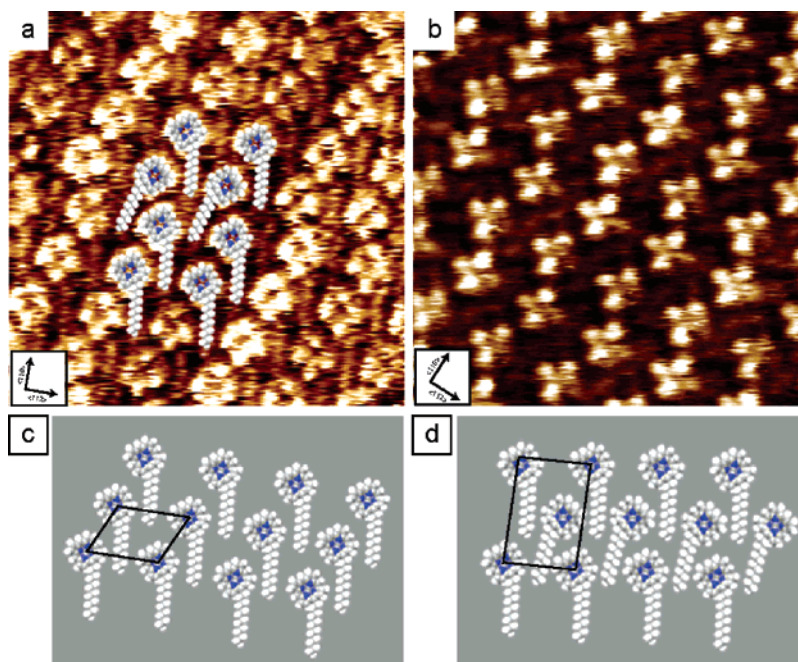
**Figure 3.** High-resolution STM images of $H_2P$ on Au(111) and corresponding packing models. (a) Physisorbed alkyl chains are visible through the use of a high $i_T$, which favors imaging of insulating aliphatic moieties. Only one alkyl chain per $H_2P$ molecule adsorbs. On that image most alkyl chains physisorb in the $\langle 110 \rangle$ direction (α-type of packing). $9.5 \times 9.5$ nm$^2$, $V_T = 575$ mV, $i_T = 42$ pA. (b) The alternate orientation of physisorbed alkyl chains is at the origin of a zigzag pattern (β-type). $8.4 \times 8.4$ nm$^2$, $V_T = 581$ mV, $i_T = 7$ pA. (c) Proposed packing model and corresponding unit cell for α-type packing. The unit cell, which contains one molecule, is described by $a = (1.7 \pm 0.1)$ nm, $b = (1.1 \pm 0.1)$ nm, $\gamma = (105 \pm 1)°$. (d) Proposed packing model and corresponding unit cell for β-type packing. The unit cell, which contains two molecules, is described by $a = (1.5 \pm 0.1)$ nm, $b = (2.3 \pm 0.1)$ nm, $\gamma = (96 \pm 1)°$.

on Au(111). This was observed, for example, in the image of Figure 3a, which confirmed that partial solvation of the alkyl chains by the solution occurs at the Au(111)/*n*-tetradecane interface also. In the STM image of Figure 3a, most of the observable physisorbed alkyl chains are oriented parallel to the $\langle 110 \rangle$ direction of Au(111), which is known to be the favored direction of adsorption for alkanes.[19] However, five alkyl chains in the center of the picture adsorb in a direction equivalent to the $\langle 112 \rangle$ direction (they form a 30° angle with $\langle 110 \rangle$). Two of these molecules with an alkyl chain having a different orientation are highlighted by the molecular structures superimposed in Figure 3a. Depending on the regular or alternate direction of packing of the alkyl chains, it consequently appears that $H_2Ps$ can form two different lattices on Au(111). The regular packing of the alkyl chains (α-packing) leads to the formation of an oblique unit cell, as in the major part of Figure 3a, whereas their alternate packing (β-packing) forms a regular zigzag arrangement visible in Figure 3b. Both 2D-crystalline structures and corresponding unit cells are represented schematically in Figure 3c and d. The $(1.8 \pm 0.1)$ nm$^2$ surface density of $H_2P$ molecules is the same in both domains.

