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Evidence of Charge Transfer at the Cu-phthalocyanine/Al(100) Interface[†]

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Electronic and structural properties of the CuPc/Al(100) organic−inorganic interface were investigated by means of a multitechnique experimental approach based on synchrotron radiation. The chemical selectivity of X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structure of copper-phthalocyanine (CuPc) as a function of the molecular thickness ranging from the submonolayer to 40 Å. Photoemission from core levels shows a dramatic alteration of the electronic structure of molecules localized at the interface. At the lowest CuPc coverages, the complete reduction of the oxidation state of copper was observed, while C 1s and N 1s shake-up satellites were no longer visible. Both findings are explained with a sizable charge transfer from the substrate to the molecule involving the b_{1g} (Cu 3d-derived) and the LUMO hybridized with the substrate conduction band. The linear polarization of the synchrotron light was employed in X-ray absorption near-edge spectroscopy (XANES) to determine the orientation of CuPc molecules. Molecular planes oriented almost perpendicular with respect to the metal surface were observed from the second layer on.

I. Introduction

In recent years, organic−inorganic complex structures were recognized as technologically important because of their application in optoelectronics, solar cells, sensors, and organic semiconductor devices. By using organic−inorganic complexes, it is possible to exploit not only the individual merit of each material but also the interfacial properties between the components. These are intimately connected to the nature of the interaction between the molecule and the substrate that depends on the chemical composition and/or the geometry of the surface. Despite the amount of works concerning the characterization of organic thin films deposited on several substrates, an in-depth comprehension of the interaction at the interface is still lacking. At the interface, a variety of possibilities can be observed, moving from a strong to weak interaction that affects or does not affect the electronic structure of involved molecules and substrates. For example, charge-transfer mechanisms testify that the electronic equilibrium at the interface is reached upon the filling of some empty states of the molecule. On the other hand, an interface dipole is observed when the equilibrium is reached upon a rigid shift of the electronic structure of the adsorbate with respect to the substrate.[1] Another interesting effect due to a significant molecule−substrate interaction is the mixing between molecular orbitals and metal electronic states[2−4] that can give rise to new electronic states localized at the interface. An intermediate case where a sort of weak interaction is present was recently observed in the CuPc/Au(110) interface; in this case, minor changes in the core level line shapes were visible for monolayer and submonolayer coverages.[5] Nonethe-less, the formation of interface states in the valence band spectra and the corresponding Au surface rearrangement[5,6] testify to the presence of a sizable interaction not referable to a simple van der Waals picture.

The interaction occurring at the interface between the adsorbate and substrate can also influence the growth morphology in the early stages of adsorption; when the molecule−substrate interaction is strong, a flat-lying deposition is favored,[7,8] while when the molecule−molecule interactions become more important, a different growth morphology can be observed.[9] Upon molecular deposition, the surface structure of the substrate can also undergo a rearrangement of the topmost atoms.[5,10] In some cases, an overgrowth evolution characterized by different molecular orientations was detected; in particular, the adsorption starts from a planar arrangement at low coverage, when the substrate−molecule interaction dominates, to progressively change into an out-of-plane orientation at higher coverage, where the molecule−molecule interaction overcomes the molecule−substrate one.[11] These findings are particularly relevant as electronic and optical properties are strongly dependent on the molecular orientation, mutual distance and molecule−substrate interaction. Within this picture, understanding molecular aggregation and the interaction with the substrate is a prerequisite for controlling long-range ordering of the molecular film, which is a fundamental issue to enhance electrical conductivity in an organic molecule thin film, as shown in the case of a pentacene thin film.[12]

Metal-phthalocyanines (MPc's) are planar organic molecules characterized by an extended π-electron distribution and by the presence of a metallic central atom. Thick MPc films generally grow in columnar stacks, and in several cases, self-ordering processes were detected.[13] Over the past decade, MPc overlayers interfaced with noble metals,[7,13−15] semiconductors,[7,16,17] and layered compounds were studied.[15,18,19]

In this work, we study ultrathin films of copper-Pc molecules grown on an aluminum(100) surface. Among the MPc's, CuPc

exhibits the half-filled b_{1g} orbital (Cu 3d-derived) located in energy between the filled a_{1u} orbital and the lowest unoccupied molecular orbital (LUMO).[20] As a substrate, aluminum was not yet considered with the proper attention; in fact, only a few works are devoted to growth MPc's on Al, and only one gives particular attention to the electronic properties of the molecule at the interface with the substrate.[21] Nonetheless, Al is a very peculiar and attractive metal due to the fact that its external s and p electrons form a nearly free electron system; then, the study of the CuPc/Al interface compared to CuPc grown on metals with the d band partially or totally filled can contribute to point out the role of localized electrons in an organic−inorganic interface.

In order to understand the modification of the electronic structure inside of the molecule, the chemical specificity gained by means of the creation of a core hole is of fundamental relevance. Therefore, X-ray photoemission spectroscopy (XPS) and X-ray absorption near-edge spectroscopy (XANES) were employed. The core level binding energy and line shape in XPS can give indirect information on the external molecular orbitals directly involved in the interaction with the metallic substrate.[3,7] Shake-up satellites (when they are present) can give further insight into the strength of the interaction at the interface.[22]

On the contrary, information on the delocalized outer orbital can be gained by means of ultraviolet photoemission spectroscopy (UPS). In this work, UPS spectra of bulk and Al-interfaced CuPc were compared to the gas-phase spectrum in order to gain information on the modification of the electronic structure occurring for the molecule at the interface.

XANES is commonly employed to study the empty states of the system, but in the case of molecules adsorbed on surfaces, it can be useful also to determine the orientation of the molecule with respect to the substrate.[23] The orientation of organic planar molecules was often determined by means of the well-defined symmetry of the 1s−σ^* and 1s−π^* transitions.[24] Nonetheless, the complexity of the spectra allows one to give only a qualitative determination of the molecular orientation. On the contrary, in the case of the CuPc, the XANES spectra of the Cu L_3 edge shows a white line strongly polarized in the plane of the molecule that allows one to quantitatively determine the orientation of the molecule with respect to the surface.[7,25]

II. Experimental Section

XPS and XANES were performed at the ALOISA beamline located at the Elettra Synchrotron in Trieste, where the UHV chambers (base pressure of 10^{-10} mbar) allow in situ preparation and characterization of ultrathin films under controlled conditions. Among the wide range of the available photon energies at the beamline (130−8000 eV), we employed 210 (Al 2p core level spectra), 500, (C 1s and N 1s core level spectra) and 1100 eV (Cu 2p core level spectra). Photoelectron spectra have been measured for different thicknesses of the overlayer, having calibrated the binding energy scale versus the Al $2p_{3/2}$ core level (72.70 eV). Photoelectrons were analyzed by a hemispherical analyzer working in constant pass energy mode and in normal emission geometry.[26] For each core level photoelectron spectrum, a fitting procedure was applied where each individual spectral component was described by a Voigt profile as a result of the convolution of a Gaussian contribution, mainly accounting for the experimental resolution, and a Lorentzian contribution related to the natural line width of the excitation. The program had the possibility to fit also the line shape asymmetry that is necessary for C 1s and N 1s core levels as measured at the lowest coverages and for the clean Al 2p. The background was

described with an integral function, which takes into account for the loss process that a photoelectron may undergo in escaping from the molecule to the vacuum. The background parameters are part of the fitting program, and they can be used in the optimization procedure. All of the XPS spectra are presented with their original background.

