Molecule Length-Induced Reentrant Self-Organization of Alkanes in Monolayers Adsorbed on Au(111)

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We report the observation by scanning tunneling microscopy of the reentrant self-organization of n-alkanes (C_nH_{2n+2}) in monolayers adsorbed on Au(111) induced by a variation of the chain length. In the investigated range of lengths ($10 \leq n \leq 38$ with even n values), the presence of self-assembled monolayers which consist of a close-packed arrangement of molecules lying flat on the surface is evidenced except for alkanes with $18 \leq n \leq 26$. The unexpected transition between ordered and disordered phases is related to the mismatch between Au(111) lattice and the CH_2-group period along the chain.

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Thin overlayers deposited onto the surface of a solid substrate play a critical role in many domains of technological applications ranging from corrosion inhibitors to biocompatible materials or from lubrication to adhesion. Properties of these overlayers often depend on the arrangement of adsorbates onto the substrate. For ultrathin films, various structures have been observed during the monolayer growth onto crystal surfaces. For example, overlayers of physisorbed rare gas [1] or of alkali atoms deposited on metal surfaces [2] exhibit very different structures depending on the adsorbate coverage. In fact, the overlayer structure is governed, in a simplified picture, by the competition between the lateral adsorbate/adsorbate interaction and the surface corrugation potential of the substrate at thermodynamic equilibrium. For linear adsorbates such as alkane and substituted-alkane molecules deposited on the basal surface of graphite, some scanning tunneling microscopy (STM) studies have evidenced the sensitivity of the monolayer structure to changes in the molecule/molecule interaction and/or in the molecule/substrate one [3–12]. For example, the monolayers of long alkane ($n > 24$) and the ones of long-chain alcohols present a similar structure consisting of lamellae separated by troughs. However, these monolayers display different angles between molecule axes and troughs, 90° for alkanes [5–8,11] and 60° or 76° for alcohols [5,9,12]. These differences are related to changes in intermolecular interaction since the alkane packing is due to lateral van der Waals interaction between chains whereas the alcohol self-organization is mainly governed by the hydrogen bonds between the OH groups. The molecule arrangement is also sensitive to changes in the alkyl-chain/graphite interaction as shown by the following examples. For increasing temperatures, a self-assembled alkane monolayer on graphite displays an increasing disorder and disappears near the melting point of the 3D alkane crystal [4,7]. For some liquid crystal molecules, a small increase of their alkyl chain length provokes changes in the molecule packing as observed for the alkylcyanobiphenyl series (nCB) [13,14] or for discotic molecules for which a chiral ordering transition is induced [15]. In a very recent STM study of the adsorption of $C_{36}H_{74}$ molecules in solution in $C_{12}H_{26}$ onto Au(111) at 300 K, we have evidenced the formation of a self-organized monolayer [16]. Interestingly, some $C_{12}H_{26}$ molecules are coadsorbed with $C_{36}H_{74}$. Keeping in mind the observations of alkane layers on graphite, this rather surprising result ($C_{12}H_{26}$ crystal melts at 263 K [17]) raises the question of the dependence of the alkane/Au(111) interaction with the molecule length.

In this paper, we report a STM study of the overlayers formed with a series of alkanes (C_nH_{2n+2}) with a length ranging from $10 \leq n \leq 38$ (even n values) adsorbed at the interface between a liquid and the Au(111) surface. At 300 K, we have found that all the alkanes self-assemble in ordered monolayers except for a particular range of lengths. This reentrant self-organization of alkane on Au(111) when increasing the molecule length is related to the existence of a misfit between the adsorbate and substrate lattices.

Two kinds of liquid were used: pure liquids for alkanes with $10 \leq n \leq 16$ and solutions in $C_{14}H_{30}$ for alkanes with $n \geq 16$ with long alkane concentration ~0.1 mg/ml (alkanes used as received from Aldrich). Some mixtures of $C_{16}H_{34}$ and $C_{18}H_{38}$ in $C_{12}H_{26}$ with different concentrations were also investigated. Au(111) surfaces were prepared from gold films (thickness ≈20 nm) deposited in ultrahigh vacuum onto a freshly cleaved mica surface heated at ~650 K followed by a careful annealing in a gas flame (propane + air). Measurements were carried out by using STM in air [18] with a mechanically sharpened Pt/Ir tip, which was immersed into a drop of the alkane solution deposited onto a freshly annealed Au(111) surface. For each alkane, several STM images recorded in the constant current mode were obtained with different samples and tips to check reproducibility.

