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Copper-phthalocyanine based metal–organic interfaces: The effect of fluorination, the substrate, and its symmetry

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Metal–organic interfaces based on copper-phthalocyanine monolayers are studied in dependence of the metal substrate (Au versus Cu), of its symmetry [hexagonal (111) surfaces versus fourfold (100) surfaces], as well as of the donor or acceptor semiconducting character associated with the nonfluorinated or perfluorinated molecules, respectively. Comparison of the properties of these systematically varied metal–organic interfaces provides new insight into the effect of each of the previously mentioned parameters on the molecule–substrate interactions. © 2010 American Institute of Physics. [doi:10.1063/1.3509394]

I. INTRODUCTION

Phthalocyanines are among the most intensively studied semiconducting oligomers. On the one hand, they serve as excellent model systems due to their outstanding stability and the tunability of their properties.^{1,2} The latter is easily achieved via molecular functionalization, or exchanging their coordination metal cation. On the other hand, phthalocyanines have shown remarkable success in their integration into organic-based devices.¹ The performance of these devices is particularly dependent on the properties of their various interfaces including the metal–organic interface between the contacts and the active semiconducting material.³

A detailed knowledge of these interfaces is thus of paramount importance for the establishment of correlations between their properties and device performance, which could eventually allow a directed optimization of the devices via interface engineering. Among potential contact materials for optoelectronic devices we find, for example, Au and Cu. Therefore, we have investigated the interfaces between copper-phthalocyanines with Au and Cu model surfaces of different symmetries, in particular their sixfold (111) and fourfold (100) surfaces. Copper-phthalocyanine (CuPc, Fig. 1) is a typical p-type organic semiconductor widely used in organic field effect transistors, organic light emitting diodes, and solar cells.^{4–6}

However, upon molecular fluorination, the energies of the molecular orbitals close to the Fermi level are lowered, leading to an increase of both its ionization potential and electron affinity (Fig. 1).^{7,8} As a consequence, perfluorinated copper-phthalocyanine (F₁₆CuPc, Fig. 1) presents a preferred acceptor behavior and has shown remarkable performance in devices as n-type semiconductor.^{9–11} In this work, we have used both the donor CuPc and the acceptor F₁₆CuPc. Although some of the interfaces addressed in this work have been studied previously, no direct comparison among them has been performed so far. By doing so, further complemented with the newly investigated metal–organic combinations, and making use of a variety of complementary techniques such as scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), x-ray standing waves (XSW), and density functional theory (DFT) calculations, we provide a systematic study which gives new insight into the effect of molecular fluorination, of different substrates, and of their symmetry, on the properties of the various metal–organic interfaces.

II. EXPERIMENTAL

The samples have been prepared by standard Ar sputtering (E = 600–1000 eV) and annealing cycles (T = 350–450 °C) of the single crystals under ultrahigh vacuum, followed by molecular deposition from resistively heated Knudsen-cells onto substrates held at room temperature. The deposition rates, unless explicitly stated, were in the range of ~0.1 ML/min. All STM, XPS, and XSW experiments were

