Site-Dependent Donation/Backdonation Charge Transfer at the CoPc/Ag(111) Interface

Marius Toader,*[,†] Pavel Shukrynau,[†] Martin Knupfer,[‡] Dietrich R. T. Zahn,[§] and Michael Hietschold[†]

[†]Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany
[‡]Leibniz Institute for Solid State and Materials Research IFW Dresden, D-01171 Dresden, Germany
[§]Chemnitz University of Technology, Institute of Physics, Semiconductor Physics, D-09107 Chemnitz, Germany

ABSTRACT: The organic/metal interface formed upon adsorption of cobalt(II) phthalocyanine (CoPc) molecules on a flat Ag(111) single crystal was investigated using a combination of scanning tunneling microscopy (STM) and photoemission spectroscopy (PES). A flat-lying molecular adsorption with the π conjugated phthalocyanine ligand parallel to the substrate was found to lead to an effective molecule−substrate coupling which governs a template-guided molecular growth. A voltage polarity dependence at the cobalt ion site was emphasized and correlated with the Co 2p core level spectra evolution which sustains an interface-confined reduction effect of the cobalt oxidation state. The formation of interface dipoles was observed via monitoring the changes in the work function (WF) upon deposition. The observations are discussed on the basis of a site-dependent donation/backdonation charge transfer at the molecule−substrate interface.
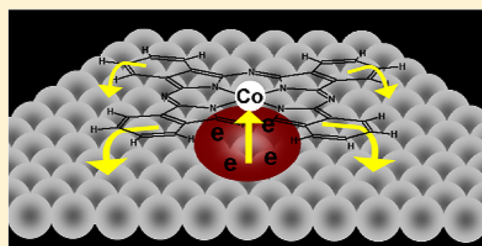
INTRODUCTION

There is no doubt nowadays that organic materials are well suited for novel hybrid electronics, since they already found their way into distinct industrial applications. However, the hybrid technology obeys the high demanding scaling down tendency where not only the small size issues turn into high challenges but also finding suitable and novel candidates requires intense research. For a successful development of ultimate future organic based nanodevices, the nowadays mostly used thick and bulky organic films will be presumably replaced with a limited number of individual molecules (or even with single molecules) which can self-assemble in well-defined defect-free arrays. The consequences could be outstanding in what concerns predicting, tuning, and controlling morphological and electronic properties down to the nanoscale. However, the final integration of only few organic molecules with inorganic counterparts toward developing a novel hybrid technology down to the nanoscale is definitely a process full of challenges. Therefore, the understanding of the organic/inorganic interface is strongly required; especially the corresponding importance grows tremendously at the nanoscale. Moreover, possible effects confined down to submolecular parts become of great precedence, since they might change or define the general behavior of the nanodevice. Among the organic materials, the family of metal phthalocyanines (MePc's) was intensively studied lately, since their huge variety of geometrical and electronic properties recommends them as suitable candidates to be used as active elements in organic based nanodevices. From p-type[1−3] to n-type[4−6] planar MePc's suited for OFET[7,8] or photovoltaic cell[9] applications toward nonplanar single-decker[10−12] or double-decker[13,14] MePc's appropriate as single-molecule switches[15,16] or single-

molecule magnets,[17−19] respectively, the class of MePc's is intensively addressed in research studies which emphasize the actuality, the novelty, and the almost unrestricted great potential for future hybrid technology. Starting with the pioneering work of Hipps et al.,[20] the protonated cobalt substituted phthalocyanine (CoPc), the molecule of interest in this work, became slowly an attractive system to be investigated due to highly interesting effects highlighted during the time. The corresponding suitability for spintronics, an area of great novelty and actuality, was emphasized using spin-polarized STM.[21,22] The protonated CoPc exhibits a ferromagnetic exchange interaction with underlying cobalt magnetic nano-leads,[21] while, in thin films, antiferromagnetic chains were found due to a superexchange mechanism pathway involving an E_g orbital of the phthalocyanine ring, the d_z^2 of the same molecule and the d_z^2 of the neighboring molecule.[22] With the same goal, a spin manipulation between the spin states "1/2" and "0" was recently reported by Wäckerlin et al.[23] in cobalt based phorphyrins via chemically induced NO attachment at the cobalt ion site. A first successful integration of the CoPc molecules with inorganic nanowire field effect transistors was proven by Duan et al.[24] where a bistable system switching between high and low conductance states was obtained. The fluorinated n-type counterpart $F_{16}CoPc$ is poorly reported in the literature.[3,6,25,26] We recently addressed an extended study of the system formed upon its corresponding adsorption on Ag(111).[25] The work is of importance, since very often analogies will be made with the present study in order to

