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Synthesis and properties of mono-*O*-[(*N*-(aminoalkyl)aminocarbonyl)-methoxy]thiacalix[4]arenes and novel mono-O-bridged bisthiacalix[4]arene

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ABSTRACT

A simple method for thiacalix[4]arene *O*-monoamide preparation with high yields using 5,11,17,23-tetra-*tert*-butyl-28-(ethoxycarbonyl)methoxy-2,8,14,20-tetrathiacalix[4]arene reaction with diaminoalkanes is reported. The solid state cyclization reaction of the acylethylenediamines function of 5,11,17,23-tetra-*tert*-butyl-28-*O*-[(*N*-(2-aminoethyl)aminocarbonyl)-methoxy]thiacalix[4]arene leading to the formation of the 5,11,17,23-tetra-*tert*-butyl-28-[2-methoxy-imdazoline]thiacalix[4]arene compound is described for the first time for the calixarene macrocycle family. Finally, preliminary results show that *O*-mono-amide-thiacalixarene derivatives are promising candidates for the production of self-assembled materials and efficient precursors for the synthesis of bisthiacalix[4]arenes.

RÉSUMÉ

Nous reportons la préparation de dérivés *O*-monoamide thiacalixarènes obtenus à partir de la réaction entre le 5,11,17,23-tetra-*tert*-butyl-28-(ethoxycarbonyl)methoxy-2,8,14,20-tetrathiacalix[4]arene et différents diamino-alcanes. La réaction, à l'état solide, de cyclisation de la fonction acyléthylènediamine du composé 5,11,17,23-tetra-*tert*-butyl-28-*O*-[(*N*-(2-aminoethyl)aminocarbonyl)-methoxy]thiacalix[4]arene conduisant au composé 5,11,17,23-tetra-*tert*-butyl-25-[2-imdazoline-methoxy]thiacalix[4]arene est décrite pour la première fois pour la famille des macrocycles calixarèniques. Enfin, des réactions préliminaires attestent que les dérivés *O*-monoamide-thiacalixarènes sont de bons candidats pour l'obtention de matériaux auto-assemblés ainsi que de bons précurseurs pour la synthèse de bisthiacalix[4]arènes.

1. Introduction

Thiacalixarenes are molecules in the calixarene family in which the methylene bridge of the classical calixarenes is replaced with epithio groups [1]. Their ease of preparation and high potential for numerous applications has increased the interest in this class of macrocycles and, in particular, for the preparation of polynuclear metal complexes, an endeavor in which our research group has been involved for several years [2,3]. In a previous publication, we reported the first quantitative syntheses of several mono-*O*-alkylated-thiacalix[4]arenes in order to

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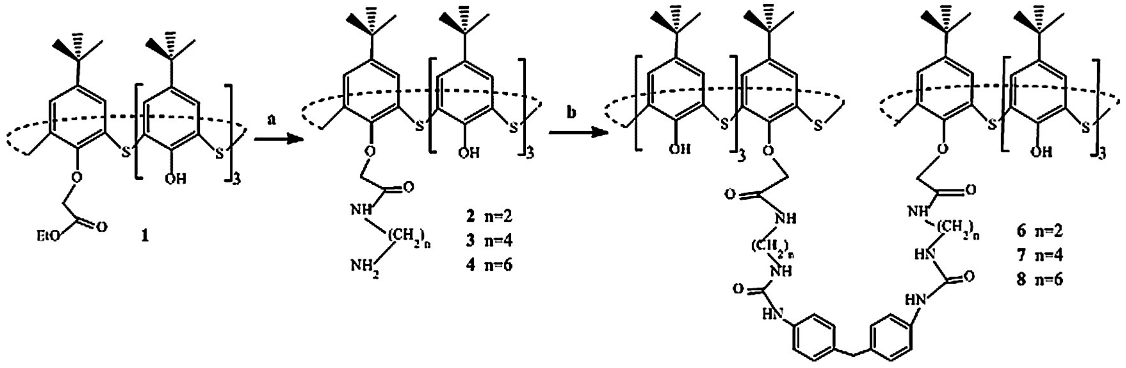

Scheme 1. (a) Aminolysis reactions of 5,11,17,23-tetra-*tert*-butyl-25-*O*-(ethoxy)methoxy-2,8,14,20-tetrathiacalix[4]arene **1**. (b) 4,4′-methylenebis (phenylisocyanate), catalyst (dibutyltin dilaurate), THF, RT, N_2.

break the symmetry of the phenolic crown and thus, obtain a multichelating asymmetric ligand [4]. To increase the complexing power of this mono-O-alkylated ligand, we decided to introduce additional complexing functionality by adding a diaminoethane group via aminolysis of the 28-*O*-(ethoxycarbonyl)methoxy-2,8,14,20-tetrathiacalix[4]-arene **1**. The expected products could be used as ligands, but also as intermediates, which could lead to the bridging of two macrocycles.