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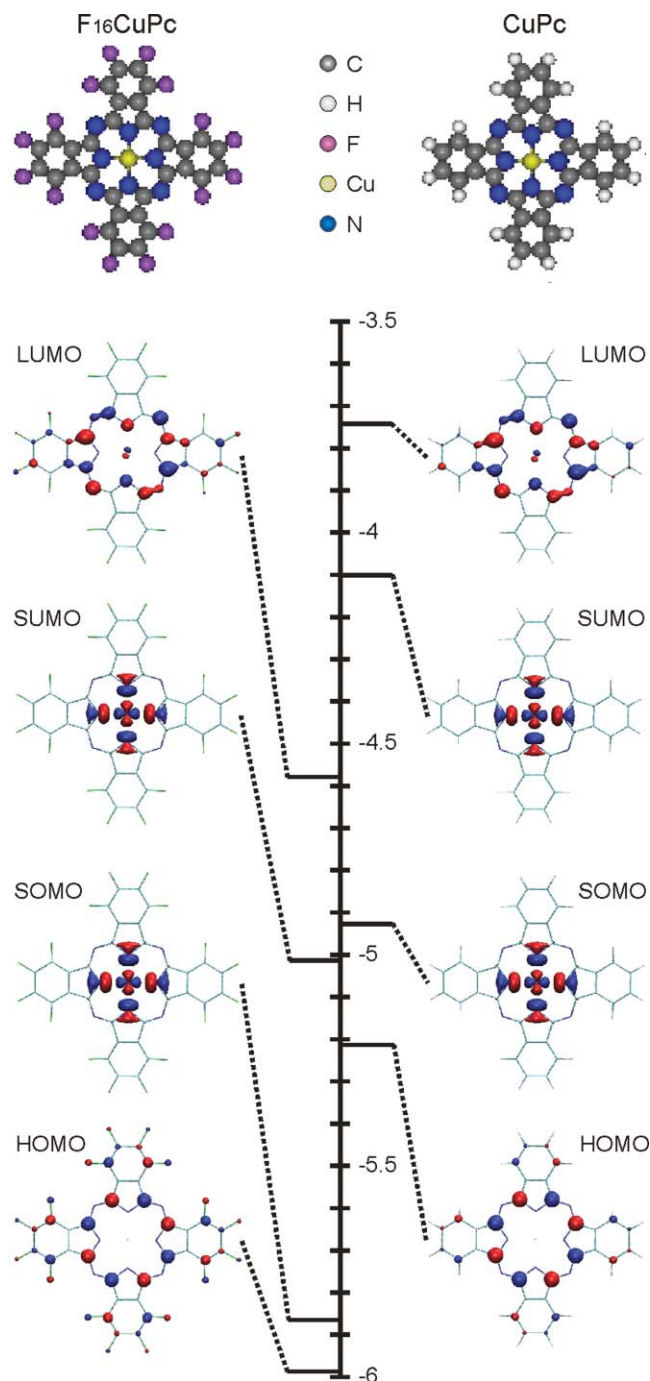


FIG. 1. Molecular structures, spatial distribution, and energies (in eV) of the molecular orbitals closest to the Fermi level of gas phase $F_{16}CuPc$ (left) and $CuPc$ (right). SOMO, SUMO, HOMO, and LUMO stand for single occupied, single unoccupied, highest, and lowest (doubly) occupied molecular orbitals, respectively.

performed at room temperature without breaking the vacuum between growth and characterization.

The STM experiments have been carried out in a commercial JEOL system, in constant current mode and with chemically etched tungsten tips. Data analysis was performed with the WSXM freeware.¹² The XPS measurements have been performed with a SPECS ESCA setup equipped with a hemispherical electron analyzer (Phoibos100), and making use of $Mg K_{\alpha}$ radiation. The XSW measurements have been performed at beamline ID32 of the European Synchrotron

Radiation Facility (ESRF) in Grenoble equipped with a hemispherical electron analyzer (Physical Electronics) at an angle of 45° relative to the incoming x-ray beam. Only the yields of $F1s$ and $C1s$ were measured, as those of Cu and N were too low to obtain a sufficient signal to noise ratio adequate for the XSW analysis within our available time.

DFT calculations were carried out by means of the Amsterdam density functional code.¹³ All atoms were described through basis sets of TZP quality (triple-z Slater-Type orbitals plus one polarization function) given in the program database, including all the core electrons in the calculation (i.e., with no frozen core approximation). The exchange-correlation energy was computed according to the local density approximation by means of the Vosko–Wilk–Nussair functional.¹⁴ The calculations were performed only for isolated molecules, without taking into account the substrate, in order to make them affordable. The structures were relaxed until a maximum force below $0.03 \text{ eV}/\text{\AA}$ was obtained.

