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Metal d-Orbital Occupation-Dependent Images in the Scanning Tunneling Microscopy of Metal Phthalocyanines

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A strong d-orbital dependence in the scanning tunneling microscopy image of metal phthalocyanines is demonstrated. Unlike copper phthalocyanine (CuPc) wherein the central metal appears as a hole in the molecular image, the cobalt atom in CoPc is the highest point (about 0.3 nm) in the molecular image. On the other hand, the benzene ring regions of CoPc and CuPc appear to have the same height. These data are consistent with theoretical calculations that predict a large contribution of cobalt d-orbitals near the Fermi energy. An intriguing aspect of this work is that it may be possible to chemically identify the different metal phthalocyanines simply by their appearance. This is demonstrated for the case of a mixed monolayer of CuPc and CoPc on Au(111).

Introduction

Metal phthalocyanines are of great technological and fundamental interest. A schematic structure of a typical metal(II) phthalocyanine is presented in Figure 1. Recent theoretical studies of the electronic structure of metal phthalocyanines include, but are not limited to, density functional treatments,^{1,2} unrestricted (open-shell) Hartree–Fock calculations,³ multiconfiguration SCF,⁴ and extended Huckel MO-based elastic scattering quantum chemical calculations.⁵ The phthalocyanines are models for biologically important species such as porphyrins, hemoglobin, and chlorophyll, and they are extensively used as pigments and dyes. They can serve as the active elements in chemical sensors⁶ and are of great interest in optoelectronic devices⁷ and solar cells.⁸ Their catalytic properties have been of interest for some time,⁹ most recently for redox catalysis such as in fuel cell applications.^{10–12} They have interesting semi-conductivity and can be used to form well-behaved field effect transistors.^{13,14}

An understanding of the interaction between metal phthalocyanines (MPc) and surfaces is a critical element required for optimizing their use in many of the applications listed above. Two elements of interest are the nature of the bonding between the MPc and the support, and the structure of the MPc–support entity. In principal, both of these issues can be addressed by obtaining submolecular-resolution images of MPc adsorbed on the substrate of interest. Until now, however, only limited information about the chemical nature of the adsorbed MPc was extracted by STM studies.

STM images of individually distinguishable copper phthalocyanine (CuPc) molecules have been presented by Gimzewski and co-workers,¹⁵ Moeller,¹⁶ Lippel et al.,¹⁷ Ludwig and associates,¹⁸ Fritz and co-workers,¹⁹ Kanai et al.,²⁰ and Petracek.²¹ In addition, images of the free acid (H₂Pc) coadsorbed on graphite with a liquid-crystalline carrier have also been published by Freund and associates.²² While there have been reports of PbPc studied by STM, no molecular images have been observed.^{23,24} To our knowledge, no other phthalocyanine systems have been studied by STM. In all of these cases, the predominant features of the molecular image could be under-

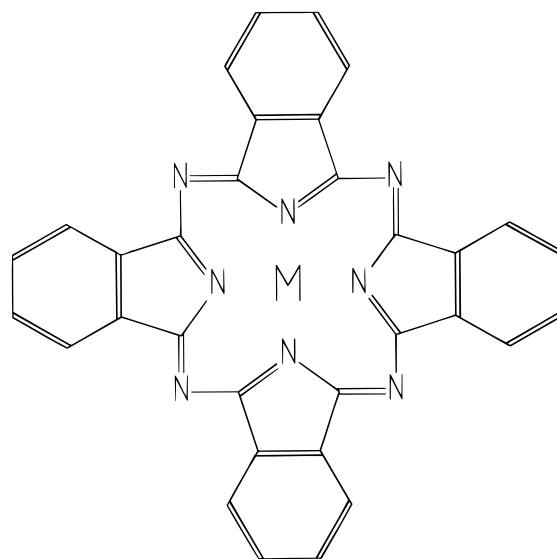


Figure 1. Molecular structure of a typical metal(II) phthalocyanine.

stood based on the organic material alone. Theoretical calculations of the STM image of CuPc predict that there should be an apparent hole in the center of the molecule,^{5,17} and this is what is normally observed.^{17,19} Even for H₂Pc, there is an apparent hole in the center of the molecule.²² Since STM measures the local density of states, the “height” in constant-current mode is a complex function of the density of electrons with energy near the Fermi energy—it may deviate significantly (in either a positive or negative direction) from the overall electron density. The explanation for these “holes”, it seemed to us, was that both the occupied and unoccupied orbitals localized on Cu lay 1 eV or more from the Fermi energy, while the MPc ligand LUMO lay close to the Fermi energy.^{25,26} We reasoned that MPc systems having a greater metal d-orbital participation in molecular orbitals near the Fermi surface should show profoundly different STM images. Alternatively, dramatic changes in the apparent molecular shape might also occur in systems where interactions between the metal d-orbitals and a metallic substrate were significant. In the latter case, the metal surface density of states might “shine through”, giving enhanced height to the central metal.

