Remarkable Acidity Independent Actinide Extraction with a Novel Both-side Diglycolamide-functionalized Calix[4]arene in Room Temperature Ionic Liquid: Complexation and Fluorescence studies

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ELECTRONIC SUPPLIMENTARY MATERIAL

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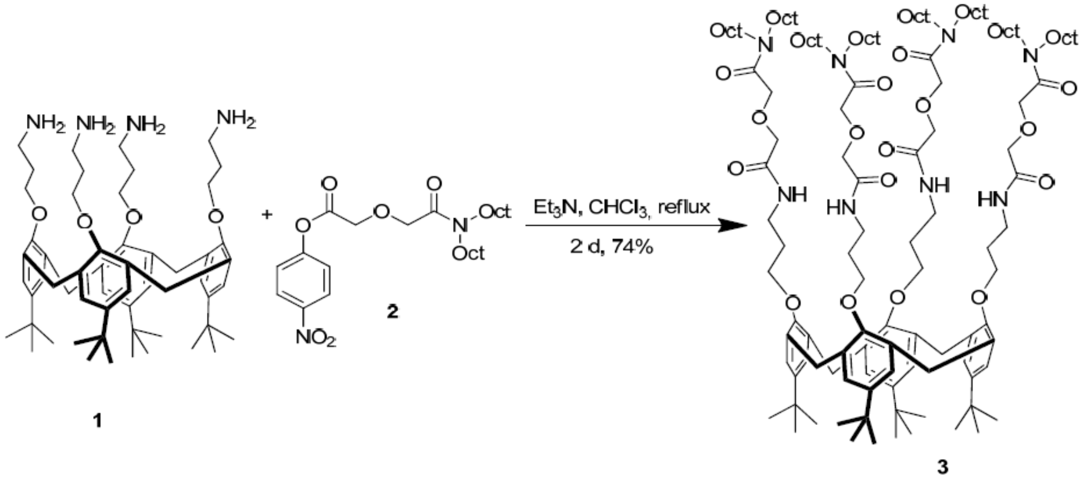
1. Experimental

1.1 *General.* All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Compound **2** (Scheme I in manuscript) was prepared according to a literature procedure. Solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. All NMR measurements are recorded in $CDCl_3$ as a solvent. Electrospray Ionization (positive mode) high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminum). Column chromatography was carried out with Merck silica gel 60 (230–400 mesh). Detailed synthetic protocols are elaborated in Supplementary information.

1.1.1 Synthesis DGA-functionalized calix[4]arenes[i]

Narrow rim DGA-functionalized calix[4]arene ***3 (L-II)***

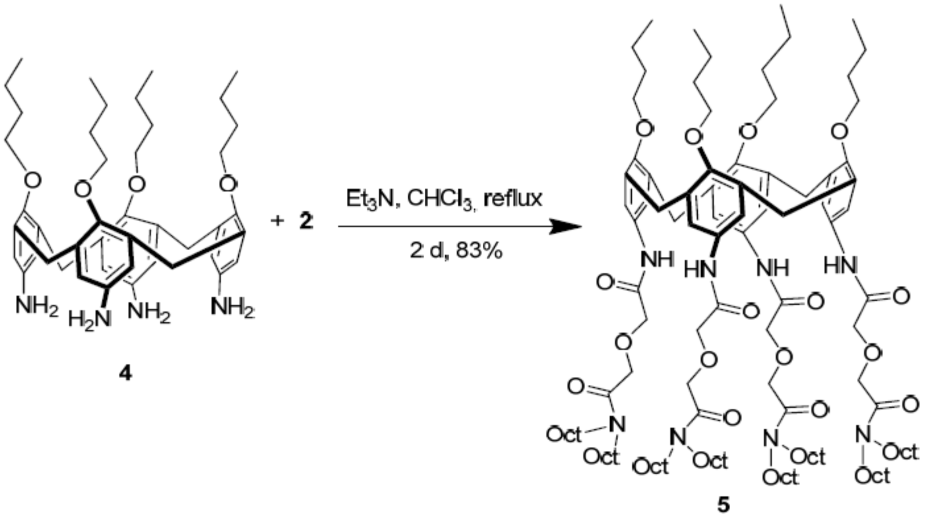
Tetra-DGA-calix[4]arene (**3**) was prepared by reaction of cone tetrakis(aminopropoxy)calix[4]arene **1**[ii] with *p*-nitrophenol activated DGA **2** (Scheme 1). The formation of **3** clearly followed from the shifts of the CH_2NH methylene protons from 2.91 ppm in **1** to 3.46 ppm in **3** in the ^{1}H NMR spectra. In addition, the $[M+H]^+$ peak was found at *m/z* 2234.7507 in the ES$^+$ HRMS mass spectrum, which corresponds to the calculated *m/z* of 2234.7665 for $C_{136}H_{233}N_8O_{16}$.



