Complexation of Tetraalkyl Diglycolamides with Trivalent *f*-cations in a Room Temperature Ionic Liquid: Extraction and Spectroscopic Investigations

S.A. Ansari, R.B. Gujar, P.K. Mohapatra

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, INDIA

Electronic Supporting Information

Contents

S1. Assaying of Am and Eu:

^{241}Am and ^{152,154}Eu were assayed radiometrically using a well type NaI(Tl) scintillation counter which was interphased with a multi-channel analyzer. For experiments where the extraction of Am or Eu were very large or very low, the aliquot size from the phase containing low counts was kept large enough to have more counts. Additionally, counting time was increased (some cases, >10 h counting time was used as against only one minute of counting time used for most samples). The counter was calibrated with known standards before the counting was done. Enough counts were collected (>10,000 counts) to neglect the counting statistics errors (<1%).

S2. Solvent extraction studies

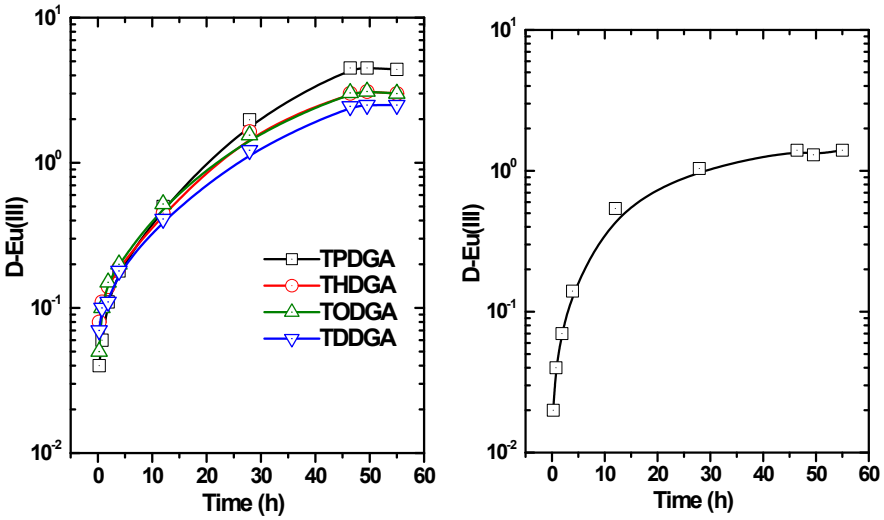

Figure S1. Extraction kinetics of Eu(III) by DGA ligands (Right: T2EHDGA). [Ligand]: 0.5 mmol/L in $[C_8mim][Tf_2N]$; Aqueous phase: 1 M HNO_3; Temperature: 25°C

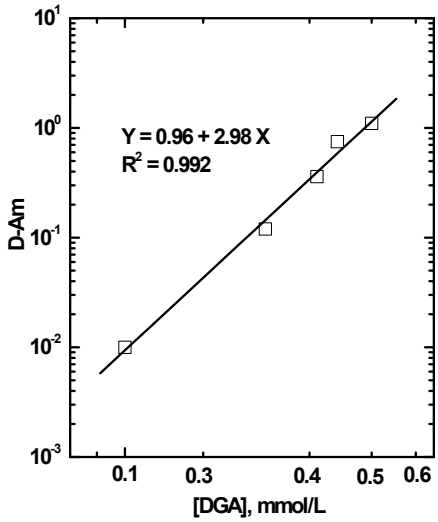

Figure S2. Distribution behaviour of Am(III) with varying concentration of T2EHDGA for analyzing the stoichiometry of the extracted species. RTIL: $[C_8mim][Tf_2N]$; Aqueous phase: 1 M HNO_3; Temperature: 25°C.

Table S1. Extraction behaviour of Am^{3+} and Eu^{3+} by TODGA and T2EHDGA. Ligand: 0.5 mmol/L in $[C_8mim][Tf_2N]$; Temperature: 25°C; S.F. = $D_{Eu(III)}/D_{Am(III)}$.

