Supramolecular Hydrophobic−Hydrophilic Nanopatterns at Electrified Interfaces

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ABSTRACT

We have developed hydrophobic−hydrophilic nanopatterns at electrified surfaces via the self-assembly of amphiphilic molecules. For this purpose, we selected 5-hexadecyloxy isophthalic acid: this neutral amphiphile forms hydrogen-bonded rows that are commensurate with the Au(111) surface. The alkyl chains are interdigitated. The molecular organization of these nanopatterns depends strongly on the substrate potential, which reveals the hierarchical nature of the assembly. The new hydrophobic−hydrophilic nanopatterns are of special interest as templates for the formation of nanostructures of higher complexity.

Currently, the formation of functionalized surfaces with periodicities on the nanometer scale (1−5 nm) attracts a lot of interest.[1,2] Molecules are ideal building blocks for the formation of such well-organized and functional surfaces via self-assembly, as they are tunable in size, shape, and functionality.[3,4] Van der Waals interactions, hydrogen bonding, and metal coordination are the most important modes of interaction for the formation of self-assembled architectures on surfaces.[1,3] Most often, competitive interactions play simultaneously and the successful outcome of the self-assembly process requires not only balanced intermolecular interactions but also favorable molecule−substrate interactions.

One of the ways to tune these molecule−substrate interactions is the use of well-defined atomically flat surfaces, which direct the molecular ordering via specific geometric and electronic effects. There are many successful examples of this approach under UHV conditions[1] and at the interface between an organic liquid and a substrate.[2,3] Electrified surfaces offer a further dimension to influence the molecule−surface interactions by controlling the electrochemical potential of the substrate when immersed in aqueous electrolyte. Electrochemical scanning tunneling microcopy (EC-STM) is the technique of choice to unravel with submolecular resolution the surface-potential-induced ordering.[5−12]

Molecules substituted with linear alkyl chains are in particular useful to tune the periodicity of surface nanostructures. By changing the length of the alkyl chains that adsorb parallel to the substrate, the intermolecular distance can be modified in a controlled way.[13] In combination with their affinity for graphite and metal substrates, alkylated molecules are fine building blocks for the formation of functional patterns.[14] Furthermore, functionality is often automatically induced as the alkyl chains are by definition hydrophobic and often are linked to hydrophilic molecular parts.

So far, these patterns of alternating hydrophobic alkyl chains, lying parallel to the substrate, and hydrophilic units have been formed exclusively at the interface between a hydrophobic liquid and (semi)metallic substrates. The formation of such supramolecular patterns in a polar environment turned out to be extremely challenging, even at electrified surfaces. For instance, alkylated compounds with thiol groups do not adsorb parallel to the substrate (gold) but rather form chemisorbed self-assembled monolayers.[15−18] Detergent molecules also do not form 2D crystals but tend to organize into hemispherical micelles, as reported for sodium dodecylsulfate (SDS) on Au(111).[19] Recently, lipids were reported to form a metastable 2D crystalline lamellar phase on Au(111), which in time transformed into a hemispherical micellar phase.[20] Among compounds bearing hydrocarbon chains, only alkanes were reported to adsorb parallel to the electrified metal−

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electrolyte surface, forming well-ordered 2D crystals on a Au(111) surface.[21]

To overcome the problem of hemispherical micelle- or SAM-like assembly at the water−Au(111) interface, we selected an amphiphilic molecule composed of an alkyl chain (hexadecyloxy) coupled with a planar, aromatic head group selected to form multiple H-bonds (isophthalic acid). Such head groups are expected to interact particularly favorably with one another to form stable networks. While the planarity and aromaticity favor the interaction with gold and hamper micelle formation, the intermolecular hydrogen-bonding interactions stabilize the network, as elegantly demonstrated for trimesic acid (1,3,5-benzene tricarboxylic acid).[22] The molecule of the present study, 5-hexadecyloxy-isophthalic acid (ISA16), is known to form lamellar structures on HOPG. The alkyl chains are interdigitated and oriented parallel to the main symmetry axes of graphite, while the isophthalic acid (ISA) residues form intermolecular H-bonding chains.[23]

