

Adsorption and Self-Organization of CuOEP on Heterogeneous Surfaces: Tuning the Molecule-Substrate Interaction



# Adsorption and Self-Organization of CuOEP on Heterogeneous Surfaces: Tuning the Molecule-Substrate Interaction.

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## Abstract

The adsorption and self-organization of copper(II) octaethyl porphyrin (CuOEP) have been studied in detail on heterogeneous surfaces by Scanning Tunnelling Microscopy (STM), Low Energy Electron Diffraction (LEED) and Ultraviolet Photoelectron Spectroscopy (UPS).

The research has been focussed both on the adsorption of CuOEP on clean metals as well as on ultrathin sodium chloride films grown on metals. For this reason, in a first stage, the growth of NaCl films on Cu(111), Ag(111) and Ag(001) has been carefully investigated. For submonolayer coverages the samples show the formation of NaCl islands with a characteristic rectangular shape, which coexist with clean metal regions. Salt structures 1 to 3 ML thick can be identified.

CuOEP molecules have been deposited on the so prepared heterogeneous salt-metal surfaces. STM reveals that the molecules self organize in ordered monolayers on the bare metal areas as well as on the NaCl islands. Series of observations performed by increasing the CuOEP coverage in steps from 0 to 1 ML revealed that the assembly develops in a hierarchical fashion. Molecules sequentially adsorb and assemble first on the bare metal, then on the 1-layer and 2-layer thick NaCl areas. From these observations it can be inferred that the adsorption energy of CuOEP decreases by introducing an insulator layer and by increasing its thickness. Moreover, the investigation of the STM appearance of CuOEP as a function of the bias voltage, indicates a weaker adsorbate-substrate interaction on the NaCl/metal system than on the bare metal.

The adsorption of CuOEP on the clean metal has been further investigated by LEED and UPS. Combining LEED and STM, the structure of the molecular layer formed on Cu(111), Ag(111) and Ag(001) is determined. Information on the adsorption conformation of CuOEP has also been gained by high resolution STM. In these measurements several intramolecular features can be recognized and they fit very well with simulated STM images based on DFT calculations. The theoretical predictions of the molecular orbital energies fit also very well with the UPS measurements. In particular the position and the relative intensity of HOMO and HOMO-1 levels show a very good agreement between experiment and calculation.

UPS has also been used to measure the work function change of the various metal substrates upon CuOEP adsorption. These experiments prove that, for all metal investigated, a charge transfer from the molecule to the substrate takes place. This charge transfer is found to depend on the work function of the substrate. In particular the comparison between the Ag(111) and Ag(001) cases demonstrates that the observed work function change does not depend only on the chemistry of the substrate but also on the details of the surface electronic structure.

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# Abbreviations

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
CuOEP	Copper(II) octaethyl porphyrin
DFM	Dynamic force microscopy
$\mathrm{DFT}$	Density functional theory
DOS	Density of states
EA	Electron affinity
EELS	Electron energy loss spectroscopy
EFM	Electrostatic force microscopy
ESCA	Electron spectroscopy for chemical analysis
HOMO	Highest occupied molecular orbital
IP	Ionization potential
LDOS	Local density of states
LEED	Low energy electron diffraction
LUMO	Lowest unoccupied molecular orbital
MFM	Magnetic force microscopy
ML	Monolayer
OLED	Organic light emitting diode
PES	Photoelectron spectroscopy
SNOM	Scanning Near Field optical microscopy
SEM	Scanning electron microscopy
SPM	Scanning probe microscopy
STM	Scanning tunnelling microscope
STS	Scanning tunnelling spectroscopy
SubPc	Chloro[subphthalocyaninato]boron(III)
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
vdW	van der Waals
XPS	X-ray photoelectron spectroscopy

## 1. Introduction

### 1.1. Motivation and Outline

The concept of molecule has historically been developed in the field of chemistry and for a long time molecules have almost exclusively been investigated by chemists. However, the development of powerful investigation tools as well as quantum theory allowed the scientists to gain a deep understanding of the physics at the molecular scale. Hence molecules started to be in the focus of physicists too.

