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Electronic Structure of Co-Phthalocyanine on Gold Investigated by Photoexcited Electron Spectroscopies: Indication of Co Ion–Metal Interaction

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The electronic properties of the interface between cobalt phthalocyanine and gold substrate were investigated by photoexcited electron spectroscopies (UPS, XPS, and XAES). The experimental data indicate a quite strong interaction between the organic molecules and the metallic substrate, which is concluded from the different shape of the XPS Co 2p and Co LVV Auger spectral lines, as well as a splitting of the HOMO in the UP spectra. Initial and final state effects in photoemission and a possible change of the crystal field symmetry at the interface are discussed.

Introduction

In recent years, organic materials have been considered as technologically important due to their beneficial properties. In organic electronic devices, the interfaces between the electrodes and the organic films play a significant role, as they determine the injection efficiency by establishing barriers for carrier injection in the organic active layer. Therefore, interface studies contribute significantly to the understanding and improvement of the device performance. A variety of interactions can be observed right at the interface as going from a strong chemical interaction, which could affect the electronic structure of the organic molecules and/or the substrate, to a weak interaction without any impact on the properties of the materials in contact.^{1,2}

For the investigation of the chemical reactivity at interfaces, photoemission spectroscopies such as X-ray and Ultra-Violet Photoemission Spectroscopies (XPS, UPS) as well as X-ray Excited Auger Electron Spectroscopy (XAES) are quite valuable methods. The core level binding energy and line shape in XPS can give information on molecular orbitals which are directly involved in the interaction with the metallic substrate. The combination of XPS and XAES can give valuable insight on the nature of a possible interaction at interfaces via the analysis of the screening mechanism of holes.^{3,4} Furthermore, basic electronic properties such as the formation of interface dipole layers, the determination of the valence band structure, the energy band alignment at the interface, as well as the position of the highest occupied molecular orbital (HOMO) for the organic semiconductor, which are significant for the determination of the characteristics of devices based on these materials, can be determined by UPS.

Organic dyes have attracted significant attention as novel materials in applications in microelectronics due to their chemical stability, low heat conduction, diversity of optical properties, easy process ability, and low cost of preparation.⁵ In particular, phthalocyanines (Pc) are a family of organic semiconductors which possess excellent stability against heat, light, moisture, and oxygen. Their physical properties are controlled by traps, which are associated with imperfections,

grain boundaries, and surface topology of the material films.⁶ Although electronic properties of metal Pcs (MPcs), which are planar molecules formed by stable π -conjugated macrocycles coordinating a central metal atom, have been extensively investigated by photoemission spectroscopies,^{7–12} the nature of the interaction at several interfaces is still under discussion. In particular, even if the adsorption configurations are well-known for several MPc molecules, the involvement of the central metal atoms seems to be a key issue for the electronic interface properties.^{10,11,13}

In the present study the interfaces between cobalt phthalocyanine (CoPc), which is a transition metal phthalocyanine, and gold substrate (polycrystalline and (100) single crystal) are investigated by XPS, XAES, and UPS. CoPc is already applied in gas sensor and optoelectronic devices and it is considered a promising material for the development of low-dimensional molecular magnets.^{14,15} The magnetic properties of the Pc complexes depend on the number of unpaired electrons (d-electrons in the case of the Fe(d⁶), Co(d⁷), Ni(d⁸), Cu(d⁹)-phthalocyanines). Our focus is on the role of the 3d transition metal atom in the molecule–substrate interaction. The results are compared with those obtained for other studied interfaces between MPcs as well as metallo-tetraphenylporphyrins (MTPP), which cover the series of 3d⁵–3d¹⁰ complexes (e.g., FePc, CuPc, ZnPc, MgPc, CoTPP), and metallic substrates.^{3,4,13,15–21}

