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Adsorption geometry, conformation, and electronic structure of 2H-octaethylporphyrin on Ag(111) and Fe metalation in ultra high vacuum

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Due to the growing interest in the ferromagnetic properties of Fe-octaethylporphyrins (Fe-OEP) for applications in spintronics, methods to produce stable Fe-porphyrins with no Cl atoms are highly demanded. Here, we demonstrate the formation of Fe-OEP layers on Ag(111) single crystal by the ultra high vacuum *in situ* metalation of the free-base 2H-2,3,7,8,12,13,17, 18-octaethylporphyrin (2H-OEP) molecules. The metalation proceeds exactly as in the case of 2H-5,10,15,20-tetraphenylporphyrin (2H-TPP) on the same substrate. An extensive surface characterization by means of X-ray photoemission spectroscopy, valence band photoemission, and NEXAFS with synchrotron radiation light provides information on molecular conformation and electronic structure in the monolayer and multilayer cases. We demonstrate that the presence of the ethyl groups affects the tilt of the adsorbed molecules, the conformation of the macrocycle, and the polarization screening in multilayers, but has only a minor effect in the metalation process with respect to 2H-TPP. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798934>]

I. INTRODUCTION

The key advantages of organic materials over their inorganic counterparts are the possibility to tune their chemical and electronic properties through the tailored synthesis of their molecular constituents and the possibility of forming ordered structures on various substrates by means of self-assembly.^{1–5} In view of this, porphyrins are excellent candidates for growing organic active layers since molecular functionalization can be easily achieved by exchanging the meso-substituents or the metal ion at the center of the macrocycle.⁶ This in turn allows changing the intermolecular interactions as well as the interactions between molecules and the substrate, which are critical parameters for the proper growth of several layers and for device performance.^{7–11}

Amongst porphyrins, Fe-octaethylporphyrin (Fe-OEP) has recently attracted the attention of the scientific community due to its ferromagnetic coupling to ultrathin Co and Ni magnetic films.^{12–14} Experiments have shown that specific porphyrins may be used to form long range ordered 2D arrays of switchable magnetic elements, opening the possibility of their use in applications in spintronics. In these experiments, however, only Fe(III)-octaethylporphyrin-Cl molecules have been employed, since the presence of Cl attached to the Fe atom is required to stabilize the highly reactive metal at the center.¹⁵ Furthermore, several calculations demonstrate that the ferromagnetic vs antiferromagnetic coupling of porphyrins with

the magnetic substrate strongly depends on the presence of Cl and on the way the Cl atoms in the molecules are adsorbed on the surface (Cl up or Cl down).^{12,16} Hence, the possibility to produce stable Fe-porphyrins with no Cl atoms attached and characterize them *in situ* is of fundamental interest for further understanding the magnetic properties of the Cl-free compound.

Recently, the *in situ* metalation of 2H-5,10,15,20-tetraphenylporphyrin (2H-TPP) with Fe atoms was successfully reproduced on Ag(111) in ultra high vacuum (UHV).^{17,18} In particular, Di Santo and co-workers¹⁸ showed that through the use of synchrotron radiation-based techniques it is possible to obtain information on the complex electronic structure and geometrical conformation of both the multilayer and the monolayer (ML) films during metalation. Based on the flat configuration of both the macrocycle and the phenyl groups in the monolayer on Ag(111), a simple adatom hopping instead of a substrate surface mediated dopant diffusion to the reaction sites was proposed as a possible explanation for the metalation process. Nevertheless, while the metalation by Fe,^{17,18} Zn,¹⁹ Co,²⁰ Ni,²¹ and Ce²² of free-base tetraphenylporphyrins has already been assessed by STM and photoemission studies, no similar metalation experiments have been reported so far on free-base octaethylporphyrins (2H-OEP). In addition, a comparison between the metalation process of 2H-TPP and 2H-OEP is highly desirable since the presence of different side groups in the two molecules could affect the geometrical adaptation on the surface and hence the metal diffusion to the reaction sites.

Herein, by following the established recipe for Fe metalation of 2H-TPP on Ag(111),¹⁸ the progressive *in situ* metalation of pure 2H-OEP monolayers and multilayers on

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Ag(111) in UHV environment is demonstrated. Core level spectroscopies (XPS and NEXAFS) directly substantiated the synthesis along with information on the complex electronic structure. Moreover, apart from the characterization of the electronic states and the geometrical adaptation of the molecules during the synthesis of Fe-octaethylporphyrin, a detailed study of the XPS and NEXAFS spectra of pure and Fe metalated 2H-OEP and a comparison with the corresponding metalation of 2H-TPP on Ag(111)¹⁸ and with the adsorption of Co-OEP on Ag(110)²³ evidence the role of ethyl side groups in the adsorption, conformation, and electronic structure of OEP on metal substrates, as well as their possible influence on the metalation process.

