Enhanced Magnetism through Oxygenation of FePc/Ag(110) Monolayer Phases

E. Bartolomé,[1][*] J. Bartolomé,[2] F. Sedona,[3] J. Lobo-Checa,[2] D. Forrer,[3] J. Herrero-Albillos,[4] M. Piantek,[5] J. Herrero-Martín,[6] D. Betto,[7] E. Velez-Fort,[7] L.M. García,[2] M. Panighel,[8] A. Mugarza,[9,10] M. Sambi,[3,11] F. Bartolomé[2]

[1] Escola Universitària Salesiana de Sarrià (EUSS), Passeig Sant Joan Bosco 74, 08017 Barcelona, Spain; Phone: +34 932 80 52 44; e-mail: ebartolome@euss.es

[2] Instituto de Ciencia de Materiales de Aragón and Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

[3] Dipartimento di Scienze Chimiche, Università Degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy

[4] Centro Universitario de la Defensa. Academia General Militar, Zaragoza, Spain

[5] Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Zaragoza, Spain

[6] ALBA synchrotron, Bellaterra, 08193-Barcelona, Spain

[7] ESRF-The European Synchrotron Radiation Facility, Grenoble, France

[8] CNR-IOM Laboratorio TASC, S.S. 14 km 163, Basovizza, I-34149 Trieste, Italy

[9] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[10] ICREA - Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain

[11] Consorzio INSTM, Unità di Ricerca di Padova, Padova, Italy

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ABSTRACT: Iron-phtalocyanines (FePc) adsorbed onto a Ag(110) substrate self-assemble into different monolayer phases going from rectangular to different oblique phases, with increasing molecular density. We have investigated the oxygen uptake capability of the different phases and their associated magneto-structural changes. Our study combines scanning tunneling microscopy and spectroscopy (STM/STS), X-ray magnetic circular dichroism (XMCD), and density functional theory (DFT) calculations. STM measurements reveal that the oxygenation reaction of the FePc/Ag(110) generally involves a displacement and a rotation of the molecules, which affects the electronic state of the Fe centers. The oxygen intercalation between FePc and the substrate is greatly obstructed by the steric hindrance in the high-density phases, to the point that a fraction of oblique phase molecules cannot change their position after oxydizing. Depending on the oxidation state and adsoption geometry, the STS spectra evidence clear differences in the Fe local density of states, which are mirrored in the XAS and XMCD experiments. Particularly, XMCD spectra of the oxidized phases reflect the distribution of FePc species (non-oxygenated, oxygenated-rotated and oxygenated-unrotated) in the different cases. Sum rule analysis yields the effective spin (m_s^{eff}) and orbital (m_L) magnetic moments of Fe in the different FePc species. Upon oxygenation, the magnetic moment of FePc molecules increases about an order of magnitude, reaching $m_{TOT} \sim 2.2$ μ_B per Fe atom.

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1. INTRODUCTION

Molecular overlayers on crystalline substrates have a broad field of application in catalysis, sensing, molecular electronics, light-to-energy conversion, etc. In particular, bio-inspired oxygen-binding metalated macrocycles, such as iron-phtalocyanines (FePc), are investigated as viable substitutes for precious metals in catalysis of the Oxygen Reduction Reaction in low-temperature fuel cells[1].

Recently, the spontaneous assembly and the electronic and magnetic properties of FePc have been studied on a variety of substrates: $Au(111)^{2-4}$, $Au(001)^5$, $Au(100)^6$, $TiO_2(110)^7$, $InAs(100)^8$, $InSb(100)^8$, $Cu(110)^9$, $NaCl/Cu(111)^{10}$, $Ag(111)^{11,12}$, $graphite^{13}$ and graphene/Cu(111), $Ni(111)^{14}$. In particular, FePc/Ag(110) has been intensively investigated to shed light into the self-assembly, interaction mechanisms, structural transformations upon thermal treatments, and its capacity to accommodate small molecules like O_2.

After deposition on a metal substrate, FePc may react with different ligands. For example, in NH_3/FePc/Au, the NH_3 is weakly bonded with the Fe atom on the external side of the FePc molecule, The coordination of the Fe atom is modified and a reorganization of the Fe charge takes place, pairing electrons to a quenched spin $(S=0)^{15}$. In contrast, in NO/FePc/Au, where NO is adsorbed on the external side of the FePc molecule, the spin quenching seems to be partial $(S=1/2)^{16}$. The exposure to oxygen of a 1ML FePc deposited on Ag surface has been explored previously. It has been found that its dissociation and location, whether on-top of the Fe atom, on $Ag(100)^{17}$, or sandwiched between the FePc and the substrate, on $Ag(110)^{18}$, actually depends on the different self-organization schemes of the FePc on the each type of Ag surface. The difference between the two modes of oxygen absorption, on top or sandwiched, are clearly distinguished by STM, since when on-top an increase in the intensity at the Fe site is viewed, while when sandwiched the intensity decreases. At any rate, the oxygen atoms react only with the Fe, in no case has it been observed to react with other moieties of the molecule.

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The properties of FePc sublimated onto Ag(110) were first investigated by Palmgren *et al.*[19] by low energy electron diffraction (LEED). Casarin *et al.*[20] reported coverage-dependent structural and self-assembly properties of FePc based on STM direct observations, and DFT simulations. They found that in the monolayer regime, FePc molecules lie flat on the Ag(110) surface. At molecular densities below 0.449 molecules per nm^2, a mixture of two structurally distinct, equally dense phases coexist, namely c(10x4) = R1, and p(10x4) = R2 phases. Both phases stabilize upon annealing in UHV between 410 and 520 K. The R1 phase has a centered rectangular unit cell, as shown in Figure 1. In this phase, Fe centers ocupy sites on-top of a silver atom (OT sites) and all the molecules are oriented alike, with the molecular axis bisecting the phenyl rings forming a 45° angle with the substrate $[1\bar{1}0]$ direction (OT-45 positions, see Figure 2a). The R2 phase is formed by the ordered and alternated sequence of singly oriented rows parallel to the [001] direction of the Ag substrate (see Figure 1). In this phase, Fe centers occupy short-bridge sites between two silver atoms (SB sites), and the FePc phenyl rings are rotated 30° (either clockwise or anticlockwise) with respect to the substrate $[1\bar{1}0]$ direction (SB-30 positions, see Figure 2b).

At higher molecular density ($\approx$0.449 molecules per nm^2) the thermal treatment stabilizes an oblique phase (OB1), as reported by Sedona *et al.*[18]. The molecular adsorption site and possible local orientations in the OB1 phase with respect to the substrate are those described for the R2 phase: in the OB1 phase the Fe centers occupy SB sites and all of them have the same orientation, either $+30^o$ or -30° within the same ordered domain. Cai *et al.*[21] did observe two additional "oblique" arrangements of FePc on Ag(110), which we have not found reproducibly as stable phases.

Interestingly, low-density R1 and R2 phases have been shown to be catalytically active[18]. Upon oxygenation of these two phases, oxygen atoms intercalate between the FePc and the substrate, forming the FePc-(η^2-O_2)-Ag coordination complex. The oxygen uptake in R2 phase involves shifting and rotating the molecules from its original SB-30 to an OX(OT-45) position, and adsorbing two

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oxygen atoms at the neighboring SB sites, as shown in Figure 2c (in the pristine R1 phase the FePc molecule is already positioned on OT-45). Remarkably, this process decouples the molecular electronic states from the metal surface resulting in a concomitant increase of one order of magnitude of the Fe magnetic moment (from $m_{TOT}{\approx}0.26$ μ_B to $m_{TOT}{\approx}2.1$ μ_B), as demonstrated by XMCD. Notably, the molecular arrangement and the Fe magnetic moment is reversible upon oxygenation-annealing cycles[22].

However, the oxygenation of high-density FePc phases on Ag(110) is still unreported. It is known that in the related case of high-density FePc on Ag(100)[17], oxygen is adsorbed (as di- and mono-oxygen) on-top of the Fe centers instead of being intercalated between the molecular layer and the substrate[23]. In this case, the FePc reactivity to oxygenation seems to be mediated by the presence of Ag adatoms between the molecules, therefore involving a completely different reaction mechanism with respect to Ag(110). A temptative explanation for this difference assumes, on one hand, that Ag(100) is atomically "flat" compared to the corrugated Ag(110), which hinders the dissociation and transport of oxygen underneath the FePc molecules, and on the other hand that on Ag(110) there is no evidence of the presence of Ag adatomns in-between the FePc molecules.

In this paper we report the formation of new high-density FePc/Ag(110) phases in the sub-ML to ML regime, which, despite their steric limitations, still present catalytic activity, at variance with the saturated Fe/Ag(100) monolayer. The oxygen intercalation capability and associated magnetization changes of these high-density phases are reported by correlating high-resolution STM images, STS spectra, XMCD measurements and DFT calculations, and systematically compared with the analogous results obtained on the low-density phases, thereby obtaining a more detailed description of this complex and intringuing system.

2. METHODS

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Samples. FePc molecules were evaporated on a Ag(110) single crystal substrate in several ultrahigh vacuum (UHV) chambers (base pressures in the low 10^{-10} mbar range), containing equipment for sample sputtering, thermal annealing, FePc deposition, and connected to the XAS & XMCD experimental chamber. The Ag(110) single-crystal was cleaned by repeated cycles of 1keV Ar^+ sputtering and annealing at 550°C (10 min). The surface quality and order was monitored by LEED.

A few mg of FePc (Alfa Aesar GmbH, 95% purity) were loaded into a pyrolytic boron nitride (PBN) crucible connected to the preparation chamber. The FePc sample was carefully degassed while monitoring the UHV base pressure. The crucible temperature was raised to 540 K in approximately 30 h, held at this temperature for 25 h and increased to 560-570 K for additional 6 h. Depositions were performed with the crucible temperature at 550 K. The Ag substrate was held at room temperature (RT) during molecular deposition. Different sub-ML phases of FePc/Ag(110) were prepared, and the structure controlled *in situ* by LEED.

The oxygenation of the FePc deposited on the Ag substrate was achieved by exposing the sample surface to an oxygen pressure P, for a time t (P x t Langmuir) in the closed chamber at room temperature. The exposures for the samples used in this paper are collected in Table 1.

STM. The structural evolution of FePc phases up to the full ML with the oxygen dosing was monitored by Scanning Tunnelling Microscopy (STM). The experiments were performed using two different instruments: a room-temperature setup (Omicron VT-STM) at the University of Padova, and a low temperature equipment (Omicron LT-STM) operated at 4.6 K at the *Laboratorio de Microscopías Avanzadas* (LMA, Zaragoza).

STS. Differential conductance (dI/dV) curves at the Fe centres were obtained using the Omicron LT-STM at 4.6 K in two different operating modes: with open feedback loop at constant tip height (CH) and in constant current (CC) mode. While the CH mode is generally used to measure the local density of states (LDOS) around the Fermi level, we found more convenient to close the feedback-

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loop (CC mode) for extended voltage ranges in order to avoid structural damage of tip and sample by excessive electric fields and/or electron injection. Here we combined the two modes in order to obtain the spectra over the entire range of interest. For better visualisation, the CC data is multiplied by a constant factor in order to stitch the experimental curves. It should be noted, that we refrain from comparing different phases' spectra measured in separate experimental runs since the tip apex termination was found to be altered. Given that the surface was saturated with molecules, we did not have full control over the tip nanostructuring that ultimately influence the dI/dV spectral lineshape (the observed signal is a convolution of both the sample and tip LDOS).

