Advanced separation strategies for spent nuclear fuel reprocessing studied at Politecnico di Milano Radiochemistry Lab within European Projects

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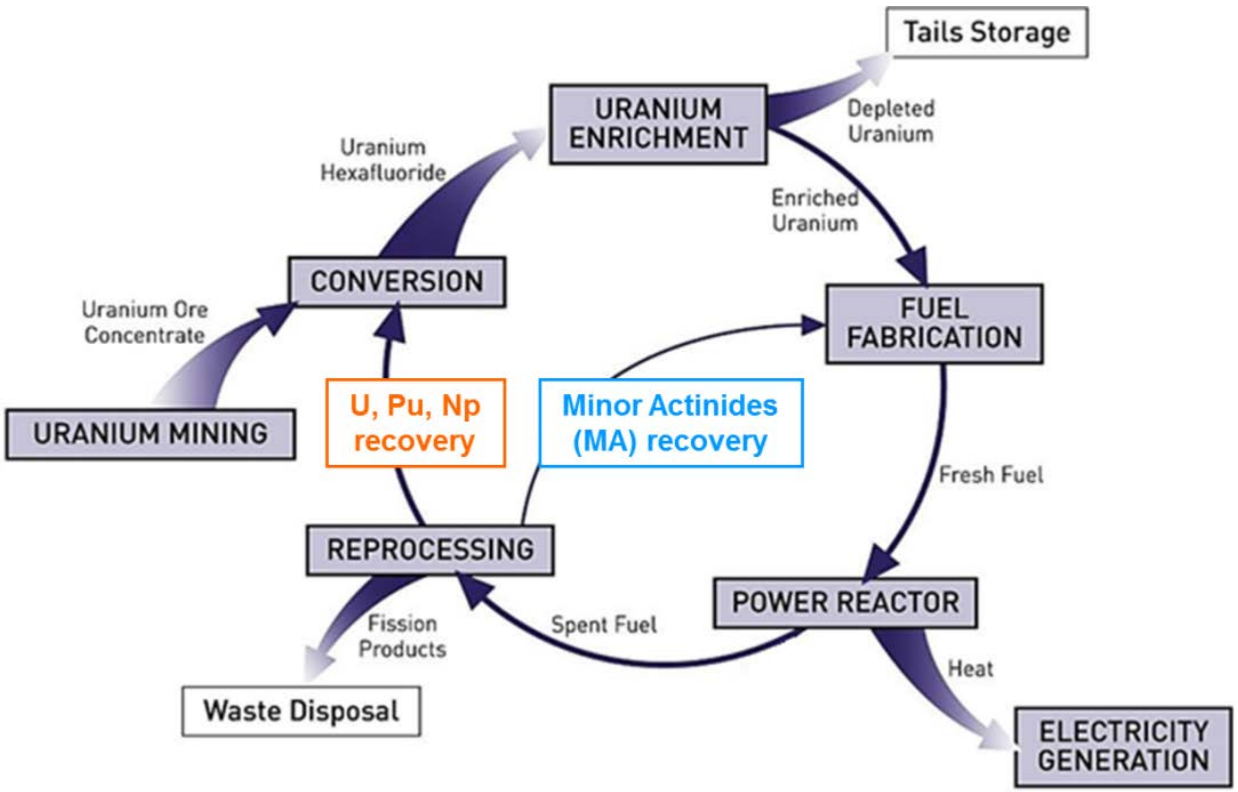
MILANO 1863

CHERNE 2018
29/5-1/6, 2018, Macugnaga, Italy



CLOSED NUCLEAR FUEL CYCLE OPTION

To improve Sustainability – Acceptability of nuclear energy worldwide

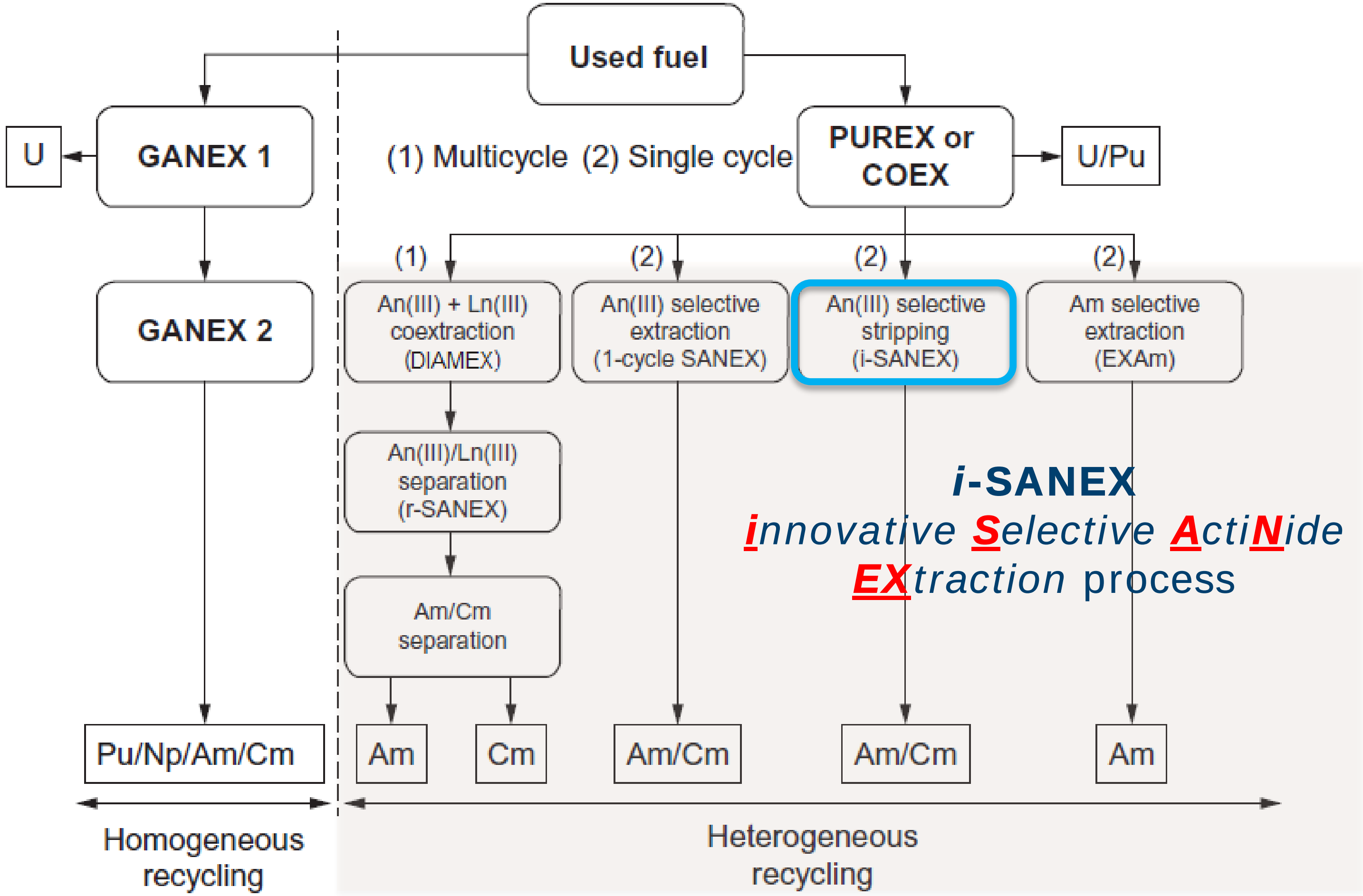
ADVANCED CLOSED CYCLE

- Recycling of reusable material
- Better waste management
- Radiotoxicity reduction
- Proliferation resistance

