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Conclusively Addressing the CoPc Electronic Structure: A Joint Gas-Phase and Solid-State Photoemission and Absorption Spectroscopy Study

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Supporting Information

ABSTRACT: The occupied and empty densities of states of cobalt phthalocyanine (CoPc) were investigated by photoelectron and X-ray absorption spectroscopies in the gas phase and in thin films deposited on a Au(111) surface. The comparison between the gas-phase results and density functional theory single-molecule simulations confirmed that the CoPc ground state is correctly described by the $^2A_{1g}$ electronic configuration. Moreover, photon-energy-dependent valence photoemission spectra of both the gas phase and thin film confirmed the atomic character of the highest occupied molecular orbital as being derived from the organic ligand, with dominant contributions from the carbon atoms. Multiplet ligand-field theory was employed to simulate the Co *L*-edge X-ray absorption spectroscopy results.

1. INTRODUCTION

Phthalocyanines (Pcs) consist of four isoindole groups connected by nitrogen atoms to form a planar ring structure (see Figure 1a). A metal atom can be hosted in the center of the molecular ring of transition-metal phthalocyanines (TMPcs), or alternatively, two hydrogen atoms can be hosted in metal-free phthalocyanine (H_2Pc). Because their chemical and physical properties are tunable through the choice of different central metal ions or through functionalization, phthalocyanines can be exploited in a large variety of applications, such as optoelectronics [organic light-emitting diodes (OLEDs)], solar cells, catalysis, and gas sensing. This versatility, in addition to their high chemical and thermal stability, which makes them suitable for sublimation and thus investigation in ultrahigh-vacuum (UHV) environments, have allowed for a huge amount of characterizations of different Pcs by several techniques^{1–11} since their discovery.¹² More recent works have highlighted that phthalocyanines can also play a major role in molecular spintronics. In fact, TMPcs are considered archetypes of molecular nanomagnets or single-

molecule magnets (SMMs),^{13–16} namely, organic molecules having one or several metal centers with unpaired electrons. Different central metal ions, such as the 3d transition metals Fe, Mn, and Co, result in molecular magnets with different magnetic properties, which are strictly related to the d-electron population of the metal ion and the electronic structure resulting from the coordination of the metal ion with the molecular ligand. The magnetic properties can, moreover, be affected by adsorption on metallic surfaces and by the different polymorphs in which the molecules can arrange in films.

The symmetry of flat CoPc belongs to the D_{4h} point group, which, according to ligand-field theory, causes the splitting of the degenerate 3d states of the transition-metal atom into b_{1g} ($d_{x^2-y^2}$), a_{1g} (d_{z^2}), e_g (d_{zx} , d_{yz}), and b_{2g} (d_{xy}) levels, where e_g is doubly degenerate (Figure 1b). The $3d^7$ open-shell config-

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Figure 1. (a) Molecular structure of cobalt phthalocyanine (CoPc), with C atoms shown in black, Co atom in yellow, and N atoms in blue. (b) Schematic representation of the d-level splitting in a D_{4h} ligand field and a simplified depiction of the Co 3d electronic configuration corresponding to the DFT-calculated CoPc ground-state. (c) DFT-derived density of states for the CoPc ground state with atomic-orbital- and spin-resolved contributions. A Gaussian broadening of 0.3 eV fwhm was added to the DOS, and the metal 3d PDOS was multiplied by a factor of 4 for clarity.

uration of the Co ion in CoPc preserves a total spin of $S = 1/2$ resulting from the Co a_{1g} (d_{z^2}) unpaired electron.

In this study, we present conclusive results on the electronic structure of CoPc. Among the reasons driving our research were the recent works of Atxabal et al.¹⁷ and Niu et al.,¹⁸ who have suggested spin-doping and spin-filtering applications for CoPc. A convincing description of the CoPc electronic structure, especially focusing on the energy positions of the Co 3d levels, is clearly crucial for future applications of such molecules in spintronics. So far, experimental and theoretical studies have provided controversial results. Investigations of CoPc thin films have indicated that the electronic ground-state configuration is $^2A_{1g}$ (Figure 1b)⁵ or a mixture of $^2A_{1g}$ and 2E_g , where the 2E_g represents the first excited state at slightly higher energy.^{1–3} On the other hand, other studies have proposed the 2E_g configuration with a 3d hole in the e_g state as the ground state⁴ of CoPc. In addition, the character of the highest occupied molecular orbital (HOMO) of CoPc molecules has been under debate for a long time. This orbital has been suggested either to be of metal 3d-like character and localized on the central Co atom^{4,19} or to originate from the organic ring of the molecule.^{6,7}

Whereas a large number of photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) studies of CoPc thin films have been reported,²⁰ only a very few gas-phase measurements have been performed.^{8–10} Whereas the molecule in thin films can have a strong interaction with the substrate,

gas-phase experiments are aimed at elucidating the electronic structure of pristine CoPc and identifying the modifications induced when the molecules are adsorbed on a surface.

