Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Dalton Trans.*, 2018, **47**, 15164

A diglycolamide-functionalized TREN-based dendrimer with a 'crab-like' grip for the complexation of actinides and lanthanides†

Arunasis Bhattacharyya,[a] Andrea Leoncini,[b] Prasanta K. Mohapatra,*[a] Parveen K. Verma,[a] Avinash S. Kanekar,[a] Ashok K. Yadav,[c] Sambhunath Jha,[c] Dibyendu Bhattacharyya,[c] Richard J. M. Egberink,[b] Jurriaan Huskens[b] and Willem Verboom*[b]

Received 26th July 2018,
Accepted 24th September 2018

DOI: 10.1039/c8dt03051k

rsc.li/dalton

A generation 1 dendrimer, based on tris(2-aminoethyl)amine (TREN), containing six diglycolamide (DGA) pendent arms (termed TREN-G1-DGA) was synthesized and evaluated for the extraction of actinides and fission product ions. Solvent extraction studies indicated preferential extraction of Eu^{3+} over Am^{3+} with a separation factor value of *ca.* 4.5 in line with the extraction behaviour of multiple DGA ligands in previous reports. The distribution values of Am^{3+} and Eu^{3+} were about 12 and 9 times higher, respectively, than those obtained in the case of TREN-DGA using the 1×10^{-3} M ligand in 5% iso-decanol/95% *n*-dodecane at 3 M HNO_3. The 1 : 1 (M : L) extracted species suggested 'inclusion' complex formation where more than one DGA moiety participates in the complex formation. The extracted species were devoid of any inner-sphere coordinated water molecules as confirmed by luminescence spectroscopy. The structure of the complex was also studied by DFT computations and EXAFS which suggested binding of three DGA arms around the central metal ion in the absence of any inner-sphere nitrate ions.

Introduction

Minor actinide partitioning is an accepted strategy for the safe management of high level liquid wastes (HLLW) emanating from the spent nuclear fuel reprocessing.[1] HLLW contain >95% of the radioactivity present in the nuclear wastes, which have the fission products and the transuranics, *viz.* Np, Pu, Am and Cm, as the major constituents.[2] Over the years, a great deal of efforts have been made to develop efficient extractants for minor actinide partitioning[3] and only recently, it was reported that diglycolamides (DGA),[4] such as TODGA (*N*,*N*,*N*′,*N*′-tetra-*n*-octyl diglycolamide), are the most potent of them all; this has been validated by several counter-current extraction studies using 'hot' solutions.[5] Subsequently, several multiple DGA-containing extractants have been studied for the extraction of trivalent lanthanides and actinides. Encouraging results have been reported with tripodal DGA ligands,[6] calix[4]arenes[7] and pillar[5]arenes.[8] Amongst the tripodals, a N-pivot tripodal ligand (TREN-DGA; Fig. 1a) showed entirely different results as compared to a C-pivot tripodal ligand (T-DGA).[9] The extraction of metal ions with the former in molecular diluents was rather poor compared to that with T-DGA, which showed a dramatic reversal in the extraction behaviour in an ionic liquid as the diluent.

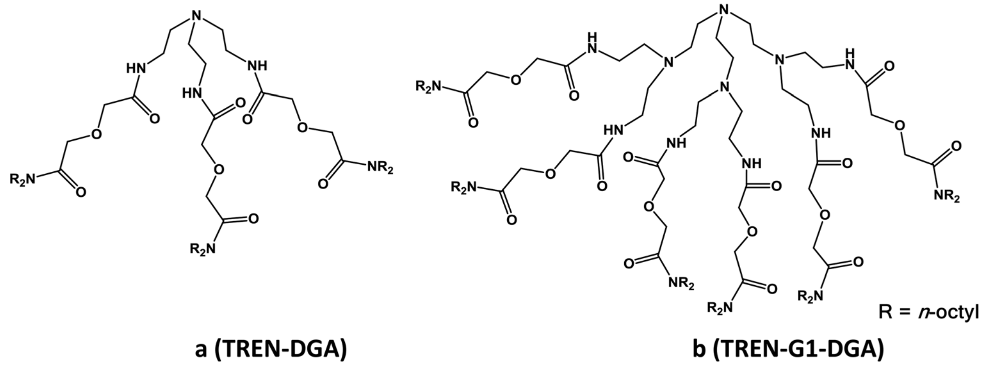
Recently, we have reported the first DGA–functionalized dendrimers[10] which showed a significantly improved metal ion extraction at millimolar concentrations. Though the generation 0 (Gen 0) ligand (TREN-DGA; Fig. 1a) gave only a modest increase in the extraction of metal ions with respect to that of TODGA, the use of the generations 1 and 2 dendrimers resulted in a large enhancement in metal ion extraction. This enhancement upon going from the Gen 1 to the Gen 2 dendrimer was, however, much less than that going from the Gen 0 to the Gen 1 dendrimer. Therefore, it was thought of interest to design a generation 1 dendrimer based on TREN-DGA (TREN-G1-DGA; Fig. 1b); the corresponding generation 2 dendrimer would have too many DGA arms making the complexation stereochemically untenable.

The newly prepared TREN-G1-DGA was evaluated for metal ion extraction, particularly the lanthanides, actinides and

---

[a] *Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India. E-mail: mpatra@barc.gov.in*
[b] *Molecular Nanofabrication group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. E-mail: w.verboom@utwente.nl*
[c] *Atomic & Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India*

† Electronic supplementary information (ESI) available: Solvent extraction, luminescence and DFT data and coordinates of free ligands and complexes. See DOI: 10.1039/c8dt03051k



a (TREN-DGA) b (TREN-G1-DGA)

Fig. 1 Schematic structures of TREN-DGA and TREN-G1-DGA.

some fission product ions such as Cs^+ and Sr^{2+}. This novel ligand, with six DGA arms, appeared to be a robust ionophore capable of making 'inclusion' complexes where the metal ion becomes completely buried inside the ligating arms. As the six DGA pendent arms can make the complex quite 'stressed', several possible structures were evaluated where a lower number of ligating moieties can participate making the complex sterically more 'relaxed'. This has been attempted by DFT computations and the best fit structure model was subsequently used for obtaining structural information from EXAFS.

Apart from liquid–liquid extraction studies, which have direct relevance in minor actinide partitioning applications, luminescence studies were carried out to understand the number and nature of the extracted complexes. For comparison with our previous results, a mixture of 95% *n*-dodecane and 5% iso-decanol was used as the diluent which also eases the ligand solubility.

