Perfluorinated Phthalocyanines on Cu(110) and Cu(110)-(2 × 1)O: The Special Role of the Central Cobalt Atom

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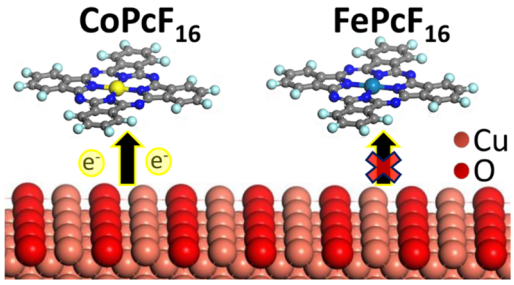
ABSTRACT: Interface properties of $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O were investigated by X ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), X ray absorption spectroscopy (XAS), and scanning tunneling microscopy (STM). The results are compared to $FePcF_{16}$ on Cu(110) (2 × 1)O. A charge transfer from both substrates to the central Co ion of $CoPcF_{16}$ is observed. Unlike to $FePcF_{16}$ and related molecules, the strong interaction between $CoPcF_{16}$ molecules of the first layer and the Cu(110) substrate is only partially suppressed by oxygen termination. The special nature of the electronic structure of the Co ion in Co phthalocyanines is discussed. The analysis of the fluorine Auger parameter enables the discussion of initial and final state effects of core level binding energy shifts in photoemission. A bidirectional charge transfer also involving the macrocycle of $CoPcF_{16}$ molecules is concluded.



1. INTRODUCTION

The tuning of electronic interface properties between organic molecules and metallic substrates is of enormous importance for a broad variety of applications.[1−3] Strong interactions including chemical reactions may especially alter the molecular electronic structure of the frontier orbitals, which are important for charge carrier transport and injection. Routes to avoid chemical interactions at interfaces include, among others, the optimization of the surface preparation or the introduction of intermediate layers.[4−9] Copper surfaces are among the more reactive substrates, where a strong chemisorption is observed for many organic molecules.[9−17] For some systems, such interactions can be avoided by an oxygen termination of the copper surface.[16,18]

The interface properties of cobalt phthalocyanine (CoPc) seem to be different compared to other transition metal phthalocyanines: In many cases, interaction at the interfaces between $CoPcF_X$ (X = 0, 16) and noble metals is governed by a local interaction between the Co $3d_{z^2}$ orbital and states of the metal substrate,[19,20] and a charge donation was observed for many interfaces (e.g., refs 19−22). In this study, we compare interface properties of $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O. To assess the special role of the central Co ion, the results are compared to $FePcF_{16}$ on Cu(110) (2 × 1)O.

2. EXPERIMENTAL SECTION

The Cu(110) single crystal was cleaned by several cycles of Ar^+ ion sputtering and subsequent annealing. The sputtering was performed at a voltage of 1.0 kV for typically 30 min at an argon partial pressure of 5×10^{-5} mbar, and the annealing was performed for 30 min at a temperature of 750 K. The crystal cleanliness and orientation were checked by X ray photo emission spectroscopy (XPS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). The Cu(110) (2 × 1)O surface was prepared by exposing the clean surface to 20 langmuirs of oxygen at room temperature, followed by heating to 570 K for 4 min.

$CoPcF_{16}$ (Sigma Aldrich) and $FePcF_{16}$ (SYNTHON Chem icals GmbH & Co. KG) powders were evaporated at rates of 0.2−0.4 nm/min and a temperature of 650−670 K from a temperature controlled crucible. The evaporation rates were estimated from a quartz microbalance. The nominal film thickness was estimated from XPS intensity ratios by using sensitivity factors from Yeh and Lindau[23] assuming layer by layer growth for each deposition step.

The photoemission measurements (XPS and ultraviolet photoemission spectroscopy (UPS)) were performed in the home lab by using a multichamber UHV system (base pressure of 2×10^{-10} mbar) equipped with a Phoibos 150 hemi spherical energy analyzer (SPECS), an X ray source with monochromator (XR 50 M, SPECS), and a helium discharge lamp (SPECS). The energy resolution for XPS (excitation energy $h\nu$ = 1486.7 eV) and UPS ($h\nu$ = 21.22 eV) was 400 and

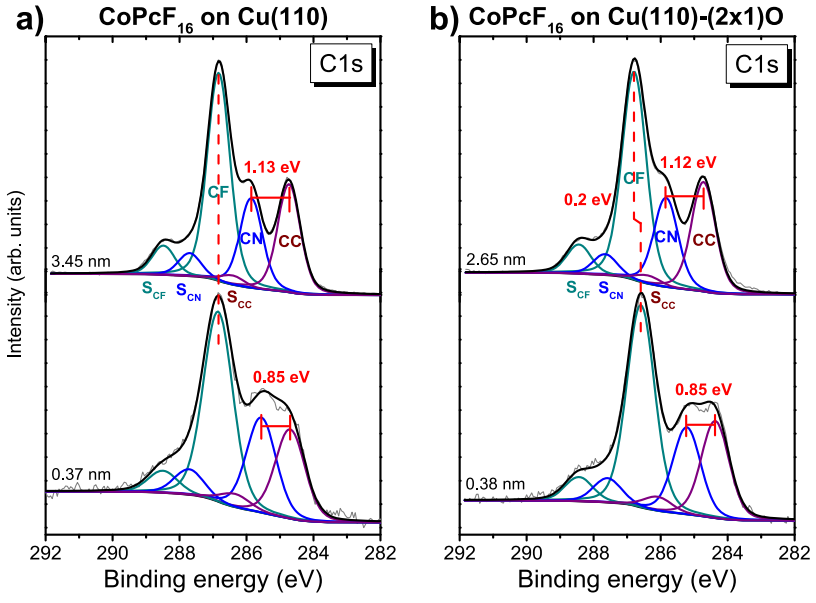


Figure 1. Thickness dependent C 1s core level spectra for $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O. Except for minor differences in the relative energy position of the components, the same model can be applied for the description of all spectra.

