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Review

Two-dimensional functional molecular nanoarchitectures – Complementary investigations with scanning tunneling microscopy and X-ray spectroscopy

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ABSTRACT

Functional molecular nanoarchitectures (FMNs) are highly relevant for the development of future nanotechnology devices. Profound knowledge about the atomically controlled construction of such nanoscale assemblies is an indispensable requirement to render the implementation of such components into a real product successful. For exploiting their full potential the architectures' functionalities have to be characterized in detail including the ways to tailor them. In recent years a plethora of sophisticated constructs were fabricated touching a wide range of research topics.

The present review summarizes important achievements of bottom-up fabricated, molecular nanostructures created on single crystal metal surfaces under ultra-high vacuum conditions. This selection focuses on examples where self-assembly mechanisms played a central role for their construction. Such systems, though typically quite complex, can be comprehensively understood by the STM+XS approach combining scanning tunneling microscopy (STM) with X-ray spectroscopy (XS) and being aided in the atomic interpretation by the appropriate theoretic analysis, often from density functional theory. The symbiosis of the techniques is especially fruitful because of the complementary character of the information accessed by the local microscopy and the space-averaging spectroscopy tools. STM delivers sub-molecular spatial-resolution, but suffers from limited sensitivity for the chemical and conformational states of the building-blocks. XS compensates these weaknesses with element- and moiety-specific data, which in turn would be hard to interpret with respect to structure formation without the topographic details revealed by STM. The united merit

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of this methodology allows detailed geometric information to be obtained and addresses both the electronic and chemical state of the complex organic species constituting such architectures. Thus, possible changes induced by the various processes such as surface interaction, thermal annealing, or molecular recognition can be followed with unprecedented level of detail.

The well-understood nanoarchitecture construction protocols often rely on the 'classic' supramolecular interactions, namely hydrogen bonding and metal-organic coordination. Further examples include rarely encountered special cases where substrate-mediated processes or repulsive forces drive the emergence of order. The demonstrated functionalities include tuning of the electronic structure by confining surface state electrons and atomically defined arrays of magnetic complexes. Moreover, the high-quality templates can be utilized for imposing novel thin film growth modes or act as basic constituents of nanoswitches. Finally, the aptitude of the STM+XS approach for the emerging field of creating nanoarchitectures by on-surface covalent coupling is addressed.

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