

On-surface synthesis of polymeric low-dimensional structures with tailorable architecture and functions has been recently one of the most intensively studied topics in nano/surface science. Suitable chemical modification of organic building blocks, for example via selective halogenation, has enabled the creation of diverse monomeric units ready to polymerize in a sterically specific manner when adsorbed on catalytically active metal surfaces. Manipulation of molecular size, shape and intramolecular distribution of active atoms/groups in such monomeric units is thus a powerful method to direct the surface-confined synthesis of 2D polymers. As in numerous cases, the formation of 2D covalent polymers is preceded by the corresponding labile metal-organic precursors (e.g. in the Ullmann coupling reaction) the structure of these coordination connections affects directly the 2D polymer which usually forms next upon thermal treatment. To date, encoding of active centers (e.g. halogen atoms) into the monomeric building blocks has been based mostly on systematic synthesis and testing of various candidate molecules – a procedure which is usually time and resource consuming.

The ultimate objective of the project is to construct a general theoretical model which would enable fast prediction of self-assembled metal-organic superstructures created by halogenated polyaromatic hydrocarbon (PAH) molecules adsorbed on catalytically active metallic substrates. The proposed research focuses on theoretical modeling of the metal-mediated self-assembly of PAH derivatives into diverse low-dimensional superstructures being precursors of 2D covalent polymers with precisely tuned size and shape. The main research subject are the adsorbed overlayers comprising simple mono and poly-halogenated PAH building blocks which can form metal-mediated reversible intermolecular bonds to produce adsorbed nanostructures with tailorable properties. An important objective of the project is to study the influence of such factors as size, shape and functionality of the organic building blocks (number and distribution of halogen substituents), adsorbate density and temperature on the morphology of the resulting assemblies.

Our main intention is to formulate simple and general rules which would facilitate designing 2D organic polymers formed via metal-organic intermediates, based on individual properties of the molecular bricks at play. Using Monte Carlo computer simulations and simple lattice models we are going to test the hypothesis assuming that accurate de novo structure prediction of such self-assembled metal-organic precursors can be made without detailed knowledge about atomic/electronic structure of the interacting components.

An important motivation for running the project is the growing importance of practical methods to fabricate low-dimensional organic polymers which are an alternative to the conventional conducting/semiconducting materials used in (nano)electronics/optics. The results of the project will broaden our understanding of the mechanisms governing the structure formation in adsorbed metal-organic precursor systems and they will provide hints on how to design new 2D polymers with predefined architecture. As we believe, an important output will be the prediction of yet unknown superstructures with intriguing geometric properties. If true, our theoretical research will stimulate or accelerate experimental studies on the corresponding surface-confined molecular/polymeric systems with unique properties.