Table 1. $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O: Thickness Dependent C 1s Binding Energies as Obtained from Peak Fits in eV

substrate	thickness (nm)	CF	SCF	CN	SCN	CC	SCC
Cu(110)	3.45	286.83	288.48	285.86	287.70	284.73	286.42
	0.37	286.85	288.50	285.55	287.72	284.70	286.35
Cu(110)-(2 × 1)O	2.65	286.79	288.44	285.84	287.66	284.72	286.38
	0.38	286.59	288.44	285.22	287.59	284.37	286.09

150 meV, respectively. The binding energy was calibrated with respect to the Au $4f_{7/2}$ (84.0 eV) and the Cu $2p_{3/2}$ (932.6 eV) peak positions. The peak fitting of XP spectra was performed by using the program Unifit.[24] A Voigt profile peak shape (convolution of Gaussian and Lorentzian peaks) and a Shirley model background were used.

The corresponding X ray absorption spectroscopy (XAS) measurements of the N K and Co L edges have been performed at the PM4 beamline (LowDose PES endstation) at BESSY II (Helmholtz Zentrum Berlin, Germany) and the measurements of the Fe L edge at the WERA beamline at the Karlsruhe Research Accelerator (KARA, Karlsruhe, Germany). The energy resolution at the PM4 beamline was set at 100 meV at a photon energy of 400 eV and at the WERA beamline at 220 and 340 meV at photon energies of 400 and 710 eV. The XA spectra at both beamlines were monitored indirectly by measuring the total electron yield (sample current).

The STM measurements were performed in a two chamber UHV system equipped with a low energy electron diffraction (LEED) system from OCI Vacuum Microengineering Inc. and a variable temperature (VT) STM from Omicrometer GmbH. For the STM measurements, mechanically cut Pt/Ir tips were used. All given tunneling voltages are referenced to the sample. The WSxM program was used to tune the image contrast.[25]

3. RESULTS AND DISCUSSION

3.1. Interaction between the $CoPcF_{16}$ Macrocycle and the Substrates. Different interaction channels are observed between phthalocyanines and a variety of substrates, involving both the macrocycle and the central metal atom; often the charge transfer is bidirectional.[15,26−28] First, we will discuss interactions between the $CoPcF_{16}$ macrocycle (i.e., the C and N atoms) and the copper substrates.

In Figure 1, we show C 1s core level spectra for $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O at about one monolayer coverage (0.37 nm) compared to bulklike thin films. 0.32 nm corresponds to one monolayer of flat lying perfluorinated phthalocyanines, as can be inferred from the crystal structure.[29] Data for additional thicknesses are provided as Supporting Information (Figure S1). As for related perfluorinated phthalocyanines,[15,30] the C 1s core level spectra for the bulklike, thickest films can be fitted by using three main components in sequential order from high to low binding energy: carbon bonded to fluorine (CF), bonded to nitrogen (CN), and bonded to other carbon (CC). All main peaks are accompanied by their respective satellites, denoted S_{CF}, S_{CN}, and S_{CC} in Figure 1. The intensity ratio estimated from the peak areas CF:CN:CC (including related satellites) of 4:1.9:2 is in reasonable agreement with the stoichiometric composition (4:2:2). Energetic positions obtained from the peak fits shown in Figure 1 are summarized in Table 1.

Essentially the same model can be applied for the description of the spectra for low coverages of about 0.37 nm. The intensity ratio CF:CN:CC agrees well with the expectation according to stoichiometry: 4:2.3:1.9 and 4:2:2 for Cu(110) and Cu(110) (2 × 1)O, respectively. The energetic position of satellites with respect to the main lines as well as the Lorentzian widths (0.2 eV) were kept constant. Generally higher Gaussian widths were obtained for the low coverages (about 0.9 eV; thicker films: about 0.7 eV), which might be

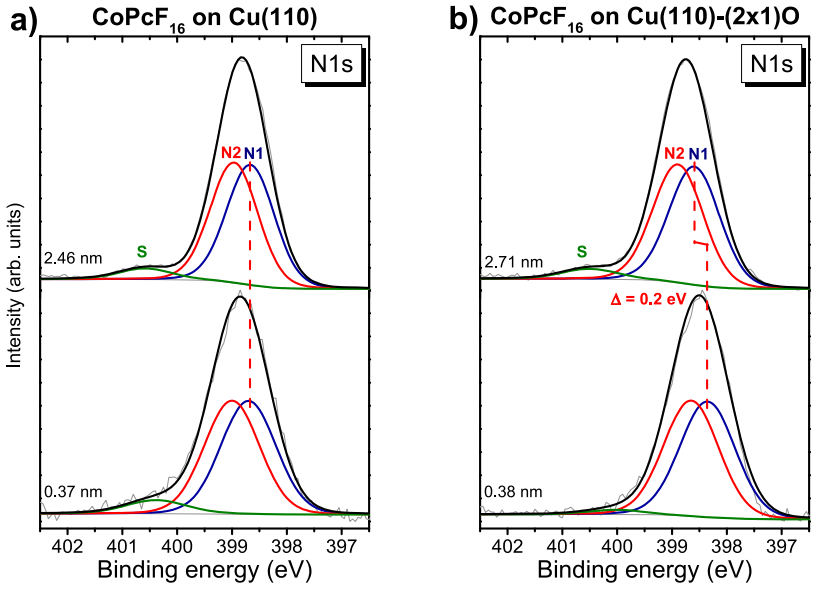


Figure 2. Thickness dependent N 1s core level spectra for $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O.

