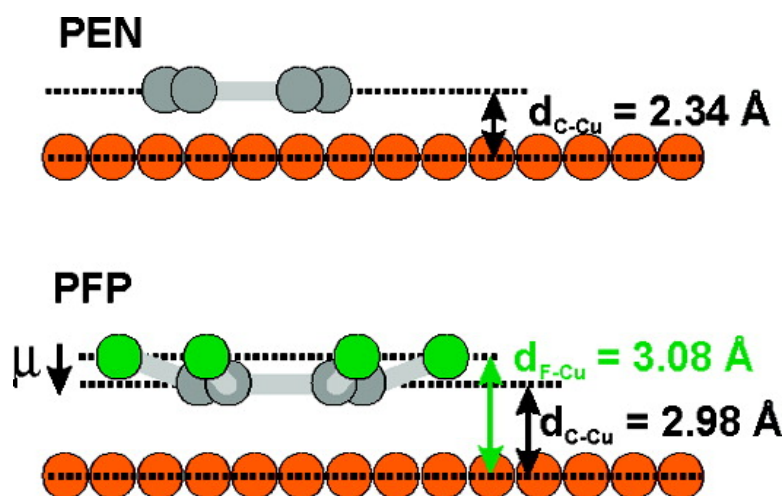


## Adsorption-Induced Intramolecular Dipole: Correlating Molecular Conformation and Interface Electronic Structure

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## Adsorption-Induced Intramolecular Dipole: Correlating Molecular Conformation and Interface Electronic Structure

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**Abstract:** The interfaces formed between pentacene (PEN) and perfluoropentacene (PFP) molecules and Cu(111) were studied using photoelectron spectroscopy, X-ray standing wave (XSW), and scanning tunneling microscopy measurements, in conjunction with theoretical modeling. The average carbon bonding distances for PEN and PFP differ strongly, that is, 2.34 Å for PEN versus 2.98 Å for PFP. An adsorption-induced nonplanar conformation of PFP is suggested by XSW (F atoms 0.1 Å above the carbon plane), which causes an intramolecular dipole of  $\sim 0.5$  D. These observations explain why the hole injection barriers at both molecule/metal interfaces are comparable (1.10 eV for PEN and 1.35 eV for PFP) whereas the molecular ionization energies differ significantly (5.00 eV for PEN and 5.85 eV for PFP). Our results show that the hypothesis of charge injection barrier tuning at organic/metal interfaces by adjusting the ionization energy of molecules is not always readily applicable.

### Introduction

The magnitude of electron (hole) injection barriers (EIBs and HIBs) at organic semiconductor/metal interfaces is crucial for the performance of organic (opto-) electronic devices.<sup>1,2</sup> Consequently, considerable effort has been directed toward developing a coherent picture of organic/metal interface energetics<sup>1–6</sup> and approaches to control the energy level alignment.<sup>7–10</sup> One strategy believed to decrease the EIB (HIB) at organic/metal interfaces is to increase (decrease) the ionization energy (IE) of the organic material by  $\Delta_{IE}$ . Such an increase of the molecular

IE can, e.g., efficiently be facilitated by fluorination substitution. Within the simple model of the Schottky-Mott limit, the EIB (HIB) of the molecular layer then decreases (increases) by the amount  $\Delta_{IE}$  for any metal contact. Because the invalidity of the Schottky-Mott limit (i.e., vacuum level alignment) for organic/metal interfaces is well documented,<sup>3,4</sup> the applicability of this simple model can be challenged. The actual value of charge injection barriers is governed by the type and strength of organic/metal interaction, often accompanied by metal surface charge redistribution due to the adsorbed molecules and also charge transfer between metal and molecules. In addition, the molecular charge reorganization energy, charge polarization by surrounding matter, and changes of molecular conformation (possibly inducing/changing intramolecular dipoles) strongly influence charge injection barrier heights. This complex combination of several effects makes it practically impossible to predict injection barriers based on simple models. Therefore, it is necessary to draw on complementary information that yield electronic and structural properties of interfaces between an organic molecule and a metal surface.

Using different experimental techniques we have studied the interfaces formed between two prototypical organic semiconductor materials, that is, pentacene (PEN, C<sub>22</sub>H<sub>14</sub>) and perfluoropentacene (PFP, C<sub>22</sub>F<sub>14</sub>), and Cu(111). Both are widely studied materials today, as they are used in organic field-effect transistors with high hole (PEN)<sup>11</sup> and electron (PFP)<sup>12</sup> mobility.

