PHYSICAL REVIEW B **90**, 045406 (2014)

Coverage-dependent surface magnetism of iron phthalocyanine on an O-Fe(110) surface

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(Received 17 May 2014; published 14 July 2014)

Iron phthalocyanine adsorbed on an oxygen covered Fe(110) surface shows a complex coverage-dependent spin polarization during growth of a molecular monolayer. Spin polarization is modified at low submonolayer coverages, absent at intermediate submonolayer coverages, and reappears in modified form for a complete monolayer. This is attributed to coverage-dependent adsorption configurations from a random adsorption system to a packed monolayer with a well-defined interfacial spin polarization. In addition, we report on the observation of a rotation of the spin direction of photoelectrons in the presence of molecules which is attributed to molecular modifications of surface magnetic anisotropy.

DOI: 10.1103/PhysRevB.90.045406 PACS number(s): 75.70.Ak, 75.50.Xx, 75.70.Rf, 75.30.Gw

I. INTRODUCTION

Magnetism in molecular materials offers intriguing opportunities to control spin-dependent charge transport for organic and molecular spintronics [1–3]. Numerous observations of magnetoresistive effects have been reported for traditional organic semiconductors over the past decade, including giant magnetoresistance in tris(hydroxyquinolate) aluminum (Alq3) [4] and tunneling magnetoresistance in Alq3 [5–7], rubrene [8], and C_{60} [9]. Designer magnetic molecules such as single molecule magnets [10–13], ferrimagnetic coordination polymers [14,15], and various paramagnetic coordination compounds exhibiting spin crossover [16–19] have illustrated the tremendous diversity that can be harnessed in explorations of organic and molecular spintronics. Moreover, even relatively weak paramagnetism in molecules can have important impacts on charge transport processes in organic molecules [20].

An important challenge in organic and molecular spintronics is the control of interfaces for efficient spin-polarized carrier injection [21,22]. This is due to the conductivity mismatch problem that was first identified in the context of poor efficiency of spin injection into inorganic semiconductors [23]. For organic materials, an ohmic contact to a metal electrode would be expected to lead to severely inefficient spin injection due to this effect. This must be overcome by designing spin-dependent interface resistances that promote spin-polarized carrier injection. For this purpose, the notion of hybrid interface states formed by electronic interactions between a conducting magnetic substrate and an organic film has arisen as among the most important concepts in organic spintronics [6,24,25]. One may envision harnessing spontaneous interface states that form by direct substrate-organic hybridization to promote spin injection [25].

Characterization of electronic interactions at interfaces for organic spintronics applications has focused significantly on metal phthalocyanines (MPc's, where M is typically a 3*d* transition metal). These planar organic semiconductors have the interesting property of a central, square-planar-coordinated metal ion that can directly interact with a conducting substrate when the molecule is in a flat-lying adsorption geometry. This has already been shown to lead to efficient metal-organic interface hybridization for CoPc adsorbed on cobalt using spin-polarized scanning tunneling microscopy (SPSTM) [26]. Brede *et al.* showed submolecular spin contrast indicative of adsorption-geometry-dependent hybridization for CoPc adsorption on iron using SPSTM [27]. A study of the weakly magnetic CuPc using SPSTM and spin-polarized photoelectron spectroscopy showed that this molecule creates hybrid interface states on an Fe substrate [28]. Thus, the molecular design strategy of using MPc's to engineer coupling seems to be a plausible route toward systematically controlling magnetic interactions at organic spintronic interfaces. Moreover, there is evidence from two-photon photoelectron spectroscopy that spin-polarized transport can occur into relatively thick phthaocyanine films [29], though this is still a topic of significant discussion [30].

Comparative photoelectron spectroscopy studies of different phthalocyanine interactions on magnetic surfaces have shown that indeed there is a significant dependence of interfacial spin polarization on the chemical identity of the central metal atoms. Lach *et al.* found molecule-induced spin polarization near the Fermi level of a cobalt substrate that is connected to the symmetry and occupation of the MPc metal ion *d* orbitals, which varies across the 3*d* series [24]. A related dependence on the metal center is also reported based on computational studies of iron phthalocyanine (FePc) and manganese phthalocyanine (MnPc) adsorption on Fe(001) [31].

