Electronic Supplementary Material (ESI) for RSC Advances.

Speciation of Lanthanide Ions in the Organic Phase after Extraction from Nitrate Media by Basic Extractants

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Supplementary information

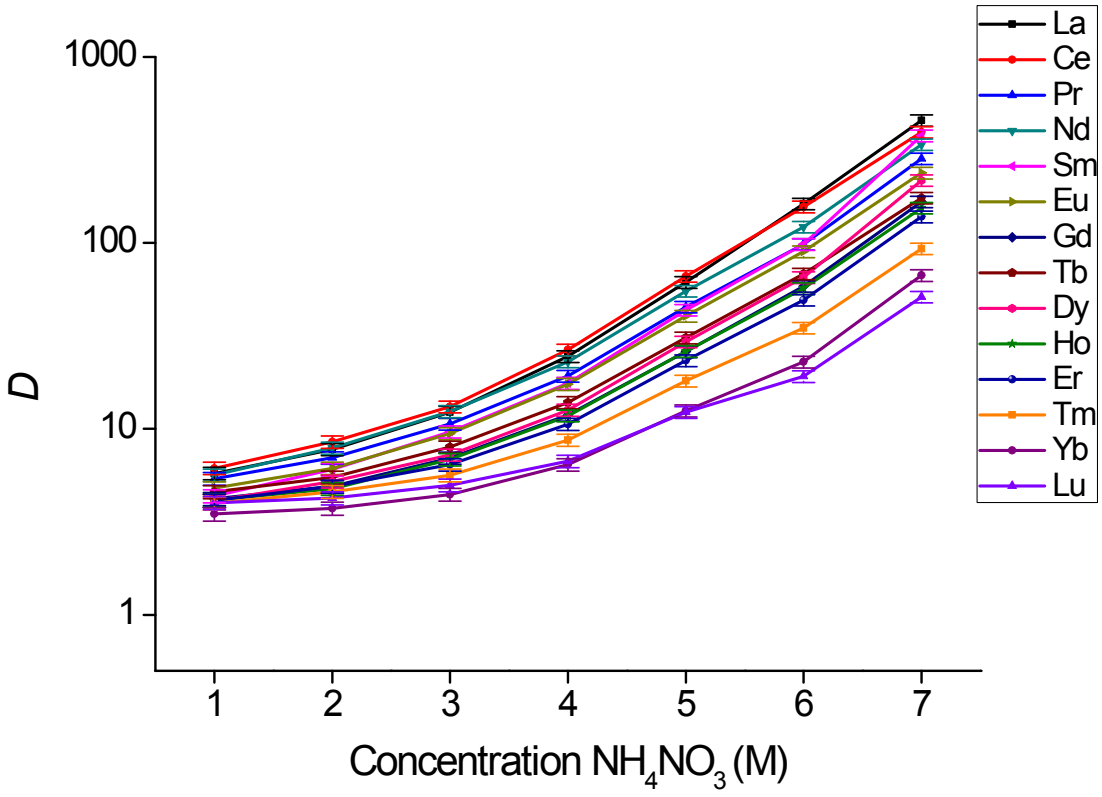

Figure S1: Distribution ratio *D* for the extraction of lanthanide ions with trihexyl(tetradecyl)phosphonium nitrate as a function of the concentration of NH_4NO_3 in the aqueous phase. $[Ln^{3+}]_{aq,in}$ = 0.01 mol L^{-1}.

