

# SURFACE CHEMISTRY IN COMPLEX ORGANIC LAYERS

H.-P. Steinrück

Physikalische Chemie, Universität Erlangen-Nürnberg  
Egerlandstraße 3, D-91058 Erlangen, Germany

Chemical reactions on surfaces can be followed in detail using X-ray photoelectron spectroscopy (XPS or ESCA), in particular in combination with scanning tunneling microscopy (STM). From the XPS binding energies of the adsorbate and substrate core levels, detailed information on the chemical composition, chemical state (e.g. oxidation state), adsorption sites, but also on the photoemission process itself can be derived. STM provides information on surface order and intramolecular conformation but also on the chemical state. Based on the understanding obtained for simple adsorbate systems, now complex molecular systems can be studied in great detail. One specifically interesting group of materials are metalloporphyrins. These metallotetrapyrrole complexes are versatile functional building blocks in many biological and biochemical processes. Moreover, there are several examples where such molecules were utilized in technical applications, retaining their highly functional nature within an inorganic framework. Examples include gas sensors, solar cells and catalysts. In this presentation the surface chemistry of porphyrins on metal and oxide substrates will be addressed. Specific topics are the interplay between porphyrin-substrate and porphyrin-porphyrin interactions, the role of the substrate, surface diffusion, and the synthesis of metalloporphyrin monolayers by direct metalation of free base porphyrins.<sup>[1-7]</sup>

*Keywords:* Porphyrins; Metalation; XPS; STM

## References

- [1] S. Ditze, M. Stark, M. Drost, F. Buchner, H.-P. Steinrück, H. Marbach, *Activation energy for the self-metalation reaction of 2H-tetraphenylporphyrin on Cu(111)*, *Angew. Chem. Int. Edition* 51 (2012) 10898.
- [2] M. Röckert, M. Franke, Q. Tariq, S. Ditze, M. Stark, P. Uffinger, D. Wechsler, U. Singh, J. Xiao, H. Marbach, H.-P. Steinrück, O. Lytken, *Coverage- and Temperature-dependent Metalation and Dehydrogenation of Tetraphenylporphyrin (2HTPP) on Cu(111)*, *Chem. Eur. J.* 20 (2014) 8948.
- [3] M. Stark, S. Ditze, M. Lepper, L. Zhang, H. Schlott, F. Buchner, M. Röckert, M. Chen, O. Lytken, H.-P. Steinrück, and H. Marbach, *Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenyl-porphyrin on Cu(111)*, *Chem. Commun.* 50 (2014) 10225.
- [4] M. Röckert, M. Franke, Q. Tariq, H.-P. Steinrück and O. Lytken, *Evidence for a Precursor Adcomplex During the Metalation of 2HTPP with Iron on Ag(100)*, *Chem. Phys. Lett.* 635 (2015) 60.
- [5] M. Franke, F. Marchini, H.-P. Steinrück, O. Lytken, F. J. Williams, *Surface Porphyrins Metalate with Zn Ions from Solution*, *J. Phys. Chem. Lett.* 6 (2015) 4845-4849
- [6] J. Schneider, M. Franke, M. Gurrath, M. Röckert, T. Berger, J. Bernardi, B. Meyer, H.-P. Steinrück, O. Lytken, O. Diwald, *Porphyrin Metalation at MgO Surfaces: a Spectroscopic and Quantum Mechanical Study on Complementary Model Systems*, *Chem. Eur. J.* 22 (2016) 1744-1749
- [7] M. Franke, F. Marchini, N. Jux, H.-P. Steinrück, O. Lytken, F. J. Williams, *Zinc Porphyrin Metal Center Exchange at the Solid-Liquid Interface*, *Chem. Eur. J.* (in press)