

Interaction of ultra-thin CoTPP films on Fe(001) with oxygen: Interplay between chemistry, order, and magnetism F

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ABSTRACT

This work focuses on the stability against the oxidation of the chemical, structural, and magnetic properties of the system consisting of a layer of Co tetra-phenyl porphyrins grown on the top of Fe(001) – $p(1 \times 1)$ O. Such a system is characterized by a very high degree of structural order and the existence of magnetic coupling between the molecules and the substrate, even at room temperature, as we recently reported [Jagadeesh *et al.*, Appl. Phys. Lett. **115**, 082404 (2019)]. We highlight, by using x-ray photoemission spectroscopy, the effect of porphyrins in screening the substrate from oxidation. The coupling between the magnetic response of the system and the order of the molecular layer is investigated by means of spin-resolved UV photoemission spectroscopy and low-energy electron diffraction, respectively. As a result, a link is eventually found between this response and the chemical and structural stability of the interface.

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I. INTRODUCTION

Ultrathin molecular films on crystalline substrates are interesting model systems to investigate the relevant physical phenomena taking place at the organic/metal hybrid interface.¹ If the substrate is ferromagnetic, the electronic interactions at the interface can (i) induce a net magnetic moment on the molecules and/or (ii) orient the molecular moments in a preferential direction.^{2–4} The latter phenomenon has been observed, among others, with porphyrin or phthalocyanine molecules containing a transition metal (TM) ion and thus bearing a localized magnetic moment.^{5–8} Conversely, examples in literature can be found where magnetic moments have been induced in non-magnetic molecules such as H₂ phthalocyanines or C60.^{9–11} These peculiar interactions are active in ultra-thin films having ideally the thickness of a single molecular layer [or monolayer (ML)], disclosing possible spintronic applications such as magnetic memories, coupling layers in magneto-resistive devices, spin valves, etc.,^{12–15} if long-range magnetic ordering can be stabilized at room temperature (RT).

The tuning of the magnetic behavior of the molecules can be potentially realized by letting their TM ion interact with gaseous

species, trying to preserve a regular pattern previously obtained onto the substrate, which depends on the structure and local arrangement of the molecules.^{16–18} However, reactive gases can potentially damage the molecular layer and the supporting substrate, considering also that traditional ferromagnets are among the most reactive metals.¹⁹ Assessing the stability of the hybrid interface against common gases is, therefore, important, for instance, to set some minimum requirements in the processing conditions, in terms, e.g., of the cleanliness of the growth environment (background pressures) for the reproducible fabrication of devices.

Tetra-phenyl porphyrins are aromatic compounds featuring a ring-like structure with four pyrrole units. They can be considered free bases since they can host different metals in their central core. The metalated compound is called a metallo-tetra-phenyl porphyrin (MTPP, where M is a general metal ion).^{8,20} At ML coverage, these molecules lie flat and ordered on the surface of the Fe(001) – $p(1 \times 1)$ O substrate^{21–23} obtained after the passivation of the pristine Fe(001) surface with a single layer of oxygen atoms filling the (001) hollow sites in between the Fe atoms.^{24,25} The coverage of the substrate is typically uniform, i.e., a molecular “wetting

layer” is usually formed.²⁶ In the following, we consider the CoTPP/Fe(001)- $p(1 \times 1)$ O system because Fe is one of the most important substrates for inorganic spintronics²⁷ and CoTPP, among the MTPP, a porphyrin carrying a non-null magnetic moment and consequently used as a prototypical molecule to study the interactions with different magnetic substrates.^{17,28,29} As we have recently shown, the CoTPP ML is magnetically coupled to the Fe(001)- $p(1 \times 1)$ O substrate, even at RT.²⁹

In this work, we study the effect of exposing the 1 ML CoTPP/Fe(001)- $p(1 \times 1)$ O system to an increasing amount of molecular oxygen by simultaneously monitoring its chemical modifications and magnetic behavior. The growth of the molecular layer, its exposure to O₂, and its characterization are accomplished *in situ* under well-controlled experimental conditions. The chemical analysis is performed by means of x-ray photoemission spectroscopy (XPS), the morphology is checked with low-energy electron diffraction (LEED), while the magnetic ordering is detected with spin-resolved UV photoemission spectroscopy (SR-UPS). Our results highlight the presence of a link between the observation of a magnetic response and the system integrity.

