Predicting the concentration-dependent self-assembly of weakly interacting molecules at surfaces

The self-assembly of 1,3,5-tris(pyridine-4-ylethynyl)benzene derivatives on graphite was recently shown by STM imaging to be highly concentration-dependent. These molecules, which are flat C3-symmetric compounds, are thought to arrange into highly ordered architectures through weak hydrogen-bonding interactions. Here, we explore the concentration-dependent self-assembly of these molecular tripods by calculation using the Merck Molecular Force Field (MMFF) and an explicit model of the substrate. A series of 2D ordered arrangements, which were produced based on chemical intuition, are analysed by comparing the MMFF energy of the unit cell. The results indicate that the concentration dependence of weakly interacting molecules arises from the interplay between the strength of molecular recognition in the self-assembled monolayer, which favours the porous architecture, and the strength of the interaction with the substrate, which favours the densely packed parallel arrangement, in agreement with the STM analysis. We predict that an antiparallel architecture, which was never observed in the experiments, should arise in an intermediate range of concentrations.