Site-Specific Organic/Metal Interaction Revealed from Shockley-Type Interface State

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ABSTRACT: In order to discuss the site specificity in the organic/metal interfacial interaction, the electronic structure of the well-ordered interface of cobalt phthalocyanine (CoPc) adsorbed on Au(111) is studied by angle-resolved photoemission spectroscopy (ARPES) with synchrotron radiation. The core-level and valence-band ARPES spectra show an evidence for the strong CoPc/Au(111) chemical interaction localized at the Co site and the resultant formation of the interface states. The CoPc/Au(111) interface states are formed around the highest occupied molecular orbital (HOMO) and just below the Fermi level (E_F) with the nondispersive and dispersive characteristics, respectively. The nondispersive interface state around the HOMO is attributed to the intramolecular π_{Pc}–d_{Co} mixed orbital induced by the site-specific interfacial interaction. The dispersive interface state below E_F originates from the adsorbate-induced modification of the Au(111) Shockley state, which shows difference between CoPc and metal-free Pc (H_2Pc) and dependence on the temperature. The Shockley-type interface state enables us to characterize organic/metal interface energetics quantitatively in terms of the site-specific interfacial interaction.
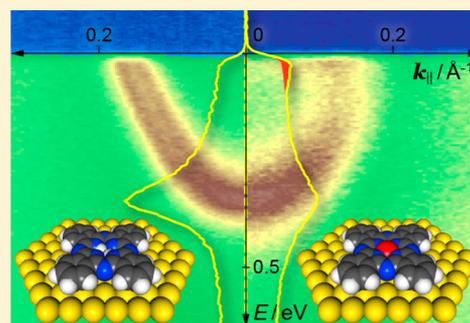
1. INTRODUCTION

The Shockley state is a well-known surface state associated with the breakdown of the periodic bulk crystal potential and the symmetry at the surface and can be observed as a free-electron-like parabolic dispersion for normal metal and semiconductor surfaces by using angle-resolved photoemission spectroscopy (ARPES). Recent technical advances of the photoelectron analyzer and the photon source (e.g., synchrotron radiation and laser) improve experimental data significantly in energy resolution, in angular (wavevector) resolution, and in photo-electron detection efficiency (i.e., surface sensitivity),[1−3] giving the opportunity to discuss new surface physics and chemistry such as the Rashba spin−orbit splitting and the kink structure by the electron−phonon (e−ph) interaction. The Shockley state is in principle observable also in adsorbed-surface systems, and indeed the Shockley state has been recently reported for single-crystalline surfaces adsorbed by rare gases,[2,4] metals,[4,5] and organic molecules[6−10] with modified dispersion parameters relative to the parameters of clean surfaces. It is understood that the modified Shockley states are derived from the rearrange-ment of surface electron systems and the resultant surface potential induced by complex interfacial interactions between adsorbates and solid surfaces. In some cases, the Shockley state shows a band gap opening at the Brillouin zone boundaries of adsorbate's superlattices.[4]

Organic monolayers adsorbed on metal surfaces are regarded as a model system for the study of fundamental physical and chemical properties related to organic electronics. In particular, the energetics in organic/metal interfaces is dominated by the complex interplay of various interfacial electronic phenomena such as the charge transfer, the mirror force effect, the Pauli repulsion (exchange interaction), the chemical reaction, and the intramolecular dipole.[11] Some of these factors have been already demonstrated for the control of organic/metal interface energetics. As a surface-sensitive method, the Shockley state measurement has recently been thus applied to organic/metal interfaces for the quantitative characterization of the interfacial bonding strength,[6] ultrafast dynamics,[7−9] and doping effects[10] related to organic/metal interface energetics.

In the present work, we have carried out the Shockley state measurement of well-ordered organic/metal interfaces of metal phthalocyanine [MPc; M = Co, H_2 (metal-free)] molecules adsorbed on Au(111), in combination with high-resolution core-level and valence-band ARPES measurements. MPc molecules are a class of important organic semiconductors especially for organic photovoltaics, and in particular the planar CoPc molecule shows unique molecular electronic and magnetic properties.[12−14] Therefore, various CoPc/metal interfaces have been investigated by using photoelectron/X-ray spectroscopies and the scanning tunneling microscopy (STM).[15−25] The present high-resolution core-level and valence-band ARPES spectra show a clear evidence for the site specificity in the CoPc/Au(111) interfacial interaction. The relatively strong chemical interaction at the Co site in the molecule with the Au(111) surface introduces the core-level shift and the interface state formation around the uppermost

molecular electronic states. Moreover, we have succeeded in observation of the difference in the shape of the modified Shockley state at the CoPc/Au(111) interface as compared to that at the H_2Pc/Au(111) interface. On the basis of the present observations for the core-level and valence-band electronic structure, we reveal a possible origin of the modified Shockley state at the CoPc/Au(111) interface in terms of the site-specific organic/metal interfacial interaction and discuss its impact on organic/metal interface energetics.

