High-Resolution Imaging of Copper-Phthalocyanine by Scanning-Tunneling Microscopy

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Scanning-tunneling microscopy (STM) images of isolated Cu-phthalocyanine molecules on a Cu(100) substrate exhibit atomic scale features which agree well with Hückel molecular-orbital calculations. Images which show a molecule atop a measurably corrugated Cu(100) surface, a hopping molecule, packed molecular arrays, and a novel molecular binding site at a Cu step edge further illustrate the potential of STM for molecular observations.

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Although molecular imaging by scanning-tunneling microscopy (STM) has been of interest for several years,[1,2] it has only recently been shown that STM can resolve internal structure of molecules.[3,4] These observations of close-packed arrays of coadsorbed benzene and CO on Rh(111) suggest a strong potential for STM as a tool for observing molecular phenomena, provided STM image contrast is understood and molecular motion, induced either thermally or by the STM,[2,3] can be overcome. To further assess this technique, we have imaged Cu-phthalocyanine (Cu-phth) molecules on a Cu(100) surface at various coverages. This distinctively shaped molecule, shown in Fig. 1(a), has been imaged previously by field-emission microscopy,[6] STM,[2] and transmission-electron microscopy.[7] Phthalocyanines are chemically stable and form crystalline solids which sublime around 550 °C. They are analog to biological molecules important to photosynthesis and respiration, and are of interest as pigments, catalysts, and photosensitive semiconducting organics.[8]

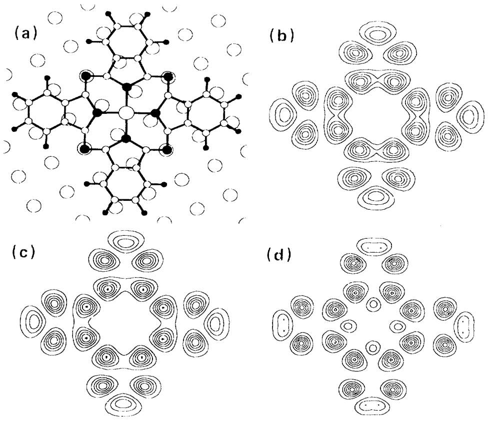

FIG. 1. (a) Model of the Cu-phth molecule above a Cu(100) surface. Small (large) open circles are C (Cu) atoms and small (large) filled circles are H (N) atoms. The Cu(100) lattice is shown rotated by 26.5° (Ref. 5). (b) and (c) Contour plots of the charge densities of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) 2 Å above the molecular plane. (d) Charge density of the HOMO, 1 Å above the plane.

Our results include the first STM observation of the internal structure of an isolated molecule. We find that Cu-phth molecules adsorb in the expected flat-lying configuration, but with two different rotational orientations. Tip-induced motion of isolated molecules is sometimes observed, as are isolated molecules above a corrugated metal surface. Near 1-monolayer (ML) coverage the two domains evident in low-energy electron diffraction[9] (LEED) are observed, each corresponding to one of the molecular orientations present at low coverages. We compare the observed image contrast to simple valence charge densities calculated for free molecules, obtaining surprising agreement. Finally, we discuss problems with images of Cu-phth at coverages above 1 ML on Cu(100), and at low coverage on Si(111) and Au(111).

STM images were obtained with constant current, slow scan (2 sec/line) techniques[10] with an ultrahigh vacuum (UHV) STM system described previously.[11] The Cu(100) single crystal was cleaned by repeated sputter-anneal cycles. The final cycles employed 500-eV Ar ions incident on a room temperature sample, followed by annealing to 500 °C. Cu-phth was sublimed, at a rate of 0.5 ML/min, onto the room temperature sample from a quartz crucible heated radiatively by a tungsten spiral. LEED patterns of the dosed Cu(100) sample were consistent with, but inferior to, those previously reported.[9] Tungsten tips, heated by e^- bombardment with use of a filament, the tip, or the sample as the source, were usually sharpened by brief operation at elevated voltages. Unless otherwise noted, data processing has been limited to simple filtering with thresholded averaging of surrounding pixels.

