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Substrate-induced symmetry reduction of CuPc on Cu(1 1 1): An LT-STM study

H. Karacuban [a,b,*], M. Lange [a,b], J. Schaffert [a,b], O. Weingart [c], Th. Wagner [a,b,1], R. Möller [a,b]

[a] Fachbereich Physik, Center for Nanointegration Duisburg-Essen, Duisburg-Essen, 47048 Duisburg, Germany
[b] Universität Duisburg-Essen, Lotharstr. 1-21, D-47048 Duisburg, Germany
[c] Fachbereich Chemie, Universität Duisburg-Essen, Universitätsstr. 5, D-45117 Essen, Germany

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ABSTRACT

The adsorption of copper phthalocyanine (CuPc) on Cu(1 1 1) was studied by means of low-temperature scanning microscopy. At very low coverage, individual molecules are randomly distributed over the surface. Increasing the coverage, the molecules align in chains before forming ordered domains with a rectangular unit cell. The molecules are centered on top of a copper atom aligning two opposite lobes with a principal axis of the substrate. The topographic images of the molecules show a reduction of the fourfold to a twofold symmetry. At negative sample bias, a switching between two states at a typical rate of 500 Hz is observed for isolated molecules, which are neither adsorbed at defects nor forming chains or domains.

1. Introduction

In the past decades, more and more low cost, mechanically flexible, large-scale electronic devices have been made using organic semiconductors [1]. Metal phthalocyanines are archetype molecules for fundamental research in this field because of their high thermal stability, their symmetric geometrical structure and their electronic structure, which can be easily modified [2]. They are used in organic solar cells [3], organic light emitting diodes [4] and organic field-effect transistors [5]. The interaction of copper phthalocyanine (CuPc) with different substrates has been investigated intensively. The monolayer growth of CuPc on Cu(1 1 1) was studied by low-energy electron diffraction at room temperature [6]. Gimzewski et al. [7] were the first to image individual CuPc molecules on polycrystalline silver by means of scanning tunneling microscopy (STM). High resolution STM images were presented by Lippel et al. [8], showing a fourfold symmetry for CuPc on Cu(1 0 0). The term *n*-fold symmetry is used in this work as a synonym for C_{nv}-symmetry, meaning there are *n* mirror planes and *n* equivalent adsorption sites within a rotation of the molecule around its center by 360°. At room temperature, individual CuPc molecules are mobile on flat crystalline metal surfaces. Stable images of well ordered closed-packed layers of CuPc have been obtained on Au(1 1 1) [9] as well as on Ag(1 1 1) [10]. Multiple layers of CuPc deposited on Au(1 1 1) were characterized by means of STM and scanning tunneling spectroscopy (STS) [11]. For individual CuPc molecules on closed-packed islands of C_{60} on Au(1 1 1), a hindered rotation was observed by Stöhr et al. [12]. The results were compared to force field calculations by Fendrich et al. [13]. Recently, after post-deposition annealing of CuPc adsorbed on Ag(1 1 1), dendrite-like chains were investigated by Manandhar et al. [14].

While STM images of CuPc on Au(1 1 1) [15] show a fourfold symmetry according to the D_{4h}-symmetry of the gas phase [2,16,17], a reduction to a twofold symmetry was reported by Qui et al. [18] based on *dI*/*dV*-data of CuPc adsorbed on an ultrathin Al_2O_3 film grown on a NiAl(1 1 0) single crystal. A reduced symmetry of CuPc molecules was also found for well ordered mixed phases with 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) on Cu(1 1 1) [19].

In this paper, low-temperature STM measurements of CuPc on Cu(1 1 1) at 10 K are presented for various coverages in the submonolayer regime. The adsorbed molecules show a twofold symmetry. In addition, isolated molecules appear to switch between two states when the occupied electronic states contribute to the tunneling current.