II. EXPERIMENTAL

Data for octaethylporphyrin thin films were collected at BACH beamline in the Elettra Synchrotron facility (Trieste). All the experiments were performed in ultra-high vacuum experimental chambers at a base pressure of 10^{-10} mbar. Highly purified (99.999%) commercial 2H-OEP was used and sublimated on Ag(111) directly by a home made, resistively heated, Ta evaporator at 520 K. The Ag(111) surface was prepared by Ar⁺ sputtering at 1 keV and annealing at 700 K. The absence of contaminants and the ordering of the surfaces was checked by means of X-ray photoemission spectroscopy and Low-Energy Electron Diffraction (LEED) techniques.

The 2H-OEP monolayer was obtained by annealing a free-base multilayer film on Ag(111) at 530 K. We therefore define 1 ML of 2H-OEP as the maximum amount of molecules adsorbed on the substrate surface after the above-described procedure. Iron evaporation was carried out by means of a highly focused electron bombardment evaporator (Omicron). After each Fe evaporation the substrate was annealed at about 400 K for metal diffusion.

NEXAFS spectra were collected in partial electron yield by means of a 16-channel detector, while scanning the photon energy across the N K-edge with an energy resolution of 100 meV. The electrons were collected by a hemispherical energy analyzer using a pass energy of 100 eV and a kinetic energy of 370 eV, close to the N KLL Auger. The absorption spectra were recorded by simultaneously collecting the photocurrent emitted by the sample and the reference current I_0 from the horizontal refocusing mirror of the beamline as a function of the incident photon energy. The NEXAFS data were normalized by the reference I_0 to the absorption edge jump and the energy scale was calibrated with XPS photoemission spectra in the region of the Ag $3d_{5/2}$ peak at BE = 368.1 eV (the analyzer's work function is known). To observe dichroism, the NEXAFS spectra were recorded at RT with two different geometries; in both cases horizontally polarized radiation was used (better than 99%) changing the direction of the incident radiation from normal (90° with respect to the surface plane) to grazing angle (30° with respect to the surface plane). This corresponds to an angle θ between the light polarization vector and the normal to the surface of 90° (in plane polarization) and 30° (out-of-plane polarization), respectively.

The XPS data for 1ML of 2H-OEP on Ag(111) were collected by means of a VSW CLASS 150 hemispherical electron energy analyzer. The analyzer was at 60° from the incident photon beam, in the horizontal plane. The photoemission measurements were collected with a $\pm 4^\circ$ angular acceptance and a total resolution of 150 meV and 360 meV for a photon energy of 175 eV and 530 eV, respectively.²⁴ The binding energies (BEs) of the photoemission spectra were calibrated using the Fermi level of Ag(111).

The measurements of the 2H-TPP and 2H-OEP molecules in gas phase were carried out at the gas phase photoemission beamline in Elettra (Trieste)²⁵ using a 6-channel, 150 mm hemispherical electron energy analyzer mounted at 54.78° with respect to the electric vector of the light. The valence band (VB) spectrum of the 2H-OEP was collected with an incident photon energy of 130 eV, while for the N 1s core level spectra of the 2H-OEP and of the 2H-TPP molecules the photon energy was set at 500 eV. The overall energy resolution (photons+analyzer) for these photoemission spectra was 0.25 eV. The energy scale was calibrated by introducing N₂ in the chamber, collecting an N₂+molecule spectrum, and using the N₂ reference value²⁶ to align the energies.

III. RESULTS AND DISCUSSION

A. Fe metalation

A direct indication of Fe coordination to 2H-OEP molecules is provided by the N 1s X-ray photoemission spectra. While the 2H-OEP molecule contains two N species (iminic and pyrrolic) producing two separate peaks in the N 1s spectrum, the coordination of a Fe ion at the porphyrin macrocycle center renders the all N atoms equivalent, leading to a single N 1s peak.

The 2H-OEP multilayer sample corresponds to approximately four layers, as estimated from the attenuation of the Ag 3d signal in XPS spectra. A film this thin should allow following the Fe metalation across the entire thickness of the film via surface sensitive techniques (in this work, XPS and NEXAFS). After depositing 2H-OEP molecules on Ag(111), the N 1s XPS spectrum (Fig. 1(a)) displays two components separated by 2 eV: according to previous studies,^{27,28} the peak at higher binding energy corresponds to the two pyrrolic nitrogen atoms (–NH–) while the lower BE component is ascribed to the two iminic ones (–N=).