HOOC

HOOC   ISA16
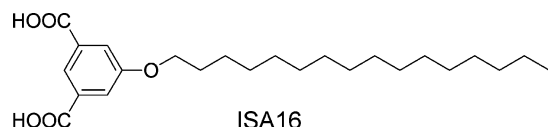
The present results show that this noncharged amphiphile forms a stable 2D crystalline lamellar phase at the electrolyte−Au(111) interface close to the potential of zero charge (pzc). At more positive potentials, unique dynamics are observed, revealing the hierarchical nature of the assembly. The obtained nanopatterned surfaces that expose both hydrophilic and hydrophobic regions may find applications as a template for constructing organized functional surfaces.

Nanopattern Formation. The ordering of ISA16 on Au-(111) was studied by a home-built EC-STM[24] in two different electrolytes, 0.1 $HClO_4$ and 0.05 H_2SO_4, at an electrode potential (E_w) of 300 mV vs SCE, where the gold reconstruction is not observed.[25] According to our STM data, both electrolytes gave very similar results. In the STM images, we observed lamellae, where bright double rows can be assigned to the aromatic residues of the ISA head groups (Figure 1). The less bright but long features can be assigned to the hydrocarbon alkyl chains. Thus, ISA16 forms lamellae with a head-to-head arrangement. The hydrophobic tails of the molecules are packed parallel to each other and are interdigitated (see model in Figure 1A). The distance between aromatic groups along the long lamella axis is 0.96 ± 0.06 nm, which is evidently twice the distance between two adjacent alkyl chains measured along the same direction. The width of a lamella (ΔL) measures 3.4 ± 0.2 nm (Figure 1A), which is similar to the value measured for ISA16 on graphite. Therefore, one could draw the preliminary conclusion that the arrangement is similar to that observed for ISA16 and its analogs on HOPG in organic solvents.[23]

However, close inspection of the images reveals peculiar differences. While the isophthalic acid groups are well aligned, the absolute value of the angle between the alkyl chains and the lamella director varies between 60° and 90°.
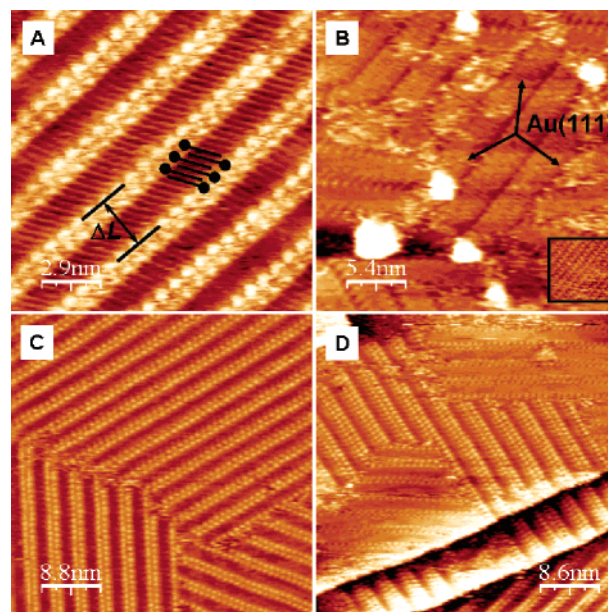

Figure 1. STM images of ISA16 on Au(111) in 0.1 M $HClO_4$ (A, C, and D) and in 0.05 M H_2SO_4 (B). (A) Tunneling current (I_t) is 1 nA, bias voltage (U_{bias}) is −250 mV, and work potential (E_w) is 300 mV vs SCE. ΔL stands for the distance between the lamellae. A few molecules are schematically indicated on top of the STM image. (B) Arrows show the three nearest-neighbor directions (NN) of the Au(111) lattice. The inset in the bottom-right corner is an STM image of a sulfate adlayer recorded at a work potential of 900 mV vs SCE. $I_t = 1$ nA, $U_{bias} = -850$ mV. (C,D) $I_t = 1$ nA, $U_{bias} = -250$ mV, $E_w = 300$ mV vs SCE.