A typical STM image of self-assembled $C_{30}H_{62}$ monolayers at the liquid/gold interface is shown in Fig. 1. The layer consists of a close packing of lamellae. Each lamella is formed by a side-to-side arrangement of sticks, the length of which corresponds well to the $C_{30}H_{62}$ one

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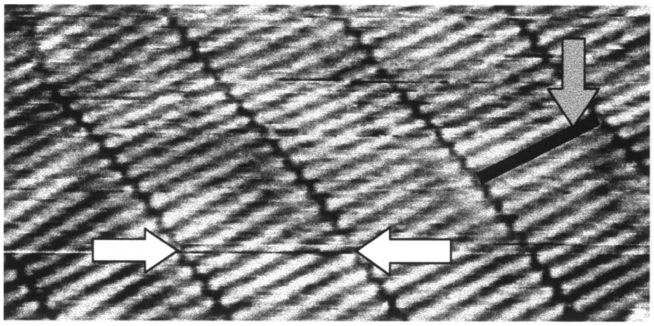

FIG. 1. Typical STM image of a self-organized $C_{30}H_{62}$ monolayer at the interface between a solution of these molecules in $C_{14}H_{30}$ and a reconstructed Au(111) surface. The monolayer is formed by an arrangement of lamellae, which consists of a side-to-side packing of $C_{30}H_{62}$ imaged as parallel sticks. Two white arrows show a lamella and a grey arrow shows a single molecule (17.6×8.3 nm^2), Vt = 133 mV, It = 0.2 nA).

(3.75 nm). So, each stick is identified with an individual molecule with its main axis parallel to the surface. All the molecules are parallel to $\langle 110 \rangle$ of Au(111) as shown by their orientation with respect to the gold reconstruction stripes. The lateral intermolecular separation is equal to 0.5 ± 0.05 nm which corresponds well to the distance between second-nearest neighbor $\langle 110 \rangle$ rows of Au surface. Therefore, $C_{30}H_{62}$ molecules involved in a self-assembled monolayer are in true epitaxy perpendicular to the $\langle 110 \rangle$ direction on Au(111) with a main axis parallel to this direction as observed in the $C_{36}H_{74}$ monolayer [16]. In fact, this description is valid for all the self-assembled monolayers of alkanes on Au(111) observed in this study.

Surprisingly, we have found that C_nH_{2n+2} molecules form self-assembled monolayers for two separated ranges of even n values (Fig. 2). For short alkanes with $10 \leq n \leq 16$, well-organized monolayers were observed either at the interface between pure alkanes and gold or for mixtures of alkanes on this substrate. We stress for these ordered monolayers of short alkanes on Au(111) are formed at temperatures higher than the bulk melting point of these molecules (T_m varies from 243 K for $n = 10$ to 291 K for $n = 16$ [17]). This is the first observation of self-assembled monolayers of short alkanes at 300 K on a solid surface. For $C_{16}H_{34}$ molecules, monolayers obtained from either a pure liquid or a diluted solution in $C_{12}H_{26}$ display similar structures. In the other domain of n values, long alkanes with $26 < n \leq 38$ self-organize on Au(111).

For $16 < n < 28$, we point out that no ordered molecular structure due to C_nH_{2n+2} in solution in $C_{14}H_{30}$ could be detected despite hundreds of interface images. All the attempts to obtain images of ordered films for these particular alkanes were also unsuccessful with $C_{12}H_{26}$ as a solvent. Since the Au(111) reconstruction pattern was clearly imaged during these investigations, such a lack of ordered monolayer cannot be related to a poor resolution due to a blunt STM tip. At this point, the question of the origin of this absence raises up since, at a given temperature on an "ideal noncorrugated" surface, entropic contributions to the monolayer disorder must monotonically decrease when n increases. Then, the stability of alkane monolayers should increase with increasing n, which is clearly in opposition with the results obtained here. One hypothesis could be the formation of a new phase at the interface of these particular mixtures with Au(111), which could be a 2D solid solution less stable than the lamellae made of one kind of alkane. For 3D crystals, solid solutions of binary mixtures of alkanes appear only for small differences in molecule lengths (ΔL) [19]. In fact, both the absence of ordered monolayer of the longer alkane for the $C_{26}H_{54}/C_{14}H_{30}$, $C_{24}H_{50}/C_{14}H_{30}$, and $C_{22}H_{46}/C_{14}H_{30}$ mixtures with large ΔL and the presence of pure $C_{16}H_{34}$ lamella for the $C_{16}H_{34}/C_{12}H_{26}$ system with small ΔL are in opposition with this hypothesis. Another possibility is that the lack of self-organized monolayers could be due to changes in intermolecule and/or in molecule-substrate interactions with the alkane length. As lateral intermolecular distances have the same value (0.5 nm) for any ordered monolayer, such an absence for $16 < n < 28$ (even n) is probably related to changes of the molecule/gold interaction with the chain length.

