Chemisorption of Pentacene on the Pt(111) with little molecular distortion

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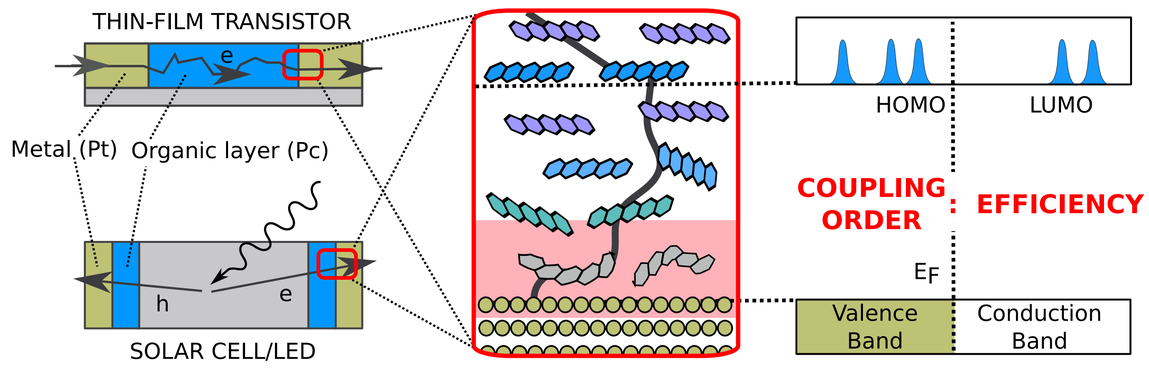
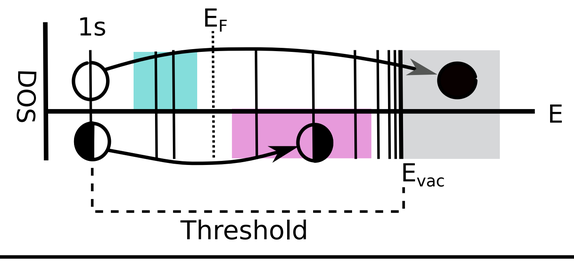
IN BRIEF - Here we investigate the adsorption of an aromatic molecule, Pentacene (Pc, $C_{22}H_{14}$), onto the (111) surface of Platinum (Pt). We probe the surface using the Scanning Tunnelling Microscopy (STM) to define the most favored configurations of the molecule. We use X-ray absorption techniques as X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy to investigate the chemical environment and the electronic configuration of C atoms. We simulate the interface by means of density functional theory (DFT), also accounting for the van der Waals (vdW) interaction, to support the experimental results and address the features observed in the measurements.

BACKGROUND - Organic molecules have attracted much attention as building blocks for active layers in opto-electronic devices because the large number of compounds and production techniques available can bring new interesting properties at lower costs compared to inorganic semiconductors[1]. Hybrid organic-metal interfaces are formed at the electrodes and their properties are key factors in defining the performance of the device either in a thin-film or as a support for the growth of a more extended multilayer[2]. The Pc/Pt(111) junction seems promising because of the high charge mobility of bulk Pc and the reactivity of Pt surface.



COMPUTATIONAL METHODS - We performed the simulations with Quantum ESPRESSO (QE) distribution. We calculated the ground state within the DFT framework, using PBE(+vdW$_{surf}$)[3,4] and vdW-DF2-C09[5,6] (vdW$_{nl}$) exchange correlation functionals. We focused on the K-edge C 1s transitions and we constructed the excited states by setting the proper PAW[7] pseudopotential at every inequivalent C atom and relaxing the electronic configuration. For the XPS simulated spectra the core level shifts (CLS) are calculated within the ΔSCF method[8], by considering a full core hole (FCH). For the NEXAFS simulations we considered the transition potential approach[9] by setting a half core hole (HCH) into the pseudopotential and calculated the spectra using Xspectra tool within QE; here we referred the binding energy (BE) to the Fermi level.



FCH

Probing valence states modifications:
sensitive to chemical environment of atoms

HCH

Probing unoccupied states:
sensitive to density of states (DOS)