Valence band spectra, in the solid phase, were collected at the BEAR beamline (Elettra, Trieste) with a photon energy of 20 eV and an overall resolution of 200 meV. The reported photoemission spectrum from the isolated molecule was collected at the GAS PHASE beamline (Elettra Trieste) with a photon energy of 21 eV and an overall resolution of 160 meV.

The peculiar ALOISA experimental setup, associated with a grazing incidence geometry, allows one to keep fixed the incidence angle between the photon beam and the sample surface while varying the polar angle of the sample defined by the polarization vector and the normal to the sample surface. The incidence angle was kept fixed at 10.5°, while the azimuthal angle of the Al substrate was oriented by means of photoelectron diffraction from the Al 2p core level in order to align the [001] direction with the scattering plane. Absorption measurements were performed by measuring the total electron yield as a function of the photon energy. The intensities of the 2p−b_{1g} transition were normalized to a reference signal below the L_3 edge, accounting for the variable field of view of the detector and the variable illuminated sample area when the polar angle is varied.

A clean Al(100) surface was obtained by sputtering (1 h, 3 keV, I_{sample} = 20 μA) and annealing at 420 °C and checked by monitoring the presence of the chemically shifted oxidized Al component. CuPc films were evaporated in situ from a PBN crucible; during the evaporation, the pressure in the preparation chamber was about 1×10^{-9} mbar, the crucible was heated up to 350 °C, and the resulting evaporation rate on the sample was estimated to be about 0.2 Å/min. The stability of the evaporation rate was checked by means of a quartz microbalance. After several hours of photon irradiation, we did not have any evidence of radiation damage of the CuPc film independent of its thickness.

III. Results

A. Photoemission: Al 2p. In Figure 1, Al 2p spectra of a clean Al surface and after deposition of 4 Å of CuPc are reported. The spectrum of the clean surface presents the typical spin−orbit splitting of the 2p core level ($2p_{1/2}$ and $2p_{3/2}$). In order to disentangle different contributions, each peak was fitted with two asymmetric curves, accounting for the bulk and the surface components. The best fitting parameters are reported in Table 1; in the case of a clean surface, they agree with previous results.[27] The bulk component is roughly twice as intense as the surface one that lies at a lower binding energy. The Al spectrum after the deposition of CuPc shows some changes; at lower binding energy with respect to the bulk $2p_{1/2}$ and $2p_{3/2}$ components, we still observe, with a reduced intensity, two peaks shifted by about 100 meV and slightly larger compared to the surface components of the clean surface. A similar effect was already observed in the case of C_{60} grown on the Al(111) surface,[28] where the presence of a peak at the low binding energy side was attributed to Al atoms not bound to C_{60} having a different symmetry with respect the (111) surface.

The second relevant modification of the spectrum upon CuPc deposition is the presence of a widespread structure that extends at the high binding energy side; the origin of this signal will be discussed in the Discussion section.
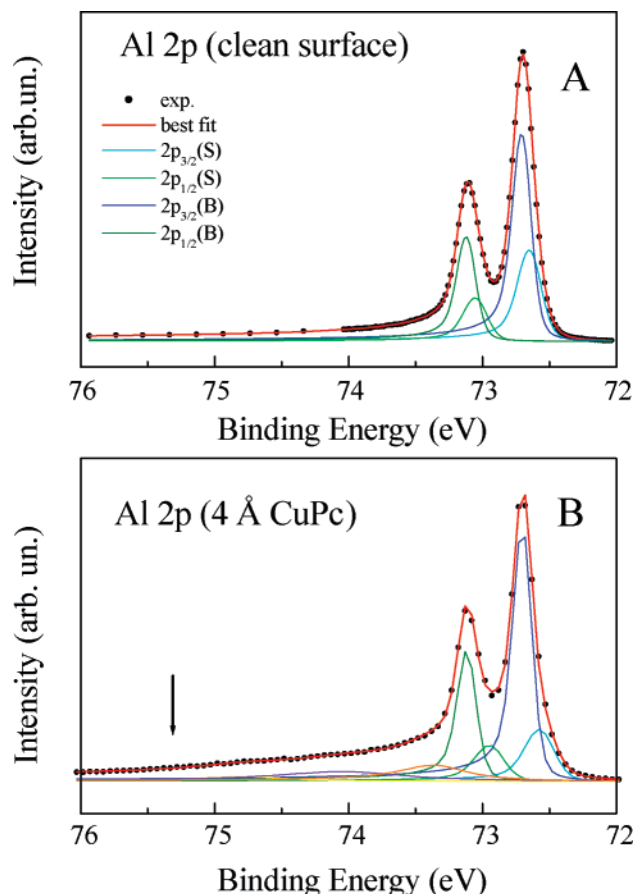
Figure 1. Results of the fitting procedure applied to the Al 2p core level spectra for the clean surface (A) and after a deposition of 4 Å (B) of CuPc. The arrow indicates the position of the expected oxidized Al.

TABLE 1: Best-Fit Parameters of the Al 2p Core Level Recorded in the Case of the Clean Surface ($\theta = 0$) and after a CuPc Deposition of 4 Å. Each Column Represent the Binding Energy (BE), the Area of the Peak (A), the Intrinsic Width (LW), the Gaussian Broadening (Full Width at Half-Maximum) (GW), and the Asymmetry Parameter (α), while Each Row Refers to Different Components of the Spectrum (B and S Indicate the Bulk and Surface Component). All Energies Are in eV

peak	BE	A	LW	GW	α	θ
$2p_{3/2}$ (B)	72.70	1	0.04	0.13	0.10	
$2p_{3/2}$ (S)	72.64	0.53	0.04	0.18	0.10	0 Å
$2p_{1/2}$ (B)	73.11	0.49	0.04	0.13	0.10	
$2p_{1/2}$ (S)	73.05	0.25	0.04	0.18	0.10	
$2p_{3/2}$ (B)	72.70	1	0.04	0.13	0.10	
$2p_{3/2}$ (S)	72.57	0.29	0.04	0.22	0.10	4 Å
$2p_{1/2}$ (B)	73.12	0.51	0.04	0.13	0.10	
$2p_{1/2}$ (S)	72.95	0.20	0.04	0.22	0.10	