elucidate similarities and differences such that a final under-standing will be achieved more easily. Due to the π conjugated molecular backbone, the CoPc molecules are expected, upon adsorption on a flat Ag(111) surface, to self-assemble in well-defined molecular arrays. To kick the hybrid technology one step forward, the present work addresses an extended study at the CoPc/Ag(111) interface. To help getting an enlarged overview of the system with no limitation to morphological/electronic or localized/averaged information, the actual study makes use of a combination of STM and PES. Moreover, the targeted molecular coverage is in the submonolayer regime for the STM study such that it facilitates the investigation from isolated toward a limited number of self-assembled molecules. Ultimately, effects confined to submolecular parts and their importance for the molecule/substrate coupling are emphasized and discussed. The observations are correlated with the PES study which helps to sustain and to complementarily interpret the results. The molecular coverage is tuned here from a submonolayer regime until a few stacked layers such that the interface-confined effects can be easier distinguished.

■ EXPERIMENTAL DETAILS

Both sample preparation and investigation as well as STM and PES experiments were performed *in situ* under similar ultrahigh vacuum (UHV) conditions (base pressure low 10^{-10} mbar). While for the first type of investigations an UHV variable-temperature STM was used, the PES experiments were carried out at the Material Science end-station at the Elettra synchrotron radiation facility in Trieste. All STM results were achieved at a temperature of 30 K using electrochemically etched tungsten tips (cut from a polycrystalline W wire). The photoemission spectroscopy (PES) data were recorded in the normal emission mode at room temperature. The Al Kα line (1487 eV) of an X-ray source was used to excite the XP spectra, while the used synchrotron radiation energy values are addressed later on. Prior to any deposition, the metal single crystal was cleaned *in situ* by repeated cycles of Ar$^+$ sputtering and subsequent annealing. For a high quality and purity molecular film, the organic material must be preliminarily degassed to reduce the amount of contaminations, since the impurities may have a strong negative impact on the self-assembled molecular structure. Therefore, thermal gradient sublimation was employed for the purification of the organic material purchased from Aldrich GmbH with purity larger than 97%. The molecular layers were grown using organic molecular beam deposition (sublimation temperature around 670 K) on the freshly cleaned metal substrate held at room temperature. While for the STM study a quartz microbalance thickness monitor was used to carefully control the amount of deposited organic material, for the PES experiments, the attenuation of the Ag 3d core level signal was used for the thickness estimation.[27] This procedure is known to be reliable only for layer-by-layer growth in the early deposition stage. Therefore, at higher coverage, the average estimation may deviate considerably from reality. However, for our study of ultrathin molecular films, this issue should not represent a drawback especially for the very first monolayers.

■ RESULTS AND DISCUSSION

A typical high resolution STM image for CoPc on Ag(111) is shown in Figure 1a. At the investigated submonolayer coverage, an agglomeration of the molecules to the step edges (the most energetically favorable regions) is observed. Besides the disordered areas, typical for these regions and coverage regime, highly oriented molecules can be identified as single molecules as well as arrays. Adsorbing with the π conjugated molecular plane parallel to the metal surface, the corresponding molecular orientation is guided by the substrate symmetry. Therefore, template-guided isolated molecules are found to align one molecular axis with one of the three main crystallographic
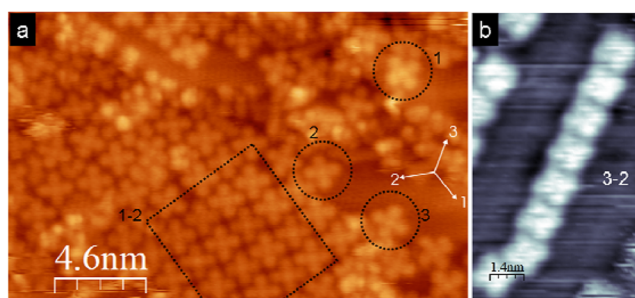

Figure 1. STM images of CoPc adsorbed on Ag(111) denoting a molecular agglomeration in the step edge proximity ($V_{sp} = -1$ V, $I_{sp} = 100$ pA) (a) and a highly oriented molecular nanochain ($V_{sp} = +1.8$ V, $I_{sp} = 150$ pA) (b).

directions of the silver substrate (refer to the marked molecules 1, 2, and 3 within Figure 1a). The surface symmetry directions depicted in Figure 1a are valid for all STM images used in this work. Individual molecules can be identified as four-leaf patterns (refer to the inset of Figure 5 for the molecular structure) due to the outer π orbitals delocalized over the phthalocyanine ligand. However, an insight into the inner π orbitals was not possible most probably due to a corresponding rehybridization with the underlying surface states, highly sustainable by the flat-lying molecular adsorption. The effect is less pronounced for the nonplanar MePc's like single-decker SnPc[11] or double-decker LuPc$_2$,[13] where the nonplanarity of the phthalocyanine ligand counteracts a strong rehybridization process via an effective decoupling from the underlying surface states. As a result, for both systems, more submolecular features could be emphasized under certain voltage conditions and correspondingly correlated with the 16 delocalized π orbitals as obtained from the DFT calculations.

