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Safety of actinide separation processes

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Complex structure of An and Ln complexes with modified diglycolamides in solution and solid state using different analytical techniques

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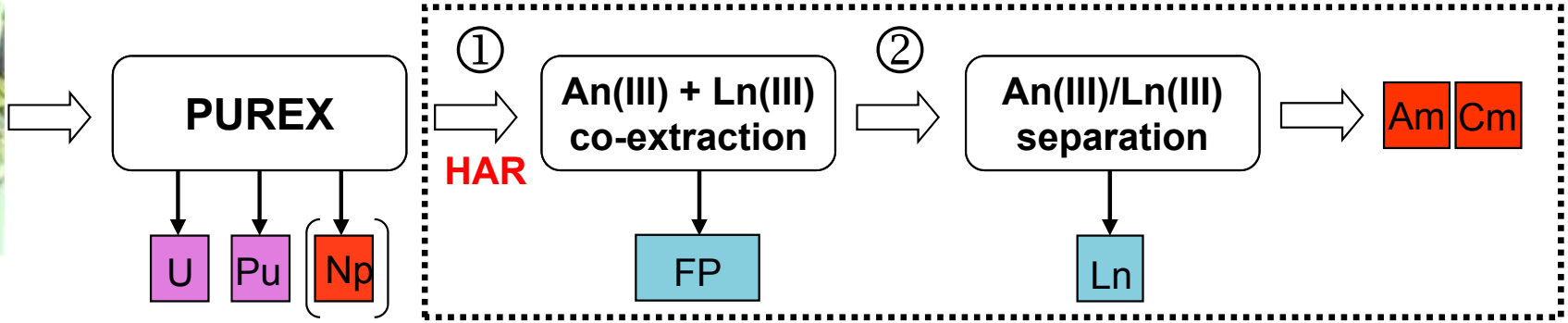
An(III) recovery: the multistep strategy

used nuclear fuel

Heterogeneous Recycling of MA



- Highly Acidic: 3 - 4 mol/L HNO_3
- Very Radioactive: (FP: $5 \cdot 10^{12}$ Bq/L)
- Rather large volumes : 6 to 7 m^3 / t_{HMi}
- Contains 100% of the MA and 80% of FP
- Large inventory of elements (>40) in different concentrations
- An(III) behave like Ln(III)

High Active Raffinate (HAR)

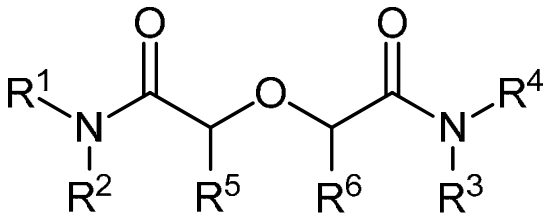
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*Ln*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	*An*	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Major Actinides | Minor Actinides (MA)

Fission products | Activation products

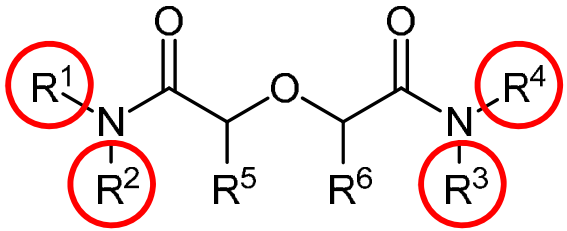
Introduction - Diglycolamides



- High affinity for An(III)/Ln(III)
- High distribution ratios of An(III)/Ln(III) at process relevant HNO_3 concentrations
- Easy/Cheap synthesis with various possible modifications
- CHON
- Good hydrolytic/radiolytic stability
- Several process demonstrations, e.g.
  - TODGA/TBP (Jülich (spiked) and ITU, Karlsruhe (genuine fuel))
    Modolo, G. et a. Solvent Extr. Ion Exch. **2008**, *26* (1), 62-76.
    Magnusson, D. et al. Solvent Extr. Ion Exch. **2009**, *27* (1), 26-35.
  - SANEX-TODGA (CEA, France)
    Hérès, X. et al. Proceedings of GLOBAL **2009**, Paris, France, 1127-1132.
  - T2EHDGA (India)
    Gujar, R.B. et al. Solvent Extr. Ion Exch. **2010**, 28 (6), 764-777.

Stephan, H. et al. Solvent Extr. Ion Exch. **1991**, *9* (3), 435-458 and 459-469.

Diglycolamides - Solubility

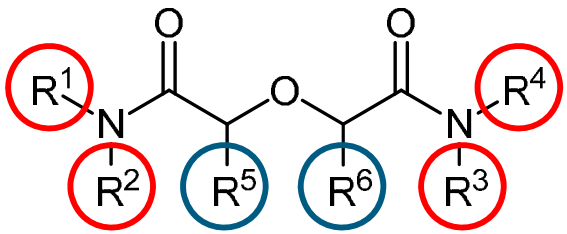


$$D = \frac{c_{org}(M)}{c_{aq}(M)}$$

DGA	Solubility in H_2O (mmol/L)	Solubility in n-dodecane	D_{Am} by 0.1 M DGA (1 M HNO_3)
TPDGA	57	Very poor	
TBDGA	2.3	Poor	
TADGA	0.27	Soluble	100
THDGA	0.11	Soluble	40
TODGA	0.042	Freely soluble	30
TDDGA	0.042	Freely soluble	18
TdDDGA	0.040	Freely soluble	11

Sasaki, Y. et al. Solvent Extr. Ion Exch. **2001**, *19* (1), 91-103.

Diglycolamides - Derivatisation

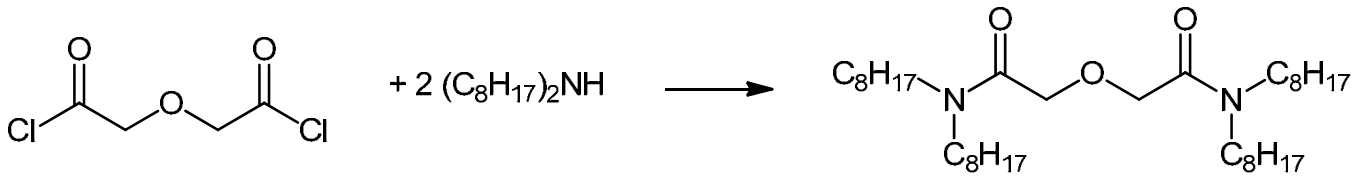


- A lot of effort was drawn to vary R^1-R^4 [1]
  - Effect on solubility
  - Branching improves 3rd phase formation boundaries
  - Higher loading of the solvent
  - Selectivity
- Effect of substituents R^5/R^6 was not studied yet!
  - Synthesis of derivatives within the ACSEPT project[2-3]

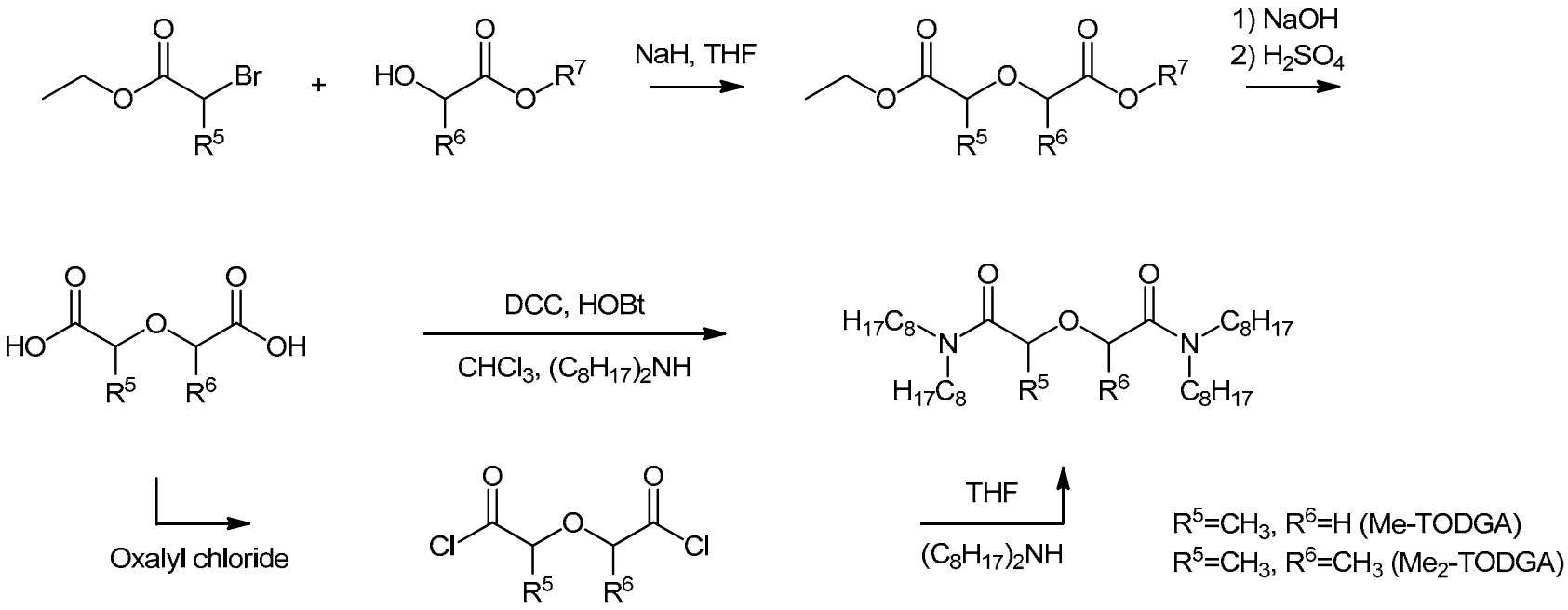
[1]Ansari, S.A. et al. Chem. Rev. **2012**, *112* (3), pp. 1751-1772
[2]Iqbal, M. et al. Supramol. Chem. **2010**, *22* (11), pp. 827-837
[3]Wilden, A. et al. Solvent Extr. Ion Exch. **2014**, *32* (2), pp. 119-137

