Chapter 6

Intermolecular Repulsion through Interfacial Attraction: Polymorphism in Self-Assembled Monolayers

A comparative study of the structure of molecular monolayers is reported, formed spontaneously at the interface between a series of atomically flat surfaces and a solution containing a Schiff-base derivative (PHB). Scanning tunneling microscopy (STM) at the liquid/solid interface shows that PHB forms well-ordered monolayers characterized by a columnar packing on all surfaces employed, including highly oriented pyrolytic graphite (HOPG), Au(111), MoS$_2$ and pentacontane-modified HOPG. Notably, a polymorphic monolayer is formed on Au(111), where in addition to the columnar arrangement, PHB molecules form dimeric structures also. It is shown that the formation of a dimeric 2D crystal on Au(111) is associated with a decrease in the surface density of the molecules. The decrease in surface density is ascribed to a strong interaction between PHB and the Au(111) surface, which induces partial charging of the aromatic moieties of PHB. These results suggest that polymorphism on Au(111) originates from molecule/surface attraction, which in turn induces molecule/molecule repulsion. They highlight the importance of considering molecule/molecule and molecule/substrate interactions both as independent and interdependent phenomena in understanding the mechanisms behind the formation of polymorphous 2D crystals on a surface.

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6.1 Introduction

Crystal polymorphism, which embodies the ability of molecules to form various packing arrangements displaying different physical and chemical characteristics, is of paramount importance in fields such as pharmacology, solid-state chemistry, and material science. In particular, understanding which interactions drive the formation of 2D polymorphic crystals is a key to achieve control over nanofabrication methods, which utilize the bottom-up molecular approach to build organic devices. The interactions, which are involved in 2D self-assembly, on top of solid surfaces, are divided most commonly into molecule/molecule, and molecule/substrate interactions. Recent studies have highlighted that slight modifications in these interactions can induce structural transformations in the self-assembled monolayer formed at the liquid/solid interface. The parameters, which have been investigated include length and position of alkyl chains, modification of the aromatic core, physico-chemical properties of the solvent, and addition of guest molecules. Alternatively, the influence of substrates on the structure of self-assembled monolayers, in particular at the liquid/solid interface, has not been addressed systematically and was limited to a comparison of two substrates only.

In addition to the strength of molecule/surface interactions, several factors are responsible for the structure of a 2D crystal formed on a given substrate. Geometric factors e.g., lattice constants of the substrate, can affect packing geometry, generally because monolayers are formed so as to maximize commensuration. However, this trend can be counterbalanced by the fact that high packing densities also favor energy gain by adsorption. Additionally, self-assembly is influenced by molecule/molecule interactions. The formation of less densely packed adlayers can be favored when intermolecular interactions, such as H-bonding or electrostatic interactions between longitudinal dipolar moments of the molecules dominate the self-assembly process. If molecule/molecule repulsion is too strong, self-assembled monolayers do not form at the liquid/solid interface, however, deposition of molecules in UHV results in the formation of individually stabilized nanostructures. Identifying which of the aforementioned factors dominates the self-assembly process is challenging since, in the comparison of self-assembled monolayers on different substrates, several parameters are varied.

In this chapter, the effect of a systematic variation of substrate on the geometry of self-assembled monolayers formed at the liquid/solid interface is discussed. The polymorphism observed on Au(111) exclusively, is rationalized by consideration of the substrate-induced intermolecular interactions. The structures of the 2D crystals formed spontaneously at liquid/solid interfaces are rationalized, typically, on the basis of independent analysis of...
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molecule/molecule and molecule/substrate interactions, and on the interplay between these contributions. However, molecule/molecule and molecule/substrate interactions are not independent, and hence here we show that molecule/substrate interactions can be used to tune molecule/molecule interactions. A range of substrates were employed to investigate the interdependence of these interactions: metallic Au(111), semi-metallic highly oriented pyrolytic graphite (HOPG), semiconducting MoS$_2$ and pentacontane-modified HOPG. Surface-adsorbate coupling is expected to vary between each of the substrates because they have different geometrical patterns, corrugations and electronic characteristics.

The molecule that is used is a Schiff-base derivative, 4-(n-dodecyloxy)-N-(4-n-dodecyl)-phenyl-2-hydroxybenzaldimine (PHB, Figure 1). Schiff bases can be considered as molecular switches because they undergo cis/trans photoisomerisation. The 2D molecular organization of simple alkylated Schiff bases has been reported on HOPG. PHB constitutes a more complex photochromic molecular switch belonging to the sub-class of N-salicylideneanilines, which comprise hydroxy-substituted derivatives of Schiff bases (Figure 1). These compounds have attracted considerable attention recently due to their photochromic, thermochromic and aggregative properties and their ability to act as versatile metal-binding ligands. The central unit of PHB, composed of aromatic cores, is functionalized by two alkyl chains with a length of 1.5 nm, incorporated to stabilize the monolayer. The hydrogen of the hydroxyl group can interact with the adjacent nitrogen atom forming an intramolecular hydrogen bond or it can interact with another molecule in its proximity, thus creating an intermolecular hydrogen bond (Figure 1).