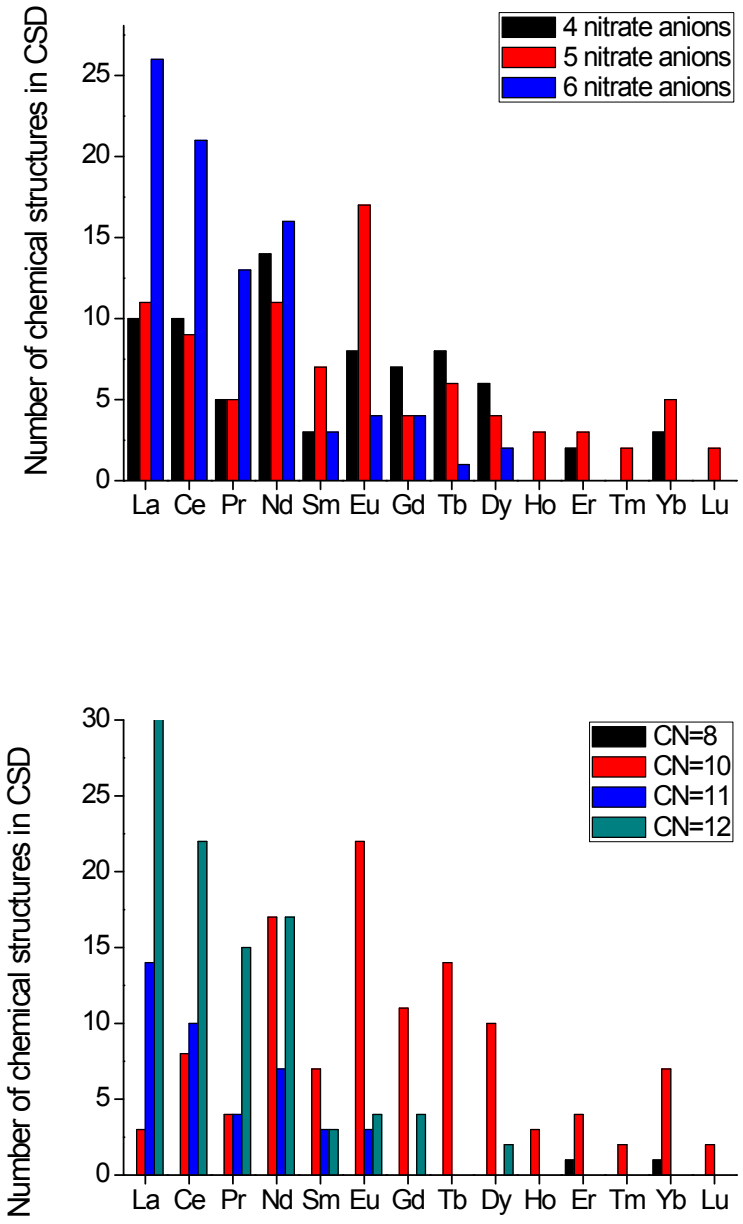

Figure S2: Systematic overview of the number of crystal structures of trivalent lanthanide complexes in the Cambridge Structural Database with (a) 4, 5 or 6 coordinating bidentate nitrate ligands, and (b) with a coordination number (CN) of 8, 10, 11 or 12.

