

Self-metalation of 2H-Tetraphenyl Porphyrin and 2H-Porphine on Magnesium Oxide films

F. Schwarz, T. Bone, L. Egger, M. Hollerer, C. Kern, F. Presel, P. Puschnig, M. G. Ramsey, M. Sterrer

Institute of Physics, University of Graz, Universitätsplatz 5, 8010 Graz, Austria

florian.schwarz@uni-graz.at

Porphyrins and metalloporphyrins are versatile molecules, which offer a large variability of their properties due to the possibility to attach different ligands or metal atoms to the porphyrin macrocycle. The surface-confined self-metalation reaction describes the replacement of two aminic protons in the macrocycle of the porphyrin molecule by a metal atom of the substrate. This reaction was first observed on metal surfaces, but more recent investigations show that it also occurs on oxides such as magnesium oxide (MgO). Previous work has shown that the self-metalation of 2H-tetraphenyl porphyrin (2H-TPP) on MgO is strongly dependent on the morphology of the material and occurs only on surface irregularities but not on a perfect planar surface.

By a combination of results obtained with scanning tunneling microscopy, photoemission spectroscopy, and DFT computations, we show that the self-metalation reaction on MgO can also be induced on planar MgO surfaces. The key to this is the use of only few atomic layers thin MgO films, which are grown on a metallic substrate. Because of the reduction of the work function of the silver substrate by the MgO film, electron transfer occurs into adsorbed 2H-TPP molecules, which then leads to the self-metalation reaction. By chemical tuning of the work function we could furthermore show that states where the molecules are charged and metalated or uncharged and non-metalated can deliberately be generated. These results suggest a method to control the electric and chemical properties of porphyrins on surfaces, which opens the way for selective surface functionalization.

To understand the role of charging, we compare the self-metalation of 2H-TPP and 2H-porphine on ultrathin MgO films. Our results suggest, that charging helps to bring the macrocycle closer to the MgO surface, which facilitates the transfer of an Mg ion from the oxide lattice into the molecule.

Keywords: Charge Transfer, Photoemission Tomography, Porphyrins, Self-Metalation, Thin Films