

Synthesis and characterization of aryl ether derivatives of *p*-*tert*-butyl calix[4]arenes as a capable receptors of Ag⁺ and Pb⁺² ions

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Abstract: The synthesis and characterization some tetra-aryloxy derivatives of calix[4]arenes have been reported in this paper for promoting of cation binding activities. Obtained receptors have been characterized by ¹HNMR, ¹³CNMR and FTIR. The Calix[4]arene structures were extended via lower rim by etherification and sulfoesterification and the ionophoric capability of synthetic receptors were investigated toward Ag⁺ and Pb⁺² cations by spectroscopic methods.

Keywords: Arylether Calix[4]arene, Ion receptor, Lower rim modification.

Introduction

Supramolecules are widely used in host-guest chemistry for the construction of various receptors for charged or neutral molecules or ions [1]. Calixarenes are cyclic oligomers composed of phenol units and are very well known as excellent ionophores because they provide a unique three-dimensional structure with almost unlimited derivatization possibilities [2].

Investigations of molecular recognition [3-5] and ionic recognition [6-9] by calixarenes and their derivatives as synthetic receptors have attracted increasing attention in recent years because of their potential to serve as molecular devices and functional materials [10]. Some of calixarenes were tested as metal ion extractors and applied as selective ligands in ion selective electrodes [11-30].

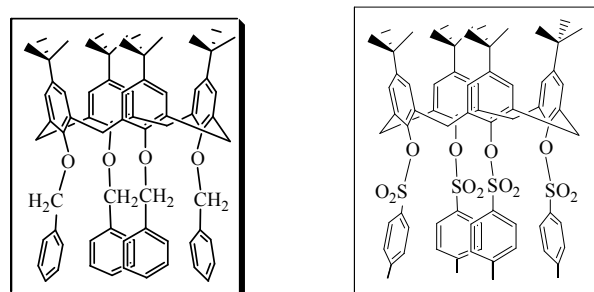
In this work, two derivatives of *p*-*tert*-butyl calix[4]arene were synthesized by lower rim reaction in presence of NaH and alkyl halide and aryl sulfonyl chloride (as alkylating agent), in DMF. The ionophoric capabilities of synthetic receptors were investigated toward Ag⁺ and Pb⁺² cations by spectroscopic methods.

Results and discussion

One of the best ways for promoting of solubility and

conformational rigidity of calixarenes is lower rim modification via esterification and etherification reactions on parent calixarene. In this reaction, the number of aromatic rings which were inserted in lower rim is very important because the π -stacking interactions are depending on the phenyl moieties.

For this mean, we have synthesized, 25, 26, 27, 28-tetra-benzyloxy-5, 11, 17, 23-tetra-*tert*-butyl-calix [4] arene, **2**, and 25, 26, 27, 28-tetra-tosyloxy-5, 11, 17, 23-tetra-*tert*-butyl-calix[4]arene, **3** with 8 aromatic rings in each structures in lower rim (Scheme 1). With these ligating groups in the lower rim of receptors the binding abilities of them towards the metal cations were increased.



Scheme 1: Structures of modified lower rim calixarenes **2** and **3**

The etherification of calixarene was generally achieved by the Williamson reaction, but the strength

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of the base may govern the reactions. The use of other bases do not obtain the tetra-alkylethers of *p-tert*-butyl calix[4]arene because other anions are not able to attain complete deprotonation of phenolic OH and it can form strong hydrogen bonds with acidic protons. Calix[4]arene **2** was prepared by alkylation of parent calixarene **1** with benzyl chloride in the presence of NaH in DMF. The solubility of **2** is fair in wide range of organic solvents with different polarities.

The best solvent for preparing of compound **3** in arylation reaction is THF and it has fair solubility in general organic solvents as well.

The cone conformer of calix[4]arenes usually show the highest affinity for metal ions [31]. The $^1\text{H NMR}$ shows two doublets at 3.45, 4.27 ($\Delta\delta = 0.81$ for **2**), and 2.4, 3.9 ($\Delta\delta = 1.5$ for **3**) for methylene bridge protons. The $^1\text{H NMR}$ show that **2** and **3** have cone conformation ($\text{Ar-CH}_2\text{-Ar } \Delta\delta > 0.8$) [1].