The present work, comprising both gas-phase and thin-film results, provides conclusive descriptions of both the electronic structure of CoPc and the contribution of the Co d states to the valence density of states. Valence photoemission data of molecular films on a gold single crystal, Au(111), definitely elucidate the ligand character of the CoPc HOMO.

2. EXPERIMENTAL DETAILS

The gas-phase measurements were performed at the GasPhase beamline of the Elettra synchrotron in Trieste, Italy. The experimental chamber is equipped with a home-built effusive molecular oven nozzle²¹ and a Scienta SES200 spectrometer mounted at the magic angle (54.7°) with respect to the linearly polarized incident light beam.

A few milligrams of cobalt(II) phthalocyanine (CoPc) (powder, 97% purity, Sigma-Aldrich) was put into the oven nozzle and further purified in situ by annealing at about 200 °C for more than 24 h before the experiments. In this way, contaminants within the CoPc sample, notably H_2O and phthalonitrile fragments, were removed. During the measurements, a cold trap, filled with liquid nitrogen, was employed to improve the background pressure of the experimental chamber. CoPc was sublimed at 435 °C during the PES and XAS measurements, resulting in a pressure in the high 10^{-8} mbar range.

The binding-energy scale of the PE spectra was calibrated by simultaneously measuring CoPc and a reference gas introduced into the experimental chamber (giving a pressure of about 10^{-5} mbar). The Ar $3p_{3/2}$ line, set to its nominal binding energy of 15.76 eV,²² was used to calibrate the valence spectra taken at $h\nu = 50$, 100, and 150 eV. The resolution of the valence photoemission spectra varied with photon energy but was always better than 100 meV. For the comparisons, the different valence spectra, including the simulated ones, were normalized to their total area between binding energies of 5.5 and 12.4 eV.

The C 1s and N 1s PE spectra and the N K-edge XA spectrum of gas-phase CoPc are very similar to the already published results for other TMPs in the gas phase⁸ as well as CoPc in the solid state.¹¹ We include these spectra (to our knowledge, the first PES and XAS measurements of CoPc in the gas phase) in the Supporting Information. CO_2 and N_2 gases were used to calibrate the C 1s ($h\nu = 382$ eV) and N 1s ($h\nu = 495$ eV) spectra, respectively. Both types of spectra were recorded with an overall resolution of about 390 meV.

XA spectra were obtained by integrating the constant-final-state (CFS) spectra with a Scienta SES200 analyzer set to the fixed kinetic energy windows of the N KVV and Co $L_{3M_{23}M_{23}}$ Auger electrons while the photon energy was scanned across the N K-edge and Co L-edge XAS regions, respectively. The absorption intensity was normalized to the transmitted photon flux measured with a calibrated Si photodiode. The photon energy was calibrated using the absorption structure of N_2 (N 1s to π^* , $\nu' = 1$) at 401.10 eV measured simultaneously with the CoPc N K-edge spectrum. In the case of the Co L-edge spectrum, an absolute photon energy calibration was achieved by measuring the Ar 2p photoemission core level, whereas the kinetic-energy window was calibrated with Xe MNN Auger lines. The overall resolution of the absorption spectra was approximately 110 meV for the N K-edge and 600 meV for the Co L-edge.