Considering the average surface areas occupied by each molecule, it appears that the surface density of $H_2P$ molecules is considerably higher on Au(111) than on HOPG. These results thus show either that the stabilization provided by adsorption of the conjugated core is stronger on Au(111) than on HOPG or that it is weaker for aliphatic chains. Although there is no general consensus in the literature, recent investigations suggest that the aliphatic chains engage in a more favorable interaction with Au(111) than on HOPG.[20] This is supported in part by the fact that short alkanes (such as dodecane) do not physisorb on

HOPG at room temperature, whereas they do physisorb on Au(111) under the identical conditions.[21] Despite the fact that alkyl chains are expected to be more stabilized by physisorption on Au(111) than on HOPG, we observe that for each $H_2P$ molecule, the number of physisorbed alkyl chains is smaller on Au(111) than on HOPG. Consequently, we conclude that the free energy gain of adsorption of $H_2P$ to the surface is maximized by a favorable interaction between the porphyrin heterocycle and Au(111), rather than by physisorption of alkyl chains. Such a strong stabilization by adsorption of the free-base porphyrin aromatic core on Au(111) is surprising and, to the best of our knowledge, has not been previously reported for other porphyrins. The presence of reconstruction stripes behind the adsorbed monolayer indicates that adsorption occurs without lifting of Au(111) reconstruction, ruling out the possibility of modification of the surface structure by formation of a gold metalloporphyrin.[17]

The four-lobes contrast observed for $H_2P$ molecules on Au(111) gives some insight into this phenomenon. Whereas on HOPG each porphyrin core creates one bright feature suggesting that the electrons are well delocalized around the $H_2P$ core, four distinct lobes are visible for each molecule on Au(111) under different scanning conditions. Within each $H_2P$ molecule, some of these lobes appear less pronounced than the other ones. In particular, in Figure 3b, the lower-right lobe is always darker than the others. We can exclude the possibility that this is a consequence of the dissymmetry of the tip because it was observed on pictures registered in different scanning directions. This contrast could also be a consequence of interactions between porphyrins through their alkyl chains, thus putting restrictions on other molecule's orientations. However, not only the bottom-right lobes but also part of the top-left lobes present a noticeably darker contrast. We attribute this two-fold contrast

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to a conformational distortion of the H$_2$P heterocycle out of planarity. The sub-angstrom conformational dissymmetrization created upon adsorption would generate the nonuniform four-lobe structure. In solution, the porphyrin heterocycle has been found to distort from planarity by the introduction of sterically crowded substituents at its periphery or by metalation.[1] On surfaces, conformational changes upon adsorption have been reported for porphyrins with bulky substituents creating steric hindrance.[22] Conformational interconversion by voltage pulses has also been reported in a (Zn)etioporphyrin on NiAl(110)[23] and in a brominated Zn(II)TPP.[24] However, to the best of our knowledge, distortion of the porphyrin core of a TAP by coordination to a metallic surface is unknown.

In light of these results, we sought a explanation that accounted for both the strong interaction between the porphyrin aromatic core and Au(111) and its deformation upon physisorption. We propose that the increased heterocycle/Au(111) interaction is a consequence of the interaction of iminic (−C=N−) nitrogen lone pairs with the surface, whereas the pyrrolic (−NH−) nitrogens are not involved. The coordination of the iminic nitrogen onto the surface would induce a conformational distortion. In contrast to TAPs, the coordination of iminic nitrogens to Au(111) is unlikely to occur with TPPs because of the large distance between the porphyrin cores and the surface on which they physisorb.

To obtain further evidence for the coordination of iminic nitrogen lone pairs to Au(111), we performed X-ray photoelectron spectroscopy (XPS) of the porphyrin monolayers, thus providing information regarding the chemical state of the nitrogen atoms in a H$_2$P monolayer on Au(111). The N 1s photoemission signal was recorded for a H$_2$P monolayer formed by depositing the molecules from a 0.1 mM solution of H$_2$Ps in dichloromethane onto reconstructed Au(111). After deposition of a droplet of solution, the surface was dried in argon and introduced in UHV. Formation of multilayers in significant amount is unlikely to occur at the liquid/solid interface because of solvation of molecules in excess. This is not the case for dried films because inhomogeneous films containing multilayers are formed during evaporation of dichloromethane. Therefore, to desorb excessive porphyrin molecules from the second or higher layers formed after drying and to obtain a surface as homogeneous as possible, the samples were heated in UHV in a range of temperatures comprised between 400 and 500 K. This annealing step was used previously to form porphyrin monolayers on Ag(111)[25] or other monolayers on Au(111).[26] The samples were subsequently allowed to cool to room temperature and remained in UHV before being transferred to the spectrometer. In Figure 4, fitting of the experimental spectrum was carried out by a deconvolution using a minimum number of peaks. The fitting reveals the presence of three distinct chemically inequivalent N 1s core-level emissions at 397.5, 399.3, and 400.2 eV.
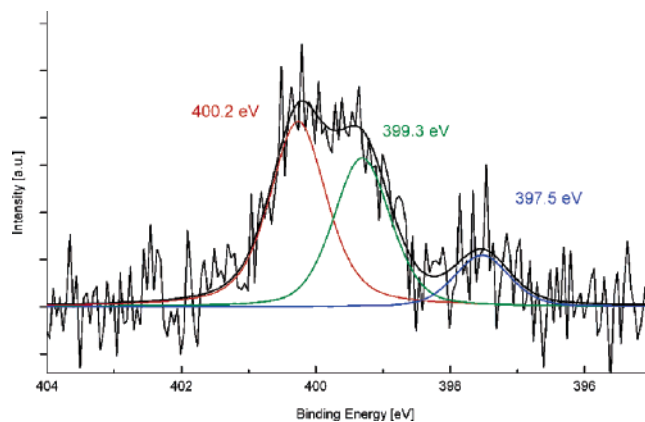


