PHYSICAL REVIEW B **78**, 233409 (2008)

Symmetry reduction of metal phthalocyanines on metals

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(Received 29 October 2008; revised manuscript received 24 November 2008; published 29 December 2008)

The temperature-dependent adsorption behavior of fourfold symmetric metal phthalocyanines (*M*Pcs) on metals with commensurate and incommensurate symmetries was investigated by scanning tunneling microscopy. On the fourfold symmetric Cu(100) surface, planar and fourfold molecular structures in two equivalent orientations were found for *M*Pcs when prepared at room temperature. In addition, two metastable orientations were identified when prepared at low temperature, which can be depopulated upon annealing. *M*Pcs adsorbed on the sixfold symmetric Cu(111) surface showed a disturbed molecular appearance. The symmetry of molecular structures changed from fourfold to twofold, which is discussed in terms of molecule-substrate interaction.

DOI: 10.1103/PhysRevB.78.233409 PACS number(s): 68.37.Ef, 68.43.Fg, 61.46.−w

The study of organic molecules has received remarkable attention during the last decades for the development of thin-film transistors.[1–3] Among them metal phthalocyanines (*M*Pcs) and their derivatives, also known as dye molecules, are utilized in a broad field of applications especially for optical and organic electronic devices.[4] *M*Pcs are metal-organic complexes with a single metal ion in the central position of a macrocycle of alternating carbon and nitrogen atoms. Four outer benzene rings are rigidly attached to the macrocycle via two C-C bonds for each ring. As a result, *M*Pcs have a fourfold symmetry when being planar. Thanks to their stable molecular structures, investigations of *M*Pcs in an ultrahigh vacuum (UHV) environment through thermal sublimation become attainable. Besides volume-averaging techniques used for thick molecular films and bulk materials, local probes with a high spatial resolution such as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are intensively applied to determine geometric and electronic structures, as well as magnetic properties of *M*Pcs from isolated *M*Pcs to a coverage up to a few monolayers.[5–21]

Imaging of *M*Pcs and of their intramolecular structures by STM was first achieved by Gimzewski *et al.*[5] and Lippel *et al.*[6] under UHV condition. Until now, many *M*Pcs [M=Cu,[5–8] Co,[9–11] Fe,[12–17] Ni,[14] Pd,[18] Zn,[19] Mn (Ref. 20)] have been studied on various surfaces: they adsorb in a planar configuration on surfaces and exhibit four-lobed cross shapes in STM images, which are consistent with their molecular structures. The metallic centers appear either as a dip or as a protrusion in STM images depending on the electronic structure of the central metal ion, i.e., the energy of the d_Z^2 orbital with respect to the Fermi level.[14] For larger ionic sizes of metallic centers of *M*Pcs, such as SnPc, the metallic ion sticks out of the molecular plane resulting in a nonplanar configuration on surfaces.[21] For the growth behavior on metallic surfaces (Cu, Au, Ag, and graphite), no ordered structures are found at low coverages. With increasing coverage, ordered molecular domains start to appear and form a complete molecular monolayer before the formation of the second molecular layer.[12,14,16–19,21] Upon further increase of coverage, self-assembling in higher layers can be observed with the molecular plane to be parallel[22] or tilted[12,16] to the surface plane.

In the low-coverage regime, many physical properties of isolated *M*Pcs on metallic substrates are dominated by the molecule-substrate interaction. For instance, *M*Pcs with a magnetic center, such as Fe, Co, or Mn, adsorbed on nonmagnetic substrates are highly fascinating, as spin-scattering processes are manifested as a Kondo resonance in STS and thereby reflecting molecule-substrate interactions and molecular excitations.[9,13,20] The distance between magnetic centers of *M*Pcs and substrate[11] as well as the exact adsorption site[13] were found to strongly modify the Kondo temperature. For metallic substrates, three orientations of FePcs have been reported for the adsorption on Cu(111) (Ref. 12) and Au(111) (Ref. 13) in the submonolayer regime, which are directly attributed to the substrate symmetry. Low-energy electron-diffraction (LEED) observations exhibited two orientations for CuPcs and FePcs on Cu(100) of ±22.5° relative to the ⟨001⟩ direction.[23] Later, this was reconfirmed by STM experiments for CuPc on Cu(100).[6] In addition, one metastable configuration of FePc is reported to occur when FePc is adsorbed on Au(111).[13]

However, in the above experiments molecules were evaporated onto surfaces being held either at room temperature or at elevated temperatures and, therefore, *M*Pcs adsorbed in stable configurations. It remains a question whether there are more metastable configurations, which might have different properties than stable ones when adsorbed on surfaces at low temperatures. In addition, the adsorption of fourfold symmetric *M*Pcs on substrates with commensurate and incommensurate symmetries, as Cu(100) and Cu(111), respectively, can provide a valuable contribution to the understanding of molecule-substrate interactions.