Let us now consider one C_nH_{2n+2} molecule as a linear and rigid array formed by n CH_2 groups (differences between CH_2 and CH_3 are neglected). Along the molecule axis, the distance between second-nearest CH_2 neighbors defines a period ($T_a = 0.251$ nm). This linear

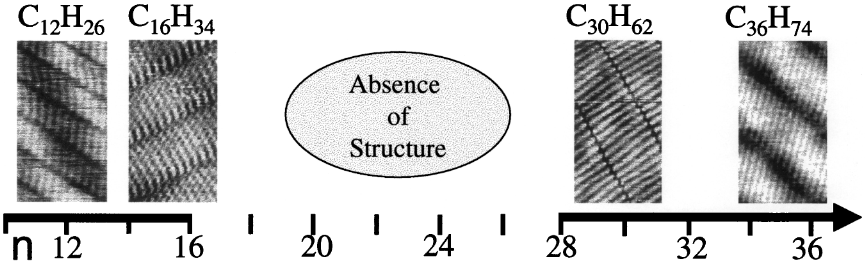

FIG. 2. Diagram showing the absence of self-assembled monolayers at the liquid/Au(111) interface for some particular length of C_nH_{2n+2}. While ordered layers are observed for molecules with $10 \leq n \leq 16$ and $n \geq 28$, no structure due to alkanes with $16 < n < 28$ can be detected on the Au(111) surface. For the different lamellae shown, the variation of the angle between a molecule and a trough is due to different relative shifts of neighboring molecules along their axes [16].

lattice placed onto a Au⟨110⟩ direction with a period equal to the interatomic distance ($T_s = 0.288$ nm neglecting the reconstruction of gold) generates a new period T:

$$T = T_a T_s / |T_s - T_a| \,. \tag{1}$$

With the values of T_a and T_s, we obtain $T = 1.95$ nm to compare to $7^* T_a = 1.76$ nm and $8^* T_a = 2.01$ nm which correspond to $C_{16}H_{34}$ and $C_{18}H_{38}$ molecules, respectively. Clearly, T would play a critical role in the arrangement of these molecules onto the surface. For example, molecules with a length shorter than T are expected to exhibit different behaviors during their adsorption than the longer ones since some CH_2 groups of longer molecules will be located on top of some substrate atoms. Calculations of the potential energy of such a linear and periodic lattice deposited on a crystal surface characterized by a different period have attracted a lot of attention since the pioneering works of Frenkel-Kontorova [20]. However, these calculations require different parameters as the coupling forces between molecules in the overlayer and between molecules and substrate or as the amplitude of the surface corrugation, etc. [20–22]. In the case of a physisorbed alkane onto reconstructed gold surfaces, no accurate data on these parameters are available.

To point out the physical origin of this reentrant self-organization of alkanes, we present a simple geometrical model based on a molecule-substrate misfit. In this one-dimensional model, a molecule is described as a rigid and periodic arrangement of interacting centers in coincidence with CH_2 positions including the ends (CH_3). By using a 6-12 Lennard-Jones potential to describe the molecule-substrate interaction, the potential energy of the ith CH_2-group W_i for a molecule with an infinite length can be numerically calculated for an arbitrary molecule/surface distance.

$$W_i = \sum_j U_j \,, \tag{2}$$

where U_j corresponds to the potential of the jth atom of gold. Because of the misfit, the potential energy of CH_2 groups exhibits a long-period oscillation with a period T. Deeper insight on changes in the potential energy when increasing the chain length can be obtained by calculating the average potential energy per CH_2, $\langle W(n) \rangle$, for a rigid molecule with n carbons:

