



# Photoelectron spectroscopy study of the electronic structures at CoPc/Bi(111) interface



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## ABSTRACT

Self-assembly of functional molecules on solid substrate has been recognized as an appealing approach for the fabrication of diverse nanostructures for nanoelectronics. Herein, we investigate the growth of cobalt phthalocyanine (CoPc) on a Bi(111) surface with focus on the interface electronic structures utilizing photoelectron spectroscopy. While charge transfer from bismuth substrate to the molecule results in the emergence of an interface component in the Co 3p core level at lower binding energy, core-levels associated to the molecular ligand (C 1s and N 1s) are less influenced by the adsorption. In addition, density functional theory (DFT) calculations also support the empirical inference that the molecule-substrate interaction mainly involves the out-of-plane empty Co 3d orbital and bismuth states. Finally, valence band spectra demonstrate the molecule-substrate interaction is induced by interface charge transfer, agreeing well with core level measurements. Charge transfer is shown to be mainly from the underlying bismuth substrate to the empty states located at the central Co atom in the CoPc molecules. This report may provide a fundamental basis to the on-surface engineering of interfaces for molecular devices and spintronics.

## 1. Introduction

The manipulation of self-assembly of functionalized molecules on solid surfaces has been extensively exploited because it facilitates the convenient fabrication of low-dimensional nanostructures with great flexibility [1]. Furthermore, not only the physical nanostructures but also the related electronic properties, can be tailored as demanded [2,3]. In particular, the family of phthalocyanines, as one of the most widely investigated conjugated ring complex, has been proposed for an increasingly promising range of applications in the field of biological processes, gas sensing, thin-film transistors, photovoltaic devices and so on [4–8]. For example, considerable interests have been paid to the transition-metal phthalocyanines (TMPcs) as a representative model system because of the possibility of tuning both electronic and optical properties, owing to the presence of partially filled d orbitals of the transition metal atom [9–11]. As a result, numerous investigations have proliferated in the past regarding on the adsorption of TMPcs on solid substrates, for example, CoPc and MnPc on Ag(111) [11–15], CoPc on graphene [16], CoPc on Ag/Si(111) [17], CoPc on Cu(111)

[18], FePc on Ag(111) and Au [19–21], CoPc on Au [22–25], CuPc on Ag [26], and their application to spintronics and data storage devices has also been demonstrated [27,28].

It has been realized that, the performance of transitional metal phthalocyanines in devices can be strongly affected by interface interaction, which in turn can be altered both in strength and nature by choosing specific substrates [16,22–32]. Bismuth (Bi), a heavy element semimetal, has interesting properties such as strong spin orbital coupling [33] and plays a major role in topological insulators (for instance, Bi<sub>2</sub>Se<sub>3</sub> or Bi<sub>2</sub>Te<sub>3</sub>). Meanwhile, efforts have also been devoted to prepare transition metal phthalocyanines on Bi substrates, based on the relatively inert activity of bismuth as compared to other metals such as Cu, Ni or Ag [34–36]. Because of the strong spin-orbit interaction, Bi surfaces have unusual spin properties [36] and one of the most appealing applications could be the construction of spin-filters for spintronics. Importantly, Bi(111) is the natural cleavage plane of Bi crystal and turns out to be the preferred direction of epitaxial growth [37]. Consequently, the CoPc/Bi(111) interface could be an ideal combination to study the interface electronic and magnetic

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properties. Since the molecule-substrate interaction is expected to be predominantly between the partially filled 3d orbitals of cobalt ion and the spin-orbit coupled bismuth substrate, the investigation of the CoPc/Bi(111) system may also shed new light on the understanding of interfacial interactions between atoms both with strong spin-orbital interactions. Therefore, we focus on the interface exploiting between CoPc and Bi(111) in this work, by carrying out photoelectron spectroscopy (PES) and density function theory (DFT) to understand the interference of the Co 3d states on the interface electronic properties.

## 2. Material and methods

All the experiments were performed under ultra-high vacuum with the base pressure better than  $5 \times 10^{-10}$  mbar at room temperature (RT). Photoelectron spectroscopy measurements were carried out at the Centre for Storage Ring Facilities (ISA) in Denmark at “Matline”, while the valence band spectra were also repeatedly measured in the lab using the helium lamp (He I,  $h\nu=21.2$  eV). The photon energies were calibrated by comparing the binding energy of Ta 4f and the metal Fermi level ( $E_F$ ) from the sample holder. The Bi(111) substrate (Mateck) was cleaned prior to organic film deposition by cycles of Ar + sputtering at 800 eV and post annealing to about 400 K while the surface cleanliness was checked by XPS. The CoPc molecule (Sigma-Aldrich, the molecular structure is shown in Fig. 1) was thermally evaporated onto the Bi(111) surface from a temperature controlled evaporation cell after overnight outgassing. The thickness of the CoPc films varies from submonolayer to multilayer as was determined using quartz microbalance together with the attenuation of the intensity of the Bi 4f substrate peak in XPS, suggesting an almost layer-by-layer growth mode of CoPc on Bi(111). Herein, one monolayer is defined to have a thickness of about 3 Å (consistent with other studies for such planner ring macrocycles [18,20,35]). After background subtraction, XPS spectra were fitted using Voigt functions with XPSPEAK software.

