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Unique selectivity reversal in Am^{3+} - Eu^{3+} extraction in a tripodal TREN-based diglycolamide in ionic liquid: Extraction, luminescence, complexation and structural studies†

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An *N*-pivot diglycolamide extractant (DGA-TREN) was synthesized for the first time and its complexation behaviour was studied towards trivalent lanthanide / actinide ions. The solvent extraction studies suggested a unique selectivity reversal in the extraction of trivalent actinides *versus* trivalent lanthanides which was observed performing extraction studies in an ionic liquid vis-à-vis a molecular diluent for a tripodal TREN-based diglycolamide extractant which may have great significance in radioactive waste remediation. The nature of the bonding to Eu^{3+} ion was investigated by EXAFS as well as by DFT calculations.

Introduction

Diglycolamides (DGA)[1] are a class of organic ligands which are found to be the most promising for the selective extraction of trivalent actinides and lanthanides from high level radioactive waste. Apart from showing a preference for trivalent actinide / lanthanide ions over tetravalent actinide ions such as Pu^{4+}, the extraction of UO_2^{2+} ion is reported to be significantly lower, which is in sharp contrast to the general trend seen with other analogous extractants such CMPO (carbamoyl methylene phosphine oxide)[2] and malonamides.[3] This has been attributed to a special aggregated reverse micellar structure,[4] which facilitates size-selective complexation.[5] The uranyl ion, in view of its special requirement for complexation along the equatorial plane, experiences steric constraints to bind effectively with the DGA aggregate. Several DGA extractants have been tested extensively and 'hot engineering scale runs' have been carried out.[6] The extraction of Eu^{3+} with TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) has been reported to be an order of magnitude higher than that of Am^{3+} suggesting interesting separation possibilities under acidic feed conditions using *n*-dodecane, a commonly used process molecular solvent.[7]

Room temperature ionic liquids have been proposed as benign alternatives to the generally hazardous molecular diluents.[8] Ionic liquids, apart from having a low vapour pressure and a lower tendency for inflammability, show very large enhancements in the metal ion extraction as compared to molecular diluents.[9] Favourable extraction of Eu^{3+} vis-à-vis Am^{3+}, seen with DGA ligands in molecular diluents also takes place when the solvent system contains room temperature ionic liquids as the diluent.[10] In general, though selectivities in ionic liquids are found to improve manifold as compared to molecular diluents for the Am^{3+} - UO_2^{2+} (or Am^{3+} - Pu^{4+}) pair in DGA extractants, similar observations were not made for the Am^{3+} - Eu^{3+} pair.[11] We have used several multiply DGA-functionalized calix[4]arenes with an amazing increase in selectivities for Am^{3+} vis-à-vis actinide ions such as UO_2^{2+}, while there was only a slight decrease in the selectivities with respect to the Eu^{3+} ion.[12] In view of the involvement of three diglycolamide extractants in the extraction of trivalent lanthanide ions, it was thought of interest to study the separation behaviour of tripodal DGA ligands.[13] Previous studies with a C-pivot tripodal diglycolamide (T-DGA) ligand have indicated very high D_{Am} values at 3 M HNO_3 (usual feed acid concentration for high level radioactive wastes) in

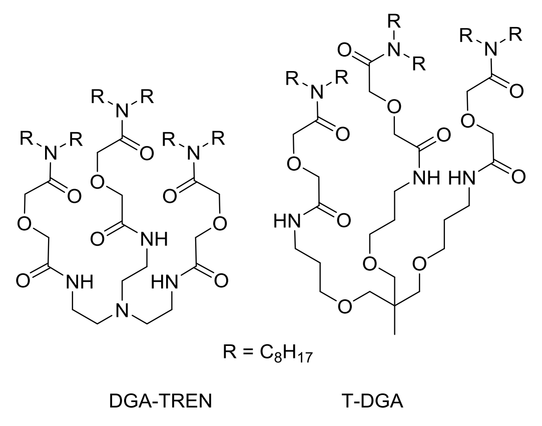


Table 1 Distribution ratio and separation factor values of lanthanides, actinides and important fission product elements using 1.0 x 10^{-3} M ligands. Aqueous phase: 3 M HNO_3. Separation factor (S.F.) values with respect to Am (S.F. = D_{Am} / D_M) are given between parentheses. IDA = isodecanol

Metal ion (M)	D_M values with DGA-TREN		D_M values with T-DGA	
	n-Dodecane + IDA (9:1)	$[C_4mim][Tf_2N]$	*n*-Dodecane + IDA (9:1)	$[C_4mim][Tf_2N]$
Am^{3+}	0.36 ± 0.02	161 ± 2.3	11.1 ± 0.06	0.081 ± 0.21
Eu^{3+}	1.16 ± 0.01 (0.31)	126 ± 1.8 (1.28)	98.5 ± 2.6 (0.11)	0.087 ± 0.02 (0.93)
Pu^{4+}	0.25 ± 0.01 (1.44)	4.0 ± 0.1 (40.2)	19.0 ± 1.1 (0.58)	--
UO_2^{2+}	0.02 ± 0.00 (18)	0.01 ± 0.00 (16,100)	0.06 ± 0.01 (185)	1.00 ± 0.01 (0.81)
Sr^{2+}	<0.001 (>2430)	0.006 (>2.68 x 10^4)	0.02 (555)	0.002 ± 0.00 (40)
Cs^+	<0.001 (>2430)	0.097 (>1.65 x 10^3)	<0.001 (>1.1 x 10^4)	0.009 (9)