Figure 2(a) is an image at nominal 0.3-ML coverage. Two orientations of the fourfold Cu-phth molecules are evident. The molecular corrugation is typically 2 Å and hints of internal structure are visible with a 0.4-Å corrugation. Figure 2(b) is a higher magnification image

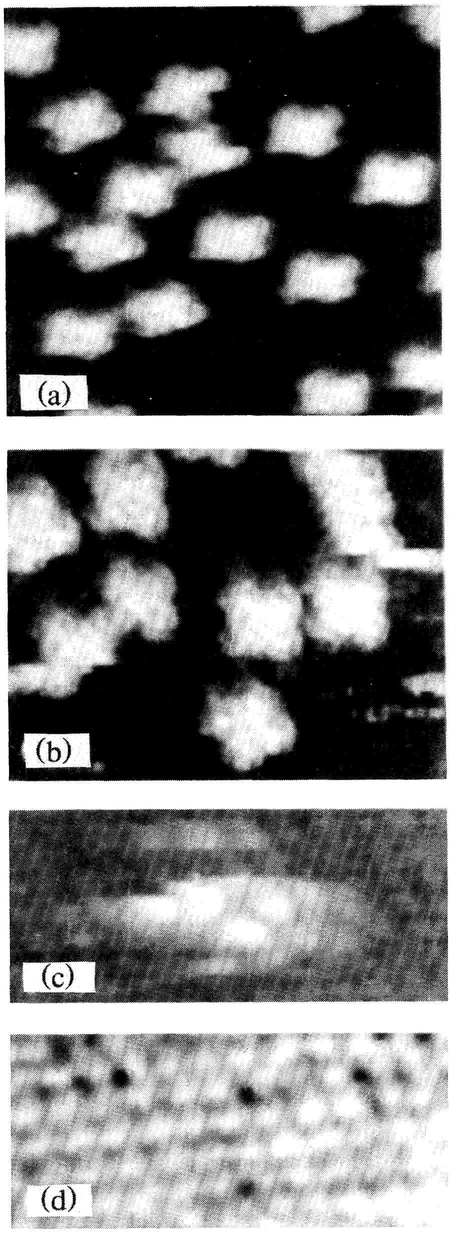

FIG. 2. STM images of isolated Cu-phth on Cu(100). (a) A 150×150-Å^2 image recorded at $(V_T,i_T)=(-0.30\text{ V}, 4\text{ nA})$. (b) A 90×75-Å^2 image for $(-0.39\text{ V}, 4\text{ nA})$. (c) Section of an image at $(-0.10\text{ V}, 2\text{ nA})$ showing a fourfold molecule superimposed on a weak Cu(100) corrugation. (d) Image at $(-0.12, 2\text{ nA})$ showing strong Cu(100) corrugation. The Cu atom spacing is 2.55 Å.

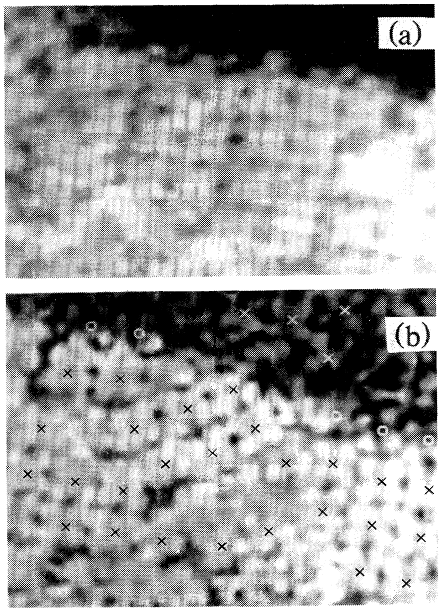

FIG. 3. Images near 1-ML coverage. (a) A standard gray scale image showing the upper terrace of a stepped region. The molecules are spaced 13.7 Å apart (Ref. 9). (b) A processed image showing upper and lower terraces of a two-domain region. Crosses are superimposed on those features which can be readily associated with Cu-phth molecules. Both images are recorded with $(-0.61\text{ V}, 8\text{ nA})$.