Calculations were performed in the framework of Density Functional Theory (DFT) [38,39] by using CASTEP package [40] with the gradient-corrected Perdew-Burke-Ernzerhof (PBE-GGA) exchange-correlation functional [41]. To obtain a more exact description of interaction between CoPc and substrate, the van der Waals (vdW) were included using Tkatchenko-Scheffler method [42]. The convergence criterion for electronic self-consistent relaxation is set to  $2 \times 10^{-5}$  eV/atom. The Bi atoms in the substrate are fixed while the atoms in the

adsorbate macrocycles are fully relaxed with a force convergence criteria of 0.01 eV/Å.

## 3. Results and discussion

As revealed from previous reports, CoPc is expected to lie flat on metal surfaces for layer thickness of up to a few monolayers, thus maximizing the interaction of the molecule's extended  $\pi$ -electron system and d orbitals of the Co atom with the underlying substrate [23,24,31]. Owing to its high sensitivity to changes of chemical environment, XPS is therefore a powerful tool for monitoring any chemical state change of CoPc upon adsorption on bismuth substrate. To start with, the Co 3p core level was recorded in sequence as a function of coverages and plotted together in Fig. 2. Due to the upper limit of photon energy at the Matline beamline, the monitoring of Co 2p core level was unfortunately not possible even though it has a relatively high photoionization cross section compared to the Co 3p. For the convenience of comparison, the raw Co 3p spectra with background included are plotted and presented separately in Fig. 2a. As seen, the Shirley background feature is apparent for thick CoPc film. However, a linear background is observed at low coverages (below 2.5 ML) due to the fact that the spectrum background (at low CoPc coverage) is mainly dominated by the contribution from the Bi(111) surface, which shows a similar linear background at the binding energy region between 70 eV and 50 eV. The best fitting parameters of Co 3p spectra are listed in Table 1, with the peak position, line width and the relative percentage of peak area included. At first glance, apparent changes can be identified for the cobalt chemical state from submonolayer to multilayer coverage. At the initial stage of about 0.4 ML CoPc deposited onto the Bi(111) substrate, a peak located at about 59.5 eV binding energy can be clearly resolved. Further deposition of another 0.8 ML CoPc (1.2 ML in total) results in a visible change of the Co 3p peak shape with an additional component located at higher binding energy (60.5 eV), which is about one fifth in intensity of the original component at 59.5 eV. When the coverage reaches about 2.5 ML, these two components are still well resolved while the relative percentage of peak intensity of individual component changes significantly: the component at higher binding energy gets 3 times stronger compared to the peak at lower binding energy, meanwhile the line shape of both peaks keeps constant. Furthermore, for thick film of about 4 ML, the component at 60.7 eV becomes absolutely dominant and the one locating at 50.7 eV almost vanishes.

In the case of the free CoPc molecule, the macrocycle has  $D_{4h}$  symmetry and Co is divalent ( $\text{Co}^{2+}$ ) [14,18,31]. As compared to previous studies from literature [24,43], the Co 3p peak locating at 60.5 eV should be attributed to the Co(II) oxidation state, and in our case it is assigned to the Co ion in the center of CoPc molecule at thick coverage (Peak T), where the majority of CoPc molecules have no interaction with the Bi substrate and hence the CoPc behaves more or less as in gas phase [22,23,44]. Based on this, it can be concluded now that the appearance of Co 3p component at 59.5 eV at thin coverage of CoPc on Bi(111) should be related to the interface molecular-substrate interaction, which consequently results in a new chemical state for the cobalt ion. As seen in Fig. 2b, when less than one monolayer of CoPc was deposited onto the bismuth substrate, the Co 3p core level presents only one single peak located at 59.5 eV (interface component, Peak I), indicating that the first layer of CoPc is directly contacted with the underlying bismuth surface and the interface charge transfer involves the central Co ion interacting with the underlying bismuth states, as similar behavior has also been reported for the analogous systems of CoPc on Ag(111) and Au(110) [12,23]. In addition, the presence of both the Co(II) state and the interface component in the case of 1.2 ML and 2.5 ML coverages is again an evident proof for the strong molecule-substrate interaction between CoPc and Bi(111). While the first monolayer of CoPc has covered the whole surface, additional layers of CoPc do not contact or interact with the substrate, which in the end gives the pristine Co(II) state for multilayer CoPc.

