Bonding and electronic structure of self-assembled metal-organic networks on metal surfaces

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Controlling supramolecular self-assembly is a fundamental step towards molecular nanofabrication with potential applications in different fields ranging from surface patterning, heterogeneous catalysis, magnetism and host-guest chemistry. It is known that complex nanostructures with molecular-level accuracy and long-range order can be efficiently obtained by assembling appropriate organic molecules and transition metal atoms on well-defined substrates. The presence of the bridging metal atoms introduces new functionalities due to the distinct charge and spin states of the metal centers and their associated redox and magnetic properties.

Here, we show recent investigations of two-dimensional metal-organic networks in contact with a metal surface performed by scanning tunneling microscopy and spectroscopy as well as x-ray absorption spectroscopy. The examples provide molecular-level insight into the bonding and growth phenomena of the adlayers revealing the importance of the relative strength of the interactions between the constituents and with the underlying substrate. Further, the chemical state of the coordination centers shows a hybrid character being partially atomic like as in free complexes and on the other hand partially hybridized with the surface metal states. This has intriguing consequences for their magnetic properties and chemical reactivity. The latter renders these compounds interesting candidates for functionalized electrodes in biomimetic heterogeneous catalysis.