

Review

Arunasis Bhattacharyya*, Prasanta K. Mohapatra* and Willem Verboom

Understanding the separation of trivalent lanthanides and actinides using multiple diglycolamide-containing ligands: a review

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Abstract: The complexation and separation behaviour of trivalent actinides and lanthanides with various multiple diglycolamide (DGA) group-containing ligands are compiled in the present review. The DGA arms are anchored on various scaffolds, viz., C- and N-pivot tripodal backbones, benzene-centred tripodal backbones, calix[4]arene, pillar[5]arene and azamacrocyclic scaffolds. Dendrimers of different generations having DGA arms were also evaluated for the extraction and complexation studies of trivalent actinide and lanthanide ions. The extraction efficiency of the DGA units increases significantly when they are grouped together on a single backbone/scaffold. Furthermore, the selectivity was found to improve in many cases, particularly with respect to the UO_2^{2+} ion. This is very important for the development of suitable ligands for the extraction/separation of the actinide and lanthanide ions. Combined experimental, luminescence and DFT studies on the complexation of trivalent actinides and lanthanides with these DGA-based ligands are quite useful to understand their extraction and separation behaviour and this review article gives a critical analysis of the results available in the literature.

Keywords: diglycolamides; molecular scaffolds; actinide/lanthanide separation; multipodal ligands

1 Introduction

Early actinides (upto plutonium) show variable oxidation states whereas heavier actinides (americium onwards) are

mostly trivalent similar to the lanthanides due to the non-availability of the 'f' orbitals for bonding.^{1–3} Trivalent actinides are produced as the activation product of the fuel elements or the decay products of the activated species in a nuclear reactor and the lanthanides are the fission products of relatively higher yield.⁴ These trivalent actinides and lanthanides need to be separated not only for safe nuclear waste management, but they can also be used for the societal benefit, viz., ^{241}Am as smoke detector^{5,6} a heat source for thermoelectric devices.⁷

Over the years, a large number of ligands have been explored for the extraction of the trivalent actinides and lanthanides with a view to employ in nuclear fuel cycle applications.^{8–11} Some of them are phosphorus-based extractants, whereas the others are amide-based. Among the phosphorus based extractants, trialkyl phosphine oxide (TRPO) and carbamoyl methylene phosphine oxide based ligands were studied extensively for the coextraction of trivalent actinides and lanthanides.^{10,12–16} The amide based extractants possess the advantage of complete incinerability.¹⁷ Malonamide based extractants were evaluated extensively for the extraction of trivalent actinides and lanthanides.^{18,19} The malonamide based extractants, however, possess the limitation of poor extraction capability and these extractants are required to use in much larger concentration. In view of the low extraction capability of the malonamide based extractions, diglycolamide (DGA) derivatives were explored where another coordinating ethereal 'O' donor site is incorporated beside the two amidic 'O' donors. Stephan et al. observed significantly high extraction efficiency of the DGA derivatives for the trivalent lanthanide ions.²⁰ Sasaki et al. synthesized a series of DGA derivatives and evaluated for the extraction of trivalent actinides and lanthanides.²¹ Beside the higher extraction efficiency, these DGA based extractants have multiple advantages over the other amide as well as phosphorus based extractants, viz. improved third phase and stripping behaviour.¹¹ *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA; Figure 1) is found to be most suitable and hence most studied amongst all the DGA derivatives evaluated by different research groups.^{11,21–23}

TODGA shows an interesting extraction ability of actinides of different oxidation states viz. trivalent actinides are

*Corresponding authors: Arunasis Bhattacharyya and Prasanta K. Mohapatra, Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India, E-mail: arun12@barc.gov.in (A. Bhattacharyya), mpatra@barc.gov.in (P.K. Mohapatra)

Willem Verboom, Laboratory of Molecular Nanofabrication, Department for Molecules & Materials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

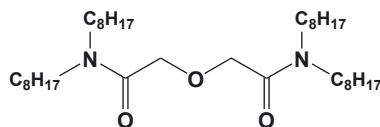


Figure 1: Molecular structure of TODGA.

extracted to a higher extent than the tetra- and hexavalent actinides in spite of the lower ionic potential values of the latter ones. This was explained on the basis of the formation of reverse micellar structures with 3–4 TODGA molecules.^{24,25} Presence of three TODGA molecules in the inner-coordination sphere of the actinide or lanthanide ions saturates the coordination number of the metal ions. The counter anions remain beyond the primary coordination sphere of the actinide or lanthanide ions in their extracted complexes²⁶ and the extraction behaviour of these actinide and lanthanide ions cannot be predicted solely based on the metal-ligand complexation behaviour in their primary coordination spheres. Solvation-desolvation behaviour of the counter anions present in the secondary coordination sphere should also be accounted for the prediction of the overall extraction behaviour.²⁷ Accumulation of 3–4 TODGA molecules around the metal ions is unfavourable due to loss of entropy (including a significant part as conformational entropy). However this can be overcome if the multiple DGA arms are preorganized on a molecular platform. Significant effort is therefore directed towards the development of different types of scaffolds having multiple DGA units. A review covering the literature till mid-2017 is available where the extraction behaviour of ligands consisting of active sites as CMPO (carbamoylmethylphosphine oxide), diamide, DGA connected to different backbones is discussed.²⁸ After that quite a number of papers appeared on the development and application of this type of ligands.

In addition several other more specific reviews appeared on the development of ligands for nuclear waste treatment.^{29–32} The present review deals with the recent developments on the extraction and complexation of trivalent actinides and lanthanides with different types of multiple DGA-functionalized ligands. In addition to molecular diluents, special attention is paid to the use of room temperature ionic liquids (RTILs) as extraction medium.^{33–35} Both luminescence and DFT studies are used to understand the extraction and separation

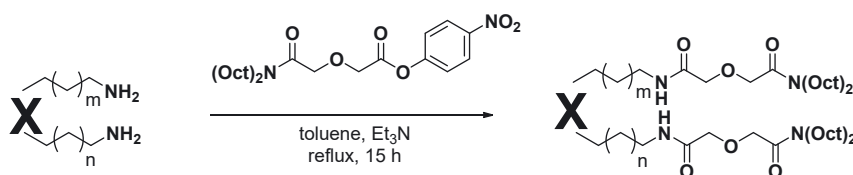
behaviour of these DGA-containing ligands. In this review, the application of this type of DGA ligands in membrane transport^{36,37} and extraction chromatography^{38,39} studies are not included.

Due to the favourable entropy changes, pre-organisation of the ligating sites results in better extractants and higher metal ion selectivities which is discussed later. The structure of the scaffold on which these sites are tethered, influence the performance of these ligands.⁸ The choice of the scaffolds is determined by their structure (rigidity, accessible attaching points) and their availability. The presence of amino groups allows relatively easy connection of the DGA moieties. This is performed by refluxing in toluene with *p*-nitrophenyl-activated DGA as in the general method outlined in Scheme 1.

The more flexible scaffolds comprise tris(2-aminoethyl) amine (TREN) and its generation 1 dendrimer (TREN-G1), giving N-pivot tripodal DGA ligands, and three generations (0, 1 and 2) poly(propylene imine) diaminobutane dendrimers. Both types of these scaffolds are commercially available. Different generations of the dendrimers have two, four and eight available primary amino groups, respectively, for further functionalization. A C-pivot tripodal diglycolamide (T-DGA) was prepared in several steps, the last one being the attachment of the DGA via an amino group.⁴⁰

Another class is the aza-crown ethers in which the (in this case secondary) nitrogen atoms are incorporated in a macrocyclic ring. In the same way as described in Scheme 1, DGA units were attached to 1,4,7-triazacyclononane and 1,4,7,10-tetraazacyclododecane. The macrocycle hinders the movement of the tethered DGA groups. This reflected in a broadening of the methylene signals in the ¹H NMR spectra. The macrocyclic scaffolds can have high flexibility and the binding can be easier compared to more rigid scaffolds such as the benzene centred DGA ligands. Furthermore, it was proposed that the 'N' atoms in the aza-crown ethers can bind to softer metal ions such as Am³⁺ leading to a better separation efficiency with respect to the trivalent lanthanide ions such as Eu³⁺.

Benzene rings were selected as a flat scaffold to which (via a spacer) DGA sites can be attached. Different types of tripodal benzene-centred DGA ligands were prepared. They differ in the connection to the benzene ring influencing the flexibility of the ligating sites and consequently, the extraction behaviour.



Scheme 1: Schematic representation of the attachment of DGA moieties to molecular scaffolds.

