X-ray absorption and photoemission spectroscopy of zinc protoporphyrin adsorbed on rutile TiO 2 (110) prepared by in situ electrospray deposition

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Zinc-protoporphyrin, adsorbed on the rutile TiO$_2$(110) surface, has been studied using photoemission spectroscopy and near-edge absorption fine structure spectroscopy to deduce the nature of the molecule-surface bonding and the chemical environment of the central metal atom. To overcome the difficulties associated with sublimation of the porphyrin molecules, samples were prepared *in situ* using ultrahigh vacuum electrospray deposition, a technique which facilitates the deposition of nonvolatile and fragile molecules. Monolayers of Zn protoporphyrin are found to bond to the surface via the oxygen atoms of the deprotonated carboxyl groups. The molecules initially lie largely parallel to the surface, reorienting to an upright geometry as the coverage is increased up to a monolayer. For those molecules directly chemisorbed to the surface, the interaction is sufficiently strong to pull the central metal atom out of the molecule. © *2010 American Institute of Physics*. [doi:10.1063/1.3336747]

I. INTRODUCTION

At the heart of dye-sensitized solar cells lies a charge transfer interface comprising a photoactive dye molecule adsorbed to a wide band gap semiconductor surface.[1,2] Absorption of light induces electron excitation to previously unoccupied molecular orbitals on the dye molecule from which they can tunnel into the conduction band of a semiconductor substrate.[1] The charge transfer dynamics of such an interface is determined by both the chemical and electronic coupling of the molecule and the surface.[3] It is possible to conceive of a single molecule sensor based on the coupling to a semiconductor surface of a photoactive molecule, where either the chemical or electronic coupling can be modified by an interaction with another molecule. Metal porphyrins are excellent candidates for such an arrangement. They are photoactive and have already been identified as candidates for solid state dye-sensitized solar cells.[4] Moreover, metal porphyrins can reversibly bind small molecules to the central metal atom,[5] and in doing so, inevitably change their electronic structure which in turn may well modify the charge transfer coupling to a surface to which they are adsorbed. In addition, metal porphyrins are promising molecular building blocks for the self-assembly of functional layers and macrostructures on surfaces,[6,7] and thus have real potential in the realization of devices for chemical sensors and nanoscale optical and magnetic materials.[8] A detailed understanding of the adsorption of metal porphyrins on a variety of surfaces, and in particular of the chemical functionality of the adsorbed molecules, is

therefore key to progress in this area. In this paper we turn our attention to the adsorption of zinc protoporphyrin on the TiO$_2$(110) surface.

In order to fully explore the interaction between various porphyrins and the surface of TiO$_2$(110) and other wide band gap semiconductors, we can use a range of high resolution ultrahigh vacuum (UHV) techniques such as scanning tunneling microscopy (STM) and synchrotron radiation based electron spectroscopies to probe the adsorption bonding, molecular orientation, and electronic structure of the adsorbed molecules. However, the range of porphyrin molecules that can be studied under UHV conditions through evaporation onto well-defined surfaces is limited by the fragile and nonvolatile nature of many porphyrins. A few specific, volatile porphyrins have been successfully studied in this way and typically show well-ordered molecular layers in which the porphyrin molecules have a flat orientation with the molecular plane lying parallel to the substrate.[9] Combined STM and near edge x-ray absorption fine structure (NEXAFS) spectroscopy have also demonstrated the ability of such molecules to address molecular recognition and self-assembly on metal surfaces.[10] In addition, a wide range of metal atoms can be incorporated into the center of the molecule, which present active sites to reversibly form porphyrin-ligand complexes,[11,12] and thus the possibility to tune the selectivity of porphyrin-based functional surfaces.

In this paper we describe the first *in situ* study of zinc-protoporphyrin (ZnPP) adsorption on a rutile TiO$_2$(110) surface. The molecule has been chosen in the context of the above discussion due to the two carboxylic acid groups on only one side of the porphyrin ring which can be used to

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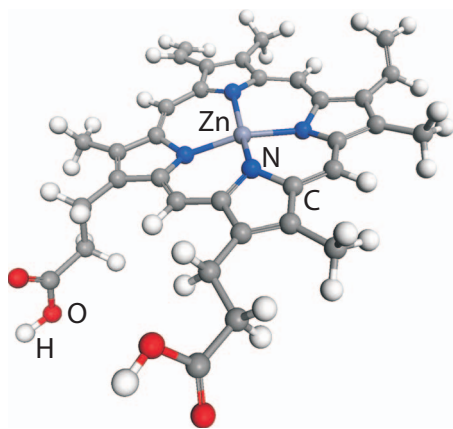
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FIG. 1. Schematic representation of the zinc-protoporphyrin IX complex, showing the largely planar structure of the porphyrin ring containing the Zn^{2+} central metal ion. A key feature of the molecule is the two carboxylic anchor groups on one side of the ring.

