

Influence of molecular conformation on organic/metal interface energetics

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Abstract

Using ultraviolet photoemission spectroscopy (UPS), we show that the conformation of a conjugated organic molecule can be changed significantly upon adsorption on a metal surface, even in the case of weak interactions with the metal. This is accomplished by comparing the thickness-dependent spectral evolution for a non-rigid non-planar molecule (*p*-sexiphenyl) deposited onto Ag(111), with those of a coplanar molecule (α -sexithienyl) and a rigid non-planar one (1,3,4,6,7,9,10,12,13,15,16,18-dodecylmethyl-hexa-*peri*-hexabenzocoronene). Molecular conformation changes can influence hole injection barriers by at least 0.1 eV. These results have a direct impact on the detailed understanding of organic/metal interfaces.

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1. Introduction

The importance of a detailed understanding of energy-level alignment mechanisms at interfaces between metals and conjugated organic materials has been well recognized over the past few years in the context of realizing novel electronic and opto-electronic devices. The impact of, e.g., chemical reaction (charge transfer and covalent bond formation), polarization, interface dipoles, and diffusion on measured charge injection barriers has been pointed out in numerous experimental and theoretical studies [1–5]. However, another effect possibly influencing the energy level alignment at organic/metal interfaces has not yet been addressed adequately in the literature: metal surface-induced conformational

changes of molecules. Such changes could occur even in the case of rather weak interactions between the metal and the organic molecule (e.g., physisorption), and might modify the effective conjugation of a molecule in direct contact to the metal surface as opposed to one located in the organic bulk. The consequence would be a modified charge-injection barrier. Actually, energetic disorder at organic/metal interfaces due to different local molecular adsorption geometries (in particular on polycrystalline substrates) has sometimes been invoked to explain broadened or poorly resolved features in photoemission experiments [6,7].

In the present work, we compare the photoemission spectra obtained on monolayer-range and multilayer films of organic molecules on an Ag(111) surface. We find varying relative shifts of the peaks in the UPS spectra, which depend on the nature of the molecular backbone. These results are attributed to changes in

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molecular conformation induced by the metal surface, which implies that such effects must be considered to fully understand the energetic changes of molecular levels as a function of the distance from the metal substrate.

2. Methodology

Ultraviolet photoemission spectroscopy (UPS) experiments were performed at the end-station of the Flipper II beamline at Hasylab (Hamburg, Germany) [8]. This system allows the transfer of samples between the preparation and analysis chambers (base pressure: 4×10^{-9} and 2×10^{-10} mbar, respectively) without breaking ultrahigh vacuum conditions. Before every organic deposition, the Ag(111) single crystal substrate was cleaned by repeated Ar-ion sputtering and annealing cycles until a clear low-energy electron diffraction pattern could be observed. α -Sexithienyl (Aldrich), *p*-sexiphenyl (Tokyo Kasei Kogyo, Co., Ltd.), and 1,3,4,6,7,9,10,12,13,15,16,18-dodecamethyl-hexa-*peri*-hexabenzocoronene (DM-HBC) [9] were evaporated from resistively heated pin-hole sources. The chemical structures of these molecules are shown in Fig. 1. The mass-thickness was monitored with a quartz crystal microbalance. No correction was made for possible differences in sticking coefficient on the quartz and Ag crystals. UPS spectra were recorded with a double-pass cylindrical mirror analyzer, set to an energy resolution of 150 meV (80–20% intensity drop at the Ag Fermi-edge). The photon energy was set to 22 eV. For better visibility, spectra are shown with five-point averaging. Curve fitting was done with the program *Winspec*, developed at the University of Namur, Belgium).

The molecular orbital energies for isolated molecules have been calculated within the framework of density functional theory at the fully relaxed geometry for any given (fixed) inter-ring twist angle. The mPW-LYP exchange-correlation functionals were used [10,11], in conjunction with a 4-31G** basis set. All calculations have been performed with GAUSSIAN98 [12]. The electronic density-of-states has then been obtained by convolution with Gaussian functions with a full width at half maximum of 0.35 eV.