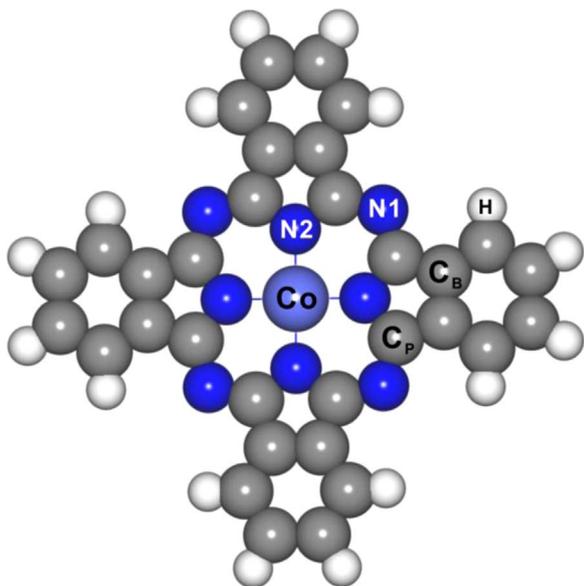
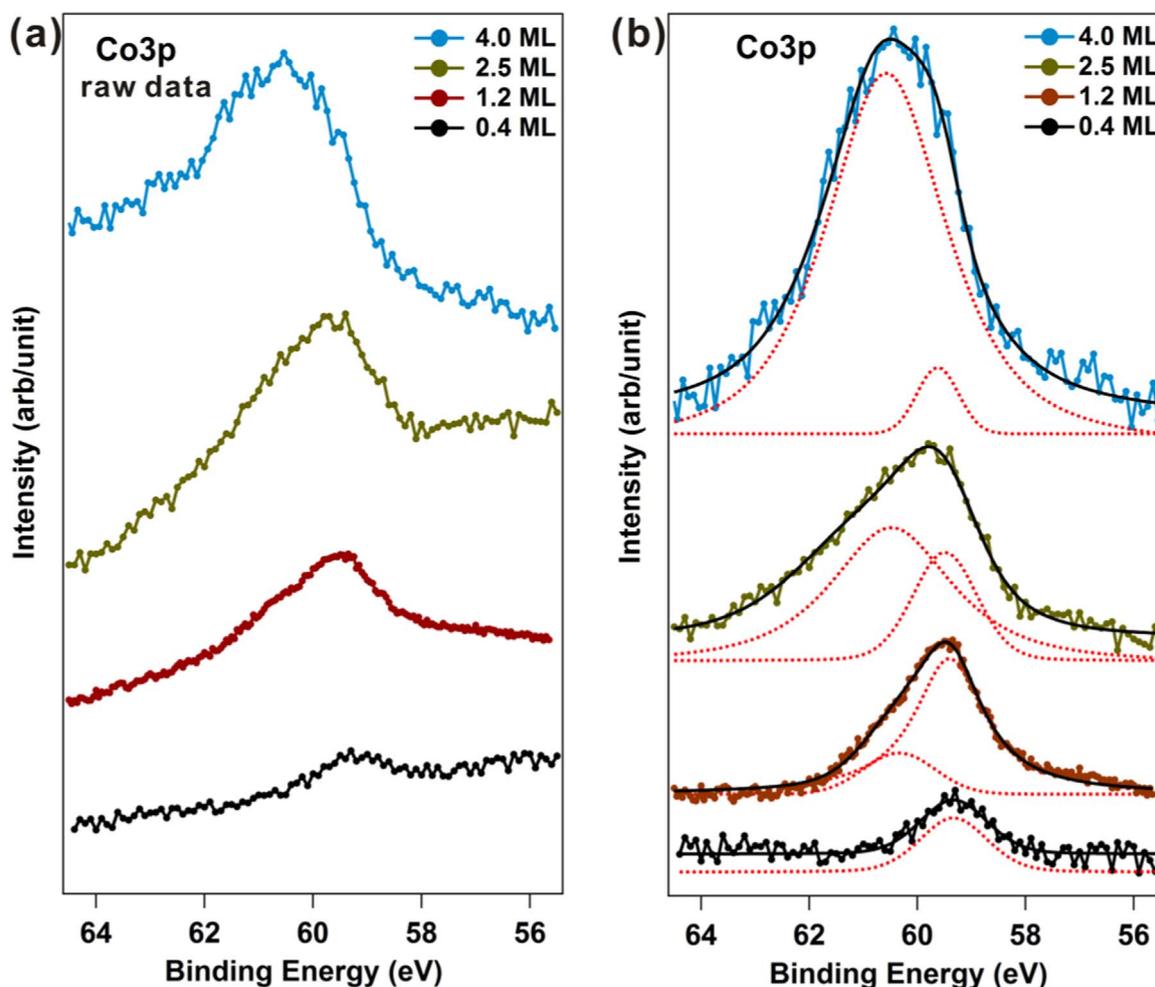


Fig. 1. The molecular structure of CoPc in gas phase. N1 and N2 indicate two different chemically bonded nitrogen sites, while  $C_B$  and  $C_P$  represent carbon atoms in benzene ring and pyrrole, respectively.



**Fig. 2.** Core level spectra of the Co 3p as a function of CoPc film thickness adsorbed on Bi(111). The raw data is plotted separately in panel (a) while the fitting curves are present in panel (b).

**Table 1**

The best fitting results for Co 3p spectrum at varying CoPc coverages from Fig. 2. ‘T’ means the component originating from thick film CoPc (bulk-like), while ‘I’ stands for the interface component which interacts with substrate, FWHM: full width at half-maximum. I: relative percentage of peak area.