III. RESULTS AND DISCUSSION

Core-level spectroscopy spectra of $CuPc$ and $F_{16}CuPc$ monolayers on $Au(100)$ are shown in Fig. 2. $CuPc$ molecules comprise one Cu , two N , and four chemically different C atoms, as marked in the inset of Fig. 2. However, $C1s$ spectra are characterized by two main peaks (and their corresponding shake-up satellites). The high binding energy peak corresponds to the pyrrole ($C1$), and the low binding energy to the aromatic ($C2$, $C3$, and $C4$) atoms (Fig. 2). As extensively described in previous studies, molecular fluorination leads to a decrease of the aromatic peak, shifting the contribution of the F-bonded atoms ($C3$, $C4$) to higher binding energies as a result of the increased electron transfer to the fluorine atoms (Fig. 2).^{15,16} On the contrary, $N1s$ and $Cu3p$ core-level spectra are hardly affected by fluorination.¹⁵

The crystalline structures characteristic of the various metal–organic interfaces between $CuPc$ ($F_{16}CuPc$) and the Cu substrates as observed by STM are summarized in Fig. 3. In all of them, as commonly observed for most metal–organic systems, the strong interaction between the metal d-bands and the molecular π orbitals causes the molecules to lie down with the molecular plane parallel to the substrate surface.

$CuPc$ on $Cu(100)$ forms a disordered layer with the molecules azimuthally oriented along two discrete directions (Fig. 3).¹⁷ In particular, the molecular diagonal is oriented $17.5 \pm 2^{\circ}$ off the high symmetry $[001]$ or $[010]$ directions. The fourfold symmetry of both substrate and molecule allows the presence of only these two azimuthal orientations. Although no long-range order is observed by STM neither in our measurements nor in those previously published by Lippel *et al.*,¹⁷ previous works by Schuerlein and Armstrong and Buchholz and Somorjai evidenced the presence of crystalline $CuPc$ areas with a square unit cell by means of low energy electron diffraction (LEED).^{18,19} Our measurements reveal a few areas presenting short-range order with the molecules arranged into a square unit cell, as highlighted in Fig. 3, which might be related to the crystalline structure observed with the LEED. However, the lack of larger crystalline clusters, which must be necessarily present to obtain a LEED

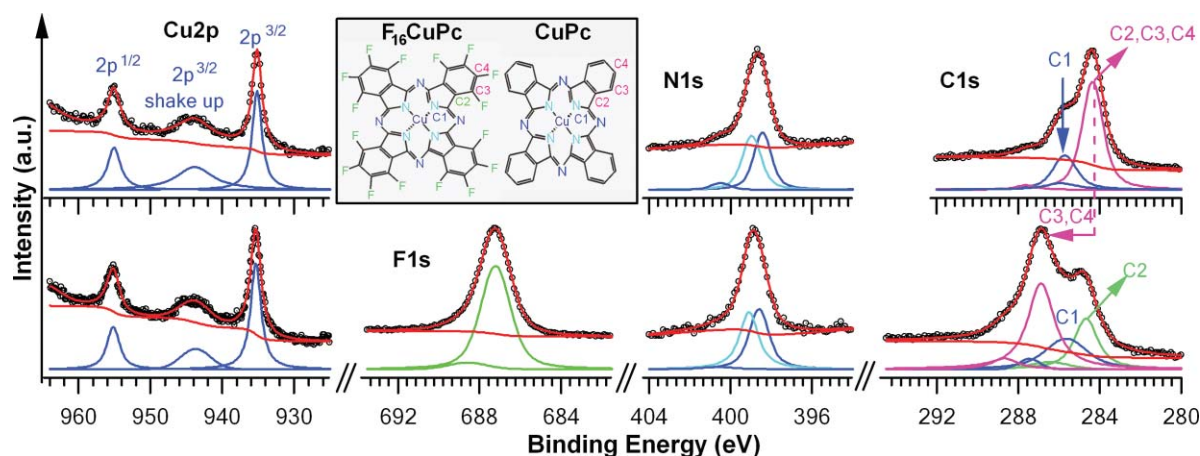


FIG. 2. Characteristic XPS spectra for CuPc and F_{16} CuPc monolayers on Au(100), with the different components associated with chemically distinct atoms (main peaks and associated HOMO–LUMO shake-ups) following the color code of the molecular structures in the inset.

pattern, might be ascribed to the different preparation conditions, as are the higher substrate temperatures in the case of Schuerlein and Armstrong ($T = 130^\circ\text{C}$) and higher growth rates in the case of Buchholz and Somorjai (up to 1 ML/min).

