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# Review of 2H-tetraphenylporphyrins metalation in ultra-high vacuum on metal surfaces

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**Abstract.** The formation and conformational adaptation of self-assembled monolayer of 2H-tetraphenylporphyrins (2H-TPPs) on metal surfaces, as well as their metalation processes in ultra-high vacuum (UHV), are reviewed. By means of XPS, NEXAFS and STM measurements we demonstrate that, after the annealing at 550 K, a temperature-induced chemical modification of 2H-TPP monolayer on Ag(111) occurs, resulting in the rotation of the phenyl rings parallel to the substrate plane. Moreover, independently of the conformation, we report three different methods to metalate 2H-TPP monolayers in UHV. Experimental evidence indicates that the presence of a metal atom in the TPP macrocycle influences both the conformation of the molecule and its adsorption distance.

## 1. Introduction

The self-assembly of molecular building blocks on crystalline surfaces allows the creation of highly ordered nano-architectures, which cannot be achieved by conventional methods. In this context, organic-inorganic interfaces, due to their flexibility, are very promising for the realization of new compounds with controllable and tunable properties [1].

Porphyrins and similar macrocycle molecular systems are extremely suitable for this task, because they combine the ability to self-assemble with the presence of active sites of interaction for metals [2–4]. 2H-tetraphenylporphyrins (2H-TPPs), for example, can be deposited in ultra-high vacuum (UHV) in well-ordered monolayers on different substrates and, in the last years, it has been demonstrated that metal ions can be incorporated and stabilized inside the macrocycle with the substrate-mediated formation of metallo-porphyrins [5–31]. Actually, there is a large number of studies on this subject, in particular taking into account the role of the substrate metal atoms in structural and electronic properties of the formed adlayer and metallo-adlayer. For this purpose, synchrotron radiation techniques, such as X-ray photoemission spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) – due to their extreme chemical and electronic selectivity – combined with scanning tunnelling microscopy (STM), allow a deep understanding of the chemical and conformational properties of the adsorbed molecules and of their metalation on crystalline metal substrates.



Here we review the formation of a monolayer of 2H-TPPs on several metallic substrates, the adsorption geometry and the conformation of the molecule and the possible ways to obtain metallo-porphyrins in UHV starting from the adsorbed free-base species.

## 2. Thermal-induced conformational adaptation

As shown in many experiments on 2H-TPP multilayer [8, 13, 25], as well as in gas-phase measurements [32], the presence of an intact macrocycle can be determined by photoemission spectroscopy, through which the existence of two atomic species of nitrogen (N) can be detected (iminic and pyrrolic). The pyrrolic N is bonded to an hydrogen atom, while the iminic is not, resulting in a binding energy (BE) difference in the N 1s core level spectrum of about 2 eV.

Actually, 2H-TPP molecules have been deposited on several metallic substrates, but Au [4, 19, 26] and Ag [5–7, 10, 18, 20, 33] are those on which it is possible to obtain a single layer without any modification of the macrocycle. In both cases, when deposited at room temperature (RT) or when the monolayer is obtained after the sublimation of a multilayer in the range  $525 \div 580$  K, the XPS analysis shows the presence of two unaffected N 1s peaks, indicating that in the monolayer the molecule macrocycle is still protonated.

However, a remarkable effect on the phenyls adsorption geometry was observed on the monolayer (or sub-monolayer) of 2H-TPPs, after annealing above 525 K. On the Ag(111) and Au(111) surfaces, the macrocycle of 2H-TPP deposited at RT has been shown to be adsorbed parallel to the substrate surface, adopting a saddle shape conformation [29], whereas its phenyl legs exhibit a tilt angle of about  $45^\circ \div 55^\circ$  with respect to the surface plane [29, 33]. Differently, after annealing above 525 K, Di Santo et al. [33] predicted and observed a temperature-induced conformational adaptation of the porphyrin molecules on the surface, resulting in the rotation of the phenyl rings parallel to the substrate plane.

