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Intermolecular Repulsion through Interfacial Attraction: Toward Engineering of Polymorphs

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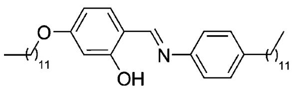
Abstract: Understanding the formation of crystalline polymorphs is of importance for various applications of materials science. Polymorphism of Schiff base derivatives has recently attracted considerable attention because of its influence on photochromic and thermochromic properties of their 3D crystals. The present investigation extends the study of Schiff base polymorphism to the molecular level by using a combination of scanning tunneling microscopy at the liquid/solid interface and molecular modeling. It is demonstrated that polymorphism of 4-(dodecyloxy)-*N*-(4-dodecylphenyl)-2-hydroxybenzaldimine (PHB), a Schiff base substituted by alkyl side chains, can occur in 2D crystals when PHB is adsorbed on a surface that is able to exchange charge with the molecule. In particular, on Au(111), PHB molecules self-organize not only into a columnar packing but also in dimer structures. Theoretical and experimental results demonstrate that the dimer-based structure observed on Au(111) originates from molecule/surface interactions, which in turn modify molecule/molecule interactions. The results highlight that the Au(111) substrate is far from being a passive part of the self-assembled system and plays a crucial role in the morphology of 2D polymorphs.

Introduction

Crystal polymorphism, which embodies the ability of molecules to form various packing arrangements with different physical and chemical properties, is of importance in fields such as pharmacology, solid-state chemistry, and materials science.[1] In particular, understanding which interactions drive the formation of 2D polymorphic crystals is crucial to achieve control over nanofabrication methods, which utilize the bottom-up molecular approach to build organic devices. Polymorphism of a class of molecules called Schiff bases, whether in 3D crystals[2] or in glassy films, has attracted considerable interest because of the photochromic and thermochromic properties of these molecules.[3] Previous studies have shown that for these molecules, some crystalline polymorphs exhibit thermochromic properties (their color is modified by a change in temperature), whereas another class of polymorphs is photochromic (their color is modified by irradiation with light).[4] This difference in behavior was attributed to different conformations of the molecules in the polymorphs. The polymorphs in which the molecules adopt a planar conformation display thermochromism because of a hydrogen transfer from the oxygen to the nitrogen, to form the keto isomer.[5] Alternatively, in the second class of polymorphs, the molecules adjust to nonplanar conformations; therefore, they can undergo trans−cis isomerization and display photochromism.[6] In the present investigation, we extend studies on Schiff base polymorphs to the molecular level by using scanning tunneling microscopy (STM) at the liquid/solid interface.[7] In particular, we demonstrate that polymorphism of these molecules can also occur in two-dimensional crystals formed on an atomically flat surface.

Scheme 1. Structure of 4-(Dodecyloxy)-*N*-(4-dodecylphenyl)-2-hydroxybenzaldimine (PHB)



The hydroxy-substituted Schiff base used in the frame of this investigation is 4-(dodecyloxy)-*N*-(4-dodecylphenyl)-2-hydroxybenzaldimine (PHB, Scheme 1). The 2D molecular organization of alkylated Schiff bases on highly oriented pyrolytic graphite (HOPG) has previously been reported.[8] The central unit of PHB, composed of aromatic cores, is functionalized by two alkyl

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10.1021/ja901718q CCC: $40.75