Experimental Methods

The measurements were performed with a multichamber UHV system (base pressure 2×10^{-10} mbar), equipped with a Phoibos 150 hemispherical analyzer (SPECS), a monochromatic Al K α source, and a high-flux He discharge lamp (UVS 300, SPECS). The energetic resolution determined from the width of the Fermi edge for XPS and UPS was about 400 and 100 meV, respectively. The binding energy (BE) scale of the spectra was calibrated to reproduce the BE of Au 4f_{7/2} (84.0 eV), Ag 3d_{5/2} (368.3 eV), and Cu 2p_{3/2} (932.5 eV). UPS measurements were performed with a He discharge lamp, He I β and He I γ satellites were subtracted from the data. As substrates, we use polycrystalline Au and single crystal Au(100) surfaces. Prior to organic film deposition both surfaces were cleaned by repeated argon ion sputtering and annealing cycles (in the case of the single crystal). The cleanliness of the gold surface was

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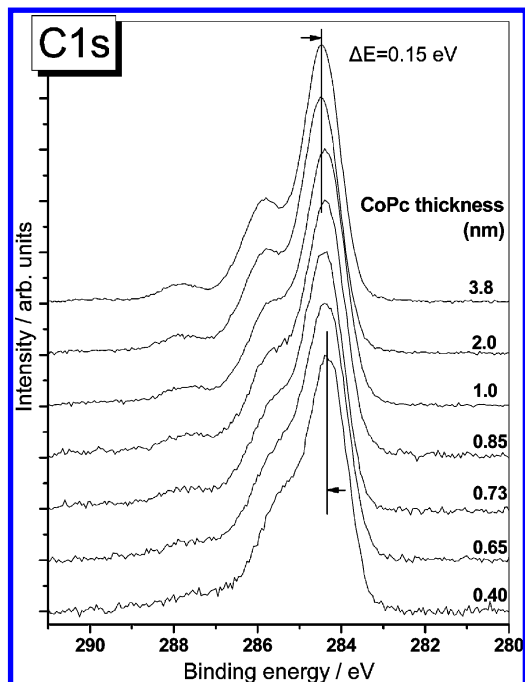


Figure 1. XPS spectra for the C 1s core level as a function of the CoPc coverage. The spectra are normalized to the same height.

checked by XPS and UPS, and no traces of contamination were detected. Thin films of cobalt phthalocyanine, purchased from Aldrich, were thermally evaporated in ultrahigh vacuum in a stepwise manner on both substrates. The pressure during the evaporation was less than 5×10^{-8} mbar and the evaporation rate was about 0.001 nm/s. The film thickness (maximum about 4 nm) was controlled by a quartz microbalance, which was calibrated using the attenuation of XPS intensities during the initial deposition steps. A nominal monolayer corresponds to ~ 0.34 nm for lying MPc molecules considering crystal structure data.²² During the UPS measurements, a negative bias of 5 V was applied to the sample in order to determine the absolute work function value from the high binding energy cutoff of the spectra.

Results and Discussion

In Figure 1, the evolution of the C 1s core level spectra for CoPc on Au foil as a function of the layer thickness is displayed. The intensities of the spectra are normalized to the peak height of the most intense component in order to highlight changes in the line shape. Only a slight change in the energetic position occurs, whereas the peak shape is almost not affected by the coverage. In particular, a total energy shift of about 0.15 eV toward higher binding energies is observed (indicated by arrows in Figure 1) with increasing coverage, which can be attributed to enhanced screening effects from the metallic substrate acting on the initial monolayers only similar to the related system ZnPc/Au. For a better understanding of the line shape evolution, we compare in Figure 2 fitted C 1s spectra of a monolayer and multilayer coverage. The spectra can be described analogous to other metal phthalocyanines.^{3,23,24} The C 1s peak consists of three main components which are quite clearly distinguished even at submonolayer coverage. The features C1 and C2 in Figure 2 are attributed to aromatic carbon of the benzene rings and to pyrrole carbon linked to nitrogen, respectively. There are also two lower intensity components (S1, S2) attributed to $\pi-\pi^*$ satellites from the main contributions to the C 1s overall signal (C1 and C2, respectively). A slightly smaller peak

