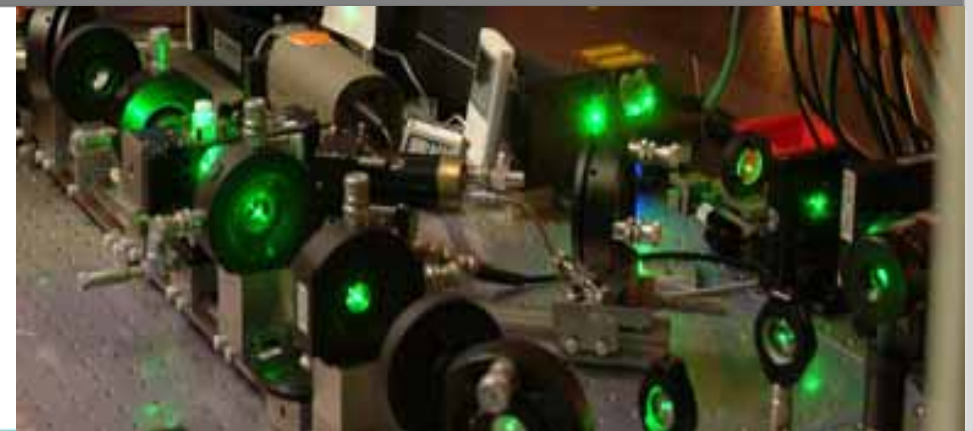
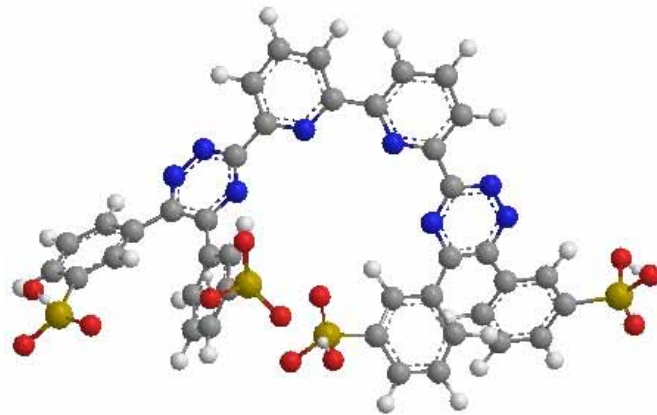


The AmSel Process – Selective Separation of Americium from PUREX raffinate

Christoph Wagner, Udo Müllich, Andreas Geist, Petra J. Panak



cf
Am

Bk

Np

U

Th

Cm

Pu

INE

Institut für Nukleare Entsorgung

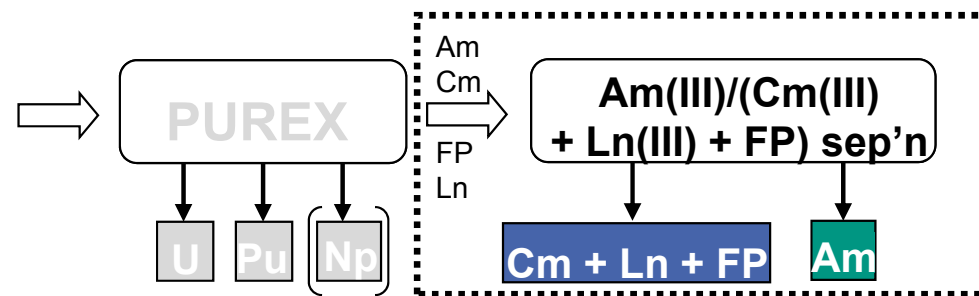
Introduction

- **Partitioning and Transmutation:**
 - Strategy to reduce long term radiotoxicity and heat load of nuclear waste.
 - Aim: separation of Pu and minor actinides (Np, Am and Cm) and transmuting them into short-lived or stable nuclides.
- Our goal: **selective extraction of Am(III) from PUREX raffinate**
 - separation of Am(III) from Cm(III), Ln(III) & other fission products (FP) and corrosion products (CP)

Why separate americium from curium?

- Curium:
 - no significant impact on long-term radiotoxicity or heat load of nuclear waste
 - High neutron dose rates and decay heat complicate production of new nuclear fuel

→ disposal in high active waste
- Separation of Am(III) should be performed early in the process



- EXAm process already successfully tested



Bollesteros, M.-J.; Calor, J.-N.; Costenoble, S.; Montuir, M.; Pacary, V.; Sorel, C.; Burdet, F.; Espinoux, D.; Hérès, X.; Eysseric, C., *Procedia Chem.* **2012**, 7, 178–183.

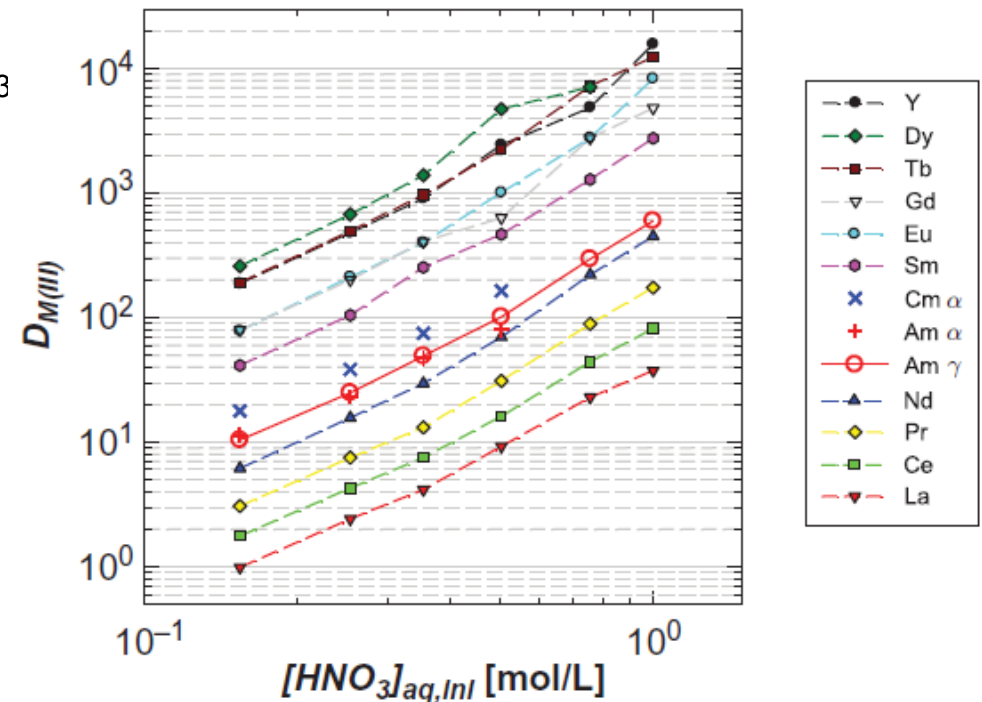
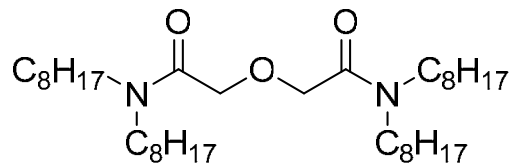
Strategy

- Co-extraction of Am(III), Cm(III) and Ln(III)
- Selective Am(III) stripping

Strategy

- Co-extraction of Am(III), Cm(III) and Ln(III)
- TODGA

- Extracts An(III) + Ln(III) from HNO_3
- Rejects most non-Ln fission products
- Rejects corrosion products
- Successfully used in DIAMEX and *i*-SANEX processes



Strategy

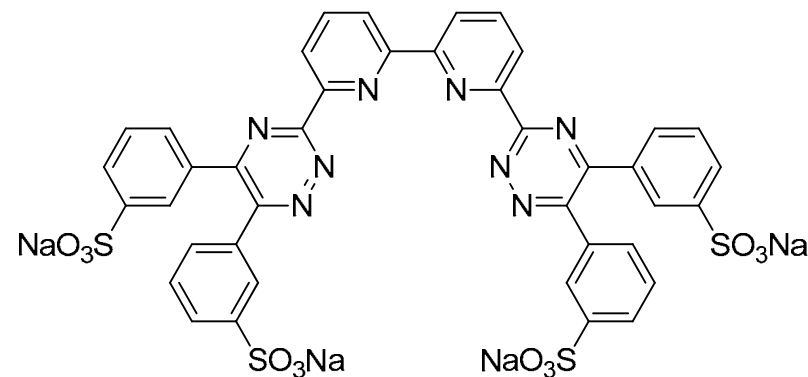
■ TODGA prefers Cm(III) over Am(III) $SF_{\text{Cm(III)/Am(III)}} = 1.6$

■ Requirement for selective Am(III) stripping:

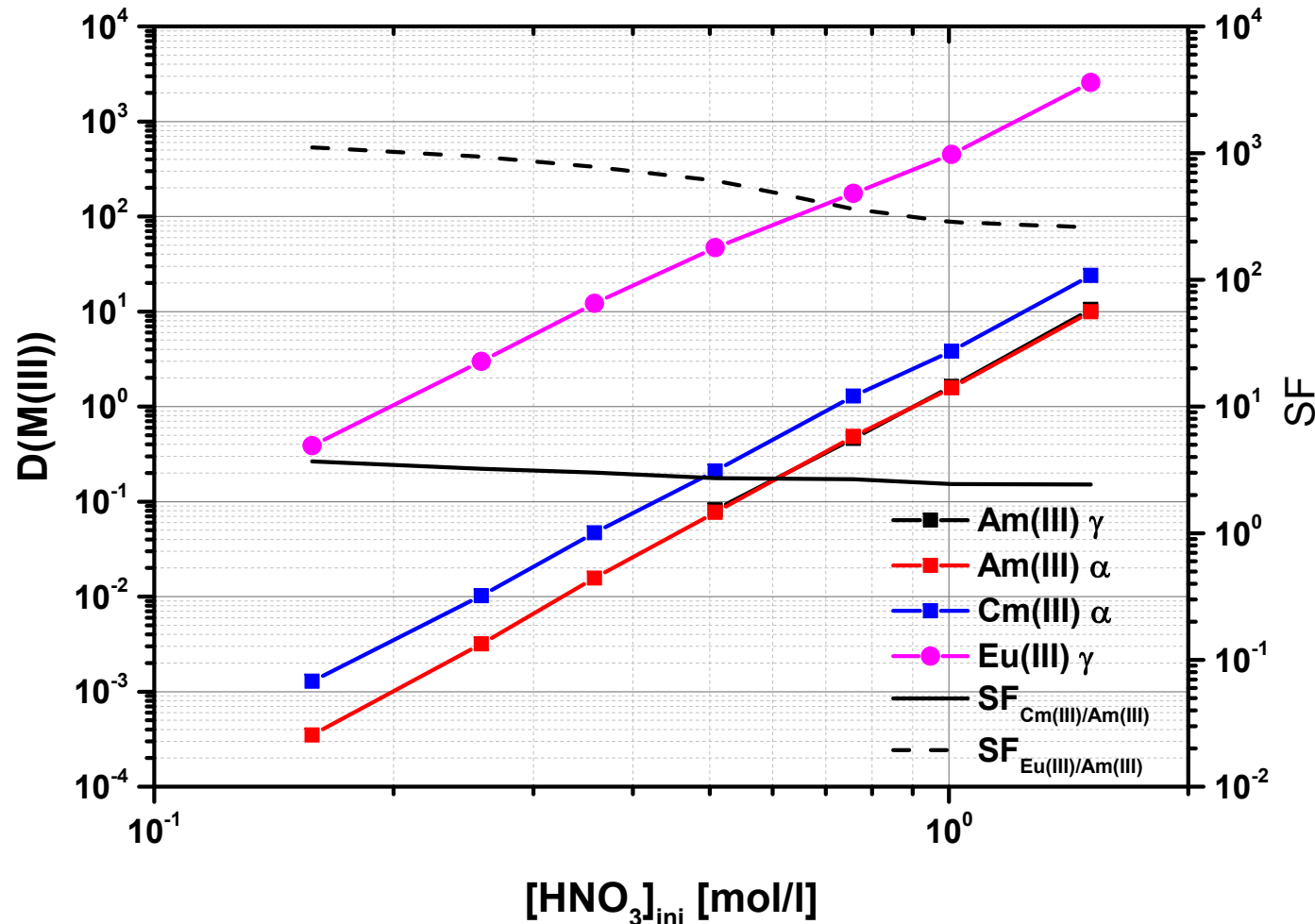
- Ligand has to prefer Am(III) over Cm(III)
- Well soluble in water / nitric acid

