



# Synthesis of calixamide nanofibers by electrospinning and toxic anion binding to the fiber structures



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## ABSTRACT

This study reports the synthesis of three novel polyacrylonitrile (PAN) nanofibers based calixamide containing pyridine groups by electrospinning. The structures of the newly prepared nanofibers were clarified using spectroscopic techniques. Analysis indicated that preparation of nanofibers based calixamide was successfully achieved. The presence of calixarene molecules in the nanofiber backbones was confirmed by Fourier transform infrared (FTIR-ATR), scanning electron microscope (SEM), and thermogravimetric analyses (TGA and DSC). The toxic anion binding studies exhibited that the nanofiber-based calixamide could be efficiently used for the binding of chromate anions as a model toxic oxoanion. Nanofiber based calixamide may be a good candidate as a filter material for water purification and waste treatment owing to their very large surface area as well as the inclusion complexation capability of all surfaces associated with the calixarene skeleton.

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## 1. Introduction

Nanofibers are ultrafine solid fibers notable for their very small diameters (lower than 100 nm), large surface area per unit mass, and small pore size. Due to the inherent properties of the electrospinning process, which can control the deposition of polymer fibers onto a target substrate, nanofibers with complex, and seamless three-dimensional shapes could be formed.<sup>1</sup> Nanofibers are used in numerous areas, including catalysis,<sup>2,3</sup> biosensors,<sup>4</sup> power sources,<sup>5,6</sup> biotechnology,<sup>7</sup> membranes/filters,<sup>8</sup> and optical materials.<sup>9</sup> They also have flexibility for chemical/physical functionalization.<sup>10</sup> There are three available techniques for the preparation of nanofibers electrospinning, self-assembly, and phase separation. From these techniques, electrospinning is the most widely used and studied technique.<sup>11</sup> In electrospinning, a continuous filament is spun from a polymer solution under the influence of a very high electrical field, resulting in ultrafine fibers.<sup>12,13</sup> The solution is held at the tip of a capillary tube by virtue of its surface tension. The applied electrical potential provides a charge to the polymer solution. Mutual charge repulsion in the polymer solution induces a force that is directly opposite to the surface tension of the polymer solution. An increase in the electrical potential initially leads to

the elongation of the hemispherical surface of the solution at the tip of the capillary tube to form a conical shape known as the Taylor cone.<sup>14</sup> A further increase causes the electric potential to reach a critical value, at which it overcomes the surface tension forces to cause the formation of a jet that is ejected from the tip of the Taylor cone. The charged jet undergoes instabilities and gradually thins in air primarily due to elongation and solvent evaporation. The charged jet eventually forms randomly oriented nanofibers that can be collected on a stationary or rotating grounded metallic collector.<sup>15</sup>

Careful examination of the literature reveals that considerable work has been reported on the design and synthesis of nanofibers with cyclodextrins and their analytical applications.<sup>16–19</sup> But very little information (only two published results) has appeared in the literature concerning nanofibers derived from calixarene supramolecular and their possible applications.<sup>10,20</sup> Calixarenes are often referred to as the third generation of supramolecular receptors after crown ethers and cyclodextrins.<sup>21,22</sup> Calixarenes are cyclic oligomers made of several phenolic units bound with methylene bridges.<sup>23–26</sup> The phenolic OH groups of the calixarene lower rim can be further functionalized to give various ionic receptors for anions, cations, as well as hosts of neutral molecules.<sup>27–29</sup> This excellent skeleton enables calixarenes to act as ‘molecular baskets’ toward neutral or ionic guests. Nowadays many researchers are interested in surface modification of all kinds of materials such as nanoparticles,<sup>30</sup> resin,<sup>31</sup> and silica gel<sup>32</sup> with calixarene compounds

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to obtain new composite materials. Therefore, simple nanofibers containing calixarenes may result in composites having a range of useful and interesting properties. Electrospinning of nanofibers with calixarene units is of particular interest, since in this way, nanofibers with specific functions can be produced. Even though surface modifications of fibers by calixarene compounds were reported,<sup>10,20</sup> to the best of our knowledge, the synthesis of nanofibers with calixamide containing functional pyridine groups and their extraction studies were not reported previously. With this in mind, we set out to synthesize nanofiber-based calixamide containing pyridine units and explore its anion binding properties toward chromate anion as a model toxic oxoanion.

