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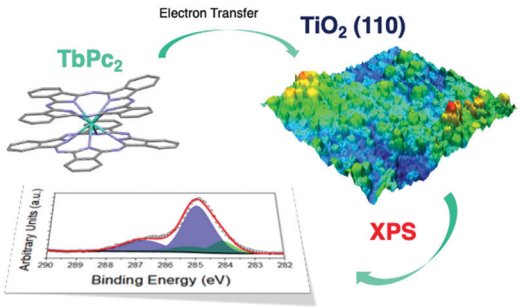

Substrate mediated interaction of terbium(III) double-deckers with the TiO_2(110) surface

Giulia Serrano,* Andrea Luigi Sorrentino, Lorenzo Poggini,* Brunetto Cortigiani, Claudio Goletti, Roberta Sessoli and Matteo Mannini

STM and XPS characterization studies were used to deeply investigate the chemical environment of $TbPc_2$ molecules on the TiO_2 rutile surface, probing a strong interfacial interaction independently from surface preparation.

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Giulia	Serrano		0000-0001-7953-7780
Andrea Luigi	Sorrentino		0000-0002-9476-4583
Lorenzo	Poggini		0000-0002-1931-5841
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Substrate mediated interaction of terbium(III) double-deckers with the TiO_2(110) surface†

Cite this: DOI: 10.1039/d1cp00928a

Giulia Serrano, *[ab] Andrea Luigi Sorrentino, [ab] Lorenzo Poggini, *[ac] Brunetto Cortigiani,[a] Claudio Goletti,[d] Roberta Sessoli [a] and Matteo Mannini [a]

Received 1st March 2021,
Accepted 1st May 2021

DOI: 10.1039/d1cp00928a

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A terbium(III)-bis(phthalocyaninato) neutral complex was deposited on the rutile TiO_2(110) surface, and their interaction was studied by Scanning Tunneling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS). It was found that the TiO_2 rutile surface favours the adsorption of isolated molecules adopting a lying down configuration with the phthalocyanine planes tilted by about 30° when they lie in the first layer. The electronic and chemical properties of the molecules on the surface were studied by XPS as a function of the TiO_2(110) substrate preparation. This study evidences that strong molecule–substrate interactions are present and a charge transfer process occurs from the molecule to the surface.

Introduction

Single-molecule magnets (SMMs) are a peculiar class of molecules characterized by magnetic bistability at low temperature and, therefore, show magnetic hysteresis properties.[1] They hold promise for quantum computations and spintronics.[2–5] However, their use is strictly related to the interaction with a solid surface that often alters the molecular structure or magnetic properties.[6–9] Terbium(III)-bis(phthalocyaninato) molecules, hereafter $TbPc_2$, represent an archetypal single ion magnet – that is, an SMM achieved exploiting only the anisotropy and the crystal field of a mononuclear-based complex – whose structure consists of a Tb^{III} ion sandwiched between two phthalocyanines (Pc) as ligands.[10–12] The deprotonation of both Pc ligands and an additional unpaired electron delocalized on the two ligands[13] impart to the molecule a neutral character. The delocalized electron plays a crucial role in the SMM behaviour[14] and is also significantly participating in the strong surface–molecule interaction with metal substrates leading to the appearance of Kondo features.[15,16] The structural and magnetic properties of $TbPc_2$ films were extensively investigated on various metal surfaces, and it was evidenced that surface–molecule interactions, probably interfering on the delocalization of this unpaired electron, cause the quenching of the SMM magnetic properties on metals.[7,17–21] Recently, thin insulating layers, *e.g.* graphene,[17,20] or chemisorption strategies, introduction of a molecular spacer (an alkyl chain group),[22] were used to reduce this interaction. It was also reported that the interaction of $TbPc_2$ with silicon substrates can play an additional role in enhancing the SMM properties (*i.e.* an increased hysteresis opening) due to the stabilization of electron-depleted molecular species.[22] Furthermore, an even more pronounced hysteresis opening can be obtained by decoupling the SMM deposit from the metal substrates with a magnesium oxide multilayer.[18,23] Indeed, MgO films are extensively used to investigate the quantum properties of single atoms on surfaces,[24–26] evidencing the key role of metal oxides in these studies.

