

Impact of an interface dipole layer on molecular level alignment at an organic-conductor interface studied by ultraviolet photoemission spectroscopy

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The effect of an interface dipole layer on the energy level alignment at organic-conductor interfaces is studied on a copper phthalocyanine (CuPc) monolayer/electric dipole layer/graphite system via ultraviolet photoemission spectroscopy (UPS) and metastable atom electron spectroscopy. An oriented monolayer of the OTi-phthalocyanine molecule, which has an electric dipole moment, is grown on graphite to yield a well-defined dipole layer with the vacuum side negatively charged. The CuPc monolayer is sequentially deposited on the dipole layer kept at 123 K. This weakly interacting system made of a very thin organic layer on top of a very thin dipole layer is in thermodynamic equilibrium. The UPS data from the system grown with and without the interface dipole layer show that the binding energy of the highest occupied state of the CuPc monolayer decreases when the dipole layer is inserted. The binding energy shift is in excellent agreement with the increase in vacuum level energy of the graphite substrate upon deposition of the dipole layer. The results show that the Fermi level of the CuPc shifts toward the valence states when the interface dipole layer is inserted.

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I. INTRODUCTION

Small molecule and polymer organic semiconductors^{1,2} have attracted considerable attention for over a decade in view of their promising applications in electronics and optoelectronics.³⁻¹² Organic-metal contacts play a key role in the performance of thin film organic devices. Research on organic interfaces is therefore particularly important,^{8,10-12} and several groups have investigated a number of organic-metal systems using techniques such as ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and Kelvin probe (KP) contact potential difference measurements.^{10,11,13-35} The goal of these investigations is to understand interface electronic states, energy level alignment,^{5,12,17-30} chemical reactions,³¹⁻³³ and diffusion phenomena.^{36,37} The experimental determination of the binding energies (E_B) of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states of organic layers with respect to the Fermi level (E_F) of the metal substrate is a central part of this work, since these values define the energy barriers for hole and electron injection from the metal to the organic layer. In that context, a comprehensive understanding of the mechanisms that control the energy-level alignment at organic-metal interfaces, which remains elusive to date, requires the elucidation of the role of the dipole layer that generally forms at these interfaces.

A related issue that arises when investigating organic interfaces is that of thermodynamic equilibrium across the interface and through the organic layer. If thermodynamic equilibrium is achieved, E_F in the organic layer aligns with that of the metal. The experimental difficulty, however, is that UPS cannot detect E_F in a band gap material, as there

are generally no electron at the Fermi energy. Thus thermodynamic equilibrium can often only be assumed for organic/metal and organic/organic systems. Instances of nonequilibrium have been reported. Harima *et al.*^{20,21} pointed out mismatch in E_F from KP studies performed in air. Ito *et al.*¹⁸ observed via KP a ~ 28 V built-up of surface potential for a thick layer of tris(8-hydroxyquinolino) aluminum (Alq_3) on metal, which may have originated from the orientation of the molecular electric dipoles, indicating that thermodynamic equilibrium was not achieved in this system. Koch *et al.*³⁰ recently pointed out a lack of thermodynamic equilibrium in an alkali-metal-intercalated para-sexiphenyl system. Campbell *et al.*³⁴ and Alloway *et al.*³⁵ demonstrated that the Schottky barrier can be manipulated by the insertion of an oriented dipole layer between the metal and the organic material, using self-assembled monolayers (SAM) with alkyl chains to attach the dipole layers to the metal. However, thermodynamic equilibrium is not clear even for these metal/SAM/organic systems because of the strong insulating nature of the alkyl chains.

Finally, the unambiguous identification of the effect of the dipole layer on the interface electronic structure is difficult because of the various interactions, e.g., chemical reactions, which take place at interfaces and induce new electronic states in the energy gap of the molecular film.²⁹⁻³³ Thus molecular electronic states near the interface are modified according to the interaction. Organic-metal interfaces are therefore often quite complex, and investigating simplified and well-characterized interface systems is necessary in order to clarify the role of the interface dipole layer. The study of a system that is unambiguously in thermodynamic equilibrium requires the use of a very thin organic layer on a well-defined thin interface dipole layer.