## 2. Results and discussion

### 2.1. Synthesis of calix[4]arene derivatives

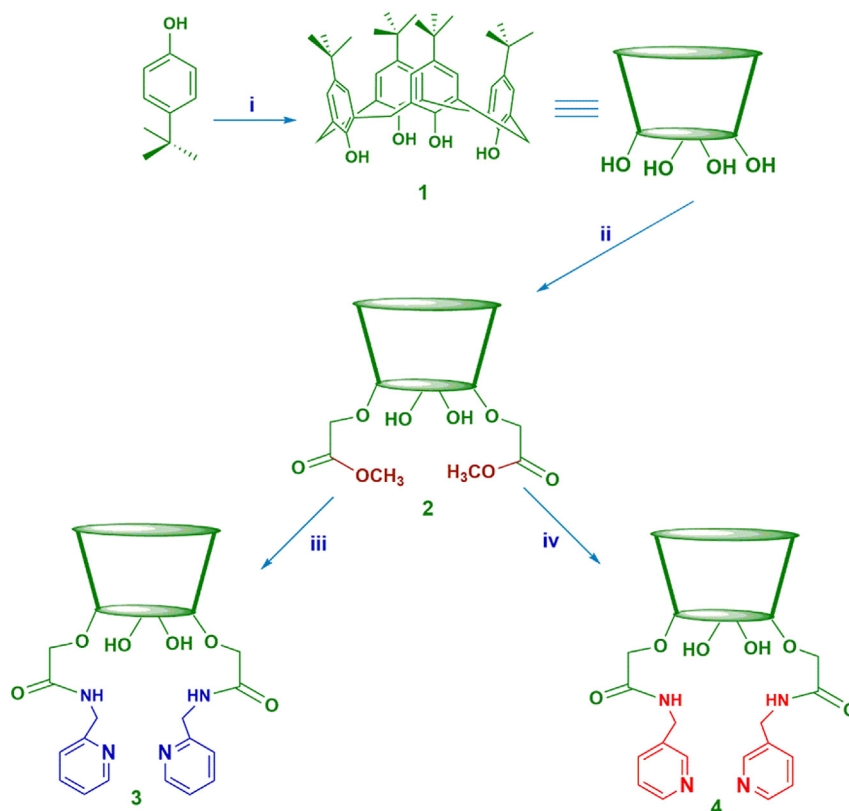
We are interested in the synthesis and preparation of calixamide nanofibers having pyridinium binding sites in order to investigate their binding ability toward dichromate anions. For the synthesis of calix[4]arenes based on pyridinium units, the required starting material, *p*-*tert*-butyl-calix[4]arene **1** was obtained by following the procedure available in the literature.<sup>33</sup> Compounds **3** and **4** contain pyridinium moieties in their structures, and therefore they may provide an effective binding site for toxic chromate anions in highly acidic media. Calix[4]arene derivatives **1–4** have been prepared in two steps as shown in Scheme 1. Firstly, *p*-*tert*-butyl-calix[4]arene was functionalized with bromomethylacetate in presence of K<sub>2</sub>CO<sub>3</sub> in dry acetonitrile to obtain the disubstituted methylester derivative of **1** by O-substitution on the lower rim of calix[4]arene in 1,3-(distal) position.<sup>34</sup> The diester calixarene derivative **2** was then treated with suitable amine compounds,

2-aminomethylpyridine and 3-aminomethylpyridine, to synthesize target calix[4]arene amide derivatives **3** and **4** in a mixture of toluene/methanol.<sup>26</sup> All of the structures were in the cone conformation in solution.

### 2.2. The synthesis and characterization of nanofibers based calixarene

In this study, calixester and amide nanofibers were obtained by electrospinning of 40% (w/v) PAN solution in DMF, as schematically shown in Scheme 2. The chemical reaction cannot occur between calixarene compounds and PAN nanofibers directly, since the PAN polymer backbone does not contain free reactive groups. Therefore, we modified the surface of the PAN nanofibers by the electrospinning between PAN and calixarene molecules. For a comparison study, PAN-calixester, PAN-calix2AMP, PAN-calix3AMP, and PAN nanofibers without calixarene were also electrospun. All of the fiber structures were characterized by SEM and FTIR (ATR) spectra. Scanning electron microscopy (SEM) analysis was performed to investigate any morphological changes after the surface modification of PAN nanofibers with calixarene derivatives.

Fig. 1 shows the representative SEM images and average fiber diameter (AFD) of the pure PAN, PAN-calixester, PAN-calix2AMP, and PAN-calix3AMP nanofibers. Fig. 1 clearly reveals that there are non-beaded randomly grown fibers with diameters ranging from 261 to 311 nm. The fiber diameters are not homogeneous and uniformly distributed. The increase in the average of PAN-calixester, PAN-calix2AMP, and PAN-calix3AMP nanofibers compared to pure PAN nanofiber could be due to the coating of the calixarene onto PAN nanofibers. Additionally, slight swelling of nanofibers during the modification process might also have resulted in the fiber diameter increase. Compared with the



**Scheme 1.** Schematic illustration of the synthesis of *p*-*tert*-butyl-calixarene derivatives. (i) Formaldehyde, NaOH, diphenyl ether, (ii) bromomethylacetate, CH<sub>3</sub>CN, reflux, 48 h, (iii) 2-(aminomethyl)pyridine, toluene/methanol (1:2) reflux, (iv) 3-(aminomethyl)pyridine, toluene/methanol (1:2) reflux.

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