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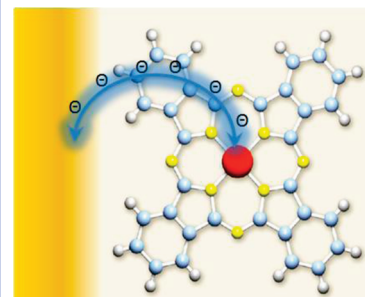
# Interaction between Cobalt Phthalocyanine and Gold Studied by X-ray Absorption and Resonant Photoemission Spectroscopy

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**ABSTRACT** Cobalt phthalocyanine (CoPc) monolayer films evaporated on Au(100) are studied by photoexcited electron spectroscopies: X-ray absorption (XAS) and resonant photoemission spectroscopy (ResPES). According to XAS data, the Co 2p absorption spectra look different for monolayer and thicker organic films, pointing to a possible interaction of the molecules with the substrate via the Co d electrons. The contribution of Co-related states in the valence band of CoPc was observed with ResPES. The conclusions are discussed in combination with core-level X-ray photoemission spectroscopy (XPS), X-ray excited Auger electron spectroscopy (XAES), and valence band ultraviolet photoemission spectroscopy (UPS) results previously obtained.

**SECTION** Surfaces, Interfaces, Catalysis



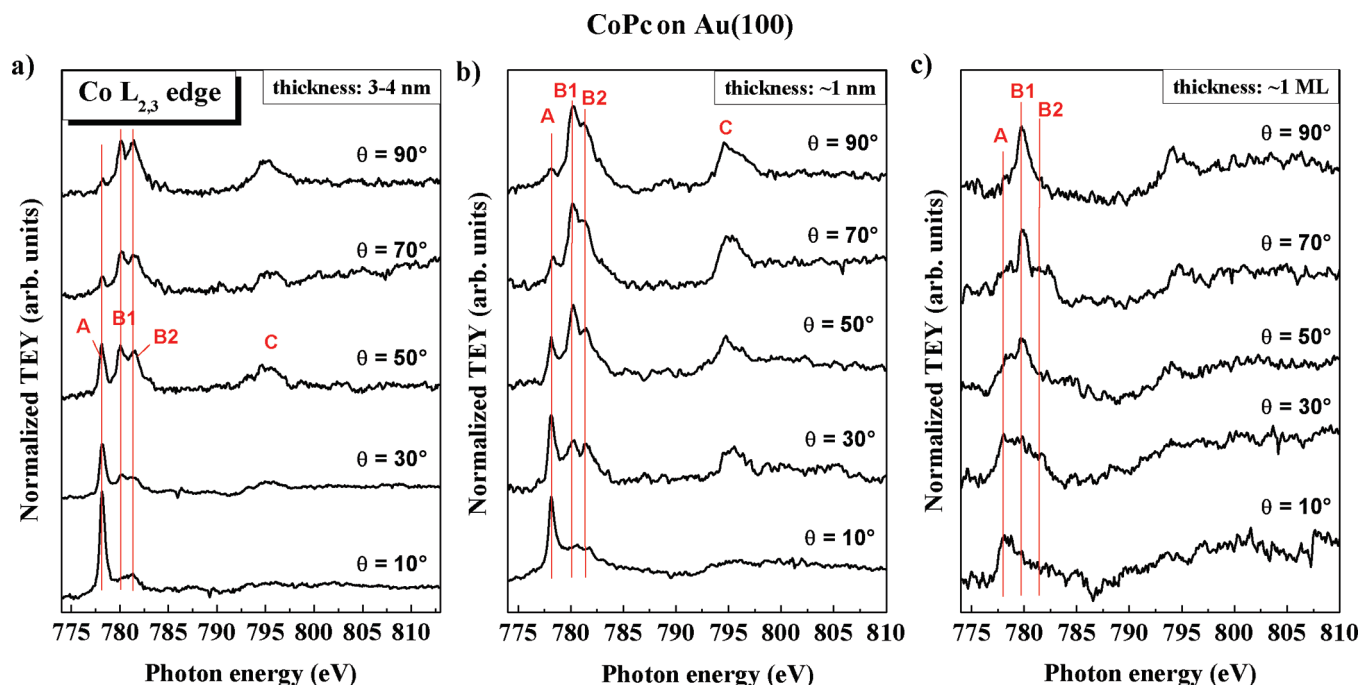
The understanding of the processes occurring at the interface between an organic film and a metallic substrate is crucial for many technological applications because the structural and morphological details of the organic-metal interface play a fundamental role in optimizing the performance and efficiency of organic-based devices.<sup>1–4</sup> Metal phthalocyanines (MPcs) are a family of quite stable molecules that form organic semiconductors in their solid state, and they have a wide range of applications in organic electronic devices (e.g., solar cells, gas sensors, light emitting diodes, and thin film transistors).<sup>5</sup> Transition-metal phthalocyanines are of particular interest because they exhibit magnetic properties<sup>6–8</sup> and could be of significant importance in the field of molecular spintronics.<sup>9,10</sup> In the present study, the focus is on a transition MPc, cobalt phthalocyanine (CoPc), and its interface with a single crystalline gold Au(100) substrate. The electronic structure of ultrathin films of CoPc is investigated by high-energy spectroscopic techniques: X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and resonant photoemission (ResPES). ResPES is used for the experimental analysis of the contribution of different chemical species to spectral valence band features.

