Extraction and speciation studies of new diglycolamides for selective recovery of americium by solvent extraction

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Electronic Supplementary Information (ESI)

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S1. Synthesis and characterization of unsymmetrical diglycolamide extractants

General procedure of the synthesis

1 eq of diglycolic anhydride was reacted with 1 eq of didodecylamine in dry Me-THF. The reaction mixture was kept under N_2 atmosphere and was stirred at room temperature for 15 hours. Then, 1.2 eq of the coupling agent (1-Cyano-2-ethoxy-2-oxoethylideneaminooxy)di-methylamino-morpholino-carbenium hexafluorophosphate (COMU) and 2 eq of *N,N*-diisopropylethylamine (DIPEA) were added and the mixture was stirred for another 15 minutes. Finally, 1.1 eq of the second diamine were added, and the mixture was stirred for another 15 hours. The reaction mixture was then quenched with 50/50 water/ethyl acetate mixture. This was further washed with water, 10 wt% HCl solution, and saturated potassium carbonate solution. Finally, the organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated under vacuum.

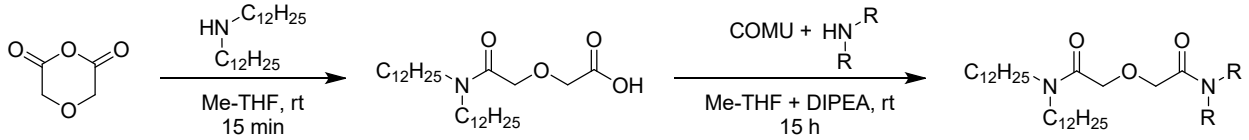

Figure S1: Reaction scheme for the synthesis of UDGAs with COMU

The main side product found was *N,N,N',N'*-tetradodecyldiglycolamide. Purification of the unsymmetrical diglycolamide was done by flash chromatography. The column was packed with 0.030−0.200 mm, 60 Å, silica gel. The column was eluted with a mixture of 30-40% ethyl acetate in heptane (concentration depending on the compound being purified). Fractions of ca. 15 mL were collected and analyzed with TLC. The pure fractions were collected together and evaporated yielding a viscous, yellowish oil in all cases.

NMR spectra were recorded on a Bruker Avance III HD 400 NMR spectrometer.

HPLC was performed on a C18 column with a temperature of 50 °C. The more polar solvent consisted of H_2O containing 0.1% of hydrogen fluoride, and the less polar solvent consisted of isoproanol (iPrOH) with 3% 1-octanol. The column was conditioned with a 50/50 H_2O solvent/iPrOH solvent solution. 5 µL of sample was injected at a flow rate of 0.2 mL/min. The gradient was varied between 50/50 and 20/80 H_2O solvent/iPrOH solvent. The measurement time was 50 minutes.

***N,N*-dipropyl-*N',N'*-didodecyldiglycolamide (PDdDGA)**

Yield: 33%

FTIR: ν_{max}/cm^{-1} 1659 (C=O), 1466 and 1377 (C-N), 1122 (C-O-C)

HRMS (ESI-Q-TOF): m/z $[M + H]^+$ calcd. for $C_{34}H_{69}N_2O_3$: 553.5303 found: 553.5297

^{1}H NMR ($CDCl_3$):

δ 4.31 (s, 2 H), 4.30 (s, 2 H), 3.28 (q, J = 7.4Hz, 4H), 3.17 (t, J = 7.7 Hz, 4H), 1.57 (m, 4H), 1.51 (m, 4H), 1.26 (m, 36H), 0.89 (m, 12H)

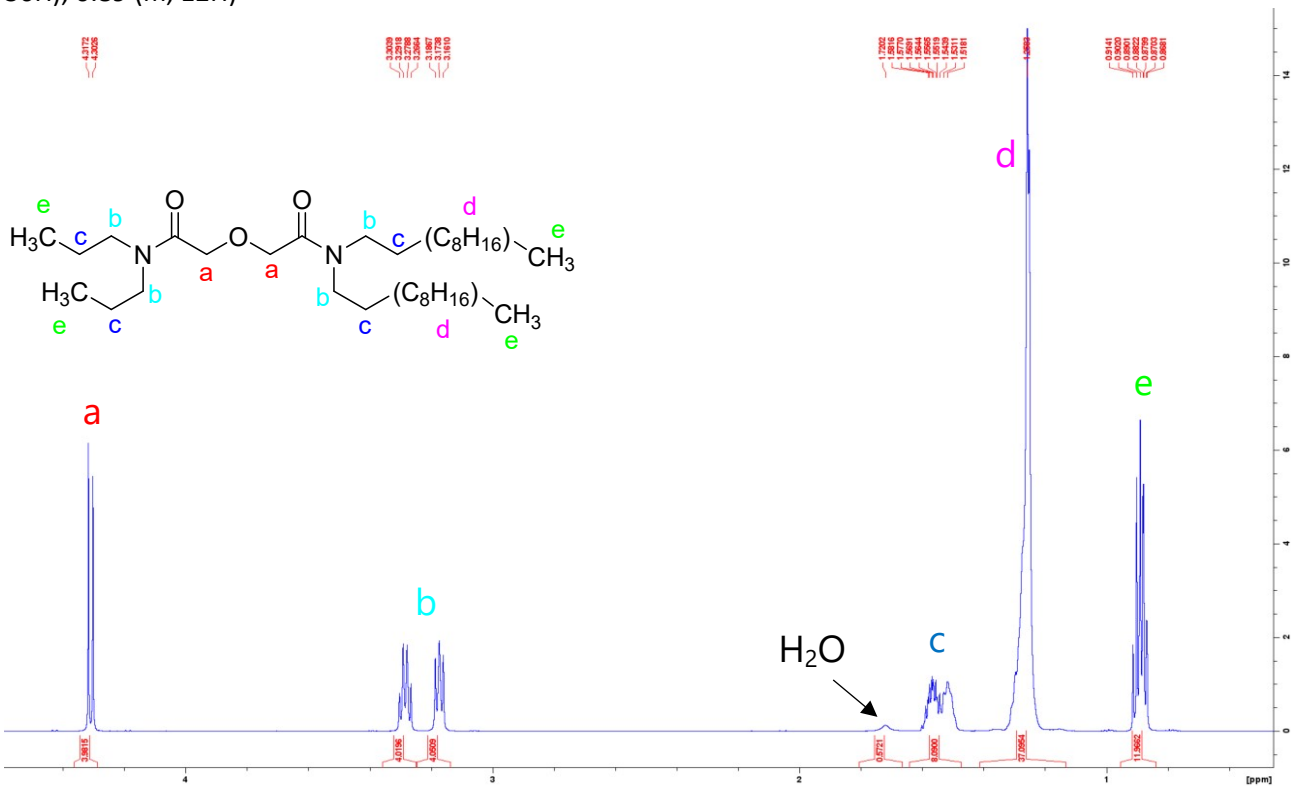

Figure S2: ^{1}H NMR spectrum of N,N-dipropyl-N',N'-didodecyldiglycolamide.

^{13}C NMR ($CDCl_3$):

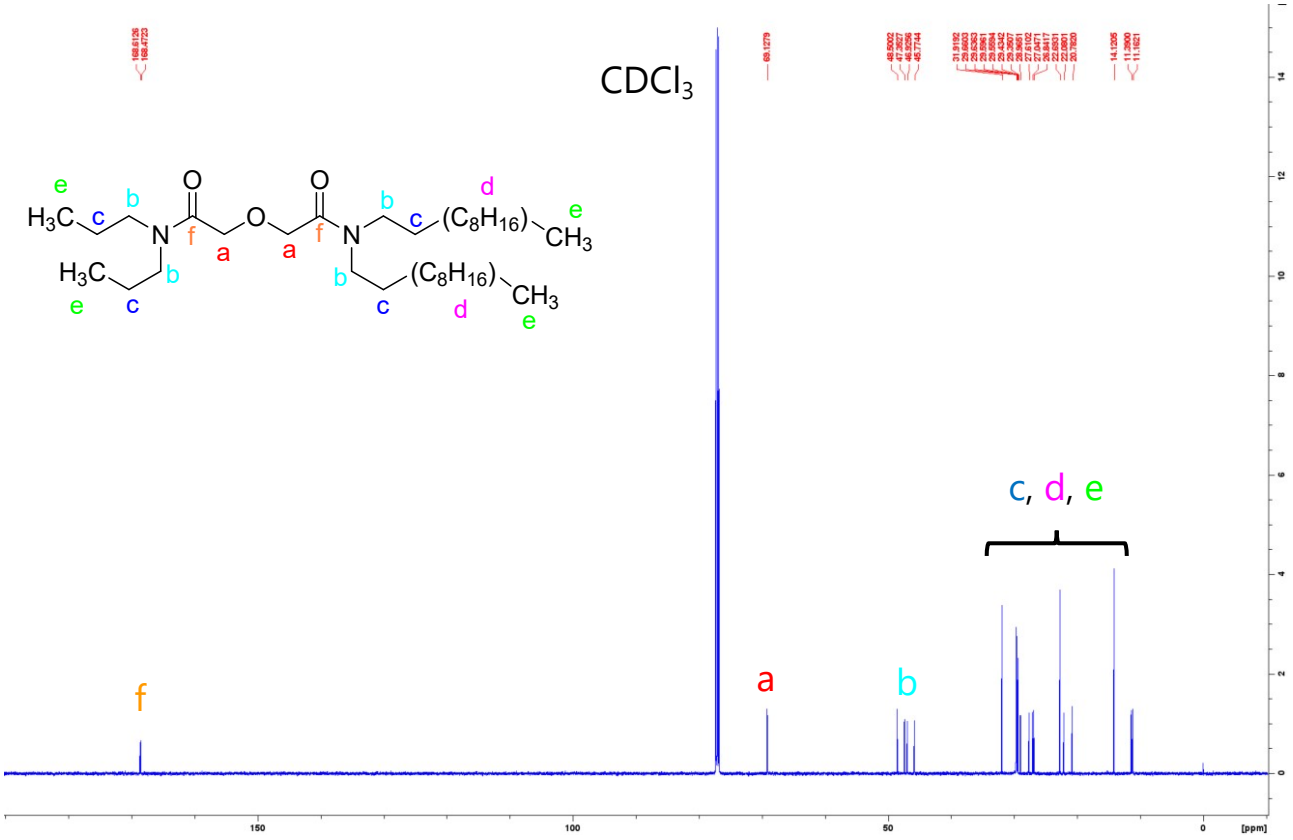

Figure S3: ^{13}C NMR spectrum of N,N-dipropyl-N',N'-didodecyldiglycolamide.