It is important to recognize that interfacial coupling between organic molecules and metal surfaces can fundamentally change the nature of molecular magnetism. This could be an advantage as a means of magnetic and spintronic control. Such subtle interfacial control has been already explored for phthalocyanine adsorption on copper and cobalt surfaces with submonolayer oxygen functionalization of the metal substrates. Direct adsorption of FePc on $p(2 \times 1)$-O-Cu(110) results in a change in sign of the zero-field splitting parameter compared to a bulk FePc crystal [32]. This has the remarkable physical consequence of changing the easy axis of molecular magnetization from the plane of the molecule to perpendicular to the plane and has been predicted to be switchable by an applied electric field [33]. For a related case of an Fe-porphyrin

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molecule, direct adsorption on Co(100) was found to lead to very strong ferromagnetic molecule-substrate interactions, while adsorption on *c*(2 × 2)-O-Co(100) leads to antiferromagnetic interactions [30]. These dramatic consequences illustrate the value of careful interfacial design well beyond the creation of hybrid interface states.

In this work we report a study of magnetic interactions with FePc adsorbates by using spin-polarized photoelectron spectroscopy to characterize the electronic structure of their interfaces with a partially oxygenated Fe(110) crystal. We report strongly coverage-dependent spin polarization in the valence band that is controlled by molecular ordering in the first monolayer. We also report the unusual observation of coexisting spin polarization of photoelectrons in both [110] and [001] directions that indicates a subtle molecular modification of surface magnetic anisotropy.

II. EXPERIMENTAL METHODS

Experiments were carried out in an ultrahigh vacuum system (base pressure $\sim 2 \times 10^{-10}$ Torr) on beamline U5UA of the National Synchrotron Light Source at Brookhaven National Lab. A W(110) single crystal was cleaned in a preparation chamber by electron beam heating to 920 °C in 4×10^{-8} Torr O_2 background pressure followed by annealing to 1500 °C. Films of Fe approximately 5 nm thick were deposited from a rod-style electron beam evaporator onto the clean W(110) substrate. Exposure to oxygen during Fe growth resulted in a *c*(3 × 1) oxygen overlayer on this Fe film as described in Sec. III A.

Iron phthalocyanine (Sigma Aldrich, 90%) was loaded as-received into a quartz crucible housed in a home-built thermal evaporator. The material was outgassed extensively prior to evaporation and the temperature was monitored at a point near the crucible with a thermocouple to ensure stability and reproducibility of molecular flux. Molecular coverage on the surface was monitored using measurements of the change in work function due to adsorption. The "monolayer" is defined here as the coverage where there is an obvious change in slope of the work function decrease as described in the next section. Work functions were measured by observing the position of the secondary electron cutoff in photoelectron energy distribution curves with the sample biased at −15 V.

Photoelectron spectra were measured with a 120 mm mean radius hemispherical analyzer (Omicron EA120). Samples were magnetized with a pulsed magnetic field of ∼300 Oe applied in the plane of the surface along the [110] direction and then spin-polarized photoelectron spectra were measured in remnance. The detector was a home-built "mini-Mott" spin polarimeter operated at 27 kV and capable of resolving spin polarization of photoelectrons in the plane of the sample surface with four orthogonal backscattering detectors. Spectra are reported with instrumental asymmetries corrected by sequential measurements of oppositely magnetized samples [34]. Synchrotron light from the U5UA undulator was used as an excitation source and the monochromatized photon energy was measured to be 41.4 eV by observing the energy difference between equivalent photoelectron peaks in the Fe *d* band resulting from the first and second harmonics of the undulator. Spin-integrated spectra were measured with a pass energy of 5 eV, while spin-resolved spectra were measured with a higher pass energy of 10 eV to increase the photoelectron count rate.

III. RESULTS

A. Substrate characterization and coverage calibration

Analysis of the shape of the valence band photoelectron spectra of the Fe(110) films grown on W(110) shows a clear O 2*p* peak at ∼5.5 eV binding energy as shown in Fig. 1. The ratio of *d*-band peak height near the Fermi level to O 2*p* peak height in this spectrum is indicative of the well-known *c*(3 × 1) oxygen overlayer on Fe(110) [35]. This structure has one chemisorbed oxygen atom for every three Fe atoms on the surface. It has been shown not only to introduce the O 2*p* peak in Fig. 1, but to also slightly modify the shape of the Fe(110) *d* band [36], the spin polarization at the surface [37], and the surface contribution to the magnetic anisotropy [38].

The starting O-Fe(110) substrate was measured to have a work function of about 5 eV using the secondary electron cutoff with a negatively biased sample. Adsorption of FePc reduces this work function as expected based on the combined effects of direct charge transfer and "Pauli pushback" by which molecular layers tend to reduce the amount of electron density spillout from the metal into vacuum [39–41]. These effects reduce the surface electrostatic dipole layer and hence the work function.