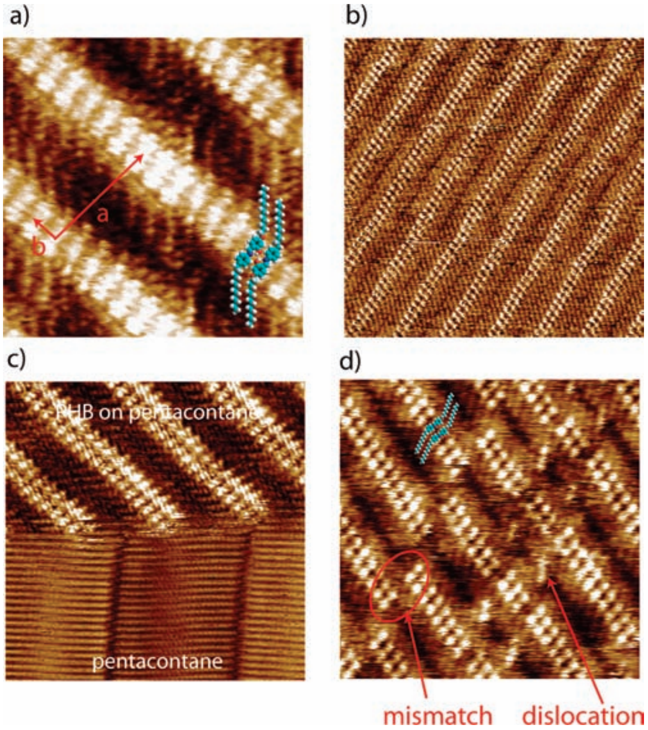

Figure 1. STM images of monolayers with columnar structure formed by self-assembly of PHB on various substrates: (a) on HOPG, $V_T = 374$ mV, $i_T = 9.2$ pA, 7.2 × 7.2 nm^2; (b) on MoS$_2$, $V_T = 2830$ mV, $i_T = 19$ pA, 27.2 × 27.2 nm^2; (c) on n-$C_{50}H_{102}$/HOPG, $V_T = 520$ mV, $i_T = 21$ pA, 15 × 15 nm^2; and (d) on Au(111), $V_T = 290$ mV, $i_T = 24$ pA, 14.1 × 14.1 nm^2.

chains with a length of 1.5 nm in the extended conformation, incorporated to stabilize the monolayer.[9]

Results and Discussion

We investigated the self-assembly of PHB on a range of substrates having different atomic arrangement, corrugation, and electronic characteristics: metallic Au(111), semimetallic HOPG, semiconducting MoS$_2$, and pentacontane-modified HOPG.[10] On all these substrates, including Au(111), PHB forms stable monolayers with a columnar structure. The corresponding STM images show regularly spaced bright columns separated by darker stripes (Figure 1). The bright STM contrast of the columns stems from the two aromatic moieties of PHB, whereas the lower contrast areas are assigned to the adsorbed alkyl chains. Within one bright column, the aromatic moieties are regularly positioned, with an intermolecular spacing of $b = 0.60 \pm 0.05$ nm. In all these columnar structures, alkyl chains adopt a *transoid* orientation with respect to the central aromatic unit (see Figure 1). The intercolumnar periodicity is characterized by a lattice parameter $a = 3.15 \pm 0.20$ nm on HOPG and on pentacontane, and by $a = 3.30 \pm 0.20$ nm on Au(111) and on MoS$_2$. On HOPG, alkyl chains are aligned along one of the main ⟨100⟩ axes of HOPG and tilted by 46 ± 2° with respect to the main axis of the molecular columns.[11] This tilt angle allows the chains to reach the well-known periodicity of densely packed alkanes on HOPG (∼0.43 nm).[12] Alternatively, on Au(111), the angle between alkyl chains and the main columnar axis is 52 ± 3°, i.e., it is increased by 6° with respect to the angle observed on HOPG. Consequently, intercolumnar periodicity on Au (111) is increased to 3.30 ± 0.2 nm. The tilt angle allows the alkyl chains to reach the well-known periodicity of densely packed alkanes on Au(111) (∼0.48 nm)[13] and to align along ⟨110⟩,[11] which is known to be the favored direction of adsorption for alkanes on Au(111).