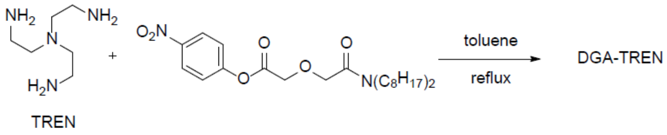
molecular diluents,[14] while significantly lower D_{Am} values were obtained under identical conditions when room temperature ionic liquids were used as the diluent.[15]

In the present study, the extraction / separation behaviour of a new type of *N*-pivot DGA ligand, DGA-TREN (Fig. 1), was studied both in a molecular diluent mixture of *n*-dodecane and isodecanol (IDA) (9:1 volume ratio) and in a room temperature ionic liquid, $[C_4mim][Tf_2N]$ (1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonamide), and the results are compared with those obtained using T-DGA. Attempts have been made to compare the separation behaviour of Am^{3+} vis-à-vis Eu^{3+}. In addition, structural studies were carried out using EXAFS and DFT calculations were done to arrive at the most feasible structure of the Eu^{3+}-DGA-TREN complex. In literature, an analogous ligand with CMPO ligating groups connected to TREN has been studied, though the results were rather routine.[16]

Results and discussion

Synthesis

DGA-TREN was prepared in 73% yield by the reaction of the commercially available tris(2-aminoethyl)amine (TREN) as a scaffold with *p*-nitrophenyl-activated DGA in refluxing toluene (Scheme 1).



Scheme 1

Solvent extraction studies

Solvent extraction data for Am^{3+} and Eu^{3+} with DGA-TREN and T-DGA are listed in Table 1 for both the molecular diluent and the ionic liquid. Extraction data of some other metal ions relevant in nuclear waste viz. UO_2^{2+} and Pu^{4+}, Sr^{2+} and Cs^+ are also presented in Table 1. An equilibration time optimization study was carried out in both the molecular diluent and in $[C_4mim][Tf_2N]$. It took about 2 h to attain an equilibrium D_{Am} value in the ionic liquid medium, while much lesser time was needed in the molecular diluent (Fig. S5). DGA-TREN displays a rather low D_{Am} value in the molecular diluent mixture of *n*-dodecane and IDA. However, an unprecedented enhancement in the D_{Am} value by ca. 450 times was seen by changing the diluent to the ionic liquid under identical experimental conditions which is quite remarkable. Though such large enhancements have been reported previously at lower acidities[9a] (which is due to the manifestation of the difference in the extraction mechanism[17]), such observations are rare at higher acidities.[18] In case of DGA-based extractants, lower extractions of actinide and lanthanide ions are reported for ionic liquids as the diluent compared to molecular diluents when the aqueous phase acid concentration is moderate to high. For example, though D_{Eu} was reported to be ca. 9 at 4 M HNO_3 when 7 x 10^{-3} M TBDGA (tetrabutyl diglycolamide) was used in 1-octanol, it decreased by an order of magnitude to ca. 1 when $[C_4mim][Tf_2N]$ was used as the diluent and the other conditions were kept constant.[10a] Similarly, the extraction of both Am^{3+} and Eu^{3+} with DGA-functionalized calix[4]arenes was reported to be lower[12] in an ionic liquid than in molecular diluents.[19] It may be pointed out that if a cation exchange mechanism is operative similar to that reported with T-DGA in the ionic liquid $[C_4mim][Tf_2N]$,[15] rather low D_{Am} values are expected for DGA-TREN as well at 3 M HNO_3. To our best knowledge, this extraction behaviour is unique at moderate acid concentrations (1 - 6 M HNO_3)

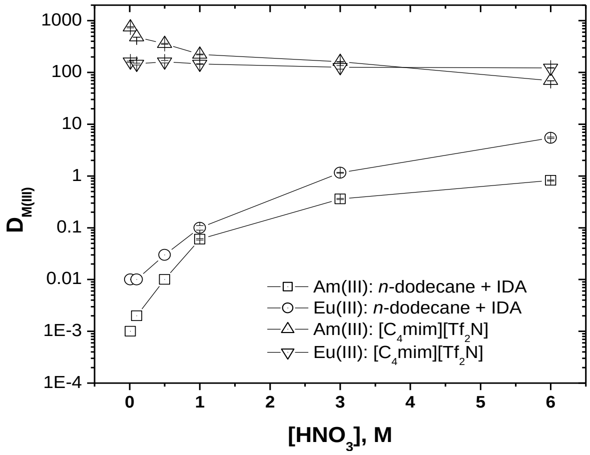


Fig. 2 Extraction of Am(III) and Eu(III) from varying concentrations of HNO_3. [DGA-TREN] = 1.0 x 10^{-3} M

and may be relevant in the radioactive waste processing by tuning the solvent system.

The extraction of Am(III) was studied at 3 M HNO_3 at varying concentrations of DGA-TREN in both the molecular diluent as well as the ionic liquid (Fig. S6). Slope analysis revealed a change in the composition of the extracted species, the slope values being ca. 1 and 2, respectively.

Unique separation behaviour

Another unique observation is a very significant change in the selectivity of Am^{3+} *vs* Eu^{3+} in both classes of tripodal DGA extractants. Though a similar extraction behaviour was seen for Eu^{3+} ion, the selectivity, as defined by the S.F. values (Table 1), shows a reversal. Selectivity reversal is also observed in case of Pu^{4+}. In case of DGA-based ligands, the extraction of Eu^{3+} is always favoured over that of Am^{3+}.[3] The comparative evaluation of the extraction behaviour of Am^{3+} vis-à-vis Eu^{3+} over a wide acidity range is presented in Fig. 2. Though for DGAs, the well-known favourable extraction of Eu^{3+} over Am^{3+} is observed in molecular diluents, the opposite takes place in the ionic liquid for the greater part of the acidity range investigated. Reversal of the selectivity in an ionic liquid is a unique observation of this study, which again reverts back to the expected trend at 6 M HNO_3. Another unique observation is the acidity independent extraction of Eu^{3+} in the ionic liquid in the wide HNO_3 concentration range of 0.01 - 6 M (Fig. 2). This holds significance as selective extraction of trivalent actinides from lanthanides is a challenging problem.