Results and discussion

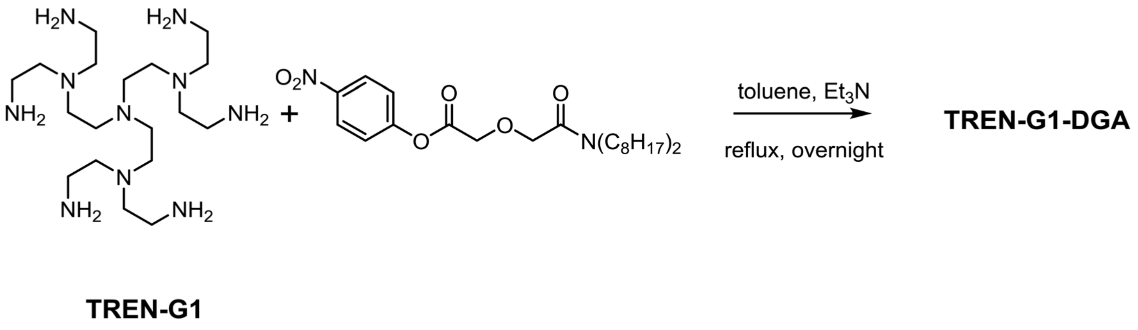
Preparation of the ligand

TREN-G1-DGA was prepared in 42% yield by reaction of TREN-G1 with *p*-nitrophenyl-activated DGA in refluxing toluene (Scheme 1). The ^1H NMR spectrum of TREN-G1-DGA is very similar to that of the previously reported TREN-DGA.[9] The signals of the DGA moiety and the external NCH_2CH_2N chains of TREN-G1-DGA almost exactly superimpose those of TREN-DGA. The peak belonging to the amidic protons around 8.00 ppm appears as a broad signal instead of a clear triplet. The internal NCH_2CH_2N chains of TREN-G1-DGA have some broad signals between 3.20 and 2.53 ppm, partially overlapping with the peaks at 3.09 and 2.68 ppm.

Solvent extraction studies

Identification of extracted species of Am^{3+} and Eu^{3+}. The extraction of the metal ion was <0.001 when no extractant was used. On the other hand, 1×10^{-3} M ligand enhanced the metal ion enormously, the D_{Am} value being *ca.* 2.5 at 3 M HNO_3. In order to determine the time to attain the equilibration, a two-phase liquid–liquid extraction study was carried out involving Am^{3+} ions where aliquots were taken out at regular intervals for radiometric assay by gamma ray counting. The results (Fig. S1; ESI†) indicated that the equilibrium was attained within 5 minutes. For the subsequent experiments, however, extraction studies were carried out for 1 hour, for the sake of convenience. The extraction of both Am^{3+} and Eu^{3+} was carried out varying the TREN-G1-DGA concentration in the organic phase. The log–log plot of the distribution ratio *vs.* the ligand concentration (Fig. S2; ESI†) showed a slope value of *ca.* 1 indicating the involvement of one ligand molecule in the extracted complex as per the following equation:

$$M^{3+}{}_{aq} + 3NO_3{}^-{}_{aq} + L_{org} \rightleftharpoons [M(NO_3)_3 \cdot L]_{org} \quad (1)$$



Scheme 1 Synthesis of TREN-G1-DGA.

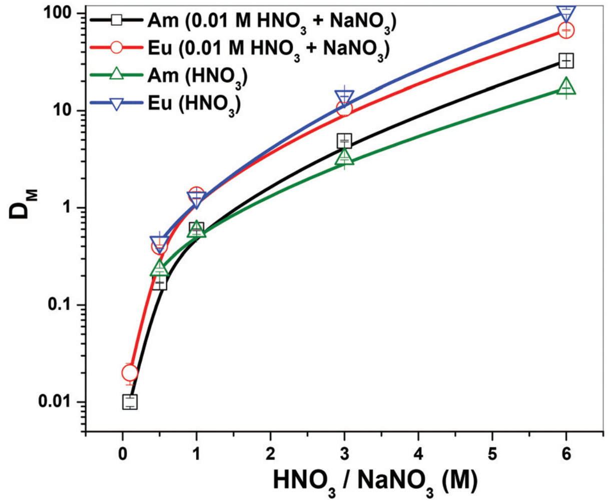


Fig. 2 Effect of the HNO_3 and $NaNO_3$ concentration on the extraction of Am^{3+} and Eu^{3+} using 1 mM TREN-G1-DGA in 5% iso-decanol/*n*-dodecane.

where L represents the TREN-G1-DGA ligand and 'aq' and 'org' represent the respective species in the aqueous and organic phases.

The distribution ratio was also determined at varying nitric acid concentrations, where the distribution ratio values for both metal ions increased even up to 6 M HNO_3 (Fig. 2). In order to further understand the role of the H^+ concentration, the extraction of both Am^{3+} and Eu^{3+} was carried out varying the $NaNO_3$ concentration at a fixed 0.01 M HNO_3 concentration (Fig. 2). It is interesting to note here that for Am^{3+} the extraction is only marginally higher in the presence of $NaNO_3$ than that in HNO_3 solutions, which is expected because of the competition of H^+ in the complexation with TREN-G1-DGA. In the case of Eu^{3+}, on the other hand, surprisingly, the extraction was higher in HNO_3 than in the $NaNO_3$ medium. This clearly shows that, unlike the cases for other neutral donor ligands, competition from H^+ plays an insignificant role in the lowering of the extraction efficiency of TREN-G1-DGA, which is an interesting observation. This may be due to the higher affinity of TREN-G1-DGA towards Eu^{3+} as compared to Am^{3+} and therefore the competition from H^+ for the complexation with TREN-G1-DGA is much weaker in the case of Eu^{3+} as compared to Am^{3+}. Moreover, increasing the HNO_3 concentration makes the dehydration of Eu^{3+} easier leading to enhancement in its extraction from the organic phase.