Here, we explore the structural and electronic properties of $TbPc_2$ SMMs adsorbed on a metal oxide of widespread use, namely titanium dioxide, where both the decoupling effect and electron depletion can occur.[27,28] This material has a high technological significance, thanks to its photocatalytic and electron transport properties of relevance for sensors or photovoltaic applications.[27–29] The efficiency of the catalytic and transfer electron processes can be tuned by doping agents or creating surface defects as oxygen vacancies (O-vac), causing excess electrons to be distributed on the surface and introducing defect states within the bandgap.[27] The interaction of the most stable surface of titanium dioxide, that is the rutile TiO_2(110) surface,[27] with phthalocyanine (Pc) systems has been already thoroughly studied. It reveals strong interactions and

[a] *Department of Chemistry "U. Schiff" and INSTM Research Unit, University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy*
[b] *Department of Industrial Engineering and INSTM Research Unit, University of Florence, Via Santa Marta 3, 50139 Florence (FI), Italy. E-mail: giulia.serrano@unifi.it*
[c] *Institute for Chemistry of OrganoMetallic Compounds (ICCOM-CNR), Via Madonna del Piano, 50019 Sesto Fiorentino (FI), Italy. E-mail: lpoggini@iccom.cnr.it*
[d] *Dipartimento di Fisica, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133, Rome, Italy*

† Electronic supplementary information (ESI) available: Additional XPS, STM and LEED characterization of the sample. See DOI: 10.1039/d1cp00928a

the charge transfer processes occurring at the surface–molecule interface.[30–32] Electron depletion from the highest occupied molecular orbital of the TiOPc molecules was observed on TiO_2(110), and this effect was reduced by the use of pyridines as an interlayer between the materials.[33] The charge transfer processes were also observed for the electron acceptor molecular layers like PTCDA (3,4,9,10, perylene tetracarboxylic dianhydride, $C_{24}O_6H_8$)[34,35] or PTCDI (perylene-tetra-carboxylic-diimide)[36] deposited on TiO_2(110). In many cases, O-vacs were found to act as the catalytic sites for molecular dissociation[37] or the preferential adsorption sites favouring the surface–molecule charge transfer processes.[38]

To investigate the interaction of $TbPc_2$ SMMs with a titania substrate, we deposited a $TbPc_2$ sub-monolayer on the rutile TiO_2(110) surface in Ultra High Vacuum (UHV) and we studied their chemical and electronic properties by X-ray Photoemission Spectroscopy (XPS) and Scanning Tunnelling Microscopy (STM) measurements. To understand the role of surface defects in the surface–molecule interactions, we tuned the defect amount by preparing TiO_2 surfaces with different procedures: by (i) sputtering and high-temperature annealing in UHV (TiO_2-HT),[39,40] (ii) exposing TiO_2-HT to oxygen (TiO_2-HT_{Ox})[39,40] and (iii) performing low-temperature annealing after air exposure (TiO_2-LT)[40] (for full description, see the Experimental Methods).

Experimental methods

TiO_2(110) surface preparations

The TiO_2-HT surface was prepared by cycles of Ar sputtering (1.5 keV energy) and annealing at 1000 K in UHV for 60 min and slowly cooled down to room temperature by 10 K min^{-1}. The surface was then studied by XPS and STM measurements as reported in the text. TiO_2-HT_{Ox} was prepared by following the same procedure of TiO_2-HT but, to completely suppress oxygen vacancies on the surface (see Results and discussion), the surface was exposed to an oxygen partial pressure of 2×10^{-7} mbar at room temperature for 15 min afterwards. The TiO_2-LT surface was prepared by exposing the TiO_2-HT sample to air for several days to recover the TiO_2 stoichiometry. The sample was then placed in UHV and gently annealed at 570 K for 60 min. The surface was then checked by XPS and STM measurements. The Au(111) surface, used as a reference substrate for $TbPc_2$ deposition, was prepared in UHV by cycles of Ar sputtering (1.5 keV energy) and annealing at 770 K. All the surfaces were studied by XPS and STM measurements after preparation. In the TiO_2-HT_{Ox} case, this control was performed before and after oxygen exposure.