HPLC:

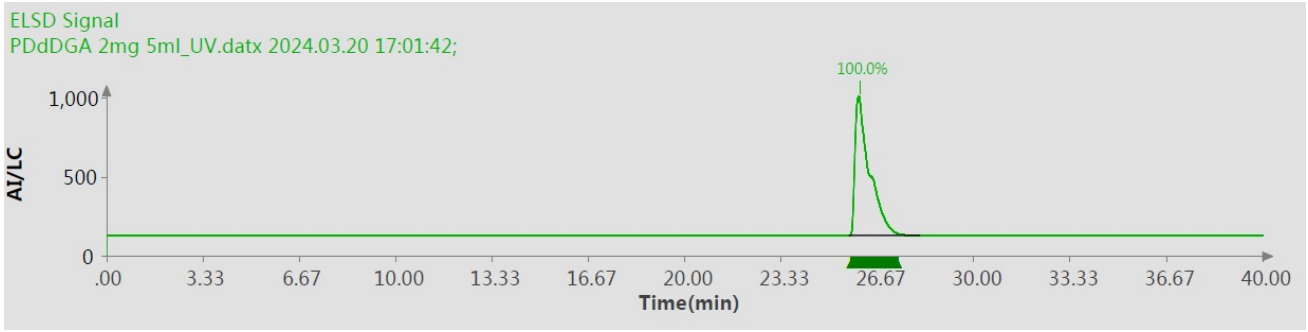

Figure S4: HPLC chromatogram of N,N-dipropyl-N',N'-didodecyldiglycolamide.

***N,N*-dibutyl-*N',N'*-didodecyldiglycolamide (BDdDGA)**

Yield: 27%

FTIR: ν_{max}/cm^{-1} 1655 (C=O), 1466 and 1377 (C-N), 1124 (C-O-C)

HRMS (ESI-Q-TOF): m/z $[M + H]^+$ calcd. for $C_{36}H_{73}N_2O_3$: 581.5616 found: 581.5618

^{1}H NMR ($CDCl_3$):
δ 4.31 (s, 2 H), 4.30 (s, 2 H), 3.30 (m, 4H), 3.18 (q, J = 7.7 Hz, 4H), 1.51 (m, 8H), 1.26 (m, 42H), 0.93 (q, J = 7.2 Hz, 6H), 0.88 (t, J = 6.9 Hz, 6H)

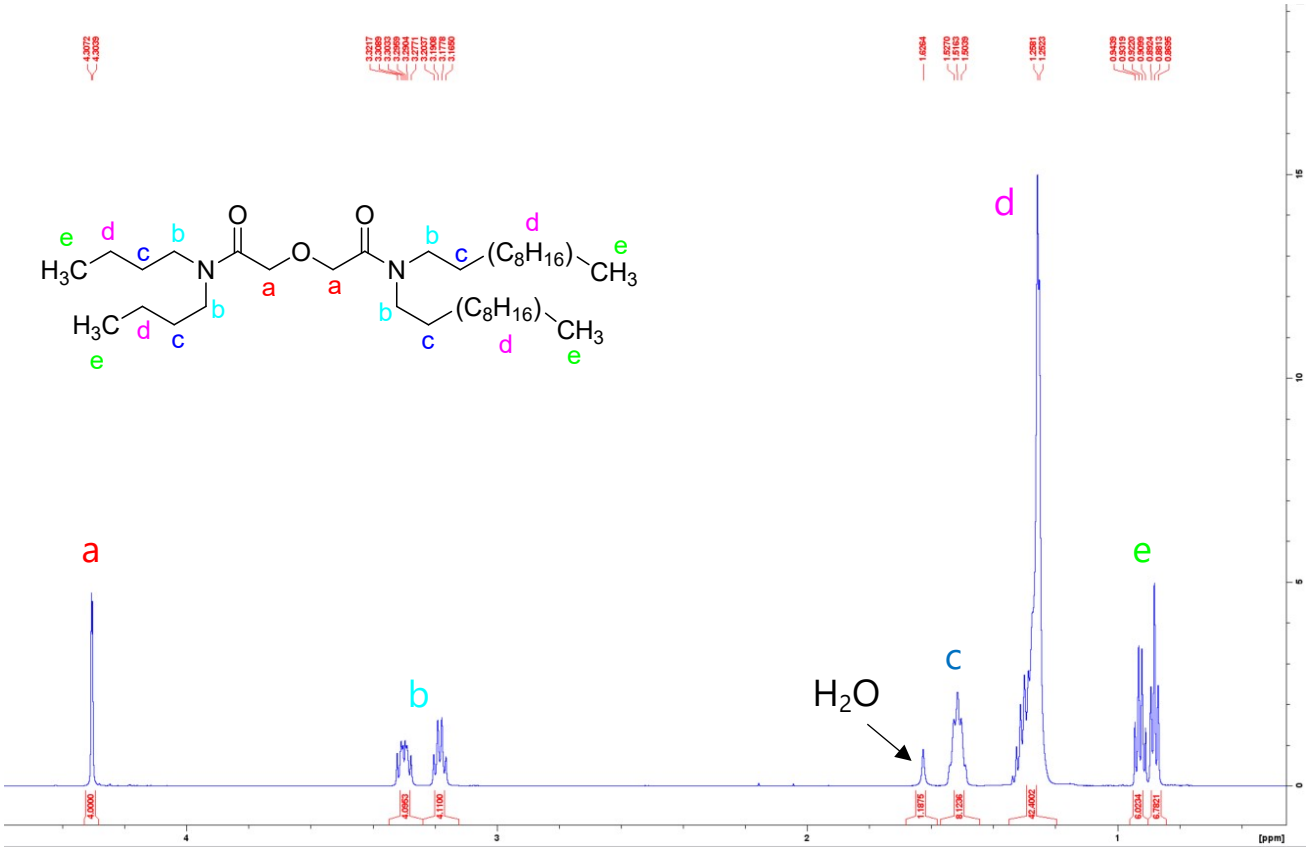

Figure S5: ^{1}H NMR spectrum of N,N-dibutyl-N',N'-didodecyldiglycolamide.

^{13}C NMR ($CDCl_3$):

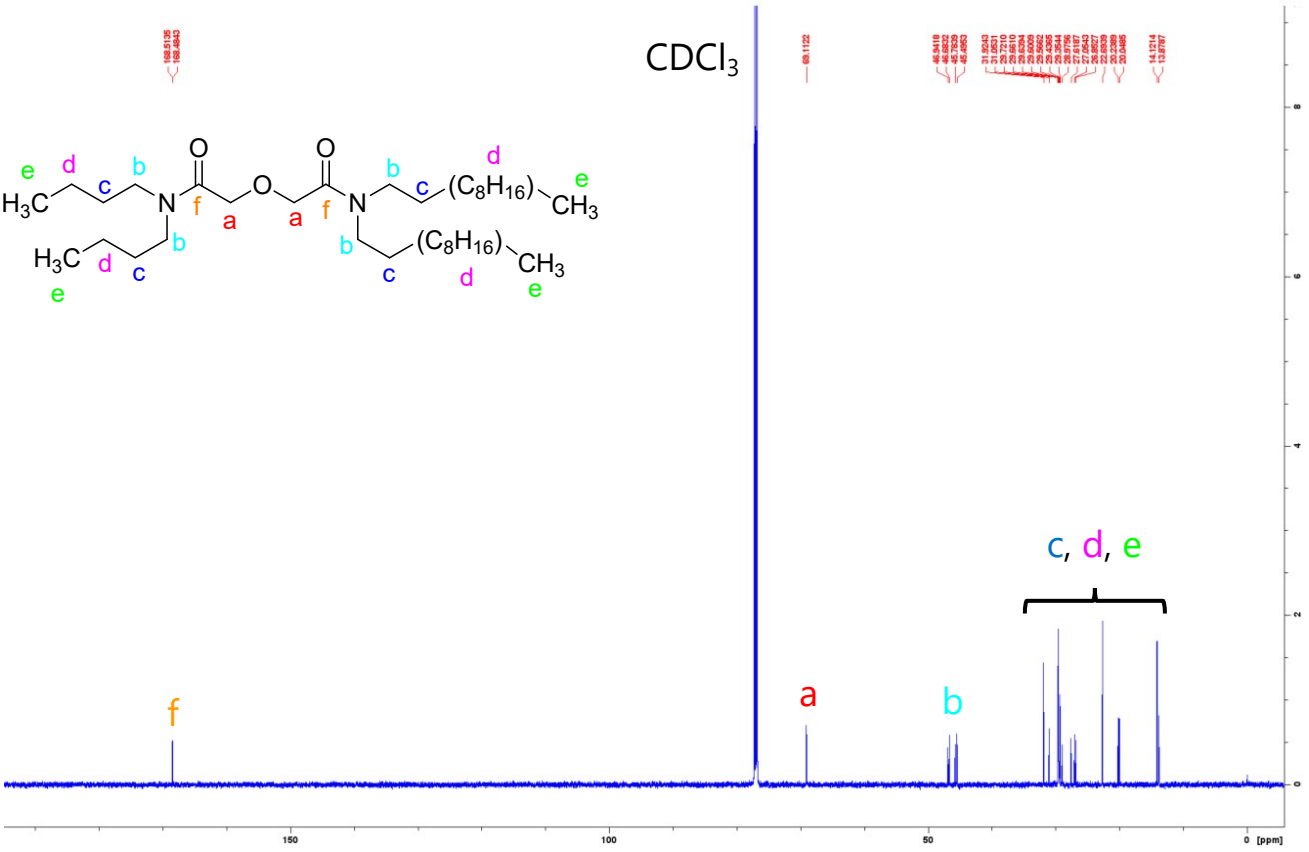

Figure S6: ^{12}C NMR spectrum of N,N-dibutyl-N',N'-didodecyldiglycolamide.

