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A combined scanning tunneling microscopy and reflectance anisotropy spectroscopy investigation of tetraphenylporphyrin deposited on graphite

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Abstract

The ordering properties of tetraphenylporphyrin molecules sublimated on a highly oriented pyrolitic graphite surface have been investigated. The morphological information obtained by scanning tunneling microscopy has been linked with the optical spectra by reflectance anisotropy spectroscopy. Measurements were performed *in situ* as a function of the nominal coverage.

Keywords: Scanning tunneling microscopy; Reflection spectroscopy; Light scattering; Self-assembly

1. Introduction

In the last few years extensive studies have been performed on assemblies from organic molecules onto solid surfaces in view of potential application in molecular-based nanodevices [1] as well as in the field of materials science research [2]. Porphyrin-derivatives play nowadays an important role in the design of extended self-assembled adlayers of controlled size and shape. In particular, surface assemblies from porphyrins are of special interest because of their ample electronic and photonic properties that have been already applied in the creation of optical devices [3], chemical sensors [4] and functional supramolecular materials [5]. Several strategies can be followed for the preparation of porphyrin layers with controlled properties. Self-assembly of monolayers (SAMs) on gold [6], Langmuir–Blodgett (LB) or Langmuir–Schaefer (LS) depositions [7], have found extensive application, while ultra high vacuum (UHV) sublimation has been used to deposit, under controlled conditions, individual molecules on a solid substrate [8].

The research in this field is performed primarily by scanning tunneling microscopy (STM) that allows to assess directly position, orientation, and packing arrangement of single or complex molecules on solid substrates, correlating this information to the electronic properties [9]. Among non-destructive spectroscopies suitable for monitoring *in situ* the growth process of organic materials, reflectance anisotropy spectroscopy (RAS) has recently demonstrated [10] to represent an excellent choice. Due to the millimeter-sized spot of the light used, RAS measures the average anisotropy signal on a macroscopic scale. Nonetheless, it has been verified theoretically [11] and experimentally [12] that RAS is sensitive to the local interaction between molecules and consequently to the morphology of the deposited layer. So it is meaningful to compare the spectroscopic data of the optical anisotropy with the local information obtained from STM images of the adlayers.

Up to now, studies mainly have dealt with porphyrin adlayers involving either simple metalloporphyrins [13] or

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free-base porphyrin derivatives bearing ad hoc functional groups, such as peripheral alkyl chains [14], or carboxylic substituents [15], which exert stabilization and ordering by Van der Waals forces or hydrogen bonding, respectively.

A notable exception is found in a recent paper, which reports STM studies on adlayers from simple octaethylporphyrin derivatives on highly oriented pyrolitic graphite (HOPG) in dichlorobenzene solution [16]. The resulting packing geometries were strongly influenced by subtle differences in molecular structures. Although a detailed explanation for this observation was not given, it appears that moderately functionalized porphyrins tend to give unpredictable and intriguing arrangements. In this paper, we focused on the simple 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (tetraphenylporphyrin, H_2TPP hereafter), sublimated under UHV conditions on HOPG and studied with STM and RAS as a function of the quantity of deposited molecules.

2. Experimental details

5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine (H_2TPP), 99% purity, was purchased from Aldrich and used as received.