$[HNO_3]$, mol/L	**TODGA**			**T2EHDGA**		
	$D_{Am(III)}$	$D_{Eu(III)}$	***S.F.***	$D_{Am(III)}$	$D_{Eu(III)}$	***S.F.***
0.1	44.6	58.2	1.3	4.31	5.91	1.4
1	2.20	3.03	1.4	1.22	1.44	1.2
3	0.04	0.44	11	0.02	0.16	8.0
4	0.01	0.18	18	0.005	0.087	17
6	0.002	0.056	28	0.001	0.031	31

S3. UV-VIS Spectrophotometry

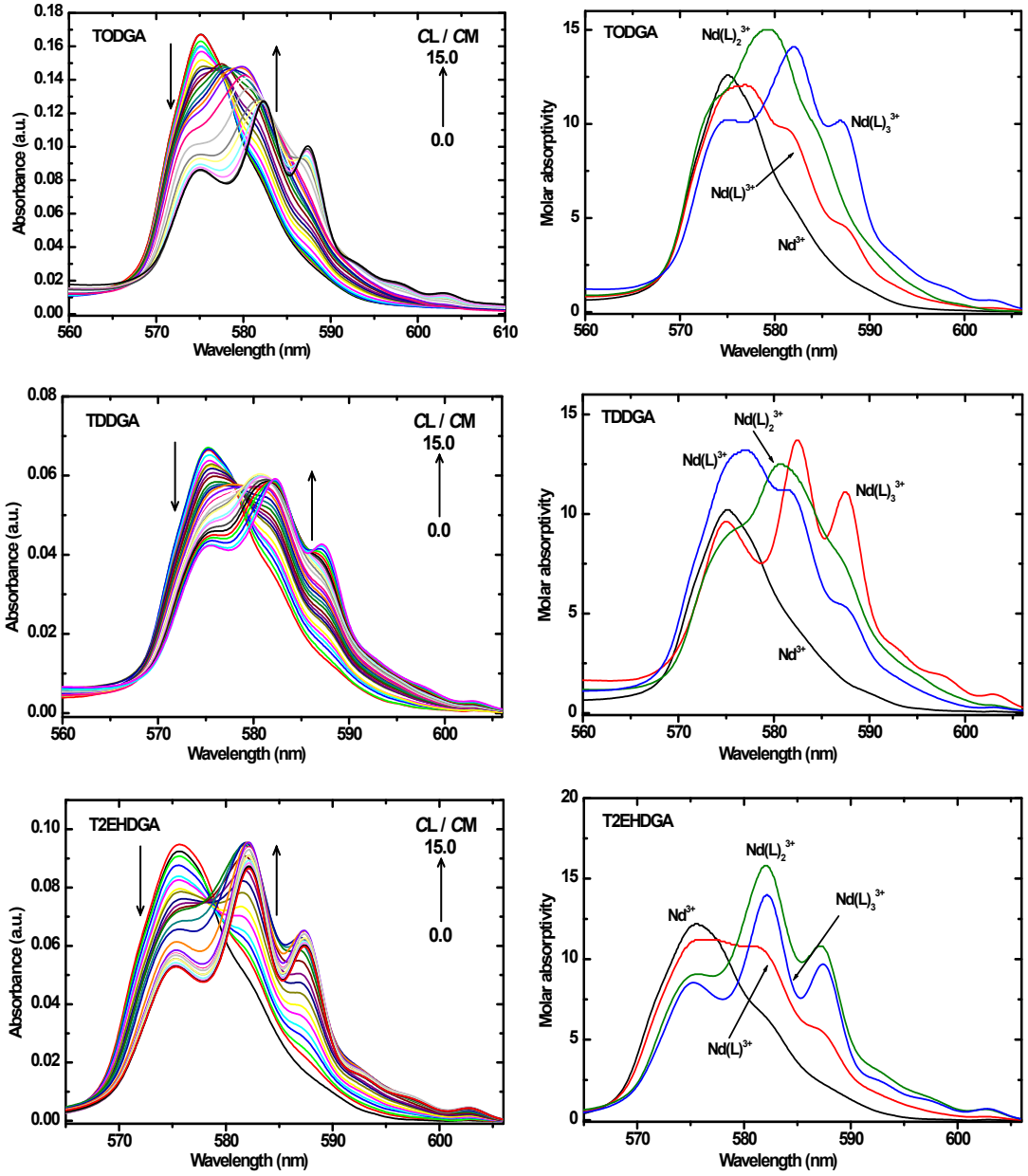

Figure S3. Representative spectrophotometric titrations of Nd^{3+} with TODGA, TDDGA and T2EHDGA ligands (Left) in $[C_8mim][Tf_2N]$, and deconvoluted spectra of M, ML, ML_2 and ML_3 species (Right).