The process of metalation is tracked by inspecting a sequence of N 1s spectra taken during Fe evaporation (Figs. 1(b) and 1(c)). It is evident that when Fe atoms are evaporated the two inequivalent nitrogen components change towards a single peak. As already pointed out, this is the primary evidence of Fe metalation, since the single peak configuration indicates that the N atoms are all unprotonated and equivalent, due to the N–Fe bond formation.

The fit analysis of the multilayer was made using a Shirley background and Voigt integral functions. According to the fit analysis, the pyrrolic peak (–NH–) is found at BE = 400.2 ± 0.05 eV, the iminic N one (–N=) at BE = 398.2 ± 0.05 eV, and the peak corresponding to the N–Fe bond at BE = 398.9 ± 0.05 eV. The BE values obtained by fitting all

FIG. 1. N 1s XPS spectra of a 2H-OEP multilayer before (a) and after (b) and (c) Fe deposition steps. The photon energy was $h\nu = 530$ eV. The formation of the peak at BE = 398.9 ± 0.05 eV gives evidence of the N–Fe coordination.

the spectra of Fig. 1 are reported in Table I. The degree of metalation at every Fe evaporation step is evaluated by considering the area of the N–Fe component relative to the total area of the N 1s profile. The metalation of the multilayer film is mostly accomplished, since the relative area corresponding to the N–Fe component is about 68% of the total, as indicated in Table I. Similar results for the Fe metalation efficiency were obtained in the case of a 2H-TPP multilayer of comparable thickness.¹⁸

The same metalation experiment done for a multilayer was reproduced for a monolayer. The starting 2H-OEP monolayer was obtained by annealing a free-base multilayer film on Ag(111) at about 530 K. Again, the N 1s spectrum of the 2H-OEP monolayer (Fig. 2(a)) consists of two peaks separated in energy by 2 eV. However, according to the fit analysis, the BEs of both the N 1s peaks (see Table II) shift by -0.2 eV with respect to peaks of the 2H-OEP multilayer spectrum. A downward shift with respect to multilayer films is not

TABLE I. Formation of Fe-OEP multilayer on Ag(111): normalized intensity and BE of the N 1s components of XPS spectra in Fig. 1.

Evaporation step	Normalized peak area		
	–N=	–NH–	NFe
No Fe (2H-OEP)	0.52 ± 0.03	0.48 ± 0.03	...
1st ($t_{\text{evap}} = 45$ s)	0.23 ± 0.03	0.23 ± 0.03	0.54 ± 0.03
2nd ($t_{\text{evap}} = 90$ s)	0.16 ± 0.03	0.16 ± 0.03	0.68 ± 0.03
BE (eV)	398.2 ± 0.05	400.2 ± 0.05	398.9 ± 0.05

FIG. 2. N 1s XPS spectra of a 2H-OEP ML before (a) and after (b)–(d) Fe deposition steps. The used photon energy was $h\nu = 530$ eV. The formation of the peak at BE = 398.7 ± 0.05 eV gives evidence of the N–Fe coordination.

unexpected in monolayers on metallic surface and can be ascribed to the more efficient core-hole screening by the metal substrate as compared with the poorer dielectric screening in multilayers.^{18,29–31}

For the monolayer N 1s spectra (Fig. 2(a)), the fit procedure was accomplished by means of a Shirley background and Doniach-Sunjc integral functions. The latter are chosen to account for any peak asymmetry typical of metallic systems, which originates from the intrinsic excitation of the Fermi sea in the core-hole creation process.³³ A low energy tail in XPS components is observed in strongly interacting organic/metal interfaces, such as TPP/Ag(111)¹⁸ or Fe-Terephthalic acid/Cu(100).³² A non zero asymmetry parameter ($\alpha = 0.05 \pm 0.01$) is indeed obtained in the best fit of the N 1s spectrum of the 2H-OEP monolayer (Table II), suggesting that a significant interaction with the metal substrate already occurs in the free-base monolayer. As Fe atoms react

TABLE II. Formation of Fe-OEP monolayer on Ag(111): normalized intensity, BE, and Doniach-Sunjc asymmetry of the N 1s components of the photoemission spectra in Fig. 1.