Synthesis

- TODGA

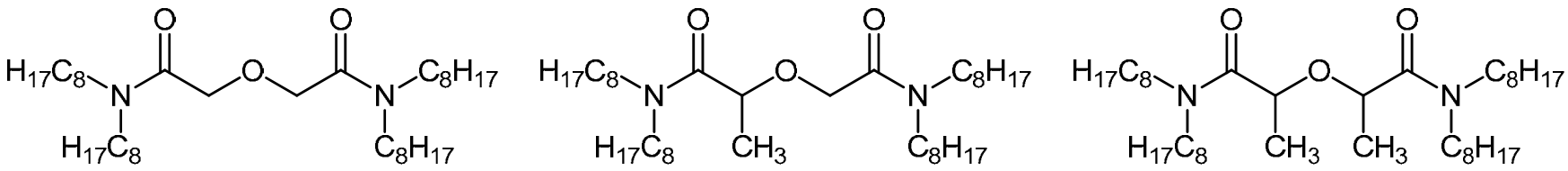


- R^5/R^6 derivatized TODGA

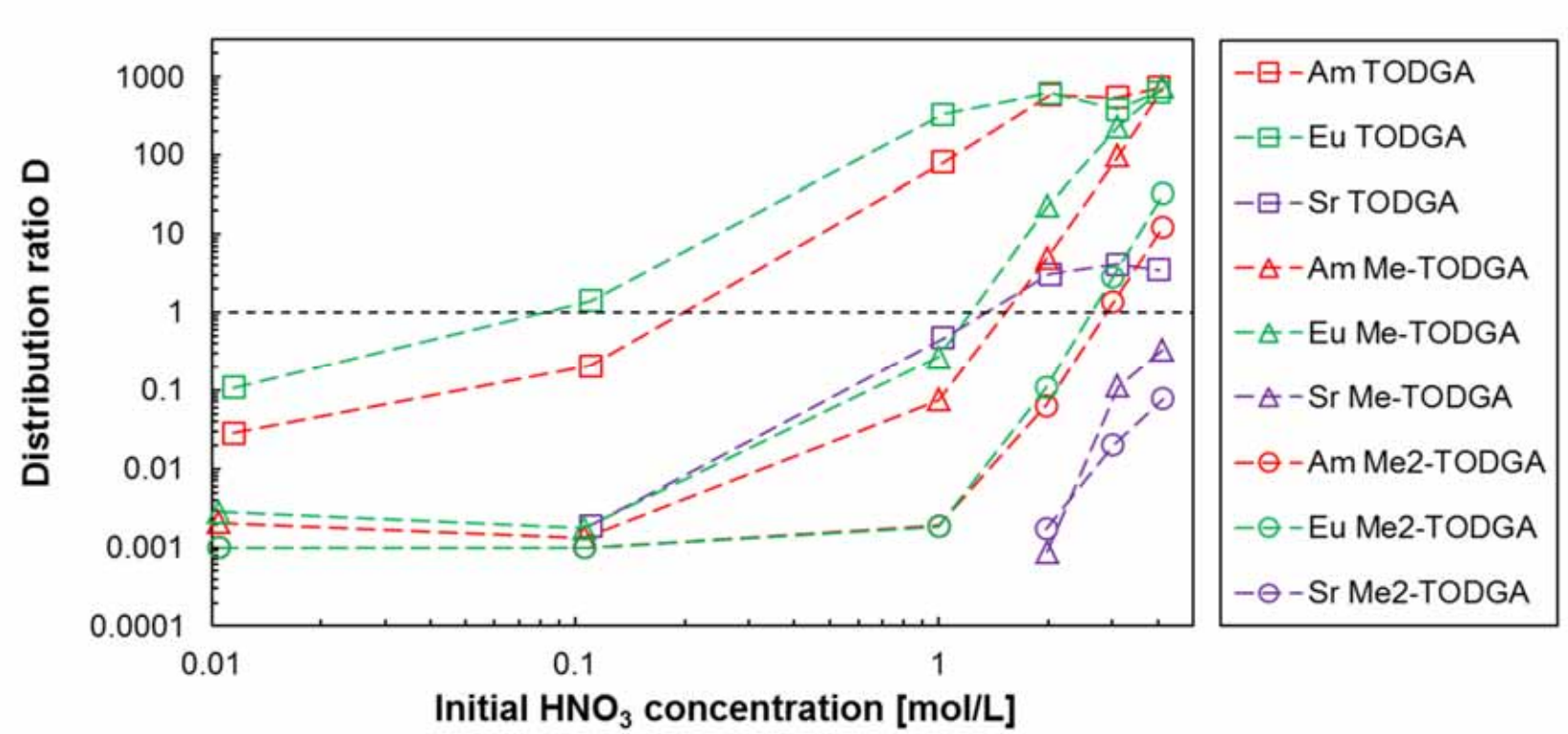


Iqbal, M. et al. Supramol. Chem. **2010**, *22* (11), pp. 827-837

Solvent Extraction



TODGA Me-TODGA Me_2-TODGA

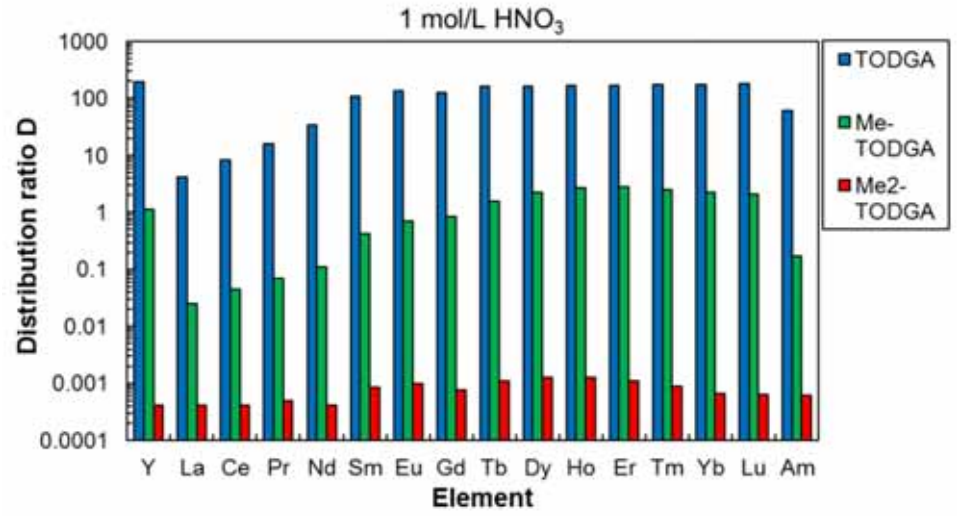


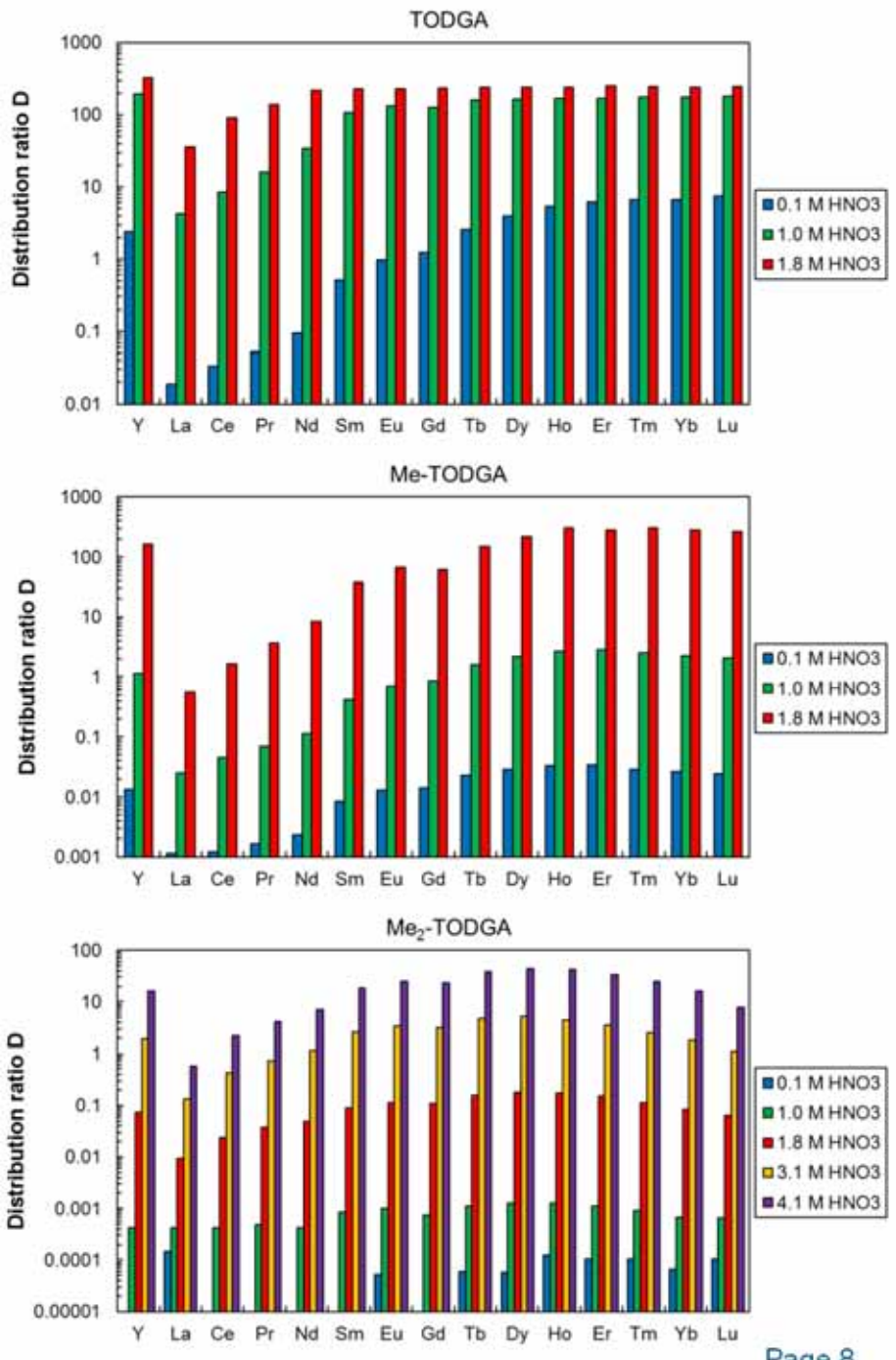
- Distribution ratios decrease with introduction of additional Me groups
- reduced Sr co-extraction

Org. 0.1 mol/L ligand in TPH
Aq. var. HNO_3 concentrations, 10^{-4} M Sr, + ^{241}Am, ^{152}Eu tracer, 15 min., 22°C

Extraction of Ln(III)

- D-ratios strongly depend on degree of substitution