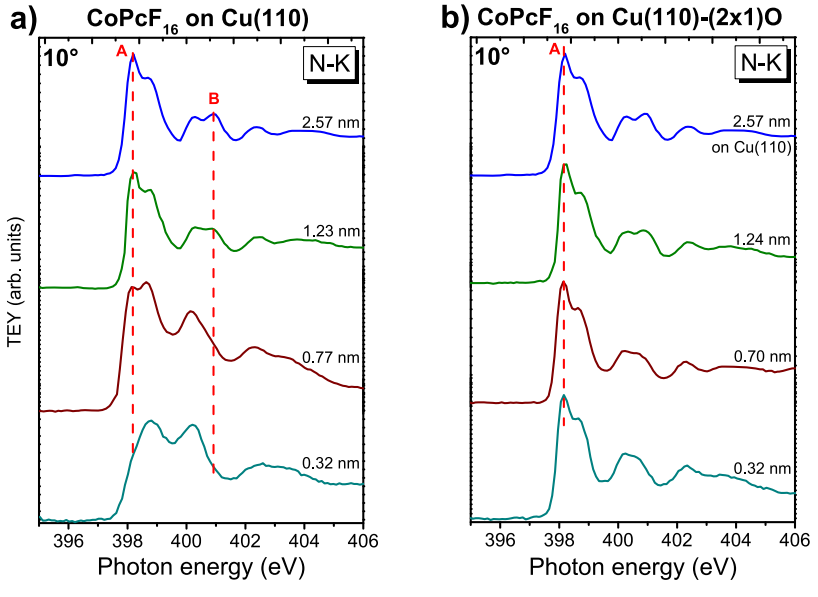


Figure 3. Thickness dependent N 1s excitation spectra at grazing incidence (10°) for $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O. The reference for the bulklike spectrum of the thickest film in (b) is taken from (a). Because of a complex background treatment, the exact determination of the step height is complicated.

ascribed to adsorption at inequivalent adsorption sites or another kind of disorder, which may cause a statistical distribution of orbital energies.[31]

However, the detailed analysis of energetic positions of the C 1s components in Figure 1 (cf. Table 1) reveals distinct differences between monolayer coverages and thicker films. Generally, in close proximity to metallic substrates, a shift of core level binding energies to lower values is expected due to final state screening effects of the photohole as the additional mirror charge screening. Such energetic shifts are often in the range 0.3−0.6 eV.[32−35] For the investigated samples these effects may affect the observed binding energies. However, additional effects must influence the observed energetic positions because the peak components are not shifted by equal amounts. Most visible in Figure 1, the distance between CC and CN is decreased by more than 0.25 eV for molecules directly at the interface (monolayer coverage), compared to thicker films, similar to $FePcF_{16}$ on Cu(111).[15] A possible reason might be a site dependent screening or a redistribution of electrons for molecules of the first layer on both substrates.[36] The stronger shift of CN to lower binding energies compared to CC at the interface would imply a relative increase of electron density at the CN atoms of the interface layer.

Also, N 1s spectra, shown in Figure 2, exhibit almost no thickness dependent changes of the peak shape (complete series shown in Figure S2). The main line consists of two signals of the same intensity for the pyrrole and the bridging nitrogen atoms, denoted N1 and N2 in Figure 2. Because their energy separation is small for related phthalocyanines (0.3−0.5 eV),[37−42] they cannot be clearly resolved by XPS. Peak fit parameters are given as Supporting Information (Table

S1). Similar to C 1s (cf. Figure 1), all N 1s spectra can be fitted by using the same model, independent of the layer thickness. Only the Gaussian width is slightly increased for low coverages (by about 0.1 eV), most likely due to adsorption at inequivalent sites of the substrate surface (cf. discussion of the C 1s peak shape). Similar to C 1s, peak shifts to lower binding energy are observed for low coverages $CoPcF_{16}$ on Cu(110) (2 × 1)O, most likely due to screening effects.

The corresponding N 1s XA spectra taken at grazing incidence are shown in Figure 3. The $CoPcF_{16}$ molecules grow in a preferred flat lying adsorption geometry, as concluded from the angular (polarization) dependence of N K XA spectra at higher film thicknesses (see Figure S3). Thus, at the chosen measurement geometry, features below 404 eV arise predominantly from transitions into π^* molecular orbitals. For phthalocyanines, most intense π^* resonances (denoted A) are assigned to transitions from N 1s to LUMO e_g orbitals.[43,44] The complex structure of feature A arises from an involvement of the ligand LUMO in the hybridization with the central metal atom of the Pc.[42,43,45−49]

It was shown that π^* resonances in N K edge absorption spectra are very sensitive on involvement of nitrogen in the interfacial interactions.[20,45,50,51] Indeed, for $CoPcF_{16}$ on Cu(110) distinct changes of the peak shape as a function of the film thickness are visible in Figure 3a. The ratio between the intensities of features A and B at photon energies of 398.2 and 400.9 eV decreases for lower coverages, reminiscent of $FePcF_{16}$ on Cu(111) or FePc on Ag(111).[15,50] This may indicate (partial) charge transfer from the Cu(110) substrate to the (ligand) LUMO of $CoPcF_{16}$. Because the corresponding N 1s core level photoemission spectra are almost unaffected by the interface interaction, the charge transfer may occur into the (delocalized) LUMO; in other words, the electron density is not (only) localized at the nitrogen atoms. In contrast to the Cu(110) substrate, for $CoPcF_{16}$ on Cu(110) (2 × 1)O (Figure 4b), the peak shape is almost the same for all thicknesses, indicating that nitrogen is not involved in the interaction at the interface.

A localized, strong interaction between nitrogen and the Cu(110) substrate may result in the breaking of chemical bonds within the macrocycle of $CoPcF_{16}$. To further investigate the interface interaction in more detail, we performed STM measurements for the apparently most reactive interface $CoPcF_{16}$/Cu(110). In Figure 4, an STM image of a $CoPcF_{16}$ submonolayer is shown. Clearly, the typical 4 fold symmetry of the phthalocyanine molecules can be identified. Similar to $CoPcF_{16}$ on Ag(110),[52] the molecules are aligned along the $[1\bar{1}0]$ direction of the substrate. Thus, we conclude that the $CoPcF_{16}$ molecules appear intact upon adsorption on the Cu(110) surface.