HPLC:

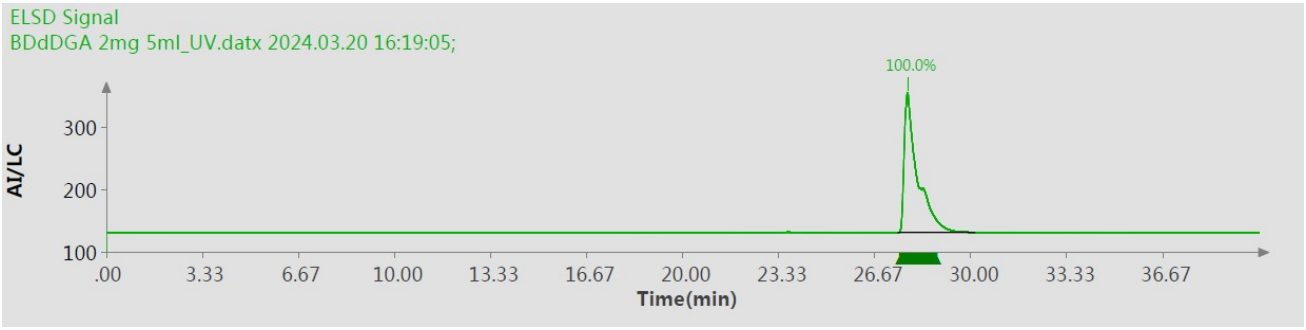

Figure S7: HPLC chromatogram of N,N-dibutyl-N',N'-didodecyldiglycolamide.

***N,N*-diisobutyl-*N',N'*-didodecyldiglycolamide (iBDdDGA)**

Yield: 38%

FTIR: ν_{max}/cm^{-1} 1659 (C=O), 1466 and 1379 (C-N), 1120 (C-O-C)

HRMS (ESI-Q-TOF): m/z $[M + H]^+$ calcd. for $C_{36}H_{73}N_2O_3$: 581.5616 found: 581.5616

^{1}H NMR ($CDCl_3$):
δ 4.35 (s, 2 H), 4.30 (s, 2 H), 3.22 (dt, J = 7.7 Hz, 4H), 3.12 (dd, J = 7.6 Hz, 4H), 1.97 (dm, J = 6.9 Hz, 2H), 1.51 (m, 4H), 1.26 (m, 36H), 0.88 (m, 18H)

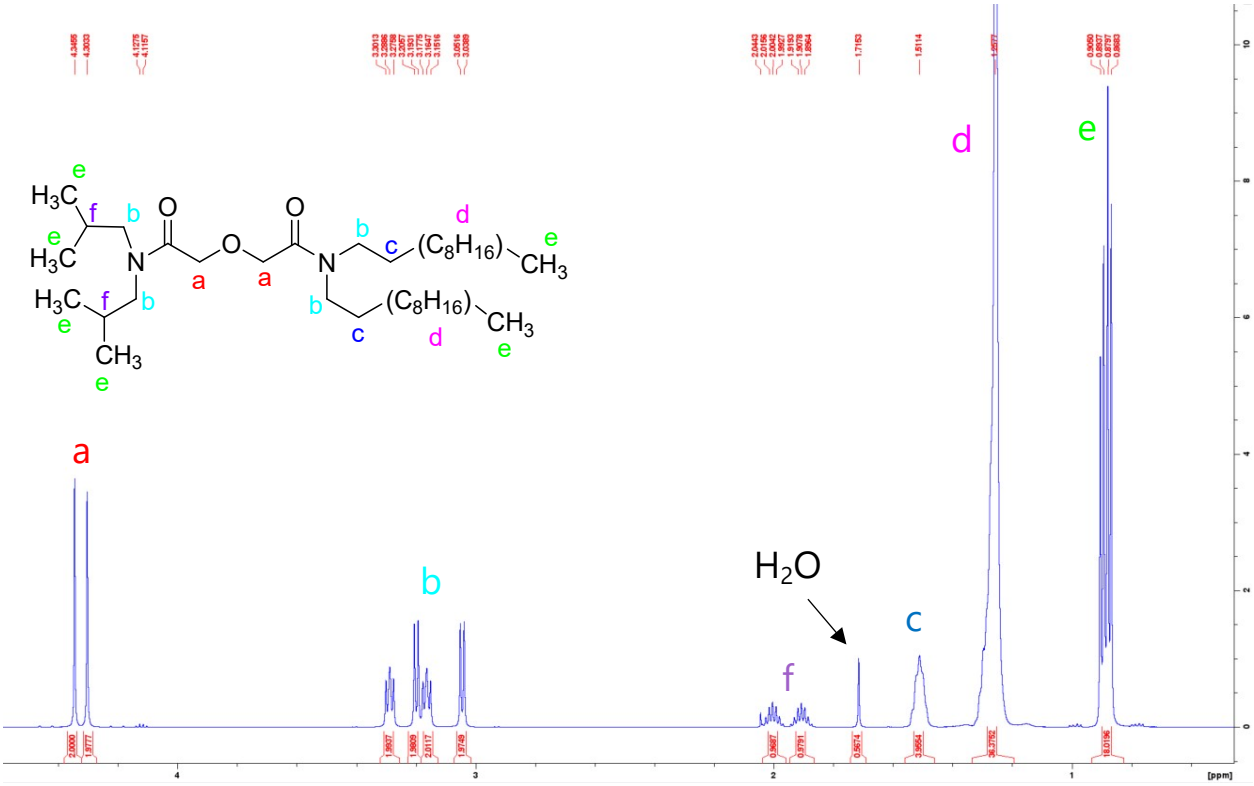

Figure S8: ^{1}H NMR spectrum of N,N-diisobutyl-N',N'-didodecyldiglycolamide.

^{13}C NMR ($CDCl_3$):

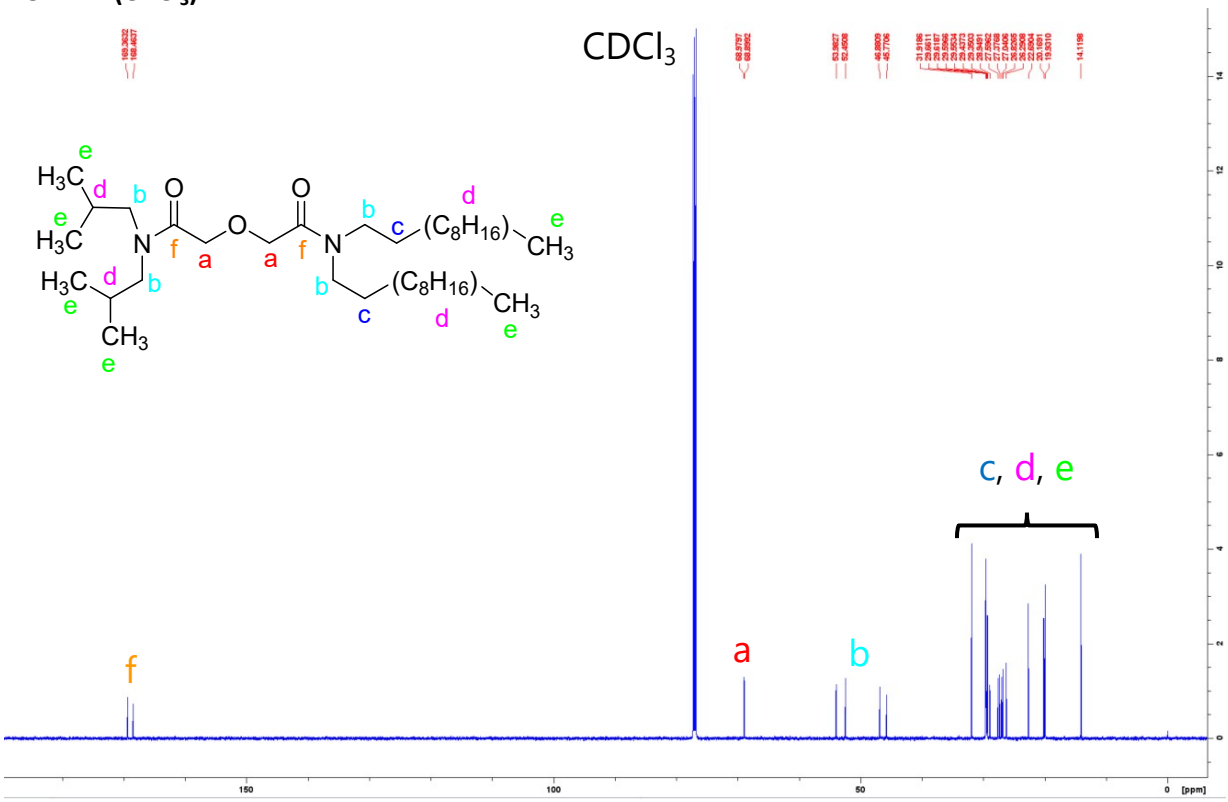

Figure S9: ^{13}C NMR spectrum of N,N-diisobutyl-N',N'-didodecyldiglycolamide.

HPLC:

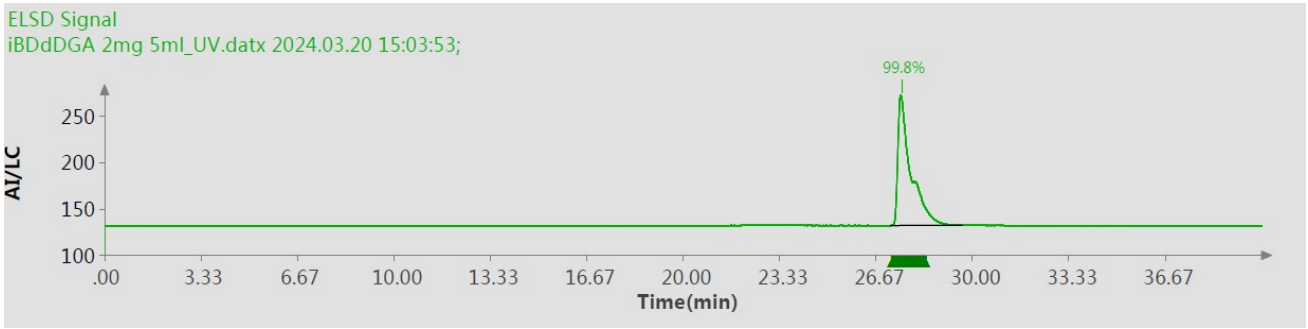

Figure S10: HPLC chromatogram of N,N-diisobutyl-N',N'-didodecyldiglycolamide.