2. EXPERIMENTAL SECTION

The present experiment was performed on a highly brilliant in-vacuum undulator beamline of BL6U, which covers the photon energy ($h\nu$) from 40 to 700 eV, of the UVSOR Synchrotron in the Institute for Molecular Science (Okazaki, Japan). The ARPES endstation consists of the measurement, preparation, and load–lock chambers. The ARPES spectra were acquired from the energy-versus-angle image by using a microchannel-plate (MCP) detector of a hemispherical electron energy analyzer (MB Scientific A-1).

In the present work, the Au(111) single crystal (5N purity) and the highly oriented pyrolytic graphite (HOPG, ZYA grade) were used for the substrate. The clean Au(111) substrate was obtained by repeated cycles of the Ar^+ sputtering and the subsequent annealing at 700 K. The HOPG substrate was cleaved in air just before loading into the load–lock chamber and cleaned by heating at 700 K for 5 h in the preparation chamber. The cleanliness of these substrates was confirmed by the core-level and valence-band ARPES spectra and the low-energy electron diffraction (LEED) with the MCP detector (OCI BDL800IR-MCP).

The well-ordered organic layers of CoPc and H_2Pc were prepared by the vacuum deposition of highly purified powders onto the clean substrate kept at the room temperature. After the deposition, the sample was annealed at about 420 K to improve the lateral ordering. The deposition rate (<1 Å/min) and the layer thickness were measured using a quartz crystal microbalance, which was calibrated by the spectral shape in ARPES. The lateral ordering of organic layers was confirmed by MCP-LEED. Note that, because of the use of MCP, all displayed LEED images in this paper were distorted.

3. RESULTS AND DISCUSSION

Figure 1 shows high-resolution N 1s, C 1s, and Co 3p photoemission spectra measured for the clean Au(111) surface [labeled (0)], the CoPc/Au(111) interface [labeled (1)], the CoPc thin (15 Å) and thick (300 Å) multilayers on Au(111) [labeled (1)′ and (2), respectively], and the CoPc/HOPG interface [labeled (3)] at 20 K. The CoPc thick multilayer shows well-known spectral features, where the N 1s peak is attributed to both the azaporphyrin and the pyrrole nitrogen sites with a small energy difference, the first and second C 1s peaks are attributed to the benzene ring and pyrrole carbon sites, respectively, and the third C 1s peak is attributed to the π–π^* shakeup satellite at the pyrrole carbon site. Although the first C 1s peak for the CoPc/HOPG interface consists of carbon components of both the molecule and the substrate, the binding energy (E_b) positions of the N 1s, second C 1s, and Co 3p peaks for the CoPc/HOPG interface agree well with those for the CoPc thick multilayer, suggesting a weak core–hole screening at the physisorbed CoPc/HOPG interface. On the other hand, the N 1s, C 1s, and Co 3p peaks for the CoPc/
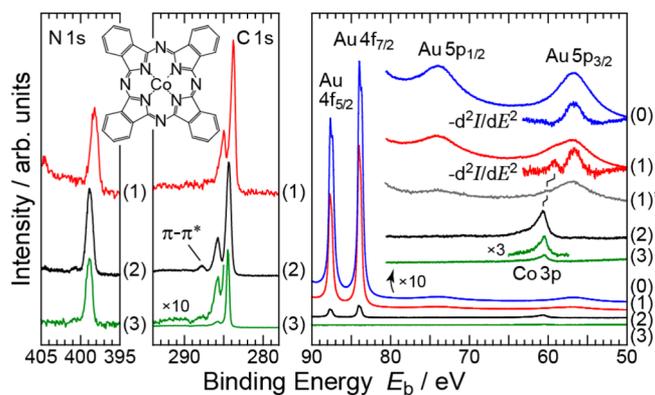
Figure 1. High-resolution core-level photoemission spectra at the normal emission measured for the clean Au(111) surface [labeled (0)], the CoPc thin films on Au(111) with the film thicknesses of 2.5, 15, and 300 Å [labeled (1), (1)′, and (2), respectively], and the 2.5 Å thick CoPc thin film on HOPG [labeled (3)] at 20 K. $h\nu = 500$ eV for the N 1s and C 1s measurement and $h\nu = 170$ eV for the Co 3p measurement were used. The molecular structure of CoPc is shown in the inset.

