CALIX[6]ARENES FUNCTIONALISED WITH MALONDIAMIDES AT THE UPPER RIM AS POSSIBLE EXTRACTANTS FOR LANTHANIDE AND ACTINIDE CATIONS

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Abstract

Lipophilic malondiamides have been recently employed successfully as extractants for lanthanide and actinide cations from strongly acidic media. Many complexes between malondiamides and lanthanide-actinides cations have been studied by different techniques. For many of these complexes it has been observed that more than one malondiamide ligand participates in the complexation of each metallic cation. Incorporation of two or three malondiamide moieties into a calixarene platform would probably improve both extraction and selectivity with respect to the already tested malondiamides. According to CPK examination, a calix[6]arene substituted at the upper rim with two or three malondiamide moieties should constitute a promising ligand for lanthanide and actinide cations due to co-operative complexation with the malondiamides. Based on these considerations, we synthesised calix[6]arenes functionalised with malonic acid derivatives.

1. Introduction

The separation of lanthanides and specially actinides from the nuclear fuel and the transmutation of long-lived isotopes to short lived ones are very important for the reprocessing of spent nuclear fuel.

The DIAMEX process in which malondiamides are used as extractants is one of the most promising one because these kind of extractants are well-suited compounds to extract trivalent actinides from nitric acid solutions. On the other hand, they are completely incinerable and have very low water solubility.

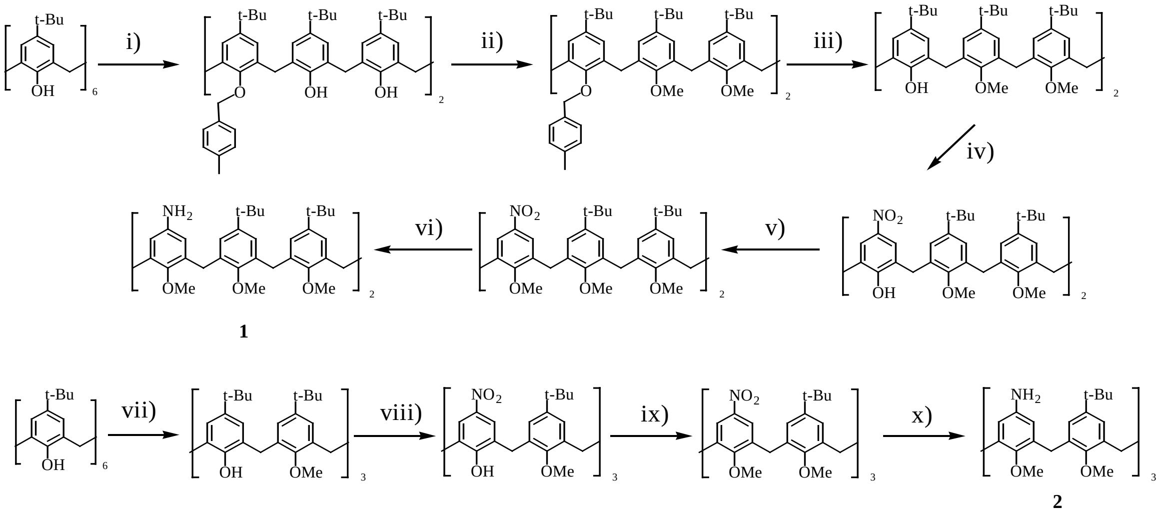
Lipophilic malondiamides have been recently employed successfully as extractants for lanthanide and actinide cations from strongly acid media. It has been observed that more than one malondiamide ligands participates in the complexation of each metallic cation [1]. For that reason it was decided to synthesize calix[6]arenes functionalised with malonic acids derivatives.

2. Malondiamide calix[6]arenes

As starting materials for this proposal, a variety of amines on the calixarenes were used with different acyl chlorides.

Amines **1** and **2** were synthesised starting from p-tert-butyl calix[6]arene [2], as described in Figure 1, by successive selective alkylation, nitration, total alkylation of the platform and finally reduction to the desired amine [3].

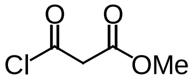
Figure 1**. Synthesis of amines 1 and 2**



i) Me_3SiOK, $BrCH_2C_6H_4CH_3$.
ii) NaH, Me_2SO_4.
iii) H_2, Pd/C.
iv) HNO_3/H_2SO_4.
v) NaH/Me_2SO_4.
vi) H_2/PtO_2.
vii) Na_2CO_3/IMe.
viii) HNO_3/H_2SO_4.
ix) K_2CO_3/Me_2SO_4, x) H_2/PtO_2.