which reveals more internal structure, and includes a molecule which appears to be making stepwise displacements across the surface. Such motion could often be induced by a lowering of the bias voltage so as to reduce the tunnel gap, but the specific bias voltage and tunnel currents required to observe this effect were tip dependent and tip damage was difficult to avoid. Figure 2(c) shows a single molecule, its fourfold symmetry presumably broken by a displacement into a previously scanned region during the image, above a weakly corrugated Cu(100) surface. The molecular image differs significantly from those where metal corrugation is absent. When strong metal corrugation was observed, as in Fig. 2(d), no molecules were detected.

Figure 3(a) shows a partially ordered region obtained by one increasing the coverage to near 1 ML. The gray levels have been adjusted to provide adequate contrast on the upper terrace, making the terrace at the bottom of the Cu step appear dark. Pairs of protrusions corresponding to two of the four lobes of Cu-phth are seen at the step edge. Figure 3(b) shows a similar region, with statistical differencing used to increase the contrast and reduce the apparent step height so that both terraces can be examined.[12] This image shows that Cu-phth molecules near step edges, indicated by open circles, prefer a rather different binding geometry, so that variations in their chemical properties might be expected.

We have performed simple Hückel calculations of the charge distributions of free molecule states nearest to the Fermi level.[13] Charge-density contours evaluated 2 Å above the molecular plane are shown in Figs. 1(b) and 1(c) for the HOMO and LUMO. These can be compared to the high-resolution STM data of Fig. 4. In Fig.

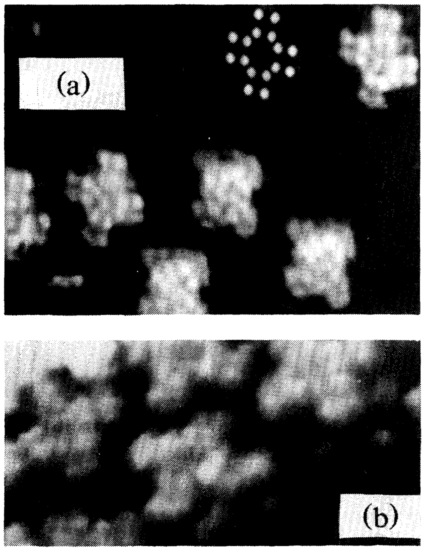

FIG. 4. (a) High-resolution image at submonolayer coverage for (−0.15 V, 2 nA). Fine structure has been emphasized by baseline subtraction, and a gray scale representation of the HOMO, evaluated 2 Å above the molecular plane, has been embedded in the image. (b) High-resolution image near 1-ML coverage with (−0.07 V, 6 nA).

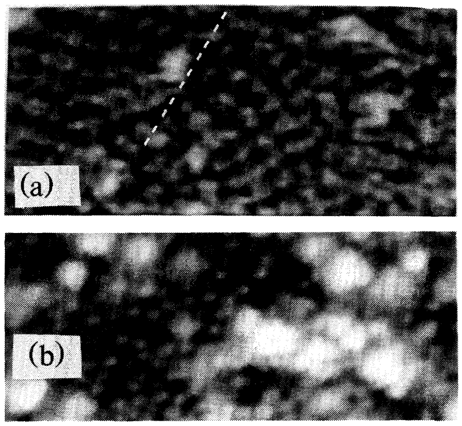

FIG. 5. (a) A 300×150-Å^2 image at a nominal 1.5-ML coverage on Cu(100) recorded with (−1.4 V, 2 nA). A dashed line marks a rotational domain boundary. (b) A 150×75-Å^2 image of Cu-phth on Si(111) 7×7 for (2.0 V, 1 nA).

