

# **Controlling a chemical reaction on a surface: applications for scanning probe microscopy**

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Two-dimensional (2D) polymers are expected to have a great impact on many fundamental and applied aspects of science. Some recent demonstrations of covalent polymerization performed directly at surfaces have opened promising perspectives.[1] The polymer formation is usually obtained by deposition of the molecular precursors on the surface followed by thermal activation of the polymerization reaction. In particular, boronic acids can undergo a self-condensation (dehydration) reaction to create rigid boroxine rings and a planar polymer sheet. By using 1,4-benzenediboronic acid (BDBA) evaporated onto a well-defined metal surface, extended nanoporous 2D networks could grow. I will present recent scanning tunneling microscopy (STM) results in ultrahigh vacuum (UHV) reflecting various efforts to control the growth process of these two-dimensional covalent organic frameworks (influence of the deposition parameters, local activation of the reaction, coupling with an Ullmann reaction, nanopatterning).[2]

In a second part I will show how the probe of an atomic force microscopy (AFM) can locally and selectively initiate a chemical reaction. Scanning probe lithography (SPL) is a highly promising tool for the creation of specific nanosized patterns on a surface with high spatial resolution. We reported a novel approach to chemically selective lithography using AFM probe with immobilized homogeneous catalyst, potentially opening an access to a diversity of nanoscale transformations of the surface-bound functional groups.[3] This new concept was proven for local epoxidation of alkene-terminated self-assembled monolayer on silicon using  $H_2O_2$  as an oxidant and a catalytic silicon AFM tip charged with manganese complexes with 1,3,7-triaza-cyclononane type ligand. By varying the reaction parameters (scanning speed, force applied), important insights into the reaction mechanism could be obtained.

## References:

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- [3] D. Valyaev et al., Chemical Science **4**, 2815 (2013)