

Formation of Two-Dimensional Crystals of Alkanes on the Au(111) Surface in Neat Liquid

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Organic thin films of single molecular thickness (monolayer) at the solid/liquid interface play important roles in many phenomena such as crystal growth, lubrication, wetting, and chemical reactions, and it is essential to understand the structure of the monolayer to clarify its role in these phenomena. Furthermore, the arrangement of the organic monolayer in an ordered manner is a key step for the construction of molecular devices. Although a number of reports on the formation of ordered monolayers of organic molecules on solid surfaces at solid/liquid interfaces by in situ scanning tunneling microscopy (STM) are available,¹ the adsorbing molecules are dissolved in other solvents in all cases except for liquid crystal monolayer formation on graphite^{2,3} and other layered materials.⁴ In these situations, the origin of the monolayer formation is rather complicated because the adsorption is controlled by not only molecule–molecule and molecule–substrate interactions but also molecule–solvent, solvent–solvent, and solvent–substrate interactions. Furthermore, the adsorption of solvent molecules makes the interpretation of the STM image more difficult. The adsorption of alkanes on a metal surface is particularly interesting because the molecule–molecule as well as the molecule–substrate interactions are rather weak. Although the structure of adsorbed alkane monolayers on metal has been studied under UHV conditions,^{5,6} that in neat liquid has not been previously reported. Here, we report the first observation of formation of two-dimensionally ordered monolayers, i.e., two-dimensional (2D) crystals, of alkanes on Au(111) in neat liquid, i.e., above the melting point, by in situ STM.

Figure 1a shows an STM image of an Au(111) surface obtained in neat hexadecane ($C_{16}H_{34}$: C_{16}) at room temperature (ca. 25 °C).⁷ In addition to the herringbone structure seen as elevated regions due to the reconstruction of the gold surface,^{8,9} a row structure (lamella) crossing the herringbone was observed. The lamella consists of rods 2.2 nm in length and separated by 0.43 nm. The 2.2 nm length is comparable with the length of C_{16} , 2.2 nm, showing that the rod corresponds to an individual C_{16} molecule in an all-trans conformation with the molecular axis parallel to the surface plane. Thus, one can conclude that the two-dimensionally ordered adlayer, i.e., 2D crystal of C_{16} , is formed on the reconstructed Au(111) surface above the melting point of C_{16} , which is ca. 18 °C, and that adsorption of alkanes does not affect the surface energy and the charge density of the gold surface

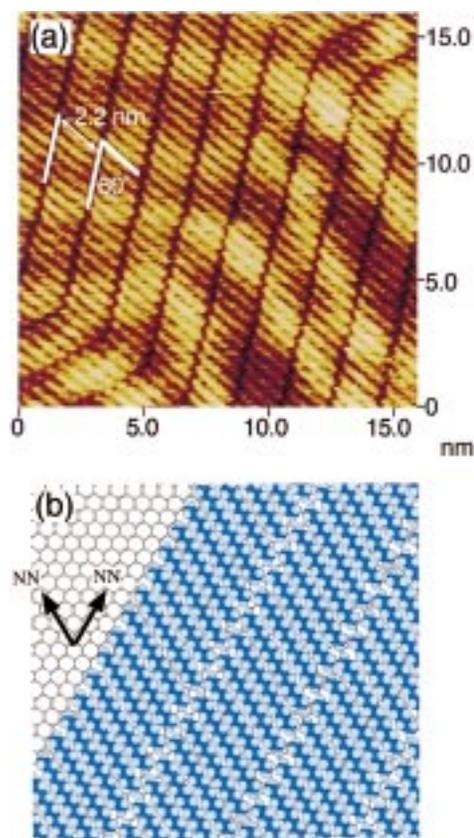


Figure 1. (a) An STM image of the Au(111) surface in $C_{16}H_{34}$. Bias 50 mV, tunneling current 0.2 nA. (b) Proposed model of the 2D crystal of $C_{16}H_{34}$.

significantly as the gold reconstruction is not lifted after the formation of the alkane adlayer. In most cases, domains of the ordered structure were rather large and each Au(111) terrace was covered with a single domain of the ordered adlayer.

The alignment of alkane molecules seems to be affected by the structure of the underlying gold. Although we were not able to observe individual gold atoms, we can determine the registry of the adlayer to the atomic arrangement of the gold surface by considering the rows of the herringbone structure which are known to align to $\langle 1\bar{2}1 \rangle$, i.e., the next nearest neighbor (NNN) direction of Au(111).^{8,9} The direction of the lamella of the adlayer is either ca. 90° or ca. 30° with respect to the bridging rows of Au(111) and is, therefore, the nearest neighbor (NN) direction of the Au(111) surface. The rod, i.e., the molecular axis, crosses the lamella by ca. 60°, indicating that the molecular axis also lies along the NN direction. A proposed model for the adlayer structure based on this information is schematically shown in Figure 1b.¹⁰ If one considers the anisotropy of the gold surface due to the reconstruction, there are two different NN directions, i.e., the NN direction perpendicular to the bridging rows of the gold surface and the one crossing the bridging row of the gold surface by 30°. We call them the NN(90°) and NN(30°) direction, respectively. The STM investigation in the present study shows that the molecular axis of alkanes is preferentially oriented in the NN(30°). This is because the deformation of the gold surface is maximum in the NN(90°) direction and it would be unfavorable to adapt the molecular skeleton to the winding surface.

