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PAPER

# Heteroditopic *p*-*tert*-butyl thiacalix[4]arenes for creating supramolecular self-assemblies by cascade or commutative mechanisms†

Elena A. Yushkova,<sup>a</sup> Ivan I. Stoikov,<sup>\*a</sup> Arkadiy Yu. Zhukov,<sup>a</sup> Joshua B. Puplampu,<sup>a</sup> Ildar Kh. Rizvanov,<sup>b</sup> Igor S. Antipin<sup>a</sup> and Alexander Konovalov<sup>a</sup>

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New *p*-*tert*-butylthiacalix[4]arenes functionalized with hydrazides of nicotinic, isonicotinic, 3-nitrobenzoic acids, 2-hydrazinopyridine, phenylhydrazine, benzotriazole groups at the lower rim in *cone*, *partial cone* and *1,3-alternate* conformation have been synthesized. The mechanism of self-assembly of supramolecular nanosized particles based on functionalized *p*-*tert*-butylthiacalix[4]arenes with silver nitrate and or dicarboxylic acids (oxalic, malonic, succinic acid) has been determined by dynamic light scattering. For the first time, it has been shown that nanoscale particles based on *p*-*tert*-butylthiacalix[4]arenes, capable of recognizing metal cations and dicarboxylic acids can form cascade or commutative three-component supramolecular systems. Also for the first time, it has been shown that *p*-*tert*-butylthiacalix[4]arenes containing *N*-substituted hydrazide and heterocyclic fragments are coreceptors, capable of simultaneously binding silver (I) cations and dicarboxylic acids. The formation of cascade systems: “macrocycle-silver (I) nitrate-dicarboxylic acid” is a characteristic of *p*-*tert*-butyl thiacalix[4]arenes containing *N*-substituted hydrazide fragments.

## Introduction

The development of self-assembled micro- and nano-sized supramolecular systems with a given property is one of the most rapidly developing fields in organic and supramolecular chemistry.<sup>1–4</sup> The structure and properties of supermolecules and supramolecular assemblies can be predetermined during the covalent receptor synthesis.<sup>3–12</sup> Designed synthetic receptors capable of recognizing different types of “guests” have been employed in the construction of sensors, catalysts, biomimetic systems, selective extractants, drug delivery systems and programmable materials.<sup>12–20</sup>

Various macrocyclic “building” platforms *e.g.*, crown ethers, cyclodextrins and calixarenes, are currently used in the development of synthetic receptors.<sup>3,4,16,21,22</sup> The uniqueness of thiacalix[4]arenes, analogues of classical calixarenes, is that: (1) the initial macrocycles are easily obtained by one-step synthesis,<sup>21–23</sup> (2) they have sulfide bridged fragments capable of coordinating transition metal cations,<sup>24</sup> (3) the upper and lower rims of the macrocycle can be modified by various functional groups,<sup>21,22</sup> (4) they exist in multiple conformations that can position binding

sites in desired spatial orientations<sup>25–27</sup> and, (5) allosteric effect can be realized during the binding of “guests.”<sup>28,29</sup>

Recently, Lotak’s research group demonstrated that thiacalix[4]arenes containing alkoxy groups (n-PrO– and MeO–) formed solid-state assemblies during their interaction with silver triflate (I).<sup>24</sup> The aggregation of *p*-*tert*-butylthiacalix[4]arene stereoisomers with alkali metal nitrate, p- and d-elements in dichloromethane has been studied by dynamic light scattering.<sup>30–32</sup> The hydrodynamic diameters of nanoaggregates, polydispersity index (PDI, particle size distribution), and molecular weights (for the determination of the number of structural fragments, N, *i.e.* *p*-*tert*-butylthiacalix[4]arene molecules and metal cations, which form nanoscale associates) have been determined.<sup>33,34</sup> It has been shown that depending on the conformation of the macrocycle, the nature of binding sites and the nature of metal cations, *p*-*tert*-butylthiacalix[4]arenes and metal nitrates are capable of forming not only “guest–host” complexes, but also dimers, spherical, ellipsoidal and elongated nanosized particles.<sup>33,34</sup>

However, there has been no report on the possibility of supramolecular assemblies forming during the interaction of cationic, anionic and neutral substrates with the simultaneous participation of both the sulfide bridges and the functional groups of *p*-*tert*-butylthiacalix[4]arenes. Thus, we propose that the ability of the thiacalix[4]arene platform to form nanoscale aggregates with metal cations and dicarboxylic acids with the participation of different coordination sites, and the realization of allosteric effect during binding of “guests” should be exploited in the development of cascade and commutative (three-component) nanoscale systems (Fig. 1).

<sup>a</sup>Kazan (Volga Region) Federal University, A.M. Butlerov Chemical Institute, 420008, Kremlevskaya, 18, Kazan, Russian Federation. E-mail: Ivan.Stoikov@mail.ru; Fax: +7-8432-752253; Tel: +7-8432-337463

<sup>b</sup>Russian Academy of Sciences, A.E. Arbuзов Institute of Organic and Physical Chemistry, Kazan, Russian Federation

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