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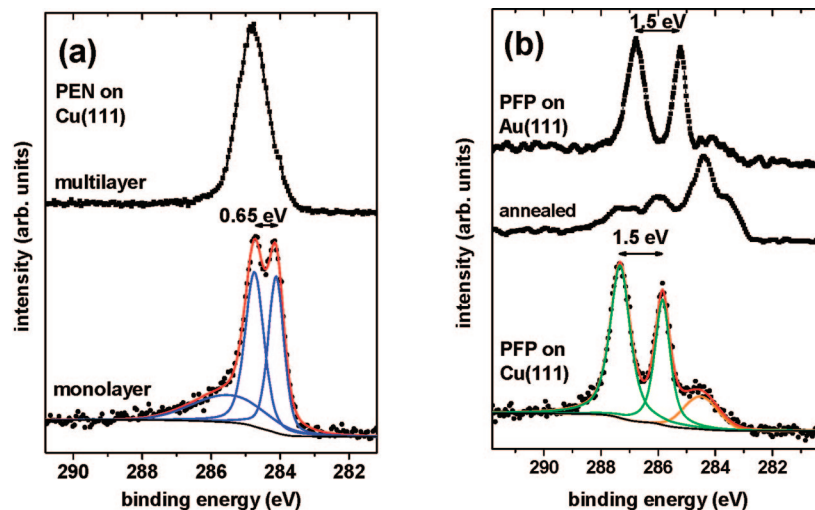
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**Figure 1.** C1s core levels of (a) PEN monolayer (bottom) and multilayer (top) on Cu(111), and (b) PFP monolayer on Cu(111) (bottom) and on Au(111) (top), and PFP monolayer on Cu(111) after annealing to 150 °C (center curve), providing evidence for a temperature-induced reaction. All spectra were taken at beamline PM4 (BESSY), the photon energy was 630 eV.

Employing ultraviolet and X-ray photoelectron spectroscopy (UPS, XPS), X-ray standing wave (XSW) measurements, scanning tunneling microscopy (STM), supported by quantum chemical modeling, allows to assess hole injection barriers, sample work function changes, strength of organic/metal interaction, molecular order, and molecule-metal bonding distances, molecular distortions, and distortion-induced intramolecular dipoles. This comparative study thus enables providing a comprehensive picture of interfacial phenomena for the two archetypal molecules.

## Experimental Section

UPS and XPS experiments were performed with the endstation SurfCat at beamline PM4 (BESSY),<sup>8</sup> for XSW experiments we used beamline ID32 (ESRF),<sup>13</sup> and STM measurements were done using an Omicron VT-STM attached to a custom vacuum system at the HU-Berlin. In all cases, ultrahigh vacuum (UHV) conditions were preserved during sample preparation and measurements (base pressure  $< 5 \times 10^{-10}$  mbar), and a higher base pressure in the evaporation chamber of SurfCat ( $5 \times 10^{-9}$  mbar). Cu(111) crystals were cleaned by repeated Ar-ion sputtering/annealing cycles. PEN (Sigma-Aldrich) and PFP<sup>14</sup> were evaporated from resistively heated pinhole sources, and the deposited mass-thickness was monitored by quartz crystal microbalances. Density-functional theory (DFT) calculations on isolated, fully geometry-optimized PEN, and PFP molecules were performed at the B3LYP/6-31G\*\* level.<sup>15</sup> Additionally, PFP was geometry-optimized under the constraints that the F atoms are located 0.1 Å above the plane of the C atoms. The intramolecular dipole was then extracted from this model PFP conformation (as suggested by our experiments).

## Results and Discussion

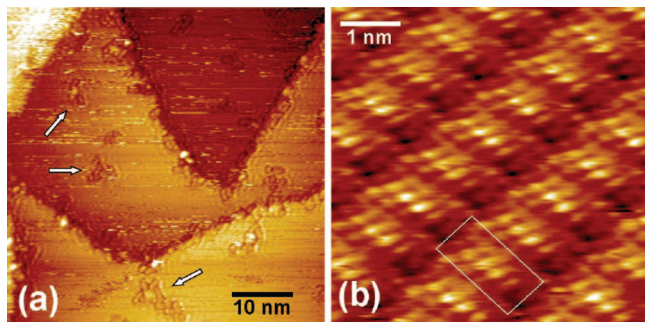
The C1s core-level of the PEN monolayer on Cu(111) [bottom curve in Figure 1a] is split by 0.65 eV into two

