Theoretical modeling of the surface-confined self-assembly of functional molecules with directional interactions

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Controlled self-assembly of organic molecules adsorbed on solid supports has been an attractive method of fabrication of functional surfaces with programmable architecture. In this contribution, with the help of theoretical modeling, we show how steering of directional intermolecular interactions which are encoded in a simple organic building block allows for the creation of 2D assemblies with largely diversified morphologies. To that purpose we use the canonical ensemble Monte Carlo method to simulate the self-assembly of a model tripod-shaped molecule adsorbed on a triangular lattice. The calculations were carried out for flat, rigid building blocks built of four discrete segments (core plus three arm segments) and equipped with adjustable peripheral interaction centers providing directional intermolecular bonds. The simulated results demonstrated that the changes in the directionality of interactions assigned to the active centers are responsible for the formation of largely diversified molecular structures including ordered porous networks, chain and ladder structures and chiral patterns. The obtained assemblies were characterized and classified with respect to their structural and energetic properties. Our theoretical studies revealed that small changes in the position of the outer interaction centers in a tripod functional molecule can have crucial influence on the morphology of the resulting adsorbed structures. These findings can be helpful in designing and optimization of the surface-confined self-assembly of organic tripod molecules with the different interaction patterns. This information can facilitate screening of molecular libraries to select the optimal building block able to self-assembly into a 2D superstructure with predefined properties.

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