The CoPc film measurements were performed at the LowDosePES endstation at the PM4 dipole beamline of the BESSY II synchrotron in Berlin, Germany. This beamline is equipped with a novel angle-resolved time-of-flight (ArTOF) spectrometer.²³ The clean Au(111) surface was prepared by sputtering and annealing cycles, and the CoPc films were grown by thermal evaporation from a quartz crucible that was resistively heated by a tantalum wire. The CoPc monolayer (1 ML) sample shown in Figure 4 was achieved by deposition of a multilayer onto the Au(111) substrate and subsequent flashing to 410 °C, a temperature well above that needed for desorption of the multilayer (i.e., ~300 °C).²⁴ The thickness of the “flashed” sample was further confirmed by the attenuation of the XPS Au 4f signal. The valence-band spectrum of the flashed sample was used as a reference for determining the coverage obtained using different deposition times and assuming a constant evaporation rate at the applied current of 4.65 A. Under our experimental conditions, 100 min of deposition was needed to reproduce the 1 ML flashed sample. Other samples thicknesses, namely, 0.3, 0.6, 0.9, and 4.5 ML, were determined by evaluating the times needed for their preparation, namely, 30, 60, 90, and 450 min, respectively. However, for the very long deposition time (450 min), the actual evaporation rate could be different from the considered constant rate, and therefore, 4.5 ML should be considered only as a nominal value. Aside from the possible lower coverage than we assumed, a Stransky–Krastanov growth (1 ML + islands) could explain the fact that both the Fermi level and the interface state (IntS) are still clearly visible in the spectrum of 4.5 ML (Figure 4). The island-growth mechanism is also supported by a previous study.¹¹ The spectra shown in Figure 4 were normalized to the intensity of the Au Fermi level.

3. THEORETICAL METHODS

The molecular geometry of CoPc was optimized within density functional theory (DFT) using an optimally tuned range separated hybrid (OT-RSH) functional^{25–31} based on the exchange–correlation functional of Perdew, Zunger, and Ernzerhof,^{32,33} as implemented in the Gaussian 09 quantum chemistry software.³⁴ The 6-31G(d,p) basis set³⁵ was used for H, C, and N, whereas cc-pVTZ³⁶ was used for Co. The range-separation parameter (γ) and amount of exact exchange (α) were tuned as to fulfill the ionization energy theorem for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The optimal parameters obtained in this way were³¹ $\alpha = 0.1$ and $\gamma = 0.146 \text{ bohr}^{-1}$. Using the relaxed geometry, the electronic structure was calculated, and a full population analysis was performed. The atomic contributions to each molecular orbital were determined using the c^2 method,³⁷ as performed in previous studies.^{8,38,39} The DFT-derived density of states for the CoPc ground state with atomic-orbital- and spin-resolved contributions, for both occupied and unoccupied valence states of CoPc, is shown in Figure 1c. To facilitate the comparison with the experiment (as shown in Figure 3a), the total eigenvalue spectrum was obtained by summing the atomic contributions multiplied by the dipole photoionization cross sections.^{38–40} The C 2p, N 2p, and Co 3d atomic components multiplied with cross sections are also shown separately. All calculated spectra were broadened using Gaussian functions of 0.3 eV constant full width at half-maximum (fwhm). Using the optimal parameters $\alpha = 0.1$ and $\gamma = 0.146 \text{ bohr}^{-1}$, the HOMO was calculated at a binding energy of 6.15 eV, in good agreement with the

measured value of 6.38 eV. The ground-state electronic configuration obtained in this way consists of a ligand HOMO and a singly occupied a_{1g} (d_z^2) orbital, corresponding to the $^2A_{1g}$ electronic structure (Figure 1b).

The simulated XAS results were generated using multiplet ligand-field theory (MLFT) with the Quanty package^{41–43} through a fit to the experimental L -edge spectrum. Because the propagation of a 2p electron into unoccupied 3d states can be regarded as a local process and the 2p wave function has strong overlap with the 3d wave function,⁴⁴ a wave function approach employing a model Hamiltonian can accurately describe the multiplet effects in 2p XAS and provide further information on the electronic states of the CoPc molecule. In contrast to DFT, MLFT obtains an exact solution, but the model is simplified. Only 2p and 3d states of the impurity, here, the Co atom, and 10 ligand states accounting for the Pc macrocycle are used. Within MLFT, the relative energies between the 3d levels are described by the Ballhausen parameters,⁴⁵ which, in the case of D_{4h} symmetry, are the three parameters 10Dq, Dt, and Ds. We determined them by fitting to experiment. The simulated spectra were then obtained with the Ballhausen parameters set to 10Dq = 2.8 eV, Dt = −0.15 eV, and Ds = 1.0 eV assuming D_{4h} symmetry of the ligand field, a charge-transfer energy of 8 eV, and monopole (multipole) Slater parameters reduced to 75% (88%) of their Hartree–Fock values. Lifetime broadening was added to the L_2 and L_3 parts of the spectra with fwhm values of 0.4 and 0.2 eV, respectively. The effects of the vibrations and of the experimental broadening were taken into account together by a convolution with Gaussian curves with a fwhm of 0.1 eV increasing to 0.60 at 17 eV from the first transition.