Evaporation step	Normalized peak area			α
	–N=	–NH–	NFe	
No Fe (2H-OEP)	0.55 ± 0.03	0.45 ± 0.03	...	0.05 ± 0.01
1st ($t_{\text{evap}} = 10$ s)	0.35 ± 0.03	0.33 ± 0.03	0.32 ± 0.03	0.06 ± 0.01
2nd ($t_{\text{evap}} = 20$ s)	0.17 ± 0.03	0.15 ± 0.03	0.68 ± 0.03	0.12 ± 0.01
3rd ($t_{\text{evap}} = 30$ s)	...	...	1.0 ± 0.03	0.20 ± 0.01
BE (eV)	397.9 ± 0.05	399.9 ± 0.05	398.5 ± 0.05

FIG. 3. N K-edge NEXAFS spectra of a multilayer (a) and (b) and a monolayer (c) and (d) before and after Fe metalation. Spectra were collected for $\theta = 90^\circ$ and $\theta = 30^\circ$ (where θ is the angle between the light polarization vector and the normal to the surface).

with the deposited monolayer, the two components of the N 1s spectrum merge into a single peak at $BE = 398.4 \pm 0.05$ eV. The values of the relative area of the N-Fe component are reported in Table II, showing that the evaporation procedure led to a completely metalated monolayer (Fig. 2(d)). The complete Fe metalation of a monolayer has also been reported for 2H-TPP/Ag(111).¹⁸ It is worth pointing out that a substantial increase in the asymmetry parameter value α occurs during Fe complexation (see Table II) suggesting that the presence of the Fe in the molecule enhances the metallic character of the monolayer.

Additional information on the electronic structure of the metalated and unmetalated films can be obtained by analyzing the N K-edge NEXAFS spectra of multilayers and monolayers (Fig. 3). The N K-edge π^* region of the 2H-OEP multilayer (Fig. 3(a)) displays an isolated peak at $h\nu = 397.7 \pm 0.05$ eV, followed by four peaks detected between 399.8 ± 0.05 eV and 403.8 ± 0.05 eV. These data are in accordance with the NEXAFS N K-edge spectra of 2H-TPP multilayers,^{18,30,34} which indicates that the side groups hardly have any direct influence on the electronic structure of the macrocycle. In particular, the first two peaks at $h\nu = 397.7 \pm 0.05$ eV and $h\nu = 399.8 \pm 0.05$ eV correspond

to the N 1s $\rightarrow$ LUMO transition for the iminic ($-N=$) and pyrrolic ($-NH-$) groups,^{18,30} respectively. All these structures exhibit a similar dependence on light polarization, showing a higher intensity when the light polarization is almost perpendicular to the Ag(111) surface, i.e., for $\theta = 30^\circ$, where θ is the angle between the light polarization vector and the normal to the surface. After Fe evaporation, the first two π^* peaks related to the two non-equivalent N 1s core levels of the unmetalated multilayer are reduced to a single peak at $h\nu = 398.6 \pm 0.05$ eV (Fig. 3(b)), as was observed in the N 1s XPS spectra. In Fig. 3(b), the presence of unmetalated molecules is indicated by the small but distinct feature at $h\nu = 397.7 \pm 0.05$ eV, which derives from the $-N=$ groups of the unmetalated 2H-OEP molecules. The structure of the N K-edge NEXAFS spectrum after Fe evaporation is in good agreement with that reported for metalloporphyrins in general^{23,30,35} and Fe-TPP in particular,¹⁸ which further confirms the coordination of Fe atoms with 2H-OEP molecules.

A similar behavior is observed for the N K-edge NEXAFS spectrum of a 2H-OEP monolayer (Figs. 3(c) and 3(d)). At $\theta = 30^\circ$, the structure of N K-edge NEXAFS spectrum of the monolayer before Fe evaporation (Fig. 3(c)) strongly resembles that of the multilayer (Fig. 3(a)), suggesting that Ag(111) has a secondary influence on the electronic structure of the molecules. The N K-edge NEXAFS spectrum of a 2H-OEP monolayer after metalation is shown in Fig. 3(d). In this case, the same Fe evaporation procedure as that monitored during the XPS measurements of Fig. 2 was repeated on a new ML. Again, the effect of Fe evaporation is that the first two π^* peaks related to the two non-equivalent N 1s core levels of the unmetalated monolayer at $h\nu = 397.9 \pm 0.05$ eV and $h\nu = 399.9 \pm 0.05$ eV (Fig. 3(c)) converge to a single peak at $h\nu = 398.4 \pm 0.05$ eV (Fig. 3(d)), as was observed in the N 1s XPS spectra (Fig. 2). Finally, in Fig. 3(d) a small pre-edge is identified at the same photon energy as the first π^* peak of the unmetalated monolayer, indicating that the metalation of this monolayer is almost but not completely accomplished.

B. Molecular adsorption and conformation

In this section, we complete the study of the molecular conformation and electronic structure of the unmetalated and metalated 2H-OEP films by using angle-resolved NEXAFS measurements. We also make a detailed comparison between the results obtained for OEP layers to their TPP counterparts reported in Ref. 18, as well as to Co-OEP/Ag(110) studied in Ref. 23. This comparison allows to evaluate the influence of different side groups (like ethyls and phenyls) on the Fe metalation, packing configuration, and electronic properties of porphyrin films deposited on non-reactive metal surfaces such as silver.

