

Electronic supplementary information

**Separation of samarium and europium by solvent extraction
with an undiluted quaternary ammonium ionic liquid:
towards high-purity medical samarium-153**

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Analysis anion purity of [A336][NO₃] after metathesis

The final chloride content after conversion of the commercially available [A336][Cl] to [A336][NO₃] was determined by total reflection X-ray fluorescence (TXRF) spectroscopy, using a Bruker Picofox S2 TXRF spectrometer. A sample of [A336][NO₃] was prepared by the addition of 100 μL of a Cu²⁺ standard solution, 100 μL of a NH₃ solution (25 wt%) and 750 μL of ethanol to 40 mg of the ionic liquid. A droplet (2.5 μL) of this mixture was placed on a quartz glass carrier after vigorous homogenization. Subsequently, the quartz glass carrier was dried in a hot air oven at 60 °C for 30 min and measured in the TXRF spectrometer for 200 s. The results were processed using the Bruker Spectra Picofox software (version 7.5.3.0).

Anion source and anion concentration for the extraction of Sr²⁺ and Eu²⁺

In a first series of screening experiments, the extraction behavior of Sr²⁺ by the crown ether containing ionic liquid was studied as a simulant for Eu²⁺. Different anion concentrations were used in the aqueous feed solution, *i.e.* 0, 1, 3, 6 and 8 M. Three different sources were used to vary the anion concentration, *i.e.* HX, NH₄X and LiX (with X = Cl⁻ or NO₃⁻). Extractions were performed using [A336][NO₃] + 0.05 M DCH18C6 (IL+CE) (Figure S1). Significant extraction of Sr²⁺ was only reached in case of high lithium salt concentration, *i.e.* ≥ 6 M. The extraction of Sr²⁺ was negligible at lower salt concentration. In these conditions, fractions of > 70% were extracted. The use of HX and NH₄X resulted in much lower extraction efficiencies. It is also clear that extraction from nitrate media occurs much more efficiently than extraction from chloride media. This is most probably due to the higher hydration energy of the chloride, which hampers the co-extraction to ensure charge neutrality. Distribution ratios were negligible when no DCH18C6 was present in the ionic liquid phase, regardless the origin and concentration of the anions.

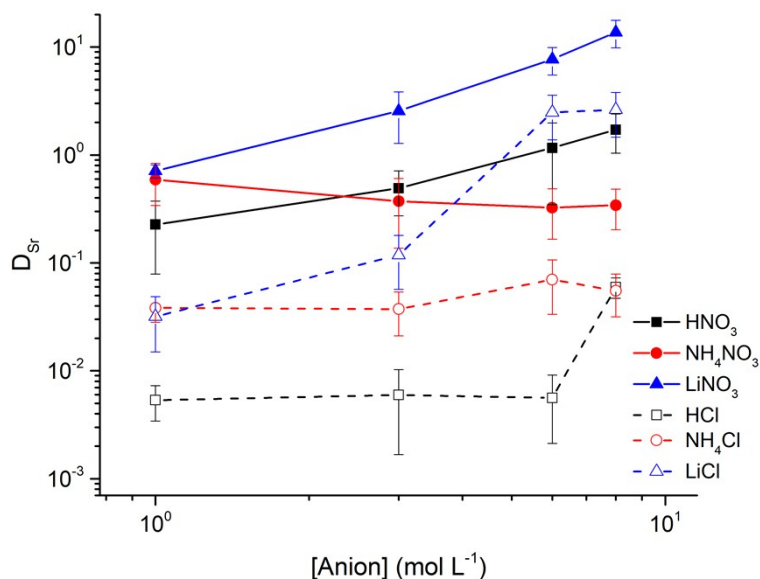


Figure S1: Distribution ratio of Sr^{2+} as a function of the concentration added anions (0, 1, 3, 6 and 8 M) anions using HX (black, squares), NH_4X (red, circles) and LiX (blue, triangle) in the aqueous feed solution, with X being nitrate (solid line, solid symbol) or chloride (dashed line, open symbol). The organic phase consisted of $[A336][NO_3] + 0.05$ M DCH18C6 (1L+CE₇). Extraction parameters: o/a 1:1, 60 min, 60 °C and 1700 rpm.