4. RESULTS AND DISCUSSION

Accurate information on the electronic structure of the free CoPc molecule is fundamental for clearly identifying the effects of various substrates on the electronic and magnetic properties of CoPc. This knowledge is, in turn, crucial for implementing CoPc in single-molecule devices for electronics or spintronics.

Figure 2a shows the XA spectrum of CoPc in the gas phase at the Co $L_{2,3}$ edge, which is, to the best of our knowledge, the first such spectrum ever published. The energy separation between the L_3 peak (generated by a Co 2p core hole with quantum number $j = 3/2$) and the L_2 peak (with $j = 1/2$) amounts to 15 eV. The L_3 peak is formed by two components that originate from two main subgroups of transitions: at lower photon energy (778.2 eV), a π^* resonance (A), and at higher photon energies (780.2 and 781.4 eV respectively), two σ^* resonances (C1, C2).

To better understand the origin of these peaks, we performed an angle-resolved MLFT simulation of the spectra, also shown in Figure 2a, where the in-plane (IPL, blue-filled curve) and the out-of-plane (OPL, green line) contributions are resolved. The calculated angle-resolved spectrum also agrees well with previous X-ray linear dichroism measurements performed on CoPc films,^{1,46} indicating the accuracy of our theoretical model. As an aid for the discussion, we also report the unoccupied DOS (Figure 2c), which is an enlargement of Figure 1c, where atomic-orbital- and spin-resolved ground-state DFT calculations of the filled and empty valence states of CoPc are given.

We observe that the three main peaks of the Co L -edge XA spectrum (A, C1, and C2) correspond to the same unoccupied d orbitals (a_{1g} spin-down, b_{1g} spin-up, and b_{1g} spin-down) as predicted by our ground-state DFT calculations, in good

Figure 2. (a) Co L -edge X-ray absorption spectrum (shown in red) in comparison with the multiplet ligand-field theory (MLFT) angle-resolved simulation (shown in black), where the in-plane (IPL, blue filled) and out-of-plane (OPL, green) contributions are resolved. (b) Enlargement of the Co L_3 -edge X-ray absorption spectrum. (c) Enlargement (from Figure 1c) of the DFT orbital- and spin-resolved atomic contributions to the unoccupied valence states. A Gaussian broadening of 0.3 eV fwhm was added to the DOS, and the metal 3d contributions were multiplied by a factor of 4 for clarity.

agreement with the results from ref 47. Therefore, according to our MLFT and ground-state DFT simulations, the main peak A is an out-of-plane feature, and it is associated with a $2p_{3/2}$ transition into the spin-down a_{1g} (d_z^2) level, whereas the C1 and C2 peaks correspond to excitations from $2p_{3/2}$ into in-plane orbital b_{1g} ($d_{x^2-y^2}$), having their lobes directed toward the nitrogen ligand, with spin up and spin down, respectively. Analogously, the A', C1', and C2' peaks of L_2 are related to the transitions from Co $2p_{1/2}$ to a_{1g} spin-down, b_{1g} spin-up, and b_{1g} spin-down states, respectively. In comparison to the L_3 peaks, these L_2 features are broader, but the energy differences between A' and C1' and between C1' and C2' are roughly the same as observed for the L_3 edge. This represents an additional important confirmation that the $^2A_{1g}$ electronic configuration is the ground-state electronic configuration of the CoPc molecule. It is important to note that there is an interesting low-intensity feature in our XAS results, labeled B in Figure 2b, that has also been observed in previous studies on CoPc thin films⁴⁶ and attributed to transitions to the e_g state. However, this does not imply that the e_g d orbital is the one where the 3d hole is located (see the discussion in the Introduction, as well as refs

39 and 48). In fact, our ground-state DFT calculations reveal that the LUMO of CoPc contains a small contribution from the e_g Co states, which hybridize with the p_z orbitals of the pyrrole and aza-bridge N atoms (Figure 2c). It is very likely that feature B in our L_3 -edge XAS spectrum is due to the transition of the Co $2p_{3/2}$ electron to this hybrid molecular orbital. The switch in energy positions of peaks B and A compared to the ground-state case (where the a_{1g} orbital is above the LUMO) is most probably due to the presence of the core hole (absent in the DFT calculations). The core hole created in the X-ray absorption process is known to cause an energy shift of the empty valence levels, likely affecting the energy positions and populations of the a_{1g} orbital and the LUMO.