II. EXPERIMENTAL METHODS

All the results shown in this paper were collected in an ultra-high vacuum system working at a base pressure in the low 10^{-10} Torr range.³⁰ The Fe(001)- $p(1 \times 1)$ O substrate was prepared by first

growing a thick (about 500 nm) Fe layer on top of an MgO(001) crystal, thus perfectly mimicking the electronic and magnetic behavior of a bulk Fe crystal.^{31,32} The surface is then modified by dosing 30 L (1 L = 10^{-6} Torr · s) of O₂, with the sample kept at 450 °C, and then annealed at 700 °C to remove the oxygen in excess of a single layer.³³ Co porphyrins (bought from Merck KGaA) were purified in vacuum and then sublimated from a quartz crucible at a rate of about 1 Å/min with the sample kept at RT.^{34,35} We decided to grow a film with a thickness slightly in excess of a single molecular layer (nominally 1.3 ML, with a monolayer thickness of 3.06 \AA ²³) to be sure about the complete covering of the substrate surface. Oxygen was admitted into the system by means of a leak valve at a maximum pressure of 10^{-7} Torr for the highest dose.

Photoemission spectra were acquired with a 150 mm hemispherical electron analyzer from SPECS GmbH, equipped with a Mott detector for spin-resolved measures. Mg K α ($h\nu = 1253.6 \text{ eV}$) and HeI ($h\nu = 21.2 \text{ eV}$) photon sources were used for XPS and UPS, respectively, with a full width at half maximum (FWHM) resolution of 0.9 eV for XPS and 0.05 (0.15) eV for UPS (SR-UPS).

III. RESULTS AND DISCUSSION

In order to investigate the effect of oxidation on the bare passivated substrate and after the CoTPP deposition, we have acquired the XPS spectra shown in Fig. 1. Two samples, the bare passivated substrate [panel (A)] and another with the molecules [panel (B)],