components, very similar to the case of PEN/Cu(110)<sup>16</sup> and PEN/Cu(119),<sup>17</sup> where strong organic/metal chemisorption involving a hybridization of molecular orbitals and metal states has been suggested.<sup>18</sup> The broad high binding energy component required for adequate spectral fitting indicates pronounced shakeup processes for PEN chemisorbed on Cu(111), that is, low-energy losses of emitted photoelectrons due to electron-hole pair creation within the new hybrid molecule/metal density of states close to the Fermi level ( $E_F$ ).<sup>17,19</sup> PEN multilayers yield only a single but asymmetric C1s peak (top curve in Figure 1a) due to a superposition from the chemically slightly inequivalent C atoms in pristine bulk PEN,<sup>20</sup> whose binding energy differences are too small to be resolved experimentally in the solid state.<sup>17</sup> The continuum-like shakeup processes occurring for the chemisorbed PEN monolayer are absent for the multilayer because no hybrid molecule/metal states close to  $E_F$  exist in multilayer PEN. Consequently, the binding energy of inequivalent carbon species in PEN is significantly altered due to the strong interaction with the Cu(111) substrate. The C1s core-level of the PFP monolayer on Cu(111) also has two components, separated by 1.5 eV (bottom curve in Figure 1b). The low binding energy (BE) C1s component in this spectrum (at 284.4 eV BE) is due to some residual carbon contamination, which adsorbed on the metal surface during PFP sublimation and sample transfer that was necessary for XPS and UPS measurements. In addition, a few PFP molecules (less than 5% of a monolayer) may have reacted on the substrate at defect sites/step edges, as suggested by STM in Figure 2a and discussed below. However, the vast majority of adsorbed PFP molecules remains intact at room temperature, as only annealing to 150 °C leads to a significantly changed C1s spectrum (center curve

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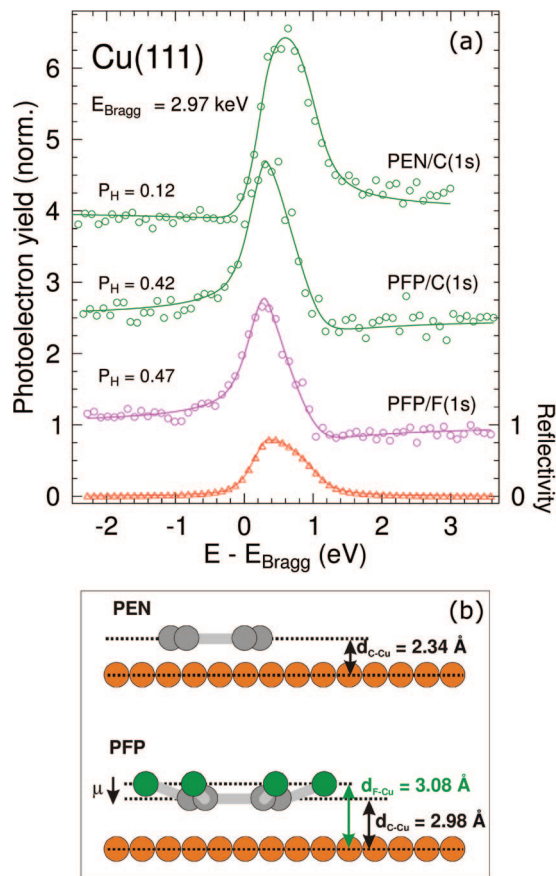


**Figure 2.** STM micrographs of (a) a liquid-like submonolayer of PFP on Cu(111) including several reaction-induced pinning centers (arrows) (imaging parameters:  $-1.2$  V,  $0.5$  nA), and (b) of an ordered monolayer PFP on Cu(111) with submolecular resolution, unit-cell (containing one PFP) parameters:  $a = (1.6 \pm 0.1)$  nm,  $b = (0.8 \pm 0.1)$  nm,  $\alpha = (96 \pm 2)^\circ$  (imaging parameters:  $-0.8$  V,  $0.5$  nA). Images were obtained at room temperature.