UV-Vis spectroscopic studies of synthesized receptors in present of metal iones:

For investigation of binding abilities of **2** and **3** towards cation ions, Ag^+ and Pb^{+2} were selected for their size compatibility with synthesized receptors **2** and **3**. Spectral titrations were performed in THF-H₂O (99:1/V:V) solution. The metal nitrates did not show any significant absorption in the scanned spectral range. **2** and **3** consist of four benzene rings, which are arranged conically, so four aromatic rings in lower rim benzyloxy for **2** and tosyloxy for **3** groups form a coordination sphere where metal cations can be bound. Typical UV spectral changes by addition of Ag^+ and Pb^{+2} to **2** and **3** solutions are shown in Figure 1-4.

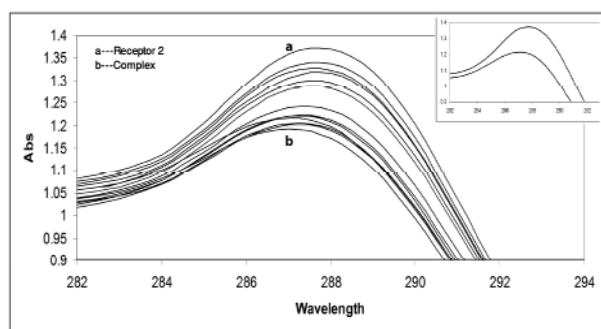


Fig. 1. UV spectra of **2** (10^{-3} M) in the presence of Pb^+ (10^{-2} M). The Pb^{+2} were added stepwise (0-0.6 Mm) at 288.0 nm.

Absorbance of Host **2** in $\lambda = 288$ nm was decreased with addition of Ag^+ and Pb^{+2} ions. Fig 1 and 2 show the binding interactions of **2** with Ag^+ and Pb^{+2} respectively. Fig 3 illustrates the dependence of absorbing variations of **2** with Ag^+ and Pb^{+2}

concentrations and show the better affinity of receptor **2** toward Pb^{+2} ion.

According to Fig 3 receptor **2** is poor extractant for Ag^+ cation but shows better affinity toward Pb^{+2} cation. Table 1 shows the removal ability of Ag^+ and Pb^{+2} ions by receptors **2** and **3**.

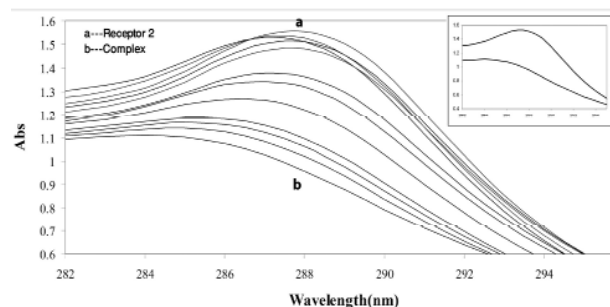


Fig. 2. UV spectra of **2** (10^{-3} M) in the presence of Ag^+ (10^{-2} M). The Ag^+ was added stepwise (0-0.6 Mm) at 288.0 nm.

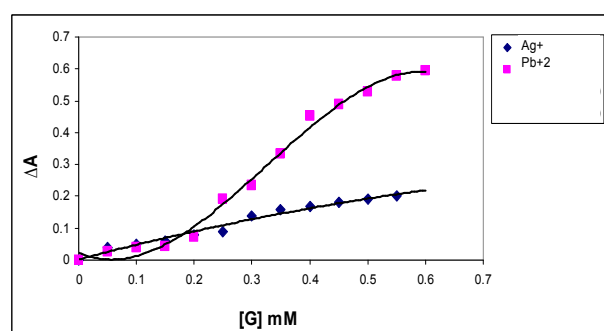


Fig. 3. The dependence of absorbing variations of **2** with Ag^+ and Pb^{+2} concentrations.