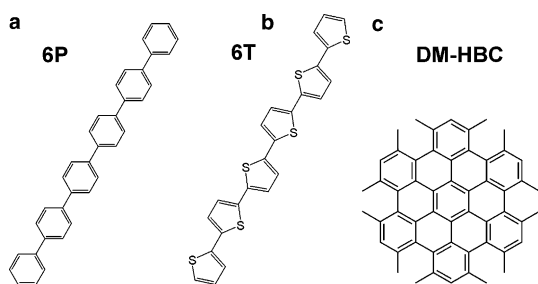


Fig. 1. Chemical structure of: (a) 6P, (b) 6T and (c) DM-HBC.

3. Results and discussion

UPS spectra of *p*-sexiphenyl (6P) for varying nominal coverage (θ) are shown in Fig. 2a. The first maximum (at 2.34 eV binding energy in the 150 Å film) is related to an ionization processes from the highest occupied molecular orbital (HOMO), that at 2.84 eV to the HOMO–1 and that around 4 eV is mainly due to localized π -orbitals [13]. The various peaks exhibit differential shifts as θ increases, which is more clearly visible in the inset in Fig. 2a, where the contributions from the Ag substrate were subtracted [6]. These otherwise influence the apparent position of the peak near 4 eV binding energy (BE). The respective peak positions and the total shift Δ when going from monolayer coverage ($\theta < 10$ Å) to thick 6P films are listed in Table 1, together with the values for the two other organic materials studied. The shift of HOMO and HOMO–1 is ca. 0.1 eV larger than for the emission of the localized π -states (loc.- π). As the film thickness increases, the energy separation between loc.- π and HOMO and HOMO–1, respectively, becomes smaller. The observation of differential shifts indicates that 6P molecules in the monolayer are different from those in the thick film. The interaction between Ag and 6P is rather weak as no new states in the 6P energy gap are observed even at very low coverage, ruling out charge transfer [14]. In addition, core level photoelectron spectroscopy performed for 6P on Ag(111) did not show the appearance of new C1s peak components for monolayer coverage compared to multilayers, thus ruling out covalent bond formation or strong chemisorption [15]. Hence, the differential changes in molecular level BE are likely to come from differences in the molecular conformation of 6P between the monolayer and the thick film (although small differences in the interactions between the Ag substrate and the localized and delocalized π -orbitals cannot be excluded). Note that 6P molecules are oriented with they long molecular axis parallel to the Ag(111) surface [16]. At room temperature, 6P molecules in the bulk exhibit librational motion, resulting in angles between neighbouring benzene ring planes (α) different from zero. Biphenyl (as an example for oligophenylenes) displays an inter-ring twist angle of 42° in the gas phase [17] and 32° in solution and the molten state [18], whereas it is found to be planar on average [19] in the solid state as a result of ring librations at room temperature. More in-depth investigations, however, yield a twist of 18° between the central and the outer rings in *p*-terphenyl at low temperature [20]. For *p*-quarterphenyl, Baudour et al. [21] find an average twist of 22.7° between the two inner rings and 17.2° between the inner and outer rings in the low temperature phase. Slightly larger values are estimated at room temperature [22].

As is very well established, larger α leads to smaller conjugation (inter-benzene π -electron overlap) along