Calix[4]arenes represent a class of versatile, three-dimensional platforms that have been used for a variety of applications.^{41,42} Functionalization is possible in two ways, at the narrow (lower) rim (smaller cavity) which was having 'OH' functionalized in the simple calixarene backbone and at the wide (upper) rim (larger cavity). An example will be shown that DGA groups are attached to both rims. Related to this are the three-dimensional pillar [5]arenes⁴³ to which 10 DGA groups were attached with varying spacer lengths. Another class of three-dimensional platform is resorcin[4]arenes in which also four DGA arms were attached and evaluated for the extraction of trivalent lanthanides.^{44–46}

2 Bis-diglycolamide derivatives

The simplest form of the multiple DGA based ligands we can imagine is the bis-DGA derivatives. Murillo et al. synthesized a series of bis-DGA derivatives (Figure 2a–c).⁴⁷ These ligands were evaluated for the extraction studies of Am^{3+} and Eu^{3+} from the nitric acid media and found to be seven times more selective for Eu^{3+} as compared to Am^{3+} . Their preference for Eu^{3+} was subsequently exploited for the selective extraction of Am^{3+} by nitrilo triacetamide (NTAamide) based ligand through the selective complexation of Eu^{3+} in the aqueous phase using aqueous soluble bis-DGA derivative. A S.F. value of 26 for Am^{3+} over Eu^{3+} was observed using TEE-DGA (Figure 2c, $n = 0$) in the aqueous phase when used in combination with N,N,N',N',N'',N''-hexaocetylnitrilotriacetamide (HONTA).⁴⁸ Ren et al. reported further enhancement in the selectivity for Eu^{3+} over Am^{3+} when ethyl or isopropyl substitution was incorporated on the central 'N' atoms of TEE-DGA ligand.⁴⁹ Recently, using an aromatic aqueous

soluble bis-DGA derivative ($\text{SO}_3\text{-TEX(p)-BisDGA}$, Figure 2d), the decontamination factor (DF) more than 500 was reported between Am^{3+} and most of the lanthanide ions.⁵⁰

3 DGAs on tripodal backbones

Two different ligands having C- and N-pivot tripodal DGA arms, T-DGA and TREN-DGA, respectively (Figure 3a and b), were explored for the extraction of actinides and lanthanide ions both in molecular solvent and room temperature ionic liquid (RTIL) media. T-DGA, where three DGA units are anchored through an ethereal oxygen linkage (Figure 3a), shows the highest extraction for Eu^{3+} ion followed by Pu^{4+} and Am^{3+} in the molecular diluent (Table 1). Extraction of UO_2^{2+} was however found to be negligible.⁵¹ In RTIL ($\text{C}_4\text{mim.NTf}_2$) medium, the extraction of tri- and tetravalent metal ions significantly decreased. The extraction of UO_2^{2+} , on the other hand, enhanced resulting in lowering of the separation factor (S.F.) of Am^{3+} over UO_2^{2+} .

In the case of N-pivot tripodal DGA ligand (TREN-DGA), extraction of tri- and tetravalent metal ions just increases in the RTIL medium.⁵¹ This reversal of the extraction behaviour of these lanthanide and actinide ions in these two media might be attributed to the formation of different extractable species in the case of these two ligands.^{51,52} EXAFS and DFT studies suggested that one of the three DGA arms of two TREN-DGA ligands coordinates to the metal ion.⁵¹ A similar observation along with the coordination of three monodentate nitrate ions was also reported while studying the extraction behaviour of several N-pivot tripodal DGA ligands of varying alkyl substituents at the amidic nitrogen atom and spacer length. Single phase complexation studies in acetonitrile showed the presence of both 1:1 and 1:2 complexes.⁵³

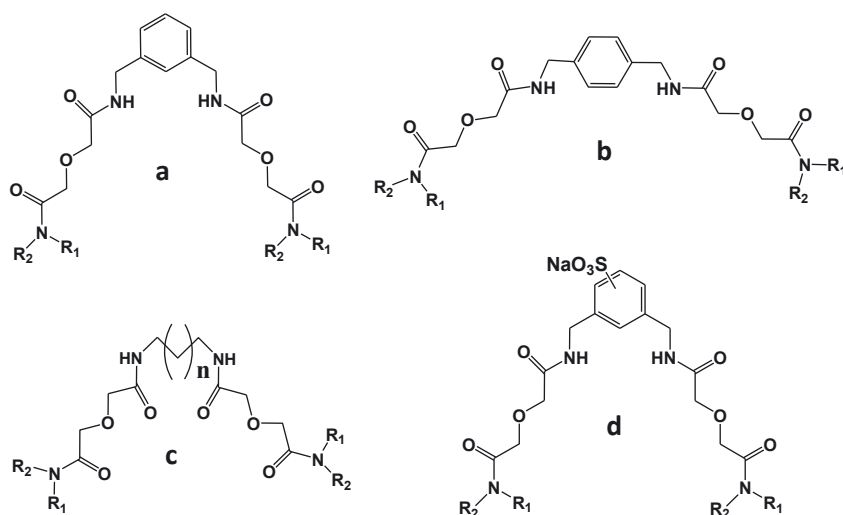


Figure 2: Schematic structures of different bis-DGA derivatives evaluated for the extraction studies of trivalent actinides and lanthanides. (a) 2-[(N'-alkylcarbamoyl)methoxy]-N-[3-[(2-(N''-alkyl carbamoyl) methoxyacetyl amino) methyl] benzyl] acetamide, (b) 12-[(N',N'-Dialkyl carbamoyl) methoxy]-N-[4-[(2-(N'',N''-dialkyl carbamoyl) methoxy acetyl amino) methyl] benzyl] acetamide, (c) 2-Dialkyl carbamoyl methoxy-N-[5-(2-dialkyl carbamoyl methoxy acetyl amino)alkyl] acetamide, (d) Sulphonated-2-[(N'-alkyl carbamoyl) methoxy]-N-[3-[(2-(N''-alkyl carbamoyl) methoxy acetyl amino) methyl] benzyl] acetamide.

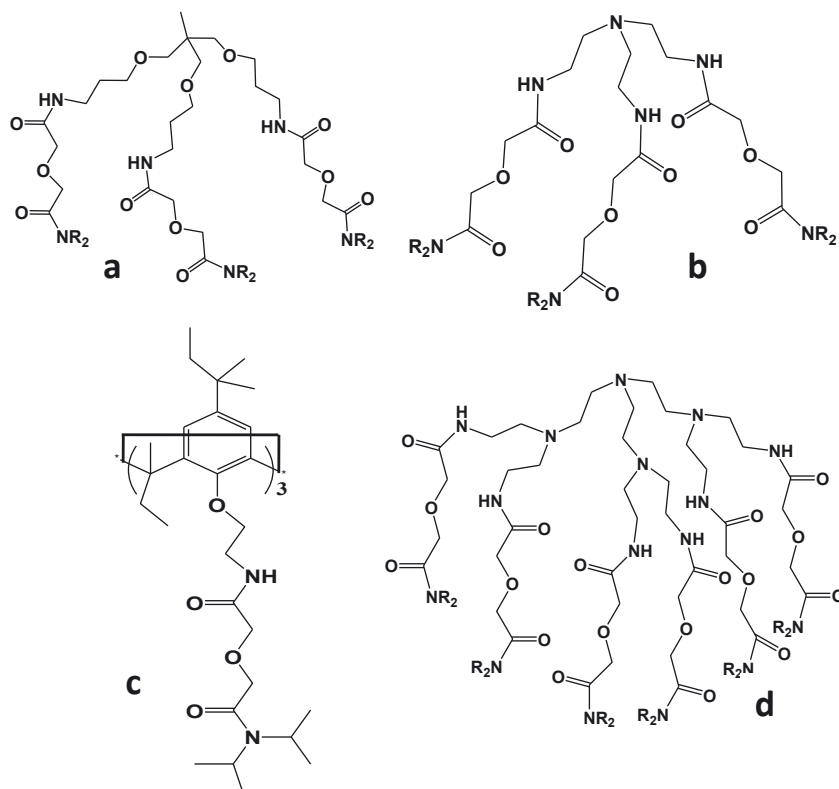


Figure 3: Molecular structures of (a) T-DGA, (b) TREN-DGA, (c) C3-Tripod-DGA and (d) TREN-G1-DGA ($R = n$ -octyl).

Table 1: Distribution ratio, separation factor values of lanthanides, actinides and important fission product elements. Org. phase: 1.0×10^{-3} M ligand in 5 % isodecanol/95 % n -dodecane (DD-IDA) mixture and in $C_4mim.NTf_2$. Aqueous phase: 3 M HNO_3 . S.F. values with respect to Am (S.F. = D_{Am}/D_M) are given between parentheses. Enhancement factor (EF) is the enhancement in extraction in $C_4mim.NTf_2$ as compared to that in DD-IDA mixture.