When the molecules adsorb close to each other, the additional molecule−molecule interaction contributes to the final formation of the 1D or 2D molecular ordered arrays which are found to preferentially grow along the substrate symmetry directions. Consequently, crystallographically equivalent arrays are formed. They can be easily distinguished according to the same labeling procedure proposed for the adsorption of the F$_{16}$CoPc on Ag(111).[25] For example, refer to the highly oriented 1D molecular nanochain (3−2) and 2D molecular array (1−2) depicted within the Figure 1b and a, respectively. Here, the aligned molecules with one molecular axis oriented along the substrate direction 2 grow preferentially along the direction 3 or 1, respectively.

Despite the template-guided adlayer structure formation which is an indication for an effective molecule−substrate coupling, a conservation of the 4-fold molecular symmetry within the self-assembled molecular arrays was found. Therefore, compared to the substituted n-type counterparts (F$_{16}$CoPc), the protonated CoPc molecules assemble in a 4-fold symmetric square structure. The adlayer structure parameters, depicted within Figure 2, are summarized in Table 1. They are highly consistent with the work reported in the literature.[28] It was recently shown that FePc molecules obey a similar self-assembly mechanism.[29] However, the commensurate adlayer structure was reported to have higher packing density (0.55 molecules/nm^2)[29] compared to CoPc (0.46 molecules/nm^2).[28]

In conclusion, the effective molecule−substrate coupling together with the flat-lying molecular adsorption emphasized by
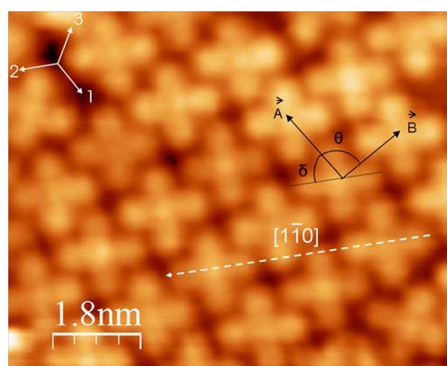
Figure 2. CoPc on Ag(111): highly resolved STM image of the corresponding close-packed adlayer structure (V_{sp} = −1 V, I_{sp} = 100 pA).

Table 1. Adlayer Structure Parameters

A (nm)	B (nm)	Θ (deg)	δ (deg)
1.58 ± 0.05	1.52 ± 0.05	94 ± 3	60 ± 1

the STM study sustain reasonably a better overlap between the out-protruding molecular wave functions (namely, the π orbitals of the aromatic stage and the d orbitals of the Co ion) and the underlying surface states. Consequently, site-dependent charge transfer effects are expected to occur at the interface, as will be shown later on.

The valence band (VB) evolution as a function of the CoPc molecular thickness is shown in Figure 3a. Similar to $F_{16}CoPc$,[25] molecular features are found to develop within the entire energy range with increasing film thickness while the Ag electronic states (between 4 and 8 eV) are gradually disappearing. However, the strong molecular features detected in the energy range (9−12 eV) for $F_{16}CoPc$ are missing, proving thus their origin and correlation to the fluorine atoms. Opposite to its n-type counterpart, a systematic work function decrease occurs for the p-type protonated CoPc upon stepwise deposition (see inset of Figure 3a). For a final investigated molecular thickness (1.67 nm), a work function value of 4.1 eV is reported. Variations in the work function defined as the difference between E_F and the vacuum level are consistent with the formation of interface dipoles. The corresponding

orientation (the sign of the induced dipole) is an indication for the doping character at the interface. Therefore, the induced interface dipole of Δ = −0.39 eV indicates a p doping character at the CoPc/Ag(111) interface accompanied with a hole injection from the metal surface states into the molecular orbitals. This scenario for the interface charge transfer is reasonably expected to appear, since according to DFT calculations[30] E_F for the CoPc free molecule was found to be located above the Fermi level of the silver single crystal. The reported value is in good agreement with previous work (Δ = −0.4 eV)[26] where a molecular film of ~2 nm CoPc was grown on a gold foil.