MA Partitioning and **Transmutation** (P&T) strategy

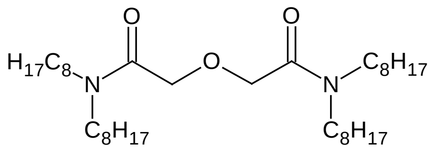
Hydro-metallurgical processes

Solvent extraction

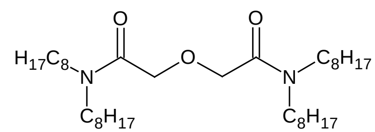


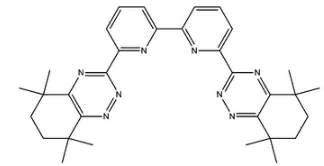
HETEROGENEOUS RECYCLING

TODGA + *regular*-SANEX processes



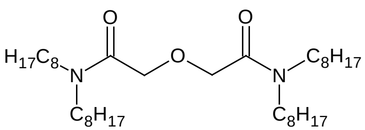
0.2 M TODGA in kerosene with 5% of 1-octanol

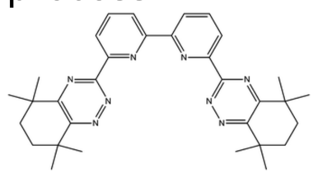




0.005 M TODGA + 0.015 M **$CyMe_4BTBP$** in 1-octanol

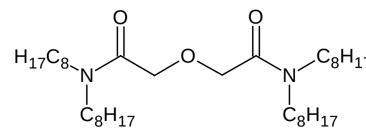
1cycle-SANEX process



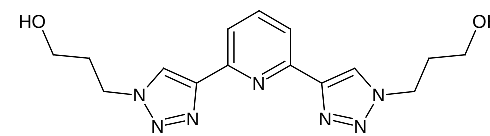


0.005 M TODGA + 0.015 M **$CyMe_4BTBP$**
in TPH/1-octanol 40/60 mixture

innovative-SANEX process



0.2 M TODGA in kerosene
+ 5 vol.% 1-octanol



0.08 M **PyTri-Diol** in
HNO_3 0.44 M

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PoliMi is involved in **EU** projects dedicated to the **Advanced Partitioning of Spent Nuclear Fuel *since 2002***

Extracting performances

solvent extraction experiments with **simulating feeds**

Solvent degradation (ligand/diluent)

- Ageing
- Hydrolysis
- Radiolysis

Fluid dynamic properties (density, viscosity)

Speciation

TRFLS

HPLC/ESI-MS

UV-Vis

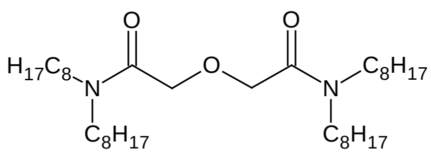
ACSEPT innovative solutions for sustainable nuclear energy

SACSESS

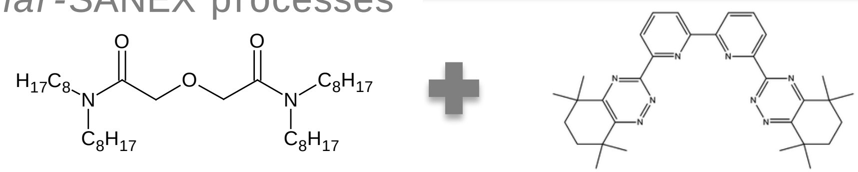
GENIORS GEN IV integrated oxide fuels recycling strategies

HETEROGENEOUS RECYCLING

TODGA + *regular*-SANEX processes



0.2 M TODGA in kerosene with 5% of 1-octanol



0.005 M TODGA + 0.015 M **$CyMe_4BTBP$** in 1-octanol

1cycle-SANEX process

0.005 M TODGA + 0.015 M **$CyMe_4BTBP$**
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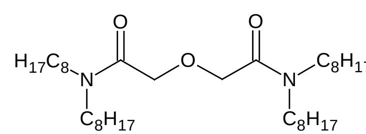
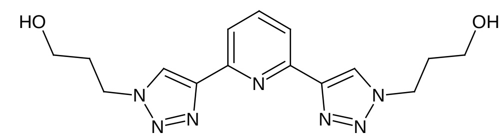
innovative-SANEX process

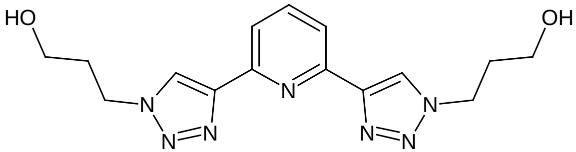


0.2 M TODGA in kerosene
+ 5 vol.% 1-octanol

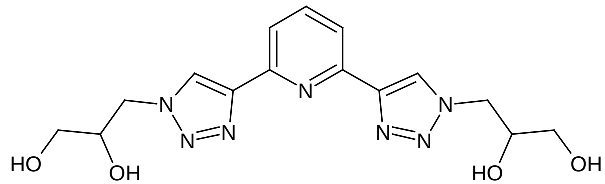


0.08 M **PyTri-Diol** in
HNO_3 0.44 M

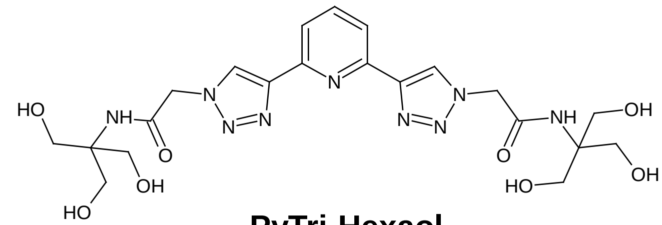
Pyridine-2,6-bis(1h-1,2,3-triazol-4-yl) based ligand



PyTri-Diol



PyTri-Tetraol

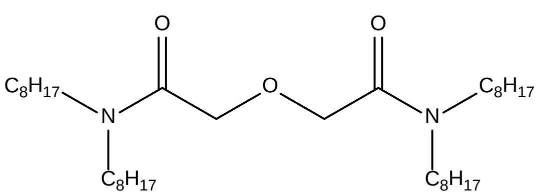


PyTri-Hexaol

- ✓ CHON principle
- ✓ High MAs selectivity
- ✓ Fast kinetics
- ✓ High hydrolytic and radiolytic stability

Novel *i*-SANEX / GANEX reference system

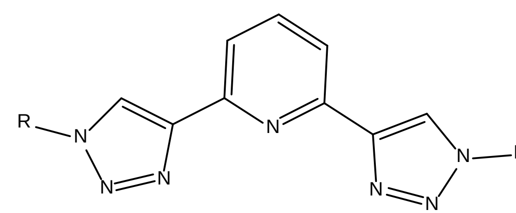
An and Ln co-extraction
from feed solution