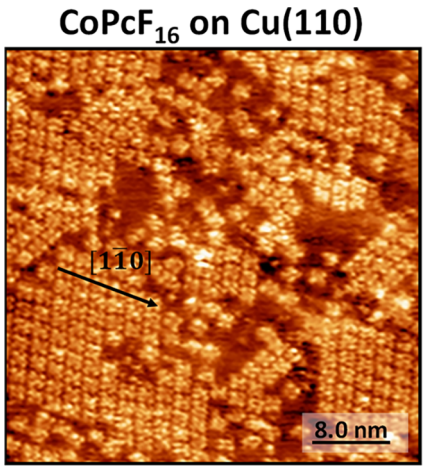


Figure 4. STM image of a submonolayer coverage of $CoPcF_{16}$ on Cu(110) (about 0.7 ML). The 4 fold symmetry of the molecules is typical for phthalocyanines, indicating that the molecules remain intact upon adsorption on Cu(110). Measurement parameters: I = 300 pA and U = 0.7 V.

3.2. Interactions between the Central Metal Atom of the Phthalocyanines and the Substrates. For transition metal phthalocyanines, the study of both 2p photoemission and X ray absorption spectroscopy yields valuable information about the electronic structure of the central metal atom at interfaces. In Figure 5, we show Co $2p_{3/2}$ core level photoemission for $CoPcF_{16}$ on Cu(110) (Figure 5a) and on Cu(110) (2 × 1)O (Figure 5b) as a function of thickness. On both substrates the spectrum of the thickest layer shows the typical multiplet structure, as known for Co phthalocyanines.[26,40,53,54] Clearly visible, with decreasing layer thickness an additional (interface) peak at lower binding energy develops, located at 778.4 and 778.1 eV for $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O, respectively. The lower binding energy compared to the main component implies a higher electron density or, in other words, a reduction of the Co^{2+} ion at the interface. The different binding energy on both substrates is most likely caused by a different energy level alignment of the first layer. Thus, a charge transfer from the substrate to the central metal atom of the phthalocyanine occurs on both substrates, similar to $CoPcF_{16}$ on other metals.[5,26,53]

Also visible in Figure 5, the intensity of the interface component is clearly different for the about monolayer coverages (0.37 and 0.38 nm) on the two substrates. On the Cu(110) substrate (Figure 5a), the shape of the spectrum is typical for reduced Co at reactive metal substrates;[26,27,53,55] the intensity at binding energies >780 eV can be assigned to satellite (i.e., multiplet) structures.[40] In contrast, for the same $CoPcF_{16}$ coverage on Cu(110) (2 × 1)O (Figure 5b), the relative intensity at binding energies >780 eV is distinctly increased, indicating remaining intensity from the Co^{2+} multiplet, which is similar to $CoPcF_{16}$ at a copper intercalated graphene/Ni(111) interface.[5] Thus, it seems that not all molecules of the first monolayer on Cu(110) (2 × 1)O undergo a charge transfer; apparently the interaction strength depends crucially on the adsorption site. The importance of different adsorption sites has been shown in detail for other large organic molecules as, for example, 4′ (4 tolyl) 2,2′:6′,2″ terpyridine on Au(111).[56]

Additional information about the (unoccupied) electronic structure of the central metal atom can be gained from the corresponding Co 2p excitation spectra. Thickness dependent Co L_3 edge XA spectra of $CoPcF_{16}$ on both substrates are shown in Figure 6 for grazing (10°) and normal (90°) incidence of the incoming linearly polarized synchrotron light. The angular dependence can be understood by polarization rules for transitions into different orbitals. For the almost flat lying molecules (cf. discussion of the angular dependence of N K XA spectra, Figure S3), transitions into orbitals with out of plane components (e.g., d_{z^2}) are strongest at grazing incidence, while at normal incidence transitions into orbitals with in plane components ($d_{x^2-y^2}$ and d_{xy}) are most intense. For a detailed

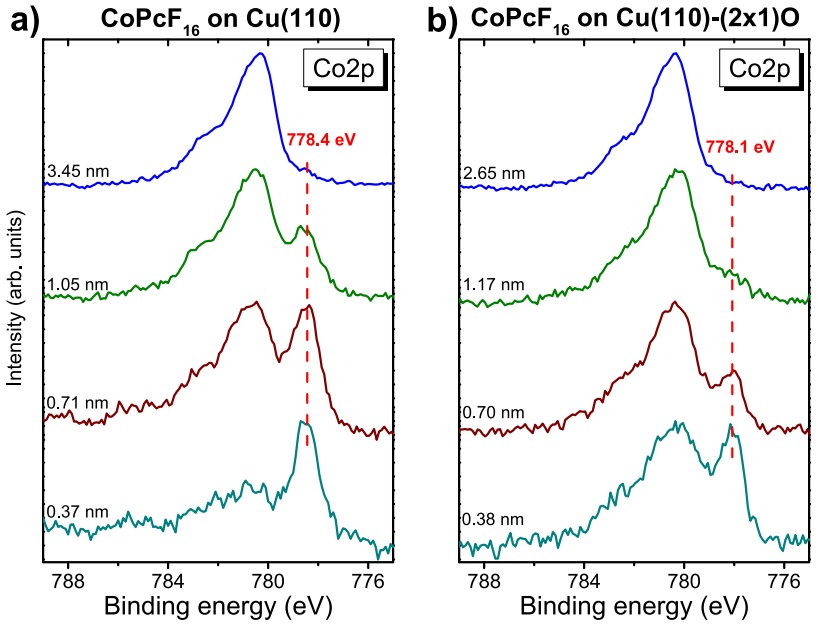


Figure 5. Thickness dependent Co $2p_{3/2}$ core level spectra for $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O.

