

## MPc/Au(111) interface electronic structure investigated by high-resolution photoemission spectroscopy

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**Summary.** — We study the adsorption and the growth of FePc and MnPc layer(s) on the Au(111) surface. The evolution of the Au(111) Shockley surface state by molecular deposition has been investigated by means of photoemission spectroscopy. The Shockley surface state undergoes a shift at lower binding energy upon FePc adsorption, indicating a charge redistribution, while for the MnPc molecules the surface state binding energy is constant up to the completion of a single layer. The interaction is mainly driven by the central metal atom and the different orbital configuration induces a charge redistribution of the Fe central atom, while the Mn atoms seem unaffected by the process. Interaction of the central metal atom and charge redistribution are fundamental parameters to control the magnetic state of the single layer of FePc and MnPc on the metal surface.

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### 1. – Introduction

The design of organic nanostructures at surfaces is a topic of intense research for nanotechnology and organic-based molecular devices. Organic molecules can organize into long-range-ordered structures on surfaces, forming a variety of molecular 1D and 2D superstructures [1]. The vast range of available building blocks with diverse functional properties yields to the possibility to design supramolecular architectures with desired optical, magnetic and transport properties. Metal phthalocyanines (MPcs) are planar molecules formed by four pi-conjugated macrocycles coordinating a central metallic atom. MPcs are known as promising systems not only for optical and electronic applications, but also for spin-related mechanisms. Molecules with magnetic properties have gained great appeal, as they offer an ideal platform to advance the fundamental understanding of magnetism at the nanoscale, and can act as templates for molecular spintronic device fabrication. MPcs with a magnetic central atom can be anchored on a metal surface, exploiting the interaction of the macrocycles, and the spin-state of the central atom could be

changed by modifying the molecular conformation. Manganese phthalocyanine (MnPc) molecular magnet in the solid  $\beta$ -phase presents a ferromagnetic phase below 8.6 K, while FePc presents ferromagnetic ordering only at 3 K in the solid phase. The Curie-Weiss temperature strongly depends on the structural configurations and can be amplified in bi-dimensional (2D) structures [2]. The control of the interaction process is a fundamental step for a better understanding of the magnetic properties of 2D organic layers deposited on surfaces. The magnetic moment of FePc supported on the Au(111) substrate is preserved upon adsorption [3] and the mixing of Fe-localized molecular orbitals with the underlying free electron gas can give rise to a Kondo resonance, as observed by single-molecule STS spectroscopy [4]. However a detailed experimental study of the electronic structure of the FePc/Au(111) interface is still lacking and the comparison with MnPc can enlighten the driving mechanism of the interaction process. In the past, we have successfully employed high-resolution photoemission spectroscopy (HR-PES) to investigate the long-range-ordered MPc/Au(110) (M=Fe, Co, Ni, Cu, Zn) electronic structure [5-7]. Here we report of a HR-PES study of FePc and MnPc molecules deposited on a Au(111) surface to form 2D-ordered interfaces. The formation of interface spectral features at the single layer for the FePc can be ascribed to the interaction of 3*d*-like molecular orbitals with the underlying substrate. The shift of the Au(111) Shockley surface state to lower binding energy at the formation of a FePc single layer is related to charge redistribution at the interface.

## 2. – Experimental

Experiments have been carried out at the surface physics laboratory LOTUS in Rome in an ultra-high-vacuum (UHV) chamber equipped with high-resolution ultraviolet photoelectron spectroscopy (UPS) and all the ancillary facilities for sample preparation. Photoelectron spectra have been excited with a He discharge lamp ( $h\nu = 21.218$  eV and 40.814 eV). The photoemitted electrons were analyzed in the plane of incidence, with a high-resolution Scienta SES-200 hemispherical analyzer, by using a two-dimensional multi-channel-plate detector. Angular integration has been obtained over around normal emission. The intrinsic energy resolution is 16 meV. The Au(111) clean surface has been obtained by means of a sputtering-annealing treatment Ar<sup>+</sup> ions at 1000 eV,  $T = 500$  °C. The MPc layers were prepared by evaporation from quartz crucibles after purification obtained by degassing cycles of several hours. The nominal thickness was estimated by means of a quartz microbalance. The thickness of the first MPc layer is about 3.5 Å nominal coverage and it corresponds to completion of the first SL.

## 3. – Results and discussion

In fig. 1, we report normal-emission ultraviolet photoemission spectra in the valence-band energy region for the FePc and MnPc deposited on the Au(111) surface as a function molecular coverage. Data are obtained with FePc and MnPc deposition on the substrate kept at room temperature. The Au(111) Shockley surface state dominates the spectral density for the Au(111) surface. After MnPc and FePc deposition the intensity of the surface state decreases and its binding energy undergoes a shift of about 120 meV to lower binding energy at the completion of the SL for the FePc/Au(111) system, while it is constant for the MnPc/Au(111) interface. A tiny structure at about 0.8 eV for