The sample work function decreases rapidly during the growth of a complete monolayer of FePc on the surface as shown in Fig. 2. The total reduction in work function after adsorption of a full monolayer of FePc is 1.2 ± 0.1 eV. This magnitude is similar to the work function decrease that results in phthalocyanines adsorbed on other metal surfaces [42] and is an important parameter in ultimately defining energy level alignment in organic devices [39]. In our experiment, the coverage dependence in Fig. 2 serves the important goal of precisely defining the monolayer FePc coverage as coverage at which the work function shows a dramatic reduction in slope. Moreover, the systematic dependence of work function

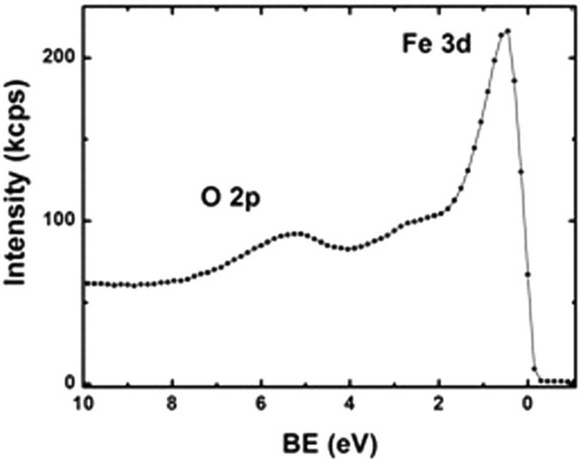

FIG. 1. Spin-averaged photoelectron spectrum of the O-Fe(110) substrate with O 2*p* and Fe 3*d* peak indicated. The ratio of peak heights and shape of the spectrum is consistent with a *c*(3 × 1) O overlayer on the Fe(110) surface.

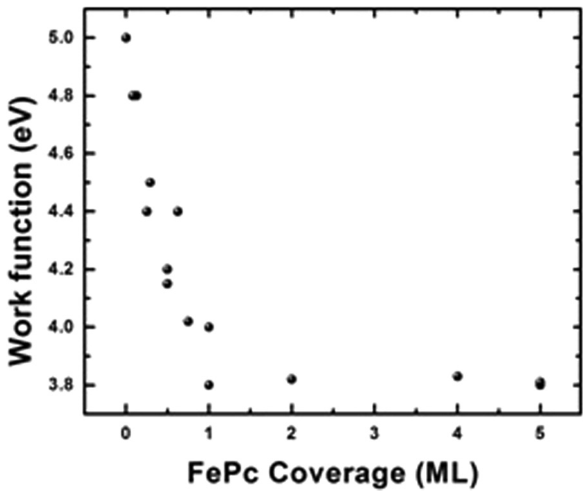

FIG. 2. Work function measurements during sequential FePc adsorption on the O-Fe(110) substrate. The coverage where the slope of this dependence shows a large reduction is taken as the full monolayer molecular coverage.

through sequential deposition steps is evidence for a minimal impact of photon beam damage during combined spin-averaged and spin-resolved photoemission at each coverage.

B. Spin-integrated valence band spectra

Figure 3 shows the coverage-dependent evolution of the valence band from 0 to 1 ML of FePc on O-Fe(110). An important feature of these spectra is the enhancement in intensity on the high binding energy side of the Fe *d* band near 1 eV. In addition, numerous new peaks arise deeper below the Fermi level that are assigned as molecular orbitals of FePc. To emphasize the molecular origin of spectral features in Fig. 3, we plot in Fig. 3(b) a difference spectrum where the intense *d*-band peak region near the Fermi level due to the Fe(110) substrate is subtracted by normalizing all spectra to the substrate *d*-band maximum.

In the difference spectra in Fig. 3(b), the added weight on the high-binding side of the substrate *d* band around 1 eV is resolved into a shoulder that can be assigned as due to the highest occupied molecular orbital (HOMO) of the adsorbed FePc. This shoulder increases in intensity as FePc coverage increases. The same is true for more deeply bound molecular states. In addition, the substrate *d*-band background subtraction is very imperfect just around and slightly below the Fermi level. This is evidence for some modification of the density of electronic states near the Fermi level due to molecular adsorption. Interestingly, there is an abrupt sharpening of the HOMO-derived peak 1.5 eV below the Fermi level at precisely 1 ML coverage that is obvious in the difference spectra but also visible in the raw spectra [Fig. 3(a)]. This change will be important to note in our later discussion of the coverage dependence of spin polarization.