Scheme 1

Wide rim DGA-functionalized calix[4]arene ***5 (L-III)***

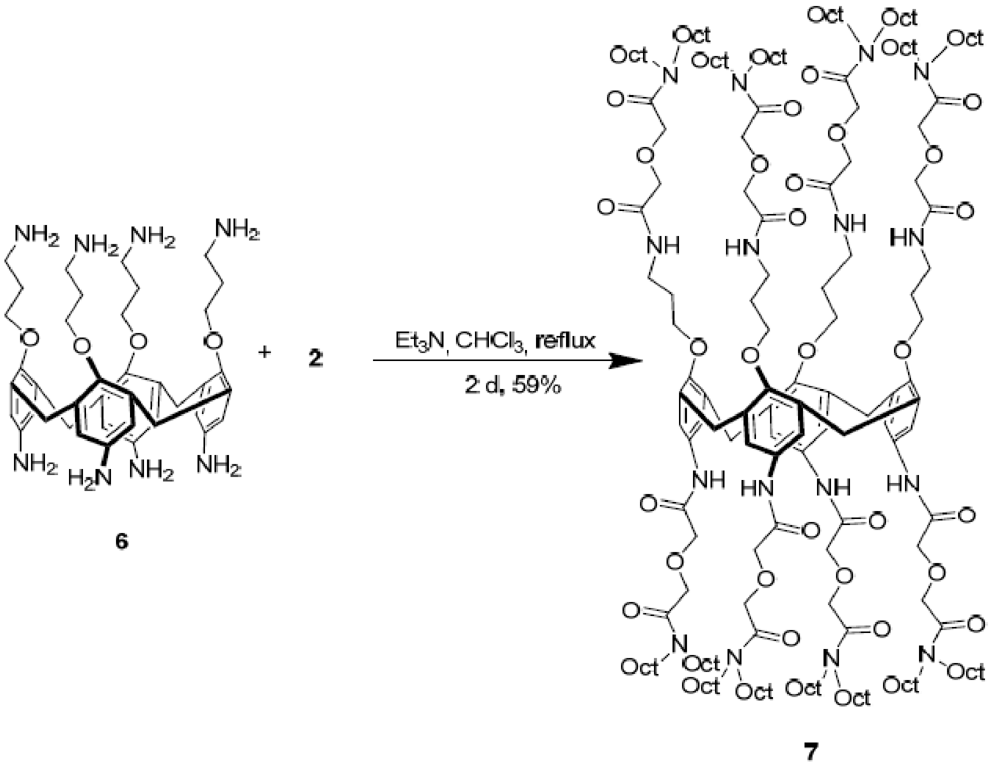
Wide rim DGA-functionalized calix[4]arene (**5**) was prepared accordingly by reaction of the known[iii] tetrabutoxycalix[4]arene tetraamine **4** with *p*-nitrophenol activated DGA **2** (Scheme 2). The formation of **5** clearly followed from the ES$^+$ HR mass spectrum showing a characteristic $[M+Na]^+$ peak at m/z 2089.7678, which corresponds with the calculated m/z of 2089.7715 for $C_{124}H_{208}N_8O_{16}Na$. In addition, its formation was demonstrated by the downfield shift of the aromatic protons in the ^1H NMR spectrum from 6.12 ppm in **4** to 6.83 ppm in **5**.



Scheme 2

Wide and narrow rim DGA-functionalized calix[4]arene **7** *(**L-I**)*

Octaaminocalix[4]arene **6** was reacted with *p*-nitrophenol activated DGA **2** to afford the desired ligand **7** (Scheme 3). The ES$^+$ HR mass spectrum exhibited the $[M+H]^+$ peak at m/z 3427.6606. In the ^1H NMR spectra shifts occurred of the NCH_2 protons from 2.87 in **6** to 3.48 ppm in **7**, and of the aromatic hydrogens from 6.07 in **6** to 6.97 ppm in **7**.