The angular-dependence of NEXAFS signatures on the linear polarization of the light allows to determine the molecular orientation of the 2H-OEP molecules on Ag(111), both in the unmetalated and metalated phases.³⁶ This is due to the fact that porphyrins are planar aromatic molecules whose π^* states mainly originate from a combination of atomic-like p_z orbitals that lie perpendicular to the porphine plane: from the linear polarization dependence of NEXAFS spectra, the

spatial orientation of the π^* states, and consequently the orientation of the molecular plane with respect to the supporting surface can be directly probed. In particular, the π^* states generated by the four central nitrogen atoms are a good choice to study dichroism because they are well separated in energy from the remaining empty orbitals.

In Fig. 3, the N K-edge NEXAFS spectra of the 2H-OEP multilayer and monolayer are shown for the angles $\theta = 90^\circ$ and $\theta = 30^\circ$ between the polarization vector and the normal to the surface. All the spectra are normalized to the intensity of the σ^* states at $h\nu = 415$ eV. The linear polarization dependence of the NEXAFS spectra is first analyzed for a monolayer system. As was discussed in Sec. III A, the first two π^* transitions of the free-base 2H-OEP monolayer spectrum (Fig. 3(c)) correspond to the two peaks visible in photoemission and exhibit a clear dependence on light polarization. The intensity of these peaks is higher when the light polarization is almost perpendicular to the Ag(111) surface ($\theta = 30^\circ$) while when the light polarization is parallel to the surface ($\theta = 90^\circ$) a strong quenching is observed.

In order to determine the polarization dependence of the peak area, we deconvoluted the NEXAFS spectra by performing a nonlinear least-squares fitting of the experimental data, using a set of Gaussian functions. An additional integral background was included in order to account for transitions to the continuum of free electron states.³⁶ Then, the total area of each π^* peak was fitted as a function of the linear polarization angle with the equation given by Stöhr,³⁶ assuming a threefold symmetry of the substrate. Starting with the 2H-OEP monolayer, the fit indicates the same average tilt angle of $17^\circ \pm 3^\circ$ between the first two π^* states and the surface normal. In principle, the determined value may arise either from a distortion of a macrocycle parallel to the surface or from a tilt of the whole molecule, but it is not possible to distinguish these two cases based solely on the analysis of the N K-edge. Nonetheless, a macrocycle tilt angle of about 17° with respect to the substrate plane would not be unexpected for octaethylporphyrins on silver surfaces. In fact, Fanetti *et al.* studied the dichroic behavior of the NEXAFS spectra at both the N and C K-edges of a monolayer of cobalt octaethylporphyrins on Ag(110) with the result that the whole molecular macrocycle is undistorted and tilted by about 20° with respect to the metal surface.²³ In that study, calculations on the possible orientation of a 2H-OEP (without Co) monolayer were also performed.²³ By considering only the steric interaction (thus neglecting the Ag substrate), the minimum-energy configuration is achieved when the molecules are tilted about 17° with respect to the surface plane. This combined study suggests that the experimental geometry of the Co-OEP monolayer arises from a trade-off between the molecule/metal interaction (which determines the periodicity of the interface) and the repulsive molecule/molecule interaction (which determines the tilt of the molecules) and is not governed by the specific metal center or by the presence of a weakly interacting surface. The good agreement between the tilt angles reported by Fanetti *et al.*²³ and that found for the 2H-OEP monolayer suggests that the latter is indeed the tilt angle of the whole undistorted 2H-OEP molecule on Ag(111). In this case, it seems unlikely that factors such as the metal center or the

FIG. 4. N K-edge NEXAFS spectrum of 2H-OEP molecules in gas phase (a). N 1s XPS spectra of 2H-OEP (continuous line) and 2H-TPP (dashed line) molecules in gas phase measured at $h\nu = 500$ eV (b). The inset shows the N 1s XPS spectra of 2H-OEP (continuous line) and 2H-TPP (dashed line) multilayers (4 layers) deposited on Ag(111). Data of the 2H-TPP multilayer are taken from Ref. 18. A sketch of the molecular structures for 2H-OEP and 2H-TPP is shown on the top right side.

presence and orientation of the surface could determine the adsorption angle. Rather, the important role is played by the steric interaction between the various moieties in the monolayer. In other words, it is the presence of the ethyl groups that is responsible for the adsorption angle of the OEP macrocycle in the monolayer.