Given these considerations, we perform here UPS experiments on a very thin organic system, i.e., a monolayer of copper phthalocyanine (CuPc) deposited on a graphite surface with and without dipole interlayer of OTi-phthalocyanine (OTiPc). These measurements demonstrate the effect of the dipole layer on the interface energy level alignment. We use graphite to obtain a well-defined dipole layer in an oriented OTiPc monolayer^{38–40} and to minimize substrate-molecule interactions and the resulting changes in the molecular electronic states. We confirm that the change in substrate vacuum level is negligibly small when CuPc is deposited directly onto the graphite surface, indicating that the molecule-substrate interaction is weak, and that the formation of a dipole layer due to molecule-substrate interaction can be neglected in the present system. We then investigate the formation and molecular orientation of monolayers of OTiPc and CuPc/OTiPc by combined use of UPS and metastable atom electron spectroscopy (MAES). The latter technique is recognized as the most sensitive spectroscopy to the outermost surface layer.^{38–42} We discuss the true effect of the interface dipole layer on E_F matching and energy level alignment between the organic layer and the substrate in the presence of an interface (OTiPc) dipole layer. We demonstrate that a shift in E_B (referenced to E_F) equal to the potential difference introduced by the dipole layer is observed for the valence levels of CuPc when a dipole layer is intentionally inserted between CuPc and the substrate. The results lead to the conclusion that equilibrium between substrate and molecular film is maintained and that the Fermi level in the CuPc overlayer aligns with the substrate E_F . The HOMO level of the CuPc layer moves according to the dipole sign and magnitude relative to the Fermi level of the entire system.

II. EXPERIMENT

UPS and MAES were performed in ultrahigh vacuum (UHV) with a hemispherical deflection analyzer. The entire apparatus has been described elsewhere.⁴¹ The position of the substrate E_F was determined by UPS on an evaporated Au film. Both UPS and MAES binding energy (E_B) scales are referenced to that energy. The total UPS energy resolution (spectrometer and incident light) using the He I resonance line was 210 meV, as determined from the Fermi edge of the Au sample at 295 K. The metastable atoms of He* (2^3S ; 19.82 eV, 2^1S ; 20.62 eV) were produced by cold discharge of pure He gas. The He* (2^1S) component was quenched by a dc helium lamp (quench lamp) in order to measure the spectra excited by He* (2^3S) only, as reported previously.⁴¹

The substrate was ZYA grade highly oriented pyrolytic graphite (HOPG) cleaved in the air, immediately introduced into the preparation chamber, and heated in UHV at 620 K for 15 h. MAES measurements just before the deposition of OTiPc confirmed the cleanliness of the substrate surface. The synthesis of OTiPc was described in a previous paper.³⁹ CuPc was obtained commercially and purified by repeated sublimation. The same OTiPc and CuPc source materials were used throughout the present experiments, eliminating

eventual effects of a change of impurity concentration on the energy level alignment in the CuPc/HOPG and CuPc/OTiPc/HOPG systems.

Thin films of OTiPc and CuPc were deposited on the HOPG substrate by sublimation in the preparation chamber (base pressure = 10^{-9} Torr). The deposition of these compounds was monitored with a quartz oscillator calibrated in advance. The deposition rate was about 0.1 monolayer equivalent (MLE)/min. Here, 1 MLE is defined as a closely packed layer of molecules forming a monolayer with their plane parallel to the substrate. The molecular orientation in the 1 MLE film was determined by MAES as described in a previous paper.^{38–42} The detail of the molecular orientation of the present films and formation of the dipole layer are discussed later.

III. RESULTS AND DISCUSSION

Prior to showing experimental results, we briefly summarize previous results on the growth of OTiPc thin films on HOPG, the change in molecular orientation with film thickness, and the effects of annealing on the molecular orientation.^{38–40} In the as-grown OTiPc film (monolayer range) on HOPG, molecules form bilayer islands in which most of the molecules in the outer layer are oriented flat with the oxygen atom directed inward (downward orientation). Annealing at 373–423 K for 3h–12 h (depending on the OTiPc island size and actual film thickness) spreads the molecules from the islands over the substrate surface to form a monolayer in which all the molecules are oriented with the oxygen atom directed outward (upward orientation). When the second layer of OTiPc is deposited on this monolayer, molecules in the outer layer have the downward orientation. In the oriented monolayer, the electric dipoles of the molecules are parallel and form a dipole layer, while in the bilayer, the electric dipoles of the first and second layers cancel each other. These changes in molecular orientation were detected with high sensitivity by MAES,⁴⁰ and the vacuum level shift due to the formation of the dipole layer was observed by UPS (Ref. 43) and low-energy electron transmission (LEET) spectroscopy.⁴⁴

