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Scanning Tunneling Microscopy Observations of [7]Thiahelicene Adsorbed on Au(111)

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Molecular images of [7]thiahelicene on gold single crystal surfaces were observed for the first time by scanning tunneling microscopy under high-vacuum condition at room temperature. The thiahelicene molecules took a quasi-ordered arrangement, in which the molecules were almost hexagonally packed with their molecular planes parallel to the suface. The interaction between the physisorbed thiahelicene and gold surface was rather weak.

Keywords: [7]thiahelicene; gold single crystal surfaces; scanning tunneling microscopy

INTRODUCTION

Helicene derivatives have been attracting considerable attention mainly due to the spectral and chiroptical properties. These derivatives possess helicity originating from their special helix structure. The enantiomers show large specific rotatory power. Hence many efforts have been focused on the preparation of various helicene series such as optically active ones which could be used as polarizers or chiral sources.[1-5] However, the molecular image of helicene has not hitherto been published. In this paper we will report the first scanning tunneling microscopy (STM) observations of a helicene derivative on Au(111) surface.

EXPERIMENTAL

[7]Thiahelicene was synthesized by the reported procedures[1-3] and purified by column chromatography and recrystallization. The purified compound was identified by the measurements of melting point (267 - 269 °C, ref.[1] 268 - 270 °C), ^{1}H-NMR spectra (300MHz, $CDCl_3$/TMS, δ = 7.9 - 8.1 (m, 6H), 6.91 (d, J = 5.5, 2H), 6.74 (d, J = 5.5, 2H)), and mass spectra (M^+ = 402, 100%). The structure of [7]thiahelicene is shown in Chart. The diameter of this molecule is *ca.* 12 Å considering van der Waals radii. This molecule has a coil-shaped structure due to the steric hindrance between the hydrogens at both ends.

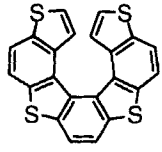

Chart. [7]Thiahelicene.

Single crystal Au(111) surfaces were prepared by vacuum deposition of gold onto mica at 350 °C with a thickness of *ca.* 1000 Å followed by annealing in H_2 flame. STM measurements were performed by using a JEOL 4500 XT at room temperature under high-vacuum conditions with electrochemically polished tungsten wires. Typical operation conditions were: bias voltage in the range of 0.6 - 2.0 V and tunneling current in the range of 0.1 - 1.5 nA. The samples of [7]thiahelicene were prepared by exposing the Au (111) surface to the vapor of the helicene in a closed vessel with a volume of *ca.* 5 cm^3 for a few minutes at *ca.* 70 °C under ambient pressure.

RESULTS AND DISCUSSION

Molecular images of [7]thiahelicene were observed on Au(111) by STM. A typical example is shown in Figure 1. The entire Au surface is covered with small circles, not coils, assigned to helicene molecules. This is probably due to the rotation of helicene molecules on the surface at room temperature. The average diameter of these circles was 13 Å, which is in good agreement with that of the molecule. This film has a monolayer structure because the height of the film consisting of these circles was less than 5 Å by the STM measurements. These results suggest that the molecules are adsorbed with a flat-lying configuration on Au (111). We have tried to investigate the orientation of thiahelicenes on gold surfaces by IR reflection-absorption spectroscopy. However, that has not been successful at present.

The arrangement of molecules is quasi-hexagonal as shown in Figure 1. The distance between the adjacent circles ranges from 13 to 30 Å, with the average of 24 Å. This suggests that the lateral interaction between the adjacent thiahelicene molecules is not large enough to arrange the adsorbed molecules in a well-defined manner. The interaction between the helicene and Au surface was rather weak since the images of the molecules disappeared under high-vacuum conditions (*ca.* 10^{-9} torr) at room temperature within a few days probably due to the sublimation of the molecules.

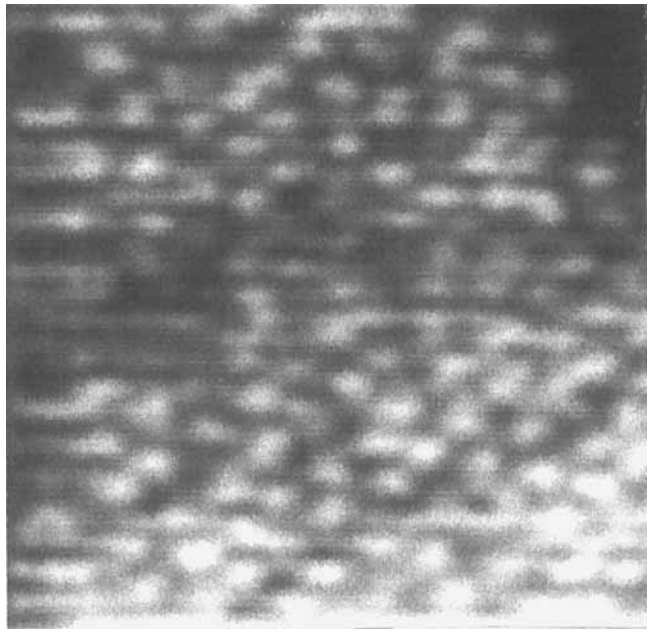

FIGURE 1. STM images of [7]thiahelicene on Au surface at room temperature. The exposing time was 5 min. Images were taken with the constant current mode: V_b = 0.64 V, I_t = 1.4 nA. 290 Å x 290 Å.

We have observed helicene molecules on gold surface using STM for the first time. The study along this line will open the possibilities of investigating physical properties of the coil-shaped single molecule on solid substrates.

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