

Understanding the unique paradigm in the extraction of tri- and tetravalent actinide/lanthanide ions by a diglycolamide-functionalized dendrimer in RTIL medium

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Electronic Supporting Information

Experimental

General

C₄mim.NTf₂ was procured from Iolitec, Germany. Suprapur nitric acid (Merck) was used for the preparation of all HNO₃ solutions using MilliQ water (Millipore), which were standardized using a standard NaOH (BDH) solution and phenolphthalein (Fluka) indicator. TREN-G1-DGA was prepared according to a literature procedure.¹ All other reagents were of AR grade.

Radiotracers

²³³U, Pu (mainly ²³⁹Pu) and ²⁴¹Am radiotracers were used after purification of the laboratory stocks and were stored in nitric acid medium. ²³³U was purified from its daughter products using an anion exchange-based separation method.² The Pu stock solution was freshly purified from its decay products like ²⁴¹Am (beta decay of ²⁴¹Pu) using the standard TTA (thenoyl trifluoroacetone) extraction method reported in the literature.³ ²⁴¹Am was purified from ²³⁷Np (alpha decay product) by first adjusting the oxidation state of the latter to the +4 state by a mixture of Fe(II)-sulphamate and hydroxylamine hydrochloride followed by TTA extraction.⁴ ²³⁹Np was purified by extracting in 0.5 M HTTA in xylene at 1 M HNO₃ and was subsequently stripped by 8 M HNO₃. The aqueous solution was given several xylene contacts to remove any traces of the organic solvent. The valency of Pu, taken in 1 M HNO₃, was adjusted to the +4 state by the addition of a few drops of 0.05 M NaNO₂ followed by selective extraction of the converted Pu⁴⁺ ions by TTA. The extract was subjected to contact with 8 M HNO₃ to yield a stripped fraction of Pu⁴⁺, which was used as the stock solution of the tetravalent ion. ^{152,154}Eu, ¹³⁷Cs and ^{85,89}Sr were procured from BRIT (Board of Radiation and Isotope Technology), Mumbai. All radiotracers were used after ascertaining their radiochemical purity. ²³³U and Pu tracers were assayed radiometrically by a liquid scintillation counting system (Hidex, Finland) using the Ultima Gold (Perkin Elmer) scintillation cocktail, while the gamma ray emitting radionuclides, viz. ²⁴¹Am, ^{152,154}Eu, ¹³⁷Cs, and ^{85,89}Sr were assayed using a well type NaI(Tl) scintillation counter (Para Electronics) interfaced with a multi-channel analyzer (ECIL, India).

Synthesis of the ligand

The ligand was synthesized as reported before.¹ The characterization was done by NMR and ESI-MS and the relevant data are given below

¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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.

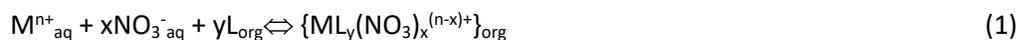
ESI-MS: *m/z* 2442.3 [M+H]⁺; HRMS: *m/z* calcd for C₁₃₈H₂₇₃N₁₆O₁₈: 814.6985 [M+3H]³⁺; found 814.6971.

Solvent extraction studies

Two-phase liquid-liquid extraction studies of lanthanide (Eu³⁺), actinide (UO₂²⁺, Np⁴⁺, Pu⁴⁺ and Am³⁺) and other fission product (Cs⁺) 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 C₄mim.NTf₂, and the aqueous phase, containing the required tracer in HNO₃ solutions in leak-tight Pyrex tubes in a thermostated water bath at 25 ± 0.1 °C for 2 h as the extraction of Am³⁺ was found to be completed within 1 h (Fig. S1). Subsequently, the tubes were centrifuged and aliquots (usually 0.1 mL) were taken out from both 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, 10^{-5} M for Eu, U. The distribution ratio (D) values were calculated as the ratio of the concentration of metal ion 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.