XAS monitors transitions from a core level into unoccupied (valence) and following orbitals, most notably to the LUMO (lowest unoccupied molecular orbital). Peaks in XAS spectra therefore correspond to the resonance energies for the excitation of an electron from a core level of a specific atomic site to unoccupied molecular orbitals ( $\pi^*$  and  $\sigma^*$  orbitals). The core-electron molecular excitation is subject to strict selection rules, and the spectra of oriented samples show significant dependence on the polarization of the incident light.<sup>11–14</sup>

From polarization-dependent N 1s absorption spectra (not shown here), we conclude that the CoPc molecules are lying flat with their molecular plane parallel to the surface of the single-crystalline Au(100) substrate, in good agreement with previous publications.<sup>8,15,16</sup> The dipole selection rules for core excitations into various vacant states enable angle-dependent XAS to be used as a sensitive probe of the anisotropy of these systems and provide detailed insight into bond orientation, the unoccupied electronic structure, and the symmetry of the frontier orbital states. Moreover, multiplet effects play an important role in XAS and XPS; the reason is the strong overlap of the core wave function with the valence wave functions. For example, for the Co 2p excitation spectra, the final state of an X-ray absorption process consists of a partially filled 2p<sup>5</sup> core state and incompletely filled 3d valence states. The wave function overlap between 2p and 3d holes now leads to several largely screened final states, which determine the shape of the XAS spectrum. For a detailed discussion of so-called multiplet effects, see, for example, ref 17. In Figure 1, the Co 2p excitation spectra of CoPc on Au(100) are depicted for nominal film thicknesses of (a) 3 to 4 nm,<sup>15</sup> (b) 1 nm, and (c) 1 monolayer (ML). Features A and B in Figure 1 are attributed to transitions from the Co 2p<sub>3/2</sub> level into unoccupied molecular levels, whereas transitions from the Co 2p<sub>1/2</sub> level are visible in the photon energy range of 794 to 795 eV

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**Figure 1.** Co 2p excitation spectra of a (a) 3 to 4 nm, (b) 1 nm, and (c) 1 ML (about 0.35 nm) CoPc film on Au(100), taken with different angles of beam incidence. ( $\Theta = 90^\circ$  corresponds to normal and  $\Theta = 10^\circ$  corresponds to grazing incidence.)