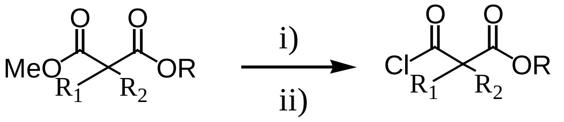
These compounds were reacted with acyl chlorides **3**, **4** and **5**. Compound **3** is commercially available and compounds **4** and **5** were obtained from commercially available di-esters by monohydrolysis with MeOH/H_2O/KOH followed by treatment of the resulting carboxylic acids with Cl_2SO (Figure 2).

Figure 2. **Formula 3 and synthesis of compounds 4 and 5**



Commercially available

3

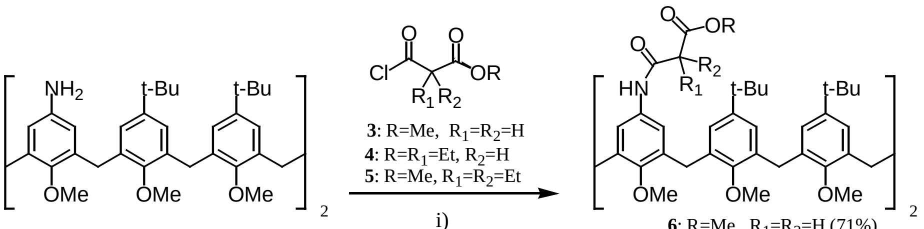


4: R=R_1=Et, R_2=H (88%)
5: R=Me, R_1=R_2=Et (86%)

i) KOH,
ii) Cl_2SO

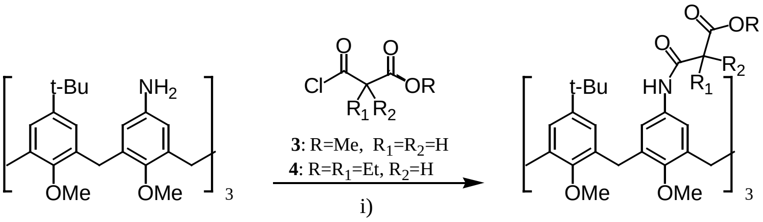
The reaction of acyl chlorides **3**, **4** and **5** with the amines **1** and **2** in CH_2Cl_2 in the presence of Et_3N at room temperature gave the ester derivatives **6-10** (Figure 3).

Figure 3. **Synthesis of esters 6-10**



1

6: R=Me, R_1=R_2=H (71%)
7: R=R_1=Et, R_2=H (51%)
8: R=Me, R_1=R_2=Et (36%)



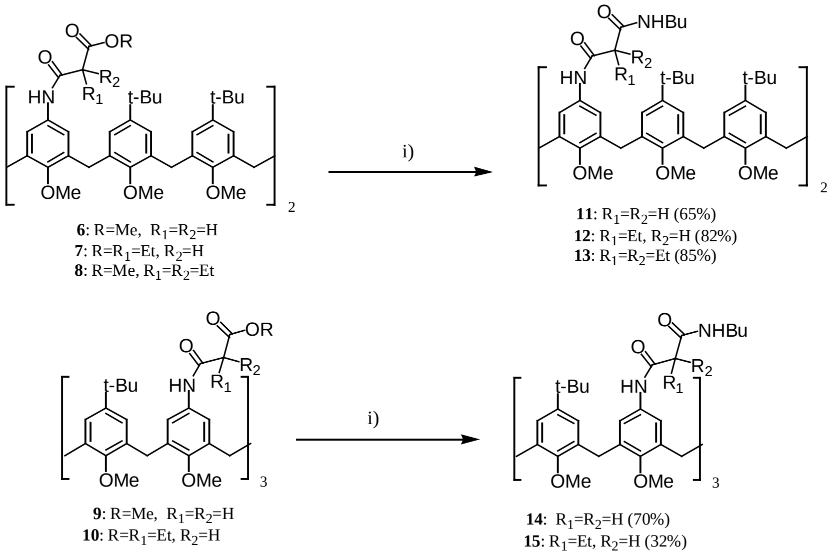
2

9: R=Me, R_1=R_2=H (23%)
10: R=R_1=Et, R_2=H (57%)

i) Et_3N, CH_2Cl_2, r.t.

Aminolysis of these compounds with butylamine at reflux temperature gave malonamide derivatives **11-15**, as described in Figure 4.

Figure 4. **Synthesis of amides 11-15**



6: R=Me, R_1=R_2=H
7: R=R_1=Et, R_2=H
8: R=Me, R_1=R_2=Et

11: R_1=R_2=H (65%)
12: R_1=Et, R_2=H (82%)
13: R_1=R_2=Et (85%)

9: R=Me, R_1=R_2=H
10: R=R_1=Et, R_2=H

14: R_1=R_2=H (70%)
15: R_1=Et, R_2=H (32%)

i) NH_2Bu/Δ

These compounds are currently being tested in lanthanide-actinide extraction.

Acknowledgements

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