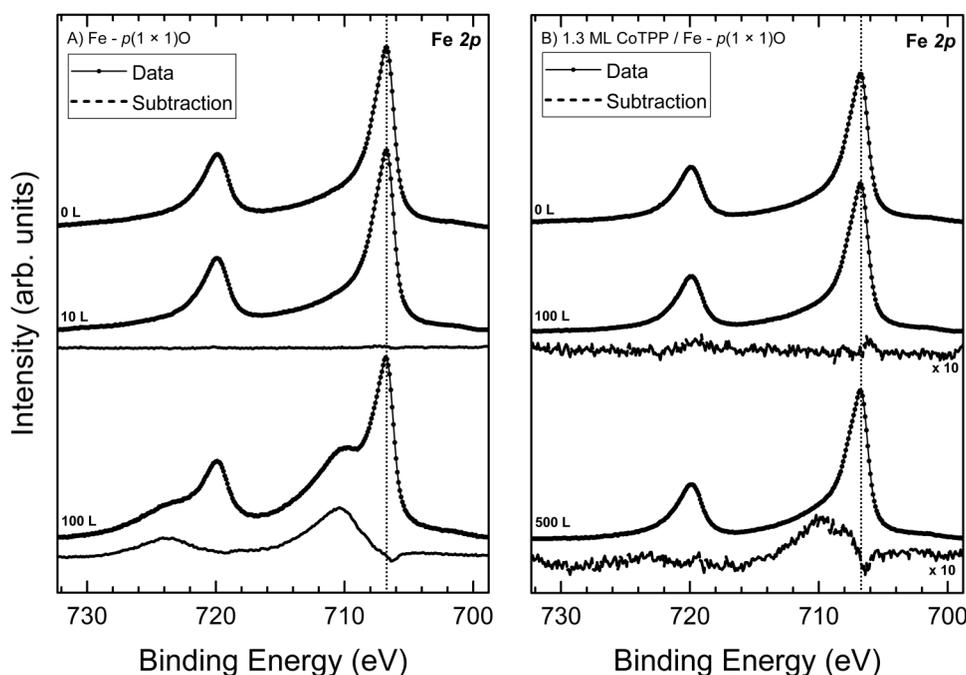


FIG. 1. XPS spectra (lines plus dots) of the Fe 2p spectral region for (A) Fe- $p(1 \times 1)$ O and (B) 1.3 ML CoTPP/Fe- $p(1 \times 1)$ O for different O₂ exposures. The spectra are plotted after the subtraction of an integral (Shirley) background and normalized to their peak intensity. For the spectra related to non-zero exposures, the difference with the spectrum acquired on the as-prepared substrate is shown with lines. In panel (B), the difference spectra at 100 L and 500 L have been multiplied by 10. The vertical dotted line marks the binding energy of the $2p_{3/2}$ states of metal iron.

have been analyzed at increasing oxygen exposure. To highlight possible differences, the spectra from the unexposed samples have been subtracted from the ones obtained after the O_2 exposure. As it can be seen from panel (A), for $Fe-p(1 \times 1)O$, there are no appreciable differences up to 10 L. When the exposure reaches 100 L, a strong feature attributable to photoemission from Fe cations appears,³⁶ and it is even more evident when the contribution of the spectrum from the unexposed sample is subtracted, in good agreement with the literature.^{37,38} This situation changes when the substrate is covered by 1.3 ML of CoTPP. Indeed, no differences whatsoever can be detected in the spectra for exposures between 0 and 100 L. When the sample is exposed to 500 L of oxygen, a very weak feature appears in the difference spectrum, compatible with the one shown in panel (A) for a 100 L exposure. In view of a cross-check of the partial oxidation of the substrate underneath, spectra in the $O 1s$ region have been also acquired on the same sample at 0 and 500 L, and the results are shown in Fig. 2(A). The position of the peak is not modified, but its intensity grows with exposure by a factor 1.5. This leads to the conclusion that, at 500 L, some extra oxygen has been incorporated in the sample.

Figure 2(B) reports the spectra acquired in the $Co 2p_{3/2}$ spectral region. Within the experimental uncertainty, the intensity of the peak does not change when the exposure reaches 500 L, and the peak position remains practically unmodified. We can, therefore, conclude that the molecular layer is not directly affected by the interaction with the reactive gas and it also allows for a “screening” effect, preventing the substrate from oxidation. Indeed, when the bare passivated substrate is exposed to 100 L, it is almost completely oxidized, while at the same exposure the sample covered by 1.3 ML of CoTPP does not show any sign of oxidation. The O_2 exposure can be increased by up to one order of magnitude without affecting the sample.

In order to understand whether the oxidation of the sample plays a role in the ordering of the layer, we have acquired LEED images at different exposures. Figure 3 shows the LEED pattern related to 1.3 ML of CoTPP grown on top of $Fe-p(1 \times 1)O$ at different O_2 exposures. It is known²¹ that the molecules arrange commensurately on the top of the $Fe-p(1 \times 1)O$ substrate and indeed

the LEED image obtained before exposing the molecular layer to oxygen (top left panel) shows the typical pattern for CoTPP on top of this substrate.^{23,29} This is compatible with the presence of two square (5×5) super-lattices rotated by $\pm 36.9^\circ$ with respect to the substrate in-plane cubic crystallographic axes, as it is shown with the simulation obtained by LEEDpat42.³⁹ No visible variation of the pattern is observed after a 10 L exposure, while after 100 L, although the pattern is still visible, the diffraction spots are less intense. When a 500 L exposure is reached, the pattern due to the molecules is not present any longer, while it is still possible to mark the spots arising from the substrate, which are, nevertheless, strongly attenuated with respect to those shown in the other panels. This evolution is compatible with a progressive loss of order of the molecular layer above the substrate, which we attribute to partial oxidation of the substrate leading to a loss of the crystalline order of the topmost layers of the substrate.¹⁹ In fact, at 500 L, the effects of O_2 exposure are barely detectable with XPS, while the LEED super-pattern representative of the long-range order of the molecules has already completely disappeared. On the contrary, when no oxidation effects whatsoever can be guessed from the XPS spectra, even the LEED (5×5) pattern is preserved.

