

## **Structural studies of the supramolecular systems based on pillar[*n*]arenes**

Helena Butkiewicz

Carboxylated pillar[*n*]arenes ( $n = 5, 6$ ; CPA5, CPA6) are highly symmetrical pillar-shaped macrocycles, composed of hydroquinone units linked by methylene bridges at the *para*-positions of aromatic rings, decorated by carboxylic acid groups. Their hydrophobic, electron-rich cavities combined with water solubility make them great candidates as host molecules for various electron deficient, cationic or neutral guest molecules. Moreover, the presence of carboxyl groups at the both rims, that can be deprotonated, gives the possibility of formation of different supramolecular synthons based on hydrogen bonds with both donor and acceptor groups, and thus creating complex, multidimensional structures.

Carboxylated pillar[5,6]arenes and their complexes in the solution have been in the center of interest of supramolecular chemists for many years. Complex systems based on pillar[*n*]arenes can be used in drug delivery, dyes and hormone transporters or in supramolecular catalysis. Despite the very interesting properties, they have been an unexplored class of building blocks in crystal engineering.

The aim of the dissertation was to obtain crystalline host-guest and coordination complexes of CPA5 and CPA6 and to analyse their structures by single crystal X-ray diffraction. Structural studies on the CPA5-viologen complexes show that the self-assembly is dictated by strong carboxylic-carboxylate hydrogen bonds. Altering the guest with competitive functional groups changes main synthon into amidinium-carboxyl/ate and guanidinium-carboxyl/ate hydrogen bonds. The addition of the metal cations results in the formation of coordination polymers, which may be perturbed by the addition of a coligand, for example phenantroline. One of the greatest achievements of this work is the first structural authentication of carboxylated pillar[6]arene in its host-guest complexes with dimethyl viologen and pentamidine. The most interesting finding is the deformation of CPA6 molecule, that mimics pentagonal shape due to the presence of two intramolecular hydrogen bonds. The information on the intermolecular interactions in the pillar[5,6]arenes complexes and their self-assembly allows for more precise design and construction of hierarchical architectures based on CPA5 and CPA6. In a broader perspective these results may have potential applications in the building of molecular machines, MOFs and HOFs, for drug delivery or gas storage.