Table 1 Distribution ratio and separation factor values of lanthanides, actinides and important fission product elements. Org. phase: 1.0×10^{-3} M ligand in 5% iso-decanol/*n*-dodecane mixture. Aqueous phase: 3 M HNO_3. S.F. values with respect to Am (S.F. = D_{Am}/D_M) are given between parentheses

Metal ion	D_M values with DGA-TREN[9]	D_M values with TREN-G1-DGA (p.w.)
Am^{3+}	0.36 ± 0.02	3.20 ± 0.09
Eu^{3+}	1.16 ± 0.01 (0.31 ± 0.02)	13.99 ± 0.08 (0.23 ± 0.01)
Pu^{4+}	0.25 ± 0.01 (1.4 ± 0.1)	6.5 ± 0.1 (0.49 ± 0.02)
UO_2^{2+}	0.02 ± 0.00 (18 ± 1)	0.040 ± 0.001 (74 ± 3)
Sr^{2+}	<0.001 (>2430)	0.010 ± 0.001 (319 ± 33)
Cs^+	<0.001 (>2430)	<0.001 (>8 × 10^3)

Comparison of extraction behaviour of different metal ions. The extraction behaviour of different metal ions, *viz.* Am^{3+}, Eu^{3+}, Pu^{4+}, UO_2^{2+}, Sr^{2+} and Cs^+, was studied with 3 M HNO_3 using 1×10^{-3} M TREN-G1-DGA. The results were compared with those obtained using TREN-DGA, reported previously (Table 1).[9] It is interesting to note here that of all the metal ions the extraction efficiency of TREN-G1-DGA is significantly higher than that of TREN-DGA, in the case of Pu^{4+} even 26 times. While Pu^{4+} was extracted to a marginally lesser extent than Am^{3+} with TREN-DGA, an opposite trend was seen with TREN-G1-DGA, the D_{Pu} value being more than twice the D_{Am} value (Table 1). For both ligands, the highest extraction was observed for Eu^{3+}. The separation behaviour is very interesting as the separation factor (S.F.) values of Eu with respect to Am (S.F. = D_{Eu}/D_{Am}) were found to be close to 2 at any concentrations of $NaNO_3$ (containing 0.01 M HNO_3 to prevent hydrolysis of the metal ions) up to 6 M. They increased continuously with the aqueous phase HNO_3 concentration with a maximum value of 6.1 at 6 M HNO_3 (Table S1; ESI†). It is interesting to note that the trend of increasing S.F. values with HNO_3 concentration is a unique feature of this class of ligands (TREN-based)[9] as an opposite trend was recently reported by us with the benzene-centred tripodal DGA ligands.[6b] In contrast to other DGA derivatives, the order of extraction was found to be $Eu^{3+} > Pu^{4+} > Am^{3+} > UO_2^{2+} > Sr^{2+} > Cs^+$. The selectivity of Am^{3+} ion extraction with respect to UO_2^{2+} ion extraction also was *ca.* 4 times that reported with TREN-DGA. The selectivity of simple DGA derivatives (TODGA) for the trivalent lanthanide ions across the series was recently studied in detail employing solvent extraction, EXAFS, DFT and molecular dynamics simulations, where both the inner sphere complexation of the DGA derivatives and outer sphere interactions of the counter anions along with their hydration shell are found to be responsible for the selectivity of the DGA derivatives.[11] It will, therefore, be interesting to evaluate the role of counter anions and solvents in the selectivity of these multipodal DGA derivatives, *viz.* TREN-DGA and TREN-G1-DGA. These interesting separation possibilities suggest the possible application of this multi-podant extractant to the nuclear fuel cycle activities at the back end. Furthermore, an aqueous complexing agent with a preference for Am^{3+} can possibly enhance the S.F. values further, as demonstrated by tetrazolylpyridine,[12] sulphonated BTP,[13] *etc.*

Luminescence studies

A metal–ligand stoichiometry of 1 : 1 was determined from the solvent extraction study. In order to further understand the coordination environment around the Eu^{3+} ion in its complex, luminescence studies were carried out on the extracted complex in the 5% iso-decanol/*n*-dodecane medium. The most intense peak in the excitation spectra was found to be at 394 nm due to the $^7F_0$–$^5L_6$ transition. Other metal centred excitation peaks, due to the $^7F_0$–$^5D_4$ and $^7F_0$–$^5G_2$ transitions, were observed on the shoulder of the ligand to metal charge transfer band. The emission spectra of the Eu^{3+} extract, recorded at an excitation wavelength of 394 nm, were similar to the typical emission spectra reported for EuL_3^{3+} complexes with TODGA or EuL_n^{3+} types of complexes with various multiple DGA-functionalized ligands.[14] Kou *et al.*[15] reported the emission spectra of EuL_3^{3+} complexes of symmetric (*N*,*N*,*N*′,*N*′-tetramethyl diglycolamides (TMDGA)) and asymmetric (*N*,*N*′-dimethyl-*N*,*N*′-dioctyl-diglycolamide (DMDODGA)) DGA derivatives. Interestingly, they have pointed out that their emission spectra are very similar, except for the position of the hypersensitive $^5D_0$–$^7F_2$ transition peak. In both complexes, this emission peak was split into a doublet and the relative intensity ratio of these two peaks (doublet) was significantly affected by the symmetry of the DGA derivatives. In the present work, we also recorded the luminescence spectra of the TODGA and T2EHDGA (*N*,*N*,*N*′,*N*′-tetra-2-ethylhexyl diglycolamide) complexes of Eu^{3+} in the organic extract of 5% iso-decanol/*n*-dodecane (Fig. S3 and S4; ESI†) to compare the results with that obtained for the Eu^{3+} complex of TREN-G1-DGA. The asymmetry is also reflected in the higher asymmetric ratio (A.R.) value in the Eu^{3+} complex of TREN-G1-DGA (Fig. 3 and Table 2) as compared to that of the other symmetric DGA derivatives, *e.g.* TODGA.[16] Time-resolved luminescence spectra of the Eu^{3+} extract were recorded and the results indicated that the decay of the luminescence intensity of the Eu^{3+} complex of TREN-G1-DGA in 5% iso-decanol/*n*-dodecane followed a lifetime (τ_{obs}) value of 1.527 ms. The absence of any water molecules in the first coordination sphere of the Eu^{3+} was confirmed according to the following empirical relationship:[17]

$$N_{H_2O} = (1.05 \times \tau_{obs}^{-1}) - 0.44 \tag{2}$$

Table 2 Asymmetric ratio (A.R.) and luminescence decay lifetime of the Eu^{3+} complex of DGA derivatives

Ligand	A.R. ($^7F_2/^7F_1$)	τ (ms)	N_{H_2O}	Ref.
TREN-G1-DGA	2.20[a]	1.527[a]	0.25	p.w.
TREN-DGA	2.70[b]	1.037[b]	0.57	9
TODGA	1.96[a]	2.075[a]	0.07	p.w.
	2.07[c]	2.57[c]	−0.03	16
T2EHDGA	2.53[a]	1.630[a]	0.20	p.w.

[a] 5% iso-decanol/*n*-dodecane. [b] 10% iso-decanol/*n*-dodecane. [c] *n*-Dodecane.

where N_{H_2O} is the number of water molecules. It is interesting to note here that the lifetime of the Eu^{3+} complex of T2EHDGA (1.603 ms) is close to that of the Eu-TREN-G1-DGA complex, whereas the lifetime of the Eu-TODGA complex (2.075 ms) is relatively higher in the same medium (Fig. 4). A detailed study is required to understand this enhancement in lifetime in the case of the Eu-TODGA complex.