As we recently proved,²⁹ when an ultra-thin film (about 1 ML-thick) of CoTPP is grown on top of $Fe-p(1 \times 1)O$, a magnetic coupling between the molecules and the substrate is present, likely due to the non-zero total spin carried by the Co porphyrin. In that work,²⁹ searching for a spin imbalance between the majority and minority populations of the molecular states, we have focused our analysis in a precise region of the UPS spectrum, between 5 and 6 eV, as pointed out in Fig. 4(A). In this figure, it is possible to compare the UPS spectra acquired on the bare $Fe-p(1 \times 1)O$ substrate and after the deposition of the molecules. The features arising in the latter spectrum are due to photoemission from the phenyls or the tetra-pyrrole ring [Fig. 4(B)]. By comparison with theoretical simulations,⁴⁰ we identified two main features attributable to the inner ring of the CoTPP molecule, hosting the Co ion, and we have labeled them as “ring 1” (around 2 eV) and “ring 2” (around 5.5 eV) in Fig. 4(A).^{23,41} By using SR-UPS, we detected in the “ring 2” region an imbalance between majority- and minority-spin populations.²⁹

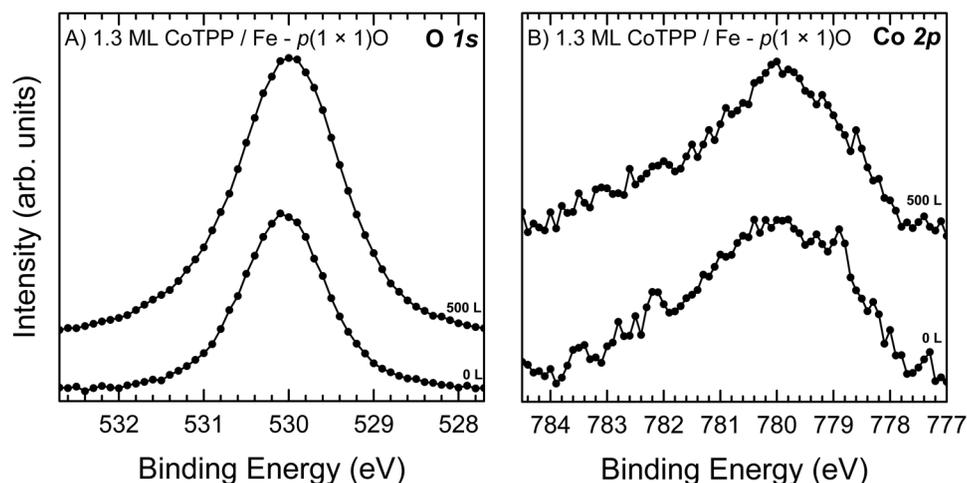


FIG. 2. XPS spectra acquired for 1.3 ML CoTPP/ $Fe-p(1 \times 1)O$ in the (A) $O 1s$ region and in the (B) $Co 2p_{3/2}$ region. In both panels, data obtained after 0 and 500 L oxygen exposure are shown. An integral (Shirley) and a linear background has been subtracted from the spectra in (A) and (B), respectively.