To identify the chemical characters of the different molecular valence states and, in particular, of the debated HOMO, we collected valence-state photoemission data for gas-phase CoPc at different photon energies. In this way, we could take advantage of the different photon-energy dependences of the photoemission cross sections of the C 2p and N 2p orbitals as compared to the Co 3d states.⁴⁰ In particular, the intensity of Co photoemission peaks increases with increasing photon energy (as expected for heavier elements). The validity of the method has largely been shown in previous studies.^{8,9,38,49} The photon-energy-dependent valence-level photoemission spectra recorded with photon energies of 50, 100, and 150 eV are shown in Figure 3a, together with theoretical PE spectra where the different PDOS were normalized for the corresponding experimental photoemission cross sections. In Figure 3b, the ground-state calculated DOS is shown. The different photoemission features are labeled with letters from A to I. In all experimental spectra, one can clearly distinguish the HOMO (A, A' in Figure 3) located at 6.38 eV. The intensity of the HOMO decreases with increasing photon energy. Similarly, features D and E become weaker when the excitation energy is increased from 50 to 150 eV. On the other hand, features B, B', and C are clearly increasing in intensity, as are shoulders C' and F', which become more visible as the photon energy increases. Therefore, from these experimental results, we can already conclude that the HOMO, as well as the D and E features, mostly originate from the organic ring of the molecule, formed by C and N atoms, whereas the B, B', C, C', F, and F' features have a larger Co character.

The DFT calculations provide an analogous picture for the organic versus metallic occupation of the valence levels; however, the binding-energy values of the peaks below the HOMO are generally overestimated by theory. The $^2A_{1g}$ electron configuration, determined using an OT-RSH functional with $\alpha = 0.1$ and $\gamma = 0.146 \text{ bohr}^{-1}$, was used for ground-state CoPc. The theoretical data resolving different atomic contributions (C, N, and Co) are also shown in Figure 3, allowing the respective atomic contributions to be assigned in detail to the features observed in the experimental valence spectra. The comparison with the DFT results indicates that the HOMO, predicted at 6.15 eV in very good agreement with the experimental binding energy, fully originates from the C 2p states. The computed HOMO is an a_{1u} molecular orbital coming from the C–C hybridization of π -type orbitals, as already proposed in previous studies.^{6,7} Furthermore, peaks B, B', C, C', F, and F' have significant Co 3d contributions, in agreement with our experimental results. On the other hand and as observed in the experiment, peak D mostly originates from 2p ligand states. A slightly different situation is observed for feature E, whose intensity does not drop as much as for

Figure 3. (a) Experimental valence-state photoemission spectra of CoPc in the gas phase, taken with photon energies of 50, 100 and 150 eV (black points) compared with the calculated valence spectrum (reported only for 50 and 150 eV) for a ground-state configuration of $^2A_{1g}$, determined using the OT-RSH functional with $\alpha = 0.1$ and $\gamma = 0.146 \text{ bohr}^{-1}$ (black line) and multiplied by cross sections. The spectra were normalized to the total area, and the calculated results were broadened using Gaussian functions of 0.3 eV fwhm. The most significant spectral features are labeled using capital letters from A to I. The arrows emphasize the positions of shoulders F' and C', barely visible at 50 eV but more evident at higher photon energies. The calculated C 2p (green), N 2p (blue), and Co 3d (orange) contributions are also shown. (b) Calculated valence electronic structure with orbital- and spin-resolved atomic contributions. The intensities of the metal d states were multiplied by a factor of 4 for clarity.

other ligand peaks in the experiment. This could suggest a metal–ligand mixed character, as shown, for example, in the region at about 9 eV in Figure 3b.

An analysis of the individual Co 3d levels as obtained from the DFT calculations (Figure 3b) suggests that the binding-energy region of peaks B, B', and C comprises mostly e_g states, whereas the b_{2g} spin-up and spin-down components can be associated with part of the C and C' features, respectively. The singly occupied a_{1g} state, along with b_{2g} , contribute mostly to the F and F' features.