Molecular deposition and experimental setup

Molecular deposition was performed in UHV using a home-built molecular evaporator in which the molecules were contained in a quartz crucible and heated by a tantalum filament. Molecules were heated to about 683 K, and the TiO_2 substrate was exposed to a molecular flux after having determined the deposition rate using a quartz microbalance (about 0.4 nm h^{-1} for all the depositions). Substrates were kept at room temperature during all the deposition processes. The deposition time was chosen to ensure the deposition of a sub-monolayer quantity of molecules. The integrity and coverage of the molecular deposit were first checked on the Au(111) substrate by STM, showing a coverage of about 15% (see text). Accordingly, similar deposition times were used for the TiO_2 substrates (20 minutes for TiO_2-HT and TiO_2-HT_{Ox}, and 30 min for TiO_2-HT). The STM characterization was carried out using an Omicron Variable-Temperature STM in which the sample was cooled down to 30 K by a liquid helium flux to stabilize molecular deposits. STM images of all clean substrates were collected at room temperature. XPS analyses were performed using a micro-focused monochromatic Al Kα radiation source, $h\nu$ = 1486.7 eV, (XR-MF + Focus 600, by SPECS), and a multi-channel detector electron analyser (SPECS Phoibos 150 1DLD). The X-ray monochromatic beam was set at 54.44° with respect to the analyser. XPS measurements were recorded in normal emission and using a pass energy of 40 eV. XPS spectra were analysed using the CasaXPS software and fitted using a Shirley background. Single-peak components were deconvoluted using a mixed Gaussian and Lorentzian function (70/30). The Spectra were calibrated using the Ti^{IV} component at 458.5 eV. LEED images were acquired using Omicron SpectaLEED rear-view optics.

Results and discussion

TiO_2-HT, TiO_2-HT_{Ox}, and TiO_2-LT samples were characterized by XPS before and after molecular deposition to determine the chemical environment of the titania surface and evaluate its interaction with the $TbPc_2$ sub-monolayer. Fig. 1a shows the Ti2p XPS core-level spectra of these three UHV-prepared surfaces before the deposition of $TbPc_2$.

The most characteristic peak of the XPS spectrum of TiO_2-HT is found at about 458.5 eV. It comprises the $Ti2p_{3/2}$ components associated with the Ti^{IV} species in the bulk and fivefold-coordinated Ti atom (Ti5c) rows and bridging-oxygen rows, respectively, that are characteristic of the TiO_2(110)-(1 × 1) reconstruction.[27,39,41] The shoulder at a lower binding energy (about 456.6 eV) is associated with the $Ti2p_{3/2}$ component of the Ti^{III} species (see Fig. 1b) that could arise from (i) the sputtering and annealing treatment in UHV causing the formation of surface oxygen vacancies, (ii) the migration of Ti interstitial atoms from the bulk towards the surface, or (iii) the presence of hydroxyl groups.[42–45] The percentage of Ti^{III} in the TiO_2-HT sample is about 3.2% of the total Ti^{III} and Ti^{IV} $Ti2p_{3/2}$ components (see Table S1, ESI†). The spin–orbit component of Ti^{IV} is found at a binding energy of about 5.7 eV above the main components, while that of Ti^{III} is found at 5.2 eV.[46] Shake-up at 460.3 eV and plasmons at 471.8, 477.5, and 483.6 eV peaks are also observed in agreement with the literature reports.[47–49] The O1s core-level spectrum (Fig. S1, ESI†) of the clean TiO_2-HT surface is characterized by the main component at about 529.7 eV due to the bulk oxygen species, and a small shoulder (at

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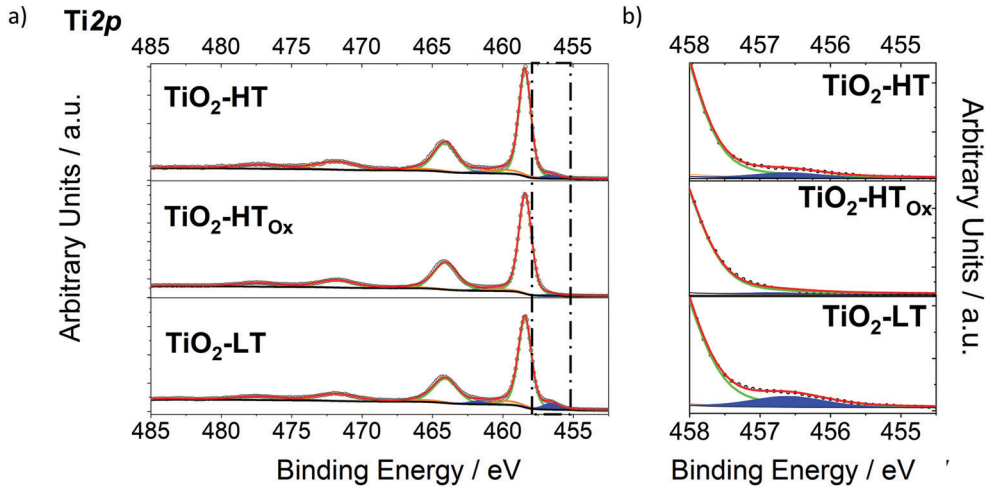

