ChemComm

Extraction of lanthanides and actinides by a magnetically assisted chemical separation technique based on CMPO-calix[4]arenes†

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Received (in Cambridge, UK) 4th December 2000, Accepted 23rd January 2001
First published as an Advance Article on the web 14th February 2001

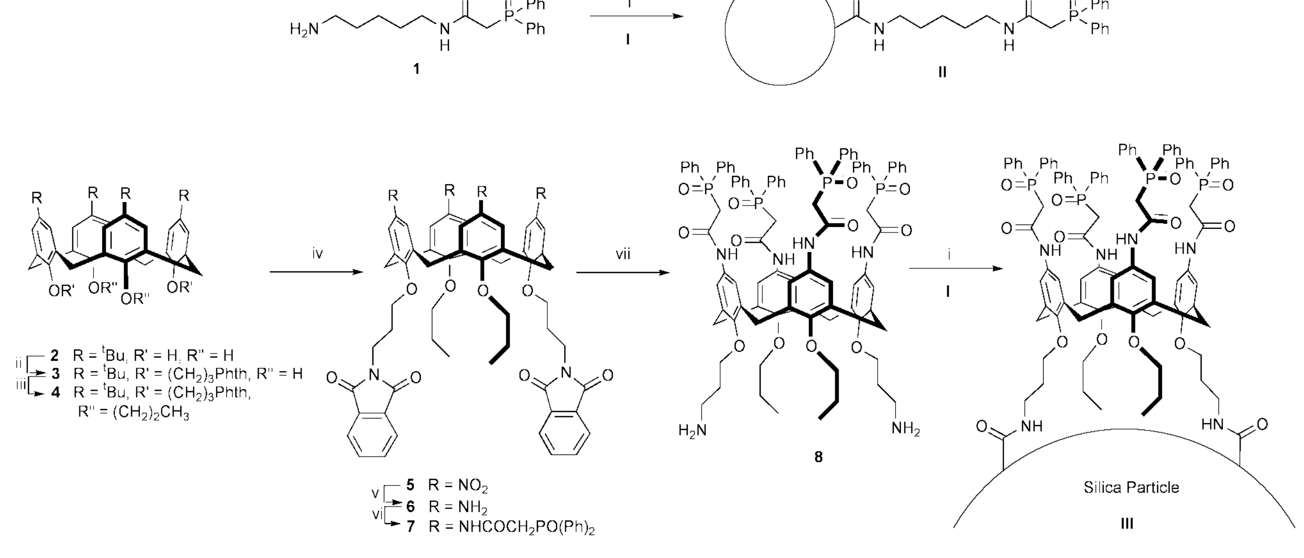
A novel particulate system carrying CMPO ligands pre-organised on a calixarene scaffold has been synthesised and demonstrated to extract Eu^{3+}, Am^{3+} and Ce^{3+} at high efficiency from simulated nuclear waste streams.

The recovery of lanthanides and actinides from high level nuclear waste is an area of world-wide concern. Current approaches are based on the TRUEX process which utilises the highly efficient, neutral, organophosphorus ligand; octyl(phenyl)(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide (CMPO).[1] Previously, we have reported calix[4]arene-based extractants which incorporate CMPO moieties at either the wide[2,3] or narrow rim.[4] Such pre-organisation of the chelating ligands leads to a 100-fold (or greater) increase[2] in extraction efficiency combined with an enhanced selectivity for actinides and lighter lanthanides.[5]

Recently, interest has been focused on magnetic fluidised bed separation technology and the development of magnetically assisted chemical separation (MACS) systems for nuclear waste remediation.[6] These combine the selectivity of a ligand developed for liquid/liquid extraction with improved separation due to the magnetic field, resulting in an effective system suitable for use at low concentrations. Adsorption of CMPO to magnetic polyacrylamide particles enhances extraction of americium and plutonium through a putative synergistic relationship between the extractant and magnetic particle.[7–9]

Here we report the first extraction results, for lanthanides and actinides, obtained with magnetic and non-magnetic silica particles[10] which allow evaluation of the role of pre-organisation of chelating groups through direct comparison of CMPO-substituted calixarenes and derivatives with single CMPO groups. Unlike previously reported systems, in which the extractant is adsorbed onto magnetic particles, our system uses covalent attachment of ligands to the particle surface, allowing controlled ligand loading with defined orientation.

Ligands carrying amines were developed for straightforward attachment to silica particles modified with carboxylic acids. The simple ligand **1** was easily synthesised by monoacylation of 1,5-diaminopentane with 4-nitrophenyl(diphenylphosphoryl)-acetate.[2] In contrast, the calix[4]arene-based system[11] **8** was designed to allow chelation at the wide rim and attachment *via* a two-point interaction at the narrow rim. The multi-step synthesis is outlined in Scheme 1.¶ Selective 1,3 alkylation at the narrow rim with *N*-(3-bromopropyl)phthalimide enabled incorporation of masked amines, whilst subsequent treatment of the remaining 2,4-positions with bromopropane fixed the calix[4]arene in the desired *cone* conformation. *ipso*-Nitration[12]



Scheme 1 Synthesis of CMPO particles. *Reagents and conditions*: i, preactivated polymeric beads (I), quant.; ii, $Br(CH_2)_3Phth$, K_2CO_3, MeCN, reflux, 48 h, 68%: iii, $Br(CH_2)_2Me$, NaH, DMF, 2 d, 82%; iv, TFA, HNO_3 (fuming), CH_2Cl_2, 30 min, 65%; v, Sn(II)Cl_2, EtOH, reflux, 18 h, 89%; vi, *p*-nitrophenyl(diphenylphosphoryl)acetate, toluene, 50 °C, 68%; vii, hydrazine hydrate, EtOH, reflux, 1 h, 96%.