Figure 1 Structure of PHB monomer and dimer.
6.2 Scanning Tunneling Microscopy (STM) at the Liquid/Solid Interface

6.2.1 The Tunneling Effect, a Short Introduction

Let us consider an electron with an energy $E$ which collides with a barrier of potential energy $V_0 > E$. Classical mechanics predict that the electron will not overcome the barrier. Alternatively, in quantum mechanics, the probability that this electron, which can be considered as a propagating wave, goes through the barrier of potential is not zero. Because everything happens as if the electron was using a tunnel to go through the barrier, this effect is known as the "tunneling effect". This effect was predicted early by quantum theory, but its first observation was not made until 1958 in p-n junctions of germanium.\(^{17}\)

STM is based on the tunneling of electrons between two polarized electrodes, through an insulating medium such as vacuum, air or a carefully chosen liquid (Figure 2).\(^{18}\) If we simplify the system by assuming that the two electrodes are made from the same metal, then the potential barrier that electrons have to overcome corresponds to the workfunction $\Phi$ of the metal, i.e. the energy which is necessary to take an electron from the metal. If the bias $V$ applied between the two electrodes is small enough ($eV << \Phi$), the barrier of potential has a trapezoidal shape and a simplified expression of the tunneling current can be given:\(^{19}\):

$$I_{\text{tunnel}} = V e^{-2 \kappa d} \text{ with } \kappa \approx \sqrt{\Phi} \text{ and } d \text{ the distance between the two electrodes.}$$

This expression highlights that the tunneling current depends exponentially on the distance between the two involved electrodes, which means that its intensity is sensitive to this distance.
In the configuration used for STM, the two electrodes which are used are a metallic tip and a conductive surface. Given a certain number of approximations Tersoff and Hamann have provided a more detailed expression of the tunneling current for this particular configuration. In the expression they obtained it is of importance that the intensity of the tunneling current is directly proportional to the local density of states (DOS) of the tip and of the surface. Therefore, the variations of tunneling current on a surface cannot be interpreted strictly as topological variations, because they are directly related to the variations of DOS of the surface.

6.2.2 STM: the Experimental Setup
Basically, STM consists in using a sharp tip in order to probe the surface of a conductive material (Figure 3), the tunneling current being localized between the apex of the tip and the planar conductive surface of the second electrode. By scanning the surface with the tip, it is thus possible to register the (amplified) variations of tunneling current, which are related to variations of topography and to spatial distribution of density of states. The main challenges in the implementation of such a concept lies in, first, the necessity to measure low intensities of tunneling current (typically lower than 50 pA), and, second, to control the displacement of the tip with nanoscale precision. These difficulties have been overcome by the development of ever more efficient preamplifiers and by the use of piezoelectric ceramics to displace the tip. In the work described hereafter, the STM was operated in “constant current” mode, where the tip scans the surface while a regulation loop imposes a setpoint value for the tunneling current. Therefore, the feedback loop readjusts the vertical position of the tip for each measuring point. These variations of height of the tip are the data which allows obtaining information about the structure of the conductive surface.
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particular, provided that the tunneling barrier has the same height everywhere, this allows mapping the repartition of electronic states of the surface. In STM images, the tip height variations are converted into coded colors in order to give a 2D representation.

Figure 3 Schematic description of a STM setup for experiments at liquid/solid interface.

6.2.3 STM of Molecular Monolayers at the Liquid/Solid Interface

In the years following the birth of STM, the technique has been used mainly to study surfaces of metal or semiconductors, which requires the use of ultra high vacuum (UHV) conditions because of the reactivity of these surfaces to atmospheric components. However, UHV experiments are quite expensive and time-consuming. Alternatively, it is possible to use STM under ambient conditions, in air or at the liquid/solid interface. At the liquid/solid interface, the surface is scanned while the tip is immersed in an insulating liquid (Figure 3). These experimental conditions are well adapted to the study of molecular monolayers formed on conductive surfaces, because the liquid not only protects the tunneling gap from atmospheric impurities, but it can also be used as a solvent for the molecules to be studied. Upon deposition of a droplet of a solution on an atomically flat and conductive surface, the solubilized molecules are free to diffuse towards the surface and thus to form molecular monolayers by self-assembly. Since molecular monolayers are quite insulating, it is not strictly possible to study them directly by STM. What is registered by STM is in fact the DOS of a conductive surface modulated by the DOS of the adsorbed molecules. This conductive surface is also referred to as the substrate.
6.2.4 Description of the Solvent
The solvent should be commercially available, and apolar (and consequently hydrophobic) in order to avoid the creation of ion-mediated “leakage” currents between the tip and the surface. Moreover, it should not be too volatile over the timescale of the experiment. For the experiments described in this chapter n-tetradecane was used as a solvent, meeting these requirements.