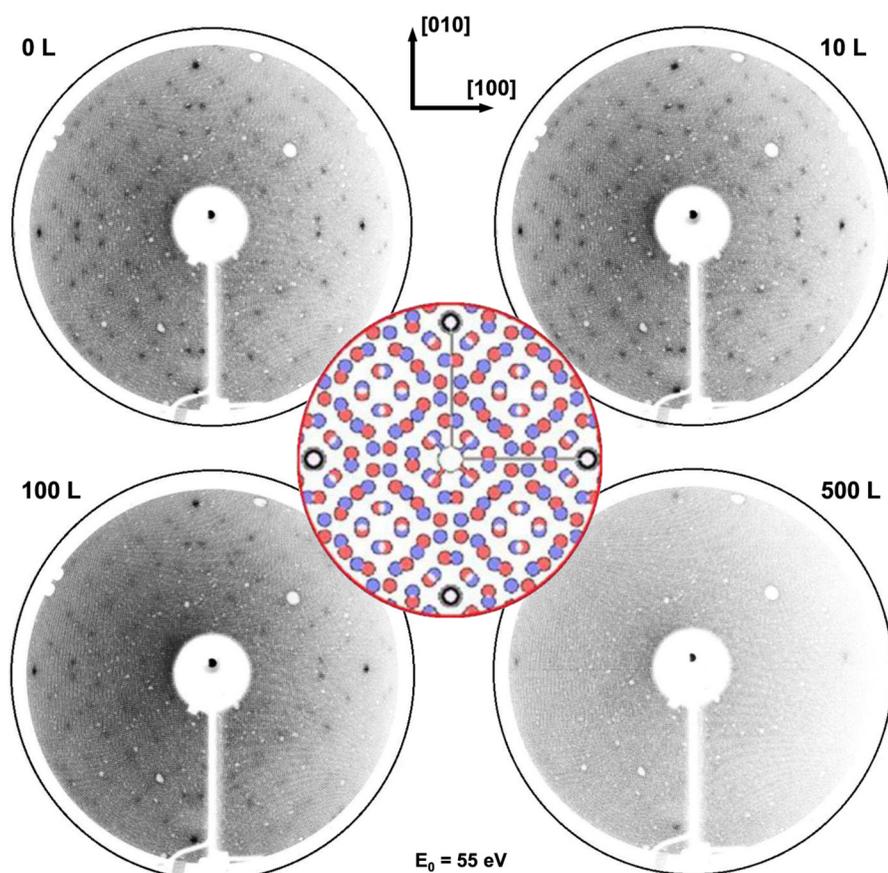


FIG. 3. LEED images for 1.3 ML CoTPP on Fe- $p(1 \times 1)$ O at different O_2 exposures. The arrows indicate the main crystallographic directions of the substrate. All the images were acquired with a beam energy of 55 eV. In the center, a simulation with LEEDpat42 is shown where the white spots are due to the substrate, and the red/blue ones are due to the molecules.

The results are shown in Fig. 5(A) for different exposures, while in Fig. 5(B), we report the photoemission spectra of our previous work on 1 ML CoTPP/Fe- $p(1 \times 1)$ O.²⁹ In all spectra, a linear background has been subtracted. In the present data, we observe a slight shift of the photoemission features associated with the molecular ring toward larger binding energies, together with a slight

increase in the majority to minority splitting, possibly related to the larger molecular coverage. The spectral spin polarization is still clearly detectable at 10 L becomes progressively less pronounced at 100 L and eventually vanishes completely at 500 L, where the peak becomes also broader. This observation can be directly linked to the loss of structural order and the onset of surface oxidation, as

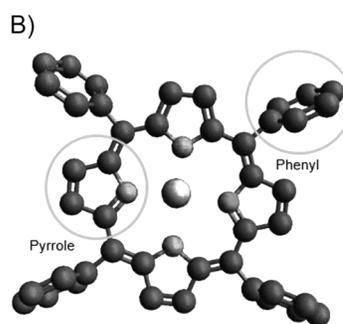
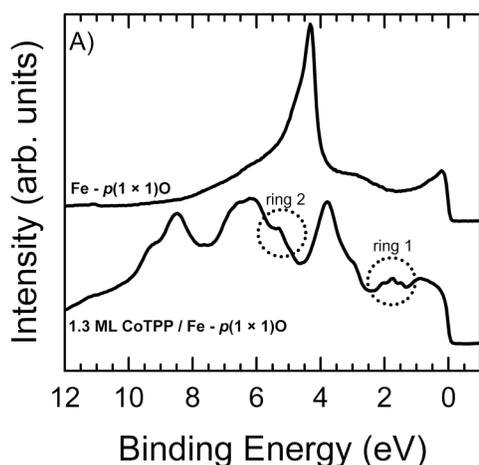


FIG. 4. (A) UPS spectra acquired on the bare Fe- $p(1 \times 1)$ O substrate and after the deposition of 1.3 ML of CoTPP. The two dotted circles represent the features attributable to the tetra-pyrrole ring of the molecule, namely, "ring 1" (around 2 eV) and "ring 2" (around 5.5 eV). (B) Scheme of the CoTPP molecule, the phenyl aromatic group, and the one of the four pyrroles that compose the central ring are highlighted.