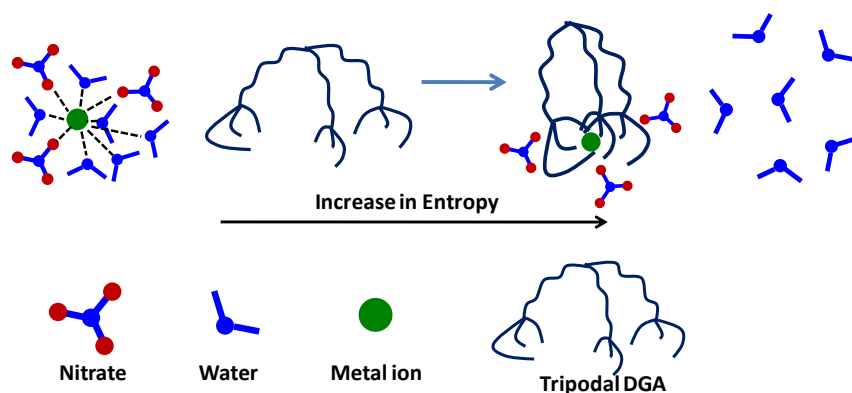
Metal ion	D_M with TODGA ⁵⁷		EF	D_M with T-DGA ⁵¹		EF
	DD-IDA	$C_4mim.NTf_2$		DD-IDA	$C_4mim.NTf_2$	
Am ³⁺	0.003	0.25	83	11.1 ± 0.1	0.081	0.1
Eu ³⁺	–	–	–	98 ± 3 (0.11)	0.09 ± 0.02	<0.001
UO ₂ ²⁺	<0.01	0.04 (6.25)	>4	0.06 ± 0.01 (185)	1.00 ± 0.01 (0.081)	16.7
Pu ⁴⁺	0.03	18 ± 1 (0.014)	600	19 ± 1 (0.58)	3227 ± 40 (2.5×10^{-5})	170
Np ⁴⁺	–	–	–	–	–	–

Metal ion	D_M with TREN-DGA ⁵¹		EF	D_M with TREN-G1-DGA		EF
	DD-IDA	$C_4mim.NTf_2$		DD-IDA ⁵⁸	$C_4mim.NTf_2$ ⁵⁹	
Am ³⁺	0.36 ± 0.02	161 ± 2	447	3.2 ± 0.1	89 ± 3	28
Eu ³⁺	1.16 ± 0.01 (0.31)	126 ± 2 (1.28)	109	14.0 ± 0.1 (0.23 ± 0.01)	175 ± 4 (0.5 ± 0.04)	12
UO ₂ ²⁺	0.02 (18)	0.01 (16100)	0.5	0.040 ± 0.001 (74 ± 3)	0.11 ± 0.01 (809 ± 7)	2.8
Pu ⁴⁺	0.25 ± 0.01 (1.44)	4.0 ± 0.1 (40.2)	16	6.5 ± 0.1 (0.49 ± 0.02)	9.8 ± 0.4 (9.1 ± 0.5)	1.5
Np ⁴⁺	–	–	–	9.3 ± 0.4 (0.34 ± 0.03)	7.7 ± 0.1 (11 ± 3)	0.8

The extraction efficiency of T-DGA decreased with increasing the length of the alkyl chain attached to the imidazolium ring of the RTIL. A similar observation was also noticed in the case of TODGA.⁵⁴ The increase in extraction with increasing alkyl chain length of the cationic part of the RTIL suggests the solvation mechanism for the extraction of these metal ions. Determination of thermodynamic parameters

suggested that the extraction is highly entropy driven. This indicates the removal of a large number of water molecules from the inner-coordination sphere (Scheme 2). Moreover, the RTIL-based solvent systems were found to be radiolytically more stable.⁵⁴

Matloka et al.^{55,56} have synthesized and evaluated a new tripodal DGA-based ligand where three DGA arms are



Scheme 2: Entropy driven complexation of the metal ion with tripodal DGA-based ligands.

tethered to the triphenoxymethane scaffold varying spacer length (Figure 3c). This class of ligands, in general, showed increasing extraction efficiency for the heavier lanthanides as compared to the lighter ones. However, the selectivity between the heavier to the lighter lanthanide ions was significantly affected by the alkyl groups present in the DGA arms, viz. isopropyl substituted DGA showed much higher selectivity as compared to the *n*-butyl substituted DGA. Change of spacer length, however, did not have much effect on their extraction behaviour.⁵⁶ They have also incorporated 'S' by replacing the ethereal 'O' atoms of the DGA moieties to enhance the softness of the ligand to achieve the selectivity between trivalent actinides and lanthanides. The thio derivative, however, showed poor extraction for both these trivalent 'f' block elements.⁵⁶

With the aim to further increase the number of DGA arms, a TREN-DGA ligand of higher generation, TREN-G1-DGA (Figure 3d), was also synthesized where six DGA arms are attached to the tripodal backbone. In the molecular diluents (mixture of *n*-dodecane and isodecanol in the present case), a significant enhancement in the extraction of tri- and tetravalent metal ions is observed in the case of TREN-G1-DGA as compared to TREN-DGA. Such regular increase was not

observed in the RTIL medium. Detailed extraction studies indicated that the trivalent metal ions are extracted as a 1:1 complex in the case of TREN-G1-DGA. EXAFS studies showed that three out of the six DGA arms coordinate to the Eu^{3+} ion, which was further supported by DFT studies.

4 Benzene-centred DGA ligands

A series of ligands having three DGA arms anchored to the alternate positions of a benzene ring was investigated for the extraction of actinide and lanthanide ions. Ligand **L_I** (Figure 4a) shows much higher extraction than the C- or N-pivot tripodal DGA ligands in the molecular diluent, but follow the regular extraction trend of $\text{Eu}^{3+} > \text{Am}^{3+} > \text{Pu}^{4+} \gg \text{UO}_2^{2+}$ (Table 2). The other two benzene-centred tris-DGA ligands, **L_{II}** (Figure 4b) and **L_{III}** (Figure 4c), however, show different trends in the extraction. The highest extraction was observed for the Pu^{4+} ion as compared to the trivalent Am^{3+} and Eu^{3+} metal ions.⁶⁰ The presence of three ethyl groups resulted into more pre-organization in the ligand structure in **L_I** and consequently into different trends in the extraction behaviour. In case of **L_{II}** and **L_{III}**, on the other hand, the preorganization is expected to be

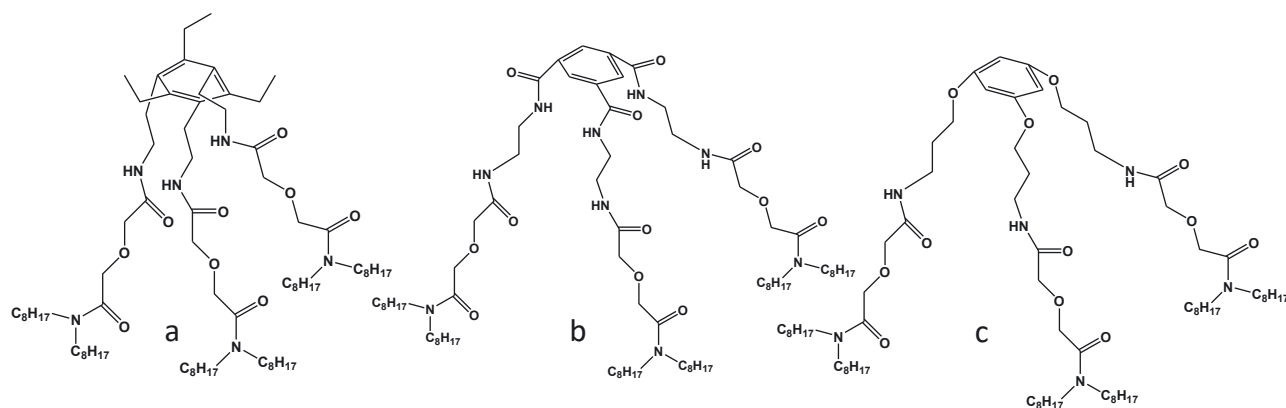


Figure 4: Molecular structures of (a) **L_I**, (b) **L_{II}** and (c) **L_{III}**.

Table 2: Extraction of different actinides and Eu^{3+} from 3 M HNO_3 using three different benzene-centred tris-DGA ligands in DD-IDA (Ligand: 1 mM; Ref.⁶⁰).

Metal ion	Ligand		
	L_I	L_{II}	L_{III}
Eu^{3+}	$(3.9 \pm 0.3) \times 10^2$	110 ± 5.5	32.7 ± 1.6
Am^{3+}	$(2.3 \pm 0.2) \times 10^2$	14.3 ± 0.3	4.06 ± 0.11
Pu^{4+}	$(1.0 \pm 0.1) \times 10^2$	$(1.9 \pm 0.1) \times 10^2$	$(1.15 \pm 0.06) \times 10^2$
UO_2^{2+}	0.04 ± 0.01	0.08 ± 0.001	0.04 ± 0.001
PuO_2^{2+}	0.08 ± 0.01	0.11 ± 0.01	0.05 ± 0.01

less and their extraction behaviour is dictated by the ionic potential of the metal ions resulting in highest extraction of Pu^{4+} followed by Eu^{3+} and Am^{3+} . The lowest extraction of hexavalent actinyl ions is due to the stringent steric requirement of their coordination through the equatorial plane beside the relative order of the hydration entropies of the tri, tetra and hexa valent actinide ions³.