Figure 1 shows the upper valence band region measured with He I UPS and He* MAES on: (1) OTiPc (~2–3 MLE) as-grown on HOPG kept at room temperature (RT) (measured at RT), (2) OTiPc film (oriented monolayer) on HOPG obtained by annealing (1) at 573 K for 9 h (measured at RT), (3) annealed OTiPc film (oriented monolayer) after cooling (2) to 123 K (measured at 123 K), (4) CuPc (1 MLE) deposited on the OTiPc monolayer kept at 123 K (CuPc/OTiPc/HOPG) (measured at 123 K), and (5) CuPc/OTiPc/HOPG heated up to 373 K (measured at 373 K). The HOPG substrate spectrum is also shown for comparison in the bottom of Fig. 1. The MAES spectra (2) and (3) clearly show that the oxygen nonbonding state n_O (peak C) appears after annealing, indicating that the film consists of OTiPc molecules with upward orientation. When 1-MLE CuPc layer is deposited on the oriented OTiPc monolayer kept at 123 K, peak C disappears, indicating that the

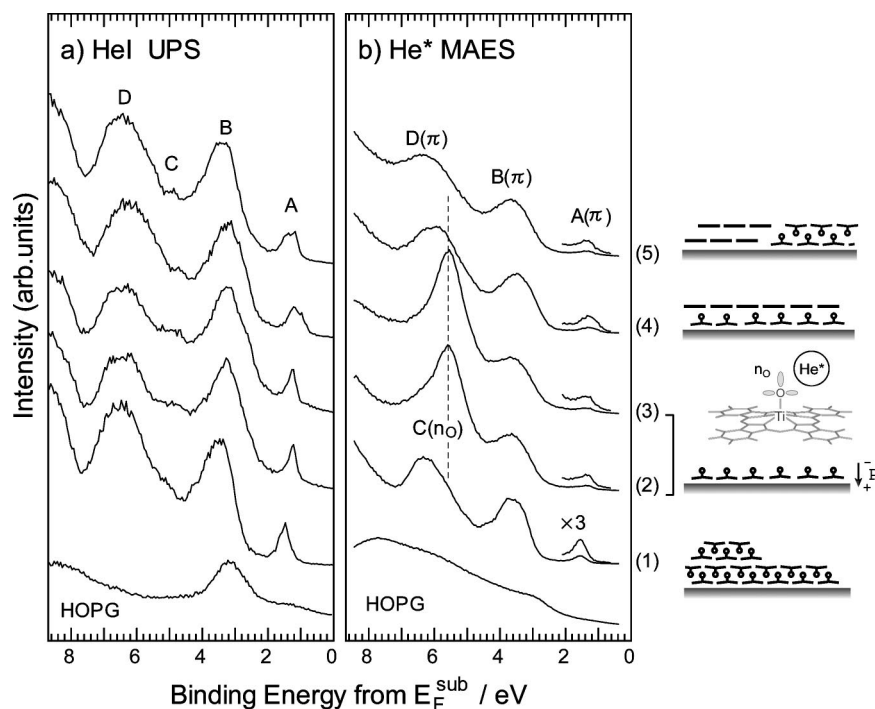


FIG. 1. He I UPS (a) and He* MAES (b) spectra of the upper valence band region of (1) the as-grown OTiPc film (2–3 MLE), (2) the oriented OTiPc monolayer obtained by annealing film (1) at 573 K for 9 h, (3) the annealed OTiPc film (oriented monolayer) measured at 123 K, (4) CuPc(1 MLE) deposited on the OTiPc monolayer kept at 123 K and (5) the CuPc/OTiPc/HOPG measured at 373 K. The schematic film structure and molecular orientation are shown on the right.

outermost surface of the OTiPc film is covered by CuPc molecules. Peak C remains undetectable even at 373 K. Furthermore, no increase is observed in the intensity of the $\sigma(\text{C-H})$ bands that are effectively excited by He* only when the molecular plane is tilted (not shown).^{41,42} These results indicate that (i) the outermost surface of the CuPc/OTiPc/HOPG consists of molecules oriented flat with respect to the substrate and (ii) there are few, if any, OTiPc molecules in the outermost surface layer. In UPS, the most characteristic change of the spectral feature is seen in the HOMO band A. The molecular orientation corresponding to each spectrum is depicted in Fig. 1 and discussed below.

