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Scanning Tunneling Microscopy of Metal Phthalocyanines: d^7 and d^9 Cases

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Abstract: Scanning tunneling microscopy (STM) images of cobalt(II) phthalocyanine (CoPc), copper(II) phthalocyanine (CuPc), and mixtures of the two adsorbed on the Au(111) face are reported. Based upon the stability and ease of obtaining molecular images, CoPc appears to adsorb more strongly than CuPc on Au(111), but both species provide images showing submolecular structure. The mixed CoPc and CuPc films also provide high-quality images showing details of the internal structure of the metal phthalocyanine. A particularly exciting aspect of this work is the strong influence of the metal ion valence configuration on the observed tunneling images. Unlike 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. These data are interpreted as indicating that the Co(II) d^7 system has significant d-orbital character near the Fermi energy while the Cu(II) d^9 system does not. This interpretation is consistent with theoretical calculations that predict a large contribution of cobalt d-orbitals near the Fermi energy, and with inelastic electron tunneling spectra that show d-orbital-related bands within 1 eV of 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 can be used to advantage in the study of surface diffusion, 2-d sublimation, and the surface thermodynamics and kinetics of adlayer formation.

Introduction

Metal(II) phthalocyanines are planar complexes with a structure shown schematically in Figure 1. They are of great technological and fundamental interest, both because of their own properties and because of their similarity to other classes of compounds. 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 Hückel MO based elastic scattering quantum chemical calculations.[5] The phthalocyanines are extensively used as pigments and dyes, and they are models for biologically important species such as porphyrins, hemoglobin, and chlorophyll. They can serve as the active elements in chemical sensors, especially for the detection of NO$_2$.[6,7] They are of great interest for use in optoelectronic devices[8] and solar cells.[9] Their catalytic properties have been studied for some time,[10] most recently for redox catalysis such as in fuel cell applications.[11−13] They are semiconducting, and can be used to form well-behaved field effect transistors.[14,15] 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. Of particular interest are the nature of the bonding between the MPc and the support, as reflected in the electronic charge distribution, and the geometric configuration of the MPc−support entity. Both of these issues can, in principal, 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.

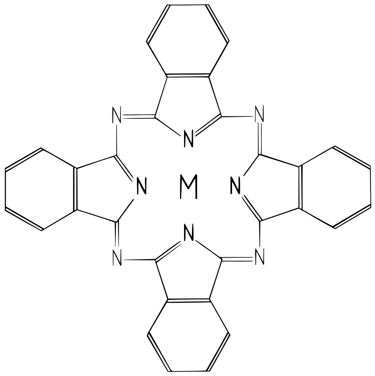

Figure 1. Molecular structure of a typical metal(II) phthalocyanine.

STM images of individually distinguishable copper phthalocyanine (CuPc) molecules have been presented by a number of researchers. Gimzewski and co-workers studied CuPc adsorbed

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on polycrystalline silver.[16] Moeller and associates observed single molecules of CuPc on GaAS(110).[17] Lippel et al. reported excellent submolecular resolution images of CuPc adsorbed on Cu(100).[18] Ludwig and associates found highly resolved images of CuPc could be obtained on graphite and MoS_2.[19] Kanai et al. studied CuPc on Si(100) and Si(111).[20] Fritz and co-workers studied hetero-epitaxial layers of CuPc on Au(111),[21] as did Petracek.[22] In addition, images of the free acid (H_2Pc) co-adsorbed on graphite with a liquid crystalline carrier have also been published by Freund and associates.[23] While there have been reports of PbPc studied by STM, no molecular images have been observed.[24,25] 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 understood 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,[5,18] and this is what is normally observed.[18,21] Even for H_2Pc, there is an apparent hole in the center of the molecule.[23] The explanation for these "holes", it seemed to us, was that both the occupied and unoccupied orbitals localized on Cu lay more than 1 eV from the Fermi energy, while the MPc ligand LUMO lay close to the Fermi energy.[26,27] 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.