Au(111) interface are observed at the lower E_b side with respect to those for the CoPc thick multilayer. The E_b difference for N 1s and C 1s between the CoPc/Au(111) interface and the CoPc thick multilayer of 0.6 eV is explained by the core–hole screening in the photoemission final state.[16] The Co 3p signal for the CoPc/Au(111) interface appears as a shoulder structure in the Au $5p_{3/2}$ peak, which is not observable in the Au $5p_{1/2}$ peak, excluding the possibility of the surface core-level shift by adsorbates. The Co 3p signal appears at $E_b = 59.2$ eV in the second derivative curve ($-d^2I/dE^2$) at the CoPc/Au(111) interface, and is getting strong and shifted to the higher E_b side with increasing the film thickness; $E_b = 60.1$ and 60.6 eV for the CoPc thin and thick multilayers, respectively. The E_b difference for Co 3p between the CoPc/Au(111) interface and the CoPc thick multilayer of 1.4 eV is larger than that for N 1s and C 1s of 0.6 eV. This evidence indicates the presence of the site-specific interaction at the CoPc/Au(111) interface, where the strong charge-transfer interaction with Au(111) exists at the Co site via an unpaired electron, as is pointed out using STM.[24,25] A similar evidence has been demonstrated for the ZnPc/Cu(111) interface using core-level photoemission and X-ray standing wave (XSW) experiments.[26]

On the basis of the presence of the site-specific chemical interaction at the CoPc/Au(111) interface, we discuss the valence electronic structure. Figure 2 shows the photoemission angle (θ) dependence of ARPES and the LEED image measured for the CoPc/HOPG, CoPc/Au(111), and H_2Pc/Au(111) interfaces at 20 K. The LEED image of CoPc/Au(111) and H_2Pc/Au(111) shows a typical diffraction pattern of flat-lying MPc molecules on the Au(111) surface,[27] indicating the formation of the well-ordered MPc/Au(111) interface. The hexagonal spots just around the (0,0) spot are ascribed to the $22 \times \sqrt{3}$ herringbone reconstruction of the Au(111) surface. The LEED spots arising from the molecular ordering, indicated by the arrows in the LEED image, suggest that the CoPc (H_2Pc) molecules on Au(111) form a square lattice with a distance of ca. 14.7 Å. At the CoPc/HOPG interface, the LEED spots due to the molecular ordering are appeared as a ringlike pattern by the azimuthally averaging effect of the HOPG surface. These well-ordered organic layers introduce the clear θ dependence in the ARPES peak intensity
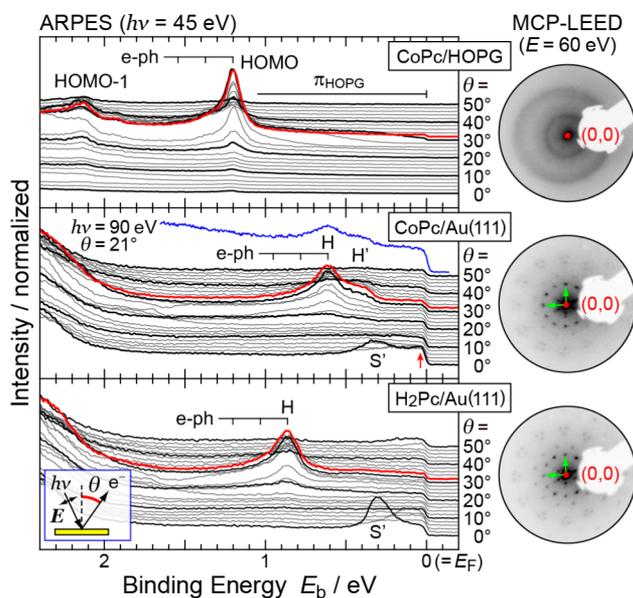
Figure 2. Photoemission angle (θ) dependence of ARPES ($h\upsilon = 45$ eV) and the LEED image ($E = 60$ eV) measured for the interfaces of CoPc/HOPG, CoPc/Au(111), and H$_2$Pc/Au(111) at 20 K. ARPES spectrum with $h\upsilon = 90$ eV and $\theta = 21°$ for CoPc/Au(111) is shown for comparison.