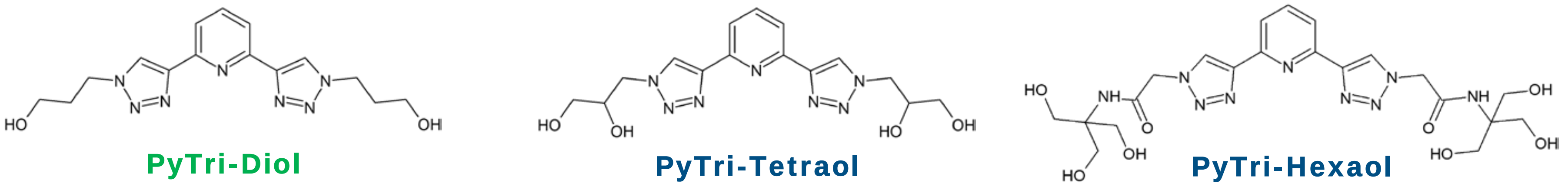
0.2 M TODGA extractant
in kerosene + 5 vol.% 1-octanol

- Affinity for An and Ln;
- CHON principle;
- High stability;
- Fast kinetics;
- Hydrodynamically safe.

New An stripping solvent
PyTri-compounds in nitric acid



Macerata E. et al., *Hydrophilic Clicked 2,6-bis-Triazolyl-Pyridines Endowed with High Actinide Selectivity and Radiochemical Stability: towards a Closed Nuclear Fuel Cycle*, **J. Am. Chem. Soc.**, **2016**, *138* (23), pp 7232-7235, DOI: 10.1021/jacs.6b03106

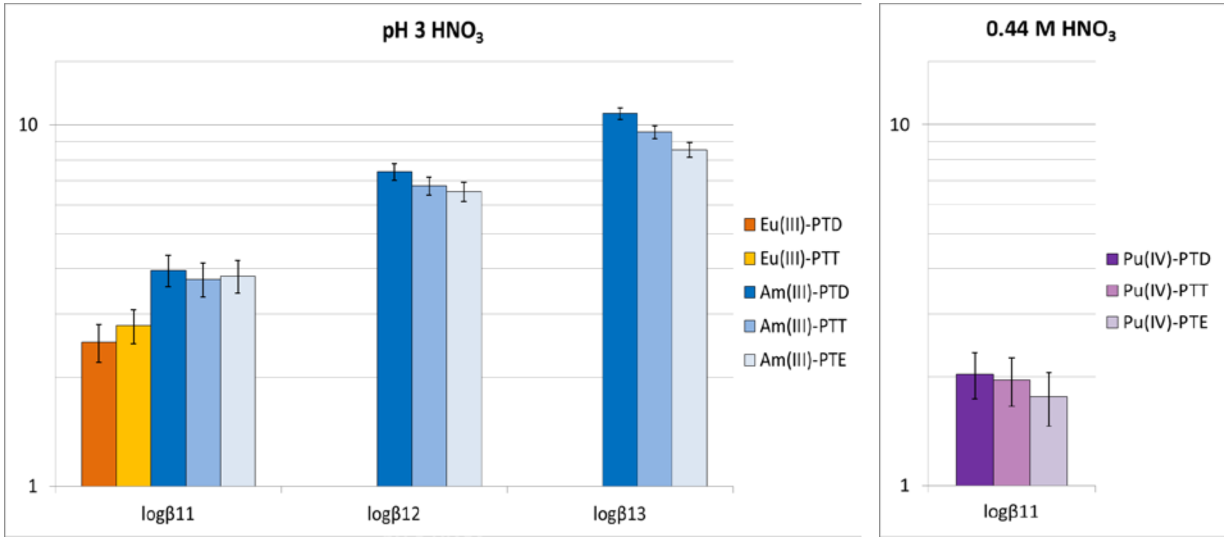


The investigation on **novel stripping agents** confirmed the previous results:

Best ligand within the PyTri-family

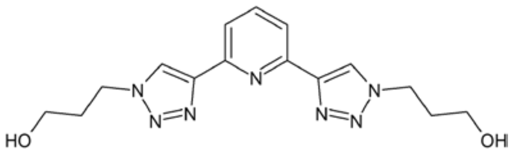
Within the family, PyTri-Diol is slightly **more selective** for An towards Ln

Monophasic UV-Vis experiments

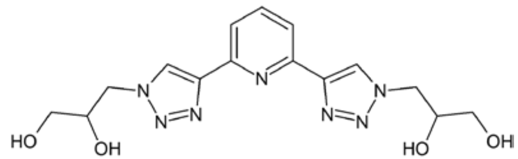


Am(III) and **Pu(IV)** experiments **following the cation** signal: stepwise addition of ligand to the cation solution

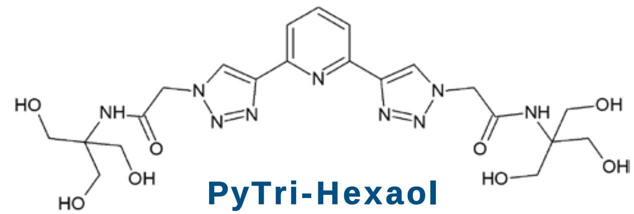
Eu(III) experiment **following the ligand** signal: stepwise addition of cation to the ligand solution



PyTri-Diol



PyTri-Tetraol

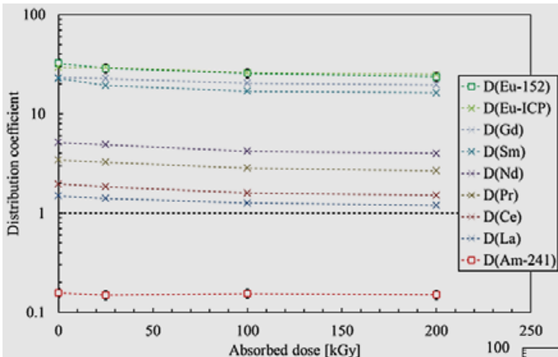


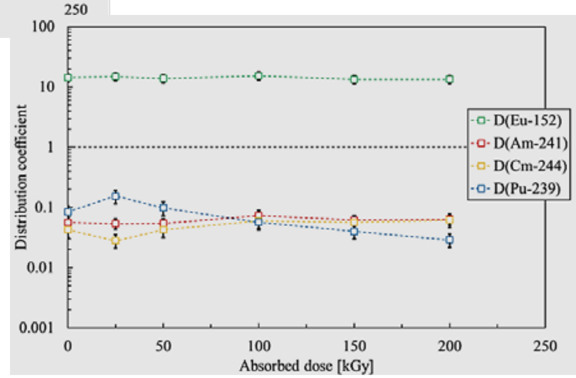
PyTri-Hexaol

The investigation on **novel stripping agents** confirmed the previous results:

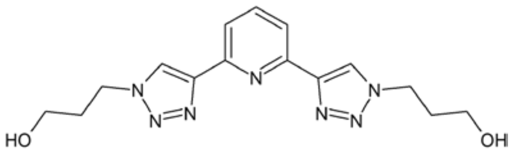
Radiochemical stability

Stability constants unaltered in solutions aged for months and/or irradiated up to 200 kGy