DFT. DFT+U calculations were performed on FePc adsorbed on Ag(110) before and after the oxygen dosage, using the Quantum-ESPRESSO suite of codes[24]. As we need to deal with two different adsorption configurations, i.e. the SB-30 and rotated OT-45, simulations were run on a p(6x4) rectangular cell, which can allocate both geometries. The PBE[25] exchange-correlation functional was adopted and wavefunctions were expanded on a plane-wave basis set with a cut-off of 27 Ry, while the cut-off on the density was 250 Ry and a 2x2 mesh of k-points was used. The interaction between valence electrons and ion cores was described through ultrasoft pseudopotentials[26]. The Hubbard U was used on the Fe site only and was set to 3.9 eV[27]. STM images were simulated within the Tersoff-Hamann approach[28], while STS curves were compared to the density of states (PDOS) projected on the Fe $3d_z^2$ atomic orbital. PDOS on the $d_{//}$ and $d\pi$ atomic orbitals were also calculated (see S3). Atomic charges, magnetizations and holes were computed within a Löwdin approach as in our previous work[22].

XAS and XMCD. Soft X-ray absorption and magnetic dichroism experiments at the Fe $L_{2,3}$ and N K edges were carried out at ALBA (BOREAS beamline[29]) and ESRF (ID-32[30,31]) synchrotron radiation facilities. The sample was placed perpendicular to the synchrotron orbital plane. To perform angle-dependent experiments the sample was rotated about a vertical axis to the synchrotron orbital plane, so as to vary the γ angle of incidence between the X-ray beam and the substrate-normal

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between $\gamma=0°$ (normal incidence) and $\gamma=70°$ (grazing incidence). The detection mode was total electron yield (TEY). Linear polarization X-ray absorption (XAS) measurements were carried on at $B=6$ T, $T=3.4$ K, with the polarization of the incident electric field either vertical, E_V (i.e. perpendicular to the synchrotron orbital plane, and parallel to the sample surface), or horizontal, E_H (i.e. horizontal to the synchrotron ring plane, and perpendicular to the x-ray beam), see schematics in Figure 5c.

X-ray magnetic circular dichroism (XMCD) spectra were measured at ALBA (BOREAS, $B=6$ T, $T=3.4$ K) and ESRF (ID8, $B=4$ T, $T=6.0$ K) end stations, respectively, to guarantee magnetic saturation. To rule out experimental artifacts and reduce drift phenomena, XMCD was measured by either changing the light helicity or the field direction. To increase statistics, the XMCD (μ^+-μ^-) and normalized XAS (μ^++μ^-)/2 spectra were determined from 16 x-ray absorption spectra measured under right-handed (μ^+) and left-handed (μ^-) circular polarizations.

To determine the FePc signal, the background contribution from the Ag substrate has to be carefully subtracted. X-ray absorption spectroscopy experiments on pristine Ag substrates were performed under the same experimental conditions used for FePc/Ag(110) samples. The background-subtracted XAS spectra were subsequently normalized to the atomic continuum signal well above the Fe $L_{2,3}$ absorption edges.

3. RESULTS

3.1 Modification of FePc/Ag(110) Phases upon Oxygenation. At room temperature, FePc on Ag(110) self-assembles up to the ML in several ordered phases, all of them characterised by flat-lying molecular overlayers. We detect five FePc phases when increasing the surface density, with occupation densities ranging from 0.421 to 0.527 molecules per nm^2. Figure 1 summarizes these arrangements by showing their STM topography, LEED pattern, structural model and matrix notation with respect to the Ag(110) substrate.

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At low densities, the surface is characterised by a mixture of the rectangular R1 and R2 phases, that show the same centred unit cell dimensions. By increasing the FePc density, the oblique OB1 phase is stabilized with 0.449 molecule/nm^2. At even higher densities, two other phases appear (with a unit cell almost squared but slightly distorted): R3 phase, and a new oblique phase OB2. Among the five phases reported in Figure 1, only in R1 the Fe is found in OT-45 configuration, whereas in all the other phases the Fe is in SB-30 positions. The R3 and OB2 phases often coexist, likely because of their similar structure (see also Figure S1). Due to this similarity, in the subsequent discussion regarding oxygenation they are treated as equivalent (R3^{OX}/OB2^{OX}).

Figure 3 shows STM images exhibiting the effect of exposing to oxygen the different phases. Before oxygenation (Figure 3, top panel), the FePc molecules characteristically show a bright central spot corresponding to the Fe atom. Oxygen uptake has the effect of "dimming" this central point (Figure 3, mid panels). This phenomenon was earlier reported for low-density phases R1/R2. The formation of the FePc-(η_2-O$_2$)-Ag complex is accompanied by a downward pull of the Fe atom, which is well below the macrocycle plane (as visible in Figure 2c, 2d side views). The oxidized Fe atoms present also a different electronic configuration, and appear as dark spots in the STM images. The high-resolution STM image Figure 3g shows the R1/R2^{OX} phase contains a distribution of non-oxidized molecules and oxidized molecules, OX(SB-30), see green box.

We have found that OB1, R3 and OB2 high-density phases are also catalytically active and behave similarly to R1 and R2, as evidenced in the middle and bottom rows of Figure 3.

Figure 3i displays a high-resolution STM image of a highly oxygen-dosed phase R3^{OX}, where approximately 80% of the molecules were oxidized. In comparison with previously reported oxidized R1^{OX} and R2^{OX}, the high-density oxidized R3^{OX} phase shows considerable disorder. Indeed, numerous vacancies appear and occasionally phenyl rings of neighboring oxidized molecules overlap. Figure S2 (top) shows a zoom into a non-oxidized molecule (SB-30) and an oxidized one, OX(OT-45). The oxygenation mechanism in the R3^{OX} phase therefore resembles the one found in R2^{OX} phase,

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although the increased molecular density strongly distorts the initial arrangement by introducing disorder due to steric hindrance.

In the case of the oblique phase after oxygenation (OB1^{OX}) shown in Figure 3h, the system largely maintains its initial arrangement. As extracted from this Figure, we can distinguish mainly three FePc species: i) a majority of non-oxidized molecules, which remain at their original SB-30 positions (bright centers); ii) oxidized, rotated molecules in OX(OT-45) positions (green box in Figure 3h), resembling the oxidized molecules in R2^{OX} and R3^{OX} phases, and iii) oxidized, non-rotated molecules maintaining their original positions, OX(SB-30), blue box in Figure 3h. This last species had not been previously reported. In Figure 3i we find 70% of non-oxidized molecules, 22% of OX(SB-30) and 8% of OX(OT-45) oxidized species. It is not surprising that the OB1 order is preserved by the SB-30 species, while grain boundaries are generated around FePc's shifting into OT-45 sites upon oxygenation. It is evident that in the OB1^{OX} phase the FePc molecules struggle to accommodate oxygen underneath, as seen by the STM image of oxidized molecules and their corresponding profiles along the pyrrole rings (Figure S2, bottom). Even if all non-oxidized molecules for the high-density phases start from SB-30 configuration, the oxidizing activity of this OB phase is significantly lower compared to the R3 and OB2 phases, even when these two present a higher molecular density. Therefore, the local molecular environment might be the key for a higher reaction efficiency, as it can probably control the ultimate molecular degrees of freedom.

3.2 Spectroscopy of Molecular Species in Selected Phases. STS experiments and DFT calculations have been performed to follow the changes upon oxidation in the local density of states of the Fe centers. The square planar symmetry around Fe in the non-oxidized molecules is modified when oxidized, since the Fe is shifted downwards and has 4 N and 2 O atoms as nearest neighbors, with local C2 symmetry[32]. One may expect therefore a strong change in the electronic states. As opposed to the case of CuPc on Ag(100), where the interaction with the substrate is mediated by the peripheral ^2e_g ligand orbital that is sensitive to the weak intermolecular interactions[33], we expect the

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effects of the latter to be negligible for FePc on Ag(110) for the following arguments. On the first hand, the interaction with the substrate is in this case mediated by the out-of-plane metal ion d_π orbitals near the Fermi level [a_{1g} (d_{z^2}) and ^2e_g (d_{xz},d_{yz})][6], which are protected by the ligand core from weak intermolecular interactions. On the second hand, the molecular lattices we find in Ag(110) are less dense than in Ag(100), making the intermolecular interactions even more negligible.

We have considered the three types of molecular species that have been identified in partially oxidized R2^{OX} and OB1^{OX}: non-oxidized SB-30, oxidized OX(OT-45) and OX(SB-30) FePc molecules. Their STS spectra are measured with the tip of the microscope on top of the Fe atoms, either oxidized and non-oxidized. The energy positions of the spectral features are summarized in Table S1. The experimental STS under the Fermi energy can be rationalized in terms of the d_{z^2} and d_π orbitals PDOS predictions mainly, as displayed in Figures 4c and d, and are less sensitive to $d_{//}$ orbitals, depicted in Figure S3.1 for completeness.

Figure 4a shows the STS spectra corresponding to the partially oxidized R2^{OX} low-density phase. The non-oxidized SB-30 molecules are found at SB-30 positions either clockwise or counter-clockwise rotated. They are found to exhibit identical conductance spectra. Their spectrum (red line) exhibits resonances at -1.15 V (a) and -0.32 V (b) below the Fermi level. Weaker features corresponding to unoccupied states can be found above the Fermi level: peak (c) at +0.80 V and an incomplete peak (d) in the proximity of +2 V.

In contrast, the spectrum at the Fe center of the oxidized molecule OX(OT-45) (green line) shows only one dominant feature (e) above the Fermi level at +1.52 V, and another below the Fermi level (a) at -1.14 V.

For the oxidized high-density OB1^{OX} phase (Figure 4b), we acquired the STS of the three different species. In the case of the pristine (non-oxidized) FePc (red line), despite the different tip LDOS, we find a close resemblance to the R2-phase spectrum, which is expected since in both cases molecules

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have the Fe centers at SB-30 adsorption sites. In contrast, the oxidized species can correspond either to rotated molecules OX(OT-45), green line, or to unrotated FePc species, OX(SB-30), blue line.

The spectrum of Fe in OX(SB-30) molecules shows a new resonance at -0.80 V, peak (f), absent in the rotated molecule OX(OT-45), but no other peak is found in the occupied PDOS region (note we assign the small features between -0.5 V and the Fermi energy to tip contributions). In the region above the Fermi level, the dominant peaks (e') and (e) are found at +1.58 eV for the OX(SB-30) and at +1.78 eV for OX(OT-45), respectively. Moreover, the spectrum of OX(OT-45), blue line, exhibits a broad resonance (c) close to +1.0 eV. Importantly, these energy differences allow us to spectroscopically distinguish the two oxidized species.