B. Photoemission: Cu $2p_{3/2}$. We report in Figure 2 the evolution of the Cu $2p_{3/2}$ line shape as a function of the CuPc nominal coverage. The spectra are normalized to the same height in order to highlight changes in the line shape. To better understand the line shape evolution, we fit each spectrum reported in Figure 2. For the lowest coverage (1 and 3 Å), we observe only one peak (I) centered at a 933.4 eV binding energy. Upon increasing the coverage, a second peak appears on the high binding energy side. For higher coverages, the second component becomes dominant, while the peak (I) decreases its intensity and is completely absent in the spectrum of 40 Å; at this coverage, peak (II) is found at 935.0 eV.
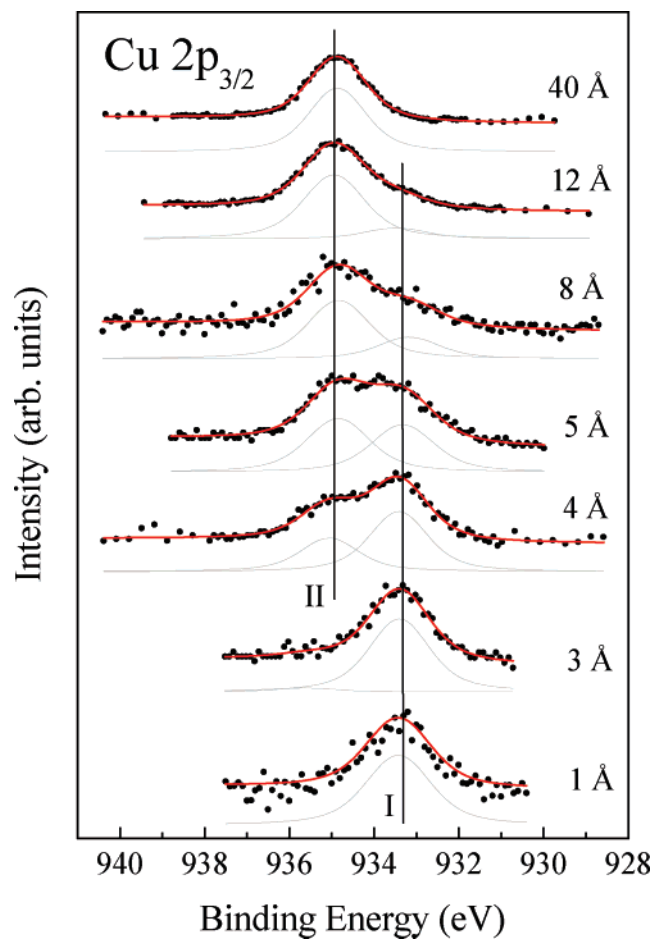

Figure 2. XPS spectra from Cu $2p_{3/2}$ core level as a function of CuPc coverage. Copper atoms in different oxidation states are denoted with (I) and (II); see the text for discussion. Spectra were normalized to the same height in order to highlight changes in the line shape.

The two peaks correspond to copper in two different electronic states. The peak (II) at 935 eV originates from divalent copper (hereafter, called Cu(II)) in the CuPc molecular solid phase,[7,29] that is, in the $3d^9$ initial state and $2\bar{p}3d^{10}\bar{L}$ final state (the overline indicates a hole in the corresponding orbital). The $2\bar{p}3d^9$ final state has much higher binding energy, and it is found around 945 eV (not reported in our spectra). At lower CuPc coverage, we observe only the peak (I) that is ascribed to copper in the $2\bar{p}3d^{10}$ final state,[7] corresponding to a filled 3d orbital already in the initial state. A filled 3d orbital is observed in two possible oxidation states,[30] namely, the monovalent copper Cu(I) and the metallic copper Cu(0); the binding energy of Cu $2p_{3/2}$ in the two oxidation states, Cu(0) and Cu(I), are almost identical,[31,32] and both are separated by about 1.5 eV from the same core level in Cu(II). For this reason, the results from XPS alone are not sufficient to distinguish between the two oxidation states.

Copper in the divalent state is visible only starting from 4 Å; the signal from Cu(I) observed at higher coverage (>4 Å) comes from molecules buried at the interface, as suggested by the attenuation of this signal as the CuPc thickness is increased. A partial reduction of the oxidation state of copper in CuPc was already observed in the CuPc/Si(111)[7] interface, while in the case of the Si(100)[7] and Au(110)[5] substrates, the reduction of Cu was not observed. To our knowledge, the CuPc/Al(100) interface represents the first case where a complete reduction of copper in the phthalocyanine occurs.
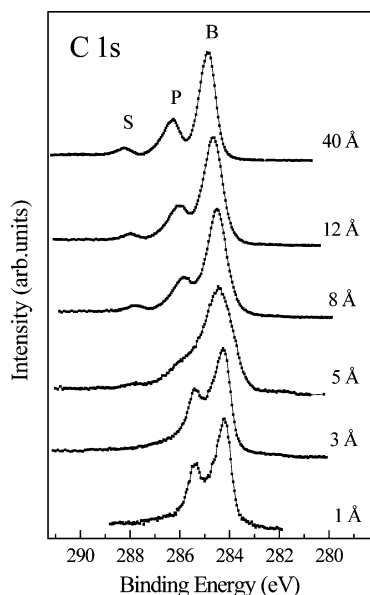
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Figure 3. XPS spectra from the C 1s core level as a function of CuPc coverage. Spectra were normalized to the same height in order to highlight changes in the line shape. The benzene and the pyrrolic components are denoted with B and P, respectively, while S indicates the shake-up satellite associated with the pyrrolic component, as discussed in the text.

C. Photoemission: C 1s. In Figure 3, the evolution of the C 1s core level is reported as a function of the CuPc coverage. In the submonolayer spectra (1 and 3 Å) a resolved doublet is present. The two peaks are labeled B and P, respectively. Upon increasing the coverage (8 and 12 Å), a smaller peak appears around 288 eV, the ratio between the two main peaks (B and P) changes, and the valley between the peaks is less pronounced. At the highest coverage (40 Å), the line shape is still different; the peak at 288 eV (S) is now more evident, and the valley between the main peaks is deeper. This spectrum is due to CuPc in its standard solid phase, that is, for this coverage, molecules are no longer influenced by the presence of the substrate. The two main peaks are attributed[7] to carbon in the benzene rings (B) and to carbon bound to nitrogen in the pyrrole rings (P). The peak S is a shake-up satellite related to the pyrrole peak.

Photoemission results from Cu 2p, presented in the previous section, suggest that coverages of 40 and 1 Å are representative, respectively, of molecules in the bulk-like phase and molecules bound to the Al substrate. In order to highlight the differences between the two phases, we focused our attention on these two extreme cases. The main differences between the two spectra are the presence of the peak S in the bulk-like coverage, the energy distance between the two main peaks and the ratio between the B and P peaks. In order to disentangle the contribution of each atom and/or excitation to the spectra, we deconvolute the experimental curves by means of a fitting procedure. The analysis of spectra corresponding to a coverage of 1 Å and the bulk CuPc is reported in Figure 4.