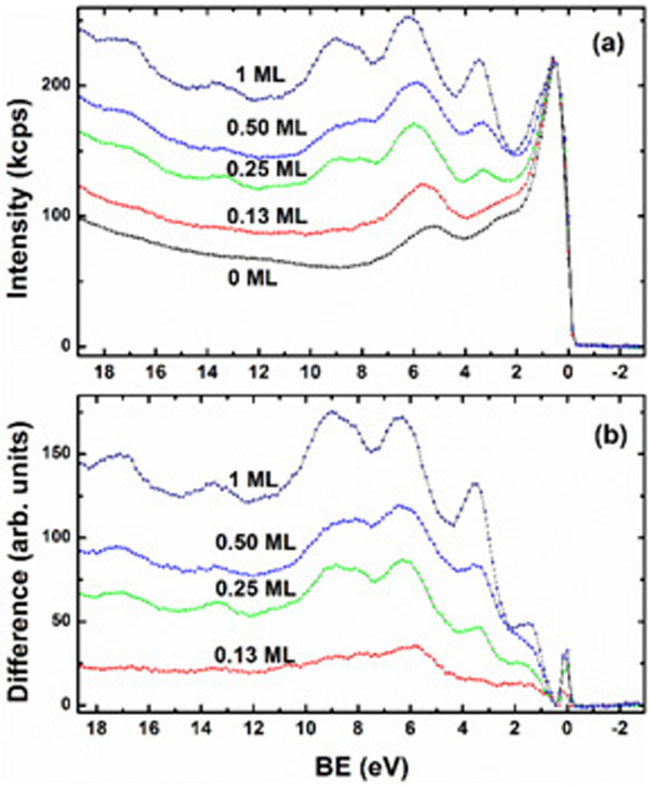

FIG. 3. (Color online) (a) Valence band spectra measured for submonolayer to single monolayer films of FePc on O-Fe(110). All spectra are normalized to the peak in the *d* band on the starting substrate. (b) Difference spectra obtained by subtracting the normalized 0 ML spectrum from the finite coverage spectra in part a to remove the dominating influence of the *d*-band peak.

Further support for the molecular origin of the various electronic states in the difference spectrum is shown in the valence band spectrum measured for a multilayer FePc film in Fig. 4. In this spectrum, photoelectrons from the substrate are attenuated sufficiently that they do not interfere with peak assignments. Here we clearly see the HOMO peak defined at 1.35 eV below the Fermi level very close to the region expected based on observation of the HOMO shoulder in Fig. 3(b). Moreover, the higher binding peaks are also clearly defined and can be associated in a one-to-one manner with peaks in the difference spectra.

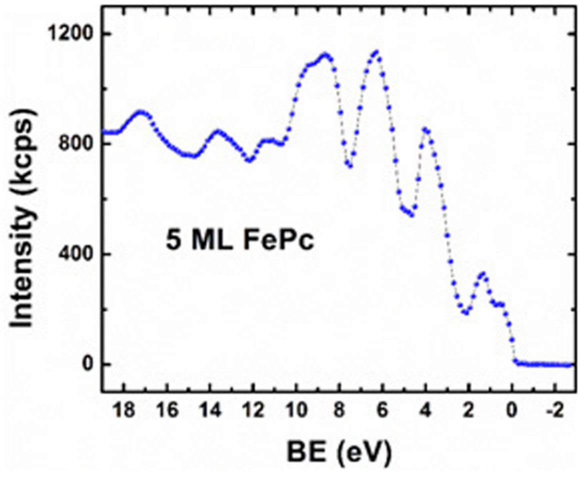

FIG. 4. (Color online) Valence band photoelectron spectrum of a 5 ML think FePc film.

