Effect of fluorination on the molecule-substrate interactions of pentacene/Cu(100) interfaces.

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Abstract: By means of scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS), we study and compare the crystalline and electronic structure of fluorinated and non-fluorinated pentacene fims on Cu(100). Pentacene perfluorination strongly affects its electronic structure both in the bulk and at the metal-organic interface. While the azimuthal anisotropy of the molecule-substrate interactions on Cu(100) remains unaffected by the fluorination, the interaction mechanisms, as concluded from their effect on the core-levels and on the conduction band of the respective molecules, show a completely disparate behaviour.

1. Introduction

Molecular electronics has attracted intense interest because of its potential for producing inexpensive optoelectronic devices (LEDs, thin film transistors, solar cells), and because of the possibility of tailoring the electronic structure by synthesizing new variations of organic molecules. In particular, perfluorination of semiconducting oligomers is long known as an effective route to modify their electronic structure in a controlled way.[1-4] It enhances both the ionization potential and the electron affinity, and commonly entails a change in their charge transport properties which favors n-type semiconducting behaviour. However, only recently this method was applied to one of the so far most popular and successful organic semiconductors, as is the case of pentacene (PEN, Fig 1a).[5] Perfluoropentacene (PFP, Fig. 1a) showed a remarkably good performance in n-channel field effect transistors[5]. In combination with pentacene it produced high performance complementary circuits and ambipolar transistors.[5] Ever since, PFP has been receiving increasing attention and has become the target of numerous research efforts.[6-14] Nevertheless, many important aspects remain unexplored. In particular, the electronic structure of unoccupied molecular orbitals has never been addressed so far. Other relevant questions, such as the crystalline structure of films on metallic substrates or the electronic structure of core-levels, have been studied only for very limited cases.[13,14] Therefore, we have performed a comparative study of the epitaxial growth and electronic structure of PFP thin films with respect to PEN, using a Cu(100) single crystal as substrate. To obtain a complete picture, we have combined scanning tunneling microscopy (STM), core-level photoelectron spectroscopy (XPS), and near edge X-ray absorption fine structure spectroscopy (NEXAFS).

2. Experimental

The substrates have been prepared by repeated Ar sputtering (E=600-900 eV) and annealing cycles (T=350-450ºC). PEN and PFP molecules were purchased from Aldrich and Kanto Denka Kogyo Co., respectively. The STM experiments have been performed under UHV in constant current mode, at room temperature, with chemically etched tungsten tips, in a commercial JEOL system. The measurements were carried out on full coverage monolayer samples. The XPS measurements have been performed with a

SPECS ESCA setup, making use of Mg K_{α} radiation. The NEXAFS measurements have been performed in total electron yield detection mode at beamline 8.0 of the ALS (Berkeley) for the monolayer samples, and beamline VLS-PGM of the SRC (Wisconsin) for the thick film samples. The polarization angle between the electric field vector and the surface plane was of ~0º and ~40º for the samples on SiO_2 and Cu(100), respectively. The intensity of the NEXAFS spectra is normalized to the high energy vacuum level, except for the PFP/SiO_2 spectrum, which is additionally scaled by 0.5 because of the high intensity of the π* resonances with the geometry used.

3. Results and discussion

The STM results on the crystalline structure of PFP monolayers on Cu(100) after room temperature deposition are summarized in Fig. 1. The molecules lie down with the long molecular axis presenting only two discrete, orthogonal orientations on the surface plane, namely the [011] and [01-1] substrate directions. As previously reported, the same applies for monolayers of PEN, [15-17] or even of other elongated molecules such as tetracene or diindenoperylene (DIP).[18,19] The orientational dependence of the molecule-substrate interactions on Cu(100) is thus the same for PEN and PFP, unaffected by molecular fluorination. However, while PEN only forms a disordered layer,[15,16] PFP shows long-range crystalline order, evidencing significant differences in the interrelated molecule-substrate and intermolecular interactions which drive the self-assembly. In particular, two crystalline polymorphs coexist in the molecular monolayers, as observed on each of the two Cu terraces in Fig. 1. One is formed by rows of collinearly oriented molecules (lower terrace in Fig. 1), while the other presents a more complex unit cell and includes molecules aligned along both directions (upper terrace in Fig. 1). Their unit cell vectors are overlaid on the close-ups of each of the polymorphs, and the parameters are given by a = 9.4±0.5 Å, b = 17.6±0.9 Å, and γ = 57±2º, and a = 35.4±1.5 Å, b = 26.4±1.2 Å, and γ = 90±2º, respectively. Tentative epitaxial models are shown on the lower panels.