since the angular distribution of the photoelectron intensity reflects the spatial distribution of molecular orbitals, as has been applied to the determination of the molecular orientation and the orbital tomography.[28,29] At the CoPc/HOPG interface, the dispersive and nondispersive ARPES peaks appear. The dispersive feature at $E_b = 0-1$ eV around $\theta = 30°$ is attributed to the well-known π band of the underlying HOPG substrate (π_{HOPG}). The nondispersive peaks at $E_b = 1.2$ and 2.1 eV are attributed to the highest occupied molecular orbital (HOMO) of a C 2p character and the HOMO − 1 of a Co 3d character, respectively. The HOMO intensity shows a sharp θ dependence with the maximum at $\theta = 32°$, which corresponds to $k_\parallel \sim$ 1.7 Å^{-1}. This is the reflection of the spatial electron distribution of the HOMO in the well-ordered CoPc monolayer. The maximum intensity of the HOMO is stronger than that of the HOMO − 1 when $h\upsilon = 45$ eV, which is flipped when $h\upsilon > 60$ eV due to the different photoionization cross section between C 2p and Co 3d orbitals.[30] On the other hand, the tail structure at the higher E_b side in the HOMO peak is attributed to the e−ph coupling,[31,32] of which the energy separation is about 170 meV (1370 cm^{-1}) from the main peak and corresponds to CH and CNC in-plane bending vibrations of MPc molecules. The conservation of vibrational progressions in the HOMO peak rules out the presence of the strong hybridization between the molecular orbital at the Pc ligand and the substrate wave function.

At the CoPc/Au(111) interface, the nondispersive HOMO peak exhibits the clear θ dependence with the intensity maximum at $\theta = 32°$ ($k_\parallel \sim 1.7$ Å^{-1}) as CoPc/HOPG, while no clear Co 3d-derived peaks appear below the HOMO-derived peak, indicating the modification of the Co 3d orbital. The HOMO-derived peak at CoPc/Au(111) has two prominent components with the main peak H at $E_b = 0.6$ eV and the shoulder peak H′ at $E_b = 0.4$ eV, which is not observable for CoPc/HOPG, H$_2$Pc/Au(111), ZnPc/Au(111),[33] and CoPc multilayers on Au(111).[30] The intensity distribution with θ of

peak H′ is slightly different from that of peak H, suggesting the different orbital character between peaks H and H′. If peak H′ is mainly derived from the Co 3d orbital, peak H′ should be stronger than peak H at $h\upsilon > 60$ eV;[30] however, peak H′ is weaker than peak H even at $h\upsilon = 90$ eV and $\theta = 21°$ ($k_\parallel \sim 1.7$ Å^{-1}). Judging from the previous STM[24,25] and present ARPES data, peak H′ is attributed not to the predominant Co 3d orbital but to the interface-induced π_{Pc}−d$_{Co}$ mixed orbital derived from the strong interfacial interaction at the Co site. On the other hand, the e−ph coupling is visible for peak H of CoPc/Au(111) as CoPc/HOPG and H$_2$Pc/Au(111), suggesting the weak interfacial interaction at the Pc-ligand site. Therefore, the observed HOMO line shape is explained by the site-specific interfacial interaction with the weak interaction at the Pc-ligand site and the relatively strong interaction at the Co site.

In addition to the HOMO line shape, the other CoPc/Au(111) interface state is observed. In Figure 2, for both the CoPc/Au(111) and H$_2$Pc/Au(111) interfaces, the Shockley-type electronic state (S′) appears at $\theta = 0°$ and disappears when $\theta = 4°$ due to its free-electron-like dispersion to the lower E_b side with increasing θ. We found that the dispersion of band S′ is deduced to originate from the modified Au(111) Shockley state as discussed below. Furthermore, only at the CoPc/Au(111) interface, a quite weak adsorption-induced feature is observed just below the Fermi level (E_F) at $\theta = 0°$ as indicated by the upper arrow in Figure 2.