^{1}H NMR titration with TREN-G1-DGA

Qualitative ^{1}H NMR titrations of TREN-G1-DGA with lanthanum triflate were performed in deuterated methanol (CD_3OD). Due to the low solubility of the salt in apolar solvents such as toluene-*d*$_8$, the polar solvent CD_3OD was used. Upon addition of salt, at first instance the broad triplet like signals at δ 3.22 and 3.36 (NCH_2) and the singlets at δ 4.16 and 4.41 (OCH_2) broadened until a M : L ratio of about 2 : 1 (Fig. 5a–f). Subsequently, these signals almost (partly) disappear. Upon further addition of salt it looks like that the system is set at a M : L ratio of 6 : 1 with broad peaks at δ 3.33 and 3.52 (NMe_2) and δ 4.65 and 4.81 (OCH_2) (Fig. 5h). During the titration, the broad signal at δ 1.60 slowly shifts to δ 1.69 (CH_2). The M : L ratio found in this way deviates from the results obtained from solvent extraction. This will be caused by the much higher

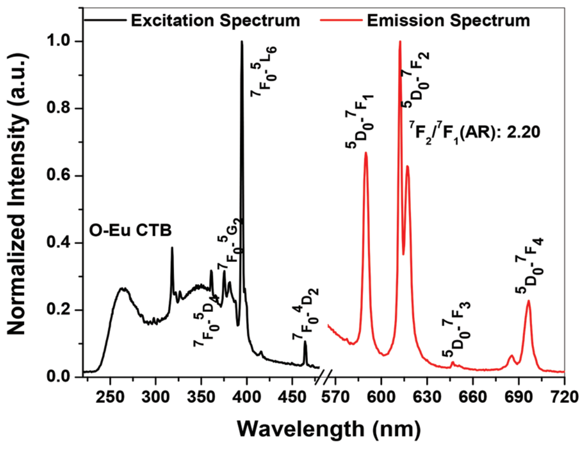


Fig. 3 Luminescence (excitation and emission) spectra of the Eu^{3+} extract using 1 mM TREN-G1-DGA in 5% iso-decanol/*n*-dodecane (λ_{em}: 614 nm in the excitation scan and λ_{ex}: 394 nm in the emission scan).

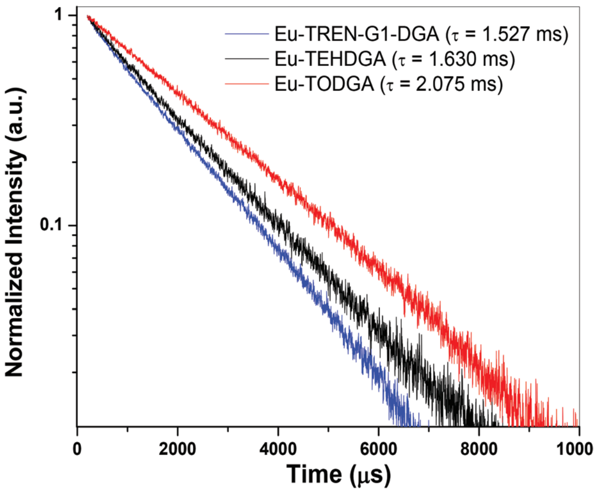


Fig. 4 Decay of the fluorescence intensity of the Eu^{3+} extract using 1 mM TREN-G1-DGA, 10 mM TEHDGA and 10 mM TODGA in 5% iso-decanol/*n*-dodecane (λ_{em}: 614 nm and λ_{ex}: 394 nm).

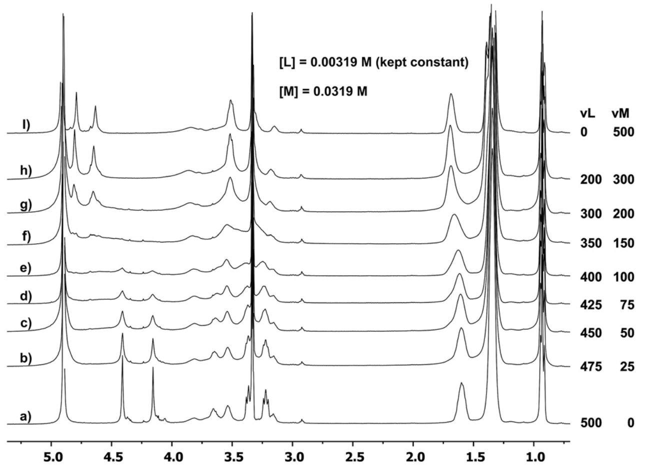


Fig. 5 ^1H NMR titration of TREN-G1-DGA with lanthanum triflate in deuterated methanol.

ligand concentration needed for ^1H NMR spectroscopy. Assuming that for La complexation three DGA moieties are required, the found M : L ratio of 6 : 1 points to the formation of clusters under these conditions.

Structural investigation of the Eu complex of TREN-G1-DGA: EXAFS studies

The luminescence study indicated that the emission spectrum of the Eu^{3+} extract in the organic phase containing TREN-G1-DGA is very similar to those obtained for EuL_3^{3+} types of complexes of other simple DGA derivatives, *viz*. TMDGA, TODGA or DMDODGA (*vide supra*). However, it was different from that of other multiple DGA functionalized ligands.[14] In order to further understand the metal ion coordination and to find out the structural parameters, an EXAFS study was carried out supplemented with the help of DFT-based calculations (*vide infra*). Fig. 6 indicates that the fitting of the EXAFS results is quite good up to a second peak for a phase corrected *R*-value of 3.49 Å. The EXAFS study reveals the presence of six nearest neighbouring atoms (oxygens) to the central Eu^{3+} ion at a distance of 2.46 Å. Three oxygen atoms were found at a distance of 2.69 Å and *ca.* 10 carbon atoms were observed at a distance of 3.49 Å. This result is slightly different from that reported in the case of the TODGA complex of Eu^{3+}, where all nine coordinating oxygen atoms from both the carbonyl and the ethereal groups of three TODGA molecules appeared at an equal distance of 2.40 Å.[11,18] This suggests that coordination around the central Eu^{3+} ion is more symmetrical in the TODGA complex with 9 equidistant 'O' atoms as compared to the Eu^{3+} complex of TREN-DGA or TREN-G1-DGA. This higher symmetry in the TODGA complex is also reflected in the lower asymmetric ratio values (Table 2). However, in this study two distinct peaks were observed for the two sets of carbon atoms ('$\underline{C}{=}O$' and $\underline{C}H_2$) at 3.34 and 3.55 Å, respectively.