Looking at the structure of the molecule, reported in the inset of Figure 9, we note that C atoms are not equivalent; the main difference is between C_4 bound with nitrogen in the pyrrole ring and the group made by C_1, C_2, and C_3 belonging to the benzene ring. At first glance, the C 1s spectrum of bulk CuPc could be fitted with three components,[7,33] the first (B) representing C_1, C_2, and C_3, the second (P) C_4, and the last one (S) accounting for the shake up of the C_4 peak. With respect to this model, we need two more components in order to properly reproduce the line shape.[34] The two new components are located,
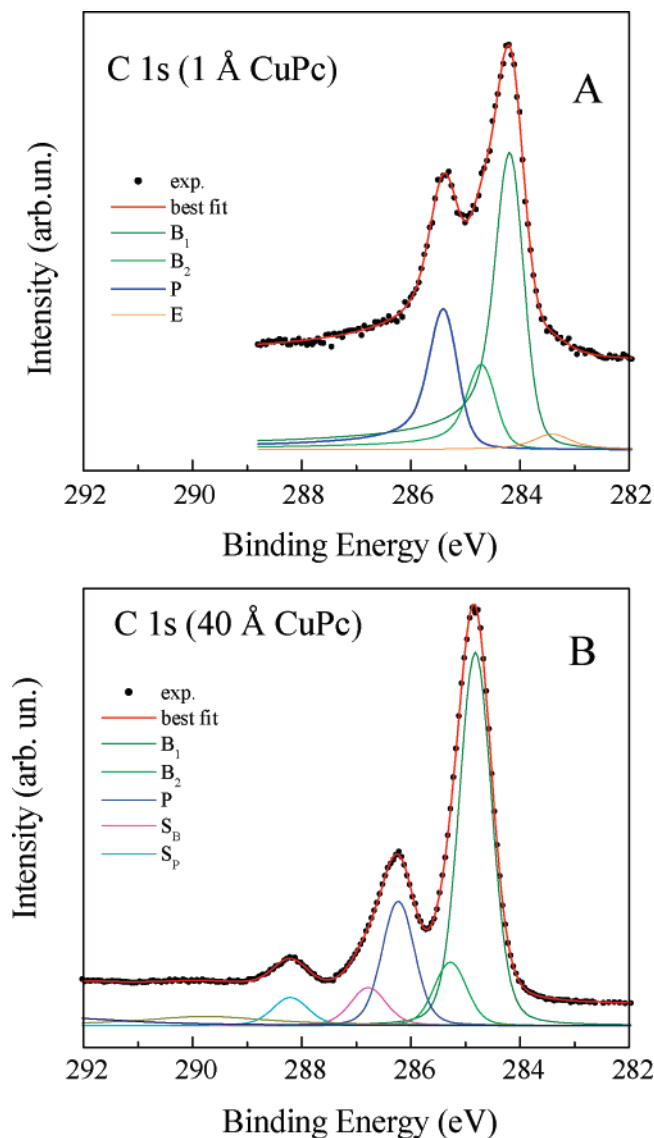

Figure 4. Results of the fitting procedure of the C 1s core level spectra for a 1 (A) and 40 Å (B) CuPc thickness.

TABLE 2: Best-Fit Parameters of the C 1s Spectra Recorded for CuPc Coverages (θ) Equal to 1 and 40 Å. Each Column Represent the Binding Energy (BE), the Area of the Peak (A), the Intrinsic Width (LW), the Gaussian Broadening (Full Width at Half-Maximum) (GW), and the Asymmetry Parameter (α), while Each Row Refers to Different Components of the Spectrum. All Energies Are in eV

peak	BE	A	LW	GW	α	θ
B_1	284.20	1	0.14	0.49	0.14	
B_2	284.71	0.28	0.14	0.49	0.14	1 Å
P	285.41	0.45	0.14	0.49	0.14	
E	283.45	0.06	0.60	0.49	0	
B_1	284.81	1	0.15	0.61	—	
B_2	285.26	0.18	0.15	0.61	—	
P	286.22	0.33	0.15	0.61	—	40 Å
S_B	286.76	0.12	0.25	0.61	—	
S_P	288.20	0.09	0.25	0.61	—	

in both cases, on the higher binding energy side of the main peaks B and P. The best fit is reported in Figure 4, and the corresponding parameters are reported in Table 2.[35]

The S_B component in Figure 4B represents the shake-up satellite of the main peak B, that is, the carbon atom in the

benzene ring. The assignment of the S_B peak is derived essentially from the analogous separation from the main peak observed in both S_B and S_P satellites and equal to 1.9 eV, corresponding to the energy separation of the a_{1u}−LUMO transition as pointed out theoretically[20] and experimentally.[21] Further support of this interpretation is derived from a recent calculation of the C 1s photoemission line shape of free phthalocyanine;[36] in this work, the presence of the S_B shake-up satellite hidden in the peak P is pointed out.

The origin of the component B_2 is less evident. In principle, it can be due to the inequivalence of carbon atoms in the benzene ring; in fact, C_1 and C_2 are bound with hydrogen, while C_3 belongs to both pyrrolic and benzene rings. Such a hypothesis is not supported by the numerical results of the fit: the ratio between the area of peaks B_1 and B_2 is far from the expected stoichiometric ratio of 2. Moreover, recent calculations show the equivalence of the C atoms in the benzene rings,[37] thus ruling out such a picture. Recently, the B_2 peak was attributed to the excitation of the in-plane C−H stretching mode.[34] This hypothesis is consistent with the results of the fit; in fact, if we guess that the signal from B_2 originates from carbon in benzene rings, then the ratio between the intensity from the group made by B_1, B_2, and S_B and the group P and S_P is equal to 3.1, close to the expected value (3) determined by the number of C atoms in the two rings.

The analysis of the C 1s spectrum collected for a thickness of 1 Å is reported in Figure 4A. The best agreement is obtained with three main components, whose energies are reported in Table 2, plus a weak extra component (E) at lower binding energy. The comparison with the bulk-like spectrum suggests that the component at a higher binding energy (P) is due to carbon in the pyrrole ring. The other two components (B_1, B_2) are attributed to carbon atoms in the benzene ring. In contrast with the bulk-like phase, this spectrum is well-fitted with asymmetric line profiles ($\alpha = 0.14$). Usually, an asymmetric line profile is used to fit core level peaks from metals, and it takes electron excitations near the Fermi level into account. The weak extra component (E) is found at 283.3 eV; it is probably due to carbon not belonging to phthalocyanine molecules; in any case, the intensity of this peak is only 5% of the benzene component, thus suggesting that the validity of the results is not compromised.