Previous works on CuPc layers on Cu(111) report disparate results. Karacuban *et al.* observe by STM a rectangular unit cell oriented along the high symmetry substrate directions.²⁰ Its parameters change from $a = 15.5 \text{ \AA}$ and $b = 17.6 \text{ \AA}$ (with a parallel to the $[-110]$ direction), for low temperature measurements and submonolayer coverage, to $a = 14.2 \text{ \AA}$ and $b = 13.5 \text{ \AA}$ for room temperature measurements and full monolayer coverage.²⁰ In contrast, at room temperature Buchholz and Somorjai observed by LEED an oblique unit cell with parameters $a = 12.6 \pm 0.5 \text{ \AA}$, $b = 12.6 \pm 0.5 \text{ \AA}$, and $\gamma = 85^\circ$, with the a axis oriented 8° off the $[-110]$ and equivalent directions.¹⁸ Our STM measurements unambiguously reveal the presence of six equivalent domains (three rotational and three mirror domains). The parameters are $a = 13.2 \pm 0.6 \text{ \AA}$, $b = 13.4 \pm 0.6 \text{ \AA}$, and $\gamma = 89 \pm 3^\circ$, with the a axis oriented 8° off the $[-110]$ and equivalent directions (Fig. 3). Our domain orientations are thus in perfect agreement with those reported by Buchholz and Somorjai. However, our proposed unit cell size is somewhat in between those claimed by Buchholz and Karacuban, with a square unit cell well within the limits of experimental error.

F_{16} CuPc on Cu(111) assembles into ordered layer characterized by an oblique unit cell of parameters $a = 14.5 \pm 0.5 \text{ \AA}$, $b = 14.5 \pm 0.5 \text{ \AA}$, and $\gamma = 75 \pm 2^\circ$ (Fig. 3).²¹ The a axis is oriented along the high symmetry $[-110]$ and equivalent directions. The obliqueness of the unit cell leads to the presence of mirror domains, consequently with a change in molecular orientation.^{21,22} In fact, in analogy to F_{16} CuPc layers on Ag(111),²³ long-range order is observed only along the direction of the a axis, as a consequence of the frequent change between the two mirror domains along the perpendicular direction (marked by arrows in the STM image).

In contrast, on the Cu(100) substrate the F_{16} CuPc deposition results in well ordered molecular overlayers in two dimensions (Fig. 3).² The unit cell is a square, with a lattice parameter of $14.8 \pm 1 \text{ \AA}$, and therefore fulfills excellently a

commensurate epitaxial relation with the substrate as marked in Fig. 2. Two enantiomorphic domains form, related to the mirror symmetry along the $[011]$ and $[0\bar{1}1]$ directions.²⁴

Comparing the different structures for the various interfaces with Cu substrates we find that both CuPc and F_{16} CuPc molecules adopt two (six) discrete azimuthal orientations on the Cu(100) [Cu(111)] substrate with fourfold (sixfold) symmetry. Interestingly, we find that the individual molecule orientations on each substrate are the same (within the error margins of our measurements), whether fluorinated or not. These orientations are schematically outlined on the lower panels of Fig. 3. From our measurements we cannot conclude on the translational position of the molecules with respect to the surface lattice, and remind the reader of its arbitrariness in the provided models.

The same orientations observed for both molecules evidence a similar azimuthal dependence of the molecule–substrate interactions independently of fluorination, as previously found comparing the structures of pentacene and perfluoropentacene on Cu(100) surfaces.²⁵ These interactions might be dominated either by dispersion forces or by an electronic coupling of the molecular orbitals closest to the Fermi energy and the substrate. The strong electronic coupling observed in previous studies of some of these interfaces points to the latter.^{18,22} In the case of copper-phthalocyanines, those orbitals correspond to the single occupied and single unoccupied molecular orbitals (SOMO and SUMO, respectively), followed by the highest and lowest (doubly) occupied molecular orbitals (HOMO and LUMO, respectively) as outlined in Fig. 1.^{26,27}