- Heavier Ln are better extracted
- Maximum in Ln-series shifts (Lu – Er – Dy)





Extraction mechanism: slope analysis

- Solvating mechanism is assumed

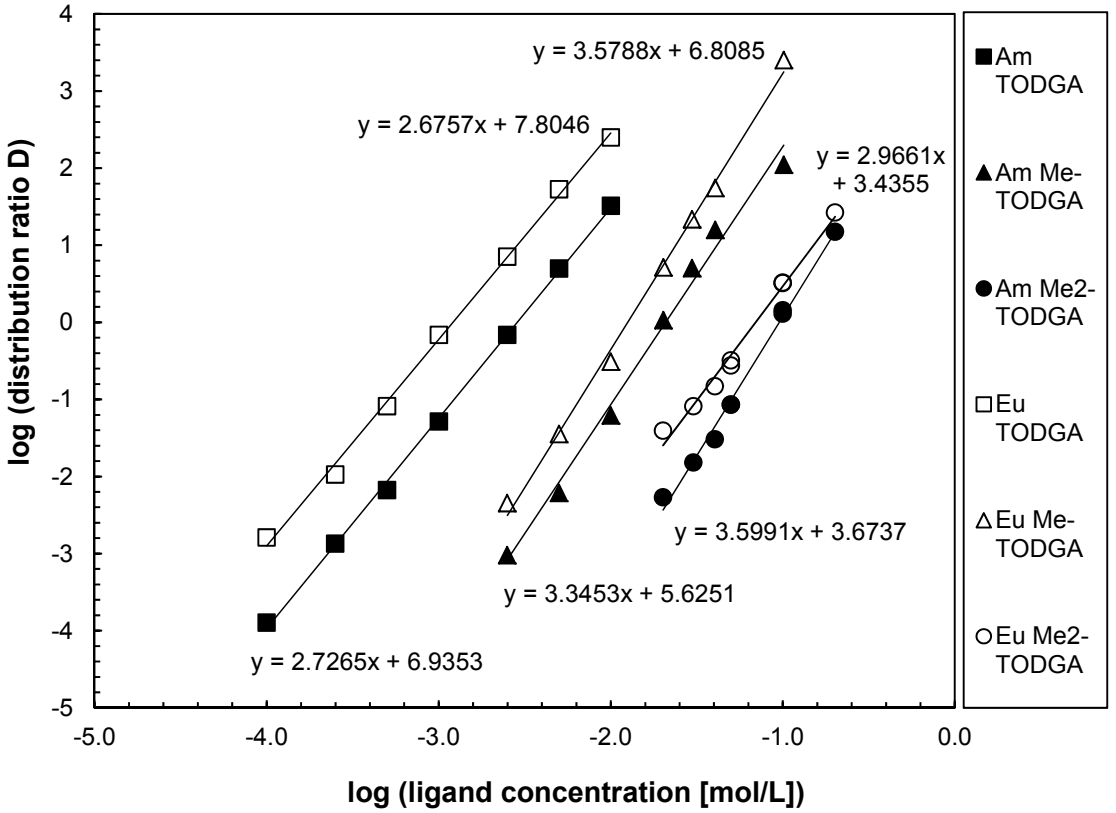
$$M_{aq}^{n+} + nNO_{3,aq}^{-} + mL_{org} \overset{K_{ex}}{\rightleftharpoons} M(NO_3)_n L_{m,org}$$

$$K_{ex} = \frac{\left[M(NO_3)_n L_{m,org}\right]}{\left[M_{aq}^{n+}\right] \cdot \left[NO_{3,aq}^{-}\right]^n \cdot \left[L_{org}\right]^m}$$

$$\log D = m \cdot \log\left[L_{org}\right] + n \cdot \log\left[NO_{3,aq}^{-}\right] + \log K_{ex}$$

$$D = \frac{\left[\left(M(NO_3)_n L_m\right)_{org}\right]}{\left[M_{aq}^{n+}\right]}$$