To estimate the Eu^{3+} selectivity of these ligands over Am^{3+} , separation studies were performed in 1 M HNO_3 . Ligand L_{III} showed the highest selectivity with a S.F. value ($\text{Eu}^{3+}/\text{Am}^{3+}$) of 10.⁶⁰ Time-resolved luminescence spectroscopy (TRFS) and DFT studies were carried out on the Eu^{3+} and Am^{3+} complexation with these benzene-centred tris-DGA ligands. The results indicated the presence of one water molecule in the inner-coordination sphere of the metal ion in case of L_{III} , whereas the complexes of L_I and L_{II} do not contain any inner-sphere water molecule. Comparing the species responsible for the extraction of Eu^{3+} or Am^{3+} , it was interesting to observe the formation of a 1:1 complex in the case of L_I and a 1:2 complex in case of L_{II} .

Higher extraction of trivalent metal ions (Am^{3+} and Eu^{3+}) with L_I as compared to that with L_{II} can be explained based on the calculation of the extraction free energies with DFT. Three ethyl groups at the alternate positions in the benzene ring point in the same direction and consequently also the ligating DGA sites. This makes the free energy for preorganization of the ligand in the organic phase more favourable in case of L_I , which results into its higher extraction efficiency. The preorganized structure of L_I , by

virtue of the presence of the three ethyl groups, makes the approach of two ligands towards the metal ion sterically hindered.⁶¹ X-ray absorption spectroscopic (XAS) studies suggest the presence of ~4–5 oxygen atoms at 2.30 Å and ~4–5 oxygen atoms at 2.35 Å in the Eu^{3+} complex of L_I . In the case of L_{II} , on the other hand, these bond lengths are somewhat shorter.⁶¹

5 DGA ligands attached to aza-crown ether

Nitrilo-triacetamide (NTA) derivatives were found to show selectivity towards trivalent actinides over lanthanides. This was attributed to the involvement of the central nitrogen atom in the bonding with the metal ions.^{62–65} Another class of DGA derivatives was then developed where the DGA arms are attached to an aza-crown ring having three and four 'N' atoms. In the case of the ligand where three DGA arms are attached to the three 'N' atoms of the triaza-crown ring (T9C3ODGA; Figure 5a) both Am^{3+} and Eu^{3+} are extracted as ML_2 type of complexes in a 5 % isodecanol/*n*-dodecane mixture. Luminescence studies showed the absence of any water molecule at the inner coordination sphere of the Eu^{3+} ion.

Using these clues from the experimental studies, DFT studies were performed on eight different possible structures varying the coordination modes of the DGA arms and the number of inner-sphere nitrate ions from 0 to 3. In the most stable complex however one DGA arm of each of the two ligands coordinates through all three oxygen (two O_{amid} and one O_{ether}) atoms present in a DGA arm. Three nitrate ions are present in the inner coordination sphere of the Eu^{3+} ion to saturate its coordination number. Out of these three nitrate ions, one is bidentate and the remaining two are monodentate. The energetics from the solution phase complexation studies considering the COSMO model show that the extraction of Eu^{3+} is more preferable than that of Am^{3+} , which corroborates the results of the solvent extraction study.⁶⁶

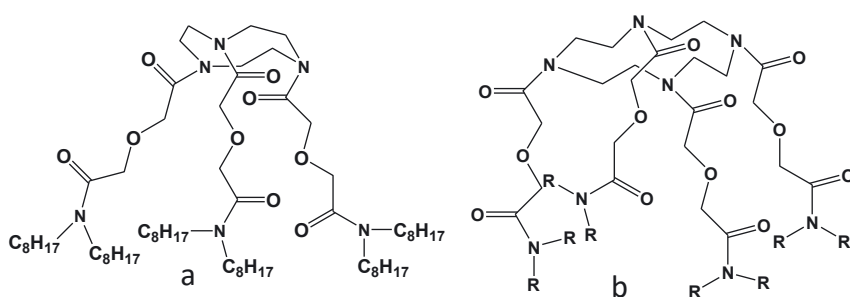


Figure 5: Molecular structures of (a) T9C3ODGA, (b) T12C4ODGA ($\text{R} = n\text{-octyl}$) and T12C4MDGA ($\text{R} = \text{methyl}$).

In the case of the ligand, where four DGA arms are attached to the four 'N' atoms of the tetraaza-crown ring (T12C4ODGA; Figure 5b) mixed 1:1 and 1:2 complexes were observed for both Am^{3+} and Eu^{3+} from the solvent extraction studies. This indicates the increasing tendency to form the lower stoichiometric complexes as the number of DGA units increased from 3 (T9C3ODGA) to 4 (T12C4ODGA). The proportion of 1:2 complex is, however, higher in the case of Eu^{3+} than that of Am^{3+} . When extraction studies were carried out in RTIL medium, only 1:2 complex formation was found to be responsible for both the metal ions (Am^{3+} and Eu^{3+}) in case of both the ligands, i.e., T9C3ODGA and T12C4ODGA. However unlike in the case of molecular diluents, the extraction in RTIL medium decreased with increasing HNO_3 concentration. This suggests a cation-exchange mechanism for the extraction of the trivalent metal ions in the RTIL.⁶⁷ Extraction of Eu^{3+} was marginally higher than that of Am^{3+} in the case of both the ligands both in molecular diluent and RTIL medium. The separation factor for Eu^{3+} over Am^{3+} , however, is higher in the 5 % isodecanol/*n*-dodecane medium than in $\text{C}_8\text{mim.NTf}_2$ (Table 3).⁶⁷ It is to be mentioned here that in the molecular diluent T9C3ODGA shows higher extraction than T12C4ODGA. In the RTIL medium, on the other hand, extraction of both the metal ions are higher with T12C4ODGA than with T9C3ODGA. This can be explained on the basis of the complexes responsible for their extraction. Two T9C3ODGA molecules are present in the extraction complex, whereas T12C4ODGA extracts both Am^{3+} and Eu^{3+} as a mixture of 1:1 and 1:2 complexes in the molecular diluent. This results in more hydrophobicity of the metal complex of T9C3ODGA leading to higher extraction.

In case of RTIL medium both the ligands extract both the metal ions as 1:2 complex. The metal complex becomes more hydrophobic because of the presence of more octyl-DGA units in T12C4ODGA which results into higher extraction. Luminescence studies on the Eu^{3+} complexes in the organic extract for both *n*-dodecane and $\text{C}_4\text{mim.NTf}_2$ media show

that the excitation spectra are significantly different (Figure 6). However, in a particular diluent, either *n*-dodecane or $\text{C}_4\text{mim.NTf}_2$, similar excitation spectra were observed in the case of both the ligands, viz., T9C3ODGA and T12C4ODGA.⁶⁷

Their emission spectra are different even in the same diluent indicating the difference in local symmetry around the Eu^{3+} ion (Figure 6). Single-phase complexation studies in methanol showed the formation of both 1:1 and 1:2 complexes of Eu^{3+} ion with T9C3ODGA with stability constant ($\log \beta$) values of 4.75 and 9.12, respectively. In $\text{C}_8\text{mim.NTf}_2$, however, only 1:2 complex is observed for both the ligands with comparable stability constant values.⁶⁷ This suggests that the affinity for the Eu^{3+} ion is not altered much when the number of DGA arms are increased from three to four. This

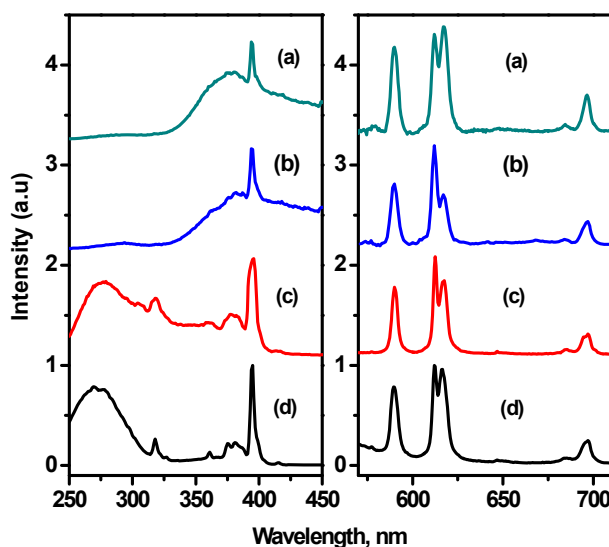


Figure 6: Left: Excitation spectrum of Eu^{3+} complex with emission (λ_{em}) at 612 nm. Right: Emission spectrum of Eu^{3+} complex with excitation (λ_{ex}) at 394 nm. (a) T9C3ODGA, (b) T12C4ODGA in $\text{C}_8\text{mim.Tf}_2\text{N}$, (c) T9C3ODGA, (d) T12C4ODGA in *n*-dodecane (Reproduced from Ref.⁶⁷).