Scheme 3

1.2 *Distribution studies*. Equal volumes of the tracer (^{241}Am, ^{233}U, Pu (mostly ^{239}Pu), ^{152}Eu, ^{137}Cs and ^{85,89}Sr) spiked aqueous solution and ionic liquid containing the C4DGA ligand were vertexed in Pyrex stoppered equilibration tubes in a thermostated water bath at 25±0.1 °C for about 3 h which was optimized after the studies with varying equilibration time (vide infra). The phases were separated after centrifugation, and assayed radiometrically (alpha counting for U and Pu and gamma counting for the rest).

Pu was converted to its +4 oxidation states using $NaNO_2$ and the ionic species was selectively extracted using TTA (2-thenoyltrifluoroacetone) from 1 M HNO_3 followed by stripping into 8 M HNO_3 which was used as Pu^{4+} stock solution. All subsequent studies with Pu^{4+} involved ammonium metavanadate as the holding oxidant. PuO_2^{2+} was obtained by adding AgO as the oxidizing agent.

For the calculation of the distribution ratio of a particlar metal ion M (D_M), defined as the ratio of the activity per unit volume in the ionic liquid phase to that in the aqueous phase, aliquots were removed from the aqueous phase only before and after the extraction experiments.

$$D_M = (C_i - C_f)/(C_f)$$

where, C_i and C_f are the initial and final concentrations of the metal ion, respectively. This method has been reported previously in such studies and we have reported good agreement between the D_M obtained by the difference method (above) and that obtained by carefully taken aliquots from the IL phase. The experiments were carried out in duplicate and the precision was within ± 5%. This was required to minimize errors associated with ionic liquid phase sampling due to their relatively high viscosity. Stripping studies were carried out in a manner analogus to the extraction studies with the difference that the aqueous phase was either 0.05 M DTPA / EDTA in 1 M guanidine carbonate or a buffer mixture containing 0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate while the organic phase was the metal ion loaded ionic liquids. The radiolytic degradation of the ionic liquid based solvents was done by exposing those in a gamma chamber (with ^{60}Co source) for a given period of time at a dose rate of 1.6 kGy/h.

The distribution experiments were carried out in triplicate and the reported data are within error limits of 5% and with >98% mass balance compared to the blanks.

1.3 *Fluorescence studies*. Emission spectroscopic studies of the Eu^{3+} complexes, in dilute nitric acid as well as in the ionic liquid extracts, were carried out using a spectrometer (Edinburgh Analytical Instruments, UK) controlled by CD 920 controller and equipped with OPO laser. While the samples were excited at 395 nm, the emission spectra were recorded in the range of 575–750 nm. The emission decay curves were fitted into the exponential function to obtain the lifetimes / decay rates of the excited states using inbuilt software GEM/3 (Edinburgh) with reproducibility of lifetimes of the excited states within ±3μs.

Table S-1: Composition of high level waste of PHWR (pressurized heavy water reactor) origin. Data indicate bulk concentrations of important fission product elements, structural materials (Fe, Zr, Cr, etc.) and process chemicals (Na) at 3 M HNO_3.

Element	Concentration (g/L)	Element	Concentration (g/L)
Na	5.50	Pd	0.03
K	0.22	Mo	0.14
Cr	0.12	Ba	0.06
Mn	0.43	Y	0.06
Fe	0.72	La	0.18
Sr	0.03	Ce	0.06
Cs	0.22	Pr	0.09
Zr	0.09	Nd	0.12
Ru	0.04	Sm	0.09

2. Results

2.1 Solvent extraction studies

2.1.1 Comparative extraction data

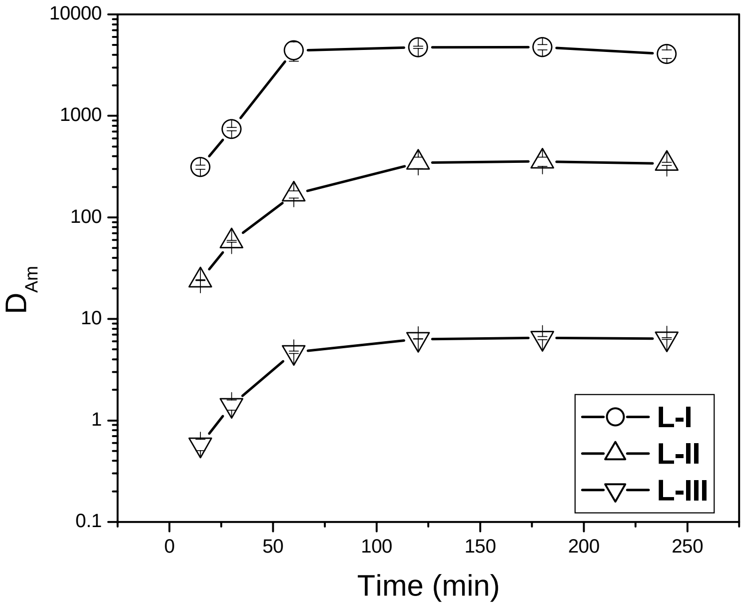
Table S-2 Distribution data of Am(III) using $5.0\text{x}10^{-4}$ M C4DGA ligands in room temperature ionic liquids[a] as well as *n*-dodecane from aqueous nitric acid feed solutions.