Though UO_2^{2+} extraction is quite significant with TODGA,[7] DGA-TREN showed very poor extraction of this metal ion, which decreased further in $[C_4mim][Tf_2N]$ (Table 1). However, Pu^{4+} extraction increased in the ionic liquid by an order of magnitude, in addition giving a very impressive selectivity value (S.F. = 40.2), which is more than 4 and 16 times the selectivity values reported using a DGA-functionalized calix[4]arene and TODGA, respectively, in $[C_8mim][PF_6]$.[11] On the other hand, the poor extraction of UO_2^{2+} is reflected in a very high selectivity value. Selectivities with respect to Sr^{2+} and Cs^{+} ions, investigated in view of the significant dose imparted by the ^{90}Sr and ^{137}Cs radionuclides,[20] were also spectacular in the ionic liquid (Table 1).

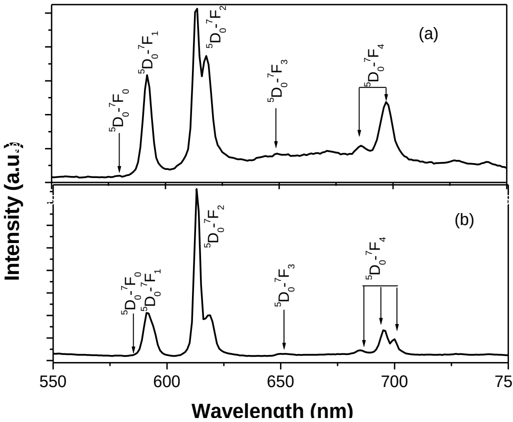


Fig. 3 Luminescence spectra of the Eu^{3+} extracts in 1.0 x 10^{-3} M DGA-TREN in a) molecular diluents: *n*-dodecane + IDA (9:1) and b) $[C_4mim][Tf_2N]$

Stripping behaviour

The extracted trivalent actinide ion (Am^{3+}) was stripped from the ionic liquid medium using a buffer mixture (0.4 M formic acid + 0.4 M hydrazine hydrate + 0.1 M citric acid) and a complexing agent (0.05 M EDTA in 1 M guanidine carbonate) resulting in 85% and 99.8% stripping, respectively, in a single contact. On the other hand, the buffer mixture was able to back extract about 99.8% of the extracted Am^{3+} from the solvent containing a 9:1 mixture of the molecular diluents, *n*-dodecane and IDA. It was not required to use the complexing agent for an effective stripping of the metal ion and even a pH 2 solution could result in 99.6% back extraction. Stage wise stripping efficiency is given in Table S1.

Complexation studies

Solution phase complexation studies were performed using FT-IR, ^1H-NMR and luminescence techniques. The FT-IR spectra of the free DGA-TREN ligand and its $LaTf_3$ complex, recorded in the apolar toluene-d_8 (Figs S7 and S8), show a shift in the carbonyl 'C=O' stretching frequency from 1652 cm^{-1} to 1617 cm^{-1} due to complexation. The shift in the etheric 'C-O' stretching frequency from 1129 cm^{-1} to 1163 cm^{-1} is an indication of the participation of the etheric oxygen atom in the metal ion binding. Peak broadening in the ^1H-NMR spectra of DGA-TREN in toluene-d_8 after complexation with La(III) points to fast exchange phenomena. The OCH_2 methylene protons at 4.25 and 4.37 ppm (Fig. S9) in free DGA-TREN, are shifted to 4.33 and 4.98 ppm, respectively (Fig. S10), in the $LaTf_3$ complex with a metal to ligand ratio of 1:1. Splitting of the signals and shifts to 4.05, 4.08 and 4.69, 4.79 ppm (Fig. S11), respectively, were observed for a metal to ligand ratio of 1:1. This clearly indicates fast exchange between the complexed and the uncomplexed ligand molecules in the $LaTf_3$ complex.

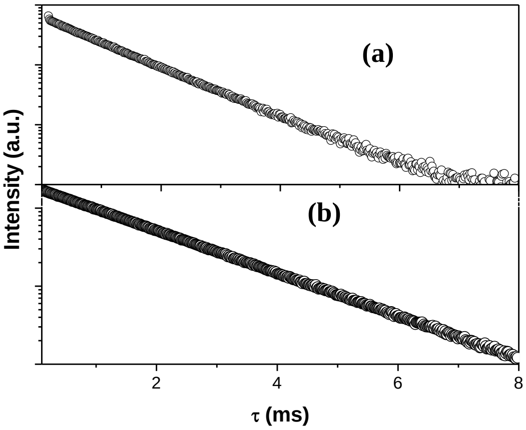


Fig. 4 Decay profiles of Eu^{3+}-DGA-TREN in the (a) molecular diluent mixture (*n*-dodecane + IDA (9:1)) and (b) $[C_4mim][NTf_2]$