Table 3: Comparison of the extraction and S.F. data for Am^{3+} and Eu^{3+} in molecular diluent as well as in ionic liquid using 1×10^{-4} M DGA-functionalized aza-crown solutions.

Ligand	HNO_3	D_{Am}	D_{Eu}	$\text{SF}_{(\text{Eu}/\text{Am})}$	Comment
T9C3ODGA-DD-IDA ^a	0.5 M	1.3 ± 0.1	4.3 ± 0.1	3.3	Increasing extraction with HNO_3 concentration in <i>n</i> -dodecane, whereas decreasing extraction in $\text{C}_8\text{mim.NTf}_2$ for both the ligands
	3.0 M	71 ± 6	$(3.0 \pm 0.3) \times 10^2$	4.2	
T9C3ODGA- $\text{C}_8\text{mim.Tf}_2\text{N}^c$	0.5 M	5.9 ± 0.3	14.8 ± 0.6	2.5	
	3.0 M	0.01 ± 0.001	0.04 ± 0.01	4.0	
T12C4ODGA-DD-IDA ^b	0.5 M	0.30 ± 0.05	2.0 ± 0.1	6.7	
	3.0 M	3.0 ± 0.3	20.8 ± 2.1	6.9	
T12C4ODGA- $\text{C}_8\text{mim.Tf}_2\text{N}^c$	0.5 M	15.1 ± 0.7	47.9 ± 2.4	3.2	
	3.0 M	0.67 ± 0.04	1.6 ± 0.2	2.4	

^aRef.⁶⁶, ^bRef.⁶⁸, ^cRef.⁶⁸. 5×10^{-4} M (Reproduced from⁶⁷).

is because all the DGA arms are not participating in the coordination with the metal ions. Time-resolved luminescence indicated that three water molecules are present in the first coordination sphere of the metal ion in the 1:1 complex observed in molecular diluent in case of T12C4ODGA (Table 7). No signature of inner-sphere water molecules was noticed from the lifetime values of all the 1:2 Eu^{3+} complexes in both the diluents.^{66–68} In the 1:1 complex six coordination sites of the metal ion are occupied by one DGA arm of the ligand molecule and three water molecules. The remaining coordination sites are satisfied by three nitrate ions. Whereas in the case of the 1:2 complex, two DGA arms from two ligand molecules satisfy six coordination sites and the remaining sites are fulfilled by nitrate ions.

With this information, different possible structures were considered for DFT calculations and the final optimized structures of the Am^{3+} complexes are provided in Figure 7. Similar structures were also obtained for the Eu^{3+} complexes. No significant changes in the ligand coordination behaviour were noticed upon replacement of the methyl group with the *n*-octyl group (T12C4ODGA). Only in the complexes of T12C4MDGA, the interaction of Am^{3+} with the nitrate ion was found to be stronger than that of Eu^{3+} in the 1:2 complex, whereas this was not observed in the complexes of T12C4ODGA. After inclusion of the dispersion corrections and the solvent effects using the COSMO model, it was observed that the Eu^{3+} complexation with T12C4ODGA was stronger than that of Am^{3+} . This clearly explained its higher extraction of Eu^{3+} over Am^{3+} .⁶⁸

6 DGA sites attached to calix[4]arenes

Several multiple DGA-based ligands on a calix[4]arene scaffold with varying number and position of the DGA arms were evaluated for the complexation and extraction of actinide and lanthanide ions. In the simplest ligand of this class, DGA arms are attached to only two alternate positions of the lower rim of *p*-*tert*-butylcalix[4]arene (C2DGA, Figure 8a). The remaining two 'OH' groups of calix-2DGA were substituted with *n*-butyl groups (C2DGA-R, Figure 8b). In the third and fourth ligands of this class, DGA arms are attached to all the four positions of the lower rim (C4DGA-L, Figure 8c) and upper rim (C4DGA-U, Figure 8d). Finally, DGA arms are attached to all the eight positions of both rims of calix[4]arene (C8DGA, Figure 8e). In the case of C2DGA, the extraction of both tri- and tetravalent metal ions (Am^{3+} , Pu^{3+} , Eu^{3+} and Pu^{4+}) increased significantly as compared to that of TODGA.⁶⁹ To further enhance the lipophilicity, C2DGA-R was used for the extraction studies. A significant decrease in the extraction of all the metal ions was, however, noticed as compared to that of C2DGA. This decrease in extraction efficiency in spite of increasing lipophilicity of the ligand molecules suggests that the incorporation of the two butyl groups at the lower rim adversely affected the complexation ability of C2DGA-R as compared to that of C2DGA due to higher steric hindrance.

In the case of C4DGA-L, the extraction increased by more than an order of magnitude as compared to that of C2DGA.

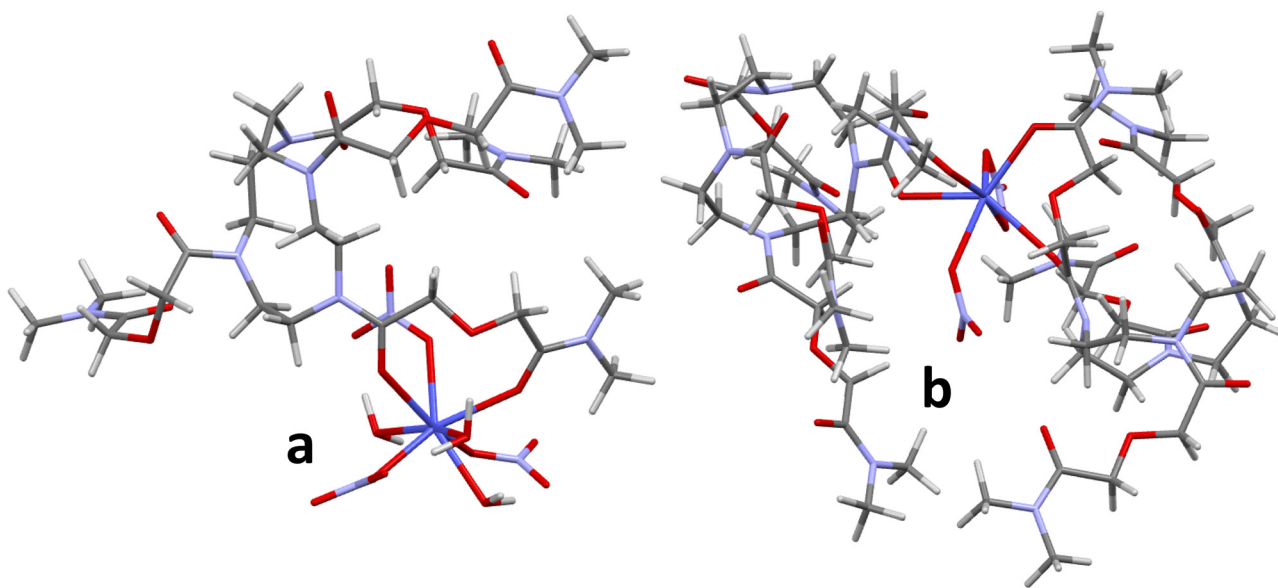
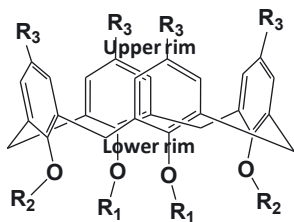


Figure 7: Optimized structures of (a) 1:1 and (b) 1:2 complexes of Am^{3+} with T12C4MDGA using DFT calculations.



Ligand	R ₁	R ₂	R ₃
C2DGA (a)	H		<i>t</i> Bu
C2DGA-R (b)	<i>n</i> Bu		<i>t</i> Bu
C4DGA-L (c)			<i>t</i> Bu
C4DGA-U (d)	<i>n</i> Bu	<i>n</i> Bu	
C8DGA (e)			

Figure 8: Molecular structures of calix[4]arene-based ligands with DGA arms with varying number and position. (a) C2DGA, (b) C2DGA-R, (c) C4DGA-L, (d) C4DGA-U and (e) C8DGA.

