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**Self-organization of *para*-sulfonatocalix[*n*]arenes and selected aromatic amines
in heteromolecular crystals: structural studies.**

Supramolecular chemistry is an interdisciplinary field of science that deals with the design, formation and exploration of complex chemical systems of smaller building blocks joined by non-covalent intermolecular interactions. One of its tasks is to look for new molecular receptors, and acquiring knowledge about molecular recognition which involves the formation of selective bond between a receptor and the substrate molecules, resulting in the host-guest complex formation. The dissertation presents research results concerning construction of inclusion complexes of *p*-sulfonatocalix[*n*]arenes ($n = 4, 6, 8$). Aromatic amines such as 4,4'-bipyridine, 1,2-bis(4-pyridyl)-ethane, 1,3-bis(4-pyridyl)-propane, and 1,10-phenanthroline were selected as potential guest molecules. Structures of crystalline guest-host complexes were determined by means of X-ray diffraction. Intermolecular interactions were analyzed and the organization of ions and molecules in the crystal lattice was described.

p-Sulfonatocalix[*n*]arenes ($n = 4, 6, 8$) show a great ability to interact with the mentioned above aromatic amines. The obtained supramolecular systems are organic salts formed from deprotonated calixarene and protonated guest molecules. Anion receptors form inclusion complexes with substrates mainly by π - π , C-H $\cdots\pi$ and N-H $\cdots\pi$ interactions. New, not described before, conformations of the *p*-sulfonatocalix[8]arene anion was observed and described and it has been shown that this particular anion may substantially change its conformation depending on the type and the amount of complexed cations. In the obtained complexes, the mechanism of induced fitting is observed in cases where the substrate forces the conformational change of the receptor and the mechanism of mutual induced fitting is observed, when there is a mutual adjusting host and guest molecules.

Ions and molecules in described supramolecular compounds contribute to the formation of various structural motifs, such as dimers, trimers, tetramers, infinite stacks, capsules, columns, ribbons, polymeric chains, channels. The obtained inclusion complexes are characterized by diverse molecular packing in the crystal lattice and diverse topologies from simple, stepped and a "zig-zag" bilayers through the column packing to the three-dimensional network of intersecting channels. In the studied systems a following relationship is observed: the larger differences are between the molecular conformations of the calixarene, the major

differences are observed in the supramolecular self-assembly, in the found structural motifs and in crystal packing.

On the basis of the obtained supramolecular assemblies it can be stated that *p*-sulfonatocalix[*n*]arene/aromatic amine systems are able to spontaneous generation of well-defined, structured supramolecular architectures. The obtained results show structural diversity of these compounds, a great richness of supramolecular chemistry, and demonstrate that these compounds are promising "building blocks" to construct further supramolecular architectures of high complexity. The information gained about the crystal and molecular structures of *p*-sulfonatocalix[*n*]arenes complexes with aromatic amines can contribute significantly to the development of supramolecular chemistry and crystal engineering – a field, that deals with obtaining–crystal structures with designed properties, and also for materials chemistry, aimed at obtaining new functional materials.