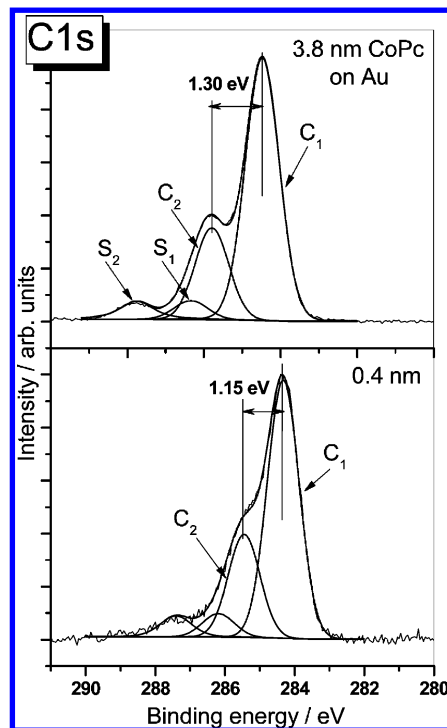


Figure 2. Analysis of the C 1s peak for a ML (0.4 nm) and multilayer (3.8 nm) CoPc film deposited on polycrystalline Au foil by fitting procedure.⁵¹

separation of the C1 and C2 carbon components at monolayer coverage is present, which can be understood by site-specific screening effects.^{3,4} The peak fit provides an increase of the peak separation at high coverage compared to monolayer coverage by 0.15 eV. Thus, the total BE shift from the ML to the multilayer film (~ 4 nm) is about 0.15 eV for the case of the benzene C1 carbons, while this shift is about 0.30 eV in the case of the pyrrole-based C2 component. No additional component is observed during the analysis of the ML and multilayer C 1s related spectra, which might point to a chemical interaction of the carbon atoms with the substrate.

As for other Pcs, the N 1s spectra (not shown) consist of a single peak centered at about 398.9 eV at 4 nm of CoPc coverage representing the two chemically slightly different N atoms in CoPc. No significant change is observed for the N1s spectra during the evaporations, except of a BE shift of 0.30 eV toward higher binding energies going from monolayer to multilayers. Interestingly, the size of the N1s peak shift matches closely the related shift of the pyrrole carbon (C2), i.e. the site specific screening is similar for the inner nitrogen and carbon atoms, whereas it is slightly different for the benzene carbons (C1). A similar effect in the case of MgPc and ZnPc on polycrystalline Au was observed recently.^{3,4} Also, the energetic shifts between mono- and multilayer in the order of ~ 0.3 eV, which fit reasonably well to the range of observations reported for other MPcs, can be understood essentially by polarization effects due to image charge screening at metal interfaces.^{3,4,25}

The spectra displayed in Figure 3 represent the development of the Co 2p_{3/2} signal on polycrystalline Au substrate with increasing CoPc film thickness. Again, the spectra have been normalized to equal peak heights of the maxima above the background. The bottom spectrum corresponds to about half a monolayer. In contrast to the other core level spectra, the Co 2p_{3/2} line shape looks completely different between the monolayer and the subsequent layers. The spectrum taken after the first CoPc deposition is dominated by an intense, sharp peak at

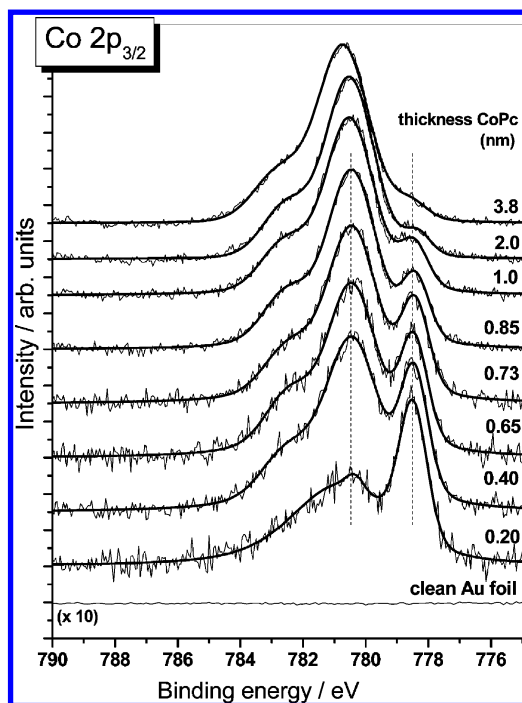


Figure 3. XPS spectra for the Co $2p_{3/2}$ core level peak as a function of the CoPc coverage on Au foil. Spectra were normalized to the same height for better comparison.