As a test of this concept, a study of various metal phthalocyanines was initiated. The first system chosen was cobalt(II) phthalocyanine (CoPc), wherein cobalt has a d^7 configuration. The calculations of Rosa and Baerends,[1] for example, show that the half-filled CoPc d_{z^2} orbital lies very near the ligand HOMO and at least 1 eV below the CuPc half-filled $d_{x^2-y^2}$ orbital. These calculations also place the filled CuPc d_{z^2} orbital about 2 eV below the ligand HOMO. According to Rosa and Baerends,[1] there is no significant d orbital contribution within a band 1 eV above and 2 eV below the ligand HOMO in CuPc. Figure 2 depicts the contrasting situation in the case of CoPc wherein is presented 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] Because the Figgis calculation is for gas-phase molecules, we have added a constant 1.5 eV to the calculated energy in order to roughly correct for the polarization energy associated with formation of a crystalline solid. The correction is associated with the dielectric stabilization of the ion and has been found to range between 0.8 and 2 eV in a broad range of compounds.[28−30] 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 observing direct d-orbital charge density. In this article 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.

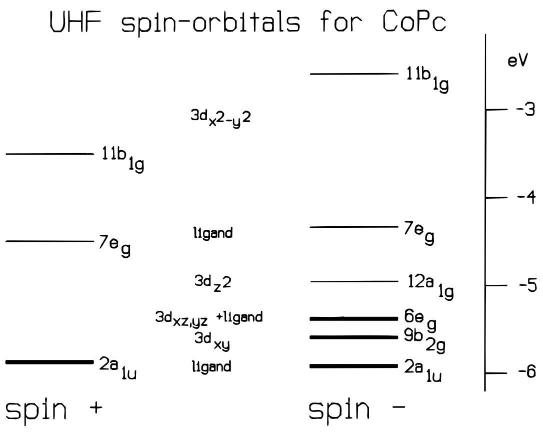

Figure 2. Spin−orbital energies of cobalt(II) phthalocyanine near the Fermi energy. Heavy lines depict occupied levels while the thinner ones represent virtual (empty) orbitals. This diagram is based on data taken from ref 3. The energy scale has been shifted by 1.5 eV.

Experimental Section

The metal phthalocyanines were purified by multiple sublimation before use. The gold was purchased from Cerac and was 99.999% purity. Mica sheets were purchased from Ted Pella and were freshly cleaved just before use. In a single continuous operation, 0.3 to 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. A 100 nm thick Au layer was deposited onto the mica (still at 375 °C) at a rate of 7.8 nm/min. The substrate was then allowed to cool to either 180 or 50 °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 to room temperature in vacuum and then rapidly transferred to the UHV chamber.

In the case of the mixed phthalocyanine film, the total amount could be measured using a thin film quartz microbalance, but the relative amounts of CuPc and CoPc were not determined. While approximately equal amounts of the CoPc and CuPc were mixed and added to an ME-1 source, neither the vapor pressures nor the sticking coefficients are the same at any given temperature. Our intent was to produce films that had a qualitatively significant mixture of CoPc and CuPc. Quantitative studies will be pursued in the future.

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. We also heated a CoPc on Au(111)/mica sample to 180 °C in the STM chamber (partial pressure of $O_2 < 2 \times 10^{-10}$ Torr) and then allowed it to cool for 6 h prior to STM image acquisition. Both W and Pt/Ir tips were used for STM analysis. The W tips (0.5 mm in diameter) were electrochemically etched in 1.0 M KOH using about 30 V AC, while the Pt/Ir tips (0.25 mm in diameter) were cut with scissors. Once the tips were in vacuum, they were cleaned by electron bombardment from a hot filament. Typically 4 mA of current at 1200 V was passed through each tip for a period of 30 s. The McAllister STM is based on the slip-stick principal and is controlled by a Digital Instruments Nanoscope III. Typical images were acquired in constant current mode at a scan rate