The changes in the electronic structure upon molecular fluorination are addressed by XPS and NEXAFS. XPS spectra of the C1s and F1s core levels for PEN and PFP films on Cu(100) are shown in Fig. 2a for various coverages during stepwise thin film deposition. Previous

investigations of PEN on Cu(100) reported strong molecule-substrate hybridization, including partial charge transfer into the LUMO.[20] As a consequence, the C atoms participating most strongly in the hybridization (those numbered 2 and 4 in the inset of Fig. 2b) exhibit a chemical shift to lower binding energies in the XPS spectra, which disappears for multilayer films.[21] A detailed peak shape analysis of the 1 and 2 ML coverage data in Fig. 2b confirms those findings. Deconvolution of the 1 ML spectrum into four components (each corresponding to the C atoms numbered in the inset of Fig. 2b as 1, 2-4, 3, and 5-6, respectively) leads to an excellent fit (Fig. 2b). While a lesser number of components could have provided a satisfactory fit as well, we have opted to follow the model based on previous findings of Baldachini et al.,[21] which were supported by theoretical calculations and have been corroborated in a number of studies.[20,22] For the 2 ML sample, the data are well fitted by simply doubling the intensity of the various components, except that of the 2-4 C atoms. This peak is kept unchanged, taking into account the first layer 2-4 C atoms hybridized with the surface, while a new component is required for the non-hybridized 2-4 C atoms of the second layer. The absence of width changes in the 1, 3, and 5-6 C atom components for the second layer prove their lower contribution to the interactions with the Cu substrate.[23]

Interestingly, the PFP spectra and their evolution with coverage is very different from the case of PEN, evidencing thoroughly different molecule-substrate interaction mechanisms. The spectrum of the monolayer appears as a triple peak, each centered at 286.74 eV, 284.98 eV and 283.56 eV, respectively (Fig. 2b). As previously suggested by Koch et al. for XPS spectra of PFP on Cu(111) and Au(111),[13] we ascribe the high binding energy peak to the C atoms bonded to F, since, as already observed for other fluorinated molecules such as phthalocyanines,[3,24,25] fluorination gives rise to a pronounced chemical shift as a result of the increased electron transfer to the F atoms. The component at 284.98 eV corresponds to the non-fluorinated atoms presenting a triple C bond, while we ascribe the small, low binding energy contribution to some residual carbon contamination adsorbed during PFP sublimation (due to e.g. low purity source material), in line with the previous interpretation by Koch et al.[13] In contrast to PEN, the signal arising from the second layer upward presents a rigid shift of those features to higher binding energies (Fig. 2b).

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The contribution from the first layer can be discerned at the low binding energy side (best observed for the 2 ML sample). A fit to the 2 ML spectrum does indeed reveal the same components as for the 1 ML sample, plus new components for the second layer with similar intensities, shifted down by 1.15 eV and about 35% narrower (Fig. 2b). No major shifts are observed for further layers. Similar observations are made upon analysis of the F1s spectra. Comparing fits of the 1 ML and 2 ML films, we find that the latter contains the same component as the 1 ML film, plus a new component for the second layer, characterized by a similar intensity, a width reduced by about 8%, and a shift down in energy by 0.65 eV (Fig. 2b).

In contrast with the localized interactions between PEN and Cu(100), which involve considerable charge transfer and can be considered on the limit to chemisorption, PFP shows a more delocalized nature of the molecule-substrate interactions involving the whole molecule. The narrowing of the XPS components of the second layer evidences the decreased interaction with the substrate, while their shift is related to the diminished screening by the metallic surface. Also the disparate behaviour of the F and C core levels versus coverage is expalined by atom-specific dynamic screening at the metal-organic interface as the potential cause. In reference to the evolution of the F1s core levels, the stronger shift and the reduced width of the C1s levels in the second layer provides evidence that the PFP-Cu(100) interaction takes place primarily via the C atoms, which might be related with the localization of both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) essentially on the C atom backbone.[12]