■ BTBP prefers Am(III) over Cm(III) $SF_{\text{Am(III)/Cm(III)}} = 1.6$

- Water soluble BTBP? $SF(\text{TODGA}) \cdot SF(\text{BTBP}) = 2.6?$



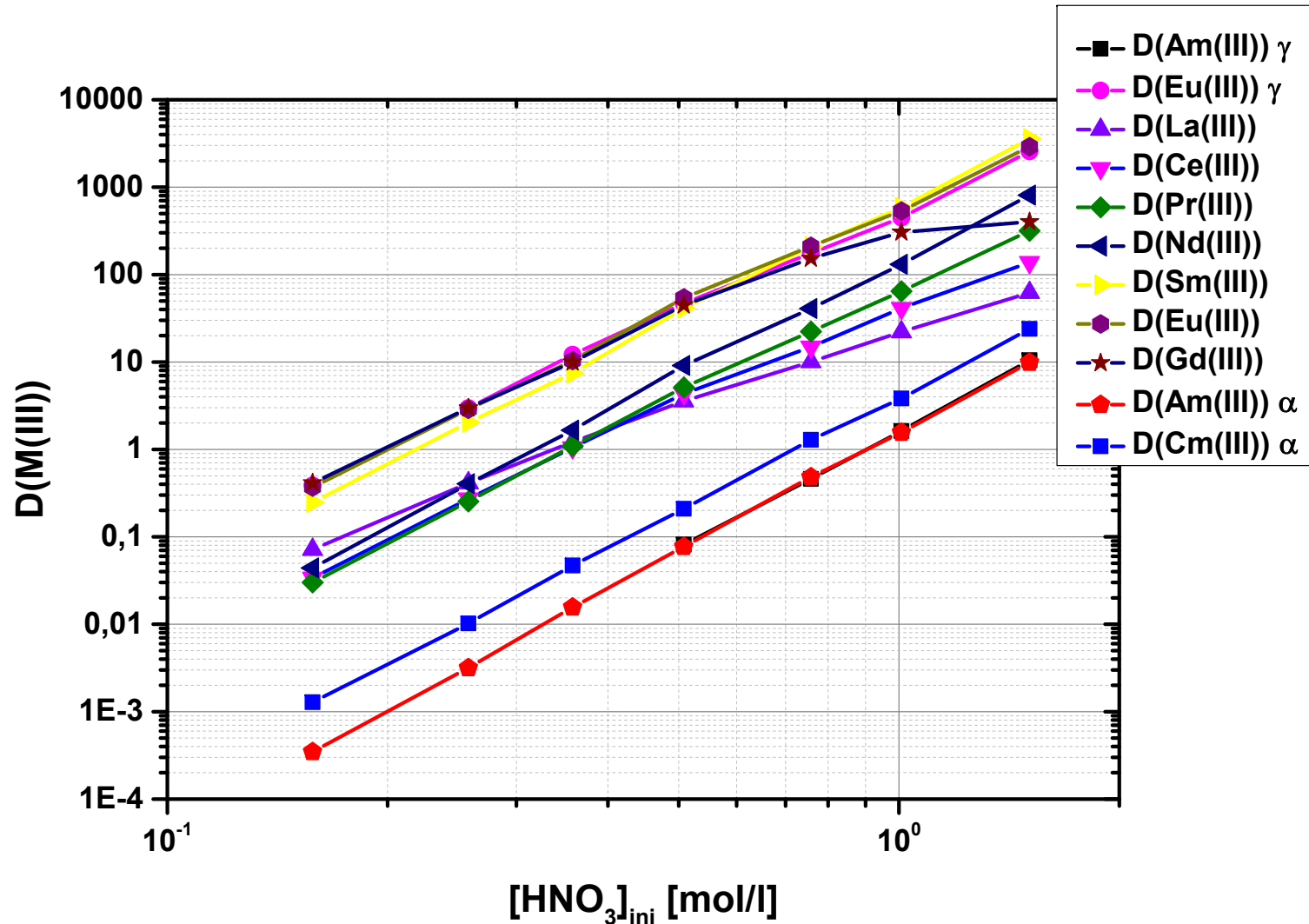
Extraction experiments with TODGA and SO₃-Ph-BTBP



$$SF_{\text{Cm(III)/Am(III)}} = 2.5-3$$

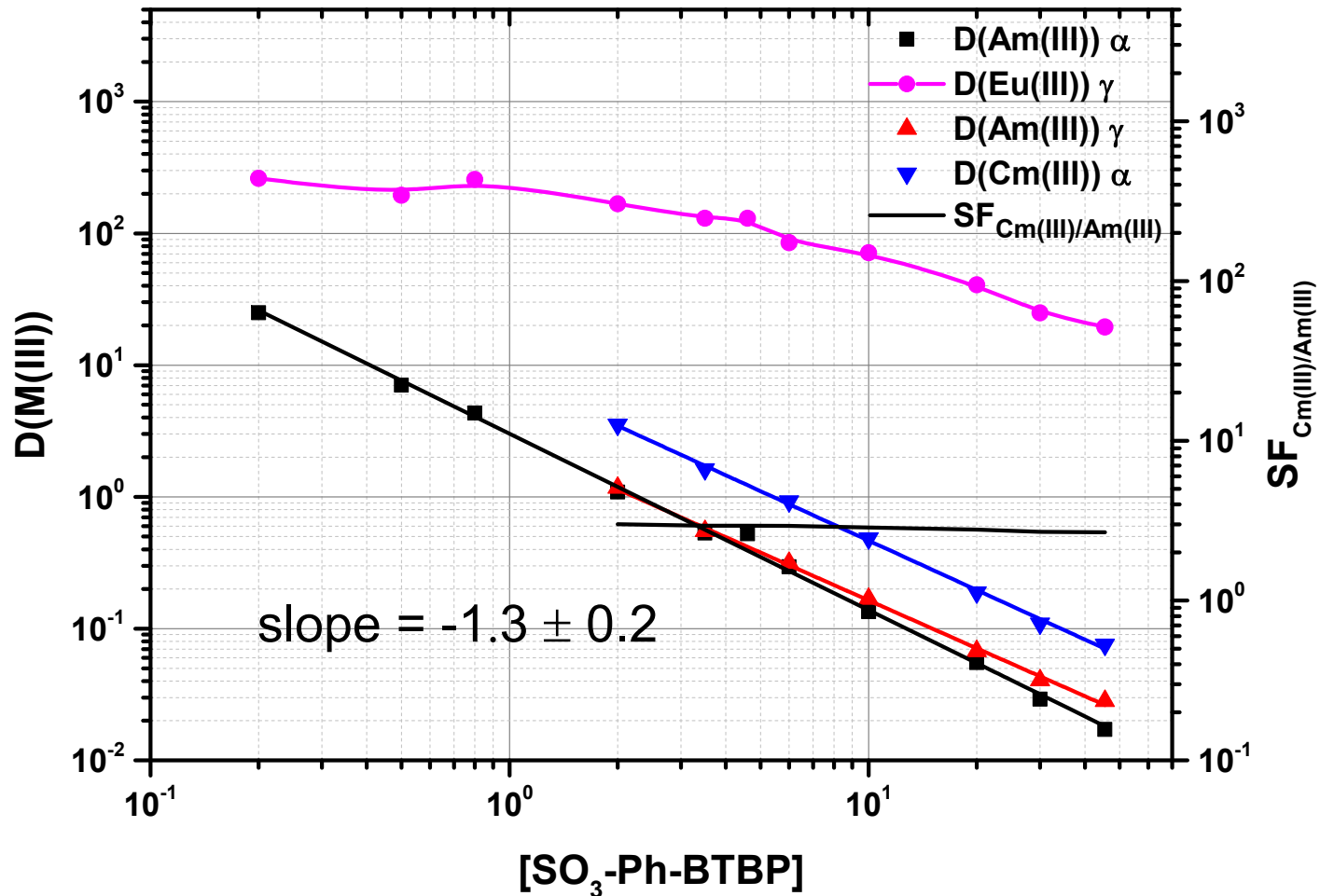
Aq. phase: 20 mM SO₃-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) in HNO₃
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

Extraction experiments with TODGA and SO₃⁻ Ph-BTBP



Aq. phase: 20 mM SO₃⁻-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) and 6 mg/l of each Ln(III), Y(III) and La(III) in HNO₃
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