The extent of the observed variation in the orientation of the alkyl chains is much larger compared to that observed for ISA16 and its analogs with longer alkyl chains on HOPG: for those systems, the absolute value of the angle between the alkyl chains and the lamella director only varies between 85° and 90°.[23] In our experiments, we could not resolve the gold lattice underneath the ISA16 adsorbate; therefore, we used the sulfate adlayer as a calibration lattice. These adlayers were visualized by applying highly positive substrate potentials. The ISA16 lamellae run parallel to the nearest-neighbor (NN) direction of the sulfate adlayer, which is equivalent to the next-nearest-neighbor (NNN) direction of the Au(111) lattice,[26] also called the "$\sqrt{3}$" or $\langle 112 \rangle$ direction.[12] The NNN direction is perpendicular to the NN direction of Au(111) (see Figure 2). The same conclusion can be drawn from the orientation of ISA16 lamellae with respect to step edges. The ISA16 lamellae run perpendicular to the step edges that appear along the NN direction of Au-(111) (Figure 1D). Because the angle between the alkyl chains and the lamellae covers a large range, we can safely conclude that the alkyl chains of ISA16 do not follow the Au(111) lattice. Not only are the ISA moieties lying along the NNN direction, but the distance between two of these groups (0.96 ± 0.06 nm) corresponds well also to two times the distance between two gold atoms along the NNN direction (1.00 nm). Moreover, the calculated distance between the carbon atoms of the two carboxyl groups in an ISA moiety is 0.495 nm, which fits ideally the distance between two Au atoms along the NNN direction.
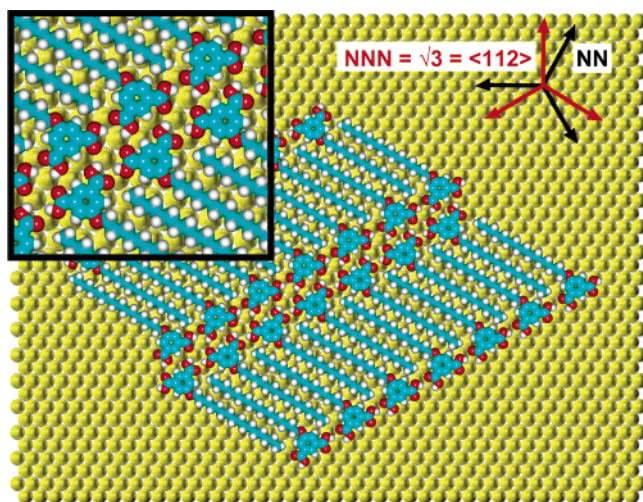
Figure 2. Tentative model of the molecular arrangement of a lamella of ISA16 on Au(111). Note that the isophthalic acid groups are arranged along the NNN direction.

A tentative model of the assembly of ISA16 molecules with respect to the Au(111) substrate is presented in Figure 2. The commensurate alignment of the ISA groups with the gold lattice along the NNN direction fits well with the formation of hydrogen bonds of ca. 2 Å long between ISA groups within the same row. In addition, hydrogen bonding between lamellae is also supported. The latter hypothesis is confirmed by the observation of a uniform short distance between the lamellae. Formation of intermolecular H-bonds is in line with previous studies of alkylated isophthalic acid derivatives at the graphite−organic liquid interface.[23] Moreover, a more recent study of trimesic acid by EC-STM also indicates the important role of intermolecular H-bonding in molecular self-assembly at the Au(111)−water interface.[22] Thus, we can conclude that the observed perfect alignment of the ISA16 lamellae along the NNN direction of Au(111) is a result of the commensurability of the ISA aromatic residues with the gold substrate and also due to intermolecular H-bonding of the ISA residues.