Inspection of the spatial distribution of occupied and unoccupied molecular orbitals of F_{16} CuPc and CuPc as obtained from DFT calculations reveals a remarkable resemblance, with little influence of the fluorine atoms (Fig. 1). Thus, the similar azimuthal dependence of the energy landscape is tentatively ascribed to the comparable spatial distribution of those molecular orbitals that dominate the molecule–substrate interactions. As observed from Fig. 1, this reasoning remains valid even considering different molecular orbitals to be dominant in the interactions of the substrate with either molecule (the occupied HOMO or SOMO for CuPc and the

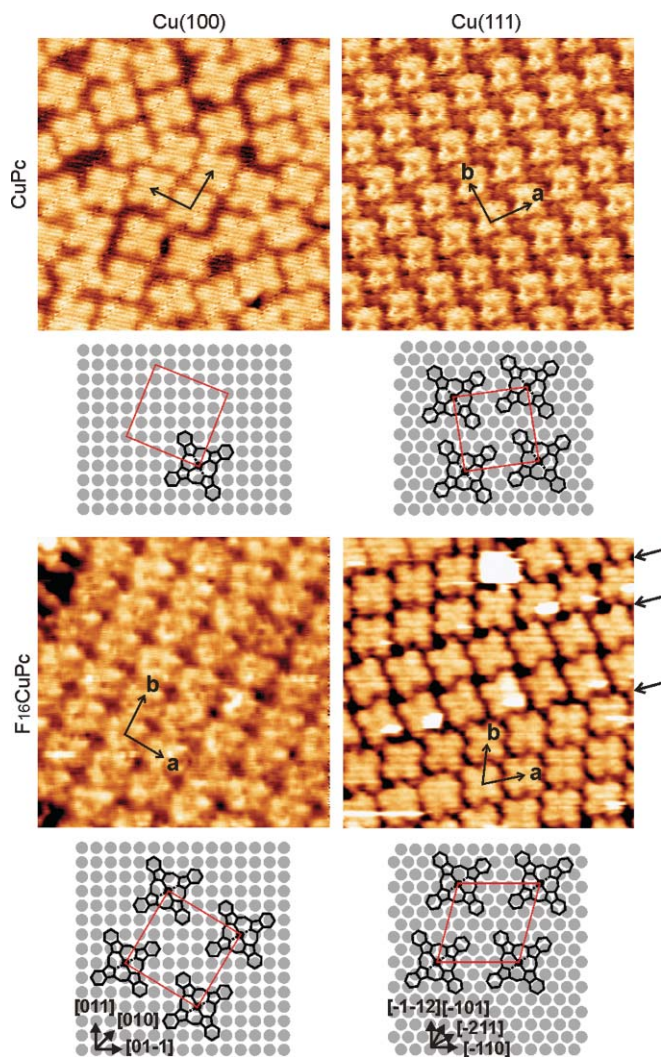


FIG. 3. $10 \times 10 \text{ nm}^2$ STM images of the film structures resulting from CuPc and $F_{16}\text{CuPc}$ deposition on Cu(100) and Cu(111) surfaces. At the bottom, schematic drawings of the proposed structural models in relation to the respective substrates are shown for the various systems. For CuPc on Cu(100), in the absence of a long-range ordered structure observed by STM, the unit cell of the crystalline structure reported based on LEED measurements is outlined.

unoccupied LUMO or SUMO for $F_{16}\text{CuPc}$), as a result of the respective donor and acceptor character of CuPc and $F_{16}\text{CuPc}$. Calculations including the impact of the substrate, and therefore charge transfer and energy level alignment issues, have been published in a previous work for $F_{16}\text{CuPc}$ on Cu(111) and will be published in forthcoming papers for other interfaces.²² However, the small changes observed in the spatial distribution of the molecular orbitals upon consideration of the substrate, in spite of the relatively strong molecule–substrate interactions, justify our hypothesis based on calculations for gas phase molecules.

Figure 4 summarizes the observed structures at the metal–organic interfaces for Au surfaces. Both the Au(100) and Au(111) surfaces are reconstructed. In the case of Au(100) the surface layer is compressed by 20% with a quasi-hexagonal atomic arrangement and a periodic corrugation along the [011] or [01-1] directions.^{28,29} This reconstruction is clearly observed prior to molecular deposition.