Extraction experiments with TODGA and SO₃-Ph-BTBP

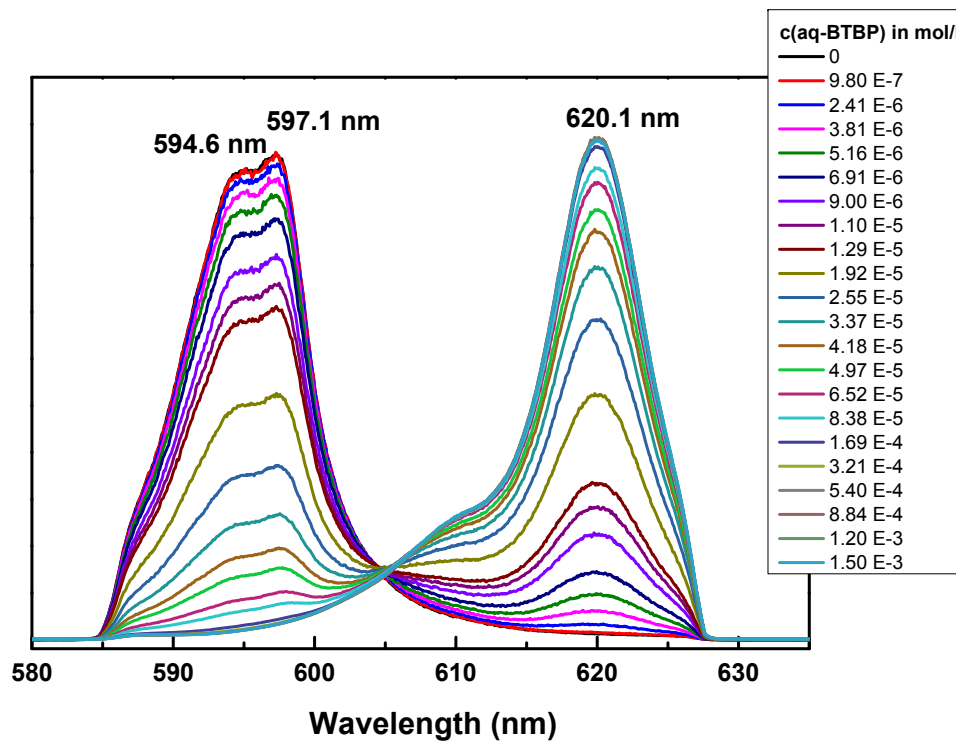


Formation of 1:1 complex? → TRLFS studies

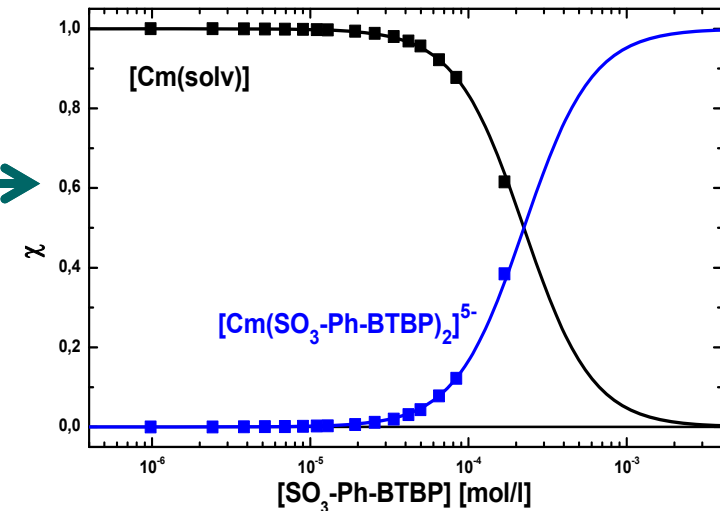
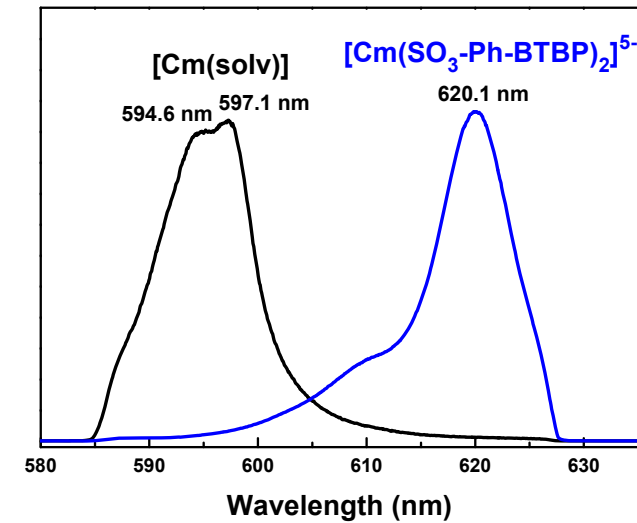
Aq. phase: SO₃-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) in 0.51 M HNO₃
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

Complexation of Cm(III) with SO₃-Ph-BTBP

Cm(III) emission spectra with increasing SO₃-Ph-BTBP concentration in 0.5 M HNO₃

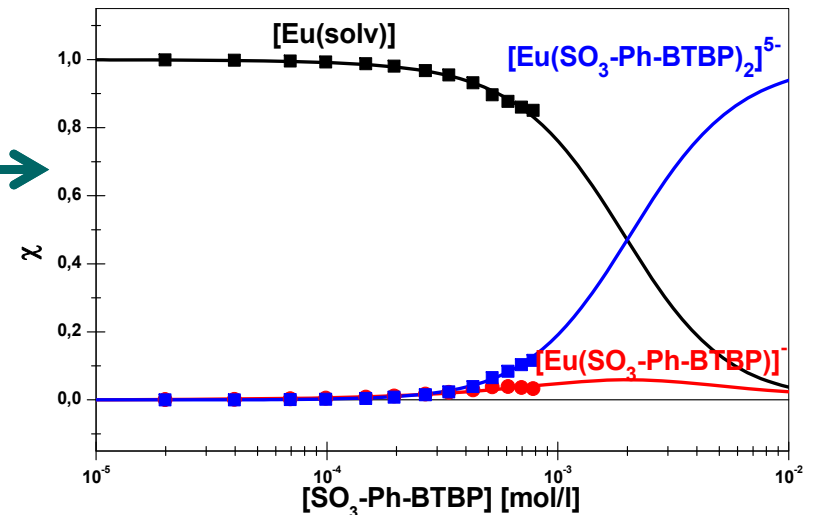
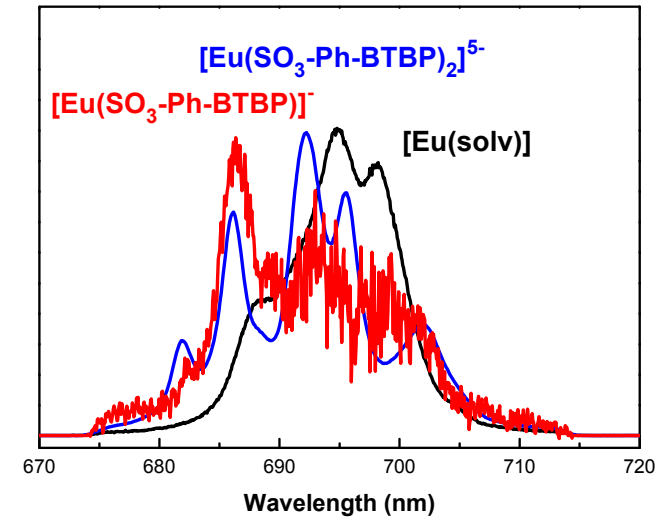
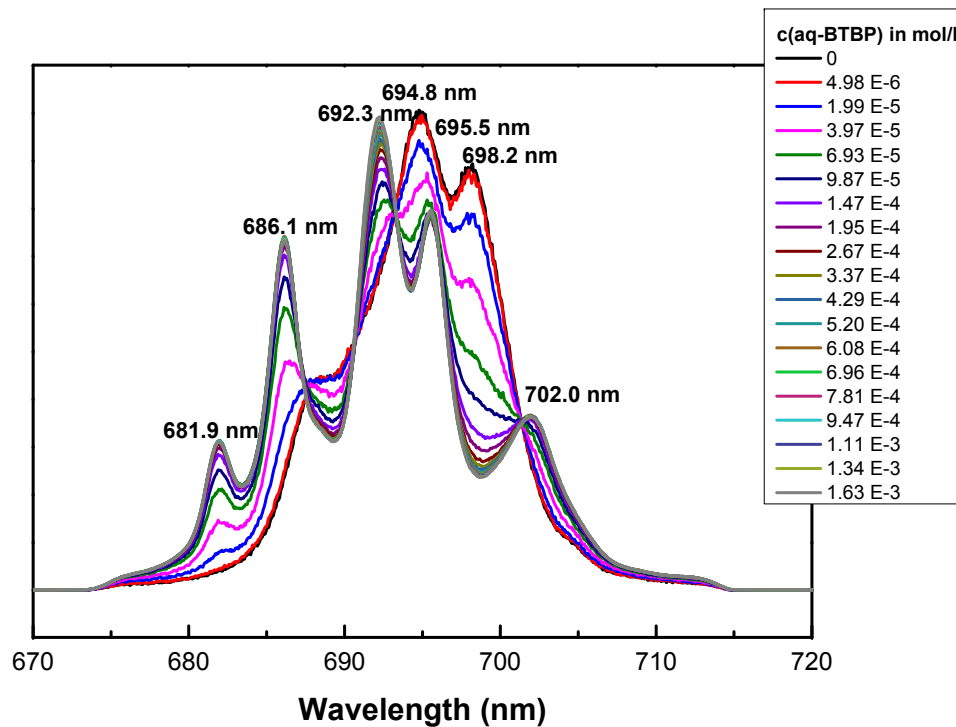


only one complex species



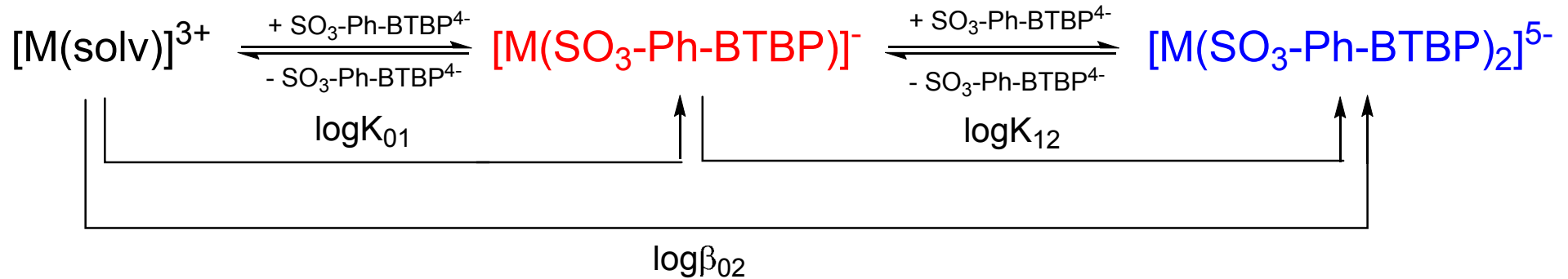
Complexation of Eu(III) with SO₃-Ph-BTBP

Eu(III) ⁷F₄ band emission spectra with increasing SO₃-Ph-BTBP concentration in 0.5 M HNO₃