Expanded views of the UPS HOMO band regions corresponding to various molecular configurations are presented in Fig. 2. Separately prepared OTiPc(bilayer)/HOPG and CuPc/HOPG systems are compared to the layers described above. One can see a very narrow photoemission HOMO bands (the full-width-at-half maximum is 0.26 eV, which includes the experimental energy resolution of 0.21 eV), as was already observed in high-resolution UPS of CuPc/HOPG,⁴⁵ OTiPc/HOPG, PbPc/HOPG,⁴³ and CIAIPc/HOPG.⁴⁶

The OTiPc HOMO peak shifts markedly ($c \rightarrow d$) between the UPS spectra of the OTiPc(monolayer)/HOPG [spectrum (3)] and OTiPc(monolayer)/HOPG [spectrum (4)]. Moreover, peak c is very small in the UPS spectrum of the bilayer [spectrum (4)], in spite of the fact that the overlayer is only one monolayer thick, indicating that E_B of the HOMO in the underlying layer has been changed by the deposition of the second layer. This is due to the cancellation of the dipole in the bilayer, which results in the elimination of the dipole-related electric field. The E_B difference between these two films is 0.24 eV. The MAES spectra of Fig. 1 give similar indications, although it is difficult to discuss precise peak

positions since the kinetic energy of the emitted electron is affected by the interaction potential between the probe and the target surface.⁴¹ The shift of the UPS peak position in Fig. 2 is related to the formation of the electric-dipole layer on the HOPG surface due to a change in molecular orientation and evaporation of excess molecules. Thus an electric dipole layer with the vacuum side negatively charged is formed.⁴³ This kind of large E_B difference between the oriented OTiPc monolayer and the bilayer is not observed in the case of CuPc thin films on HOPG [spectra (1) and (2)],⁴⁴ as the molecule does not have a permanent electric dipole.

The UPS spectrum of the CuPc(monolayer)/OTiPc(oriented monolayer)/HOPG [spectrum (5)] has a prominent new band a at $E_B=0.94$ eV. This binding energy is smaller by 0.23 eV than that of band b of the CuPc(monolayer)/HOPG ($E_B=1.17$ eV). Band a is observed only for the CuPc(monolayer)/OTiPc(oriented monolayer)/HOPG system. Furthermore, the difference in binding energy between bands a and b is nearly similar to that between bands c and d . These facts indicate that the E_B shift of band a is due to the dipole layer. On the other hand, the HOMO band b' of the CuPc bilayer appears at $E_B=1.21$ eV, which is higher by 0.04 eV than that of the CuPc monolayer [spectra (1) and (2)]. Furthermore, band c in the OTiPc(oriented monolayer)/HOPG is located near bands b and b' . Thus the band at $E_B=1.21$ eV in spectrum (5) is ascribed to the overlap of bands b , b' , and c . The fact that the intensity of this band is stronger than that of band a in spectrum (5) indicates that the sandwich structure shown schematically on the right is not perfect in the present specimen. We conclude therefore that (i) band a , which is observed only for the CuPc(monolayer)/OTiPc(oriented monolayer)/HOPG, is assigned to the HOMO band of the CuPc overlayer and (ii) the 0.23 eV E_B shift of band a is due to the potential step corresponding to the underlying dipole layer.