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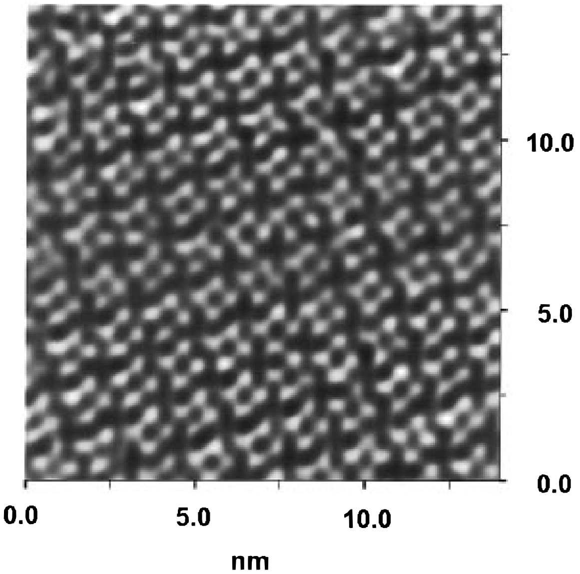

Figure 3. Top view STM image of a 0.3-nm layer of CuPc on Au(111) obtained with a W tip, +0.94 V sample bias, and 140 pA tunneling current. The image was Fourier filtered to reduce noise.

of 2 to 6 Hz. High bias/low current (±0.95 V/200 pA) and low bias/high current (±0.1 V/2 nA) conditions were used depending upon the tip and sample. No clear cut universal "best" conditions were observed. The images were manually plane-fit to account for sample tilt and then either low-pass filtered or Fourier filtered. In either case, the Nanoscope III software (version 3.2) was used. If not otherwise indicated in the figure caption, only plane fitting and low pass filtering was applied.

Results and Discussion

A 0.3-nm layer of copper(II) phthalocyanine on Au(111) forms a near monolayer. While it is easy to observe the individual molecules as fuzzy disks by STM, it is more difficult to resolve structure on the submolecular scale. One of our better images is shown in Figure 3. The 4-leaf pattern of the phthalocyanine ring is clearly observed, as is the previously reported depression (hole) in the center of the macrocycle. The Cu atom is not participating in the tunneling process. This result was also obtained with Pt/Ir tips and a variety of bias voltages and currents. To date, it appears that cut tips require higher currents and lower bias voltages than sharp etched (W) tips to obtain the same image.

A 0.3-nm layer of CoPc on Au(111) gives a somewhat clearer image. As seen in Figure 4, small domains of CoPc form on the gold surface. The high plateau on the right is a monatomic gold step underlying the CoPc monolayer. Note that in the center of Figure 4 where three domains meet there is a region of disorder where no single molecule can be identified. This is, we believe, due to a higher degree of molecular mobility in this region. Zooming in to an ordered region, one obtains images like that shown in Figure 5. The 4-fold structure is again clearly identified, but the central region is dramatically different. (We note here that the apparent elongation of some of the CoPc arms in Figure 5 is probably due to piezo creep.) Instead of a hole in the center of the CoPc, a pronounced high point is observed. Changing the tip material, bias voltage, or set point current changes the amount of resolution observed, but the CoPc images were always highest in the center.

It appears from the STM images of the pure materials that our conjecture concerning the role of the metal orbital configuration is correct. However, one must constantly be alert for possible artifacts in the STM image arising from tip imperfections and/or contamination. A surer test, it seemed to us, would be to image a mixed MPc layer. In that way the substrate and tip are identical and any image differences must be due to the local density of molecular states. Figure 6 is the image of a small section of such a surface. As expected, the CoPc molecules are easily identified by their high centers. In a gray scale image like Figure 6, they stand out like beacons. The CuPc molecules, on the other hand, have dark centers as expected. A more quantitative indicator of the difference between CoPc and CuPc is the sectional plot shown in Figure 7. The cross section was chosen to pass through the center of a CoPc molecule at the upper left, through the center of a CuPc (central region), and finally through the center of another CoPc. The markers in the sectional plot indicate the positions of Co^{2+} and Cu^{2+} ions, respectively. In this image, the benzene rings of both the CoPc and CuPc are of equal height but the Cu^{2+} ion appears as a roughly 0.1-nm hole in the molecular center while the Co^{2+} ion appears to be a 0.15-nm hill. The total molecular height appears to be about 0.3 nm. Of course, the apparent height depends on a number of parameters, not the least of which are the sharpness of the tip and the sample−tip