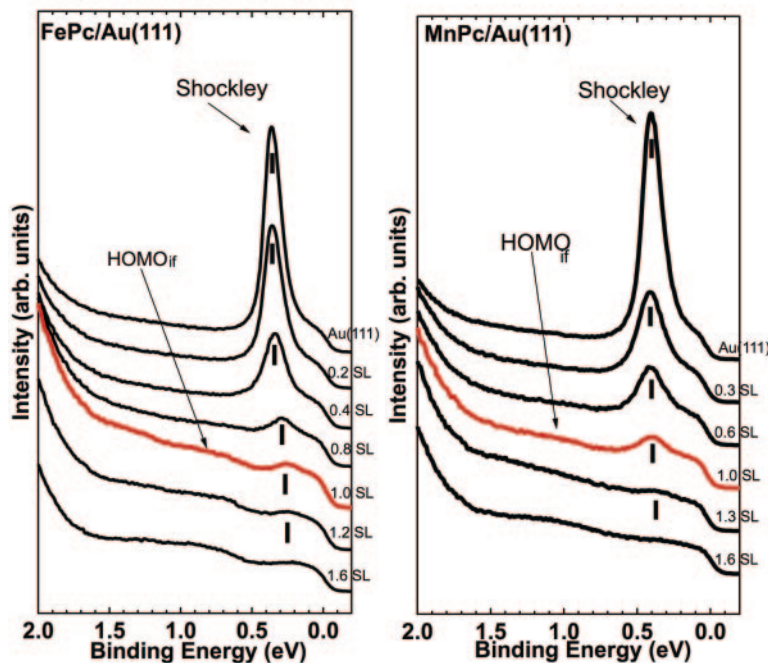


Fig. 1. – FePc (left) and MnPc (right) growth on Au(111) at room temperature condition. These spectra are taken with a photon energy:  $h\nu = 21.218$  eV. In the case of FePc we can observe an energy shift of Shockley state toward lower binding energies, while for MnPc there is no Shockley energy shift.

the FePc single layer and at 1.0 eV for the MnPc single layer can be assigned to the interface-HOMO ( $\text{HOMO}_{\text{if}}$ ) localized on the pyrrole rings, as previously observed for other MPC/Au interfaces [5].

The energy shift and the modification of the surface states depend on the strength of the interaction between the organic molecules and metallic substrates. The nature and the strength of the bonding and charge redistribution can influence the Shockley surface state, as observed in similar hybrid interfaces, like pentacene on Cu(110) surface [8] and PTCDA and NTCDA on Au(111) [9]. In the case of pentacene the shift is toward higher binding energy and it is related to a mixing of the electronic state, the polarization of the adsorbate and the Pauli repulsion, in the case of PTCDA and NTCDA the shift goes in the opposite direction and it has been justified as due to Pauli repulsion. In our case, we hypothesize a main contribution due to a charge transfer from the underlying metallic substrate to the Fe central atom. In fact, the Pauli repulsion is expected to affect both the organic molecules and the absence of an energy shift for the MnPc can exclude this effect. The charge redistribution and the mixing of the underlying metallic state for the MnPc is confirmed by high-energy resolution photoemission spectra in the energy region close to the Fermi level. In fig. 2 the spectral density reveals a feature at about 0.1 eV for the FePc/Au(111) interface, while any contribution to the density of state related to the molecular orbitals can be observed for MnPc/Au(111). This state is well defined and intense at the interface, then the intensity decreases and the peaks disappear after the

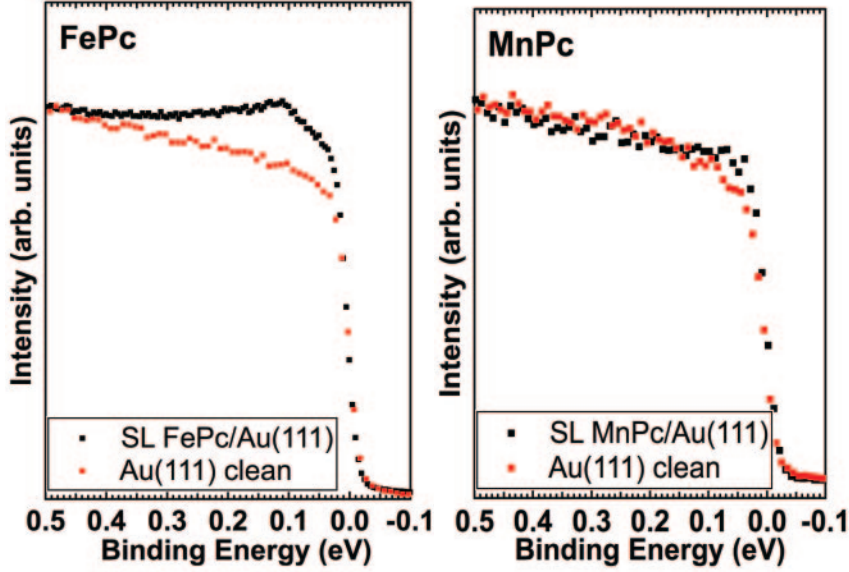


Fig. 2. – FePc (left) and MnPc (right) single layers deposited on Au(111) surface. These spectra are taken with a photon energy:  $h\nu = 21.218$  eV. The FePc/Au(111) interface presents an interaction state in the energy region close to the Fermi level.

formation of the thin FePc films. The attribution to a specific molecular-derived level is not straightforward, although we can hypothesize a relation with states residing on the Fe atom, involved in the interaction with the underlying Au states.

#### 4. – Conclusions

The electronic properties of FePc and MnPc layers grown on the Au(111) surface have been investigated by high-resolution photoemission spectroscopy. The charge redistribution at FePc/Au(111) interface induces an energy shift to lower binding energies of the free-electron-like Au(111) Shockley surface state, as a function of the molecular coverage. We observe an increased spectral density near the Fermi level for the FePc/Au(111) as a consequence of a rehybridization at the interface. Such behavior is not observed for the MnPc/Au(111) interface, where the Shockley state binding energy is not affected by molecular deposition. This evidence suggests a direct involvement of the metallic centers orbitals in the interaction with the gold substrate for the FePc. In particular, the reduced symmetry of the  $3d$ -like frontier orbital plays a crucial role and influences the magnetic properties at the interface.

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