Luminescence spectroscopy

Luminescence spectra of the extracts of Eu^{3+} in 1.0 x 10^{-3} M DGA-TREN in molecular diluents and the ionic liquid $[C_4mim][Tf_2N]$ are presented in Fig. 3. The high intensity of the $^5D_0$-$^7F_2$ transition reveals that the Eu^{3+} ion resides in an asymmetric environment with respect to the center of symmetry. It was quantified as asymmetry factor,[21] which shows that the same extracted species in the RTIL is more asymmetric compared to that in the molecular diluents. The complex formation constants were calculated from the titration of the Eu^{3+} solution (1.0 x 10^{-3} M in water) by incremental addition of DGA-TREN (1.0 x 10^{-2} M in methanol medium). The Job's plot (Fig. S14) shows the formation of ML_2 type species and the log β_2 was calculated to be 9.6 ± 0.5. The β values match very well with the data reported by Pathak et al.[22] suggesting that only one DGA arm from the DGA-TREN may be taking part in the complexation reaction. The monoexponential nature of the decay profile of the complex (Fig. 4) reveals the predominant presence of single species (which is the ML_2 complex alone rather than a mixture of ML and ML_2 species). The number of water molecules present in the primary coordination sphere of Eu^{3+} can be evaluated from the lifetime (τ) data using the empirical formula given by Choppin and Peterman ($N_{H2O} = (1.05/\tau) - 0.7$),[23] showing that there is no water molecule in the inner sphere of Eu^{3+} when the complex is either in the molecular diluents or in $[C_4mim][Tf_2N]$. These studies indicate that the extracted complex contains two DGA-TREN units and no water molecules (Table S2). Though both the extraction media and the extracted complexed species are quite different, the absence of water molecules in the coordinated spheres also indicates a difference in the nature of the binding of the DGA pendant arms. Apparently, while one DGA arm of each DGA-TREN (in a ML_2 complex) is binding the metal ion, this leads to only six-coordination leaving another three coordination sites vacant around the metal ion. In view of the fact that no inner-sphere water molecule is present on the basis of the luminescence data, we included three nitrate anions in the complex (for charge neutralization) to obtain the resultant complex as: $Eu(DGA\text{-}TREN)_2(NO_3)_3$.

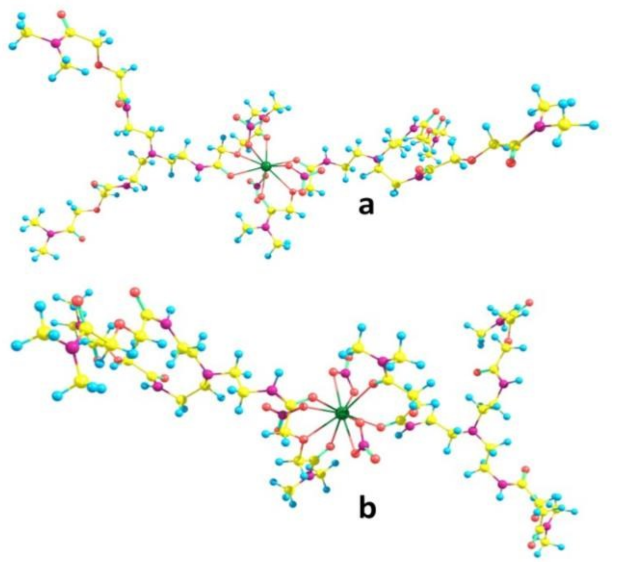


Fig. 5 Optimized geometries of two probable structures of the Eu^{3+} complex of DGA-TREN considered with the stoichiometry $Eu(DGA\text{-}TREN)_2(NO_3)_3$; Eu^{3+} complex with (a) three monodentate nitrates; (b) two bidentate and one monodentate nitrates (DGA: diglycolamide unit with methyl instead of octyl chains)

Computational studies

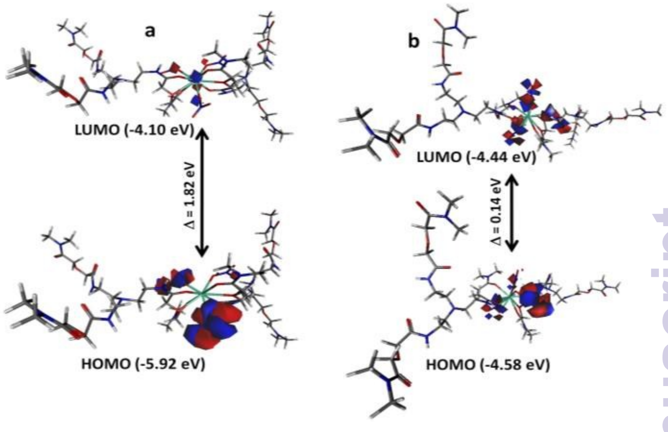


Fig. 6 Frontier orbitals (HOMO and LUMO) of two probable Eu^{3+} complexes of DGA-TREN considered with the stoichiometry $Eu(DGA\text{-}TREN)_2(NO_3)_3$ (used cut off: 0.01 e/Bohr^3); Eu^{3+} complex with (a) three monodentate nitrates; (b) two bidentate and one monodentate nitrates

Geometry optimization

The optimized geometries of two probable structures of the Eu^{3+} complex of DGA-TREN are shown in Fig. 5. The extracted species in the ionic liquid are cationic and hence, may not have charged neutralized species. On the other hand, in the molecular diluents, solvated charge neutralized species are extracted. As the EXAFS studies refer to the extracts in the molecular diluents (vide infra), the computations were carried out using species containing three nitrate anions. In complex 'a' all the three nitrate ions were considered as monodentate. In complex 'b', on the other hand, two nitrates were considered as bidentate, while the third one was considered as monodentate. Complex 'a' was found to be lower in energy than complex 'b' only by 6.1 kcal.mol^{-1}. This indicates that both the structures may be possible. The distances between the central Eu^{3+} ion and the atoms present in the first and second shell obtained in the geometry optimized structures of complexes 'a' and 'b' are shown in Table 2.