Ligand concentration variation experiments suggested that the calix[4]arenes having two DGA arms, viz., C2DGA and C2DGA-R, extracted the Eu³⁺ ion as an 1:2 complex, whereas C4DGA-L extracted it as an 1:1 complex. In the case of Am³⁺, however, an 1:2 complex was also noticed with C4DGA-L in some of the diluents.⁷⁰ Luminescence spectroscopic studies indicated the absence of any water molecule in the inner-coordination sphere of the Eu³⁺ ion. DFT calculations on the Eu³⁺ complexes of these three ligands showed that the metal-ligand bond distances were higher in the complex of C4DGA-L. However, coordination of more DGA arms made the complex more stable as indicated from the higher interaction energies in the case of C4DGA-L.⁷⁰ Huang et al. also evaluated lower rim DGA functionalized calix-4-arene (C4DGA-L) derivative for the extraction of Am³⁺ and Eu³⁺.⁷¹ A separation factor values for Eu³⁺ over Am³⁺ was found be dependent on the nitric acid concentration in the aqueous

phase and at 2 M HNO₃ medium, a S.F. value > 7 was reported.⁷¹ DFT based calculations were performed on their complexes with the C4DGA-L both in the gas and solution phase to understand this selectivity for Eu³⁺ over Am³⁺.⁷² Results from this calculations showed that the complexation free energy is more negative for Eu³⁺ as compared to Am³⁺ when the inner sphere coordination of the nitrate ions was considered. This clearly supports the experimental observation of selectivity of C4DGA-L for Eu³⁺ over Am³⁺.⁷²

Presence of more number of DGA units at the lower rim of the calix[4]arene helps the complexation due to a favourable entropy factor. Moreover, these two extra octyl-DGA units provide additional lipophilicity to the ligand molecule leading to higher extraction in case of C4DGA-L. It was of interest to evaluate the ligands having four DGA arms on the other side of the calix[4]arene moiety (C4DGA-U, Figure 8d) and eight DGA arms on both sides of the calix[4]

Table 4: Extraction behaviour of different actinides and Eu³⁺ using various multiple DGA-based ligands on calix[4]arene scaffold.

Ligand	Distribution ratio (<i>D_M</i>)					
	Am ³⁺		Eu ³⁺	Pu ³⁺	Pu ⁴⁺	UO ₂ ²⁺
	Mol. Dil.	RTIL	Mol. Dil.	Mol. Dil.	Mol. Dil.	Mol. Dil.
C2DGA	1.06 ± 0.01 ^a	0.69 ± 0.01 ^c	5.28 ± 0.02 ^a	1.67 ^a	6.86 ± 0.2 ^a	0.05 ± 0.01 ^a
C2DGA-R	0.04 ± 0.01 ^a	0.23 ± 0.06 ^c	0.28 ± 0.01 ^a	0.29 ± 0.0 ^a	1.12 ± 0.1 ^a	0.04 ± 0.01 ^a
C4DGA-L	26.5 ± 1.4 ^a	194 ± 2 ^c	155 ± 1 ^a	30.4 ± 0.8 ^a	67.9 ± 1.4 ^a	0.17 ± 0.01 ^a
	402 ^b	1.06 ^d	356 ^b			
C4DGA-U	0.58 ^b	0.3 ^d	0.43 ^b	–	–	–
C8DGA	54.2 ^b	7700 ^d	375 ^b	–	–	–

^aDiluent: *n*-dodecane, Feed: 3 M HNO₃, Concentration of the ligand: 3 mM⁶⁹, ^bDiluent: 5 % isodecanol/*n*-dodecane, Feed: 3 M HNO₃, Concentration of the ligand: 11 mM⁷³, ^cDiluent: C₈mim.PF₆, Feed: 3 M HNO₃, Concentration of the ligand: 0.5 mM⁷⁴, ^dDiluent: C₈mim.NTf₂, Feed: 3 M HNO₃, Concentration of the ligand: 0.5 mM⁷⁵.

arene (C8DGA, Figure 8e). Table 4 clearly shows a significant decrease in the extraction capability when the four DGA arms are attached at the upper rim (C4DGA-U) as compared to that having them at the lower rim (C4DGA-L). In the case of C8DGA, however, there are marginal changes in the extraction of Am^{3+} and Eu^{3+} ions compared to that in the case of C4DGA-L.^{69,73}

To understand the extraction behaviour of the DGA-anchored calix[4]arene derivatives, a complexation study with Eu^{3+} ion was carried out in acetonitrile, where only 1:1 complex formation was noticed in the cases of C4DGA-L, C4DGA-U and C8DGA. The stability constant values, however, were reported to be the highest for C4DGA-L ($\log \beta = 7.35 \pm 0.03$), which decreased to as low as 1.10 ± 0.02 for C4DGA-U, while that of C8DGA being 6.71 ± 0.02 . The trend in the stability constant values nicely corroborates with the extraction efficiency of these three ligands.⁷⁶

DFT calculations on the Eu^{3+} complexes showed that the Eu–O bond distances with all the coordination sites of the DGA arms were shorter in the case of C4DGA-L than those in C4DGA-U. This suggests a stronger interaction of Eu^{3+} ion with the former. This was also reflected in the higher free energies of complexation with C4DGA-L as compared to that with C4DGA-U. Frontier orbital analysis revealed that the close matching of the $E_{\text{HOMO-LUMO}}$ of Eu^{3+} with C4DGA-L resulted into its stronger interaction and higher charge transfer to the Eu^{3+} ion.⁷⁶ This charge transfer clearly suggests that the presence of DGA units at the upper rim of the C4DGA cannot complex as effectively as the DGA units at the lower rim. This is attributable to the shorter spacer length between the DGA and calix[4]arene moieties, which makes the DGA units more rigid. This more rigid ligand then complexes and extracts metal ions less efficiently.

The extraction behaviour of these ligands significantly modifies in RTIL media. The most interesting phenomenon is the significant enhancement of the extraction of Am^{3+} by C8DGA (Table 4). The distribution ratio values are reported to remain almost unaltered when the aqueous phase acidity was varied in the range of 0.5–3 M HNO_3 .⁷⁷ In the case of the ligands C4DGA-L and C4DGA-U, however, the extraction was found to have decreased with increasing acid concentration, which is typically observed in RTIL media where a cation-exchange mechanism is operative.⁷⁸ Luminescence studies on the Eu^{3+} extract in the $\text{C}_8\text{mim.NTf}_2$ medium indicated the absence of any inner-sphere water molecule in the cases of C4DGA-L and C8DGA, whereas there were around five inner-sphere water molecules in the case of C4DGA-U, which clearly explained its poor extraction efficiency.⁷⁷

7 DGA-based dendrimers of three generations

DGA-functionalized poly(propylene imine) diaminobutane dendrimers (DGA-Den) of three generations, viz., DGA-Gen0 (Figure 9a), DGA-Gen1 (Figure 9b) and DGA-Gen2 (Figure 9c) were synthesized having two, four and eight DGA arms, respectively. Similar to other DGA-based ligands, all the three dendrimeric ligands show marginally higher extraction for Eu^{3+} over Am^{3+} with varying separation factor values in the range of 1.9–5.5 (Table 5). Irrespective of the diluents used, the extraction of both the trivalent f-cations increased by orders of magnitude moving from DGA-Gen0 to DGA-Gen1 or DGA-Gen2.^{79,80}

Solvent extraction studies indicated that the trivalent metal ions were extracted as 1:2 complex in the case of DGA-Gen0, whereas in the case of the other two dendrimer ligands the extraction occurred through the formation of only an 1:1 complex in 5 % isodecanol/*n*-dodecane.⁸¹ Single-phase complexation studies of Eu^{3+} ion in methanol using UV–Vis spectrophotometric titrations showed the formation of 1:1 and 1:2 complexes with stability constant ($\log \beta$) values of 5.2 and 9.4, respectively, in the case of the DGA-Gen0. In the cases of the higher generations DGA-Dens the presence of only 1:1 complexes was noticed with similar $\log \beta$ values as obtained for DGA-Gen0. The remarkable enhancement in the extraction of the DGA-Dens of higher generation, in spite of similar $\log \beta$ values, was attributed to their higher lipophilicity compared to that of DGA-Gen0.⁸¹ A luminescence study also indicated the formation of a 1:2 complex for DGA-Gen0 and a 1:1 complex for the other two ligands.⁸¹ Similar $\log \beta$ values for the 1:1 complexes of all the three DGA-Den ligands suggests that the nature of bonding is similar for all the three DGA-Dens, viz., the same number of DGA units of a ligand molecule participate in the bonding with the metal ion in spite of the presence of more DGA arms in the higher generation DGA-Dens.