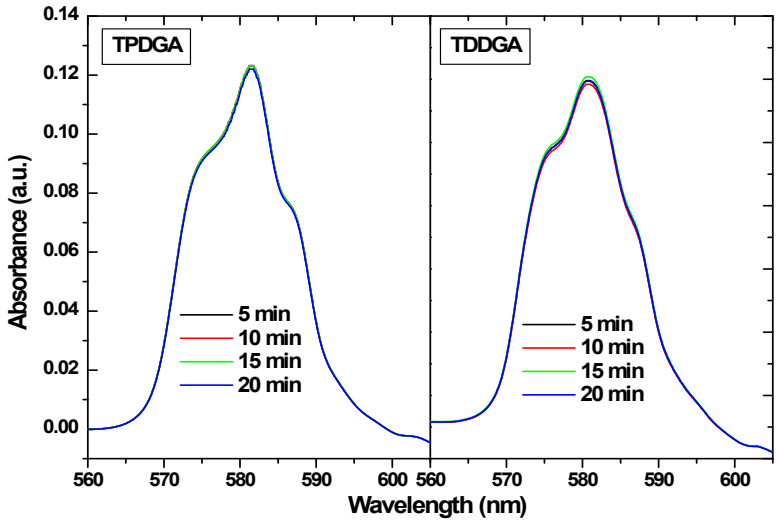

Figure S4. Representative spectra of Nd^{3+} after addition of titrant recorded over 20 minutes to establish the kinetics of complexation in $[C_8mim][Tf_2N]$. Spectra were recorded at Nd^{3+}/DGA = 1.