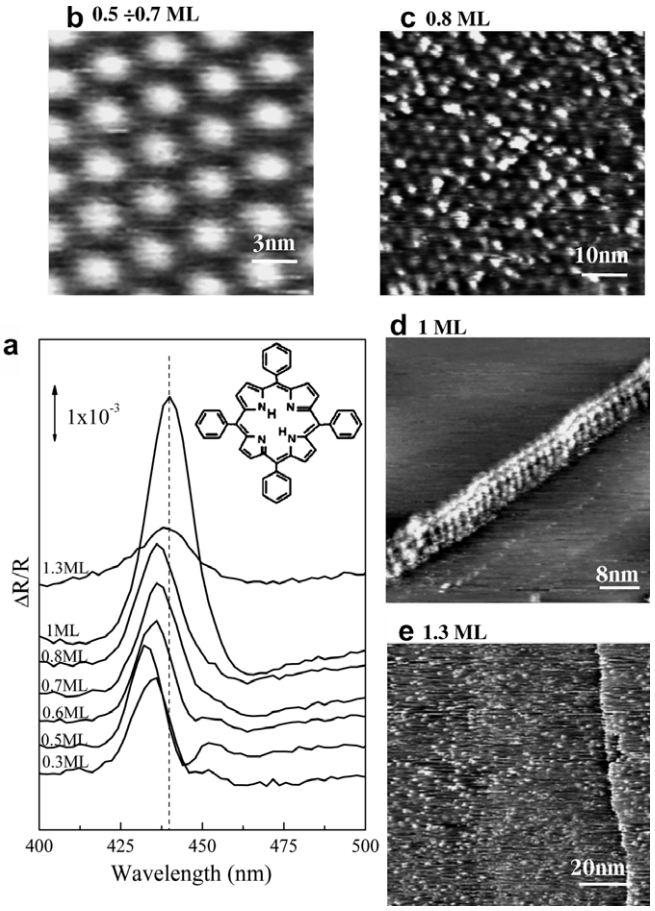

Fig. 1. RAS spectra as a function of the amount of deposited H_2TPP (a), and corresponding STM images (b–e) recorded at the same coverage rate. The inset in figure 1a reports the molecular structure.

The structure of the molecule is reported in the inset of Fig. 1.

Freshly cleaved highly oriented pyrolitic graphite was introduced in the UHV chamber (base pressure low 10^{-10} Torr). The sublimation in vacuum was performed by heating a tungsten filament previously dipped in a H_2TPP solution at a concentration lower than 1%. During the sublimation cycles, the base pressure was kept as low as 10^{-7} Torr and the H_2TPP molecules deposition was estimated from the exposure time and partial pressure, calibrated during preliminary experiments.

The HOPG samples, after molecules deposition, were transferred in the STM chamber and imaged to investigate their modification. RAS spectra were recorded after imaging, in the same experimental chamber. After each experimental session, the HOPG sample was brought back to the preparation chamber for additional H_2TPP deposition.

STM imaging was performed with an Omicron-STM system operating at room temperature. Electrochemically etched tungsten tips were employed. A dependence of image contrast on the polarity of the applied voltage was not observed. STM calibration was done by comparing images of molecular adsorbates with atomically resolved pictures of graphite. All images were unfiltered, the only treatment being a rigid plane subtraction.

Reflectance anisotropy spectroscopy (RAS) measures the difference of the sample reflectivity (ΔR) in near-normal incidence, for light polarized along two perpendicular directions (a and b). The signal is expressed as:

$$\frac{\Delta R}{R} = 2\frac{R_a - R_b}{R_a + R_b} \tag{1}$$

where R_i ($i = a, b$) is the square modulus of the Fresnel complex coefficients for reflection (r_i) of polarization i [10]. Usually, a and b coincide with well-defined symmetry directions of the sample, but in this experiment the linearly polarized electric fields were aligned parallel to the edges of the rectangular graphite substrate. This experimental configuration has been chosen measuring the dependence of RAS spectra upon the azimuthal rotation by an angle ϕ around an axis perpendicular to the substrate and looking for the maximum signal amplitude. All the spectra have been recorded in the photon wavelength range 200–800 nm (1.5–5.5 eV). Particular attention has been used to measure the signal around the Soret band region (400–500 nm−2.5–3.1 eV), where the main π–π^* transition of the aromatic porphyrin cycle is [17].

3. Results and discussion

In agreement with similar studies already performed by applying STM with other spectroscopies (X-ray photoemission spectroscopy (XPS) and electron energy loss spectroscopy (EELS)), which are sensitive to the chemical and electronic structure of the molecules, we have found out that vacuum deposited H_2TPP molecules adsorb intact