To carefully address the character of the HOMO and to investigate whether any metal contributions could be hidden underneath the HOMO peak, we studied CoPc films of different thicknesses grown on a Au(111) surface. The comparison of the gas-phase valence-state photoemission spectrum with that of a thick Pc film is justified by the observation that CoPc maintains its molecular character in the latter configuration, in analogy with what was observed for other PCs; see, for example, the results for FePc films.⁸ This is important in allowing us to adapt the conclusion drawn about

the ligand character of the CoPc HOMO in the solid phase to the molecular case. The detailed comparison between the CoPc gas-phase and film valence-band PE spectra is shown in the Supporting Information.

In Figure 4, we present the valence PE spectra of a clean Au(111) substrate and of CoPc films of about 0.3, 0.6, 1, and

Figure 4. Valence-band photoemission spectra of CoPc deposited on Au(111) at the given molecular thicknesses, taken with a photon energy of 80 eV. Inset: Comparison of valence-band photoemission spectra of the 1 ML sample taken with photon energies of 57 and 80 eV. All spectra were normalized and calibrated at the Fermi edges. The features due to the molecular HOMO and to the interface state (IntS), formed between the Co 3d out-of-plane orbital (a_{1g}) and the gold valence states, are indicated in the figure.

4.5 ML thicknesses grown on the Au(111) surface, recorded with an ArTOF spectrometer. The comparison of the spectra highlights the evolution of the HOMO peak for increasing molecular coverage, with a final binding energy of 1.15 eV for the 4.5 ML deposition. However, the spectra also show another less intense peak at a binding energy of about 0.6 eV (labeled IntS in Figure 4) that can be distinguished very clearly beginning in the early stages of deposition. This state has been ascribed to an interface state (IntS), a pure metal state originating from the interaction between the Co 3d out-of-plane orbital (a_{1g}) and the delocalized states of the gold surface.^{11,46}

We subsequently performed a further photon-energy-dependent valence photoemission investigation to carefully address the character of the HOMO by following the intensity variations of the HOMO as compared to those of the purely metallic interface.^{11,46} The inset in Figure 4 shows the comparison of the photoemission spectra of the 1 ML sample recorded at two different photon energies, namely, 57 and 80

eV. The intensity of the interface state at about 0.6 eV does not change much in the spectra, as expected because of the quite similar photoionization cross sections of the Co 3d states at such photon energies. In contrast, the HOMO peak is more intense in the spectrum taken at lower photon energy (57 eV). Indeed, the photoionization cross sections for Co 3d and C 2p levels imply that the intensity of the C 2p-related features almost doubles when passing from 80 to 57 eV.⁴⁰

For a more quantitative analysis, we performed a simple fit (shown in the Supporting Information) of the two features, namely, the HOMO and IntS, for 0.6, 0.9, and 1 ML samples measured at 57 and 80 eV. Using this fitting procedure, we found that the HOMO/IntS intensity ratios measured at the two different photon energies correlate well with the corresponding C 2p/Co 3d cross section ratio.⁴⁰ These values and their reproducibility for the different coverages represent more solid evidence for the conclusion that we drew previously from gas-phase and theoretical results, namely, that the HOMO is due to only the organic ligand of the molecule and that the metallic contribution is negligible. The IntS peak is instead assigned to a pure metallic interface state, with contributions from the Co atom, in agreement with previous studies.^{6,11,46}

5. CONCLUSIONS

Gas-phase CoPc was characterized by core and valence PES and XAS; the valence PE and Co *L*-edge XA spectra were compared to theoretical calculations. The calculated electronic structure is in good agreement with the experimental findings. The DFT simulations indicate that the CoPc ground state is well-described by the ²A_{1g} configuration. DFT simulations were also used to assign which atoms contribute to the different valence states. By comparing valence photoemission results for the gas phase and thin films of CoPc on a single-crystal Au(111) surface, we definitively assigned the HOMO of CoPc to the organic ligand of the molecule alone, as also predicted by our DFT calculations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b08524.

C 1s and N 1s core-level photoemission (PE) spectra of gas-phase CoPc with fits, N *K*-edge NEXAFS spectrum of gas-phase CoPc, comparison between the valence PE spectra of gas-phase and thick-film CoPc, fits of the CoPc 1 ML VB measured at 57 and 80 eV with the HOMO and the interface state (IntS) features (PDF)

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Notes

The authors declare no competing financial interest.

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