To understand the adsorption-induced charge transfer mechanism, highly resolved VB spectra close to the Fermi energy are shown in Figure 3b. At the very initial growth stage, a double shoulder feature is emphasized by arrows with a peak-to-peak splitting of 0.5 eV. Upon thickness increase, the higher binding energy (BE) feature assigned as the highest occupied molecular orbital (HOMO) develops into a broad double-shouldered feature, indicating the very-early formation of molecular bands characteristic for thicker films. Moreover, the doubled feature is due to the formation of multiple molecular domains or different molecular orientation within multilayers, changes which are reasonably expected to be emphasized at one glance by the average character of the PES technique. A relaxation from the flat-lying orientation while crossing from monolayer to multilayer regime was previously reported for CoPc adsorbed on gold single crystal by Takada and Tada.[28] Opposite to the previously discussed behavior, the lower BE feature is progressively quenched upon increasing thickness, which is denoted to be an interface effect caused by the molecule coupling to the metal surface states. A similar adsorption-induced gap state confined at the interface was observed for the n-type counterpart $F_{16}CoPc$.[25] We assume the reason behind it to be identical for both systems, namely, an electron injection from the surface states into the d orbital of the cobalt ion. Although this assumption seems to contradict the already mentioned hole injection into the molecular orbitals, we will show in the following that the effect is highly localized at the cobalt ion site and occurs regardless of the studied cobalt based phthalocyanines.
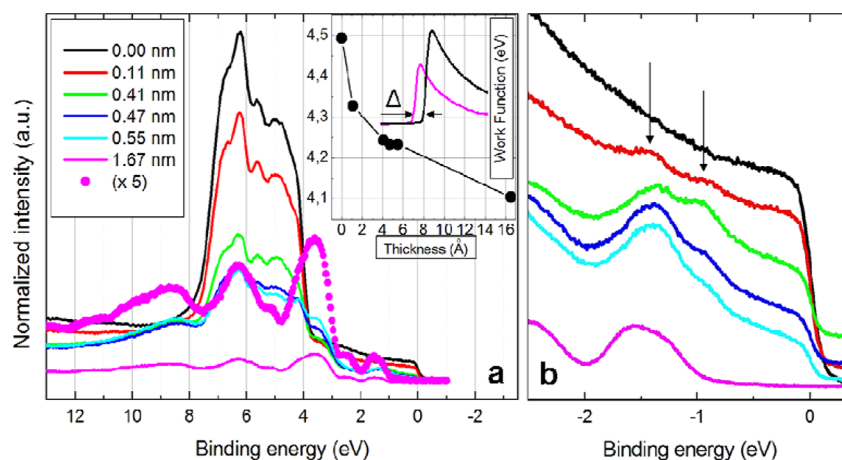

Figure 3. Valence band spectra (55 eV) evolution at the CoPc/Ag(111) interface as a function of the molecular thickness; the corresponding WF evolution is shown in the inset together with the secondary electron cutoff for the bare substrate and the highest coverage (a); region below the Fermi energy (b).

As already observed for $F_{16}CoPc$,[30] the appearance of the protonated CoPc in the STM imaging exhibits as well a voltage polarity dependence at the cobalt ion site (Figure 4a). The
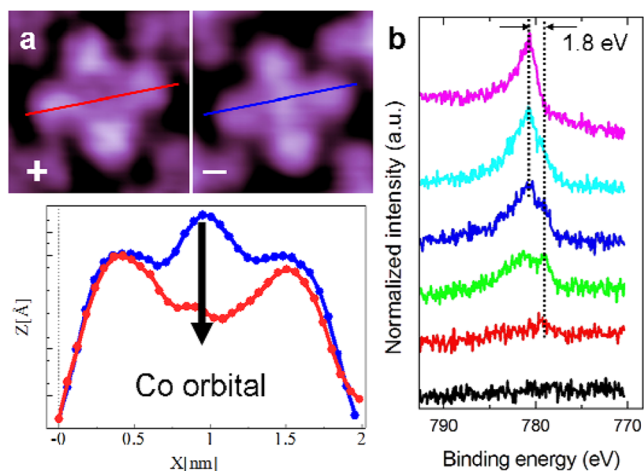

Figure 4. Voltage polarity dependent (±1 V) STM images of the CoPc molecules (a); Co $2p_{3/2}$ (1487 eV) core level spectra evolution as a function of the molecular thickness (b).

polarity-dependent orbital tunnelling imaging reveals a tunnelling mechanism strongly mediated by the cobalt ion. In pioneering works, Hipps et al.[1,26,31] have explained the difference in the tunnelling contrast for MePc's as a consequence of the different degree of occupation of the d orbital. The increased height appearance of the molecular central cavity when negatively biased sustains a correspondingly high density of filled states localized at the cobalt ion site. The observation is likely to appear due to an electron injection from the substrate into the out-protruding d orbitals of the cobalt ion which overlap favorably with the underlying surface states strongly supported by the flat-lying adsorption geometry of the Pc ligand. Consequently, a reduction effect of the cobalt oxidation state is reasonably expected to occur for the molecules directly in contact with the metal surface.

