Application of nano-baskets for extraction of lanthanides Bahram Mokhtari and Kobra Pourabdollah*

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Eight proton di-ionisable diacid conformers of nano-baskets including 25,26-di(carboxymethoxy)calix[4]arene-crown-3, -crown-4, -crown-5 and -crown-6 in the cone conformation have been synthesised and shown to extract lanthanide cations effectively. Their selectivities were greatly influenced by the acidity of the solution and the conformations of the calix-crown. The extraction loading was improved by having the *p-tert*-butyl-moiety in the upper rim. The scaffold bearing the crown-4 ether moiety showed the least loading, while scaffolds with crown-3- and crown-5-ether moieties had the best selectivities.

Keywords: calixcrown, calixarenes, lanthanides, extraction, nano-baskets

Nano-baskets of calixarenes and calixcrowns are a versatile class of macrocycles, which have been subject to extensive research in the development of many extractants, transporters and stationary phases.¹⁻⁸ Functionalisation of calix[4]arenes at both the upper and lower rims has been extensively studied. Attaching donor atoms to the lower rim of a calix[4]arene can improve the binding strength of the parent calixarene dramatically. The two main groups of lower-rim functionalised calix[4]arenes are calix[4]arene podands and calixarene-crown ethers.^{9,10} Distal hydroxyl groups can be connected to give 1,3-bridged calix[4]crowns, while connection between proximal hydroxyl groups leads to 1,2-bridged calix[4]crowns.

It was observed that calixarenes with phosphorus-containing pendant arms are the best extractants for lanthanides and actinides. Moreover, it was found that the 1,3-bridged calix[4]crowns exhibit high binding affinity and selectivity toward alkali and alkaline earth metal cations.¹¹ However, researches on 1,2-bridged calix[4]crowns lag far behind.

Attachment of proton-ionisable groups to calixcrowns can further improve their extraction properties because the ionised group not only participates in metal ion coordination, but also eliminates the need to transfer aqueous phase anions into the organic phase.¹² Combining crown ethers with calix[4]arenes increases the cation binding ability of the parent calixarenes^{3,14} The selectivity can be affected by the crown ether size, the identity of donor atoms on the crown ether moiety and the conformation of the calixarene platform.¹⁵⁻²¹ To further explore the influence of these factors on the extraction characteristics of *p-tert*-butylcalix[4]-1,2-crown ethers toward metal ions, a series of di-ionisable *p-tert*-butylcalix[4]-1,2-crown-3 compounds in the cone conformation and the 1,2-alternate conformation, as well as *p-tert*-butylcalix[4]arene-1,2-thiacrown-3 in the cone conformation have now been synthesised.

Two kinds of side chain in the calixcrown skeleton have been studied, including two ionisable carboxylic acid moieties and the crown-ether moieties. The ionisable moieties not only participate in cooperative metal ion coordination, but also eliminate the need to transfer the anions from the aqueous phase into the organic phase by operating in a cation-exchange mode with the metal cation. In this work, two proton-ionisable function groups were incorporated into a calix[4]arene scaffold. A special feature of such modification is that the acidity of the ionisable moiety can be tuned by changing the functional group from hydroxyl to other groups having different electron-withdrawing abilities of the functional group. A wide range of pH environments can be examined when these ionisable groups are incorporated into the calixcrown skeleton. These extractants exhibit excellent extraction selectivity for alkali and alkaline earth metals.

In the work reported here, eight diacid proton-ionisable calixcrowns have been synthesised including cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene1,2-crown-3

(10), cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene 1,2-crown-4 (11), cone *p-tert*-butyl-25,26-di(carboxymethoxy) calix[4]arene1,2-crown-5 (12), cone *p-tert*-butyl-25,26-di (carboxymethoxy)calix[4]arene1,2-crown-6 (13), cone 25,26-di (carboxymethoxy) calix[4]arene1,2-crown-3 (23), cone 25,26-di (carboxymethoxy)calix[4]arene1,2-crown-3 (24), cone 25,26-di (carboxymethoxy)calix[4]arene1,2-crown-5 (25), and cone 25,26-di (carboxymethoxy)calix[4]arene1,2-crown-6 (26). Some of the synthesised scaffolds have also been reported as intermediates for preparation of N-pheny-sulfonyl oxyacetamide derivatives, and their extraction of alkaline earth metals described.²²⁻²⁶

In the following, the synthesis and the extraction procedures of eight conformers are presented, respectively. Figure 1 depicts the chemical structure of eight calixcrown scaffolds studied as extracting agents.