The clear difference in the ordering of the alkyl chains of ISA16 between HOPG and Au(111) highlights the far better commensurability of these alkyl chains with HOPG compared to Au(111).[27−29] Nevertheless, it was recently shown that alkanes can align parallel to the NN direction of 1×1 Au(111) at the electrolyte−metal interface.[21] The absence of this alignment in the case of ISA16 underlines the decisive role of the ISA group in the formation of ordered structures. The ISA residues interact strongly with the Au(111) substrate and dominate the packing. The role of the alkyl chains seems limited to chain−chain hydrophobic interactions, which do not control the direction of the lamellae with respect to the substrate.

Remarkably, this assembly results in a stable 2D nano-patterned surface containing both hydrophilic and hydrophobic rows exposed to aqueous solvent. Previous reports showed that these kind of adlayers are not stable and convert into hemispherical micelle forms.[19,20] The surprising stability
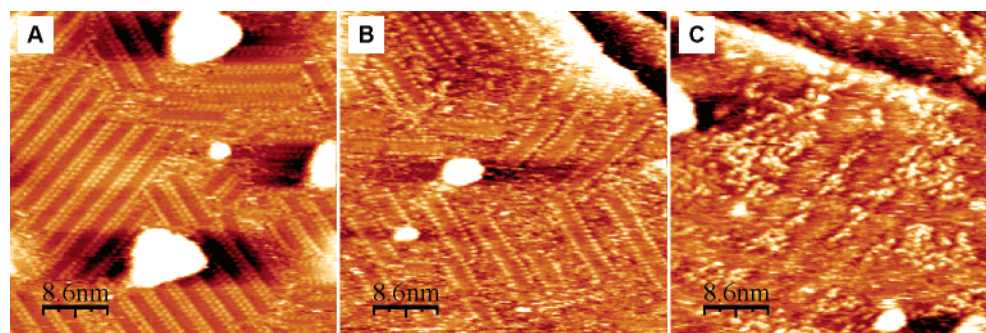

Figure 3. Potential dependent assembly of ISA16 on Au(111) in 0.1 M HClO$_4$. (A) $I_t = 1$ nA, $U_{bias} = -250$ mV, and $E_w = 300$ mV vs SCE. (B) $I_t = 1$ nA, $U_{bias} = -450$ mV, and $E_w = 500$ mV vs SCE. (C) $I_t = 1$ nA, $U_{bias} = -650$ mV, and $E_w = 700$ mV vs SCE.
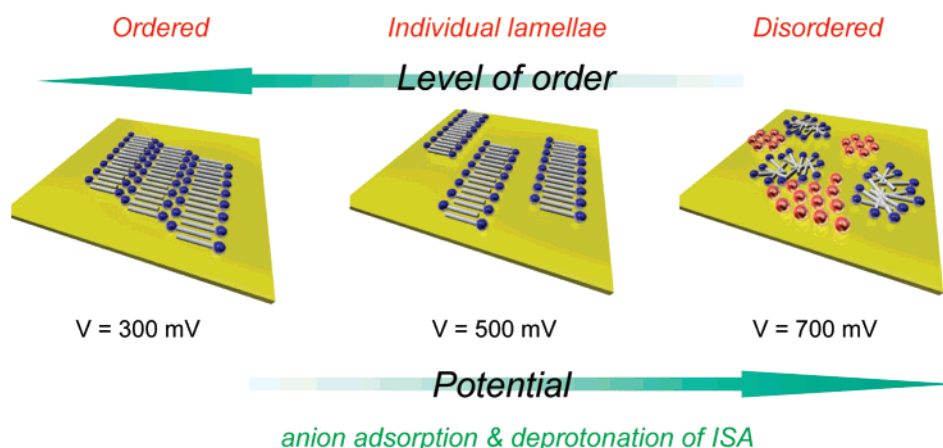

Figure 4. Schematic of the potential dependence of the hierarchical self-assembly.

of the adlayers formed by ISA16 originates probably from the strong in-plane H-bonds.