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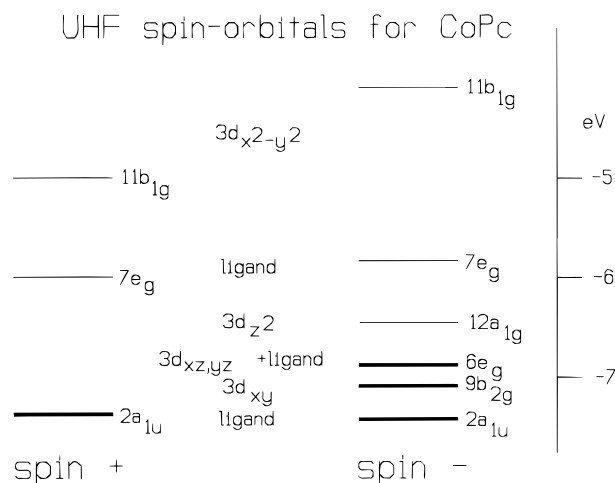


Figure 2. Spin-orbital energies of cobalt(II) phthalocyanine near the Fermi energy. Heavy lines depict occupied levels while the thinner ones represent virtual (empty) orbitals. This diagram is based on data taken from ref 3.

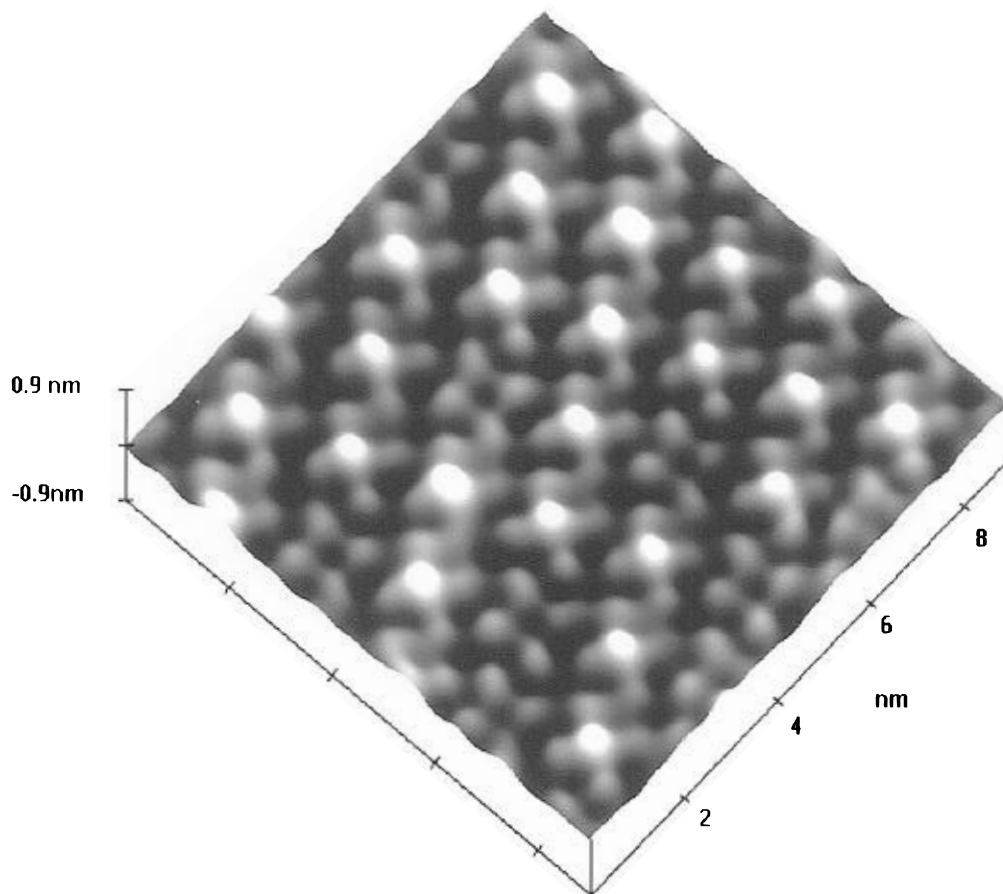
As a test of this concept, a study of various metal phthalocyanines was initiated. The first system chosen was cobalt phthalocyanine (CoPc), wherein cobalt has a d^7 configuration. Figure 2 depicts the occupied (heavy lines) and unoccupied levels close to the Fermi energy as determined by the UHF- $X\alpha$ calculation of Reynolds and Figgis.³ (This is a gas-phase calculation, so the apparent value of E_f is about 2 eV too negative.) It is clear from this open-shell calculation that there

should be considerable d-orbital participation in both the HOMO and LUMO orbitals, making CoPc an excellent candidate for directly observing d-orbital charge density. In this letter we will demonstrate that the submolecular-resolution STM image of CoPc on Au(111) is dramatically different from that of CuPc on the same substrate.

