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# XPS studies of the adsorption characteristics of 2H-TPP at Fe/Si interface

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Porphyrinic nanomaterials have emerged as potential candidates of various applications in the fields of molecular electronics, photonics and semiconductor sensitization. There has been a great interest in utilizing supramolecular chemistry as a means to fabricate components for nanoscale devices. Metalloporphyrins control the decisive steps in various natural and technological processes which often involve the reversible attachment of a molecular ligand to the central metal ion. This work presents a study of metalation of 2H-Tetraphenylporphyrin (2H-TPP) on Fe metal films onto well reconstructed Si(111)-7× 7 surfaces. In-situ metalation reaction proceeds at 550K to form metalloporphyrin. X-ray Photoelectron Spectroscopy (XPS) studies provide evidence for the Fe coordination with TPP macrocycle and result monolayer formation of metalloporphyrin (Fe-TPP).

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## 1. Introduction

Porphyrins are involved in important biological processes ranging from oxygen transport to photosynthesis and from catalysis to pigmentation changes [1].The common basic structure of the macrocycle consists four pyrrolic subunits bridged by four (meso) carbon atoms. This is an aromatic system of the size which is perfect to bind almost all metal ions, specially the first row of transition metal atoms. Therefore a number of metals (e.g., Fe, Zn, Cu, Ni, and Co) can be inserted in the center of the macrocycle forming metallo-porphyrins. These molecules can be produced via metalation reactions in Ultra High Vacuum (UHV) or many of them are commercially available.

The construction of molecular assemblies which have well-defined shapes dimensions (molecular objects) and pattern formations by self-assembly of molecules are of great interest [2, 3]. Porphyrins are attractive building blocks to form such molecular materials since they are (photo) catalytically active and have interesting electronic properties [4, 5].

The possibility to tailor their physical and chemical properties of porphyrins at the molecular level makes porphyrins and metalloporphyrins extremely versatile in many disciplines of chemistry and physics [6]. It requires a high thermal stability and a sufficiently low reactivity of the complexes for deposition of metalloporphyrins by thermal evaporation. Fe(II)-tetraphenylporphyin is one example for such a very reactive metalloporphyrin. It is particularly interesting with respect to oxygen adsorption but also extremely sensitive toward oxidation and therefore difficult to handle and to obtain as a pure compound [7, 8].

An understanding of the porphyrin/inorganic interface with specific properties is required for optimizing their use in Organo-electronic devices [9. 10] and in realizing new types of organic molecular devices. Nature of the bonding between porphyrin molecules and substrate surfaces is of particular interest which is reflected in the electronic charge distribution and the geometric configuration at the interface. Most of the studies of porphyrins on metal surfacesare on scanning tunneling microscopy/ spectroscopy investigationsin Ultra High Vacuum (UHV) conditions, where the macrocycle is adsorbed flat and the conformation of the meso-substituents changes as a function of the surface termination and the interaction with the substrate [11 – 14].There are only a few studies on semiconductor surfaces [15, 16] and even fewer experiments using other techniques to extract the porphyrin orientations on surfaces [17, 18].

In the present work electronic structure of the interface between 2H-Tetraphenylporphyrin (2H-TPP) and iron on Si (111) substrate is studied using X-ray Photoelectron Spectroscopy (XPS). The choice of these substrates is guided by the fact that the magnetic properties of the molecules are altered by deposition on metal surfaces or metal on semiconductor, suggesting a possibility of engineering magnetic nanostructures for potential use in spintronics.

## 2. Experimental section

The measurements were performed in the UHV experimental chamber (base pressure of $10^{-10}$ mbar) at

Micro & Nano-Carbon Lab of the Elettra Synchrotron facility. First Si(111)-7x7 surface was prepared by removing the natural oxide through annealing at ~ 1200 K. The 7x7 reconstruction of Si is confirmed by Low Energy Electron Diffraction (LEED). The absence of contaminants and ordering of the surface were checked by means of XPS and LEED techniques. Subsequent Fe films were deposited using homemade E-beam evaporator (filament power = 4.7 Amp x 1.5 Volt, High Voltage = 1250 Volt & $I_{emission}$ = 13 Milliamp) for 15 minutes and monitored by XPS. The molecular films are prepared by *in-situ* evaporation of commercial 2H-Tetraphenylporphyrin (2H-TPP) (99.95%, Sigma Aldrich) by an outgassed Ta crucible on a freshly deposited Fe film. The amount of deposited iron and molecules is monitored by XPS. The specimen was annealed at 550 K to see interaction of the iron with TPP macrocycle and yielded metalloporphyrin monolayer at the system. The 2H-TPP monolayer (ML) was obtained by sublimating a predeposited thick film of 2H-TPP molecules on Fe/Si(111) interface at 550 K. We therefore define 1 ML of 2H-TPP as the maximum amount of molecules adsorbed on the substrate surface after the above procedure.