These experimental results can be compared to the PDOS predictions for the different d orbitals, calculated for the three molecular species depicted in Figure 2. The experimental STS appears to follow closely the d_z^2 orbital PDOS predictions, as displayed in Figure 4c, and to be less sensitive to the other calculated orbitals that are shown in Figure S3.1. A reason for this orbital selection relates to the instrumental response since the tip is prone to interact predominantly with vertically protruding wavefunctions, which are fulfilled by the d_z^2 and d_π orbitals predominantly.

In the case of the pristine FePc in SB-30 (red line in Figure 4c), the dominant peak (b) in the occupied region corresponds to contributions form d_z^2 and d_π orbitals closest to the E_F, which energetically agrees well with the experimental spectra observed for the R2 and OB1 phases (Table S1). The occupied peak (a), which is clearly observed in R2 but barely visible in OB1 at a lower energy, is neatly present in the calculation, in good agreement with the experimental result in R2. Above the Fermi level, peaks (c) and (d) can also be correlated with the experiments, albeit these peaks are weak and show slight energy shifts.

Noteworthy is that in the occupied region we find experimentally that the oxidized rotated species OX(OT-45) in the R2^{OX} exhibits the state (a) below the Fermi energy, but peak (b) disappears. The same feature can be observed in the OX(OT-45) of the OB1^{OX} spectra. The absence of this peak in

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the OX(OT-45) species of both R2^{OX} and OB1^{OX} is correctly predicted in the DFT calculations (Figures 4c, d). Contrarily, the existence of peak (f) in OB1^{OX} (SB-30) in proximity to (b) suggests a gentle electronic reconfiguration of this state whenever the oxidized molecules are unable to rotate. In the unoccupied region, both oxidized species experimentally show dominant peaks (e) and (e') close to +1.8 V, which find its match in the calculations even if slight energy deviations are observed.

In essence, the STS main experimental features are well reproduced by our theoretical calculations. Importantly, the vanishing of the pristine peak (b) and concomitant appearance of the dominant unoccupied states ((e) and (e')) evidences a strong reconfiguration of the electronic density of metallic d- states upon oxidation that simply depend on the adsorption position (determined by the molecule rotation) of the individual oxidized molecules. To understand the extent of the electron transfer of the central Fe-ion upon oxygen adsorption we complement our findings by studying these systems using surface averaging XMCD.

3.3 Probing Oxygenation of a High-Density Phase using Linearly Polarized XAS. Linearly polarized XAS measurements at the N K-edge were first performed to reassess the planar arrangement of the FePc molecules on the studied samples. In each of the samples, the vertical (V) and horizontal (H) N K-edge spectra in grazing incidence ($\gamma=70^\circ$) were clearly different, exhibiting the characteristic peaks corresponding to π^* and σ^* resonances which allows us to confirm the planar adsorption of the FePc molecules at the Ag(110) surface[32] once placed in the XAS sample holder.

Figure 5a displays the linearly polarized XAS at the Fe L$_3$ edge for the freshly deposited highest density phase OB2. At normal incidence ($\gamma=0^\circ$), V and H spectra are coincident (as expected), while in grazing incidence ($\gamma=70^\circ$), the linear absorption is strongly dichroic. In particular, the intense peak B in the H configuration is practically quenched in the V one. This behavior was previously observed in R1 and R2 phases, where the B peak was identified with the excitation of the Fe 2p$_{3/2}$ electrons to the empty antibonding d$_z{}^2$(up) state hybridized with the N-s and N-p$_{xy}$ states of the next neighbor

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nitrogen atoms[22]. Features A-E, which were also found in R1 and R2, are less pronounced in the OB2 phase.

Figure 5b shows the evolution of the H-V linearly polarized XAS spectra obtained in grazing incidence ($\gamma=70^o$) for four different stages in an oxygenation-annealing cycle: OB2→OX1→OX2→ANN, where the O_2 dosing of oxidized samples are given in Table 1. The evolution observed in the linearly polarized XAS spectra reflects the evolution of the oxidation reaction, i.e. OB2^{OX1} sample was less oxidized than OB2^{OX2}: as the OB2 phase gets oxidized, peak B fades while an intense peak D emerges. The reverse process occurs upon annealing, although the initial state was not completely recovered. The strong structural disorder observed in OB2 upon oxygenation by STM (see Figure 3i) probably justifies the incomplete recover of the pristine sample after annealing.

Qualitatively, a similar behavior was observed upon oxygenation of the R2 phase[22], although in that case the D peak was more pronounced, and the process was completely reversible after annealing. In the R2 phase, the FePc molecules have, in principle, space enough to change from SB-30 to OT-45 and back upon oxygenation and annealing respectively without much steric hindrance (although collisions between molecules shifted in opposite directions may occur). We associate the intensity transfer from peak B to D upon oxygenation with a ~2 eV peak shift, compatible with an increase in the hole density above the Fermi Energy, E_F, which is compatible with the LDOS changes observed in STS on the Fe sites (cf. Figure 4). It is feasible that that the formation of the FePc-(η^2-O_2)-Ag complex has associated a charge transfer from Fe towards oxygen, increasing the hole density.

Figure 5c shows the H linearly polarized XAS spectrum of the oxidized sample OB2^{OX2} (black thick line). The experimental spectrum can be qualitatively approximated by a weighted sum of the spectra obtained for the pristine sample, where non-oxidized FePc molecules are on SB-30 positions (green line), and that of a fully oxidized R2^{OX} sample made of 100% oxidized, rotated OX(OT-45) molecules[22]. By this procedure, we could estimate a yield of 20% of oxidized molecules for OB2^{OX1}

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and 50% in OB2^{OX2}. We conclude that the oxygenation of the denser phase OB2 is less effective than for the low-density R2 (comparing these results with those reported in ref.[22] for similar O_2 dosing level, see Figure 10a). We note that we could reach up to 80% of oxidized species when the sample was exposed in a different chamber to a higher oxygen dosing, as shown by the STM image in Figure 3i.

3.4 Magnetic Properties of Oxygenized High-Density Phases. The XAS and XMCD spectra were measured on OB2 and OB1 pristine and oxidized samples at the Fe $L_{2,3}$ edges, under different incident angles from normal to grazing incidence, including the so called "magic angle" to allow the separate determination of Fe spin magnetic moment. The applied field was $\mu_0 H$=6 T and T=3.4 K or 6 K), since at this field and temperatures magnetic saturation is practically complete (see S5).

Figure 6 shows the XAS & XMCD spectra obtained for pristine and oxygenized OB2 and OB1 phases (upper and lower panels respectively). For the OB2 phase, the peaks observed in the circularly polarized XAS spectrum (Figure 6a) coincide in energy with the peaks at 709.1 (A), 709.7 (B), 710.6 (C) and 712 eV (E) measured in the linearly polarized XAS spectrum, shown in Figure 5a. Peak B, not visible at normal incidence, appears clearly as the incident angle increases, as expected for a peak associated with the excitation to the d_z^2 (up) state. In contrast, the XAS spectra of OB2^{OX} measured with circularly polarized light are less dependent of incident angle (Figure 6b). They feature a prepeak, shoulder and high main peak at A, B and 711.3 eV (D). Thus the shape and evolution with incident angle of OB2^{OX} phase is completely different from that of pristine OB2. Qualitatively, the XAS behavior of the OB2 phase upon oxygenation is similar to that earlier described for the R2 phase[22]. For the pristine OB1 phase, the XAS peaks appear at the same energies as in the OB2, at A, B, C' (710.8 eV) and E, with peak B growing with the incidence angle, but in this case C and E have a similar intensity (Figure 6c). Upon oxygenation, the XAS spectrum of OB1^{OX} exhibits peaks at A, B, C' and D (Figure 6d). In comparison with the XAS of the OB2^{OX} phase, peak B is more pronounced, and peak C' appears, with an intensity close to that of peak D.

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Regarding the results of dichroism, it is first noted that the XMCD signal of the pristine phases is very small, (see Figure 6a, c), similar to that of the R1/R2 phases reported earlier[22]. Such reduction in Fe moment, or spin, is caused by hybridization between the Fe d_z^2 orbital and the Ag-sp$_z$ orbital[34,4].

In contrast, the Fe XMCD signal of the oxygen dosed samples is much larger than that of pristine FePc/Ag(110). For example, O_2 dosing produces an increase in the XMCD signal in OB1 phase of a factor ~7 at $\gamma=55^o$. Determination of the fraction of oxidized molecules on each sample and sum rule analysis allows us to properly quantify the orbital and spin magnetic moment of each configuration. Second, it is interesting to remark that although pristine OB2 and OB1 XMCD spectra are essentially equal, and very similar to the XMCD of the R1 and R2 samples[22], the line shape of XMCD spectra in the oxidized OB1^{OX} phase is clearly different to that observed in samples R1^{OX}, R2^{OX} (Figure S8) and OB2^{OX} (Figures 6 and S6): the intensity of the peak at E=710 eV is uniquely strong in comparison with all the other samples, which is indicative of the presence of a fraction of Fe species with a different electronic structure. This observation correlates with the spectral differences obtained in STS of the different oxidized species previously discussed.

Figure 7 (left) compares the XMCD spectra along the cycle OB2→OX1→OX2→ANN obtained at $\gamma=0^o$ and $\gamma=70^o$. The XMCD of pristine FePc on Ag(110) has a L$_{2,3}$ line shape very similar to that of metallic Fe, suggesting the strong hybridization of Fe in FePc with the metal substrate. Similar results were obtained for other investigated incidence angles (see Figure S6). The analysis of the spectra evidences an evolution from the as-deposited phase to the most oxidized configuration. The XMCD obtained at the OB2^{OX1} and OB2^{OX2} phases present a progressively larger intensity and a shape evolving towards that observed for non-metallic Fe(III) in a crystal field. After the annealing process, the XMCD recovers the metallic aspect, although the line shape is not exactly coincident with that of the as-deposited sample. Qualitatively, the same behavior was observed along the oxygenation -reduction reaction of the R1 and R2 phases[22].

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The sum rules allow us to determine the orbital and effective spin magnetic moment per hole in the 3d band as a function of the incident angle. The right side of Figure 7 yields the angular dependence of the orbital and effective spin magnetic moments per 3d hole, m_s^{eff}/n_h and $m_L/n_h(\gamma)$, determined for the OB2, OB2^{OX1}, OB2^{OX2} and OB2^{ANN} phases. For the sake of comparison, the previously determined dependencies for pristine and oxidized low-density R2 phases are also shown.