As an example, figure 1 shows the NEXAFS spectra for two polarized beams at the N 1s (left panel) and C 1s (right panel) thresholds of the 2H-TPP monolayer adsorbed on Au(111) at room temperature (top) and after the annealing at 550 K (bottom). Regardless of the temperature, the N 1s spectra show enhanced or suppressed  $\pi^*$  features respectively for light polarized perpendicular or parallel to the surface. This suggests that the macrocycle, in which the N atoms are located, is adsorbed parallel to the substrate surface.

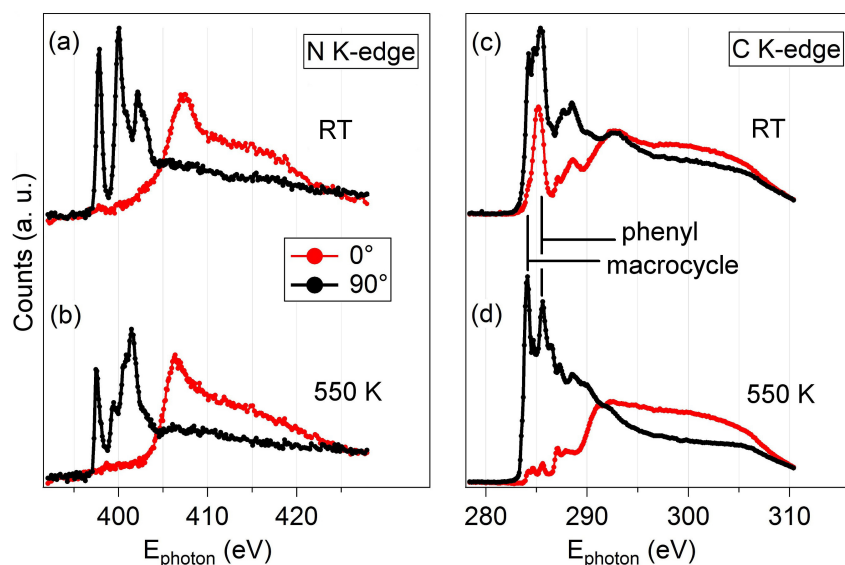
The C 1s NEXAFS spectrum in 2H-TPP can be seen as the superposition of the macrocycle and the benzene (phenyl) spectra [34]: in particular, the first  $\pi^*$  peak at 284.1 eV belongs to the macrocycle, whereas the large peak at 285.2 eV is mainly related to the phenyl  $\pi^*$  absorption spectrum.

For the monolayer deposited at RT (figure 1c) the macrocycle peaks follow the same behaviour as the N 1s NEXAFS spectra, again indicating that it is adsorbed parallel to the substrate surface. The large phenyl peak shows instead a very small dichroism suggesting that the phenyl rings have an average angle very close to  $50^\circ$ .

For the monolayer after the annealing at 550 K (figure 1d), the situation is completely different: all of the  $\pi^*$  peaks are suppressed when  $\theta = 0^\circ$ , indicating that in this case the phenyl rings are parallel to the surface. This situation is actually quite strange because the rotation of the phenyl rings is inhibited by the steric interaction between the hydrogen atoms in the molecule.

A possible reaction and modification of the porphyrins able to explain this configuration is a dehydrogenation of eight carbon atoms (four in the phenyl rings and four in the macrocycle) with the formation of four new aryl-aryl carbon bonds. In this way, with the rotation of the benzene moieties, the molecule becomes flat and, therefore, reduces the distance from the substrate, making new and stronger bonds between their molecular  $\pi$  orbitals (both from phenyls and macrocycle) and the bands of the substrate. The details of this configuration can be described within the density functional theory (DFT) formalism [33].