To verify this assumption, a detailed evolution of the Co 2p core level spectra was monitored as a function of the molecular thickness (Figure 4b). A strong change in the line shape of the Co $2p_{3/2}$ core level spectra was observed with increasing thickness. In the very early growth stage, in the submonolayer regime, the line shape is defined by a single-peak feature, while upon subsequent deposition an additional feature at higher binding energy arises. Characteristic to the Co(II) oxidation state, the higher BE feature increases gradually with the coverage while the lower BE feature close to metallic Co(0) is strongly confined at the interface, since its appearance is increasingly quenched in the multilayer regime. This is a strong indication for a reduction effect of the cobalt oxidation state characteristic for the organic molecules directly in contact with the metal substrate sustaining a corresponding site-specific electron injection into the central part of the molecule. This observation is consistent with and complementarily sustains the voltage polarity dependence of the molecular appearance observed in the STM imaging. Moreover, the evolution of the Co 2p core level spectra with increasing thickness of the molecular film is strongly correlated with the evolution of the VB spectra close to E_F. The low binding energy feature in the Co 2p core level spectra vanishes in the same manner as the

induced gap state in the "filled" region below E_F, emphasizing a direct correlation. Therefore, all three observations, namely, the polarity-dependent STM imaging, the newly induced gap state, and the lower BE feature in Co 2p core level spectra, are consistent with the previous report on $F_{16}CoPc$.[25] Regardless of the investigated Co containing phthalocyanine molecules, a site-dependent interface confined effect occurs at the cobalt ion site. Previous reports on CoPc adsorbed on Au(111) made use of scanning tunneling spectroscopy to emphasize the same observation.[32,33] Therefore, the tunneling spectra recorded at the Co ion site contain a clear feature below and close to the Fermi energy which vanishes in the case of the spectra recorded on top of the molecular lobes. If we consider the ~1.8 eV splitting between the lower and higher BE features for the submonolayer and multilayer regime, respectively, it can be concluded that the effect is slightly weaker for the protonated CoPc as compared to fluorinated $F_{16}CoPc$, where a larger value of ~2 eV was measured.[25] However, as was assumed for the latter case, a quenching of the spin moment is reasonably expected to occur for CoPc, resulting most probably in a nonmagnetic cobalt center. Such an observation was previously reported by Chang et al.,[34] being valid only for the molecules directly in contact with the metal surface. The assumption can be further sustained by the smaller spin−orbit splitting (with a relative value of ~0.9 eV) measured for the lower and higher BE features of the Co $2p_{3/2}$ and $2p_{1/2}$ core level spectra.

The two opposite charge transfer effects confined at the interface intrigued us to check if the molecules get partially decomposed when evaporated and therefore the average character of the PES could emphasize signals from distinct molecular parts which might behave differently when coupled to the surface states. Despite the fact that the STM images show molecules being intact on the surface, the local character of the technique combined with the different location of the PES experiments motivated our study. Therefore, the C1s and N1s core level spectra were monitored for various thicknesses of the molecular film. No significant changes in the spectra were observed with increasing film thickness (data not shown). For a detailed analysis, the C1s spectrum for the multilayer system is shown in Figure 5. Each of the carbon atoms
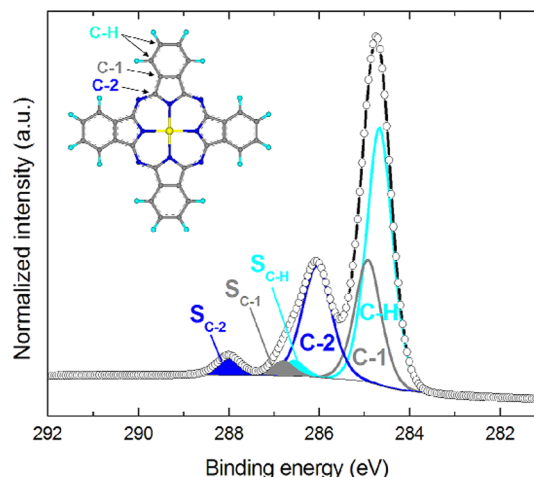

Figure 5. C1s core level spectra for 1.67 nm thick film of CoPc adsorbed on Ag(111) measured using synchrotron radiation (450 eV); the inset depicts the molecular structure of CoPc where the corresponding different types of C atoms are indicated.