778.5 eV (see the vertical bar in Figure 3), which is accompanied by a rather broad structure with a maximum at ~ 2.3 eV higher BE. The spectra taken at increasing film thickness still exhibit this sharp peak at low BE, but more intense and broader peak structures develop at lower BE, between ~ 779 and ~ 784 eV. Finally, in the top spectrum of Figure 3 at a film thickness of 3.8 nm the relative intensity of the peak at low BE has attenuated and the spectrum is dominated by a broad peak located at 780.6 eV and a well-resolved shoulder at about 2 eV higher energy. All the spectra taken at coverage in between may be described by a superposition of the bottom and top spectrum, essentially. The Co 2p energy position for the multilayer is very similar to the BE of Co(II) in oxide materials.^{26,27} However, the well-known, prominent satellite structures at higher BEs (>784 eV), which are observed in bulk oxides, are missing here.²⁸ We would like to mention that a very similar spectrum has been reported for the case of Co porphyrines (CoTPP) on the more reactive Ag substrate²¹ and very recently also on Au.²⁹

The narrow peak width and the low BE of the Co 2p monolayer peak (Figure 3, bottom) fit reasonably well to a metallic-like nature Co(0). On the contrary, metallic Co peaks do not possess satellites typically and exhibit asymmetry due to Fermi surface excitations. There is no evidence for such a metallic-like asymmetry in the CoPc monolayer spectrum here in Figure 3, but very similar satellite features as observed in the monolayer spectrum have been reported for submonolayer Co deposited on Cu metal as well as for diluted Co embedded in Cu and Au bulk.^{16,17} This has been attributed to the coupling of d-orbitals of Co to s-type wave functions of the substrate or bulk noble metal materials.³⁰ Nevertheless, again a very similar monolayer spectrum has been reported for the case of CoTPP (Co 2p spectrum)²¹ as well as FePc (Fe 2p spectrum)¹⁶ on Ag(111) substrate pointing to a similar nature of both interfaces with the CoPc/Au interface. Following those arguments, both the metal-like main peak position and the appearance of the satellite indicate a significant Co central atom–Au substrate

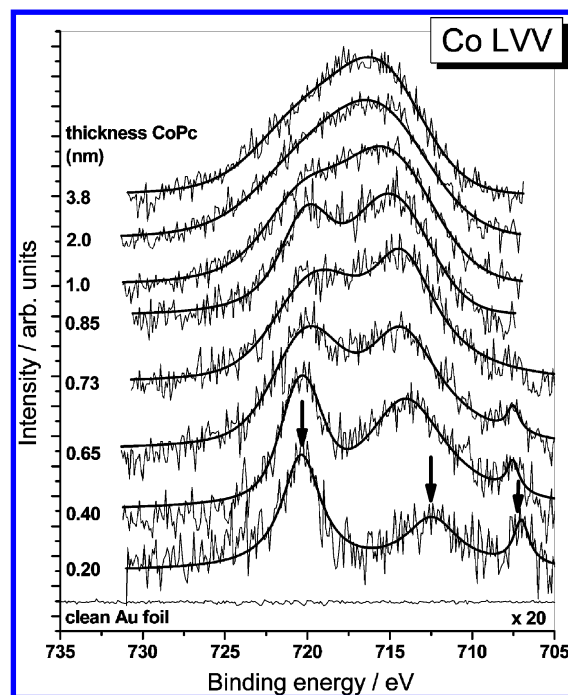


Figure 4. XPS spectra for the Co LVV Auger peak as a function of the CoPc coverage on Au foil. Spectra were normalized to the same height.

interaction and charge redistribution at least at Co sites at the immediate CoPc/Au interface.

Additional information on the different electronic situations of the central metal atoms of CoPc in the monolayer at the interface and within the organic multilayer system may be obtained from the Co LVV Auger peak shapes as displayed in Figure 4. In general, broad band-like, narrow atomic-like and intermediate structures can be present in Auger spectra depending on the ratio of the on-site Coulomb repulsion U to the bandwidth W .^{15,31,32} For open shell systems like Co, broad band-like spectra could be expected in contrast, e.g., to narrow atomic-like $Zn L_3M_{4,5}M_{4,5}$ spectra.^{4,33} From literature data, broad LVV Auger spectra are known for both metallic Co and Co oxides,^{34,35} and the Auger peak shape depends only weakly on the oxidation state.