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† Electronic supplementary information (ESI) available: full synthetic procedures and extraction studies. See http://www.rsc.org/suppdata/cc/b0/b009679m/

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DOI: 10.1039/b009679m

followed by reduction [Sn(II)Cl$_2$] yielded the tetraamine derivative **6** which could be effectively acylated to give the pre-organised ligand **7**. Removal of the phthalimide protecting groups gave the required amino ligand **8**.

The amino CMPO derivatives **1** and **8** were covalently bound to the surface of carboxylic acid modified magnetic ($\mathbf{I_m}$) and (for comparison) non-magnetic ($\mathbf{I_n}$) silica particles *via* carbodiimide activation. The optimal binding capacity of *ca.* 50 μmol CO$_2$H functions per g particles was determined by preliminary electrokinetic studies. An equivalent loading of CMPO units on the particle surface was achieved through stoichiometric treatment of the particles with either 50 μmol g^{-1} of compound **1** containing a single CMPO unit or with 12.5 μmol g^{-1} of calixarene **8** containing four pre-organised CMPO units.

Solid–liquid extraction experiments were performed under conditions that simulate European nuclear waste streams (4 M NaNO$_3$, 1 M HNO$_3$). Separation of europium, cerium or americium, as representatives of the early lanthanides and actinides, was evaluated. γ-Ray spectroscopic measurements of the initial nuclide activity in the aqueous phase and the activity after shaking with the particles were used to calculate the percentage extraction (%E = $100(A_0 - A)/A_0$ where A_0 and A symbolise the initial and final activity of the aqueous phase) (Table 1).[‖]

Table 1 Percentage extraction of lanthanides and actinides by CMPO and CMPO–calix[4]arene silica particles

	^{152}Eu	^{241}Am	^{139}Ce
Non-magnetic silica particles			
$\mathbf{I_n}$	0	0	—
$\mathbf{II_n}$	3	12	—
$\mathbf{III_n}$	62	88	—
Magnetic silica particles			
$\mathbf{I_m}$	4	0	9
$\mathbf{II_m}$	2	1	9
$\mathbf{III_m}$	78	82	92

Attachment of simple CMPO ligands directly onto the particle surface (**II**) enables extraction of the trivalent cations, albeit at a very low level which is only slightly higher than for the untreated silica particles (**I**). However, the calix[4]arene-based particles (**III**), with a comparable concentration of ligating functions, show a significantly higher level of extraction of all cations studied. This demonstrates the importance of pre-organisation of the chelating ligands on a suitable macrocyclic scaffold, prior to their attachment at the particle surface.

Partition coefficients for europium extraction are comparable to those seen for the particulate systems with adsorbed ligands.[13] However, in contrast, larger K_D values per mass of particles are found for americium. Taking into account the lower density of ligands on the particle (50 μmol g^{-1} *vs.* 4.8 mmol g^{-1}), the apparent K_D ($\approx$ 425 ml g^{-1} *vs.* 3500 ml g^{-1}) represents a *ca.* 12-fold advantage in extraction. This reinforces the importance of initial pre-organisation in imparting selectivity. CMPO extractants, such as octyl(phenyl)(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide are unable to discriminate greatly between actinides and lanthanides showing only a slight preference for the heavier lanthanides. In contrast, it has previously been shown, with non-particulate systems,[2,3] that incorporation onto a calix[4]arene allows differentiation between the actinides and lanthanides based on their cationic radii, the actinides and lighter lanthanides with larger radii being extracted more efficiently.

Interestingly, preliminary results on the extraction of ^{139}Ce for the magnetic particles are in marked contrast to those found previously for flexible wide-rim CMPO-calix[4]arenes.[3] The minimal extraction of cerium by CMPO-calix[4]arenes, has been rationalised by the oxidation of Ce^{3+} to the smaller radius Ce^{4+} in the extremely acidic extraction conditions. However, with the solid–liquid extraction conditions reported here, 90% extraction of cerium is achieved within 19 h of shaking, providing an opportunity for effective and selective separation of this cation.

Both non-magnetic and magnetic particles proved effective in the extraction of lanthanides and actinides. However, the ease of separation of magnetic particles from the waste stream using magnetic fluidised bed techniques makes this system more attractive for future industrial development.

These preliminary results are the starting point for a novel MACS process based on particles bearing pre-organised CMPO-calix[4]arenes as ligands. Efficient extraction of americium and europium from simulated nuclear waste conditions has been achieved together with surprisingly high levels of cerium sequestration. Currently, we are developing a range of particulate systems based on suitably functionalised conformationally mobile and narrow-rim CMPO-calix[4]arenes and extending the system to industrial applications.

These studies were supported by the Commission of the European Communities (contract F12W-CT96-0022).

Notes and references

[¶] Full synthetic procedures are given in the supplementary material (ESI†).

[‖] Methods for extraction studies are reported in the supplementary material (ESI†). Distribution coefficients are defined as $K_D = (A_0 - A)V/Am$ with V = volume of the aqueous phase and m = mass of the particles.

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