introduces a specific feature line in the C1s spectra, the so-called main core level components. Additionally, small features called *shakeup* satellites appear at higher energies caused by kinetic-energy loss via simultaneously excited $\pi-\pi^*$ transitions.[35] A value of 2:1.92:3.98 is reported for the fitted intensity ratio described as $(C\text{-}1 + S_{C\text{-}1}):(C\text{-}2 + S_{C\text{-}2}):(C\text{-}H + S_{C\text{-}H})$ which is in very good agreement with the numerical ratio of distinct types of carbon atoms identified within the molecular ligand: 2:2:4 (C-1:C-2:C−H). This is a clear indication that the molecules are intact on the surface which is information of great importance, since it comes from a much larger scale than the one accessible with the STM. An energy splitting of 1.9−2 eV was found between the main lines and the corresponding *shakeup* satellites. These values are around ∼0.2 eV higher than the one obtained for the F_{16}CoPc system. According to Piper et al.,[36] this is an indication for a larger molecular gap. The observation is highly consistent with a previous report on copper based phthalocyanines.[37] Here, it was shown using PES and IPES that a systematic increase of the number of fluorine atoms leads to a corresponding decrease of the molecular gap. This might be attributed to a weaker molecule−substrate coupling for the protonated CoPc as compared to F_{16}CoPc which sustains the slightly lower energy splitting observed in the Co 2p core level spectra between the two features correlated with different coordination states of the cobalt ion.

It can be concluded that the apparently contradictory charge transfer effects confined at the interface are exclusively valid and characterize an intact deposited molecule of CoPc on Ag(111). The observations can be rationally explained by assuming a site-dependent donation/backdonation charge transfer at the organic/metal interface. Due to the flat-lying adsorption geometry, the coupling of the molecules with the metallic surface states is reasonably expected to be mediated by the out-protruding orbitals. An electron injection from the substrate into the molecule is achieved via the d orbital of the cobalt ion, while a backdonation effect is realized via the π orbitals of the phthalocyanine stage. A donation/backdonation effect was previously reported for the nonplanar SnPc adsorbed on Ag(111).[10] We recently reported on the same system, showing that the donation/backdonation effect can be further induced into a more complex configuration where the SnPc molecule was "sandwiched" by two metal electrodes, namely, the substrate Ag(111) and the metallic tip, respectively.[15] Making an analogy, the out-protruding d orbital of the cobalt ion sustains a good overlap with the underlying surface states, as it can be achieved via the out-protruding metal ion in the nonplanar MePc's, leading to similar site-specific effects. Furthermore, the local interaction of the Co d orbital might also be present for other phthalocyanines that have open or half-filled 3dz orbitals like, for example, FePc or MnPc.

CONCLUSIONS

A template-guided growth was observed in the early stage of deposition of CoPc on Ag(111) where isolated molecules, molecular nanochains, and molecular domains appear highly oriented with respect to the substrate. Compared to the fluorinated n-type counterpart, the attractive molecule−molecule interaction preserves the corresponding 4-fold symmetry within the molecular arrays. The flat-lying molecular adsorption emphasized by STM supports an effective coupling of the out-protruding molecular orbitals with the underlying surface states mediated by the delocalized molecular π orbitals on one side and the d orbitals of the Co ion on the other side.

As a result, an electron injection from the substrate into the molecule via the cobalt ion is sustained by the voltage polarity dependence, the reduction effect of the cobalt oxidation state detectable within the Co 2p core level spectra and the adsorption induced gap state below E_F. However, as the WF evolution shows, the protonated CoPc molecules get positively charged via a hybridization of the π electrons delocalized over the molecular ligand with the metal surface states. This charge relocalization scenario within the molecule is very similar with the one proposed for the F_{16}CoPc. On the other side, there, the high electronegativity of the fluorine atoms will compensate the backdonation effect and consequently the molecular ligand gets negatively charged as well. The suggestion is strongly sustained by the different WF evolution for the two systems.

AUTHOR INFORMATION

Corresponding Author

*E-mail: marius.toader@physik.tu-chemnitz.de (M.T.); hietschold@physik.tu-chemnitz.de (M.H.). Fax: +49 371 531 21639 (M.H.).

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Lu, X.; Hipps, K. W.; Wang, X.; Mazur, U. Scanning Tunneling Microscopy of Metal Phthalocyanines: d^7 and d^9 Cases. *J. Am. Chem. Soc.* **1996**, *118* (30), 7197−7202.

(2) Song, F.; Wells, J. W.; Handrup, K.; Li, Z. S.; Bao, S. N.; Schulte, K.; Ahola-Tuomi, M.; Mayor, L. C.; Swarbrick, J. C.; Perkins, E. W.; Gammelgaard, L.; Hofmann, Ph. Direct Measurement of Electrical Conductance through a Self-Assembled Molecular Layer. *Nat. Nanotechnol.* **2009**, *4*, 373−376.

(3) Lindner, S.; Treske, U.; Grobosch, M.; Knupfer, M. Charge Transfer at F_{16}CoPc and CoPc Interfaces to Au. *Appl. Phys. A: Mater. Sci. Process.* **2011**, *105*, 921−925.

(4) Chen, L.; Li, H.; Wee, A. T. S. Nonlocal Chemical Reactivity at Organic-Metal Interfaces. *ACS Nano* **2009**, *3*, 3684−3690.

