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## Original Article

# Conformational adaptation of 2H-Tetraphenylporphyrin at Fe/Si(1 0 0) interface during metalation

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### ABSTRACT

Many recent studies have highlighted the possibility to tailor the physical and chemical properties of porphyrin at the molecular level to design novel catalysts, sensors and devices with applications in electronics, opto-electronics, etc. In the present work we study the electronic properties of 2H-Tetraphenylporphyrin (2H-TPP) on iron (Fe) and iron silicide (Fe<sub>3</sub>Si) onto Si (1 0 0) substrate using X-ray and Ultraviolet photoelectron spectroscopy (XPS & UPS). The results revealed that the iron atom is coordinated by TPP molecules at Fe/Si system. XPS results provide evidence of the iron coordination with TPP molecules. The UPS analysis show the fine structure in the electronic spectra related to HOMO states below the Fermi level.

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## 1. Introduction

The adsorption of functional molecules on solid substrates has become important in the field of nanoscience strategies by which the nanostructures are grown in a controlled way. It is known that the position and dimension of the molecular assemblies can be tuned and controlled with high precision down to the atomic level on metals [1–3] and semiconductors [4–7]. Developing technologically robust families of adsorbed assemblies on semiconductor surfaces is challenging, especially because the electronic skeleton of molecules is slightly altered after the adsorption [8,9].

Organic/inorganic interfaces are intriguing and challenging because of the wide variety of phenomena they exhibit and these interfaces have evolved as a potential alternative to conventional electronic devices. The flexibility afforded by organic molecular films in terms of modes of deposition, chemical functionalization, molecular mixing and doping opens a number of routes to tailor the interface properties, which would not be possible with inorganic materials [10]. Porphyrins are a flexible class of molecules with a square symmetry planar core conformation (macrocycle) and two-dimensional conjugated  $\pi$  electron delocalization [11–13]. These organic molecules are one of the most studied systems because of their ability to absorb light, to interact with gases, and their involvement in

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many biological systems. However they combine a structure-forming element the porphyrin framework with an active site of the porphyrin core [13].

The intrinsic functionality of porphyrins is given by their ability to bind 1st transition row metal atoms at the center of the macrocycle to form a metalloporphyrin. Many of these molecules are commercially available or can be produced via metalation reactions in Ultra High Vacuum (UHV). The metalation reaction is, in many cases, energetically proved independently on the order of deposition, e.g. adsorbed 2H-TPP molecules react with metal atoms irrespective of which reactant is deposited first.

The commercially available Fe-porphyrins have also a Cl bonded to the iron to stabilize the highly reactive metal that can easily oxidize. The possibility to produce stable Fe-porphyrins with no Cl atoms and to characterize them in situ is an intriguing challenge because of their key role as main building blocks in important biological molecules as well as for magnetic systems and catalytic processes [14,15].

The formation of cobalt (II) and iron (II) tetraphenylporphyrins (MTPP's, M=Co, Fe) from the direct reaction of the bare metal atoms (Co or Fe) and adsorbed tetraphenylporphyrin (2H-TPP) molecules have been reported by Gottfried et al. [16,17]. The adsorbed porphyrin monolayer was efficiently on to the metal atom, which increase the possibility to study metalloporphyrins using surface science techniques at low sample temperatures.

Pure Fe-tetraphenylporphyrin (Fe-TPP) was produced under UHV conditions by in situ metalation of free-base 2H-5, 10, 15, 20-tetraphenylporphyrin (2H-TPP) monolayers with Fe atoms deposited by an electron beam evaporator [17]. STM micrographs showed the appearance of intramolecular protrusions consequent to Fe evaporation and the evidence of the TPP metalation. Similar experiments have been performed for Co and Ce [18]. Moreover, photoemission studies, performed with laboratory X-ray sources, have demonstrated metalation by Fe, Zn and Co of free-base porphyrins by collecting the N 1s core level signal together with the metal peak [19].