$$\langle W(n) \rangle = 1/n \sum_{i=1}^{n} W_i \,. \tag{3}$$

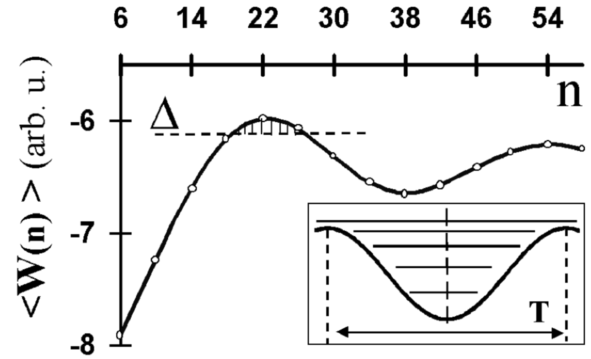

FIG. 3. Variation of the average potential energy of a CH_2 group, $\langle W(n) \rangle$, for rigid alkane molecules with increasing lengths ($8 \le n \le 58$). The line is a guide for the eyes. The line Δ that connects $\langle W(18) \rangle$ and $\langle W(26) \rangle$ corresponds to a critical value of $\langle W(n) \rangle$ at 300 K: Above this line, monolayers are disordered while below they are ordered. The inset shows schematically the positions of different molecules in a period of the potential curve, W_i, calculated from Eq. (2). For clarity, the positions along the Y axis of the different molecules are magnified.

For chains located in the potential curve as shown in the inset, the variation of $\langle W(n) \rangle$ when n increases presents a nonmonotonic dependence (Fig. 3). For alkanes with $10 \le n \le 22$, $|\langle W(n) \rangle|$ decreases continuously for increasing molecule lengths up to chains longer than T. For molecules smaller than T, the CH_2 groups of the chain can lock on the gold lattice despite the misfit between the two lattices [Fig. 4(a)]. Consequently, molecules are stabilized and ordered monolayers can be formed as observed in STM images. For molecules with n increasing from 16 to 22, $|\langle W(n) \rangle|$ decreases gently. This smooth variation around T is probably related to the hypothesis of a rigid lattice for the alkane chain. In fact, a strong variation of $\langle W(n) \rangle$ was expected since adsorption of molecules with a length equal to T causes the formation of stacking faults due to CH_2 resting on top of Au atoms, named discommensurations [Fig. 4(b)]. Here, two explanations can be proposed for the absence of ordered monolayers for

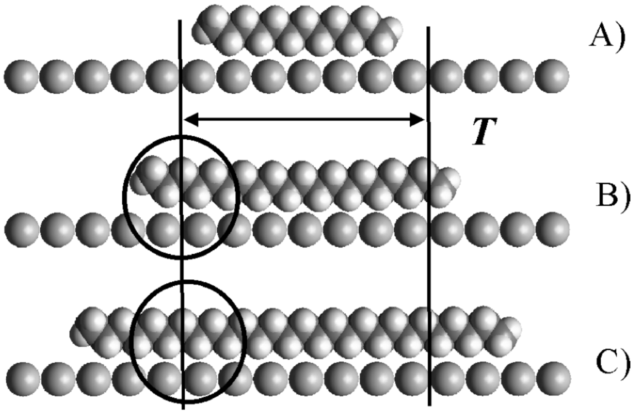

FIG. 4. Schematic models showing possible arrangements of rigid alkanes with different lengths on top of a ⟨110⟩ row of Au(111) (grey circles). The distance between the two continuous lines corresponds to the coincidence period T. (a) For $C_{12}H_{26}$ shorter than T, the CH_2 groups located near the surface can lock in between gold atoms; (b) for $C_{20}H_{42}$ slightly longer than T, the molecule cannot lock on the surface because of stacking faults or discommensurations. These defects correspond to some CH_2 groups located on top of gold atoms. (c) For $C_{28}H_{58}$ well longer than T, CH_2 groups at the two ends can lock again onto the gold lattice despite the presence of stacking faults. The large circles show discommensurations. For clarity, we orient the carbon skeleton of alkane perpendicular to the surface, but similar misfit effects are expected for any nonparallel orientation of the skeleton.

$16 < n < 28$. The first one is related to the decrease of $|\langle W(n)\rangle|$ that would yield a high rate of molecule exchange between the interface layer and the liquid: So, STM cannot image the overlayer structure. However, we reject this hypothesis because molecular dynamics calculations have evidenced the formation of a monolayer at the liquid/solid interface [23]. In the other explanation, molecules trapped by van der Waals forces on Au(111) cannot lock on the gold lattice because of discommensurations. In other words, the interface is a liquid monolayer characterized by a high surface mobility of these molecules along Au(111), which prevents STM observation.

For alkanes with $22 < n \leq 38$, $|\langle W(n)\rangle|$ increases with n while STM images show that molecules self-organize again for $n = 28$. In fact, two different contributions can stabilize these long molecules on Au(111). The first one is that $|W_i|$ of the chain ends becomes large enough to lock these parts of the molecule on gold [Fig. 4(c)]. This locking will become more efficient if the alkane chain presents some flexibility. As a result, the surface mobility of the whole molecule decreases despite the presence of two discommensurations. The second reason is related to the increasing of the molecule mass with n, which decreases its mobility along the surface.