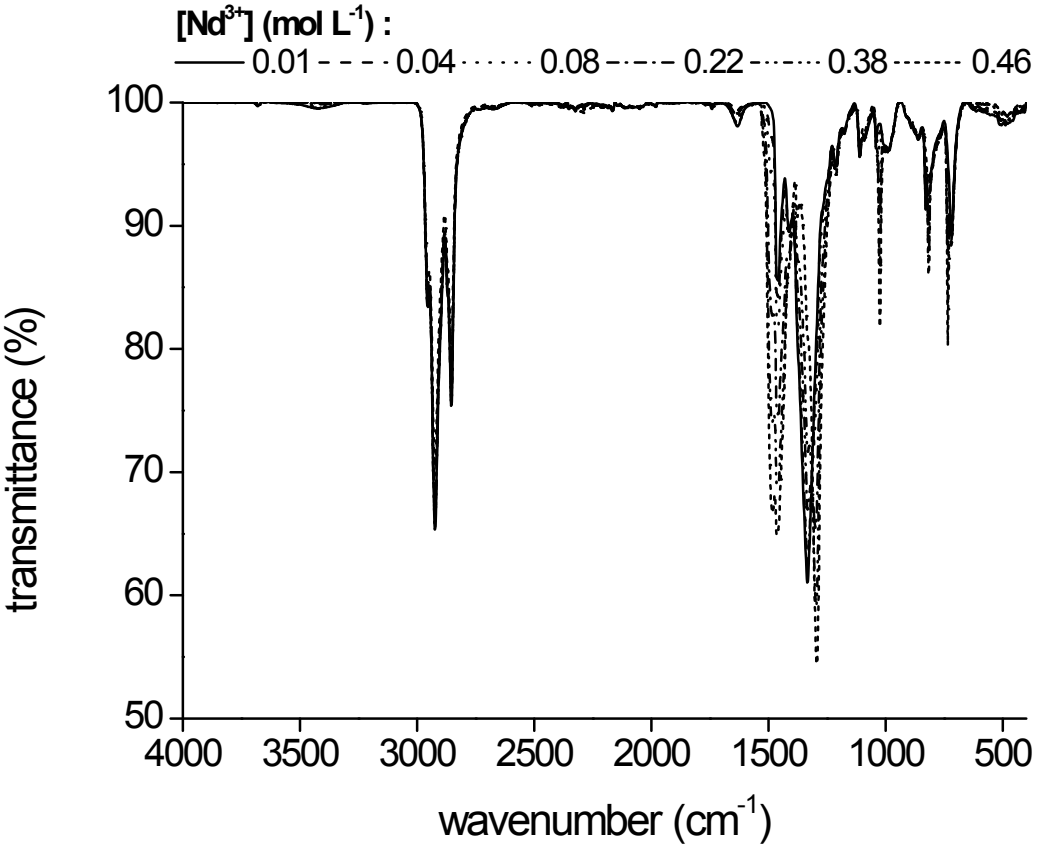

Figure S3. FTIR spectra of the trihexyl(tetradecyl)phosphonium nitrate phase after extraction of increasing concentrations of Nd^{3+} from nitrate solution.

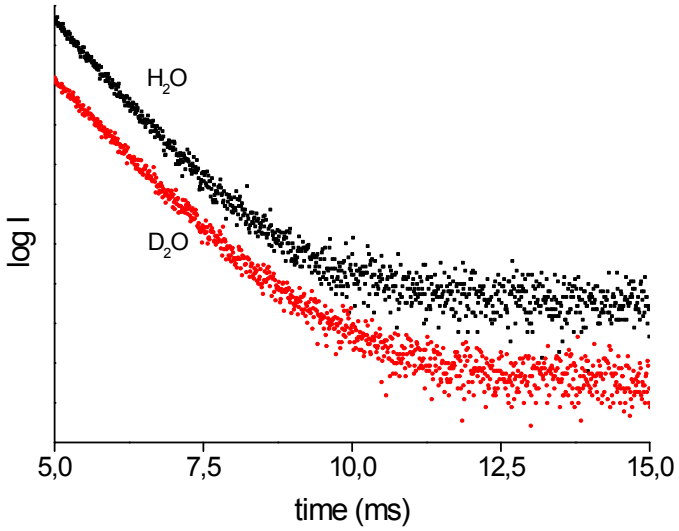

Figure S4. Luminescence decay curves of Eu^{3+} (0.05 mol L^{-1}) extracted to trihexyl(tetradecyl)phosphonium nitrate in H_2O and D_2O.

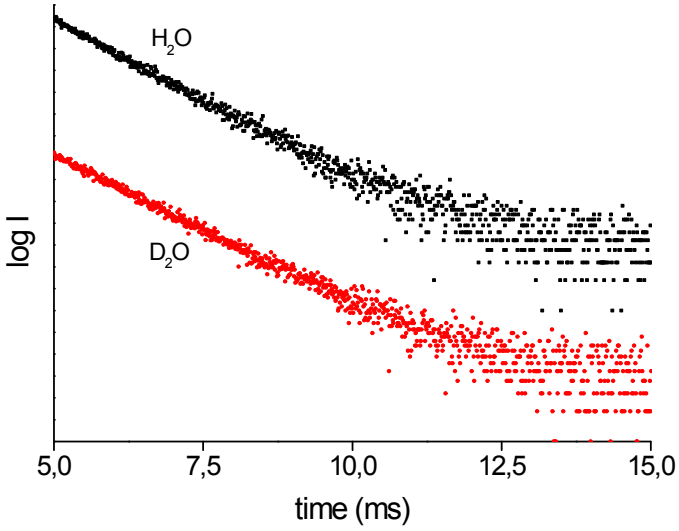

Figure S5. Luminescence decay curves of Tb^{3+} (0.05 mol L^{-1}) extracted to trihexyl(tetradecyl)phosphonium nitrate in H_2O and D_2O.