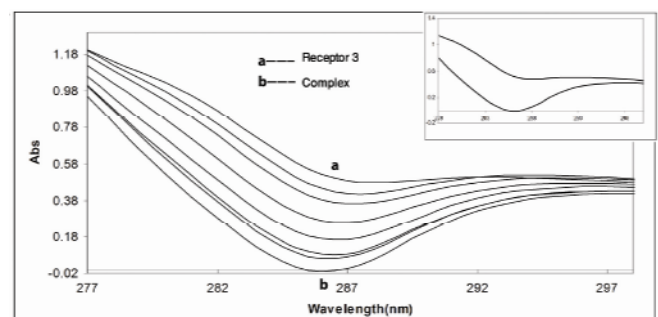


Fig. 4. UV spectra of **3** (10^{-3} M) in the presence of Pb^{+2} (10^{-2} M). The Pb^{+2} were added stepwise (0-0.6 Mm) at 288.0 nm.

Absorbance of Host **3** in $\lambda = 286$ nm was decreased with addition of Ag^+ and Pb^{+2} ions. Fig 4 and 5 show the binding interactions of **3** with Ag^+ and Pb^{+2} respectively. Fig 6 illustrates the dependence of absorbing variations of **3** with ions concentrations.

According to Fig 6 and Table 1, the removal capability of receptor **3** towards Ag^+ and Pb^{+2} ions is very good (90.5% for Ag^+ and 99.3% for Pb^{+2}).

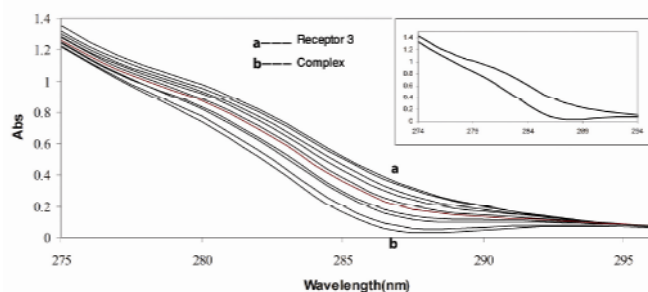


Fig. 5. UV spectra of **3** (10^{-3} M) in the presence of Ag^+ (10^{-2} M). The Ag^+ was added stepwise (0-0.6 Mm) at 288.0 nm.

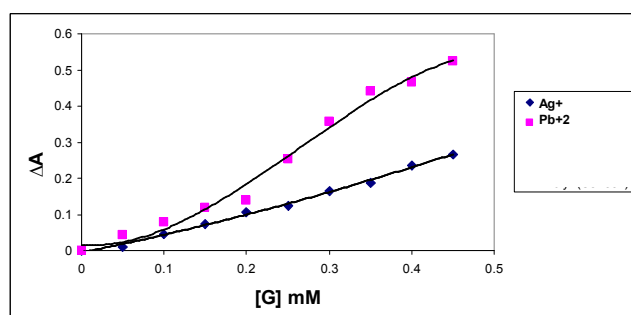


Fig. 6. Dependence of absorbing variations of **3** with Ag^+ and Pb^{+2} concentrations.

Table 1. The ion removal capabilities of **2** and **3**

Receptor	Ion	ΔA	E%
2	Ag^+	0.20	14.6
2	Pb^{+2}	0.59	38.2
3	Ag^+	0.26	90.5
3	Pb^{+2}	0.52	99.3

It is well known that the cation binding ability and selectivity upon complexation with calix[4]arene and its derivatives are influenced by many factors, such as the ion surface charge density, spatial arrangement of the donor atoms, size-fit relationship between cation and calix[4]arene, as well as the cooperative binding of the appended side-arms, and so on [32]. In this work, it is considered that the induced three-dimensional cavity of the parent calixarene platform and the attached side arms upon complexation play an important role in cation binding ability and selectivity.

Conclusion

In this study, two synthesized receptors have shown potential in extracting Ag^+ and Pb^{+2} cations. The

receptor **3** that has sulfoesteric functionalities shows excellent behavior toward Ag^+ and Pb^{+2} cations. This field of cations recognition and extraction is a relatively important to analytical and biochemical activities.

The variety of functional group which joint to phenolic OH that occur in these calix[4]arene derivatives may be of considerable importance for the future design of novel calix[4]arene-based receptors, carriers or supramolecular structures.

Experimental

All the reagents were purchased from Merck Company. NMR spectra were recorded on a Bruker spectrometer in CDCl_3 with TMS as internal standard. IR spectra were recorded on Bruker Tensor 27 and Perkin Elmer. UV-vis. spectra were obtained on a T90 UV-visible spectrophotometer, PG Instrument ltd.

