

## STM imaging and spectroscopy of single copperphthalocyanine molecules

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### Abstract

A low-temperature ultrahigh-vacuum scanning tunneling microscope (STM) is used to image individual copperphthalocyanine (CuPc) molecules and to perform local spectroscopic measurements on these molecules. Evaporation of CuPc on liquid-nitrogen-cooled graphite substrates leads to nonclustered individual molecules at random positions. STM images at 35 K show protrusions with a height of about 0.2 nm and a diameter of about 1.0 nm, consistent with CuPc molecules that lie flat on the substrate. Current-voltage curves acquired with the STM tip positioned over CuPc show a pronounced peak in  $dI/dV$  vs  $V$  at a tip voltage of  $0.4 \pm 0.1$  V. This is attributed to resonant tunneling through a molecular level of CuPc.

*Keywords:* scanning tunneling microscopy, scanning tunneling spectroscopy, copperphthalocyanine

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### 1. Introduction

Scanning tunneling microscopy (STM) has been widely used to image organic molecules [1]. STM can also be used as a spectroscopic tool for measurements of the local electronic structure which may be deduced from current-voltage curves between tip and sample. This technique of scanning-tunneling spectroscopy (STS) has been applied to atomic adsorbates on semiconductors [2] and metals [3], but very little has been done on organic molecules. With the atomic resolution of STM/STS, it is possible to study the electronic structure of organic adsorbates on a metallic substrate at a submolecular scale. Here, we report preliminary STS data on single molecules of copperphthalocyanine (CuPc, see inset of Fig.1b) that indicate tunneling through a molecular level.

### 2. Experimental details

CuPc is evaporated from a Knudsen cell at 400 °C through a liquid-nitrogen-cooled diaphragm onto highly-oriented pyrolytic graphite (HOPG) substrates in an ultrahigh vacuum (UHV) system. A low deposition rate was used, viz.,  $\sim 0.01$  monolayer per minute. Pressure was  $< 10^{-7}$  mbar during deposition. CuPc was studied at very low coverage ( $\ll 1$  monolayer) to allow imaging and spectroscopy of single molecules.

A difficulty in STM and STS on molecules is adsorbate mobility on the surface which leads to clustering. For this reason, substrates were kept at about 200 K during evaporation. Immediately after deposition, samples were transferred in situ to the precooled UHV STM. STM images

show nonclustered individual CuPc molecules at random positions for samples prepared in this way.

An Omicron variable-temperature STM was used for imaging and spectroscopy at 35 K. Base pressure during imaging was  $\sim 10^{-11}$  mbar. STM tips were hand-cut from Pt(10%Ir) wire.  $I$ - $V$  curves were acquired as follows. Curves were collected at a grid of  $20 \times 20$  pixels within a  $15 \times 15$  nm<sup>2</sup> image, at a spot where a few CuPc molecules were located. At every pixel where a curve is collected scanning is interrupted, feedback is turned off, and the voltage is ramped from -0.8 to 0.8 V in 80 steps. After each voltage step, data acquisition is halted for 300  $\mu$ s to allow stabilization of the current preamplifier, and data are taken during 640  $\mu$ s. In between subsequent  $I$ - $V$  curves feedback is on. The  $I$ - $V$  curves presented here are an average of 14 separate curves acquired at adjacent pixel sites. Individual  $I$ - $V$  curves show the same features, albeit with decreased signal-to-noise ratio.

### 3. Imaging and spectroscopy of CuPc

A typical STM image of an isolated CuPc molecule is given in Fig.1a. A protrusion with an apparent height of 0.2 nm and a diameter of 1.0 nm is observed. This shows that the CuPc molecule lies flat on the HOPG substrate. No intramolecular structure is observed. Both findings are in accordance with previous reports of CuPc on HOPG [5].

Whereas topographic STM images of CuPc are abundant in the literature [4,5], STS has rarely been reported. Figure 1b presents current-voltage curves taken with the STM tip positioned over a CuPc adsorbate as well as 3 curves taken at the bare substrate. Bias parameters are  $I = -0.5$  nA and  $V_{tip} = -0.6$  V. The three substrate  $I$ - $V$  curves were taken at different spots. The excellent overlap indicates the good reproducibility of the data.