2. Experimental setup

The experiments were performed under ultra high vacuum conditions using a self-built low-temperature STM (LT-STM). Similar

* Corresponding author. Address: Universität Duisburg-Essen, Center for Nanointegration Duisburg-Essen, Fachbereich Physik, Lotharstr. 1-21, D-47048 Duisburg, Germany. Tel.: +49 203 3792178; fax: +49 203 3791727.
E-mail addresses: hatice.karacuban@uni-due.de (H. Karacuban), thorsten.wagner@jku.at (Th. Wagner).
[1] Present address: Institut für Experimentalphysik, Johannes Kepler Universität Linz, Altenbergerstr. 69, A-4040 Linz, Austria.

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to the setup used by Stipe et al. [20], our system is cooled by a liquid He continuous flow cryostat (Helitran LT-3B). The LT-STM chamber is connected to a preparation chamber equipped with self-built evaporation cells.

The Cu(1 1 1) single crystal was cleaned by several cycles of Ar^+-sputtering and thermal annealing at about 900 K. Subsequently, various amounts of CuPc molecules were evaporated onto the copper substrate at room temperature. The evaporation rate was determined by a quadrupole mass spectrometer. Prior to the first preparation, the evaporator was degassed until the correct ratio of the primary peaks (575 and 577 amu) to the fragment masses and background peaks was achieved. During the LT-STM measurements, the temperature of the complete STM system including sample, tip and piezo scanner was held at about 10 K. The sample was biased while the tunneling current was measured at the tip. The tunneling tips used for the experiments were cut from a PtIr wire and cleaned by heating and field emission. The scanner was calibrated in the lateral directions by acquiring STM images of Au(1 1 1) and atomically resolved Cu(1 1 1) leading to an error of less than 5%. To measure the tunneling current as a function of time it was recorded with a digital storage oscilloscope while the feedback loop was turned off to keep the tip-sample distance constant. The topographic data were acquired by the open-source system GXSM [21] and processed by the free software WSxM [22].

The electronic orbitals of the CuPc molecule in the gas phase were calculated by unrestricted open shell DFT algorithms and, for comparison, with restricted open shell Hartree–Fock methods. The CuPc structure was geometry optimized at the unrestricted B3LYP/6-31G** level of theory [23].

3. Results

Fig. 1A shows a characteristic image of a submonolayer CuPc on Cu(1 1 1) obtained at about 10 K. The coverage is equivalent to approximately 0.1 monolayers (ML). On the free substrate terraces, the molecules lie flat and show a random lateral arrangement. Some molecules are trapped at the edge of a monoatomic step of the Cu(1 1 1) substrate or by other adsorbates. No motion of the molecules is observed. Fig. 1B and C shows a small area at higher resolution for two different bias voltages, +0.4 V and −1.3 V. It can be seen that two opposite lobes of the molecules appear brighter than the other two, hence the fourfold symmetry of the molecule is broken and reduced to a twofold one. Fig. 1B was measured at a sample voltage of +0.4 V, thus the empty molecular electronic states are contributing to the tunneling current. The observed topography is very smooth. A close inspection reveals standing waves around the molecules which are due to the scattering of the electronic surface state of the Cu(1 1 1) surface at the molecules. At a negative sample voltage of −1.3 V, the free surface is still very smooth but the molecules appear rough due to fluctuations. These are particularly strong at the two dimmer lobes of the molecules. The fluctuation does not depend on the direction of the scan. The molecule marked by an arrow is pinned at a defect. This one, as well as the neighboring molecule, appears less noisy. Fig. 1D–F show the geometrical structure of the CuPc molecule and it's LUMO states.

To analyze the exact adsorption geometry of the CuPc molecule on the copper substrate in more detail, a high resolution scan was acquired. Fig. 2 shows an STM image resolving the underlying atomic structure of the substrate as well as the intramolecular structure of the CuPc. A careful analysis reveals that the molecule is centered on top of a copper atom. In addition, it is oriented such that the line connecting two bright lobes is aligned parallel with a row of copper atoms, i.e. to a base vector of the Cu(1 1 1) substrate. Hence, there are three equivalent adsorption sites. The analysis of a large number of data sets reveals that all molecules which are not pinned by a defect are adsorbed in this geometry. The combination of the symmetries of molecule and substrate leads to the twofold symmetry reflected in the STM images.

