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STM study of $C_{60}F_{18}$ high dipole moment molecules on Au(111)

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ABSTRACT

Scanning tunneling microscopy and spectroscopy studies of $C_{60}F_{18}$ molecules deposited on Au(111) are reported and compared to C_{60} molecules both at liquid helium temperature and room temperature (RT). Whereas adsorption and electronic properties of $C_{60}F_{18}$ single molecules were studied at low temperature (LT), self-assemblies were investigated at RT. In both cases, the fluorine atoms of the $C_{60}F_{18}$ molecules are pointed towards the surface. Individual $C_{60}F_{18}$ molecules on Au(111) have a HOMO–LUMO gap of 2.9 eV. The self-assembled islands exhibit a close-packed hexagonal lattice with amorphous borders. The comparison with C_{60} molecules clearly demonstrates the influence of the $C_{60}F_{18}$ electric dipole moment (EDM) on the electronic properties of single molecules and on the thermodynamics of self-assembled islands. Besides, the apparent height value of a separate molecule increases in a self-assembly environment as a result of a depolarization phenomenon.

1. Introduction

Nowadays the scientific community shows considerable interest in fullerene derivative molecules. In addition to the research of various properties of such molecules, special interest is attracted to the self-assembly of such molecules on various surfaces. For example, by means of scanning tunneling microscopy experiments, the organization of C_{60} monolayer and bilayer were probed [1,2].

Although many fullerene derivatives are known around the world, the fluorofullerenes stand out because of their unusual geometric structure. They also present interesting properties as local fluorine source [3] or in relation to self-assembly [4]. The structural peculiarity of $C_{60}F_{18}$ molecules consists in that one part of the molecule is actually a carbon hemisphere similar to C_{60} but the other moiety of its carbon skeleton has fluorine atoms attached to it (Fig. 1). Since all 18 fluorine atoms are located in one part of a molecule, the spherical carbon cage is considerably deformed in contrast to the "spherical-shaped" C_{60} molecule. Due to this asymmetry, the $C_{60}F_{18}$ molecule has a substantial electric dipole moment (EDM) that could be as high as 10 D as suggested by quantum-chemical estimates [5,6]. Its space orientation coincides with the 3-fold molecular axis as schematically shown by the arrows in Fig. 1. Due to its unusual structure and geometry, $C_{60}F_{18}$ are promising molecules for the creation of nanoscale ordered structures which could be used in nanoelectronics, nonlinear optics, and so on.

This paper presents the first results obtained by scanning tunneling microscopy and spectroscopy (STM/STS) of $C_{60}F_{18}$ molecules deposited on Au(111). At low temperature, we focus on the adsorption sites and electronic properties of individual $C_{60}F_{18}$ molecules, while at room temperature we investigate a self-assembly of $C_{60}F_{18}$ molecules. In both cases, C_{60} molecules on Au(111) were used as a reference. Comparison between individual molecules and self-assembled islands shows a global picture of the $C_{60}F_{18}$/Au(111) system and emphasizes, in both cases, the influence of its huge molecular EDM.

2. Experiment

$C_{60}F_{18}$ molecules with a purity of 99% (about 1% C_{60}, $C_{60}F_{36}$, etc.) were evaporated at 250 °C from a nickel Knudsen cell under ultra-high vacuum (UHV) conditions. The molecular flux was previously calibrated by a quartz microbalance (0.2 ML per hour). Prior to the molecular deposition, the Au(111) substrates (i.e. Au(111) single crystal and Au(111) on mica) were cleaned by a standard argon etching (900 eV) and annealing (450 °C and 330 °C for single crystal and Au/mica, respectively) under UHV. The STM measurements were performed at RT and LT (4.6 K) on two different Omicron STM apparatus working in UHV below 10^{-10} mbar. The dI/dV spectra were acquired using a lock-in detector at a frequency of 676 Hz and a modulation amplitude of 24 mV. The resulting STM data were processed by the WSxM software [7].

3. Results and discussion

3.1. Electronic properties of individual $C_{60}F_{18}$ molecule at low temperature

We investigated the adsorption and the electronic properties of individual $C_{60}F_{18}$ molecules on Au(111) at low temperature (4.6 K). To

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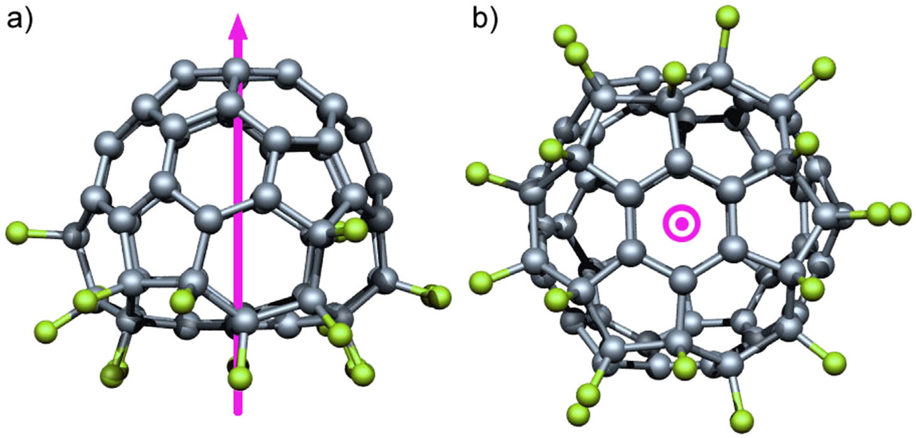