6.2.5 Description of the Substrates
6.2.5.1 Highly Oriented Pyrolytic Graphite (HOPG)
Graphite occurs naturally but the graphite which is commonly used for research is a synthetic material called highly oriented pyrolytic graphite (HOPG). HOPG is composed of layers of carbon with hexagonal symmetry, called graphene sheets (Figure 4a). Because graphene sheets are held together by relatively weak van der Waals interactions, HOPG is easily cleavable, i.e. it is possible to dissociate graphene layers by use of scotch tape. Freshly cleaved surfaces of graphite are composed by very large (typically a few hundreds of nanometers) and atomically flat terraces.

Figure 4  a) Structure of the cleaved surface of HOPG. Full circles represent the α atoms of the graphene sheet, which are placed on top of an underlying carbon atom. Open circles represent the β atoms. By using typical scanning conditions, usually only the β atoms are visible by STM. b) STM image (1.7x 1.7 nm$^2$) of HOPG with atomic resolution ($V_T = 180$ mV, $i_T = 46$ pA).

The structure of the cleaved surface of HOPG as observed by STM is a centered hexagonal (Figure 4b), whereas it should be a simple hexagonal (honeycomb structure, Figure 4a). Moreover, the distance observed between two bright spots on the STM image (0.246 nm) is
higher than the expected interatomic distance within a sheet of graphene (0.142 nm). This phenomenon is illustrative of the fact that STM does not provide a measure of geometrical structures but of electronic structures. In fact, this peculiar STM contrast is due to the fact that not all carbon atoms of a graphene sheet are equivalent. Due to a shift between adjacent graphene sheets some atoms are on top of an atom of the underlying sheet (α type), but some are not (β type). Consequently, with most scanning conditions, the β type atoms are generating a much brighter contrast and are thus the ones which are visible by STM.25

6.2.5.2 A Gold Substrate: Au(111)

Figure 5 shows typical STM images that can be obtained on the Au(111) surface. At large scale, the morphology of this substrate is characterized by triangular terraces which can reach areas of a few nm². These terraces are triangular because the step edges delimiting them follow lines which are oriented at 120° with each other. These lines correspond to <110> directions of a (111) surface of gold. The step edges have a height of 0.25 nm, which is close to the distance between two (111) crystallographic planes of gold. At medium scale, the typical feature of the Au(111) surface lies in its reconstruction lines, which correspond to relaxation of the surface atoms of gold.26 Usually, these 22x√3 reconstruction lines follow a herringbone pattern. Observation of these lines is of crucial importance to ensure for cleanliness and quality of the prepared substrate. Atomic scale resolution is not possible to obtain by STM at the liquid/solid interface, but is achievable in ultra high vacuum, where it reveals the hexagonal centered structure shown on Figure 5c.

Figure 5 Structure of Au(111). a) STM image (500x 500 nm²) of Au(111) triangular terraces in air (V T = -418 mV, i T = 59 pA), b) STM image (78 x 78 nm²) of Au(111) herringbone reconstruction in air (V T = 630 mV, i T = 30 pA), c) Schematic representation of the structure of the Au(111) surface. Each yellow dots represents one atom of gold.
6.2.5.3 Molybdenum disulfide (MoS$_2$)

MoS$_2$ is a semi-conducting material found in nature as “molybdenite”. It crystallizes with a layered structure shown in Figure 6a. Each layer is composed of sheets of molybdenum atoms sandwiched between sheets of sulphur atoms. As for HOPG, MoS$_2$ can be easily cleaved, but unlike HOPG this cleaving forms large 2D monocrystals. On the MoS$_2$ cleavage surface, sulfur atoms form a centered hexagonal network (similar to the network of Au(111)) with an interatomic distance of $a = 0.316$ nm.

![Figure 6](image)

**Figure 6** Structure of the surface obtained by cleaving of MoS$_2$. a) The layered structure of MoS$_2$. Open circles represent sulfur atoms, the closed circles molybdenum atoms. b) STM image (7.7 x 7.7 nm$^2$) of the MoS$_2$ surface in n-tetradecane, with atomic resolution ($V_T = 400$mV, $i_T = 20$ pA). c) Zoomed in area of the previous STM image (2.0 x 2.0 nm$^2$), filtered by cross-correlation. This image shows a hexagonal network of bright spots corresponding to the location of the sulphur atoms.