The fits of the two spectra presented in Figure 4 provide evidence for several differences that reflect changes in the CuPc electronic structure between the solid phase (40 Å) and the monolayer phase. In particular, in the spectrum at 1 Å, the shake-up satellites are not observed, thus indicating that the a_{1u}−LUMO excitation is not possible when molecules directly interact with Al. We observe a general shift of the P, B_1, and B_2 peaks in the spectrum at 1 Å with respect to the spectrum at 40 Å. Besides, the amount of the shift is not equal for the three components. In particular, we observe a shift of 610 meV for B_1 in the bulk-like phase with respect to the interface, while the relative distance between B_1 and P changes from 1.41 to 1.21 eV.

The spectrum at intermediate coverage (5 Å) has a different line shape with respect to both the bulk-like and submonolayer regime. This line shape originates from the superposition of signals coming from molecules bound to the substrate and from molecules from second layer on.[38]

From the analysis of the C 1s spectra, it is evident that the electronic structure of the molecule is strongly influenced by the interaction with the Al substrate, and this interaction seems to be confined to the molecules directly bonded with aluminum.
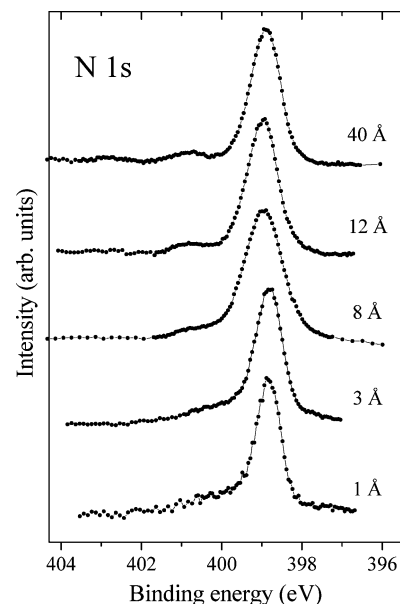

Figure 5. XPS spectra from the N 1s core level as a function of CuPc coverage. Spectra were normalized to the same height in order to highlight changes in the line shape. For the highest coverages, the shake-up satellite becomes visible.

D. Photoemission: N 1s. In Figure 5, we present the evolution of the N 1s core level as a function of the CuPc thickness; for the highest coverage, the main peak is slightly asymmetric, and two small satellites are present. As observed in the case of the C 1s spectra, also the photoemission from the N 1s shows changes induced by the interaction of the molecule with the Al substrate; in fact, at the lowest coverage, we observe a narrow asymmetric peak and the absence of satellites. The intermediate spectra show a continuous evolution between the two extreme coverages. Finally, the center of the peak does not substantially vary its energy position that is found around 398.8 eV.

Similar to the C 1s core level spectra, the data reported in Figures 5 and 6 are not background subtracted, and the parameters that describe the background are included in the optimization procedure. In Figure 6A, the result of the fitting procedure for the highest coverage is reported. An attempt to fit the main structure with only one component was made, but the slightly asymmetric shape of the peak can be well reproduced only with two components that reflect the presence of two inequivalent nitrogen atoms in the molecule located in the pyrrole ring (N_1 in Table 3) and in the aza bridging positions (N_2 in the Table 3).[39] In order to obtain equal intensity for the two components, we allowed the fit program to use two different values for the intrinsic width; the slightly different value, obtained in the best fit (see Table 3), can be ascribed to different screening of the N 1s core hole in the two different locations. To properly fit the measured spectra, we used two components for the main peak and two other components for the satellite region. The energy differences between the main peak and the satellites suggest, in analogy with the C 1s spectrum, that the observed structure are shake-up. In particular, they correspond to the Q and B absorption bands observed in optical[40] and in EELS[21] spectra; with respect to the carbon 1s spectrum, we observe a less-intense satellite related to the a_{1u}−LUMO transition (the ratio is 0.15 in the case of N and 0.27 in the case of C in the pyrrole ring), suggesting a minor participation of N atoms to the a_{1u} orbital, in agreement with calculations reported in the literature.[41]
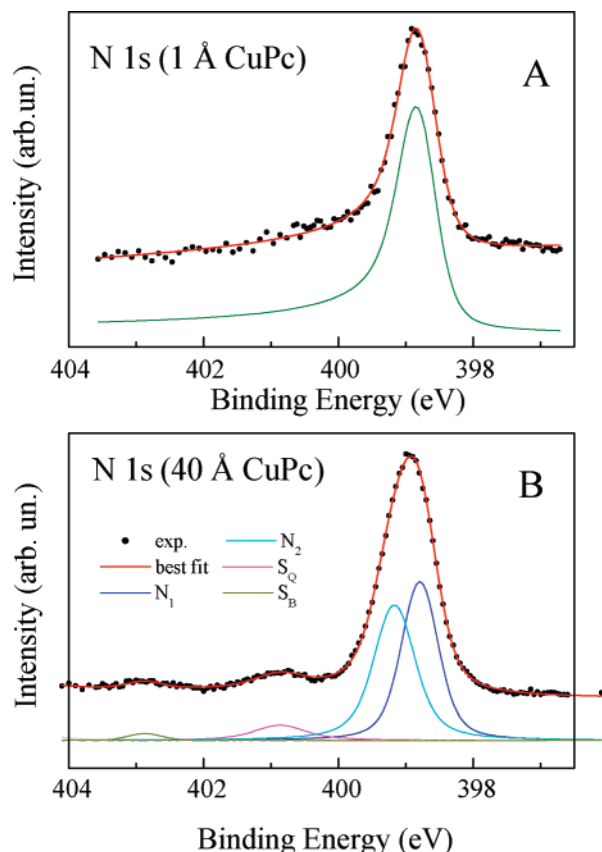
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Figure 6. Results of the fitting procedure of the N 1s core level spectra for a 1 (A) and 40 Å (B) CuPc thickness.

TABLE 3: Best-Fit Parameters of the N 1s Spectra Taken for CuPc Coverages (θ) Equal to 1 and 40 Å. Each Column Represent the Binding Energy (BE), the Area of the Peak (A), the Intrinsic Width (LW), the Gaussian Broadening (Full Width at Half-Maximum) (GW), and the Asymmetry Parameter (α), while Each Row Refers to Different Components of the Spectrum. All Energies Are in eV

peak	BE	A	LW	GW	α	θ
N	398.84	1	0.24	0.49	0.17	1 Å
N_1	398.80	1	0.25	0.50	—	
N_2	399.18	1	0.36	0.50	—	40 Å
S_Q	400.88	0.15	0.63	0.50	—	
S_B	402.86	0.04	0.53	0.50	—	

Analogously to what happens in the case of carbon, the spectrum at low coverage is different from the bulk one. At the interface, we use again an asymmetric profile to reproduce the main peak ($\alpha = 0.17$), and with respect to the spectrum of bulk CuPc, we need only one component. This is the best choice among the different models that were tested.[42]

E. Valence Band Photoemission. In Figure 7, the photoemission spectra of the valence band for 1 ML of CuPc compared with that of the bulk CuPc (50 Å) and CuPc in gas phase are reported. The lower spectrum, taken as a reference, was collected from the clean Al(100) surface; this spectrum has a single broad peak, thus enabling us to easily distinguish molecular contribution even at the lowest CuPc coverage. The gas-phase spectrum (reported in ionization energy (I.E.)) was aligned to the CuPc in the bulk phase by means of the emission from the a_{1u} orbital (6.38 of I.E. and 1.54 of B.E.).