discussion of the spectral shape, see refs 5, 57, and 58. Out of plane transitions are labeled with "A", while in plane transitions are labeled with "B" in Figure 6. The spectra for the thickest, bulklike film of 2.57 nm are typical for flat lying CoPc or $CoPcF_{16}$ molecules on different substrates.[5,20,57] However, for lower coverages the peak shape of Co 2p excitation spectra changes distinctly. While the feature A dominates the bulklike spectra at grazing incidence, a new feature, denoted A0, appears for lower coverages in Figure 6a,b. Such a feature A0 was observed for CoPc on other reactive substrates, such as Ag or Ni, and can be understood by a hybridization of the Co d_{z^2} orbital with substrate related orbitals.[20,59] At the same time, at normal incidence feature B2 disappears for low coverages (Figure 6c,d), indicating that the charge transfer is accompanied by a redistribution of the d electrons at the central metal atom of the phthalocyanine at the interface.[20]

Comparing the Co L_3 edge XA spectra for monolayer coverages in Figure 6, it becomes evident that the shape distinctly depends on the substrate. Feature A0 completely dominates the spectrum at grazing incidence on Cu(110), whereas A is still the most intense feature on Cu(110) (2 × 1)O. At normal incidence, feature B2 disappears on Cu(110), while it is still visible on Cu(110) (2 × 1)O. The behavior indicates that for a portion of the molecules of the first layer on Cu(110) (2 × 1)O no charge transfer occurs at the interface.

Thus, both 2p photoemission and excitation spectra reveal that the oxygen termination of the Cu(110) (2 × 1)O substrate prevents the interfacial charge transfer to the Co^{2+} ion only partly. This is somewhat surprising, since for even smaller molecules like hexacene,[18] an almost complete electronic decoupling by the oxygen rows is observed. The one dimensional Cu−O rows, aligned along the [001] direction of the Cu(110) surface, have a distance of about 0.51 nm, i.e., distinctly smaller than the size of CoPc or $CoPcF_{16}$ molecules. For details of the Cu(110) (2 × 1)O reconstruction, see Figures S7 and S8 and refs 60−62. Thus, one might conclude that the charge transfer occurs between atoms of the Cu−O rows and the Co ion of the phthalocyanine.

The different behavior of $CoPcF_{16}$ compared to other molecules might be the special nature of the half filled d_{z^2} orbital of the Co ion of Co phthalocyanines, which is oriented toward the substrate for flat lying molecules. Recent experimental and theoretical works demonstrate that charge transfer occurs from the formation of a molecule−metal hybrid state, which is most likely due to a local bond between the Co $3d_{z^2}$ orbital and metal states.[19,53,55,63,64] In addition, the observation of similar interface interactions for cobalt octaethylporphyrin and cobalt tetraphenylporhyrin on different substrates suggests they are almost independent of the ligand or macrocycle.[65−67]

To study the particular role of the central Co ion in $CoPcF_{16}$ for interface interactions, we compare our results to $FePcF_{16}$ on Cu(110) (2 × 1)O. Fe 2p XP spectra and Fe L_3 edge XA spectra for $FePcF_{16}$ on Cu(110) (2 × 1)O as a function of the film thicknesses are shown in Figure 7. For a detailed discussion of the peak shape, we refer to the literature on FePc and $FePcF_{16}$.[20,43,47,51,68,69] Although most literature confirms for Fe^{2+} in FePc a ^3E_g ground state with a configuration $(b_{2g})^2(e_g)^3(a_{1g})^1$, the electronic configuration is much more flexible compared to Co^{2+} in Co phthalocya nines.[70−72]

The Fe 2p XP spectrum of a multilayer (0.83 nm) in Figure 7a exhibits a broad multiplet structure; similar spectra were reported for both FePc and $FePcF_{16}$.[50,51,68] Most important, no interface component can be detected in the related monolayer spectrum, which might be expected at about 707 eV (compare, e.g., FePc on Ag(111)[50] and $FePcF_{16}$ on Cu(111)[15]). Also, the peak shape of the corresponding XA spectra is almost independent of the film thickness; differences may also arise from artifacts due to the complex background subtraction procedure. For example, a feature similar to "A0" observed on Cu(110) (Figure 6a) and related reactive interfaces[15,50] at grazing incidence of the incoming p polarized synchrotron light is not detectable.

Therefore, we conclude that the first monolayer of $FePcF_{16}$ is widely decoupled from the Cu(110) (2 × 1)O substrate surface. There is no evidence for a substantial charge transfer