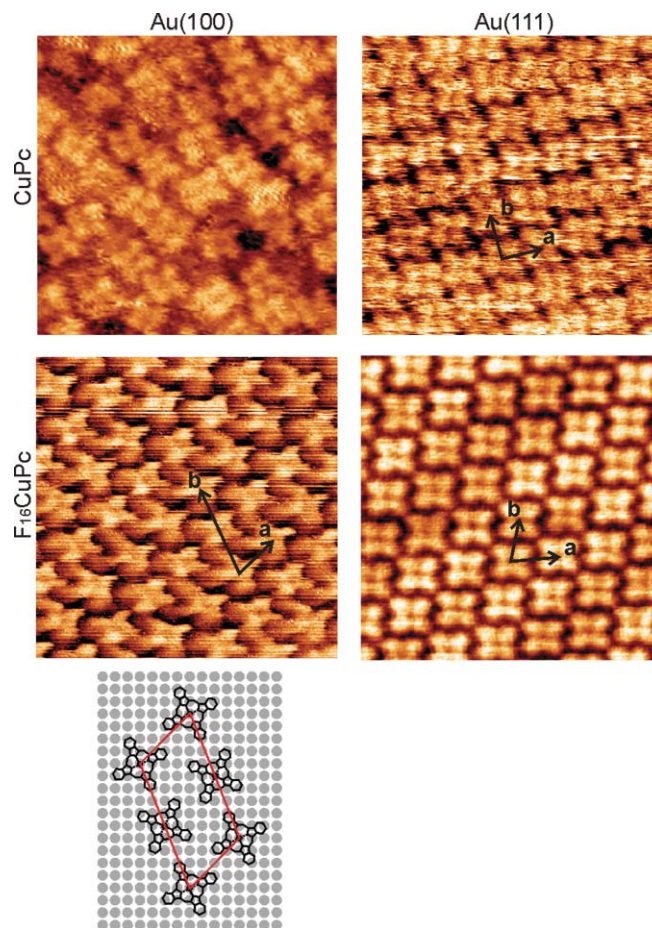


FIG. 4. $10 \times 10 \text{ nm}^2$ STM images of the film structures resulting from CuPc and $F_{16}\text{CuPc}$ deposition on Au(100) and Au(111) surfaces. For $F_{16}\text{CuPc}$ on Au(100) also the schematic drawing of the proposed structural model in relation to the substrates is shown. This is not the case for CuPc on Au(100) due to the absence of order, nor for CuPc or $F_{16}\text{CuPc}$ on Au(111) due to the difficulty in the modeling of the epitaxial relation in the presence of the herringbone reconstruction, especially as a result of the extension of the molecular domains throughout multiple rotational domains of the substrate reconstruction.

However, no trace of the reconstruction is observed underneath the organic monolayer upon growth of CuPc. This is in contrast to the scenario observed for CuPc (and many other molecules) on Au(111).^{30–32} This suggests that the Au(100) reconstruction is lifted upon CuPc deposition in spite of the weak molecule–substrate interactions determined by energy loss spectroscopy.³³ Rearranging the compressed overlayer into an unreconstructed surface leads to an excess of 0.2 ML Au on the surface. Its accommodation into the step edges competes with CuPc adsorption, making it plausible to expect that some of the Au forms clusters on the surface and thereby reduces its order.

No crystalline layer is observed for CuPc molecules on Au(100) (Fig. 4). Although they exhibit two preferential azimuthal orientations on the substrate, the broad angular distribution around each direction points to a smooth energetic landscape for the molecule–substrate interactions. One of the possible reasons for hindering the formation of an ordered organic overlayer is the suspected disorder of the substrate surface. However, while to the best of our knowledge no other STM measurements have been published so far on this sys-

tem, previous LEED measurements evidenced formation of a crystalline CuPc overlayer with square unit cell.^{34,35} The reason behind such discrepancy remains unclear, but can most probably be ascribed to different preparation conditions.

