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Paramagnetic Character in Thin Films of Metal-Free Organic Magnets Deposited on $TiO_2(110)$ Single Crystals

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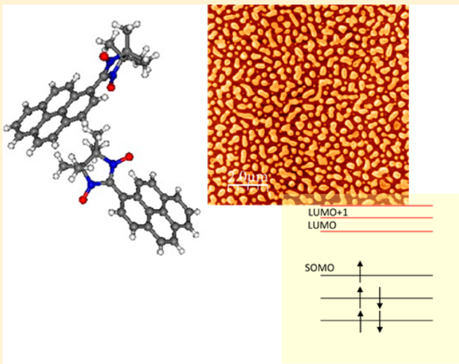
Supporting Information

ABSTRACT: Metal-free organic magnets are a class of emerging materials interesting for their potential use in electronics. We investigate the paramagnetic character of thin films of a pyrene derivative of the nitronyl nitroxide radical deposited on rutile $TiO_2(110)$ single crystals. By using X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, we find that the paramagnetic character is kept going from "molecule to material". In particular, we evidence the transitions related to the singly occupied molecular orbital, as expected in open shell materials, by using NEXAFS spectroscopy.



INTRODUCTION

Electronics have changed our life in the last decades. From the advent of the first personal computer (due to the pioneer work of a few creative scientists developing a new idea, a desktop computer,[1] at a time when computers were "big cupboards"), in around 50 years, the high degree of electronic development has made science fiction a reality. In the past decade, a huge benefit has been gained by the use of materials of different natures, as in the case of organic electronics, where the flexibility of synthetic chemistry becomes very useful.[2,3] Engineering a device implies the design of new molecules, the tuning of the characteristics of existing molecules, or testing a new class of materials.[4−7] In this respect, we are focusing our efforts on defining and controlling the thin-film processes of nitronyl nitroxide-based molecules.[8−13] These are stable radicals with an unpaired electron whose stability is due to its complete delocalization over both NO groups[8] (Figure 1). The importance of organic radicals is that they are purely organic molecules with at least one unpaired electron. This originates a magnetic moment: only light elements are coupled to the magnetic properties of the molecules. The technological potential of this class of materials is easily foreseen because they bring together magnetism and the flexibility of chemical synthesis.[3] We have previously demonstrated by using X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy that paramagnetic nitronyl nitroxide radicals are thermally stable and it is possible to use organic molecular beam deposition (OMBD) to grow their thin films, keeping their paramagnetic character.[14]

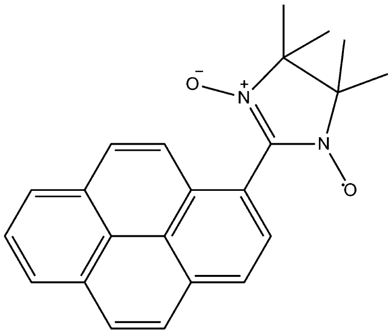


Figure 1. NitPyn molecular structure.

Aiming at their use in electronics, in the present work, we use soft X-ray techniques like XPS and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to explore the paramagnetic character of thin films of a pyrene derivative of the nitronyl nitroxide radical (4,4,5,5-tetramethyl-2-(pyrenyl)-imidazoline-1-oxy-3-oxide, NitPyn, Figure 1) deposited on rutile $TiO_2(110)$ single crystals.

At the interface between NitPyn and rutile $TiO_2(110)$ single crystals, in the sub- and monolayer regimes, a strong chemisorption of the molecules occurs. The chemisorption perturbs the nitronyl nitroxide radical. The first layer of NitPyn deposited on rutile $TiO_2(110)$ has a mixed nature consisting of paramagnetic molecules and molecules that lost their paramagnetic character. This depends on their adsorption site, that is, ideal versus hydrolyzed sites.[15] In this work, we explore the film characteristics beyond the first layer. As the substrate