Experimental Section

In a single continuous operation, 0.4 nm of CoPc, CuPc, or a mixture of both was deposited onto a 100 nm thick layer of Au(111) epitaxially grown on mica. This was accomplished in a liquid nitrogen trapped diffusion pumped bell jar system having a base pressure of about 2×10^{-7} Torr. In detail, the mica was heated to 550 °C in vacuum for a period of 2 h and then allowed to cool to 375 °C. The Au layer was deposited at this temperature at a rate of 7.8 nm/min. The substrate was then allowed to cool to 180 °C and the MPc was vapor deposited at a rate of 1.8 nm/min from an ME-1 source (R. D. Mathis). The sample was then allowed to cool in vacuum. The metal phthalocyanines were purified by multiple sublimation before use.

The completed sample was removed from the preparation chamber, mounted on a sample carrier, and immediately inserted through a load lock into the UHV chamber housing a McAllister STM. Both W and Pt/Ir tips were used after electron bombardment in UHV. The STM is controlled by a Digital Instruments Nanoscope III. All the data were obtained in constant current mode using a Pt/Ir tip, but similar results have been obtained



CoPc and CuPc adsorbed on Au(111)

Figure 3. Surface plot of a mixed CoPc and CuPc monolayer on Au(111). The gray scale extends over a range of 0.5 nm. The image was Fourier filtered.

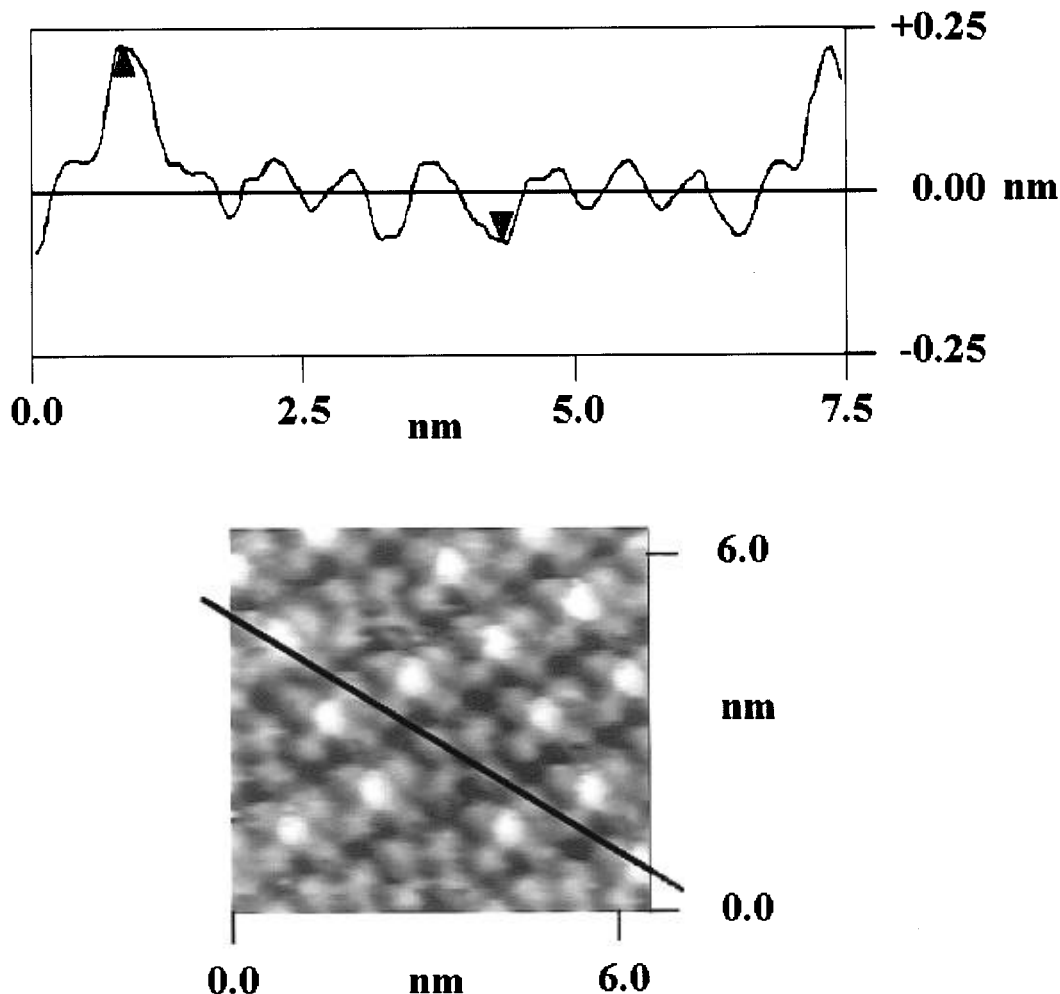


Figure 4. Top view and cross-sectional plot of a mixed CoPc and CuPc monolayer on Au(111). The gray scale extends over a range of 0.5 nm. These data were not Fourier filtered.