(5) Huang, Y. L.; Li, H.; Ma, J.; Huang, H.; Chen, W.; Wee, A. T. S. Scanning Tunneling Microscopy Investigation of Self-Assembled CuPc/F_{16}CuPc Binary Superstructures on Graphite. *Langmuir* **2010**, *26*, 3329−3334.

(6) Toader, M.; Gopakumar, T. G.; Abdel-Hafiez, M.; Hietschold, M. Exploring the F_{16}CoPc/Ag(110) Interface Using Scanning Tunneling Microscopy and Spectroscopy. Part 1: Template-Guided Adlayer Structure Formation. *J. Phys. Chem. C* **2010**, *114*, 3537−3543.

(7) de Oteyza, D. G.; Barrena, E.; Ossó, J. O.; Dosch, H.; Meyer, S.; Pflaum, J. Controlled Enhancement of the Electron Field-Effect Mobility of F_{16}CuPc Thin-Film Transistors by Use of Functionalized SiO_2 Substrates. *Appl. Phys. Lett.* **2005**, *87*, 183504.

(8) Bao, Z.; Lovinger, A. J.; Dodabalapur, A. Organic Field-Effect Transistors with High Mobility Based on Copper Phthalocyanine. *Appl. Phys. Lett.* **1996**, *69*, 3066−3068.

(9) Jiang, X.; Dai, J.; Haibo, W.; Geng, Y.; Yan, D. H. Organic Photovoltaic Cells Using Hexadecafluorophthalocyaninatocopper (F_{16}CuPc) as electron acceptor material. *Chem. Phys. Lett.* **2007**, *446*, 329−332.

(10) Stadler, C.; Hansen, S.; Kröger, I.; Kumpf, C.; Umbach, E. Tuning Intermolecular Interaction in Longrange-Ordered Submonolayer Organic Films. *Nat. Phys.* **2009**, *5*, 153−158.

(11) Toader, M.; Hietschold, M. SnPc on Ag(111): A Scanning Tunneling Microscopy Study at the Submolecular Level. *J. Phys. Chem. C* **2011**, *115*, 12494−12500.

(12) Steele, M. P.; Blumenfeld, M. L.; Monti, O. L. A. Experimental Determination of the Excited-State Polarizability and Dipole Moment in a Thin Organic Semiconductor Film. *J. Phys. Chem. Lett.* **2010**, *1*, 2011−2016.

(13) Toader, M.; Knupfer, M.; Zahn, D. R. T.; Hietschold, M. Initial Growth of Lutetium(III) Bis-phthalocyanine on Ag(111) Surface. *J. Am. Chem. Soc.* **2011**, *133*, 5538−5544.

(14) Zhang, Y. F.; Isshiki, H.; Katoh, K.; Yoshida, Y.; Yamashita, M.; Miyasaka, H.; Breedlove, B. K.; Kajiwara, T.; Takaishi, S.; Komeda, T. A Low-Temperature Scanning Tunneling Microscope Investigation of a Nonplanar Dysprosium-Phthalocyanine Adsorption on Au(111). *J. Phys. Chem. C* **2009**, *113*, 14407−14410.

(15) Toader, M.; Hietschold, M. Tuning the Energy Level Alignment at the SnPc/Ag(111) Interface Using an STM Tip. *J. Phys. Chem. C* **2011**, *115*, 3099−3105.

(16) Wang, Y.; Kröger, J.; Berndt, R.; Hofer, W. A. Pushing and Pulling a Sn Ion through an Adsorbed Phthalocyanine Molecule. *J. Am. Chem. Soc.* **2009**, *131*, 3639−3643.

(17) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. Lanthanide Double-Decker Complexes Functioning as Magnets at the Single-Molecular Level. *J. Am. Chem. Soc.* **2003**, *125*, 8694−8695.

(18) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets: Bis-(phthalocyaninato)terbium and Bis(phthalocyaninato)dysprosium Anions. *Angew. Chem.* **2005**, *117*, 2991−2995.

(19) Vitali, L.; Fabris, S.; Conte, A. M.; Brink, S.; Ruben, M.; Baroni, S.; Kern, K. Electronic Structure of Surface-Supported Bis-(phthalocyaninato) terbium(III) Single Molecular Magnets. *Nano Lett.* **2008**, *8*, 3364−3368.

(20) Hipps, K. W.; Lu, X.; Wang, X.; Mazur, U. Metal d-Orbital Occupation-Dependent Images in the Scanning Tunneling Microscopy of Metal Phthalocyanines. *J. Phys. Chem. C* **1996**, *100*, 11207−11210.