6.3 Synthesis of PHB

Schiff-base derivative PHB was prepared according to the Scheme 1 from known 4-$n$-dodecyloxy-2-hydroxybenzaldehyde$^{27}$ by reacting it with commercially available 4-$n$-dodecylaniline in ethanol with the presence of a catalytic amount of acetic acid. The resulting PHB was fully characterized by means of $^1$H and $^{13}$C NMR spectroscopy and mass spectroscopy (experimental section).
6.4 Columnar Packing on HOPG

Deposition of PHB from \( n \)-tetradecane onto highly ordered pyrolytic graphite (HOPG) leads to the formation of highly ordered self-assembled monolayers (Figure 7a). Within each domain, typically extending over a few hundreds of nanometers, STM images show regularly spaced bright columns separated by darker stripes, with an intercolumnar periodicity of \( a = 3.15 \pm 0.05 \) nm. A mismatch between the columns is observed only rarely (Figure 7c). The relatively higher STM contrast is assigned to the two aromatic moieties of PHB (Figure 7b), whereas the lower contrast areas are assigned to the absorbed alkyl chains.\(^2\) The intermolecular spacing within one bright column is \( b = 0.60 \pm 0.01 \) nm. The regular spacing of the molecules within the columns suggests that intermolecular hydrogen bonding is not present between the molecular units.
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Figure 7  

a) STM image (20.1 x 20.1 nm$^2$) of a self-assembled monolayer of PHB on HOPG, $V_T = 761$ mV, $I_T = 58$ pA.

b) High resolution STM image (7.2 x 7.2 nm$^2$) of PHB on HOPG, $V_T = 374$ mV, $I_T = 9.2$ pA.

c) STM image (35.1 x 35.1 nm$^2$) of the monolayer of PHB on HOPG showing a “mismatch” between the columns within one domain, $V_T = 827$ mV, $I_T = 32$ pA.

d) Schematic representation of the packing model proposed, and associated unit cell.

Alkyl chains are aligned along one of the main <100> axes (determined by the direction of the periodicity of $\beta$ atoms of HOPG, see Figure 4) of HOPG$^{28}$ and tilted by $46 \pm 1^\circ$ with respect to the main axis of the molecular columns. This tilt angle allows the chains to reach the well-known periodicity of densely packed alkanes on HOPG ($\sim 0.43$ nm).$^{21}$ This implies that the self-assembly is dominated by alkyl chains through their 2D crystallization and their interaction with the surface. This is confirmed by the observation of inter-columnar spacing, which, instead of emulating the periodicity of the underlying substrate, is determined by the tilt and length of the alkyl tails.

6.5 Polymorphism on Au(111)

In order to compare the effects of different substrates on self-assembly, a solution of PHB in n-tetradecane was also deposited onto Au(111). As on HOPG, PHB molecules self-
assemble into parallel columns (Figure 8a,c). Within each column, the intermolecular spacing is the same as observed on HOPG. However, the angle between alkyl chains and the main columnar axis is 52 ± 2°, i.e. it is increased by 6° with respect to the angle observed on HOPG. Consequently, inter-columnar periodicity on Au (111) is increased up to 3.30 ± 0.05 nm. The tilt angle allows the alkyl chains to reach the well-known periodicity of densely packed alkanes on Au(111) (~0.48 nm)\textsuperscript{29} and to align along the <110> axis,\textsuperscript{28} which is known to be the favored direction of adsorption for alkanes on Au(111).\textsuperscript{29} The mismatch between the periodicity of the Au(111) lattice and the inter-columnar and intermolecular periodicities of PHB molecules, indicates that alkyl chain adsorption is again the dominating factor determining the packing geometry. However, mismatches and other packing defects are observed more frequently on Au(111) than on HOPG. Typically, the columns are formed by less than a dozen molecules. The presence of these defects could be interpreted as the stronger adsorption of PHB molecules on Au(111) than on HOPG, which would render the repair of defects by either diffusion on the surface, or by desorption and subsequent re-adsorption from solution, energetically unfavorable. However, this hypothesis can be excluded as during scanning, we observed in real time the formation of a misfit dislocation within an ordered area (Figure 9), which suggests that the adsorption/desorption processes are sufficiently fast for the monolayer to reach thermodynamic equilibrium. Consequently, we conclude that the formation of defects on Au(111) is not a kinetically driven phenomenon.
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Figure 8  

a) STM image (24.7 x 24.7 nm$^2$) of the self-assembled monolayer of PHB on Au(111), $V_T = -300$ mV, $i_T = 34$ pA.  
b) High resolution STM image (9.3 x 9.3 nm$^2$) of PHB on Au(111) showing the area with molecules associated into the dimers, $V_T = 340$ mV, $i_T = 37$ pA.  
c) High resolution STM image (14.1 x 14.1 nm$^2$) of PHB on Au(111) showing the “mismatch” of the columns and the dislocations within one domain of columnar packing, $V_T = 290$ mV, $i_T = 24$ pA.  
d) Tentative model of PHB packing on Au(111) associated with areas of dimer formation. In this proposed model distances and angles fit the anticipated geometries.

