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Binary Molecular Layers of C₆₀ and Copper Phthalocyanine on Au(111): Self-Organized Nanostructuring**

By Meike Stöhr, Thorsten Wagner, Markus Gabriel, Bastian Weyers, and Rolf Möller*

The binary molecular system of C₆₀ and copper phthalocyanine(CuPc) molecules has been investigated by scanning tunneling microscopy (STM) at room temperature and at 50 K. As substrate Au(111) was chosen. When C₆₀ and CuPc molecules are sequentially deposited, it is found that well-ordered domains of both molecules may coexist simultaneously. Hence hexagonal ordering of C₆₀ and quadratic ordering of CuPc is observed side by side but no ordered mixed layer of both molecules or heteroepitaxy from one molecule on the other is found. Instead the boundaries of the CuPc domains are often decorated by C₆₀ molecules and for a particular choice of parameters, with regard to the film preparation, individual CuPc molecules may adsorb on top of a C₆₀ layer. The interaction with the underlying C₆₀ layer permits the molecules to perform a localized, hindered rotation. At room temperature the hopping frequency is so high that only the time average of the rotation is seen by STM while at 50 K the rotation is frozen and the CuPc molecule is trapped in one definite position.

1. Introduction

Thin organic films have received an increasing interest in the last years because of the possible application for optical or electrical devices. For further improvements and a general understanding a detailed analysis of the interaction between the surface and the molecules, as well as the interaction between molecules, is required. The development of scanning tunneling microscopy (STM) has improved the possibilities of investigating such films and has even enabled the examination of individual molecules. The adsorption of organic molecules on inorganic surfaces has been successfully investigated for a broad variety of systems.^[1] The pioneering work has been done for copper phthalocyanine (CuPc) by Gimzewski et al.^[2] and by Lippel et al.^[3] They were able to image individual molecules with intramolecular resolution. Although one of the earliest experiments performed by Ohtani et al.^[4] dealt with coadsorption of benzene and CO on Rh(111), binary molecular layers have rarely been investigated. Cuberes et al.^[5] analyzed C₆₀ on a monolayer of dimethyl-bianthron on Cu(111) and performed C₆₀ manipulation on an organic layer. Epitaxial growth of two planar molecules has been demonstrated by Schmitz-Hübsch et al.^[6] for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on hexabenzocoronene and by Staub et al.^[7] for PTCDA on decanethiol.

An organic molecule that has been intensely investigated is C₆₀. It has been grown on various metal and semiconductor

surfaces and a broad spectrum of surface techniques has been applied. However, so far only few experiments have been carried out for the combination of CuPc and C₆₀ molecules on a substrate. One example in the literature is the testing of phthalocyanines and C₆₀ for solar cells.^[8]

The present paper deals with the combination of C₆₀ and CuPc molecules adsorbed on a Au(111) substrate. This is a particularly interesting system for several reasons. First of all, it is known that both molecules form well-ordered monolayers on this substrate. The size of the molecules is roughly comparable but their shape is completely different. While the C₆₀ molecule may be considered in good approximation as a sphere with a diameter of 0.7 nm, the CuPc molecule is a flat planar molecule with the form of a cross and a diameter of about 1.2 nm. In consequence, C₆₀ prefers a hexagonal ordering whereas CuPc usually attains a quadratic ordering when adsorbed on (111) oriented surfaces of noble metals. One of the goals of the investigation was to analyze the concerted action of these two different ordering schemes, with six and fourfold symmetry, and to find out if mixed layer or epitaxial growth of one molecule on a layer of the other occurs.

2. Results

Firstly, the preparation of monolayers of either C₆₀ or CuPc on Au(111) was studied. Figure 1 shows the typical appearance of a C₆₀ layer at a coverage of slightly less than one monolayer. Large domains with perfect hexagonal packing are formed in agreement with findings previously reported (see e.g., Altman and Colton^[9]). For the given bias voltage $V = -1.85$ V at the tip some of the C₆₀ molecules appear brighter than the majority of the molecules. It has been proposed that this is due to a different orientation of the C₆₀ relative to the substrate.^[10] The slight fuzziness at the boundary indicates that the molecules at the edges are somewhat mobile.