Details about the origin of different structures are given elsewhere (ref 37 and reference therein). Here, we concentrate our attention on the emission near the Fermi level and on the similarity between spectra in the gas phase, in the solid phase,
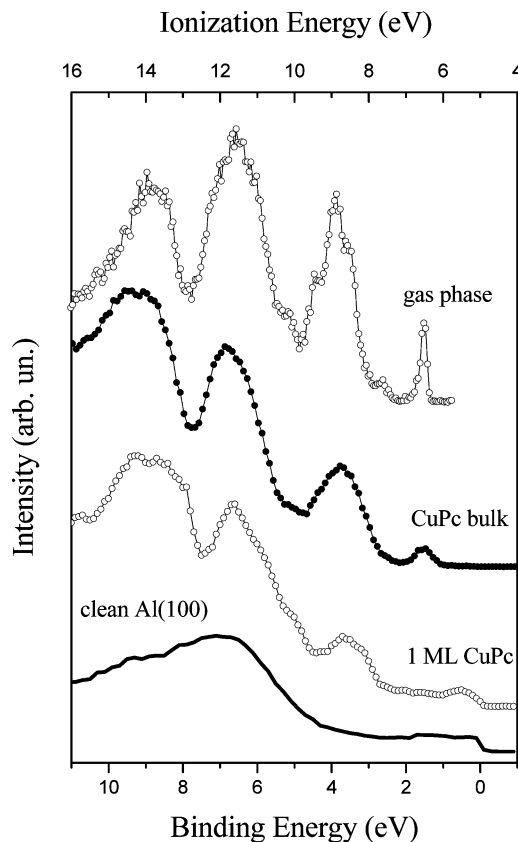

Figure 7. Photoemission spectra from the valence band of CuPc in the gas phase (upper X scale in ionization energy, $h\nu = 21$ eV), the bulk phase (estimated thickness of 50 Å), and for 1 ML of CuPc grown on an Al(100) substrate (lower X scale in binding energy, $h\nu = 20$ eV). For reference, the spectrum of the clean Al(100) surface is also reported.

and at the interface with the substrate. We observe a close similarity between the spectra in the gas phase and that in the solid phase, suggesting that the formation of a solid CuPc film does not significantly alter the electronic structure of the CuPc molecule, in accord with previous results.[37,43] For the CuPc at the interface, the most relevant differences are located close to the Fermi edge. In particular, we observe that emission from the a_{1u} orbital is completely smeared out, while we observe a significant emission close to the Fermi level.

The interface spectrum, in this region, is different from both the gas and the bulk phases, while the latter two are very similar. As a consequence, variations in the photoemission spectrum at this coverage can be related to the interaction of CuPc with the substrate; as expected, this interaction influences mostly the outer orbitals, and this will be further discussed later on.

F. Absorption Spectroscopy. Absorption spectroscopy from the Cu L_3 edge offers the possibility to investigate the empty states of the metal in the center of the molecule and the orientation of the molecule. In the free molecule and in its molecular solid phase, copper is in 3d^9 configuration, and the half-filled 3d-derived state (i.e., the b_{1g} molecular orbital) is located between the a_{1u} orbital and the LUMO.[20] The 2p$-b_{1g}$ transition gives rise to a sharp white line in the absorption spectra;[7] this transition has a well defined associated dipole moment parallel to the plane of the molecule.[25] It is then possible to investigate the orientation of the molecule by varying the polarization of the light with respect to that dipole moment. In this section, the absorption spectra (Cu 2p$-b_{1g}$ transition) will be presented as a function of the molecular thickness and of
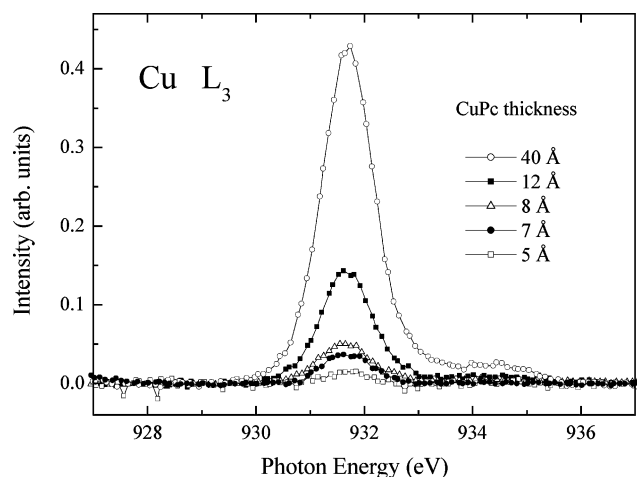
Figure 8. Absorption spectra of the Cu L_3 edge in the region of the $2p-b_{1g}$ transition for several thicknesses ranging from 5 to 40 Å.
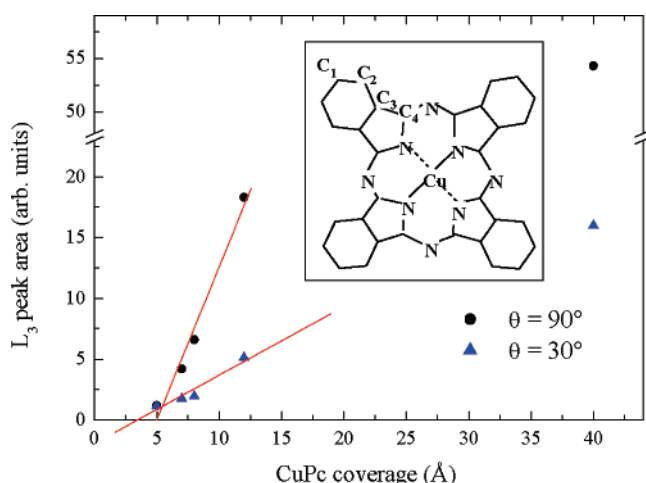

Figure 9. Intensity of the Cu $2p-b_{1g}$ transition as a function of the thickness for two different orientations of the sample with respect to the polarization of the incident photon beam. A picture of the CuPc molecule with the indication of the four inequivalent carbon atoms is reported in the inset.

the polar angle θ, that is, the angle between the polarization of the light and the surface of the Al substrate.