In Figure 4, the background has been subtracted from the spectra in order to emphasize the Auger spectral features. The bottom spectrum representing (sub)monolayer coverage displays three significant peak structures in the range between 705 and 725 eV at 707.0, 712.5, and 720.35 eV on the BE scale (see vertical arrows). With increasing nominal surface coverage by CoPc these peaks become attenuated. In addition, a rather broad spectral feature centered near 715 eV grows in intensity. At the highest CoPc coverage (3.8 nm, top spectrum) a broad peak structure that extends from 710 to 725 eV with a tail toward higher energies on the BE scale is obtained. The peak shape and position are strikingly similar to reported Co LVV spectra.³⁵ However, completely different Auger spectra including new peaks have been obtained for the first monolayer at the CoPc/Au interface as mentioned above. Thereby, the peak shape cannot be simply explained by the “metallic” or “metal-like” Co, as could be concluded from the Co 2p core level photoemission spectra above, the electronic situation seems to be significantly different. A possible reason for this phenomenon could be the more localized nature of Co d-states in CoPc³⁶ compared to Co metal connected with charge transfer processes or/and the different screening at the interface to a metal. These

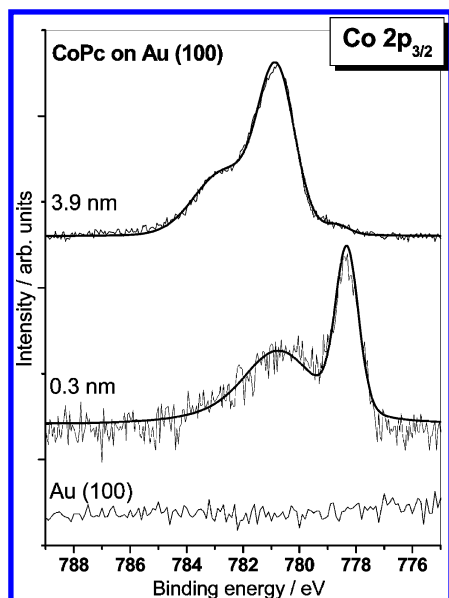


Figure 5. The XPS normalized spectra for the Co $2p_{3/2}$ core level peak for ML and about 4 nm CoPc coverage on Au (100).

effects may change the on-site Coulomb repulsion U^{15} and/or the bandwidth W , which can result in more atomic-like features.

Alternatively, the coordination symmetry for Co may change at the Au interface. The transition metal atoms, embedded in the molecular environment with a tetragonal symmetry as in the case of MPcs, break the degenerate 3d level symmetry with two levels E_g and T_{2g} known from the octahedral field symmetry.^{37,38} It is customary to use lower case symbols to describe the symmetry of orbitals and therefore we refer to the two sets of d-orbitals as the e_g and t_{2g} sets. In particular, the e_g is splitted into b_{1g} ($d_{x^2-y^2}$) and a_{1g} (d_{z^2}) and the t_{2g} into b_{2g} (d_{xy}) and e_g (d_{yz}, d_{zx}).^{37,41} The filled b_{2g} and the empty b_{1g} states are hybridized with the π -orbital localized on the neighbor nitrogen atoms, while the occupancy of the a_{1g} and e_g states is still under investigation^{13,39,40} and may change at the interface. Different terms for the multiplet splitting only due to the change of the symmetry for Co from tetragonal D_{4h} to C_{4v} at the interface cannot be expected, since the change from D_{4h} to C_{4v} upon adsorption does not lead to a further splitting of the degenerate e_g level. However, due to hybridization with substrate-derived states, energy split interface states may arise²⁹ at different energies.

In this manner the Auger spectra provide strong evidence indicating a redistribution of charge density for the Co d-states and appearance of new terms, e.g. due to charge transfer. The peak at lowest BE in the monolayer Co LVV Auger spectrum is at significantly lower energy than the lower edge of the multilayer spectrum. As in the case of the Co 2p spectra, also the Auger spectra point to a rather local interaction (including the Co atom only), which is confined to the monolayer CoPc–Au interface.