Experimental

The synthesis scheme for the preparation of cone *p-tert*-butyl-25,26di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**10–13**) and cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**23–26**) is presented in Fig. 2. The synthetic and characterisation details of all compounds in Figs 1 and 2 have been deposited in the Electronic Supplementary Information.

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH₂ and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. Cs₂CO₃ was activated by heating at 150 °C overnight under reduced pressure and stored in a desiccator. Melting points were determined with a Mel-Temp melting point apparatus. IR spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH₂Cl₂ solution on NaCl plates. The ¹H and ¹³C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (¹H 500 MHz and ¹³C 126 MHz) spectrometer in CDCl₃ with Me₄Si as internal standard unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants (*J*) values are in Hz.

Lanthanide perchlorates (99%), lanthanide hydroxide, perchloric acid (1.0 N) and chloroform were obtained from Aldrich. Chloroform was shaken with deionised water to remove the stabilising ethanol and stored in the dark.

Lanthanide cations were loaded into the aqueous solutions by adding stock solutions containing six lanthanide cations. The solutions of six cations were made up as Nd³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Er³⁺ and Yb³⁺ perchlorate solutions (0.1 mM in each). 0.1 mM lanthanide hydroxide and 0.01–1.0 M perchloric acid solutions were used to adjust the pH values of the aqueous phases. The extraction ability of calixcrown scaffolds was determined in eight solutions with pH range of 1.0–10.0, in 15 mL conical polypropylene centrifuge tubes. The samples contained 2.0 mL of the aqueous phase of 0.1 mM lanthanide cation solution and 2.0 mL of 5.0 mM calixarene solution in chloroform.

A preconcentration method was used in the solvent extraction procedure. The combined aqueous and organic phases were shaken for 5 minutes and were centrifuged for 5 minutes. The pH of the aqueous phase was measured using a pH-meter with a Corning 476157 combination pH electrode. In the stripping step, 1.5 mL of the organic phase

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Fig. 1 The chemical structure of eight calixcrown scaffolds.



Fig. 2 Synthesis of cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**10–13**) and cone 25,26-di(carboxy methoxy)calix[4]arene-1,2-crown-3,4,5,6 (**23–26**).

was transferred to a capped conical centrifuge tube containing 3.0 mL of 0.10 M HClO₄. The stripping process involved 5 minutes of mixing, then 5 minutes of centrifuging. After that, 1.0 mL of the aqueous phase was diluted to 10.0 mL for analysis by ICP-AES.

The percent of cation extraction (E%) was defined as:

$$E\% = \frac{[M^{3+}]_{org} \times V_{org}}{[M^{3+}]_{aq} \times V_{aq}} \times 100$$
(1)

where $[M^{3+}]_{\text{org}}$ and $[M^{3+}]_{\text{aq}}$ represent the concentration of cations in the organic phase and the aqua solution (before extraction), and V_{org} and V_{aq} depict the corresponding volume of phases respectively.

An ICP-AES spectrometer (model Seiko SPS-1500R) was used in the experiments. The spectrometer was equipped with a computercontrolled sequential Czerny-Turner scanning monochromator with the focal length of holographic grating 3600 grooves per mm. From the emission intensity data for the sample and standard solutions, the concentrations of solutes were calculated and corrected for spectral interferences among solutes. Table 1 presents the wavelengths of the emission lines used in the ICP-AES measurements. It was found that blank corrections were unnecessary. The recovery tests showed that the cations were recovered by $96\pm 3\%$. The average coefficients of variation for lanthanide cations were calculated from the replicate analyses of the six samples and are listed in Table 2. The maximum and minimum CV values were determined as 5.5% for Tb³⁺ and 1.0% for Yb³⁺, respectively. The average CV values of all lanthanide cations were calculated to be $3\pm1\%$.

Results and discussion

Upon ionisation, the di-ionisable cone calix[4]crowns form metal ion complexes with two anionic centres on the same side of the crown unit. The perchlorate anions in the solution neutralise the last positive charge in the complex and enhance the extraction of uncharged complexes to the organic media. Therefore, 1:1:1 ligand:metal:perchlorate complexes are formed and transferred.²⁷

Competitive solvent extractions of lanthanide cations (Nd³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Er³⁺ and Yb³⁺) were performed for 5.0 mM solutions of di-ionisable calix[4]crown ligands **10–13** and **23–26** in chloroform, and plots of metal ion loading of the organic phase *vs*. the equilibrium pH of the aqueous phase were obtained, as depicted in Figs 3 and 4, respectively. All of the

 Table 1
 The wavelengths of emission lines used in the ICP-AES measurements.