In between the present 2H-Tetraphenylporphyrin (2H-TPP) and iron or iron silicide on Si(100) substrate is studied using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS). 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

Measurements were performed in the UHV chamber at a pressure of  $<10^{-10}$  mbar in Micro and Nano-Carbon Lab, Elettra Synchrotron facility, Trieste Italy. Sample preparation was made by in situ evaporating 2H-TPP (99.95%, Sigma Aldrich) by a resistively heated Ta evaporator on magnetic layers at Si(100) substrate. Before the deposition of magnetic layers, Si(100)- $2 \times 1$  substrate surface was first reconstructed by removing the natural oxide by annealing at  $\sim 1200$  K.  $2 \times 1$  reconstruction of Si was confirmed by Low Energy Electron

Diffraction (LEED). The absence of contaminants and ordering of the surface were checked by means of XPS, LEED and UPS. Two different systems were prepared for the spectroscopy measurements in the following ways.

Hundreds of monolayers of Fe atoms were deposited using homemade E-beam evaporator having Filament power =  $4.7 \text{ A} \times 1.5 \text{ V}$ , H.V. = 1250 V,  $I_{\text{emission}} = 13 \text{ mA}$  for 20 min on Si(100) and then evaporated multilayer of 2H-TPP molecules.

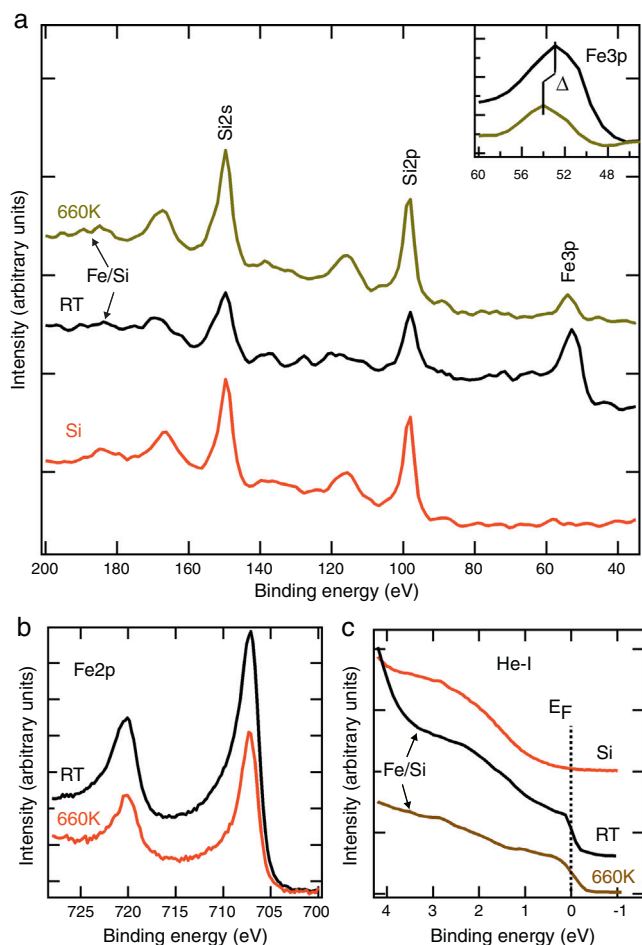
In the second type of sample, first the Fe/Si system was annealed at 660 K for 45 min to form iron silicide ( $\text{Fe}_3\text{Si}$ ). Thereafter multilayer of 2H-TPP molecules was deposited on iron silicide onto Si substrate.

Both specimens were heated at 550 K for 5 min to study the adsorption of the Fe atoms in the TPP macrocycle and yielded metalloporphyrin monolayer at the system.

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

## 3. Results and discussion

The growth of iron and the formation of iron silicide on Si(100) have been followed by XPS and UPS, as shown in Fig. 1. The Fe overlayer thickness can be estimated by the quantitative evaluation of the Si 2p core level peaks area attenuation ( $\sim 90\%$ ). In Fig. 1a a comparison is shown between the wide energy spectrum including Si 2s, Si 2p and Fe 3p core level peaks in the case of clean Si (red), Fe/Si measured at RT (black) and after annealing at 660 K (brown). It is worth noting that Fe 3p rigidly shifts of 1.3 eV toward higher BE (inset of Fig. 1a), while Si 2p & 2s are not shifted after annealing at 660 K. Fig. 1b shows the Fe 2p core shifts of Fe/Si system at room temperature (RT) and 660 K. The binding energy of Fe  $2p_{3/2}$  is located at 707 eV corresponding well to the metallic iron Fe  $2p_{3/2}$  peak for the RT growing sample. An asymmetry iron arises due to an increase in the state density at the Fermi level [20]. The asymmetric line shape indicates the formation of metallic silicides namely  $\text{Fe}_3\text{Si}$  and  $\epsilon\text{-FeSi}$ . The value of the binding energy for a given core level measured by XPS depends on its chemical environment. The XPS spectra show a change in intensity of the silicon peak and the chemical shift occurred for the Fe 3p. The shift in energy toward higher binding energy is observed as 0.11 eV for Fe  $2p_{3/2}$  peak. Moreover, the value of the full width at half maxima is reduced in comparison to the RT case. These shifts and the narrowed line-width of the Fe  $2p_{3/2}$  indicate the formation of the iron silicide ( $\text{Fe}_3\text{Si}$ ) through the reaction between silicon and iron at 660 K. In fact, the value of 0.11 eV is in good agreement with previous reports [21]. However, the silicon 2p and 2s does not show any significant shift after the iron silicide phase formation, disagreeing with the previous reported results [22,23]. Fig. 1c shows the valence band spectrum of Si and Fe/Si system at RT and 660 K. Clean Si shows the well-known surface state band at 0.85 eV below the