***N,N*-dipentyl-*N',N'*-didodecyldiglycolamide (PnDdDGA)**

Yield: 25%

FTIR: ν_{max}/cm^{-1} 1657 (C=O), 1466 and 1377 (C-N), 1124 (C-O-C)

HRMS (ESI-Q-TOF): m/z $[M + Na]^+$ calcd. for $C_{38}H_{76}N_2NaO_3$: 631.5748 found: 631.5750

^{1}H NMR ($CDCl_3$):
δ 4.31 (m, 4 H), 3.29 (m, 4H), 3.16 (m, 4H), 1.52 (m, 8H), 1.26 (m, 46H), 0.88 (m, 12H)

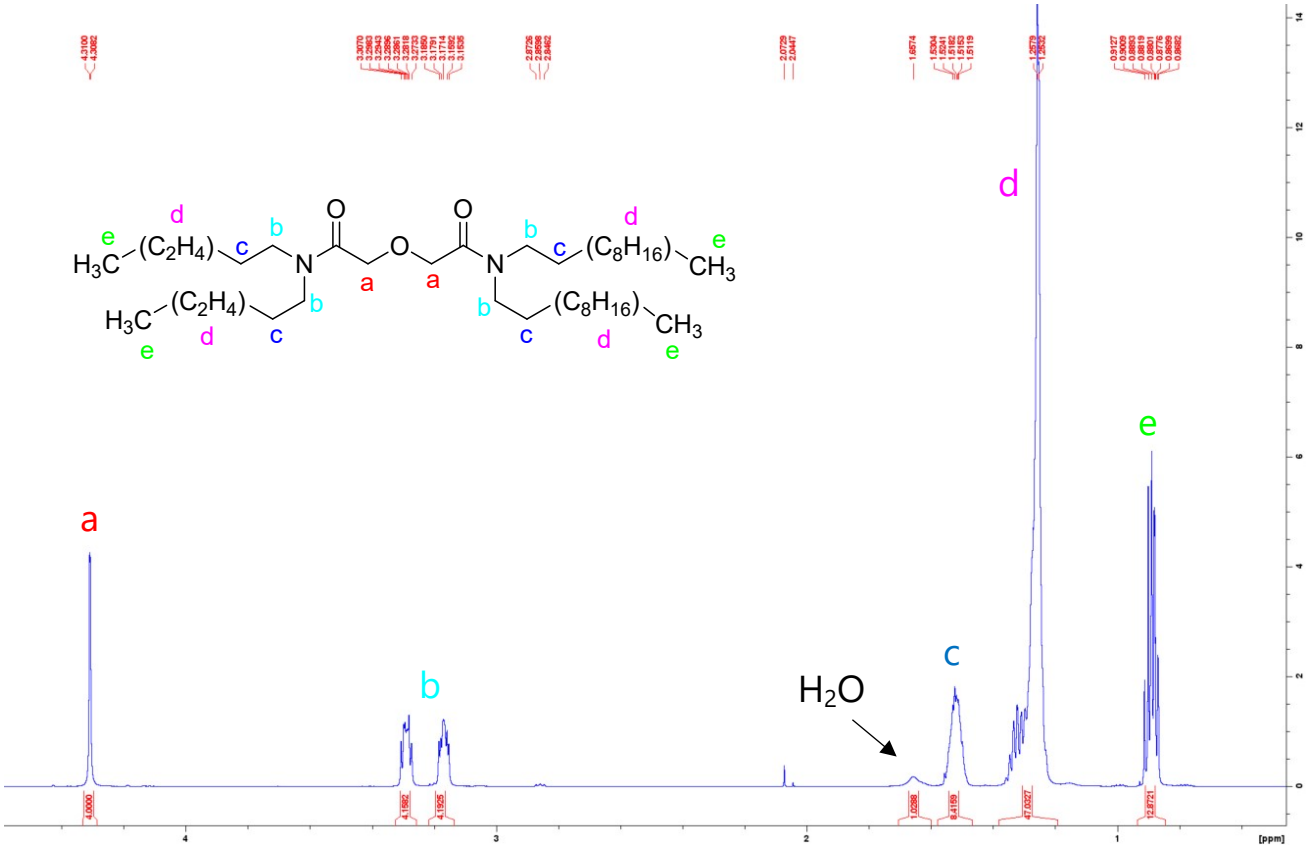

Figure S11: [1]H NMR spectrum of N,N-dipentyl-N',N'-didodecyldiglycolamide.

[13]C NMR ($CDCl_3$):

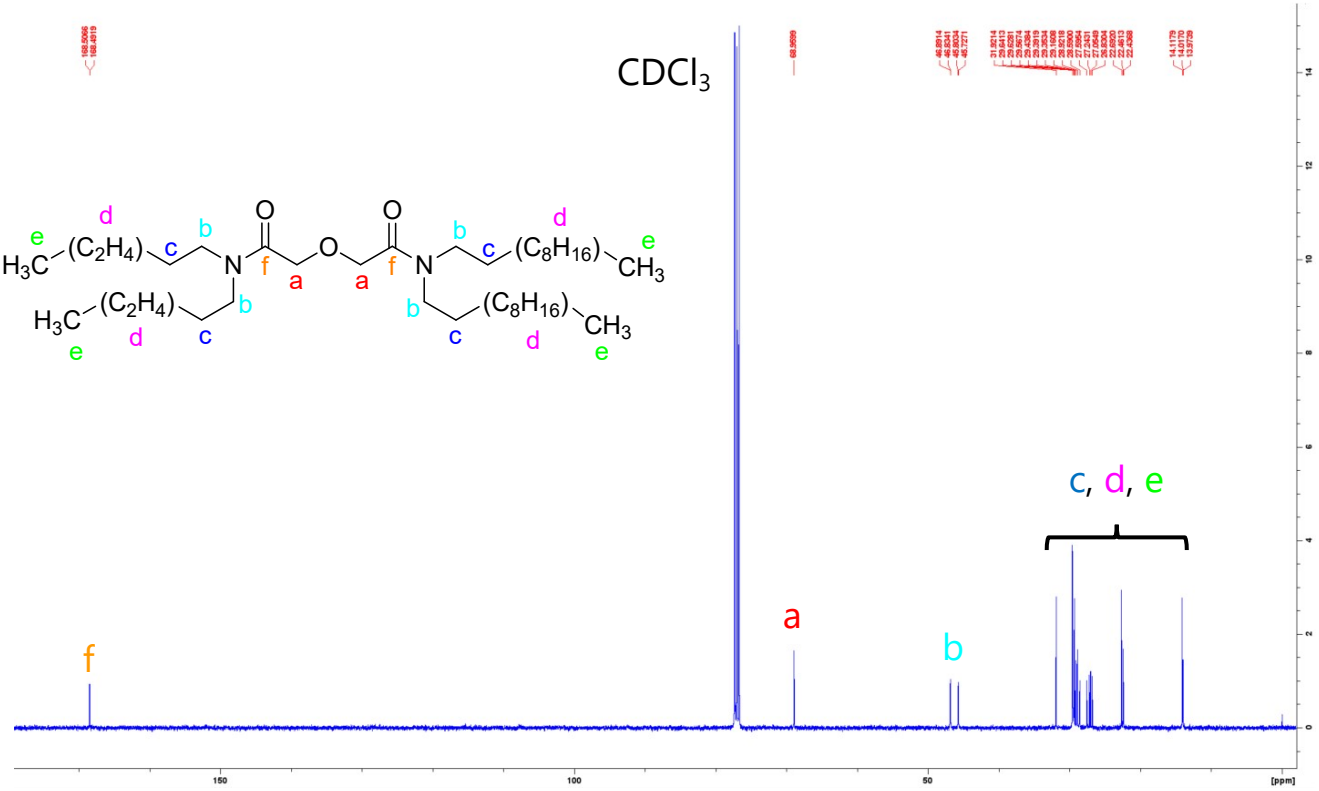

Figure S12: [13]C NMR spectrum of N,N-dipentyl-N',N'-didodecyldiglycolamide.

HPLC:

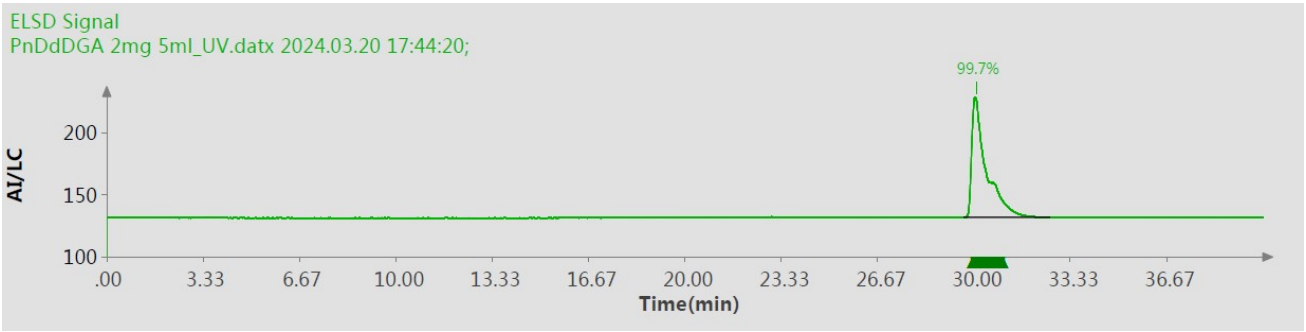

Figure S13: HPLC chromatogram of N,N-dipentyl-N',N'-didodecyldiglycolamide.

S2. Titration data of extraction experiments

To better understand the extraction of acid by the different DGA extractants, the aqueous and organic phases were titrated to measure the equilibrium acid concentration. Potentiometric titrations were performed with a Metrohm 905 Titrando autotitrator. The used titrant was 0.1 mol·L^{-1} NaOH solution. Both aqueous and organic phases were diluted with a 0.1 mol·L^{-1} sodium oxalate solution to complex the lanthanide ions and to avoid hydrolysis during titration. Additionally, Triton X-100 was added as a surfactant to organic dilutions to improve the transfer of HNO_3 to the aqueous phase. The results are reported below.

Table S1: Titration data of aqueous and organic phases after extraction.

DGA	Equilibrium Acid concentration Aqueous phase (M)	Equilibrium Acid concentration Organic phase (M)
TODGA[1]	2.96	0.28
PnDdDGA[1]	2.99	0.31
iBDdDGA[1]	2.99	0.32
BDdDGA[1]	3.00	0.26
PDdDGA[1]	2.97	0.25
iPDdDGA[1]	2.92	0.36
pipDdDGA[1]	2.98	0.25

Table S2: Titration data of aqueous and organic phases after stripping.