Fig. 1 (a) Ti2p XPS spectra of the TiO_2(110) substrate before molecular deposition for all the three different preparation procedures; (b) zoom in the rectangular region of panel a to emphasise the $Ti2p_{3/2}$ Ti^{III} component obtained from the fitting procedure.

about 530.6 eV) that is attributed to the presence of the Ti^{III} sites and oxygen species (OH groups, water).[50]

The Ti2p and O1s XPS spectra after molecular deposition are reported in Fig. S1, ESI.† We notice that after the deposition of a sub-monolayer of $TbPc_2$ molecules, the Ti^{III} component of the TiO_2-HT sample is significantly suppressed from 3.4 to 1.7% (see Table S1, ESI†), as observed when molecular species are preferentially bound to the oxygen vacancy sites.[32] The high energy component of the O1s signal is only faintly altered by molecular deposition (see Table S1, ESI†). The C1s and N1s core level XPS spectra after $TbPc_2$ deposition on TiO_2(110) are shown in Fig. 2. The reference spectra of a thick $TbPc_2$ film (about 14 nm) on Au(111) are shown in the top of Fig. 2 and labelled as $TbPc_2$ bulk (in the bulk reference spectra, we have omitted the Tb3d peaks, due to an overlap between this signal and the KLL Carbon Auger peaks[51]). The bulk reference C1s spectrum for $TbPc_2$ is characterized by two main components, one at 284.0 eV corresponding to the benzene carbon species and the second one at 285.2 eV attributed to the pyrrole carbon, and two shake-up components at 286.9 and 287.9 eV. The N1s spectrum of $TbPc_2$ bulk shows a single component at 398.0 eV and a shake-up component at 399.4 eV. The C1s and N1s contributions of the reference spectra agree with the expected bulk features of phthalocyanines-based compounds,[32,51–53] thus indicating the integrity of molecules upon thermal sublimation.[32,52] Interestingly, both N1s and C1s signals are strongly altered when $TbPc_2$ molecules in the sub-monolayer are in contact with titanium dioxide. On the TiO_2-HT substrate,

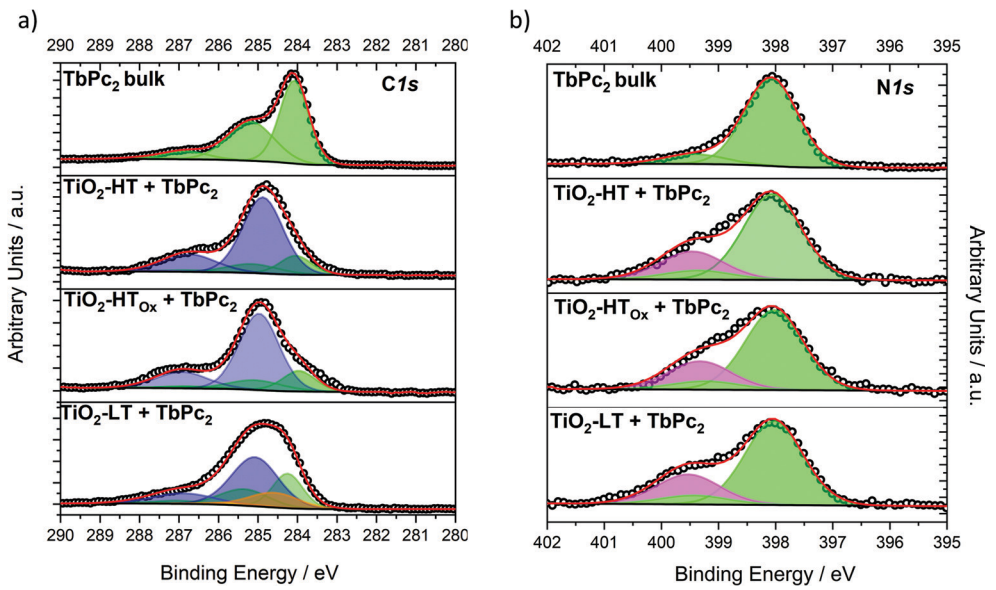

Fig. 2 (a) C1s and (b) N1s core level XPS spectra of a $TbPc_2$ thick film on Au(111) ($TbPc_2$ bulk) and $TbPc_2$ sub-monolayer films on the TiO_2(110) surfaces prepared using different procedures (see text). Bulk-like molecular components are shown in green, while interacting components are shown in blue and pink.