All experiments were performed with a commercial x-ray photoelectron spectrometer (VG-ESCALAB-II) equipped with an Al Kα X-ray source (1486.6 eV) and a hemispherical energy analyzer with base pressure in this UHV system is below $1\times10^{-10}$ mbar. In addition to the XPS spectrometer, the system is equipped with a differentially pumped gas discharge lamp for UV photoelectron spectroscopy (UPS), LEED optics (SPЄCS ErLEED-1000A) and evaporators.

## 3. Result and discussion

The sketch of the metalation reaction of 2H-tetraphenylporhyrin (2H-TPP) are shown in figure a, the metalation reaction is completed at 550 K and metalloporphyrin is achieved as a resultant.

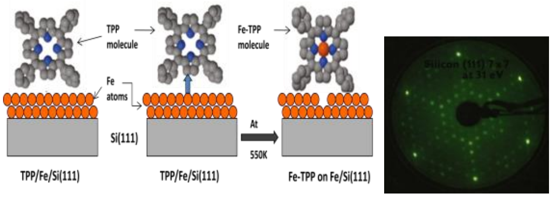

*Fig. 1. Sketch of the proposed metalation reaction at the interface and 7x7-LEED pattern of Si.*

**X-ray Photoelectron Spectroscopy (XPS) Study**: For the spectroscopic investigation, we prepared ~10 ML of 2H-TPP on a Fe deposited Si(111)-7x7 surface. Chemical analysis of the reaction system was carried out by XPS. For studying metalation with Fe, we monitored two core level signals, N1*s* and C1*s*.

XPS spectra provide the straightforward evidence of the Fe coordination with TPP. In particular, the N1*s* spectrum of the 2H-TPP is expected to change when the iron is bound at the center of the macrocycle. In fact, the N1*s* spectrum of 2H-TPP has two easily resolved components because of the two N species (iminic and pyrrolic), whereas the N atoms are equivalent in Fe-TPP, and just one peak is expected.

The 2H-TPP spectra for multilayer and monolayer, reported in Fig.1a and 1b, are composed by two peaks: the one at higher binding energy is assigned to the two pyrrolic N atoms (-NH-), while the lower BE peak corresponds to the two iminic ones (-N=) [19]. The BE values obtained by fitting the spectra are in good agreement with similar results already reported in the literature [20]. Since molecule-surface interactions are not taken into account in the XPS calculations, the theoretically determined values and spectra are compared only to measurements of multilayer where it can be assumed that the substrate hardly has any direct influence on the molecules. While the calculated ionization potentials are referenced to the vacuum level, the measured binding energies are referenced to the Fermi level which leads to an intrinsic difference of several eV between the respective values.