DFT-based calculations on the Eu^{3+} and Am^{3+} complexes of DGA derivatives, however, clearly indicated that the carbonyl and ethereal oxygen atoms are present at two different distances from the central metal ion.[19] In our study in the Eu^{3+} complex, the carbonyl and ethereal oxygen atoms are present at a distance of 2.42 and 2.62 Å, which is expected from the geometric considerations as a lot of strain is imposed on the DGA moiety in order to bring all the three coordinating oxygen atoms at equidistance from the central metal ion.

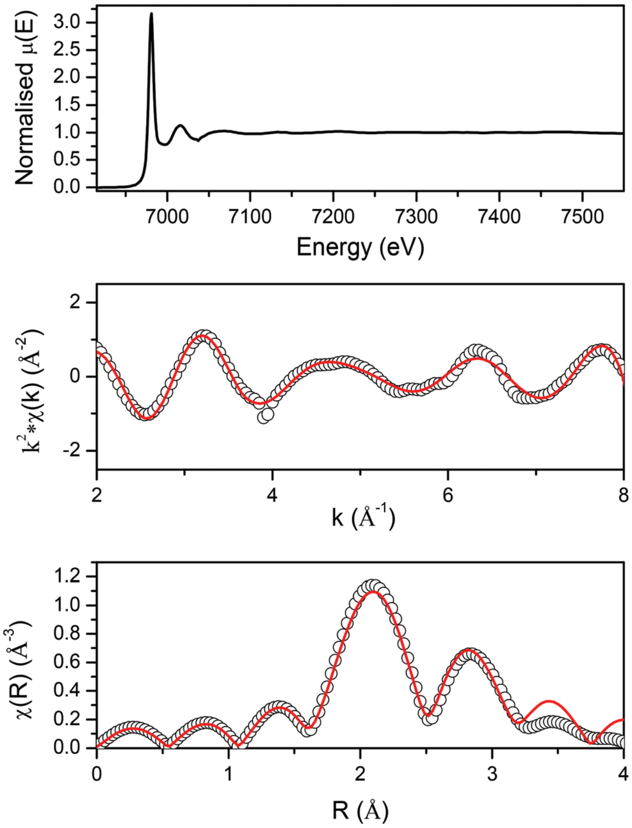


Fig. 6 Fourier transformed EXAFS spectra of the Eu(III)-TREN-G1-DGA complex at the Eu L3 edge (scatter points) and theoretical fit (solid line).

DFT computations

DFT calculations on the free TREN-G1-DGA molecule indicated that out of the six DGA arms, three DGAs point in one direction, whereas the other three face another direction. During complexation with Am^{3+} or Eu^{3+} ions, the three DGAs which are facing in one direction coordinate with the metal ions with a similar coordination mode to that observed in the cases of simple DGA derivatives, *viz*. with a nine-coordinated metal ion devoid of any water molecules or nitrate ions in the inner coordination sphere. This makes a wrapping around or 'inclusion' complex structure for the trivalent *f*-cations.

The other three arms of the TREN-G1-DGA molecule remained uncoordinated (Fig. 7). This is because of the fact that when three arms coordinate to a metal ion, the other three arms go far apart and as a result they become unable to coordinate a metal ion in a similar fashion to that of the other three DGA arms. Fig. 8 shows the optimized structures of the

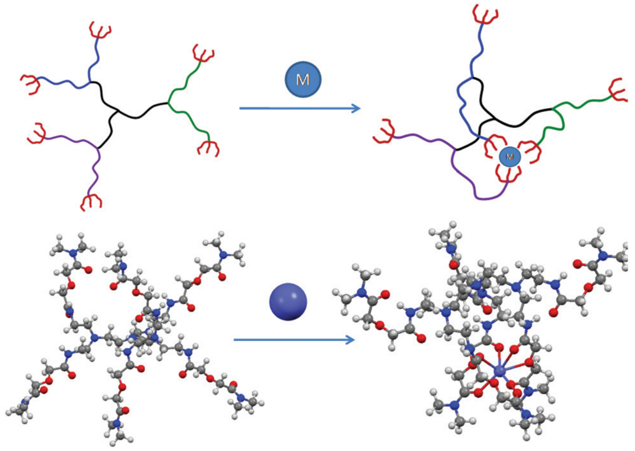


Fig. 7 Binding mode of TREN-G1-DGA for Am^{3+} and Eu^{3+}.

Am^{3+} and Eu^{3+} complexes of TREN-G1-DGA, where the distances between the terminal amidic 'N' atoms of the three co-ordinated DGA arms are in the range of 5–7 Å, whereas those of the non-coordinated DGA arms are in the range of 17–20 Å. Hydrogen bonding was noticed between the amidic (N–H) proton and the carbonyl (C=O) oxygen atoms for all the non-coordinated DGA arms with a "O···H" distance of *ca.* 1.7–1.8 Å. The other carbonyl (C=O) oxygen of the three non-coordinating DGA units of TREN-G1-DGA remained free in its complexes with Am^{3+} and Eu^{3+}. These free oxygen atoms can be protonated at higher HNO_3 concentration with a minimal effect on the metal ion coordination sites of the TREN-G1-DGA moiety. This results in lowering of the competition from H^+ to the complexation of TREN-G1-DGA with Am^{3+} and Eu^{3+}. The extraction of Am^{3+} and Eu^{3+} by TREN-G1-DGA is, therefore, affected insignificantly by the presence of HNO_3 in place of $NaNO_3$, as observed from the solvent extraction study (Fig. 2). This is similar to the 'intramolecular buffering' seen in the case of CMPO (carbamoylmethyl phosphine oxide) ligands.[20]

Table 3 Structural parameters of the Eu^{3+} complex obtained from EXAFS and DFT calculations

Parameter	Path	Structural parameters (experimental)	Structural parameters (theoretical)
R (Å)	Eu–O	2.46 ± 0.01	2.52 ± 0.04
N		6.0 ± 0.24	6
σ^2		0.0012 ± 0.0011	—
R (Å)	Eu–O	2.69 ± 0.01	2.699 ± 0.008
N		3.0 ± 0.18	3
σ^2		0.0012 ± 0.0008	—
R (Å)	Eu–C	3.49 ± 0.03	3.5 ± 0.1
N		10.0 ± 0.60	12
σ^2		0.0086 ± 0.0021	—

As shown in Table 3, the structural parameters of the Eu^{3+} complex of TREN-G1-MDGA obtained from the DFT calculations corroborate well with the experimental results obtained from the EXAFS study with the Eu^{3+} complex of TREN-G1-DGA, except the number of the carbon atoms in the second coordination sphere. Estimated coordination numbers from EXAFS data (*vide supra*), however, are always associated with an error of *ca.* 20%. In the present case, also the variation between the DFT calculations and EXAFS results is within this error limit.

