Site-Specific Geometric and Electronic Relaxations at Organic-Metal Interfaces

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The rapid recent progress in organic semiconductor devices is expected to pave the way for next-generation nanoelectronics. Organic-metal (O-M) interfaces are essential for device performance, and they also represent a formidable testing ground for complex fundamental effects related to (partially) delocalized electron and hole states and their transfer between molecules and metals. In this context, the energy level alignment near the Fermi energy ($E_F$), such as the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO), is crucial. However, O-M interface energetics are rather complicated because of the existence of interface dipoles (ID) and interface states (IS) [1,2], which are either intrinsic due to the interface formation or extrinsic due to the presence of impurities and/or defects. These effects are not well understood on a fundamental level, yet several possible factors of ID and IS, such as O-M charge transfer (CT) [3], have been demonstrated for the control of O-M interface energetics. For the further elucidation towards the intentional control of O-M interfaces, a more pertinent approach would be to use a well-characterized system for quantitative complementary measurements.

The x-ray standing wave (XSW) technique is a high-precision method to probe site-specific adsorption heights between adsorbate atoms and substrate surfaces [4–12]. The O-M distance is an important factor in the formation of ID [13] and IS [14]. Therefore, the XSW technique has recently been applied to large $\pi$-conjugated systems. In this Letter, we focus on the important question of how the adsorbate configuration affects the interfacial electronic structure. In order to explore this question, we applied the combination of XSW and angle-resolved photoemission spectroscopy (ARPES), which enables the comprehensive understanding of the correlation between geometric and electronic structures, to Zn-phthalocyanine (ZnPc) on a Cu(111) surface. Since organometallic compounds, such as Pc’s, contacted with metals show various electronic and magnetic properties, the present study can be regarded as an archetypal model wherein the influence of a metal atom in the molecule on the geometric and electronic structures can be studied. From the XSW data, we infer the ZnPc-Cu(111) bonding configuration, and find significant molecular distortion with the central Zn atom in the molecule protruding towards the substrate. The ARPES data reveal the formation of two IS derived from the substrate surface modification and the molecular distortion. Furthermore, these geometric and electronic phenomena can be substantially modified by fluorination of the molecule (F$_{16}$ZnPc). Based on these results, we address the importance of site-specific geometric and electronic relaxations at O-M interfaces.

The experiments were performed at the synchrotron radiation facilities ESRF ID32 for XSW and UVSOR BL8B2 for ARPES. The experimental setup and data analysis procedures are described in Ref. [6] for XSW and Ref. [15] for ARPES. For XSW, we used the (111) Bragg reflection in normal incidence geometry. All XSW and ARPES data were measured at 300 K. The clean Cu(111) was obtained by repeated cycles of Ar$^+$ sputtering and annealing at 750 K, as confirmed by core-level peaks in XSW and by the surface state and the work function ($\Phi$) in ARPES. Purified ZnPc and F$_{16}$ZnPc was evaporated onto the clean Cu(111) at a rate of 1 Å/min. The monolayer (ML) coverage was determined from the core-level peaks in XSW and the $\Phi$ change in ARPES.

First, we discuss the site-specific O-M interaction at ZnPc/Cu(111), which was examined by XSW (Fig. 1). By measuring the photoelectron yield of Zn 2$p_{3/2}$, N 1$s$,
molecule. Compared to ZnPc, the XSW data for Cu(111) are significantly changed by fluorination of the organic molecules on Cu(111); the strongly chemisorbed pentacene (2.34 Å) [11], a small compared to the Pc ligand. Moreover, and exhibits a nonplanar conformation on Cu(111), with the Zn atom. Hence, the planar ZnPc is significantly distorted. Furthermore, the molecular distortion of ZnPc modifies the molecular dipole and angular distribution. Shown at the bottom.

C 1s and C 1s for the photon energy (hv) around the substrate Bragg condition (2.97 keV), characteristic XSW signals are obtained at 0.7 ML. Compared to the C and N data sets, the Zn atom shows a notably different signal. Analysis of the XSW data gives the coherent fraction (f_{coh}) and coherent positions (P_{eff}) used to determine the bonding configuration, shown at the bottom.