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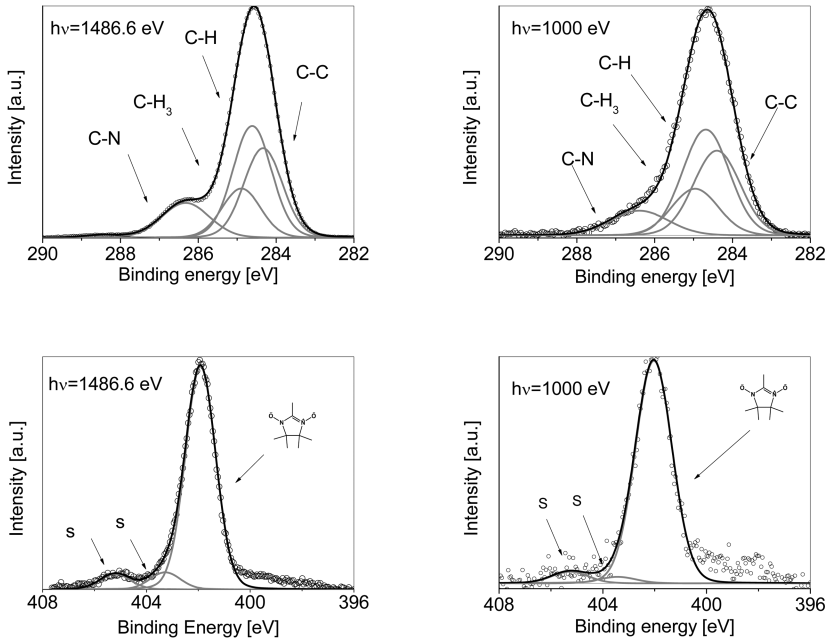

Figure 2. Thickness-dependent C1s and N1s core-level spectra (together with their peak-fit analysis) of NitPyn thin films deposited on rutile $TiO_2(110)$ single crystals. Left: 2 nm nominally thick film. Right: 3.5 nm nominally thick film.

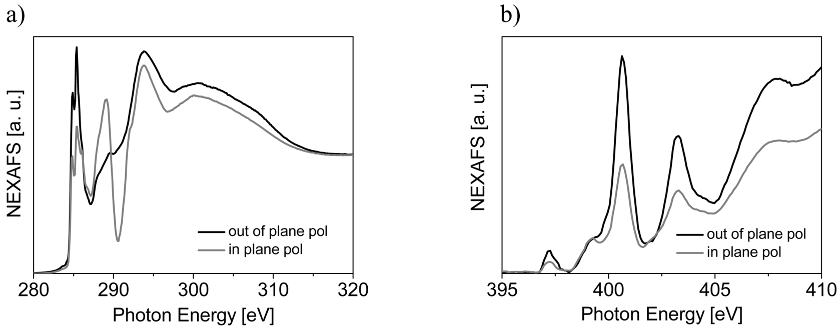

Figure 3. (a) C−K and (b) N−K edge NEXAFS spectra obtained from a 4.5 nm nominally thick film. The spectra were taken in grazing incidence for out-of-plane (black curve) and in-plane (gray curve) polarization.

contains oxygen, we concentrate on the carbon and nitrogen atomic species.

■ EXPERIMENTAL METHODS

The measurements were carried out at the third-generation synchrotron radiation source BESSY II (Berlin) at the UE52-PGM undulator beamline. The measurements have been performed in low-alpha and in single bunch (ring current at injection = 100/15 (mode B/mode A), and 20 mA, cff = 2.5, analyzer resolution = 0.1 eV). Clean $TiO_2(110)$ single crystals were prepared by multiple cycles of argon ion sputtering and UHV annealing at ∼830 K for 30 min,[16] with cleanness monitored by XPS and NEXAFS. The colorless as-received defect-free surfaces changed to light blue/gray after successive cleaning cycles, indicating the occurrence of an oxygen-deficient surface.[17] The thin films were deposited in situ under UHV conditions by OMBD (evaporation rate = 1 Å /min). The evaporation rate was determined by a quartz microbalance. The peak fit analysis was carried out with the Unifit package.[18] The end station at the beamline had separated preparation and analysis chambers (base pressure = 4×10^{-10} mbar) equipped with a SCIENTA R 4000 electron energy analyzer. The NEXAFS spectra were measured in total and partial electron yield, normalized by the clean substrate signals. All spectra were scaled to give an equal edge jump. Details of NEXAFS normalization and molecular orientation calculations are given elsewhere.[19] NitPyn thin films revealed radiation sensitivity on a relatively short time scale evidenced by a clear broadening of the main lines and appearance of additional features upon strong X-ray exposure. (See the Supporting Information.) Thus, we have taken all precautions necessary to avoid radiation damaging (i.e., short beam exposure, short acquisition time, a freshly prepared film for each spectrum).

■ RESULTS AND DISCUSSION

Figure 2 shows the XPS C1s and N1s core-level spectra of a 2 and a 3.5 nm nominally thick film together with their fitting curves. The fitting procedure has been discussed in detail in ref 14 for NitPyn films, while the application of specific constrains to perform a best fit of the XPS spectroscopic lines is discussed in ref 20. The aromatic carbon sites (C−C and C−H bounded carbons), the carbons of the methyl group (CH_3), and the carbons bound to nitrogen (C−N) contribute to the spectroscopic lines in the C1s core-level spectra. The components, assigned according to ref 14, are in good stoichiometric agreement. (See Tables 1 and 2 in the

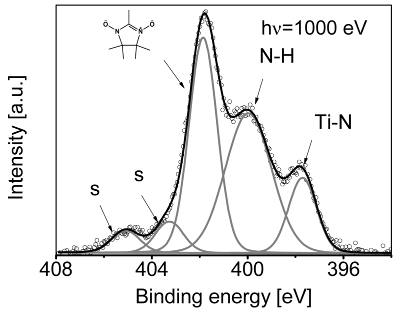

Figure 4. N1s core level spectrum of the NitPyn film at the interface.