In addition to a columnar structure, a second type of packing of PHB was observed on Au(111), in which molecules associate into dimers and create a regular zig-zag pattern (Figure 8 a,b). Within a dimer, the intermolecular distance, 0.60 ± 0.02, nm is comparable to the intermolecular distance in the columnar structure. Despite this similar spacing between molecules, it is likely that the dimers are stabilized by hydrogen bonding (Figure 8d). Alkyl chains adopt a cis orientation with respect to the central aromatic unit and align parallel to the $<110>$ direction of Au(111). The distance between alkyl chains within a

* The hypothesis of the stabilization by intermolecular hydrogen bonding has to be further confirmed by molecular modeling calculations.
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dimer $0.49 \pm 0.02$ nm is the same as the spacing between alkanes adsorbed on Au(111), which means that they occupy optimal adsorption sites on the surface. The unit cell consists of four molecules and the average area per molecule is $2.40 \pm 0.04$ nm$^2$, which is 21% more than for columnar packing $1.98 \pm 0.04$ nm$^2$.

**Figure 9** Series of STM images (9.3 x 9.3 nm$^2$) highlighting the formation of a misfit dislocation in real time. The time scale of the measurement is 24 s per picture. $V_T = -300$ mV, $i_T = 37$ pA

### 6.6 Origin of Polymorphism on Au(111): Driving Force for Dimer Formation

It is noticeable that compared to columnar packing (Figure 8c), the dimeric structure formed on Au(111) (Figure 8b) shows an increase of average area per molecule of 21%. Throughout the STM measurements partial interconversions between columnar and dimeric structures were observed as can be seen in Figure 10 (dimer to column interconversion) and Figure 11 (column to dimer interconversion). Since the interconversion between both structures can be observed on the timescale of the STM measurements, we conclude that the activation energy of the interconversion is low and that adsorption energies are comparable for both structures. Consequently there must be an additional stabilizing effect in the dimer structure, which compensates for the loss in free energy associated with the lower density of packing. We propose that the formation of dimers on Au(111) is made possible by the presence of repulsive forces between the aromatic cores of PHB. Compared to (hypothetical dimers in) columnar packing, dimer packing allows additional stabilization because the equilibrium distance between dimers of PHB is increased: as dimers are separated from each other by insulating alkyl chains, destabilization through repulsion is minimized. Intermolecular hydrogen bonding is likely to contribute to the stabilization of dimers, however, since the spacing between the aromatic moieties within a dimer remains...
unchanged with respect to the spacing between two molecules in columnar packing, it is unlikely that this factor would be sufficient to account for dimer formation.

**Figure 10** Consecutive STM images of the same area (24.7 x 24.7 nm²). During scanning, part of the dimer-packed area (top right part of the image) transforms into an area of columnar packing. \( V_T = -300 \text{ mV}, i_T = 34 \text{ pA} \).

**Figure 11** Consecutive STM images of the same area (22.4 x 22.4 nm²). During scanning, part of the columnar-packed area (right part of the image) is transformed into an area of dimer packing. \( V_T = 350 \text{ mV}, i_T = 21 \text{ pA} \).

In the light of these results we sought an explanation to account for the occurrence of repulsive forces and consequently for polymorphism within the self-assembled monolayer. We propose that molecule/molecule repulsive forces arise from molecule/substrate interactions, through either van der Waals or charge transfer interactions, or both of them. * 

* In order to validate this hypothesis complementary experimental and theoretical investigations on interfacial dipole moments and possible charge transfer interactions are currently being conducted by means of XPS and UPS spectroscopies and molecular modeling calculations. Also see discussion below.
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In physisorbed systems, attractive van der Waals interactions are present between the adsorbate and the substrate.\textsuperscript{30} It is well known that when a molecule adsorbs on a substrate its permanent and induced dipolar moment create opposite image charges in the substrate. This leads to the formation of interfacial dipole moments, which are oriented perpendicularly to the surface.\textsuperscript{31} Given that all interfacial dipoles are oriented in the same direction, lateral repulsive forces between dipoles increase the Gibbs free energy of the system. The strength of the induced dipole moment, and consequently of the repulsion, for different parts of the molecule interacting with the substrate, is a function of their polarizability. Since the polarizability of alkanes is low compared to that of aromatic compounds\textsuperscript{32} we can assume that repulsions resulting from the induced dipole moment of the alkyl chains are negligible. This assumption is supported by the well-known formation of highly organized and densely packed adlayers of alkanes at different liquid/solid interfaces.\textsuperscript{16,28,33}