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Zn 2p_{3/2}, N 1s, and C 1s photoelectron and x-ray reflectivity [R(E)] profiles as a function of hv relative to the Bragg energy for ZnPc(0.7 ML)/Cu(111). The best fits to the experimental data (C) yield the coherent fractions (f_{coh}) and coherent positions (P_{eff}) used to determine the bonding configuration, shown at the bottom.

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FIG. 1 (color online). Zn 2p_{3/2}, N 1s, and C 1s photoelectron and x-ray reflectivity [R(E)] profiles as a function of hv relative to the Bragg energy for ZnPc(0.7 ML)/Cu(111). The best fits to the experimental data (C) yield the coherent fractions (f_{coh}) and coherent positions (P_{eff}) used to determine the bonding configuration, shown at the bottom.

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FIG. 2 (color online). Coverage dependence of ARPES and its intensity map for (a) ZnPc and (b) F16ZnPc on Cu(111) measured at 
\( h\nu = 20 \, \text{eV} \). (c) \( \theta \) dependence of ARPES and its intensity maps of 1 ML ZnPc on Cu(111). (d) Energy diagrams of ZnPc/Cu(111) and
F16ZnPc/Cu(111), where the LUMO energy for F16ZnPc is estimated from that for F16CuPc [2].

unexpected. If peak \( X_1 \) originates either from the
eruder LUMO as reported for potassium-doped ZnPc [19] or from
the level splitting due to orbital hybridization as reported
for pentacene/Cu [15], deeper-lying energy levels should
be affected as well. These scenarios seem unlikely for the
present interfaces since (i) deeper-lying valences do not
show a significant shift for 1–5 ML, and (ii) the C 1s and N
1s PES for 0.7 ML are similar to those for 10 ML (see,
Fig. 1).

Based on the bonding configuration, the MOs related to
the Zn-N bond may play a crucial role for peaks \( X_{1,2} \). We
examined the electronic structure of an isolated ZnPc
molecule as a function of the Zn-N bond length perpen-
dicular to the Pc plane (\( \delta_\perp \)) by a MO calculation using
GAUSSIAN03 [20]. In Fig. 3, it is seen that the calculated
spectrum for \( \delta_\perp = 0 \, \text{Å} \) (optimized geometry) agrees well
with the experimental spectrum of the ZnPc thick film. In
contrast to the HOMO (\( H \)) and LUMO (\( L \)), an unoccupied
MO derived from Zn 4s (\( Z \)) shows a large energy shift with
\( \delta_\perp \). Most likely, this effect is more pronounced by the
substrate, i.e., the site-specific O-M wave function overlap
due to the anisotropic spatial distribution of MOs. In the
present case, the Zn-N bond changes from covalent to a
more ionic character, and thereby, Zn 4s states can be
occupied by CT from the substrate at the Zn site, which
is supported by the Zn 2p3/2 photoemission spectra with
relatively large shift at 0.7–10 ML in Fig. 1. These site-
specific geometric and electronic relaxations may con-
tribute to peaks \( X_{1,2} \). Such evidence also appears for
deeper-lying valences. In the experimental data at \( \theta = 0^\circ \nolimits
[Fig. 2(a)], there is an interface-specific shoulder around
\( E_b = 5 \, \text{eV} \) labeled by \( * \), wherein the modification of
the MOs related to Zn 3d with \( \delta_\perp \) exists. This evidence also
supports the present scenario with the site-specific O-M
interaction.