the C1s region (Fig. 2a) shows two main peaks around 284.9 and 286.9 eV and a small shoulder around 284.0 eV. The main features are ascribed to the benzene and pyrrole carbon signals (blue components) shifted from the bulk ones (green components) towards higher binding energies of 1.1 and 1.8 eV, respectively, thus denoting a strong interaction with the surface. Bulk components arise from the shoulder at 284 eV and are fitted in addition to the interacting components.[32] The coexistence of interacting and bulk-like components was found in the XPS C1s core-level spectrum of metal or free-base phthalocyanines on TiO_2.[30–33] The high binding energy components were attributed to strong interfacial interactions between the surface and molecules in the first molecular layer, indicating that molecules undergo an oxidation process.[30–33] Interacting components were found to vanish with increasing film thickness, where bulk-like feature dominated.[30,32] In analogy with phthalocyanine deposits,[30–33] also in the present case, bulk-like components in the C1s spectrum of $TbPc_2$ on TiO_2-HT could arise from molecules in the second layer, whose presence is further confirmed by STM experiments reported below. Besides, the absence of shake-up signals related to the interacting components of the C1s signal (Fig. 2a) suggests an electron depletion from the molecular layer.[30–33]

In line with the C1s spectrum, the XPS N1s signal of the $TbPc_2$ monolayer on TiO_2-HT deviates from the bulk behaviour (Fig. 2b). The spectrum is characterized by two components, the first one at 398.1 eV and the second one of a lower intensity at about 399.4 eV. The low energy component (green) is characteristic of bulk-like or non-interacting $TbPc_2$ molecules, while that at 399.5 eV (pink) indicates the presence of oxidized molecular species, in line with previous observations of Pc species on TiO_2[30–33] or oxidized $TbPc_2$ complexes grafted on silicon.[22]

To clarify whether this interaction arises from the specific TiO_2 reactive sites, such as O-vac,[38] we performed the study on the O-vac-free TiO_2(110) surface (TiO_2-HT_{Ox} sample). O-vac defect suppression due to oxygen exposure (see Experimental methods) results in the almost total disappearance of the Ti^{III} component as evident in the Ti2p XPS spectrum (see Fig. 1 TiO_2-HT_{Ox} and Table S1, ESI†) and the high binding energy (defect-related) component detected in the O1s spectrum (529.8 eV, Fig. S1, ESI†). After $TbPc_2$ deposition, the XPS C1s and N1s (TiO_2-HT_{Ox}, Fig. 2) signals look similar to those obtained for TiO_2-HT, showing no significant variation in energy and intensity. Furthermore, the Ti2p and O1s signals are not significantly altered by the deposition. These results indicate that the O-vac sites do not play a central role in the charge transfer process between the $TbPc_2$ molecules and the surface. This is at variance with other molecular compounds, such as 4-*tert*-butyl pyridine,[38] but in line with previous observations on similar systems as the Zn-phthalocyanine films.[32] Furthermore, it was shown by XPS that FePc/$FePcF_{16}$ deposited on TiO_2 on differently prepared substrates was not affected by surface oxidation.[54] However, in this case, the Pc rings weakly interacted with the substrate.[54]