In order to discuss the Shockley-type electronic state below E_F at the CoPc/Au(111) interface in more detail, the energy-versus-wavevector ($E−k_\parallel$) maps of the CoPc/Au(111), H$_2$Pc/Au(111), and Au(111) at 20 K are shown in Figure 3, as obtained using the relation of

$$k_\parallel = \sqrt{2m_0(h\upsilon - E_b - \Phi)} \sin\theta/\hbar$$

where m_0 and Φ are the free-electron mass and the work function, respectively. From the LEED analysis as discussed above, the Brillouin zone boundaries of the CoPc (H$_2$Pc) molecular unit cell exist at varied $k_\parallel$ positions of ±0.15−0.21 Å^{-1} due to the multidomain ordering structure. The Shockley state of the clean Au(111) surface (S) shows a parabolic dispersion with the Rashba spin−orbit splitting, which can be fitted by two free-electron-like parabolas with the effective mass (m^*) of 0.27m_0, the surface state energy at $k_\parallel = 0$ Å^{-1} (E_0) of 465 meV, and the Rashba momentum offset (Δk_R) of ±0.013 Å^{-1}. Upon adsorption of H$_2$Pc on Au(111), the Au(111) Shockley state S is quenched and the new Shockley state (S′) appears at the lower E_b side. The observed Shockley state S′ at the H$_2$Pc/Au(111) interface can be fitted by modified dispersion parameters of the increased m^* (0.27m_0 → 0.29m_0) and the upshifted E_0 of 345 meV, while Δk_R is unchanged, with respect to the original Au(111) Shockley state. According to the earlier ARPES studies on the Shockley state at rare-gas/Au(111) and organic/Au(111) interfaces,[6] the modified Shockley state with the upshift in E_0 is in general ascribed to the Pauli repulsion of surface electron systems by adsorbates, and has been interpreted as the Shockley-type interface state. This modification of the Shockley state enables us to determine the interfacial adsorption energy (E_a) quantitatively, and the observed shift in E_0 ($\Delta E_0 = 120$ meV) at the H$_2$Pc/Au(111) interface gives $E_a = 12.7$ meV/Å^2 (= 0.106ΔE_0), suggesting a physisorption-type interaction as in rare-gas/Au(111) systems.[6] The CoPc/Au(111) interface also forms the modified Shockley
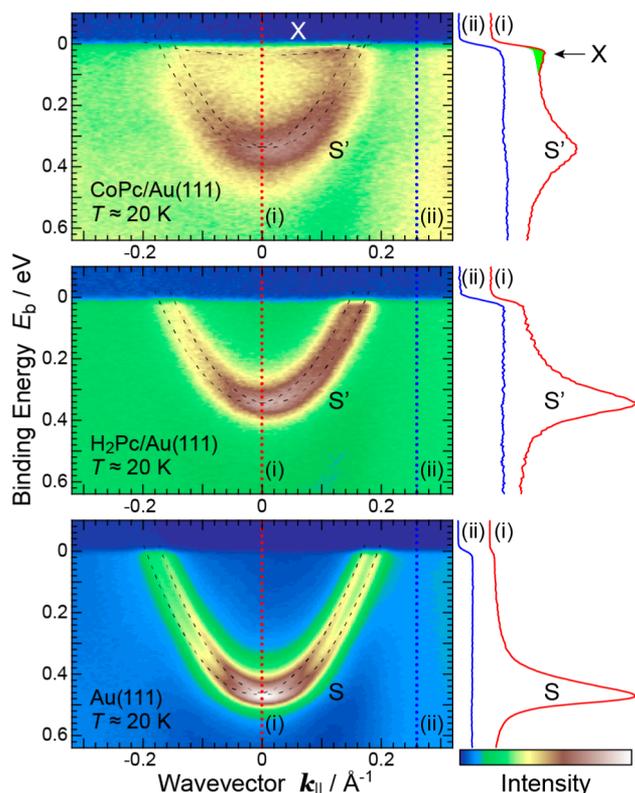
Figure 3. $E-k_\parallel$ map of the Shockley-type electronic state along $\bar{\Gamma}-\bar{M}$ of CoPc/Au(111), H$_2$Pc/Au(111), and Au(111) at 20 K, measured with $h\nu$ = 45 eV, which gives a maximum intensity for the Shockley state (ref 34). The black dashed line in the $E-k_\parallel$ map represents the parabolic fitting to the observed dispersion. The energy distribution curves at (i) $k_\parallel = 0$ Å^{-1} and (ii) $k_\parallel = 0.26$ Å^{-1} are shown in the right.