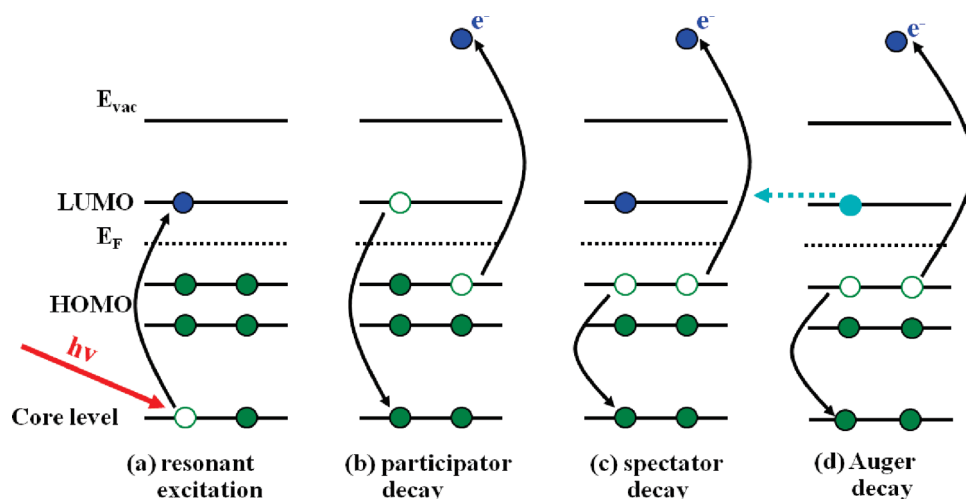
(feature C). Looking at Figure 1a, it becomes clear that two groups of Co  $2p_{3/2}$  excitations with different polarization dependence occur: at grazing incidence ( $\Theta = 10^\circ$ ), the intensity of feature A at 778.15 eV is maximal, whereas at normal incidence ( $\Theta = 90^\circ$ ), most intense features are B1 and B2 between 779 and 782 eV. Because the molecules adsorb in a lying geometry (concluded from N 1s XAS spectra<sup>15</sup>), the A transition is vertically polarized related to the molecular axis (z-polarized), whereas B1 and B2 are xy-polarized transitions (within the molecular plane). For similar films of a few nanometers, the spectra are discussed in detail in refs 15 and 16.

For the 1 nm CoPc coverage on Au(100) in Figure 1b, at first glance, the spectra look quite similar to the thicker (3 to 4 nm) film; however, distinct differences become visible. In particular, at grazing incidence, the relative intensity of feature A seems to be attenuated for the 1 nm film compared with the corresponding spectrum for a 3 to 4 nm thick layer (Figure 1a). Furthermore, at normal incidence, a clear enhancement of the B1 feature compared with all other features in the spectra of Figure 1b is quite obvious. Although the spectra appear to be more noisy for the monolayer coverage of CoPc in Figure 1c, it is clearly visible that this trend is further continued with lowering thickness. In this case, at normal incidence, the feature A has almost completely disappeared compared with the spectra acquired at grazing incidence, revealing the absence of z-polarized features. The B1 feature dominates the spectrum at normal incidence, whereas B2 is distinctly attenuated. (See Figure 1c.) In other words, there is a strong enhancement of the xy-polarized B1 feature for ML CoPc coverage at normal incidence. The disappearance of feature B2 may be likely explained by a charge transfer to CoPc at the interface to Au,

which could cause filling of the B2 (xy-polarized) Co-related states, and thus an excitation into these states is quenched. However, a possible modification of the ligand field experienced by the Co in CoPc at the interface to Au cannot be excluded, which could affect the electron redistribution at the Co site.

In the case of a charge transfer from Au to Co at the interface, the expected XAS final state of Co is  $d^9$ ; that is, the 2p hole can interact only with one hole in the d shell. This change of final-state occupation, in particular, decreases the possible number of features due to multiplet splitting. (In atomic multiplet theory, 16 transitions are allowed for  $3d^7 \rightarrow 2p^5 3d^8$ , whereas only 4 transitions appear for  $3d^8 \rightarrow 2p^5 3d^9$ .)<sup>17</sup> As a consequence, for Ni in NiPc ( $Ni^{2+}$ ;  $3d^8$ ) the  $2p_{3/2}$  absorption spectrum consists basically of a single intense feature beside weaker features.<sup>17</sup> Therefore, the observed disappearance of the above-discussed XAS features for CoPc/Au at monolayer coverage in Figure 1 supports the assumption of a charge transfer at this interface.