At this point, it is quite important to note that similar results have also been obtained from the study of the interface formed between CoPc and Au(100) single crystal. Shifts of the CoPc related core level lines toward higher binding energies and new features at the first steps of deposition for the Co $2p_{3/2}$ peak (see Figure 5) and the Co LVV Auger peak are observed. This observation depicts that the presence of an interaction between the substrate and the initial monolayer is not significantly affected by the atomic structure of the substrate. In the case of CoPc on Au(100), the features due to the interaction with Au

have completely disappeared at about 4.0 nm (see Figure 5) while in the case of the polycrystalline substrate (Figure 3) some shoulders from the monolayer spectrum can be observed also at high nominal coverage in the multilayer spectrum. This may be explained tentatively by the orientation of the organic molecules and details of film morphology, which according to previous studies may be different at thicknesses beyond a few monolayer thickness on well-oriented and ill-defined surfaces.¹⁰

The question now arises, whether or not the possible strong molecule–substrate interaction leads to the creation of additional features (gap states) in the UP spectra. Figure 6a presents the evolution of the He I UP spectra during the development of the CoPc/poly-Au interface. The bottom spectrum represents the clean metallic substrate. Starting at the first CoPc deposition, the intensity of the Au surface electronic states is increasingly quenched and electronic features of the hybrid interface appear in the energy region across the Au metal d- and s-bands. The valence band structure of CoPc is fully developed at about >2 nm thickness and is composed of several peaks, noted as A–E in Figure 6a. According to previous spectroscopic data as well as theoretical calculations^{42,43} the valence band shape between 0 and 5 eV results from the interaction of the metal d-electrons with the four central N atoms. The intensity of the upper UP spectra in the 5–12 eV range is attributed to orbitals from benzene and pyrrole which are common for all Pc molecules.^{11,44} More detailed information can be obtained by zooming to the upper valence band region (see Figure 6b) and by subtracting the substrate-derived background, essentially Au s-derived states, from the valence spectra, as shown in Figure 6c. For a 2.0 nm thick CoPc film the HOMO (peak A) has essentially developed to its final shape and position representative for the multilayer film. This HOMO peak maximum (A) is located at 1.25 eV below the Fermi level with an onset position at 0.75 eV. The second spectrum from the bottom in panels b and c of Figure 6 represents a CoPc film of 0.4 nm thickness. At this coverage of about ~ 1.1 ML a small single peak appears at a comparably low BE of 0.7 eV. For higher coverage this peak broadens toward higher BE and a splitting into more than two peaks seems to occur at a film thickness of 0.6 to 0.9 nm (~ 2 –3 ML). The splitting of the HOMO into two or more peaks is reminiscent of the related system ZnPc/Au and might be understood by polarization screening of CoPc layers with different distances to the mirror plane of the metallic substrate.⁴ However, for CoPc on Au the total BE difference between the first monolayer valence peak and the established multilayer HOMO peak position of 0.55 eV is nearly twice as large as that observed for the core level shifts between the same coverage. Therefore, this also could be evidence for the formation of new states due to an interaction at the interface as suggested by the Co-related XPS and XAES features above. These states are most likely hybrid states with considerable contribution from the Au 6sp band of the substrate in the gap of the organic semiconductor. Note that similar results have been reported recently for CoPc/Au(110) studied by UPS(He I), where it was observed that the interaction of CoPc molecules with the Au substrate gives rise to molecular induced states close to the Fermi level unlike to the more d-filled MPcs.^{11,13}

Stronger interactions at CoPc/Au interface were most recently also suggested in refs 12, 15, and 45. Bias-dependent STM images for the CoPc/Au(111) interface revealed significant changes of the experimentally derived density of states (DOS) of the Co metal ion in the MPc molecule, when the molecule is adsorbed onto the metallic surface.^{15,46} At the interface, the