The F₁₆CuPc overlayer on Au(100) shows some similarities to its nonfluorinated counterpart. It also lifts the surface reconstruction, and the molecules present only two discrete azimuthal orientations, with the molecular diagonal 65 ± 3 degrees off the high symmetry [011] or [01-1] directions (Fig. 4). Assuming a similarly reduced surface order for lifting the reconstruction as in the case of CuPc, there must be a counter effect responsible for the crystallinity of F₁₆CuPc monolayers, plausibly found in stronger intermolecular interactions or a decreased molecule–substrate interaction leading to an enhanced molecule mobility. In contrast to CuPc, a highly ordered F₁₆CuPc monolayer is formed, with an oblique unit cell comparable to that found on HOPG comprising two molecules of disparate orientations.³⁶ The unit cell parameters are $a = 16.8 \pm 1 \text{ \AA}$, $b = 30.8 \pm 0.5 \text{ \AA}$, and $\gamma = 65 \pm 3.5^\circ$, and the a axis is oriented along the [010] or [001] directions. This arrangement is in excellent agreement with a commensurate structure with the underlying substrate as depicted below the STM image.

On Au(111) the F₁₆CuPc molecules arrange into an oblique lattice with parameters $a = 14.5 \pm 0.8 \text{ \AA}$, $b = 15.1 \pm 0.8 \text{ \AA}$, and $\gamma = 75 \pm 2^\circ$ (Fig. 4).^{26,37} The molecular diagonal is tilted $51 \pm 3^\circ$ with respect to the a axis, which in turn aligns with the [1-10] and related substrate directions (Fig. 4). However, the azimuthal orientation of the domains is often perturbed by the steps in the substrate surface, which induce the alignment of the lattice vectors with the step direction.³⁷ Previous work reported the disappearance of the Au(111) herringbone reconstruction under the F₁₆CuPc monolayers.²⁶ However, higher quality STM measurements have now proven the opposite, revealing the substrate reconstruction under the organic overlayer with an fcc/hcp periodicity measured along the [1-10] direction of $65 \pm 3 \text{ \AA}$, thus virtually unchanged with respect to the pristine Au(111). While this could be interpreted as the result of very weak molecule–substrate interactions,³¹ the reported disappearance of the Au(111) surface state upon F₁₆CuPc adsorption, as measured by valence band photoelectron spectroscopy,²⁶ still supports the picture of a significant interaction.^{31,38}

CuPc on Au(111) leads to the growth of crystalline layers characterized by a square unit cell of dimensions $a = 13.9 \pm 0.7 \text{ \AA}$, and it hardly affects the underlying Au(111) surface reconstruction.^{30,39} The unit cell vectors are directed along the high symmetry [11-2] and [1-10] directions (Fig. 4). However, as for F₁₆CuPc, the step edges affect this ordering by aligning the unit cell vectors parallel to the step directions.³⁰ The molecular diagonals are tilted $58 \pm 3^\circ$ with respect to the unit cell vectors (and thus the high symmetry directions).

Interestingly, in contrast to the findings on Cu, on Au the two molecules do not show the same orientational dependence of the molecule–substrate interactions. As Au is considerably less reactive than Cu, the molecule–substrate interactions on Au are expected to be considerably weaker, to the point of being dominated, not by electronic coupling, but

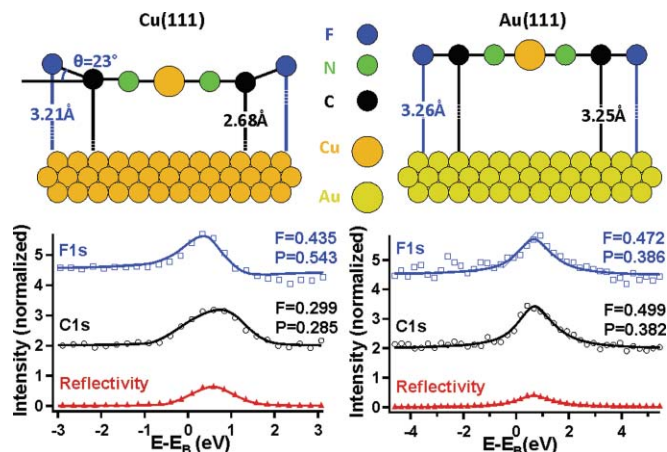


FIG. 5. Summary of the x-ray standing wave results of F₁₆CuPc on Cu(111) (left) and Au(111) (right). The atom–substrate distances are schematically given in the top part. In the absence of data referring to the N and Cu positions, we assume them to be on the same plane as C. The lower part depicts the reflectivity and photoelectron yield curves with the corresponding fits and fit parameters (coherent fraction, F; and coherent position, P) vs the relative photon energy with respect to Bragg conditions ($E_B = 2.645 \text{ keV}$).