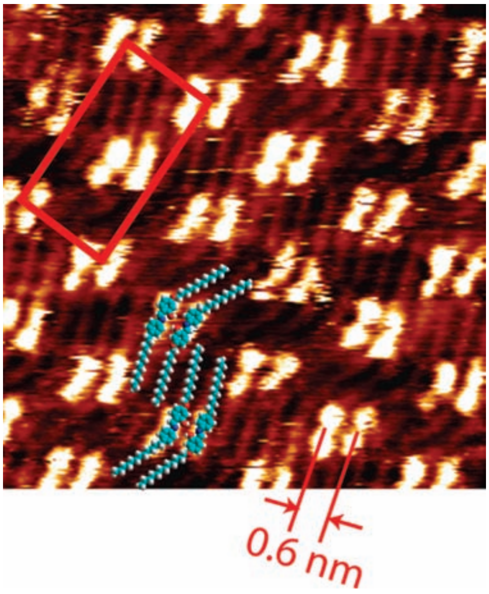

Figure 2. STM image of the dimer packing of PHB on Au(111), $V_T = 340$ mV, $i_T = 37$ pA, 9.3 × 9.3 nm^2. The unit cell is marked in red.

Of the four substrates investigated here, Au(111) is the only one where a dimer-based structure is formed in addition to the columnar structure (Figure 2). Within a dimer, the intermolecular distance of 0.60 ± 0.05 nm is comparable to the intermolecular distance in the columnar structure. In the dimer structure, in contrast to what happens in the columnar structure, alkyl chains adopt a *cisoid* orientation with respect to the central aromatic unit. They are aligned parallel to the ⟨110⟩ direction of Au(111). The distance between alkyl chains within a dimer, 0.49 ± 0.05 nm, is the same as the spacing between alkanes adsorbed on Au(111),[13] which means that they occupy optimal adsorption sites on the surface. The unit cell consists of four molecules with unit cell parameters $a = 4.2 \pm 0.20$ nm and $b = 2.15 \pm 0.20$ nm, and the average area per molecule is 2.30 ± 0.20 nm^2, i.e., 14% more than for the columnar packing (1.98 ± 0.20 nm^2).

Understanding the origin of the dimer phase on Au(111) is of general interest because controlling the formation of 2D polymorphs is a prerequisite for the design of functional molecular surfaces. To explain the formation of these dimers on Au(111), we performed comparative molecular modeling calculations on HOPG and on Au(111).

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[10] Pentacontane-modified HOPG is prepared as follows: a drop of saturated solution of pentacontane in tetradecane is deposited on HOPG. After 15 min, the surface is rinsed with tetradecane, and proper preparation of the pentacontane-modified HOPG is verified by using STM.

[11] 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 chains with respect to Au(111) was determined by using the Au(111) reconstruction stripes.

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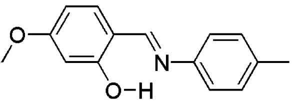
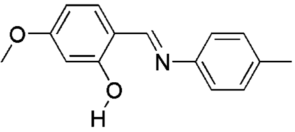
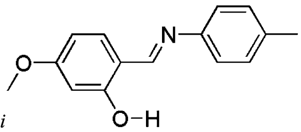
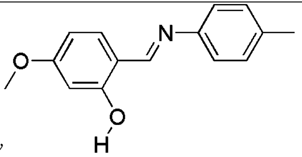
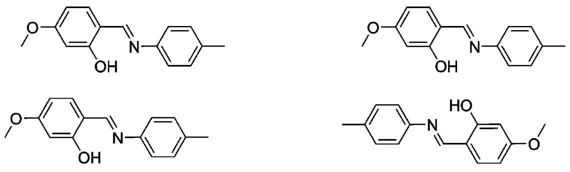
Table 1. Relative Energies and, in Parentheses, the Binding Energy to the Surface for the PHB′ Co-conformers in the Isolated Phase on Au(111) and on HOPG As Determined by Molecular Dynamics Calculations[a]

Conformer	Isolated	Au(111)	HOPG
 *i*	0.0	0.0 (-35.3)	0.0 (-20.8)
 *ii*	4.7	12.8 (-27.2)	5.5 (-15.2)
 *iii*	6.3	6.9 (-34.6)	6.7 (-14.0)
 *iv*	7.3	8.9 (-33.7)	6.4 (-14.4)

[a] All energies are in kcal mol^{-1}.

