

### s9.m3.p5 Supramolecular Chemistry of Calixarenes.

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Calixarene molecules are a category of supramolecular receptors exhibiting rigid cavities, generally in a cone conformation, which allows molecular recognition.

The supramolecular chemistry of calixarenes encompasses: host-guest species in supermolecules; molecular recognition; and inclusion and intercalation complexes. The significance of the area relates to the potential of supramolecular chemistry in building up new materials with novel function. Clearly there are many other species which are potential candidates for supramolecular chemistry, including organic P-, N- containing heterocycles, polycyclic compounds. A major part of this presentation deals with calixarenes which show a remarkable ability to self assemble via hydrogen bonds involving the C-H groups and C-H- $\pi$  interactions. Using single-crystal diffractometry, powder diffractometry and small-angle X-ray scattering the structure of new series of calixarenes and their derivatives in neutral, protonated and deprotonated forms were studied. It was shown that the structure of the calixarene moiety and three dimensional arrangement of the complexes with the same calixarene fragment depend greatly on the "guest" metal, inclusion of solvate molecules and on the type of hydrogen bonds.

It was found that the hydrophobic and hydrophilic regions are strongly localised in crystals. For crystal packing analysis a fragmentary structure, consisting of infinite one-dimensional stick, is chosen as a building units of the three dimensional packing. The stick (which can be considered as a substructure of crystal formation) consists of more hydrophobic calixarene residues, whereas polar substituents, inorganic anions and solvate molecules form hydrophilic shell around the sticks. The stick formation as well as its packing in crystals depend on the hydrogen bonding and weak interactions. Several types of superstructures which differ by the host:guest stoichiometry and the mode of metal-guest and host molecules respective disposition has been observed.

For confirmation of this model investigations of the kinetics of crystal destruction from single-crystals to polycrystals and self-associates in solution were performed. It was shown that the solid-state structure of calixarenes and complexes is reorganized upon the solvent exclusion and temperature increasing. This model is used for the comparative analysis of structure, correlation of packing and intermolecular interactions in a series of new compounds belonging to four different classes: calixarenes with substituents in upper and lower rings, phosphorus and nitrogen containing heterocycles and polycyclic natural compounds.

### s9.m3.p6 The Structural Studies on Calix[4]arene Ligands and Their Complexes with Anions.

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The study of electron deficient abiotic receptor molecules designed for non-covalent binding of anion guest species is an area of ever increasing research activity. However, theoretical studies have mainly focused on macrocyclic receptors for cations and anion chemistry has developed more slowly<sup>1</sup>. We have published the study of amide bond activation for anion complexation<sup>2</sup> and the DFT study on the structure of simple aromatic amides (Ar-CO-NH-Ar', where Ar and Ar' are (per)fluorinated phenyl or pyridil groups) and their 1:1 complexes with bromide anion<sup>3</sup>.

Several ligands on the calix[4]arene base have been prepared by modification of the calixarene framework on upper-rim by Ar-CO-NH- functional group as a multidentate neutral ligands for anion complexation. The anion - cation couples complexation was observable after modification of this skeleton by four ester groups located on the lower-rim.

The structural analysis of the ligands and their complexes with anions has been performed. The project is focused on optimization of theoretical methods for correct description of structure and properties of the man-made large molecular systems and their complexes. Crystallographic analyses of the tetraamide calixarenes and their 1:1 complexes with halides have been compared with theoretical data on DFT and *ab initio* HF level. The structural aspects of complexation and conformational modifications of the calixarene macrocycles induced by the process of complexation will be discussed.

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