Table 2 Distances of neighbouring atoms (first few shells) from the central Eu^{3+} ion in the Eu^{3+} complex of DGA-TREN obtained from DFT and EXAFS studies

'Eu-L' Bond	DFT (Complex 'a')	DFT (Complex 'b')	EXAFS
$\text{Eu-O}_{\text{(nitrate)}}$	2.38 ± 0.02	2.56 ± 0.08	2.32 ± 0.008
$\text{Eu-O}_{\text{(carbonyl)}}$	2.52 ± 0.08	2.56 ± 0.07	2.45 ± 0.02
$\text{Eu-O}_{\text{(etheric)}}$	2.82 ± 0.09	2.664, 3.865	2.99 ± 0.007
$\text{Eu-N}_{\text{(nitrate)}}$	3.39 ± 0.03	3.00 ± 0.08 (bi), 3.546 (mono)	3.55 ± 0.07
$\text{Eu-C}_{\text{(carbonyl)}}$	3.43 ± 0.01	3.47 ± 0.08	3.8 ± 0.01
$\text{Eu-C}_{\text{(etheric)}}$	3.67 ± 0.04	3.62 ± 0.03 4.21 ± 0.04	

Eu-O$_{(nitrate)}$ bond distances were found to be smaller in complex ‘a’ as compared to that in complex ‘b’ indicating a closer approach of the coordinating ‘O’ atoms from the nitrate ion when it coordinates in a monodentate fashion. The Eu-O$_{(carbonyl)}$ bond length was found to be comparable in both complexes. There is, however, a significant difference in the coordination of the ethereal ‘O’ atom in the two complexes. In complex ‘a’, the ethereal ‘O’ of both ligands coordinates and is located at a distance of 2.82 ± 0.09 Å. In case of complex ‘b’, on the other hand, the ethereal ‘O’ from one of the DGA-TRENs coordinates strongly with an Eu-O$_{(etheric)}$ distance of 2.664 Å. The other ethereal ‘O’ from the second DGA-TREN molecule is located at a distance of 3.865 Å suggesting the absence of any bonding with the central Eu^{3+} ion. EXAFS results (vide infra) were found to be matching well with complex ‘a’.

Table 3 Natural charges on europium, nitrate (mono- and bi-dentate) and DGA-TREN molecules in two different Eu^{3+} complexes of DGA-TREN (a and b), calculated using natural population analysis

Eu^{3+} complex	A	b
q(Eu)	1.839	1.418
q(NO$_3$)$_{mono}$	-0.78	-0.684
q(NO$_3$)$_{bi}$	--	-0.62
q(DGA-TREN)	0.252	0.252
Δq(NO$_3$)$_{mono}$	0.22	0.316
Δq(NO$_3$)$_{bi}$	--	0.38

Natural population analysis

The natural charges on europium, nitrate (mono- and bidentate) and DGA-TREN molecules in two different Eu^{3+} complexes of DGA-TREN, calculated using natural population analysis, are shown in Table 3. The charge on the central Eu^{3+} ion was found to be higher (1.839 e) in complex ‘a’, where all the three nitrates coordinate in monodentate fashion, than in complex ‘b’ (1.418 e), where two of the nitrate ions coordinate in bidentate fashion. If we compare the cumulative charge on the nitrate moiety in the complexes, in complex ‘a’, only 0.22 e charge is transferred (Δq(NO$_3$)$_{mono}$) from each of the monodentate nitrate ions. In case of complex ‘b’, however, more charge is transferred from both mono- (Δq(NO$_3$)$_{mono}$ = 0.316 e) and bi- (Δq(NO$_3$)$_{bi}$ = 0.38 e) dentate nitrate ions. This indicates that less electron density from the nitrate ions is transferred to the metal ion when they coordinate in a monodentate mode. Interestingly, the charge transferred (0.252 e) from the DGA-TREN moiety does not alter in these two types of complexes.

Frontier molecular orbitals of the two different Eu^{3+} complexes of DGA-TREN considered are shown in Fig. 6. The difference in energies between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is larger in case of complex ‘a’. It is the nitrate group that contributes more in the HOMO in case of both complexes. In the LUMO, however, a significant contribution from the Eu^{3+} ion is noticed.

EXAFS studies

An EXAFS study was carried out on the organic extract made in the molecular diluent mixture to elucidate the structure of the Eu-DGA-TREN complex. Unfortunately, the extract prepared in the ionic liquid failed to yield reliable data. The results were fitted considering the two probable structures ‘a’ and ‘b’ (Fig. 5), mentioned above. Other possible structures that used either two or three DGA arms of the DGA-TREN were found to be of higher energy and hence, were not considered.