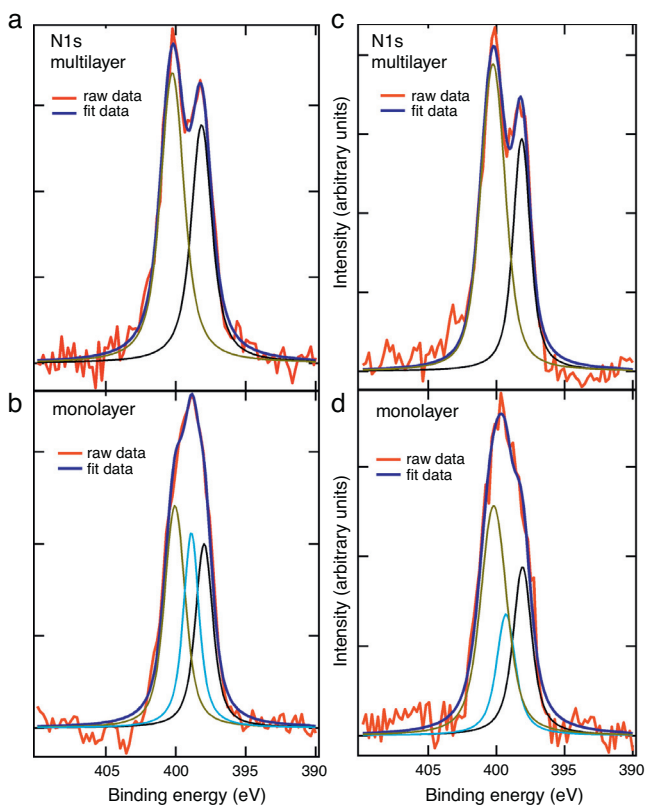


**Fig. 1 – (a) Fe3p, Si2p & Si2s represented in clean Si, Fe/Si at RT and 660 K and chemical shift in Fe3p is shown in Inset. (b) Fe2p: Fe/Si at RT and 660 K. (c) UPS spectra of Si, Fe/Si at RT and 660 K.**

Fermi level and the bulk derived state at 2.8 eV. The Fe/Si spectrum shows a high density of states (DOS) at Fermi level and d-derived peaks at 1 eV, in agreement with spectra for bulk Fe [24]. The new features, near the Fermi level edge arising in the case of iron silicide indicate an overlap between the Fe and the Si bands.

LEED measurements also carried out formation, showing  $1 \times 1$  patterns. The crystal structure ( $DO_3$ ) of  $Fe_3Si$  phase on Si substrate can be described by a cubic unit cell consisting of four bcc and four CsCl type cubes [25]. Different from a pure Fe bcc lattice, the centered iron atom in every other cube is substituted by silicon. As a result the nominal  $1 \times 1$  surface structure is observed for  $Fe_3Si$  phase. The phase diagrams also support the formation [26] of  $Fe_3Si$  on Si at 660 K and because the growth kinetics makes the properties of iron silicide films strongly dependent on the deposition methods of the iron element.

The spectroscopic investigations were undertaken on  $\sim 10$  ML of 2H-TPP on iron (Fe) and iron silicide ( $Fe_3Si$ ) onto Si(100). Chemical analysis of the reaction was carried out using XPS to study metalation with Fe, by monitoring the core level of nitrogen (N 1s) and carbon (C 1s).