chemically anchor the molecule to the oxide surface (see Fig. 1), allowing the porphyrin ring to tilt away from the surface and retain its functionality with respect to binding to a "guest" molecule. Since this molecule is too thermally labile to be deposited by evaporation, we have used the technique of UHV electrospray deposition. The electrospray apparatus, developed in-house, allows nonvolatile molecules to be deposited at pressures between 1×10^{-7} and 1×10^{-9} mbar.[13] Molecules shown to have been successfully deposited using this technique include polymers,[14–16] dye molecules,[13,17] carbon nanotubes,[18] and C_{60}.[19,20] Here, the technique has been used to deposit a wide range of surface coverages from a fraction of a monolayer to several monolayers for *in situ* analysis using synchrotron radiation based photoemission and x-ray absorption spectroscopy.

II. METHODS

Experiments were performed at the undulator beamlines 5U.1 of the SRS Daresbury Laboratory (UK) and I311 of the MAX-laboratory synchrotron radiation facility[21] (Sweden). The photon energy ranges of the beamlines are 100–1000 and 30–1500 eV, respectively, both delivering radiation with such a high degree of elliptical polarization that it may be considered as linearly polarized. The base pressures in the analysis and preparation chambers were $<1 \times 10^{-10}$ mbar for both beamlines and each was equipped with a hemispherical electron analyzer.

The zinc-protoporphyrin IX (ZnPP), formally referred to as 3,7,12,17-tetramethyl-8,13-divinyl-2,18-porphinedipropionic acid (Sigma-Aldrich) was deposited by *in situ* UHV electrospray deposition, from a solution of ~1 mg of ZnPP in 10 ml of a 1:1 methanol/toluene mixture. The apparatus used and the process by which the molecules are taken from *ex situ* solution to *in situ* vacuum are described in detail in Ref. 13. Briefly, the liquid is pushed through a hollow stainless-steel emitter held at ~2 kV. Here, the liquid becomes ionized and a jet emerges consisting of multiple charged droplets. The resulting plume enters a series of differentially pumped molecular beam skimmer apertures via a grounded entrance capillary and gradually

loses its solvent molecules through evaporation and a cascade of Coulomb fission events. Between depositions, the electrospray system was sealed off from the preparation chamber using an UHV gate valve. With the valve open, but the emitter voltage off and thus no electrospray process occurring, the pressure in the preparation chamber was $\sim 2 \times 10^{-8}$ mbar. With the voltage turned on, the preparation chamber pressure rose to $\sim 5 \times 10^{-7}$ mbar, the additional pressure being due to residual solvent molecules in the molecular beam. Different surface coverages were obtained by varying the deposition time.

The rutile $TiO_2(110)$ crystals ($10 \times 10 \times 1$ mm^3), mounted on a tantalum backplate, were cleaned by repeated cycles of sputtering with 1 keV Ar$^+$ ions for 10 min, followed by annealing by electron bombardment at a temperature of ~ 550 °C for 10 min until no carbon signal could be observed in the C 1s photoemission. For the experiment carried out at beamline I311, Auger-yield NEXAFS spectra were measured at the N 1s absorption edge using a Scienta 200 analyzer. For the experiment carried out at beamline 5U.1, total yield NEXAFS spectra were measured by recording the sample drain current. The photon energy was calibrated by taking the energy separation of the C 1s core-level photoemission peaks excited by x rays in first and second orders. For all measurements, the sample was swept continuously at a rate of at least 1.25 μm/s, following beam damage studies to determine a safe exposure time. All photoemission spectra were calibrated to the substrate O 1s peak at 530.05 eV (Ref. 22) unless otherwise stated, and for curve-fitted spectra, a Shirley background was subtracted before fitting to a combination using Voigt functions.