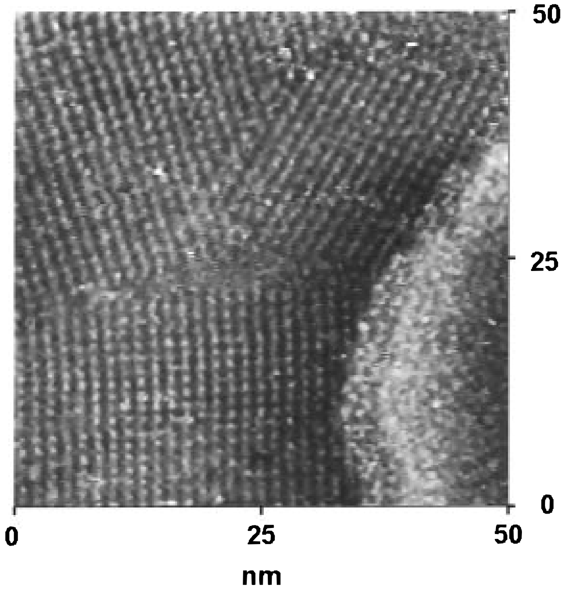

Figure 4. Top view STM image of a 0.3-nm layer of CoPc adsorbed on Au(111). The image was obtained with a W tip at a sample bias of +0.9 V and a fixed tunneling current of 192 pA.

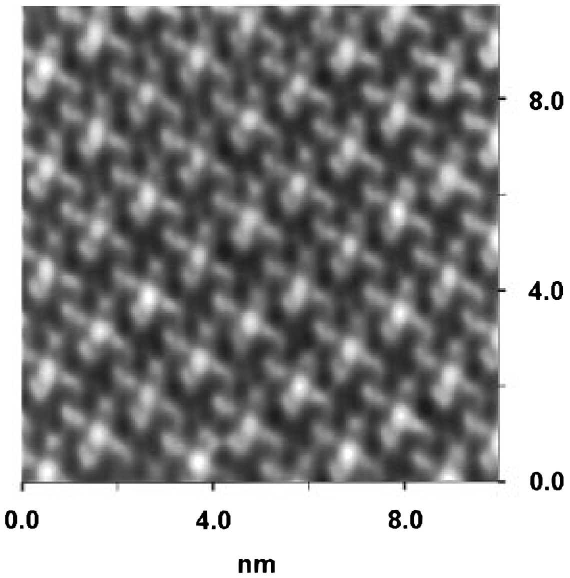

Figure 5. Top view STM image of 0.3 nm of CoPc on Au(111) obtained with a W tip, +0.90 V sample bias, and 200 pA tunneling current. The image was Fourier filtered to reduce noise.

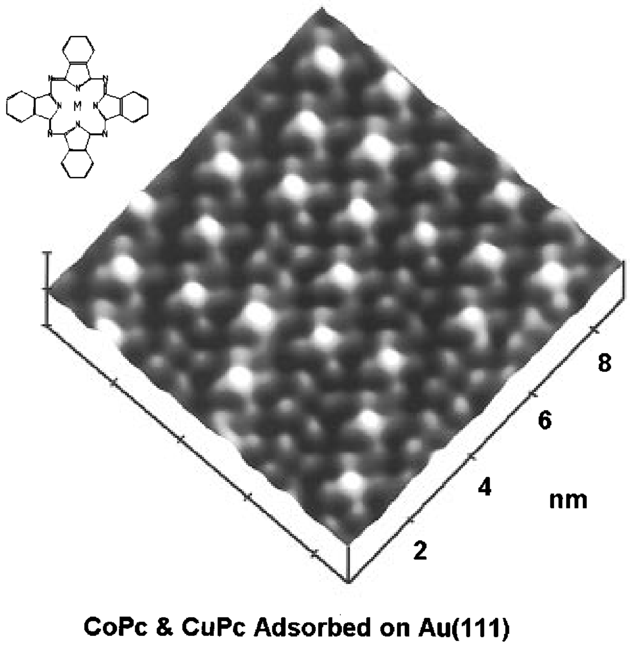

Figure 6. Surface plot STM image of 0.4 nm of a mixture of CuPc and CoPc on Au(111) obtained with a Pt/Ir tip, −0.10 V sample bias, and 1 nA tunneling current. The image was Fourier filtered to reduce noise.