$[HNO_3]$, M	D_{Am} with different DGA ligands in $C_8mim^+NTf_2^-$				D_{Am} with different DGA ligands in *n*-dodecane			
	L-I	**L-II**	**L-III**	TODGA[b]	**L-I**	**L-II**	**L-III**	TODGA[b]
3	1.06	7710	0.60	30.1	1.43	6.04	1.16	0.003
0.5	397	5533	0.37	0.05	0.92	2.22	0.57	0.002
$1.0\text{x}10^{-2}$	2490	2301	6.72	0.02	0.11	0.11	0.099	$5.0\text{x}10^{-4}$

[a] The D_{Am} values in the absence of the extractants were typically <0.01 in all three ionic liquids; [b] Extraction data with TODGA ($1.0\text{x}10^{-3}$ M) are included for comparison purposes. TODGA concentration used for these studies was $1.0\text{x}10^{-3}$ M and assuming extraction of a predominantly 1:2 (M:L) complex species, the effective ligand concentration was 5.0x10-4 M which was comparable to the C4DGA concentration as the C4DGA ligand formed 1:1 (M:L) species.

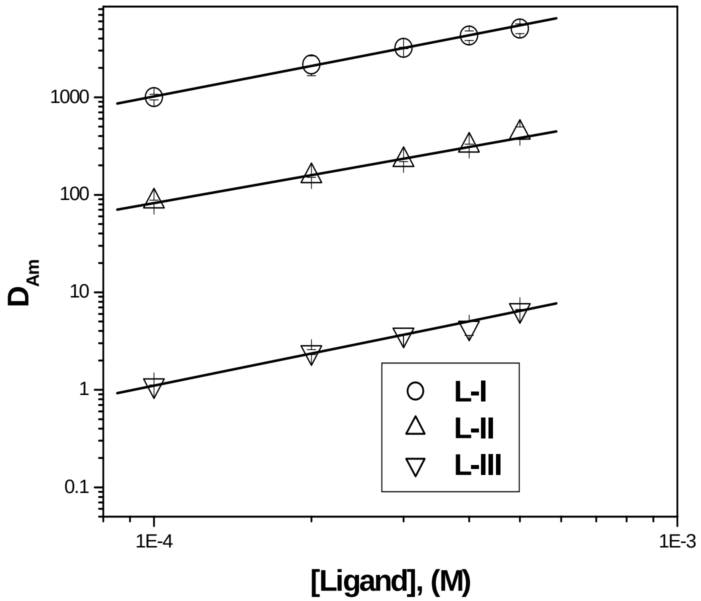
2.1.2 Kinetics of extraction

Fig. S-1 Extraction kinetics of Am(III) from 0.5 M HNO_3 feed into $5.0\text{x}10^{-4}$ M of the three C4DGA ligands in $C_8mim^+.NTf_2^-$. Feed acidity for **L–III** was $1.0\text{x}10^{-2}$ M HNO_3.



2.1.3 Nature of extracted species

Fig. S-2 Dependence of Am(III) extraction on varying C4DGA **L-I** – **L-III** concentrations from 0.5 M HNO_3 and in case of **L-III** 1.0×10^{-2} M HNO_3 feed into $C_8mim^+NTf_2^-$.