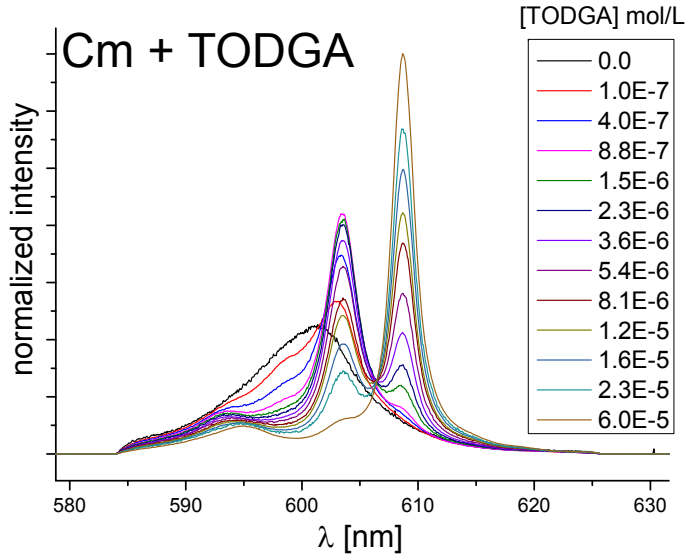
- At constant nitrate concentrations linear relationship
- Slopes ~3 observed
- Am/Eu slopes not parallel for Me_2-TODGA

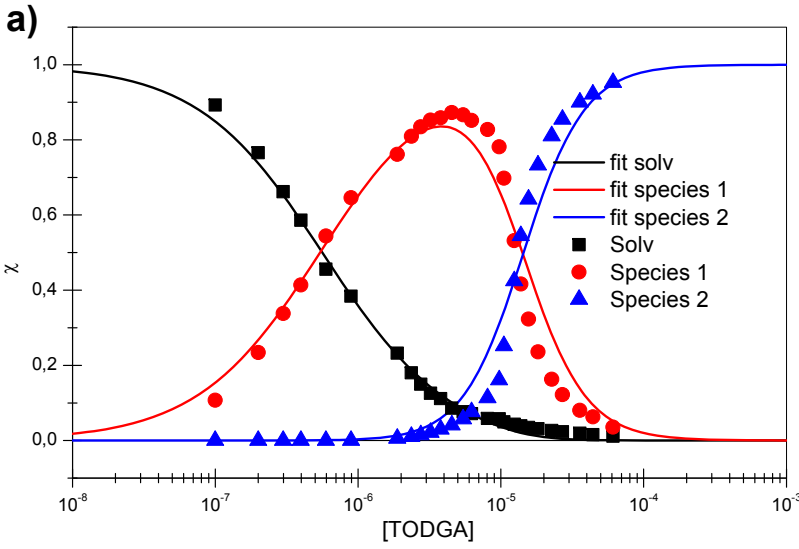


Org. var. ligand concentrations in TPH
Aq. 3.1 mol/L HNO_3, ^{241}Am, ^{152}Eu tracer, 15 min., 22°C

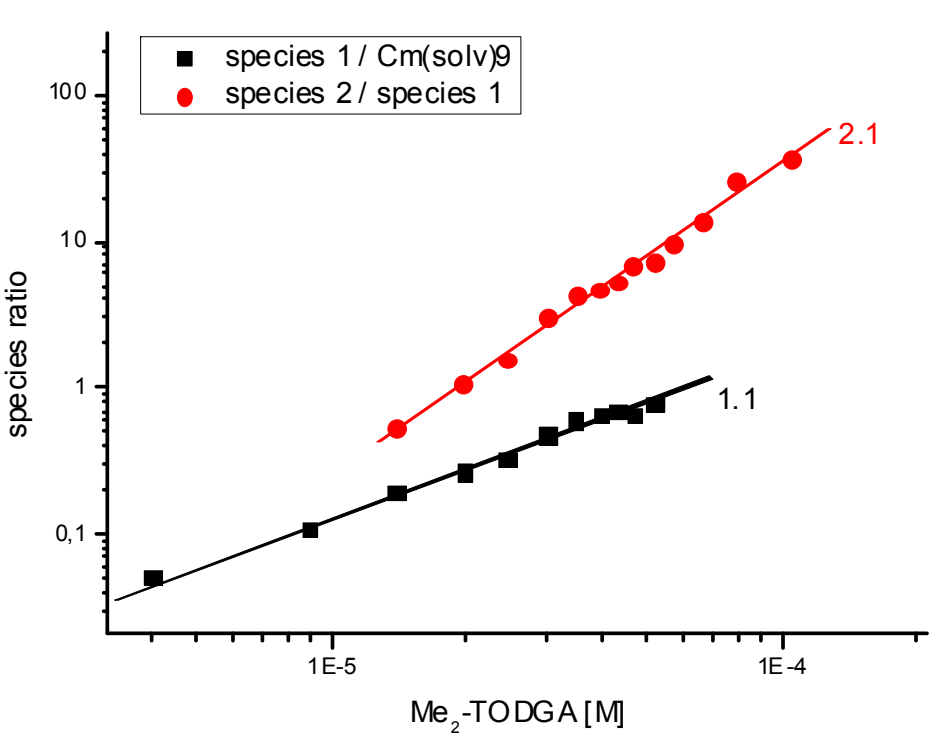
Additional insight into the complexation by TRLFS investigations

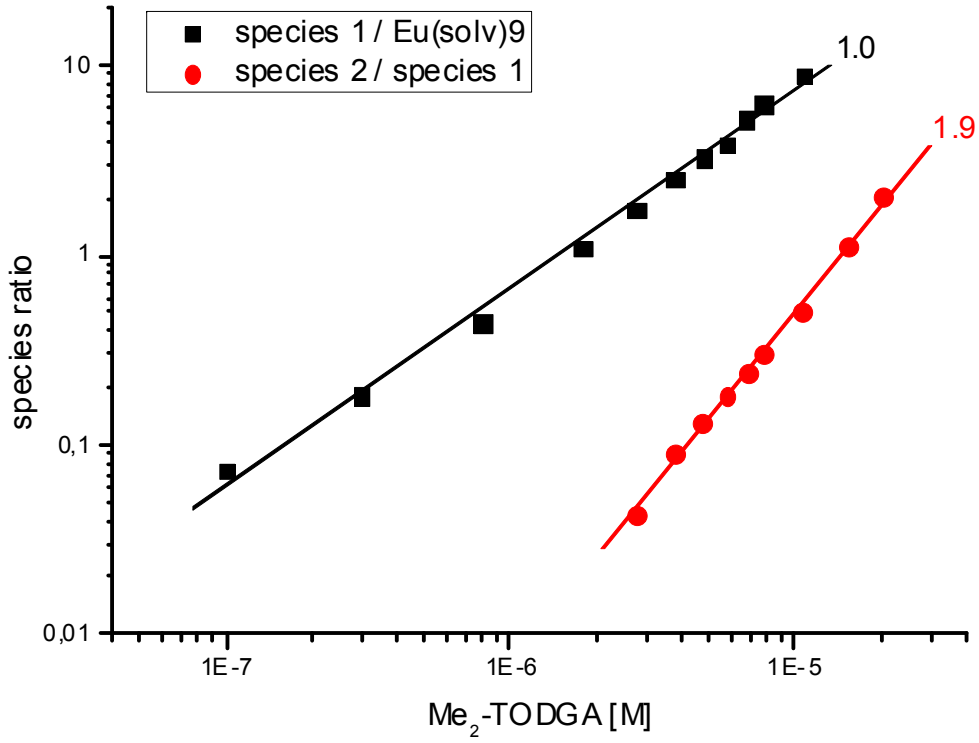
- Time Resolved Laser induced Fluorescence Spectroscopy
- Cm(III) and Eu(III) fluorescence is measured after excitation using monochromatic laser light
- Complexation of the metal ions with different ligands changes the fluorescence emission spectrum
- Single phase titration experiments in EtOH and extraction experiments into kerosene solution of ligand to confirm single phase data





TRLFS slope analysis





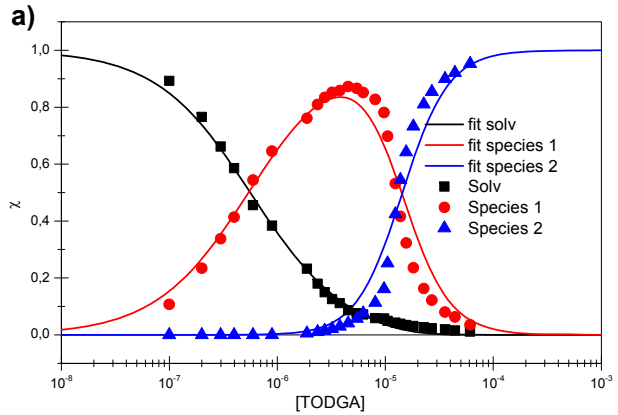
- Species 1 identified as the 1:1 metal:ligand complex
- Species 2 identified as the 1:3 metal:ligand complex
- Same results for TODGA and Me-TODGA