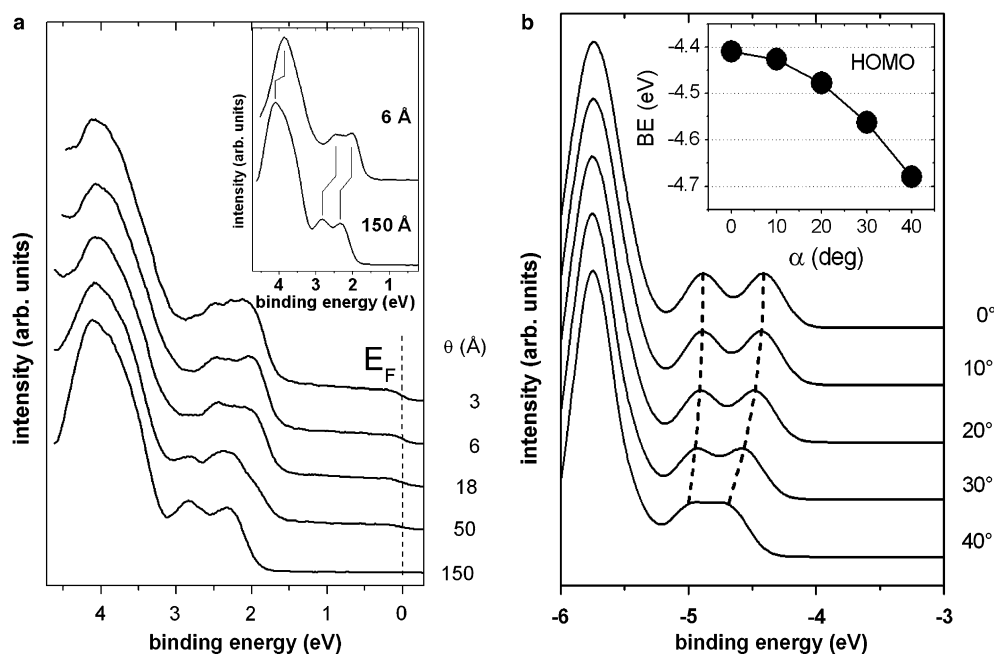


Fig. 2. (a) UPS spectra of 6P on Ag(111) for increasing coverage θ . Inset: contribution from Ag subtracted. (b) DFT-calculated density of states of 6P for different inter-ring twist angles α . Energy reference is the vacuum level, not corrected for solid state effects. Inset: Evolution of the binding energy of the maximum associated with the HOMO level as a function of the inter-ring twist angle.

Table 1

Peak maxima (derived from HOMO, HOMO–1, and localized π -orbitals) for organic films on Ag(111) in the monolayer range (ML) and thick films (thick), and the difference Δ

	ML (eV)	Thick (eV)	Δ (eV)	HIB _{ML} (eV)	HIB _{Thick} (eV)	Δ_{HIB} (eV)
<i>6P</i>						
HOMO	2.02	2.34	0.32	1.63	1.90	0.27
HOMO–1	2.47	2.84	0.37			
Loc.- π	3.85	4.09	0.24			
<i>6T</i>						
HOMO	1.62	1.83	0.21	1.23	1.38	0.15
HOMO–1	2.31	2.49	0.18			
Loc.- π	3.89	4.07	0.18			
<i>DM-HBC</i>						
HOMO	1.62	1.83	0.21	1.19	1.31	0.12
HOMO–1	2.12	2.31	0.19			
Loc.- π	3.07	3.29	0.22			

Maxima positions are obtained by peak fitting (where applicable), or visual inspection; the error is estimated to be ± 0.03 eV. Hole injection barriers (HIB) are determined as linear extrapolation of the HOMO low BE onset towards the background. Δ_{HIB} is the difference of HIB's for ML and Thick films (not corrected for analyzer resolution). The error for HIB's is estimated to be smaller than ± 0.05 eV.

the 6P molecule, and consequently to a shift of energy levels and a larger energy gap [23]. A simple theoretical model describes this behaviour qualitatively (see Fig. 2b). In particular, an increase of α leads to a decrease in the energy separation between the delocalized HOMO and the localized π -states, which are at ca. 5.7 eV below the vacuum level in Fig. 2b (and around 4 eV binding energy in Fig. 2a). The inset of Fig. 2b highlights this trend, which we also observe experimentally (cf. Table 1: for increasing film thickness, the energy separation between HOMO and loc.- π

decreases). This observation is consistent with the fact that 6P molecules in direct contact with the Ag surface can have a smaller inter-ring twist angle α than bulk 6P. This is confirmed by a recent scanning tunnelling microscopy study on 6P/Ag(111) performed at 6 K, where $\alpha = 11.4^\circ$ was reported [16]. We attribute this to the small, but yet finite interaction between the metal surface and 6P, forcing the molecule into a more coplanar conformation with increased π -electron overlap. We also note that Koller et al. [24] also found that the majority of 6P molecules adopted a conformation close

to coplanar when adsorbed on an Ni(110)(2×1)-O surface.

