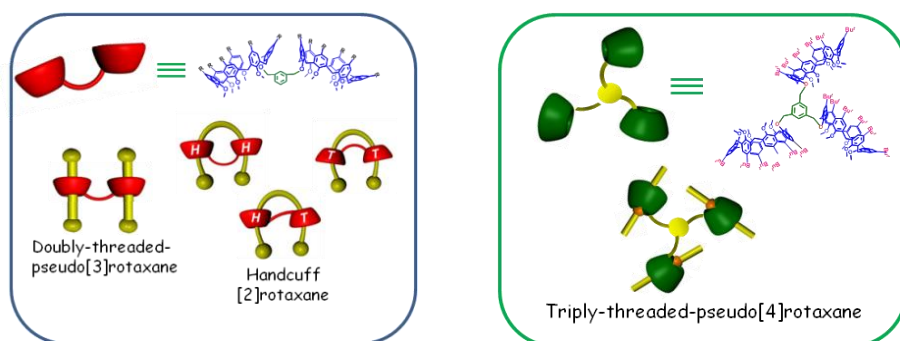


Abstract

Recently, Neri et al. have introduced an efficient method to obtain *endo*-cavity complexation and *through-the-annulus* threading of large calixarenes by exploiting the inducing effect of the weakly coordinating tetrakis[3,5-bis-trifluoromethyl)phenyl]borate (TFPB⁻) anion. The corresponding calix[6]-arene/dialkylammonium pair can be considered a versatile recognition motif, which can be used for the construction of a large variety of calixarene-threaded architectures.

This Ph. D. thesis deals with the exploration of the stereochemical features of the threading of hosts containing multiple cavities. Therefore, the synthesis of double- and triple-calixarenes is reported, which is followed by the subsequent study of their threading abilities with dialkylammonium axles.



The results confirmed the now well-known *endo-alkyl* rule of calix[6]arenes that give the inclusion of alkyl chains inside the calix-cavity. On this basis, we were then able to build new attractive chemical topologies. In particular, doubly-threaded pseudo[3]rotaxane structures have been obtained by the threading of double-calixarene hosts with mono-ammonium axles. The subsequent extension to triple-calixarene hosts, in which three macrocycles are covalently linked to one another by means of an appropriate spacer, gave triply-threaded pseudo[4]rotaxane structures.

Because of the three-dimensional nonsymmetrical nature of the calix[6]arene wheels, by threading double-calixarene hosts with bis-ammonium axles three examples of beautiful stereoisomeric calixarene-based handcuff rotaxanes were obtained, which could be termed as *head-to-head* (*H,H*), *head-to-tail* (*H,T*), and *tail-to-tail* (*T,T*).

On the basis of these results, it is conceivable that the extension of this approach could lead to novel mechanically interlocked architectures with high-order topologies.