4(a), obtained at low bias, the molecules appear as delocalized pedestals with weak internal structure. The inequivalent appearance of the two molecular orientations implies a strong tip asymmetry. Figure 4(b) shows a stepped region with gray levels chosen to highlight the fine structure within individual molecules. Although the resolution is poorer than in the previous image, the symmetry of the two orientations is better represented. Allowing for image distortions, the fine structure appears as four protrusions on each of the four lobes of the molecule. The calculated images also show four predominant protrusions per lobe, each originating from a highly populated carbon atom *p* state, in surprising agreement with the data. We find little dependence of low-voltage images on the bias polarity, as expected since the half-filled HOMO differs only slightly from the LUMO. The central Cu atom is not seen in the calculated image and a central protrusion does not appear in most of our data. We thus consider the central protrusions in some of the molecules in Fig. 4(a) to represent tip artifacts, which will be difficult to eliminate for unknown or asymmetric molecules. When metal corrugation appears, the image contrast changes to that shown in Fig. 2(c). For comparison, Fig. 1(d) shows charge densities for the HOMO evaluated only 1.0 Å above the molecular plane. Substantial charge density has appeared on the four nitrogen atoms bonded to the central Cu atom. Our Hückel wave functions show that the charge density on these N atoms continues to grow as the molecular plane is approached. The fact that maxima are seen near the positions of these N atoms in Fig. 2(c), as deduced from the known molecular structure and orientation, suggests that the metal corrugation appears at very small tunnel gaps. When large metal corrugation is present,[14] tip-induced forces may thus be strong enough to move molecules or induce localized states.[15] Detailed interpretation of STM data becomes uncertain under such conditions, because the observed protrusions may not correspond to metal atoms.

We have not obtained good images of Cu-phth at coverages much above 1 ML on Cu(100), or at submonolayer coverage on Si(111) or Au(111). Figure 5(a) shows an image obtained for 1.5-ML coverage on Cu(100). Domain structures and defects are seen, as well as small islands which may correspond to a second layer of molecules. We could not maintain lateral resolution adequate to allow us to definitively identify second-layer molecules. Poor lateral resolution was typically accompanied by anomalously large gap variations ($\delta z = 20$ Å) for small bias voltage changes (from 0.5 to 1.5 V). Such artifacts could sometimes be eliminated by a short period of unstable operation at 4.0 V, but they reappeared during attempts to record images. We associate this problem with a build up of molecules on the tip, which is exacerbated by the presence of defects and of additional poorly conducting overlayers which reduce the tip-molecule gap. Our initial measurements, which employed easily prepared Au(111) and Si(111) crystals[10,13] and low Cu-phth coverages, were similarly disappointing. It was easy to see protrusions atop the Si(111) 7×7, as exemplified by Fig. 5(b). Unfortunately, most of the protrusions do not show fourfold symmetry and there is little structure within molecules. For Au(111), preliminary images of isolated molecules showed less repeatability than those reported for

Ag(111).[2] We suspect that low activation barriers allow rotations or translations of molecules to smear these images. If this is the case, then UHV instruments have an important advantage in that more reactive substrates, which form strong chemisorption bonds as for Cu-phth/Cu,[9] can reduce molecular motion. For Si(111), the situation is more complex and interesting because the 7×7 surface offers several binding sites and may itself be locally modified by interactions with the molecules.[16]

Our results can be summarized as follows. The choice of a substrate upon which molecules are bound by a highly corrugated molecule-surface interaction potential appears to be essential for high-resolution imaging of isolated molecules. When molecular motion is inhibited, high-resolution images can give insight into the molecular electronic structure. Simultaneous observation of molecules and of the corrugation of the metallic substrate is made difficult by strong tip-surface interactions which accompany small tunnel gaps. These data suggest that, with further development, STM can become a valuable technique for observing relatively simple molecules.