The experiments presented were performed in an UHV system equipped with a home-built variable-temperature STM (VT-STM) operated at ∼25–28 K and with a preparation chamber for substrate cleaning and deposition of molecules.[24] Electrochemically etched tungsten tips were used as STM probes and cleaned by standard procedures. Cu(100) and Cu(111) surfaces were cleaned by repeated cycles of Ar^+ ion etching and annealing to ∼900 K. Surface cleanness was directly checked before evaporation of *M*Pcs by STM. In this study three kinds of *M*Pcs (M=Co, Cu, and Fe) were used.[25] *M*Pcs were evaporated onto surfaces through home-made evaporators, and the evaporation rates

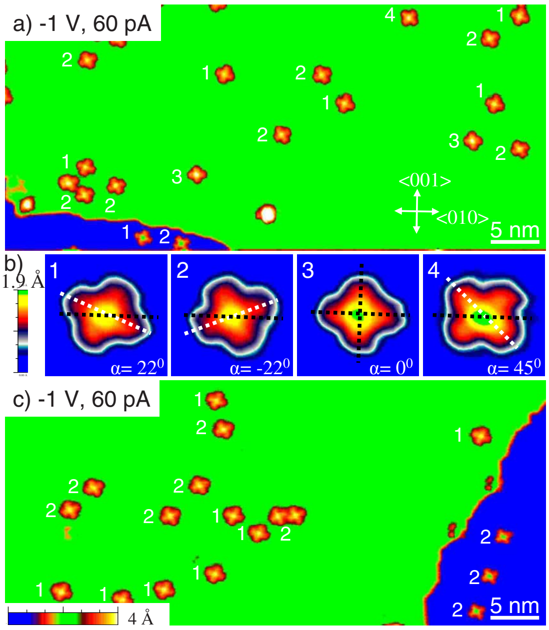

FIG. 1. (Color online) STM images of CoPc on Cu(100) (a) as prepared at ~29 K and (c) after post annealing to room temperature (c). (b) Higher magnification of four different adsorption orientations as marked by 1, 2, 3, and 4 in (a), 3×3 nm^2. In (a), a set of arrows reflects the crystallographic axes of Cu(100) as determined from the bare surface. In (b) one crystallographic axis (black dotted line) and one molecular axis (white dotted line) are indicated.

were measured by a quartz-crystal microbalance. Prior to the sample preparation, all *M*Pcs were heated for 70 h just below their evaporation temperatures for purification. For evaporation onto cold surfaces, samples were stored in the cooled STM with tips fully retracted. During evaporation, sample temperatures rose to ~29 K. To investigate the effect of temperature-controlled reorientation processes, samples were afterward annealed to room temperature and reinvestigated. Bias voltages refer to the sample potential with respect to the tip. Thermal drift and scanner piezocreep result in an estimated lateral error of ±3% and an angular error of ±1.5°.

Figure 1(a) shows a STM image of a stepped Cu(100) surface with adsorbed CoPcs. CoPcs are arbitrarily distributed but Cu steps remain uncovered. Four different adsorption orientations are identified. For each orientation, enlarged images of representative CoPcs are plotted in Fig. 1(b). CoPcs appear in their characteristic four-lobe structure with a bright center similar to those adsorbed on other metals.[9–11] This suggests a planar structure. With a closer inspection, the molecular axes of configuration 3 are found to be parallel with the crystallographic axes of Cu(100). The molecular axes of configurations 1 and 2 are rotated by ~±22° and of configuration 4 by ~45° with respect to configuration 3 and to the crystallographic axes, respectively. Relative frequencies of molecular configurations clearly manifest two groups of distributions as shown in Fig. 2: orientations 1 and 2 (~87%) significantly dominate over orientations 3 and 4 (~13%). Within each group different orientations have almost identical appearing rates. Within the limits of statistical significance, an identical distribution of molecular orientations can be found for CuPc and FePc on Cu(100) (see Fig. 2).

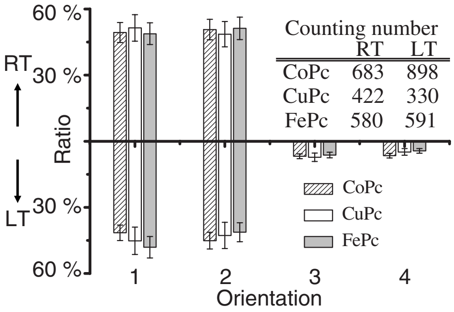

FIG. 2. Relative frequencies of adsorption orientations for CoPcs, CuPcs, and FePcs on Cu(100) after preparation at room temperature and at low temperature. The statistical error is indicated.