Conclusions

A generation 1 dendrimer, based on tris(2-aminoethyl)amine (TREN), containing six diglycolamide ligating sites (TREN-G1-DGA) was successfully prepared and evaluated for its extraction behaviour toward actinides and lanthanides. Under the same conditions, the *D*-values for Am^{3+} and Eu^{3+} were about 12 and 9 times larger than those of TREN-DGA (generation 0). In the case of Pu^{4+}, the enlargement is even 26 times showing an even larger *D*-value than Am^{3+}. In the case of Am^{3+} and Eu^{3+}, 1 : 1 complexes were formed indicating that of the six pendent arms only three are used for binding to yield an 'inclusion' complex. This is clearly confirmed by DFT computations and an EXAFS study demonstrating that three DGA arms are

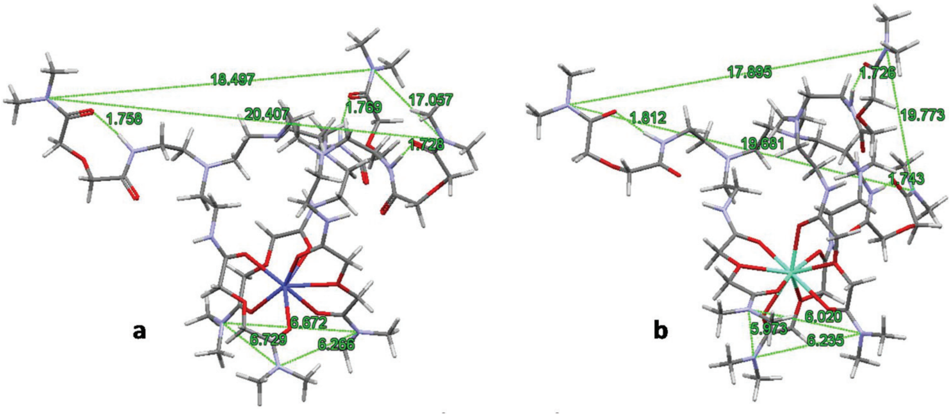


Fig. 8 Geometry optimized structures of the (a) Am^{3+} and (b) Eu^{3+} complexes of TREN-G1-DGA at the BP86/SVP level of theory.

wrapped around the central metal ion in the absence of an inner-sphere nitrate ion.

Experimental

General

n-Dodecane (99%; Lancaster) and iso-decanol (>99%; SD Fine Chem) were used as obtained. Suprapur nitric acid (Merck) was used for the preparation of all HNO_3 solutions using MilliQ water (Millipore), which were standardized using a standard NaOH (BDH) solution and phenolphthalein (Fluka) indicator. Triethylamine, Amberlyst® A21, lanthanum triflate and SiO_2 60 (230–400 mesh) were bought from Sigma-Aldrich and used without further purification. Triethylamine was stored on KOH. Toluene 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. 4-Nitrophenyl 2-(2-(dioctylamino)-2-oxoethoxy)acetate,[21] G1 tris(2-aminoethyl)amine-dendrimer (TREN-G1),[22] TODGA[23] and *N*,*N*,*N*′,*N*′-tetra-2-ethylhexyl diglycolamide (T2EHDGA)[23] were prepared according to literature procedures. All other reagents were of AR grade.

^1H- and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. ESI mass spectra were recorded on a WATERS LCT mass spectrometer.

Radiotracers

^{233}U, Pu (mainly ^{239}Pu) and ^{241}Am radiotracers were used after purification of the laboratory stocks and were stored in nitric acid medium. ^{233}U was purified from its daughter products using an anion exchange-based separation method.[24] The Pu stock solution was freshly purified from its decay products like ^{241}Am (beta decay of ^{241}Pu) using the standard TTA (thenoyl trifluoroacetone) extraction method reported in the literature.[25] ^{241}Am was purified from ^{237}Np (alpha decay product) by first adjusting the oxidation state of the latter to the +4 state by using a mixture of Fe(II) sulphamate and hydroxylamine hydrochloride followed by TTA extraction.[26] The valency of Pu, taken in 1 M HNO_3, was adjusted to the +4 state by the addition of a few drops of 0.05 M $NaNO_2$ followed by selective extraction of the converted Pu^{4+} ions by TTA.[24] The extract was subjected to contacts with 8 M HNO_3 to yield a stripped fraction of Pu^{4+}, which was used as the stock solution of the tetravalent ion. $^{152,154}Eu$, ^{137}Cs and $^{85,89}Sr$ were procured from BRIT (Board of Radiation and Isotope Technology), Mumbai. All radiotracers were used after ascertaining their radiochemical purity.

^{233}U and Pu tracers were assayed radiometrically by using a liquid scintillation counting system (Hidex, Finland) using the Ultima Gold (PerkinElmer) scintillation cocktail, while the gamma ray emitting radionuclides, *viz.* ^{241}Am, $^{152,154}Eu$, ^{137}Cs, and $^{85,89}Sr$ were assayed using a well type NaI(Tl) scintillation counter (Para Electronics) interphased with a multi-channel analyzer (ECIL, India).

Synthesis of TREN-G1-DGA

A solution of 4-nitrophenyl 2-(2-(dioctylamino)-2-oxoethoxy) acetate (1.90 g, 3.9 mmol), TREN-G1 (200 mg, 0.65 mmol) and triethylamine (673 mg, 6.65 mmol) in dry toluene (30 mL) was refluxed overnight. 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 piece of cotton was placed. After removal of the toluene 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). After evaporation of the solvent, the residue was further purified by preparative thin layer chromatography (SiO_2, CH_2Cl_2/MeOH 87 : 13) to give the product as a thick oil in 42% yield.