III. RESULTS AND DISCUSSION

Figure 2 shows the O 1s photoelectron spectra obtained for a range of ZnPP surface coverages, from submonolayer to thick film. Taking first the spectrum for the submonolayer (which we estimate to be approximately 0.5 ML), we see that while it is clearly dominated by the substrate oxide signal, there is only a single molecule O 1s peak. This arises due to the deprotonation of the carboxyl groups and the subsequent bonding of the oxygen atoms to titanium atoms in the surface. Both oxygen atoms of the molecule are thus in chemically equivalent states. Deprotonation and the formation of a so-called 2M-bidentate bond to the surface[23] are common features of aromatic carboxylic acid molecules adsorbed on TiO_2 and indeed larger molecules with carboxylic anchor groups.[13,22,24,25] The same situation is observed for the monolayer spectrum with an enhancement in the O 1s molecule component relative to the substrate contribution due to an increased number of molecules on the surface. For the multilayer, which was estimated to be two or three layers thick, however, two molecular components are observed. The high binding energy component is assigned to the —OH oxygen group, while the low binding energy component is attributed to the =O oxygen of the carboxylic group. As the coverage is further increased, the ratio of these two components reflects the 1:1 ratio of these chemical states in the intact molecule. The results show that only the molecules in
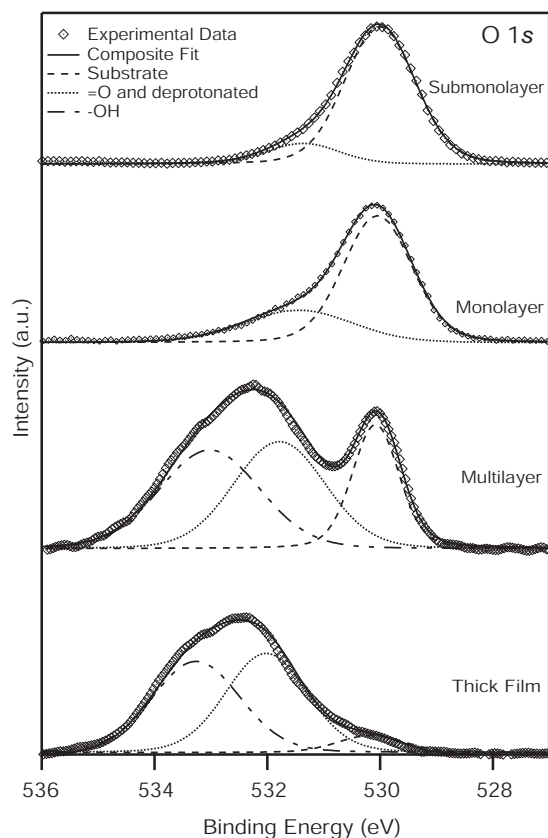
FIG. 2. O 1s core-level photoemission spectra measured using a photon energy of hν=600 eV for different surface coverages of the Zn protoporphyrin on TiO$_2$(110). Spectra are calibrated to the oxide substrate peak.

FIG. 3. C 1s core-level photoemission spectra, measured using hν =340 eV, for a very low submonolayer, submonolayer, monolayer, and a multilayer of Zn protoporphyrin on the TiO$_2$(110) surface.

the layer closest to the surface contain deprotonated carboxylic groups, which form covalent bonds to the oxide surface. The bond formation requires some degree of commensurability with the titanium atoms in the underlying oxide surface, as with the case of bi-isonicotinic acid,[26] which is probably facilitated in the case of ZnPP by the flexibility of the side chains on which the carboxylic groups are located (see Fig. 1). The flexibility of these chains also makes the simultaneous interaction of the porphyrin ring with the surface a possible secondary bonding mechanism. Information concerning this possibility can be found in the C 1s data (Table I).