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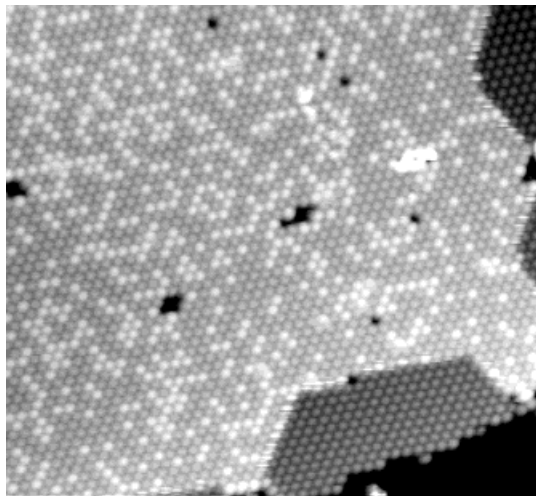


Fig. 1. Monolayer of C₆₀ on Au(111), the area is 47 × 44 nm², the tunneling current is 13 pA at -1.85 V tip bias.

In contrast to the C₆₀ molecule, CuPc on Au(111) prefers an ordering with a quadratic unit cell.^[11] Figure 2 displays the typical structure of CuPc at a coverage of about one monolayer. The planar CuPc molecules lie flat on the surface and the apparent height is about 0.3 nm. It can clearly be seen that the underlying “herringbone” reconstruction of the Au(111) is not lifted.

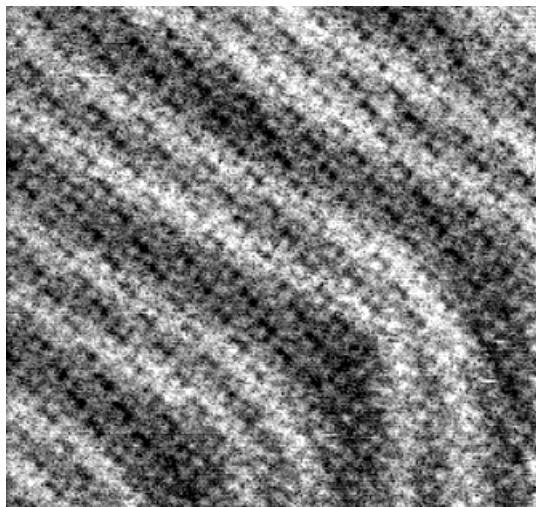


Fig. 2. Monolayer of CuPc on Au(111), the area is 23 × 21 nm², the tunneling current is 9 pA at -2.1 V tip bias.

Both C₆₀ and CuPc show a commensurate superstructure on Au(111), which indicates that the interaction between the molecules and the substrate is stronger than van der Waals bonds between the molecules. In the case of C₆₀ the reconstruction of the Au substrate can be lifted as can be seen in Figure 1. A detailed description of this phenomenon is given by Gimzewski et al.^[12]

Figure 3 displays the combination of both molecules. The upper left corner exhibits the quadratic superstructure of CuPc. It can be seen that one axis of the unit cell is parallel to a step line of the Au(111) substrate running from the left to the right

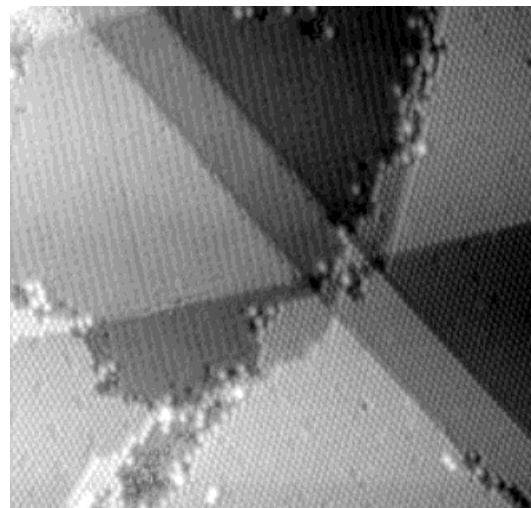


Fig. 3. A mixed layer of CuPc and C₆₀ at 50 K; the area is 93 × 86 nm², the tunneling current is 10 pA at -2.1 V tip bias, the STM data have been partially shaded to enhance the visibility of small details, the quadratic ordering of the CuPc is visible at the upper left, and to the lower right the hexagonal ordering of the C₆₀ molecules can be seen.

of the image. The latter coincides with one axis of the unit cell of the Au(111) substrate. To the lower right the hexagonal ordering of C₆₀ is found, which is also aligned with one axis of the unit cell to the same direction. Hence the hexagonal unit cell of the superstructure of the C₆₀ molecules and the quadratic one of the CuPc molecules may share a common axis, which is induced by the substrate.