The linear polarization dependence of the NEXAFS spectra is considered also for a free-base multilayer (Fig. 3(a)). As in the monolayer case, a strong quenching of all the π^* states at $\theta = 90^\circ$ is observed. However, we note that the first absorption peak is certainly composed of two components, since it shows a shoulder at $\theta = 30^\circ$ and two clear peaks at $\theta = 90^\circ$. This shoulder is absent in the monolayer spectrum and in the gas-phase NEXAFS of 2H-OEP (see Fig. 4(a)) and therefore is a consequence of the formation of the multilayer. Before analyzing the NEXAFS data, it is worth noting

FIG. 5. (Top panel) N 1s XPS spectrum of a 2H-OEP multilayer (a). This spectrum has been fitted with three components, one for -NH- (C, weighting about 50%) and two for the peak -N= (A and B, weighting roughly 25% each). (Bottom panel) N K-edge NEXAFS spectra of a 2H-OEP multilayer for $\theta = 30^\circ$ (b) and $\theta = 90^\circ$ (c). According to the fit procedure applied to (a), the NEXAFS spectra has been fitted using two components for the first π^* transition (A and B) and one for the second π^* peak (C).

that in the corresponding XPS N 1s core level spectrum, the -N= peak is much larger than the =NH- component and larger than the corresponding peak in the 2H-TPP multilayer or in the XPS spectra of 2H-OEP in gas-phase (see, for example, Fig. 4(b)). Therefore, we decided to reproduce the 2H-OEP N 1s XPS spectrum of the multilayer using three components, one for -NH- and two for the -N= peak (Fig. 5(a), top panel). This type of deconvolution does not affect the results on metalation of Sec. III A. The component C of -NH- remains as in the previous fit and weights 50% of the spectrum, while the two components A and B of the -N= peak are weighting, roughly, 25% each. Both components are associated with -N= atoms of the macrocycle, but since the component B is shifted toward the -NH- peak a possible assignment may be to -N= atoms forming hydrogen bridge bonds with the ethyl groups of the molecules in the layer above or below. A similar situation, but for a different porphyrin molecule, was reported by Garcia-Lekue *et al.*³⁷ According to this model, we actually fitted the NEXAFS spectrum of the multilayer using two components for the first π^* transition (A and B) and one for the second π^* transition (C) (Fig. 5, bottom panel). By fitting the areas of these components for

TABLE III. Average tilt angles of the macrocycle with respect to the surface normal for multilayer and monolayer 2H-OEP films on Ag(111), before and after Fe evaporation. The average angles of Co-OEP monolayer on Ag(110) (NEXAFS measurements) and of 2H-OEP monolayer (calculations) are also reported from Ref. 23.

Evaporation step	Film	Substrate	Average tilt angle
No Fe (OEP only)	Multi	Ag (111)	A= $31^\circ \pm 3^\circ$ B= $42^\circ \pm 3^\circ$ C= $22^\circ \pm 3^\circ$
Fe evaporation (t = 90 s)	Multi	Ag (111)	$27^\circ \pm 3^\circ$
No Fe (OEP only)	Mono	Ag (111)	$17^\circ \pm 3^\circ$
Fe evaporation (t = 30 s)	Mono	Ag (111)	$21^\circ \pm 3^\circ$
CoOEP ²³	Mono	Ag (110)	$20^\circ \pm 3^\circ$
2H-OEP (simulations) ²³	Mono	No	$17^\circ \pm 3^\circ$

$\theta = 30^\circ$ (Fig. 5(b), bottom panel) and $\theta = 90^\circ$ (Fig. 5(c), bottom panel), we obtain average tilt angles of $31^\circ \pm 3^\circ$ for component A, $42^\circ \pm 3^\circ$ for component B, and $22^\circ \pm 3^\circ$ for component C, indicating a distortion of the macrocycle of 2H-OEP in the multilayer. If we assume that the tilt angle of the macrocycle is around 22° (as explained later), the B component shows a further tilting of 20° due to the possible hydrogen bonding with the layer underneath (or above), while the A component is tilted a further 9° .