These observations are also strongly supported by previously acquired XPS, XAES, and UPS data concerning the CoPc/Au interface.<sup>18</sup> According to these measurements, the shapes of the XPS and XAES spectra appear to be different for monolayer CoPc coverage and the subsequent layers of thicker films. This can be understood in the frame of charge transfer processes at the interface or by a different splitting of the transition-metal 3d states.<sup>18–21</sup> This suggestion has been further supported by results of UPS measurements where a layer-dependent splitting of the CoPc HOMO is observed beyond ML coverage on Au. To some extent, this apparent splitting may be assigned to polarization screening of the CoPc layers with different distances to the mirror plane of the



**Figure 2.** Schematic overview of the working principle of the core-hole spectroscopy. (a) A core level electron is resonantly excited into adsorbate unoccupied molecular orbital (LUMO). This excited electron can (b) participate in the decay process leading to a one-hole final state (participator decay), (c) be passive as a spectator leading to a two-hole one-electron final state (spectator decay), or (d) follow the normal Auger process (Auger decay).

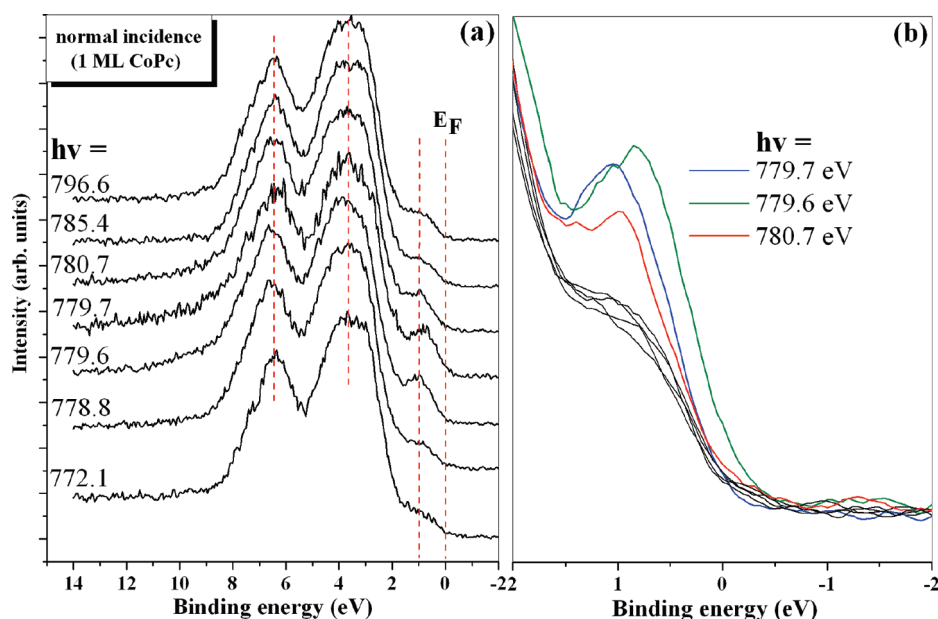
metallic substrate at the interface,<sup>18</sup> but it may also point to a formation of molecule-induced states close to the Fermi level due to an interaction of the Co d states with states of the metallic substrate.<sup>18,22</sup> A local charge transfer toward the Co atom from the metal substrate affects the charge state of the Co ion.

Different Co-related valence states can be distinguished by ResPES.<sup>15</sup> ResPES is carried out by sweeping the photon energy in discrete steps over the respective absorption edge while detecting electrons emitted from the valence region. Therefore, this technique will enhance features in the valence region originating from the element carrying the original (X-ray absorption induced) core hole, allowing a “site specific” analysis of the valence band.<sup>23–25</sup> The working principle of this synchrotron-based method is summarized in the Figure below (Figure 2). When a photon with energy of  $h\nu$  is absorbed, the core-level electron is excited into an empty conduction band state or an unoccupied molecular orbital, leading to the formation of an excited electron in previously unoccupied level and a core-hole (Figure 2a). If this electron is localized in the unoccupied molecular orbital during the lifetime of the core-hole, then the core-hole decays through the participator (Figure 2b) or spectator (Figure 2c) processes. Therefore, a particular valence state or HOMO level of the molecule is enhanced at a certain photon energy, called “resonant enhancement”. (The resonantly enhanced peak possesses a constant binding energy (BE).) If this electron becomes delocalized over many atomic centers or it is delocalized at interfaces, then the core-hole decays via the normal Auger process (Figure 2d). In the participator decay channel (Figure 2b), the resonantly excited electron fills the core-hole; then, an electron in a particular valence level takes up the excess energy released in the above transition process, and it is ejected. The final system in this case has a single photoemission.