Figure 4 shows a smaller area of the same sample. The intramolecular structure of the CuPc molecule is now clearly visible, e.g., in the lower part of the figure. Two different superstructures can be distinguished. In between isolated CuPc are found forming a dense but irregular pattern, e.g., in the middle on the right side. Although no C₆₀ is found within a CuPc domain, they may be observed at domain boundaries of ordered areas of CuPc. The size of the observed protrusions seems to be

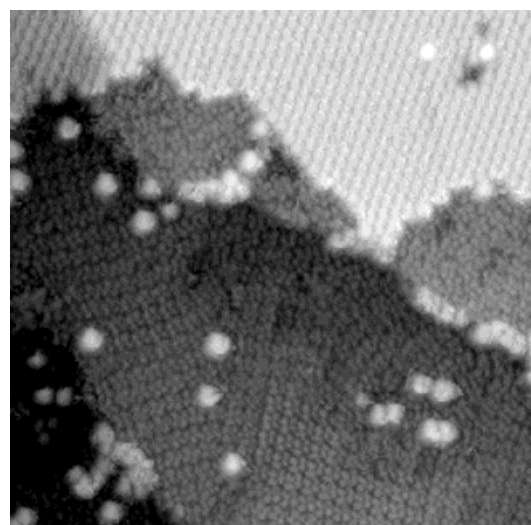


Fig. 4. Smaller area of a mixed layer of CuPc and C₆₀ at 50 K; the area is 47 × 47 nm², the tunneling current is 24 pA at 1.8 V tip bias, the STM data have been partially shaded to enhance the visibility of small details.

much larger than the one of a molecule that is incorporated in an ordered area. However, this is an effect that is due to the “convolution” of the investigated structure with the shape of the tunneling tip.

When the preparation is slightly modified, by increasing the amount of CuPc or by evaporating CuPc, new features may be observed. Figure 5 shows a large area of the corresponding molecular layer. To the lower right a domain of

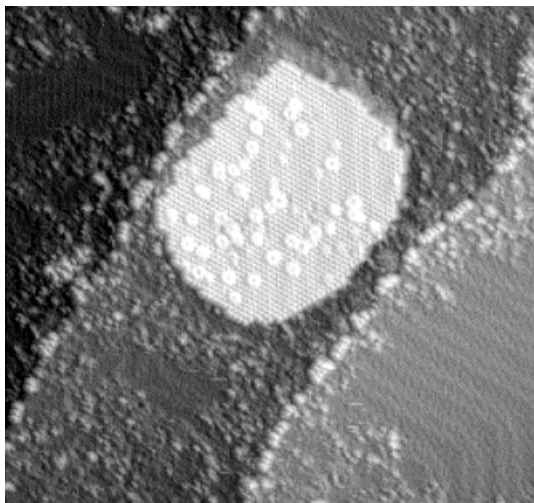


Fig. 5. Mixed layer of C₆₀ and CuPc for a slightly different preparation; the area is 87 × 80 nm², the tunneling current is 9 pA at 2.1 V tip bias, the domain boundary of the CuPc (lower right) is decorated by C₆₀ molecules, on top of the C₆₀ island individual CuPc molecules are found.

CuPc is found. Its edge is decorated by C₆₀ molecules. They tend to form linear clusters of 3–5 molecules. The most astonishing features are the rings that are found on top of the C₆₀ domain. Since they can only be found if CuPc is present, they have to be attributed to the CuPc molecule. However, the topography seems to contradict the fourfold symmetry of the CuPc molecule. Figure 6 shows another island of C₆₀ molecules, where three of these rings are present. The area surrounding the island seems to be rather disordered, nevertheless, a closer look reveals a partially ordered area of CuPc.

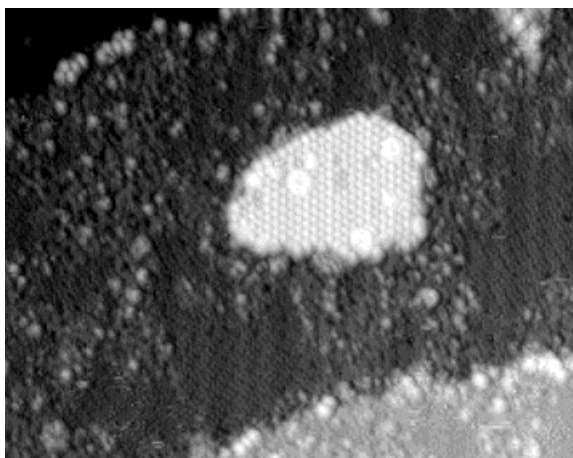


Fig. 6. Another C₆₀ island on the same sample; the area is 65 × 56 nm², the tunneling current is 8 pA at 1.4 V tip bias.