The study of a sub-monolayer of CoTPP evaporated on Ag(111) demonstrated that the



**Figure 1.** NEXAFS spectra for the angle of incidence  $\theta = 0^\circ$  (red) and  $\theta = 90^\circ$  (black) at the N 1s (left panel) and C 1s (right panel) absorption threshold for 2H-TPP monolayer deposited on Ag(111) at room temperature (top) and after annealing at 550 K (bottom).

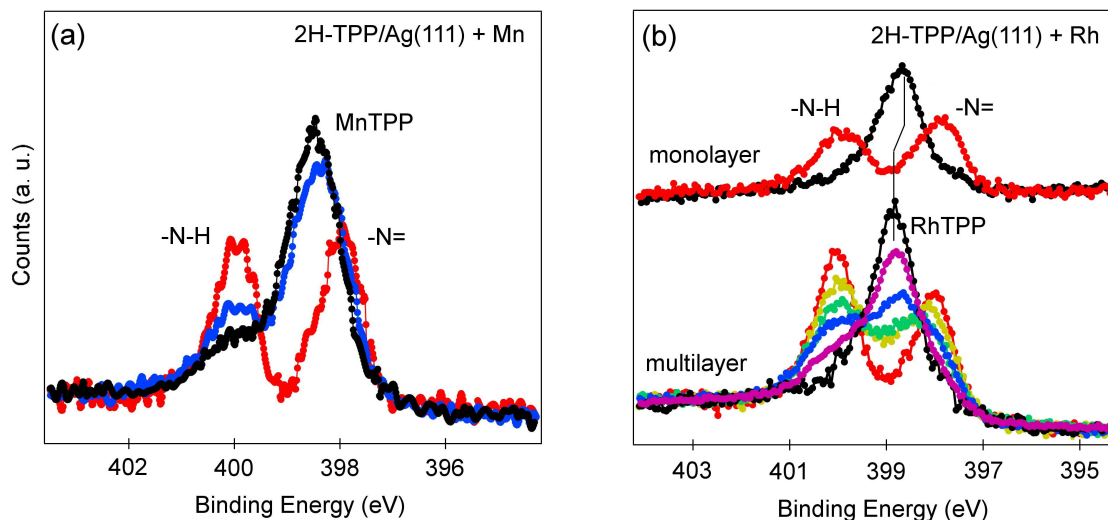
molecule increases the number of bonds and reaches a more stable energetic configuration via this mechanism. The Co at the centre of the macrocycle, like other 3d metals (Fe, Ni, Mn, Cu), has a strong interaction with the substrate via the perpendicular  $d_{z^2}$  orbital, inducing the molecule to form bonds with the  $\pi$  orbitals. Indeed, after annealing up to 600 K, the CoTPP molecule does not change the orientation of the phenyl rings, that remain rotated by about  $40^\circ$  with respect to the macrocycle, which instead is parallel to the substrate surface [24]. A strong interaction with the substrate prevents this reconfiguration of the molecule; otherwise, when the interaction is weaker, like in the case of Zn, the rotation of the phenyl rings of ZnTPP is allowed as for the 2H-TPP molecule [35].

The hypothesis of 2H-TPP modification is supported by several recent analyses [12, 18], among which the most complete was by Papageorgiou et al. [18], who observed all the predicted dehydrogenation configurations through STM [33].

### 3. UHV in-situ metalation of the macrocycle

In-situ metalation of porphyrin molecules in UHV is of great interest for the characterization of pure species in a controlled environment. Generally the inclusion of metal atoms in porphyrin molecules is obtained in solution via wet chemistry, and typically most of the metallo-porphyrin molecules need a ligand coordination to the metal atom in order to reduce its reactivity and prevent oxidation. The possibility to produce in-situ stable pure metallo-porphyrins without any ligand and to characterize them is an intriguing challenge of fundamental interest. Furthermore, the capability of this type of molecules to bind various metal ions opens the discussion on how the presence of this central metal atom modifies the interaction with the substrate as well as on the modeling of the metalation process.