However, it is likely that the intensity of induced surface dipoles formed through van der Waals interactions alone is not strong enough to explain polymorphism in PHB monolayers on Au(111). Calculations on the adsorption energy of cyanobiphenyl self-organized monolayers on MoS\textsubscript{2} have shown that neither the STM nor the XRD observations can be explained by dipolar and quadripolar interactions arising from the van der Waals interactions between molecule and substrate.\textsuperscript{34} This suggests that in some cases the surface-induced intermolecular repulsion, and as a consequence the 2D crystal reorganization, arises from strong repulsive forces mainly created by partial charge transfer at the interface. Charge transfer between aromatic compounds and a conductive surface has been established recently with several techniques including photoemission spectroscopy,\textsuperscript{35} reflectance absorption infrared spectroscopy,\textsuperscript{36} scanning tunneling spectroscopy in UHV\textsuperscript{37} or at the liquid/solid interface.\textsuperscript{38} As a consequence, partially charged adsorbates of the same sign repel each other and increase the Gibbs free energy of system.

Whether charge transfer or van der Waals interactions are dominant features involved in the adsorption, both induce greater charging of the adsorbate on Au(111) than on HOPG. Therefore it is anticipated that stronger intermolecular repulsions between PHB molecules on Au(111) induce defects and strains within the columns of columnar packed structures and consequently increases the energy of the columnar lattice. This facilitates formation of the dimer lattice, which has a lower packing density and allows the aromatic units to be spaced further apart than in columnar packing. Both columnar and dimeric structure can thus coexist on Au(111) due to the similar energies unlike on HOPG where the columnar structure is more stable.

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As discussed above, substrate-induced polymorphism can originate not only, as is shown, from substrate-induced intermolecular interactions, but also from simple geometric factors. In this particular case, the decreased surface density of the dimer packing on Au(111) could be due to the fact that the Au(111) lattice has a higher periodicity than the hexagonal HOPG lattice. However, these geometric factors do not play a significant role in the expansion of the molecular monolayer on Au(111) since the aromatic units of the molecules do not emulate the periodicity of the substrate, i.e. they show a low degree of commensuration with the substrate. STM experiments with PHB monolayers on other substrates, for example on MoS$_2$, on which the density of packing of alkanes has been shown previously to be the same as on Au(111), and on pentacontane-($n$-C$_{50}$H$_{102}$)-modified HOPG were carried out to exclude this possibility further.

6.7 Possible Influence of Geometrical Factors: Self-Assembly on MoS$_2$ and C50/HOPG

Deposition of PHB was performed on MoS$_2$ to exclude the influence of a modification in lattice periodicity and thereby to confirm the importance of the substrate-aromatic core interaction in the polymorphism observed on Au(111). Linear alkanes form self-organized monolayers on MoS$_2$ with an intermolecular distance of 0.48 ± 0.02 nm. In contrast to HOPG and Au(111), the periodicities of adsorbed alkanes and of the substrate do not correspond on MoS$_2$: the periodicity of alkanes on MoS$_2$ mimics the spacing of alkanes in the bulk phase. This periodicity of packing for alkanes on MoS$_2$ is comparable to that reported on Au(111). Therefore, if only geometrical factors would be involved in the formation of bimorphic structures on Au(111) and assuming that 2D crystallization of alkyl tails is the prevailing factor of the self-assembly on MoS$_2$ as on Au(111), then a polymorphic monolayer with two different structures should be observed on MoS$_2$, as on Au(111). Since only columnar structures are observed on MoS$_2$ (vide infra), this experimental result supports that geometrical effects are not involved in polymorphism on Au(111).

Figure 12a shows a typical STM image of a self-organized monolayer of PHB on MoS$_2$. Within experimental uncertainty, the lattice constants are the same as those determined for self-organized monolayers on Au(111). The inter-columnar periodicity is 3.3 ± 0.1 nm and the intermolecular spacing within each column is 0.61 ± 0.02 nm. The separation between alkyl tails is 0.49 ± 0.02 nm and they adopt an angle of 53 ± 2° with respect to the columnar axis. The monolayer displays a low degree of commensurability and large uniform domains extending over a few hundreds of nanometers, free of mismatches or dislocations. Dimer
formation was never observed. This suggests that, in contrast to Au(111), strong intermolecular repulsive forces are absent. The semi-conducting nature of MoS$_2$ and hence the large energy gap between occupied and unoccupied states, limits the ability of MoS$_2$ to interact with orbitals of adsorbed molecules. Thus, PHB molecules cannot form charge transfer complexes on MoS$_2$ as readily as on Au(111).\textsuperscript{39} We conclude that because charge transfer does not occur, the MoS$_2$ surface generates weaker adsorbate-surface interactions than those present on Au(111), and hence weaker intermolecular repulsion within the monolayer.