Our observation of four different orientations of CuPc, CoPc, and FePc on Cu(100) is in a remarkable disagreement with previous findings for CuPc and FePc on Cu(100).[6,23] There, after room-temperature preparation STM and LEED data reveal an alignment of *M*Pcs in only two orientations (±22.5°), which are in agreement with orientations 1 and 2 in this study. The disagreement suggests a decisive temperature effect. To test the influence of preparation temperature samples were annealed to room temperature and the resulting surface structures were compared to those of samples after room-temperature preparation. In both cases the observable orientations are reduced to those previously reported orientations. This is demonstrated in Figs. 1(c) and 2. As a consequence orientations 3 and 4 have to be assigned to metastable configurations.

Under the given scanning conditions ($U \leq 2$ V, $I \leq 300$ pA) the appearances of benzene groups of *M*Pcs are identical as shown in the line profiles crossing *M*Pcs in stable and metastable configurations [Fig. 3(b)]. However, the apparent height at the metallic centers varies significantly

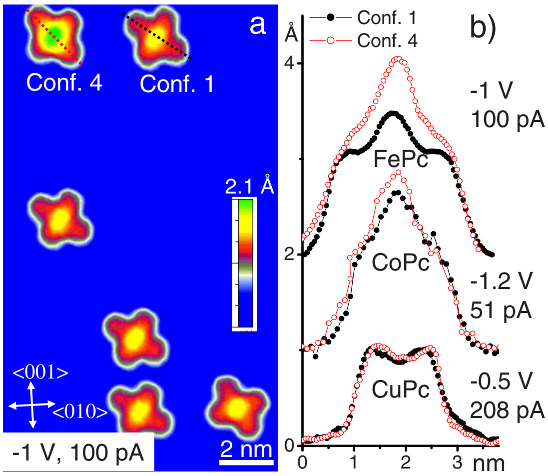

FIG. 3. (Color online) (a) STM image of FePcs on Cu(100) prepared at low temperature. (b) Line profiles crossing configurations 1 and 4 of FePc, CoPc, and CuPc. For each pair of line profiles identical tips were used.

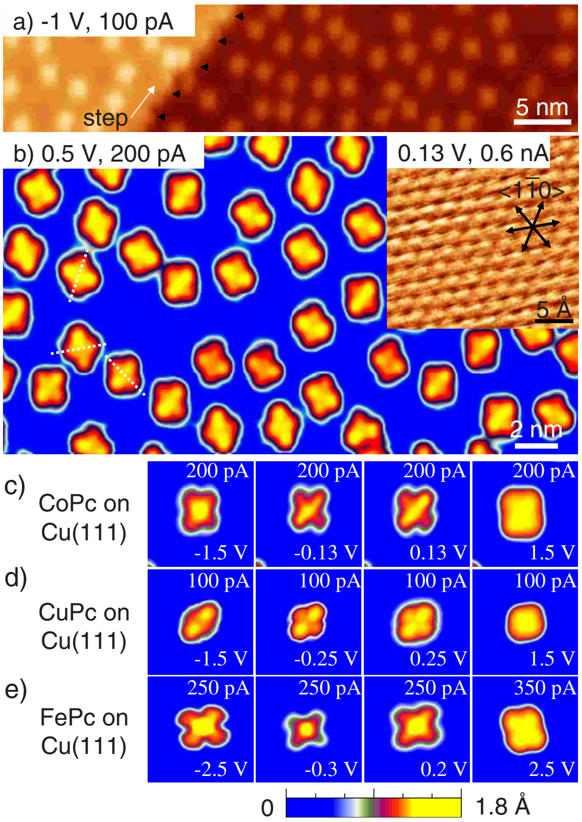

FIG. 4. (Color online) [(a)–(c)] STM images of CoPc, (d) CuPc, and (e) FePc on Cu(111). In (a) decoration of the copper step edge with CoPcs (indicated by arrows) can be observed. In (b), for each of the three observable orientations of CoPcs, the molecular axis of one molecule, which appears at reduced apparent height is marked by a white dotted line. These axes are parallel to one of the three crystallographic axes determined from atomically resolved images of the bare Cu(111) substrate [see inset (b)]. [(c)–(e)] 4×4 nm^2. [(b)–(e)] The indicated color bar for height encoding is valid for all images.

with the configuration of *M*Pcs. In Figs. 1(b) and 3(b) a pronounced center is observed for CoPcs in metastable configurations at both -1 and -1.2 V ($\Delta z \sim 0.25$ Å). The effect is more pronounced for FePcs [Fig. 3(a)] but is not observed for CuPcs.[26]