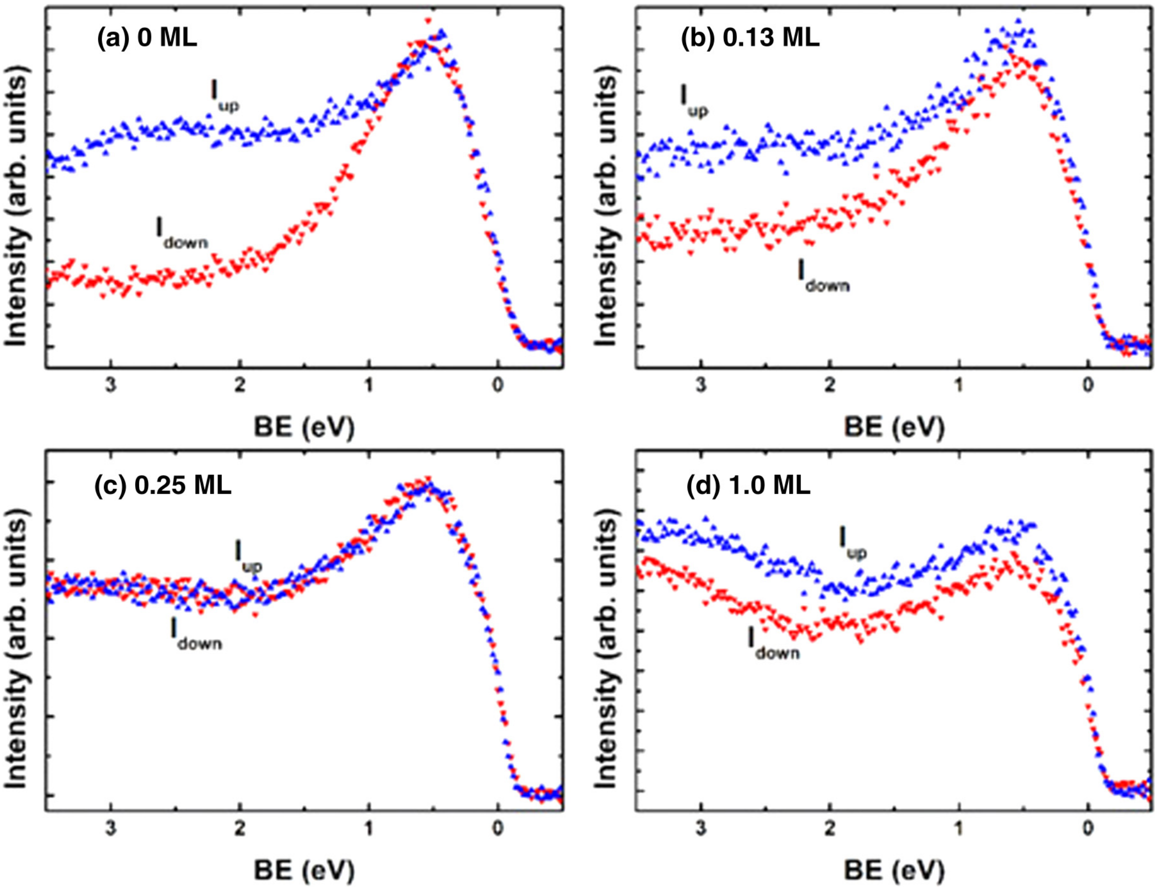

FIG. 5. (Color online) Spin-polarized valence band photoelectron spectra measured along the [1$\bar{1}$0] direction for (a) the starting O-Fe(110) substrate, (b) 0.13 ML FePc, (c) 0.25 ML FePc, and (d) 1 ML FePc. The spectra for 0.5 ML are essentially identical to those at 0.25 ML and show no measurable polarization. The applied, pulsed magnetic field is along the [1$\bar{1}$0] direction.

C. Spin-resolved valence band spectra

Figure 5 shows the spin resolved photoelectron spectra for the starting O-Fe(110) surface and several coverages building up to 1 ML in the in-plane direction parallel to the [1$\bar{1}$0] easy axis for these very thin films [38]. The initial spin polarization is expected to be aligned parallel to the applied magnetic field direction and this is in agreement with previous reports for the $c(3\times1)$-O-Fe(110) surface spin polarization [35]. In the range of our measurements this polarization is only slightly modified compared to that of clean Fe(110). With only a small addition of 0.13 ML of FePc, this polarization is reduced in magnitude and is also more uniform in the binding energy range below 1 eV when compared to the substrate. At 0.25 ML, the spin polarization is not measureable and this fact persists for an additional deposition step to an FePc coverage of 0.50 ML (not shown). Remarkably, significant spin polarization returns when the full monolayer coverage is reached as shown in Fig. 5(d). Moreover, the energy dependence of the spin polarization is different when compared to the starting substrate polarization in Fig. 5(a). It is more uniform across the entire energy window than the starting substrate.

In addition to the changes in the easy axis spin polarization shown in Fig. 5, there are also changes in the spin polarization along the hard [001] axis (which is perpendicular to the applied magnetic field direction) as shown in Fig. 6. The starting substrate has negligible magnetization in this direction since the applied pulsed magnetic field is applied along the [1$\bar{1}$0]. However, with the first deposition step of only 0.13 ML, a finite population of photoelectrons polarized along the [001] is observed. This unexpected polarization is nearly equal in magnitude to the polarization observed in the orthogonal direction [Fig. 5(b)]. It vanishes for intermediate coverage similar to the polarization along [1$\bar{1}$0] but returns for the complete monolayer. Figures 5 and 6 both illustrate significant magnetic interactions between the FePc molecule and the magnetic O-Fe(110) substrate that will be discussed in the next section.