Figure 12 a) STM image (27.2 x 27.2 nm$^2$) of the self-assembled monolayer of PHB on MoS$_2$, $V_T = 2830$ mV, $i_T = 19$ pA. b) STM image (43.8 x 43.8 nm$^2$) showing a growth of the domain composed of PHB on top of pentacontane-modified HOPG (n-C$_{50}$H$_{102}$/HOPG), $V_T = 520$ mV, $i_T = 21$ pA. c) High resolution STM image (15 x 15 nm$^2$) of the monolayer of PHB on (n-C$_{50}$H$_{102}$/HOPG), $V_T = 520$ mV, $i_T = 21$ pA.

A second approach to elimination of charge transfer interactions is to employ buffer monolayers on top of which a self-assembled monolayer can be formed.\textsuperscript{40} The buffer layer is typically composed of aliphatic alkanes\textsuperscript{41} or functionalized alkanes\textsuperscript{40,42} assembled on a surface, often HOPG. The buffer layer precludes electronic coupling of aromatic molecules with the substrate and hence limits charge transfer interactions. This strategy has been employed in the immobilization of phthalocyanines lacking the anchoring alkyl tails at the liquid/solid interface.\textsuperscript{40} The immobilization was rationalized by reduction in charge transfer interactions between the aromatic molecules and HOPG.

In the present study a buffer layer composed of pentacontane (n-C$_{50}$H$_{102}$) was employed on HOPG, to study the self-assembly of PHB. Pentacontane is known to self-assemble on
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HOPG by forming large domains of parallel lamellae (Figure 12b, bottom part). Each lamella is composed of molecules oriented perpendicular to the lamellae direction and parallel to the <100> direction of the HOPG lattice. When PHB is deposited on pentacontane-modified HOPG (n-C\(_{50}\)H\(_{102}\)/HOPG) the domain formation is initiated primarily on step edges (Figure 12b). This suggests that molecule-substrate interactions are weak, decreasing the residence time of the molecule on the n-C\(_{50}\)H\(_{102}\)/HOPG surface and hence the probability of nucleation. High resolution STM images (Figure 12c) show that the alkyl tails of PHB are located in the troughs of the underlying pentacontane lamellae. Hence the formation of PHB columns is again expected to be driven by 2D crystallization of alkyl tails. As a consequence of the underlying buffer layer, whose geometry is directed by HOPG, the columnar structure has similar lattice characteristics as in case of the columns formed on bare HOPG. The inter-columnar periodicity is 3.15 ± 0.05 nm and the intermolecular spacing within each lamella is 0.60 ± 0.01 nm. The separation between alkyl tails is 0.42 ± 0.02 nm, as for simple alkanes on HOPG and they adopt an angle of 45 ± 2° with the lamella axis. Neither defects within lamellae nor dimer formation were observed, indicating that intermolecular repulsion does not play as significant role as in the case of adsorption on Au(111) or HOPG.

6.8 Conclusions

In summary, this investigation indicates that in self-assembled monolayers, the 2D polymorphs that form spontaneously on a conductive Au(111) surface originate from surface-induced repulsion between aromatic units of the molecular building blocks. On Au(111), STM reveals two different packing types: a columnar packing, also observed on other surfaces including HOPG and MoS\(_2\), and a dimer packing of lower density observed on Au(111) exclusively. We suggest that the presence of areas with dimer packing on Au(111) is due to a destabilization of the columnar packing in which partially charged aromatic units repel each other. This is likely to be a direct consequence of the ability of the substrate to form charge transfer interactions with the molecule, which, depending on the density and proximity of states, favors more conductive substrates. Further evidence of these strong intermolecular repulsions is found in the packing defects within the columnar packing. Such defects are observed frequently on Au(111), however, only rarely on HOPG, and never on MoS\(_2\) or pentacontane-modified HOPG.

The demonstration that substrate-induced intermolecular repulsions can play a prominent role in 2D self-assembly highlights the fact that the effects of molecule/molecule and molecule/surface interactions on molecular packing cannot always be considered as independent phenomena. This also means that, in order to direct the self-assembly of
molecules into highly ordered patterns on a surface successfully, substrates must be chosen carefully.

Of particular note is the possibility of tuning the magnitude of intermolecular repulsive forces by varying the contribution of charge transfer between the substrate and adsorbed molecules and to reduce the strength of the interfacial dipole moment, which arises through physisorption of the molecules. By reducing the contribution of these effects, the need to employ strong intermolecular interactions such as coordination or hydrogen bonding, or the use of long alkyl spacer as stabilizing functional groups for monolayers at liquid/solid interface, can be reduced. In addition, it can be envisioned that when a mixture of two molecules is used to create a monolayer and one component acts as a donor forming a charge-transfer complex with the substrate and the other component as an acceptor, an evenly alternating monolayer composed of both components could be formed, which takes advantage of oppositely oriented interfacial dipoles. More generally, it is likely that by adjusting molecule/substrate interactions, intermolecular repulsion through interfacial attraction will provide an orthogonal approach to controlling the self-assembly process of monolayers.