DGA	Acid concentration Aqueous phase (M)	Acid concentration Organic phase (M)
TODGA[2]	x	0.19
PnDdDGA[2]	0.54	0.17
iBDdDGA[2]	0.55	0.19
BDdDGA[2]	x	0.20
PDdDGA[2]	0.56	0.23
iPDdDGA[2]	x	0.26
pipDdDGA[2]	x	0.25

[1] Initial conditions: Aqueous phase: 18 mmol·L^{-1} Ln(III) + 50 kBq·mL^{-1} of ^{152}Eu, ^{241}Am, and ^{244}Cm each dissolved in 3 mol·L^{-1} HNO_3 solution. Organic phase: 0.1 mol·L^{-1} diglycolamide extractant dissolved in n-dodecane + 5 vol% 1-octanol.
[2] Initial conditions: Organic phase: 0.1 mol·L^{-1} diglycolamide extractant dissolved in n-dodecane + 5 vol% 1-octanol. Loaded from a solution containing 18 mmol·L^{-1} Ln(III) + 50 kBq·mL^{-1} of ^{152}Eu, ^{241}Am, and ^{244}Cm dissolved in 3 mol·L^{-1} HNO_3 solution. Aqueous phase: 10 mmol·L^{-1} SO_3-Ph-BTBP dissolved in 0.3 mol·L^{-1} HNO_3 solution. Aqueous phases for which an insufficient amount was available for titration are marked with an x.

S3. FTIR spectra of UDGA-Nd complexes

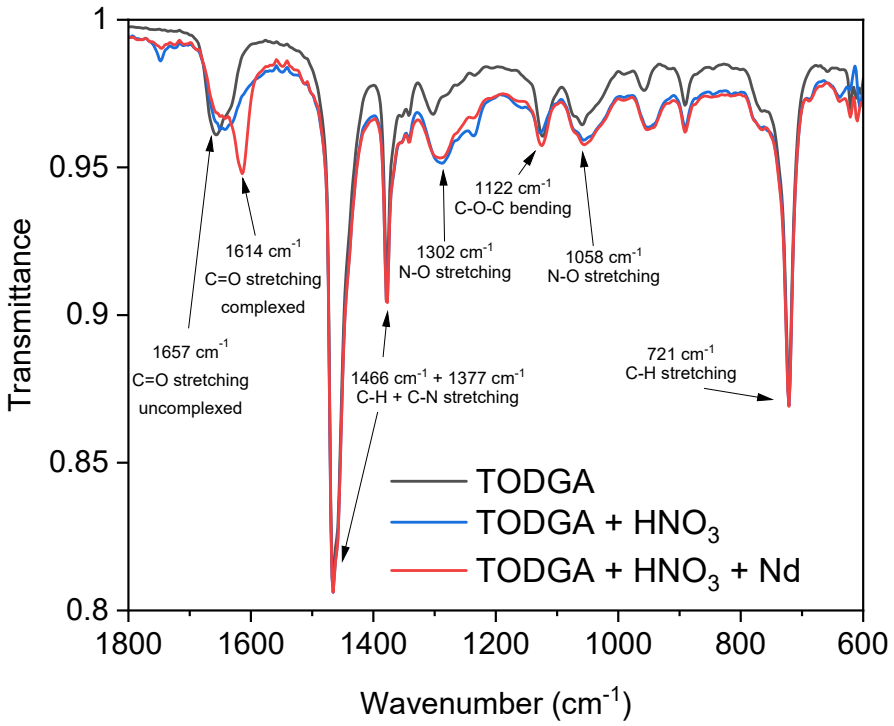

Figure S14: FTIR spectra obtained for the TODGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.28 M, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

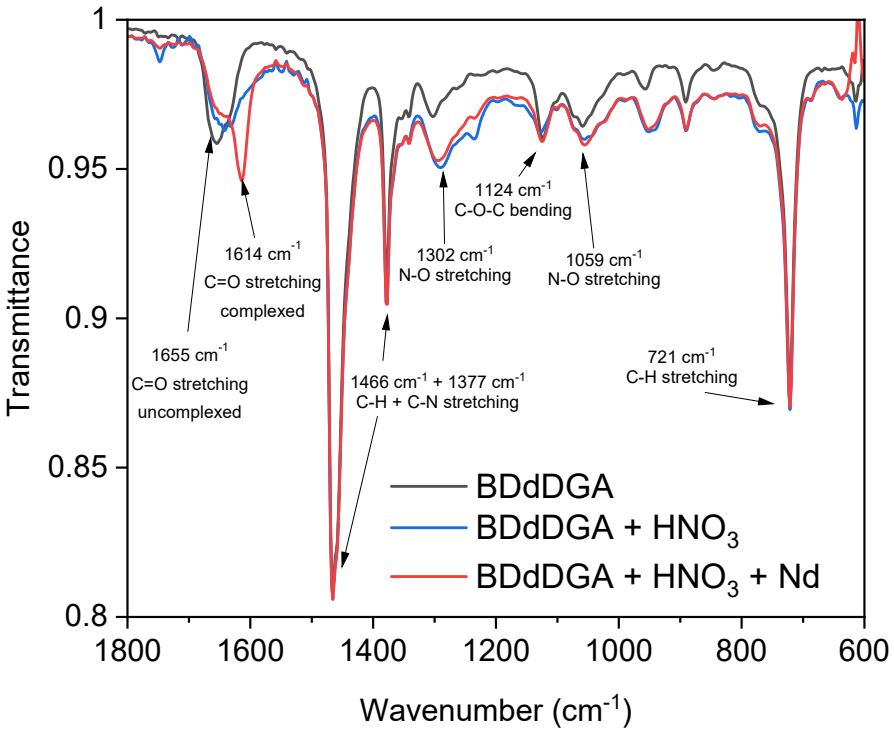

Figure S15: FTIR spectra obtained for the BDdDGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.26 mol·L^{-1}, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

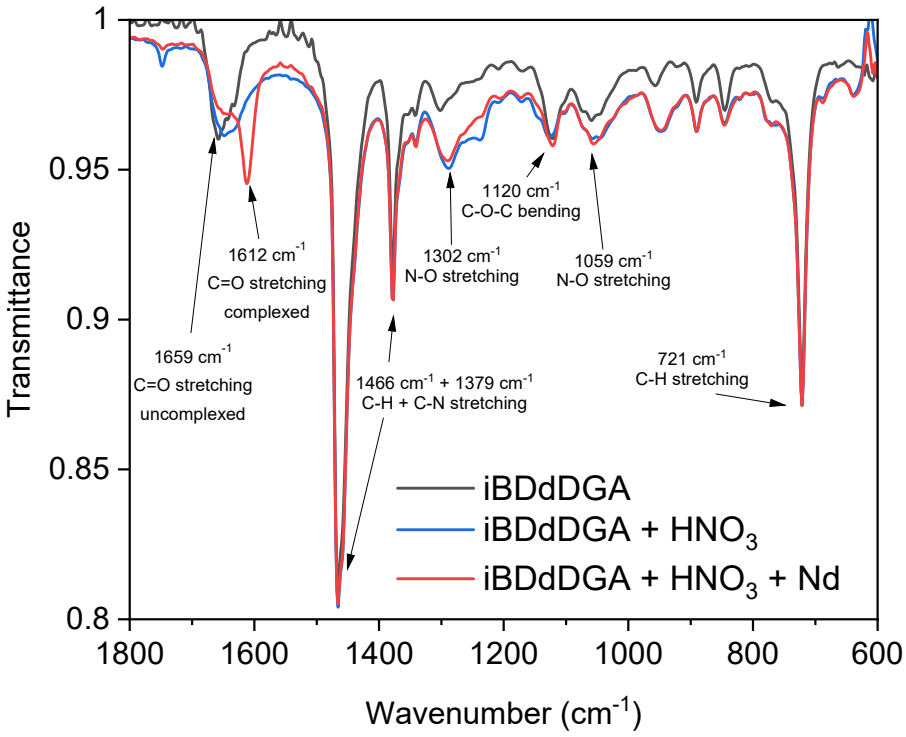

Figure S16: FTIR spectra obtained for the iBDdDGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.32 mol·L^{-1}, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

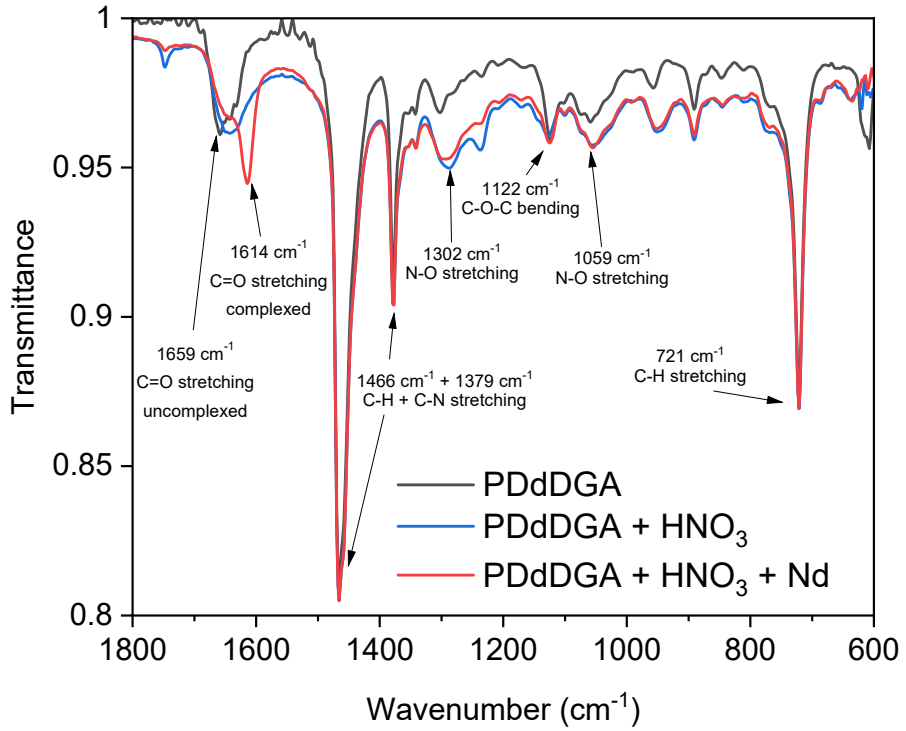

Figure S17: FTIR spectra obtained for the PDdDGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.25 mol·L^{-1}, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