Based on these results, the extraction experiments with Eu^{2+} were restricted to the use of lithium salts to increase the anion concentration in the aqueous feed solution. Figure S2 compares the distribution ratio of Sr^{2+} and Eu^{2+} for extraction by $[A336][NO_3] + 0.05$ M DCH18C6 as a function of the lithium salt concentration (0, 1, 3, 6 and 8 M). It can be seen that Eu^{2+} follows a very similar trend as Sr^{2+} , only showing reasonable distribution ratios at high salt concentrations, *i.e.* 6 and 8 M. Eu^{2+} proved to be extracted even more efficiently by DCH18C6 than Sr^{2+} . Eu^{2+} fractions of > 95% were extracted in these conditions, reaching distribution ratios well above 1. The increasing extraction efficiency with increasing anion

concentration (reflected in the rising distribution ratio), denotes that extraction to the ionic liquid phase occurs via neutral complex partitioning (Figure S2).¹ This is similar to the extraction of alkaline earth metals by crown ethers in molecular diluents, like 1-octanol.² Ion exchange mechanisms, like observed by Garvey *et al.* for [C_nmim][Tf₂N], are unlikely to happen.

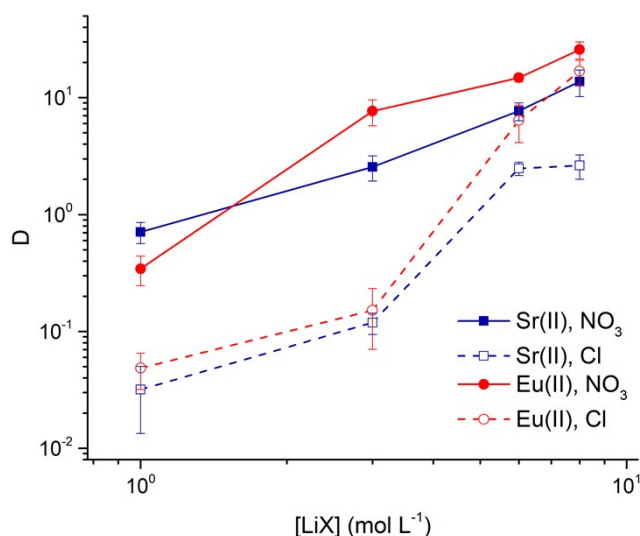


Figure S2: Distribution ratios of Sr²⁺ (dark blue, squares) and Eu²⁺ (red, circles) to the organic phase as a function of the LiX concentration (0, 1, 3, 6 and 8 M) in the aqueous feed solution, with X being nitrate (solid line, solid symbol) or chloride (dashed line, open symbol). The organic phase consisted [A336][NO₃] + 0.05 M DCH18C6 (1L+CE). Extraction parameters: O/A = 1, 60 min, 60 °C and 1700 rpm.

Extraction kinetics of Sr²⁺ and Eu²⁺

The extraction behavior of Sr²⁺ and Eu²⁺ in the [A336][NO₃] and [A336][NO₃] + 0.05 M DCH18C6 systems was studied as a function of time using various mixing times (5, 15, 30 and 60 min). This way, the minimum time required for an efficient extraction can be determined. These experiments were performed using an aqueous feed solution containing 6 M LiX (with X = Cl⁻ or NO₃⁻). In Figure S3, the distribution ratios of Sr²⁺ and Eu²⁺ from an aqueous feed

solution containing 6 M lithium salt are shown as a function of time. In Figure S3a, it is shown that the extraction of Eu^{2+} from a 6 M LiCl aqueous feed solution proceeds more efficiently than the extraction of Sr^{2+} in the presence of DCH18C6. Extraction equilibrium for Sr^{2+} and Eu^{2+} was established at 15 min contact time. At this point, a fraction of about 83% Eu^{2+} was extracted. Switching to a 6 M LiNO_3 aqueous feed solution resulted in high distribution ratios for Eu^{2+} (Figure S3b). About 90% of the initial Eu^{2+} was already extracted to the organic phase ($[\text{A336}][\text{NO}_3] + \text{DCH18C6}$) after an extraction time of 5 minutes, whereas a fraction of $> 93\%$ Eu^{2+} was extracted after longer contact times.