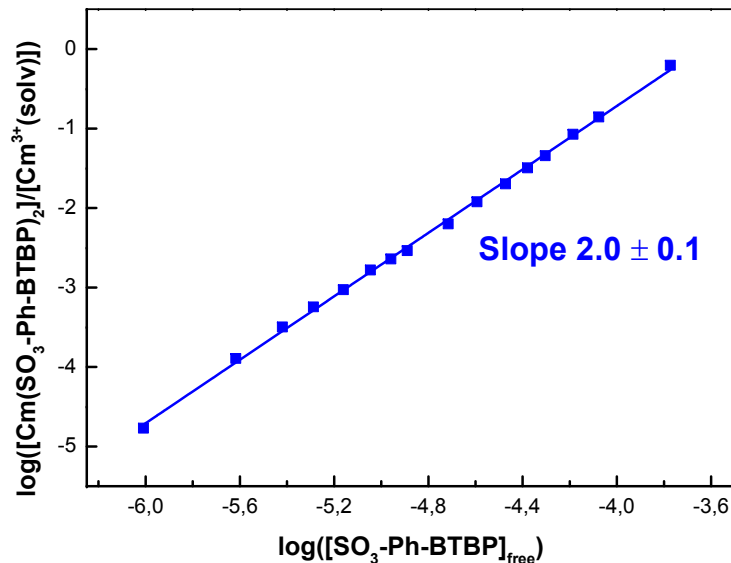


2 complex species formed, primarily 1:2 complex

Complexation of Cm(III) with SO₃-Ph-BTBP

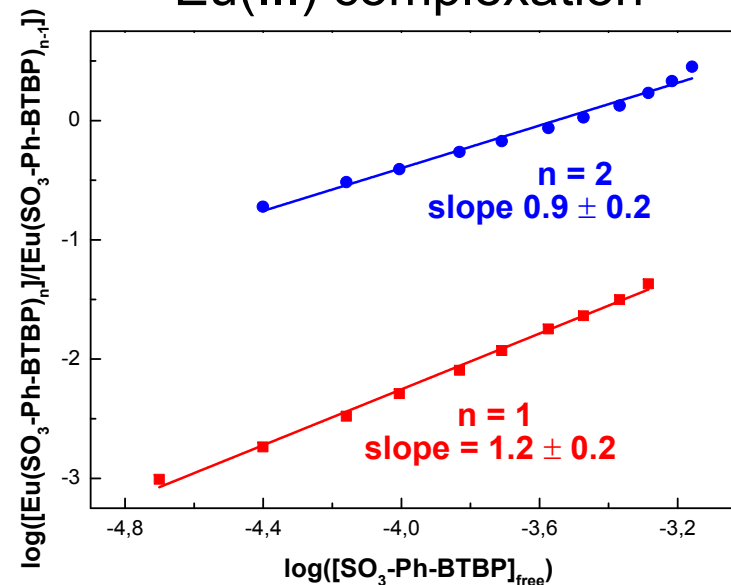


Cm(III) complexation



$$\log \beta_{02} = 7.3 \pm 0.3$$

Eu(III) complexation

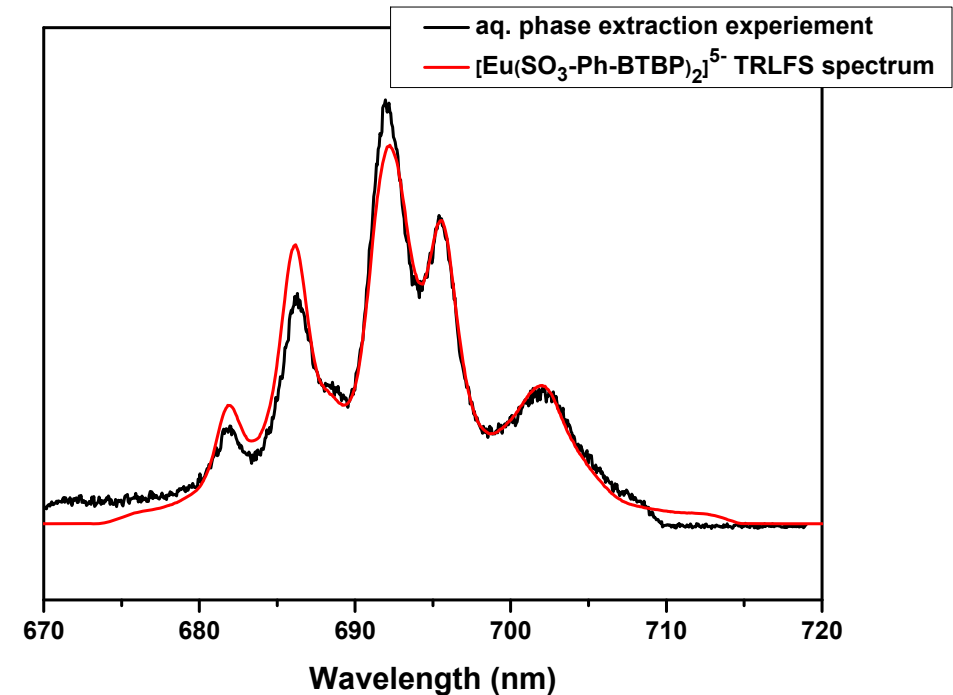
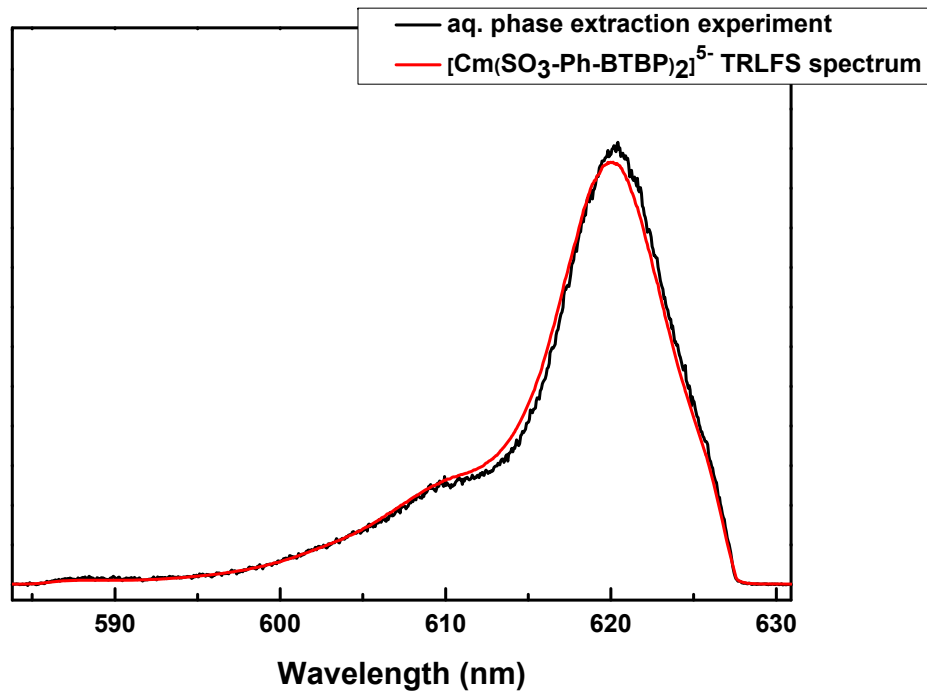


$$\log \beta_{02} = 5.4 \pm 0.5$$

$$\Delta \log \beta_{02} = 1.9$$

TRLFS with extraction experiments

2 phase extraction experiments containing Cm(III)/Eu(III) in the aq. Phase



$\text{SO}_3\text{-Ph-BTBP}$ forms 1:2 complexes in extraction experiments

Aq. phase: 20 mM $\text{SO}_3\text{-Ph-BTBP}$, Cm(III)-248 in 0.5 M HNO_3
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

Complexation of Cm(III) at pH 3

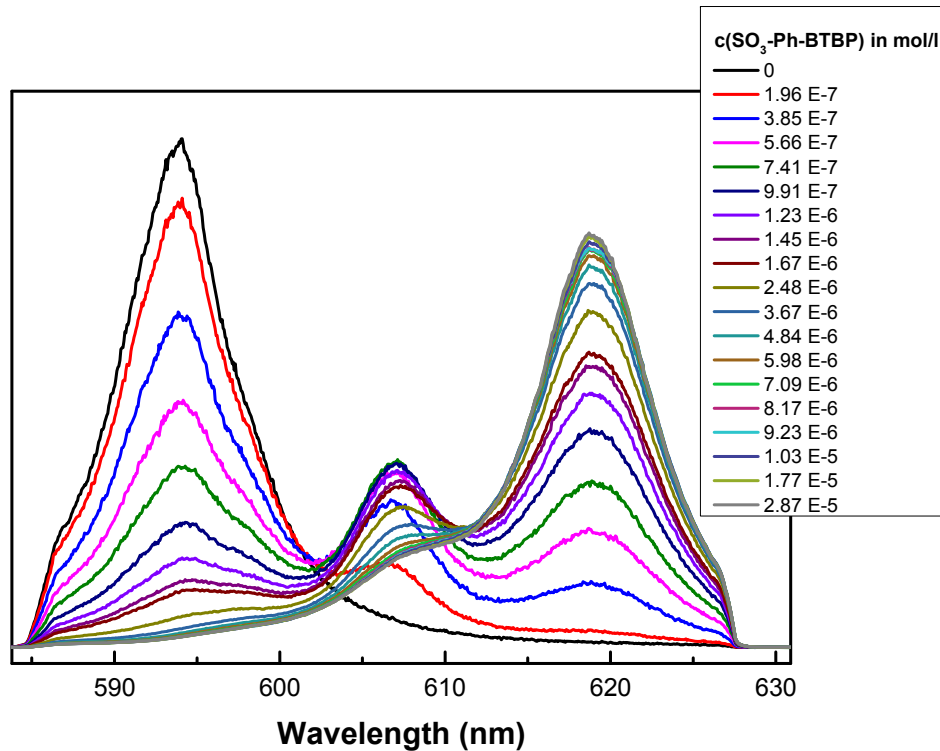
- TRLFS investigation of Cm(III) with $\text{SO}_3\text{-Ph-BTP}$ showed the formation of intermediate complexes
- studies with $\text{SO}_3\text{-Ph-BTP}$ were performed in water at pH 3

→ **investigation of Cm(III) complexation with $\text{SO}_3\text{-Ph-BTBP}$ at pH 3**