^1H NMR (400 MHz, $CDCl_3$) δ = 8.24–7.65 (m, 2H), 4.27 (s, 4H), 4.05 (s, 4H), 3.34 (q, J = 6.3 Hz, 4H), 3.27 (t, J = 7.8 Hz, 4H), 3.09 (t, J = 7.8 Hz, 4H), 3.20–2.53 (m, 4H), 2.68 (t, J = 6.3 Hz, 4H), 1.59–1.44 (m, 8H), 1.35–1.18 (m, 40H), 0.88 (t, J = 6.8 Hz, 6H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.9, 168.2, 71.3, 69.4, 53.8, 53.4, 46.8, 46.1, 37.0, 36.9, 31.8, 31.7, 29.4, 29.33, 29.28, 29.2, 29.0, 27.7, 27.1, 26.9, 22.7, 22.6, 14.12, 14.10. ESI-MS: m/z 2442.3 $[M + H]^+$; HRMS: m/z calcd for $C_{138}H_{273}N_{16}O_{18}$: 814.6985 $[M + 3H]^{3+}$; found 814.6971. (Since the ligand is symmetrical, only one-third of the number of hydrogen atoms is given for the ^1H NMR spectrum.)

Distribution studies

Biphasic extraction studies of lanthanide (Eu^{3+}), actinide (UO_2^{2+}, Pu^{4+} and Am^{3+}) and other fission product (Cs^+, Sr^{2+}) ions were carried out with equal volumes (usually 0.5–1 mL) of the organic phase, containing 1.0×10^{-3} M ligand (TREN-G1-DGA) solutions in 5% iso-decanol/*n*-dodecane, and the aqueous phase, containing the required tracer in HNO_3 solutions in leak-tight Pyrex tubes in a thermostated water bath at 25 ± 0.1 °C for 1 h. Subsequently, the tubes were centrifuged and aliquots (usually 0.1 mL) were taken out from both the phases for subsequent radiometric assay (*vide supra*). The concentrations of the actinide and fission product elements used in the solvent extraction experiments were about 10^{-7} M for Am, 10^{-6} M for Pu and Cs, and 10^{-5} M for Eu, U and Sr.

The distribution coefficient (D) values were calculated as the ratio of the concentration of metal ions in the organic phase to that in the aqueous phase (in terms of counts per unit time per unit volume). The experiments were carried out in duplicate and the accepted data points were reproducible and the errors on the data represented in the manuscript were calculated using error propagation analysis.

NMR titrations of TREN-G1-DGA with $La(OTf)_3$ in CD_3OD

A 0.00319 M solution of ligand in CD_3OD was used as the solvent to prepare a 0.0319 M solution of $La(OTf)_3$. The ligand concentration in the NMR tube was kept constant by adding varying amounts of La(OTf)$_3$ solution to the tubes and bringing the total volume to 500 μL by addition of the ligand solution. The NMR spectra were recorded 15 minutes after mixing the solutions.

Luminescence studies

Luminescence studies were performed on the organic extract of Eu^{3+} in 1.0 × 10^{-3} M TREN-G1-DGA in 5% iso-decanol/*n*-dodecane medium. In order to compare the luminescence of the Eu^{3+} complex of TREN-G1-DGA with other simple DGA derivatives, 2 mL of the organic extract of Eu^{3+} in 10 mM TODGA and TEHDGA in 5% iso-decanol/*n*-dodecane medium was taken in a fluorescence cuvette and steady state and lifetime spectra were recorded. All the luminescence studies were carried out using a Horiba PTI Quantamaster (QM 400) steady state and lifetime spectrofluorometer.

DFT computational studies

In order to lower the computational costs, the methyl derivative (TREN-G1-MDGA) of TREN-G1-DGA was considered in all the calculations. All the calculations were performed using the TURBOMOLE 7.0 program package.[27] The geometries of TREN-G1-MDGA and its Am^{3+} and Eu^{3+} complexes were optimized at the GGA level of density functional theory (DFT) by using Becke's exchange functional[28] in conjunction with Perdew's correlation functional[29] (BP86) with generalized gradient approximation (GGA). 60 Electron core pseudo-potentials (ECPs) along with the corresponding def-SV(P) basis set as implemented in the TURBOMOLE suit of program were selected for the Am^{3+} ion, whereas 28 electron core potentials (ECPs) along with the corresponding def-SV(P) basis set were chosen for Eu^{3+}. All the other lighter atoms were treated at the all electron (AE) level. In the case of Am^{3+} and Eu^{3+}, the high spin septet was found to be the ground state configuration. In the present chemical system, the close matching of the $\langle S^2 \rangle$ values with the $S(S+1)$ ideal values indicated negligible spin contamination.

EXAFS studies

The Extended X-ray Absorption Fine Structure (EXAFS) study was performed at the L3 edge of Eu^{3+} to understand the local structure around Eu^{3+} in the Eu^{3+}-TREN-G1-DGA complex. The EXAFS measurements were carried out in the fluorescence mode at the INDUS-2 Synchrotron Source (2.5 GeV, 200 mA) in the Scanning EXAFS beamline (BL-09) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The details of the beamline can be found elsewhere.[9]

The EXAFS data analysis was performed using a set of programs available within the IFEFFIT software package for background correction, normalization and fitting of the experimental EXAFS data with the guess structure. The ATHENA software was used for both data reduction and its Fourier transform of the absorption data to real space. The generation of the theoretical EXAFS spectra from the guess structure and its fitting with the experimental data were performed with ARTEMIS software using the FEFF 6.0 code.

Conflicts of interest

There is no conflict of interest to declare.

Acknowledgements

The authors (SAA, PKM, AS) are thankful to Dr P. K. Pujari, Head Radiochemistry Division, for his keen interest.

Notes and references

1 (*a*) S. A. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Sep. Purif. Rev.*, 2011, **40**, 43–76; (*b*) J. N. Mathur, M. S. Murali and K. L. Nash, *Solvent Extr. Ion Exch.*, 2001, **19**, 357–390; (*c*) B. Christiansen, C. Apostolidis, R. Carlos, O. Courson, J.-P. Glatz, R. Malmbeck, G. Pagliosa, K. Römer and D. Serrano-Purroy, *Radiochim. Acta*, 2004, **92**, 475–480.

2 (*a*) C. Madic and M. J. Hudson, *EC Report High Level Liquid Waste Partitioning by Means of Completely Incinerable extractants*, EUR 18038 EN, 1998; (*b*) C. Madic, M. J. Hudson, J. O. Liljenzin, J.-P. Glatz, R. Nannicini, A. Facchini, Z. Kolarik and Z. R. Odoj, *New Partitioning Techniques for Minor Actinides*, EUR 19149, European Commission, Luxembourg, 2000.

3 (*a*) W. Schulz and E. P. Horwitz, *Sep. Sci. Technol.*, 1988, **23**, 1191–1210; (*b*) L. Nigond, C. Musikas and C. Cuillerdier, *Solvent Extr. Ion Exch.*, 1994, **12**, 261–296; (*c*) D. Serrano-Purroy, B. Christiansen, R. Malmbeck, J.-P. Glatz and P. Baron, *Partitioning of Minor Actinides from HLW using DIAMEX Process*, Proc. Global, New Orleans, USA, 2003; (*d*) Y. Morita and M. Kubota, *Solvent Extr. Ion Exch.*, 1988, **6**, 233–246; (*e*) A. Leoncini, J. Huskens and W. Verboom, *Chem. Soc. Rev.*, 2017, **46**, 7229–7273.