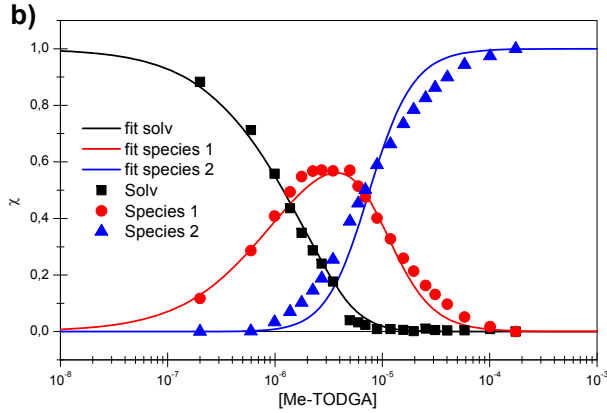
Evaluation of Me-substituted Diglycolamides

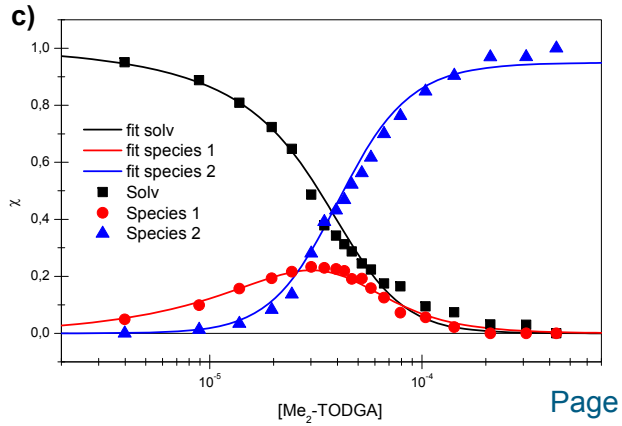
- TRLFS confirmed threefold complexation
- Same trend in stability constants
- Same trends in “SF”
- Lifetime measurements suggest 0-1 H_2O in the inner coordination shell

	$\log \beta'_3$ M = Cm	$\log \beta'_3$ M = Eu
M(III)-TODGA	14.92 ± 0.30	15.69 ± 0.22
M(III)-Me-TODGA	14.85 ± 0.31	15.45 ± 0.20
M(III)-Me_2-TODGA	12.72 ± 0.25	15.47 ± 0.24

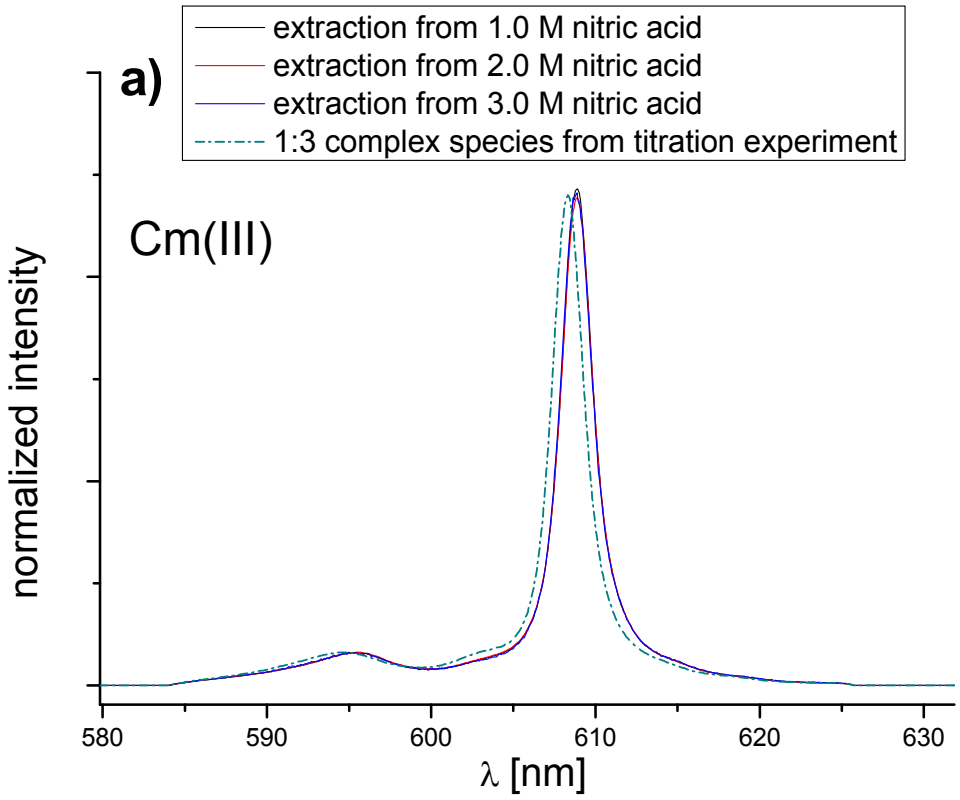
	$SF_{Eu/Am}$ solvent extraction	$SF_{Eu/Cm}$ TRLFS
TODGA	13.3	5.9
Me-TODGA	2.4	3.9
Me_2-TODGA	845	562