In order to access the electronic structure of the unoccupied molecular orbitals, we have performed NEXAFS measurements on PEN and PFP monolayers on Cu(100). The C 1s and F 1s absorption edges are shown in Fig. 3, together with reference spectra of a 90 nm thick PFP film on SiO$_2$, and of gas-phase PEN for comparison. The peaks observed represent transitions from the C1s and F1s core levels in Fig. 2 into empty molecular orbitals. For thick films and gas phase spectra, the first six peaks at low energies for both PEN and PFP stem from excitations into π^* orbitals, while the broad higher-lying features involve σ^* orbitals.[26-28] The PEN ML spectrum evidences a single, broad peak in the low energy edge as a result of the strong electronic coupling

of the molecules with the substrate. Previous studies have shown that well defined peaks appear as the coverage increases and the weaker intermolecular bonds take over, with the positions of the various features showing good agreement with PEN gas-phase spectra.[22,26-28] The PFP spectra also show broadened features for the ML as compared to the thick film sample. In addition to the peak broadening, a different lineshape evidences (as in the case of PEN) a modified electronic structure resulting from the molecule interaction at the interface with the substrate. However, in reference to PEN, the differences in the lineshape and the broadening of PFP ML spectra is much less pronounced. They contain several well defined peaks, indicating weaker interactions with the substrate. This is in line with the conclusions from previous studies on Cu(111) substrates,[13] where a stronger molecule-substrate interaction is concluded for PEN based on its lower molecule-substrate distance as measured by x-ray standing wave experiments (2.34 Å vs 2.98 Å for PEN and PFP, respectively). In fact, given that PEN on Cu(100) shows the same molecule-substrate distance (2.33 Å),[20] extrapolation of this trend to the PFP/Cu(100) interface is also in accordance with our spectroscopic measurements, which further imply a sharper metal-semiconductor transition, i.e. a sharper Schottky contact. The absorption edge is shifted downwards from the multilayer, what can most probably be ascribed to initial state effects such as those evidenced comparing the XPS spectra of monolayer and multilayer samples in Fig. 3. Altogether, this evidences a severely different electronic structure caused by fluorination of pentacene, not only in the bulk, but also at the metal-organic interface.

4. Conclusions

In conclusion, we have studied the influence of perfluorination on pentacene thin films, giving insight into its effect on the electronic structure of the molecules, the molecule-substrate interactions at the metal-organic interface, and the resulting crystalline structures. The energy levels of PFP are very different from PEN both in multilayers and at metal-organic interfaces. The azimuthal dependence of the molecule-substrate interaction is similar for PFP and PEN on Cu(100) surfaces. However, the interaction mechanisms are thoroughly different. In particular, their strength appears to be weaker for PFP, mirrored in sharper interface levels and less perturbed

orbitals by the metals. This may be beneficial for establishing sharp metal-semiconductor interfaces and well controlled Schottky barriers. These are all issues of crucial relevance for the optoelectronic performance of organic-based devices, and therefore indispensable for an understanding of the impressive success of PFP amongst the semiconducting oligomers in organic electronics.