The last $TbPc_2$ sub-monolayer deposition was carried out on the TiO_2-LT sample, presenting the most significant deviation from the expected TiO_2 stoichiometry (see Table S1, ESI†). Here the Ti2p XPS core level spectrum (Fig. 1) is still dominated by the $Ti2p_{3/2}$ component of Ti^{IV} but shows a higher intensity of the Ti^{III} component (7.3% of total signals, see Table S1, ESI†). The Ti2p shake-up features and the O1s core level spectrum (Fig. S1, ESI†) of the clean TiO_2-LT surface are similar to those observed in the previous samples. Furthermore, a residual C1s signal is detected on the surface of the TiO_2-LT sample after low-temperature annealing (see Fig. S2, ESI†). The C1s region after molecular deposition (Fig. 2) reveals a complex spectral profile that was fitted using the C1s components of the bulk $TbPc_2$ spectrum, the interaction components (two peaks around 284.9 eV and 286.8 eV), and the additional component given by the adventitious carbon present on the surface before molecular deposition. The N1s spectrum of the $TbPc_2$ sub-monolayer on TiO_2-LT (Fig. 2b) displays two components, in line with TiO_2-HT and TiO_2-HT_{Ox} (the first one at 398.0 eV and the second one of lower intensity at 399.5 eV). Therefore, both C1s and N1s XPS spectra of $TbPc_2$ on TiO_2-LT confirm the presence of the interacting components of comparable intensity with respect to the previous samples. From the XPS results, it is evident that the presence of highly interacting $TbPc_2$ molecules is independent of the TiO_2 surface preparation treatment and the presence of the Ti^{III} sites on the surface. The XPS Tb region was partially covered by the C_{KLL} Auger peak and cannot be used for the semiquantitative analysis or for understanding the possible involvement of the Tb ion in the surface interfacial interaction. The FWHM parameters and peak energy used to fit the C1s and N1s spectra of all samples are reported in Table S2, ESI.†

STM experiments were performed on the three samples to investigate the morphological properties of the TiO_2 samples before and after $TbPc_2$ sub-monolayer deposition. Fig. 3a reports an STM image of the clean TiO_2-HT surface. Here bright and dark rows along the [001] direction are associated with the Ti5c rows and bridging-oxygen rows, respectively, that are characteristic of the TiO_2(110)-(1 × 1) reconstruction.[27,39] This reconstruction was also confirmed by Low Energy Electron Diffraction (LEED) analysis (see Fig. S3, ESI†). Fig. 3a shows the presence of point defects, mainly appearing as small bright dots (labelled as type A defects) ascribed to vacant oxygen atoms in the bridging-oxygen rows. These defects are typically observed after the high-temperature annealing procedures.[27,39] Additional point defects of a greater size, type B, are shown in Fig. 3a. Line profiles taken across both A and B defects show that they have FWHM values of 0.45 and 0.55 nm, respectively (see Fig. S4, ESI†). Type A defects show the typical size of O-vac (FWHM about 0.5 nm from the literature[39]), while type B defects could be identified as the hydroxyl groups coming from water molecule dissociation at the vacancy sites.[37] Additionally, the relatively high amount O-vac (type A defects), about 20% of the surface, indicates the advanced state of the surface reduction process due to a large number of sputtering and annealing cycles in UHV. The dark colour of the TiO_2 crystal and the presence of Ti_2O_3 clusters (marked with an X in Fig. 3a) or strands growing along the [001] direction (see elongated

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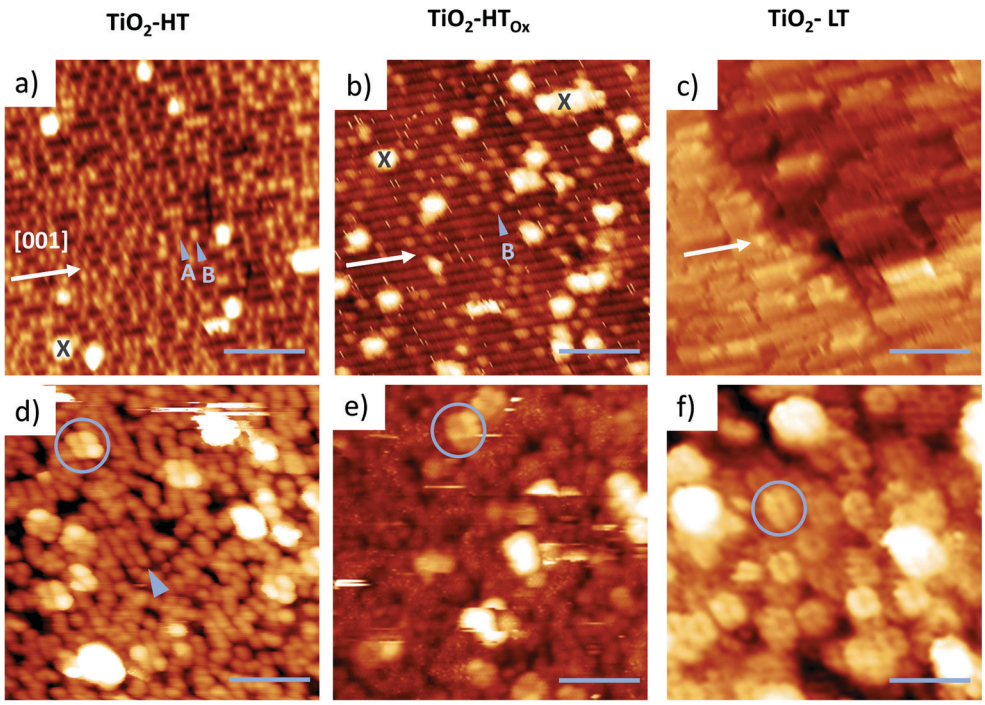

