On-Surface Synthesis – Chemistry in 2D

Roman Fasel

Empa, Swiss Federal Laboratories for Materials Science and Technology, nanotech@surfaces Laboratory, Überlandstrasse 129, 8600 Dübendorf, Switzerland
roman.fasel@empa.ch

On-surface chemistry [1] has attracted great interest as a complement to the traditional solution-based route to the fabrication of covalently bonded nanomaterials. This novel bottom-up approach aims at the fabrication of low-dimensional covalently bonded nanomaterials directly on a solid substrate surface (hence in 2D) under dry conditions (mostly UHV) via the covalent coupling of suitably functionalized molecular precursors. Since the seminal report by Grill and coworkers in 2007 [2] in which they described the successful on-surface synthesis of 0D, 1D and 2D tetraphenylporphyrin assemblies on a Au(111) surface, on-surface synthesis has experienced a tremendous development [3]. In this presentation, I will discuss some recent developments, with a focus on the structural and electronic characterization of the fabricated nanomaterials by means of scanning probe techniques.

After a brief review of the two most extensively studied and applied on-surface reactions, dehalogenative aryl-aryl coupling and (cyclo)dehydrogenation [4], I will discuss a few recent additions to the toolbox of on-surface chemistry. Oxidative ring closure involving methyl groups to establish new six-membered rings is one of the crucial steps in the formation of graphene nanoribbons (GNRs) with pure zigzag edges (ZGNRs) [5]. Ring closure involving methyl groups also plays a pivotal role in the on-surface synthesis of indenofluorene polymers from methyl-substituted terphenyl precursors. I will show that different indenofluorene isomers can be obtained by the appropriate precursor design, and will discuss recent nc-AFM and STS data characterizing these systems in great detail [6]. Another interesting class of materials is given by polycyclic aromatic hydrocarbons (PAHs) incorporating non-hexagonal rings. Recent experiments using carefully designed precursors targeting PAHs including 5- and 7-membered rings will be presented. Furthermore, it will be shown that formal [2+2] cycloaddition of *ortho*-activated acene species allows for the on-surface synthesis of four-membered rings [7]. Finally, the surface-assisted photochemical deprotection of *α*-diketone bridged acene precursors will be presented as a novel approach to the synthesis of higher acenes. Very recent data on the structural and electronic characterization of heptacene and nonacene obtained via bisdecarbonylation of the corresponding precursors will be discussed [8].

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