Fig. 1. $C_{60}F_{18}$ molecular structure. Carbon atoms are marked in gray, fluorine atoms are marked in green: a) side view, b) bottom view. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compare their properties to those of C_{60} molecules, we prepared a specific sample consisting of two consecutive evaporations of single molecules of $C_{60}F_{18}$ and then C_{60}. For this specific sample it was possible to identify the C_{60} molecules due to their known electronic properties [8]. Fig. 2 presents the apparent height of C_{60} and $C_{60}F_{18}$ molecules versus bias voltage measured on the same sample area (inset of Fig. 2). C_{60} molecules appear higher than $C_{60}F_{18}$ molecules at different voltages. The $C_{60}F_{18}$ molecules have an apparent height value between 0.45 and 0.55 nm that is below the value of 0.7 nm obtained by X-ray diffraction [9]. Also, it is worth noting that the $C_{60}F_{18}$ apparent height–voltage dependence is not monotonic, in contrast to that of C_{60}. This is most probably due to the presence of the strong dipolar field of the $C_{60}F_{18}$ molecule that decreases the local work function.

We now focus more specifically on the adsorption of $C_{60}F_{18}$ molecules. The symmetry breaking induced by fluorination leads to the increase of the possible molecular orientations on the surface. Indeed, the twelve pentagon rings of a carbon cage are not equivalent any more, leading to four possible adsorption sites depending on the position of the fluorine atoms. In the same way, six orientations are possible when a $C_{60}F_{18}$ molecule is adsorbed with a hexagon ring at the top. Besides, the adsorption can occur with apex atoms or bonds at the top. Experimentally we observed different orientations for the $C_{60}F_{18}$ molecules on Au(111). Fig. 3 presents three orientations of the $C_{60}F_{18}$ molecules: (i) with a pentagon ring at the top (Fig. 3a), (ii) an apex atom at the top (Fig. 3b) and (iii) a hexagon ring at the top (Fig. 3c). In these three cases, the adsorption configuration was found from symmetry arguments and comparison with typical STM topographies of C_{60} molecules. The last point emphasizes the fact that we can recognize features of C_{60} molecules meaning that the fluorine atoms are most probably facing the Au(111) surface. Similar molecule orientations are observed in the self-assembled islands at room temperature, as shown below. Nevertheless, the molecular EDM is always making a non-zero angle with the normal to the surface. Other orientations might be also possible, but their assignment will be found by comparing to STM topography calculation.

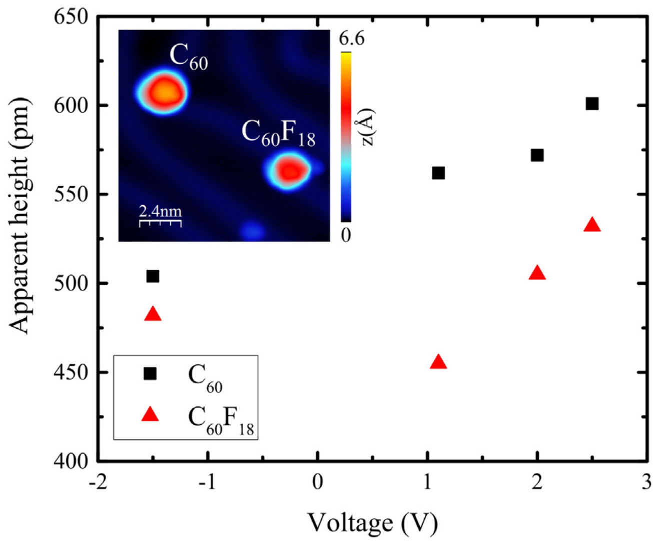

Fig. 2. Comparison of the apparent height of single C_{60} and $C_{60}F_{18}$ molecules as a function of the bias voltage. Inset: STM image (V = 1.1 V, I = 500 pA). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The STS spectra measured for the three orientations are presented in Fig. 3 and compared to the typical spectrum acquired on C_{60} molecules (green curve in Fig. 3 acquired on the single C_{60} molecule of Fig. 2). The different orientations of the $C_{60}F_{18}$ molecules lead to shifts in molecular orbital energy positions as one can see on the STS curves. The measured HOMO–LUMO gaps in the three orientations observed are equal to 2.9 eV which is slightly smaller than the C_{60} HOMO–LUMO gap (3.0 eV) and larger than the optical band gap measured for a molecular crystal (2.6 eV) [10].

It is worth noting that STM/STS study of individual $C_{60}F_{18}$ molecules on Au(111) clearly shows that the integrity of the $C_{60}F_{18}$ molecules is preserved, i.e. no decomposition occurs during the molecule evaporation and no fluorination of the surface is observed in contrast to fluorofullerene studies on Si(111) [11]. The different orientations of individual $C_{60}F_{18}$ molecules on the Au(111) surface would require theoretical calculations to understand the role of the EDM in the adsorption process and in the corresponding shift of the molecular electronic states.

3.2. Structure of $C_{60}F_{18}$ islands at room temperature

We now turn to the self-assembly of $C_{60}F_{18}$ molecules on Au(111) at RT. Typical STM topographies of $C_{60}F_{18}$ and, for comparison, C_{60} molecules deposited on Au(111) with a sub-monolayer coverage are presented in Fig. 4. The C_{60} molecules arranged in a close-packed lattice [1] form regular shaped islands that are growing from the Au(111) step edges. Indeed, the borders of the molecular islands correspond to specific directions of the C_{60} close-packed lattice, as seen in the inset of Fig. 4a. The apparent height of the C_{60} monolayer is around 0.45 nm and clearly depends on the tip state. Indeed, the bottom of Fig. 4a yields an apparent height of 0.46 nm, and on the top of the image an apparent height of 0.42 nm. A close look at the image reveals that the tip modification is

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