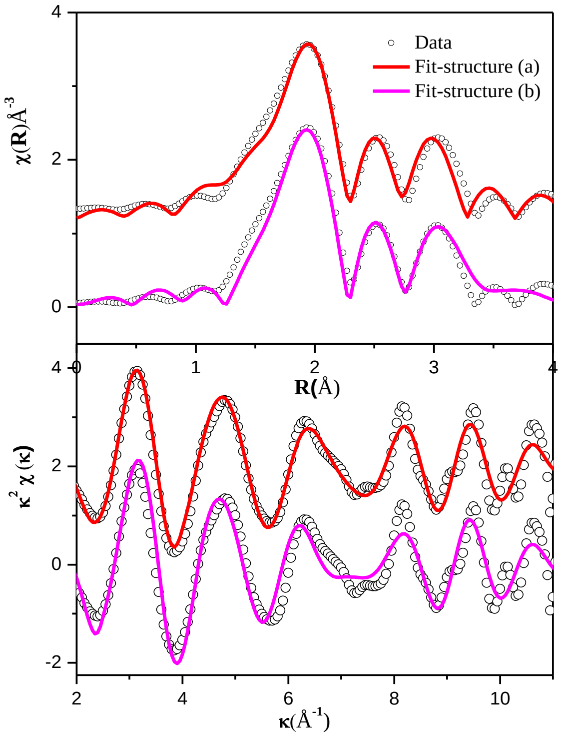


Fig. 7 Experimental $\chi(R)$ *versus* R plots and the theoretical fits of the Eu-DGA-TREN complex (Top); Experimental $k^2\chi(k)$ *versus* k plot and the theoretical fits of the Eu-DGA-TREN complex

The EXAFS data are presented in Fig. 7 with the respective fits corresponding to the two structures. The structure with the best fit in the EXAFS data showed a total coordination number of 12.28 ± 2.45 Å around Eu^{3+} in the first coordination sphere for the nitrates, carbonyl and etheric oxygen atoms (Supporting Information). In the DFT optimized structure, however, a nine-coordinated Eu^{3+} ion was observed (three from monodentate nitrate, four carbonyl and two etheric oxygens from two coordinated DGA units). Such overprediction of the coordination number from EXAFS studies is common in the literature.[24] The second shell is dominated by three nitrogen atoms at 3.55 Å from three nitrates coordinating in the monodentate mode. The structural parameters obtained from the DFT calculations and EXAFS studies are compared in Table 3, which shows a close matching in the distances of various neighbouring atoms from the central Eu^{3+} ion. ‘Eu-O’ bond distances of the nitrate and carbonyl groups are found to be a little longer from the DFT studies as compared to the EXAFS studies. All other bond lengths are, however, found to be shorter from the DFT calculations as compared to that from the EXAFS studies. The carbonyl and etheric carbons appear at different distances from the central Eu^{3+} ion from the DFT studies. In the EXAFS spectra, on the other hand, a single peak is observed in the 'R' space at a bond distance of 3.8 Å. A recent publication on an EXAFS study on the Eu^{3+} complex of TODGA has shown similar equivalent bond lengths for the amidic and the etheric 'O' atoms.[25] The detailed EXAFS results and fitting parameters are provided in the Supporting Information.

Conclusions

In conclusion, a novel *N*-pivot tripodal DGA ligand, DGA-TREN, was synthesized with an amazing extracting ability for trivalent actinide (and lanthanide) ions, particularly in ionic liquid medium. The reversal in the extraction trend of Am^{3+} and Eu^{3+} in molecular diluents vis-à-vis an ionic liquid when compared to the analogous C-pivot tripodal ligand (T-DGA) is unique and is observed for the first time. Furthermore, the selectivities with respect to Eu^{3+} showed drastic changes while moving from molecular diluents to the ionic liquid both for DGA-TREN and T-DGA. An acidity independent extraction of Eu^{3+} gives the possibility of its separation from trivalent actinides by tuning the acidity. Complexation studies indicated the formation of ML_2 species, which was further supported by TRFS, slope analysis and DFT calculations. Structural investigations using EXAFS suggest three monodentate nitrate ions bound to Eu^{3+}, while the carbonyl oxygens from one DGA arm of the ligand form stronger bonds than the 'etheric' oxygen.

Experimental

Materials and apparatus

The diluents, *n*-dodecane and isodecanol (IDA), were procured from Lancaster, UK and SRL, Mumbai, respectively. The ionic liquid, $[C_4mim][Tf_2N]$ was obtained from IoLiTech, Germany at >99% purity and was used after drying. The moisture content in the ionic liquid was <0.2%. Suprapur nitric acid (Merck, Germany) was used for the preparation of nitric acid solutions. T-DGA was synthesized following a reported procedure.[14]

Tris-(2-aminoethyl)amine, triethylamine and Amberlyst® A21 were bought from Sigma-Aldrich and used without further purification. Triethylamine was stored on KOH. Toluene-d_8 was purchased from Actu-all Chemicals and employed using a Braun MB SPS 800 dispensing machine. MeOH was obtained from Actu-all Chemicals. Et_2O was bought from VWR and distilled before use. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. FT-IR analysis was performed using a Nicolet 6700 instrument (Thermo Scientific) in transmission mode. ESI mass spectra were recorded on a WATERS LCT mass spectrometer.

Radiotracers

The radiotracers, ^{241}Am, ^{233}U and Pu (mainly ^{239}Pu), were obtained from laboratory stock after purification following literature methods.[26-28] $^{152,154}Eu$, $^{85,89}Sr$ and ^{137}Cs were obtained from BRIT (Board of Radiation and Isotope Technology, Mumbai) and were used after checking their radiochemical purity by gamma ray spectrometry using an HPGe detector. ^{241}Am tracer was purified by ion exchange methods prior to use and its purity was checked by both alpha as well as gamma ray spectrometry.[26] ^{241}Am was assayed by a NaI(Tl) scintillation detector using 60 KeV gamma ray. Plutonium tracer (mainly ^{239}Pu) was purified from ^{241}Am[27] and the ^{233}U tracer was purified from ^{229}Th using standard ion-exchange methods reported before.[28] The valency of Pu was adjusted to the +4 state by using $NaNO_2$ and ammonium metavanadate as the holding oxidant.[29] The radiometric assay of ^{233}U and Pu was done by alpha-liquid scintillation counting using the Ultima Gold scintillator cocktail, while that of $^{85,89}Sr$, ^{137}Cs and ^{241}Am was performed by gamma ray counting using a NaI(Tl) scintillation counter. Alpha-spectrometry was carried out using a silicon surface barrier detector.