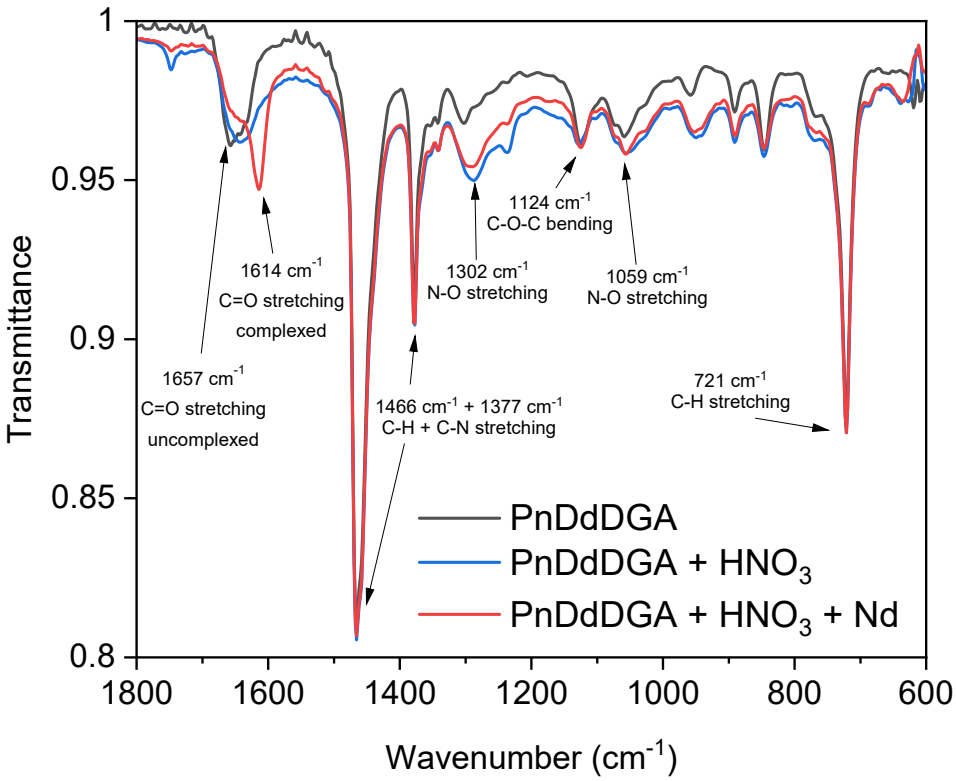

Figure S18: FTIR spectra obtained for the PnDdDGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.31 mol·L^{-1}, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

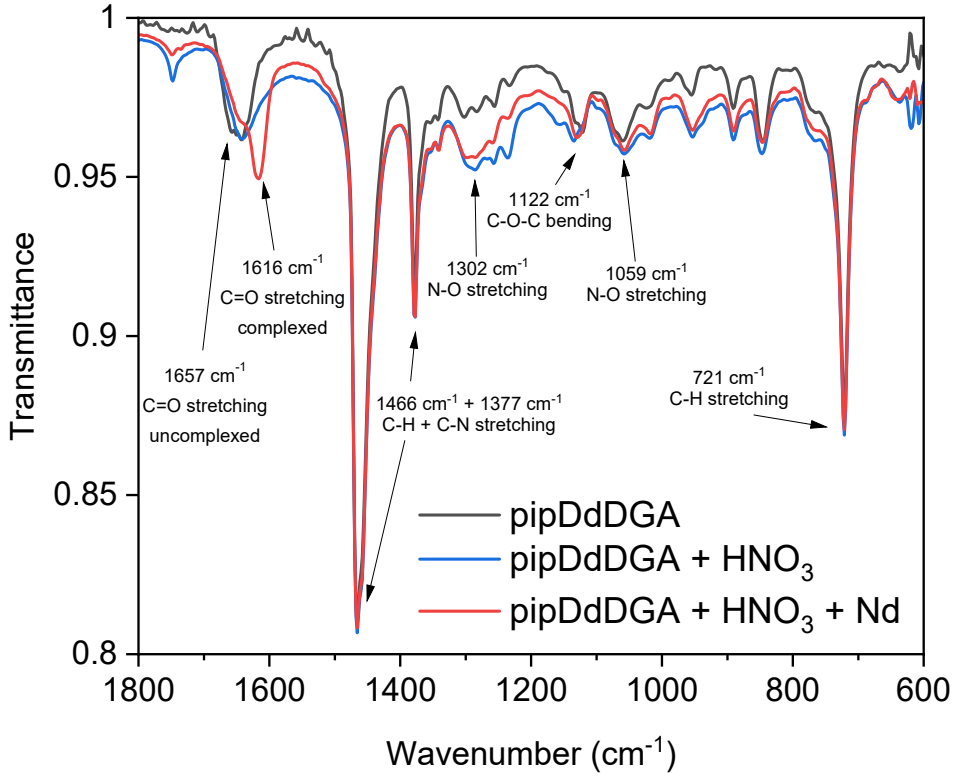

Figure S19: FTIR spectra obtained for the pipDdDGA organic phase (0.1 mol·L^{-1} DGA in n-dodecane + 5 vol% 1-octanol) before extraction, after contact with 3 mol·L^{-1} HNO_3, and after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ dissolved in 3 mol·L^{-1} HNO_3. $[H^+]_{org}$ = 0.25 mol·L^{-1}, $[Nd^{3+}]_{org}$ = 10 mmol·L^{-1}.

S4. UV-vis spectra of UDGA-Nd complexes

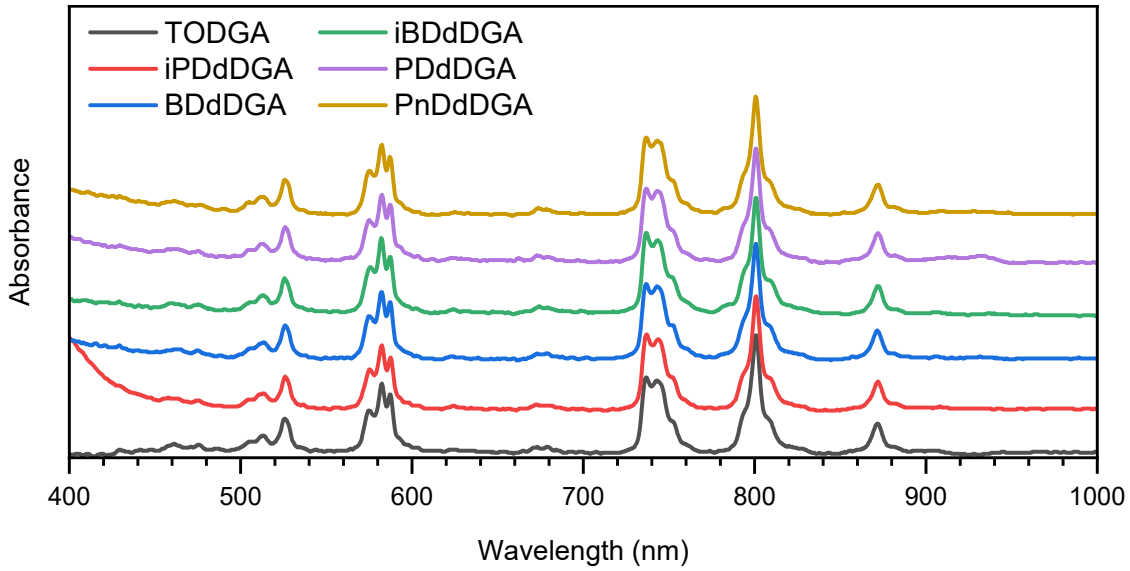

Figure S20: UV-vis spectra of the organic phases containing 0.1 mol·L^{-1} of diglycolamide extractant in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3.

S5. ESI-MS spectra of UDGA-Nd complexes

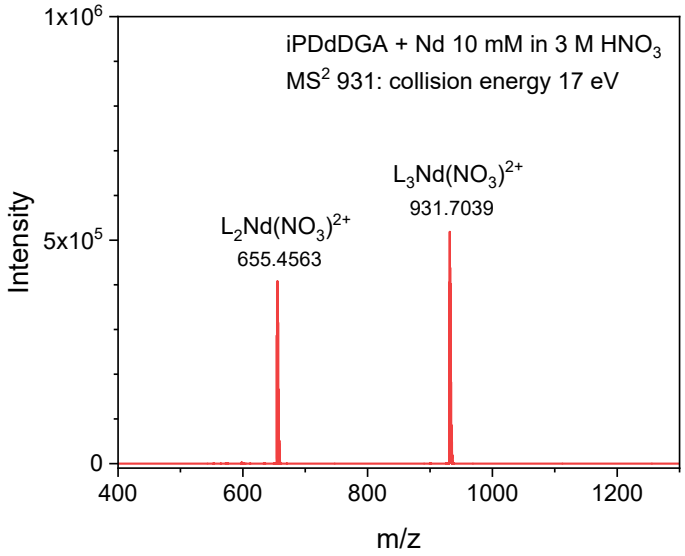

Figure S21: Tandem mass spectrum for iPDdDGA. Organic phase containing 0.1 mol·L^{-1} of iPDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 17 eV.

