



Photoelectron spectroscopy investigation of the temperature-induced deprotonation and substrate-mediated hydrogen transfer in a hydroxyphenyl-substituted porphyrin



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ABSTRACT

The temperature dependent stepwise deprotonation of 5,10,15,20-tetra(*p*-hydroxyphenyl)-porphyrin is investigated using photoelectron spectroscopy. An abundance of pyrrolic relative to iminic nitrogen and a decrease in the ratio of the amount of $-\text{NH}-$ to $-\text{N}=\text{}$ with increasing annealing temperature is found. In contrast to the molecules adsorbed on Au(111), on the more reactive Ag(110) surface, partial dissociation of the hydroxyl groups and subsequent diffusion and rebonding of hydrogen to the central nitrogen atoms resulting in a zwitterionic molecule was clearly observed. Moreover, partial C–H bond cleavage and the formation of new covalent bonds with adjacent molecules or the surface starts at a relatively high annealing temperature of 300 °C. This reaction is identified to occur at the carbon atoms of the pyrrole rings, which leads also to a shift in the N 1s signal and changes in the valence band of the molecules. Our results show that annealing can significantly alter the molecules which were deposited depending on the maximum temperature and the catalytic properties of the specific substrate. The thermal stability should be considered if a molecular monolayer is prepared from a multilayer by desorption, or if annealing is applied to enhance the self-assembly of molecular structures.

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1. Introduction

Organic materials are expected to be of crucial importance for the construction of nano-devices to address tomorrow's challenges in electronics, opto-electronics, photonics, and energy and information storage. In this sense, porphyrin-based molecules have been studied in great detail for many years because of their exceptional versatility. These organic molecules can be easily modified to change the intermolecular or molecule–substrate interaction and their optical, electronic and also magnetic properties [1–6]. This class of molecules is of outstanding importance in biological systems, in which they represent the active centre of many enzymes. Examples are iron porphyrin in heme and magnesium porphyrin in chlorophyll. Meso-tetra(hydroxyphenyl)porphyrin can be used effectively as photosensitizer, e.g. for tumour treatment [7,8]. Furthermore, the self assembly of metal-free 5,10,15,20-tetra(*p*-hydroxyphenyl) porphyrin in water leads to the formation of nano-scaled, hollow spheres [9], which have

possible applications, for example, in drug delivery and chemical storage. In nanotechnology this class of molecules is promising for various applications, for example, in non-linear optics [10,11], gas sensors [12], as catalysts [13] and in photochemical and photovoltaic cells [14,15]. The porphyrin macro-cycle exhibits a high chemical and thermal stability. Nevertheless, the effect of heating and the limit of this stability should be investigated in more detail, as production steps in the fabrication of devices might damage the molecular films or partially decompose the molecules [16] and, therewith, possibly reduce the performance. Investigations on which reactions occur for such molecules when exposed to high annealing temperatures are quite rare. It is known that at a temperature often between circa 250 °C to 300 °C desorption of porphyrin multilayer on metals starts and only the molecules which are in direct contact with the substrate remain [17–19], i.e. those with a higher adsorption energy due to the strong molecule–substrate interaction. This presents a convenient way to produce a surface fully covered with an only one monolayer thick film. It is also known that annealing increases the mobility of the molecules, which aids in or induces the formation of large highly ordered domains in the molecular film [20]. By this, the transport

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properties of devices could be improved. The desorption temperature depends on the functional groups and the coordinated metal ion of the porphyrin core, as well as the substrate. For heating at high temperatures, a change in the shape of the C 1s core level spectra was often observed, which was usually explained by the term “decomposition” without further details [17,18]. Herein, a closer look at what the nature of this decomposition really is will be taken to gain knowledge about which bond cleavage reactions occur for porphyrins at high annealing temperature.

Previously, the coexistence of two stable forms of a tetra (*p*-hydroxyphenyl)porphyrin molecule was found by scanning tunneling microscopy. Switching between them was suggested to be due to a local deprotonation or protonation reaction which changes the number of pyrrolic to iminic nitrogen [21]. Thereby, a significant change in the electronic structure near E_F was measured. To investigate also this matter further, photoelectron spectroscopy, which can give additional information about the bonding conditions in the molecule, was applied.