From these observations and the crystallographic data discussed above, it can be deduced that the interring twist angle in 6P at the Ag surface is reduced by about 10°. According to the inset in Fig. 2b, this reduction is fully consistent with the 0.1 eV change in the BE difference observed experimentally between the delocalized and localized states.

Further support for our hypothesis of α -angle reduction comes from film-thickness dependent UPS experiments with molecules that exhibit the same conformation on the Ag surface and in the bulk, i.e., α -sexithienyl [25] (6T) and DM-HBC. UPS spectra for increasing coverage of Ag(111) with 6T (Fig. 3a; the contribution from the substrate Ag is subtracted in the inset) and DM-HBC (Fig. 3b) display only a rigid shift (within the estimated error) of all molecular levels as θ increases. This can easily be seen from the peak positions listed in Table 1. (Similar to 6P, 6T and DM-HBC interact very weakly with Ag, which is deduced from the absence of differential shifts and new states in the energy gap [26,27].) 6T and DM-HBC molecules in contact to the Ag substrate exhibit the same energy level splittings, and consequently molecular conformation, as molecules in the bulk.

The observation by UPS that DM-HBC exhibits the same conformation on Ag(111) and in the bulk is supported by theoretical calculations. The density of states was calculated for the non-planar DM-HBC (Fig. 4a), unsubstituted planar hexa-*peri*-hexabenzocoronene (HBC; Fig. 4c), and HBC in the

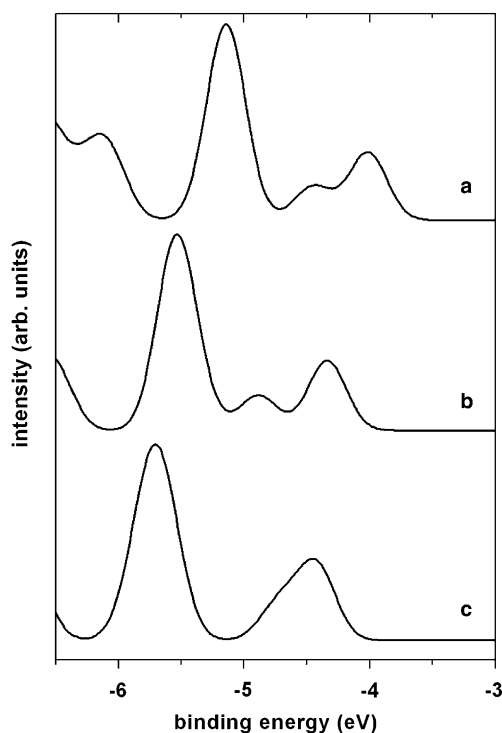


Fig. 4. DFT-calculated density of states of: (a) DM-HBC; (b) non-planar HBC (NP-HBC) and (c) planar HBC.

non-planar conformation of DM-HBC (NP-HBC; Fig. 4b; DM-HBC *cannot* be studied in its planar conformation because of steric effects). While there is essentially just a rigid shift of energy levels between DM-HBC and NP-HBC, the splitting of low-lying