Several absorption spectra relative to the Cu $2p-b_{1g}$ transition are reported in Figure 8 as a function of the CuPc thickness ranging from 5 to 40 Å. All spectra were collected with $\theta = 90°$, corresponding to the polarization vector perpendicular to the Al substrate (apart from the small tilt angle). In Figure 9, the area of the peak is reported as a function of the CuPc thickness; points corresponding to thicknesses ranging from 5 to 12 Å are aligned along a straight line that intercept the *x*-axis at about 4−5 Å; in the same figure, the intensity of the L_3 edge as a function of the thickness for $\theta = 30°$ is also reported. Actually, the two sets of data have the same intercept with the *x*-axis, thus excluding the possibility that the quenching of the signal is due a change in the molecular orientation. On the contrary, this result indicates that the $2p-b_{1g}$ transition for coverages lower than 4 Å is forbidden, and it suggests that below this thickness, a change in the electronic structure of the molecule occurs. This result is not surprising if compared with those obtained with core level photoemission. In fact, both C 1s and Cu 2p spectra show a change in the electronic structure of the molecule around 3−4 Å. A similar behavior was observed on the same system by monitoring the a_{1u}−LUMO transition by means of EELS.[21] The two spectroscopies, XANES and
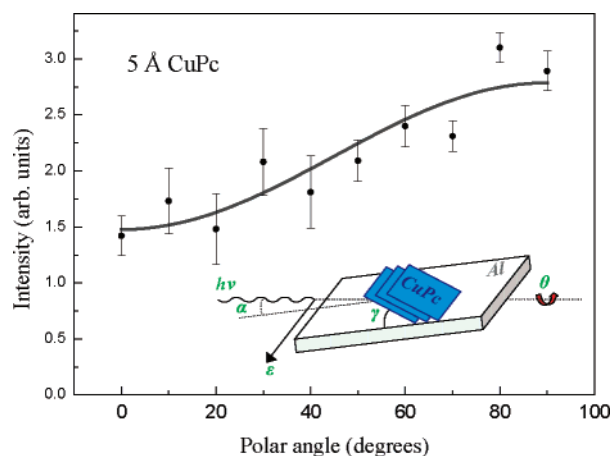

Figure 10. Intensity of the Cu $2p-b_{1g}$ transition as a function of the polar angle for a CuPc coverage of 5 Å. The gray line represents the best fit obtained with the trial function reported and discussed in the text. The best fit was obtained with a value of $\gamma = 82 \pm 6°$ (see the inset for the explanation of the geometry), which corresponds to molecules almost perpendicular to the plane of the aluminum surface.

EELS, indicate that the half-filled 3d state and the π^* orbital are not accessible in the early stage of the CuPc growth.

In order to gain information on the orientation of the molecule with respect to the Al substrate, we measure the intensity of the $2p-b_{1g}$ transition as a function of the polar angle θ. The result for a coverage of 5 Å is reported in Figure 10, where every dot represents the area of the $2p-b_{1g}$ transition. As previously discussed, the absorption signal measured for this coverage comes from molecules just above the layer of molecule bound to the Al substrate.

In these measurements, we exploited the well-defined symmetry of the Cu $2p-b_{1g}$ transition and the linear polarization of the synchrotron radiation. In the dipole approximation, the cross section for the absorption process is related to the square modulus of the scalar product between ϵ and N, where N is the normal to the plane of the CuPc molecule and ϵ is the direction of the light polarization (see the inset of Figure 10). By varying the polar angle θ, also the angle between ϵ and the orientation of the molecule N changes in a way that depends on the orientation of the molecule with respect to the substrate described by the angle γ and the tilt angle α (i.e., the grazing angle of the radiation on the surface of the sample). Also, the azimuthal orientation of the molecule influences the intensity in a polar scan; if we consider that the Al(100) substrate exhibits a 4-fold symmetry and that no ordered phase was observed for the CuPc/Al(100) interface,[21] we may integrate over the azimuthal dependence in order to consider all of the possible orientations of the molecule with respect to the substrate. As a result, the differential cross section as a function of θ can be written as[38]

$$\frac{\partial \sigma}{\partial \theta} \propto 1 - \frac{1}{2}\sin^2\gamma \sin^2\theta \sin^2\alpha - \frac{1}{2}\sin^2\gamma \cos^2\theta - \cos^2\gamma \sin^2\theta \cos^2\alpha \quad (1)$$

This expression was used to fit the experimental points reported in Figure 10, where the only free parameters were a scaling factor and the γ angle. The continuous line in Figure 10 is the best fit obtained with $\gamma = 82°$, corresponding to molecules that have their planes almost perpendicular to the surface of the substrate. The same orientation was found for a thicker molecular film,[21,38] indicating that from the second layer on (considering the first layer to be made by molecules

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interacting with the substrate) and at least up to 40 Å, the CuPc grows on an Al substrate with the same orientation.

IV. Discussion

All of the results presented in this work indicate a strong modification of the electronic structure of the CuPc molecule at the interface with respect to molecule in the bulk phase. Significant changing of CuPc is summarized by the line shape evolution of the Cu 2p core level as a function of the molecular thickness. The Cu 2p binding energy typical of the molecular solid is observed for coverages larger than 4 Å, suggesting that only the first molecular layer, whose thickness is about 3−4 Å, experiences the interaction with the substrate. After this limiting coverage is achieved, the Cu(II) peak grows in intensity while the signal from Cu(I) decreases because it is due only to molecules buried at the interface.

We ascribe the different binding energy of the Cu 2p core level, for a molecule localized at the interface, to copper in the Cu(I) oxidation state, as already pointed out in the case of the Si(111) substrate.[7] In this oxidation state, the 3d-derived orbital is completely filled, thus explaining the absence of signal from the XANES experiment at the Cu L_3 edge. In principle, the observed binding energy of Cu 2p for a molecule at the interface could be also explained by copper in the Cu(0) oxidation state. Also, in this case, the 3d-derived orbital is filled, and then, it is consistent with XANES results. The Cu(0) oxidation state is normally associated with the metallic state, which would mean in our context that, following the interaction with the substrate, the copper leaves the molecule to bond to the Al substrate or to form a copper cluster. Such a hypothesis is not consistent with the N 1s core level line shapes at the interface because the removal of Cu would imply an alteration of the N electronic environment, with consequences on the relative photoemission spectra, which basically are not observed. Also, the valence band of 1 ML of CuPc seems to indicate that copper atoms do not form clusters or metal aggregates with the substrate; in fact, the spectrum, apart from the region of the outer orbitals, is very similar to that of CuPc in the bulk phase, and the peak at about 2.5 eV from the Fermi edge, associated with the emission of Cu 3d in the metal phase, is absent.