In recent ResPES experiments,<sup>15</sup> for a 3 to 4 nm thick CoPc film deposited on Au(100), it was found that at grazing

incidence z-polarized transitions at 778.15 eV (feature A in Figure 1) related to the molecular axis cause an enhancement of a valence band feature at  $\sim 4$  eV,<sup>26</sup> whereas at normal incidence, the xy-polarized excitations between 779 and 782 eV (B1 and B2 in Figure 1) resonantly enhance, in particular, valence band features in the HOMO region<sup>27</sup> accompanied by an intensity enhancement between 7 and 10 eV. We will focus here on the nature of the B feature for CoPc monolayer coverage. Valence band spectra taken in the photon energy range at the Co  $2p_{3/2}$  absorption edge are shown in Figure 3 for an ML of CoPc on Au(100). The spectra were acquired at normal incidence, and the intensity is normalized to the intensity of the most intense feature. The spectra are dominated by Au-d band emissions. However, relative intensity changes are due to electron emission from the monolayer CoPc film and, in particular, from Co-derived states. The spectrum at  $\sim 772$  eV is well below the resonance energy, that is, below the absorption onset in the Co XAS spectra in Figure 1. Beyond 778.8 eV, the absorption onset has been passed, and there is a slight increase in the background intensity at higher BE, suggesting some resonant contribution to the signal. In the range from 779 to 782 eV (where the X-ray absorption maxima are observed in XAS) a slight increase in the background intensity beyond the Au d-band emission and a significant resonant enhancement of the HOMO peak intensity occur. This can be seen more clearly in Figure 3b, where we zoom in the low BE region. Most importantly, we observe the enhancement in the energy range of the HOMO, which is located at a BE of  $\sim 1.0$  eV for the energy around the B1 structure (at  $\sim 780$  eV) in the XAS spectra.

The occurrence of resonant enhancements for the excitation energies corresponding to the absorption structures suggest that these resonant features have their origin in Co (3d)-derived orbitals. In other words, the Co (3d) orbitals significantly contribute to the valence level structure of the CoPc molecule and, in particular, to the HOMO region.<sup>24</sup> A possible redistribution of the Co d-electrons ( $\text{Co}^{2+}$ :  $d^7$ ) results



**Figure 3.** (a) Resonant photoemission spectra acquired at normal incidence from a 1 ML pristine CoPc film deposited on a Au(100) surface. (b) Zoom into the low-energy region to highlight the enhancement of the HOMO peak.

in an unpaired hole in the  $xy$  direction and therefore in the presence of new  $xy$ -polarized states at the spectra. This is also in agreement with the previously presented XAS data. A similar behavior was also observed for a thicker (3 to 4 nm) CoPc film,<sup>15</sup> where in the absorption range of the B features the HOMO is enhanced. In contrast with the thicker (3 to 4 nm) CoPc film, no clear background increase within the resonance, due to the presence of normal Auger transitions,<sup>23</sup> is observed at the selected energies for the monolayer film. Therefore, the quite strong enhancement of the particular HOMO feature at monolayer CoPc coverage related to participator decay processes may point to a stronger localization of the corresponding Co-related states.

Synchrotron-based photoexcited electron spectroscopic measurements on the CoPc/Au(100) interface were used to elucidate the electronic structure and chemical bonding of the organic molecules. Angular-dependent XAS measurements revealed new features in the spectra for ML coverage compared with thicker overlayers, which are attributed to unoccupied states contributing to the  $xy$ -direction. A possible interaction of the d-Cobalt states with the metallic substrate could be also present.

## EXPERIMENTAL METHODS

The near-edge X-ray absorption fine structure and the ResPES measurements were carried out at the third-generation synchrotron radiation source BESSY II (Berlin) using the Optics-beamline and the end-station SURICAT. The photon energies were calibrated by comparing the BE of the Au  $4f_{7/2}$  peak excited by first- and second-order light. The XAS measurements were performed in total-electron yield (TEY) mode, measuring the drain current, with a resolution of  $\sim 100$  meV at photon energy of 400 eV. The spectra were normalized to have the same absorption edge step height well

above the threshold. The energy resolution for the ResPES measurements was set to  $\sim 200$  meV. The single-crystalline Au(100) substrate was cleaned prior to organic film deposition by repeated argon ion sputtering and annealing cycles, and the cleanliness was checked by XPS. Ultrathin films of CoPc, purchased from Aldrich, were thermally evaporated on Au(100) in ultra high vacuum (base pressure  $< 1 \times 10^{-8}$  mbar) from a temperature-controlled crucible with evaporation rates between 0.1 and 1 nm/min. The film thickness was estimated from both a quartz microbalance and the XPS intensity ratios, assuming layer-by-layer growth in each step of deposition.

