

BIOMIMETIC OXIDATIONS USING THIOL-DERIVATIZED PORPHYRINS

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Macrocyclic metal complexes, in particular metallo porphyrins have attracted attention as biomimetic catalysts in oxidation reactions. Thiol derivatized Co-Porphyrins are immobilized on Au surfaces in the study presented here. The molecular layers are studied by means of X-ray Photoelectron Spectroscopy (XPS). The results reveal a monolayer formation of the Co-porphyrins. A detailed analysis of the S2p core level at different take off angles (TOA) of the photoelectrons suggests that the molecules are preferentially adsorbed with the porphyrine core tilted up from the Au surface. A model system oxidation of hydroquinone to benzoquinone is used to measure the catalytic activity of the Co-porphyrins. The activity of the molecular layers on the surface (heterogeneous catalysis) will be compared to the activity of the molecules in solution (homogeneous catalysis).

The molecules consist of a central Co-porphyrin with four thiol linkers. In order to avoid the problems associated with disulfide formation the thiol is best handled in a protected form. S-thioacetyl has been used as a protective group.

The evaporated gold substrates on Si wafers were cleaned with Piranha solution ($H_2SO_4:H_2O_2$, 2:1) and rinsed with ultra pure water prior to molecular deposition. The porphyrin molecules (0.5mM in N,N-Dimethylformamide (DMF)) were deposited after checking the bare Au surface with XPS for remaining contaminants. Deprotection of the thioacetyl groups has been performed by using a 10 molar excess of HCl. A typical deposition time of the Au surface in the porphyrin solution was chosen to be 20h. Subsequent XPS measurements have been performed in an ESCA 300 instrument from Scienta using monochromized Al K α X-rays with a photon energy of 1487 eV.

Besides residual carbon and oxygen no additional contaminants could be observed on the bare Au surface. Figure 1 shows a survey photoelectron spectrum of deprotected Co-porphyrins obtained at a TOA of 10°. The different atomic constituents of the molecule can be related to the peaks appearing in the spectrum. The calculated ratio in the spectrum for N, S and Co agrees within the statistical error with the molecular stoichiometry. A quantity which is slightly too high has been detected for carbon and oxygen. This can be explained by the contamination of the bare Au surface and additional air contamination of the molecular layer during mounting the sample and introducing it into the load-lock chamber of the ESCA instrument. It is very likely that oxygen containing species adsorb to the Co-centre of the molecule. The XPS results show an immobilization of the molecules on the Au surface for the protected as well as for the deprotected molecules by formation of a monolayer.

Two chemically different states of the sulphur can be resolved in the S2p core level spectrum: The state with lower binding energy is attributed to the thiol bonded to the Au surface, whereas the state with higher binding energy is attributed to the free thiol. Changing the take off angle of the photoelectrons offers the possibility to change the probing depth of the analysed sample. At a TOA of 10° a higher surface sensitivity compared to a TOA of 90° is obtained. A comparison of ESCA spectra taken at those angles offers the possibility to gain insight in the orientation of the molecules on the surface. The comparison of the S2p spectra at those angles reveals that in average two thiol linkers per molecule are attached to the

surface and two are free. This behaviour suggests that the porphyrin core of the molecule is not parallel to the surface but is rather standing up.

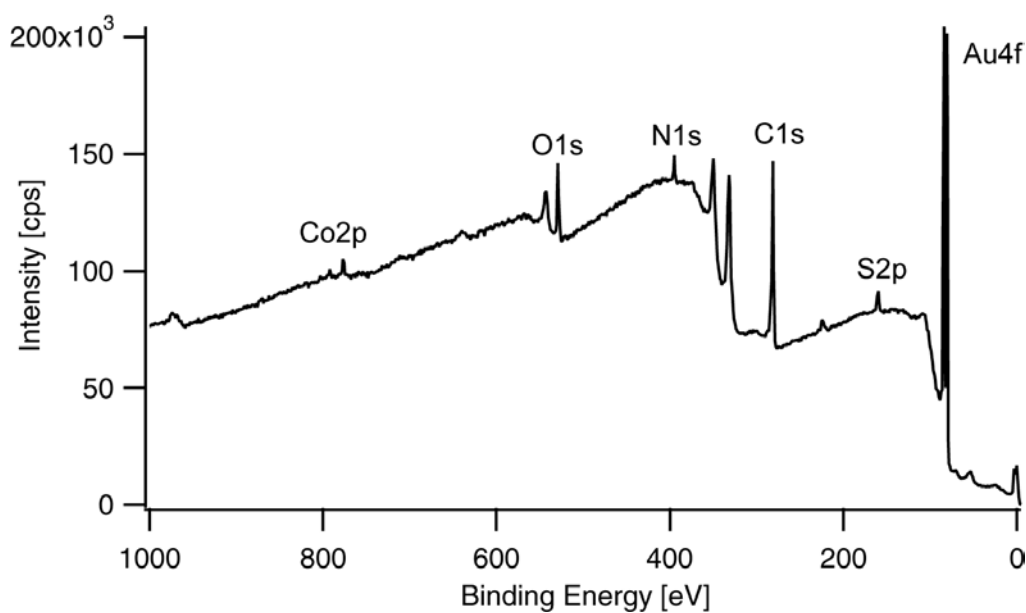


Figure 1: Photoelectron spectrum of deprotected Co-porphyrins on a Au surface obtained at a TOA of 10° . The different elements of the molecule are present in the spectrum. The main photoelectron peaks are marked.

The chemical activity of the molecules is measured in the oxidation reaction of hydroquinone to benzoquinone under the consumption of oxygen. This is a very “clean” reaction since the only by-product is water. The activity of the molecular layers immobilized on Au will be compared to the activity of the molecules in solution.