Supporting Information.) The N1s core level spectra of an intact mesomeric nitronyl nitroxide radical are characterized by a single peak,[14] as is the case for the N1s core level spectra in Figure 2, having a main peak at ~402 eV and two clear shakeup satellites. The signal tail in the lower binding energy range is due to the interface layer.[15] This layer can still contribute to the spectroscopic line because of the Stranski−Krastanow growth mode shown by the NitPyn films on rutile $TiO_2(110)$ single crystals; that is, this growth mode is defined by one or more layers that grow on the substrate, followed by island nucleation. (See the Supporting Information.)

The previous stoichiometric analysis and the XPS line shape in agreement with the correlation that we have established between EPR spectroscopy and XPS investigations performed on thick NitPyn films[14] allow the conclusion that the successive NitPyn layers, grown on the first chemisorbed layer, are characterized by intact molecules.

To further explore the electronic structure of the films, we measure NEXAFS spectroscopy. While XPS probes the occupied state, NEXAFS is the absorption of X-ray radiation close to a given edge. In NEXAFS, the photon energy is scanned in a region several tens of electronvolts above the edge, and the absorbed X-ray intensity is measured. NEXAFS is element-specific due to the fact that each element has its own binding energy. It is possible to gain information about the unoccupied states, the environment of specific chemical elements, bonding properties, and local charge distributions. An additional useful property is the possibility to calculate the molecular orientation from the NEXAFS spectra, that is, the average angular arrangement of the molecules in the film with reference to the substrate surface.[21]

The C−K edge NEXAFS spectra of a 4.5 nm nominally thick film for two different polarization directions of the incident light, as indicated, are shown in Figure 3. The relative XPS core-level spectra are given in the Supporting Information. By analogy to the NEXAFS spectra of pyrene and pyrene-based molecules,[22,23] they are characterized by two main regions: the π^* region up to ~290 eV and the σ^* region in the photon energy range above 290 eV. In particular, three resonances are visible at 284.9, 285.5, and 286.2 eV; they are due to transitions from C 1s levels mainly into the lowest unoccupied molecular orbitals (LUMOs). They have a C═C character. Features at 287.7 and 289.7 eV presumably have a mixed character (σ^*(C−H) and π^*(C═C)). Finally, the features above 290 eV have also a mixed nature due to transitions to σ^* orbitals (C−C, C═C, and C−N) and shake-up contributions ($\pi \rightarrow \pi^*$).[22,23]

The C−K edge NEXAFS dichroism is useful to calculate the average orientation of the molecular plane of the pyrene substituent with respect to the substrate.[21] The calculation, performed on the resonances at 285.5 eV, yields a value of ~48°. This orientation of the pyrene substituent is in agreement with the NitPyn crystal structure.[24] This arrangement is a compromise between the tendency of the molecules to have the major π electron sharing and the intermolecular interaction with adjacent/above/below molecules,[25] as seen in other nitronyl nitroxide radicals[26,27] and small molecules as well.[25,28−30]

Figure 3b shows the N−K edge NEXAFS spectra. They carry information about the radical nature of the molecule because the unpaired electron is delocalized over the two equivalent NO groups. We observe several sharp resonances in the photon energy range between 398 and 404 eV that may be assigned to N1s→π^* transition contributions according to previous works on NO,[31,32] amino acids,[33] and phthalocyanines.[34−36] The energy range above 405 eV is dominated by a relatively broad peak having σ^* nature due to various contributions including σ^*(N−C).[33] All features in the 398−410 eV energy range have analogy with peak energy and behavior of the features in the N−K edge NEXAFS spectra of small organic molecules. However, we observe an additional feature at 397.2 eV.

The onset of the N1s XPS core-level spectra and the N−K edge NEXAFS spectra, assuming an efficient screening of the final state, must be very similar in energy. This is the actual fact if we compare the XPS N1s main line and the NEXAFS main features. The photon energy region below 398 eV is, consequently, "pre-edge": the feature at 397.2 eV is due to contributions related to transitions of N−K electrons to the singly occupied molecular orbital (SOMO). The presence of this characteristic feature, expected in open shell systems, confirms the paramagnetic character when going from "molecule to material".