NaH was used as a 80% dispersion in oil and washed twice with n-hexane before use. Generally, solvents were dried. All aqueous solutions were prepared with deionized water.

Synthesis:

p-tert-butyl calix[4]arene (**1**):

Parent calix[4]arene was synthesized by methods reported earlier with *p*-Tert-butyl phenol and formaldehyde [1]. mp=342 – 344 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 1.21 (s, 36 H), 3.51(d, 4H, J=12.8 Hz), 4.24 (d, 4H, J=12.8Hz), 7.05(s, 8H), 10.34 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 30.5, 32.4, 34.0, 126.1, 128.2, 144.5, 146.8; IR, $\nu(\text{cm}^{-1})$ = 3155.

25, 26, 27, 28-Tetrakis Benzyloxy- 5, 11, 17, 23-tert-butyl-calix[4]arene (**2**):

To a suspension of 3 g (4.62 mmol) of **1** in 180 ml of dry DMF was added 3 g of NaH which washed with hexane (2×15 ml). The reaction mixture was stirred for 45 min at 60 °C. 30 ml (238 mmol) of benzyl chloride was added and allowed to stir and refluxed for 24h. The reaction mixture was poured into 1800 ml of water and extracted with 300 ml of CH_2Cl_2 . The organic layer was separated, washed with water twice and dried over Na_2SO_4 . The solvent was removed by evaporation. The crude was recrystallized from CH_2Cl_2 -MeOH to give white crystals of **2**. (86%) mp=236 - 238 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 1.02 (s, 36 H), 3.46 (d, 4H, J= 14.9 Hz), 4.28 (d, 4H, J= 14.9 Hz), 5.10 (s, 8H), 6.92 (s, 8H), 7.46 (d, 16H), 7.62 (d,4H, J=10 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 30.1, 31.1, 32.5, 75.2, 123.7, 127.7, 129.4,

130.5, 133.2, 135.8, 139.8, 155.0 ; IR $\nu(\text{cm}^{-1}) = 1192, 25, 26, 27, 28$ - *Tetrakis Tosyloxy- 5, 11, 17, 23- tert-butyl-calix[4]arene (3)*:

To a suspension of 2 g (3.08 mmol) of **1** in 100 ml of dry THF was added 2.5 g of NaH which washed with hexane (2×10 ml). The reaction mixture was stirred for 45 min at 60^o C. 4 g (20.5 mmol) of toluenesulfonyl chloride was added and refluxed for 5h. The solvent was removed under vacuum and the violet residue was treated with 100 ml of CH₂Cl₂ and poured into 100 ml of water. The organic layer was separated, washed with water twice and dried over Na₂SO₄. The solvent was removed by evaporation. The crude was recrystallized from CH₂Cl₂-MeOH to give cream-yellow crystals of **2**. (30%) mp=288 - 290 °C. ¹H NMR (500 MHz, CDCl₃) $\delta(\text{ppm})$ 1.05 (s, 36 H), 2.46 (d, 4 H, J= 14.0), 3.95 (d, 4H, J= 14.0), 6.69 (s, 8H), 7.46 (d, 16H, J=10 Hz), 7.62 (d, 4H, J=4.9Hz); ¹³CNMR (125 MHz, CDCl₃) δ (ppm): 22.2, 31.63, 31.66, 34.4, 126.1, 130.0, 133.1, 135.1, 142.6, 144.9, 148.7 ; IR $\nu(\text{cm}^{-1}) = 1190$.

UV-Vis Spectroscopic measurements:

The absorbing measurements were performed by UV-Vis titration experiments using a stable concentration of hosts and a varying guest concentration. All of the spectral titrations were performed in THF-H₂O (99:1/V:V) solution. 4 ml solution of the host **2** or **3** (10⁻³ M) were titrated with stepwise addition of the metal cation solution (10⁻² M). The initial and final absorbances of the host before and after titration were recorded. For both hosts **2** and **3** the data were collected over the range 200–450 nm. The ion removal by receptors can be calculated according equation 1.

$$E\% = 1 - A/A_0 \times 100 \quad \text{Equation 1}$$

Where A_0 and A are the initial and final absorbance of the host before and after the titration, respectively. Table 1 shows the extent of E% of receptors toward Ag⁺ and Pb⁺².

Acknowledgments

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