In this paper, we report the aminolysis of **1** by various diaminoalkanes. Unexpected properties of this family of compounds are presented, such as the formation of colloidal suspensions or self-assembled wires. Finally, the monoamido *p*-*tert*-butylthiacalix[4]arene derivatives are used as the precursors to synthesize a novel series of mono-*O*-bridged bisthiacalix[4]arenes.

2. Results and discussion

The reaction started from 5,11,17,23-tetra-*tert*-butyl-28-(ethoxycarbonyl)methoxy-2,8,14,20-tetrathiacalix[4]-arene **1**, which was transformed into 5,11,17,23-tetra-*tert*-butyl-25-*O*-[((*N*-aminoalkyl)aminocarbonyl)-methoxy]thiacalix[4]arene by aminolysis with an excess of an alkyldiamine under atmospheric conditions (Scheme 1).

The ^1H NMR spectra of compounds **2**–**4** reflected the ABBB ring symmetry from the signals at 1.04 ppm due to the *tert*-butyl groups (2:1:1 ratio). The three signals from the aromatic groups were also indicative of the mono-substituted structure. This prediction was also confirmed by mass spectrometry (MS–ESI). An important feature of this NMR analysis is that signals corresponding to the 4-aminoalkyl groups are absent from the spectrum when $CDCl_3$ is used as the solvent. This could be related to molecules **2**–**3** self-assembling into *meso*-structures, like micelles or vesicles (during the precipitation step of the purification, the product is usually found in the form of a colloidal suspension or of a gel). These hypotheses can be validated by measuring the diffusion coefficient from self-assembled structures using diffusion ordered spectroscopy (DOSY). The various textures of the solid obtained support the assumption of the macromolecules undergoing self-assembly on the media. A preliminary characterization carried out by scanning electron microscopy (SEM) revealed an unexpected organization of **2**. Indeed, during the purification process, the addition of water to a solution of **2** dissolved in acetone first induces a colloid suspension, then, a gel texture. The self-assembled product is composed of particles having a diameter from 0.01 to 0.5 μm and of a tangle of wires of diameter ranging from 0.1 to 0.4 μm (Fig. 1).

Compared with **3** and **4**, compound **2** reacts with an amine, such as triethylamine, for example, in the solid state or in solution by heating, to give compound **5** (Scheme 2).

Generally, 2-imidazolines are easily prepared in good yields by the reaction between aldehydes and ethylene-diamino molecules or by the cyclization reaction of the acylethylenediamine group, but, to the best of our knowledge, no thermal cyclization reaction with the carbonyl group of the amide function is known for the calixarene family [5]. Compound **5** was synthesized using two different routes: a solid state route and a solution one. Solid state reactions can be used as an efficient method for reducing reaction times. The approach consists in heating the solid state of a macrocycle whose skeleton is thermally stable, whereas its pendant arms

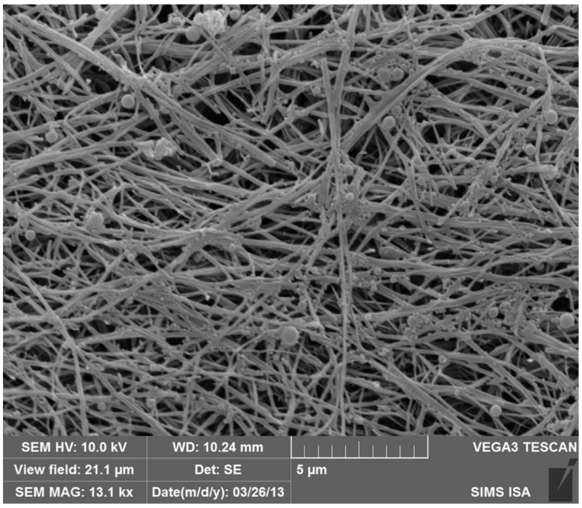

Fig. 1. SEM image of structural characterization of **2**.