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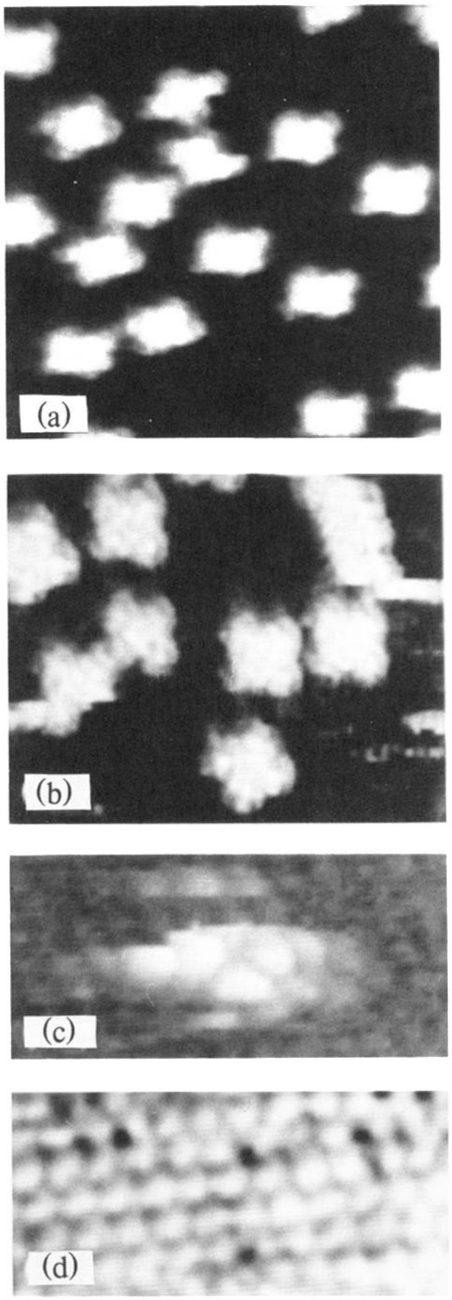

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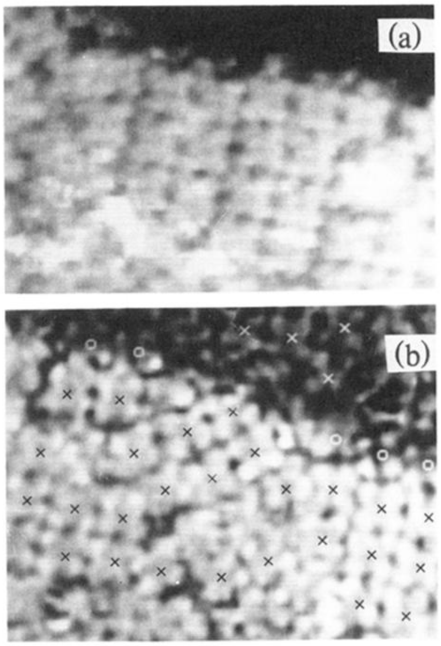

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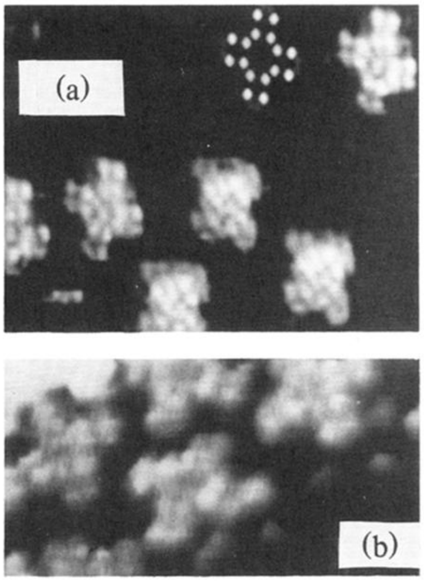

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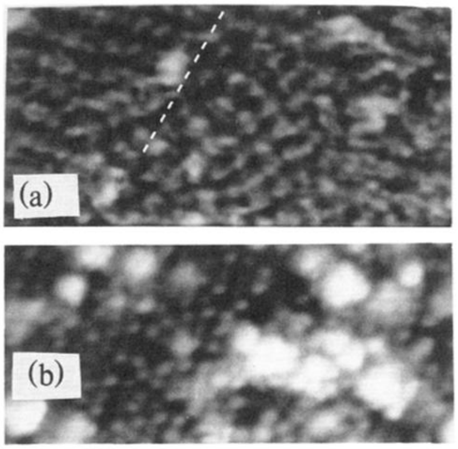

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