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Title of the doctoral dissertation: **Host–guest complexes and assemblies based on calix[*n*]arenes: structural diversity and transformations.**

Abstract

p-Sulfonatocalix[*n*]arenes have long been studied for their host–guest complexation behavior and have found applications in drug delivery, molecular sensing, supramolecular catalysis, and protein crystal engineering, etc. Their attractiveness stems from high aqueous solubility, oligo-anionic charge, conformational flexibility, and low toxicity. In the solid state, multiple sulfonate groups at the macrocyclic rim promote charge-assisted hydrogen bonding and electrostatic interactions, leading to diverse supramolecular synthons and extended multidimensional assemblies. The presence of inner cavities further enables porous material design, including molecular sieving and guest-permeable frameworks. Despite substantial progress in recent decades, many aspects of *p*-sulfonatocalix[*n*]arene complexation and crystallization remain poorly understood due to their pronounced conformational flexibility, especially in larger homologues, and sensitivity to crystallization conditions.

This dissertation aims to establish how host size and flexibility, guest functionalization, solvent composition, and counterions determine the solid-state structure of *p*-sulfonatocalix[*n*]arene complexes. The selected guest molecules include various benzamidine derivatives, which enable highly directional charge-assisted hydrogen bonding via amidinium–sulfonate synthons. Another group of guests comprises species devoid of classical hydrogen-bond donors, including pillar[*n*]pyridiniums and berberine. Structural characterization of host–guest complexes and assemblies was performed by single-crystal X-ray diffraction, supported by PXRD, TGA–DSC, and selected NMR studies in solution.

Across all benzamidine complexes, charge-assisted *N–H*⋯*O* hydrogen bonding to anionic sulfonate groups is the dominant host–guest interaction. Host size and conformational freedom strongly influence the complexation mode. Larger calix[6]arene and calix[8]arene adopt multiple conformations that create pseudo-cavities and grooves. These features support multi-guest

inclusion, external surface binding, and cooperative host–guest–solvent assemblies. Calixarene counterions, particularly sodium ions, play an important role in determining stoichiometry and supramolecular connectivity. Pronounced guest–solvent competition is observed, and the binding mode (inclusion versus exclusion) can be switched by changing the complexation or crystallization medium. Although many *p*-sulfonatocalix[*n*]arene complexes lose crystallinity upon dehydration, selected frameworks exhibit notable stability and even single-crystal-to-single-crystal transformations, suggesting potential for porous or guest-permeable materials. These outcomes establish design principles for calixarene assemblies and emphasize the usefulness of sulfonated calixarenes as building blocks for supramolecular materials and crystal engineering.