using W tips. Typical experimental parameters were a sample bias of -0.100 V, a current of 1.0 nA, and a 4 Hz scan rate. Current voltage, $i(V)$, curves were taken using the standard Nanoscope software. We also heated a CoPc on Au(111)/mica sample to 180 °C in the STM chamber (partial pressure of $O_2 < 5 \times 10^{-10}$ Torr) and then allowed it to cool for 6 h prior to STM image acquisition.

Results and Discussion

While a large number of pure CoPc/Au(111) and CuPc/Au(111) images were recorded, these results can accurately and compactly be portrayed using the mixed complex film results. Figure 3 presents a surface plot of a small section of the MPc-coated Au(111) surface. This image was Fourier filtered. Notice first that the four-leaf clover like shape of the MPc molecules is clearly apparent. Note also that some of the molecules have an intense bright (high) area in the center while others have a pronounced dark region (hole). On the basis of our experience with chemically pure samples, the bright centered molecules are CoPc while those with an apparent hole in the center are, as expected, CuPc. Thus, chemical analysis of these mixed films can be performed in a trivial way. It is also interesting to note that larger area images show the CuPc distributed in small apparently randomly sized clusters within the CoPc, suggesting weak differences in the lateral forces between the MPc species.

Figure 4 is a combined top view and cross-sectional plot of a different area of the same film. This image was not Fourier

filtered. The heavy line in the image served as the cut for the cross section. Note that (from top to bottom) it passes through a benzene ring of CoPc, the central Co, and the opposite benzene ring. It later crosses a benzene ring of a CuPc molecule, the central Cu, and the opposite benzene ring of the CuPc. The positions of the central cobalt and copper are shown by triangular markers in the sectional plot. From Figure 4, the benzene rings have an apparent height of about 0.1 nm above the gold surface, independent of the nature of the central metal. The copper appears to have near zero height while the cobalt towers over the surface with a 0.3 nm total elevation.

Since the ionic diameters of Cu(II) and Co(II) are both 0.15 nm within about ± 0.01 nm, our conjecture regarding the role of d-orbitals in the STM image must have some validity. On the other hand, there are at least three separate mechanisms (consistent with our conjecture) that could lead to the observed differences in height. If the tunneling current is primarily LUMO mediated, then the bright central region would be due to the $3d_{z^2}$ orbital of cobalt. If the HOMO is the critical participant, then the d_{xy} , d_{xz} , and d_{yz} orbitals provide the observed contrast. Alternatively, it may be that the unpaired electron on cobalt forms a partial bond with the underlying gold, as has been suggested for CoPc on platinum electrodes.¹⁰ Thus, enhanced electron density in the d_{z^2} orbital could also lead to the apparent height of the central atom. The combination of higher resolution STM images (the d_{xy} , d_{xz} , and d_{yz} orbitals should all have a small hole in their center) and current-voltage, $i(V)$, data (unoccupied orbitals enhance the current when the

sample is biased positively) should resolve this issue. To date, we have been frustrated in obtaining good $i(V)$ data by the difficulty in keeping the tip clean. Some $i(V)$ curves show a marked current increase at about +0.5 V bias, while others show a similar change at -0.5 V. We interpret this to mean that we sometimes have MPc molecules on the tip. We are currently working to solve this problem and also to obtain higher resolution images of a range of metal phthalocyanines.

An alternative explanation would involve the chemical reactivity of the partially filled d_{z^2} orbital. Iron phthalocyanine (FePc) has been shown to reversibly absorb molecular oxygen at pressures above 2×10^{-7} Torr.²⁷ Cobalt(II) tetrasulphophthalocyanine (CoTSP) reacts reversibly with oxygen in water at pH greater than 12 to form a dioxygen adduct.^{28,29} Thus, the adsorption of dioxygen on CoPc might result in the apparent increase in height of cobalt center. This explanation, of course, does not account for the hole in the CuPc complex and seems unlikely at the pressure at which these measurements were performed. Since it is known that heating FePc to 137 °C removes all traces of atmospheric exposure on the Fermi energy,³⁰ heating CoPc to 180 °C should drive off any reversibly adsorbed dioxygen. STM images taken from a heated (and then cooled to 23 °C) sample were not as well resolved as those presented here, but the large corrugation and bright centers were still apparent. Thus, we doubt that O₂ adsorption plays a role in the results presented here.

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