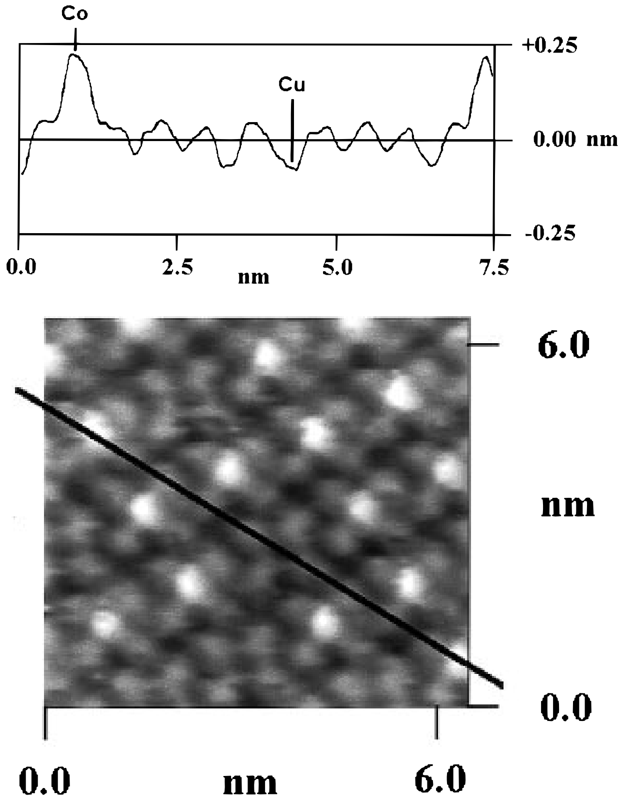

Figure 7. Top view and cross-sectional plot of a mixed CoPc and CuPc monolayer on Au(111). A Pt−Ir tip was used at a sample bias of −0.10 V and a current of 1.0 nA. The gray scale extends over a range of 0.5 nm.

separation. Figure 8 was obtained from another mixed phthalocyanine sample in a small region where only CoPc molecules were observed. Note that the central region of the molecule is more clearly separated from the periphery but the apparent height (marker to marker) is only about 0.13 nm.

The height of the molecule above the gold layer is actually greater than that determined from measurements over the ordered region alone. As shown in Figure 9, the tip is seldom

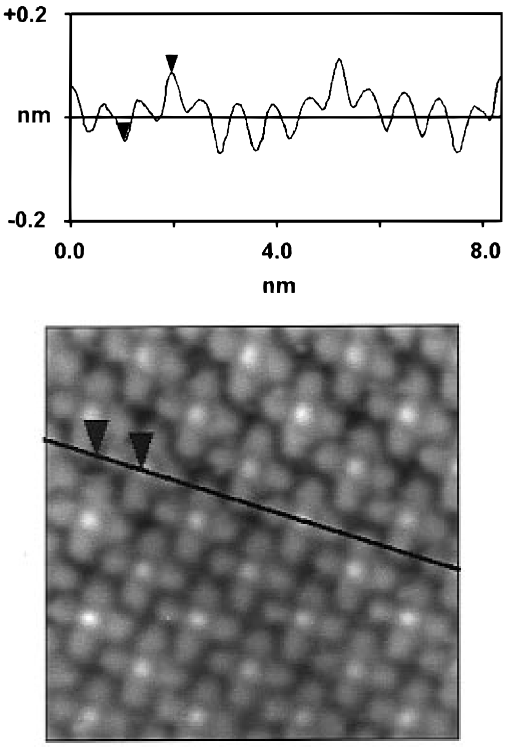

Figure 8. Top view and cross-sectional plot of a CoPc covered region of a mixed CoPc and CuPc monolayer on Au(111). A Pt−Ir tip was used at a sample bias of +0.20 V and a current of 3.0 nA.

