



## Review Article

Atomic contributions to the valence band photoelectron spectra  
of metal-free, iron and manganese phthalocyanines

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## ABSTRACT

The present work reports a photoelectron spectroscopy study of the low-energy region of the valence band of metal-free phthalocyanine (H<sub>2</sub>Pc) compared with those of iron phthalocyanine (FePc) and manganese phthalocyanine (MnPc). We have analysed in detail the atomic orbital composition of the valence band both experimentally, by making use of the variation in photoionization cross-sections with photon energy, and theoretically, by means of density functional theory. The atomic character of the Highest Occupied Molecular Orbital (HOMO), reflected on the outermost valence band binding energy region, is different for MnPc as compared to the other two molecules. The peaks related to the C 2p contributions, result in the HOMO for H<sub>2</sub>Pc and FePc and in the HOMO-1 for MnPc as described by the theoretical predictions, in very good agreement with the experimental results. The DFT simulations, discerning the atomic contribution to the density of states, indicate how the central metal atom interacts with the C and N atoms of the molecule, giving rise to different partial and total density of states for these three Pc molecules.

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## 1. Introduction

Phthalocyanines (Pcs) are a class of organic compounds widely studied due to the possibility to deposit them in supramolecular

architectures suitable for a variety of technological applications. To acquire the ability to design materials with predetermined properties by choosing proper molecular precursors requires understanding of the characteristics of the molecules used as building blocks and how they are modified when deposited in films, as has been well pointed out by Claessens et al. [1] and de la Torre et al. [2] in their review articles.

In this work we present a theoretical and experimental valence band (VB) photoelectron spectroscopy (PES) study of the electronic

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structure of metal-free phthalocyanine ( $H_2Pc$ ), iron phthalocyanine ( $FePc$ ) and manganese phthalocyanine ( $MnPc$ ) in multilayer films as well as in the gas phase. We concentrate on the comparison of the occupied valence density of states of these three phthalocyanines and we relate the observed differences to the different metal atom in the molecular central ring. By selecting proper photon energies in the experiment, we can exploit the photoionization cross sections for the photoemission of electrons from different atomic orbitals. In this way, we can disentangle in the experimental spectra the contributions given by the metallic 3d electrons from the contributions coming from the organic rings.

Our focus is on the very outermost part of the valence band which determines the electric and magnetic properties of functional materials. Although widely studied, the electronic structure, and in particular the localization of the metallic orbitals in the VB of 3d metal Pcs is still under debate since both experimental and theoretical investigations have provided ambiguous outcomes so far, see for example Refs. [3–13]. This is a crucial issue for electronic devices, since the character of the outermost molecular orbitals plays a key role in transport related phenomena [14]: for example a localized 3d metallic HOMO or a less localized molecular orbital distributed over the whole molecule would in principle be expected to behave differently [14–16]. In our previous works on  $FePc$  [9] and  $MnPc$  [11], we have shown how hybrid DFT can successfully be used to identify the metallic 3d states in the low binding energy region of the valence band, in comparison to PES measurements exploiting the photoionization cross sections. The energy positions of the outermost molecular orbitals could be reproduced with good accuracy by hybrid DFT calculations (B3LYP/DFT).

It has to be observed that for many molecules, the valence band DOS computed by means of hybrid DFT may severely differ from the experimental photoelectron spectra [17]. Approaches like GW have been used on some molecules including  $CuPc$  obtaining important improvements with respect to the hybrid DFT results [17], but this computation method is rather demanding [18]. Therefore the possibility to employ computationally cheaper methods, like hybrid functionals implemented in a Gaussian basis set description, is still an important option in several cases.

The comparison of the metal free  $H_2Pc$  with  $FePc$  and  $MnPc$  highlights the different interactions of the divalent central ion with the organic molecular ring. As shown by Grobosch et al. [6,7], the electronic structure of  $MnPc$  differs from the one of other metal Pcs because the HOMO peak in its valence band spectrum is of metallic character. Moreover the 3d electronic states contributing to this VB feature are not highly localized but hybridize with the orbitals of the organic rings, giving to this molecule potentially different electronic transport properties [6,7].

In general, as we have recently reported [11], the picture of the electronic structure of metal phthalocyanines can be further complicated:  $MnPc$  can have different electronic configurations in different types of samples, as we have seen for the gas phase with respect to a thick film. While for the thick film a single electronic structure could reproduce the energy distribution of the  $MnPc$  metallic states, in the gas phase, at least two different electronic configurations were needed. In this work we have further investigated these results by studying the symmetry and the hybridization of the outer molecular orbitals comparing  $H_2Pc$ ,  $MnPc$  and  $FePc$  molecular films. We provide a detailed determination of the orbital composition of the HOMO and HOMO-1 of  $H_2Pc$ ,  $FePc$  and  $MnPc$  by comparing hybrid DFT calculations to PE spectra for thick molecular films. This gives in addition insight into the different hybridization of the metal states with the organic rings for the two metal phthalocyanines.