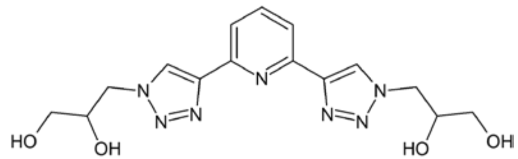




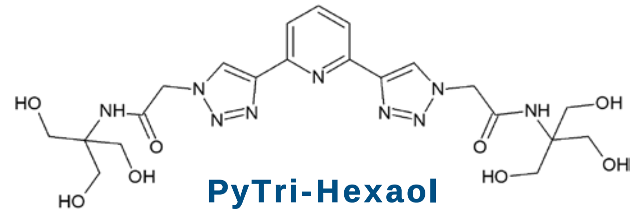
Extraction performance overview



PyTri-Diol



PyTri-Tetraol



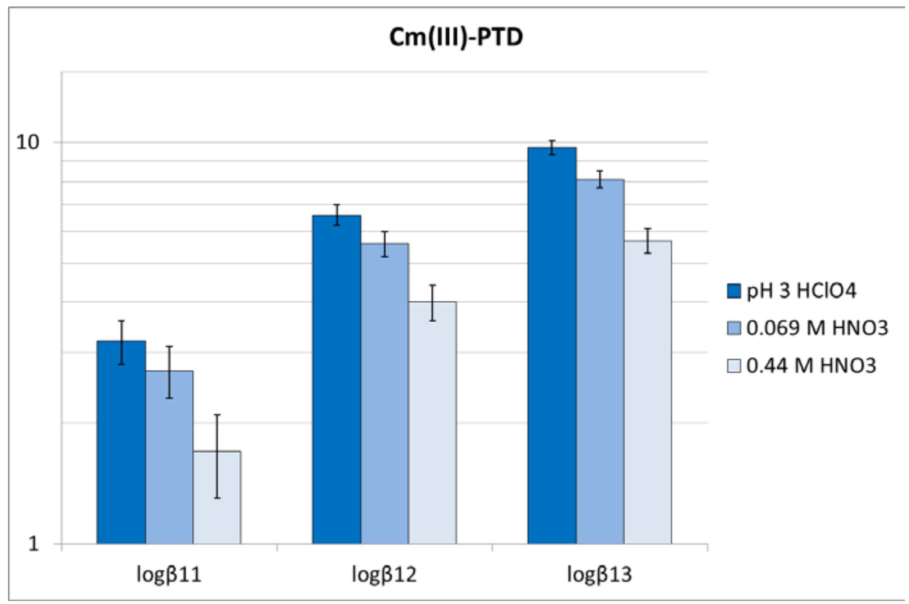
PyTri-Hexaol

The investigation on **novel stripping agents** confirmed the previous results:

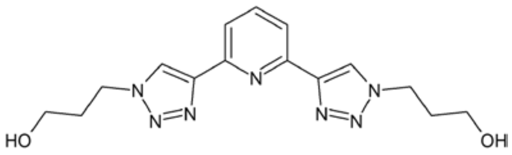
Protonation
An / Ln selectivity

PyTri-ligands form more stable complexes:
- at lower acidity;
- with An rather than with Ln

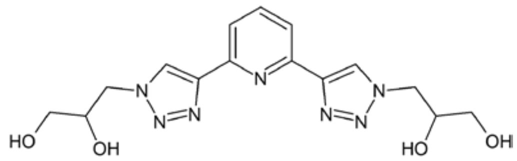
Monophasic TRLFS experiments at process conditions (0.44 M HNO_3)



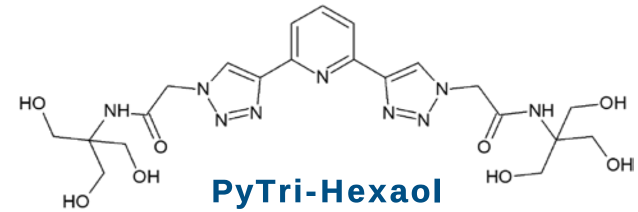
Cm(III) experiments **following the cation** signal (0.44 M and 0.069 M HNO_3, 0.001 M $HClO_4$)



PyTri-Diol



PyTri-Tetraol



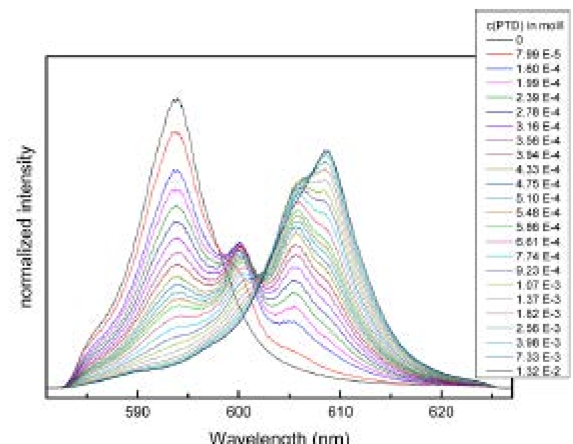
PyTri-Hexaol

The investigation on **novel stripping agents** confirmed the previous results:

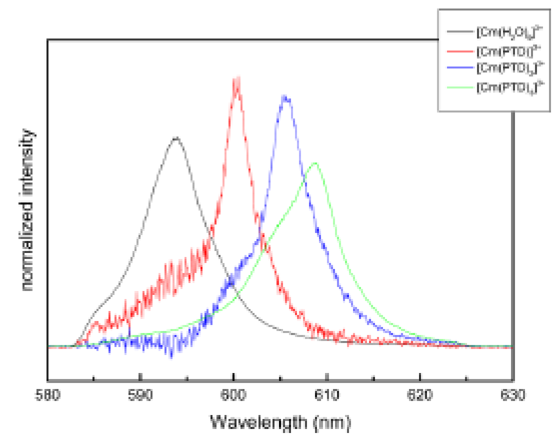
Speciation studies by TRLFS

- An increase of the ionic strength leads to the stabilization of the $M(PTD)_3^{3+}$ while the increase of the H^+ concentration leads to decomplexation;
- cH^+ plays an important role on the stability of the complexes.

Confirms the An(III)/Ln(III) selectivity observed in the extraction experiments.



Normalized fluorescence spectra of Cm(III) at increasing PTD concentration in 10−3 mol/L HClO4.