C. M. Ruff, U. Müllich, A. Geist and P. J. Panak, *Dalton Trans.*, 2012, **41**, 14594-14602.

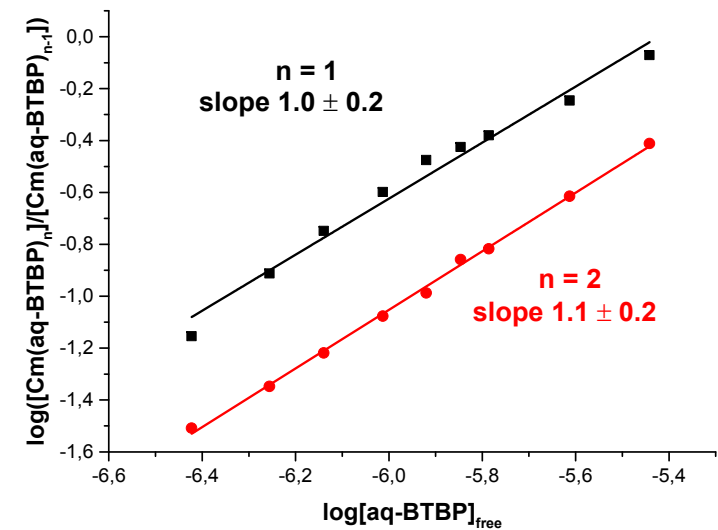
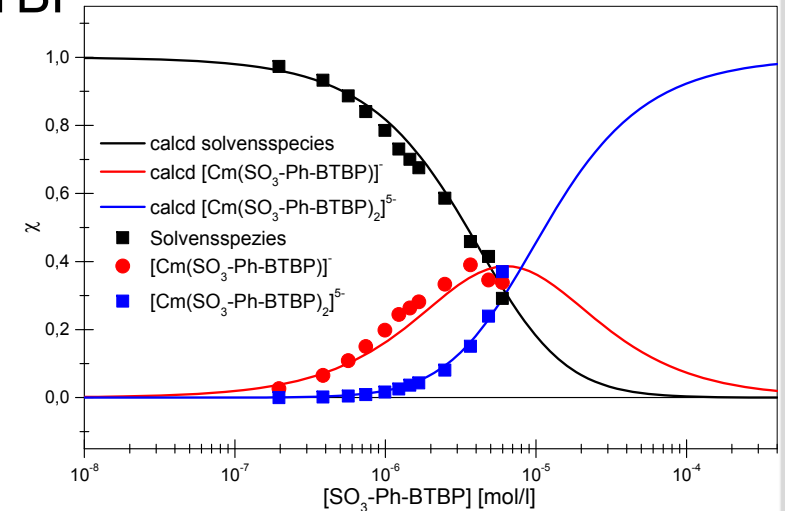
Complexation of Cm(III) at pH 3

Cm(III) emission spectra with increasing SO₃-Ph-BTBP concentration in 10⁻³ M HClO₄

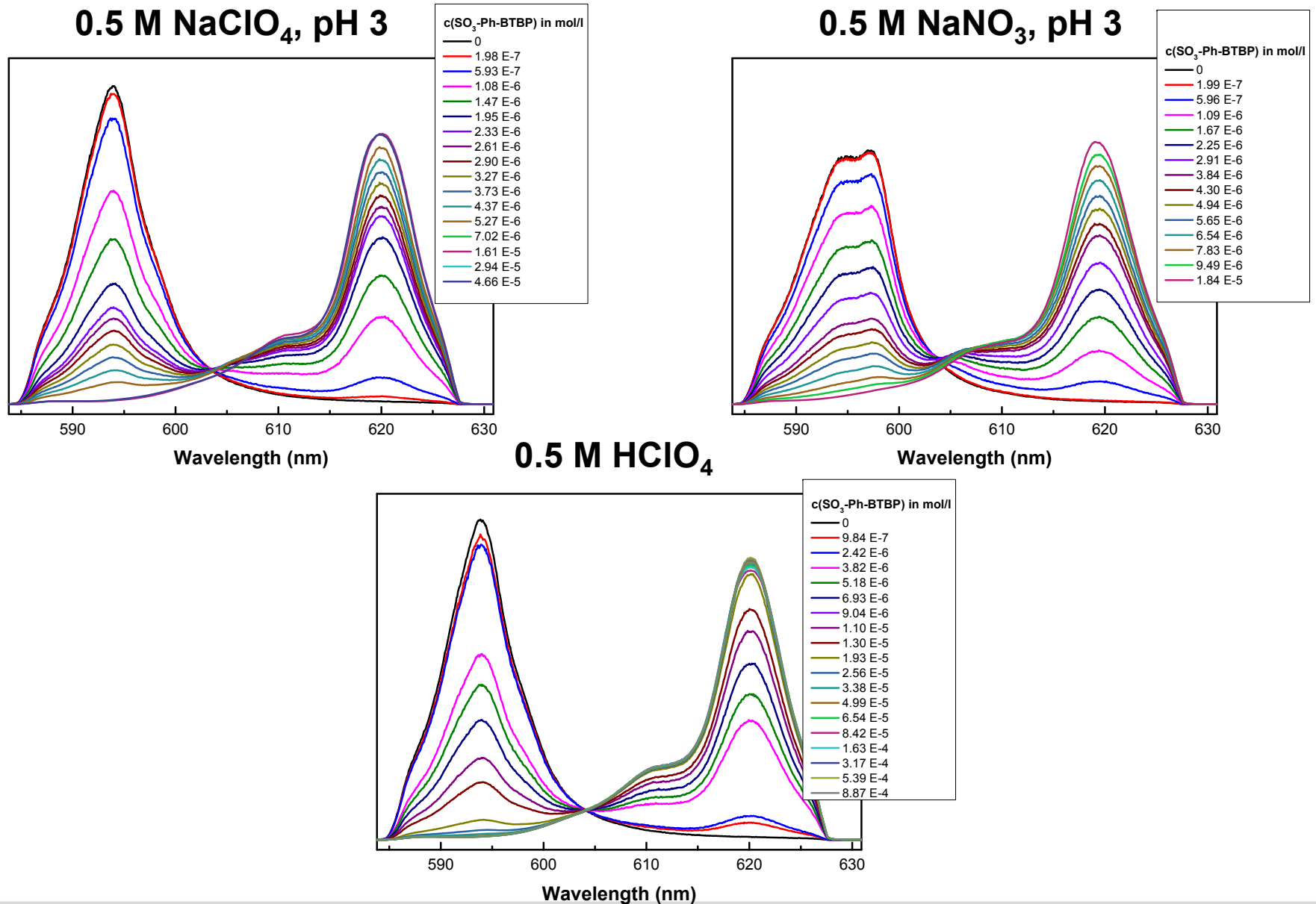


$\log\beta_{02} = 10.4 \pm 0.4$
 $(\log\beta_{02} (0.5 \text{ M HNO}_3) = 7.3 \pm 0.3)$

→ **large influence of solvent**



Complexation of Cm(III) in different media

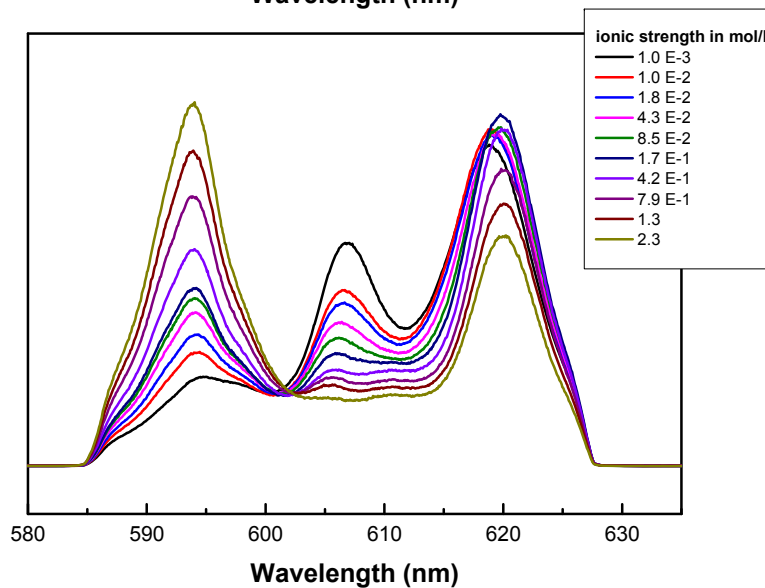
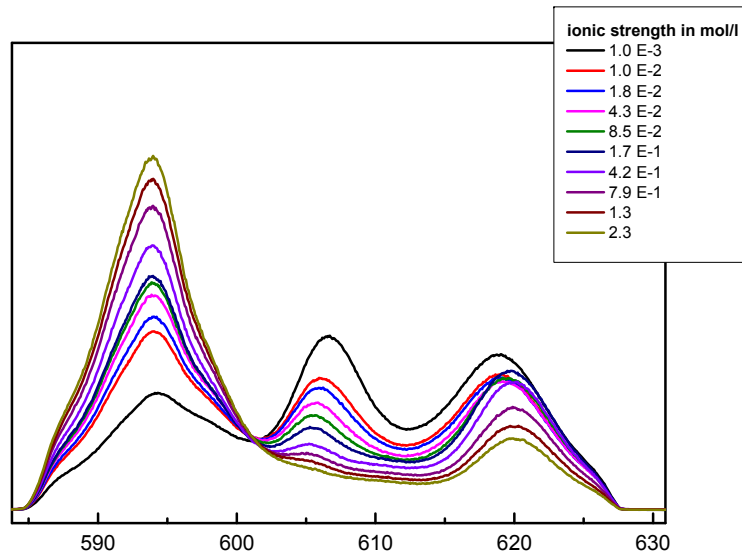


Influence of medium on conditional stability constant

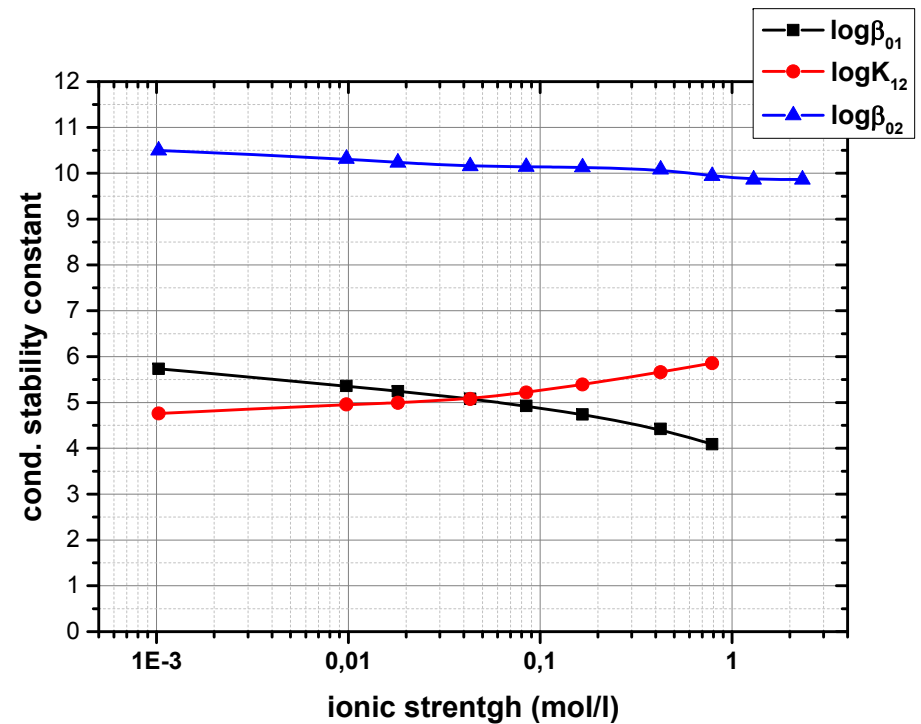
M(III)	Solvens	$\log\beta_{01}$	$\log K_{12}$	$\log\beta_{02}$
Cm	10^{-3} M HClO ₄	5.3 ± 0.3	5.1 ± 0.3	10.4 ± 0.4
Cm	0.5 M HNO ₃	-	-	7.3 ± 0.3
Cm	0.5 M NaClO ₄	-	-	9.7 ± 0.3
Cm	0.5 M NaNO ₃	-	-	9.4 ± 0.3
Cm	0.5 M HClO ₄	-	-	8.5 ± 0.4

Large effect of medium on speciation and conditional stability constant

Influence of ionic strength



Cm-SO₃-Ph-BTBP complexation with increasing ionic strength



Conclusion

- The $\text{SO}_3\text{-Ph-BTBP/TODGA}$ system shows good performance for the separation of Am(III)/Cm(III) .
- The system does not require buffers, auxiliary ligands or salting out agents.
- $\text{SO}_3\text{-Ph-BTBP}$ forms 1:2 complexes during extraction.
- Formation of the same complexes in monophasic and biphasic experiments.
- The applied medium has a large effect on the speciation and the conditional stability constants of $\text{M(III)-SO}_3\text{-Ph-BTBP}$ complexes.