		Peak position	FWHM	I
0.4 ML	Peak <sub>T</sub>	/	/	/
	Peak <sub>I</sub>	59.5	1.4	1
1.2 ML	Peak <sub>T</sub>	60.5	3.0	0.16
	Peak <sub>I</sub>	59.5	1.4	0.84
2.5 ML	Peak <sub>T</sub>	60.6	3.0	0.74
	Peak <sub>I</sub>	59.6	1.4	0.26
4.0 ML	Peak <sub>T</sub>	60.7	2.9	0.96
	Peak <sub>I</sub>	59.7	1.3	0.04

Notably, the line width of both the interface component and the thick-film component is almost constant (1.4 eV and 3.0 eV), while there is minor overall shift of peak position (0.2 eV) from thin coverage to thick film, which can be attributed to the interface dipole effect due to charge transfer [23,24]. In addition, the observed smaller width (1.4 eV) of the interface component with respect to the thick film peak (3.0 eV) can be explained by a change in the spin state of the molecules in direct contact with the Bi surface and consequently in the splitting induced by charge transfer [23,45]. As shown in the Fig. 2, the minor

Co 3p component originating from first-layer CoPc molecules interacting with the substrate is still resolved at multilayer coverage, and this can be explained by the balance between film thickness and electron mean free path. In practice, similar behavior was also reported in previous study [12].

The partially filled 3d orbitals of Co are split in energy because of the molecular field. The highest energetic state  $b_{1g}$  ( $d_{x^2-y^2}$ ) is completely empty, whereas  $d_{xy}$  ( $b_{2g}$ ),  $d_{xz}$ ,  $d_{yz}$  ( $e_g$ ) and  $d_{z^2}$  ( $a_{1g}$ ) orbitals are close in energy to each other [30,45,46]. The molecular-substrate interaction for the CoPc/Bi(111) system is expected in the form of charge transfer or charge redistribution between the substrate and molecules, while charge transfer manifests as a binding energy shift in XPS spectra. A peak shift to higher binding energy indicates donation of electrons, whereas a peak shift to lower BE indicates acceptance of electrons. As already reported from previous studies [12,23,31,45,47], CoPc molecules are strongly influenced upon adsorption with a charge transfer from the underlying metal to the  $a_{1g}$  out-of-plane Co 3d states with its partial occupation, since the completely empty  $b_{1g}$  state  $d_{x^2-y^2}$  lies too far above the Fermi level. Similarly, herein, the initially partial empty Co  $3d_{z^2}$  ( $a_{1g}$ ) energetic state is expected to be filled by electrons donated from the bismuth substrate upon adsorption for the first monolayer, which therefore results in the emerging of an interface Co 3p component at lower binding energy. In addition, charge transfer from substrate to molecules is not possible anymore for multilayer CoPc, where the pristine  $Co^{2+}$  state akin to that for a free CoPc molecule is discovered.