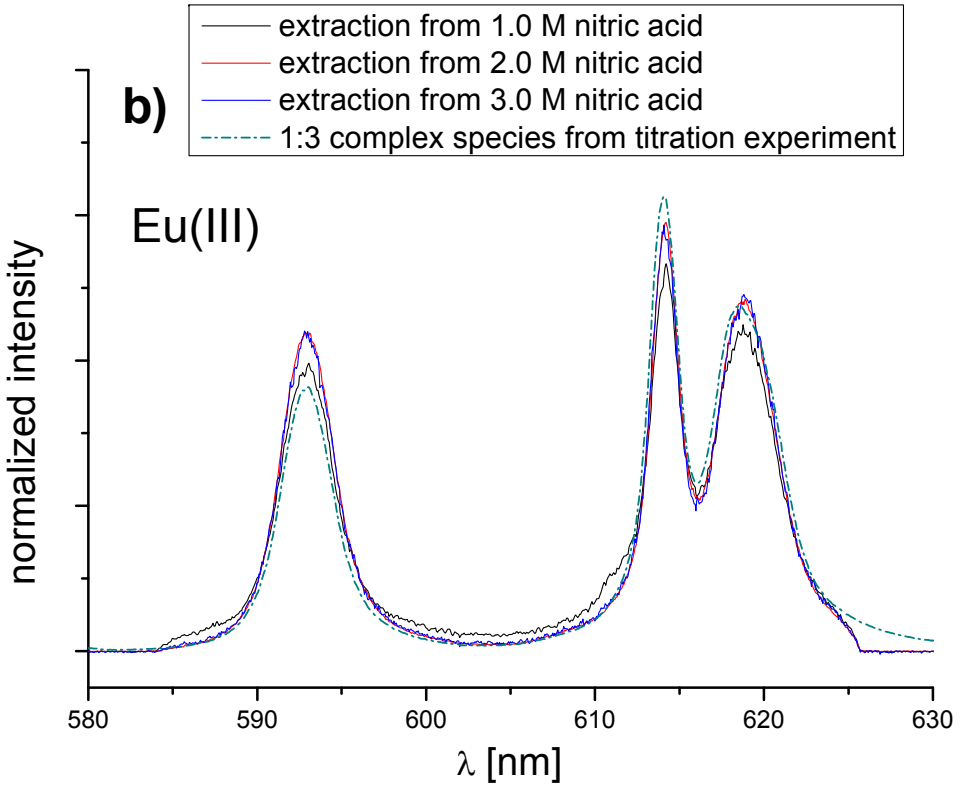






2-phase extraction experiments
Comparison to 1-phase experiments

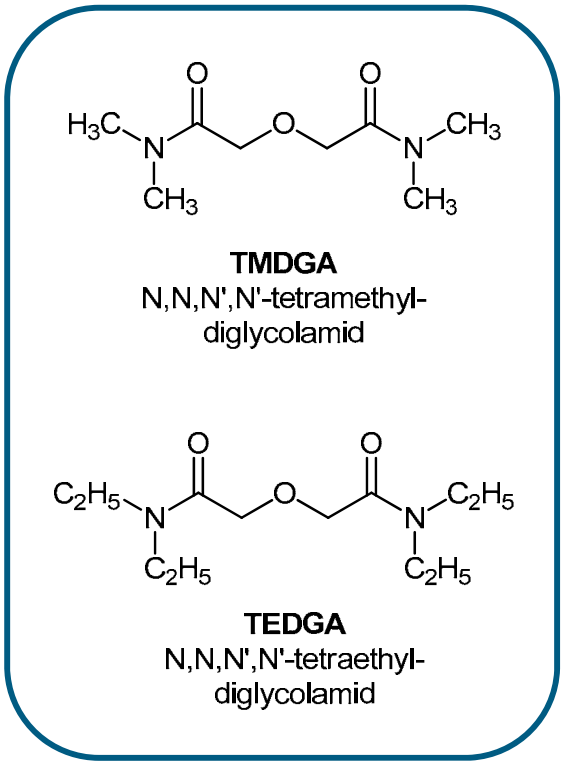


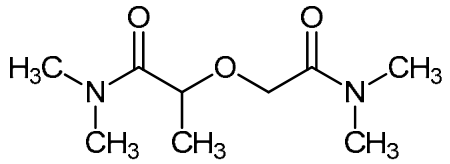


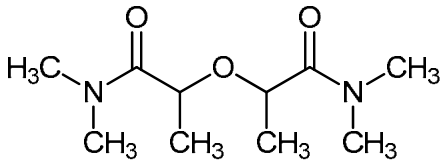
- In 2-phase extraction experiments, only the 1:3 complexes were observed
- Fluorescence lifetimes similar to single phase experiments

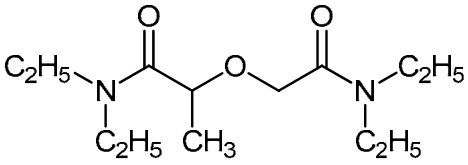
Synthesis of single crystals

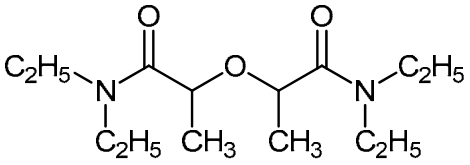
- Use of short-chained analogues of Me-TODGA and Me_2-TODGA (as lipophilic ligands don't yield crystals)
- Crystallisation experiments of Ln-complexes with these ligands
- X-ray single crystal structure analysis







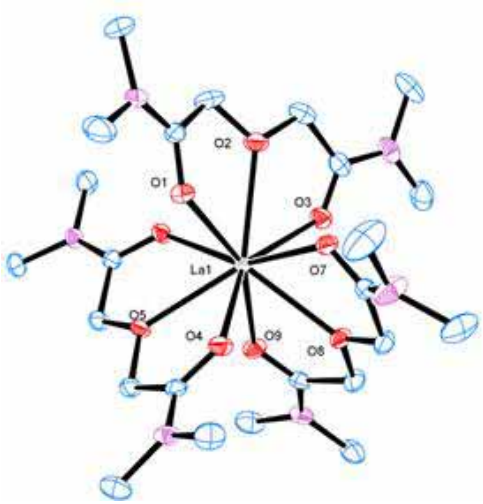




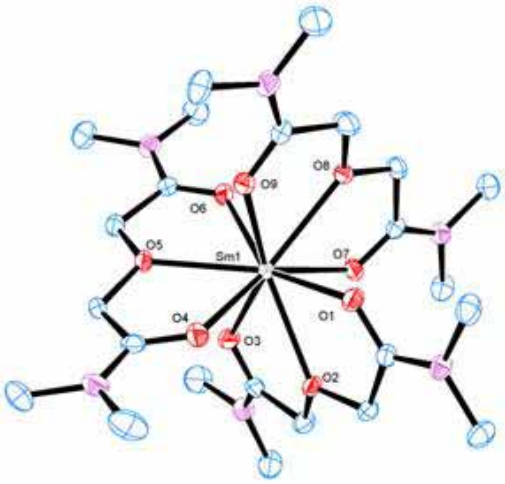
Crystal structures reported for La, Pr, Nd, Sm, Eu, and Gd with TEDGA:
Kawasaki, T. et al. Bull. Chem. Soc. Japan **2014**, 87 (2), pp. 294-300.