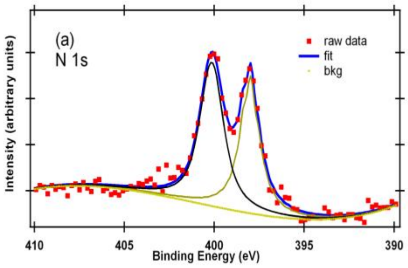

*Fig. 2. N 1s of 2H-TPP at Fe/Si(111) interface.*

The XPS calculations confirm that the binding energy of the pyrrolic nitrogen laid approximately 2 eV higher than that of the iminic nitrogen. It is observed from Fig.2 of TPP/Fe/Si(111) at room temperature (RT), that the pyrrolic peak is broader than the iminic. The fit procedure was made using a Shirley background and Voigt integral functions in multilayer thin films of TPP molecules. Using the same Gaussian function, the best fit returned a Gaussian with a full width at half-maximum (FMHM) of 0.65 eV convoluted with Lorentzian peaks associated to the two N atom components. The values for $\Gamma_N$ and $\Gamma_{NH}$ (Lorentzian width) are 0.459 eV and 0.789 eV, respectively. However, it is difficult to ascertain that the two kinds of N 1s atoms with such fwhm difference have a different core-hole lifetime that should be related to very distinct de-excitation mechanisms [21]. The core-hole de-excitations are mainly due to Auger transitions and, therefore, are controlled by the Coulomb matrix elements that might hardly be different in the two cases. On the other hand, the presence of two nitrogen's bonded with H introduces more phonon modes related to the N-H bond vibrations [21], which can be expected to broaden the pyrrolic peak because of a Franck-Condon mechanism in the photoemission process. The unresolved phonon fine structure in the measured peak can be effectively taken into account by considering a Gaussian broadening of the core level line width.

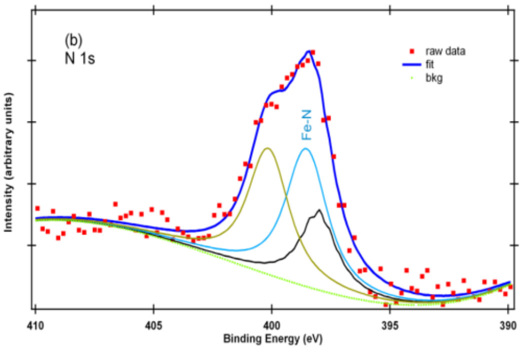

*Fig. 3. N 1s of 2H-TPP at Fe/Si(111) interface after metalation reaction completed at 550K.*

Metalation of 2H-TPP multilayer demonstrated in Fig. 1b, by the formation of Fe-TPP monolayer upon annealing at 550 K. The efficiency of the reaction is lower than for monolayer, In fact the metalation competes with the formation of Fe clusters in the multilayer [22]. Next we studied the change of the spectra induced by annealing. Fig. 3 shows a XPS spectrum of N 1s after annealing at 550 K. This core level spectrum is complicated to resolve the significant peaks in it. The simplest possible approach to interpret the signal, we assumes that it arises from a mixture of the product, Fe-TPP and unreacted TPP, accordingly, attempted a peak fitting procedure with the fitted signals of TPP and Fe-TPP. To obtain better agreement, it was necessary to introduce one additional peak, represented by the middle peak with two nitrogen (shoulders) components (position, width & ratio of intensity were held constant for fitting the peaks in the curve).The main new feature peak is observed at BE = 398.54 eV with two shoulders (-N= and –NH-) at the same BE. After annealing to 550 K the relative intensity ofthe shoulders decreases and the new feature peak is corresponding to the coordination peak of Fe and TPP. The total intensity of the signal is less than in the multilayer suggesting a desorption of the multilayer molecules with a remaining monolayer. The reduction of the two peaks of the inequivalent nitrogen species to one new main component is an indication for the metalation of the 2H-TPP since metalloporphyrins possess four chemical equivalent nitrogen atoms generating only one N1*s* peak. The binding energy of the coordinated nitrogen peak from experimental results are very close to the theoretical binding values of 398.6 eV [23].

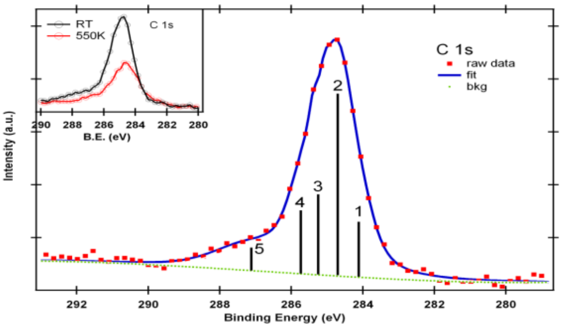

*Fig. 4. Core level of C 1s of 2H-TPP at Fe/Si(111) interface and inset show the shift in binding energy after metalation reaction complete at 550K.*