Scheme 2. Schematic Representation of Two Possible Arrangements for a PHB′ Pair on a Surface: Face-to-Face (**FF**) and Back-to-Face (**BF**) Arrangements



PHB' pair in face-to-face (**FF**) arrangement PHB' pair in back-to-face (**BF**) arrangement

From the observations described above, one can conclude that the alkyl side chains of PHB are in all cases quasi-commensurate with the substrate since their arrangement both on HOPG and on Au(111) is the same in the absence of any aromatic core. The important implication is that in either of those cases no excess strain due to the introduction of the alkyl chains is created upon deposition on the substrate. We anticipated that the difference in the arrangements formed on HOPG and on Au(111) is related to a different behavior of the aromatic cores of the molecules on these two substrates. To understand the formation of PHB polymorphs on Au(111), we consequently sought to determine the structure of a pair of PHB molecules without alkyl chains on HOPG and on Au(111). In the following discussion we define PHB′ as PHB without alkyl side chains. Given that the alkyl chains do not induce extra strain in the studied systems, the same conclusions can be drawn on polymorphism of PHB′ and PHB pairs.

Each PHB molecule can adopt four different conformations, labeled from *i* to *iv* (Table 1), and for each pair of conformers, either a face-to-face (**FF**) or a back-to-face (**BF**) arrangement is possible (Scheme 2). This stereochemical analysis shows that there are 10 (**FF**) + 10 (**BF**) possible structures for a pair of PHB′ on a surface: these 20 structures are reported in Table 2.

Two conformations of PHB′ are formed by rotation around the C−C bond that connects the hydroxybenzaldimine moiety to the rest of the molecule, and the two other conformations are formed by torsion around the aryl−OH bond. These four conformers are labeled from *i* to *iv* in Table 1. In the isolated phase, the relative energies of the conformers are within 7.3 kcal mol^{-1}. The energy of the most stable conformer *i* is used as reference and set to zero. Conformer *i* remains the most stable one when PHB is adsorbed on Au(111) and on HOPG.

Calculations were performed for all 20 possible arrangements of PHB′ pairs, both on HOPG and on Au(111).[14] The outcome of these calculations is reported in Table 2. A major component of the total energy of the system is the binding energy, E_{bind}. This energy differs from the stabilization energy because it is calculated with the molecules and the substrate distorted by their mutual interaction. Table 2 indicates that the binding energy of the molecular pairs of PHB′ is larger on Au(111) than on HOPG. The largest contribution to the binding energy is given by the electrostatic component, E_{electr}, which is at least twice as large in the case of adsorption on the metal surface as on HOPG. Finally, the electron transfer from PHB′ pairs to the substrate indicates that HOPG decreases the electron density of the molecules, whereas on Au(111) the electron density of molecules is enhanced.

On HOPG, **FF**(*i*-*i*) is the most stable pair arrangement and no other competing structure exists. Indeed, the second most stable arrangement, **FF**(*i*-*ii*), is 4.1 kcal mol^{-1} higher in energy than **FF**(*i*-*i*), and at room temperature this energy difference makes the probability of observing **FF**(*i*-*ii*) about 1000 times smaller than that of observing **FF**(*i*-*i*). It is well known that when a molecule adsorbs on a substrate its permanent and induced dipolar moments create opposite image charges in the

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(14) Experimental details are given in the Supporting Information.