The effect of nitrate ions on the extraction of Am^{3+} , Eu^{3+} and Np^{4+} was studied by varying the NaNO_3 concentration from 0.5-6.0 M at a fixed HNO_3 concentration of 0.5 M. The results indicated a significant deviation from linearity when the distribution ratios (D_M) of all the three metal ions are plotted against the nitrate ion concentration in logarithmic scale. Therefore the conditional distribution coefficient (K_d) is calculated considering the nitrate ion complexation of these metal ions. Moreover in order to take care the effect of significant change of nitrate ion concentration, K_d values were corrected with the corresponding activity coefficient (γ) of the nitrate ion as reported by Horwitz et al. . This, however, cannot explain the dependency of the conditional distribution coefficient (K_d), ratio of the concentration of metal ion in the organic phase with respect to the free (uncomplexed) metal ion concentration in the aqueous phase (equation 2), on the nitrate ion concentration, since the metal ions are complexed by the nitrate ions in both the aqueous and organic phases. In order to determine the dependence of K_d on the nitrate ion concentration, the aqueous nitrate complexation of the metal ions should be taken into consideration and in the present work, the nitrate complexation was calculated based on the data reported by Horwitz et al.⁵ In the present study, the $\log K_d$ values were also calculated using the nitrate complexation constants reported by Horwitz *et al.*⁵ and a dependence of $\log K_d$ on the $\log[\text{NO}_3^-]$ was found to be ~ 2 for both the trivalent metal ions (Am^{3+} and Eu^{3+}) and ~ 4 for Np^{4+} (Figure 2c). Based on the above results the following equilibrium is proposed for the extraction of these metal ions from the nitrate medium:



$$\text{Conditional distribution coefficient, } K_d = [\text{ML}_y(\text{NO}_3)_x]_{(\text{org})} / [\text{M}^{n+}]_{\text{aq}} \quad (2)$$

while the distribution ratio is defined as:

$$D_M = [\text{M}^{n+}]_{(\text{org})} / ([\text{M}^{n+}]\{1 + \sum \beta_i[\text{NO}_3^-]^i\}) \quad (3)$$

Where $n=3$ and $x=2$ for the trivalent metal ions (Am^{3+} and Eu^{3+}) and $n=x=4$ for Np^{4+} .

Luminescence studies

Luminescence studies of the Eu^{3+} complex were performed on the organic extracts where the extraction was performed by 1.0×10^{-3} M TREN-G1-DGA in $\text{C}_4\text{mim.NTf}_2$ medium and the aqueous phase consists of 3 M HNO_3 containing $\text{Eu}(\text{NO}_3)_3$ of varying concentration. The solution (2 mL) was taken in the fluorescence cuvette to record the steady state and lifetime spectra. In order to determine the conditional stability constant of Eu^{3+} with TREN-G1-DGA, luminescence titration was carried out following the change of the luminescence spectra of $\text{Eu}(\text{NTf}_2)_3$ upon addition of gradually increasing amount of TREN-G1-DGA in $\text{C}_4\text{mim.NTf}_2$ medium in the wavelength range of 680-720 nm. The titration data were analysed using Hypspec software to determine the conditional stability constant values of the complexes formed. All the luminescence studies were carried out using a Horiba PTI Quantmaster (QM 400) steady state and lifetime spectrofluorometer.

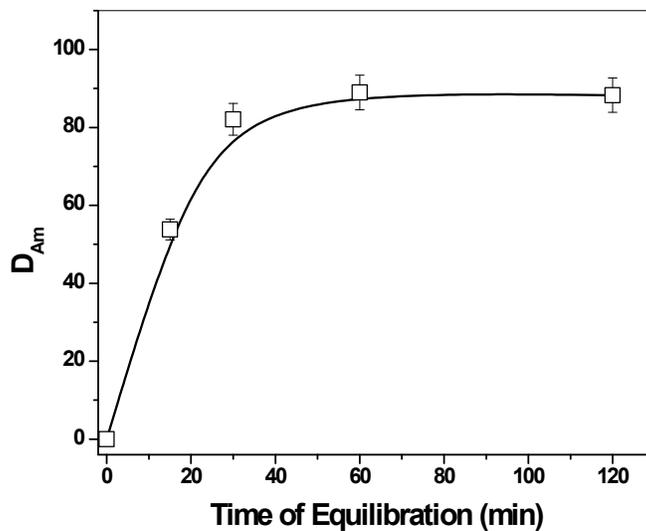


Fig. S1 Effect of time of equilibration on the extraction of Am^{3+} from 3 M HNO_3 using 1 mM TREN-G1-DGA in $C_4mim.NTf_2$.

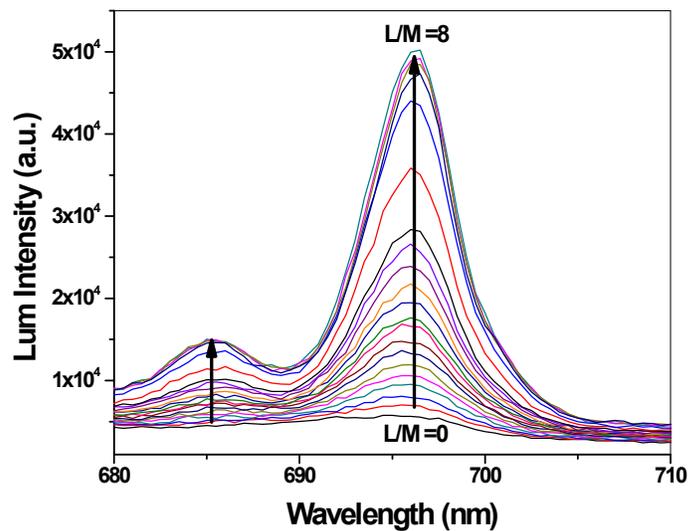


Fig. S2 Change in the luminescence spectra of $Eu(NTf_2)_3$ upon addition of increasing amounts of TREN-G1-DGA in $C_4mim.NTf_2$.

