Ullmann Coupling on Surfaces: Structure and Bonding from Computer Simulations

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Steering molecular self-assembly and polymerization in adsorbed overlayers has been a challenging task which requires detailed information on the interaction patterns associated with molecular geometry, shape and distribution of reactive groups or atoms in the contributing tectons. In this work we present the results of the Monte Carlo simulations aiming at identification of 2D metalorganic precursor structures formed by halogenated PAH molecules having diverse shape/size and differently assigned interaction centers [1-3]. These structures were modeled using the coarse-grained approach in which the PAH building blocks were treated as rigid planar units composed of a few interconnected segments, each corresponding to one benzene ring. Metal-atoms mediating the intermolecular interactions were modeled as single segments. The calculations were performed on a triangular lattice representing a (111) catalytically active metallic crystalline surface. The formation of labile metal-organic precursors, in addition to visual inspection, was monitored by means of such structural descriptors as coordination functions, radial distribution functions, cluster-size statistics and pore size distributions. The obtained findings demonstrated that a suitable halogenation of the PAH tectons enables directing the precursor self-assembly and, potentially, subsequent polymerization towards structures such as strings, ladders, ring oligomers and periodic (also chiral) and aperiodic networks. Moreover, for a spacious set of monomers it was shown that these building blocks are able to create self-similar structures resembling the Sierpiński triangle fractal. The hints gained from the simulations can be helpful in tailoring covalent polymers on solid substrates. These results can also reduce the efforts associated with preliminary selection of PAH monomers capable of formation of lowdimensional architectures with predefined properties, including periodicity, porosity, connectivity, ramification, dispersity etc.

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