Obtained crystal structures

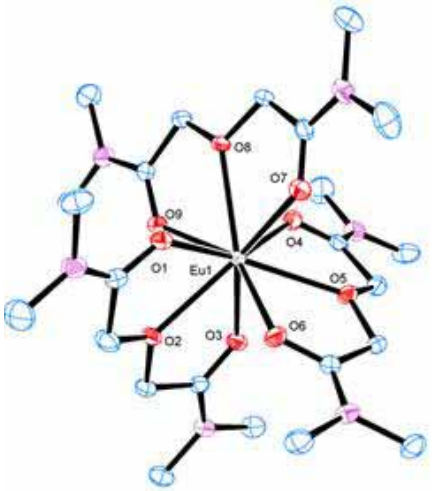
- TMDGA



La

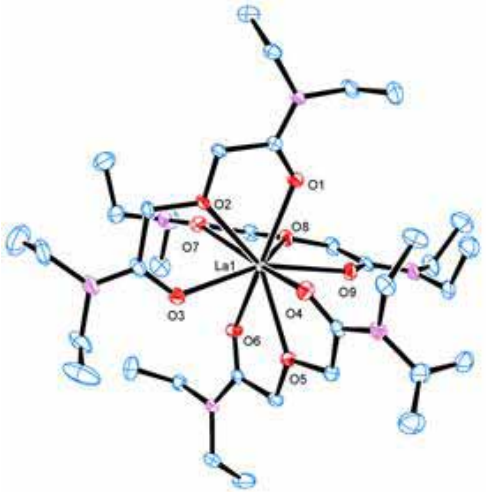


Sm

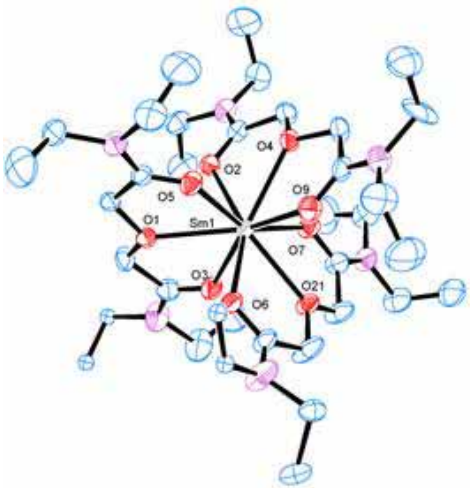


Eu

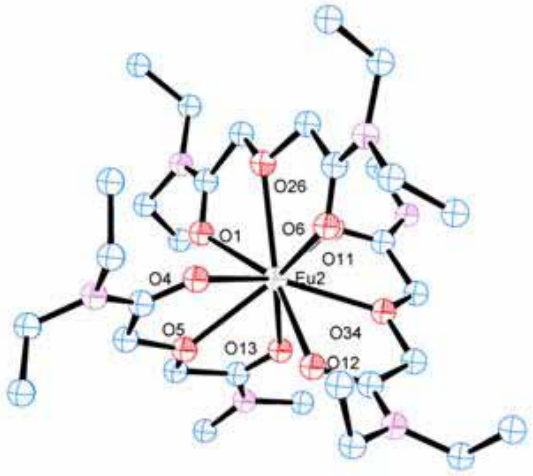
- TEDGA



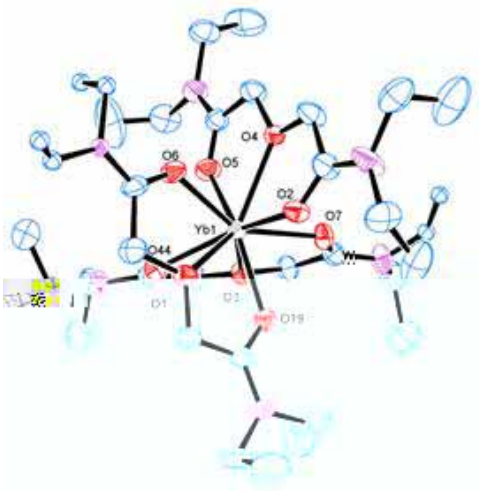
La



Sm



Eu

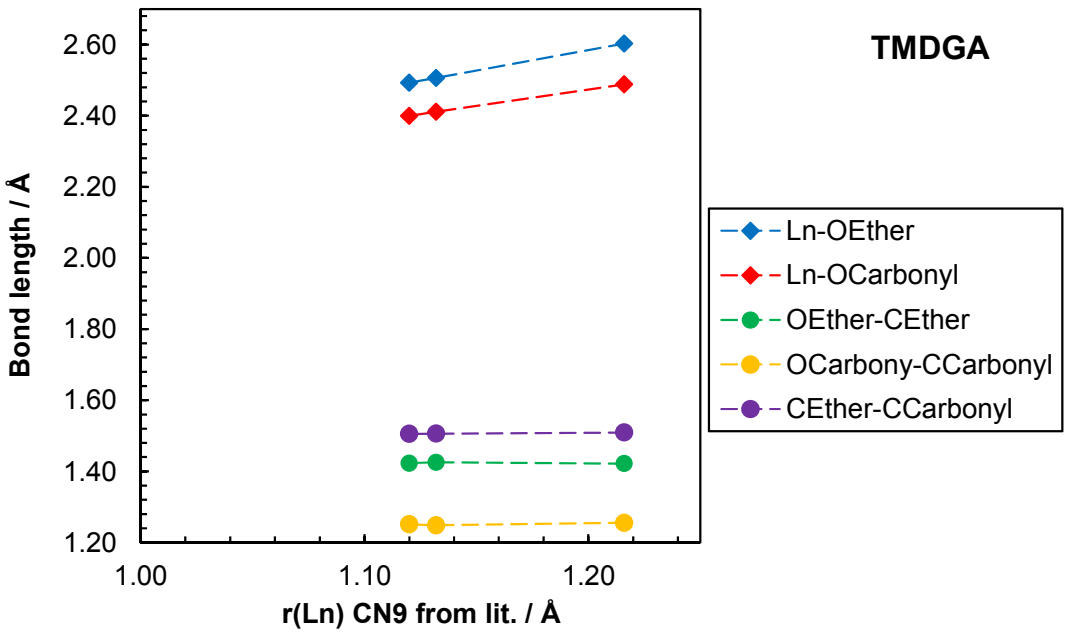


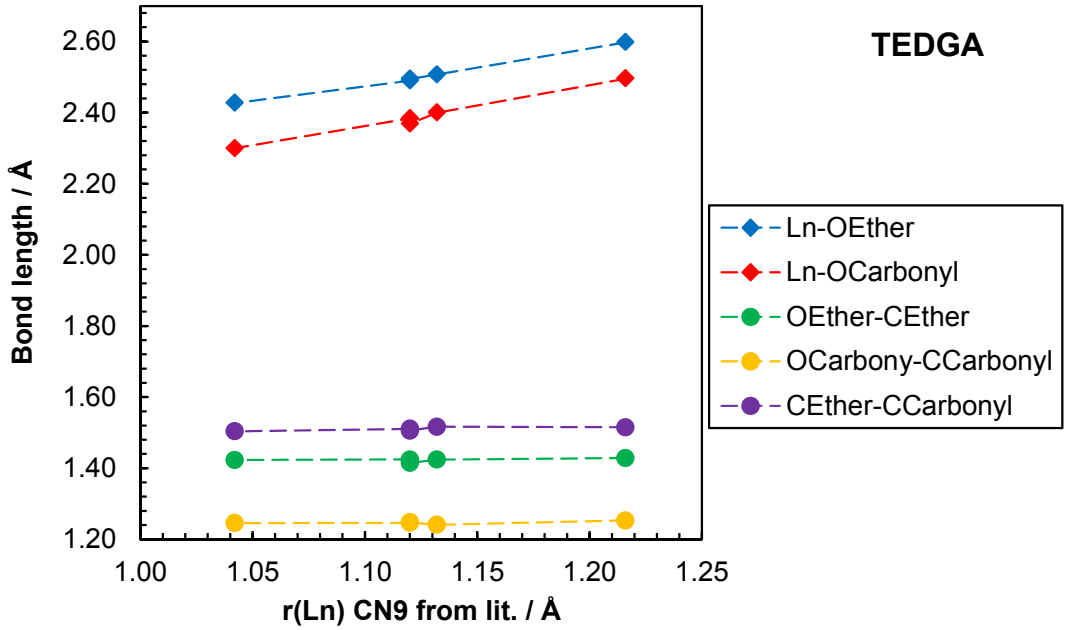
Yb

- Crystals with methylated derivatives were grown but not measured, yet.

Single crystal structure analysis

- Trends visible in Ln-O bond lengths
- Intra-ligand bond lengths constant
- $O_{Carbonyl}$-Ln-$O_{Carbonyl}$ angle decreases with increasing r(Ln)
- Isostructural to $[Pu^{IV}(TMDGA)_3]$[1] and $[Ln(TEDGA)_3]$[2] crystal structures reported for La, Pr, Nd, Sm, Eu, and Gd



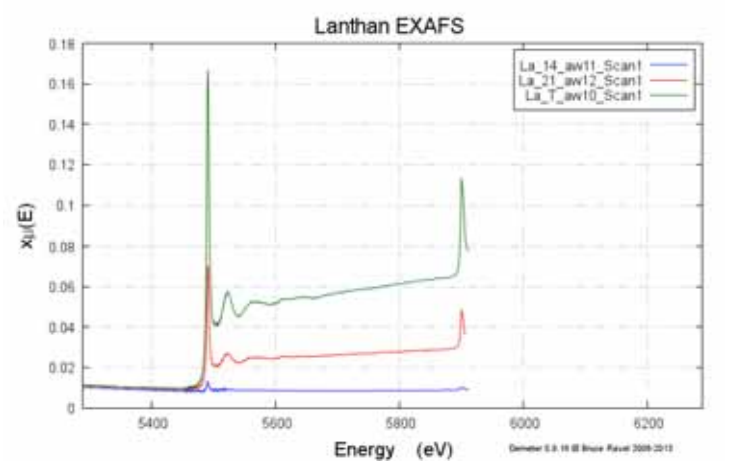


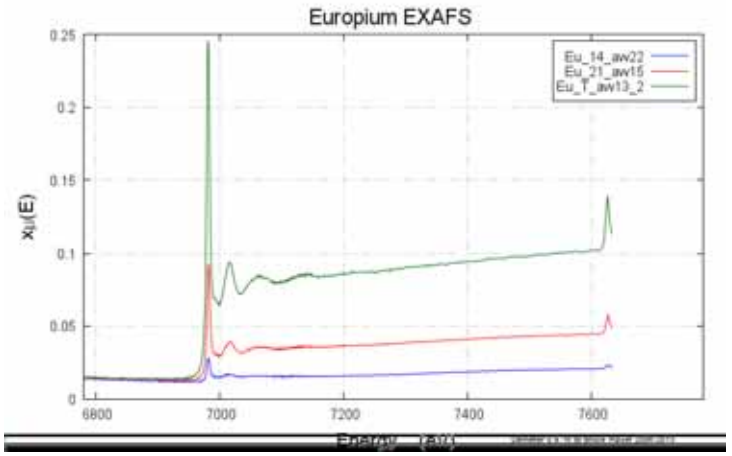
[1] Reilly S. D. et al. Chem. Comm. **2012**, *48* (78), pp. 9732-9734.

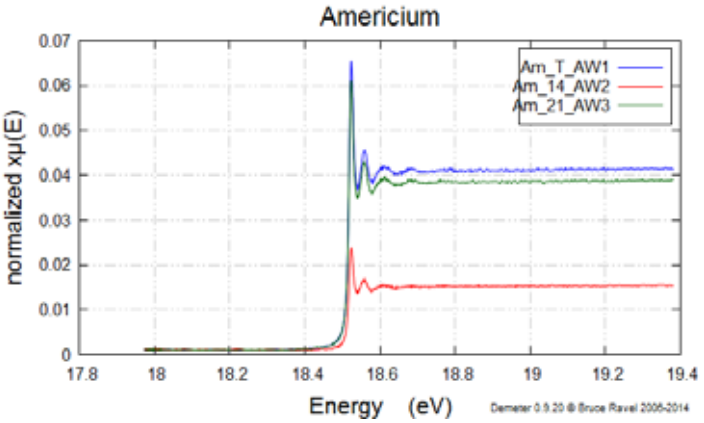
[2] Kawasaki, T. et al. Bull. Chem. Soc. Japan **2014**, *87* (2), pp. 294-300.