Studying the effects of the *in situ* Fe-metalation on the geometrical adsorption of 2H-OEP may give further information about molecular conformations and adsorption tilt angles. Again this is explored by evaluating the angular dependence of NEXAFS spectra after Fe evaporation. As reported in Sec. III A, the effect of Fe coordination on the NEXAFS N K-edge spectra is that the first two π^* orbital peaks of the 2H-OEP multilayer (Fig. 3(a)) and monolayer (Fig. 3(c)) spectra converge to a single main peak corresponding to the Fe-N component, as observed in Figs. 3(b) and 3(d), respectively. Like the -NH- and -N= π^* components of the free-base porphyrin spectra, the π^* peak of Fe-N component displays a strong angular dependence. From the deconvolution of the Fe-OEP spectra, the area of the Fe-N peak was evaluated as a function of the linear polarization angle. Accordingly, an average tilt angle of $27^\circ \pm 3^\circ$ is found for a Fe-OEP multilayer while the average tilt angle of $21^\circ \pm 3^\circ$ is obtained in case of a Fe-OEP monolayer. The average tilt angles of the 2H-OEP and Fe-OEP macrocycle with respect to the surface plane are summarized in Table III, where results from Co-OEP by Fanetti *et al.*²³ are also reported. First, for the multilayer the metalation seems to recover, at least in part, the planarity of the macrocycle, which appears to be very close to the tilt angle of 22° obtained for the C component in the 2H-OEP multilayer. In both cases, monolayer and multilayer, the metalation causes a similar change that, within the error, is a variation of the average angle of 4° . As mentioned previously, we are unable to distinguish a distortion of the macrocycle from a tilt of the entire molecule without C1s NEXAFS measurements. In any case, the effect of Fe coordination on the tilt angle of the molecular plane is small, as it was already pointed out for TPP films. The minor effect of the Fe metallic center on the tilting geometry of the macrocycle further supports the hypothesis that it is the presence of the ethyl groups

rather than the metallic center or the underlying surface determining the adsorption angle the OEP macrocycle.

Further evidence of the role of lateral groups in molecular packing comes from comparing the tilt angles of 2H-OEP and 2H-TPP on Ag(111), whose molecular structure differs only by the four phenyls groups attached to the porphyrin macrocycle. In fact, in contrast to 2H-OEP, 2H-TPP molecules lie with the molecular plane parallel to Ag(111), both in monolayers and multilayers and no distortion of the macrocycle plane are induced.¹⁸ The specific side groups therefore play an essential role on the packing configuration while, as explained below, their influence on the metalation is marginal. A complete Fe metalation is observed for both 2H-OEP and 2H-TPP monolayers on Ag(111) despite the different conformation of the molecular plane and hence the different molecule-substrate distance. Indeed, this behavior is mainly driven by the high binding affinity of the macrocycle towards metallic ions.⁶ The tendency of a heterocyclic macrocycle to bind with metal ions is characteristic also of phthalocyanines,³⁸ where metal atoms are demonstrated to coordinate exclusively with the central nitrogen atoms rather than the peripheral meso-bridging nitrogen atoms.³⁹ Hence, the metal binding affinity of porphyrins and phthalocyanines is attributed mainly to the tetrapyrrolic composition of the ring. In the case of multilayers, an equivalent ratio of metalated porphyrins is achieved in 2H-OEP and 2H-TPP films of comparable thickness. Therefore, the ability of the macrocyclic ring to coordinate with Fe atoms is negligibly affected by the orientation of the central rings, which is flat for 2H-TPP and is likely tilted (and ruffled for the multilayer) for 2H-OEP and even by the presence and orientation of side groups with respect to macrocycles. The capability to capture metal ions is recognized as an essential property of the tetrapyrrolic macrocyclic structure to such an extent that a porphyrin-like tetramer has been recently proposed as a fundamental building block of the complex and highly disordered eumelanin macromolecule,^{40,41} whose ability of accumulating, delivering, and releasing metals is widely documented.^{42–44} Indeed, the good agreement between the experimental data of eumelanin films and the calculated DOS of a possible porphyrin-like tetramer has recently been reported in the case of both unmetalated^{40,41} and metalated^{45,46} synthetic eumelanin films.

Concerning the role of side groups on molecule-substrate interaction, a set of similar results is attained for both OEP and TPP monolayers. New molecular states at the Fermi edge appear in the valence band spectra of 2H-OEP and Fe-OEP monolayers, as well as in the cases of 2H-TPP and Fe-TPP.¹⁸ This is shown in Fig. 6, where the peak close to the Fermi level, which is due to the hybridization between the 2H-OEP molecular orbitals and the continuum of density of states of the metal surface (indicated in Fig. 6(a) by an arrow), grows in intensity as the Fe atoms bind to the macrocycle (see supplementary material for a detailed analysis of VB spectra⁴⁷). This peak is likely due to a charge transfer from the substrate into the molecules, which, similar to the Co-OEP/Ag(110) case,²³ mostly involves the d_{z^2} -like orbitals localized on the central metal atom. As a consequence of the metallic character of the monolayer system, the creation of a core-hole induces an intrinsic excitation of the Fermi sea while a better core-

FIG. 6. Valence band spectra of 2H-OEP ML during Fe metalation (from (a) to (d)). The sequence of the ML valence band spectra are raw data subtracted by the valence band of the clean Ag surface taken in the same conditions. The photon energy was $h\nu = 175$ eV.

