

A time-resolved laser fluorescence spectroscopy
study of the coordination chemistry of an
hydrophilic CHON [1,2,3-triazol-4-yl]pyridine
ligand with Cm(III) and Eu(III)

Christoph Wagner^{1,2}, Eros Mossini³, Elena Macerata³, Mario Mariani³, Arturo Arduini⁴,
Alessandro Casnati⁴, Andreas Geist², Petra J. Panak^{1,2}*

¹ Universität Heidelberg, Institut für Physikalische Chemie, Im Neuenheimer Feld 253, 69120
Heidelberg (D)

² Karlsruher Institut für Technologie (KIT), Institute für nukleare Entsorgung (INE), P.O. Box
3640, 76021 Karlsruhe (D)

³ Politecnico di Milano, Department of Energy - Nuclear Engineering Division, Piazza Leonardo
da Vinci 32, 20133 Milano (I)

⁴ Università di Parma, Dipartimento di Chimica, Area delle Scienze 17/a, 43124 Parma (I)

Abstract

The complexation of Cm(III) and Eu(III) with the novel *i*-SANEX complexing agent 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine (PTD) was studied by time resolved laser fluorescence spectroscopy (TRLFS). The formation of 1:3 1:2, and 1:1 metal:ligand complexes was identified upon increasing PTD concentration in 10^{-3} mol/L HClO₄ and in 0.44 mol/L HNO₃ solutions. For all these complexes, stability constants were determined at different acid concentrations. Though under the extraction conditions proposed for an An/Ln separation process, *i.e.* for 0.08 M PTD in 0.44 M HNO₃, 1:3 complexes represent the major species, a significant fraction of 1:2 complexes was found. This is caused by ligand protonation, and results in lower Eu(III)/Am(III) separation factors compared to SO₃-Ph-BTP, until now considered the *i*-SANEX reference ligand. Focused extraction studies performed at lower proton concentration, where the 1:3 complex is formed exclusively, confirm this assumption.

Introduction

The sustainability of nuclear energy production is supported by increasing the share of recycling within the nuclear fuel cycle.¹ This way, both the extent of uranium mining operations and the volume required for finally disposing of highly radioactive waste are significantly reduced. Recycling uranium and transuranium elements (TRU: neptunium, plutonium, americium and curium) from used nuclear fuel requires their separation from other constituents such as fission products. The PUREX (Plutonium and Uranium Reduction EXtraction) process² is commercially operated for separating uranium and plutonium. Additional solvent extraction processes for separating the remaining actinides (neptunium, americium and curium) from the PUREX raffinate have been developed in many countries.^{3,4} A specific challenge is the

separation of americium and curium from fission lanthanides since both groups are present in solution as trivalent cations of similar size and similar coordination properties.

Soft-donor ligands are known to interact more strongly with trivalent actinide ions, An(III), rather than with trivalent lanthanide ions, Ln(III).⁵ This finding triggered the development of extracting agents having soft donor atoms, typically nitrogen or sulphur, to selectively extract An(III).⁶ European research programmes starting in the early 1990s furthered this development. Finally, heteroaromatic nitrogen donor ligands derived from 2,6-bis(1,2,4-triazin-3-yl)-pyridines (BTP), 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBP) and 2,9-bis(1,2,4-triazin-3-yl)-phenanthrolines (BTPhen) (see Figure 1) were found to be highly effective for selectively extracting An(III).^{7,8} One particular BTBP (6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)2,2'-bipyridine, CyMe₄-BTBP) molecule was successfully applied in laboratory scale process tests.^{4,9}