XAFS measurements

- XANES/EXAFS investigations @ ANKA synchrotron, Karlsruhe
  - “Real life” samples of ^{243}Am, ^{239}Pu(IV), La, Eu, Yb were prepared by extraction from nitric acid
  - 0.1 mol/L ligand in kerosene
  - Phase separation and measurement of the organic phase
  - Some samples have not been measured, yet
- Org-. metal concentration resembled by edge jump
- TODGA > Me-TODGA > Me_2-TODGA
- M-(Me_2-TODGA) intensities partly very low

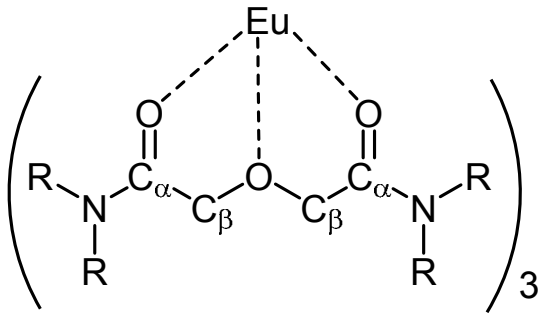




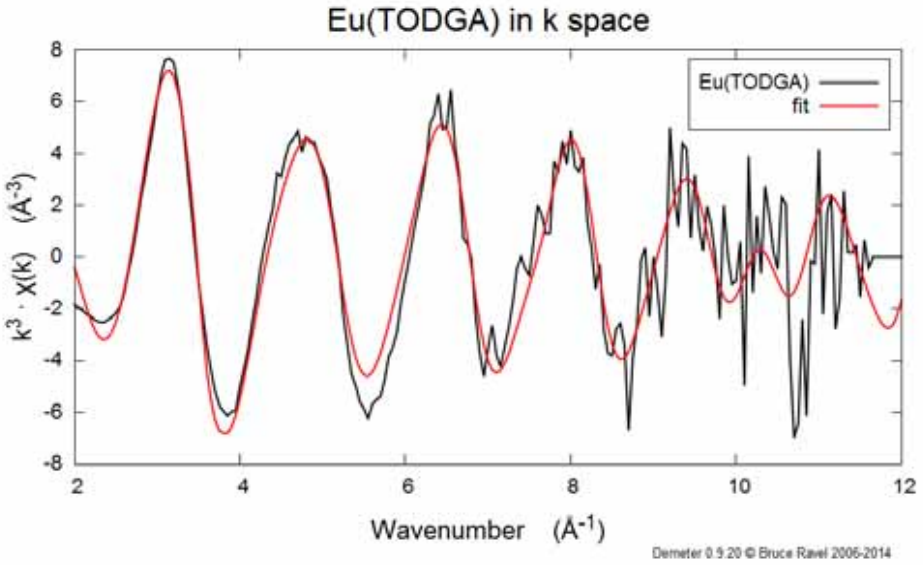


EXAFS of Eu-TODGA complex

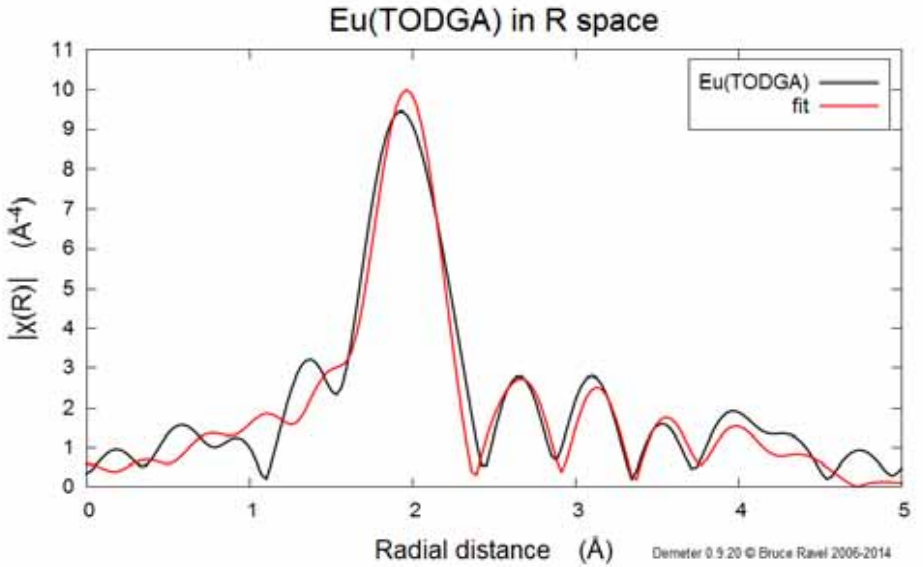
- Single crystal data of $[Eu(TEDGA)_3]$ complex was used as the structure model
- Best fit using
  - 6 O at 2.40 Å (carbonyl)
  - 3 O at 2.50 Å (ether)
  - 6 C at 3.26 Å (C_α)
  - 6 C at 3.47 Å (C_β)
  - [6 N at 4.7 Å]



- Consistent with reported EXAFS data on a solid complex of $[Eu(TODGA)_3][BiCl_4]_3$[1]



Primary $k^3\chi(k)$ Eu EXAFS data and fit

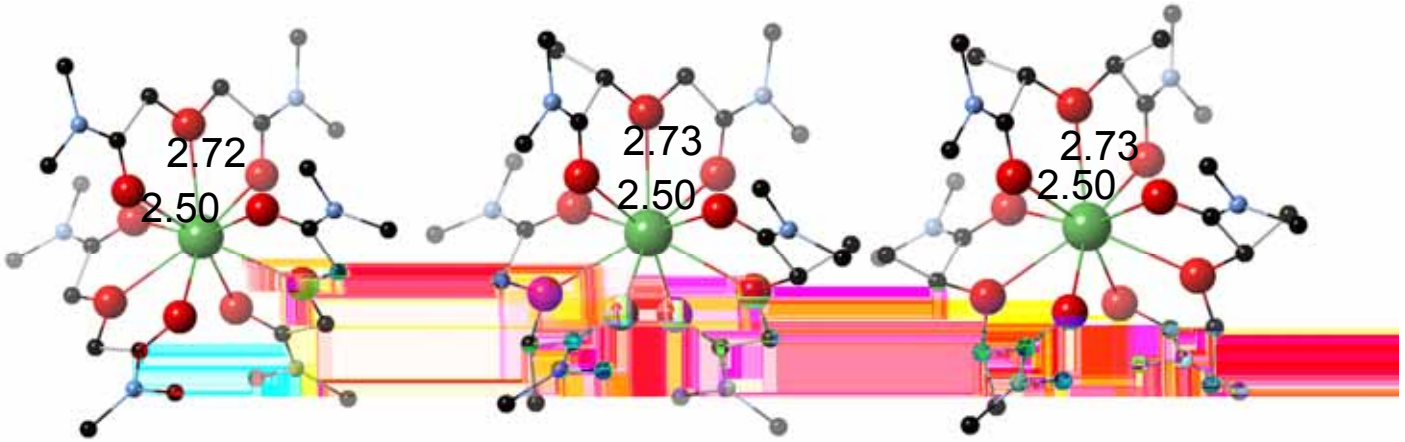


Fourier transform of the $k^3\chi(k)$ Eu EXAFS data and fit

[1] Antonio M.R. et al. Dalton Trans. **2012**, *44* (2), pp. 515-521.

Ab-initio DFT-based computational study

- TMDGA with shortest length of amide groups was used



Formation energies [kJ/mol]	La^{3+}	Eu^{3+}	Am^{3+}	
			PBE	PBE+U
TMDGA	-2750.6	-2970.5	-2888.8	-2808.8
Me-TMDGA	-2704.9	-2923.9	-2842.5	-2762.4
Me_2-TMDGA	-2700.7	-2918.4	-2837.3	-2757.1

- Trends observed in solvent extraction experiments are reproduced!

Conclusions and Outlook

- Methylated TODGA derivatives show very promising properties towards process development
  - D_{Sr}<1, but $D_{An/Ln}$>1 at high nitric acid concentrations
  - Fast kinetics
  - Stripping may be improved
- Extraction mechanism was studied by solvent extraction and TRLFS
  - Both methods show 1:3 metal:ligand complexes
  - Conditional stability constants were determined by TRLFS and show the same trends as observed in solvent extraction
- Single crystal data gives structural information in solid state (to be continued)
- EXAFS data gives structural information in organic phase (to be continued)
  - Again, both methods show 1:3 metal:ligand complexes
- DFT-based calculations support the experimental results
- This fundamental study gives a thorough insight into the impact of systematic structural changes of ligands towards their complexation and extraction behaviour
- On this basis further optimizations of the extractants will follow

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Thank you for your kind attention