

Abstract

Interaction of organic molecules with solid surfaces represents a key area of physical-chemistry research. From heterogenous catalysis to OLED displays, in numerous such systems molecules interact on interfaces, and understanding their behavior is crucial for the correct operation of such applications. In this work, I focused on the study of large π -conjugated macrocycles based on dibenzo[5]helicenes with emphasis on their behavior on graphite surface.

The chemical synthesis of the investigated macrocycles was initially impeded by a number of obstacles, particularly by their extremely low solubility. In this work, an efficient solubilization strategy based on the modification of the macrocycles with trityl groups was discovered, which effectively diminishes the intense intermolecular π - π interactions. This opened a path towards a subsequent study of the compound's properties. The attention was focused mainly on a trimer, which was successfully fully characterized, enabling further experiments. Since only a few tens of milligrams of the trimer was prepared, and some stereoisomers were isolated in only microscopic amounts, it was important to develop a suitable experimental methodology. These methods were successfully employed in the measurement of the isomerization kinetics, which allowed us to map the process of the consecutive helicity inversion, determine the rate constants and the corresponding inversion barriers. This project provided valuable insight into the relationship between the behavior of the macrocycle and its individual helicene subunits.

The attention was subsequently focused on the self-assembly on the surface of pyrolytic graphite. With the help of ambient AFM, macrocycles arranged in highly organized 2D crystals were observed, even despite the presence of the very bulky trityl groups. By using the PeakForce tapping mode, images with molecular resolution were obtained, including even individual molecules within the 2D crystals. As shown by subsequent molecular dynamics (MD) simulations, not only the trityl groups do not prevent the self-assembly, but they even substantially contribute to the stability of the formed 2D crystals, by a mechanism similar to the Velcro. The large computational cost of the MD simulations motivated us to develop an algorithm employing Lennard-Jones potential, with which a fast evaluation of the stability of the various molecular aggregates was possible. Despite its substantial simplifications, the algorithm helped us to explain several fine structural details of the observed adlayers.

Considering the trimer is formally a $4n$ π -electron system, the last part of the Thesis was dedicated to the study of its possible (anti)aromaticity. On the theoretical level, NICS and ACID calculations were performed, but the obtained results were surprisingly sensitive to the calculation parameters. The experimental investigation of the associated ring currents using NMR did not show evident global aromaticity. On surface calculations on graphite also showed a significant charge transfer from the molecule to graphite and implications on the aromatic state of the molecule were investigated. As in the solution phase, the results suggest that the global aromaticity of the macrocycle on the surface is negligible.

Keywords: Helicenes, macrocycles, chirality, self-assembly, AFM, molecular dynamics, aromaticity