Considering this reentrant self-organization of alkane monolayers induced by the molecule length, a question arises for the interface layers with $16 < n < 28$: Why do the solvent molecules, which can be locked onto Au(111), not form an ordered monolayer? The lack of ordered structure is probably related to the presence of a liquid layer due to long alkanes on Au(111) since the longest chains are known to be preferentially adsorbed from an alkane mixture [23]. Therefore, this overlayer would hinder adsorption of solvent molecules and, then, would prevent their self-organization.

Despite its simplicity, this geometrical model of alkane adsorption on Au(111) demonstrates that, at 300 K, the chain length drives transitions between 2D phases within the interface. In particular, the unexpected transition from a 2D-ordered solid to a disordered monolayer when the molecule length increases from $n = 10$ to 24 is well explained through the formation of discommensurations for chains longer than T. Such an influence of the misfit between molecules and substrate was suggested in the discussion of the factors that could affect the alkane diffusion on Pt(111) [24]. In this study, the potential-energy minimum has been calculated for isolated molecules ranging from butane to decane, but, unfortunately, the $C_{10}H_{22}$ length is shorter than T, the coincidence period of alkane/Pt(111). The alkane/Au(111) results bring evidence that properties of overlayers of linear molecules, as polymers, lying flat on a crystal surface could depend on the misfit between the period of the monomer arrangement and the one of the substrate lattice. For example, mobility of such physisorbed linear molecules along a crystal surface could be sensitive to their length since molecules with some particular lengths can be locked on the substrate. So, by tuning the molecule length, it is possible to change lubrication properties of these ultrathin films. Finally, we emphasize that these relatively simple systems open new fields for studying growth of 2D overlayers formed by linear adsorbates for experimentalists as well as for theoreticians.

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[1] K. Kern, in *Phase Transition in Surface Films 2*, edited by T. Taub, G. Torzo, H. J. Lauter, and S. C. Jain, NATO ASI Series B, Vol. 267 (Plenum, New York, 1991).

[2] A. G. Nauvomets, Chem. Phys. Solid Surf. **7**, 163 (1994).

[3] G. C. McGonigal, R. H. Bernhard, and D. J. Thomson, Appl. Phys. Lett. **57**, 28 (1990).

[4] L. Askadskaya and J. P. Rabe, Phys. Rev. Lett. **69**, 1395 (1992).

[5] Y. H. Yeo, G. C. McGonigal, and D. J. Thomson, Langmuir **9**, 649 (1993).

[6] J. P. Rabe and S. Buchholz, Phys. Rev. Lett. **66**, 2096 (1991).

[7] J. P. Bucher, H. Roeder, and K. Kern, Surf. Sci. **289**, 370 (1993).

[8] G. Watel, F. Thibaudau, and J. Cousty, Surf. Sci. **281**, 297 (1993).

[9] N. Eibel, E. Gunther, and H. Seggern, Appl. Phys. Lett. **65**, 642 (1994).

[10] D. M. Cyr *et al.*, J. Phys. Chem. **100**, 13 747 (1996).

[11] C. L. Claypool *et al.*, J. Phys. Chem. B **101**, 5978 (1997).

[12] C. Lepoulennec, Z. X. Xie, and J. Cousty, Surf. Sci. **448**, 93 (2000).

[13] D. P. E. Smith and W. M. Heckl, Nature (London) **346**, 616 (1990).

[14] E. Lacaze, P. Barois, and R. Lacaze, J. Phys. I (France) **7**, 1645 (1997).

[15] F. Charra and J. Cousty, Phys. Rev. Lett. **80**, 1682 (1998).

[16] Z. X. Xie and J. Cousty (to be published).

[17] D. M. Small, *Handbook of Lipid Research: The Physical Chemistry of Lipids,* edited by D. J. Hanahan (Plenum Press, New York, 1986), Chaps. 2 and 5.

[18] Nanoscope II (Digital) and a homemade microscope.

[19] D. L. Dorset, Macromolecules **23**, 631 (1990).

[20] J. Frankel and T. Kontorova, Phys. Z. Sowjetunion **13**, 1 (1938).

[21] F. C. Frank and J. H. Van der Merwe, Proc. R. Soc. London A **198**, 216 (1949).

[22] S. Aubry, J. Phys. (Paris) **44**, 147 (1983).

[23] T. K. Xia and U. Landman, Science **261**, 261 (1993).

[24] J. S. Raut and K. A. Fichthorn, J. Chem. Phys. **108**, 1626 (1998).