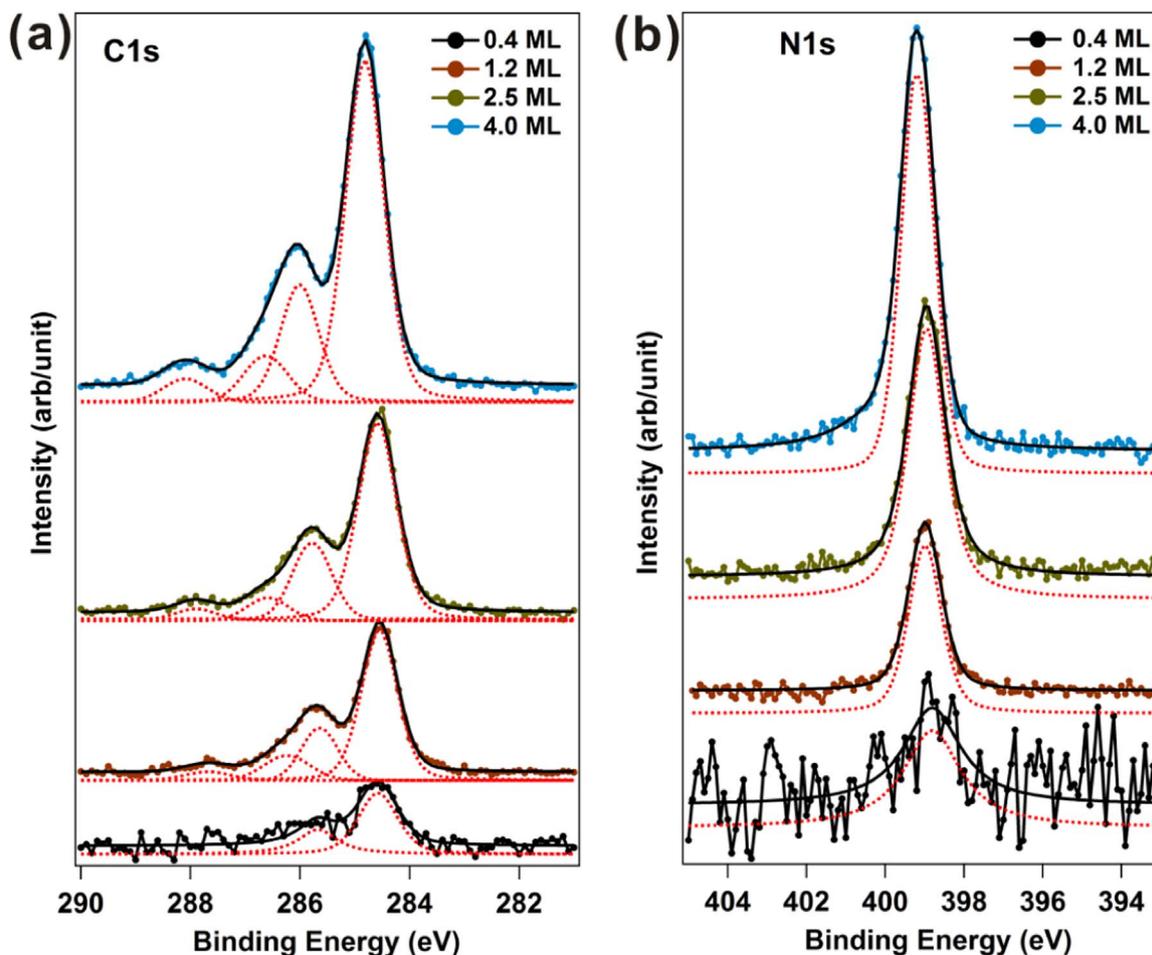
**Table 2**

The C1s fitting parameters for CoPc at varying coverages. 'B' means the component from C atoms in the benzene rings while 'P' stands for the contribution from C atoms within the pyrrole core. I: relative percentage of peak area.

		Peak position	FWHM	I
0.4 ML	Peak B	284.5	0.84	0.68
	Peak P	285.6	1.0	0.32
1.2 ML	Peak B	284.5	0.84	0.63
	Peak P	285.6	0.84	0.21
	Satellite $S_B$	286.1	0.99	0.10
	Satellite $S_P$	287.5	0.99	0.06
2.5 ML	Peak B	284.6	0.84	0.64
	Peak P	285.7	0.84	0.22
	Satellite $S_B$	286.4	0.9	0.08
	Satellite $S_P$	287.9	0.9	0.05
4.0 ML	Peak B	284.8	0.83	0.62
	Peak P	285.9	0.83	0.23
	Satellite $S_B$	286.5	0.9	0.09
	Satellite $S_P$	288.0	0.9	0.06

In order to gain more insight on the nature of the molecule-substrate interaction and the charge transfer mechanism, the evolution of C 1s and N 1s core level for CoPc adsorbed on Bi(111) is presented as a function of film thickness in Figure. Further information regarding on the adsorption mechanism can be gained by following the evolution of the C 1s and N 1s spectra, and the fitting parameters of C 1s spectra are summarized in Table 2. The C 1s spectrum at the coverage of 0.4 ML is

mainly composed by two components, which are related to the C atoms within the benzene ring (284.5 eV) and pyrrole (285.6 eV), consistent with previous related studies [23,29,48]. These features get more and more intense as the film thickness increases, and another two components are recognized lying at binding energies of 286.1 eV and 287.5 eV for the 1.2 ML thickness, which are typically attributed to the shake-up satellites corresponding to C atoms from the benzene ring and pyrrole part, respectively [13,15,18]. As also seen in Fig. 3a, such satellite peaks become quite significant when a total of 2.5 ML CoPc was deposited onto the Bi substrate, and intensify even more when the coverage reaches 4 ML. Interestingly, both the peak shape and the position of all C 1s spectra are well preserved from thin coverage to thick film, except a minor overall shift of about 0.3 eV from thin coverage to multilayer as already discovered for the Co 3p spectra. The relative intensity ratio between the benzene component and the pyrrole component is found to be around 3:1, which is also consistent with the stoichiometry. The fact that the peak position, the line width and the relative percentage of peak intensity of C 1s core level are kept constant clearly delivers a message that the carbon atoms are generally not affected by the adsorption and is therefore not involved in the interface charge transfer and molecule-substrate interaction between CoPc and Bi(111). Furthermore, the N 1s spectra illustrated in Fig. 3b also show similar behavior: no variation is found for the line shape with increasing film coverage, except that the signal to noise ratio gets much better at thick film coverage. As discovered from the analysis of the peak, the N 1s core level mainly consists of one component located at about 399 eV while it has been predicted for metal Pc that the two nitrogen atom sites (as marked in Fig. 1 by  $N_1$  and  $N_2$ ) differ in binding



**Fig. 3.** (a) The C 1s and (b) N 1s spectra plotted in sequence for varying coverages of CoPc on the bismuth substrate. Raw data: solid curves with dots; fitting results: red dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

energy by about 0.3 eV [49–51]. Due to the resolution limit, however, these two N sites cannot be well resolved using photo-electron spectroscopy, which in the end gives only one feature resulting from the combination of both N atom sites.