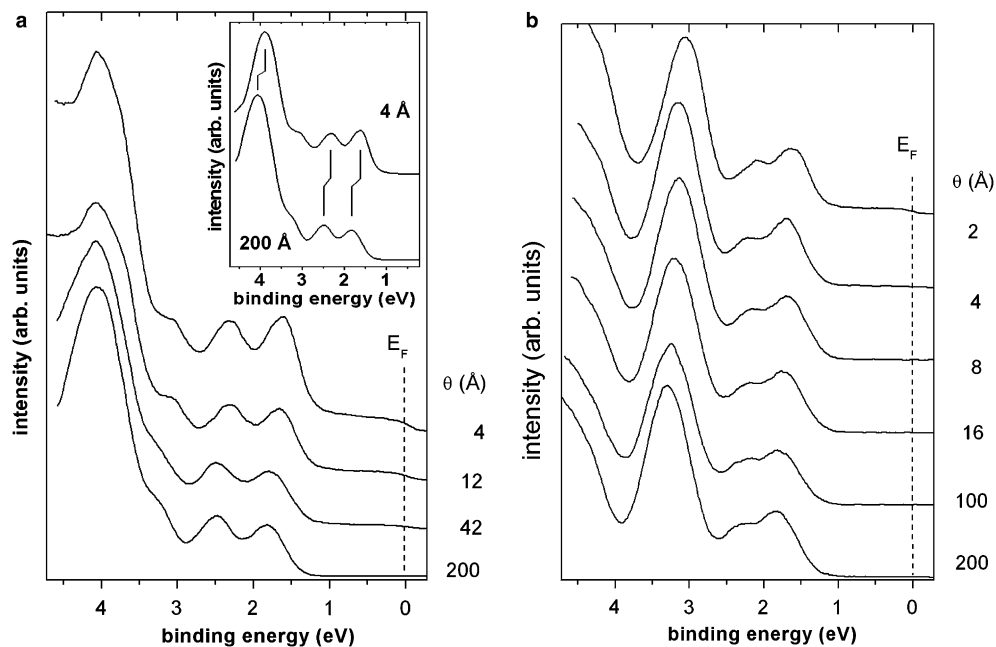


Fig. 3. (a) UPS spectra of 6T on Ag(111) for increasing coverage θ . Inset: contribution from Ag subtracted. (b) UPS spectra of DM-HBC on Ag(111) for increasing coverage θ .

energy levels for HBC is very different (BE region -5 to -4 eV). A possible planarization of DM-HBC molecules in direct contact with the metal surface can thus be ruled out, as planarization should change the photoemission features from low-lying molecular orbitals, as was the case for 6P. According to Fig. 4, these changes are predicted to be substantial but were not observed experimentally.

The reason for the *rigid* shift of molecular levels to higher BE for increasing thickness is the higher screening efficiency for photo-holes on molecules closer to the metal substrate, and has been addressed in the literature [28]. This effect also accounts for hole injection barrier (HIB) height changes (Δ_{HIB}) as a function of film thickness [6,28]. However, possible contributions to Δ_{HIB} from changes in molecular conformation have been raised only sporadically [6,7]. Comparing our results for the three different molecules, we can estimate that the contribution to Δ_{HIB} by the change in conformation of 6P molecules is ca. 0.1 eV. We propose that this contribution could be even larger for molecules at interfaces where more pronounced conformational changes are possible (e.g., large molecules with non-rigid 3-dimensional structure or chemical moieties with the capability for stronger interaction with metal surfaces).

Finally, one would expect that the values of Δ and Δ_{HIB} (Table 1) should be the same (at least for 6T and DM-HBC, where conformational effects do not contribute). However, Δ_{HIB} is notoriously smaller than Δ for all molecules investigated. The reason is the pronounced island growth mode of (nearly all) organic molecules on metal surfaces [6,29]. Therefore, UPS simultaneously probes sample regions with significantly varying film thicknesses, resulting in superimposed spectra from thin and thick regions. This can be seen particularly well in the spectrum for 50 Å 6P on Ag (Fig. 2a) that presents a clear shoulder on the low BE side of the HOMO emission. Since the thin film spectra always have their contribution on the low BE side, HIB values determined for nominally thick films are somewhat too low. In addition, energetic disorder/defects may also contribute to broadening of UPS spectra for increasing film thickness.

4. Conclusion

A comparison of the UPS spectra of 6P, 6T, and DM-HBC indicates that 6P molecules adsorbed on Ag(111) adopt a more planar conformation as compared to 6P in the bulk, where a larger inter-ring twist angle prevails. The associated changes in molecular energy levels are estimated to be on the order of 0.1 eV. This effect influences the energy position of molecular levels as a function of organic film thickness as mea-

sured by UPS. The difference in conformation of 6P molecules in close contact with the metal and those far away leads to an additional decrease of the hole injection barrier of ca. 0.1 eV compared to organic/metal interfaces where conformation changes are not observed.