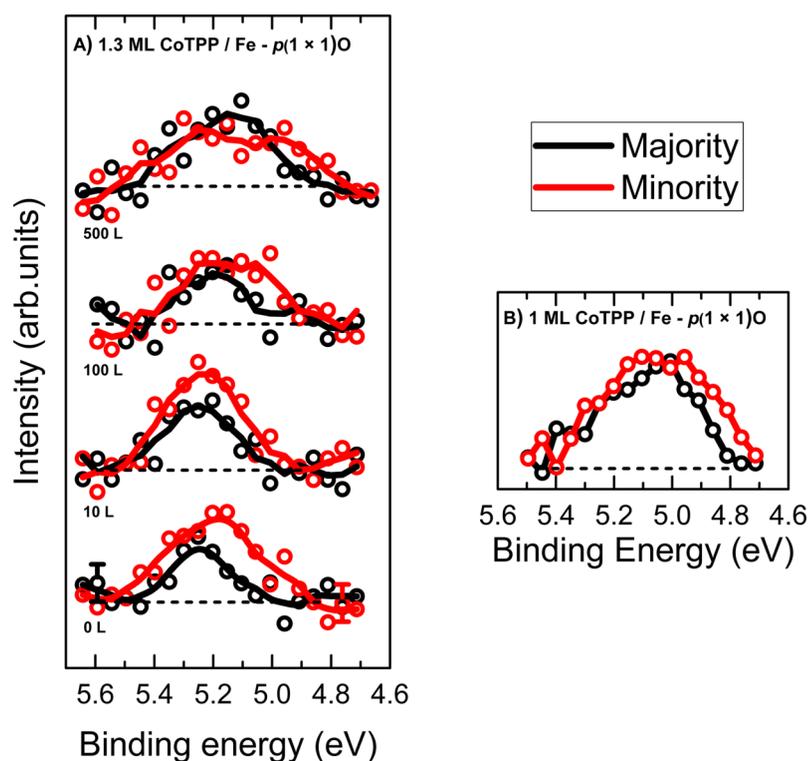


FIG. 5. (A) SR-UPS spectra acquired in the “ring 2” region on 1.3 ML CoTPP/Fe- $p(1 \times 1)$ O at different O_2 exposures, drawn after the subtraction of a linear background. Majority- and minority-spin spectra are shown with black and red colors, respectively. Experimental data (dots) and smoothing curves (solid lines) are shown. (B) SR-UPS spectra acquired in the “ring 2” region on 1 ML CoTPP/Fe- $p(1 \times 1)$ O. Reproduced with the permission from Jagadeesh *et al.*, *Appl. Phys. Lett.* **115**, 082404 (2019). Copyright 2019 AIP Publishing LLC.

evidenced by LEED and XPS, respectively. In conclusion, we can point out that the magnetic coupling between the porphyrins and the substrate is directly related to the presence of an ordered molecular array on top of it. When oxidation effects are strong enough to remove the LEED molecular pattern, the magnetic coupling also completely dies out.

IV. CONCLUSIONS

In conclusion, we have shown that when a CoTPP layer in the monolayer thickness range is deposited on top of Fe- $p(1 \times 1)$ O, its regular commensurate super-pattern measured by LEED is preserved up to 100 L oxygen exposures. By comparing the spectral evolution of the substrate signal with XPS, we observed a shift in the onset of substrate oxidation of about one order of magnitude in oxygen exposure when the latter is covered with the CoTPP layer. No detectable effects of direct interaction between the Co cation and the gas have been highlighted. Finally, the magnetic coupling between the porphyrins and the substrate is present up to 100 L of oxygen exposure and then disappears, together with the diffraction pattern, suggesting a link with the order of the molecular layer.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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