6.9 Experimental Section

General Remarks

See Chapter 2 for details on synthetic methods and information on characterization of compounds.

Preparation of Substrates

Au(111) was prepared by evaporation of 99.99% gold, Umicore Materials AG, on freshly cleaved mica sheets, Ted Paella, Inc., at $10^{-7}$ mbar in a home-built evaporator in the Materials Science Centre, University of Groningen. The thickness of the gold layer was $\sim$150 nm. Prior to formation of the self-assembled monolayer, reconstruction of the Au(111) surface was checked for by STM in $n$-tetradecane. 

Highly oriented pyrolytic graphite (HOPG) was bought from Goodfellow and freshly cleaved prior to deposition of the molecules.

MoS$_2$ single crystals were provided by Dr. E. Lacaze, for which she is gratefully acknowledged. They were freshly cleaved before use.

Pentacontane-modified HOPG ($n$-C$_{50}$H$_{102}$/HOPG) was prepared by deposition of a warm droplet of saturated pentacontane (Fluka) solution in $n$-tetradecane (Aldrich), onto a freshly
cleaved surface of HOPG. The formation of the pentacontane monolayer was observed by STM. The excess of pentacontane was washed away with few droplets of tetradecane, before addition of the PHB monolayer.

**Preparation of Samples**

A solution of PHB in $n$-tetradecane (Aldrich) was sonicated for 5 min and heated at 40°C for 20 min so as to form a saturated solution. A drop of the warm solution was applied to the prepared substrates and the STM tip was immersed into the solution for imaging.

**Scanning Tunneling Microscopy (STM)**

All experiments were performed at room temperature, using a PicoSPM (Molecular Imaging, Scientec), at the interface between the surface and tetradecane. Pt/Ir STM tips were prepared mechanically from Pt/Ir wire (80:20, diameter 0.25 mm, Goodfellow). The parameters of the unit cells were measured after drift effects were corrected with the Scanning Probe Image Processor (SPIP) software (Image Metrology ApS). However, the presented STM images contain raw data and are not subjected to any processing other than routine plane correction.

**4-(Dodecyloxy)-N-(4-dodecyl)-phenyl-2-hydroxybenzaldimine (PHB)**

The Schiff base derivative PHB was prepared by refluxing 2.34 g (7.65 mmol) of 4-dodecyloxy-2-hydroxybenzaldehyde with 2 g (7.65 mmol) of 4-dodecylaniline in absolute ethanol for 18 h, with a few drops of glacial acetic acid as the catalyst. The solvent was evaporated and the crude product was crystallized several times from hot absolute ethanol. Yield 86% (3.6 g). M. p. 102-103 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.88 (t, 6H), 1.20-1.40 (m, 34H), 1.40-1.5 (m, 2H), 1.55-1.67 (m, 2H), 1.79 (quintet, $J$=7.7 Hz, 2H), 2.62 (t, 2H, $J$=7.7 Hz) 4.00 (t, $J$=6.6 Hz, 2H), 6.47 (d, $J$=8.3 Hz, 2H), 6.51 (s, 1H) 7.16-7.21 (m, 4H), 7.23 (d, 1H, $J$=8.3 Hz), 8.52 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.1 (s), 22.7 (d), 26.0 (d), 29.1 (d), 29.2 (d), 29.3 (d), 29.5 (d), 29.6 (d), 29.6 (d), 29.7 (d), 31.5 (d), 31.9 (d), 35.5 (d), 68.2 (d), 101.5 (t), 107.5 (t), 120.7 (t), 129.3 (t), 133.3 (t), 141.4 (q), 145.8 (q), 160.5 (t), 163.4 (q), 164.0 (q) ppm; MS (EI): 549 [M+]; HRMS: calcd. for C$_{37}$H$_{59}$NO$_2$ 549.455, found 549.454.

### 6.10 References and Notes


For recent reviews on STM investigations at the liquid-solid interface, see for example:


(a) A. Gesquiere, S. de Feyter, F. C. De Schryver, F. Schoonbeek, J. van Esch, R. M. Kellogg, B. L. Feringa, *Nano. Lett.* 2001, 1, 201-206; (b) M. Surin, P. Leclere, S. De


28 The orientation of the self-assembled monolayer with respect to HOPG was determined by imaging HOPG beneath the self-assembled monolayer. The orientation of PHB alkyl
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chains with respect to Au(111) was determined by using the Au(111) reconstruction stripes which, under specific scanning conditions, can be distinguished under the self-assembled monolayer.