The site-specific electronic relaxation is also supported
by the ARPES intensity. Using the calculated MOs com-
bined with the single-scattering (SS) approximation, which
has successfully reproduced the experimental data [17], the
simulated \( I(\theta) \) of the flat-lying distorted ZnPc is shown at
the bottom of Fig. 3. The calculated HOMO (\( H \)) and
LUMO (\( L \)) derived from C 2p and N 2p show the similar

FIG. 3 (color online). Calculated electronic structure of an
isolated ZnPc as a function of the Zn-N bond length perpen-
dicular to the Pc plane (\( \delta_\perp \)), using B3LYP/6-31G(d,p) with
Gaussian broadening of 0.2 eV. The MO patterns of \( H, L, \) and \( Z \nolimits
at \( \delta_\perp = 0.3 \, \text{Å} \) and their PES-intensity \( \theta \) distribution based on
the SS/SMO approximation with HF/STO-6G/B3LYP/6-31G
(d, p) are shown at the bottom.
$I(\theta)$ pattern with a prominent maximum at $\theta \sim 45^\circ$. The Zn-derived MO ($Z$) shows a different trend, wherein two maxima appear at $\theta = 22^\circ$ and $46^\circ$. Although the perfect agreement between the present experiment (hybrid interface) and the simulation (isolated molecule) is not expected due to the possible site-specific orbital hybridization and delocalization at the interface, the simulated trends can explain the experimental $I(\theta)$ in Fig. 2(c). The $\theta$ position for the intensity maxima of the experimental HOMO peak $H_1 (\theta = 55^\circ)$ is slightly different from that of the simulated HOMO ($\theta = 46^\circ$), indicating the small orbital modification at the interface. The experimental peak $X_1$ with two intensity maxima at $\theta = 20^\circ$ and $52^\circ$ can be ascribed to the Zn-derived MO, which shows two intensity maxima in the simulation. The different relative intensity of peak $X_1$ and the simulated Zn-derived MO indicates the large orbital modification at the interface due to the protrusion of the Zn atom towards the substrate.

With the above results, the strong peak $X_1$ for ZnPc on Cu(111) can be ascribed to the Zn-derived IS due to the large molecular distortion and the corresponding electronic equilibration at the interface. Such a distortion-induced IS can be weakened by the larger O-M distance (i.e., smaller molecular distortion) as demonstrated by fluorination of the molecule ($F_{16}\text{ZnPc}$).

The site-specific geometric and electronic relaxations should also affect the Shockley state, which is sensitive to surface modifications. The Shockley state modification upon adsorption of large organic molecules is still under debate due to various physisorptive or chemisorptive bonding scenarios; e.g., PTCDA/Ag(111) shows a large upshift of 0.66 eV [21], whereas pentacene/Cu(110) shows a small upshift of 0.11 eV [22]. In fact, ZnPc/Cu(111) shows a small upshift of 0.22 eV [Fig. 2(c)], even though one might expect a larger upshift because of the strong Pauli repulsion due to the relatively small $h_C$. Since the observed modification cannot be explained only by the Pauli repulsion, the Shockley state modification for ZnPc/Cu(111) and $F_{16}\text{ZnPc}/Cu(111)$ could be dominated by the complex interplay of the O-M interactions, such as the Pauli repulsion and the site-specific CT. Based on the possible origin of the Shockley state modification for ZnPc/Cu(111) and $F_{16}\text{ZnPc}/Cu(111)$, we infer that both physical and chemical effects play a crucial role in the stabilization of the electrostatic potential at the interface.

In conclusion, using the combination of XSW and ARPES for ZnPc/Cu(111) and $F_{16}\text{ZnPc}/Cu(111)$, we have demonstrated that site-specific O-M interactions and resultant geometric and electronic relaxations yield a comprehensive energetic picture at the O-M interfaces. Among these, the observation of IS due to the change in the Zn-N bond, i.e., distortion-induced IS, is a new, important, and tunable mechanism in O-M interface energetics. We note that the site-specific electronic relaxation should occur not only for other Pc molecules but also other organic molecules when significant modifications of the molecular structure exist at O-M interfaces, such as partial rehybridization of atoms upon adsorption. Moreover, the above scenario is the intramolecular contribution to the electronic structure. Both the intra- and the intermolecular [23] site-specific contributions should affect the total energy relaxation.

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