Table 1. Fitting Parameters for the Shockley State of Au(111), H$_2$Pc/Au(111), and CoPc/Au(111) at 20 K in Figure 3 (Effective Mass m^*, Surface State Energy E_0, and Rashba Momentum Offset Δk_R) and the Determined Interfacial Adsorption Energy E_a

		m^*/m_0	E_0 (meV)	Δk_R (Å^{-1})	E_a (meV/Å^2)
Au(111)	S	0.27	465	0.013	N/A^a
H$_2$Pc/Au(111)	S'	0.29	345	0.013	12.7
CoPc/Au(111)	S'	0.29	337	0.013	13.6
CoPc/Au(111)	X	3.46	32	0	45.9

^{a}N/A, not available.

peak of the CoPc/Au(111) interface should be different from that of the CoPc multilayer of 1.4 eV due to the different chemical structure. The observed C 1s peak of the CoPc/Au(111) interface in Figure 1 shows no evidence for the dehydrogenation. Furthermore, it was reported in the case of the CuPc/Ag(111) interface that the Kondo resonance peak was observed for all emission angle (i.e., all-$k_\parallel$ region) with the nondispersive behavior.[36] Such $k_\parallel$-dependent intensity and energy distributions related to the Kondo resonance cannot be observed in the present case as judged from Figures 2 and 3. Therefore, the possibility of the Kondo resonance is completely ruled out for the origin of band X. From the analysis of the line profile in energy (i.e., energy distribution curve) for band X, we found that band X consists of a single component within the present energy and angular resolution, which is modestly visible in the temperature-dependent dispersion of band X (see, Figure 4b). Since band X shows a weak parabolic dispersion around the $\bar{\Gamma}$ point ($k_\parallel$ = 0 to ±0.2 Å^{-1}) at the CoPc/Au(111) interface, the most appropriate origin of band X is the Shockley state, which might be modified by the site-specific adsorption energy as has been observed for rare-gas/metal interfaces.[4,5] In this scenario, since band S' is observable for both the CoPc/Au(111) and H$_2$Pc/Au(111) interfaces, bands X and S' can be ascribed to the Shockley state modified by the Co site and the Pc-ligand site in the molecule, respectively. The curve fitting of band X using a single parabola gives m^* = 3.46m_0 and E_0 = 32 meV (ΔE_0 = 433 meV), which suggests the large E_a of 45.9 meV/Å^2 localized at the Co site by the site-specific interfacial interaction, as summarized in Table 1.

In order to examine the site-specific interfacial interaction at the CoPc/Au(111) interface, we measured the temperature dependence of the Shockley-type interface state at the $\bar{\Gamma}$ point ($k_\parallel = 0$ Å^{-1}), as shown in Figure 4a. The Shockley state of the clean Au(111) surface, blue dotted curve (labeled S), shifts to the higher E_b side with decreasing the temperature due to the shrink of the bulk crystal lattice.[38] A similar evidence is observed for band S' of CoPc/Au(111); however, the amounts of the energy shift are different, wherein $\Delta E_0^S(T)$ = 60 meV for Au(111) and $\Delta E_0^{S'}(T)$ = 49 meV for CoPc/Au(111) from 299 to 23 K. On the other hand, band X shifts to the lower E_b side by $\Delta E_0^X(T)$ = −25 meV from 299 to 23 K, resulting in the change in the dispersion curve as shown in Figure 4b. In the case of organic/metal interfaces, the temperature-dependent shift in the Shockley state originates from the sum of the changes in the substrate lattice constant and in the interfacial bonding distance, which modifies surface electron systems and potentials. Since $\Delta E_0^S(T)$ is regarded as the substrate–lattice contribution, the energy differences of $\Delta E_0^{S'}(T) - \Delta E_0^S(T)$ = 11 meV and $\Delta E_0^X(T) - \Delta E_0^S(T)$ = 85 meV are attributed to the magnitude of the site-specific change in the Pauli repulsion

state S' with the dispersion parameters of m^* = 0.29m_0 and E_0 = 337 meV (ΔE_0 = 128 meV). The determined E_a = 13.6 meV/Å^2 at the CoPc/Au(111) interface is slightly stronger than that at the H$_2$Pc/Au(111) interface probably due to the strong site-specific interfacial interaction at the Co site in the CoPc molecule, which may collaterally affect the overall adsorption strength and the resultant interface energetics.