$$CLS = E(N, n_{1s} = 0) - E(N, n_{1s} = 1) + E_{avg}$$

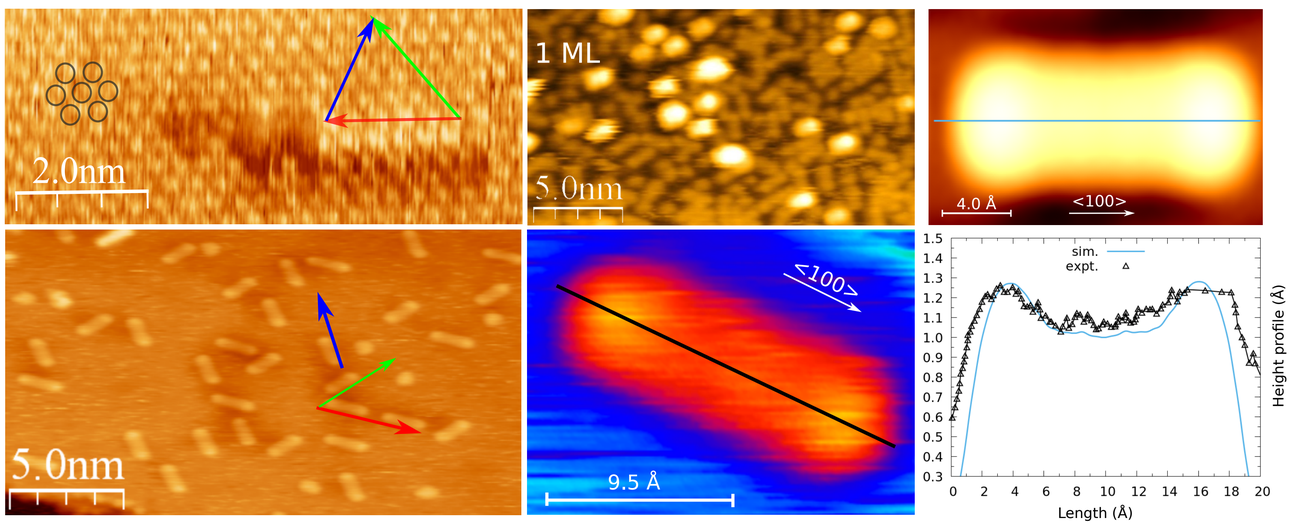
$$\sigma(E) \propto \sum_f |M_{i\to f}|^2 \delta(E_i^f - E) \qquad M_{i\to f} = \left\langle \tilde{\psi}_f \middle| \varphi \right\rangle$$

$$\sigma(E) \propto \mathrm{Im}\{\langle\varphi| \tilde{G}(E) |\varphi\rangle\} \qquad |\varphi\rangle = \sum_n P_n^\dagger \langle\phi_{1s}| \hat{D} |\psi_i\rangle$$

$$\tilde{G}(E) = (E - \mathcal{T}^\dagger H \mathcal{T} + i\eta)^{-1} \qquad |\psi\rangle = \mathcal{T} \left| \tilde{\psi} \right\rangle$$