Outlook

- Extraction experiments at elevated temperatures.
- Investigation of $\text{SO}_3\text{-Ph-BTBP}$ loading with realistic Am(III) concentrations.
- Spectroscopic investigation of Am(III)- $\text{SO}_3\text{-Ph-BTBP}$ complexes.

Thank you for your attention

Acknowledgements to:

Prof. Dr. Geckeis

The partitioning group

Tanja Kisely and Cornelia Walschburger

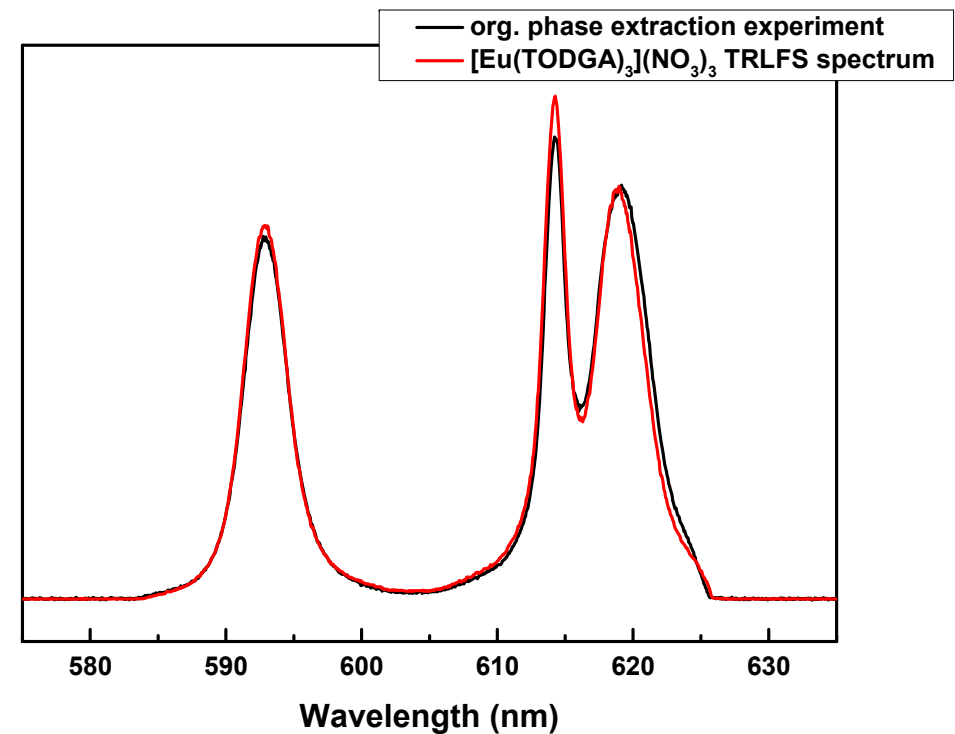
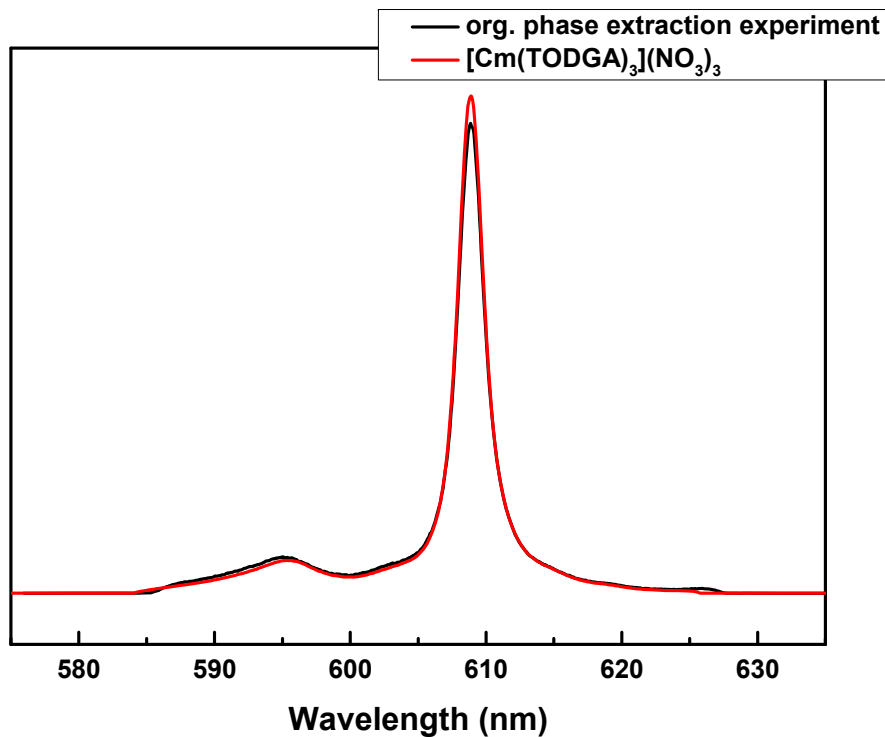
And all colleagues from INE



Acknowledgements to the Commission of European Community for financial support

Complexation of Cm(III) in the org. phase

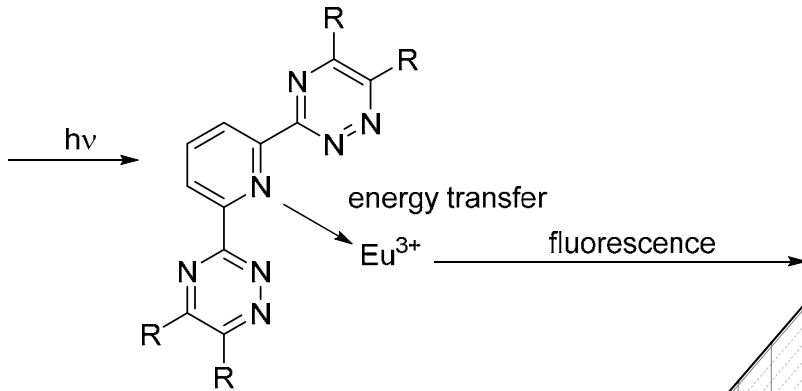
TRLFS experiments with organic phase of extraction experiment



No evidence for the formation of mixed complexes → sensitivity too low?

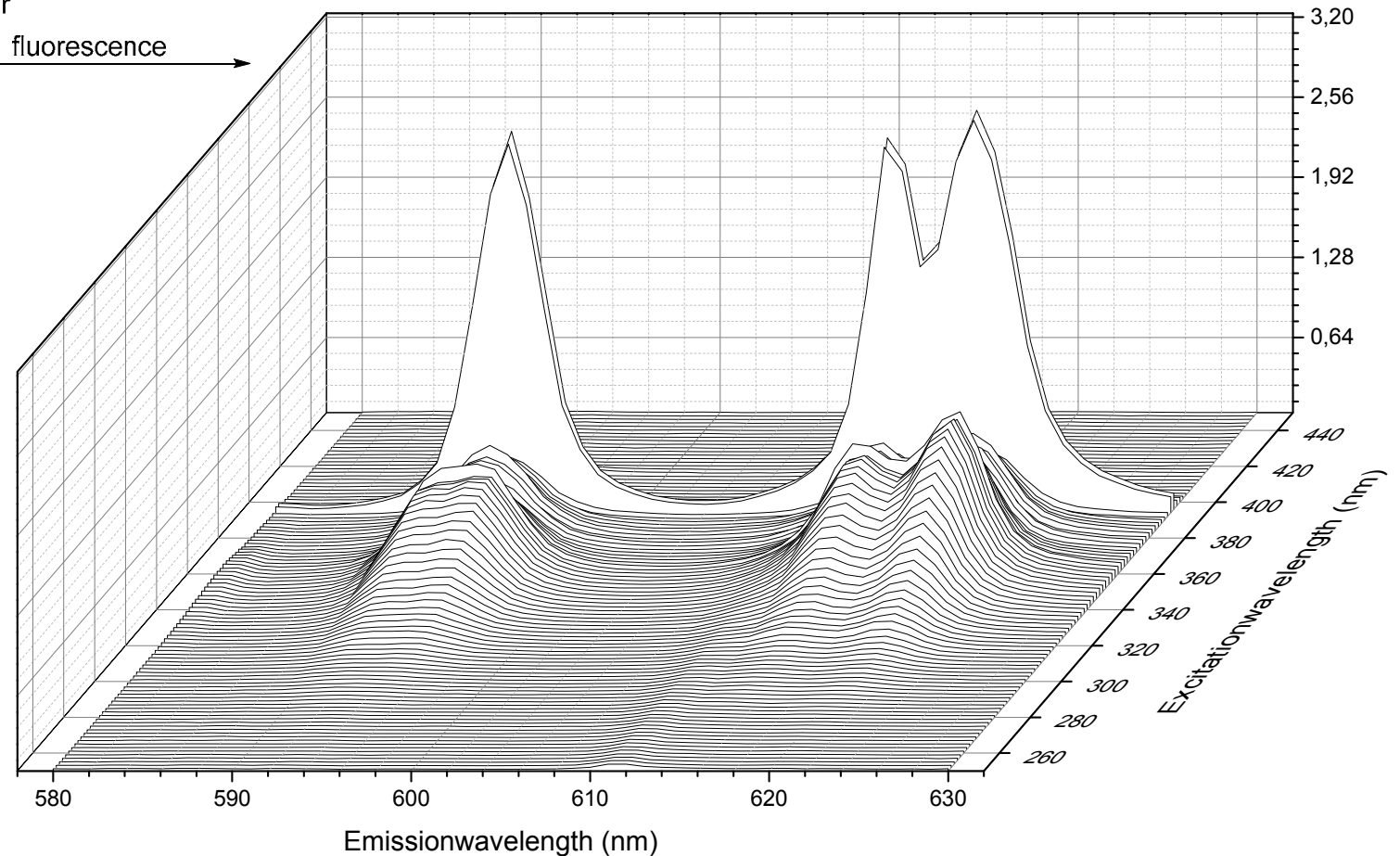
Aq. phase: 20 mM $\text{SO}_3\text{-Ph-BTP}$, Cm(III)-248 in 0.5 M HNO_3
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

