



Structural study of monolayer cobalt phthalocyanine adsorbed on graphite

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ABSTRACT

We present microscopic investigations on the two-dimensional arrangement of cobalt phthalocyanine molecules on a graphite (HOPG) substrate in the low coverage regime. The initial growth and ordering of molecular layers is revealed in high resolution scanning tunneling microscopy (STM). On low coverages single molecules orient mostly along one of the substrate lattice directions, while they form chains at slightly higher coverage. Structures with two different unit cells can be found from the first monolayer on. A theoretical model based on potential energy calculations is presented, which relates the two phases to the driving ordering forces.

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1. Introduction

Organic materials possess very intriguing properties, which make them outstanding from other functional materials used for spintronic applications, such as for example weak spin–orbit interaction and thereby implied slow spin relaxation times [1–3]. The interplay of single molecules on a substrate and their self-assembly properties were already investigated for various kinds of molecules and substrate materials [4–12]. Their small size makes them very suitable candidates to serve as building blocks of functional nanostructures. Metallophthalocyanines are in the center of current research because of their magnetic and electronic properties. The spin induced by the metal ion conveys important properties for the application in spintronic devices, for example memory elements and logic gates [13,14]. An important method for real-space topographic and spectroscopic measurements of molecular structures is the scanning tunneling microscopy, which images the electronic structure of a surface and its adsorbates with sub-Å resolution. This method requests the molecules residing on a conducting substrate in order to allow a current flow through the molecule. However, if the substrate is metallic, it may substantially alter the molecular electronic properties [15–19]. A solution to this is to use only weakly conductive substrates, such as thin insulating layers on a metal substrate [20] or intrinsically weakly conducting materials [21], where graphite is a prime candidate.

In this study, we investigate cobalt-phthalocyanine (CoPc) molecules on a highly-ordered pyrolytic graphite (HOPG) substrate in the

low coverage regime using scanning tunneling microscopy (STM). In the submonolayer regime, single molecules oriented along the substrate lattice directions as well as small chains of molecules can be found. At higher coverages, the molecules form typical ordered structures, which differ depending on the parameters of the sample preparation. Annealing of the sample leads to a higher mobility of the molecules on the surface and enhances the degree of order. The two dominant, highly ordered structures exhibit a long-range order. The grain boundaries between them form either a stripe-like pattern or two-dimensional ordered arrays. An epitaxy model combined with molecular mechanics calculations is presented and compared with the experimental results. A very good agreement between the measured data and simulated structures could be found.

2. Methods

2.1. Experimental details

CoPc molecules (Fluka, purity >97%) were degassed for purification and deposited on a HOPG substrate via organic molecular beam epitaxy in a Knudsen cell [22,23]. The evaporation took place under UHV conditions at evaporator temperatures between 350 °C and 400 °C. A quartz microbalance monitored the thickness of the deposited molecular film. The HOPG substrate was freshly cleaved and annealed up to 1600 °C prior to the deposition. The substrate temperature during the evaporation process was either kept at room temperature or held constant in a temperature range up to 100 °C. Also, further annealing of the arranged molecules at temperatures up to 200 °C was performed. To guarantee a high reproducibility of the sample preparation and the results, the investigations took place in three different microscopes and the in

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situ-preparation was done in three UHV chambers with their corresponding preparation devices.

The molecules are very mobile on the substrate surface. The mobility is reduced for the molecules assembled within a molecular layer, but to achieve stable imaging it is necessary to freeze the molecular motion by low temperatures (below 30 K in our experiments). Still, single molecules can be moved accidentally by the influence of the scanning tip (as can be seen at the separately lying molecules on the left side of the Fig. 2 (a)). The shape of these molecules is apparently strongly distorted and their position is ill-defined in the images. Therefore, throughout this paper we only discuss molecular arrangements where the overall single molecular shape is preserved in the images and where backward and forward scanning directions yield the same molecular arrangement. Significant accidental movements of the discussed molecule arrangements by the scanning tip are therefore irrelevant. Furthermore, we did not observe a significant change of topographic findings as a function of scanning parameters such as tunneling voltage/current or scan speed.

Two home-built microscopes and a commercial VT-Omicron system were used for investigation. The temperature during the measurements was 5 K/20 K/30 K depending on the microscope, the pressure in the UHV systems was less than 1×10^{-9} mbar. All shown STM pictures were obtained with electrochemically etched tungsten tips. The indicated bias voltages were applied to the sample, so that the occupied states are imaged at negative voltages. STM images were processed with the WSxM software [24].