## 2. Experimental details

This work includes VB PES measurements of both films and gas phase of phthalocyanines. The  $H_2Pc$  (98% dye content),  $FePc$  molecules (90% dye content) and  $MnPc$  (95% dye content) molecules were purchased from Sigma-Aldrich. The molecules have been carefully outgassed before all depositions and gas phase measurements. For thick film investigations, either a Au(1 1 1) single crystal (in the case of  $H_2Pc$  and  $FePc$ ), purchased from Surface Preparation Laboratory (SPL) or a gold on mica (in the case of  $MnPc$ ) substrate were used. In the case of the single crystal substrate, a clean Au(1 1 1) surface was obtained by cycles of  $Ar^+$  ion beam sputtering (900 eV) for 20 min, followed by annealing at  $\approx 550^\circ C$  for about 2 h. For the gold/mica substrate (purchased from George Albert Physical Vapor Disposition), the 300 nm thick layer of gold epitaxially grown on mica, was cleaned by cycles of sputtering and annealing (at  $445^\circ C$ ) in order to get a clean and reconstructed Au(1 1 1) surface. The cleanliness of all the surfaces was checked by PES.

The VB photoemission measurements of  $H_2Pc$  films on Au(1 1 1) ( $h\nu=130$  eV) have been performed at the undulator-based [19] beamline I511 at MAX-lab, the national synchrotron radiation facility in Lund, Sweden. The surface end-station of the beamline (at the time of our experiments) consisted of an analysis chamber and a preparation chamber, with base pressures of  $8 \times 10^{-11}$  and  $5 \times 10^{-10}$  mbar, respectively. The analysis chamber was equipped with a Scienta R4000 hemispherical electron analyzer, which could be rotated around the photon beam axis. The molecules have been deposited, *in situ*, onto the samples in an evaporation chamber under UHV conditions, using a home-built evaporator positioned a few centimeters away from the substrate. The evaporator consisted of a quartz glass tube with a diameter of about 5 mm with a heating tungsten wire twisted around. All measurements were performed with the sample at room temperature (RT), with photon energy of 130 eV and an overall resolution of about 20 meV. The binding energy (BE) scale of the  $H_2Pc$  VB spectra was calibrated by measuring the Fermi edge of the Au substrate and/or Au 4f PE spectrum (at 84.0 eV BE) keeping the experimental settings.  $FePc$  and  $H_2Pc$  films deposited by thermal evaporation on the Au(1 1 1) crystal and film of  $MnPc$  on a Au/mica substrate have also been investigated by XPS using a monochromatized Al  $K_{\alpha}$  source (1486.7 eV) and Ultra-violet photoelectron spectroscopy (UPS) with a He discharge lamp (21.2 eV) and a hemispherical analyzer at home laboratory at the University of L'Aquila, Italy. For the film thicknesses studied in this work, no signal from the Au 4f peaks was detected by XPS. The binding energy (BE) scale was calibrated considering the Au Fermi edge and the Au 4f core level peaks position (Au 4f<sub>7/2</sub> at 84 eV). The resolution of the presented valence photoemission spectra is 300 meV for photon energy of 1486.7 eV and 150 meV for photon energy of 21.2 eV.

The experimental details in acquiring the gas-phase data of  $FePc$  and  $MnPc$  are presented in details in the study by Brena et al. [9] and Brumboiu et al. [11]. The photoelectron spectroscopy (PES) measurements have been performed at the Gas Phase beamline [20] at the Elettra synchrotron, in Trieste, Italy. The valence spectra of gas phase  $MnPc$  were taken using a VG 150 mm hemispherical electron energy analyzer, equipped with six channel electron multipliers mounted at the magic angle ( $54.7^\circ$ ) with respect to the E vector of the linearly polarized incident light [21]. Valence data of gas phase  $H_2Pc$  and  $FePc$  presented in this work were instead measured with a SES-200 electron analyzer [22] also mounted at the magic angle. The molecular samples were evaporated using a custom built resistively heated furnace. The gas phase PE spectra were checked during heating procedure, comparing them to spectra for thick layers obtained by Kraus et al. [23,8] for  $MnPc$ , while for  $FePc$  they were compared to He I spectrum obtained by Berkowitz [24].

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