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References

- [1] H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* 11 (1999) 605.
- [2] C.F. Shen, A. Kahn, J. Schwartz, *J. Appl. Phys.* 90 (2001) 6236.
- [3] X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W.R. Salaneck, J.L. Brédas, *J. Am. Chem. Soc.* 124 (2002) 8131.
- [4] W.R. Salaneck, K. Seki, A. Kahn, J.-J. Pireaux, *Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and Optoelectronic Applications*, Marcel Dekker, New York, 2001.
- [5] A. Kahn, N. Koch, W.Y. Gao, *J. Polym. Sci. B* 41 (2003) 2529.
- [6] A.C. Dürr, N. Koch, M. Kelsch, A. Rühm, J. Ghijsen, R.L. Johnson, J.-J. Pireaux, J. Schwartz, F. Schreiber, H. Dosch, A. Kahn, *Phys. Rev. B* 68 (2003) 115428.
- [7] T. Munakata, T. Sugiyama, T. Mauda, M. Aida, N. Ueno, *Appl. Phys. Lett.* 85 (2004) 3584.
- [8] R.L. Johnson, J. Reichardt, *Nucl. Instr. Methods* 208 (1983) 719.
- [9] K. Müllen, et al., unpublished.
- [10] C. Adamo, V. Barone, *J. Chem. Phys.* 108 (1998) 664.
- [11] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [12] M.J. Frisch, et al., Gaussian Inc., Pittsburgh PA, 2001.
- [13] K. Seki, U.O. Karlsson, R. Engelhardt, E.E. Koch, W. Schmidt, *Chem. Phys.* 91 (1984) 459.
- [14] N. Koch, A. Rajagopal, J. Ghijsen, R.L. Johnson, G. Leising, J.-J. Pireaux, *J. Phys. Chem. B* 104 (2000) 1434.
- [15] C. Bittencourt, J. Ghijsen, private communication.
- [16] K.-F. Braun, S.-W. Hla, *Nano Lett.* 5 (2005) 73.
- [17] A. Almennigen, O. Bastiansen, L. Fernholt, B. Cyvin, S. Cyvin, S. Samdal, *J. Mol. Struct.* 128 (1985) 59.
- [18] V.J. Eaton, D. Steele, *J. Chem. Soc. Faraday Trans. 2* (1973) 1601.
- [19] B. Trotter, *Acta Cryst.* 14 (1961) 1135.
- [20] J.L. Baudour, H. Cailleau, W.B. Yelon, *Acta Cryst.* B33 (1977) 1773.
- [21] J.L. Baudour, Y. Délugeard, P. Rivet, *Acta Cryst.* B34 (1978) 625.
- [22] J.L. Baudour, *Acta Cryst.* B47 (1991) 935.
- [23] J.L. Brédas, G.B. Street, B. Thémans, J.M. André, *J. Chem. Phys.* 83 (1985) 1323.

- [24] G. Koller, S. Surnev, M.G. Ramsey, F.P. Netzer, *Surf. Sci.* 559 (2004) L187.
- [25] D. Fichou, *J. Mater. Chem.* 10 (2000) 571.
- [26] N. Koch, E. Zojer, A. Rajagopal, J. Ghijsen, R.L. Johnson, G. Leising, J.J. Pireaux, *Adv. Funct. Mater.* 11 (2001) 51.
- [27] N. Koch, J. Ghijsen, R.L. Johnson, J. Schwartz, J.-J. Pireaux, A. Kahn, *J. Phys. Chem. B* 106 (2002) 4192.
- [28] I.G. Hill, A.J. Makinen, Z.H. Kafafi, *J. Appl. Phys.* 88 (2000) 889.
- [29] G. Witte, C. Wöll, *J. Mater. Res.* 19 (2004) 1889.