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The synthesis of *p-tert*-butyl thiacalix[4]arenes functionalized with secondary amide groups at the lower rim and their extraction properties and self-assembly into nanoscale aggregates

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ABSTRACT

In this work, the synthesis of novel *p-tert*-butyl thiacalix[4]arenes functionalized with the secondary amide groups at the lower rim in *cone*, *partial cone*, and 1,3-*alternate* conformations is described. The ability of novel thiacalixarene derivatives to form dimeric associates held together by hydrogen bonds of *p-tert*-butyl thiacalixarenes and to recognize metal ions of s (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}), p (Al^{3+}, Pb^{2+}), and d (Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Ag^+, Cd^{2+}, Hg^{2+}) elements was investigated by the picrate extraction method and dynamic light scattering (DLS). As was established, the thiacalix[4]arenes investigated are poor extractants for all the metal ions. Meanwhile they self-associate to form dimers of similar size (1.1–2.7 nm) and nanoscale particles consisting of *p-tert*-butyl thiacalix[4]arenes and silver cations with hydrodynamic diameters of 70–170 nm.

1. Introduction

The design and synthesis of a variety of host molecules is an interesting topic in the field of supramolecular chemistry[1,2] because of the specified applications of these novel compounds[3] and necessity of the basic research of molecular recognition,[4–6] self-assembly,[7–10] and self-organizing[11,12] processes. These synthetic receptors are irreplaceable as base elements in the development of sensors,[13–15] and as selective carriers in industrial membrane extraction technologies,[4,16,17] highly affine and convertible effectors,[18–20] and catalysts.[21] One of the popular molecular platforms for the design of molecular receptors is the calix[4]arene.[22,23] The advantage of the host molecules consisting of the modification at the upper and lower rim of the appropriate macrocyclic platform[24] and the replacement of original methylene bridges between the aromatic units in calixarenes by sulfur,[24–26] nitrogen,[3,27] and silicon[28] atoms allows varieties of the receptor properties of these molecules over a wide range. Besides, the calix[4]arenes are able to form supramolecular aggregates consisting of two, three or more receptor molecules.[29,30] The ability of the host molecules to self-assemble is caused by H-bonding, van der Waals, π–π, donor–acceptor, and some lipophilic interactions between various substituents.[3,21] The dimeric covalent binding[3,17,31,32] and self-assembling[33–35] associates of the calix[4]arene derivatives are able to selectively include various substrates. This makes it possible to use them as containers for sensing, fixation, and storage of molecules.[17] In this work, we describe the synthesis of novel *p-tert*-butyl thiacalix[4]arenes functionalized with secondary amide groups at the lower rim in *cone*, *partial cone*, and 1,3-*alternate* conformations and study the ability of these molecules both to form dimeric associates, which are held together by a seam of hydrogen bonds of *p-tert*-butyl thiacalix[4]arenes and to recognize metal ions of s (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}), p (Al^{3+}, Pb^{2+}), and d (Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Ag^+, Cd^{2+}, Hg^{2+}) elements as shown by the picrate extraction method and dynamic light scattering (DLS).

2. Results and discussion

2.1. Synthesis of stereoisomers of tetrasubstituted at the lower rim *p-tert*-butyl thiacalix[4]arenes containing secondary amide fragments

Thiacalix[*n*]arenes provide a unique opportunity to modify the macrocyclic platform and a wide variation of hydrophilic–lipophilic properties. This is especially important because the selective

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