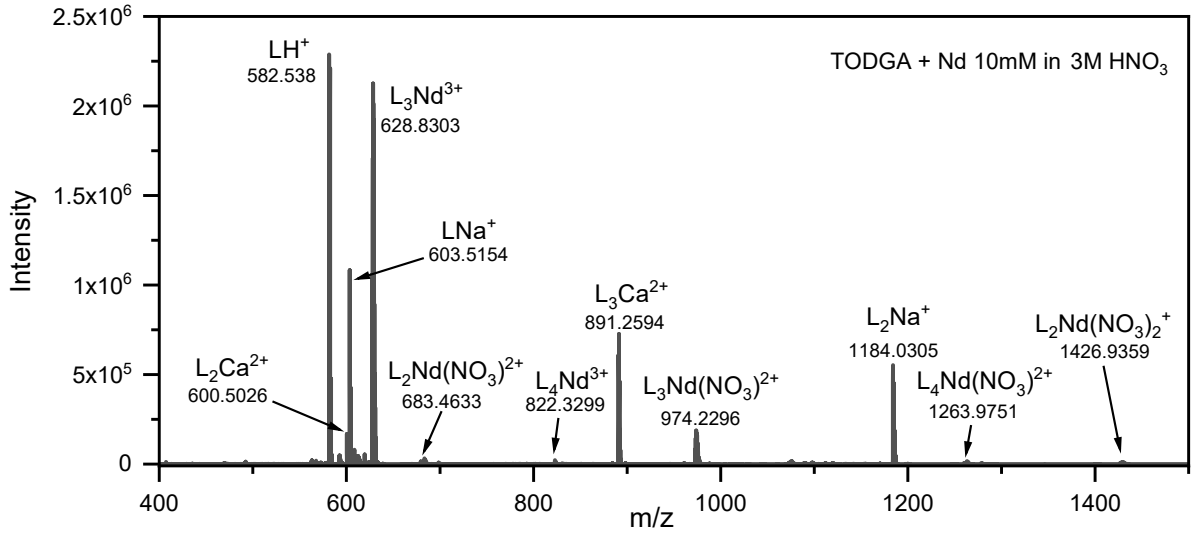

Figure S22: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of TODGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

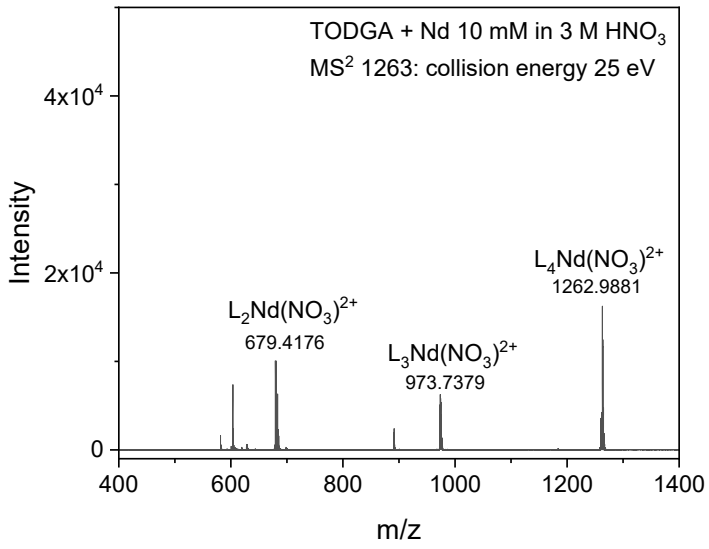

Figure S23: Tandem mass spectrum for TODGA. Organic phase containing 0.1 mol·L^{-1} of TODGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 25 eV.

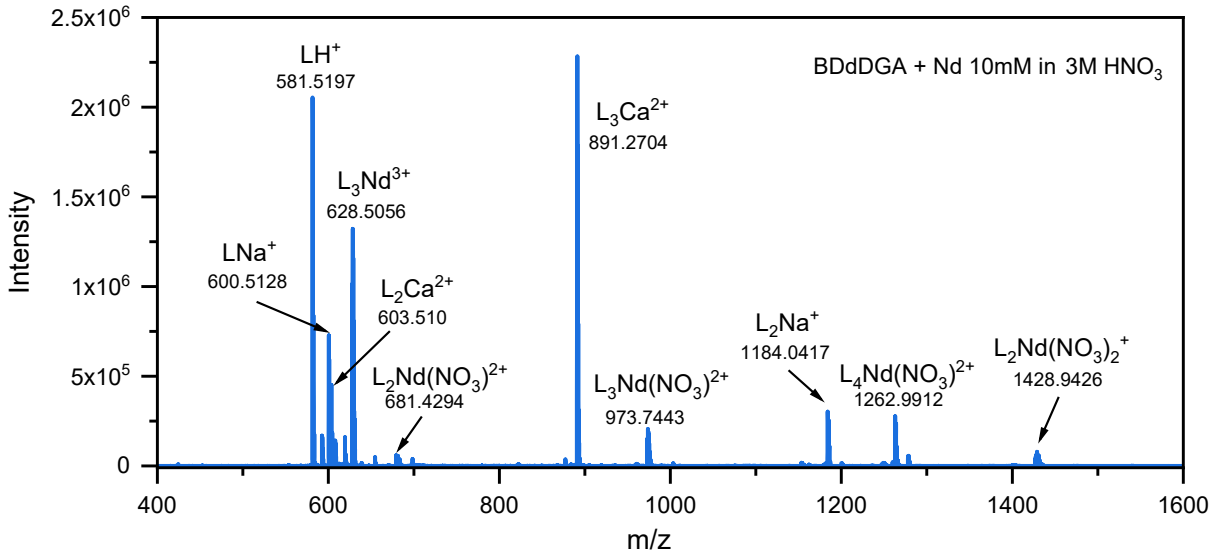

Figure S24: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of BDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

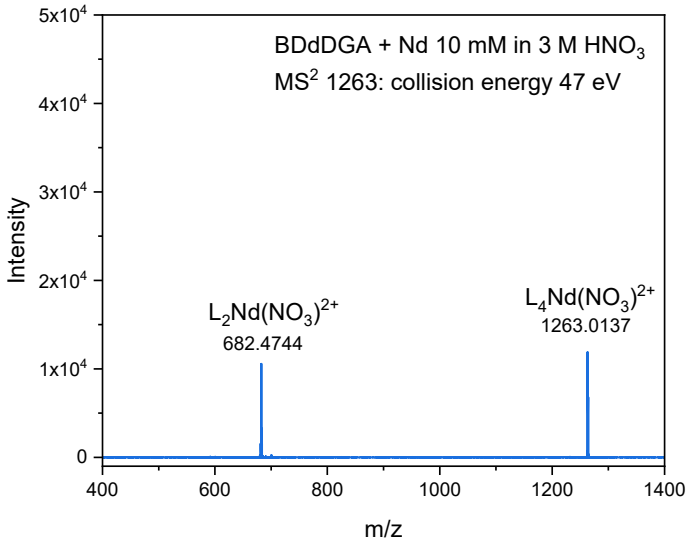

Figure S25: Tandem mass spectrum for BDdDGA. Organic phase containing 0.1 mol·L^{-1} of BDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 47 eV.

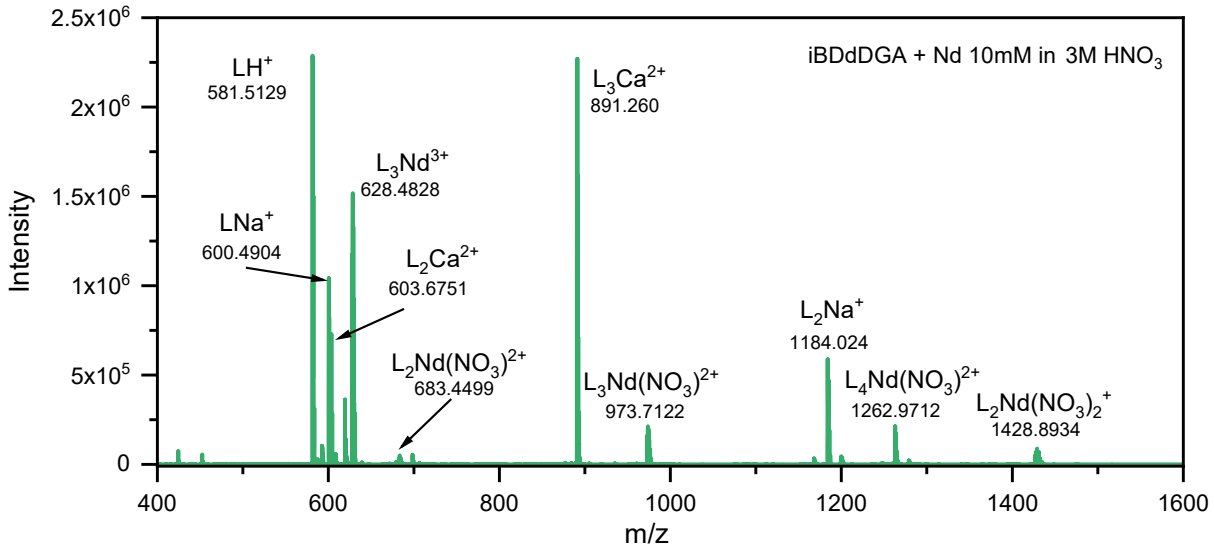

Figure S26: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of iBDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

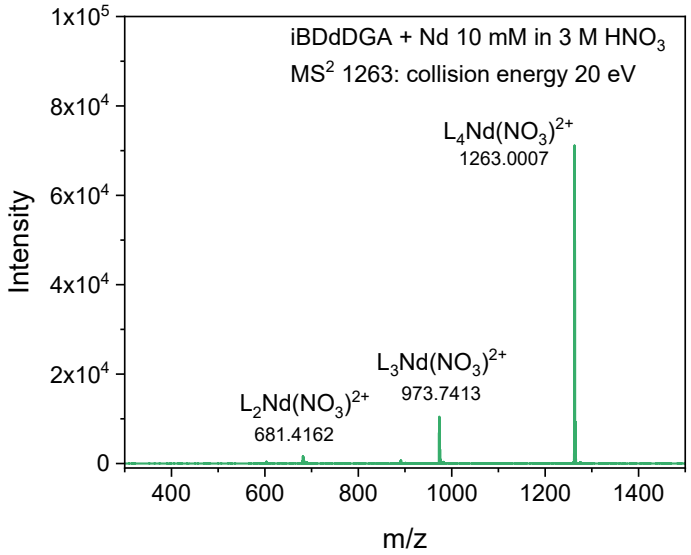

Figure S27: Tandem mass spectrum for iBDdDGA. Organic phase containing 0.1 mol·L^{-1} of iBDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 20 eV.