At a given angle of incidence, the orbital moment per hole can be expressed as a function of its components in the direction perpendicular (m_L^z) and parallel (m_L^{xy}) to the FePc molecular plane as:

$$m_L(\gamma)/n_h = m_L^{xy}/n_h \cdot \sin^2\gamma + m_L^z/n_h \cdot \cos^2\gamma. \qquad [1]$$

On the other hand, the effective spin moment is $m_s^{eff}(\gamma)/n_h = m_s(\gamma)/n_h - 7m_T(\gamma)/n_h$, where m_s is the isotropic spin moment and m_T the angle-dependent intra-atomic spin dipole moment, which is non-negligible in this case. m_T expresses the inhomogeneous spatial distribution of the spin density over the atomic unit cell, due to the anisotropic charge distribution arising from strongly directional bonds or crystal field. In the C_4 symmetry of the FePc molecule, the in-plane (m_T^{xy}) and out-of-plane (m_T^z) components of the dipolar-moment are related by $m_T^z + 2m_T^{xy} = 0$; thus, the effective moment angular dependence $m_s^{eff}(\gamma)/n_h$ can be written as:

$$m_s^{eff}(\gamma)/n_h = m_s/n_h - 7m_T^z/n_h(\cos^2\gamma - \sin^2\gamma/2). \qquad [2]$$

At the magic angle ($\gamma^*=54.7^o$), the dipolar term cancels, and so m_s^{eff} provides directly m_s [35].

The sum rules were applied to obtain the angular dependencies $m_s^{eff}(\gamma)/n_h$ and $m_L(\gamma)/n_h$ (see Figure 7c and Figure S7) and the fitting of the experimental data using Eqs. [1] and [2] allowed us to determine m_s/n_h, m_L^z/n_h, m_L^{xy}/n_h and m_T^z/n_h for Fe in pristine, oxidized and annealed OB2 and OB1 samples, which are summarized in Table 2.

All phases display planar anisotropy, in agreement with the previous findings for FePc in diverse environments. However, the highly unquenched orbital magnetic moment of FePc when the molecule

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is not in contact with a metallic surface ($m_L/m_S \approx 1$)[32],[36] is fully lost in FePc/Ag(110) phases, both in

the pristine (or annealed) phases as in the oxygenized ones.

3.5 DISCUSSION

Figure 8 shows for comparison the XMCD at $\gamma=55^{\rm o}$ of the two oxygenized high-density phases

OB2^{OX2} and OB1^{OX}. Oxygen exposure produces in both cases an increase in the dichroic signal

compared to the pristine cases. However, differences in the spectra are observed, which can be

correlated with the presence of different molecular species detected by STM, as discussed here.

The XMCD of the pristine OB1 and OB2 phases exhibits just one minimum at 710 eV,

characteristic of the hybridization between the Fe 3d electrons with the Ag 4d of the Ag atoms at the

metallic surface (Figure 6a). The XAS spectrum of the OB2^{ox} phase presents a main peak at 711.6

eV (Figure 6b). Correspondingly, its XMCD develops a new minimum in L_3 precisely at 711.6 eV,

and the L_2 peak splits in two at incident angle $\gamma=0$, as depicted in Figure 6b (black). These features

together with the order of magnitude increase in the XMCD signal point to a large variation in the

charge distribution. The XMCD of the oxidized OB2^{OX2} phases can be well fitted using a linear

combination of the experimental signals obtained from the pristine OB2 sample and the fully

oxygenized sample, i.e. a linear combination of non-oxidized FePc on SB-30 and oxidized OX(OT-

45) molecules, as shown in Figure 8a. For the OB2^{OX1} and OB2^{OX2} samples the percentages of pristine

vs. oxidized molecules are 50-50 and 80-20, respectively, matching the values found for the linearly

polarized XAS fitting (Figure 5c). In fact, this analysis is identical to that performed in our previous

paper on low density R1/R2 phases, where upon oxygenation only the OX(OT-45) species, besides

the non-oxygenated SB-30, appeared[22]. The characteristics of the XAS and XMCD spectra of the

OX(OT-45) molecules have a resemblance to Fe^{3+}, as shown by the good qualitative agreement with

Ligand Field Multiplet (LFM) calculations (ref. [22] and Figure S8).

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For the OB1 sample, the XAS at the L_3 band resembles in shape that of the OB2, although the relative intensity of the three peaks observed are slightly different (Figure 6a, c). In contrast, the XAS shape at the L_3 of the OB1^{OX} phase is different than that of the OB2^{OX}, and quite similar to its parent phase OB1 (Figure 6 c, d). Notably, the XMCD of the OB1^{OX} sample exhibits a dichroic peak at 710.6 eV, which cannot be described considering only the spectral contribution of SB-30 and OX(OT-45) species. In view of the STM images obtained in this sample (Figure 3h), the additional signal is ascribed to the OX(SB-30) molecules. This contribution can be empirically determined, as shown in Figure 8b: to obtain the XMCD of the oxidized OX(OT-30) molecules (blue line), we subtract from the experimental XMCD of the oxidized sample OB1^{OX} a weighted sum of the XMCD from non-oxidized (SB-30) molecules (red line) and from oxidized OX(OT-45) molecules (green line), see S9 for details. The clear differences observed between the two types of oxidized FePc species suggest a change in the Fe oxidation state. The spectroscopic features of the OX(SB-30) contribution, with a marked peak at 710.6 eV, and lack of splitting of the L_2 maximum point to an Fe^{2+} state, different from that of hybridized Fe^{2+} in the pristine sample.

In order to test this hypothesis, we calculated the XAS and XMCD spectra of Fe^{3+} and Fe^{2+} within a LFM model using CTM4XAS 5.5[37]. This version of the program allows only to calculate the spectra in normal incidence conditions. The results of our calculations are shown in Figure 9. The spectroscopic characteristics of the two types of oxidized FePc species are qualitatively well reproduced simulating the OX(OT-45) spectrum as Fe^{3+} ($10\,D_q$=1.8 eV, D_t=0, D_s=0) and OX(SB-30) as Fe^{2+} ($10D_q$=1.0 eV, D_t=0.03 eV, D_s=0.1 eV), under C_4 symmetry. (These last CF values are close those reported by A. Mugarza *et al.*[33] for FePc/Cu(100) with Fe^{2+}). The the experimental XAS and XMCD (at γ=0º) of the OB1^{OX} phase are nicely described by a linear combination of the pristine OB1 and the calculated Fe^{2+} and Fe^{3+} spectra.

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To complete our study, we performed DFT calculations on the three different types of FePc species relevant for our work, namely, the pristine FePc on SB-30 positions, and oxidized molecules OX(OT-45) and OX(SB-30).

The calculation yields the spin-polarized density of stated projected on the Fe d orbitals. The polarized PDOS out-of-plane components, d_{z^2} and d_π, and in-plane component ($d_{x^2-y^2} + d_{yz}$), are shown in Figure S4. The magnetic moment of Fe in each type of FePc is correlated with the uncompensated area between out-of-plane spin-up and spin-down polarized PDOS below the Fermi energy (Figure S4a-4b). Our results show that for the non-oxygenated SB-30 FePc's, the out-of-plane spin-up and spin-down PDOS curves below E_F are almost compensated, in agreement with the very small dichroic signal observed for these type of molecules while, in contrast, a huge uncompensated area is calculated for the oxidized OX(SB-30) and OX(OT-45) species, which also explains the large enhancement of dichroic observed for these two species. Table 4 summarizes the DFT-calculated 3d spin-polarized number of holes n_h, the Fe net charge, and the magnetic moment for each species. Thus, the magnetic moment increase upon oxygenation is caused by a decrease in the population of minority spin S⁻, since OX(SB-30) and OX(OT-45) lose 1.1 and 1.3 electron, respectively, while the population of majority spin S+ increase by 0.4 and 0.6 electrons, respectively. Therefore, the interaction with oxygen causes the Fe atom to gain in positive charge, from 0.1 e+ for the pristine SB-30 to 0.3 e+ and 0.6 for OX(SB-30) and OX(OT-45), respectively. These results reinforce the conclusion obtained from STS and XMCD, that interaction with oxygen in the OX(OT-45) molecule causes the Fe atom to acquire a larger positive charge, suggesting an increase in the oxidation state of Fe^{2+} [22].

We used the values in Table 2 together with the number of holes in the 3d band from DFT to obtain absolute values for the magnetic moments of the different molecular species. The results are listed in Table 4. Upon oxygenation, the total moment increases from m_{TOT}=0.27 μ_B to 1.2-1.6 μ_B in the OB2 phase, which is a factor ≈6.5, and from m_{TOT}=0.18 μ_B to 2.2 μ_B in the OB1 phase, which is a factor

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≈ 10, for both species, i.e. OX(OT-45) and OX(SB-30). We note that DFT-calculated total magnetic moment values are larger than the experimental ones, as previously reported[22]. Notably, although steric hindrance makes the accommodation of O_2 in dense phases more difficult, we find that the increase in the magnetic moment of the oxidized FePc molecules is of the same order as in the low-density phases (see Table 4).

Finally, we summarize in Figure 10 the oxygenation and magnetic moment capabilities found for the three studied FePc/Ag(110) phases upon O_2 dosing. As shown in Figure 10a, the percentage of oxidized molecules in the sample can be controlled by O_2 dosing. The oxygenation process is most efficient in the low-density R1/R2 phases, followed by the high-density R3/OB2 phases, and is more difficult in the more distorted OB1 phase. Interestingly, by virtue of the upturn in the magnetic moment produced in the oxidized FePc species, the average magnetic moment of the oxidized samples ($<m_{TOT}>$ per Fe atom) can be modified between ~ 0.2-2 μ_B by controlling the O_2 dose (see Figure 10b).

4. CONCLUSIONS

In this work we have investigated the oxygen-induced magnetic moment changes of FePc molecules of high-density sub-ML and ML phases on the Ag(110) substrate. The oxidation rate of the dense, quasi-squared R3/OB2 phases is comparable to the previously reported rectangular low-density (R1 and R2) phases. Owing to steric impediments, the oblique phase (OB1) is less effective in the oxidation-reduction reaction.

In the R3/OB2 phases, the oxidation takes place accompanied by a lateral shift of the molecule, which moves the Fe centre from SB to OT position, accompanied by a rotation of $\approx 15°$, giving rise to the FePc-(η^2-O_2)-Ag complex. This is accompanied by an increase by a factor ~ 6.5 of the Fe total magnetic moment. Upon annealing, the magnetic moment decreases to a value close to that for the

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non-oxidized phase. However, full reversibility (as found in R1 and R2 phases) is prevented by the large disorder induced by oxygenation.

For the OB1 phase, oxygen diffusion becomes even more difficult. In order to accommodate O_2, a fraction of molecules do rotate and move to OT-45 sites, while the rest is able to accommodate oxygen while keeping their initial SB-30 positions, due to the highly restricted molecular movement.

The oxygenation mode leading to the two different types of oxidized FePc species affects markedly the electronic density of states, as proven by our STS and XMCD experiments, and DFT and Ligand Field Multiplet calculations: the XMCD spectrum corresponding to the oxidized unrotated OX(SB-30) molecule shows a characteristic of the Fe^{2+} oxidation state, while that of rotated OX(OT-45) is reminiscent to that of Fe^{3+}. The Fe magnetic moment remains in all cases with planar anisotropy. Interestingly, both oxidized species show an increased magnetic moment by a factor ~10.

Even though the molecular density of the R3/OB2 phases is larger than that of the OB1 phase, we find that the oxygenation of R3/OB2 is easier, and the species of oxidized FePc resemble those found in the rectangular phases. Thus, the unit cell configuration of the ML assembly determines the oxygen capture properties.