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## REFERENCES

- Ueno, N.; Kera, S. Electron Spectroscopy of Functional Organic Thin Films: Deep Insights into Valence Electronic Structure in Relation to Charge Transport Property. *Prog. Surf. Sci.* **2008**, *83*, 490–557.
- Peisert, H.; Knupfer, M.; Schwieger, T.; Fuentes, G. G.; Olligs, D.; Fink, J.; Schmidt, T. Fluorination of Copper Phthalocyanines: Electronic Structure and Interface Properties. *J. Appl. Phys.* **2003**, *93*, 9683–9692.



- (3) Liao, M. S.; Scheiner, S. Electronic Structure and Bonding in Metal Phthalocyanines, Metal = Fe, Co, Ni, Cu, Zn, Mg. *J. Chem. Phys.* **2001**, *114*, 9780–9791.
- (4) Vollmer, A.; Jurchescu, O. D.; Arfaoui, I.; Salzmann, I.; Palstra, T. T. M.; Rudolf, P.; Niemax, J.; Pflaum, J.; Rabe, J. P.; Koch, N. The Effect of Oxygen Exposure on Pentacene Electronic Structure. *Eur. Phys. J. E* **2005**, *17*, 339–343.
- (5) Riad, S. Dark and Photoelectric Conversion Properties of *p*-MgPc/*n*-Si (Organic/Inorganic) Heterojunction Cells. *Thin Solid Films* **2000**, *370*, 255–257.
- (6) Kirner, J. F.; Dow, W.; Scheidt, W. R. Molecular Stereochemistry of Two Intermediate-Spin Complexes. Iron(II) Phthalocyanine and Manganese(II) Phthalocyanine. *Inorg. Chem.* **1976**, *15*, 1685–1690.
- (7) Molodtsova, O. V.; Knupfer, M.; Ossipyan, Yu. A.; Aristov, V. Yu. Molecular Orientation and Ordering in CoPc and FePc Thin Films Grown on Au(001)-5 × 20. *J. Appl. Phys.* **2008**, *104*, 083704–1–5.
- (8) Zhao, A.; Li, Q.; Chen, L.; Xiang, H.; Wang, W.; Pan, S.; Wang, B.; Xiao, X.; Yang, J.; Hou, J. G.; et al. Controlling the Kondo Effect of an Adsorbed Magnetic Ion Through its Chemical Bonding. *Science* **2005**, *309*, 1542–1544.
- (9) Bogani, L.; Wernsdorfer, W. Molecular Spintronics Using Single-Molecule Magnets. *Nat. Mater.* **2008**, *7*, 179–186.
- (10) Sanvito, S. Injecting and Controlling Spins in Organic Materials. *J. Mater. Chem.* **2007**, *17*, 4455–4459.
- (11) Stöhr, J. *XAS Spectroscopy*, Springer-Verlag: Berlin, NY, 1992.
- (12) Johnstone, J.; Peacock, C.; Roberts, K. J. Application of Polarised NEXAFS Spectroscopy to the Structural Characterisation of Condensed Molecular Surfaces and Interfaces. *J. Cryst. Growth* **1999**, *198–199*, 275–281.
- (13) Chen, J. G. NEXAFS Investigations of Transition Metal Oxides, Nitrides, Carbides, Sulfides and Other Interstitial Compounds. *Surf. Sci. Rep.* **1997**, *30*, 1–152.
- (14) Chen, W.; Wee, A. T. S. Synchrotron PES and NEXAFS Studies of Self-Assembled Aromatic Thiol Monolayers on Au(111). *J. Electron Spectrosc. Relat. Phenom.* **2009**, *172*, 54–63.
- (15) Peisert, H.; Biswas, I.; Aygül, U.; Vollmer, A.; Chassé, T. Electronic Structure of Cobalt Phthalocyanine Studied by Resonant Photoemission: Localization of Co-Related Valence Band States. *Chem. Phys. Lett.* **2010**, *493*, 126–129.