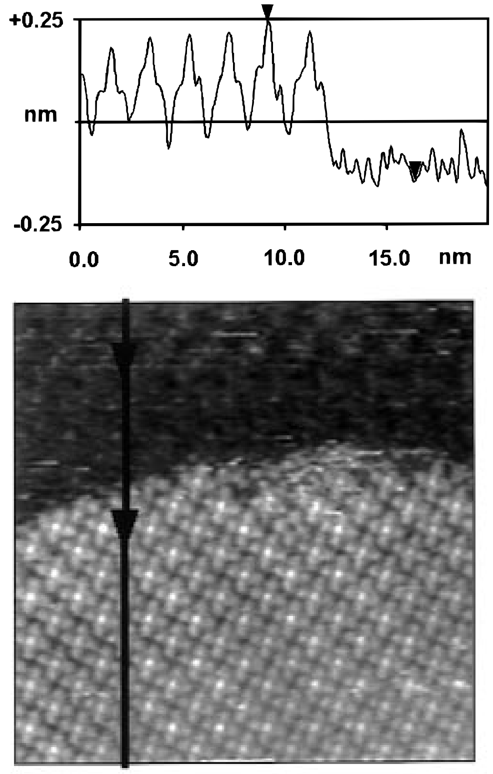

Figure 9. Top view and cross-sectional plot of an island boundary region seen on a Au(111) surface partially covered by a mixture of CoPc and CuPc. A Pt−Ir tip was used at a sample bias of +0.20 V and a current of 3.0 nA.

sharp enough to allow the tunneling current to come only from the Au surface in the region between molecules. In the "low" regions between MPc molecules, current comes both from the Au surface and a portion of the MPc in close proximity to the tip edges. If we interpret the upper dark area of the image to be due to nearly clean gold (vide infra), the height of the benzene ring portion of the MPc is about 0.21 nm. This value is quite reasonable when compared to the interplanar spacing in crystalline MPc's—about 0.38 nm in the α form.[31] The apparent Co^{2+} (0.35 nm) and Cu^{2+} (0.12 nm) heights are clearly not indicative of size in the normal sense since their ionic radii are 0.072 and 0.070 nm, respectively.[32] Thus, based on electron density alone, there should be no discernible difference between the STM images of CuPc and CoPc and the image should have only a very slight (0.03 nm) depression in the center.

It is well-known that both the electron density and the local density of surface states near the Fermi energy play a critical role in determining the STM image.[33,34] STM imaging of electronegative or electropositive elements, for example, can result in the observation of anomalous heights.[35] Another classic example is the observation of the dangling bonds on the silicon surface.[36] It is clear in the present case that the occupancy of the d-orbitals is playing a significant role in the STM image. In the simplest possible picture, Co(II) is acting as a conductor while Cu(II) is not. Since the STM images reflect contours of constant current, the tip must dip toward the Au surface above the Cu(II) center and pull back from the Co(II) in order to maintain constant current flow. There are, however, 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 empty 3d$_{z^2}$ spin-orbital on cobalt. If the HOMO is the critical participant, then the d$_{xy}$ orbital or the (d$_{xz}$, d$_{yz}$) orbital pair might provide the observed contrast. The d$_{z^2}$ and (d$_{xz}$, d$_{yz}$) orbital pair are the most likely candidates both by symmetry and since they have the largest projection out of the plane of the molecule. Moreover, as mentioned in the introduction, these orbitals are located more than 2 eV below the ligand HOMO in CuPc and are not expected to contribute significantly to the CuPc STM image. In any of these cases, the mechanism for the tunneling enhancement in CoPc would be some form of d-orbital mediated tunneling. This might be through a true resonance process,[37] where the MPc orbital coherently couples to the states of the substrate and tip. Or, it might be an incoherent transient process such as the orbital mediated tunneling seen in tunnel diodes containing metal phthalocyanines.[26,27]