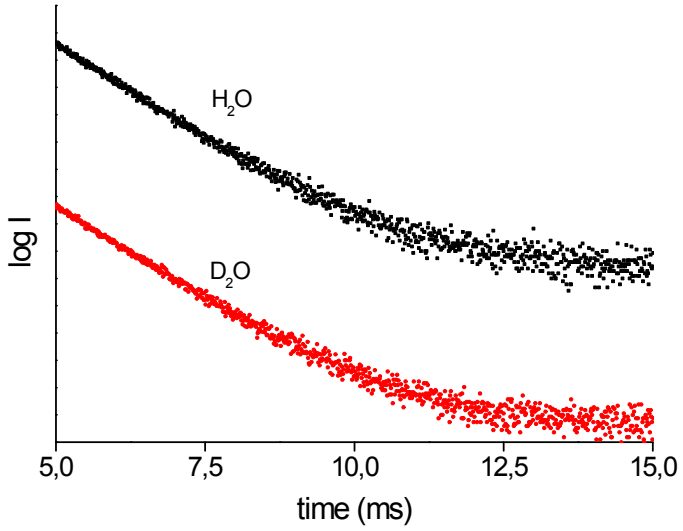

Figure S6: Luminescence decay curves of Tb^{3+} (0.5 mol L^{-1}) extracted to trihexyl(tetradecyl)phosphonium nitrate in H_2O and D_2O.

Table S1. Elemental analysis of trihexyl(tetradecyl)phosphonium nitrate, after full loading by extraction of various lanthanides from a 3.5 M $Ca(NO_3)_2$ solution (4:1 A/O phase ratio, $[Ln^{3+}]_{aq,in}$ = 0.5 mol L^{-1}).

	theoretical $[P_{66614}]_2[Ln(NO_3)_5]$					theoretical $[P_{66614}]_3[Ln(NO_3)_6]$					experimental				
	C	H	N	P/Ln	$[Ln]_{org}$	C	H	N	P/Ln	$[Ln]_{org}$	C	H	N	P/Ln	$[Ln]_{org}$
	wt%	wt%	wt%		mol kg^{-1}	wt%	wt%	wt%		mol kg^{-1}	wt%	wt%	wt%		mol·kg^{-1}
La	54.26	9.68	4.94	2	0.71	58.75	10.48	4.28	3	0.51	56.86	9.76	4.45	2.7	0.527 ± 0.005
Pr	54.18	9.66	4.94	2	0.70	58.69	10.47	4.28	3	0.51	55.53	9.85	4.55	2.3	0.593 ± 0.007
Nd	54.06	9.64	4.93	2	0.70	58.59	10.45	4.27	3	0.51	55.86	9.89	4.61	2.1	0.650 ± 0.011
Eu	53.77	9.59	4.9	2	0.70	58.37	10.41	4.25	3	0.51	54.54	9.48	4.80	1.9	0.616 ± 0.008
Ho	53.28	9.50	4.85	2	0.69	57.98	10.34	4.23	3	0.50	54.04	9.58	4.49	2.2	0.688 ± 0.011
Er	53.20	9.49	4.85	2	0.69	57.92	10.33	4.22	3	0.50	53.76	9.54	4.78	1.7	0.789 ± 0.022
Lu	52.91	9.44	4.82	2	0.69	57.69	10.29	4.20	3	0.50	55.58	9.84	4.47	1.8	0.758 ± 0.003

Table S2. EXAFS fitting results of the $[Ln(NO_3)_5]^{2-}$ complex extracted to the organic phase.