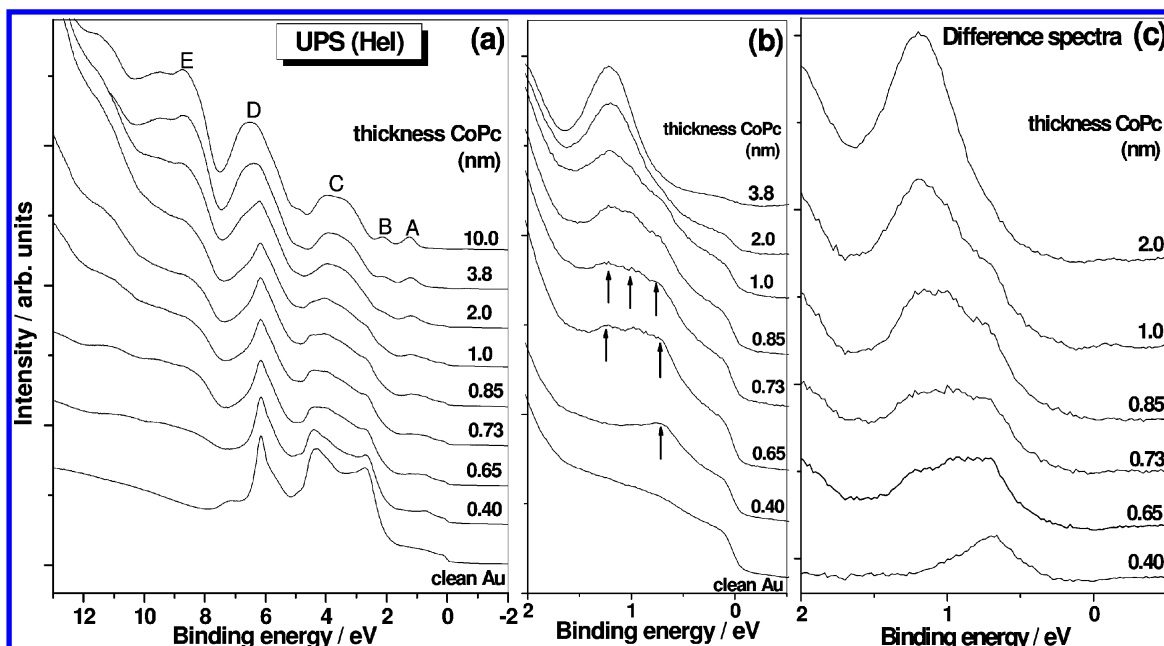


Figure 6. (a) Photoemission spectra (UPS) from the valence band of CoPc as a function of organic film thickness (CoPc/poly-Au interface), (b) zoom in the low binding energy region, and (c) the same spectra after the subtraction of the substrates signal.

magnetic moment of the Co atom is completely quenched by the molecule–substrate interaction, contrary to the free CoPc molecule. Right at the contact with Au, the DOS is changing revealing a clear Co contribution in the molecular orbitals at energy positions of 0.1 and 0.7 eV. A qualitative explanation is based on the interaction of Co 3d_{z²} and Au 6s orbitals.⁴⁵ This observation is in a good correlation with our UPS data, confirming our assumption for the formation of gap states induced by an interaction between the metallic substrate and the cobalt ion. The further, rather small DOS peak that is also present at lower BEs (0.1 eV) according to ref 15 is not present at the UPS, either because it is too weak to be detected or due to the low excitation energy that is used during the acquisition of the UPS. It is important to note that the excitation energy influences the shape of the valence band spectra significantly.⁴³ In particular, it is mentioned that with He I (21.22 eV of excitation energy, $h\nu$) the photoemission intensity in the region of the first ionization d-states for CoPc is almost negligible but it is enhanced with higher $h\nu$ (e.g., 110 eV).⁴³ Taking into consideration the above discussion, the new states at the UPS which are present up to 1–2 nm of coverage cannot be interpreted as a simple superposition of all the signals from the further deposited CoPc layers. These states are most probably related to a substrate–molecule interaction with a mixing of molecular and metal states resulting in an electronic state redistribution and surface dipole changes.