The structure of one of those rings is shown in Figure 7, which displays a high resolution scan of the C₆₀ area from Figure 6. It clearly reveals the sixfold symmetry of the struc-

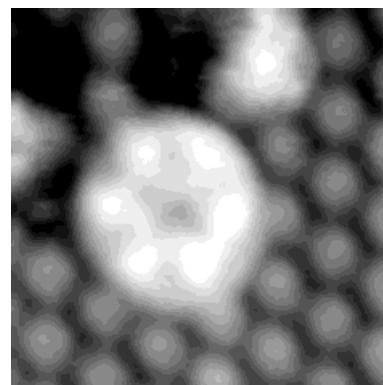


Fig. 7. Individual CuPc molecule on C₆₀ island of Figure 6, the area is 5.4 × 5.2 nm², the tunneling current is 8 pA at 1.5 V tip bias.

ture. Even if one takes into account that the size of a protrusion is always overestimated by a scanning probe microscope, the structure is too large to be a CuPc molecule that rests on the surface. To explain the observed structure we have tried to find an energetically favorable orientation by simple geometrical arguments. According to these arguments it is rather unlikely that a CuPc molecule would occupy a position centered on one C₆₀ molecule because this would be unfavorable for two of the four lobes of the CuPc molecule. It is much more probable that it occupies an asymmetric place with one of the five-membered rings consisting of four carbon atoms and one nitrogen atom centered on one C₆₀ molecule. This geometry is indeed found at low temperature as can be seen in Figure 8. Due to the symmetry of the C₆₀ layer there are six equivalent orientations of this type. If one assumes that the potential barrier is low enough^[13] the molecule may hop between the six positions at a very high rate performing a hindered eccentric rotation. Since the scan motion of the tip of the STM is several orders of magnitude slower than the molecular motion, only the time average is seen in the topographic image.

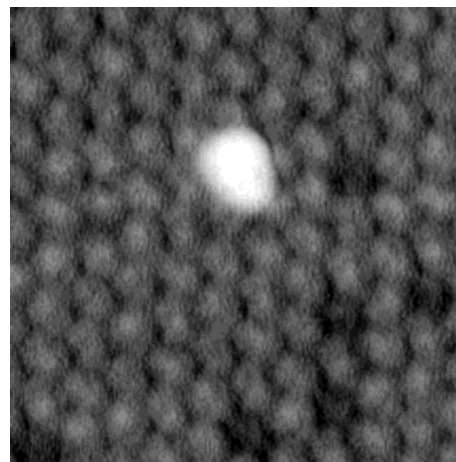


Fig. 8. Individual CuPc molecule at about 50 K; the area is 22 × 22 nm², the tunneling current is 13 pA at 2 V tip bias.

3. Conclusion

As an example of a binary system, the combination of C₆₀ and CuPc molecules deposited on Au(111) has been investigated at a coverage of about one monolayer. After thermal annealing well-ordered structures are observed, which reveal that a demixing occurs, and the molecules mainly form separated domains. Using a substrate with two types of surfaces, which differ in their affinity to the molecules, a well-defined coverage of nanostructures with either a hexagonal or a quadratic superstructure may be achieved. They may serve as a template for further processing. Possible substrates for this type of preparation may be vicinal surfaces.^[14]

A very peculiar behavior has been observed for individual CuPc molecules adsorbed onto an array of hexagonally ordered C₆₀ molecules. At room temperature they perform an eccentric rotation around one central C₆₀ molecule. From the observed topography it can be concluded that this motion is not continuous but results from the fast hopping between six equivalent positions. The observation gives rise to a speculation of using this system as a “molecular bearing”.^[15]

4. Experimental

The experiments were performed in an ultra-high vacuum (UHV) system consisting of a preparation chamber and an analysis chamber, in which the STM is situated. The preparation of the samples includes several steps. First a (111) oriented gold film was epitaxially grown onto a mica substrate heated to 600 K as described, e.g., in [16]. The mixed layers of CuPc and C₆₀ were prepared either by depositing the C₆₀ prior to the CuPc or by the inverse sequence. Surprisingly both methods lead to nearly the same findings if the surface is thermally annealed. The following description applies to the first case. The equivalent of somewhat less than one monolayer of C₆₀ was deposited by thermal evaporation. These films were annealed using a linear temperature increase of 1 K/s up to

600 K. This mainly yielded an ordered monolayer of C₆₀. In a final step a fraction of a monolayer of CuPc molecules was deposited. Again the samples were annealed, this time to 500 K.

The STM, which was used for the experiments, is a slightly modified commercial variable-temperature STM (Omicron). The results presented in this publication were obtained at room temperature and at 50 K. The tunneling tips were prepared by electrochemical etching of a tungsten wire. The tips were further processed in situ by sputtering with Ar⁺ ions and by field emission shortly before the experiment. The STM was operated at low tunneling currents in the range of 3 to 50 pA. The sample bias voltage was varied in the range from -2.5 V to +2.5 V.

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