4 (*a*) S. A. Ansari, P. N. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem. Rev.*, 2012, **112**, 1751–1772; (*b*) Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solvent Extr. Ion Exch.*, 2001, **19**, 91–103; (*c*) S. A. Ansari, P. N. Pathak, M. Husain, A. K. Prasad, V. S. Parmar and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2005, **23**, 463–479; (*d*) R. B. Gujar, S. A. Ansari, M. S. Murali, P. K. Mohapatra and V. K. Manchanda, *J. Radioanal. Nucl. Chem.*, 2010, **284**, 377–385.

5 (*a*) D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Purroy and C. Sorel, *Solvent Extr. Ion Exch.*, 2009, **27**, 26–35; (*b*) R. B. Gujar, S. A. Ansari, D. R. Prabhu, P. N. Pathak, A. Sengupta, S. K. Thulasidas, P. K. Mohapatra and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2012, **30**, 156–170.

6 (*a*) A. Leoncini, S. A. Ansari, P. K. Mohapatra, A. Boda, S. M. Ali, A. Sengupta, J. Huskens and W. Verboom, *Dalton Trans.*, 2017, **46**, 1431–1438; (*b*) S. A. Ansari, P. K. Mohapatra, A. Leoncini, J. Huskens and W. Verboom, *Dalton Trans.*, 2017, **46**, 11355–11362.

7 (*a*) P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens and W. Verboom, *Inorg. Chem.*, 2013, **52**, 2533–2541; (*b*) M. Iqbal, P. K. Mohapatra, S. A. Ansari, J. Huskens and W. Verboom, *Tetrahedron*, 2012, **68**, 7840–7847.

8 (*a*) L. Wu, Y. Fang, Y. Jia, Y. Yang, J. Liao, N. Liu, X. Yang, W. Feng, J. Ming and L. Yuan, *Dalton Trans.*, 2014, **43**, 3835–3838; (*b*) C. Li, L. Wu, L. Chen, X. Yuan, Y. Cai, W. Feng, N. Liu, Y. Ren, A. Sengupta, M. S. Murali, P. K. Mohapatra, G. Tao, H. Zeng, S. Ding and L. Yuan, *Dalton Trans.*, 2016, **45**, 19299–19310.

9 A. Leoncini, P. K. Mohapatra, A. Bhattacharyya, D. R. Raut, A. Sengupta, P. K. Verma, N. Tiwari, D. Bhattacharyya, S. Jha, A. M. Wouda, J. Huskens and W. Verboom, *Dalton Trans.*, 2016, **45**, 2476–2484.

10 (*a*) A. Leoncini, S. A. Ansari, P. K. Mohapatra, A. Sengupta, J. Huskens and W. Verboom, *Dalton Trans.*, 2017, **46**, 501–508; (*b*) S. A. Ansari, P. K. Mohapatra, A. Leoncini, Sk. M. Ali, A. Singhadeb, J. Huskens and W. Verboom, *Dalton Trans.*, 2017, **46**, 16541–16550.

11 (*a*) D. M. Bringham, A. S. Ivanov, B. A. Moyer, L. H. Delmau, V. S. Bryantsev and R. J. Ellis, *J. Am. Chem. Soc.*, 2017, **139**, 17350–17358; (*b*) A. G. Baldwin, A. S. Ivanov, N. J. Willams, R. J. Ellis, B. A. Moyer, V. S. Bryantsev and J. C. Shafer, *ACS Cent. Sci.*, 2018, **4**, 739–747.

12 A. Bhattacharyya, T. Gadly, A. S. Kanekar, S. K. Ghosh, M. Kumar and P. K. Mohapatra, *Inorg. Chem.*, 2018, **57**, 5096–5107.

13 A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden and T. Zevaco, *Solvent Extr. Ion Exch.*, 2012, **30**, 433–444.

14 A. Sengupta, S. V. Godbole, P. K. Mohapatra, M. Iqbal, J. Huskens and W. Verboom, *J. Lumin.*, 2014, **148**, 174–180.

15 F. Kou, S. Yang, H. Qian, L. Zhang, C. Beavers, S. J. Teat and G. Tian, *Dalton Trans.*, 2016, **45**, 18484–18493.

16 M. Arisaka and T. Kimura, *Solvent Extr. Ion Exch.*, 2011, **29**, 72–85.

17 P. Zhang and T. Kimura, *Solvent Extr. Ion Exch.*, 2006, **24**, 149–163.

18 M. R. Antonio, D. R. McAlister and E. P. Horwitz, *Dalton Trans.*, 2015, **44**, 515–521.

19 (*a*) J. Narbutt, A. Wodyński and M. Pecul, *Dalton Trans.*, 2015, **44**, 2657–2666; (*b*) Sk. M. Ali, S. Pahan, A. Bhattacharyya and P. K. Mohapatra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9816–9828.

20 (*a*) E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason and H. Diamond, *Sep. Sci. Technol.*, 1982, **17**, 1261–1279; (*b*) A. Sengupta, M. S. Murali, S. K. Thulasidas and P. K. Mohapatra, *Hydrometallurgy*, 2014, **147–148**, 228–233.

21 P. K. Mohapatra, M. Iqbal, D. R. Raut, W. Verboom, J. Huskens and S. V. Godbole, *Dalton Trans.*, 2012, **41**, 360–363.

22 C. Bazzicalupi, A. Bianchi, C. Giorgi, P. Gratteri, P. Mariani and B. Valtancoli, *Inorg. Chem.*, 2013, **52**, 2125–2137.

23 A. Leoncini, J. Huskens and W. Verboom, *Synlett*, 2016, 2463–2466.

24 S. S. Rattan, A. V. R. Reddy, V. S. Mallapurkar, R. J. Singh and S. Prakash, *J. Radioanal. Chem.*, 1981, **67**, 95–99.

25 M. S. Sajun, V. V. Ramakrihna and S. K. Patil, *Thermochim. Acta*, 1981, **47**, 277–286.

26 P. K. Mohapatra and V. K. Manchanda, *Radiochim. Acta*, 2003, **91**, 705–712.

27 (*a*) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169; (*b*) O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354; (*c*) TURBOMOLE V6.6 a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007 available from http://www.turbomole.com.

28 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

29 J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822–8824.