C 1s core-level photoelectron spectra for surface coverages ranging from approximately 0.2 ML (referred to as very
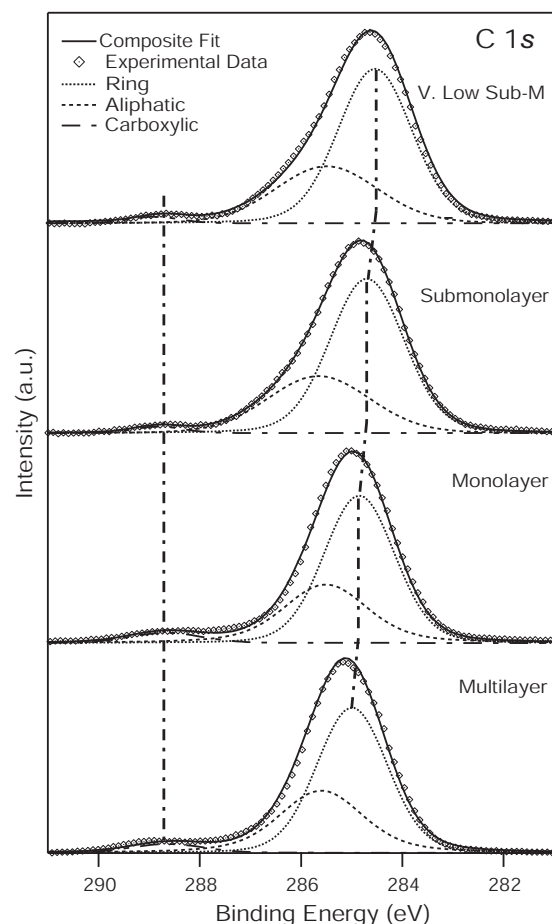
low submonolayer) to a multilayer coverage of ZnPP on the TiO$_2$(110) surface are shown in Fig. 3. These spectra were calibrated to the carboxylic group peak at 288.8 eV (in the absence of a substrate reference point at higher coverage) and illustrate the changes observed in the separation of peaks as a function of coverage. The main carbon peak can be fitted to two components representing the aliphatic carbons in the side chains at around 285.5 eV binding energy, and the ring carbons to lower binding energy. It is in the binding energy position of the ring carbons that we find the most significant change, as it varies from 284.6 eV at a fraction of a mono-

TABLE I. Parameters for the C 1s spectra [all binding energy and full width at half maximum (FWHM) values are in eV]. All the spectra are calibrated to the C 1s carboxyl peak.

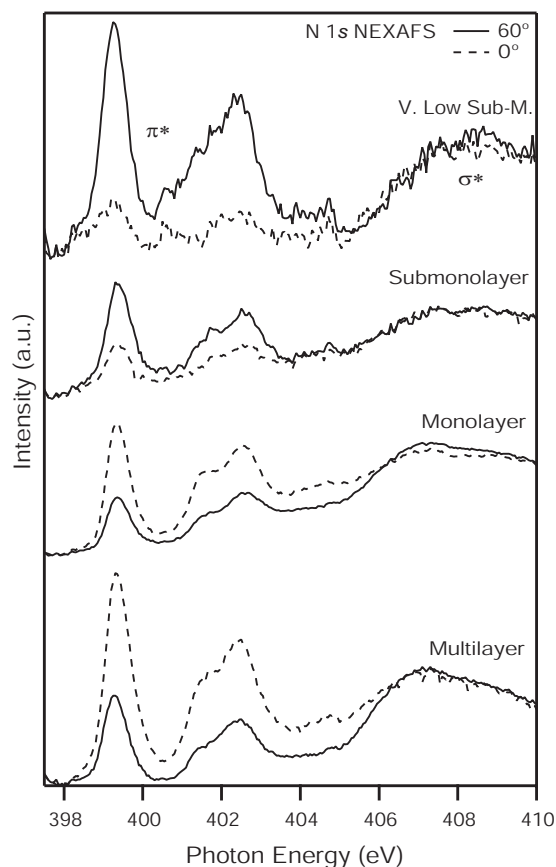|		Very low submonolayer	Submonolayer	Monolayer	Multilayer
Binding energy of	Ring C	284.6	284.7	284.8	285.0
	Aliphatic C (with respect to ring C)	+0.9	+0.9	+0.6	+0.6
	Carboxyl C (with respect to ring C)	+4.2	+4.1	+3.8	+3.6
FWHM of	Ring C	1.6	1.6	1.5	1.5
	Aliphatic C	2.2	2.2	1.5	1.5
	Carboxyl C	1.1	1.1	1.6	1.6
Normalized area of	Ring C	0.6	0.6	0.6	0.6
	Aliphatic C	0.3	0.3	0.3	0.3
	Carboxyl C	0.04	0.04	0.1	0.1

FIG. 4. N 1s NEXAFS at 0° (NI) and 60° incidence for a very low sub-monolayer, submonolayer, monolayer, and a multilayer of ZnPP. Spectra have been normalized to a point far above resonance at 425 eV.

layer coverage to 285.0 eV in the multilayer. Thus, as the coverage is increased the binding energy of the ring carbon shifts upward in energy relative to both the carboxylic carbon and the aliphatic chains. This suggests an interaction of the porphyrin ring at very low coverage which provides enhanced screening of the ring structure by the highly polarizable oxide surface, resulting in a lower binding energy. As the coverage is increased, this screening is diminished, most likely reflecting a change in the adsorption geometry of the molecule as the surface becomes more densely occupied. Due to the largely planar structure of the molecule, this is a question that can be best addressed by measuring the angular dependence of the delocalized π^* states of the molecule in the N 1s NEXAFS as a function of surface coverage.