Table 2. Relative Energies of PHB′ Pairs on HOPG and on Au(111) in a Face-to-Face (**FF**) or Back-to-Face (**BF**) Arrangement[a]

	FF		**BF**	
	Au(111)	HOPG	Au(111)	HOPG[b]
i-i	0.0 (−83.5) [−49.4] {0.63}	0.0 (−69.5) [−22.3] {−0.14}	1.1 (−77.8) [−55.8] {0.66}	6.5 (−69.8) [−20.4] {−0.15}
ii-ii	7.2 (−82.3) [−46.3] {0.55}	5.1 (−68.8) [−20.6] {−0.18}	6.7 (−76.9) [−48.7] {0.59}	−
iii-iii	17.0 (−76.1) [−45.7] {0.59}	13.1 (−69.0) [−20.1] {−0.16}	14.8 (−72.8) [−36.9] {0.62}	−
iv-iv	17.0 (−75.1) [−43.6] {0.60}	11.8 (−68.5) [−19.8] {−0.17}	20.7 (−68.6) [−34.3] {0.64}	6.5 (−68.2) [−19.3] {−0.17}
i-ii	14.5 (−77.0) [−46.0] {0.61}	4.1 (−68.2) [−19.3] {−0.18}	14.0 (−74.1) [−51.1] {0.58}	−
i-iii	17.5 (−74.1) [−40.9] {0.61}	8.9 (−68.1) [−19.5] {−0.15}	10.4 (−87.7) [−48.0] {0.61}	−
i-iv	14.8 (−75.3) [−41.1] {0.59}	9.0 (−68.0) [−19.8] {−0.15}	10.7 (−85.5) [−47.3] {0.58}	−
ii-iii	17.6 (−75.8) [−40.4] {0.61}	12.6 (−68.9) [−20.5] {−0.18}	17.3 (−75.3) [−41.5] {0.60}	7.4 (−69.7) [−20.3] {−0.22}
ii-iv	15.7 (−77.7) [−38.8] {0.56}	12.4 (−68.9) [−20.4] {−0.18}	23.1 (−62.3) [−38.3] {0.58}	−
iii-iv	18.5 (−71.9) [−43.9] {0.58}	13.2 (−68.5) [−19.1] {−0.17}	20.8 (−70.8) [−38.5] {0.64}	−

[a] The following data are provided: the binding energy to the surface (E_{bind}), the electrostatic energy [E_{electr}], and the amount of electron transfer from a PHB′ pair to the substrate {ΔE}. All energies are in kcal mol^{-1}. [b] Upon geometry optimization, only three pairs remain.

substrate. This leads to the formation of interfacial dipole moments, which are oriented perpendicularly to the surface.[15]

The interfacial dipolar moment associated with a **FF**(*i*-*i*) pair, as calculated from the value of charge transfer, $\Delta E_{\mathbf{FF}(i\text{-}i)}$, is $\mu_{\mathbf{FF}(i\text{-}i)} = 2.43$ electrons Å^{-1}. This value is sufficiently low to prevent lateral repulsive forces between interfacial dipoles. Therefore, we conclude that the dense columnar phase observed on HOPG is allowed to form by stacking of pairs of PHB in a **FF**(*i*-*i*) arrangement.

Our calculations show that the electron transfer from a PHB′ pair to Au(111) is larger than that to HOPG (Table 2). This is confirmed by ultraviolet photoelectron spectroscopy (UPS) measurements, which allow us to probe the workfunction of surfaces. Samples of PHB on HOPG and on Au(111) were prepared as for the STM measurements. Due to the necessity to operate under ultra-high-vacuum (UHV) conditions, they were dried prior to introduction under UHV.[14] Taking for clean Au(111) a workfunction value of 5.4 eV,[16] from the shift in cutoff measured for the PHB films with respect to the gold sample we determined for PHB a workfunction of 4.3 eV. Alternatively, for PHB on HOPG the workfunction amounted to 3.9 eV.

Importantly for polymorphism engineering, the high interfacial dipolar moments observed on Au(111) correspond to large charge transfer with the metal (as calculated and reported in Table 2). Charge transfer between aromatic compounds and a conductive surface has also been recently established by photoemission spectroscopy,[17] reflectance absorption infrared spectroscopy,[18] and scanning tunneling spectroscopy in UHV[19] or at the liquid/solid interface.[20]

Contrary to what happens on HOPG, on Au(111) **FF**(*i*-*i*) is not the only stable arrangement: the energy difference between **FF**(i-i) and **BF**(i-i) is 1.1 kcal mol^{-1}, which is within the accuracy of our model. Therefore, both pairs can coexist in the monolayer. These two arrangements differ by the dipolar moments $\mu_{\mathbf{FF}(i\text{-}i)}$ and $\mu_{\mathbf{BF}(i\text{-}i)}$ that they induce perpendicularly to the surface: **FF**(*i*-*i*) induces a higher dipolar moment than **BF**(*i*-*i*).