Preparation of DGA-TREN

A solution of TREN (73 mg, 0.5 mmol), 4-nitrophenyl 2-(2-(dioctylamino)-2-oxoethoxy)acetate[30] (730 mg, 1.53 mmol) and triethylamine (157 mg, 1.55 mmol) in dry toluene (15 mL) was refluxed for 15 h. A chromatography glass column (2 cm Ø) was loaded with Amberlyst® A21 (20 g) suspended in MeOH (30 mL). The resin was washed with MeOH (70 mL) and Et_2O (100 mL), at the end keeping solvent above the resin, whereupon a pluck of cotton was placed. The residue of the reaction was dissolved in Et_2O (15 mL) and loaded slowly on top of the wet resin inside the column. The solution was slowly eluted through the column with Et_2O (185 mL). The solvent was evaporated to yield the product as a slightly yellow oil (390 mg, 73%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 5.5 Hz, 3H), 4.25 (s, 6H), 4.04 (s, 6H), 3.33 (td, *J* = 6.0, 5.5 Hz, 6H), 3.27 (t, *J* = 7.7 Hz, 6H), 3.08 (t, *J* = 7.8 Hz, 6H), 2.64 (t, *J* = 6.0 Hz, 6H), 1.57–1.44 (m, 12H), 1.33–1.18 (m, 60H), 0.87 (t, *J* = 6.8 Hz, 9H), 0.86 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.87, 168.40, 71.51, 69.52, 53.91, 46.94, 46.26, 37.33, 31.93, 31.88, 29.50, 29.42, 29.38, 29.33, 29.03, 27.77, 27.18, 27.02, 22.76, 22.73, 14.21, 14.20. ESI-MS: *m/z* 1165.1 $[M+H]^+$; HRMS: *m/z* 1164.9856 $[M+H]^+$; calculated: 1164.9925 for $C_{66}H_{130}N_7O_9^+$.

Solvent extraction studies

The ligand solutions (1.0 x 10^{-3} M) were prepared in molecular diluents (90% *n*-dodecane + 10% isodecanol) as well as in the ionic liquid, $[C_4mim][Tf_2N]$, after prolonged ultra-sonification (15 – 20 min) to ensure homogeneity of the solutions. The organic phases (ligand solutions) were mixed with equal volumes of the aqueous phases (usually 0.5 – 1.0 mL) containing 3.0 M HNO_3 spiked with the respective radiotracers. The two phases were taken in leak tight Pyrex glass tubes and vortexed for about 3 h (to ensure attainment of equilibrium) in a thermostated water bath at 25 ± 0.1 °C. Subsequently, the phases were separated after centrifugation of the tubes and the metal ion concentrations in the organic and aqueous phases were determined after radiometric assay. The distribution ratio values (D_M) were calculated as the ratio of the concentration of the radionuclide in the organic phase to that in the aqueous phase. The selectivity for the radionuclides with respect to Am was expressed in terms of the Separation Factor (S.F.) defined as the ratio of D_{Am} to D_M, where M is the metal ion of interest. The D_M values reported here are the averages of duplicate measurements and the errors in the extraction percentages of the duplicate experiments are less than 5%.

Luminescence studies

The luminescence spectra of Eu^{3+} ion with increasing DGA-TREN concentrations in methanol – water mixture were recorded using an Edinburgh FLS 900 unit provided with a CD-920 controller and a micro sec (Xe) flash lamp. The data acquisition and analysis were performed by the F-900 software provided by Edinburgh Analytical Instruments, UK.

Computational methods

Geometry optimization

Gas phase geometries of the two probable Eu^{3+} complexes of DGA-TREN were optimized at the GGA level of the density functional theory (DFT) by using Becke's exchange functional[31] in conjunction with Perdew's correlation functional[32] (BP86) with generalized gradient approximation (GGA) where 28 electron core pseudopotentials (ECPs) along with the corresponding def-SV(P) basis set were selected for the Eu^{3+} ion. For the Eu atom, the def-SV(P) basis sets, present in the Turbomole basis set library, are quite large and consist of (14s13p10d8f1g) functions, contracted to [10s9p5d4f1g]. All other lighter atoms were treated at the all electron (AE) level. The nonlocal Hartree-Fock (HF) contribution is not considered in the BP86 functional and it is, therefore, quite faster for predicting the geometry and vibrational frequencies. The computed geometry and frequencies are also found to be quite accurate.[33] One can, therefore, avoid computationally expensive geometry optimizations for such a big molecular system using this functional. A high spin f^6 septet state was considered within an unrestricted framework for the Eu^{3+} complexes. Convergence criteria used for the geometry optimization step are tighter than the defaults. All the calculations were performed using the TURBOMOLE program package,[34] where a methyl group was considered instead of a long octyl chain in order to avoid convergence difficulties. Both the structures considered here were comparable in energy.

Natural population analysis

Atomic charges on the europium complexes were calculated using the natural population analysis (NPA) as it gives a satisfactory description for ranges of molcules including metal complexes. NPA provides a unified treatment of covalent and extreme ionic limits at a reasonable computational cost.[35] Some of the limitations of Mulliken's population analysis (MPA), viz. negative population values and basis set dependence, have been overcome in NPA, which is based on the construction of a set of natural atomic orbitals (NAOs) for a given molecule in an arbitrary atomic orbital basis set. The same basis set and hybrid density functional as used in case of the geometry optimization are also used for the NPA.