For the porphyrin molecule, the dipole matrix element associated with the excitation to the π^* orbitals is oriented perpendicular to the plane of the aromatic ring structure. The π^* resonance intensity will thus be maximized when the polarization vector of the light lies perpendicular to the molecular plane.[27,28] Figure 4 shows a comparison of the N 1s NEXAFS spectra measured at normal incidence (NI)—with the polarization vector of the incoming radiation in the plane of the surface—and at grazing incidence (60°)—with the polarization vector 30° off normal to the surface—as a function of coverage. The spectra were normalized to a point far above resonance at 425 eV photon energy in order to compare the intensities of the resonances at each angle and cov-

erage. For the lowest coverage (very low submonolayer), the π^* resonances, which include the lowest unoccupied molecular orbital (LUMO) at 399.3 eV and the double at peak around 402 eV, are much stronger at 60° than at NI. This indicates that the majority of molecules lie down on the surface. This is consistent with the C 1s binding energy shifts observed in Fig. 3, which suggest a stronger interaction of the porphyrin ring with the surface at very low coverage. A similar angular dependence is observed at a higher submonolayer coverage in Fig. 4, although the contrast is not as stark, indicating either less order in the adsorbed molecules or that the molecules adopt a more tilted geometry—albeit still more flat than upright. Again, this is consistent with the C 1s data which suggest a slightly reduced screening of the ring structure with increased coverage. At a monolayer coverage, we observe a dramatic reversal of the angular dependence in the NEXAFS. At this coverage, the π^* resonances are strongest at NI, indicating that the molecules are now more upright on the surface, and this continues to be the case for several multilayers until we reach a completely disordered thick film (not shown here) where no angular dependence is observed.

The picture that emerges from the photoemission and NEXAFS data therefore indicates a combination of two surface interactions. The deprotonation of the carboxylic groups observed in the O 1s photoemission indicates that the molecules are chemically anchored to the titanium dioxide surface. However, the flexibility of the side chains, which connect the carboxylic anchor groups to the rest of the molecule, allow for the porphyrin ring structure to also interact with the surface at very low coverage, where there is less steric hindrance. This is reflected in an increased screening of the ring carbons in the C 1s spectra due to this ring interaction, and confirmed by a strong angular dependence in the N 1s NEXAFS consistent with a planar molecule largely parallel to the surface. However, as the surface coverage increases toward the first complete monolayer, the molecules adopt an increasingly upright adsorption geometry as the strong chemical coupling of the deprotonated carboxyl groups to the surface dominates over the weaker interaction between the π electrons of the ring and the oxide surface. This is reflected in both the decreased screening of the ring carbons in the C 1s photoemission and the orbital angular dependence in the N 1s x-ray absorption.

In principle, the tunable orientation of the porphyrin molecules on the surface could offer a route to selectivity and specificity in surfaces functionalized with these molecules and their derivatives. However, such functionality would depend on the chemical environment of the central metal atom and its ability to bond to introduced guest molecules. The best windows onto this functionality are the N 1s and Zn 2p photoemission spectra, which are shown for a monolayer, multilayer, and thick film coverage in Fig. 5. Considering first the spectra for a thick film of ZnPP, we can see that the molecule is deposited by UHV electrospray deposition in its entirety. The N 1s spectrum exhibits a single nitrogen chemical state,[29] with a peak at 398.2 eV—reflecting the fact that all four nitrogen atoms in the molecule are coordinated to the zinc atom in their midst—and the Zn
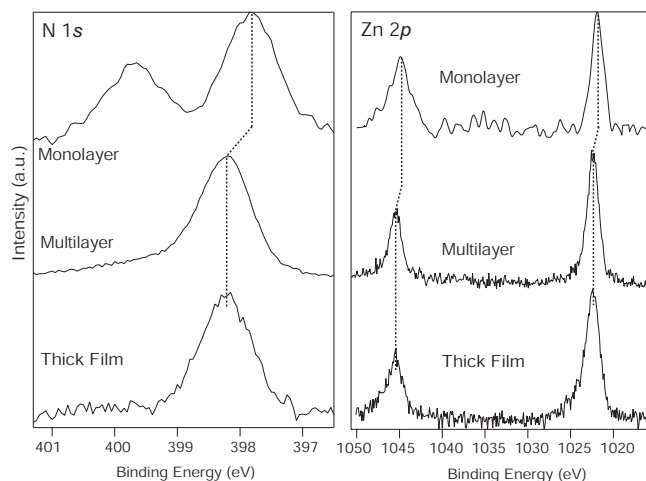
FIG. 5. N 1*s* and Zn 2*p* core-level photoemission for a monolayer, multilayer, and a thick film of ZnPP deposited on the rutile TiO₂(110) surface.