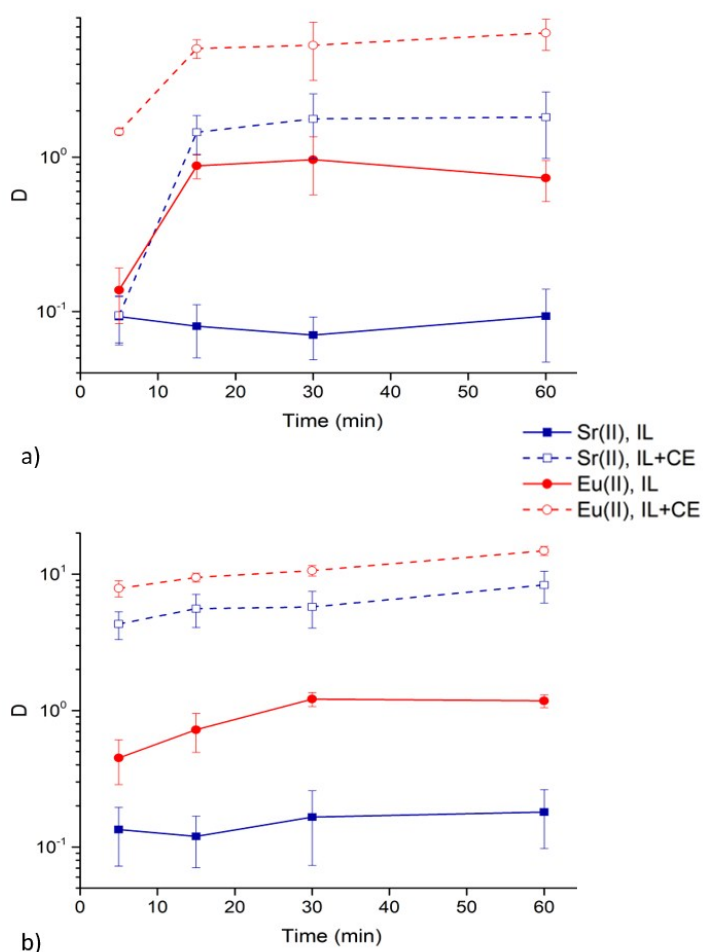


Figure S3: Distribution ratios of Sr^{2+} (dark blue, squares) and Eu^{2+} (red, circles) as a function of time (5, 15, 30 and 60 min) using 6 M LiCl (a) and 6 M LiNO_3 (b) in the aqueous feed solution. The organic

phase consisted of neat $[A336][NO_3]$ (IL, solid line, solid symbol) or $[A336][NO_3]$ containing 0.05 M DCH18C6 (IL+CE, dashed line, open symbol). Extraction parameters: $O/A = 1$, 60 °C and 1700 rpm.

Slope analysis of Sr^{2+} and Eu^{2+}

Extraction experiments with varying crown ether concentration in the ionic liquid phase were performed to support the proposed neutral complex partitioning. Aqueous phases containing $1\text{ g}\cdot\text{L}^{-1}$ Sr^{2+} and $1\text{ g}\cdot\text{L}^{-1}$ Eu^{2+} were contacted for 15 min at 60 °C with the ionic liquid phases containing different concentrations of DCH18C6 (0 – 0.1 M in $[A336][NO_3]$). LogD-log[CE] plots were constructed to investigate the extraction mechanism *via* slope analysis, *i.e.* the resulting slope gives an indication about the relation between extraction efficiency and the amount of extractant present. The increasing slope of Figure S4 denotes an increasing extraction efficiency with increasing crown ether concentration. A slope close to unity was obtained for Sr^{2+} (nitrate: 1.02, chloride: 0.82) and Eu^{2+} (nitrate: 0.72, chloride: 0.67), *i.e.* one crown ether molecule (DCH18C6) interacts with one metal ion (Sr^{2+} or Eu^{2+}).