In a second experiment, we investigated the growth of fourfold symmetric *M*Pcs on the sixfold symmetric surface of Cu(111) to find the fingerprint of the incommensurate symmetries. Figure 4(a) depicts a STM image of such a system of CoPcs adsorbed on Cu(111). Different to the adsorption on Cu(100), step edges of Cu(111) are fully covered by molecules. To study intramolecular details, Fig. 4(b) gives an enlarged view of CoPcs adsorbed on a plane terrace. At the given voltage, CoPcs evolve as parallelograms with one axis pronounced and a second perpendicular axis appearing at reduced apparent height. For all molecules, this second axis is perfectly aligned to one of the close-packed axes of the substrate, i.e., CoPcs in three different orientations are present. Independent of the preparation temperature, no other orientations are found.

The appearance of molecules in STM images, as well as the degree of observed reduced molecular symmetry, i.e., twofold symmetry, depends on the involved molecular states in the tunneling process, i.e., on the applied bias voltage as well as on the molecular center. The evolution of molecular appearances is depicted in Figs. 4(d)–4(f) for CoPc, CuPc, and FePc at representative bias voltages. Instead of sharp transitions with bias a gradual change can be observed. This is indicative for a strong hybridization of molecular and substrate states.[7,27,28] For FePc the center is most pronounced in the topography for all bias voltages between -1.5 and $+0.4$ eV. The pronounced center is attributed to the half-filled d_Z^2 state.[14] For *M*Pcs with higher atomic numbers for the central ion, i.e., for CoPc and CuPc, this d_Z^2 state is filled to a higher degree and as a consequence the onset of this state shifts to lower energies. Within the studied energy range the d_Z^2 state is not observed for CuPc. Instead, for CuPc a strong symmetry-reduction results in two pronounced protrusions at the sites of the benzene rings. A symmetry reduction of similar intensity can be observed for CoPc as long as contributions of the d_Z^2 state to the tunneling process do not become dominant. For FePc the symmetry reduction is nearly lifted but faintly present (see also Ref. 12). This observation coincides with the pronounced center for all relevant energies.

So far, the origin of the observed symmetry reduction of molecular structure remains unclear, which is present for all *M*Pcs studied. The incommensurability of molecular and surface symmetries results in a different atomic configuration underneath two perpendicular molecular axes. Therefore, electronic effects, due to the atomic structure underneath, and geometric effects, due to a structural deformation, have to be considered since STM does not distinguish between them. Indeed, indications for such a geometrically driven reduction of symmetry can be found. Although *M*Pcs on Cu(100) can be found in four different orientations with three different molecule-substrate configurations (orientations 1 and 2 are mirror symmetric), indications for a substrate-induced effect are not found in STM images and the benzene groups appear identical for all molecular orientations within the experimental accuracy [Fig. 3(b)]. When FePcs are prepared at higher coverages close to 1 ML on Cu(111) (see Ref. 12), FePcs are aligned in complex molecular structures with molecules partially rotated out of their three preferential orientations. Although the atomic configuration of the substrate underneath varies from molecule to molecule, this does neither affect the reduced symmetry nor alter the appearance of FePcs. We conclude that the driving contribution of the observed symmetry reduction is a vertical bending along one of the molecular axes. As consequence of the reduced molecular symmetry the degeneracy of molecular states is partially lifted. This is manifested as a strongly bias-voltage-dependent symmetry of molecular appearances [Figs. 4(c)–4(e)].

In conclusion, we report on the adsorption behavior of three kinds of *M*Pcs (M=Co, Cu, and Fe) on Cu(100) and Cu(111) as locally investigated by a VT-STM. On Cu(100) all *M*Pcs prefer identical orientations relative to the substrate. Two (mirror symmetric) orientations reflect stable adsorption geometries whereas two additional metastable orientations can be stabilized when prepared at low temperatures. The adsorption of *M*Pcs on Cu(111) favors one specific adsorption orientation with one molecular axis aligned with one of the close-packed-substrate axes. This adsorption orientation is accompanied with a bias-dependent reduction of symmetry in STM images. The reduction of symmetry can be driven by electronic molecule-substrate effects or by an out-of-plane deformation of the *M*Pcs. Both scenarios are discussed and indications are presented, which favor a geometrical deformation as an explanation. Albeit the simplicity of the molecular structure, our results indicate that this experimentally intensively studied (magnetic) model system of molecular adsorption is not sufficiently described when only considering electronic effects of the molecule-substrate interface but that also the impact of the interface on the molecular structure has to be taken into account as well.

This work was funded by the DFG (Grant Nos. SFB 668-A5 and GrK 611) and EU project SpiDME.

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