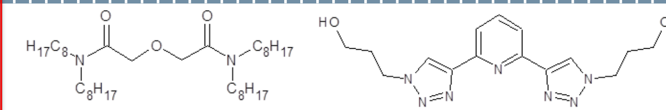
Normalized emission spectra of the $[Cm(PTD)n]^{3+}$ (n = 0, 1, 2, 3) complexes in 10−3 mol/L HClO4.

medium	log β_3 ($[Cm(PTD)_3]^{3+}$)	log β_3 ($[Eu(PTD)_3]^{3+}$)
10^{-3} mol/L $HClO_4$	9.7 ± 0.3	7.3 ± 0.4
0.44 mol/L HNO_3 (for PTD)/0.5 mol/L HNO_3 (for SO_3−Ph−BTP)	5.7 ± 0.3	3.7 ± 0.3

DOI: 10.1021/acs.inorgchem.6b02788
Inorg. Chem. 2017, 56, 2135−2144

Solvent extraction follow-up by means of **ESI-MS**

innovative-SANEX process



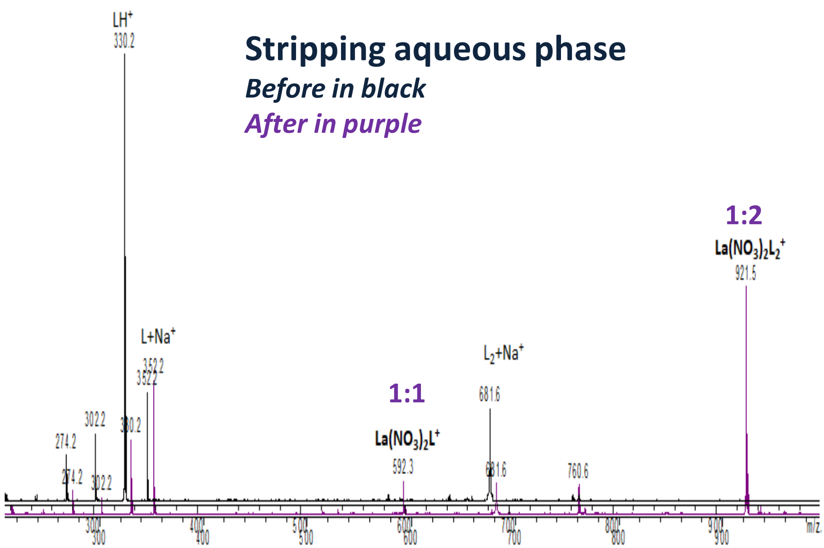
0.2 M TODGA in kerosene + 5 vol.% 1-octanol

0.08 M PyTri-Diol in HNO_3 0.44 M

- Aqueous and Organic phases coming from extraction

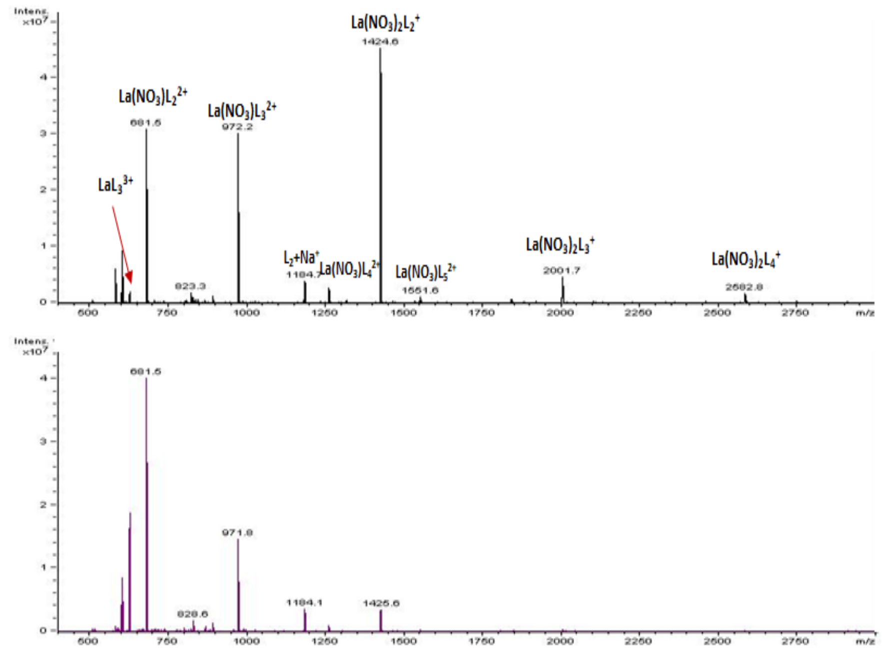
Aq. phase: 0.08 M PTD in 0.44 M HNO_3
Org. phase: loaded organic phase

Stripping aqueous phase
Before in black
After in purple



1:2 is the dominating species of the extraction

Loaded organic phase
Before in black
After in purple



The decrease in the intensity of the formed La-TODGA ion species confirms some back-extraction of La into the aqueous phase .

ESI-MS not only has the ability to:

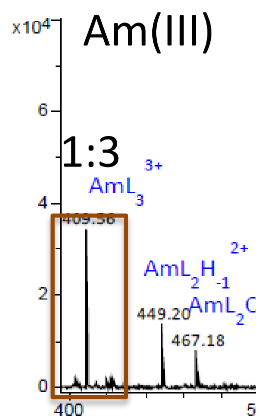
- **Preserve and transport** metal-ligand complexes from solution to the gas phase
- Determine and confirm **stoichiometry** of the complexes in solution

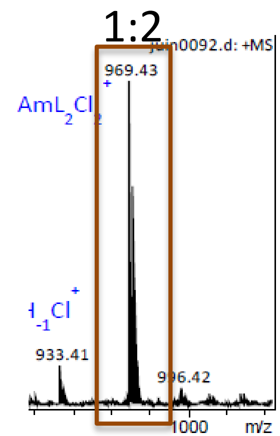
As it is also a complementary technique to:

- Evaluate the selective **affinity** of the extractants towards the metallic cations (An^{3+}/Ln^{3+})
- Contribute to the understanding of the interaction **synergism** of combining extractants (M-L competition, thermodinamic and kinetic studies)
- **Gas-phase stability** of the formed complexes

CID (collision-induced dissociation)
Cone voltage variation

Speciation studies by Electrospray Mass Spectrometry





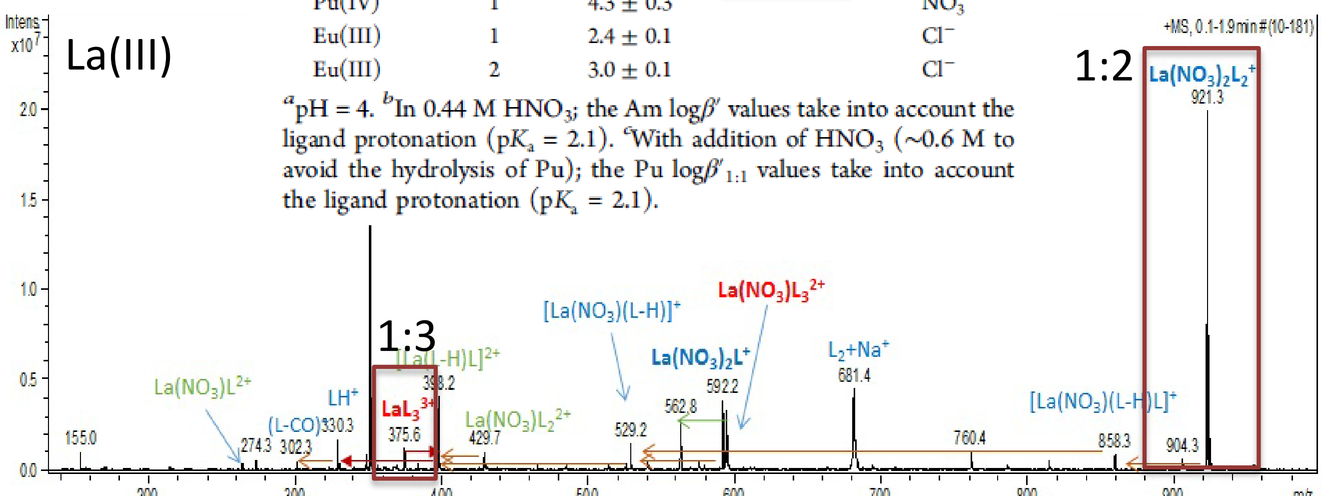
ESI-MS spectra o ...).