Potential Control. Formation of the ordered ISA16 structures is only observed for a limited range of work potentials. Upon increasing the work potential, the loss of ordering was observed (Figure 3). At 500 mV vs SCE, the ordered domains disappear and individual lamellae remain, which preserve the original direction and the structure of the lamellae in the ordered domains (Figure 3B). Also, between 500 and 1100 mV vs SCE, these isolated lamellae disappear and we observe only disordered aggregates of molecules. These effects are similar both in sulfuric and perchloric acid; however, in sulfuric acid, these effects occur at somewhat lower potentials. Importantly, the potential-driven assembly—disassembly process is totally reversible, so that the ordered nanostructures can be created from a disordered architecture in a well-controlled manner.

The potential dependence on the order of ISA16 molecules is intriguing because the molecules are not charged. One possible reason for the observed potential dependence is deprotonation of the ISA moiety at higher positive potentials. This argument is in line with recent reported data on trimesic acid.[22] It was shown that deprotonation of this acid occurs at a potential higher than 400 mV vs SCE, which is close to the potential where ISA16 looses its order. An additional explanation for this potential dependence relates to the potential of zero charge (pzc), which for 0.1 M perchloric acid on Au(111) is ca. 300 mV vs SCE.[30] The pzc is within the potential region where ordered ISA16 adlayers are observed. Therefore, at potentials above pzc, anions (perchlorate or hydroxide) and water could adsorb on the surface and thus compete with organic molecules for the interaction with the surface. At sufficiently high positive potentials, a large number of anions are adsorbed, which induces aggregation of the water-insoluble ISA16 molecules (Figure 4). A very similar conclusion was recently drawn for alkane adsorption on Au(111) in 0.1 M $HClO_4$, where the formation of ordered alkane adlayers was observed only in the potential region close to pzc.[21] Previous studies have demonstrated that hydrophobic alkyl chains interact strongly with metal surfaces only at potentials close to pzc. At other potentials, the interations of ions and dipoles with the surface dominate and thus remove hydrophobic residues from the surface[31−33] or lead to their aggregation, as observed in this study.

At intermediate potentials (500 mV vs SCE), some metastable structures appear, namely individual lamellae. Observation of individual lamellae suggests that the ordering of ISA16 on Au(111) occurs in a hierarchical manner. Thus, initially, ISA16 forms individual lamellae, and only then these lamellae organize into domains with the same orientation. The formation and stabilization of individual lamellae is probably supported by strong hydrophobic interactions between the alkyl molecules within the lamellae. Moreover, H-bonding between the ISA moieties within the same lamella and the strong interaction of this lamella with the substrate explain the observed alignment of the ISA moieties along the NNN direction. Therefore, individual lamellae of relatively small size can be immobilized and stabilized on the surface, which was, for instance, not possible at the interface between an organic liquid and HOPG.

In the present study, we have shown that amphiphilic ISA16 molecules form stable lamellar structures on Au(111) in different electrolytes, at potentials close to the potential of zero charge. We demonstrate that the key role for the ordering of the molecules in these nanostructures is played by the aromatic isophthalic acid moieties due to the commensurability of their H-bonding rows with the Au(111) lattice along the NNN direction. At more positive potentials, individual lamellae are observed, and at even higher potentials, the lamellae disassemble, suggesting the hierarchical nature of the potential-induced assembly of ISA16 molecules on Au(111) (Figure 4). Finally we expect that the obtained hydrophobic—hydrophilic nanostructures at the interface between a metal and an aqueous electrolyte can be used as templates for the advanced nanopatterning of surfaces.

Supporting Information Available: Sample preparation, EC-STM, cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org

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