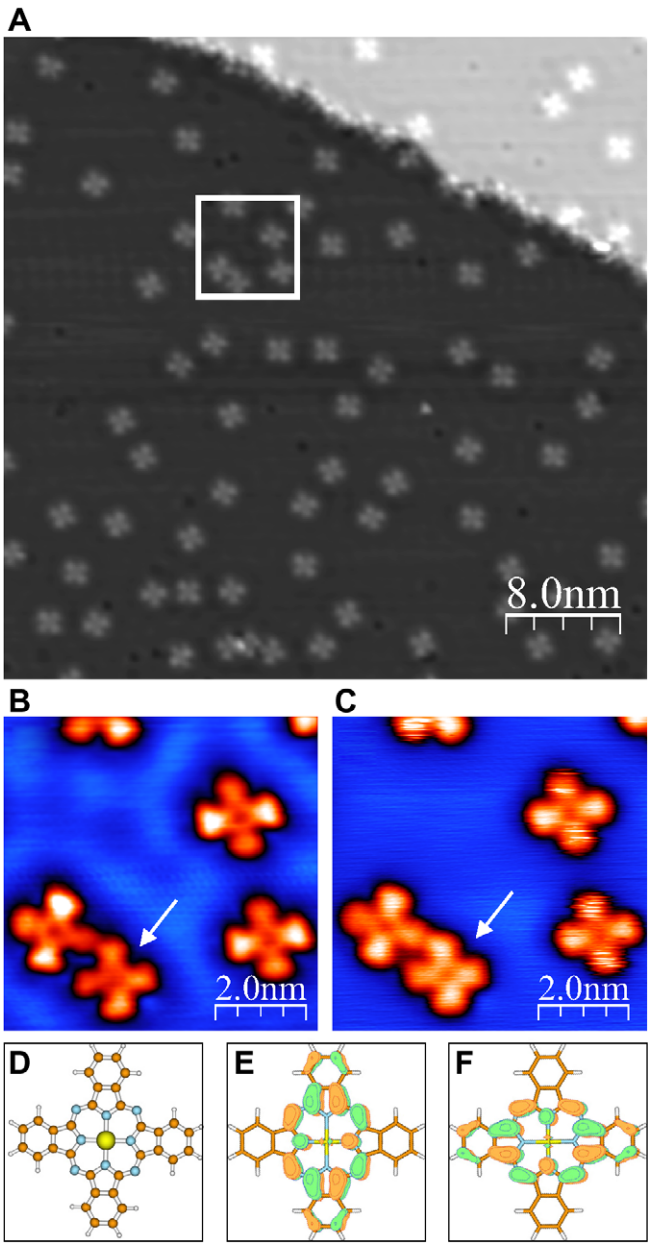

Fig. 1. STM images of a Cu(1 1 1) surface covered with an equivalent of about 0.1 monolayers of CuPc measured at 10 K. The molecules are randomly distributed over the copper surface or pinned to step edges of the substrate or to defects. (A) Displays an area of 44 × 44 nm measured at U_{bias} = +0.4 V and $I_{setpoint}$ = 20 pA. (B) and (C) Show close-ups of the region indicated in (A). For image (B) the bias voltage was +0.4 V, for (C) −1.3 V. The setpoint for the current was not changed. (D) Shows the structure of the CuPc molecule. In (E) and (F), calculations of the two degenerate e_g orbitals forming the LUMO of a free CuPc are shown. The geometry optimization has been applied by using the unrestricted open shell B3LYP functional and the 6-31G** basis set [23]. Structure and molecular orbitals were plotted using MOLDEN [31].

The fluctuations of the tunneling current at fixed positions of the tip are shown in Fig. 3. The feedback loop was turned off to maintain a constant tip-sample distance. The green dots in the insets to the right indicate where the current was measured. Fig. 3A corresponds to the bare substrate. For the given bandwidth, the noise is in the order 5%. When the tip is placed over one of the