In conclusion, the oxygenation reaction of FePc/Ag(110) depends critically on the adlayer structure. Steric hindrance affects the reaction. Despite the steric limitations, FePc molecules in high-density FePc/Ag(110) phases are able to intercalate oxygen through different mechanisms. Therefore, control of the magnetic moment of the system in a range between 0.2 to 2.2 μ_B can be easily exerted through oxygen dosing.

ASSOCIATED CONTENT

SUPPORTING INFORMATION: S1. Structural transition from R3 to OB2 phases; S2. Zoology of molecules in oxidized high-density phases; S3. DFT PDOS calculations; S4. Phase OB2, N K-edge; S5. Field-dependent XMCD curve; S6. Angular XAS & XMCD spectra for OB2^{OX1} and OB2^{ANN};

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S7. Angular dependence of magnetic moments for OB1; S8. R2^{OX} XMCD and Ligand Field Multiplet (LFM) calculations; S9. Percentages of molecular species in OB1^{OX} oxidized phase.

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Figure 1. FePc/Ag(110) sub-ML phases with increasing molecular density (from left to right). Each column identifies a phase containing an STM image acquired at room temperature, the unit cell model, the matrix notation and the LEED pattern with the corresponding simulation of the phase. STM imaging parameters for the top (75x55 Å^2) images: R1 (0.4 V, 0.3 nA), R2 (0.4 V, 0.7 nA), OB1 (3.2 V, 9.0 nA), R3 (-0.9 V, 0.8 nA), OB2 (0.6 V, 0.4 nA). LEED parameters: R1(28 eV), R2 (30 eV), OB1 (28 eV), R3 (35 eV), OB2 (30 eV).

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Figure 2. Different geometries of as deposited and oxidized molecules in FePc/Ag(110) phases (top and lateral views), as determined from high resolution STM and confirmed by DFT image simulations.

Figure 3. Catalytic activity of the different FePc/Ag(110) phases. *Top panels*: STM images of pristine phases: (a) R1/R2 ($V = 0.5$ V, $I = 0.1$ nA, 39x39 nm^2), (b) OB1 (0.5 V, 0.1 nA, 33x33 nm^2), (c) R3/OB2 (-1 V, 2.5 nA, 31x31 nm^2); *Middle panels*: images of partially oxidized phases: (d) R1^{OX}/R2^{OX} (0.5 mV, 0.2 nA, 40x40 nm^2), (e) OB1^{OX} (0.4 V, 0.1 nA, 40x40 nm^2), (f) R3^{OX}/OB2^{OX} (-1 V, 5.7 nA, 31x31 nm^2). Non-oxidized molecules are recognizable by their bright centers, while oxidized molecules have dark centers; *Bottom panels*: high-resolution STM images of oxidized phases. (g) R1^{OX}/R2^{OX} (0.5 V, 0.15 nA, 8x8 nm^2), (h) OB1^{OX} (0.5 V, 0.2 nA, 8.5x8.5 nm^2), (i) R3^{OX} (0.5 V, 0.05 nA, 8.79x8.7 nm^2). The R1^{OX}/R2^{OX} and R3^{OX}/OB2^{OX} phases contain a distribution of non-oxidized molecules (SB-30) and oxidized, rotated molecules OX(OT-45). In contrast, the OB1^{OX} phase contains a distribution of non-oxidized FePc at SB-30 and two species of oxidized FePc: OX(OT-45) (green box) and OX(SB-30) (blue box).

(a) R2^{OX}

(b) OB1^{OX}

(c) PDOS

(d)

Figure 4. STS spectra at the center of the molecule in the oxidized (a) R2^{OX} phase and (b) OB1^{OX} phase (dotted lines mark the regions measured in either CH or CC modes); (c) DFT-simulated PDOS (c) d_{z^2} and (d) $d_{\pi} = (d_{xz} + d_{yz})$ components for the SB-30, OX(SB-30) and OX(OT-45) molecular species (see also Figure S3.1 and S3.2).
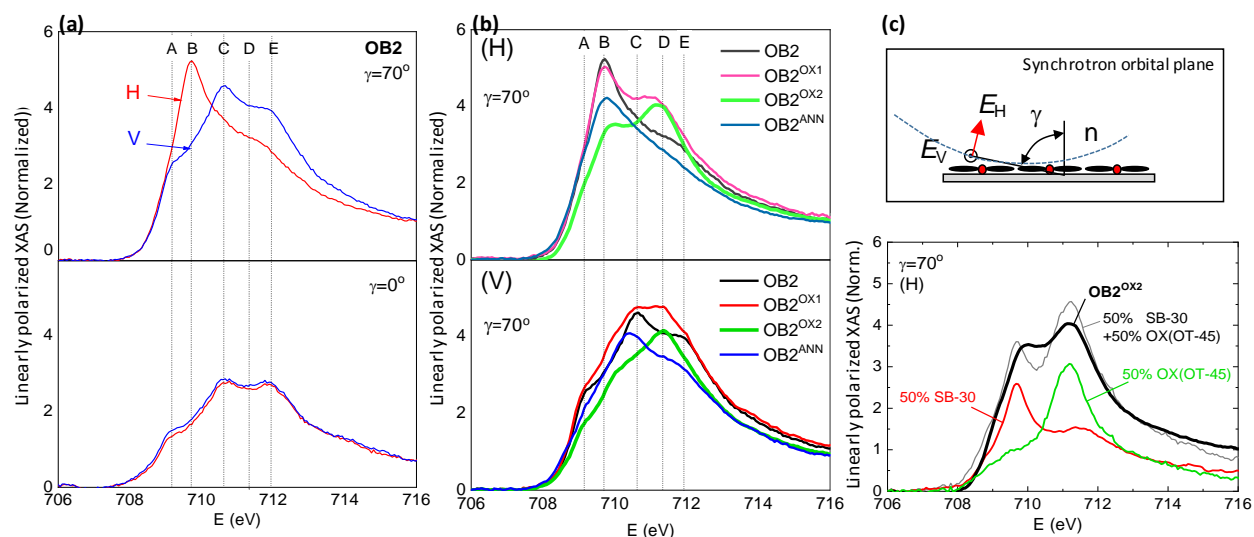
Figure 5. Normalized linearly polarized XAS of phase OB2 at the Fe L_3 edge before and after oxygenation. (a) Non-oxygenated grazing incidence ($\gamma=70°$) and normal incidence ($\gamma=0°$) spectra of two light polarizations; (b) Normalized linearly polarized XAS in grazing incidence ($\gamma=70°$), H and V polarizations, of as deposited phase OB2, oxidized phases OB2^{OX1} and OB2^{OX2} and annealed OB2^{ANN}; (c) The normalized linearly polarized XAS (H polarization) in grazing incidence ($\gamma=70°$) of the oxidized phase OB2^{OX2} is well predicted by a linear combination of 50% the linearly polarized XAS of the pristine phase OB2 (containing FePc on SB-30 positions) and 50% the spectrum of the fully oxidized R2^{ox} phase, where all molecules are OX(OT-45). Top inset: schematic view of sample FePc deposited on a Ag substrate. The incoming beam at grazing incidence is shown with the $\bar{E}$ in the H and V polarization modes.

Figure 6. Normalized XAS & XMCD spectra at the Fe $L_{2,3}$ edge measured at different beam incident angles γ, for the (a) pristine OB2 and (b) oxygenated OB2^{OX2} samples, at B=6 T, T=3.4 K, and (c) pristine OB1 and (d) oxygenated OB1^{OX} samples, at B=4 T, T=6 K.
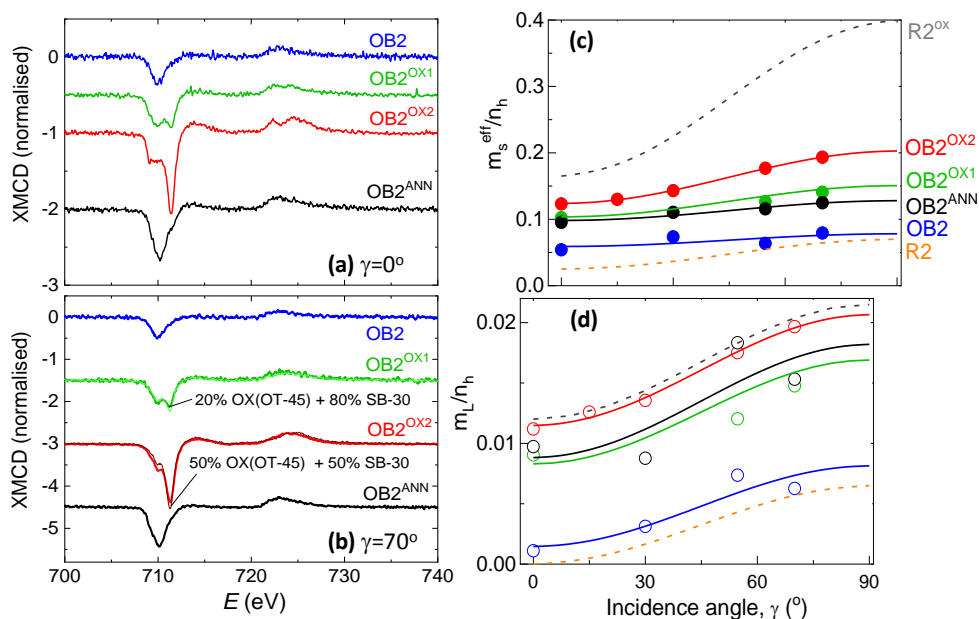
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Figure 7. Left: Normalized XMCD spectra of the OB2, OB2^{OX1}, OB2^{OX2}, OB2^{ANN} samples at the Fe L$_{2,3}$ edge, measured at B=6 T, T=3.4 K at an incident angle (a) γ=0°, (b) γ=70°. The thin lines in (b) correspond to the XMCD calculated as the linear combination with %OX(OT-45) percentage of the fully-oxidized R2^{OX} and %OX(SB-30) of the as-evaporated phase; Right: Effective spin moment (c) and orbital moments (per hole) (d) as determined with the sum rules for OB2, OB2^{OX1}, OB2^{OX2} and OB2^{ANN}. The lines in (c) and (d) show the fits using Eqs. [1] and [2], as well as curves earlier reported for low-density phases R2 and R2^{OX}, ref. [22].