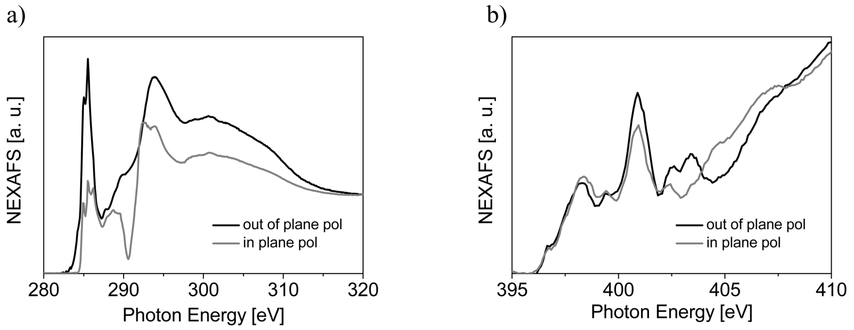

Figure 5. (a) C−K and (b) N−K edge NEXAFS spectra obtained from 0.3 nm nominally thick film. The spectra were taken in grazing incidence for out-of-plane (black curve) and in-plane (gray curve) polarization.

To make sure that this assignment is correct, we measure the N−K edge NEXAFS spectra of the first layer of NitPyn deposited on $TiO_2(110)$ single crystals. XPS N1s core-level spectra show that the layer has a mixed nature, being mainly formed by molecules whose radical character is perturbed by the strong interaction with the substrate due to chemisorption of the molecule.[15] We are able to identify three contributions for the spectra: at 401.9, 400, and 398 eV. The first contribution is due to photoelectrons emitted from mesomeric nitrogen atoms, the second one from atoms bound to hydrogen atoms, the contribution at 398 eV indicates nitrogen atoms involved in a bond with titanium. The assignment of the features in Figure 5 is done according to ref 15. We expect that the N−K edge NEXAFS spectra, shown in Figure 5, are deeply different when compared with the spectra of thicker films, with electronic and magnetic properties not influenced by the interface, as those shown in Figure 3. The N−K edge NEXAFS spectra agree with our expectation: The chemisorption of the molecule causes a strong deviation of the nitronyl nitroxide molecular orbitals from their unperturbed spatial distribution. As a consequence, the matrix element defining the NEXAFS absorption experiences a change. In particular, we do not observe any single feature at 397.2 eV. A contribution that presumably still has a SOMO nature is present, in agreement with the mixed nature of this first layer, originating a shoulder at 397 eV. To prove once more our assignment and the high sensitivity of NEXAFS to the chemical environment, we also analyze the C−K edge NEXAFS of the first NitPyn layer deposited on $TiO_2(110)$. From the XPS investigation of this layer, we know that the pyrene substituent is not perturbed by chemisorption;[15] therefore, we do not expect major differences when comparing the NEXAFS spectra of the first layer and those of the thick layers. The results are shown in Figure 4a, where the similarity of the spectra with those presented in Figure 3 is straightforward. However, we observe a difference in dichroism: The calculated molecular orientation yields a value of 33°. This value reveals a different arrangement of the molecules in the first layer deposited on $TiO_2(110)$ crystals because of a different geometry optimization due to chemisorption and a closer distance of the pyrene substituent to the interface.

CONCLUSIONS

In conclusion, we have investigated the paramagnetic character of thin films of NitPyn deposited on rutile $TiO_2(110)$ single crystals by using XPS and NEXAFS. These techniques are proved to be very sensitive to changes in the occupied and the unoccupied states due to the chemical environment. Their simultaneously use allows us (1) to prove the intactness of the molecules in the film from the XPS stoichiometry analysis; (2) to show the preserved mesomery of the N atoms in the films from the singly peaked N1s spectra; and (3) to probe the presence of the unpaired electron originating the magnetic behavior of NitPyn via the SOMO feature visible in the NEXAFS spectra. In other words, we directly observe that the paramagnetic character is maintained when going from molecules to films. We also observe a certain degree of dichroism related with the SOMO feature. This may depend on a structural lack of homogeneity related to the molecular orientation[28,37,38] or on more specific aspects of the magnetic coupling in the solid state.

Further investigations of this class of materials, together with ab initio calculations not yet available, are necessary to shed light on their solid-state properties and their magnetic character in the solid state, opening the way to consider organic radicals as real candidates for electronics.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables with fit parameters for XPS C1s core-level spectra. Growth mode investigations. The N 1s core level spectra relative to the film in Figure 3. C−K and N−K edge NEXAFS spectra obtained from 0.3 and a 2.3 nm nominally thick film, shown together for direct comparison. N1s core level spectra of a NitPyn thick film, degraded on purpose. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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