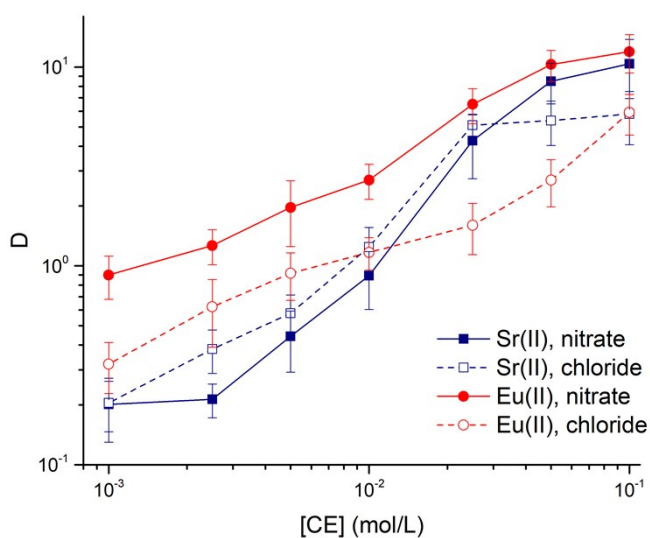


Figure S4: Distribution ratios of Sr^{2+} (dark blue, squares) and Eu^{2+} (red, circles) as a function of the DCH18C6 concentration in $[A336][NO_3]$. The aqueous feed solution consisted of 6 M LiX, with X being

nitrate (solid line, solid symbol) or chloride (dashed line, open symbol). Extraction parameters: O/A = 1, 60 °C, 15 min and 1700 rpm.

Samarium speciation in [A336][NO₃] by EXAFS

EXAFS measurement and data treatment

Extended X-ray Absorption Fine Structure (EXAFS) spectra of Sm L_{III}-edge (6716 eV) were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were done in transmission mode using Ar/He gas filled ionization chambers at ambient pressure. A brass sample holder with Kapton[®] windows and a flexible polymeric spacer (VITON[®]) with a thickness of 2 mm was used as a sample holder.

Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The EXAFS oscillations, isolated by a smoothing spline using the program VIPER, were k^4 -weighed and Fourier transformed between $k = 3.68$ and 11.13 \AA^{-1} using a Gaussian rounded ends window function (Figure S5, left).³ The data were fitted in $R + \Delta$ (\AA) space, between 0 and 2.78 \AA , using the *ab initio* code FEFF 7.0, which was used to calculate the theoretical phase and amplitude functions that were subsequently used in the non-linear least-squares refinement of the experimental data (Figure S5, right).⁴ Estimated standard deviations are shown between parentheses and calculated by VIPER. The amplitude reduction factor S_0 was fixed at 1.1.

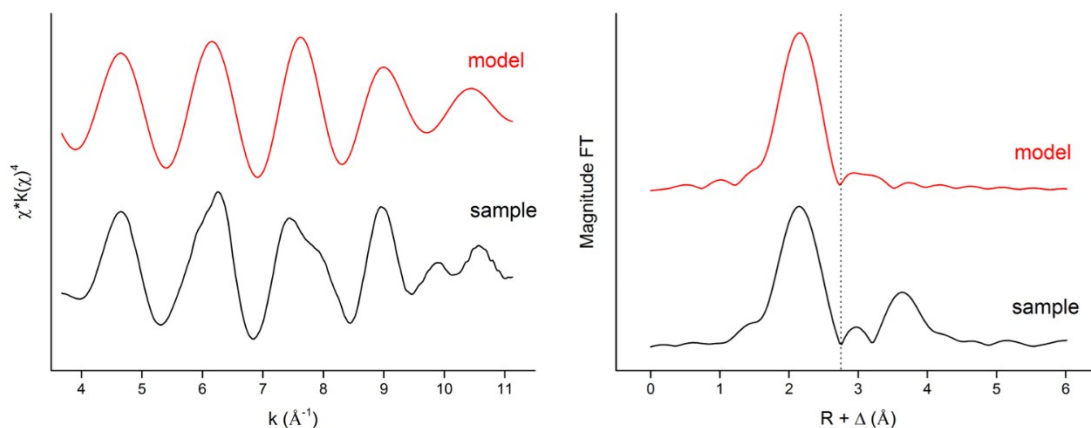


Figure S5: EXAFS function (left) and Fourier transform (right) of the $\text{Sm}(\text{NO}_3)_5$ complex extracted to $[\text{A336}][\text{NO}_3]$ and compared to the model.