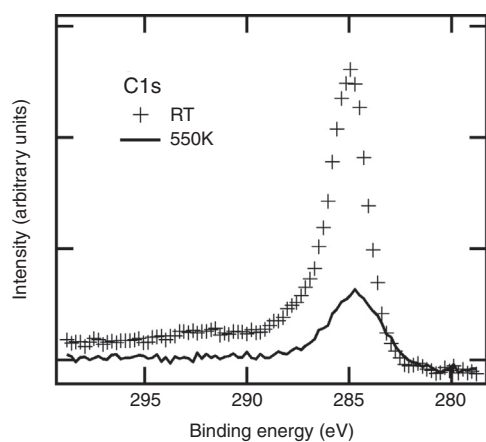


**Fig. 2 – N1s of 2H-TPP/Fe/Si(100) at (a) RT and (b) 550 K. N1s of 2H-TPP/Fe<sub>3</sub>Si/Si(100) at (c) RT and (d) 550 K.**

X-ray photoemission spectra provided 2H-TPP, allowing to follow the changes, in the N 1s core level signal. In detail the N 1s spectrum of 2H-TPP has two easily resolved components of the two N species (iminic and pyrrolic) and as the reaction proceeds, just one peak is expected for the metalated porphyrin (metalloporphyrin). This is because in the final state of metalloporphyrin complex the four nitrogen atoms are chemically equivalent. The N 1s core level XPS of TPP multilayer and formation of metalloporphyrin (Fe-TPP) on Fe and  $Fe_3Si$  onto Si is shown in Fig. 2. In 2H-TPP multilayer, the N 1s (Fig. 2a and c) has two well resolved peaks: the one at higher Binding Energy (BE) is assigned to the two pyrrolic N atoms ( $-NH-$ ), while the lower BE peak corresponds to the two iminic ones ( $-N=$ ) [27]. These two peaks were shown with their fwhm by fitting the raw data. Obtained results are reported in Table 1, which points out that the pyrrolic peak is broader than the iminic peak. These results are in good agreement with reported results

**Table 1 – N 1s components-multilayer of TPP molecules on Fe and  $Fe_3Si$  onto Si.**

Sample at RT	Normalized peaks		
	In (eV)	$-N=$	$-NH-$
2HTPP/Fe/Si	BE	398.16	400.25
	fwhm	0.8929	1.1671
2HTPP/ $Fe_3Si$ /Si	BE	398.15	400.26
	fwhm	0.8682	1.5612



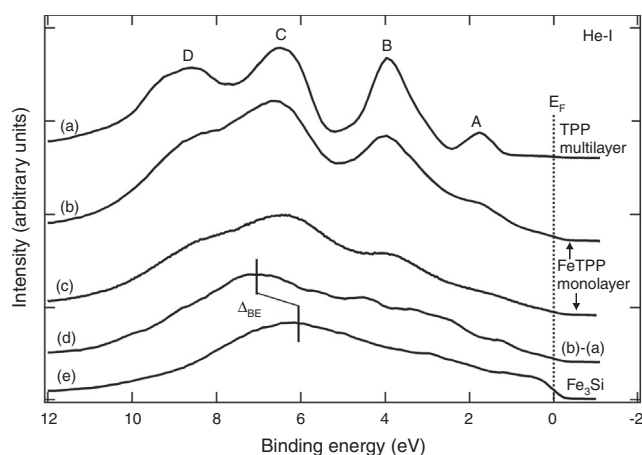
**Fig. 3 – C1s: Core level spectra of 2HTPP at Fe/Si interface at RT and 550 K.**

[16,19]. 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 [28].

Metalation of porphyrin multilayer was demonstrated by the formation of Fe-TPP monolayer upon annealing at 550 K of 2H-TPP multilayer at Fe/Si interface. The efficiency of the reaction is lower than that for monolayer. In fact, the metalation competes with the formation of Fe clusters in the multilayer [29]. The monolayer formation of metalloporphyrin (Fe-TPP) in both cases is shown in Fig. 2b and d, respectively. The simplest possible approach to interpret the signal of N 1s assumes that it arises from a mixture of the product Fe-TPP and unreacted TPP. Accordingly, a deconvolution was attempted 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 (sky blue) with two nitrogen (iminoic and pyrrolic) peaks, while separation in BE, fwhm and ratio of intensity metalloporphyrin. The position was not held constant during the fitting for better resolution and the best fit results were reported in Table 2. The shifts in peak position of iminoic and pyrrolic N atoms have been observed toward lower binding energies and represent the sign of the formation of Fe-TPP monolayer. The new component peak here represents the coordination of iron (Fe) and nitrogen (N) of TPP macrocycle. The variation in BE of the coordination peak is due to different interaction of Fe on iron and iron silicide.