hole screening is provided compared to the multilayer case. These effects are attested to OEP monolayers by the presence of the Doniach-Sunjjic asymmetry parameter in the XPS fitting functions and by the shift of the core levels to lower BE values with respect to the multilayer, akin to the XPS results presented for TPP films.¹⁸ Another indication of the core-hole screening efficiency in porphyrin monolayers is given by the energy positions of the N-related transitions in NEXAFS spectra. For a metallic or quasi-metallic system, the Coulomb interaction due to the creation of a core exciton is completely screened by the electrons near the Fermi level, so the first absorption peak should be at the same photon energy as the core level BE where the core-hole is created. This is the case of OEP monolayers: according to the values reported in Sec. III A, the lowest energy components of the NEXAFS N K-edge of both 2H-OEP and Fe-OEP monolayer spectra are detected at the same photon energy (within the error) as the BE of the correspondent components in the N 1s photoemission spectra. A similar behavior was found in the N 1s NEXAFS spectra of 2H-TPP and Fe-TPP monolayers.¹⁸ To sum up, the different tilting angle of the adsorbed macrocycles and, consequently, the different substrate-molecule distance found for OEP and TPP monolayers have only minor effects on the molecular electronic structure, which is influenced mainly by the porphyrin-Ag interaction.

On the other hand, some differences between the polarization screening of TPP and OEP (probably due to the presence of different side groups) can be identified in the multilayer spectra. As expected, no spectroscopic evidence of the metallic character is observed in multilayers. Charge injection is limited to the first layer, as deduced from the analysis of the VB spectra (see supplementary material⁴⁷), and the XPS core level shape shows no asymmetry. Nevertheless, the N 1s core levels of the unmetalated OEP and TPP multilayers have

different binding energies. The N1s level of the TPP multilayer is shifted 0.25 eV to lower BE with respect to OEP (see inset in Fig. 4(b)). By contrast, Fig. 4(b) shows that the BE of the N 1s core level measured in gas phase for the isolated molecules is higher by 0.3 eV for the TPP with respect to OEP. This indicates that the polarization screening of the N 1s core-hole in the TPP solid is more effective than in the OEP solid, probably due to the presence of aromatic electrons in the phenyl rings surrounding the excited molecule.

A similar indication comes from the N 1s NEXAFS spectra. The first absorption peak is shifted in the gap by about 0.5 eV in OEP and by about 0.3 eV in TPP,¹⁸ due to a different Coulomb interaction between the core-hole and the excited electron in the two molecules. Even when metalated with Fe, while the Fe-TPP multilayer's first absorption peak is still at the same photon energy as the core level BE,¹⁸ the Fe-OEP multilayer's is shifted below the Fermi level by 0.3 eV. These data suggest that the core-hole screening is worse in OEP than in TPP multilayers, in agreement with the reported polarizability values of these molecular species ($74.906 \times 10^{-24} \text{ cm}^3$ for TPP and $66.016 \times 10^{-24} \text{ cm}^3$ for OEP).⁴⁸

IV. CONCLUSIONS

By following the already assessed recipe of Fe metalation of 2H-TPP molecules,¹⁸ the progressive *in situ* synthesis of Fe-octaethylporphyrin (Fe-OEP) molecules on Ag(111) has been successfully carried out in UHV. The combination of synchrotron radiation-based techniques, such as XPS, valence band photoemission, and NEXAFS, allowed a comprehensive characterization of the molecular conformation and electronic structure of Fe-OEP monolayers and multilayers.

The Fe metalation seems to proceed in a manner identical to that observed on 2H-TPP on Ag(111), regardless of the presence of different side groups and of the different molecular adsorption geometry. On the other hand, the presence of the ethyl groups has a strong influence on the tilting angle of the macrocycle in the monolayer and multilayer and on the molecular conformation, in particular for the multilayer case.

In monolayers, a parallel adsorption of the macrocycle is obtained for 2H-TPP while for 2H-OEP our data indicate an adsorption geometry having the molecular plane tilted on silver surface by about 17°. Although we cannot exclude a distortion of the macrocycle, the comparison with free-standing 2H-OEP monolayer calculations²³ and CoOEP/Ag(110) experiments²³ points to a tilted and undistorted 2H-OEP macrocycle for the monolayer on Ag(111). In the case of multilayers instead we obtain a similar tilting of the molecules, but with a huge distortion of the planarity of the macrocycle, which we tentatively assign to the formation of hydrogen bridge bonds of the $\text{N}=\text{N}$ atoms with the ethyl groups of molecules in the layer above (or below), highlighting the fundamental role of lateral groups in molecular conformation. On the contrary, the addition of a central atom, such as Fe, scarcely affects the molecule orientation and seems to stabilize the macrocycle planarity in agreement with calculations.⁴⁹ Finally, the presence of different side groups

alters the polarization screening in multilayers, with a worse core-hole screening in OEP than in TPP multilayers.

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