IV. DISCUSSION

A. Coverage-dependent magnetic interactions

As a basis for discussion of magnetic interactions between FePc and O-Fe(110), we first address the details of the spin-averaged-photoelectron spectra. The molecule-derived electronic states visible in the difference spectrum of Fig. 3(b) can be clearly associated with pronounced states of the thick molecular film shown in Fig. 4. This implies that electronic modifications due to molecule substrate interactions are relatively weak and are predominantly reflected in the changes near the Fermi level in the difference spectra in Fig. 3(b). This interpretation is further supported by direct comparison with PES studies of the valence band of FePc

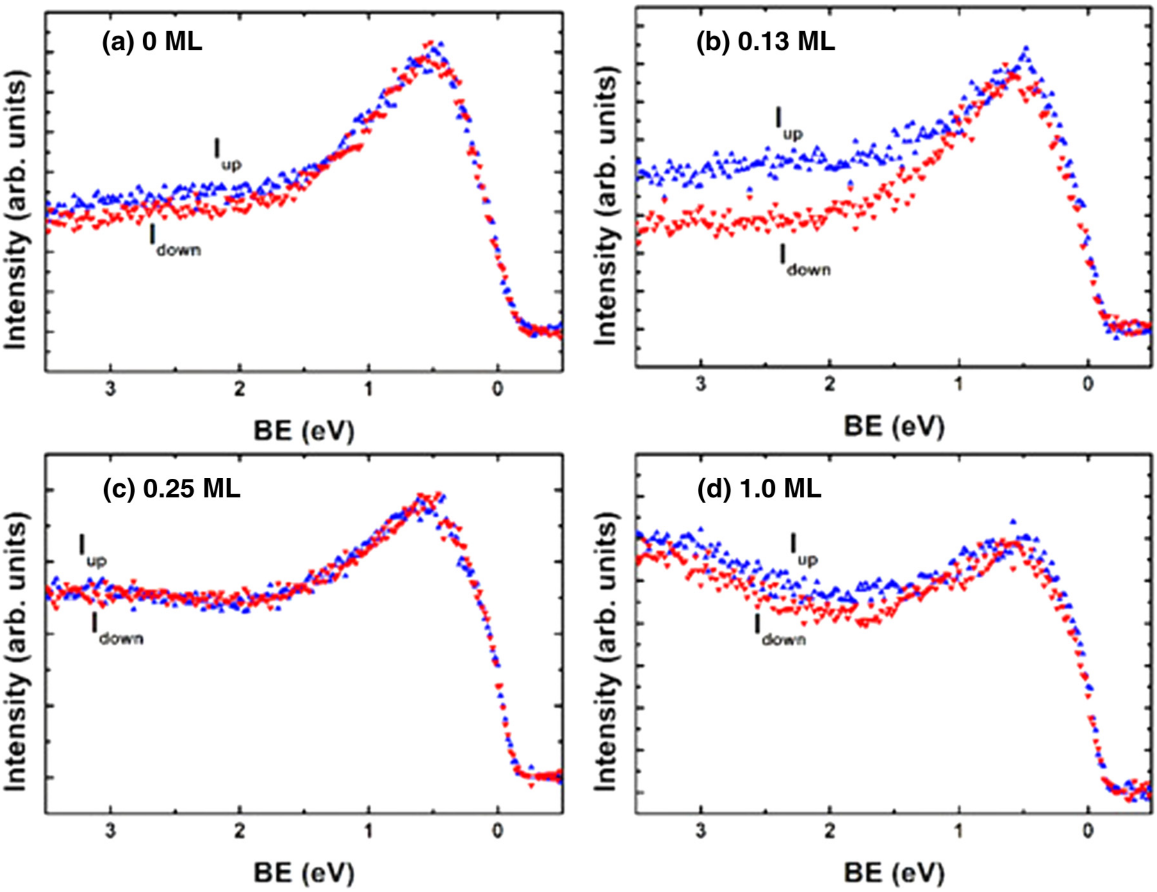

FIG. 6. (Color online) Spin-polarized valence band photoelectron spectra measured along the [001] direction for (a) the starting O-Fe(110) substrate, (b) 0.13 ML FePc, (c) 0.25 ML FePc, and (d) 1 ML FePc.

on polycrystalline Au [43] which show identical electronic features to our thick films, with the exception of the weak structure we observe near the Fermi level.

At submonolayer coverages, the HOMO feature is a broad shoulder around −1 eV rather than the more clearly peaked structure that can be seen at 1 ML. In particular, it is worth noting that the HOMO is very broad at 0.25 ML, even though other molecule-derived states at higher binding energies are reasonably distinct. We assert that the width of the HOMO feature is determined by a combination of the strength of molecule-substrate interactions and inhomogeneous broadening due to disorder. Strong molecule-substrate interactions would lead to a broad HOMO due to mixing between molecular orbital states and continuum substrate bands. In addition, local disorder can lead to small shifts in local HOMO levels that are superposed to give a broadened state in the full spectrum.