2*p* spectrum shows the spin-orbit pair with the $2p_{3/2}$ component appearing at 1022.4 eV, characteristic of the Zn^{2+} oxidation state.[30] Almost identical spectra are obtained for the multilayer coverage, which again here corresponds to between 2 and 3 MLs. However, if we look at the monolayer spectra, clearly a substantial chemical change has taken place. In the case of the monolayer, the N 1*s* spectrum now contains two nitrogen peaks at binding energies of 399.6 and 397.8 eV corresponding to protonated and deprotonated nitrogens, respectively. This is a characteristic feature of metal-free porphyrins, and the observed values are in agreement with other related works reported in Refs. 31–33. Moreover, a large chemical shift to lower binding energy is observed in the Zn 2*p* spectrum to 1021.4 eV, indicative of the reduction of zinc from its original Zn^{2+} to the neutral Zn^{0} state.[30] These two data set together confirm that for those molecules directly bonded to the surface in the chemisorbed monolayer, the interaction with the surface is sufficiently strong to pull the central metal atom out of the molecule. This process must be a complete removal since the porphyrin center is subsequently occupied by two hydrogen atoms, leading to the N 1*s* photoemission spectrum observed in Fig. 5, and the ring structure is not "tied" to the surface in a flat adsorption geometry, as evidenced by the NEXAFS data. The protons required for this process could be supplied by the deprotonation of the carboxylic anchor groups during the chemisorption of the monolayer, as observed in the O 1*s* spectra in Fig. 2. It should be noted that a change in the π^* resonances is expected to accompany the removal of the central metal atom to form the metal-free porphyrin because there are now two inequivalent nitrogen atoms, as highlighted in the N 1*s* spectrum of Fig. 5. However, Ref. 29 suggests that the results of this process would be a slight increase in the separation of the first two resonances and the appearance of two new resonances around 4–6 eV above the LUMO. The N 1*s* NEXAFS spectra shown in Fig. 4 at the lower coverages are insufficient to confirm the presence of these effects however, and further experiments are required to investigate this aspect in more detail.

IV. CONCLUSIONS

Zinc protoporphyrin has been deposited onto UHV-prepared rutile TiO₂(110) surfaces using *in situ* UHV electrospray deposition. This has allowed us to use synchrotron radiation based x-ray absorption and photoemission techniques to probe the geometric and chemical interaction of the molecule with this surface. From the O 1*s* photoemission, it is clear that the first adsorbed monolayer forms a strong chemical anchor to the titanium atoms of the oxide surface via the deprotonation of the two carboxylic acid groups in a 2M-bidentate fashion. The C 1*s* photoemission and N 1*s* x-ray absorption suggest that at low coverage the interaction of the porphyrin ring can also play a role, which becomes less significant as the coverage and thus the steric hindrance increase. This leads to an adsorption geometry which depends on the surface coverage, adopting a largely flat orientation at low coverage, rising to a more upright geometry at monolayer coverage. N 1*s* and Zn 2*p* photoemission reveals that while the UHV electrospray deposition technique can deposit the molecule intact, the strong interaction of the molecule with the oxide surface is sufficient to pull the zinc atom from the molecule. This has serious implications for the functionality of such surfaces as this process occurs for all coverages over which the adsorption geometry varies. It is therefore not possible in this case to take advantage of both the coverage-dependent molecular orientation *and* the chemical functionality of the metal porphyrin itself. The latter is only possible for surface coverages greater than 1 ML, at which point the molecule adopts a largely upright geometry on the surface. We are currently exploring the interaction of ZnPP with the Au(111) surface, where the carboxylic groups are not expected to deprotonate,[34] to address the question of whether the zinc atom remains within the porphyrin ring of the monolayer under these conditions.

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