	Ln-O_c			Ln-N		
	N	r (Å)	σ^2 (Å^2)	N	r (Å)	σ^2 (Å^2)
La*	11.6(10)	2.606(11)	0.013(1)	5.8(1.0)	3.044(11)	0.010(2)
Ce*	9.9(6)	2.549(8)	0.011(1)	4.9(6)	2.988(6)	0.007(1)
Nd	11.7(10)	2.544(14)	0.012(2)	5.8(1.0)	3.008(31)	0.016(6)
Sm	12.6(3)	2.504(4)	0.013(1)	6.3(3)	2.939(8)	0.011(1)
Eu	12.3(13)	2.500(10)	0.012(1)	6.1(1.3)	2.939(15)	0.013(2)
Gd	10.8(9)	2.472(6)	0.012(1)	5.4(9)	2.928(8)	0.009(1)
Tb	10.0(9)	2.454(7)	0.011(1)	5.0(9)	2.911(9)	0.008(1)
Dy	9.9(9)	2.433(7)	0.010(1)	5.0(9)	2.897(8)	0.007(1)
Ho	10.1(9)	2.431(7)	0.012(1)	5.0(9)	2.885(8)	0.008(1)
Er	9.8(9)	2.432(7)	0.011(1)	4.9(9)	2.889(8)	0.008(1)
Tm	9.8(9)	2.401(7)	0.011(1)	4.9(9)	2.861(8)	0.007(1)
Yb	10.0(6)	2.389(8)	0.011(1)	5.0(6)	2.853(8)	0.007(1)
Lu	10.1(3)	2.382(6)	0.011(1)	5.0(3)	2.850(7)	0.007(1)

* recorded on the K-line

Table S3. Comparison between the experimental Ln-O_c and Ln-N distances and literature data of $Ln(NO_3)_5^{2-}$ and $Ln(NO_3)_6^{3-}$ crystal structures.

	Ln-O_c					Ln-N					Ref.
	EXAFS	Literature $Ln(NO_3)_5^{2-}$		Literature $Ln(NO_3)_6^{3-}$		r (Å)	Literature $Ln(NO_3)_5^{2-}$		Literature $Ln(NO_3)_6^{3-}$		
		average	stdev	average	stdev		average	stdev	average	stdev	
La*	2.606(11)	*n.a.*	*n.a.*	2.654	0.015	3.044(11)	*n.a.*	*n.a.*	3.028	0.022	[1]
Ce*	2.549(8)	2.565	0.015	2.636	0.023	2.988(6)	2.972	0.026	3.060	0.008	[2-3]
Nd	2.544(14)	2.537	0.028	2.613	0.024	3.008(31)	3.023	0.095	3.029	0.010	[4-5]
Sm	2.504(4)	2.500	0.033	2.580	0.027	2.939(8)	2.930	0.027	3.002	0.014	[5-6]
Eu	2.500(10)	2.481	0.031	2.593	0.018	2.939(15)	2.929	0.011	3.008	0.000	[7-8]
Gd	2.472(6)	2.467	0.033	2.565	0.026	2.928(8)	2.882	0.022	2.987	0.015	[9-10]
Tb	2.454(7)	2.448	0.034	2.558	0.029	2.911(9)	2.878	0.021	2.978	0.014	[11-12]
Dy	2.433(7)	2.437	0.037	2.548	0.008	2.897(8)	2.867	0.027	2.971	0.000	[11 13]
Ho	2.431(7)	2.434	0.030	*n.a.*	*n.a.*	2.885(8)	2.880	0.014	*n.a.*	*n.a.*	[5]
Er	2.432(7)	2.416	0.034	*n.a.*	*n.a.*	2.889(8)	2.865	0.022	*n.a.*	*n.a.*	[5]
Tm	2.401(7)	2.405	0.046	*n.a.*	*n.a.*	2.861(8)	2.822	0.020	*n.a.*	*n.a.*	[5]
Yb	2.389(8)	2.399	0.032	*n.a.*	*n.a.*	2.853(8)	2.868	0.028	*n.a.*	*n.a.*	[5]
Lu	2.382(6)	2.370	0.042	*n.a.*	*n.a.*	2.850(7)	2.813	0.041	*n.a.*	*n.a.*	[5]

* recorded on the K-line

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