STM

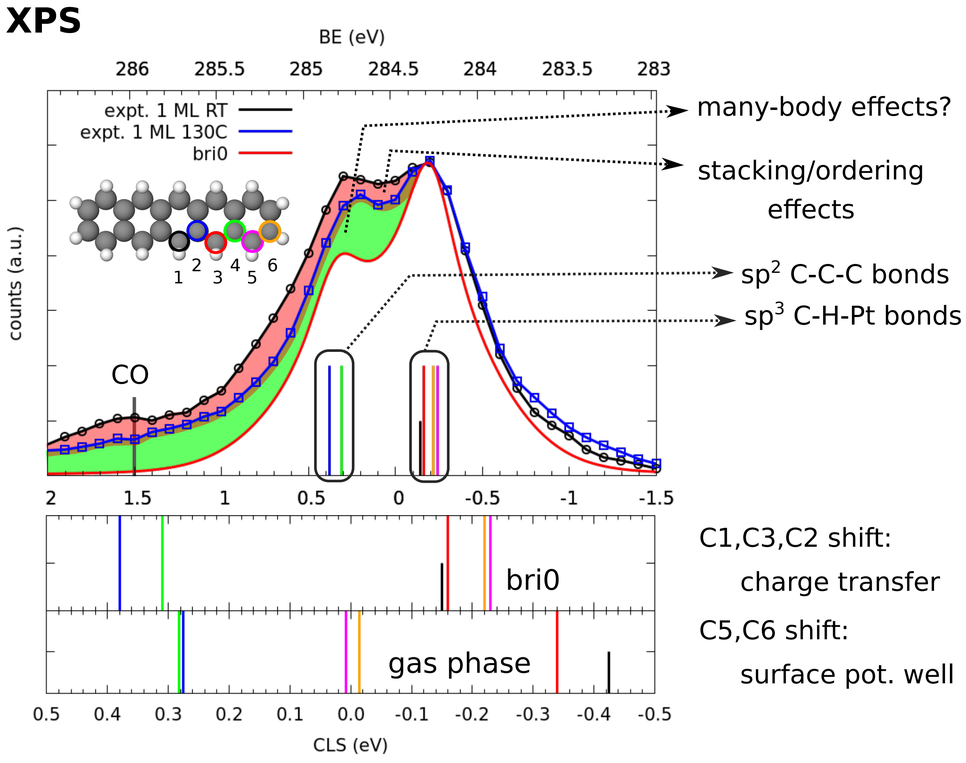
no ordered phases - stacking



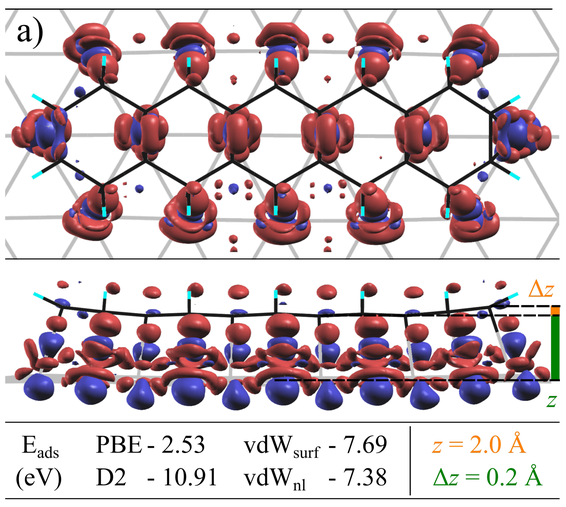
hcp lattice <100> directions

bridge site

XPS

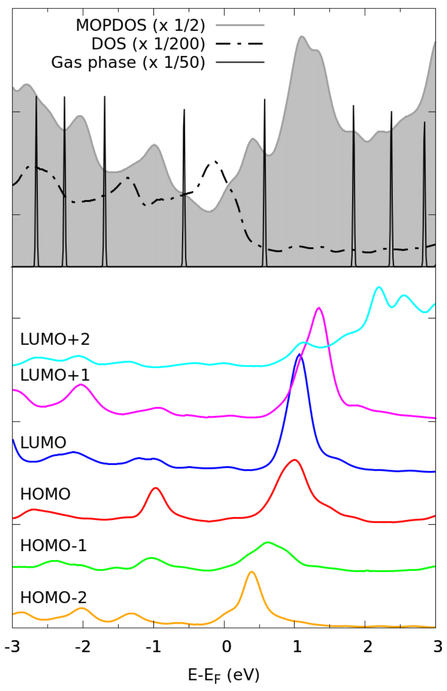


Electronic properties

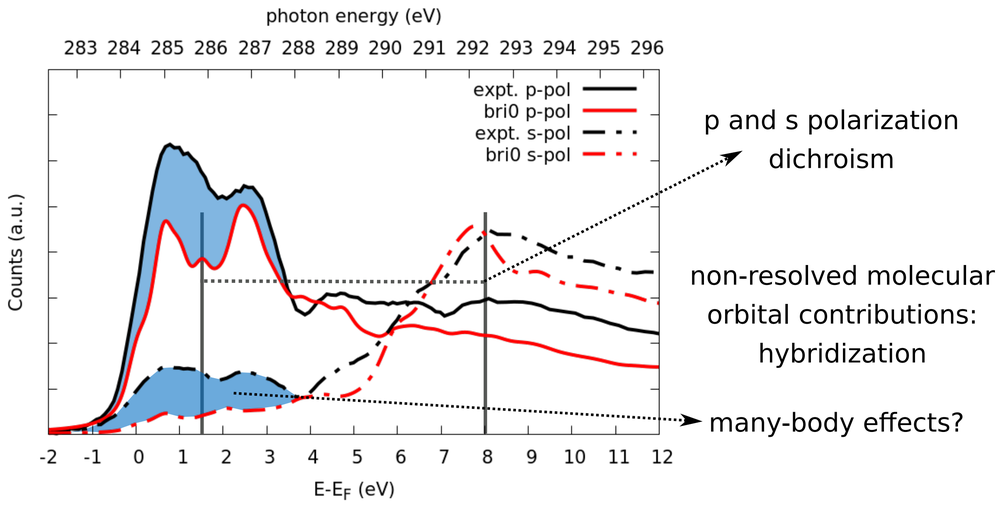


E_{ads} (eV)	PBE - 2.53	vdW$_{surf}$ - 7.69	z = 2.0 Å
	D2 - 10.91	vdW$_{nl}$ - 7.38	Δz = 0.2 Å

Charge transfer 1.5 e$^-$ from Pt to Pc



NEXAFS



CONCLUSIONS - We determined experimentally and theoretically the adsorption configuration of the molecules, which lay parallel to the hcp surface lattice, with their center onto bridge sites. We observed the formation of chemical bonds between the C atoms and the Pt ones underneath: the matching in the position of these two species, along with the high reactivity of the substrate, drives the interaction, and leads to a particularly intense chemisorption. As a consequence, the Pc adsorbs with an almost planar geometry, hybridizing its orbitals with the bands of the substrate.

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