in Figure 1b) indicating a strong chemical reaction with the metal substrate, and the appearance of more “pinned” PFP molecules in STM (not shown). The two components of the C1s core-levels assigned to nonreacted PFP are explained by the chemically highly inequivalent carbon atoms within a molecule, that is, 14 C atoms directly bound to F and 8 C atoms bound just to neighboring C atoms. The ratio of these two C species was found experimentally (from the area of the corresponding peaks) to be  $1.78 \pm 0.05$ , in good agreement with the expected value of 1.75 from the molecular stoichiometry. Peak-splitting due to strong chemisorption can be ruled out, as both spectral shape and magnitude of peak splitting for the monolayer on Cu(111) are virtually identical to those obtained for a PFP monolayer on Au(111) (top curve in Figure 1b), for which a weak interaction was found.<sup>21</sup>

The significantly weaker adsorption of PFP compared to PEN on Cu(111) is further evidenced by STM imaging. For submonolayer coverage, no stable images of laterally ordered domains could be obtained (Figure 2a). Instead, we observed a few single molecules or small clusters on terraces, and disordered larger clusters near Cu step-edges. Apparently, some PFP molecules reacted at step-edges and point-defects on terraces,<sup>22</sup> contributing mainly to the low BE component at 284.4 eV of the C1s spectrum. Most of the terraces appear featureless (at room temperature), indicating that the PFP submonolayer resembles a 2-dimensional liquid phase, where molecules can easily be moved laterally during imaging by the interaction with the STM tip. A similar phenomenon has been reported for PEN/Ag(111).<sup>23</sup> Note that for PEN on Cu(100) terraces individual molecules of a disordered phase could be imaged at room temperature, due to strong chemisorption.<sup>24</sup> Upon formation of a full PFP/Cu(111) monolayer a stable ordered structure of lying molecules is formed, as depicted in Figure 2b.

Based on these findings, one could speculate on a smaller average C–Cu adsorption distance for the chemisorbed PEN



**Figure 3.** (a) X-ray standing wave scans obtained on submonolayers of PEN and PFP on Cu(111). The symbols represent the photoelectron yield (circles) and reflectivity (triangles) data measured on both adsorbate systems. The solid lines show least-squares fits based on dynamical diffraction theory which provide the coherent position  $P_H$  and coherent fraction  $f_H$  for each element [13]. The characteristic shapes of these curves reveal the different adsorption distances  $d$  of PEN and PFP, whereas the deviation of the coherent fractions from unity, with  $f_H = 0.55$  for PEN/C1s and  $f_H = 0.41$  for PFP/C1s and PFP/F1s, is related to disorder in the adsorbate system. (b) Schematic conformation of PEN (top) and PFP (bottom) on Cu(111) derived from XSW measurements, indicating the different average positions of F and C atoms resulting in the intramolecular dipole of  $\mu \approx 0.53$  D. The long molecular axis is perpendicular to the page plane. Note that the molecule/metal and intramolecular length scales are different.

compared to the weakly bound PFP. In fact, this is confirmed and quantified by XSW measurements which probe the atomic positions of the adsorbate relative to the substrate lattice planes.<sup>13,25,26</sup> The characteristic variation of the photoelectron yield in the X-ray interference field of the Bragg reflection provides different coherent positions ( $P_H$ ) for the atoms in the PEN and PFP molecules (Figure 3a). Converting this phase information into distances and applying nondipole corrections,<sup>13</sup> we find an average C–Cu bonding length of  $(2.34 \pm 0.02)$  Å for PEN and  $(2.98 \pm 0.07)$  Å for PFP, that is, a huge difference of 0.64 Å between the positions of the carbon cores of the two adsorbates above the metal surface. Moreover, the XSW results indicate that the PFP molecule does not adsorb in its coplanar bulk conformation, as might be expected due to the weak molecule-metal interaction. We find that the F atoms of PFP