Figure 8. Comparison of XMCD (γ=55°) of oxidized phases: (a) OB2^{OX2} (B=6 T, T=3.4 K): the measured spectrum can be expressed as a linear combination of the spectra of non-oxidized SB-30 molecules, and oxidized, rotated OX(OT-45) molecules; (b) OB1^{OX} (B=4 T, T=6.0 K): the measured spectrum is a linear combination of the spectra of three molecule species: SB-30, OX(OT-45) and OX(SB-30).
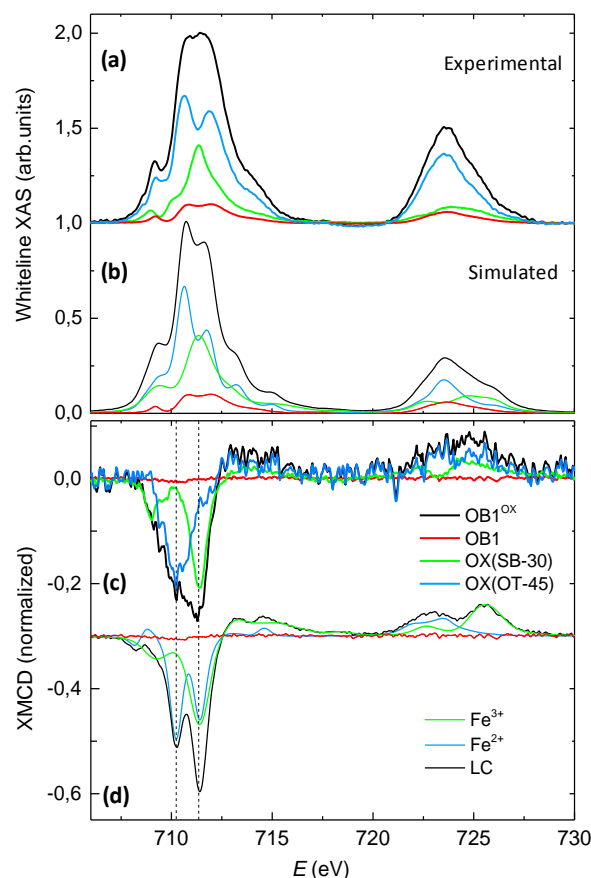
36

Figure 9. Thick lines: Experimental XAS whiteline (a) and XMCD (c) of $OB1^{OX}$ phase at $T=6.0$ K, $B=4$ T, $\gamma=0^{\circ}$. They can be described as a linear combination of the SB-30, OX(OT-45) and OX(OT-30) spectra. Vertically shifted for comparison (thin lines): Calculated (b) XAS and (d) XMCD spectra of Fe^{3+} and Fe^{2+} using with CTM4XAS 5.5 program[37] including spin-orbit coupling, crystal field (CF) effects and reduction of the Slater integrals to include the interatomic configuration interaction. Simulations were performed with Fe in C_{4v} symmetry, with the strength of the CF described by the empirical parameters $10D_q=1.8$ eV, $D_t=0$, $D_s=0$ for Fe^{3+} and $10D_q=1.0$ eV, $D_t=0.03$ eV, $D_s=0.1$ eV for Fe^{2+}. The results were convoluted by a Lorentzian of $\Gamma=0.3(0.5)$ eV for the $L_3(L_2)$ edge to account for intrinsic core-hole lifetime broadening, and by a Gaussian of $\sigma=0.2$ eV to account for instrumental broadening.
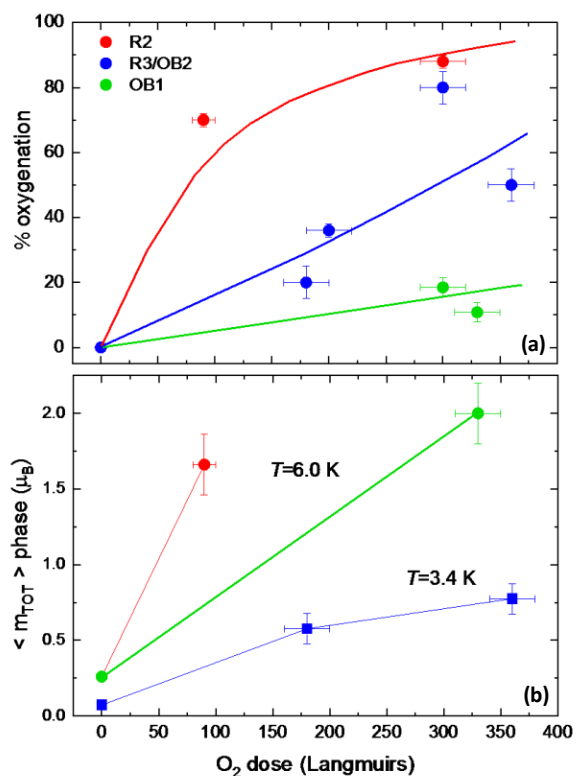
Figure 10. (a) Percentage of oxygenated molecules, and (b) average magnetic moment per Fe atom in a ML sample, as a function of the oxygen dose, for the three studied phases: the low-density R2 and high-density R3/OB2 and OB1 phases. Lines are guides for the eye.

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Table 1. Oxygenation Conditions for the Phases Reported in This Work

Phase	Figure	Chamber	O_2 dose (L)
$R2^{OX}$	Figure 3d	STM (Zaragoza)	300
$OB1^{OX}$	Figure 3e	STM (Zaragoza)	300
$R3/OB2^{OX}$	Figure 3f	STM (Padova)	200
$R1/R2^{OX}$	Figure 3g	STM (Zaragoza)	300
$OB1^{OX}$	Figure 3h	STM (Zaragoza)	300
$R3^{OX}$	Figure 3i	STM (Zaragoza)	300
$OB1^{OX}$	Figure S2.a	STM (Zaragoza)	300
$R1\text{-}R2^{OX}$	Figure S8	ID8 (ID32) [22]	90
$OB2^{OX1}$	Figures 5, 7	ALBA	180
$OB2^{OX2}$	Figures 5,6b,7,8	ALBA	360
$OB1^{OX}$	Figure 8b	ID8 (ID32)	330

* 1 Langmuir (L) corresponds to 1 s of exposure at 10^{-6} mbar. From ref. [22]

Table 2. Magnetic Moment Parameters (in Units of μB/hole) for the Different FePc/Ag(110) Samples

	m_L^z / n_h	m_L^{xy} / n_h	m_s / n_h	m_T^z / n_h	Ref.
R2	0	6.5×10^{-3}	7.1×10^{-2}	4.3×10^{-3}	22
R2^{OX}	1.2×10^{-2}	2.2×10^{-2}	3.7×10^{-1}	2.9×10^{-2}	22
R2^{ANN}	4.0×10^{-3}	1.5×10^{-2}	7.1×10^{-2}	5.9×10^{-3}	22
OB2	1.4×10^{-3}	8.1×10^{-3}	7.2×10^{-2}	1.8×10^{-3}	*
OB2^{OX1}	8.3×10^{-3}	1.7×10^{-2}	1.3×10^{-1}	4.5×10^{-3}	*
OB2^{OX2}	1.1×10^{-2}	2.1×10^{-2}	1.8×10^{-1}	7.5×10^{-3}	*
OB2^{ANN}	8.8×10^{-3}	1.8×10^{-2}	1.2×10^{-1}	2.8×10^{-3}	*
OB1	1.5×10^{-3}	1.2×10^{-2}	5.2×10^{-2}	5.6×10^{-3}	*
OB1^{OX}	2.0×10^{-3}	4.2×10^{-2}	4.9×10^{-1}	6.2×10^{-2}	*

* This work.

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Table 3. DFT Simulations of STM Images, and Fe 3d S⁺, S⁻ Holes, Fe Net Charge, Number of Holes and Total Magnetic Moment of Fe in SB-30, OX(SB-30) and OX(OT-45) FePc Species
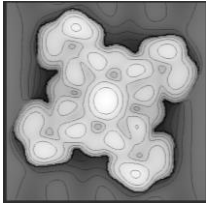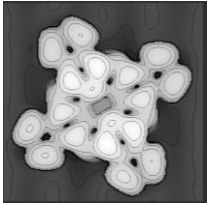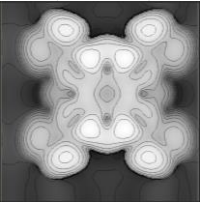
	SB-30°	OX(SB-30)	OX(OT-45)
CC mode, at 1V			
n_h^{S+}	0.7	0.3	0.1
n_h^{S-}	2.7	3.6	4.0
n_h	3.4	3.4	4.1
Fe net charge	0.1	0.4	0.6
m_{TOT}^{DFT} (μ_B)	2.1	3.3	4.0

Table 4. Magnetic Moments for the Different Types of Molecules found in the Oxygenated FePc/Ag(110) Phases

Phase	FePc	$m_L^{xy}(\mu_B)$	$m_s(\mu_B)$	$m_{TOT}(\mu_B)$	Factor
R2^{OX}	SB-30	2.2×10^{-2}	0.241	0.26	
	OX(OT-45)	1.1×10^{-1}	2.062	2.17	8.3
OB2^{OX}	SB-30	2.7×10^{-2}	0.244	0.27	
	OX(OT-45)	2.1×10^{-1}	1.59	1.80	6.7
OB1^{OX}	SB-30	4.1×10^{-2}	0.178	0.22	
	OX(OT-45)	1.1×10^{-1}	2.062	2.17	9.9
	OX(SB-30)	3.6×10^{-1}	1.87	2.23	10.1
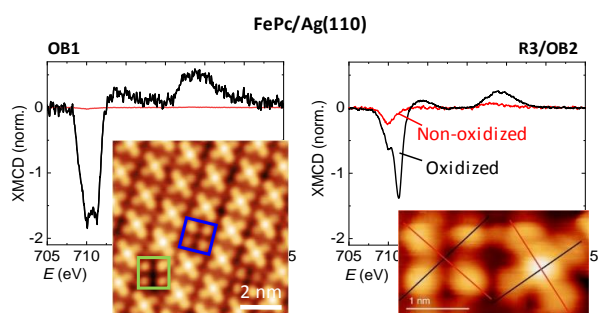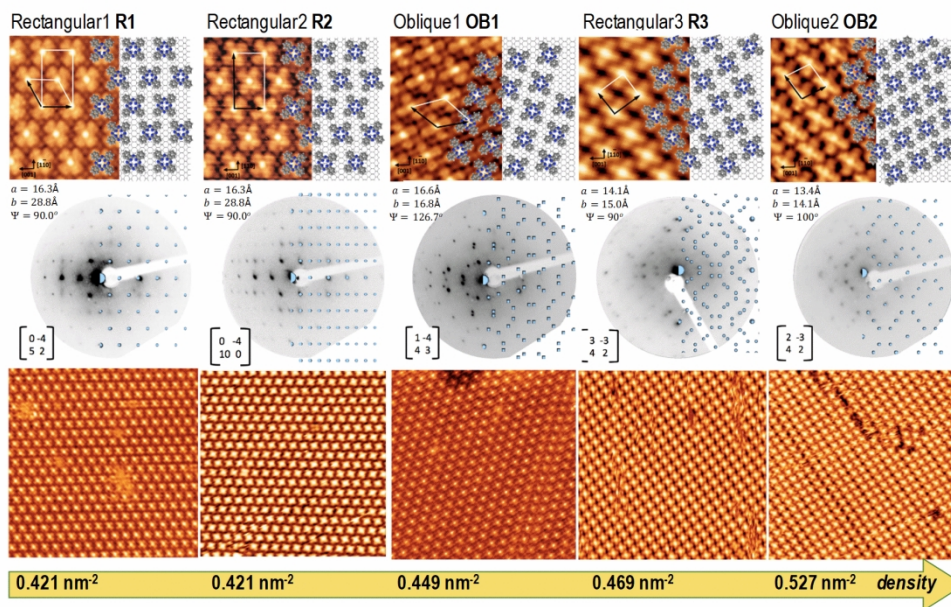
42