Fluorimetric measurements with org. Phase



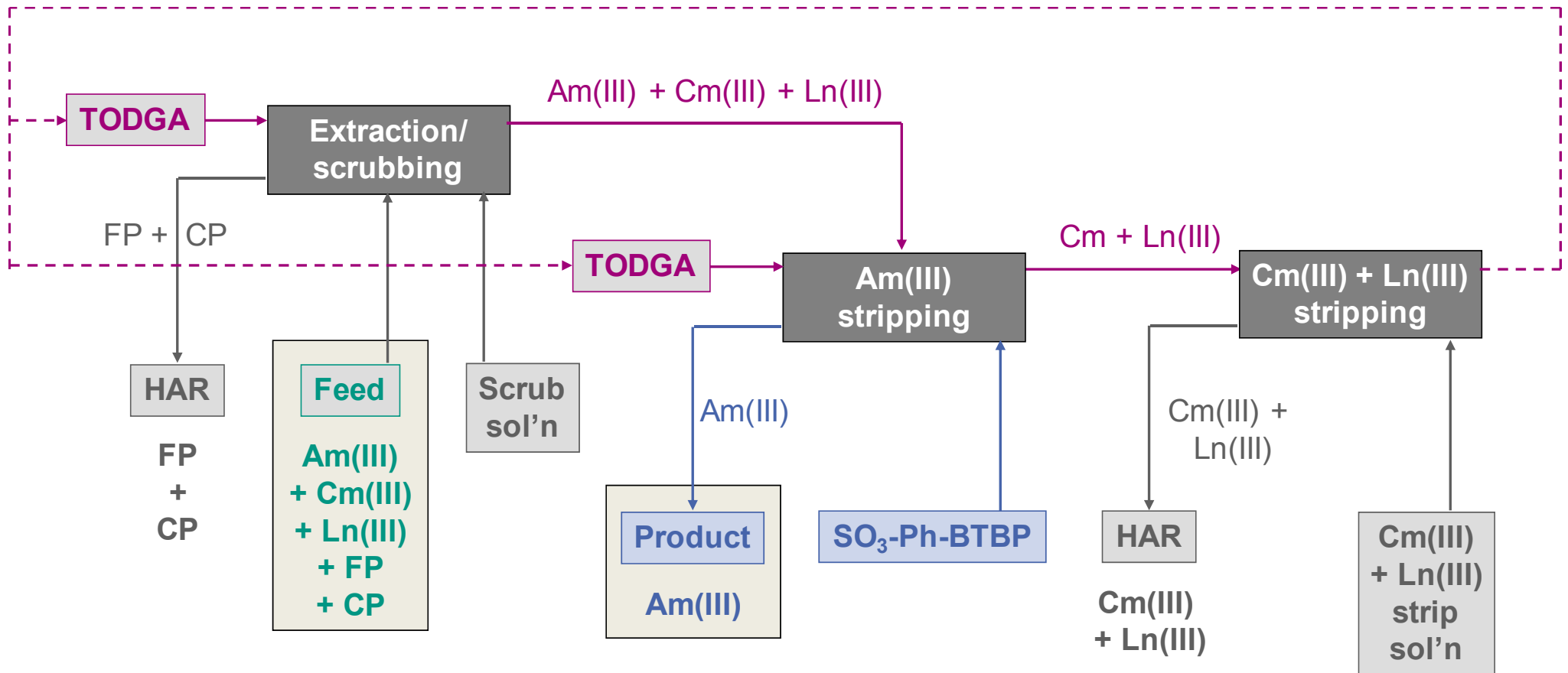
Idea:

Utilizing the energy transfer from ligand to metal to selectively excite the Eu(III) in mixed complexes

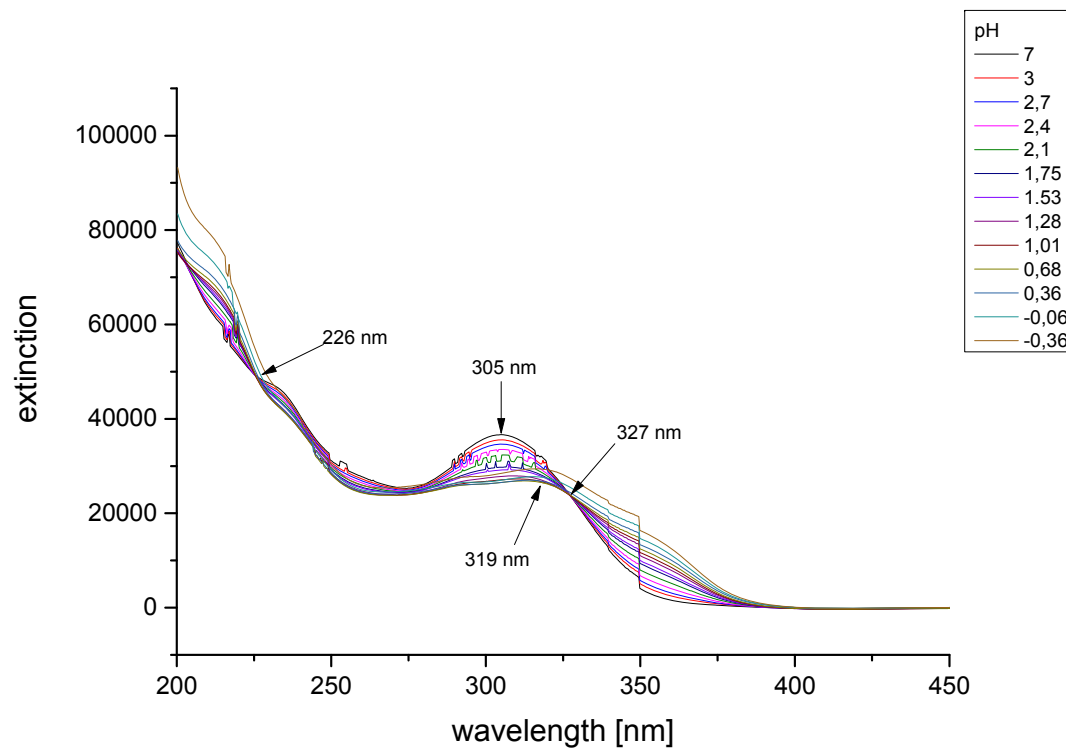


Aq. phase: 20 mM $\text{SO}_3\text{-Ph-BTP}$, 30 mM $\text{Eu}(\text{NO}_3)_3$ in 0.5 M HNO_3
 Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

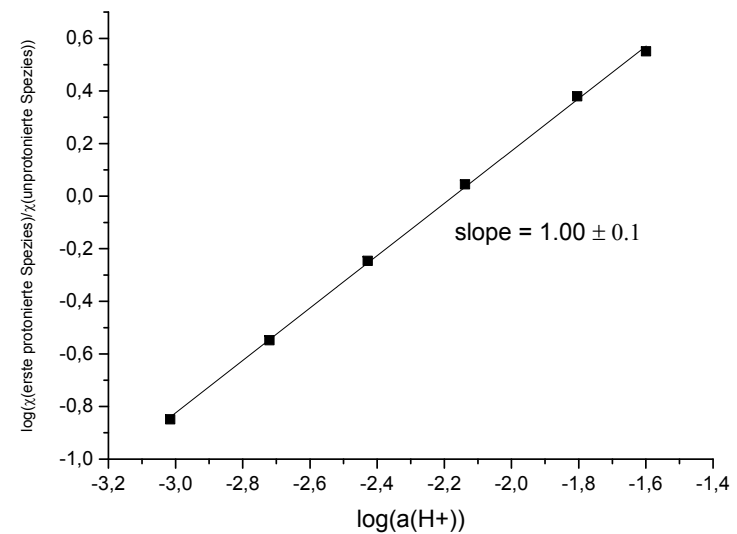
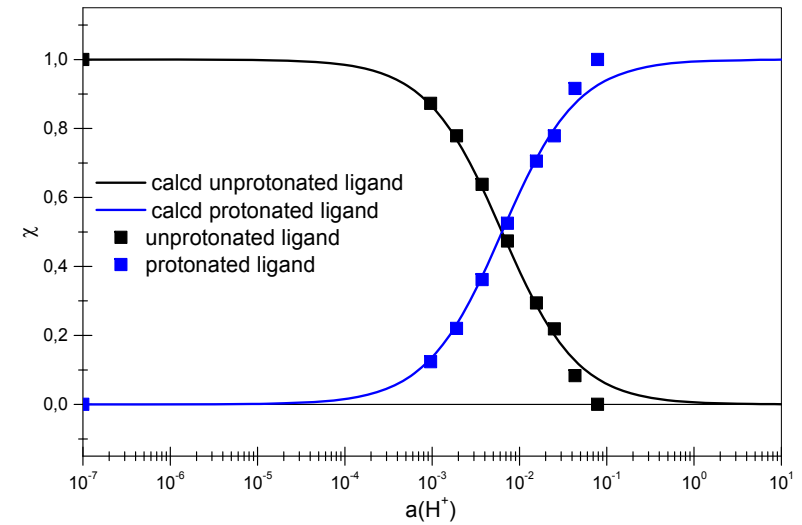
Schematic flowsheet