EXAFS studies

The local structure around Eu in the Eu-DGA-TREN complex was studied using the Synchrotron based Extended X-ray Absorption Fine Structure (EXAFS) technique. The EXAFS measurements of the sample were carried out in the fluorescence mode at the INDUS-2 Synchrotron Source (2.5 GeV, 100 mA) in the Scanning EXAFS Beamline (BL-9) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.[36] The double crystal monochromator (DCM), which works in the photon energy range of 4000-25000 eV with a resolution of 10^4 at 10 KeV, was used in the beamline. For the collimation of the beam and higher harmonic rejection, a 1.5 m horizontal pre-mirror with meridonial cylindrical curvature was used prior to the DCM. The horizontal focusing to the beam was achieved by the second crystal of the DCM in a sagittal cylinder form with a radius of curvature in the range of 1.28-12.91 m. The sample was placed at 45^0 to the incident X-ray beam, and a fluorescence detector was placed at a right angle to the incident X-ray beam to collect the signal for measurements in the fluorescence mode. One ionization chamber was placed prior to the sample to determine the incident flux (I_0) and the fluorescence detector used in this measurement is a Si drift detector (Vortex^{TM}, Hitachi High Technologies GLOBAL) with an active area of 50 mm^2 along with a digital pulse processor and the region of interest (ROI) corresponding to the fluorescence signal is chosen electronically. The absorbance of the sample as a function of energy was derived from these measurements. The EXAFS spectra of the sample were recorded in the energy range of 6916-7600 eV at the EuL_3 edge.

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Notes and references

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Unique selectivity reversal in Am^{3+} – Eu^{3+} extraction in a tripodal TREN-based diglycolamide in ionic liquid: Extraction, luminescence, complexation and structural studies

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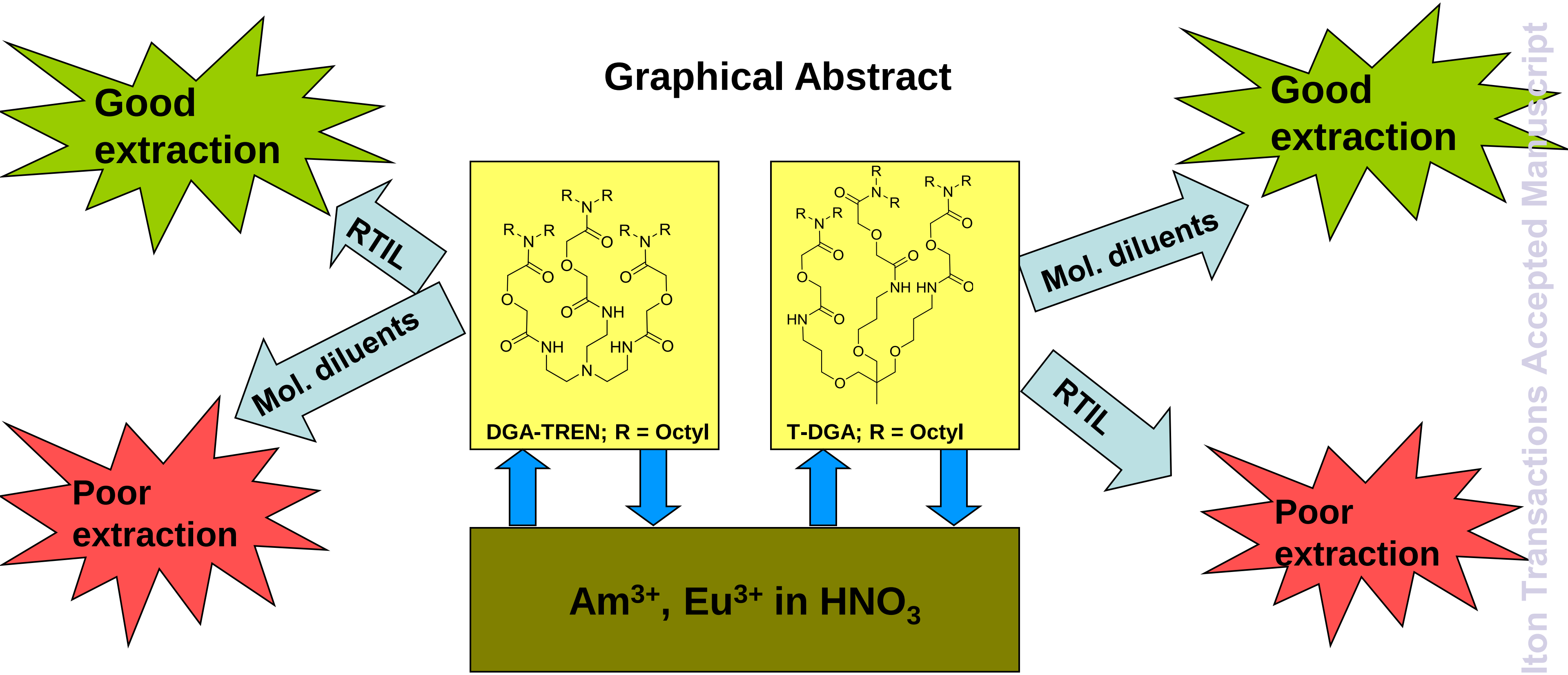
Graphical Abstract



Solvent extraction studies suggest a unique selectivity reversal in the extraction of trivalent actinides / lanthanides in an ionic liquid vis-à-vis a molecular diluent for a tripodal TREN-based diglycolamide extractant vs a tripodal DGA ligand, T-DGA.