TOC IMAGE

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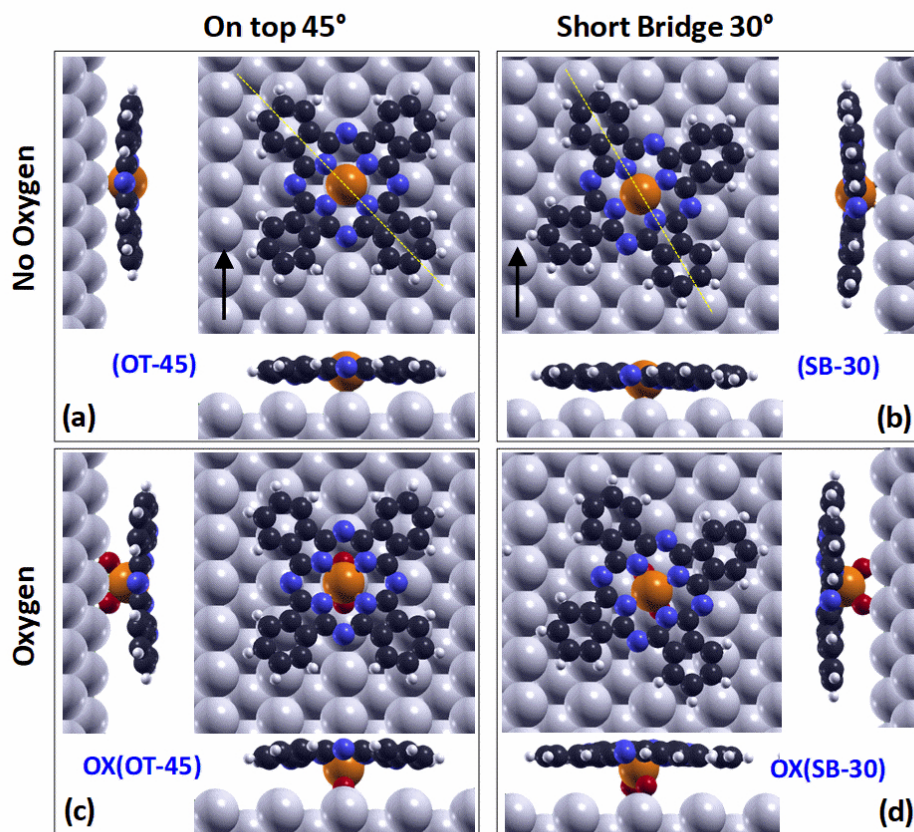
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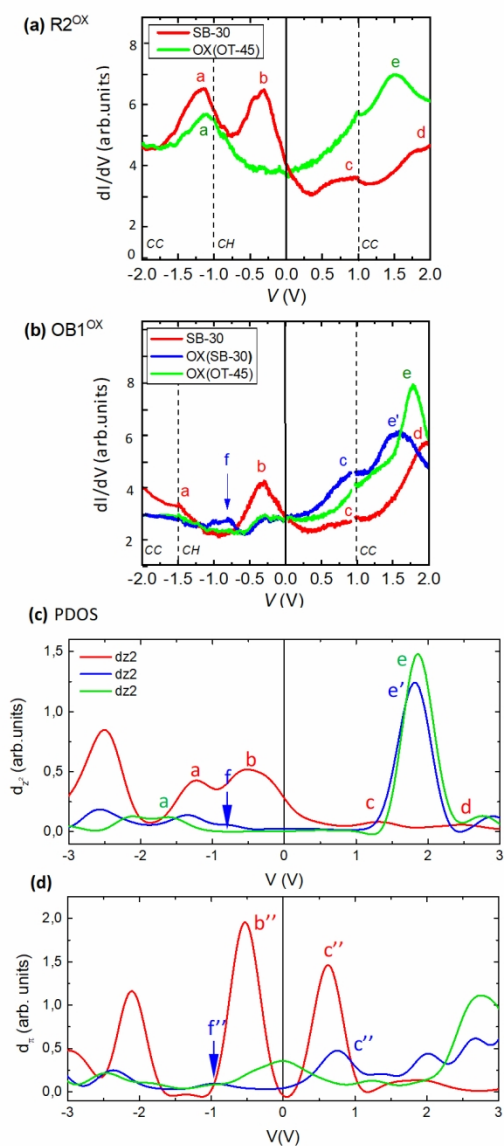
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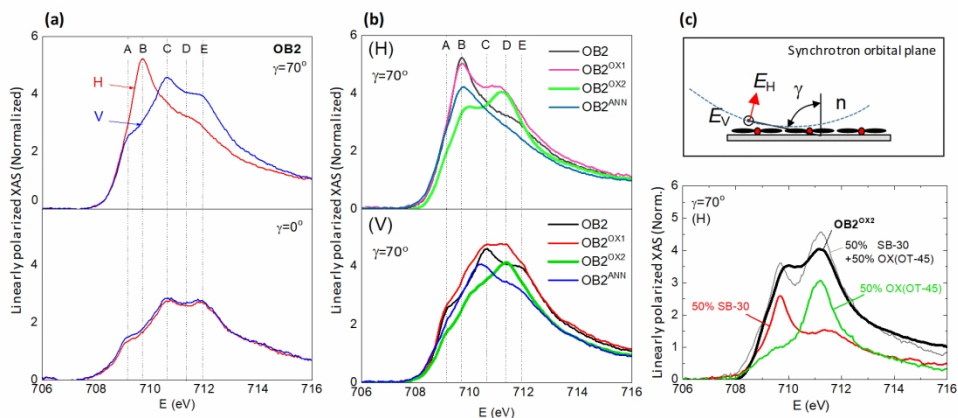
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Figure 5. Normalized linearly polarized XAS of phase OB2 at the Fe L_3 edge before and after oxygenation. (a) Non-oxygenated grazing incidence ($\gamma=70^o$) and normal incidence ($\gamma=0^o$) spectra of two light polarizations; (b) Normalized linearly polarized XAS in grazing incidence ($\gamma=70^o$), H and V polarizations, of as deposited phase OB2, oxidized phases OB2^{OX1} and OB2^{OX2} and annealed OB2^{ANN}; (c) The normalized linearly polarized XAS (H polarization) in grazing incidence ($\gamma=70^o$) of the oxidized phase OB2^{OX2} is well predicted by a linear combination of 50% the linearly polarized XAS of the pristine phase OB2 (containing FePc on SB-30 positions) and 50% the spectrum of the fully oxidized R2^{OX} phase, where all molecules are OX(OT-45). Top inset: schematic view of sample FePc deposited on a Ag substrate. The incoming beam at grazing incidence is shown with the **E** in the H and V polarization modes.
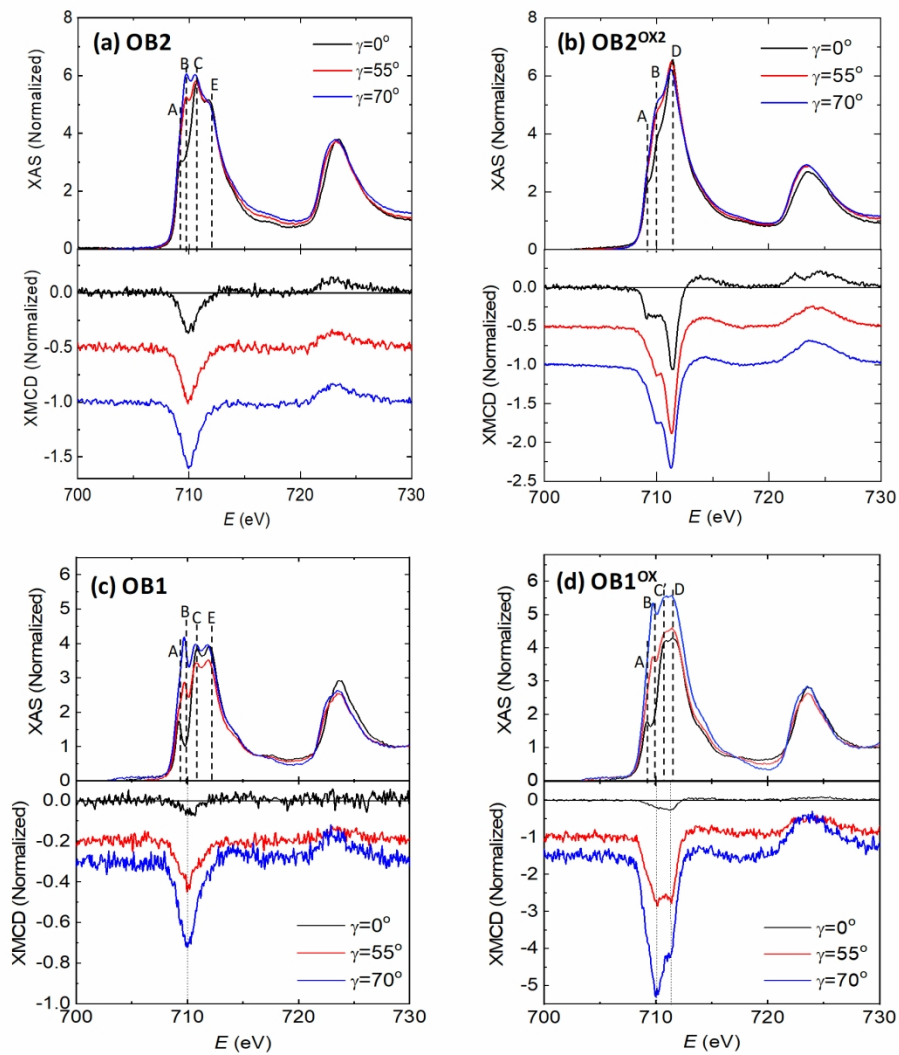
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Figure 6. Normalized XAS & XMCD spectra at the Fe $L_{2,3}$ edge measured at different beam incident angles γ, for the (a) pristine OB2 and (b) oxygenated $OB2^{OX2}$ samples, at B=6 T, T=3.4 K, and (c) pristine OB1 and (d) oxygenated $OB1^{OX}$ samples, at B=4 T, T=6 K.
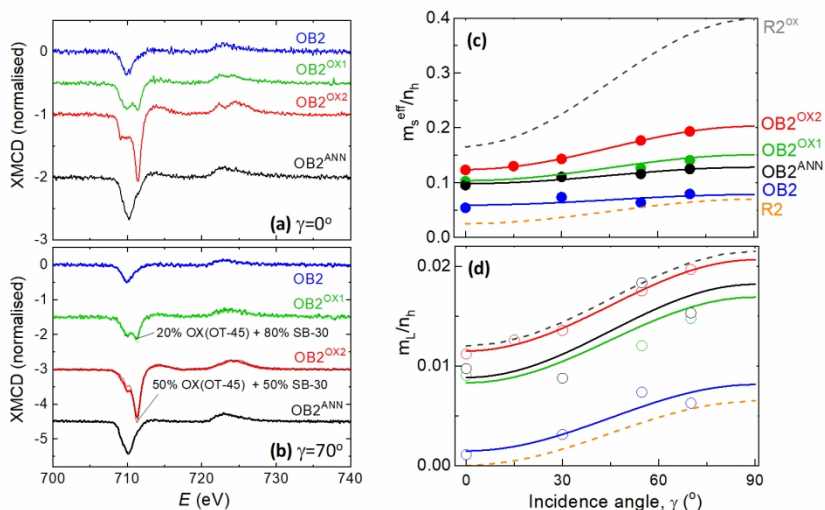