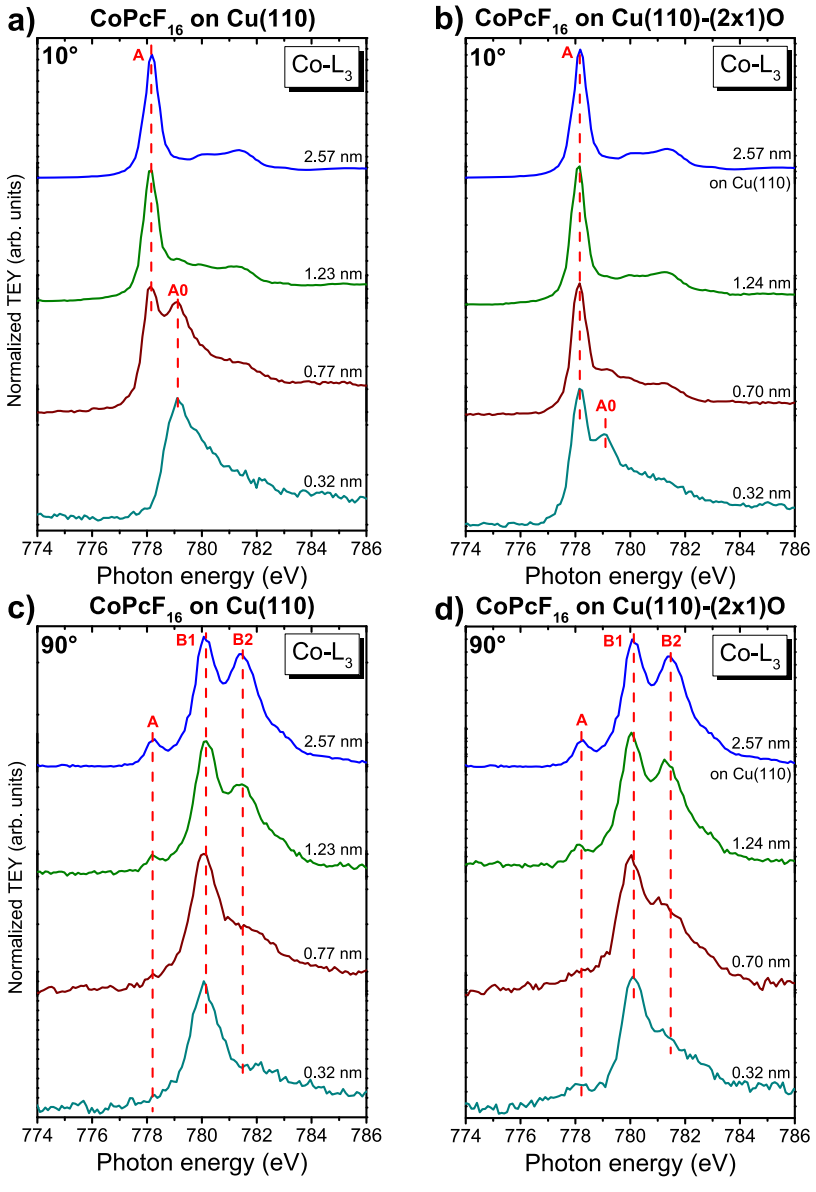


Figure 6. Thickness dependent Co 2p excitation spectra at grazing incidence (10°) for $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O and normal incidence (90°) for $CoPcF_{16}$ on (c) Cu(110) and (d) Cu(110) (2 × 1)O.

to the Fe^{2+} ion. The result is in good agreement with studies of FePc on Cu(110) and Cu(110) (2 × 1)O, where a switching of the spin state of the central Fe ion was observed on the strongly interacting Cu(110) substrate, while such spin switching is absent on the oxygen terminated Cu(110) (2 × 1)O with weak or negligible interactions.[16] As a consequence, we are left with the conclusion that the special electronic configuration of the Co ion in $CoPcF_{16}$ triggers the charge transfer at some adsorption sites on Cu(110) (2 × 1)O.

3.3. Total Interfacial Charge Transfer and Valence Electronic Structure. So far, evidence for a rather local charge transfer from both substrates to the Co ion of $CoPcF_{16}$ was provided. In addition, for the Cu(110) substrate, also a charge transfer to the LUMO of $CoPcF_{16}$ was discussed. As a consequence of such charge transfer, dipoles at the interface are formed, which can be quantitatively determined by UPS (for details, see Figure S4).

In Figure 8, the energy level alignment for $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O is summarized. In first approximation, the ionization potential (IP) can be regarded as a property of the material, although it was shown that presence of an intrinsic surface dipole may result in distinctly different values of the IP in highly ordered assemblies with differently oriented molecules.[73,74] The measured ionization potentials of $CoPcF_{16}$ in thin films (6.19 and 6.12 eV in Figure 8) are typical for fluorinated phthalocyanines and in good agreement with the literature.[5] The high IP supports charge transfer to the molecule on substrates with comparably low work function.[5] Indeed, large interface dipoles are observed on both substrates in Figure 8, indicating a total charge transfer from the substrate to the molecule. We note that not only interfacial charge transfer causes the formation of interface dipoles, an important effect is the modification of the substrate work function upon adsorption of molecules (push back effect).[32,75,76] However, for many systems values for a push back effect in the order of 0.3−0.6 eV were found,[32,34,77] which is distinctly lower than dipoles determined in Figure 8.

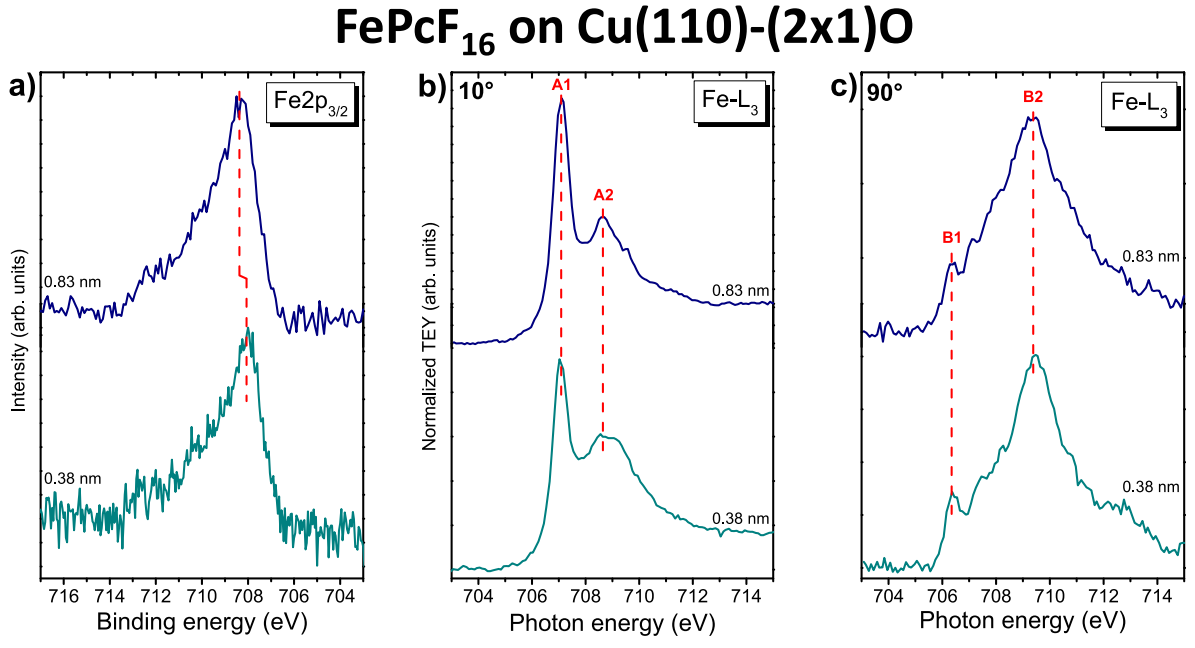


Figure 7. Thickness dependent $FePcF_{16}$ on Cu(110) (2 × 1)O. (a) Fe $2p_{3/2}$ core level spectra, (b) X ray absorption spectra at grazing incidence (10°), and (c) X ray absorption spectra at normal incidence (90°).