The C 1s and N 1s spectra at low CuPc coverage (1 Å completion) present important modifications that need a detailed discussion. With respect to the 40 Å CuPc coverage, two main differences in the line shape are evident: (a) the narrow shake-up satellites are missing, and (b) the line shape of each component is asymmetric. Both effects reflect the strong variation of the electronic structure of the molecule at the interface and, in particular, the role played by the LUMO in the formation of the bond between the molecule and the metal substrate. Our interpretation of the experimental data is based on the theoretical work of Gumhalter et al.[2] relative to the adsorption of CO on several metal substrates. According to this model, the hybridization of the localized valence orbital of the adsorbed molecule with the broad substrate band leads to the formation of a partially occupied resonance band by charge transfer from the substrate. This partially filled band is the origin of the asymmetric profile associated with the photoemission from the 1s core level because, similar to what happens in a metal, the sudden creation of the core hole can give rise to intraband transition. A similar behavior was observed in the case of complex molecules like C_{60} grown on Au and Cr[3] and in the case of simpler molecules such as CO adsorbed on metal substrates.[2] In both cases, an asymmetric profile was observed in the spectra of the C 1s and/or O 1s. In principle, extra

molecular screening (i.e., in the substrate) can give rise to an asymmetric line shape of C and N 1s core levels; however, in the case of strong coupling between the molecule and substrate, the dominant mechanism seems to be the intraresonance excitations,[2,22] that is, the excitation inside of the resonance band localized in molecules at the interface.

The presence of a partially filled band made by the hybridization of the LUMO and Al states close to the Fermi edge is also confirmed by the spectral density close to the Fermi level exhibited by the valence band spectrum at the interface (see Figure 7). Here, there is no evidence of the signal from the a_{1u}, while a broad peak appears close to the Fermi level, thus supporting a view in which the outset molecular orbitals are strongly altered at the interface.

The formation of a partially filled band in the molecule at the interface also explains the quenching of shake-up satellites in the C and N 1s spectra at low coverage; considering that the first satellite corresponds to the a_{1u}−LUMO transition, the quenching of the narrow shake-up is related to the broadening of the a_{1u} orbital and to the reduced availability of empty states in the LUMO-derived band. A similar result was obtained in the case of EELS measurements on the same system.[21]

A further issue to consider is the hypothesis that the first CuPc layer is dissociatively adsorbed on the Al substrate; we already discussed and excluded the possibility that the copper leaves the molecule; in general, we have no evidence that the dissociation process takes place. Indeed, in the case of molecule dissociation, we expect to find important variation of the core level line shape both in the case of C and N 1s, which we did not observe. An example of the dissociation of CuPc is the formation of phthalonitrile $C_6H_5(CN)_2$. The valence band spectrum of this molecule[44] is completely different from the phthalocyanine one; in our case, the valence band spectrum of 1 ML of CuPc (see Figure 7) is similar to those of the bulk and gas phase; therefore, we can exclude that we observe this important dissociation product of CuPc at the interface.

In conclusion, the observed modification of the molecule at the interface can be traced back to the hybridization and to the charge transfer from the substrate to the molecule; the hybridization and the charge transfer explain the results relative to XANES from the Cu L_3 edge and photoemission from the Cu 2p, N, and C 1s core levels. In this framework, the diffuse signal in the Al 2p core level at higher binding energy can now be related to Al atoms, directly bound to the molecule, that have donated charge to the CuPc overlayer, while the small shift of the surface component can be ascribed to a different coordination, with respect to the (100) surface, of surface atoms not bound with the CuPc molecules. Different coordination of the topmost Al atoms is compatible with a nonuniform coverage of the surface by the CuPc molecule, as inferred by the lack of long-range order observed for this system already at lower coverages.[21]

The analysis of the evolution of the C and N 1s binding energies provides further information on the electronic properties of the system. In previous sections, it was pointed out that the N 1s core level does not shift, while in the C 1s spectrum, the shift is not equal for the three main components B_1, B_2, and P (they are shifted by, respectively, 0.61, 0.55, and 0.81 eV). The relative shift between B_1 and B_2 is small, and it is not particularly significant. However, in the case of B_1 and P, the relative shift is 0.2 eV, and it could indicate a different role in the interaction of the molecule with the substrate of carbon in benzene (B_1) and pyrrole (P) rings. As previously observed, the results from EELS,[21] XANES, and the line shape analysis of XPS spectra

indicate a charge transfer from the substrate toward the LUMO and the b_{1g} orbital that could give rise to a shift of the core level binding energy relative to atoms whose orbitals host electrons from the substrate.[3] In this framework, nitrogen seems to be less involved in the charge-transfer mechanism because the 1s core level does not change its energy as a function of the CuPc thickness. This result is confirmed by the fact that the LUMO is essentially made of electronic wave functions localized on carbon atoms instead of on nitrogen atoms.[34,41] Moreover, the calculated total charge balance[20] indicates that nitrogen is negative while the four carbon atoms are all positive; this could explain why the charge transfer essentially involves the carbon atoms of the molecule. The fact that the peaks associated with inequivalent carbon atoms are shifted by a different amount suggests that the charge transfer from the substrate to molecule affects the inequivalent C atoms in the molecule in a different way.

As a final issue, the spatial localization of the a_{1u} orbital in the molecule can be inferred from the analysis of the intensity of shake-up satellites. The first satellite at 1.9 eV from the main peak, associated with the a_{1u}−LUMO transition, is more intense in the case of C_4, that is, the carbon in the pyrrole ring with respect to carbon in the benzene ring (C_1, C_2, C_3). Different intensities of the satellites reflect the fact that the molecular orbitals a_{1u} and $2e_g$ (LUMO) are preferentially distributed on C_4 atoms.[34,37,41] In the case of nitrogen, we found that the satellite at 1.9 eV from the main line is less intense with respect to shake-up in the C 1s spectra, suggesting that the nitrogen contribution to a_{1u} and the LUMO is less important. A second satellite is evident in the nitrogen spectra; this satellite (at 3.9 eV from the center of the main peak and at 3.7 eV from N_2) should correspond to the B band observed in absorption[40] and EELS spectra[21] that involves the a_{2u} (initial) and $2e_g$ (final) orbitals.

V. Conclusions

The strong interaction between the CuPc organic molecule and the Al surface was seen to deeply affect the electronic structure and the growth morphology at the interface. As molecules are deposited, a sizable charge transfer from the substrate to the molecule takes place, involving the copper-derived b_{1g} orbital and the hybridized $2e_g$ LUMO. As a consequence of such a charge transfer, at the lowest coverages, copper is in the Cu(I) oxidation state (i.e., in the $2p^63d^{10}$ configuration); the hybridization of the LUMO with the broad substrate band gives rise to a partially filled resonance band. A structural transition occurs upon moving from the monolayer to successive layers; molecules directly interacting with the substrate are likely to lie flat on the surface, while XANES as a function of polarization reveals that from the second layer on, molecules arrange themselves with the plane nearly orthogonal with respect to Al surface, in agreement with a previous EELS experiment.

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