



# 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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## ARTICLE INFO

### Article history:

Received 14 February 2008

Received in revised form 29 April 2008

Accepted 15 May 2008

Available online 17 May 2008

### Keywords:

Self-assembly

*p*-*tert*-Butyl thiacalix[4]arenes

Molecular recognition

Picrate extraction

Dynamic light scattering (DLS)

## 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 ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ), p ( $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ), and d ( $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) 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.

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## 1. Introduction

The design and synthesis of a variety of host molecules is an interesting topic in the field of supramolecular chemistry<sup>1,2</sup> because of the specified applications of these novel compounds<sup>3</sup> and necessity of the basic research of molecular recognition,<sup>4–6</sup> self-assembly,<sup>7–10</sup> and self-organizing<sup>11,12</sup> processes. These synthetic receptors are irreplaceable as base elements in the development of sensors,<sup>13–15</sup> and as selective carriers in industrial membrane extraction technologies,<sup>4,16,17</sup> highly affine and convertible effectors,<sup>18–20</sup> and catalysts.<sup>21</sup> One of the popular molecular platforms for the design of molecular receptors is the calix[4]arene.<sup>22,23</sup> The advantage of the host molecules consisting of the modification at the upper and lower rim of the appropriate macrocyclic platform<sup>24</sup> and the replacement of original methylene bridges between the aromatic units in calixarenes by sulfur,<sup>24–26</sup> nitrogen,<sup>3,27</sup> and silicon<sup>28</sup> 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.<sup>29,30</sup> The ability of the host molecules to self-assemble is caused by H-bonding, van der Waals,  $\pi$ – $\pi$ , donor–

acceptor, and some lipophilic interactions between various substituents.<sup>3,21</sup> The dimeric covalent binding<sup>3,17,31,32</sup> and self-assembling<sup>33–35</sup> 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.<sup>17</sup> 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 ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ), p ( $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ), and d ( $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) 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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