



# Synthesis and extraction results of new halide terminated 2-alkyl-*p*-tert-butylcalix[4]arenes bearing phosphine oxides or ketones on the narrow rim

Sreejit R. Menon, Joseph A.R. Schmidt\*

Department of Chemistry & Biochemistry, School of Green Chemistry & Engineering, College of Natural Sciences & Mathematics, The University of Toledo, 2801 W. Bancroft St. MS 602, Toledo, OH 43606-3390, USA

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## ABSTRACT

The synthesis of lower rim tetraphosphorylated and tetraketone calix[4]arenes with haloalkyl groups tethered to a single methylene bridge and their utilization as extraction agents for rare earth elements are reported. Synthesis of these new functionalized calix[4]arene species has been achieved in good to modest yields, and extraction of nine lanthanide nitrates has been explored using these novel calix[4]arene species. The tetraphosphorylated calix[4]arenes show better lanthanide extraction efficiency than their ketone counterparts, especially for europium (III). These experiments demonstrate that inclusion of a substituent tethered to the methylene bridge does not significantly reduce the extraction efficiency of these new calix[4]arene ligands as compared to similar unsubstituted ligands in literature, making them important precursors in the development of functionalized stationary phases for separation of lanthanides. Development of similar CMPO-bearing narrow rims and new solid-phase extraction materials for the solid–liquid separation of lanthanides remains the subject of future work.

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## 1. Introduction

The rare earth elements (REEs), composed primarily of the 15 lanthanides, find broad application in many modern devices, ranging from use as magnets in wind turbines, hard drives, and air conditioners to incorporation in hybrid car batteries.<sup>1,2</sup> These elements have proven indispensable to the sustainable and green world approach prevalent in modern society.<sup>3</sup> China has been a key player in REE production over the past several decades. Recent decisions to significantly reduce export quotas of these valuable minerals to ostensibly meet Chinese domestic requirements has resulted in increased tariffs and thereby an economic driving force to look for alternative sources of REEs.<sup>4</sup> Isolation and purification of REEs from mineral deposits has always been a lengthy and laborious task for the mining industry. Separation techniques currently employed for this processing generate undesirably large quantities of waste due to the chemical treatments that are necessary to process the raw ore and subsequently separate individual REEs, contributing significantly to their cost.<sup>5</sup> In addition to their production from raw ores, the idea of recovering REEs from stored

nuclear waste is quite attractive. High-level nuclear wastes (HLWs), obtained as secondary waste after separation of uranium or plutonium from a nuclear reactor's depleted fuel are composed of fission products including minor actinides like Am and Cm, as well as lanthanides including Nd, Gd, Eu, and Sm.<sup>6,7</sup> The recovery of lanthanides at this stage of nuclear waste management will not only help meet lanthanide production requirements, but will also reduce the total quantity of waste requiring long term storage.<sup>7</sup> Another potentially valuable source of lanthanides involves their recovery from outdated electronic devices and materials that have completed their functional lifetime. The effective utilization of each of these lanthanide sources requires improved methods and techniques that will in turn lead to better, cleaner, and more economical processes for the separation and isolation of REEs.<sup>1</sup>

Over the past decade, much effort has been invested toward improving the separation of lanthanides.<sup>8,9</sup> Primarily, research in this field has focused on liquid–liquid extraction (LLE) techniques employing coordinating solvents, ionic liquids, or multivalent coordinating ligands assembled on scaffolds such as calixarenes to separate these elements from other metals and earthly impurities.<sup>7,9</sup> In general, many of the LLE studies previously disclosed have shown significantly improved extraction efficiencies compared to the currently employed industrial separation techniques.<sup>8,10–12</sup> Despite these advances, these new methods still suffer from the

\* Corresponding author. Tel.: +1 419 530 1512; fax: +1 419 530 4033; e-mail address: [Joseph.Schmidt@utoledo.edu](mailto:Joseph.Schmidt@utoledo.edu) (J.A.R. Schmidt).

general drawbacks affiliated with LLE, including high solvent and ligand cost and large quantities of chemical waste.

Calixarenes have been widely employed in extraction chemistry over the last two decades.<sup>7,13–15</sup> These cyclic oligomers are readily produced via the condensation of *t*-butylphenol with formaldehyde under basic conditions.<sup>16</sup> The cup-shaped macrocyclic structure of a calixarene provides sites for easy modification and functionalization on its upper and lower rims (Fig. 1), making it attractive as a scaffold/platform for attachment of monovalent ligating units. The incorporation of several monovalent ligating units to a single rigid calixarene core results in the formation of a multivalent ligand system. Calixarene-based ligands have proven to be useful for applications in the biomedical field, including ion and molecular recognition.<sup>13–15</sup> They have also been used in metal recovery and waste treatment as highly selective and efficient extraction agents for alkali, transition, and heavy metals due to their ability to effectively chelate these metal ions strongly.<sup>7,17,18</sup> Upper and lower rim-functionalized calixarenes have displayed excellent extraction efficiency in various LLE processes. In particular, calixarenes with amines, amides, esters, ketones, or phosphine oxides on the lower rims have proven to be very effective in the areas of ion recognition and LLE.<sup>10,19–21</sup> Tailoring the groups present on the lower rim has led to successful extraction of alkaline, alkaline earth, or transition metals, and has also been successful in the extraction and separation of lanthanides and actinides from radioactive wastes.<sup>19,20,22,23</sup> Despite their excellent extraction capabilities, calixarenes are often overlooked industrially due to the financial drawbacks inherent with LLE. For the separation of lanthanides, this is often a laborious, time-consuming process accompanied by difficulty in layer separation due to the formation of emulsions. Also, LLE is not a green process as large quantities of organic solvents are necessary, resulting in significant amounts of waste, subsequently requiring further treatment or disposal and thus increasing costs.<sup>5–7</sup>