Fig. 3 STM characterization of the TiO_2-HT, TiO_2-HT_{OX} and TiO_2-LT samples before (a–c) and after (d–f) $TbPc_2$ deposition, respectively. White arrows indicate the [001] direction. Triangles indicate different point defects on the surface as O-vac sites (A) and OH groups or water molecules (B). Ti_2O_3 clusters or strands are marked with an X (see text). Circles indicate a single molecular unit. STM parameters: (a–c) 2 V, 200 pA; (d–f) 2 V, 3 pA. The scale bar corresponds to 4 nm.

bright features in the Fig. S5a, ESI†) are additional pieces of evidence of the advanced reduction state.[27,55]

Analogous to the TiO_2-HT case, the clean TiO_2-HT_{Ox} surface shows Ti and O rows alternating with the same regular periodicity (Fig. 3b). The greater amount of Ti_2O_3 strands (marked with X in Fig. 3b), which is more evident at larger scales (Fig. S6a and c, ESI†), is the consequence of the reiterated reduction process in UHV and subsequent exposure to molecular oxygen.[55,56] In Fig. 3b, no O-vacs are present on the surface as a consequence of the oxygen exposure.[39] At variance, small dots in Fig. 3b (type B defects) ascribed to OH groups or water molecules remain on the surface after oxygen exposure (see also line profile in Fig. S6c and d, ESI†).[37] Instead, the TiO_2-LT sample (Fig. 3c) appears to be characterized by a massive presence of Ti_2O_3 strands, while type A and type B defects are no longer evident. However, the greater surface roughness caused by the low-temperature annealing,[40] hinders the precise characterization of the TiO_2(110) surface reconstruction on the atomic scale.

Before studying the deposition of $TbPc_2$ on TiO_2, molecules were deposited in a sub-monolayer amount on a noble metal substrate, *i.e.* Au(111), to confirm the integrity, purity and dose of the molecular deposit. STM images and line profiles of the molecules on Au(111) (Fig. S7, ESI†) indeed show the presence of $TbPc_2$ molecules covering about 15% of the surface, packed in ordered molecular clusters and having a height of about 0.5 nm, in good agreement with the molecular structure and with previous studies on Au(111).[57] After depositing a similar $TbPc_2$ dose on the TiO_2-HT surface, the clean substrate's alternated bright and dark rows are no longer evident (Fig. 3d). However, the comparison of STM images and line profiles before and after deposition (Fig. S5, ESI†) confirms that monoatomic steps are still visible as expected from the sub-monolayer molecular coverage. Features with four-lobed shapes in Fig. 3d (circle) are ascribable to the presence of $TbPc_2$ molecules, similarly appearing on metals[19,57] or metal oxide surfaces.[18] Surface coverage is around 15%, compatible with that observed on the reference Au(111) surface. STM images reveal that molecules in the first layer adsorb with an inclination of the Pc planes from the surface plane of about $30^\circ \pm 5^\circ$ (see line profiles in the Fig. S8, ESI†), causing the different brightness of the four lobes characterizing the single molecular unit. Similar tilting angles could be envisioned for molecules partially sitting on bridging-oxygen sites, as observed for phthalocyanine compounds.[58] $TbPc_2$ molecules lie isolated on the surface and adopt a random distribution and orientation at variance with a high-ordered molecular packing found on most surfaces.[17,57,59] We stress that this is a further indication of a strong interaction with the surface. In contrast, a weak interaction of the molecules on TiO_2 would cause high mobility similar to what was observed by N. Ishida *et al.* for CoPc.[60] Small bright dots appearing on the surface (indicated by a triangle in Fig. 3d) have dimensions between 0.5 and 0.7 nm (see line profile in the Fig. S8b, ESI†) and may be ascribed to H atoms,[61] hydroxyl groups,[37] and water molecules[62–65] in the residual pressure of the evaporation chamber. Their massive presence on the TiO_2 surface at variance with Au(111), although