Cation	Nd ³⁺	Eu ³⁺	Tb ³⁺	Dy ³⁺	Er ³⁺	Yb ³⁺
Wavelength/nm	430.358	381.967	350.917	353.170	369.265	328.937

Table 2 The average deviations of ICP-AES measurements of lanthanide cations.										
Cation	Nd ³⁺	Eu ³⁺	Tb ³⁺	Dy ³⁺	Er ³⁺	Yb ³⁺				
Deviation/%	3.0	4.1	5.5	3.5	2.0	1.0				

extraction experiments were repeated three times and the mean value of the extraction loadings were determined and were presented in the plots.

Competitive solvent extractions by ligand **10:** For competitive extraction of such metal cations, di-ionisable 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(carboxymethoxy)-27,28-crown-3-calix[4]arene in the cone conformation (ligand **10**) showed very different selectivity from its analogues (**11–13**). All lanthanide cations were detectably extracted into the chloroform phase and the selectivity order was $Nd^{3+} > Eu^{3+} >> Tb^{3+}$, $Dy^{3+} > Yb^{3+} > Er^{3+}$ for ligand **10**. The pH for half loading, $pH_{1/2}$, is a measure of the ligand acidity. For compound **10**, the pH_{1/2} value was obtained to be in the range of 5.5–6.0 for binding to the lanthanides.

Competitive solvent extractions by ligand 11: As shown in Fig. 3, ligand 11 exhibited little selectivity for the ion species. All six lanthanide cations were extracted into the chloroform phase without any selectivity. The $pH_{1/2}$ values were obtained to be around 5.0 and 6.0 for binding to Nd³⁺ and Eu³⁺ as well as Tb³⁺, Dy³⁺, Er³⁺ and Yb³⁺, respectively.

Competitive solvent extraction by ligand 12: 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26-bis(carboxymethoxy)-27,28-crown-5-calix[4]arene in the cone conformation (ligand 12) also exhibited very different selectivity from its analogues conformers (10,11,13). All cations were extracted into the chloroform phase without selectivity. The pH_{1/2} values were obtained to be in the range of 6.0–7.0.

Competitive solvent extractions by ligand 13: Ligand 13 exhibited good selectivities. The order of loadings was $Nd^{3+} > Eu^{3+} > Tb^{3+}$, $Dy^{3+} > Yb^{3+} > Er^{3+}$. Moreover, the $pH_{1/2}$ values were around 6.0. Competitive solvent extractions by ligand 23: All cations were detectably extracted into the chloroform phase and the selectivity order was $Nd^{3+} > Eu^{3+} >> Tb^{3+}$, $Dy^{3+} > Yb^{3+} > Er^{3+}$. The $pH_{1/2}$ values were found to be in the range 5.0–8.0. Figure 4 depicts the plots of cation loading into the organic phase *versus* the equilibrium pH of the aqueous phase using ligand 23.

Competitive solvent extractions by ligand **24**: For competitive extraction of those cations, ligand **24** exhibited no selectivities and the $pH_{1/2}$ values were obtained to be around 5.0.

Competitive solvent extractions by ligand **25**: The $pH_{1/2}$ values were obtained to be in the range of 6.0–7.0 and all cations were highly extracted into the chloroform phase without any selectivity.

Competitive solvent extractions by ligand **26**: All lanthanide cations were detectably extracted into the chloroform phase. The selectivity order was $Nd^{3+} > Eu^{3+} >> Tb^{3+}$, $Dy^{3+} > Yb^{3+} > Er^{3+}$ for ligand **24**. Moreover, the pH_{1/2} values were found to be in the range 6.0–7.0.

Conclusions

Proton di-ionisable diacid conformers of cone 25,26-di(carbox ymethoxy)calix[4]arene-27,28-crown-3,4,5,6 (23–26), and their analogues including *p-tert*-butyl moieties in the upper rim (10–13), were synthesised as potential extractants for lanthanide cations. Introducing the upper rim moieties (*p-tert*-butyl-) into the scaffolds showed an enhancement in the binding tendency and extraction ability towards lanthanide cations. This was attributed to the inductive charges from aromatic rings to the donor atoms of oxygen, which are in the crown



Fig. 3 Percent of metals loading versus equilibrium pH of the aqueous phase for competitive solvent extraction of lanthanides into chloroform by conformers 10–13.



Fig. 4 Percentage of metals loading *versus* equilibrium pH of the aqueous phase for competitive solvent extraction of lanthanides into chloroform by conformers **23–26**.

ether and the acid moieties. Among different sizes of crown rings, crown-4 showed the least loading percents. The scaffolds with crown-3 and crown-5 moieties displayed the best selectivities.

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Electronic Supplementary Information

The synthetic and characterisation details of all compounds in Figs 1 and 2 have been deposited in the ESI which is available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

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