Recent high-resolution UPS studies on CuPc/HOPG and OTiPc/HOPG systems have shown that there is no time dependence in the HOMO bandwidth and its E_B position after the deposition of molecules.^{43–46} This demonstrates that the very thin organic systems investigated here is in thermodynamic equilibrium. Interesting observations can be made from the UPS spectrum of the CuPc/OTiPc(oriented monolayer)/HOPG system measured at elevated temperatures. Spectra (6) and (7) were obtained at 293 and 373 K after measuring spectrum (5) at 123 K. In spectrum (6), there is only a skewed broad band peaked at E_B similar to those of the HOMO bands in the spectra (1), (2), and (3), where band *a* is not observed. In spectrum (7) taken at 373 K, a new band appears at $E_B \sim 1.48$ eV, which is similar to the binding energy of band *d* of the OTiPc bilayer system. Band *a* is also absent. Comparing all E_B values of the HOMO band in the OTiPc(oriented monolayer)/HOPG, OTiPc(bilayer)/HOPG, CuPc(monolayer)/HOPG and CuPc(bilayer)/HOPG systems, these changes can be reasonably explained as follows. The CuPc/OTiPc/HOPG system heated up to 373 K consists mainly of a mixture of OTiPc bilayer and CuPc bilayer domains due to phase separation, as illustrated in Figs. 1 and 2. At 293 K the film structure is already affected by the phase separation, with few domains of the dipole layer. This interpretation of the film structure is supported by the MAES results, which show that the outermost surface of the CuPc/OTiPc/HOPG system at elevated temperature consists of patches of flat-lying CuPc or downward oriented OTiPc.

From these experimental observations, one concludes that (i) the sandwich structure with the dipole layer is indeed realized at 123 K, as illustrated in Figs. 1 and 2, and (ii) the system is in thermodynamic equilibrium. Accordingly the HOMO of the CuPc layer deposited on the OTiPc dipole layer appears at $E_B = 0.94$ eV, which is smaller by 0.23 eV than that of the CuPc layer without the dipole layer.

Figure 3 shows a summary of the energy levels and E_F alignment for OTiPc(oriented monolayer)/HOPG, OTiPc(bilayer)/HOPG, CuPc/HOPG, and CuPc(monolayer)/OTiPc(oriented monolayer)/HOPG. Measured vacuum level positions are also shown. The difference induced by the interface dipole between the binding energy of the HOMO of the OTiPc(oriented monolayer)/HOPG (band *c*) and that of the OTiPc(bilayer)/HOPG (band *d*), $\Delta E_{\text{HOMO}}(\text{OTiPc})$, is 0.24 eV, while the difference, $\Delta E_{\text{HOMO}}(\text{CuPc})$, between the HOMO of CuPc(monolayer)/HOPG (band *b*) and of the CuPc(monolayer)/OTiPc(oriented monolayer)/HOPG (band *a*) is 0.23 eV.

Returning to the issue of thermodynamic equilibrium, the apparent E_B shift of the HOMO band of CuPc/oriented dipole layer can be attributed to either one of two things: (i) a shift of E_F of the CuPc overlayer by about 0.23 eV toward the valence state of the molecule, to align with the substrate E_F , i.e., thermodynamic equilibrium or (ii) a mismatch between E_F of the CuPc overlayer and E_F of the substrate, i.e., lack of thermodynamic equilibrium. As described above, however, we did not see any evidence of a lack of thermodynamic equilibrium in the time dependence of high-

resolution UPS for monolayer and double layer films of various phthalocyanines.^{43–46} We conclude therefore that thermodynamic equilibrium is achieved for the present two-molecular layer sandwich system. The valence states of the CuPc overlayer shift by about 0.23 eV toward E_F when the interface dipole layer is inserted. The new E_F position in the gap of the CuPc overlayer breaks the charge neutrality condition associated with a canonical mid-gap E_F position, signaling possible charge transfer to/from the substrate through the dipole layer.

IV. CONCLUSION

Using two specific systems, i.e., CuPc monolayer/graphite and CuPc monolayer/electric dipole layer/graphite, in which a well-defined dipole layer was prepared using an oriented OTiPc monolayer, we have shown the true effect of the interface dipole layer on the energy level alignment and Fermi