Results and Discussion

Absorption spectra were recorded of the ionic liquid phase obtained after extraction of samarium from a 6 M nitrate solution to $[\text{A336}][\text{NO}_3]$. A bidentate nitrate coordinated to the Sm center was used as a model and the scattering paths Sm–O, between the Sm center and the coordinating oxygen atoms, and Sm–N were used as input for the fit. Only the first coordination shell in the Fourier transform was fitted since this provided the most accurate results on the Sm–O and Sm–N distances. The results of the Sm–O and Sm–N distances in the ionic liquid are shown in Table S1. The coordination number that was obtained from the fit was quite unreliable for two reasons. Firstly, the coordination number is highly dependent on the amplitude reduction factor S_0 , which cannot be estimated from the fit and should be chosen arbitrarily. Secondly, small changes in the extraction of the EXAFS function χ had a significant influence on the coordination number of the scattering paths. On the other hand, the coordination number can also be deduced from the Sm–O and Sm–N distances, which is much more reliable. A comparison was made with the interatomic distances found in crystal structures of $\text{Sm}(\text{NO}_3)_5$ and $\text{Sm}(\text{NO}_3)_6$ described in the literature (Table S2).^{5,6} The average Sm–O and Sm–N distances of $\text{Sm}(\text{NO}_3)_5$ corresponded best to the experimental data. Moreover, the Debye-Waller factors are expected to be higher in case a mixture of $[\text{Sm}(\text{NO}_3)_5]^{2-}$ and $[\text{Sm}(\text{NO}_3)_6]^{3-}$ would exist, as the Debye-Waller factor can be used as a

measure for the movement of the atoms in the complex. Therefore, it can be concluded that Sm is extracted to [A336][NO₃] as the pentanitrate complex, [Sm(NO₃)₅]²⁻, with bidentate nitrate ions.

Table S1: EXAFS fitting results of [Sm(NO₃)₅]²⁻ in [A336][NO₃]

Scattering path	N	r (Å)	σ ² (Å ²)
Sm–O	12.0(5)	2.515(9)	0.013(1)
Sm–N	6.0(5)	2.971(15)	0.015(3)

The data were Fourier transformed between $k = 3.68$ and 11.13 \AA^{-1} with a Gaussian rounded ends window function and fitted to the model between $R = 0$ and 2.78 \AA .

Table S2: Sm–O and Sm–N interatomic distances as determined by EXAFS analysis of the [Sm(NO₃)₅]²⁻ complex extracted to Aliquat nitrate and benzyltriethylammonium nitrate, compared to literature values

	$r_{\text{Sm-O}} (\text{Å})$	$r_{\text{Sm-N}} (\text{Å})$
[A336][NO ₃]	2.515(9)	2.971(15)
[Sm(NO ₃) ₅] ²⁻ (CN 10) ⁵	2.457 – 2.573 2.500 ^a	2.893 – 2.953 2.930 ^a
[Sm(NO ₃) ₆] ³⁻ (CN 12) ⁶	2.547 – 2.599 2.574 ^a	2.980 – 3.021 3.002 ^a

^aaverage interatomic distance in unit cell.

References

1. S. L. Garvey, C. A. Hawkins and M. L. Dietz, *Talanta*, 2012, **95**, 25-30.
2. M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, **20**, 2124-2125.
3. K. V. Klementev, *J. Phys. D Appl. Phys.*, 2001, **34**, 2241-2247

4. M. Newville, *J. Synchrotron Radiat.*, 2001, **8**, 96-100.
5. H. Cui, T. Otsuka, A. Kobayashi, N. Takeda, M. Ishikawa, Y. Misaki and H. Kobayashi, *Inorg. Chem.*, 2003, **42**, 6114-6122.
6. N. Tang, Y. Zhao, L. He, W.-L. Yuan and G.-H. Tao, *Dalton Trans.*, 2015, **44**, 8816-8823.