Macerata E. et al., ... 6b03106

Table 2. Apparent Stability Constants ($\log\beta'_{\text{metal:ligand}}$) for Am(III), Pu(IV), and Eu(III) Complexes with Ligands 1 and 2 Obtained by UV–vis Titration in Methanol/Water (75/25 v/v) at 25 °C

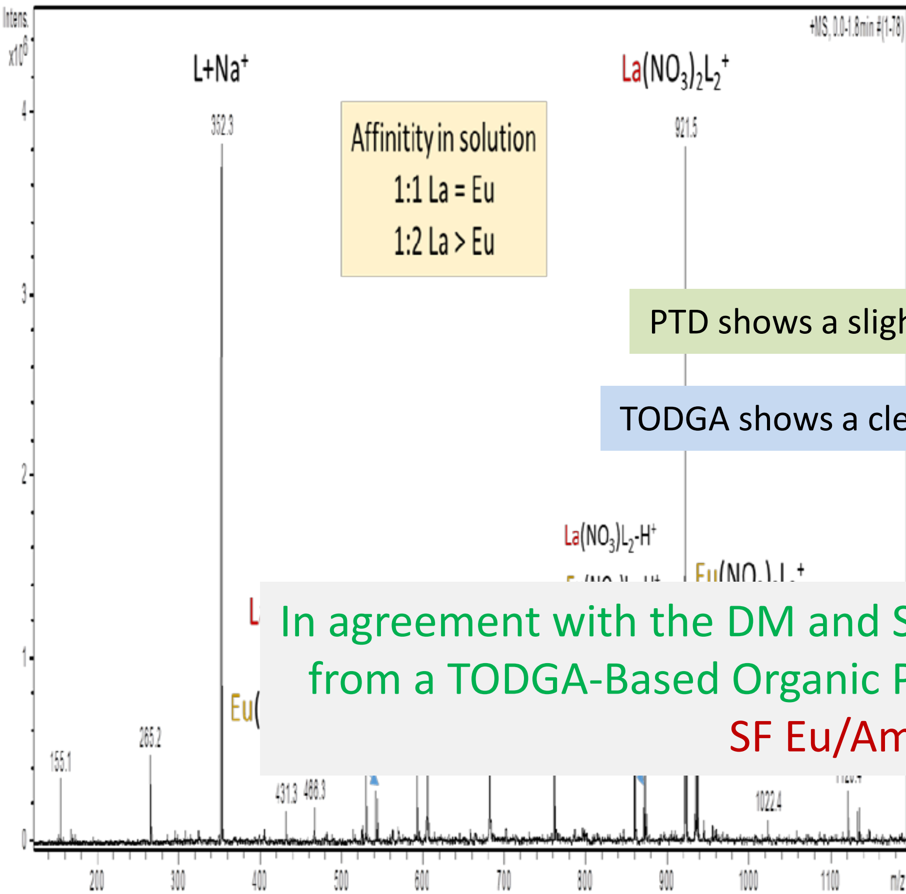
metal ion	ligand	$\log\beta'_{1:1}$	$\log\beta'_{1:2}$	counterion
Am(III)[a]	1	3.2 ± 0.3	6.2 ± 0.3	Cl^-
Am(III)[b]	1	3.5 ± 0.3	6.8 ± 0.3	NO_3^-
Am(III)[a]	2	3.1 ± 0.3	5.5 ± 0.3	Cl^-
Pu(IV)[c]	1	4.3 ± 0.3		NO_3^-
Eu(III)	1	2.4 ± 0.1		Cl^-
Eu(III)	2	3.0 ± 0.1		Cl^-

[a]pH = 4. [b]In 0.44 M HNO_3; the Am $\log\beta'$ values take into account the ligand protonation (pK_a = 2.1). [c]With addition of HNO_3 (~0.6 M to avoid the hydrolysis of Pu); the Pu $\log\beta'_{1:1}$ values take into account the ligand protonation (pK_a = 2.1).

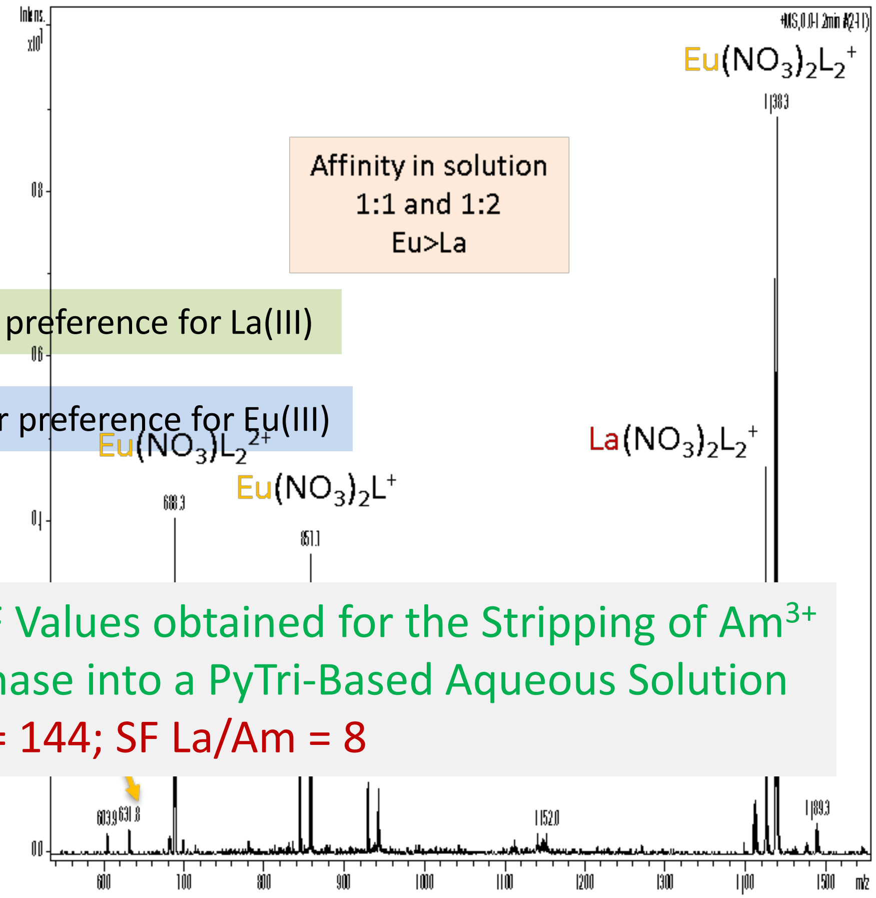


ESI-MS spectra of an equimolar solution of La(III) complexes with **PTD** in CH_3OH at 10^{-4}M.