On the basis of recent observations of metal pthalocyanine adsorption on several surfaces, we suggest that disorder is a very important factor in considering the origin of coverage-dependent spin polarization. For example, Brede *et al.* have observed that at low coverages cobalt phthalocyanine can adopt one of three different in-plane orientations of flat-lying molecules on a Fe(001) film substrate. Each of these different adsorption configurations has a slightly different local spin polarization as measured with spin-polarized STM.

Based on analogy with these STM-based studies we propose the following explanation of the coverage-dependent spin polarization seen in the measurements in Figs. 5 and 6. At the lowest coverage, spin polarization is still dominated by the substrate with some broadening induced by FePc adsorption. At intermediate coverages of 0.25 and 0.5 ML, where spin polarization is not observed, we infer that a random distribution of different molecular adsorption configurations yield photoelectrons superimposed on the substrate spectrum that wash out any observed spin polarization predominantly due to disorder.

At a full monolayer coverage, we propose that a specific adsorption configuration is selected due to intermolecular packing interactions. These create an ordered structure and well-defined molecule modified spin polarization near the surface. This is consistent with both the spin-polarized spectra and the clear sharpening of the HOMO peak in the spin-averaged spectra in Fig. 3. Based on the observed spin polarization at 1 ML we suggest that at least some (possibly all as in Brede *et al.* [27]) of the different adsorption configurations at lower coverage have spin-polarized molecular orbitals. One of these may be preferred in the full, ordered monolayer and lead to the observed finite spin polarization at this coverage. The details of adsorption configuration of FePc on O-Fe(110) cannot be ascertained from our experiments but the generic picture of a disorder-order transition with increasing coverage is consistent with all presently available data.

As identified in Fig. 7, the energy dependence of the polarization (calculated from Fig. 5) at 1 ML coverage is

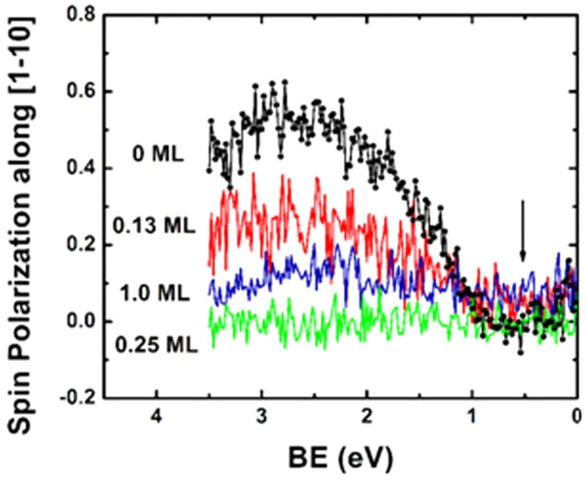

FIG. 7. (Color online) Spin polarization along the $[1\bar{1}0]$ direction for the coverages shown in Figs. 5(a)–5(d). The arrow marks the region near the Fermi level where finite polarization is induced by molecular adsorption.

different than the starting substrate suggesting that molecular orbitals are spin polarized by proximity of the substrate analogous to the case of Fe-porphyrin [30]. We note in particular that the polarization is slightly enhanced close to Fermi level compared to the starting substrate, which is important in determining spin injection properties. This spin polarization is on the order of 10% in the region between the Fermi level and 1 eV binding energy and can be interpreted as the result of a spin-polarized interface state similar to those reported for other phthalocyanines [24].

B. Spin rotation of photoelectrons

In Figs. 5 and 6 we report the simultaneous detection of photoelectrons with spin directions both parallel *and* perpendicular to the in-plane easy axis along which a magnetizing field is applied at the very low coverage of only 0.13 ML. In addition, a weak perpendicular component is also present in the 1 ML spin-polarized spectra. This observation is unusual and in this section we propose a possible origin of the effect. In simplest terms, the presence of FePc molecules changes the surface magnetoanisotropy leading to a new "easy axis" that makes a small angle with the usual $[1\bar{1}0]$ easy axis direction of the thin O-Fe(110) film substrate

In Fe(110) thin films, in-plane spin reorientation transitions (SRTs) are often observed due to changing relative contributions of surface and bulk magnetic anisotropies. However, the change is usually abrupt, with the easy axis switching from a surface-dominated $[1\bar{1}0]$ direction to a bulk-dominated [001] direction in response to film thickness changes [38,44] or adsorbate-induced changes in surface magnetic anisotropy [38,44]. These abrupt transitions result in samples that can be easily magnetized in the plane of the surface along either the $[1\bar{1}0]$ or [001] directions. Only rarely are magnetizations intermediate between these two directions observed [45].