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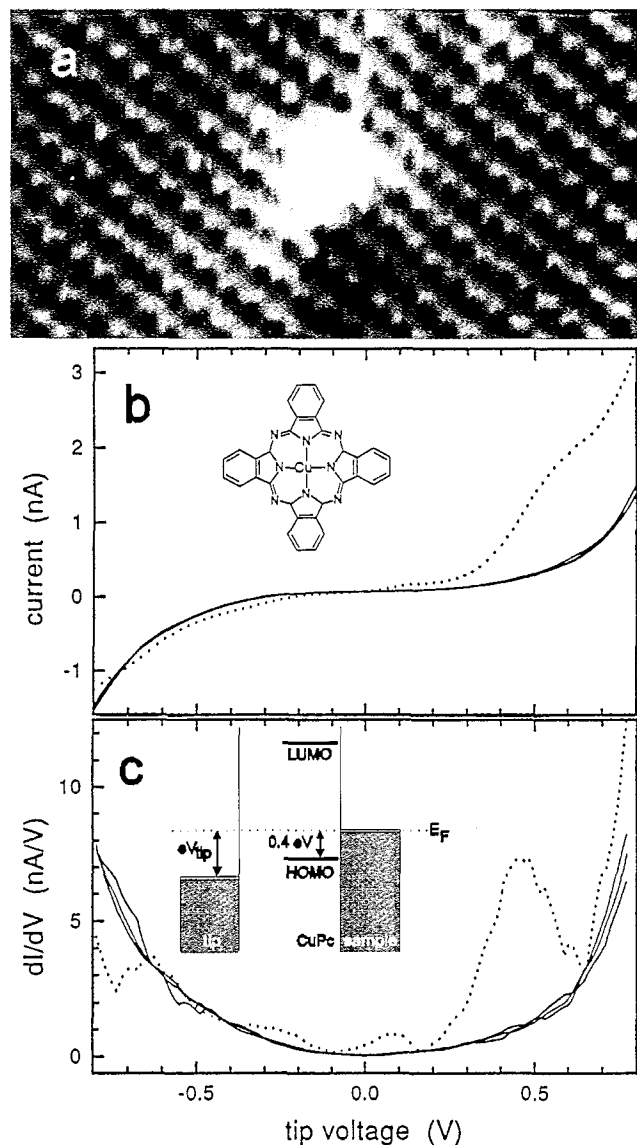


Figure 1: a. Topographic image of a single CuPc molecule on HOPG. Bias parameters are  $I = 0.5$  nA and  $V_{tip} = 0.5$  V. Image size is  $6.7 \times 3.5$  nm<sup>2</sup>.

b.  $I$ - $V$  curves on CuPc and on graphite.

c.  $dI/dV$  vs  $V$ . Dotted lines represent data taken with the STM tip positioned over a CuPc adsorbate. Solid lines denote data taken at the bare HOPG substrate. All data were taken at 35 K. Inset in b is a schematic drawing of CuPc. Inset in c is a schematic energy diagram that illustrates the proposed resonant tunneling through a molecular level of CuPc.

The  $I$ - $V$  curve taken on CuPc and those on the substrate do not differ much for tip voltages ranging from -0.8 to +0.3 V. At higher voltage, a larger current is observed if the STM tip is located over the CuPc molecule. The CuPc  $I$ - $V$  curve displays a step near 0.5 V which is absent in curves taken on the substrate.

Figure 1c shows the numerically calculated derivative  $dI/dV$  vs  $V$ . A peak is observed at a tip voltage of 0.46 V.

Data on various CuPc molecules reproduce this peak. The tip voltage where it occurs varies between 0.3 and 0.5 V. Further experiments are needed to sort out whether this variation is related to the tip electronic structure or other causes. Full width at half maximum of the peak is about 0.2 V.

#### 4. Discussion

The peak observed in STS on CuPc may be attributed to resonant tunneling through a molecular level of CuPc. This is illustrated in the inset of Fig. 1c. A location of the HOMO level at 0.4 V below the substrate Fermi level provides a straightforward explanation of the CuPc  $I$ - $V$  curves: In the STS experiment the tip Fermi level is shifted with respect to the molecular adsorbate and sample. A positive voltage on the tip lowers the tip Fermi energy. If the voltage exceeds +0.4 V, resonant tunneling through the molecular level will increase the current [6]. As a result the  $I$ - $V$  curve will display a steplike increase at 0.4 V, and accordingly  $dI/dV$  displays a peak.

HOMO and LUMO levels of free CuPc are located near 5 and 3 eV with respect to vacuum, respectively [7]. A difference of 0.4 V between the HOMO level of CuPc and the substrate Fermi level implies an effective work function of order 4.6 eV for HOPG, which is not an unreasonable value. Further experiments with a variety of tips and substrates and a larger voltage window are necessary in order to make a more definite identification of the CuPc molecular level.

The discrete CuPc molecular levels are expected to spread into broad resonances as a CuPc molecule adsorbs to HOPG [8]. The width of the resonance appears to be quite narrow ( $\sim 0.2$  eV), which suggests a relatively weak hybridization between CuPc and HOPG. Experiments on atomic adsorbates yield somewhat larger values [2,3].

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