ESI-MS of a solution containing $La(NO_3)_3$ + Eu $(NO_3)_3$ + Pytridiol at 10^{-4} M in MeOH. c[L]/c[M] = 2



ESI-MS of a solution containing $La(NO_3)_3$ + Eu $(NO_3)_3$ + TODGA at 10^{-4} M in CH_3CN. c[L]/c[M] = 2



PTD shows a slight preference for La(III)

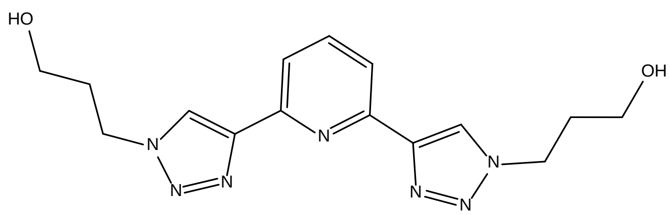
TODGA shows a clear preference for Eu(III)

In agreement with the DM and SF Values obtained for the Stripping of Am^{3+} from a TODGA-Based Organic Phase into a PyTri-Based Aqueous Solution

SF Eu/Am= 144; SF La/Am = 8

Hydrophilic ***Soft*** *N-donor ligand*

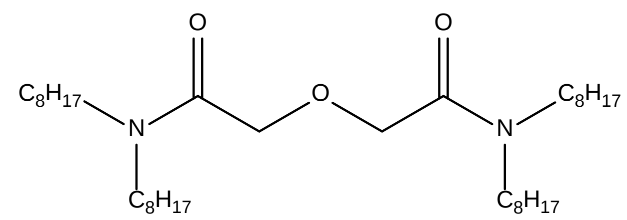
Selective Actinide stripping agent



Chemical Formula: $C_{15}H_{19}N_7O_2$
Molecular Weight: 329,36

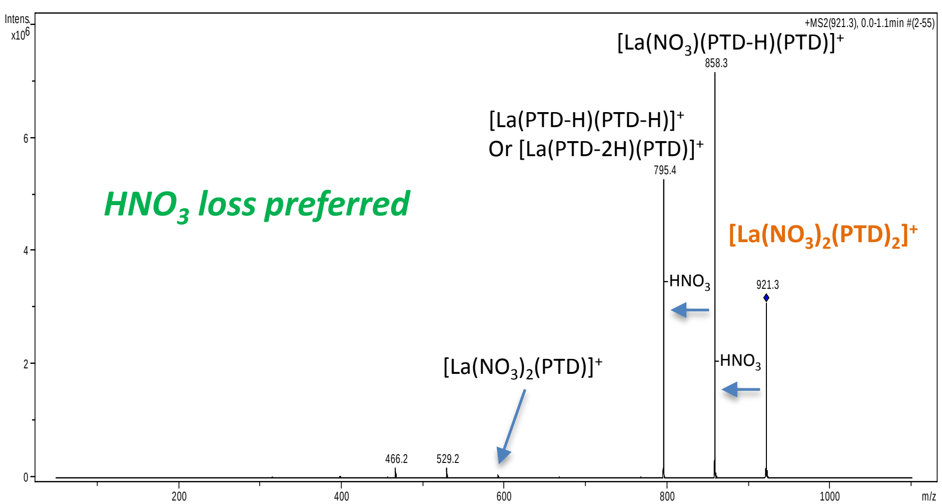
Lipophilic ***Hard*** *O-donor ligand*

Non-specific An/Ln extracting agent

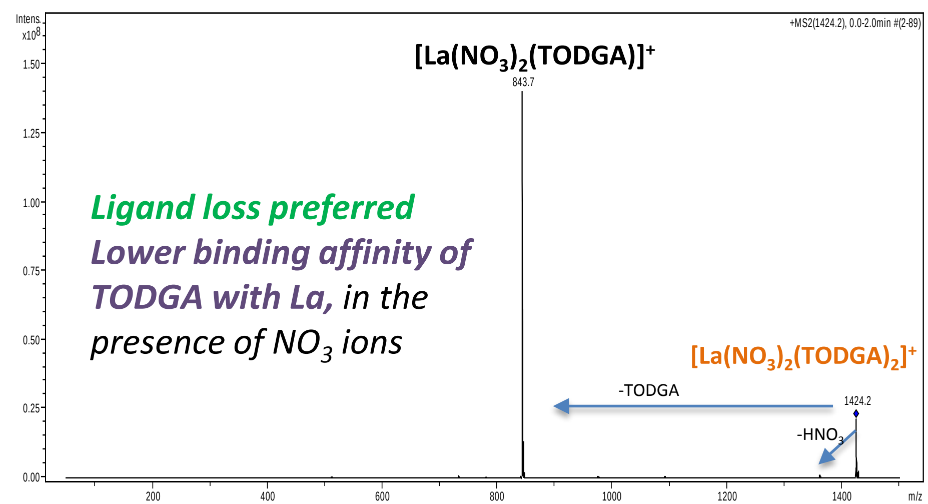


Chemical Formula: $C_{36}H_{72}N_2O_3$
Molecular Weight: 580,97

MS^2 $[La(NO_3)_2(PTD)_2]^+$



MS^2 $[La(NO_3)_2(TODGA)_2]^+$



TODGA shows a **lower binding affinity** which is in **agreement with** the observations in **solution** where the complex is solvated by nitric acid.