Also visible from the UPS data is a shift of the high binding energy cutoff, which defines the work function of the surface. According to Figure 7, the work function of the clean polycrystalline gold surface was determined to be 5.30 eV. An initial fast decrease is observed at the early stages of the deposition, in agreement with several studies of other MPcs (e.g., CuPc, NiPc, ZnPc) on Au substrate.¹³ One of the reasons for such shifts is, for example, a redistribution of the metal electron cloud due to the presence of the organic molecules, causing a reduction of the metal work function (pillow effect).⁴⁷ Alternatively, charge transfer processes may cause dipoles at interfaces. For a detailed discussion on the nature of dipoles at organic interfaces see, e.g., refs 1, 48, and 49. As the film thickness

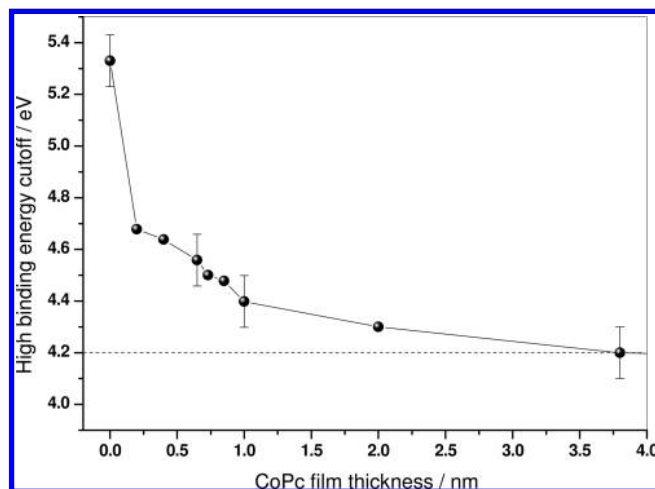


Figure 7. Variation of the high binding energy cutoff region for the CoPc/poly-Au interface as the organic layer grows thicker.

increases, the rate of the work function decrease becomes smaller. The total decrease of the work function of Au is ~ 1.1 eV, yielding a work function equal to 4.20 eV for the thick (4 nm) CoPc overlayer.

By combining all experimental data we can draw schematically the energy level diagram and estimate the electronic properties at the interface as it is displayed in Figure 8. At the CoPc/Au interface, the injection barrier (Φ_{bh}) for holes which is equal to the energy difference between the metal Fermi level (E_{F}) and the edge of the HOMO (HOMO cutoff) is found to be 0.75 eV. The ionization potential (I) is determined to be equal to 4.95 eV for the CoPc overlayer. The observed vacuum level ($E_{\text{F}}^{\text{vac}}$) shift results in the formation of an interfacial dipole layer (Δ). The total $E_{\text{F}}^{\text{vac}}$ change yields a dipole of 1.1 eV, which “points outward”. In other words, assuming a charge transfer mechanism for the dipole formation, the sign of Δ indicates a charge transfer of electrons from the molecules toward the metal surface. This is in apparent contrast to the discussion above, where a charge transfer to the Co atom was presumed. A possible explanation for this effect is a different, site-dependent partial charge transfer and back-donation related MPc on Au.⁵⁰

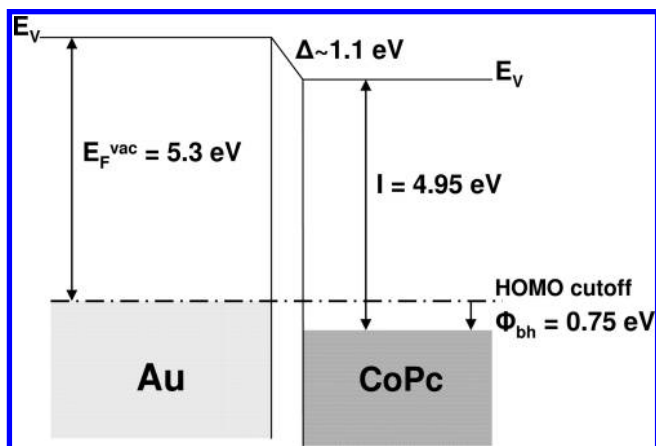


Figure 8. Schematic energy level diagram for the CoPc/Au interface deduced from photoemission measurements.

Conclusions

A quite intense modification of the electronic structure of the CoPc molecule at the interface with Au, with respect to the molecule in the bulk phase, is observed by photoexcited electron spectroscopies (UPS, XPS, and XAES). Local charge transfer toward the central metal atom of the phthalocyanine molecule from the gold substrate affects the charge state of the Co ion resulting in a different line shape of the Co related peaks and the presence of enhanced features in the energy region across the metal d-bands (UPS). This could be explained possibly by a mixing of the transition metal 3d states with the underlying metallic states of gold.

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