In Fig. 4 there are observed results which are related to partial thermal desorption of the molecule: the N 1s and C 1s core level intensities show that the total coverage is changed during heating, assuming that the molecules desorbed and monolayer of metalloporphyrin is yielded at the surface. The temperature dependent C 1s core level result has expect to reflect the information about the distance between the molecules and iron atoms on Si (111) substrate as well as the tilting of the molecules. The shift of 0.22 eV in BE of C1s core level (inset of Fig. 4) towards lower binding energy is observed and show the molecular-surface distance is decreased as a result of annealing at 550 K [24]. By the analysis of the C 1s core level, Fig. 4 show the C 1s core level photoemission spectrum of 2H-TPP multilayer on Fe/Si interface. The full-width at half-maximum (~1 eV) and the line shape (with an anomalous asymmetry on the low binding energy side) reveal the presence of several components. There are 24 carbon atoms belonging to the phenyl groups and 20 carbon atoms belonging to the macrocycle. The latter can be separated in meso-carbon bridges (4 atoms) and pyrrolic carbon atoms (16 atoms, 8 of which having a C–N bond). By fitting the core level spectrum with five components having the nearly same width and fixed intensity ratios 5:17:8:6:2, we obtain a good fit as shown in Fig. 4 and the following binding energy positions: 284.7 eV (phenyl), 285.25 eV (C-C-N, pyrrolic), 284.11 eV (C-C-C, pyrrolic), and the remaining two peaks are corresponding to meso-bridges. It is obvious that the fitting is not unique, but this one offers a plausible explanation of the C 1s line shape. In fact, the energy separation between the last two components turns out to be exactly 0.78 eV, is due to the presence of inequivalent C atoms in the macrocycle.

**Band-bending diagram of 2H-TPP at Fe/Si(111) interface**: The adsorption of metal–organic compounds and layers is useful to investigate and tune the energy level alignment at semiconductor [25] and metal interfaces [26], a decisive issue in the field of organic electronics. Recent studies revealed that conformational adaptation needs to be considered in this respect [27, 28], but many aspects remain to be explored to develop the full picture.

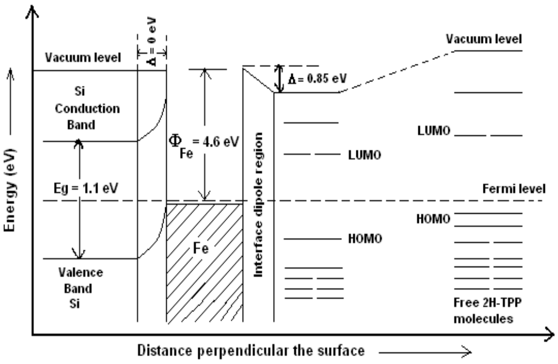

*Fig. 5. Bend-bending diagram of 2H-TPP at Fe/Si(111) interface.*

To understanding the band-bending of the 2H-TPP at Fe/Si(111) interface, we illustrated energy level diagram for this interface and are reported in Fig. 5. It is based on porphyrin/metal/Si interfaces [26], in which the energy levels of the porphyrins are fixed to the vacuum level of the metal with a finite energy shift at the interface (calculated shift in work function or vacuum level is 0.85 eV and represented by Δ). The vacuum level shifts or adsorbate-induced work function changes provide additional information about the nature of the adsorbate-surface interaction and are of potential interest to the organic electronics community [26].

Theoretically, we found work functions of 3.75 and 4.60 eV for monolayer of 2H-TPP and Fe respectively, compared to 4.95 eV for the clean Si (100) surface [29]. The resulting energy-level alignment will affect by various factors. The chemical bonding between the metal and the organic molecule involved a net electronic charge transferred to the metal due to down-shift the vacuum level by introducing a dipole-induced potential step at the interface [30, 31].

## 4. Conclusion

The *in-situ* metalation study of 2H-Tetraphenylporphyrin (2H-TPP) molecules at Fe/Si(111) interface has been studied by X-ray Photoelectron Spectroscopy (XPS). The investigations include the formation of 7x7 crystal structure of Si before the Fe deposition. The 2H-TPP was deposited Fe onto Si. The metalation reaction completes at 550K. XPS results provide the evidence to monitor the progress of the metalation of 2H-TPP. It found that as the reaction proceed the two separate peaks of 2H-TPP evolve into a single peak for the metalated porphyrin, because in the final metalloporphyrin complex, the four nitrogen atoms are chemically equivalent. The band-bending diagram has been drawn upon the experimental and theoretical reported results which is particularly important in order to understand orbital interactions, bond formation and evolution of the electronic properties with doping (oxidation and reduction) in the light of possible applications of porphyrins in donor–acceptor complexes for photovoltaic devices or, given the high molecular symmetry, as prototypical systems for the verification of recent models and phase diagrams for strongly correlated materials.

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