The possibility of an intermediate magnetization direction can be addressed phenomenologically by considering the orientation dependence of the free energy density in the Landau-like expression for a magnetic solid [44,46]:

$$f = A \sin^2 \phi + B \sin^2 \phi. \qquad (1)$$

In this expression the first order anisotropy constant A can be decomposed into surface and volume terms $A = K_{v,p} - K_{s,p}/d$ and likewise for the second order constant $B = K_{v,pp} - K_{s,pp}/d$, where d is the film thickness and the K's in A are "first order" bulk and surface magnetic anisotropy constants while the K's in B are "second order" [44,47]. The angle ϕ is the rotation of the magnetization with respect to the bulklike, in-plane [001] easy axis. The dependence of A and B on film thickness d accounts for the famous thickness-dependent SRT in Fe films [38,44,47]. In addition, temperature dependence of anisotropy constants can lead to thermal SRTs [46].

The hypothesis of an intermediate in-plane magnetization direction requires identification of a stable minimum in free energy density at an angle other than $\phi = 0$ or $\phi = \pi/2$ from Eq. (1). It has been pointed out that a second order transition leading to a broad range of intermediate angles could result from a increased second order surface anisotropy constant $K_{s,pp}$ [47]. Experimental evidence for such continuous transitions has been reported for Fe films grown on Au/W(110), where interdiffusion of Au strongly modifies the magnetic properties of the Fe film [45]. In Fig. 8 we plot Eq. (1) for values [44] corresponding to clean Fe(110) films of thickness 5 nm (note: our substrate will be modified slightly by the oxygen overlayer [38]) and also with a $K_{s,pp}$ value increased from -160 to -245 kJ/m^2 to create a broad, flat local minimum indicative of a second order phase transition. The increase in $K_{s,pp}$ by less than a factor of 2 is a plausible change given the variability that can be seen in this parameter for different capping films [44]. Moreover, magnetic anisotropy is microscopically connected to anisotropies associated with orbital angular momentum of electrons in the solid. In this context, FePc is a good candidate for inducing very strong modifications since it has been observed to have an unusually large orbital contribution to its total magnetic moment [48].

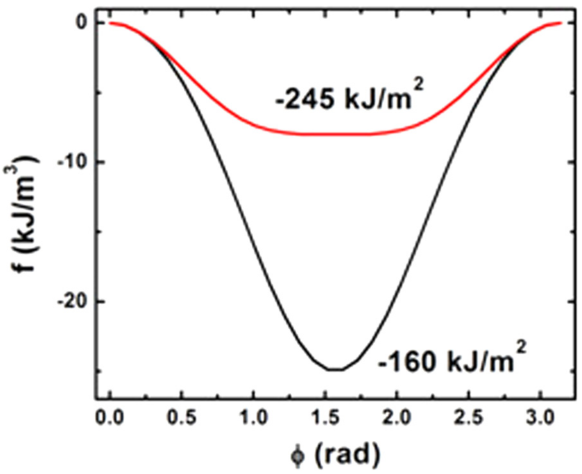

FIG. 8. (Color online) Calculated free energy density following Eq. (1) using different values of second order magnetic anisotropy as indicated along with other values taken from Ref. [45].

V. SUMMARY AND CONCLUSION

Spin-polarized photoelectron spectroscopy of the first monolayer of FePc growth on a O-Fe(110) surface shows a complex, coverage-dependent sequence of changes. Iron phthalocyanine modifies the density of states and spin polarization near the Fermi level suggesting hybrid interface state formation. At intermediate submonolayer coverages, spin polarization vanishes due to the averaged contributions from poorly ordered molecular adsorbates. Surprisingly, it returns for a full molecular monolayer coverage where intermolecular interactions drive significant ordering and thus allow a well-defined, molecule modified spin polarization at the interface.

In addition to the spin-resolved electronic structure changes, we report evidence for a significant impact of low coverage FePc adsorption on the surface magnetic anisotropy of the O-Fe(110) film. This comes from the observation of a population of photoelectrons spin polarized in the plane of the surface but orthogonal to the easy axis along which a field is applied. We attribute this to molecule-induced changes in second order magnetic anisotropies. The work described here highlights the importance and complexity of metal-molecule interfaces for controlling properties relevant to spintronics. Moreover, it points out the interesting new possibility that the basic magnetostatic properties at interfaces can be strongly modified by organic semiconductor adsorption.

ACKNOWLEDGMENTS

This work was funded by the NSF Center for Chemical Innovation: Center for Molecular Spintronics (CHE-0943975). Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886

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