Nature shows how much complexity can be borne in a very small space. A molecule is a remarkable example of an extremely small structure which has well defined characteristics and properties. Miniaturization is not only observed in nature but has been a constant trend in the technology development of our times. Researchers have continuously tried to engineer smaller and smaller devices. However so far the approach to miniaturization has mostly been quite different than the one used by nature. Scientists and engineers have mainly tried to shrink the size of objects which already exist and work at a larger scale. This approach proved to be very successful, nevertheless it is clear that there are limit to it. In fact scaling down processes which work at the macro- or micro-scale is going to face fundamental physical limits. For instance the ultimate limits for lithography processes employed in the silicon based electronics are not far from being reached[1].

The novelty of *nanoscience* consists in studying the properties and functionalities of nanoscale structures, often already known from chemistry or biology. Their understanding may lead to identify structures which can be directly used for applications or teach how to engineer new objects with the desired properties. Although very difficult, such an approach has a great potential. As pointed out by Richard P. Feynman in his famous talk "There's plenty of room at the bottom – An invitation to enter a new field of physics" gaining the ability to control and address single atoms and single molecules would allow to extraordinarily accelerate most miniaturization processes.

Among the systems available in nature organic molecules look very appealing as they are small but simultaneously complicated and structured enough to comprise interesting functionalities. Therefore, in this thesis the attention will be focussed on organic molecules adsorbed on suitable supports with a relevance for potential applications in the field of *molecular electronics*.

The use of very small functional units poses many technological challenges. Among them a very relevant one is the difficulty to handle and interconnect different units which are needed to assemble any useful device. However, the observation of nature offers a very brilliant approach to this issue. Practically all systems in nature are somehow capable to self assemble.

#### 1. Introduction

One of the goals of *nanoscience* is to understand and profitably use self assembly to form nanostructures with the desired functionalities. The smart combination of the so called *bottom up* approach (letting different substructures organize in more complicated ones) with the *top down* approach (scaling down system working at macro- and/or microscale) constitutes one of the most important peculiarities of *nanoscience* and *nanotechnology*. Of course understanding and reproducing the conditions necessary to address the self assembly in a desired way is a difficult task. Nevertheless, in recent years, the potential of such an approach triggered a lot of research in this direction. In particular, STM revealed itself to be a powerful tool to address, analyze and modify self assembled molecular structures as well as single atoms.

In this thesis different nanoscale structures have been produced, studied and combined. All the structures described have been produced following a *bottom up* scheme. As shown in the following, this indeed limits the control on the growth process. On the other hand, it has to be stressed that, due to this approach, the nanostructures investigated can be produced in a virtually countless number and in a comparably fast and cheap way. Exploiting this research direction looks therefore very important in order to open a way to the application of *nanotechnology* to any device of practical interest in everyday life.

### 1.2. Experimental Techniques

The experimental work described in this thesis has been carried out mainly by means of scanning tunnelling microscopy (STM), photoelectron spectroscopy (PES) and low energy electron diffraction (LEED). In this section a brief introduction about the working principles and some of the practical aspects of these instrumental techniques is given.

### 1.2.1. Scanning Tunnelling Microscopy

#### Introduction

Scanning Tunnelling Microscopy is a powerful tool invented at the IBM Zurich Research Laboratory in 1981 by Gerd Binnig and Heinrich Rohrer[2]. Very soon after its invention STM proved to be an extremely useful tool for the investigation of surfaces and in 1986 Binnig and Rohrer were awarded the Nobel Prize.

The STM working principle relies on the quantum mechanical tunnelling of electrons through a potential barrier between a conductive sample and a sharp metallic tip placed very close to each other (typically a few Å). A bias is applied between the tip and the sample and a tunnelling current is measured to flow across the tip-sample gap. The tip is then scanned over the sample by means of piezo-electric tubes. While moving the tip, the sample corrugation induces a variation of the sample-tip distance and therefore of the tunnelling current. The tip can be scanned on the sample at a fixed z-position above the sample while measuring the current (*constant height* mode). Alternatively a feedback system can be used to adjust the tip-sample distance in order to keep the tunnelling current constant. In this