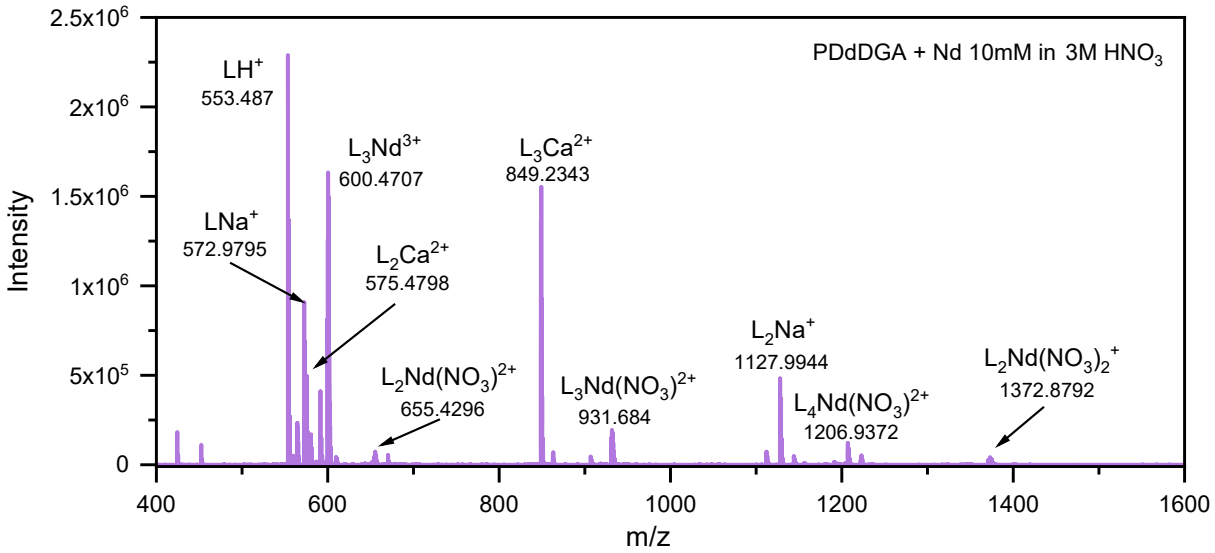

Figure S28: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of PDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

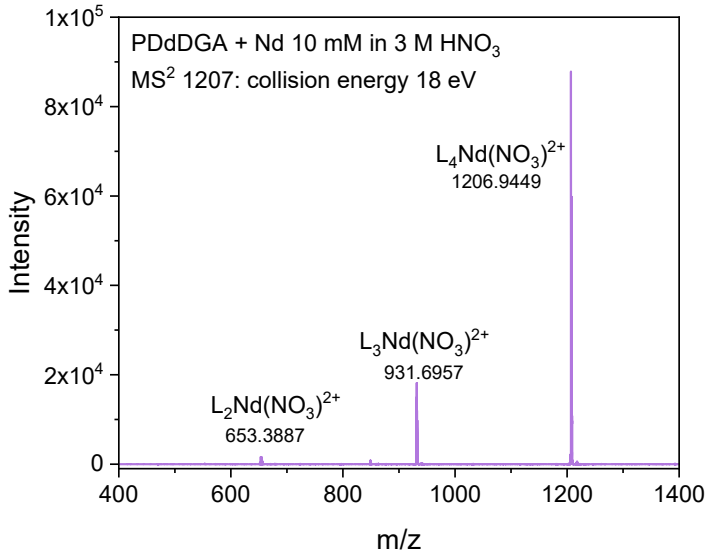

Figure S29: Tandem mass spectrum for PDdDGA. Organic phase containing 0.1 mol·L^{-1} of PDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 18 eV.

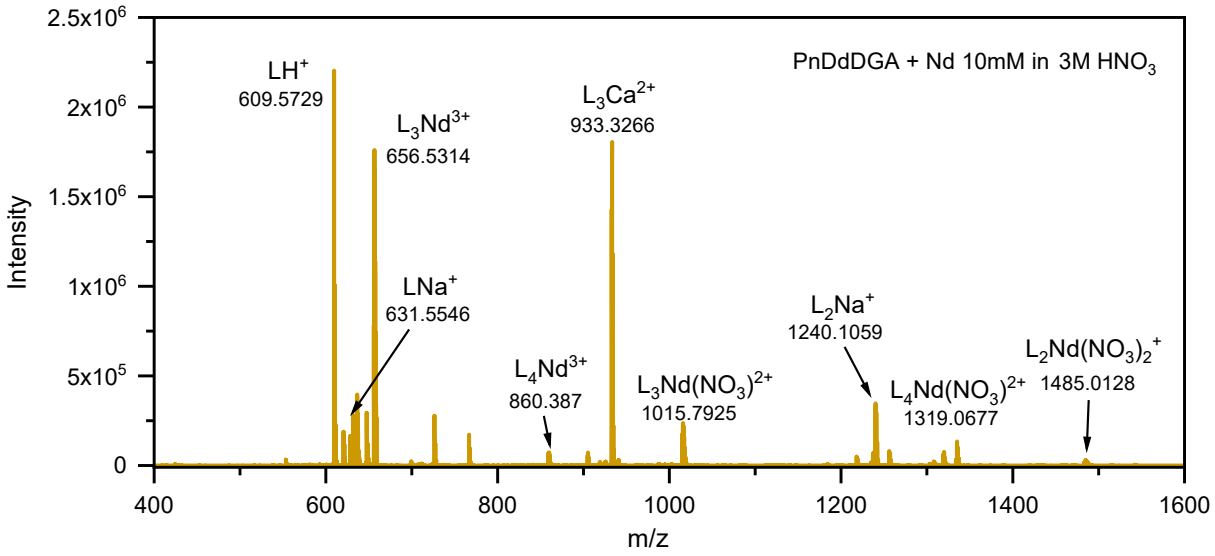

Figure S30: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of PnDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

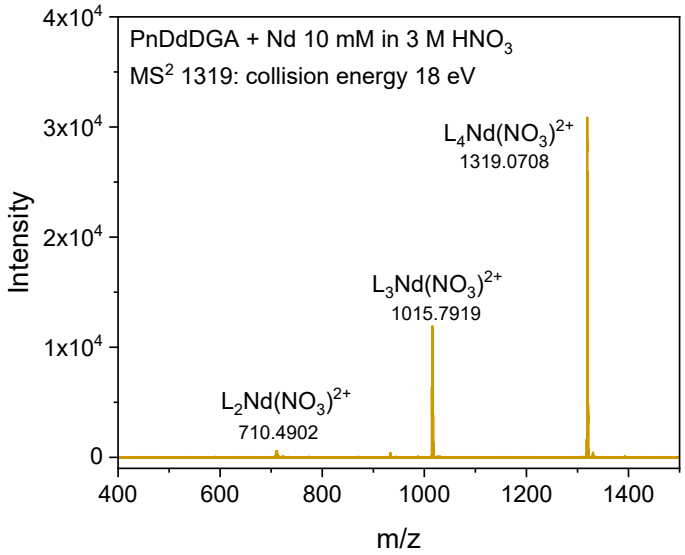

Figure S31: Tandem mass spectrum for PnDdDGA. Organic phase containing 0.1 mol·L^{-1} of PnDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 18 eV.

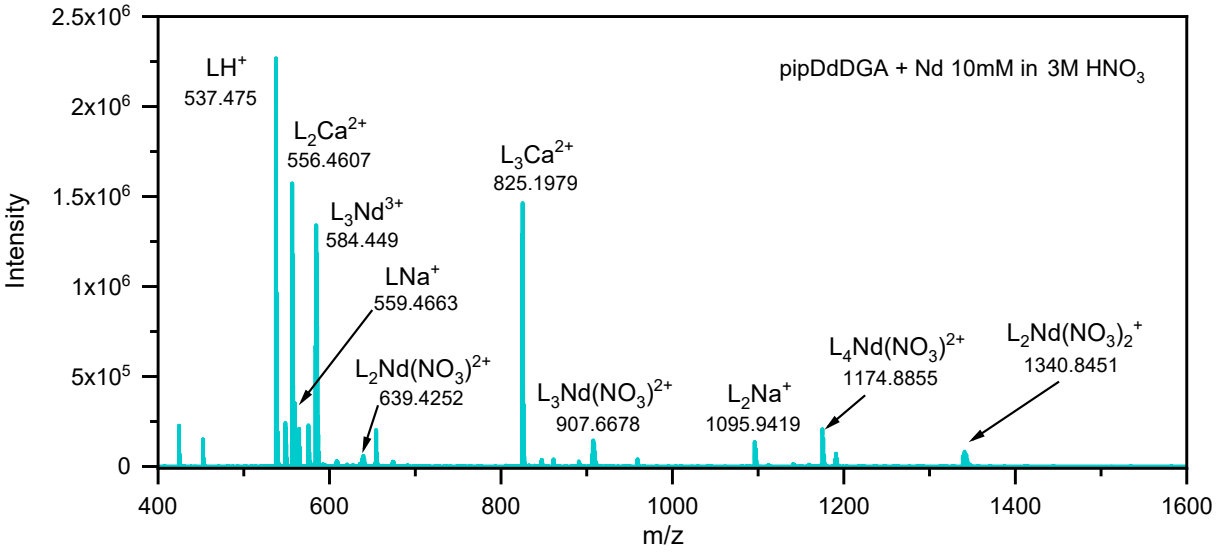

Figure S32: ESI-MS spectrum of the organic phase containing 0.1 mol·L^{-1} of pipDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile.

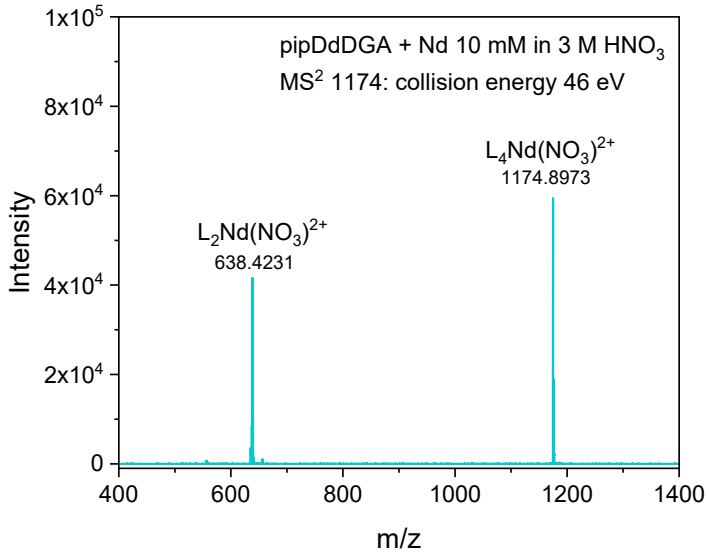

Figure S33: Tandem mass spectrum for pipDdDGA. Organic phase containing 0.1 mol·L^{-1} of pipDdDGA in n-dodecane + 5 vol% 1-octanol after contact with 10 mmol·L^{-1} $Nd(NO_3)_3$ in 3 mol·L^{-1} HNO_3. Organic phases diluted 1:10,000 in acetonitrile. Collision energy 46 eV.