



Supramolecular systems based on calixarenes

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The design, structural characterization and specific properties of (thia)calix[4]arene based supramolecular systems are considered.

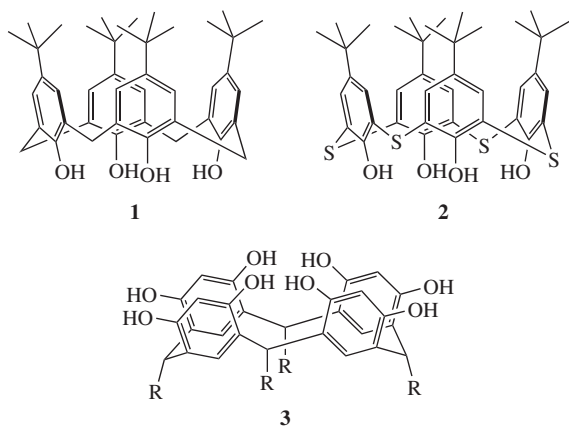
The ‘bottom-up’ technology, in which the higher organized nanosystems are spontaneously formed due to supramolecular self-organization and self-assembly from individual atoms and molecules, is promising for the design of nanomaterials. A key element of supramolecular chemistry, and now nanotechnology, is the principle of molecular recognition. It is well known that molecular recognition (or self-recognition) partners is the reason of a higher specificity of many chemical and biochemical reactions and processes. The result of the recognition is the selective binding of two or more atoms (molecules) with the formation of supramolecular assemblies. From this point of view, an urgent problem of supramolecular chemistry is the

molecular design and synthesis of preorganized receptor and amphiphilic molecules, which are capable, on the principles of molecular recognition and multipoint interactions, to form host–guest complexes, as well as self-organized supramolecular assemblies and devices.

A nanotechnological approach ‘bottom-up’ can be effectively implemented on the basis of meta-cyclophanes: calix[4]arene **1**, thiocalix[4]arene **2** and calix[4]resorcinarene **3**.¹

Supramolecular chemistry of calixarenes (phenol and aldehyde cyclic condensation products) has been intensely developed in the last two decades.^{2–4} Calix[4]arenes have several attractive properties for the design of receptor molecules, self-organized systems and nanoobjects: (i) the low cost and accessibility of parent macrocycles by one-pot synthesis; (ii) nontoxicity of calixarene platforms; (iii) calixarene ability to incorporate small hydrophobic organic molecules into their molecular cavities with the formation of the stable host–guest complexes; (iv) existence of some macrocycle conformations and ability to fix the required spatial orientation of binding centers (Scheme 1); and (v) a unique possibility to decorate the upper and lower rim of macrocycle by the suitable heteroatom groups and to form the molecular system possessing several binding centers.

Molecular design of receptor structures on the basis of a (thia)calixarene platform. The simplest type of recognition is the selective binding of spherical substrates. To perform this spherical recognition and design of the selective receptors for metal cations, the symmetric pseudo-cavity formed by eight



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