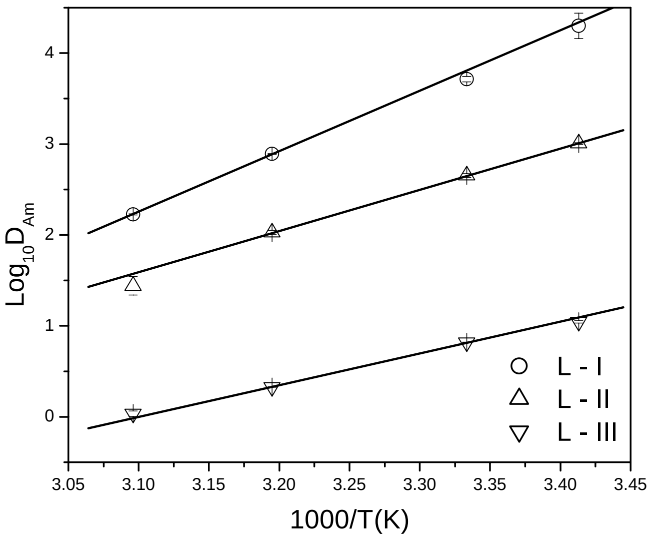


2.1.4 Temperature variation studies

Table S-3: Temperature dependence of D_{Am}.

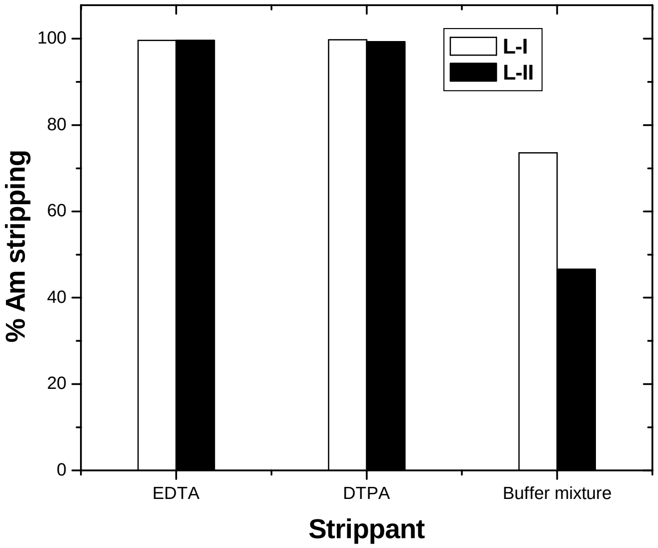
Temp(K)	D_{Am} lower rim **L-I**	both side **L-II**	upper rim **L-III**	Ligand conc. (M)	Diluent
293	7217	704	11	5×10^{-4}	$C_8mimNTf_2$
300	4913	442	6		
313	743	115	2		
323	204	38	1		

Figure S-3: Van't Hoff plots for Am(III) distribution data.



2.1.5 Stripping behaviour

Fig. S-4 Stripping behaviour of Am(III) from an extract made of 1.0x10^{-3} M C4DGAs **L-I** and **L-II** in $C_8mim^+NTf_2^-$.