The signal of pyrrolic N decreased upon heat treatment of the specimens at 550K and results indicated that a fraction of 2H-TPP molecules had undergone the metalation reaction to Fe-TPP. The N 1s core level of Fe-TPP monolayer has three components of iminoic, pyrrolic and N-Fe, while Xiao et al. [30] reported that the aminic (pyrrolic) peak completely vanishes above 450 K in sub-one monolayer systems.

Here the observed results are related to additional thermal desorption of the molecule: the N 1s and C 1s (Fig. 3) core level intensities show that the total coverage changes during heating, assuming that the molecules desorbed and monolayer of metalloporphyrin is yielded at the surface. The temperature



**Fig. 4 – Valence band of (a) TPP multilayer at Fe/Si interface. Formation of Fe-TPP monolayer on Fe<sub>3</sub>Si & Fe on Si at 550 K in (b) & (c), respectively. (d) Difference spectra and (e) Fe<sub>3</sub>Si on Si. The shift  $\Delta_{BE} = 0.99$  eV is shown here in spectra (d) & (e). Under the experimental spectra it is reported that the expected contribution of HOMO states and represented by A, B, C and D, respectively.**

dependent C 1s core level is expected to reflect the information about the distance between the molecules and iron atoms on Si(100) substrate as well as the tilting of the molecules. The shift of 0.22 eV in BE of C1s core level toward lower binding energy is observed and shows that the molecular surface distance is decreased as a result of annealing at 550 K [30].

It is both theoretically and experimentally challenging to study the valence bands of large conjugated molecules of closely spaced molecular states. Experimentally, energy positions of molecular orbitals in organic layers can be studied by Ultraviolet Photoemission Spectroscopy (UPS) or by Scanning Tunneling Spectroscopy (STS) [31,32]. UPS has the advantage that accessible binding energies are not limited to a few electron volts from the Fermi level as STS. Thus UPS is the technique of choice for studying the highest energy molecular orbitals of the metal porphyrin complexes (metalloporphyrin), where He-I (21.22 eV) was used to measure the valence band of 2H-TPP on iron (Fe) and iron silicide (Fe<sub>3</sub>Si) onto Si. The metal coordination with TPP macrocycle has been studied additionally by UPS. Fig. 4 shows the Valence Band (VB) raw data of TPP multilayer and monolayer of metalloporphyrin (Fe-TPP). The multilayer valence band results show that the Fe-TPP bonds are extremely stable and strong.

The occupied molecular orbitals (HOMO) of 2H-TPP multilayer on iron and iron silicide onto Si are shown in Fig. 4a. The peaks at BE of  $-1.765$ ,  $-3.965$ ,  $-6.495$  and  $-8.585$  eV were represented by A, B, C and D respectively and corresponding to HOMO states below the Fermi level. The monolayer of Fe-TPP is shown in Fig. 4b and c. The change in surface band of the monolayer is found at lower BE than the multilayer, in comparison with of VB spectra. The major changes are below 5 eV of BE and in particular, the growth of states near the Fermi level shows an apparent metallic behavior. The growth in intensity of DOS spectra near the Fermi level is due to the d orbitals of