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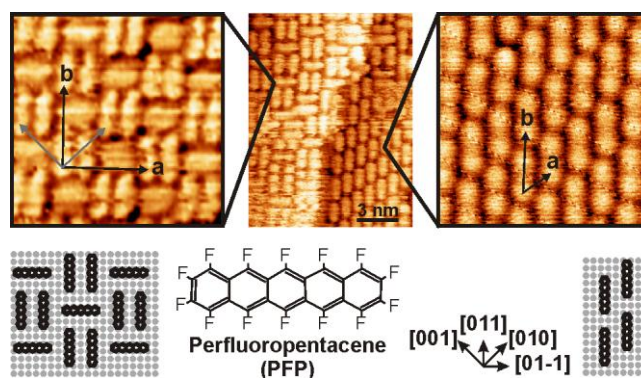
Figure 1. STM image of a PFP monolayer on Cu(100), evidencing the coexistence of two polymorphs on the higher (left) and lower (right) Cu terraces, respectively. Close-ups of each polymorph are presented at the respective sides, with the corresponding unit cell vectors overlaid on the images (the primitive unit cell is outlined by grey vectors in the left panel). At the bottom, tentative epitaxial models for the two polymorphs, as well as the molecular structure of PFP and the orientation of the crystalline directions (which apply to both the STM images and the models) are presented.
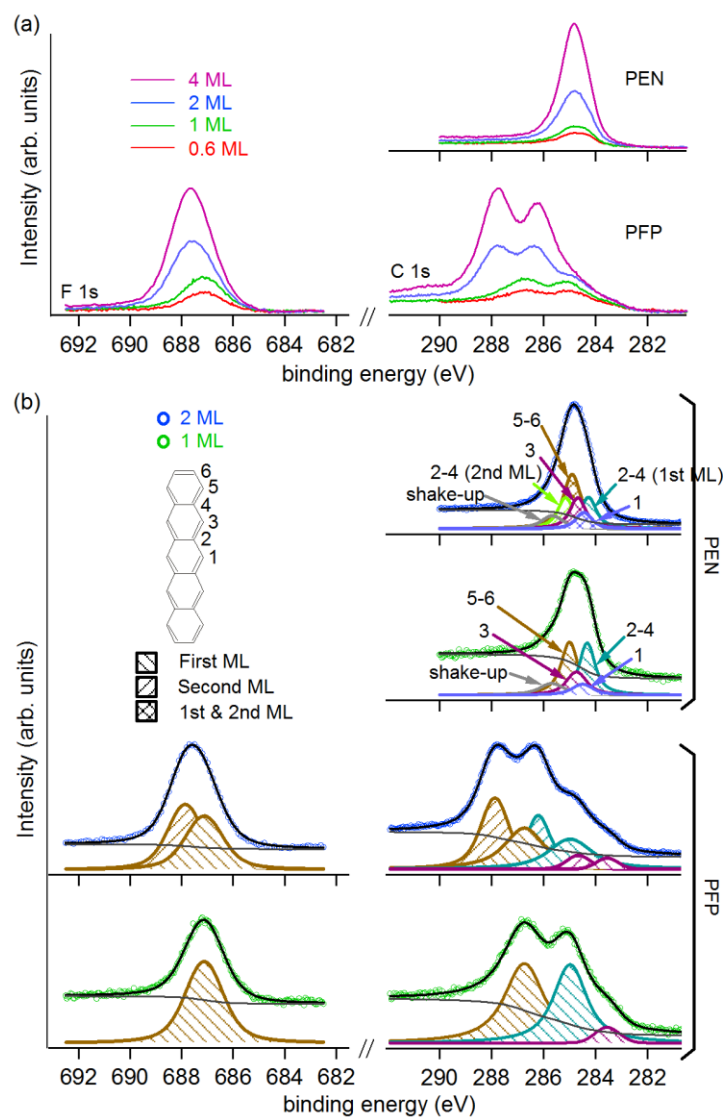
Figure 2. (a) Core level photoelectron spectra of PFP and PEN films on Cu(100) as a function of coverage. (b) Fits of the spectra corresponding to 1 ML and 2 ML samples, evidencing the contributions of the different components of the first and second layer, respectively. The molecular scheme represents the chemically different C atoms.
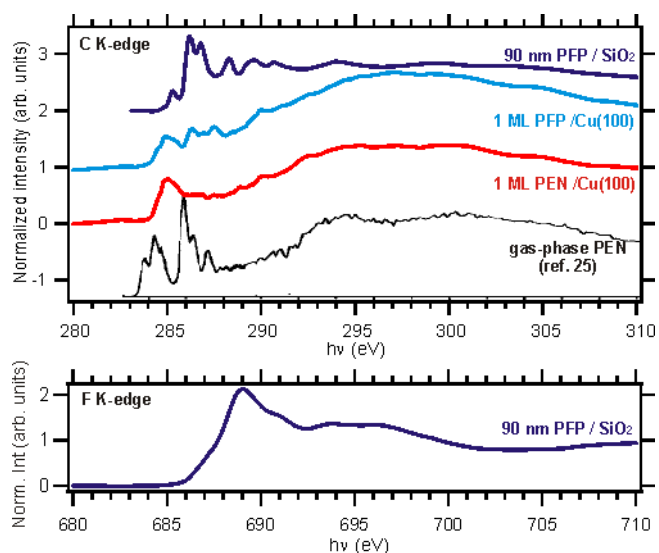
Figure 3. C K-edge NEXAFS spectra (top) taken on PEN and PFP monolayers on Cu(100), in comparison to those taken on a 90 nm thick PFP film on SiO_2 and on gas-phase PEN (from ref. 25). F K-edge NEXAFS spectrum (bottom) taken of a 90 nm thick PFP film.