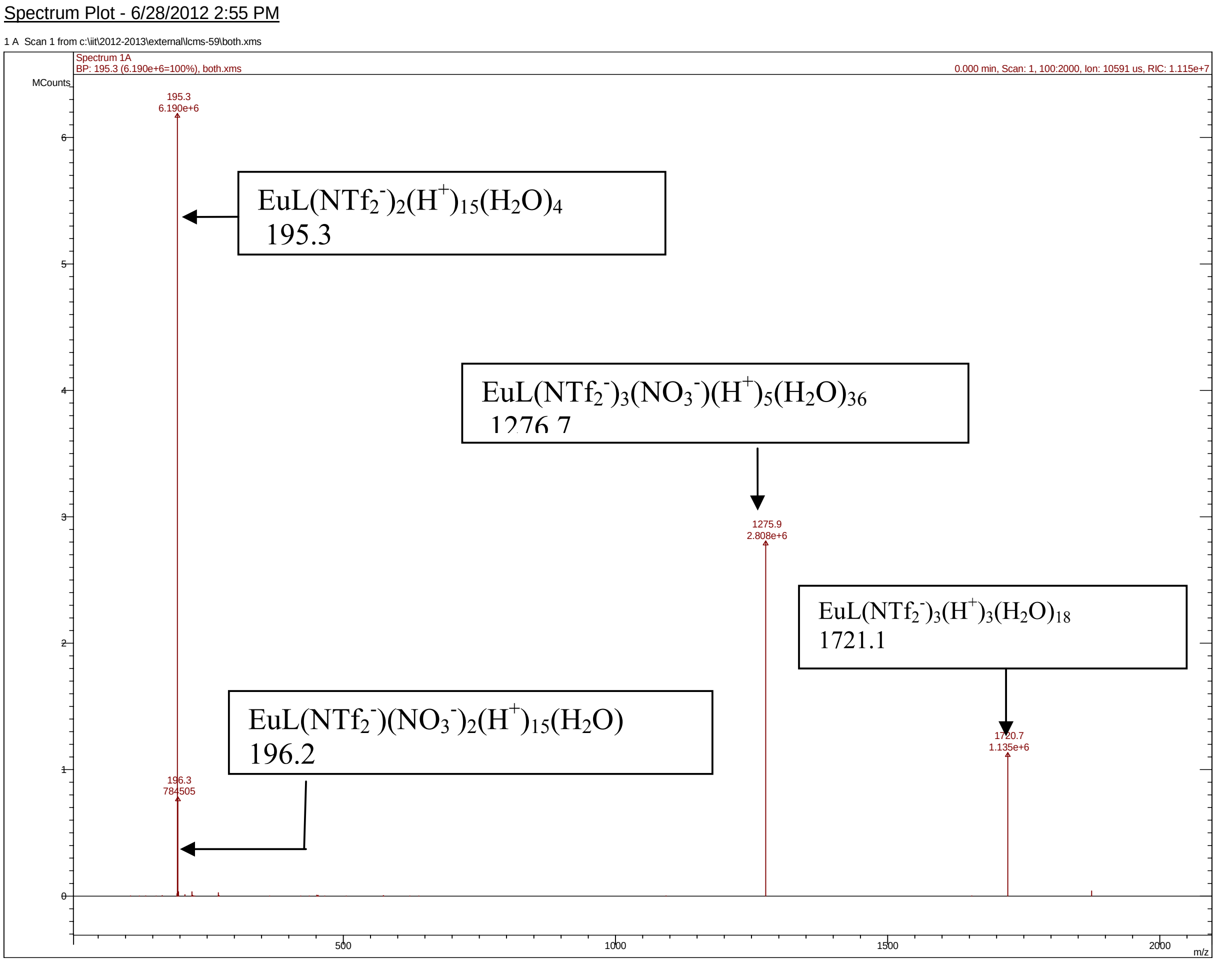
2.2. Fluorescence studies

Table S-4 Fluorescence spectroscopy data for Eu^{3+} ($1.0x10^{-3}$ M) under varying experimental conditions in the absence and presence of the three calix-DGA ligands. Excitation wavelength: 248 nm; Emission wavelength: 616 nm.

System	Transition	Peak positions	Asymmetry factor	Lifetime (ms)	No of water molecules
Eu^{3+}-Aquo	$^5D_0$-$^7F_0$	Not seen	1.649	0.114	9
	$^5D_0$-$^7F_1$	592			
	$^5D_0$-$^7F_2$	617			
	$^5D_0$-$^7F_3$	651			
	$^5D_0$-$^7F_4$	695, 700			
Eu^{3+} - **L-I**	$^5D_0$-$^7F_0$	Not seen	3.290	1.36	0
	$^5D_0$-$^7F_1$	593			
	$^5D_0$-$^7F_2$	615			
	$^5D_0$-$^7F_3$	651			
	$^5D_0$-$^7F_4$	680 (sh), 699			
Eu^{3+} - **L-II**	$^5D_0$-$^7F_0$	Not seen	2.388	1.52	0
	$^5D_0$-$^7F_1$	593			
	$^5D_0$-$^7F_2$	614, 619			
	$^5D_0$-$^7F_3$	650			
	$^5D_0$-$^7F_4$	687, 698			
Eu^{3+} - **L-III**	$^5D_0$-$^7F_0$	Not seen	2.286	0.21	5
	$^5D_0$-$^7F_1$	593			
	$^5D_0$-$^7F_2$	614, 619(sh)			
	$^5D_0$-$^7F_3$	654			
	$^5D_0$-$^7F_4$	688(sh), 690 (sh), 698			

2.3 ESI-MS Analysis

Figure S-5: ESI-MS spectra of Eu3+ extract using both side functionalized calixare (L-I) in $C_8mimNTf_2$



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[i]. For full experimental and spectroscopic data see: M. Iqbal, P. K. Mohapatra, S. A. Ansari, J. Huskens, W. Verboom, *Tetrahedron* **2012**, *68*, 7840.

[ii]. S. Barboso, A. G. Carrera, S. E. Matthews, F. Arnaud-Neu, V. Böhmer, J. Dozol, H. Rouquette, M. J. Schwing-Weill, *J. Chem. Soc., Perkin Trans. 2* **1999**, 719.

[iii]. L. Zhengyi, M. Jiejie, C. Jiawen, P. Yi, J. Juli, W. Leyong, *Chin. J. Chem.* **2009**, *27*, 2031.