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Figure 7. Left: Normalized XMCD spectra of the OB2, OB2^{OX1}, OB2^{OX2}, OB2^{ANN} samples at the Fe L$_{2,3}$ edge, measured at B=6 T, T=3.4 K at an incident angle (a) γ=0°, (b) γ=70°. The thin lines in (b) correspond to the XMCD calculated as the linear combination with %OX(OT-45) percentage of the fully-oxidized R2^{OX} and %OX(SB-30) of the as-evaporated phase; Right: Effective spin moment (c) and orbital moments (per hole) (d) as determined with the sum rules for OB2, OB2^{OX1}, OB2^{OX2} and OB2^{ANN}. The lines in (c) and (d) show the fits using Eqs. [1] and [2], as well as curves earlier reported for low-density phases R2 and R2^{OX}, ref. 22.
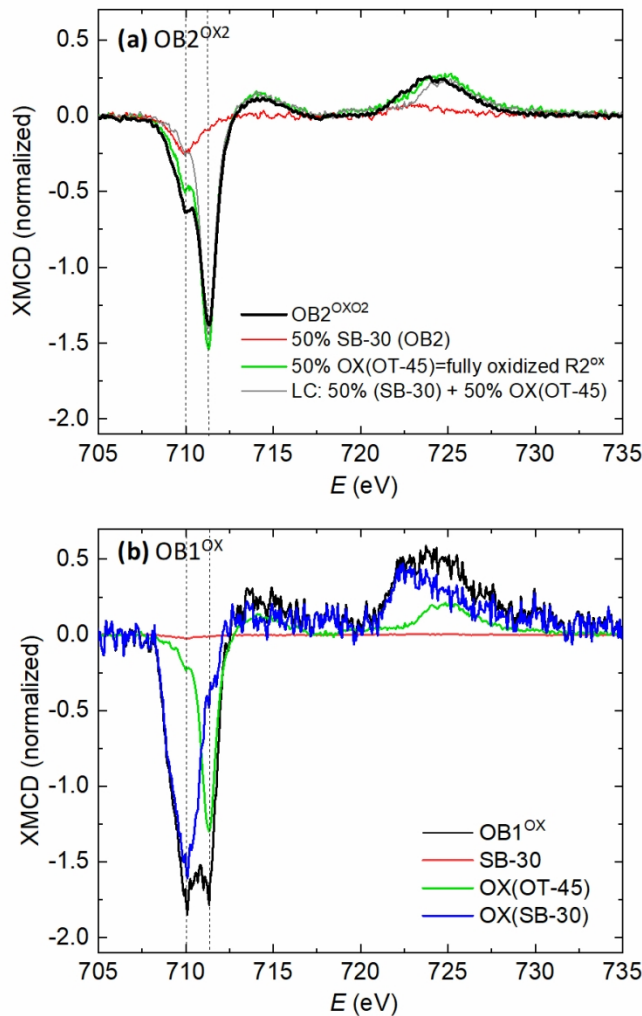
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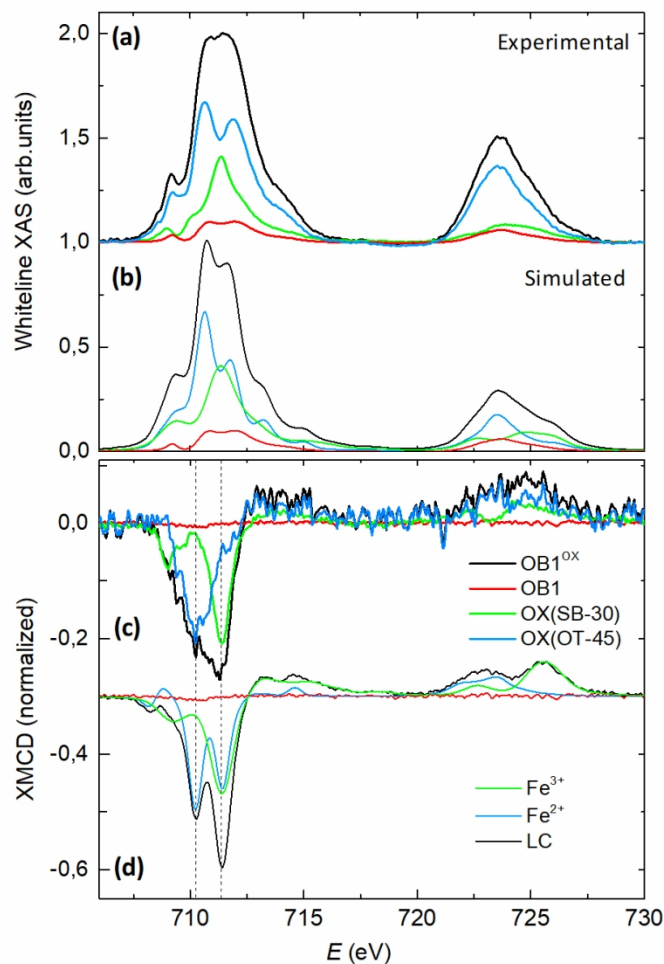
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Figure 9. Thick lines: Experimental XAS whiteline (a) and XMCD (c) of OB1^{OX} phase at T=6.0 K, B=4 T, γ=0°. They can be described as a linear combination of the SB-30, OX(OT-45) and OX(OT-30) spectra. Vertically shifted for comparison (thin lines): Calculated (b) XAS and (d) XMCD spectra of Fe^{3+} and Fe^{2+} using with CTM4XAS 5.5 program[37] including spin-orbit coupling, crystal field (CF) effects and reduction of the Slater integrals to include the interatomic configuration interaction. Simulations were performed with Fe in C4v symmetry, with the strength of the CF described by the empirical parameters 10 D_q=1.8 eV, D_t=0, D_s=0 for Fe^{3+} and 10D_q=1.0 eV, D_t=0.03 eV, D_s=0.1 eV for Fe^{2+}. The results were convoluted by a Lorentzian of Γ=0.3(0.5) eV for the L$_3$(L$_2$) edge to account for intrinsic core-hole lifetime broadening, and by a Gaussian of σ=0.2 eV to account for instrumental broadening.
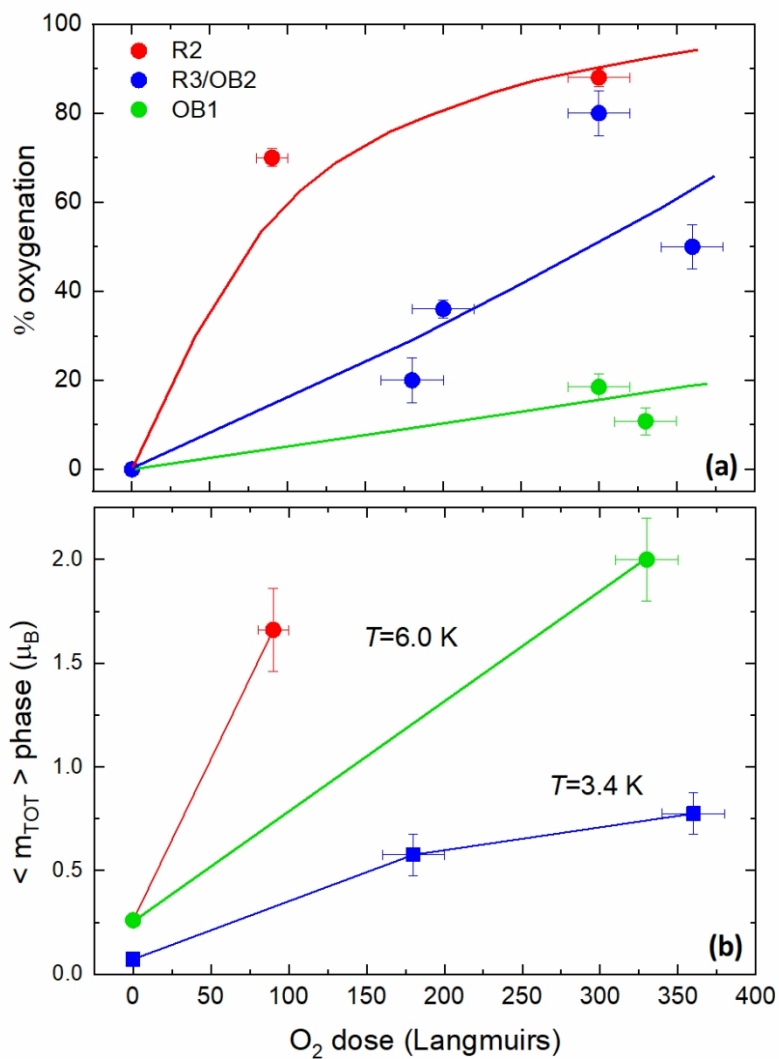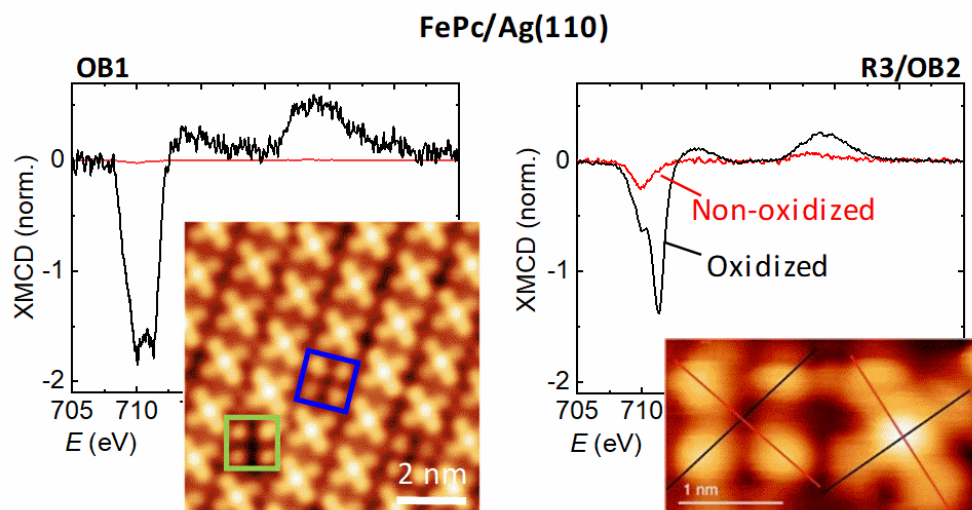
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FePc/Ag(110)

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