In addition to the presence of band S' at the CoPc/Au(111) interface, an additional dispersive band is observed just below E_F as labeled X, which is not observable at the H$_2$Pc/Au(111) interface. One of the possible origins for band X is a partially filled lowest-unoccupied molecular orbital (LUMO) by the strong charge transfer from the substrate to the molecule (i.e., electron doping).[23] If the LUMO is partially filled by the charge transfer from electron donors, the C 1s and N 1s photoemission peaks have to be significantly broadened as demonstrated previously.[35] In the present work, the C 1s and N 1s photoemission line shapes for the CoPc/Au(111) interface agree well with those for the CoPc thick multilayer as judged from Figure 1; therefore, the possibility of the filled LUMO is ruled out for the origin of band X. The other possible origin for band X is the Kondo resonance, which has been observed for some MPc/metal interfaces by using ARPES and STM.[12,36,37] In the case of CoPc adsorbed on Au(111), the Kondo resonance was realized upon dehydrogenation of the molecule by using voltage pulses from the STM tip, which recovers the localized spin state at the interface.[12] If the CoPc molecule is dehydrogenated just by the deposition on Au(111), the relative energy between the benzene ring and pyrrole C 1s

Figure 4. (a) Temperature dependence of the Shockley-type interface state of CoPc/Au(111) at $\theta = 0°$ ($k_{\parallel} = 0$ Å^{-1}), together with the Shockley surface state of the clean Au(111) surface at 23 and 299 K (dotted line). The off-normal ARPES spectra ($\theta = 33°$) of CoPc/Au(111) at 23 and 299 K are shown in the inset. (b) $E-k_{\parallel}$ map of the Shockley-type interface state of CoPc/Au(111) at 23, 133, and 299 K. (c) Secondary electron cutoff region in ARPES at $h\nu = 45$ eV, measured with a -5 V bias voltage to detect photoelectrons around zero kinetic energy.

due to the temperature-dependent interfacial bonding distance, yielding the change in the site-specific adsorption energy $\Delta E_a = 1.2$ meV/Å^2 at the Pc-ligand site and $\Delta E_a = 9.0$ meV/Å^2 at the Co site from 299 to 23 K. The determined site-specific ΔE_a with positive values can be explained by the shortening in the molecule–substrate bonding distance at the low temperature with the site specificity. The stronger interfacial interaction at the Co site than the Pc-ligand site is supported by the photoemission and XSW experiments on the CoPc/Ag(111) interface,[18,39] which suggests that the planar CoPc is distorted and exhibits a nonplanar conformation with the Co atom protruding toward the substrate. Such a site-specific strong interfacial interaction introduces the increase in the desorption temperature of MPc monolayers at metal surfaces.[17]

On the other hand, the molecular electronic states H and H′ are getting intense with decreasing the temperature, as shown in the inset of Figure 4a, due to the possible increase in the molecular ordering and the interfacial electronic coupling at 23 K, which affects the matrix element. Furthermore, from 299 to 23 K, peaks H and H′ slightly shift to the higher E_b side (ca. 16 meV). If band X originates from the partially filled LUMO by the charge transfer at the interface, band X should shift to the higher E_b side together with peaks H and H′ with decreasing the temperature, which is opposite to the observed evidence; therefore, the possibility of the partially filled LUMO is again ruled out for the origin of band X. The observed shift in H and

H′ with the temperature might be induced by the interplay of the molecule–substrate and intermolecular interactions.[40]

The expected model of the site-specific interfacial interaction and the possible molecular distortion at the CoPc/Au(111) interface are also supported by the work function Φ, which can be determined from the secondary electron cutoff in ARPES, shown in Figure 4c. The determined Φ for Au(111) of 5.46 eV is decreased by ca. 0.6 eV upon formation of the dipole layer at the CoPc/Au(111) interface due to the predominant contribution of the Pauli repulsion of surface electrons. At the CoPc/Au(111) interface, Φ at 299 K of 4.81 eV is increased to 4.86 eV at 23 K. The increase in Φ at the lower temperature is explained by the formation of the intramolecular dipole[26] and the local electron donation from the substrate at the Co site accompanied by the molecular distortion due to the site-specific interfacial interaction, which overwhelms the additional Pauli repulsion.