In RTIL medium, as usual, the extraction of both Am^{3+} and Eu^{3+} decreased with increasing nitric acid concentration in the case of all the three dendrimeric ligands.⁸⁰ The extracted species of the trivalent metal ions were reported to be similar both in molecular diluent and RTIL medium in the case of DGA-Gen0. In the case of the higher generation DGA-Dens, however, the extracted species were different in molecular diluent and RTIL media. In the case of DGA-Gen1, 0.5 equivalent of the ligand is involved in the binding with 1 equivalent of the metal ion, whereas in case of DGA-Gen2, 0.25 equivalent of the ligand is engaged. This suggested that two DGA arms were involved in the bonding with only one metal ion. Based on this assumption, DFT calculations were

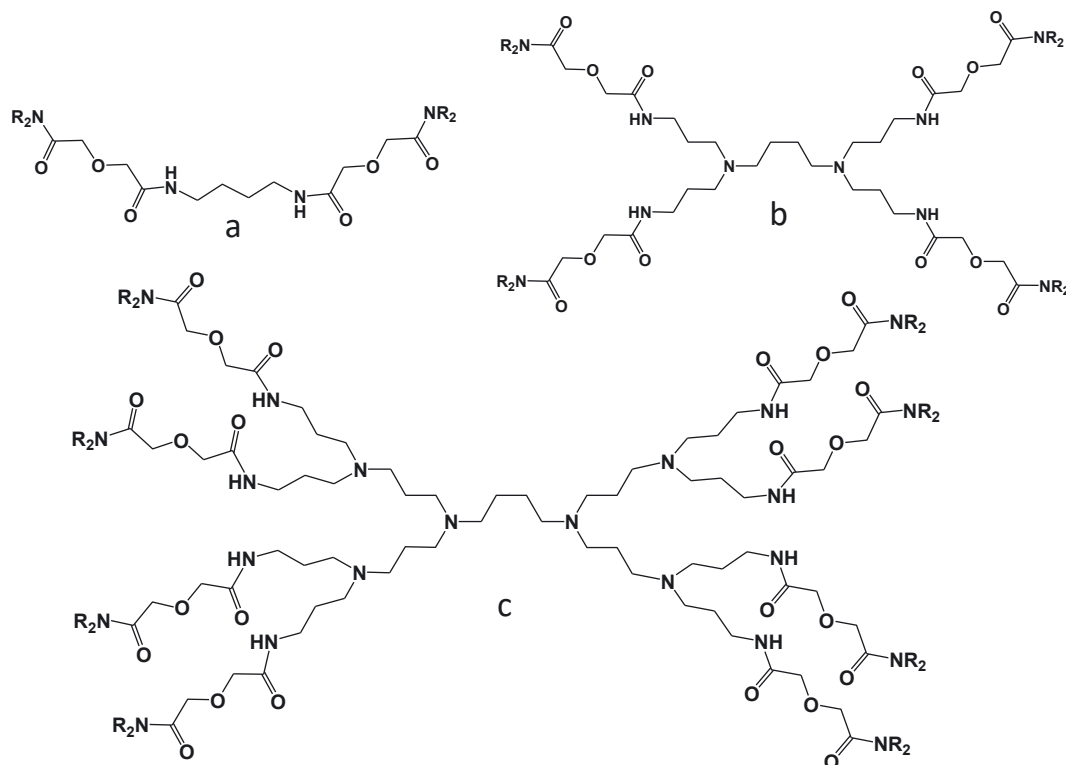


Figure 9: Schematic structures of DGA-functionalized poly(propylene imine) diaminobutane dendrimers (DGA-Den) of generations a) 0 (DGA-Gen0), b) 1 (DGA-Gen1) and c) 2 (DGA-Gen2) (R = *n*-octyl).

Table 5: Comparison of the extraction and S.F. data for Am³⁺ and Eu³⁺ in molecular diluent as well as in ionic liquid using three DGA-based dendrimers.

Ligand	DD-IDA ^a			C ₄ mim.NTf ₂ ^b		
	<i>D</i> _{Am}	<i>D</i> _{Eu}	S.F. (Eu/Am)	<i>D</i> _{Am}	<i>D</i> _{Eu}	S.F. (Eu/Am)
DGA-Gen0	0.11	0.21	1.9	0.02 ± 0.01	0.11 ± 0.01	5.5
DGA-Gen1	41.8	147	3.5	9.5 ± 0.1	23.4 ± 0.3	2.5
DGA-Gen2	110	300	2.7	52 ± 2	99 ± 5	1.9

^a1 mM Ligand, Ref.⁷⁹; ^b0.1 mM Ligand, Ref.⁸⁰.

performed on the Am³⁺ complexes of the three DGA-Dens. Two possible coordination modes are considered in the case of DGA-Gen0. The free energy of complexation indicates the preference of a structure where two DGA arms of each of the DGA-Gen0 are involved in the bonding. Based on the calculations, the order of the complexation strength is DGA-Gen2 > DGA-Gen1 > DGA-Gen0. Natural population analysis (NPA) showed the presence of some covalent contribution in the bonding of these three ligands with Am³⁺.⁸⁰ NPA data indicates small amount of orbital contribution to the inner *s* and *f* subshells and along with a significant contribution in the *d* subshells of the Am³⁺ ion.

This suggests that the interaction of the metal ion with the ligands has covalent contribution where the *d* orbitals were reported to be more diffused than the *s* and *f* orbitals.⁸⁰

8 DGA sites attached to pillar[5]arene

Another interesting class of a multiple DGA-based ligand involves the pillar[5]arenes scaffolds to which 10 DGA arms with varying spacer length (*n*) can be anchored on both sides of the scaffold (P5DGA, Figure 10). The extraction results of Am³⁺ and Eu³⁺ with these C5DGA ligands at 0.1 M and 1 M HNO₃ are provided in Table 6. Extraction of both metal ions in 1-octanol was reported to have increased up to 1 M HNO₃ for all three P5DGAs, however, beyond 1 M HNO₃ the extraction decreased with increasing acidity.⁸² Similar to the other DGA-based ligands as discussed above, the extraction of Eu³⁺ is higher than that of Am³⁺. Quite impressive selectivities for Eu³⁺ over Am³⁺ were observed specifically at 0.1 M HNO₃ in 1-octanol, which was not reported for any of the other DGA-based ligands. The extraction of both metal ions was reported to have increased by orders of magnitude in RTIL medium (Table 6).⁸³ Only 1:1 complexes are responsible

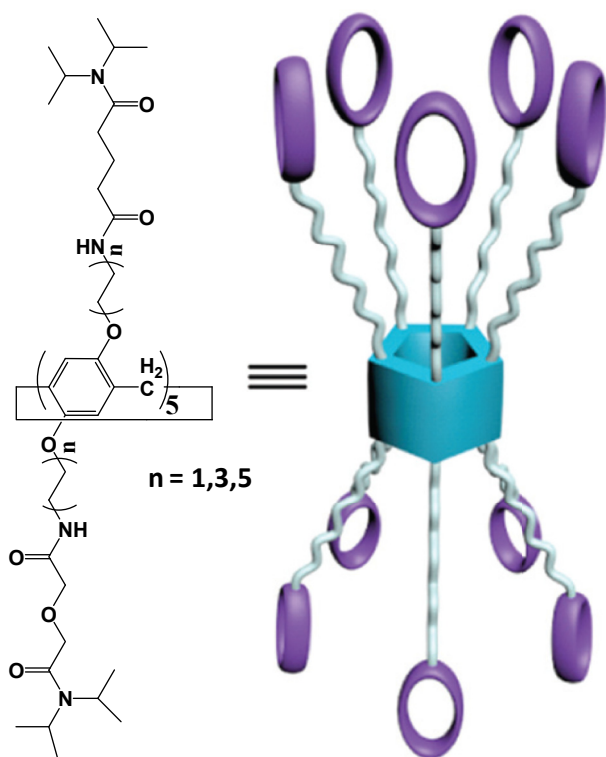


Figure 10: Schematic structure of DGA-substituted pillar[5]arenes (P5DGAs) of varying spacer lengths (reproduced with permission from Ref.⁸²).

for the extraction of the trivalent metal ions by all the three P5DGA ligands both in 1-octanol and $C_8mim.NTf_2$ media.^{82,83} The mechanism of La^{3+} ion extraction in $C_8mim.NTf_2$ was established using 1H NMR spectroscopy. Initially a C_8mim^+ cation was trapped in the cavity of the P5DGA ligand, but was subsequently replaced by a La^{3+} ion due to its stronger interaction with the ligand. The nature of the complex formed with Eu^{3+} ion was investigated employing time-resolved luminescence, which indicated the absence of any inner-sphere water molecule.⁸³

9 DGA attached to resorcin[4]arene cavitand

Very few studies are reported on the extraction and separation of trivalent lanthanides using resorcin[4]arene based DGA ligands. However, to the best of our knowledge, no report is available on the extraction of trivalent actinides using any of the resorcin[4]arene-based DGA ligands. Only one DGA anchored resorcin[4]arene derivative (Figure 11) was evaluated for the extraction studies of trivalent lanthanides. This ligand deserves mention, as it showed an enormous increase in the extraction as of the heavier lanthanides compared to that of the lighter lanthanides. This increase is much more pronounced, even as compared to the enhancement demonstrated by

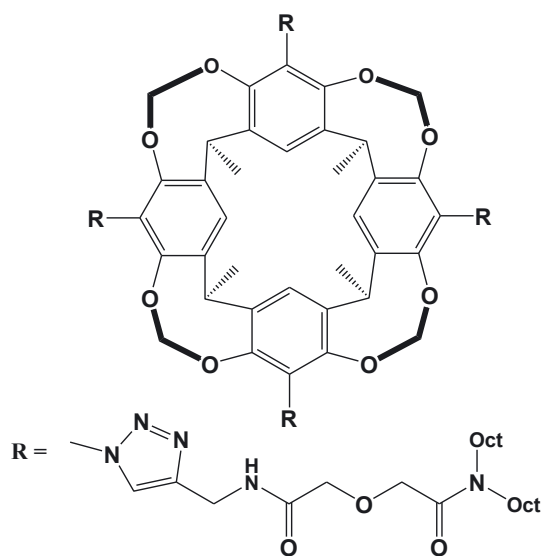


Figure 11: Schematic structure of the resorcin[4]arene-based DGA ligands (CR4-DGA) evaluated for the extraction of trivalent lanthanide ions.