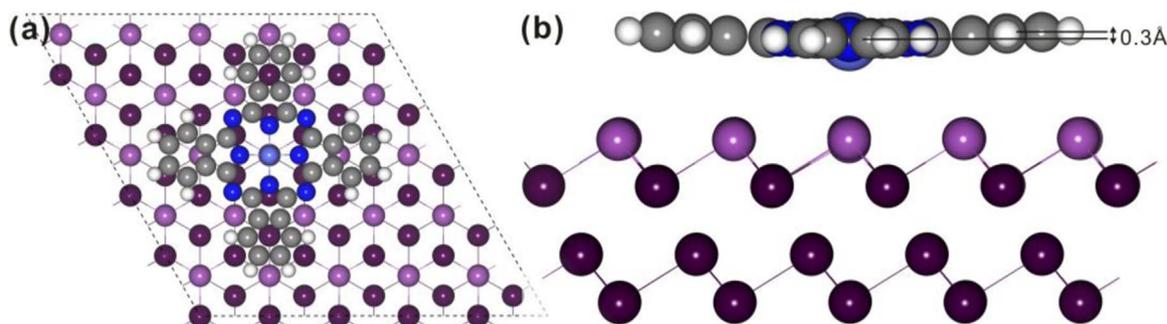
Depending on the nature of central metal atom in the Pc macrocycle and substrate, interface charge transfer might occur either from molecule to substrate or from substrate to molecule, and the molecule-substrate interaction can also be recognized either by the entire Pc macrocycle, simply the central metal atom or only the molecular ligand [11–16]. As summarized from the evolution of both C1s and N1s core level as a function of CoPc thickness, no apparent change was found in contrast to that of the Co 3p core level. Besides, the relative intensity ratio between the component from benzene ring C atoms and pyrrole C sites is also remained at around 3:1 for different CoPc thickness. Such a comparison indicates that the molecular ligand is less affected by the adsorption, and is consistent with the evolution of Co 3p spectra, which implies that only the central Co ion is directly involved in the interface interaction and charge transfer process between CoPc and Bi(111), owing to its partial empty out-of-plane  $a_{1g}$  states [23,24,31,48]. Notably, in our work, satellite peaks are also resolved for monolayer coverage as well as for thicker films, which may indicate again that the molecule-substrate interaction is mostly localized between the Co ions at the interface and the bismuth substrate, and the organic macrocycle is basically unaffected by the interface interaction. Similar reports can also be found [18,52], in which the satellite shake-up is resolved for a single layer of CoPc adsorbed on gold and copper surfaces. Nevertheless, the fitting of submonolayer spectrum does not show any shake-up satellite, and the intensity ratio between  $I_B$  and  $I_P$  differing slightly from other thickness film may give an indication that for CoPc thickness lower than 1 ML, carbon atoms participate in the interaction with the substrate, to some extent. In the end, the overall shift of spectra to higher binding energy by about 0.3 eV for both C1s and N1s, as already discovered and discussed in the case of Co 3p, is typical for the adsorption of organic film with varying thickness from thin layer to thick film on metal or semiconductor substrates. As generally recognized, such a shift to higher binding energy is usually assigned to charge transfer and the induced polarization screening effect at interface [18,23,24].

In order to verify the conclusion drawn from XPS analysis, we have also performed DFT calculations. In addition, this provides an insight into the adsorption configuration. A triclinic box is used to simulate the unit cell of the adsorption complex with a dimension of  $22.57 \text{ \AA} \times 22.57 \text{ \AA} \times 20.47 \text{ \AA}$ , including four layers of Bi and 15 Å vacuum. The CoPc macrocycles are placed into the vacuum and the absorption location of CoPc on Bi (111) surface is determined by the force field simulation method. The CoPc-Bi (111) system generated from the force field simulation is used as an input for the follow-up accurate adsorption calculation. As displayed in Fig. 4, it is apparent that the central cobalt ion is attracted towards the substrate, where the height difference between the central cobalt atom and the organic macrocycle is about 0.3 Å relative to the Bi(111) surface. Moreover, the