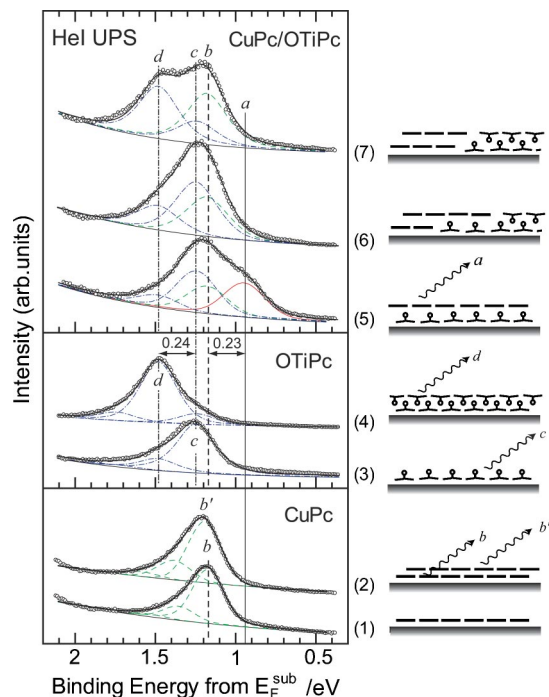


FIG. 2. (Color online) He I UPS spectra of (1) CuPc(monolayer)/HOPG, (2) CuPc(doublelayer)/HOPG, (3) OTiPc(oriented monolayer)/HOPG, (4) OTiPc(doublelayer)/HOPG, (5) CuPc(monolayer)/OTiPc(monolayer)/HOPG measured at 123 K, (6) CuPc/OTiPc/HOPG measured at 293 K after (5), and (7) the CuPc/OTiPc/HOPG measured at 373 K after (6). The schematic film structure and molecular orientation are shown in the right. The expected double layer structure shown in the schematic for spectrum (5) is approximately realized in the present specimen as understood from relative intensities of bands *a* and *b/c* in the spectrum (5). Skewed band shape in monolayer spectra (1) and (3) is due to the vibration-hole coupling (Refs. 43–46).

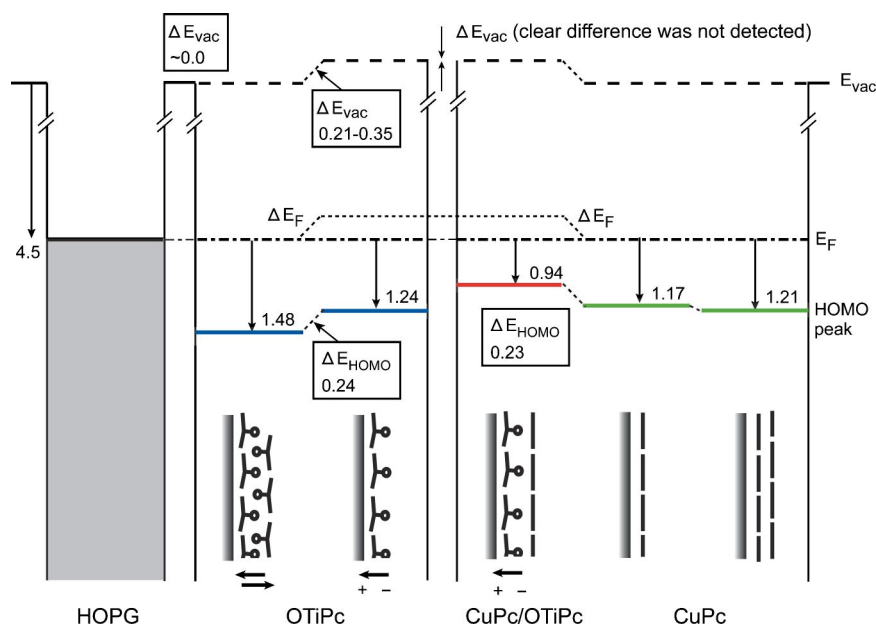


FIG. 3. (Color online) Energy diagram for the HOMO levels and Fermi level for OTiPc/HOPG, CuPc/HOPG, and CuPc/OTiPc/HOPG systems. The Fermi level shift ΔE_F is similar to the potential step produced by the dipole layer, which corresponds to the vacuum level change of the HOPG due to OTiPc-monolayer deposition (ΔE_{vac}). Although ΔE_{vac} values were slightly scattered (0.21–0.35 eV) in various measurements, no real vacuum-level shift was detected between OTiPc (oriented monolayer)/HOPG and the CuPc (monolayer)/OTiPc (oriented monolayer)/HOPG in *in situ* measurements.

level matching at an organic-conductor interface. In these systems, (i) the contribution of the electronic interaction between the substrate and the organic molecules is much smaller than the effect of the dipole layer and (ii) the systems are in thermodynamic equilibrium, as examined by high-resolution UPS. The results demonstrate that the interface dipole layer induces a change in binding energy of the valence states of the organic overlayer equal to the potential step introduced by the dipole layer in thermodynamic equilibrium.

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