- (16) Kroll, T.; Aristov, V. Yu.; Molodtsova, O. V.; Ossipyan, Yu. A.; Vyalikh, D. V.; Buechner, B.; Knupfer, M. Spin and Orbital Ground State of Co in Cobalt Phthalocyanine. *J. Phys. Chem. A* **2009**, *113*, 8917–8922.
- (17) (a) de Groot, F. M. F. Multiplet Effects in X-ray Spectroscopy. *Coord. Chem. Rev.* **2005**, *249*, 31–63. (b) Krasnikov, S. A.; Preobrajenski, A. B.; Sergeeva, N. N.; Brzhezinskaya, M. M.; Nesterov, M. A.; Cafolla, A. A.; Senge, M. O.; Vinogradov, A. S. Electronic Structure of Ni(II) Porphyrins and Phthalocyanine Studied by Soft X-ray Absorption Spectroscopy. *Chem. Phys.* **2007**, *332*, 318–324.
- (18) Petraki, F.; Peisert, H.; Biswas, I.; Chassé, T. Electronic Structure of Co-Phthalocyanine on Gold Investigated by Photoexcited Electron Spectroscopies: Indication of Co Ion-Metal Interaction. *J. Phys. Chem. C* **2010**, *114*, 17638–17643.
- (19) Lukaszczuk, T.; Flechtner, K.; Merte, L. R.; Jux, N.; Maier, F.; Gottfried, J. M.; Steinrueck, H.-P. Interaction of Cobalt(II) Tetraarylporphyrins with a Ag(111) Surface Studied with Photoelectron Spectroscopy. *J. Phys. Chem. C* **2007**, *111*, 3090–3098.
- (20) Gottfried, J. M.; Marbach, H. Surface-Confined Coordination Chemistry with Porphyrins and Phthalocyanines: Aspects of Formation, Electronic Structure, and Reactivity. *Z. Phys. Chem.* **2009**, *223*, 53–74.
- (21) Bai, Y.; Sekita, M.; Schmid, M.; Bischof, T.; Steinrueck, H.-P.; Gottfried, J. M. Interfacial Coordination Interactions Studied on Cobalt Octaethylporphyrin and Cobalt Tetraphenylporphyrin Monolayers on Au(111). *Phys. Chem. Chem. Phys.* **2010**, *12*, 4336–4344.
- (22) Gargiani, P.; Angelucci, M.; Mariani, C.; Betti, M. G. Metal-Phthalocyanine Chains on the Au(110) Surface: Interaction States Versus *d*-Metal States Occupancy. *Phys. Rev. B* **2010**, *81*, 085412–1–7.
- (23) Bruehwiler, P. A.; Karis, O.; Mårtensson, N. Charge-Transfer Dynamics Studied Using Resonant Core Spectroscopies. *Rev. Mod. Phys.* **2002**, *74*, 703–740.
- (24) Bhatt, P.; Carlegrim, E.; Kancierzewska, A.; de Jong, M. P.; Fahlman, M. Electronic Structure of Thin Film Iron-Tetracyanoethylene: Fe(TCNE)<sub>x</sub>. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 131–138.
- (25) Vilmercati, P.; Cvetko, D.; Cossaro, A.; Morgante, A. Heterostructured Organic Interfaces Probed by Resonant Photoemission. *Surf. Sci.* **2009**, *603*, 1542–1556.
- (26) Maslyuk, V. V.; Aristov, V. Yu.; Molodtsova, O. V.; Vyalikh, D. V.; Zhilin, V. M.; Ossipyan, Yu. A.; Bredow, T.; Mertig, I.; Knupfer, M. The Electronic Structure of Cobalt Phthalocyanine. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *94*, 485–489.
- (27) Grobosch, M.; Aristov, V. Yu.; Molodtsova, O. V.; Schmidt, C.; Doyle, B. P.; Nannarone, S.; Knupfer, M. Engineering of the Energy Level Alignment at Organic Semiconductor Interfaces by Intramolecular Degrees of Freedom: Transition Metal Phthalocyanines. *J. Phys. Chem. C* **2009**, *113*, 13219–13222.