# Supplementary Information

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

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### S1. Structural transition from R3 to OB2 phases

The R3 and OB2 phases often coexist, facilitated by a common cell parameter (denoted a in Figure S1); a transition from R3 to OB2 is possible simply by moving a line of FePc molecules of one Ag(110) lattice parameter along the [1-10] direction (b cell parameter in Figure S1). A curious effect is visible in the LEED pattern: starting from a coverage that clearly shows the LEED pattern of R3 phase (Figure S1 a) and increasing the FePc coverage with further deposition we obtained a peculiar LEED pattern characterized by some spots and some lines (Figure S1b) that can be well reproduced by the superposition of many LEED patterns (in the figure we used 10 patterns) obtained from incommensurate unit cells where the b parameter is positioned at all the intermediate position between the two position of R3 and OB2 phases.

This LEED indicates that at this intermediate coverage a large number of molecules are moving from R3 to OB2 position and back, whereas Figure S1c shows that a further deposition stabilize the high-density OB2 phase.



Figure S1. LEED patterns of: a) R3 phase, c) OB2 phase, and b) LEED pattern obtained for intermediate coverages with the respective unit cells used for the LEED pattern simulation.

#### S2. Zoology of molecules in oxidized high-density phases.

Figure S2 shows STM images of partially oxidized square ( $R3^{OX}$ ) and oblique ( $OB1^{OX}$ ) phases, evidencing the different types of FePc species on Ag(110). The  $R3^{OX}$  sample contains a distribution of nonoxidized FePc molecules (recognizable by their bright center) and oxidized FePc molecules (dark center). Pristine FePc are located at SB-30 positions, while oxidized molecules shift and rotate to OX(OT-45) positions, see Fig. S2, up). The OB1<sup>OX</sup> sample contains a distribution of nonoxidized FePc molecules (SB-30), oxidized molecules that shift and rotate, as in the other phase, to OX(OT-45) positions, and oxidized molecules that remain, unrotated, in their original positions, OX(SB-30). A careful inspection of this phase evidences that FePc molecules struggle to accommodate oxygen underneath, as seen by the STM image of oxidized molecules have their lobules typically *tilted* with respect to the Ag surface i.e. one lobule is more intense than its opposite, keeping the other two with intermediate brightness. Among the OX(OT-30), we find species with different pyrrole deformations: *saddle* type (#2), with opposite lobules more intense than the other two; *crab* type (#3), with two very intense and close neighboring lobules than the other two; and *extended* type (#5), with one larger lobule (more extended) than the rest.



**Figure S2.** STM images of partially high-density oxidized FePc/Ag(110), showing the different types of FePc species. *Top panel:* STM image of a highly oxidized R3<sup>OX</sup> sample (V = -0.5 V; I = 0.05 nA): (a) Oxygenating the R3 phase strongly disrupts the initial arrangement. The nonoxidized molecules are clearly recognizable for their bright centers, while the oxidized molecules (with darker centers) are found to rotate with respect to the other. (b) Detail showing the shift and rotation of a FePc molecule from a SB-30 position to an OX(OT-45) site; (c) line profiles along pyrroles of SB-30 and OX(OT-45).

*Bottom panel:* STM images of the partially oxidized oblique phase,  $OB1^{OX}$  (V = +0.04 V; I = 1 nA: (a) Distribution of non-oxidized molecules (SB-30, bright center) and oxidized, rotated molecules OX(OT-45) and unrotated molecules OX(SB-30); (b) zoology of FePc species and their corresponding line profiles, evidencing the different disposition of their pyrroles.



Figure S3.1. DFT PDOS calculations for different orbitals (indicated in the vertical axis), for the non-oxidized and oxidized molecular species.

	FePc species	а	b	с	d	e'	е	f
R2 <sup>OX</sup>	SB-30	-1.15	-0.32	+0.8	+2.0	-	-	-
	OX(OT-45)	-1.14	-	?	-	+1.52	-	-
OB1 <sup>OX</sup>	SB-30	-1.48	-0.33	+0.6	+2.0	-	-	-
	OX(SB-30)	-	-	+1.0	-	+1.58	-	-0.80
	OX(OT-45)	-	-	?	-	-	+1.78	-
Theory	SB-30	-1.23	-0.33	+1.3	+2.5			
	OX(SB-30)					+1.8		-0.8
	OX(OT-45)						+1.9	

**Table S2.** Energetic position of the appearing resonances in STS experimental and theoretical  $(d_z^2)$  spectra. Numbers are given in V with respect to the Fermi level.



**Figure S3.2.** DFT polarized PDOS calculations for different orbitals (indicated in the vertical axis), for the non-oxidized and oxidized molecular species.



**Figure S4.** Phase OB2. XLPA spectra recorded at the N-K edge with grazing angle at room temperature (RT). The two spectra correspond to the *H* and *V* polarization modes: E is parallel to the FePc plane, or forming an angle 20° with the normal to the substrate (see schematics Fig. 5c). In accordance with Ref. <sup>1</sup>, peaks A, B, C are assigned to  $\pi^*$  resonances, and D, E to  $\sigma^*$  ones.