Alternatively, the unpaired electron on cobalt may form a partial bond with the underlying gold, as has been suggested for CoPc on platinum electrodes.[11] This would also provide a mechanism for channeling Au surface electron density through the cobalt center and thence to the tip. This might be similar to the case of Xe on Ni(110) wherein Xe can be imaged because of the very slight residual density of the 6s electron at the Fermi level. This despite the fact that the peak in that resonance lies close to the vacuum state.[38] 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 sample 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 for the differences on CoPc and CuPc 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.[39] Cobalt(II) tetrasulfophthalocyanine (CoTSP) reacts reversibly with oxygen in water at pH greater than 12 to form a dioxygen adduct.[40,41] Thus, the adsorption of dioxygen on CoPc might result in the apparent increase in height of the 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,[42] 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 O$_2$ adsorption plays a role in the results presented here. On the other hand, the imaging of adsorbed oxygen is an exciting possibility for samples studied in air. While all of our studies to date have been in UHV, we are currently reconfiguring our STM to allow us to study both FePc and CoPc in air.

Another interesting aspect of the observation of unique images for CoPc and CuPc is the possibility of studying diffusion. Consider for example, the time sequence of images shown in Figure 10. Attention should be placed on the single CuPc molecule seen at the upper central edge of the island. Image 10A was taken first and 10B collected about 1 min later. Using CuPc as a marker, one observes that the island has grown by the addition of a single CoPc during the interval between scans. This growth can be interpreted in several ways. The most trivial is that the new CoPc was deposited by the tip. We view this as unlikely since we observed no significant changes in apparent image height or resolution. A second interpretation is based on the idea that the apparently bare gold surface (upper region of Figure 10) is actually partially covered with relatively rapidly moving MPc molecules—a 2-dimensional (2D) gas region. In this view, the A−B sequence is the 2D equivalent of crystal growth from the vapor. This explanation is attractive because the STM images obtained from the apparently bare regions are noisier and less stable than those obtained from truly clean Au(111) surfaces. The observed island growth might also be the result of tip-enhanced diffusion near the island boundary. In both 10A and 10B partial molecular images can be seen at the island boundary. These partial images can easily result if an edge molecule hops from under the tip during the scan. Since 10A and 10B were taken in the sequence scan-up and then scan-down, the "new" molecule in 10B might have been the same molecule seen as a partial fragment in 10A (just above its final position in 10B).

An intiguing time sequence is shown in Figure 11. The only change in the images is seen in the circled region where it

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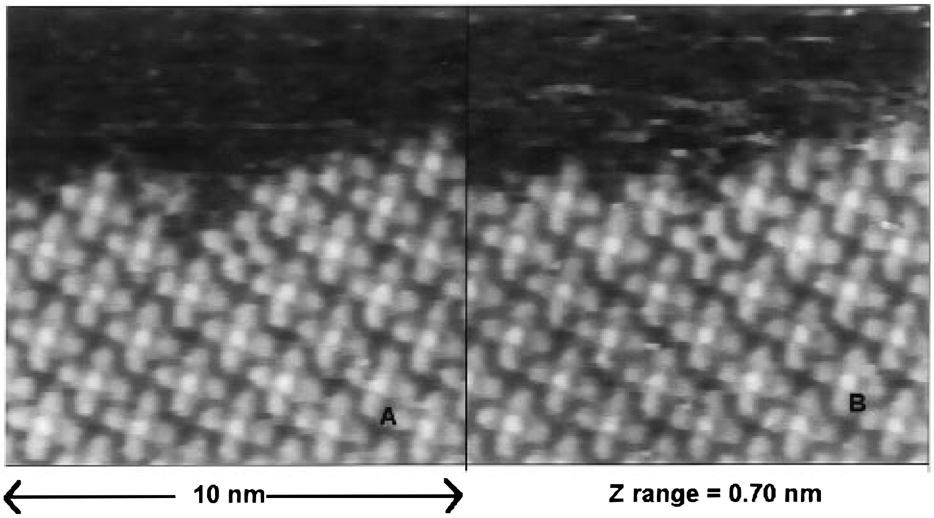

Figure 10. Time sequence top view STM images of 0.4 nm of a mixture of CuPc and CoPc adsorbed on Au(111). The images were separated in time by about 1 min, with image A being first. They were obtained with a Pt−Ir tip, +0.20 V sample bias, and 3.0 nA tunneling current.