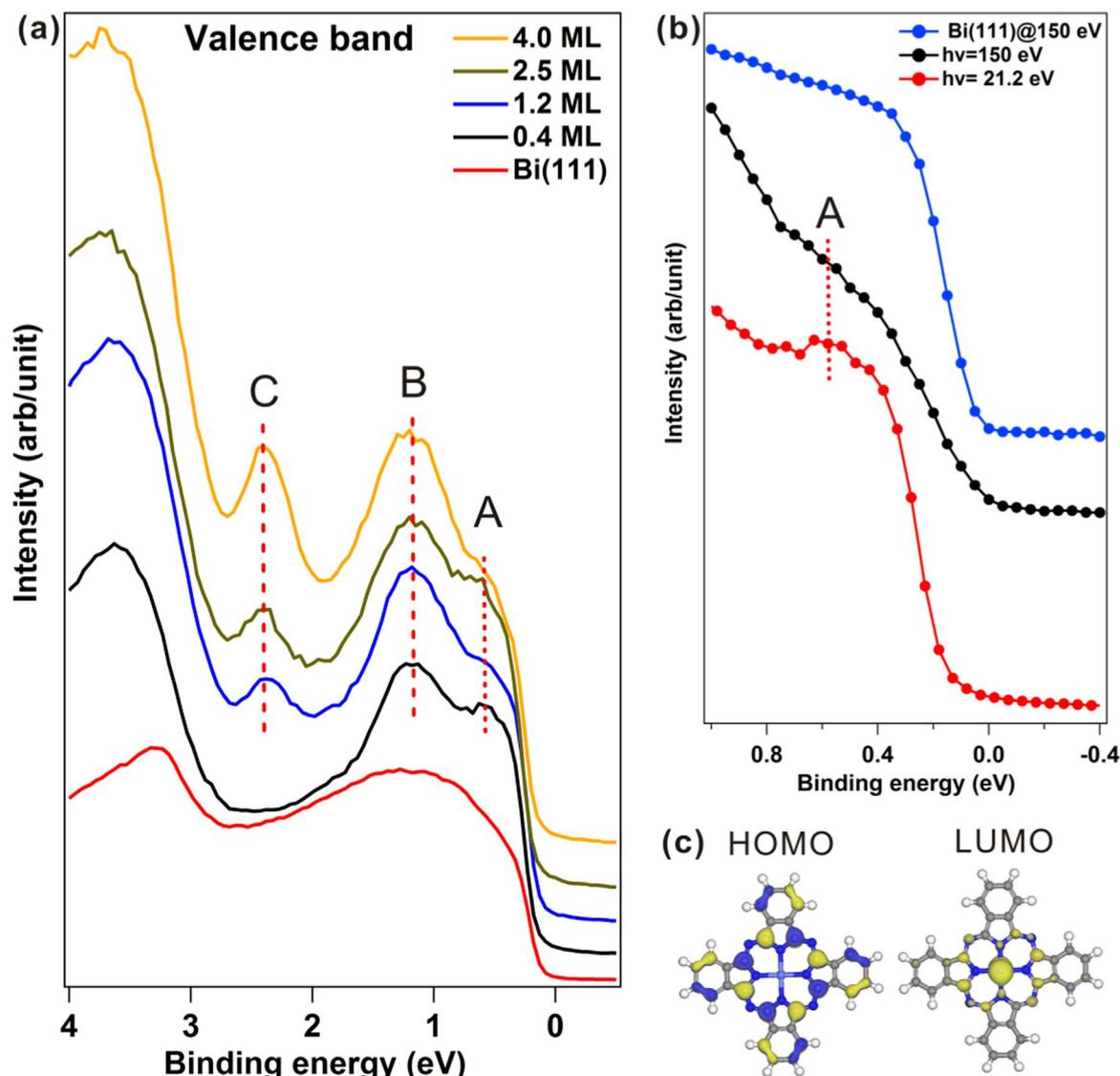
optimized adsorption site is the top site for CoPc on Bi(111), as shown in Fig. 4a, indicating that the cobalt ion is sitting just above the bismuth adatom to enhance the maximum mixing of empty Co 3d states and underlying bismuth state. In short, the adsorption configuration predicted by DFT calculations supports the conclusion drawn from XPS measurements, and is also consistent with other reports for CoPc on metal substrates [12,47].

Further, valence band spectroscopy was also carried out and is plotted in Fig. 5, in order to bring to light the character of interface interaction between CoPc and bismuth. Valence band structure, in general, depends on the properties of organic molecules and metallic substrates, as well as the nature and the strength of electronic coupling and mixing at the interface. The bottom curve in the Fig. 5 is the valence band structure from the clean Bi(111) substrate, and as expected, electronic state close to Fermi level is not clearly visible due to its semimetal properties [33]. Upon deposition, the appearance of feature A at 0.5 eV below  $E_f$  is well resolved, and as observed, feature A gets gradually broader with increasing film thickness, and becomes fairly faint at 4 ML coverage. For direct comparison, electron density distribution of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is also depicted in Fig. 5, as obtained from DFT calculations, which shows that HOMO orbital is mainly distributed around the organic macrocycle ( $a_{1u}$  symmetry) while LUMO is mostly localized on the central Co atom with  $a_{1g}$  symmetry. From this point of view, feature A can now be interpreted as an interface state due to a charge transfer from underlying Bi states to the empty LUMO with the molecular states localized on the central Co atom [22,48]. Moreover, the formerly filled LUMO state A is becoming progressively quenched with increasing film thickness due to the interface layer getting buried gradually. In fact, the hypothesis of feature A originating from the former  $a_{1g}$  LUMO with molecular states localized on the central Co atom can also be further confirmed by changing photon energy to vary the photoionization cross section of the Co 3d states. As shown in Fig. 5b, 1.2 ML-thick CoPc adsorbed on Bi(111) was measured with varying photon energies, and the feature A is somewhat attenuated but is still fairly visible at 150 eV. According to the calculations of Yeh and Lindau [54], the atomic photoionization cross sections (PICS) of the N 2p and C 2p atomic orbital decrease dramatically with increasing photon energy from 21.2 eV to 150 eV (from 6.1 to 0.05 for C 2p and from 9.7 to 0.17 for N 2p), as compared to a much more moderate decrease for the Co 3d orbital (from 4.36 to 2.96). From this point of view, it can be concluded that the feature A should be attributed to the former LUMO orbital localized on the central Co atom, as C 2p or N 2p related molecular orbitals would be difficult to detect at 150 eV photon energy and there is no surface state resolved from the clean Bi(111) substrate at this binding energy. A similar conclusion has also been drawn for CoPc adsorbed on Ag(100), where the interfacial state A was also attributed to the  $a_{1g}$  out-of-plane empty molecular states localized on the central Co atom [48].