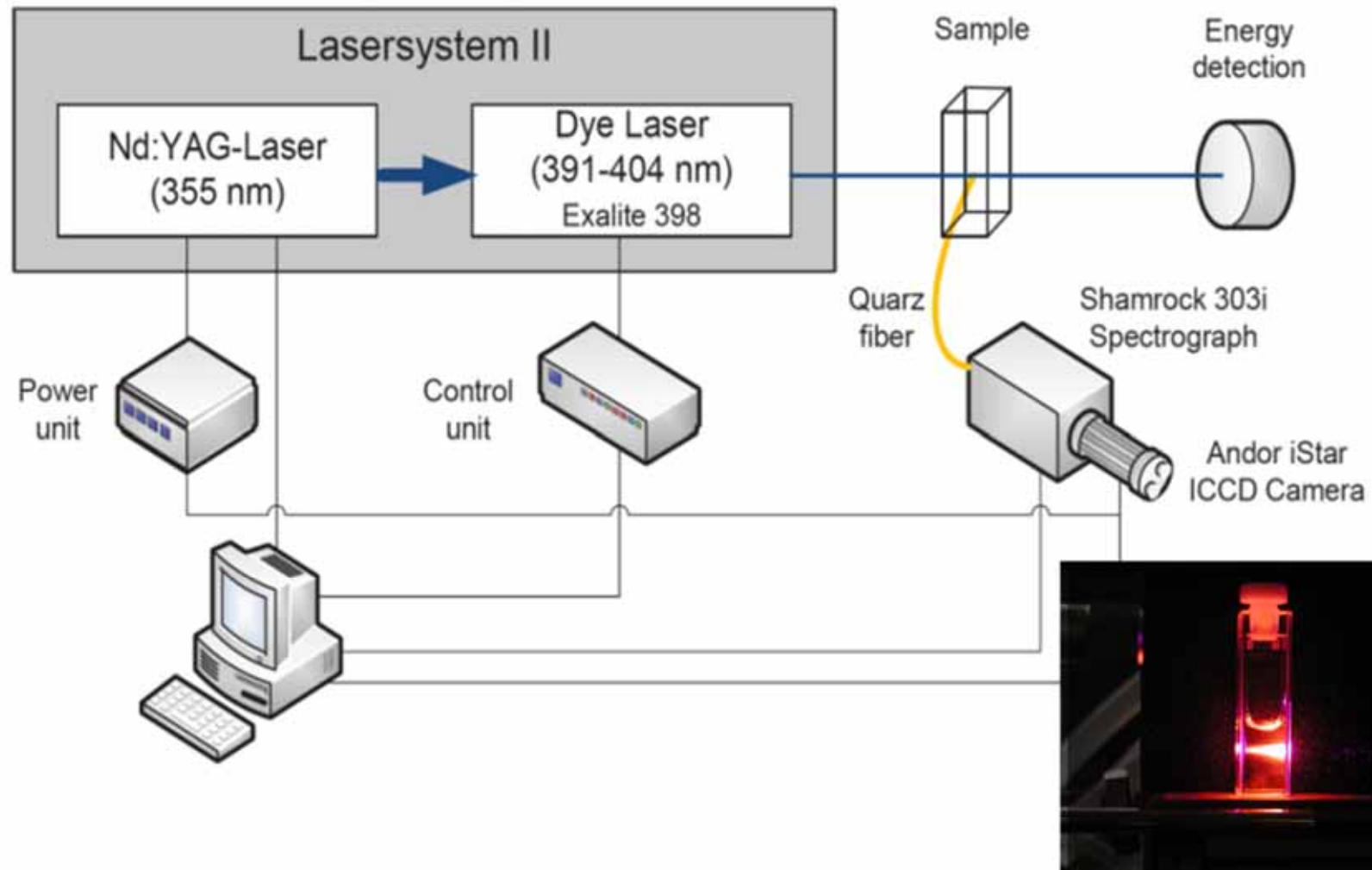
pK_a value of SO₃-Ph-BTBP



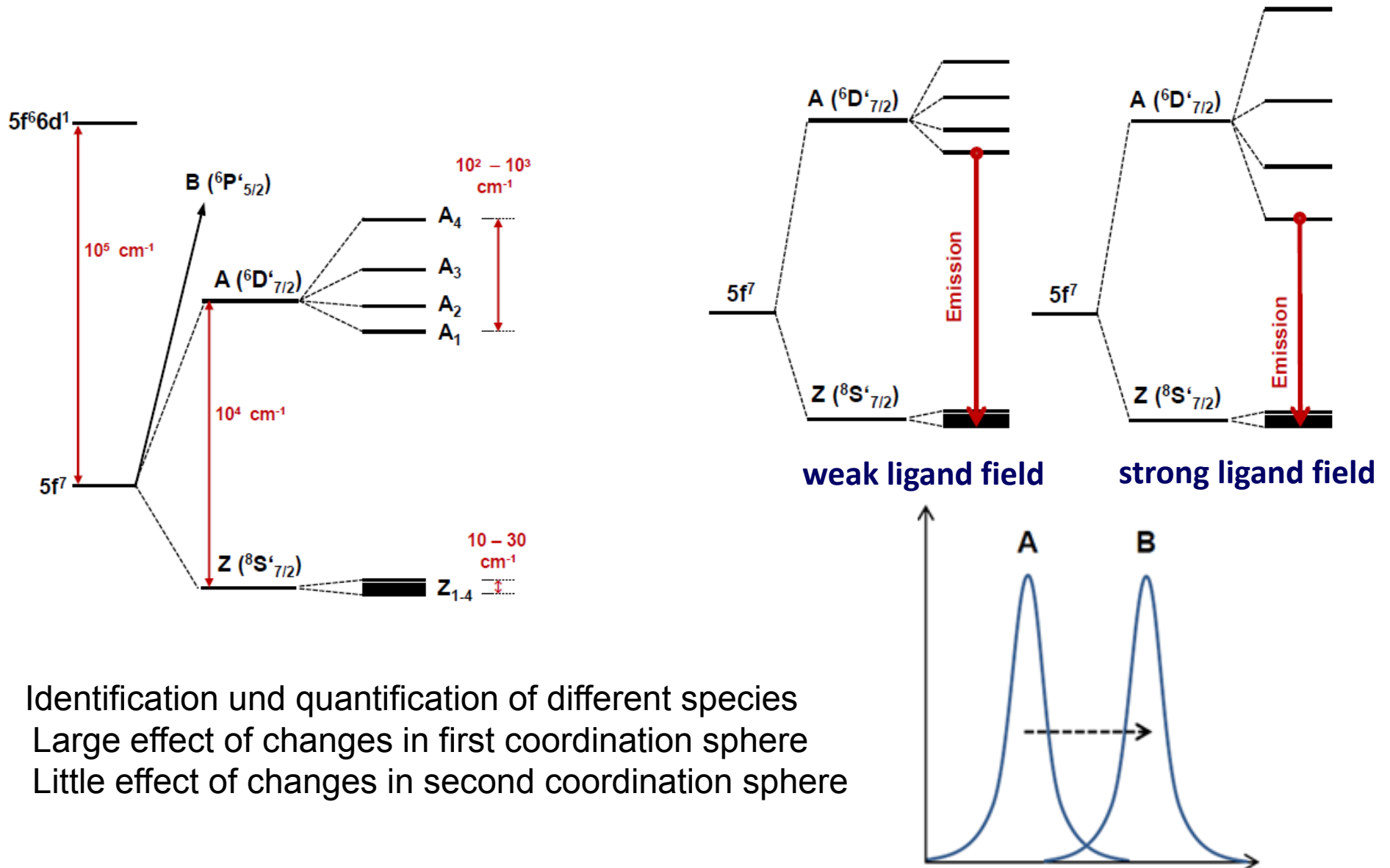
pK_a = 2.2 ± 0.2



TRLFS Setup

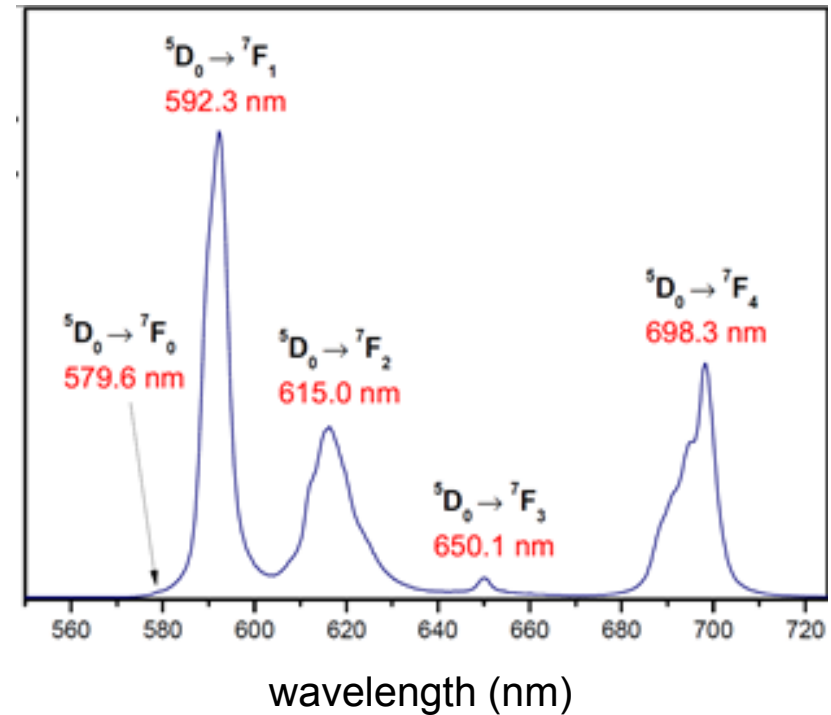
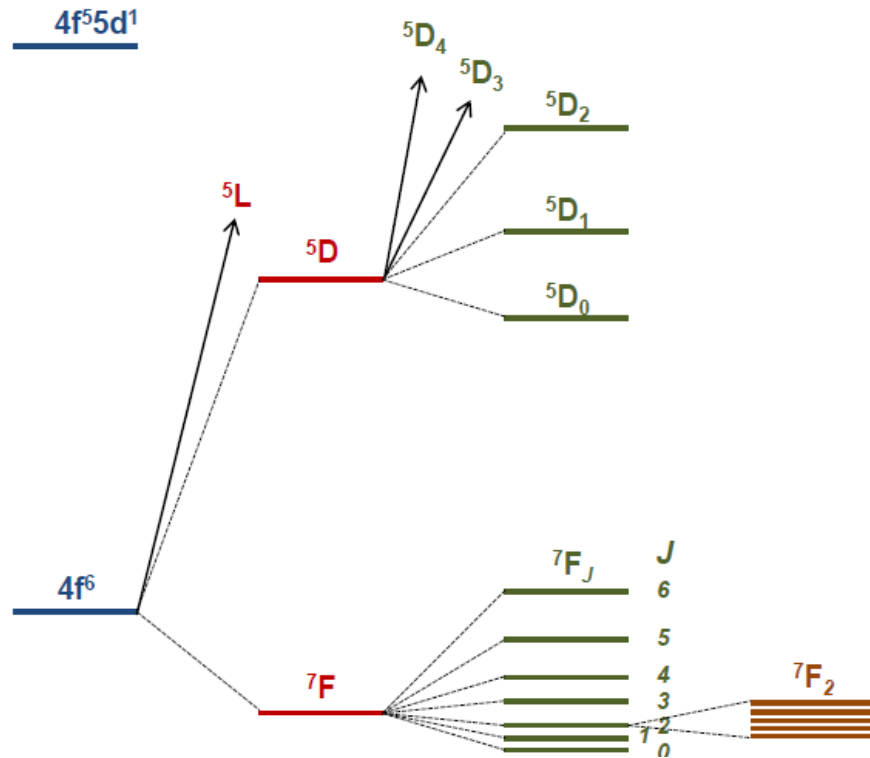


Spectroscopic properties of Cm(III)



- Identification und quantification of different species
- Large effect of changes in first coordination sphere
- Little effect of changes in second coordination sphere

Spectroscopic properties of Eu(III)



- Small shifts of the emission bands with changes in inner coordination sphere
- Characteristic splitting
- Information on the coordination structure and symmetry