molecular depositions were performed under the same molecular exposure and residual pressure conditions, can be envisioned by taking into account the greater surface reactivity of the titania substrate with respect to noble metals.[27,61] Furthermore, the great affinity of TiO_2 to water molecules has been long studied and debated, showing that water molecules can adsorb or dissociate at O-vac sites.[61,62,65,66] Fig. S8c in the ESI† shows the $TbPc_2$ molecules on TiO_2-HT at a larger scale with respect to Fig. 3d and evidences the coexistence of $TbPc_2$ molecules with different heights. By the line profile (Fig. S8d, ESI†), we observe that molecules indicated by empty triangles have a height of *ca.* 0.4 nm and width of about 2.5 nm and therefore could be ascribed to isolated molecules in the second layer.[31,57] These molecules adopt a perfect lying-down configuration with respect to those in direct contact with the surface (filled triangles in the Fig. S8d, ESI†).

Despite the increased difficulty in achieving good scanning conditions, single $TbPc_2$ molecules could be also identified for sub-monolayer deposits on the TiO_2-HT_{Ox} (Fig. 3e, coverage around 10%) and TiO_2-LT (Fig. 3f and Fig. S9, ESI,† coverage 40%) surfaces. The higher coverage observed on TiO_2-HT_{Ox} is consistent with the slightly longer deposition time used for the experiment (see Experimental methods) and a possible change of the sticking coefficient with the surface preparation. Furthermore, the presence of small dots attributed to the OH groups or water molecules in TiO_2-HT is no longer evident on TiO_2-LT, which could be explained by the higher hydrophobic properties of air-exposed TiO_2 substrates.[67]

Finally, the overall STM characterization shows that the different substrate treatments used for TiO_2 preparation induce a similar adsorption configuration and random distribution of the $TbPc_2$ molecules on the surface.

Conclusions

We investigated the structural and chemical properties of a sub-monolayer deposit of $TbPc_2$ molecules on the rutile TiO_2(110) surfaces prepared in UHV by different methods. In particular, we tested three different TiO_2 surface preparations where the annealing temperature and oxygen exposure were varied in order to modify the presence of surface defects, Ti^{III}/Ti^{IV} ratio, as well as sample stoichiometry. The XPS analysis evidenced that all samples are characterized by a strong surface–molecule interaction observed in the C1s and N1s spectra of the molecular deposits, strongly differing from the expected bulk-like behavior. The presence of interacting components at a high binging energy points towards an electron transfer from the molecule to the TiO_2 surface. We found that molecular oxidation does neither correlate specifically with the presence of oxygen vacancies on the surface nor with the Ti^{III} content detected by XPS. Still, it is more likely to be dependent on the intrinsic bulk properties of the TiO_2(110) surface as reported for other phthalocyanine-based systems.[32] The differences in the surface defects present in the investigated TiO_2 samples do not particularly affect the molecular adsorption configuration observed in the STM images. At variance with other non-metal substrates, the lying-down orientation of the Pc molecular plane is observed, and molecules lie isolated with a random distribution. This tendency to lie isolated could be interesting for local STM spectroscopy experiments intended to probe single-molecule features.[68] Additionally, the strong surface–molecule interactions detected by XPS are expected to impact the electronic and magnetic properties of the molecules. In light of the enhanced magnetic bistability observed for $TbPc_2$ on other non-metal substrates and, in particular, on MgO,[17,18,22] the investigation of the magnetic properties of the $TbPc_2$ sub-monolayers on the TiO_2 surfaces by X-ray Magnetic Circular Dichroism appears particularly interesting.

Author contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge the financial support by European COST Action CA15128 MOLSPIN and the FET Open Femtoterabyte project. The financial support by Italian MIUR for Progetto Dipartimenti di Eccellenza 2018–2022 (ref. no. B96C1700020008), for PRIN project Q-ChiSS (2017CR5WCH), for Regione Toscana POR CreO FESR 2014–2020- SENSOR, and Fondazione Ente Cassa di Risparmio di Firenze is also acknowledged.

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