In terms of the site-specific interfacial interaction, now we discuss the energy position of the HOMO-derived peak for well-ordered MPc monolayers on Au(111). It has been demonstrated that the organic–metal bonding distance plays a crucial role in interface energetics.[41] Judging from the determined site-specific adsorption energies, the overall CoPc–Au(111) bonding distance might be shorter than the H$_2$Pc–Au(111) bonding distance due to the relatively strong interfacial interaction at the Co site in the CoPc/Au(111) interface. Here, the C 2p-derived HOMO peak of physisorbed monolayers of CoPc, CuPc, ZnPc, and H$_2$Pc on HOPG appears at $E_b = 1.20 \pm 0.03$ eV.[31,32] On the other hand, the C 2p-derived peak at the CoPc/Au(111) interface (peak H in Figure 2) appears at $E_b = 0.61$ eV, which is 0.59 eV lower than that at the CoPc/HOPG interface. Unlike the CoPc/Au(111) interface, the C 2p-derived peak of the CuPc, ZnPc, and H$_2$Pc monolayers on Au(111), all of which do not form the interface-induced π_{Pc}–d$_{metal}$ mixed state, like peak H′ in Figure 2, appears at $E_b = 0.80 \pm 0.03$ eV,[42] which is 0.2 eV higher than the case of the CoPc/Au(111) interface. It is considered that the low-E_b tailing in the interface state H′ due to the site-specific organic/metal interaction plays a key role in the Fermi-level pinning at the organic/metal interface and the resultant interface energetics, which requires further systematic examination for more detailed understanding.

Finally, we briefly discuss the dispersion shape and intensity of the Shockley-type interface state S′ using Figure 3 and Figure 4b. In contrast to the H$_2$Pc/Au(111) interface, the dispersion curve of band S′ in the low-E_b region at the CoPc/Au(111) interface cannot be well-fitted by the free-electron-like parabola because of the presence of a kinklike point at around $E_b = 165 \pm 10$ meV and $k_{\parallel} = 0.14 \pm 0.02$ Å^{-1}, as indicated in Figure 4b using an eye-catching curve and arrow. The observed E_b position at the kinklike point corresponds to the e–ph coupling energy by CoPc intramolecular vibrations as indicated in the inset of Figure 4a. This evidence suggests the interaction between surface electron systems and intramolecular vibrations, which might be dominated by the site-specific molecule–substrate bonding strength. Furthermore, as seen in Figure 3, the intensity of band S′ at the CoPc/Au(111) interface is noticeably decreased at $k_{\parallel} = 0.14 \pm 0.02$ Å^{-1}, which corresponds to the Brillouin zone boundaries of the CoPc molecular unit cell as determined from LEED. The reduced intensity of band S′ near E_F can be explained by the band gap opening at the adsorbate's zone boundaries.[4] Since such a reduced intensity of band S′ is not observable at the H$_2$Pc/

Au(111) interface, the Co atom in the molecule may play a crucial role as a scatterer. The resultant band gap opening may also affect the intensity distribution of band X, which shows the higher intensity at around the zone boundaries probably due to the overlap with the low-E_b component in the gap-opened band S′. In the present work, it is quite difficult to discuss the dispersion feature of band S′ at the CoPc/Au(111) interface precisely due to the broad line shape. Low-energy ARPES experiments on high-quality samples may give a new insight into the e−ph interaction at organic/metal interfaces, as has been demonstrated for the Shockley state of the clean Cu(111) surface.[3]

4. CONCLUSION

We have characterized the electronic structure at the CoPc/Au(111) interface in terms of the site-specific interfacial interaction. The high-resolution C 1s, N 1s, and Co 3p photoemission measurements on the CoPc/Au(111) interface, as compared with those on the CoPc/HOPG interface and the CoPc multilayer, revealed the strong chemical interaction localized at the central Co atom site in the CoPc molecule with the Au(111) surface. We have found from the valence-band ARPES measurements that the site-specific chemical interaction induces the formation of the interface states near the HOMO and E_F at the CoPc/Au(111) interface. The nondispersive interface state near the HOMO is attributed to the interface-induced π_{Pc}−d_{Co} mixed orbital. On the other hand, the dispersive interface state below E_F is attributed to the Shockley state, which is modified from the original Au(111) Shockley state by the adsorbate-induced charge redistribution at the interface. The Shockley-type interface state at the CoPc/Au(111) interface shows two dispersion parabolas with the clear temperature dependence by the site-specific interfacial interaction. The dispersion parameters of the Shockley-type interface state enables us to determine the site-specific adsorption energy at the interface, which dominates the interplay of the donation/backdonation charge transfer and the resultant organic/metal interface energetics.

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Notes

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