**Table 2 – N 1s components-monolayer of Fe-TPP complex formation on Fe and Fe<sub>3</sub>Si onto Si.**

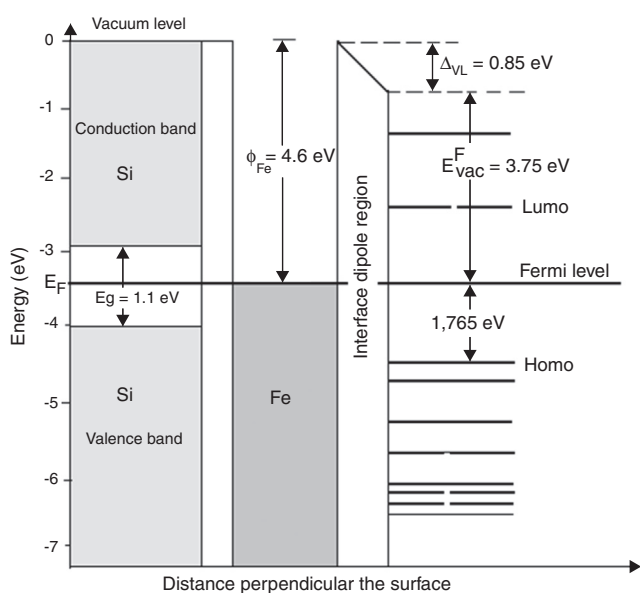
Sample at 550 K	Normalized peaks			
	In (eV)	–N=	–NH–	N-Fe
2HTPP/Fe/Si	BE	397.98	400.07	398.9
	fwhm	0.8929	1.1671	0.7142
2HTPP/Fe <sub>3</sub> Si/Si	BE	398.09	400.20	399.31
	fwhm	0.8682	1.5612	0.8886

the iron upon annealing at 550 K and evidenced that the TPP macrocycle binds the Fe atom.

To a further analysis data, a typical VB spectrum is shown in Fig. 4d. This spectrum has been obtained by subtracting the spectrum of 2H-TPP multilayer from the valence band of Fe-TPP monolayer. This procedure obviously is quite rough, but helps to highlight some important features. The Fe metalation influences the states near the Fermi level (0–2 eV) and shows that the layer tends to metallic behavior. Therefore, the Fermi level seen in monolayer valence band is due to metallization. The full UPS spectra of Fe<sub>3</sub>Si on Si have been shown in Fig. 4e. From the comparison between the spectra (d) and (e) of Fig. 4, it is concluded that the charge injection from the substrate is confined and shifts in BE (measured as  $\Delta_{BE} = 0.99$  eV), which indicates the band formation between Fe and TPP macrocycle.

From calculations, it was found that the Fe d states near the Fermi level are expected to have much less hybridization with the N states than the possible hybridization between the perpendicular d orbital. The visualization of the valence bands is also important for monitoring the Fe adatom dosing in molecular layer. The Fe metalation influences the states near the Fermi level and the Fe d states are expected to hybridize with neighboring N p states in the energy range 0–5 eV below the Fermi level [33].

To provide a quantitative analysis and understanding the band-bending of the 2H-TPP on Fe onto Si, we illustrated



**Fig. 5 – Band-bending diagram of TPP molecules at Fe/Si interface. Here A, B, C and D represent the HOMO states respectively below the Fermi level.**

energy level diagram for this interface and are reported in Fig. 5. It is based on porphyrin/metal/Si interfaces [34], 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  $\Delta_{VL}$ ). The vacuum level shifts or adsorbate-induced work function changes (extracted from the widths of the UPS spectra is 0.99 eV) provide additional information about the nature of the adsorbate–surface interaction and are of potential interest to the organic electronics community [34]. Work functions, 3.75 and 4.60 eV for monolayer of 2H-TPP and Fe, respectively, were found and compared to 4.95 eV for the clean Si surface [35]. The alignment will be affected 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 [34,36,37].

## 4. Conclusion

The in situ electronic structure of 2H-Tetraphenylporphyrin (2H-TPP) molecules on iron and iron silicide onto Si(100) substrate has been studied by XPS and UPS. The investigations include the formation of Fe<sub>3</sub>Si having (1 × 1) crystal structure on Si. This reaction needs to be activated by heating the mixed layer at 550 K, indicating a reaction barrier at room temperature. The results revealed that the Fe atom is coordinated by TPP macrocycle on iron (Fe) as well as on iron silicide (Fe<sub>3</sub>Si) onto Si. XPS results evidence the progress of the metalation of 2H-TPP, as the reaction proceeds. The two separate peaks of 2HTPP evolve into a single peak for the metalated porphyrin, because, in the final metalloporphyrin complex, the four nitrogen atoms are chemically equivalent. The fine structure is assigned in the electronic spectra related to HOMO states below the Fermi level. UPS results also support the interaction of the iron and TPP molecules on Si. Finally the band-bending diagram was drawn upon the reported results. This 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 [38].

## Conflicts of Interest

The authors declare no conflicts of interest.

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