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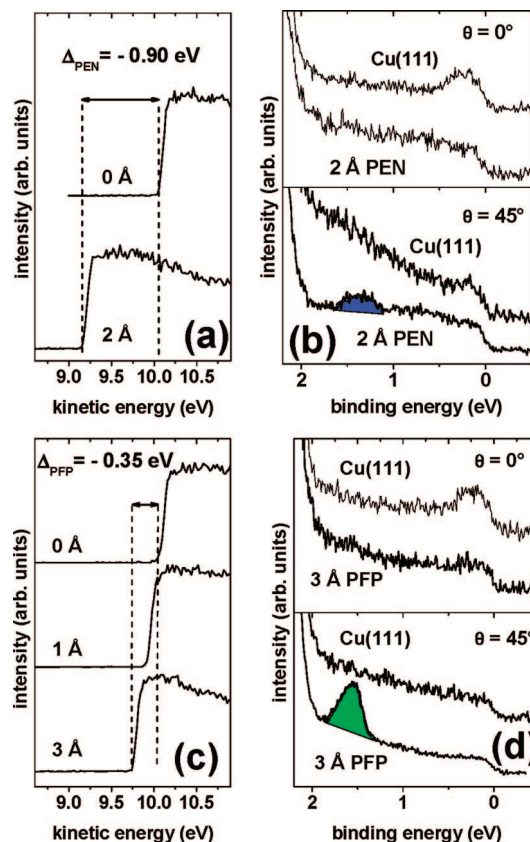
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reside above the aromatic core at a distance of  $(3.08 \pm 0.04)$  Å from the Cu surface. This distortion of the PFP molecule allows estimating the lower limit of the PFP–Cu bonding energy by comparing the total energies of a molecule in its coplanar and its measured distorted conformation. DFT calculations on isolated, fully geometry-optimized (i.e., planar) molecules, and molecules optimized under the constraint of the F-atoms being 0.1 Å above the plane of the C-atoms yield an energy difference of  $\sim 0.11$  eV. A more detailed analysis of the C1s XSW scans suggests that also the aromatic core of PFP is not perfectly coplanar. The core level splitting observed in the C1s spectra allows differentiating between the two different carbon species, that is, those bound to F and those which are not, and a comparison of their relative photoelectron yields in the XSW scan indicates that C atoms bound to F are further away from the copper substrate than C atoms not bound to F. Note that also PEN chemisorbed on Cu(111) may be nonplanar; however, the splitting of the C1s core level (Figure 1a) is rather small and thus difficult to resolve in XSW scans.

Compared to PEN, PFP molecules interact weakly with the Cu(111) surface leading to a significantly larger bonding distance. However, the adsorption geometry of PFP is nonplanar, see Figure 3b. Hence, we investigated the consequences of larger bonding distance and the distortion of PFP on the energy level alignment at the interface to the metal. With UPS we directly assessed hole injection barriers (HIBs) as the energy difference between the low-BE onset of the emission derived from the highest occupied molecular orbital (HOMO) and the Fermi level ( $E_F$ ) for both molecular monolayer/metal interfaces (Figure 4). Note that for PEN on Cu(119)<sup>18</sup> and Cu(110)<sup>27</sup> a hybridization of the PEN HOMO level and metal states was suggested, leading to new states close to  $E_F$ ; our photoemission data for 2 Å PEN/Cu(111) may also show such a hybrid gap state in the range of ca. 0.5 to 1.0 eV binding energy for  $\theta = 45^\circ$  in Figure 4b, however, at very low intensity. The HIBs for PEN (measured for the clearly visible peak at 1.1 eV) and PFP (1.35 eV) differ only by 0.25 eV, while their ionization energies differ by 0.85 eV (i.e., 5.0 eV for PEN and 5.85 eV for PFP). DFT calculations on isolated, fully geometry-optimized (i.e., planar) PEN and PFP molecules yield a difference in the HOMO energies of 0.78 eV; the adsorption-induced distortion in the PFP molecule does not significantly impact its HOMO energy. This shows that the notion that injection barriers can be easily tuned by changing molecular IEs is oversimplified, because the organic/metal interaction can change simultaneously, leading to different interface dipoles and thus unexpected injection barriers. Because of the discrepancy between differences in HIBs (0.25 eV) and IEs (0.85 eV) of PEN and PFP on Cu(111), significant differences in the sample work function ( $\phi$ ) values at monolayer coverage are observed. We find that  $\phi$  of PEN/Cu(111) is  $\Delta_{\text{PEN}} = 0.9$  eV lower than  $\phi$  of clean Cu(111) (Figure 4a). This decrease of  $\phi$  upon molecule adsorption is related to the interface charge redistribution due to strong chemisorption of PEN on Cu.<sup>18</sup> Note that the occurrence of the push-back effect of electron charge<sup>28–30</sup> alone cannot be assumed at this interface, because of the strong chemisorption.



**Figure 4.** UPS spectra. (a) Secondary electron cutoff and (b) valence region for ca. monolayer PEN on Cu(111). (c) Secondary electron cutoff and (d) valence region for ca. monolayer PFP on Cu(111). Photoemission features derived from the respective molecular HOMOs are area-filled.  $\theta$  is the angle between the surface normal and the detector. The excitation photon energy was 35 eV.