(21) Iacovita, C.; Rastei, M. V.; Heinrich, B. W.; Brumme, T.; Kortus, J.; Limot, L.; Bucher, J. P. Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules. *Phys. Rev. Lett.* **2008**, *101*, 116602.

(22) Chen, X.; Fu, Y. S.; Ji, S. H.; Zhang, T.; Cheng, P.; Ma, X. C.; Zou, X. L.; Duan, W. H.; Jia, J. F.; Xue, Q. K. Probing Superexchange Interaction in Molecular Magnets by Spin-Flip Spectroscopy and Microscopy. *Phys. Rev. Lett.* **2008**, *101*, 197208.

(23) Wäckerlin, C.; Chylarecka, D.; Kleibert, A.; Müller, K.; Iacovita, C.; Nolting, F.; Jung, T. A.; Ballav, N. Controlling Spins in Adsorbed Molecules by a Chemical Switch. *Nat. Commun.* **2010**, *1:61*, 1−7.

(24) Duan, X.; Huang, Y.; Lieber, C. M. Nonvolatile Memory and Programmable Logic from Molecule-Gated Nanowires. *Nano Lett.* **2002**, *2*, 487−490.

(25) Toader, M.; Knupfer, M.; Zahn, D. R. T.; Hietschold, M. Initial Growth at the $F_{16}CoPc/Ag(111)$ Interface. *Surf. Sci.* **2011**, *605*, 1507−1512.

(26) Scudiero, L.; Hipps, K. W.; Barlow, D. E. A Self-Organized Two-Dimensional Bimolecular Structure. *J. Phys. Chem. B* **2003**, *107*, 2903−2909.

(27) Seah, M. P.; Dench, W. A. Quantitative Electron Spectroscopy of Surfaces: A Standard Data Base for Electron Inelastic Mean Free Paths in Solids. *Surf. Interface Anal.* **1979**, *1*, 1.

(28) Takada, M.; Tada, H. Low Temperature Scanning Tunneling Microscopy of Phthalocyanine Multilayers on Au(111) Surfaces. *Chem. Phys. Lett.* **2004**, *392*, 265−269.

(29) Takami, T.; Carrizales, C.; Hipps, K. W. Commensurate Ordering of Iron Phthalocyanine on Ag(111) Surface. *Surf. Sci.* **2009**, *603*, 3201−3204.

(30) Toader, M.; Gopakumar, T. G.; Shukrynau, P.; Hietschold, M. Exploring the $F_{16}CoPc/Ag(110)$ Interface Using Scanning Tunneling Microscopy and Spectroscopy. 2. Adsorption-Induced Charge Transfer Effect. *J. Phys. Chem. C* **2010**, *114*, 21548−21554.

(31) Barlow, D. E.; Scudiero, L.; Hipps, K. W. Scanning Tunneling Microscopy Study of the Structure and Orbital-Mediated Tunneling Spectra of Cobalt(II) Phthalocyanine and Cobalt(II) Tetraphenylporphyrin on Au(111): Mixed Composition Films. *Langmuir* **2004**, *20*, 4413−4421.

(32) Takada, M.; Tada, H. Scanning Tunneling Microscopy and Spectroscopy of Phthalocyanine Molecules on Metal Surfaces. *Jpn. J. Appl. Phys.* **2005**, *44*, 5332−5335.

(33) Kröger, J.; Jensen, H.; Néel, N.; Berndt, R. Self-Organization of Cobalt-Phthalocyanine on a Vicinal Gold Surface Revealed by Scanning Tunnelling Microscopy. *Surf. Sci.* **2007**, *601*, 4180−4184.

(34) Chang, S.-H.; Kuck, S.; Brede, J.; Lichtenstein, L.; Hoffmann, G.; Wiesendanger, R. Symmetry Reduction of Metal Phthalocyanines on Metals. *Phys. Rev. B* **2008**, *78*, 233409.

(35) Peisert, H.; Knupfer, M.; Schwieger, T.; Fuentes, G. G.; Olligs, D.; Fink, J.; Schmidt, Th. Fluorination of Copper Phthalocyanines: Electronic Structure and Interface Properties. *J. Appl. Phys.* **2003**, *93*, 9683−9692.

(36) Piper, L. F. J.; Cho, S. W.; Zhang, Y.; DeMasi, A.; Smith, K. E.; Matsuura, A. Y.; McGuinness, C. Soft X-ray Spectroscopy Study of the Element and Orbital Contributions to the Electronic Structure of Copper Hexadecafluoro-Phthalocyanine. *Phys. Rev. B* **2010**, *81*, 045201.

(37) Zahn, D. R. T.; Gavrila, G. N.; Gorgoi, M. The Transport Gap of Organic Semiconductors Studied Using the Combination of Direct and Inverse Photoemission. *Chem. Phys.* **2006**, *325*, 99−112.