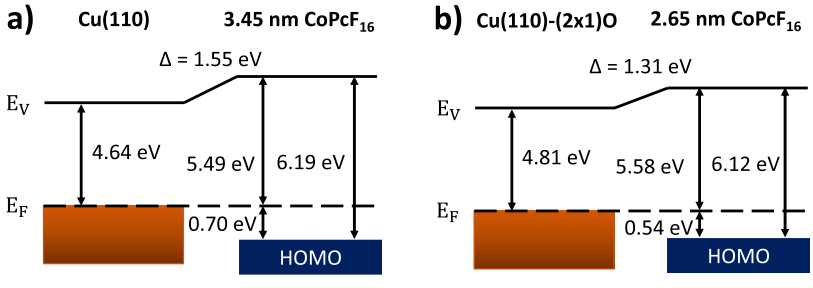


Figure 8. Energy level alignment of $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O. In both cases, the large dipoles indicate a total charge transfer from the substrate to the molecule.

The question may arise whether the charge transfer occurs unidirectionally from the substrate to the molecule or whether the interaction is bidirectional, as observed for related interfaces.[15,26−28] To discuss a possible charge transfer from the macrocycle to the substrate in more detail, we come back to the core level shifts, observed in section 3.1. Generally, such shifts can be caused by initial state effects (i.e., a different local electron density) or final state effects as a response to the formation of the photohole (screening).[36,78−80] Whereas the screening causes a lowering of the binding energy, an opposite effect is expected by an electron transfer from the molecule to the substrate (oxidation).

To distinguish between initial and final state effects, combined photoemission and X ray excited Auger electron spectroscopy (XAES) can be applied.[36,78,80−83] The basic idea is that different final states in XPS (one hole) and XAES (two holes) cause different shifts in binding energy (E_B). For the analysis of these shifts often the change of the modified Auger parameter α' is monitored according to $\Delta\alpha' = \Delta E_B(\text{XPS}) + \Delta E_{kin}(\text{XAES})$ (E_{kin} corresponds to the kinetic energy), which is correlated to the dynamical or one hole relaxation energy R_D ($\Delta\alpha' \approx 2\Delta R_D$).[79,80,84] ΔR_D can be correlated to the change of the polarization energy induced by the redistribution of environmental charges. The extra atomic relaxation energy R_D^{ea} is determined in macroscopic dielectric models by the polarization charge $(1 - 1/\varepsilon)e$, where ε is the optical dielectric constant of the environment.

For fluorinated Pcs the absence of a local charge transfer process at the fluorine atom allows the estimation of the polarization screening via the corresponding Auger parameter.[36] In addition, in contrast to C KVV and N KVV Auger spectra, F KLL Auger spectra include deeper valence levels (shallow core levels), resulting in comparably well resolved spectra. This allows a determination of the modified fluorine Auger parameter with an accuracy of about ±0.15 eV. For a discussion of the shape of F KLL Auger spectra we refer to the literature.[85,86]

We note that fluorinated phthalocyanines might be bended upon adsorption on metal surfaces. For submonolayers of $CuPcF_{16}$ on Cu(111) it was reported that fluorine atoms reside 0.027 nm above the benzene rings, which would result in an underestimation of the relaxation energy for carbon and nitrogen atoms. However, the effect is in the range of about 0.1 eV (cf. ref 36) and does not influence not the discussion below.

In Figure 9, we compare the development of the modified Auger parameter α' during the film growth of $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O. The corresponding F 1s and F KLL spectra are shown in Figures S5 and S6. Because of the mirror charge screening effect of the metallic substrate, the

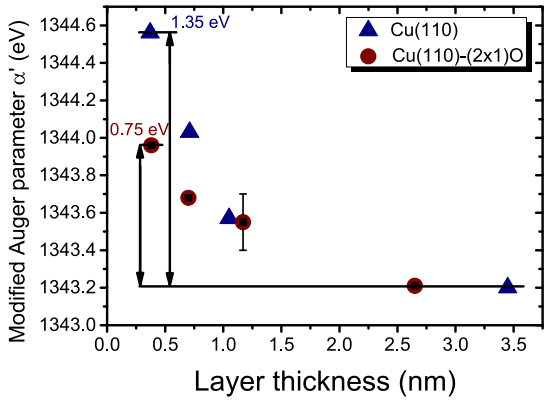


Figure 9. Modified Auger parameter α' for fluorine in $CoPcF_{16}$ as a function of film thickness of $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O. The modified Auger parameter α' is calculated from the binding energy of the F 1s core level and the kinetic energy of the related F KLL. An accuracy of ±0.15 eV is estimated.

highest value of α' in Figure 9 is found at monolayer coverages, that is, for molecules directly at the interface, where the screening ability is highest. Comparing the thickest films with monolayer coverages, changes of α' are 1.35 and 0.75 eV for $CoPcF_{16}$/Cu(110) and $CoPcF_{16}$/Cu(110) (2 × 1)O, respectively. The higher value for $\Delta\alpha'$ on Cu(110) can be well understood by the closer distance of $CoPcF_{16}$ molecules to the metallic mirror plane compared to the oxygen terminated surface.[81,87] We mention that rather similar (higher or lower) values $\Delta\alpha'$ of 1.5 and 0.7 eV were obtained on the interfaces $CoPcF_{16}$/graphene/Ni(111) and $CoPcF_{16}$/Au(111),[26,88] respectively, which were attributed to either stronger or weaker interacting interfaces. This similarity even extends to the Co 2p spectra and the apparent contributions of the interface peaks as discussed above.