2. Experimental details

5,10,15,20-tetra(*p*-hydroxyphenyl)porphyrin (H_2THPP) was synthesized as described in an earlier publication [21]. Single crystals of Au(111) and Ag(110) were cleaned in ultra-high vacuum (UHV) by cycles of Ar^+ -sputtering at an energy of 500 eV and annealing to 500 °C for 30 min. The powder of H_2THPP was purified by heating to a temperature slightly below the sublimation temperature in UHV for several days. A multilayer of the molecules were then deposited on Au(111) (layer thickness around 2.4 nm) and on Ag(110) (≈ 1.8 nm) with organic molecular beam deposition at ≈ 350 °C. The temperature of the substrate during deposition was held at room temperature. In the following, these initial layers will be denominated as “thick layer”. The thicknesses of the layers were estimated with a quartz micro-balance and from the attenuation of the respective substrate core-level peaks (Au 4f or Ag 3d). A monolayer (ML) is defined as the minimal thickness where the substrate surface is completely covered with close-packed molecules (≈ 0.35 nm). Photoelectron spectroscopy (PES) experiments were performed with synchrotron radiation at the Material Science Beamline in Elettra (Trieste, Italy). A Phoibos photoelectron spectrometer was used. All spectra were measured in a geometry for emission along the surface normal (30° incidence of beam relative to the surface plane). The excitation photon energies used for acquiring the C 1s, N 1s and O 1s core level spectra of H_2THPP were for Ag(110)/Au(111) 390 eV/400 eV, 500 eV/520 eV and 650 eV, respectively, and 22 eV for the valence band spectra. The binding energies were corrected relative to the Au 4f_{7/2} peak at 83.98 eV or Ag 3d_{5/2} at 368.21 eV. Core-level spectra were fitted with a Shirley background and Voigt peak functions using an identical width for all peaks. The full width at half maximum for example for N 1s ($E_{exc} = 520$ eV, $E_{pass} = 10$ eV) was circa 1.1 eV. The typical precision for the energy position of each peak component was ± 0.05 eV. Annealing of the sample was performed by resistive heating of a wire wound around the crystal with the thermocouple located at its backside. In each annealing step, the temperature was increased slowly till the designated maximum temperature where it was held at for 10 min and then cooled off to room temperature for the measurements.

3. Results and discussion

3.1. Protonation and deprotonation at nitrogen atoms

The evolution with annealing of the N 1s spectra, which are sensitive to the nitrogen bonded hydrogen atoms of the molecule, is

shown in Fig. 1(a) and (b) for H_2THPP on Au(111) and Ag(110), respectively. The assignment of the two-component signal is done in agreement with studies on tetraphenylporphyrin [1,22–24] with the peak at 399.8 eV corresponding to pyrrolic nitrogen, which has a bond to hydrogen ($-NH-$), and the right peak at 397.8 eV to iminic nitrogen ($-N=$). It can be seen that in the molecular films as deposited (Fig. 1(c)), the amount of pyrrolic N was clearly larger than iminic N with very similar values on both Au(111) and Ag(110) (ratio 3:2). The expected ratio of both nitrogen species from the chemical structure of H_2THPP is 1:1. Thus, both H_2THPP (80%) and a protonated form H_4THPP (20%) were likely present in the molecular layer. A similar phenomenon of non-equivalent N 1s peaks was reported for other porphyrin molecules several times before with different or no explanations given [24–27]. Diller et al. [23] found a ratio of the peak areas of the pyrrolic divided by the iminic nitrogen of 2.5 for a monolayer of H_2THPP on Cu(111) at normal emission geometry and higher ratios at other angles of emission, whereas for the multilayer the ratio was nearly 1. This behavior was explained by a photoelectron diffraction effect and a strong nitrogen-surface interaction [23]. To investigate the influence of the geometry for H_2THPP , measurements were done at angles of emission of 90°, 70° and 30° – no change in the ratio of pyrrolic to iminic nitrogen (≈ 1.6) was observed. From the different behavior with coverage and no dependence on the angle of emission in our case, photoelectron diffraction effects can be ruled out as a possible reason. It is known that some porphyrin derivatives, e.g. with sulfonatophenyl [28] or carboxyphenyl [29] groups, can exist as stable neutral zwitterionic (or “diacid”) molecules. In solutions with low pH values not only acidic groups of the molecule are partially protonated but the iminic nitrogens are protonated as well due to close pK_a values, thereby creating a positive charge in the central region and a negative charge on the periphery of the molecule. Typically, molecules with such functional groups are deposited from an acidic solution on the substrate and can then be transferred into UHV for measurements [28]. Although in our experiments, molecular films were prepared by organic molecular beam deposition, a similar hydrogenation effect was found for metal-free tetra(hydroxyphenyl) porphyrin. The additional hydrogen atoms necessary to form H_4THPP could originate from H_2 which is always present in vacuum or when the molecular powder was exposed to air.

The N 1s spectra measured after annealing to 300 °C changed their shape and are fitted the best with two peaks additional to the already discussed ones (Fig. 1(d)). These newly occurring peaks are located at a binding energy of 400.4 eV and 398.7 eV and show an intensity ratio similar to the pair of main peaks. It should be noted that these cannot be shake-up satellites because of their high relative intensity. Therefore, we assign them also to pyrrolic and iminic nitrogen, respectively, although they have a difference in the surrounding molecular frame which leads to a different partial charge of these N atoms or changed screening of the core-hole and results in a shift to higher binding energy of both N 1s peaks. This will be discussed further in the second part of this study.

The evolution of the relative amount of the N species with annealing is summarized in Fig. 2. It can be seen that after heating to 200 °C on both studied substrates the ratio of pyrrolic to iminic N decreased towards 1. This means that the two additional hydrogen atoms in H_4THPP are removed due to a smaller dissociation energy compared to the other two H atoms bonded to N in H_2THPP . On Au(111) after heating to 300 °C, the amount of respective total $-NH-$ and $-N=$ stayed constant. Whereas, after a high maximum temperature (400 °C), the total peak intensity of $-NH-$ decreased further and became lower than the one for $-N=$. This means that in H_2THPP , the two hydrogen atoms started to dissociate from the nitrogen [30] and the resulting deprotonated molecule (THPP) is stabilised on the surface. However for Ag(110), if the sample was

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