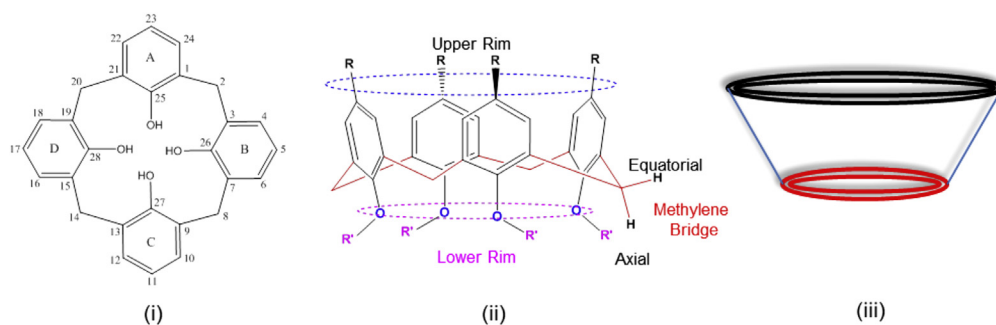


Fig. 1. Calix[4]arene: (i) flat line drawing with numbering, (ii) three dimensional perspective, and (iii) similarity to a basket.

Given the limitations of LLE, several investigators have explored the related solid phase extraction (SPE) approach.<sup>24</sup> SPE provides numerous advantages, including reduced volumes of organic solvents, capacity for large-scale separations, and automation of the extraction process, making it a much more economical and greener process. Functionalized calixarenes have been made heterogeneous by immobilization on solid supports, including silica and polymers such as polystyrene through reactions to covalently link their lower or upper rims to the solid support.<sup>24–26</sup> Unfortunately, attachment via the upper or lower rims has significantly reduced the ability of these ligands to effectively coordinate to metal centers, resulting in drastically reduced extraction efficiencies attributed to reduced flexibility in these molecules. In order to mitigate the detrimental effects resulting from covalent linkage to these solid supports, our group is investigating the methylene bridges on the calixarenes as the point of attachment. We believe that covalent attachment through these methylene units will have little or no effect on the

conformational flexibility of the calixarene in the resultant material. Fantini demonstrated a simple one-pot synthetic route to selectively monofunctionalize a methylene bridge of calix[4]arenes.<sup>27</sup> In collaboration with Fantini, our group previously designed and demonstrated synthetic routes to 2-( $\omega$ -haloalkyl)-calix[4]arenes with 3–6 carbon spacer alkyl chains.<sup>28</sup> The longer five-carbon and six-carbon alkyl tethers are preferred as they will help to physically separate the functionalized calix[4]arene ligand from a solid support like silica, upon which they will be immobilized in the future, thereby minimizing interactions between the ligand, an extracted metal ion and the surface of the solid support. Herein, we detail the incorporation of coordinating ligands such as phosphine oxides and ketones at the lower rim of the aforementioned 2-functionalized haloalkyl-calix[4]arenes. Furthermore, we report the utilization of these new molecules in LLE experiments involving lanthanide nitrate solutions as a means to investigate the effect of the long alkyl tail at the methylene bridge on extraction efficiencies of lower rim coordinating groups. These new ligands will be further modified at their halide terminated end and will ultimately be immobilized on solid supports through this modified end in our future efforts to produce improved materials for SPE of lanthanides.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Synthesis of 2-( $\omega$ -chloroalkyl)-tetramethoxy-*p*-*tert*-butylcalix[4]arenes **3a** and **3b** (Scheme 1) proceeded as reported by our group in 2009.<sup>28</sup> To extend that work, we sought to functionalize the narrow lower rim with suitable coordinating ligands for lanthanide ions, such as phosphine oxides or ketones. Ligands bearing oxygen donor atoms like phosphine oxides, phosphonates, amides, carboxylic acids, and ketones on the lower rims have been exten-

sively investigated in extraction and separation of actinides and rare earth metals in the last two decades.<sup>7</sup> As noted in previous studies, hydroxyl groups on the lower rims can be readily transformed to the desired phosphine oxide or keto groups.<sup>29,30</sup> Thus, the tetramethoxy-calix[4]arenes **3a** and **3b** were first subjected to exhaustive demethylation using  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  overnight, followed by basic hydrolysis to yield the 2-( $\omega$ -chloroalkyl)-tetrahydroxy-*p*-*tert*-butylcalix[4]arenes **4a** and **4b** (Scheme 2). The  $^1\text{H}$  NMR spectra of **4a** and **4b** each showed a resonance for the hydroxyl protons at  $\delta$  10.32 ppm, while the absence of a resonance for the methoxy protons indicated complete conversion. The NMR spectra (collected in  $\text{CDCl}_3$ ) showed that **4a** and **4b** each adopt a full cone conformation in solution, due to the strong hydrogen bonding now present at the lower rim unlike the tetramethoxy derivatives **3a** and **3b**, which were fluxional in solution.<sup>28</sup> Furthermore strong broad peaks at  $\sim 3185\text{ cm}^{-1}$  in the IR spectra also confirmed the presence of hydroxyl groups on the lower rim.

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