Several metals can be efficiently coordinated to 2H-TPP adsorbed on Ag(111) and Au(111) by in-situ metal evaporation: Fe [6, 25, 28], Co [8, 24], Zn [7], Ni [26], K [36] Ce [9], Mn and Rh [20] can be easily inserted in the macrocycle to form metallo-porphyrins. The metals can be coordinated either by direct evaporation on the 2H-TPP monolayer or multilayer, or by deposition of metal adatoms on the substrate before the molecules evaporation.



**Figure 2.** N 1s XPS spectra of 2H-TPP monolayer on Ag(111) during Mn (a) and Rh (b) evaporation (red spectra refer to the pristine 2H-TPP and black spectra to the metalated molecule). For the Rh case the metalation of the multilayer during consecutive evaporation steps is also shown.

Photoemission spectroscopy is extremely sensitive to the redox-reaction occurring at the macrocycle which leads to the metalation process. The evidence of the metal coordination comes from the changes of the N 1s XPS spectrum of the porphyrin when a metal ion is bound at the centre of the macrocycle. The spectrum of the 2H-TPP has two easily resolved components because of the two N species: 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=); in the metallo-porphyrin, instead, the four N atoms are equivalent, and just one peak is expected.

Two examples, relative to the Rh and Mn metalation, are shown in figure 2. It is worth noting that the geometrical adaptation of the tetraphenylporphyrin in the monolayer has no implications on the possible hypothesis for the metalation mechanism. The metalation of other macrocycle molecules, with different geometries, is indeed happening in a similar way [5, 24–26, 30]. Therefore, a simple ad-atom hopping instead of a substrate surface-mediated diffusion to the reaction sites could explain the metalation process.

Recently it was shown that on some reactive substrates with a small ionic radius, like the first row 3d transition metals Fe and Ni [20], Cu [12, 14, 17, 22, 23] or Al [36] substrates, the 2H-TPPs in a monolayer metalate simply by picking-up substrate atoms or ad-atoms. In the case of Ni and Fe, DFT calculations demonstrate that the molecules metalate at room temperature by incorporating a surface metal ad-atom when a monolayer is deposited on these substrates. The achievement of a complete metalation by Fe and Ni can be regarded as a test case for successful preparation of well-defined and controlled arrays of molecular-based magnets.

Finally, given the difficulty in evaporating some heavy metals (such as Rh, W, Ir or Ru) in UHV, a useful procedure to metalate the 2H-TPP in UHV has been shown by Papageorgiou et al. [18]. They demonstrated the formation of RuTPP on Ag(111) after the exposure of 2H-TPP to the carbonyl precursor molecules  $\text{Ru}_3(\text{CO})_{12}$  containing the metal and a thermal treatment to complete the reaction. This novel technique allows the engineering of new interfaces with geometrical arrangements of atoms for single-site catalysis or light-harvesting.

#### 4. Conclusions

Surface coordination of organo-metallic systems onto metal substrates in UHV has attracted great attention in the recent years due to the prospective of applications like novel catalytic systems, light-harvesting antennas, sensors and molecular magnets. Many of these systems were notably explored using macrocyclic compounds, where the tetrapyrrole macrocycle may readily incorporate several metal ions.

Here we have described how the redox reactions needed to metalate the 2H-TPP monolayer on metallic surfaces can be performed, depending on the substrate and on the inserted metal ion, resulting in different systems with various characteristics. Metal evaporation, picking-up of a substrate atom and reaction with metal precursor molecules are the three methods that allow the creation of new metallo-porphyrins on metal substrates. Finally, since the physical and chemical properties of these metallo-organic systems depend on the coordinated metal ion but also on the interaction with the substrate, annealing treatments of the original 2H-TPP or the metalated TPP monolayer may change the conformation and the adsorption geometry of the molecule, therefore modifying both the physical and chemical properties of the system, even in the case of the same metallic center.

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