rather by van der Waals interactions. In this case, the presence or absence of fluorine will cause a significant variation and might therefore be responsible for the differences among the two molecules. In a scenario in which the dominant type of interactions changes from being of chemical nature for one molecule to being van der Waals for the other, those differences would be even more justified.

Evidence for the weaker and different nature of molecule–substrate interaction on Au as compared to that on Cu is given by XSW measurements of F₁₆CuPc on Au(111) and Cu(111). An increase of the molecule–substrate distance can be taken as an indication of the reduction of the interaction strength⁴⁰ in analogy to other interactions such as hydrogen bonds.⁴¹ An example of this behavior was recently provided for the archetypal molecule perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) on Cu(111), Ag(111), and Au(111).⁴⁰ Molecule–substrate hybrid states leading to charge transfer were found by photoelectron spectroscopy to be strongest for Cu(111), weaker for Ag(111), and absent for Au(111).⁴⁰ XSW measurements showed an inverse correlation of PTCDA–substrate bonding distance and charge transfer. Furthermore, molecular distortions appeared as charge transfer took place, while the planar molecular configuration was kept on Au(111).

Figure 5 summarizes the XSW results of F₁₆CuPc on Cu(111) and Au(111). As expected, the distance on Cu(111) is much smaller than on Au(111). Furthermore, although with some disagreement in the values with previous XSW measurements and theoretical calculations,^{22,42,43} all studies coincide in the observation of a distorted, nonplanar adsorption geometry of F₁₆CuPc on Cu(111). Our measurements reveal the fluorine atoms to be located $\sim 0.5 \text{ \AA}$ further away from the surface than the C backbone. The angle between surface normal and C–F bond is thus estimated to be $113 \pm 6^\circ$. This is very close to 109.5° that would correspond to a tetrahedral sp^3 symmetry. As previously suggested by Gerlach *et al.*,⁴² this could be an indication of partial substrate-induced

rehybridization of the carbon atoms as they change from the sp^2 hybridization in the free molecule toward a more tetrahedral sp^3 symmetry upon adsorption.

In analogy to PTCDA, this distortion is presumably an additional signature of the strong interaction with the Cu(111) surface. This might arise from the electronic coupling of the molecular orbitals close to the Fermi edge, concentrated on the central molecular part and virtually absent on the outer F atoms,²⁶ with those of the substrate. In contrast, our measurements reveal that such distortion is absent on Au(111). Together with the larger molecule–substrate distance this proves the weaker $F_{16}CuPc$ –Au(111) interaction in comparison to that on Cu(111).

IV. CONCLUSIONS

In this work, we provide a compendium of different structures observed for the metal–organic interfaces composed by perfluorinated and nonperfluorinated copper-phthalocyanines on crystalline Cu and Au surfaces of different symmetries. The different strength of molecule–substrate interactions is indirectly probed by XSW, showing lower molecule–substrate distance and pronounced molecular distortions for the stronger interacting Cu. On Cu substrates, the azimuthal dependence of the molecule–substrate interactions is the same independent of molecular fluorination, tentatively ascribed to the similar spatial distribution of the molecular orbitals participating in the electronic coupling between molecules and substrate. For the less interacting Au substrates, this azimuthal dependence shows changes upon fluorination, which might in turn be traced back to changes in the molecule–substrate van der Waals interactions or even in the nature of the dominating interactions for the different molecules. Measurement and comparison of all the different systems thus provide new insight into the dependence of the molecule–substrate interactions, which are largely responsible for the final interfacial properties, on the nature of the substrate, on its symmetry, and on molecular perfluorination.

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