2.2. Model calculations

To gain insight in the delicate energetics, which are responsible for the self-organized structure formation of the CoPc molecules, molecular mechanic simulations were applied. The calculations were carried out with the Gaussian 03 package [25]. The molecular structure of the CoPc molecules was obtained by minimizing the energy using density functional theory. Potential energy surfaces for an arrangement of four CoPc molecules were calculated with the Universal Force Field (UFF) [26]. Thereby, the calculated total energy is the sum of all non-covalent energies from the Pauli repulsion and van der Waals interactions, which are expressed in a 6–12-Lennard-Jones form, and the electrostatic interaction between each non-bonded atom. The binding energy is calculated by subtracting the total energy of the arrangement from the sum of the energies of the isolated parts. To model the molecular lattice, four CoPc molecules are placed on the corners of a parallelogram which describes the unit cell as shown in Fig. 1. This model is sufficient to give qualitative results for the intermolecular interactions for one molecule with its surrounding molecules in the molecular layer. No substrate is included in the calculations, and the plane of the molecules is restricted to lie in the plane of the layer. To simulate different possible structures, calculations were done where either all molecules have the same orientation or where the orientation of the molecular axes can differ between two neighboring molecules. To obtain potential energy surfaces two parameters of the arrangement were varied while the rest remained fixed.

3. Results and discussion

3.1. Experimental data

Fig. 2 shows representative areas of CoPc molecules deposited on HOPG. The coverage is less than one monolayer. Individual molecules appear in Fig. 2 (a) in a flower-like shape with four lobes, as expected from their chemical structure. They do not exhibit a common orientation, but orientations along the plotted sketches as well as 60° rotated are preferred for most of the molecules (Fig. 2 (d)). The molecules have an apparent height of about 0.2 nm, as can be seen from the

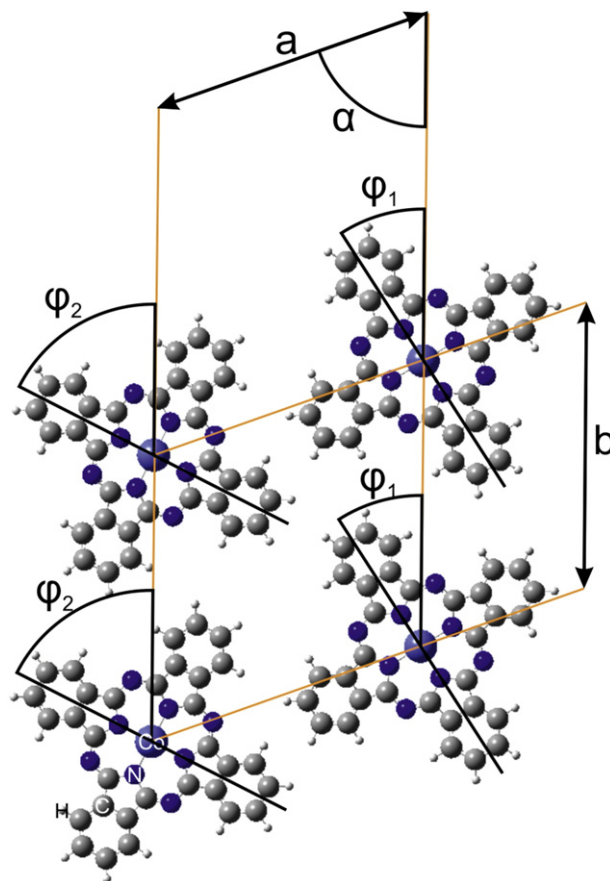


Fig. 1. One observed structure of CoPc molecules and assignment of the angles for UFF calculations and measured data.

linescan (Fig. 2 (c)) along the arrow in Fig. 2 (a). The symmetry of the molecules together with their height implies that they are adsorbed flat on the surface. Some molecules form ensembles of two or more, as can be seen in the encircled areas in Fig. 2 (a). The density of molecules in the covered area is 0.26 molecules/nm². In the STM images, at positive bias voltage the center of each molecule, which is assigned to the metal atom, often appears brighter due to an increased density of empty states at the cobalt site of the molecule. At positive bias we expect a shape of the molecules accordant to the π electron orbital of the ligands and a Co d_{z^2} orbital of the molecule, while at negative bias only the π orbital of the ligands is imaged only (e.g. in Fig. 4 (b)), similar to CoPc molecules in a stacked compound [27] or adsorbed on a gold substrate [16,28,29]. The influence of the HOPG substrate is expected to be very small due to the small binding energies of a layered material between its layers as well as towards an adsorbate on the top layer.

In order to enhance the coverage towards ~ 1 ML we prepared a second sample where we used a 25 K higher evaporator temperature (i.e. with a higher evaporation rate) for approximately the same time as has been used for the sample in Fig. 2 (a). Additionally, we heated the substrate to 100 °C during the evaporation in order to enhance the mobility and introduce a faster and better ordering of the molecules. Under these conditions, the onset of an ordering of the molecules into a closed two-dimensional arrangement takes place as can be inferred from Fig. 2 (b). At this coverage still patches with a relatively lower coverage (~ 0.24 molecules/nm²) are present at the borders of the close-packed areas. These areas contain chain-like linear arrangements of molecules. Apparently, this is an intermediate state between the disordered low-coverage and the ordered high-coverage state. The density of the molecules is the same as for the unordered agglomeration of

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