S4. Luminescence spectroscopy

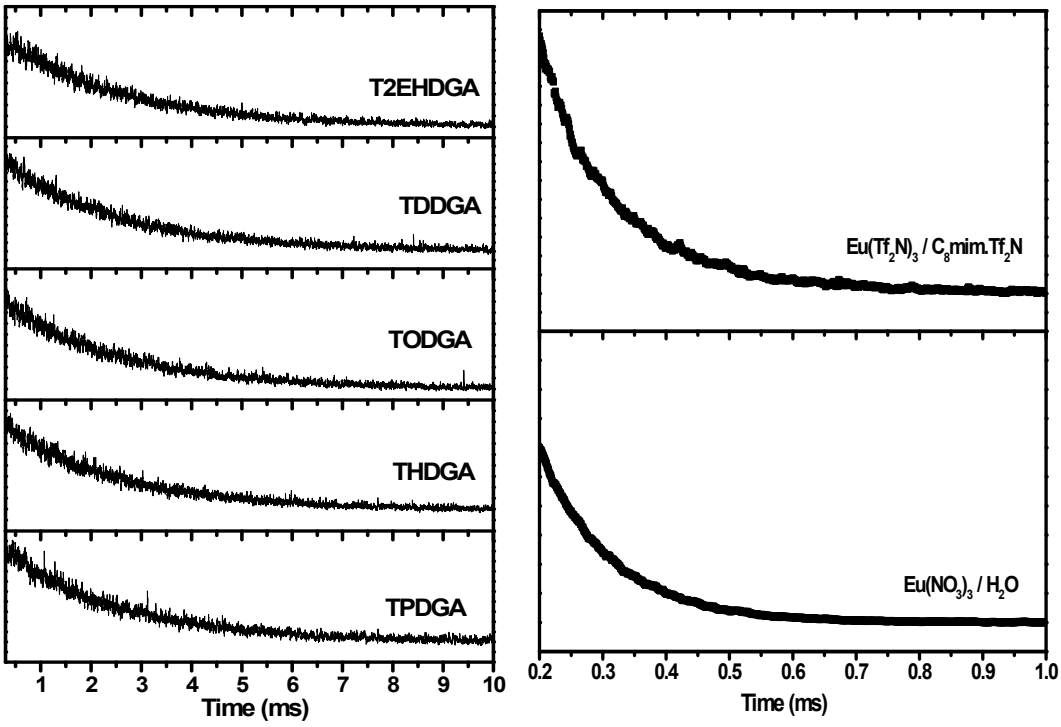

Figure S5. Fluorescence decay curve for Eu^{3+} under different environment.

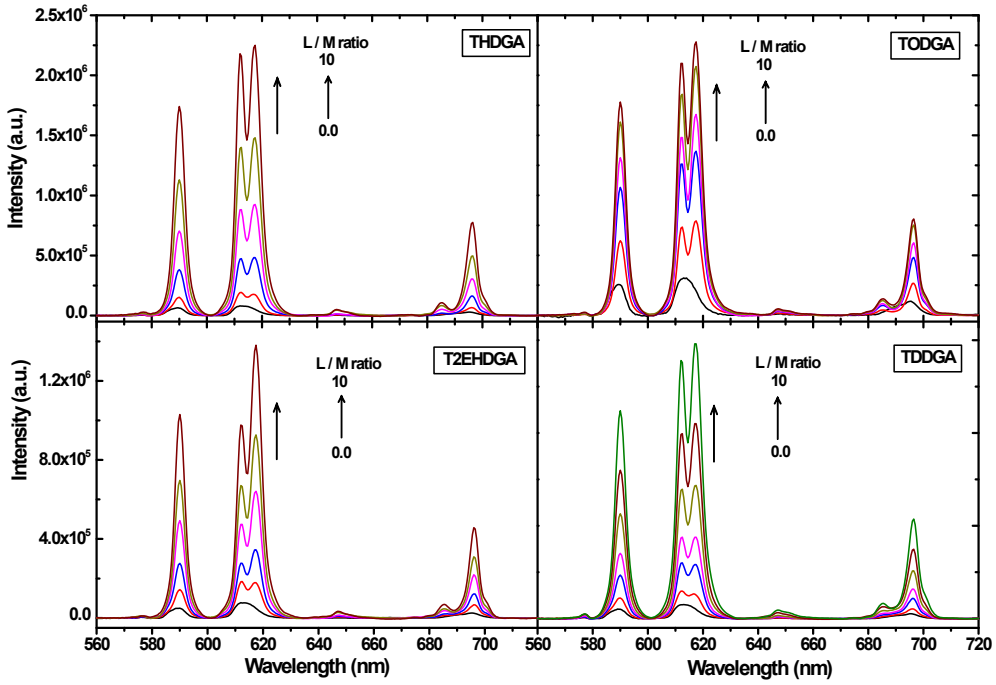

Figure S6. Luminescence spectra obtained by titration of $Eu(Tf_2N)_3$ with THDGA, TODGA, T2EHDGA and TDDGA in $C_8mim{\cdot}Tf_2N$. Cuvette: 8.0 mmol/L Eu^{3+} (1.5 mL); Ligand: 60 mmol/L in $C_8mim{\cdot}Tf_2N$; Excitation wavelength: 394 nm.

Table S2. Asymmetry factor, life-time and number of water molecules present in the primary hydration sphere of Eu^{3+} obtained at completion of complexation (ligand to Eu^{3+} ratio = 8).

Ligand	**Asymmetric factor[a]**	**Life-time (ms)**	**N_{H2O}**
TPDGA	2.25	2.11	–0.20
THDGA	2.31	1.98	–0.17
TODGA	2.36	2.13	–0.21
T2EHDGA	2.28	2.08	–0.20
TDDGA	2.34	2.14	–0.21

[a]: *Obtained as the ratio of peak area due to $^5D_o \rightarrow {}^7F_2$ to $^5D_o \rightarrow {}^7F_1$ transitions.*