Values for the relaxation energy contribution ΔR_D estimated from $\Delta\alpha'$ (Figure 9) are 0.7 and 0.4 eV for $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O, respectively. This implies that shifts of photoemission core level spectra to lower binding energies in the same order of magnitude might be expected as a function of the film thickness. Whereas shifts of C 1s and N 1s spectra of 0.2−0.3 eV are visible for $CoPcF_{16}$ on Cu(110) (2 × 1)O, on Cu(110) thickness dependent shifts are almost negligible (cf. Figures 1 and 2). Thus, we are left with the scenario that screening related shifts to lower binding energies, at least on Cu(110), are compensated to a large extent by another effect: a charge transfer from the macrocycle to the substrate at the very interface.

The complex charge transfer at both interfaces affects the valence band spectra, shown in Figure 10 as a function of the thickness. At about 3 nm $CoPcF_{16}$ film thickness, a single HOMO feature is visible in the spectra recorded from both surfaces; the energetic position (energy level alignment) is slightly different by 0.12 eV for the two surfaces (cf. Figure 8). This might be caused by the different interaction strength or energy level alignment of the first $CoPcF_{16}$ layer on both substrates. Clearly visible in the spectra is the formation of interface states (or a splitting of the HOMO) for low coverages. Such interface states may arise from a partial filling of the LUMO of the molecule as a consequence of the charge transfer,[89] or stronger changes of the electronic structure, such as the formation of new states due to hybridization between Co d orbitals and substrate related states, as proposed for other $CoPcF_{16}$/metal interfaces.[19,53] From the XA spectra (cf. Figure 6), we conclude that a hybridization occurs at both investigated interfaces. On the other hand, the shapes of monolayer valence band spectra are somewhat different for the two substrates (features A, B, and C). We ascribe these variations to the different electronic interactions involved at the respective interfaces, rather likely related to different contributions of interacting molecules of the first layer on both substrates as well as to different involvement of the macrocycle in the interaction. Feature B, only visible for $CoPcF_{16}$ on Cu(110), might be related to the interaction between the macrocycle and the substrate.

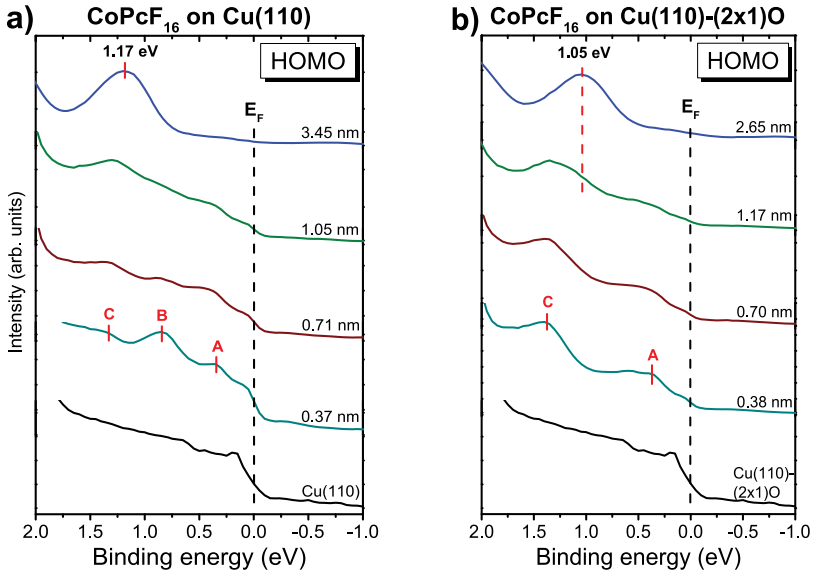


Figure 10. Thickness dependent valence band spectra (zoom into the HOMO region) of $CoPcF_{16}$ on (a) Cu(110) and (b) Cu(110) (2 × 1)O. Measured with an excitation energy of $h\nu$ = 21.22 eV.

4. CONCLUSIONS

We studied interface properties of $CoPcF_{16}$ on Cu(110) and Cu(110) (2 × 1)O. In both cases, a charge transfer from the substrate to the central Co ion of $CoPcF_{16}$ is observed, even if the oxygen termination suppresses such a strong interaction for a part of the molecules of the first monolayer. The absence of such an interaction for $FePcF_{16}$ on Cu(110) (2 × 1)O indicates that the interfacial interaction in the case of $CoPcF_{16}$ is governed by a local interaction between the Co $3d_{z^2}$ orbital and states of the substrate, similar to many CoPc and $CoPcF_{16}$ interfaces to noble metals.[5,19,20] Considering the geometry of the Cu(110) (2 × 1)O surface, the interaction occurs most likely between the Co ion of $CoPcF_{16}$ and atoms of Cu−O rows of the added row reconstruction. Thus, this study demonstrates the special nature of the Co ion in Co phthalocyanines and related compounds.

Analyzing the energetic shifts of all core levels, distinguishing between screening of the photohole and initial state effects, we propose that the charge transfer between $CoPcF_{16}$ and Cu(110) is bidirectional, involving also the macrocycle of $CoPcF_{16}$. The conclusion is supported by analysis of the shape of N K XA spectra as a function of the thickness. It is demonstrated that the application of the Auger parameter concept is a very useful tool for the estimation of polarization screening contributions in binding energy shifts of core level photoemission spectra.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Helmholtz Zentrum Berlin (electron storage ring BESSY II) for provision of synchrotron radiation at the beamline PM4. Financial travel support by HZB is thankfully acknowledged. The authors are grateful to the synchrotron light source KARA and to KNMF, both Karlsruhe, Germany, for the provision of beamtime. The Center for Light−Matter Interaction, Sensors & Analytics ($LISA^+$) at the University of Tübingen is acknowledged for technical support.

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