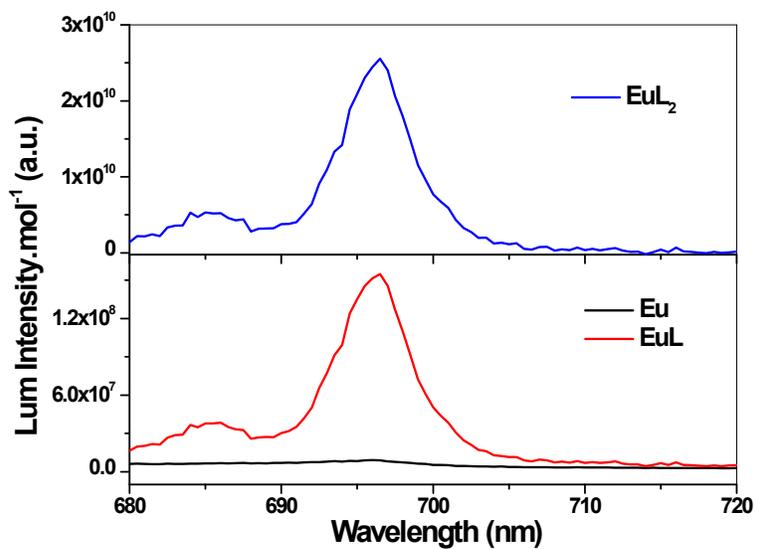


Fig. S3 Luminescence intensity per mole of different species of Eu^{3+} formed in the $\text{C}_4\text{mim.NTf}_2$ medium during its titration with TREN-G1-DGA.

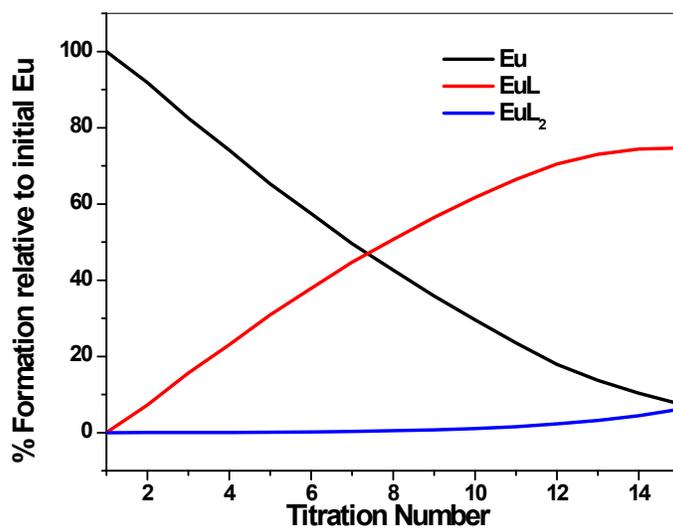
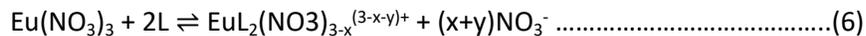
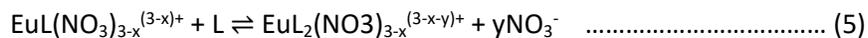
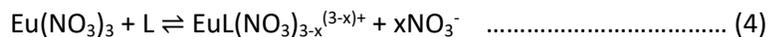


Fig. S4 Relative concentration of different species of Eu^{3+} with respect to the initial Eu^{3+} during its titration with TREN-G1-DGA in $\text{C}_4\text{mim.NTf}_2$.

The complexation equilibria



The stepwise conditional stability constant for equilibria 4 and 5 are K_1 and K_2 , respectively and their values as determined from the luminescence titration study are provided in the table below

Table S1: The conditional stability constant values for the Eu^{3+} complexes of TREN-G1-DGA obtained by fitting the luminescence titration data considering the complexation equilibria 4-6

Complexation equilibrium	$\log K_1$	$\log K_2$	$\log \beta_{1,2}$
4	4.93 ± 0.02	--	--
5	--	2.92 ± 0.08	--
6 (over all)	--	--	7.85 ± 0.08

References

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