

Theoretical Modelling of Self-Assembly of Molecular Networks

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The phenomenon of self-assembly of atomic and molecular superstructures on crystal surfaces has attracted an increasing interest in nanotechnology. Self-organised nano-templates where the self-assembled monolayer traps other molecules with selected functional properties, can be used as building blocks for larger nanoscale structures. Self-assembled superstructures can form chiral domains ranging from 1D chains to 2D monolayers.

In particular, there have been many scanning tunneling microscopy (STM) studies of self-assembly of melamine, perylene tetra-carboxylic di-imide (PTCDI) or perylene tetra-carboxylic di-anhydride (PTCDA) molecules on the Au(111) and Ag/Si(111) surfaces [1],[2] [5]. STM images of these networks do not reveal the exact details of the intermolecular bonding and process of network growth. It is therefore the task of theory to determine the exact atomic structure of these networks.

We present a theoretical study of self-assembly of molecular networks based on melamine, PTCDA and PTCDI molecules. We propose a systematic approach to building molecular superstructures based on the notion of binding sites. First, we identify all possible sites for hydrogen bonding between molecules. Then we form molecular pairs and larger structures using all possible combinations of these binding sites. In this way, we construct all possible dimers, chains and 2D monolayers of melamine, PTCDA and PTCDI. Both monomolecular and bimolecular structures are considered. The energies of these structures are calculated using the density-functional theory SIESTA code. The strength of hydrogen bonding in various molecular arrangements is analysed. The theoretically predicted monolayer structures are in very good agreement with the results of STM measurements [4][5].

References:

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