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(10) The plane formed by the carbon skeleton in an all-trans conformation is assumed to be parallel to the gold surface because the same configuration is known to be formed on Pt, Ag (see refs 5 and 6).

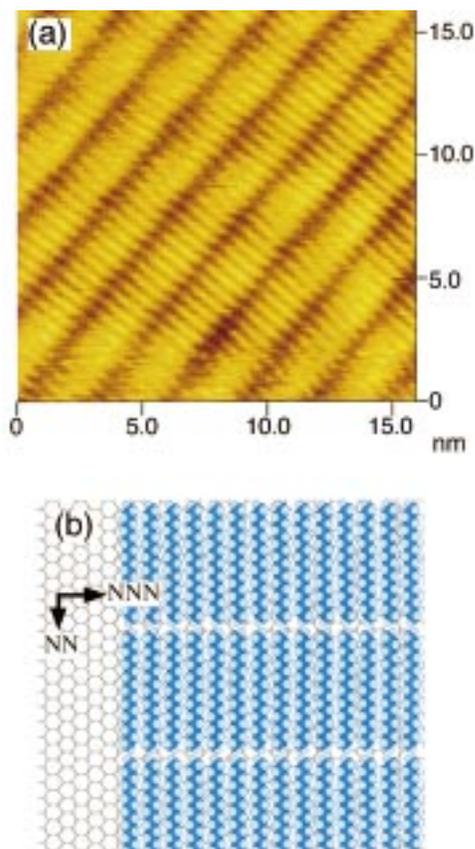


Figure 2. (a) An STM image of Au(111) in $C_{17}H_{36}$. Bias 200 mV, tunneling current 0.1 nA. (b) Proposed model of the 2D crystal of $C_{17}H_{36}$.

A 2D crystal of similar structure was observed even when the STM measurement was carried out in a liquid of an even-number alkane with a lower melting point. For example, in the neat liquid of dodecane ($C_{12}H_{26}$: C_{12} , mp = -12 °C), the rods have a 1.7 nm length, which is comparable with the length of C_{12} , 1.7 nm, and are arranged with a separation of 0.43 nm. Some disordered regions were, however, observed in this case in contrast to the results in C_{16} . This is reasonable as the C_{12} – C_{12} interaction should be weaker than the C_{16} – C_{16} interaction. Order/disorder dynamics have not yet been observed.

A different lamella structure was observed in heptadecane ($C_{17}H_{36}$, mp = 23 °C), i.e., an odd-number alkane, as shown in Figure 2a. The lamella crosses with the bridging rows of the gold surface by ca. 60° , showing that the lamella run in the NNN direction. The molecular axis crosses the lamella by ca. 90° and thus lies along the NN direction. A proposed model is shown in Figure 2b. The same lamella structure was also observed in tridecane ($C_{13}H_{28}$, mp = -5 °C) with a rod length of 1.8 nm and separation of 0.44 nm.

The adsorption of alkanes of smaller carbon numbers (C_nH_{2n+2} : $n = 6, 7,$ and 8) on Pt(111)⁵ and Ag(111)⁶ were investigated by Firment and Somorjai under a UHV environment using low-energy electron diffraction (LEED). They reported that the alkanes formed a 2D crystal whose structure is similar to the one reported here with the molecular axis parallel to the surface plane and along the NN direction. They found, however, that the detailed structure of the 2D crystal was dependent on the substrates. While a commensurate structure was observed on Pt(111), the 2D crystals of alkanes on Ag(111) were incommensurate. The direction of the lamella was along the NNN direction regardless of the molecules on Pt(111) but was dependent on the alkyl chain length on Ag(111) as the lamella of even- and odd-number alkanes ran along the direction close to the NN direction and to the NNN direction, respectively. The present result is in general agreement with the one on Ag(111). Actually, the structures of the adlayer on Ag(111) and Au(111) can be correlated with those of single crystals of alkanes which are solely determined by intermolecular interactions. The alkane single crystals (carbon numbers <26) consist of the stacked molecular layers with the molecular axis perpendicular and tilted to the molecular layer when the carbon number is odd and even, respectively.^{11,12} The odd–even effect on the structure of two- and three-dimensional crystals was explained by considering the closed packing condition by Kitaigorodskii.¹³

The origin of the effects of the substrates on the adlayer structure should be related to the electronic structure around the Fermi level, which should affect the chemical nature and potential corrugation at the surface, where Ag and Au have only s-electrons while Pt has higher density of states of d-electrons. The similarity of Ag and Au is also expected because of the same atomic size (Au and Ag: 0.289 nm, Pt: 0.277 nm).

In summary, the formation of the 2D crystal of alkanes on a metal surface in the neat liquid, i.e., above the melting point, was revealed by in situ STM investigation for the first time. The structure of the 2D crystal of alkanes showed an odd–even effect which corresponds to that appearing in single crystals of alkanes, indicating that the structure of the 2D crystal of alkanes on Au was determined by molecular–molecular force.

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