Table 6: Comparison of extraction behaviour of Am^{3+} and Eu^{3+} using P5DGA of varying spacer lengths in 1-octanol vis-à-vis RTIL media.

Diluent	Spacer length (n)	[HNO ₃] (M)	D_{Am}	D_{Eu}	S.F. (Eu/Am)
1-Octanol	1	1.0^a	1.5 ± 0.1	12.4 ± 0.9	8.27
		0.1^b	<0.001	0.68	>680
	2	1.0^a	9.6 ± 0.2	63 ± 3	6.56
		0.1^b	0.7	6.8	9.71
	3	1.0^a	15 ± 1	52 ± 3	3.47
		0.1^b	0.37	4.5	12.2
$C_8mim.NTf_2$	1	1.0^a	$(7.3 \pm 0.1) \times 10^2$	$(8.6 \pm 0.1) \times 10^2$	1.19
	2	1.0^a	$(11.6 \pm 0.1) \times 10^2$	$(17.3 \pm 0.2) \times 10^2$	1.49
	3	1.0^a	$(40.1 \pm 0.1) \times 10^2$	$(78.0 \pm 0.2) \times 10^2$	1.9

^aLigand concentration 0.5 mM, Ref.⁸³, ^bLigand concentration 1 mM, Ref.⁸².

TODGA.^{44,46} This selectivity for the heavier lanthanides was reported to be further enhanced in RTIL (*N*-octyl-*N*-ethylpiperidinium bis(trifluoromethylsulfonyl)imide ([EOPip]NTf₂)) medium where a S.F. >100 reported for Yb³⁺ over La³⁺.⁴⁵

10 Critical review on the comparative evaluation of multiple DGA ligands tethered to different scaffolds

In the present review we made an attempt to compare the extraction and complexation behaviour of multiple DGA ligands tethered at different scaffolds where the number of DGA arms are varied from 2 (DGA-Gen0, Figure 9a) to 10 (P5DGA, Figure 10). It is very difficult to directly compare their extraction behaviour as the extraction studies with these ligands were not always performed in the same experimental conditions in view of their different solubility and vast difference in their extraction performance.

All the multiple DGA-based ligands, however, showed much improved extraction behaviour as compared to

TODGA, especially in molecular diluent where in millimolar concentrations TODGA is totally inefficient to extract any of the actinide ions, whereas these multiple DGA-based ligands work very well in millimolar concentrations. The extraction efficiency does not always simply increase with increasing the number of DGA arms. Position and flexibility of these DGA arms are also important to control their extraction behaviour, viz., these DGA arms when present at the lower rim of a calix[4]arene unit showed significant enhancement in the extraction behaviour as compared to the case when they are tethered at the upper rim of the calix[4]arene moiety. In case of P5DGAs, the extraction efficiency significantly enhanced with increasing spacer length in spite of having the same number of DGA arms, whereas in case of C3 symmetric tripodal DGA ligands, the extraction efficiency is not affected when the spacer length is varied. This might be due to the fact that in case of P5DGAs, having a shorter spacer length, coordination of multiple DGA arms to the same metal ion is difficult which becomes easier when the flexibility of these arms is increased by increasing the spacer length. In case of C3 symmetric tripodal DGA ligands, on the other hand, with shorter spacer length itself, the coordination is favourable and further increasing the spacer length does not improve the extraction performance. In the RTIL

Table 7: Lifetime values and number of inner-sphere water molecules (N_{H_2O}) in the Eu³⁺ complexes of different DGA-based ligands.^a

Ligand	Condition	Lifetime (ms)	N_{H_2O}	Ref
TODGA	DD-IDA (org. extract)	2.07	0	58
T-DGA	Acetonitrile/3 M HNO ₃	2.285	0	54
	C ₄ mim.NTf ₂	2.251	0	
TREN-DGA	C ₄ mim.NTf ₂	1.60	0	84
	DD-IDA (org. extract)	1.203	0	53
TREN-G1-DGA	DD-IDA (org. extract)	1.527	0	58
Benz-DGA (L _I)		1.56	0	61
Benz-DGA (L _{II})		1.25	0	
Benz-DGA (L _{III})		0.607	1	60
T9C3ODGA	DD-IDA (org. extract)	1.18	0	66
	Methanol	0.89	1	
T12C4ODGA	DD-IDA (org. extract)	0.324 (ML) and 1.92 (ML ₂)	3 (ML) and 0 (ML ₂)	68
C4DGA-L	Acetonitrile	1.31	0	76
	C8mim.NTf ₂	1.522	0	85
C4DGA-U		0.21	5	77
C8DGA		1.364	0	
DGA-Gen0	Methanol	>2.5	0	81
	C ₄ mim.NTf ₂	1.67		80
DGA-Gen1	Methanol	>2.5	0	81
	C ₄ mim.NTf ₂	1.66		80
DGA-Gen2	Methanol	>2.5	0	81
	C ₄ mim.NTf ₂	1.65		80
P5DGA	n = 1 Ethanol/H ₂ O (5:1)	0.807	1	82
	n = 3	1.507	0	
	n = 5	1.506	0	

^aIDA, isodecanol; dd, *n*-dodecane.

medium, the extraction behaviour becomes more complicated, probably due to multiple extraction mechanisms, viz., solvation as well as cation exchange, and their contributions also vary when the RTILs are varied from C4mim.NTf₂ to C8mim.NTf₂.

The lifetime data of the Eu³⁺ complexes of most of the ligands are compared in Table 7 and we can notice that almost all the complexes extracted in the organic phase (5 % isodecanol/*n*-dodecane) are devoid of any inner-sphere water molecule, except in case of T12C4ODGA where three inner-sphere water molecules are present in the 1:1 complex, where the 1:2 complex is devoid of any inner-sphere water molecule.

11 Conclusions and future perspective

This review clearly demonstrates that the extraction efficiency of DGA ligands enhances remarkably when the ligating sites are anchored in multiple numbers onto different scaffolds. This increase is attributed to the gain in the entropy of complexation due to the preorganized structures of the ligands and their higher hydrophobicity because of the presence of multiple DGA arms having long alkyl chains. The experimentally observed trends of the extraction of Am³⁺ and Eu³⁺ with different benzene-substituted DGA derivatives can be explained successfully with the help of DFT studies.

In most cases, a significant enhancement in the extraction of the trivalent actinide and lanthanide ions was observed in an RTIL as compared to that in a molecular diluent, probably due to the different extraction mechanisms operative in these two solvent media.

In the case of all the DGA-based ligands, similar to TODGA, higher extraction was observed for Eu³⁺ as compared to that of Am³⁺, irrespective of the scaffold. An exception was TREN-DGA, where in the RTIL medium Am³⁺ extraction was superior to that of Eu³⁺.

The experimentally found trends of the extraction of Am³⁺ and Eu³⁺ ions by different calix[4]arenes, having lower rim, upper rim and both side substituted DGA units, was confirmed by single-phase complexation studies and DFT-based calculations.

The highest separation factor for Eu³⁺ over Am³⁺ was achieved in the case of a DGA-substituted pillar[5]arene (P5DGA) in 1-octanol. It can be concluded that rationally designed ligands consisting of multiple DGA moieties connected to a suitable supramolecular scaffold, have significant potential for the recognition and separation of trivalent actinides and lanthanides.

Preference of these DGA derivatives for Eu³⁺ over Am³⁺ is due to the higher ionic potential of the former owing to its smaller ionic size. This clearly opens another possible application of these class of DGA based ligands for the intra-group separation of the lanthanide ions based on their difference in ionic size as the heavier lanthanide ions are extracted to higher extent as compared to their lighter analogue.

In future, some of the ligands which showed very high affinity for these trivalent actinide and lanthanide ions can be used to develop sensors for the detection and estimation of these radiotoxic elements in environmental samples with very high sensitivity. Some of the extractants may also find application in the separation of these radiotoxic elements from nuclear waste solutions using membrane-based techniques where the separation can be achieved with very small ligand inventory, and we are also working in these directions.

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Competing interests: The authors state no conflict of interest.

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Data availability: As this is a review article raw data will be available with the authors of the cited references.

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