In the light of these results, we can propose an explanation for the polymorphism of PHB on Au(111). The interfacial dipole moment of **BF**(*i*-*i*) is sufficiently small ($\mu_{\mathbf{BF}(i\text{-}i)} = 2.22$ electrons Å^{-1}) to allow the columnar phase to grow. In contrast, the dipolar moment of **FF**(*i*-*i*) on Au(111) is relatively large ($\mu_{\mathbf{FF}(i\text{-}i)} = 3.56$ electrons Å^{-1}), and given that all interfacial dipoles are oriented in the same direction, lateral repulsive forces between dipoles increase the free energy of the system. As pairs of molecules are separated from each other by insulating alkyl chains, the destabilization through repulsion is likely to be minimized when the distance is increased. It is then concluded that the dimer packing, which has a lower packing density than the columns, is favored by self-assembly of **FF**(*i*-*i*) dimers on Au(111). Recently, ordering of molecular adsorbates mediated by repulsion between molecules has been observed on Cu(111), Cu(110), and Ag(111) under UHV conditions.[21−23] These investigations were focused on submonolayer coverages. In contrast, our investigations reveal that repulsion-mediated ordering is observed at full monolayer coverages also, while dynamic exchange of molecules between the surface and the solution occurs at the interface.

Conclusions

On Au(111), two different structures are formed by self-assembly of PHB: a columnar packing, also observed on other surfaces, and a dimeric packing of lower density, observed on Au(111) exclusively. The origin of dimeric packing on Au(111) likely lies in molecule/molecule interactions, which drive the formation of monolayers on all the surfaces we investigated. By using molecular modeling, we show that two arrangements are allowed for a pair of PHBs on Au(111), corresponding to either the back-to-face or the face-to-face arrangement of the two aromatic cores. The calculations show that these two different arrangements are at the origin of different 2D polymorphs, because the interfacial dipole moment created by a face-to-face pair on Au(111) is significantly larger than the interfacial dipole moment created by the back-to-face arrangement. UPS measurements confirm that molecule/substrate interactions modify the chemical nature of the molecule by charge transfer with the metal. These molecule/substrate interactions finally feedback to the aforementioned molecule/molecule interactions. In the dimer packing observed on Au(111), the increased equilibrium distance between pairs of PHB compensates for the

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stronger molecule/molecule repulsive interactions. This interpretation of PHB polymorphism on Au(111) is in agreement with numerous investigations reporting polymorphic structures for Schiff bases in 3D crystals.[4,6]

The reported results highlight that the Au(111) substrate is far from being a passive element of the self-assembled system; it can modify or even disrupt the interactions originally established between the molecules of the monolayer, thereby providing a first step toward engineering of 2D polymorphs. In the future, it is likely that, through molecule/molecule repulsions, adjustment of molecule/substrate interactions will provide an orthogonal approach to controlling the self-assembly process of monolayers.

We have demonstrated that polymorphism of Schiff bases, which has been extensively studied in 3D crystals, can occur in 2D crystals also, in particular on Au(111). Spectroscopic properties of the two polymorphs formed on Au(111) are not reported here; they require the use of a semitransparent layer of Au(111).[24] However, further spectroscopic investigations on these monolayers, in particular temperature-dependent investigations, could contribute to a better understanding of the molecular changes which occur during color change of these systems.

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Supporting Information Available: Experimental details, synthesis, and spectral characteristics of PHB. This material is available free of charge via the Internet at http://pubs.acs.org.

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