Dissociation pattern

MS^2 $[MX_2(PTD)_2]^+$

X = NO_3^-, Cl^-

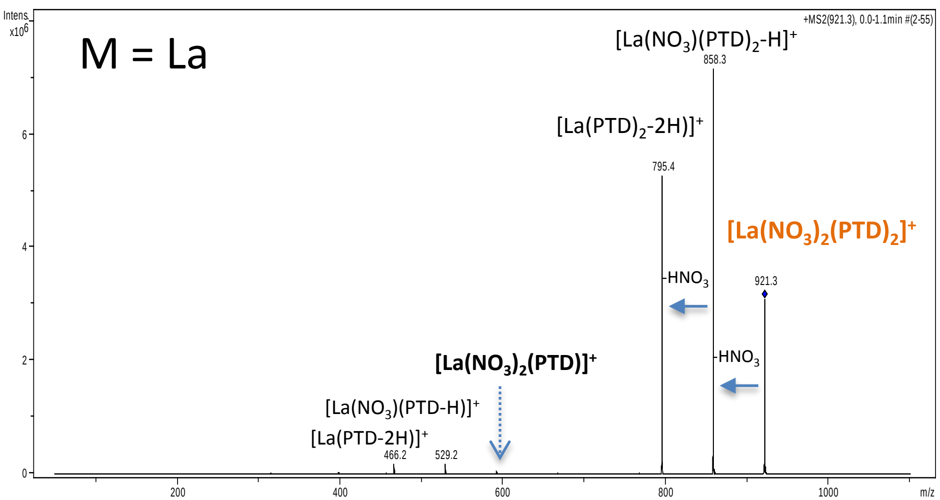
-PTD → $[MX_2(PTD)]^+$ + PTD

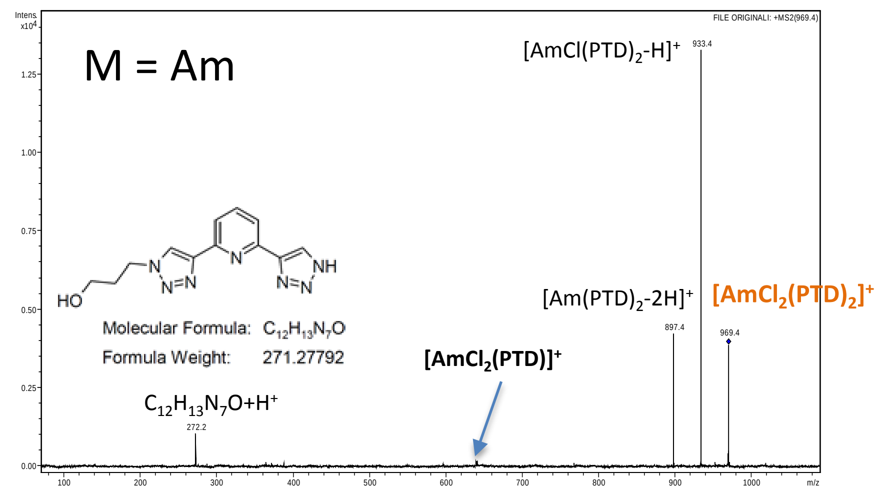
-HX → $[MX(PTD)_2\text{-}1H]^+$ + HX

-HX ↓

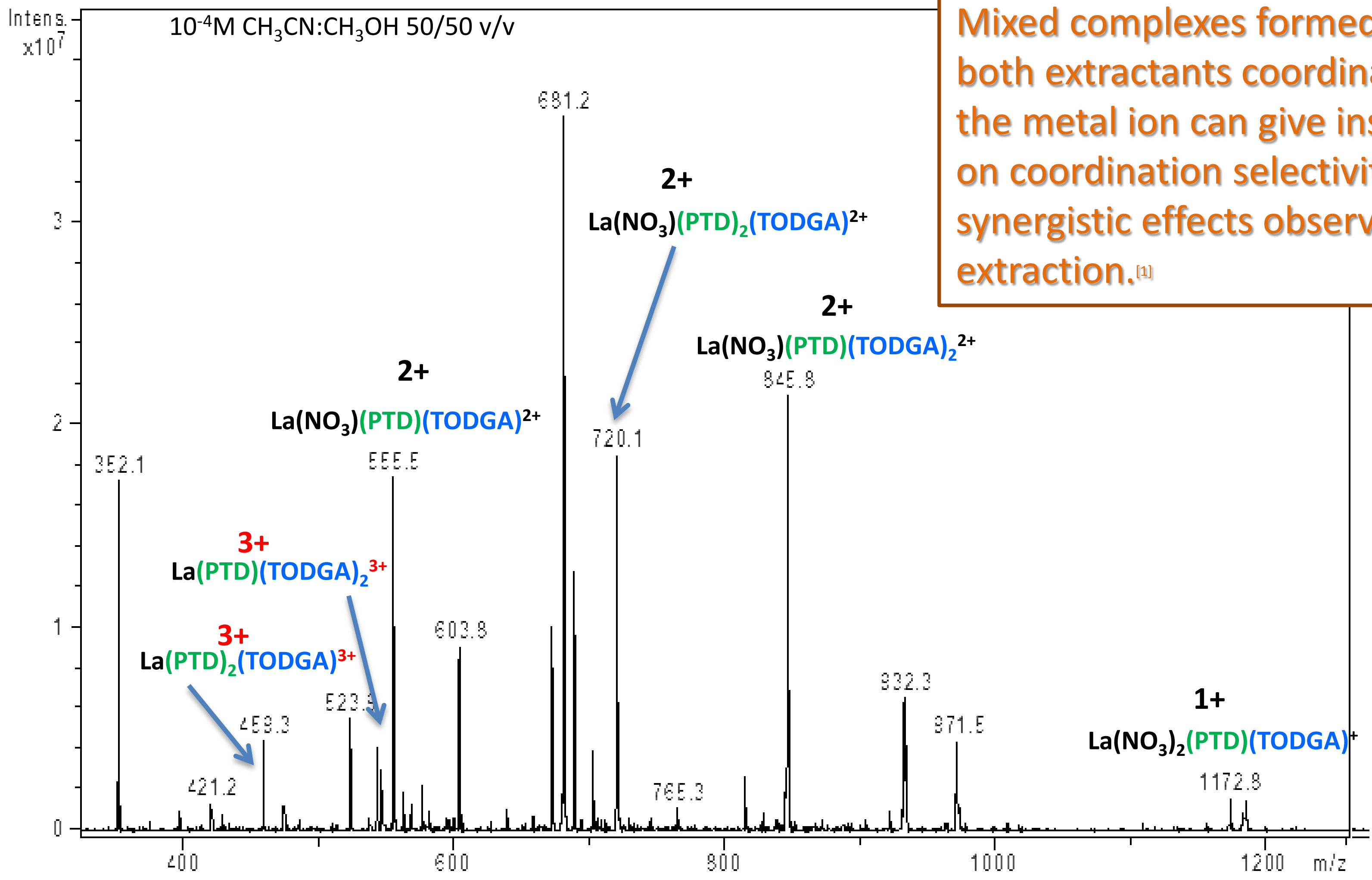
$[M(PTD)_2\text{-}2H]^+$ + HX

HX loss preferred





La:TODGA:PTD 1:1:10 ratio



Mixed complexes formed with both extractants coordinated to the metal ion can give insights on coordination selectivity and synergistic effects observed on extraction.[1]

[1] Muller, J. et al, Understanding the synergistic effect on lanthanides (III) solvent extraction by systems combining a malonamide and dialkyl phosphoric acid, Hydrometallurgy, 169 (2017) 542-551.

Conclusions and Future work

- In the heterogeneous i-SANEX process, among the tested hydrophilic PyTri-ligands, **PyTri-Diol** proved to have an **extraordinary radiolytic resistance** of the stripping phases confirmed by means of several analytical techniques;

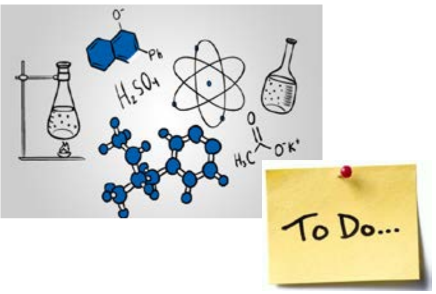
- In paralel with the other tecniques, **ESI-MS** proved to be a **valuable complementary tool**:

➢ To obtain information about the complexes formed during the solvent extraction process;

➢ To evaluate the **stability** of possible intermediary species formed upon the extraction procedure;

➢ Valuable approach for obtaining **structural information** and contribute to the **characterization of the coordination sphere**;

- The outstanding extracting behaviour of PTD-system can arise from the formation of **intermediary mixed complexes** containing both extractants (TODGA-PTD) and therefore a comprehensive understanding of such ligand selectivity is essential on a fundamental level.



- Further confirmation of the results with **computational chemistry**
- Additional complexation studies of the TODGA-PyTriDiol extracting system and **other Ln**
- **Evaluation of the gas-phase stability** of the formed complex species and the **M-L competition in mixed complexes** with both extractants and the actinides.

Work partially developed at:

cea → TALISMAn

KIT Karlsruhe Institute of Technology → SACSESS EURATOM

GENIORS GEN IV integrated oxide fuels recycling strategies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