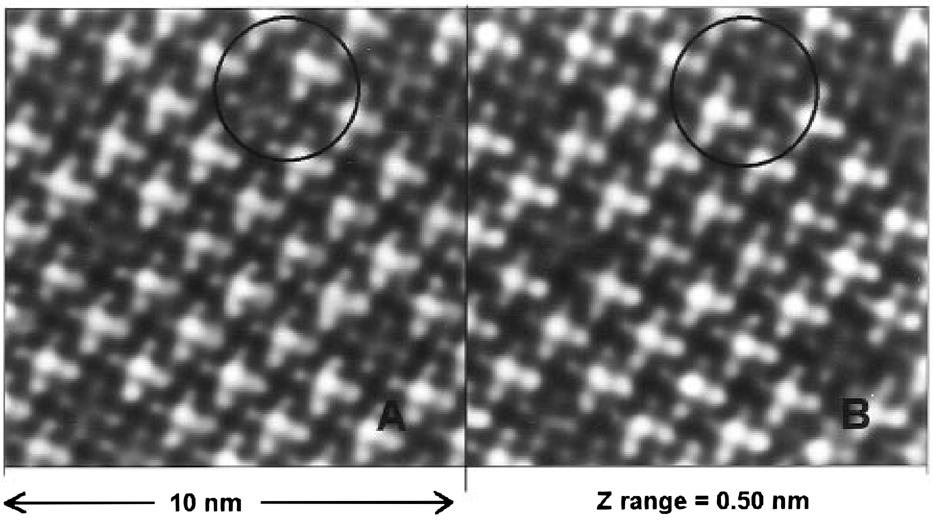

Figure 11. Time sequence top view STM images of a mixture of CuPc and CoPc adsorbed on Au(111). The images were separated in time by about 1 min, with image A being first. They were obtained with a Pt−Ir tip, +0.05 V sample bias, and 700 pA tunneling current.

appears that two phthalocyanines have exchanged position. By what mechanism could such an image change occur? Direct exchange of a CuPc and adjacent CoPc seems unlikely. Closer examination of Figure 11 suggests that these are images of a 2-layer region. The lower layer lays flat on the Au surface and neither a hole nor a hill is easily discerned at the center of each molecule. The upper incomplete layer in this particular image is composed of CoPc and appears to be tilted with respect to the surface. This tilting is the expected behavior for the second and higher layers since crystalline MPc has a herringbone structure.[31] The loss of resolution in the lower layer (almost certainly the first layer) is probably due to the finite size of the tip. Since the lower level molecules must be seen through small holes in the second layer much of the tunneling current can come from the tip edges. Thus, the tip never gets as close to them as it does to those in the top layer. The molecular motion seen in Figures 11A and 11B, therefore, is the diffusion of a second-layer phthalocyanine over the initial monolayer.

Conclusions

Contrary to the expectations set by past STM studies of CuPc and H_2Pc, more than the Pc^{2-} electronic structure must be considered in any attempt to predict and/or interpret the scanning tunneling microscopy images obtained from a general member of the class of metal phthalocyanines. Based on the results presented here, the orbital configuration of the central metal ion must be considered since it can, in certain cases, provide the dominant tunneling pathway for the molecule. This issue has special relevance for metal−macrocyclic systems where the metal ion can range through the entire periodic table providing valence shell orbitals of s, p, d, or even f type.

The use of mixed MPc adlayers provides us with a new means for studying the processes associated with film formation and diffusion in two dimensions. The results presented here show that surface diffusion processes can be monitored by using a “tracer” species differing only in the electronic configuration of the central metal. Moreover, the detailed distributions of MPc and M′Pc in a mixed film could be used to study such processes as surface diffusion, thermal annealing, 2D sublimation, and orientational changes with coverage. Another application is in the measurement of relative sticking coefficients.

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