In contrast,  $\phi$  decreases by only  $\Delta_{\text{PFP}} = 0.35$  eV upon the adsorption of PFP on Cu(111) Figure 4. At first approximation, this work function decrease might be explained by a “push-back” of metal surface-electrons. However, in the present case we also have to consider the dipole of the PFP molecule caused by the adsorption-induced distortion (see Figure 3b). DFT calculations for the nonplanar PFP yield a dipole moment normal to the molecular plane of  $\mu \approx 0.53$  D. Taking this dipole induced sample work function change ( $\Delta\phi$ ) into account via the Helmholtz equation ( $\epsilon_0$  vacuum permittivity),

$$\Delta\phi = \frac{ne \cdot \mu}{\epsilon_0 \cdot \epsilon} \quad (1)$$

and using the surface molecular density  $n = 7.8 \times 10^{13} \text{ cm}^{-2}$  obtained from STM (Figure 2b), we obtain a value of  $\Delta\phi \approx +0.15$  eV for the intramolecular dipole induced work function increase (by averaging  $\Delta\phi = +0.16$  eV for a relative dielectric constant  $\epsilon = 1$ , and  $\Delta\phi = +0.13$  eV for  $\epsilon = 1.22$ <sup>31</sup>). Because this increase counteracts the lowering of  $\phi$ , the total contribution related to electron push-back is  $-0.35$  eV ( $\Delta_{\text{PFP}}$ )  $- 0.15$  eV (intramolecular dipole contribution) =  $-0.50$  eV ( $\Delta_{\text{PFP,tot}}$ ).

Noticeably, this value of  $\Delta_{\text{PFP,tot}}$  agrees quantitatively with reported experimental<sup>30</sup> and theoretical<sup>29</sup> values for physisorbed cyclohexane ( $\text{C}_6\text{H}_{12}$ ) on Cu(111), where adsorption-induced

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lowering of  $\phi$  is related to Pauli repulsion only. This finding for PFP on Cu(111) highlights that an adsorption-induced intramolecular dipole (of an initially nondipolar molecule) must be taken into account to derive a complete picture of adsorption and energy levels. Although details of the adsorption of organic molecules on metal surfaces can coherently be assessed experimentally, a reliable theoretical description remains a challenging task.<sup>32</sup> It is anticipated that the combination of appropriate descriptions of organic/metal bonding distances and interface atomic positions with the approach to assess interface energetics from the interface charge neutrality level<sup>5</sup> should result in a refined understanding of interface phenomena that are of general importance for organic/metal interactions, regardless of specific interaction strength. In fact, recent extensions of the induced density of states (IDIS) model, allowing for inclusion of charge transfer, Pauli repulsion, intrinsic molecular dipoles, and interface screening as a function of surface coverage with molecules, have been successful for describing complex organic/metal interfaces.<sup>33</sup> This model may thus be further extended by including adsorption-induced intramolecular dipoles [i.e., as for PFP/Cu(111)], which has not yet been considered.

Following a combined experimental and theoretical approach we derive important correlations between strength of molecule/metal interaction, average bonding distances, adsorption-induced molecular conformation changes leading to intramolecular dipoles, organic/metal interface dipoles, and the resulting unexpected energy level alignment. We find a significant difference in the average bonding distances for the C atoms of

PEN (2.34 Å) and PFP (2.98 Å) on Cu(111). Furthermore, we show that even for weak organic/metal interactions [PFP on Cu(111)] distortions of the molecule occur, evidenced by the 0.1 Å larger bonding distance of F atoms compared to the average C position. This results in adsorption-induced intramolecular dipoles ( $\sim 0.5$  D), which influence the interface energetics. Adsorption-induced molecular conformational changes have to be considered as a general phenomenon at organic/metal interfaces, and will have a significant impact on charge transport across interfaces, for example, by influencing charge reorganization energies<sup>21,34</sup> of the molecular monolayer and determining the surface potential for subsequently deposited multilayers.<sup>21</sup> Furthermore, our results show that changing the molecular ionization energy by fluorination does not readily result in corresponding changes of the energy level alignment at organic/metal interfaces according to the Schottky–Mott limit, and other synthetic strategies should be developed to achieve control over interfacial energetics.

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**Supporting Information Available:** XSW confidence level plot for the atomic positions of PEN and PFP on Cu(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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