In addition, a feature (labeled as B) located at about 1.2 eV below  $E_f$



**Fig. 4.** The optimized adsorption configuration of CoPc on Bi(111) predicted by DFT. (a) Top view, (b) Side view. Purple: Bi atoms in the first layer; Dark purple: Bi in other layers; grey: Carbon; blue: Nitrogen; white: Hydrogen; light blue: Cobalt. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** (a) Valence band spectra of CoPc adsorbed on a Bi(111) surface with increasing film thickness,  $h\nu=21.2$  eV. (b) A close up view at feature A with different photon energies (21.2 eV and 150 eV) with the spectrum from the Bi(111) substrate taken at 150 eV included as well for easy comparison. (c) Plot of electron density distribution for the HOMO and LUMO of free CoPc molecule obtained from DFT calculations, yellow and blue represent positive and negative charge. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is also apparent upon adsorption, and becomes increasingly apparent with increasing film thickness. As compared to the alignment of CoPc molecular orbitals predicted by theory [22,45–48,50], feature B should be assigned to the HOMO. From the reports of  $\pi$ -conjugate ring complexes adsorbed on metal substrates, the HOMO of phthalocyanine is always resolved around the binding energy region between 1.0 eV and 1.6 eV below the Fermi level, and its feature gets more and more pronounced as a function of film thickness [51,53]. The exact HOMO position of CoPc after adsorption varies slightly depending on metal surfaces. For example, the HOMO has been identified at the binding energy of 1.37 eV for CoPc on Cu(111) [18], 1.58 eV for CoPc on Au(110) [22], 1.25 eV for CoPc on Au(110) [23], 1.2 eV for CoPc on HOPG [24] and 1.12 eV for CoPc on Au(001) [25]. While in our case, the HOMO is resolved at about 1.2 eV below  $E_f$ , indicating the rather weak interaction between the organic macrocycle and the bismuth surface similar to the adsorption of CoPc on HOPG [24]. In addition, another new feature marked as C lying at 2.4 eV is well resolved at 1.2 ML coverage and gets increasingly intense for the coverage of 4.0 ML. Similar to HOMO, feature C should therefore be attributed to one of the occupied molecular orbitals of CoPc. As compared to the

report of CoPc on Au(110) [22], where a feature at 2.43 eV below Fermi level was discovered and was assigned to the  $b_{2g}$  molecular state. Consequently, the observed feature at 2.4 eV herein should also be attributed to the  $b_{2g}$  molecular state.

In short, band measurements have revealed rich information about the interface electronic structure and the molecule-substrate interaction, and features related to different electronic states have also been discriminated in the valence band spectra. Consistent with the evolution of Co 3p core level spectra, the filled LUMO state below  $E_f$  is detected immediately upon adsorption due to a charge transfer from substrate to the central cobalt ion, and gradually gets quenched at thick coverage. Meanwhile, features related to the HOMO and other occupied molecular orbitals are recognized as well, which get increasingly intense as a function of CoPc coverage. As revealed from photoelectron measurements and DFT calculations, the main interaction is driven by the central metal Co atom and the Bi substrate while the macrocycles are less involved, though a distortion of the molecule and a breaking symmetry has been demonstrated. The HOMO and LUMO states in the VB cannot be identified with the same symmetry as in the free CoPc molecule, and the interface hybridization gives rise to new interface states.

#### 4. Conclusion

We have thoroughly investigated the adsorption of cobalt phthalocyanine on a Bi(111) surface via a combination of XPS, UPS and DFT, and discussed the relative role of the central cobalt atom and the ligand atoms (carbon and nitrogen) in CoPc in the interaction with the bismuth substrate. By exploiting, in detail, the core level spectra and the valence band structure, it is concluded that the molecule-substrate interaction is induced upon adsorption and charge transfer occurs from the bismuth substrate to the central Co atoms, due to the presence of partial filled Co 3d orbitals. The change of cobalt's chemical state due to charge transfer will clearly affect the electrical or magnetic properties at the CoPc/Bi(111) interface accordingly. In the end, our study demonstrates the presence of a molecule-substrate interaction between CoPc and the relatively nonreactive bismuth substrate, and may predict an approach towards the on-surface engineering for spintronics.

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