#### S5 Field-dependent XMCD curve

In pristine and oxygenated phases it was checked that magnetic saturation was achieved at  $\mu_0 H= 6$  T. For example, in sample OB2, the XMCD at the L<sub>3</sub> edge, at the fixed energy of the XMCD minimum, the intensity was measured as a function of applied magnetic field (Fig. S5). In all samples the XMCD(*B*) curve showed paramagnetic behaviour with saturation achieved at about  $\mu_0 H \ge 4$  T.



**Figure S5.** Field-dependent XMCD (*B*) curve measured for sample OB2, at T=3.4 K and beam incident angles  $\gamma=0^{\circ}$  and  $\gamma=70^{\circ}$ .

#### S6. Angular XAS & XMCD spectra for OB2<sup>OX1</sup> and OB2<sup>ANN</sup>



**Figure S6.** Normalized XAS & XMCD spectra at the Fe L<sub>2,3</sub> edge at *B*=6 T, *T*=5.0 K measured for the (a) oxygenated OB2<sup>OX1</sup> and (b) annealed OB2<sup>ANN</sup> samples at different incident angles  $\gamma$ .



**Figure S7.** Effective spin moment (left) and orbital moment (right) per hole as determined with the sum rules for (a) OB1 and (b) OB1<sup>OX</sup> samples. The lines show the fits to Eqs. [1] and [2].



**Figure S8.** XMCD of R2 and partially oxidized R2<sup>OX</sup> phase (*T*=2.8 K, *B*=4 T,  $\gamma$ =0°). The experimental XMCD of the R2<sup>OX</sup> phase, containing a 70% of OX(OT-45) molecules, could be fitted with the XMCD spectrum of Fe<sup>3+</sup> in tetragonal symmetry calculated with CTM4XAS<sup>1</sup>.

### S9. Percentages of molecular species in OB1<sup>OX</sup> oxidized phase

The experimental XMCD of the partially oxidized sample  $OB1^{OX}$  was described as a weighted linear combination of the spectra corresponding to the pristine molecules (SB-30), and the oxidized, rotated OX(OT-45) and unrotated OX(SB-30) species. That is, the XMCD of the OB1<sup>OX</sup> sample is written as:

 $XMCD(OB1^{OX}) = \%(SB - 30).XMCD(OB) + \%(OX(OT - 45)).XMCD(R2^{OX} \equiv OX(OT - 45)) + \%(OX(SB - 30)).XMCD(OX(SB - 30)).XMCD(OX(SB - 30))) + \%(OX(SB - 30)).XMCD(OX(SB - 30)).XMCD(OX(SB - 30))) + \%(OX(SB - 30)).XMCD(OX(SB - 30)) + \%(OX(SB - 30)).XMCD(OX(SB - 30))) + \%(OX(SB - 30)).XMCD(OX(SB - 30))) + \%(OX(SB - 30)).XMCD(OX(SB - 30))) + \%(OX(SB - 30)) + \%(OX(SB - 30)) + \%(OX(SB - 30))) + \%(OX(SB - 30)) + \%(OX(SB - 30)) + \%(OX(SB - 30))) + \%(OX(SB - 30)) + \%(OX(SB - 30)) + \%(OX(SB - 30))) + \%(OX(SB - 30)) + \%(OX(SB - 30)) + \%(OX(SB - 30))) + \%(OX(SB - 30)) + \%(OX(SB - 30)) + \%(OX(SB - 30))) + \%(OX(SB - 30)) + \%$ 

Several conditions were taken into account in order to bound the percentages of molecular species:

- (i) The percentages must be such to allow describing the experimental XMCD of the OB1<sup>OX</sup> sample determined at various incident angles (e.g. both the XMCD at  $\gamma$ =55°, in Fig. 8, and at  $\gamma$ =0°, at Fig. 9).
- (ii) The spin per hole calculated with these percentages must match the experimental  $m_x / n_b$  measured for the OB1<sup>OX</sup> sample, i.e.

 $\% OX (OT - 45) \cdot m_{e} / n_{h} [R2^{OX} \equiv OX (OT - 45)] + \% OX (SB - 30) \cdot m_{e} / n_{h} [OX (SB - 30)] = m_{e} / n_{h} [OB^{OX}] \approx 0.48 \mu_{B} / n_{h}$ 

From this equation, the spin per hole for the oxidized, unrotated molecules,  $m_s / n_h[OX(SB-30)]$ , can be deduced. Using the DFT-calculated number of holes,  $n_{\rm H}$  =3.9, the absolute spin moment  $m_s[OX(SB-30)]$  is determined. This value must be smaller than the moment ever measured for Fe<sup>2+</sup>, ~4 µB for Fe(II, high spin).

(iii) For the oxidized rotated species, OX(OT-45), it was found that the DFT-calculated magnetic moment was a factor ~1.9 larger than the experimental  $m_s$  value. Assuming that this factor will be similar for the unrotated molecule OX(SB-30), it is found an estimate for  $m_s / n_b [OX(SB-30)] = 0.45 - 0.48$ .

The percentages of oxidized molecules have been found to present some variations within a sample; however, the focus of Figs. 8-9 is to show how the XMCD reflects the existence of the three molecular species in the oxidized phase OB1<sup>OX</sup>.

#### References

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