



Supramolecular self-assemblies of stereoisomers of *p*-*tert*-butyl thiacalix[4]arenes functionalized with hydrazide groups at the lower rim with some metal cations

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ABSTRACT

Novel *p*-*tert*-butyl thiacalix[4]arenes functionalized with hydrazide groups at the lower rim in *cone*, *partial cone* and *1,3-alternate* conformations were synthesized and their receptor properties toward metal ions of p- (Al^{3+} , Pb^{2+}) and d- (Fe^{3+} , Co^{3+} , Ni^{2+} , Cu^{2+} , Ag^+ , Cd^{2+}) elements were investigated by picrate extraction and dynamic light scattering (DLS). It was shown that the *p*-*tert*-butyl thiacalix[4]arenes functionalized with hydrazide groups are effective extractants of soft metal cations. The complex stoichiometry depended on the receptor configuration. All the *p*-*tert*-butyl thiacalix[4]arene derivatives with hydrazide fragments were able to form nanoscale aggregates but did not show self-association abilities.

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1. Introduction

Chemical and physical properties of nanomaterials differ dramatically from those molecules and depend on their size, i.e., the quantity of atoms or molecules forming nanoscale structures.^{1,2} The establishment of 'structure–property' relationships that control the size, shape and chemical properties of nanoscale aggregates on the spatial level is considered an important problem. Presently, the development of approaches to the synthesis and modification of the particles from 1 nm to 1 μm , and appropriate nanomaterials is one of the priority directions in the nanotechnology area.¹ As a rule, nanoparticles of a definite size can be formed by self-association processes. This can be most effectively achieved by non-covalent self-assembly affected by specially designed ligands spontaneously connecting via metal ions. One of the appropriate classes of host molecule used for this purpose, are macrocyclic polyphenols.^{3,4} They have been successfully used for the design of a variety of receptor molecules showing complexation properties. Calix[4]arene-based receptors possessing unusual cavity dimensions have been synthesized via upper and lower rim functionalization. Their complexation properties highly depend on the nature and number of donor atoms of the substituents as well as conformation of the calix[4]arene moiety.^{3–8}

In this work, novel *p*-*tert*-butyl thiacalix[4]arenes containing hydrazide units attached to the lower rim in *cone*, *partial cone* and *1,3-alternate* conformations have been synthesized and their receptor properties toward metal ions of p- (Al^{3+} , Pb^{2+}) and d- (Fe^{3+} , Co^{3+} , Ni^{2+} , Cu^{2+} , Ag^+ , Cd^{2+}) elements were investigated by picrate extraction and dynamic light scattering (DLS).^{9,10}

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

The hydrazide fragments of the macrocycles are amenable to further modification by various reagents (Fig. 1). The introduction of the hydrazide groups at the lower rim of the *p*-*tert*-butyl thiacalix[4]arenes **1** were found to be very promising for the development of thiacalix[4]arene derivatives.

The interaction of tetraesters **2** with hydrazine hydrate in various solvents has been investigated (Table 1). The reaction was controlled by TLC. Typically, the stereoisomers of tetraesters **2** interact with the excess of hydrazine hydrate in ethanol.^{11,12}

However, the reaction of tetraester **2** with a 10-fold excess of hydrazine hydrate in boiling ethanol led to formation of the target product **1** with high yields of 95% only in the case of the *partial cone*. No reaction was observed for *1,3-alternate-2* and the initial tetraester was quantitatively isolated from the reaction mixture. The replacement of the solvent by a mixture of ethanol/THF increased the solubility of initial tetraether-**2** in the *1,3-alternate* conformation

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