**Figure 4.** X-ray photoemission spectrum of the N 1s core level for a monolayer of H$_2$P on Au(111). The raw data are plotted in black, and the fit to the experimental data is plotted in colors. We assign the blue peak to the signal of free iminic nitrogens, the green peak to the coordinated iminic nitrogens, and the red peak to pyrrolic nitrogens.

By comparison of the N 1s photoemission peak with that of a reported spectrum of a monolayer of free-base TPP on Ag(111),[25] we conclude that the 400.2 eV peak corresponds to pyrrolic (−NH−) nitrogens. Similarly, we attribute the 397.5 eV peak to free iminic (−C=N−) nitrogens, which usually present lower N 1s binding energies than pyrrolic nitrogens. The position of the third peak with an intermediate binding energy at 399.3 eV corresponds to the energy of nitrogen atoms in metalated TPPs.[12,25,27] Because the formation of gold metalated porphyrins was ruled out by the observation that the Au(111) reconstruction is not lifted under the monolayer, we suggest that this peak corresponds to the photoemission of lone pairs of iminic nitrogens coordinated onto Au(111). The fact that not all iminic lone pairs are coordinated onto Au(111) could be due either to the presence of a residual partial bilayer, or more probably to a slow exchange phenomenon occurring at room temperature. Because of the level of noise in the N 1s photoemission peak, quantitative analysis of the components within the N 1s signal is not reported.[28]

By deposition of a diluted solution (0.1 mM) of H$_2$P in dichloromethane, without annealing, it was possible to obtain a thin multilayered film on Au(111). In the corresponding N 1s photoemission line, two peaks are clearly visible at 397.2 and 399.9 eV. The 397.2 eV peak corresponds to the signal of iminic nitrogens in a multilayered film.[27] The peak centered at 399.9 eV has a full width at half-maximum of 2.0 eV, which is much larger than the experimental resolution. This reflects the presence of a number of chemically inequivalent nitrogen atoms. We attribute this signal to the contribution of bulk pyrrolic nitrogens and interfacial coordinated iminic nitrogens. However, the symmetrical shape of this peak prevents its reliable deconvolution. After annealing, the N 1s signals are better resolved and allow fitting and attribution of the peaks as described above. For both the multilayered film and the monolayer, the N/C ratio was measured and evaluated to be $(6 \pm 2)\%$, which correlates

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(28) Using XPS data, we found that about 80% of the iminic nitrogens were complexed to gold. A statistical analysis of the number of darker lobes versus lighter lobes in STM images suggests that 98% of the iminic nitrogens are in fact complexed (55% of bright lobes and 45% of dark lobes). Given the possibility of a fast exchange that would not be observed on the STM time scale, these two values compare favorably.

well with the theoretical stoichiometry of 5.8% in $H_2P$ molecules. The fact that this ratio remains constant before and after annealing strongly indicates that no structural degradation of the molecule occurred. These control experiments demonstrate that no molecular degradation occurred during annealing and suggest that coordination of iminic nitrogens already occurs before annealing, in accordance with STM observations.

In summary, we report on the structure of the self-organized monolayer formed by a *meso*-tetraalkylporphyrin on HOPG and for the first time also on Au(111). On Au(111), $H_2P$ presents a clover shape STM contrast, suggesting that the physisorbed porphyrin ring is distorted out of planarity. We suggest that this deformation arises from surface coordination of the porphyrins. This hypothesis was strengthened by the observation of a high surface density of $H_2P$ cores on Au(111) and by XPS spectra showing the presence of a chemically inequivalent nitrogen, which is likely arising from the lone pairs of iminic nitrogens coordinating onto Au(111). We conclude that, thanks to the proximity of the porphyrin plane to the surface, *meso*-tetraalkylporphyrins coordinate onto Au(111), which induces the distortion of the porphyrin macrocycles out of planarity.

This adds to our understanding of physical phenomena occurring in porphyrin monolayers on surfaces. Given the crucial role played by porphyrin coordination in supramolecular chemistry, it could also have important implications for new designs of molecular-based devices or sensors.

**Supporting Information Available:** Experimental procedures, details of synthesis, and NMR spectra of $H_2P$. This material is available free of charge via the Internet at http://pubs.acs.org.

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