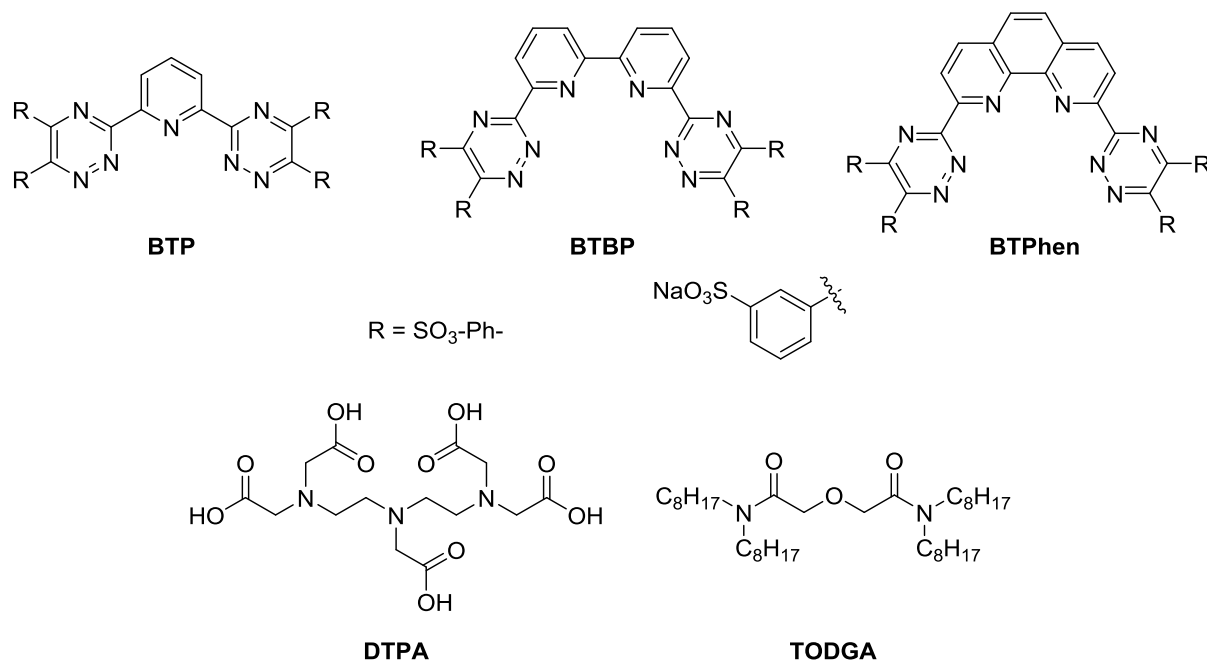


Figure 1 Molecular structures of BTP, BTBP, BTPhen, DTPA and TODGA.

Rather than selectively extracting An(III) using lipophilic soft donor extracting agents, An(III)-Ln(III) separation can also be achieved by suppressing An(III) extraction into the organic phase by a hydrophilic soft donor complexing agent present in the aqueous phase. This principle was exploited in the TALSPEAK process,^{10,11,12} developed more than 50 years ago, using DTPA (diethylenetriaminepentaacetic acid, Figure 1) to complex An(III). This principle was further developed and improved mainly in the USA,^{13,14,15} France^{16,17} and Japan.¹⁸

BTP,^{19,20} BTBP^{21,22,23} and BTPPhen^{24,25} made hydrophilic by sulfonation (*i.e.* $R = 3$ -sulfophenyl, see Figure 1) proved to be efficient and highly selective ligands for stripping An(III) from an organic phase loaded with An(III) and Ln(III) by means of *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA, Figure 1) as an extracting agent. Differently from e.g. DTPA, these hydrophilic ligands remain efficient in acidic solutions, forgoing the need for buffering agents and auxiliary ligands. The water soluble SO₃-Ph-BTP (Figure 1) was successfully implemented in spiked and hot lab-scale *i*-SANEX (innovative Selective ActiNide EXtraction) and GANEX (Group ActiNide EXtraction) processes.^{26,27,28,29} Despite preliminary results indicated that SO₃-Ph-BTP could easily be degraded by radiolysis,³⁰ it exhibits good radiolytic stability at process conditions.³¹ The analogous BTBP and BTPPhen are suitable for developing processes that extract only Am(III) but reject Cm(III) together with the Ln(III).^{21,25}

However, in the nuclear fuels recycling context their sulfur content is a disadvantage with respect to secondary waste generation. Molecules exclusively containing C, H, O and N atoms are to be preferred as they can be decomposed to gaseous products. Recently, a new CHON water-soluble ligand, 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine (PTD, Figure 2), was developed.³² Similar to SO₃-Ph-BT(B)P, PTD efficiently strips actinide ions, however with a slightly lower selectivity. Furthermore, PTD is satisfactorily stable towards radiolysis to allow

for an application under conditions encountered in solvent extraction processes for actinide recycling.³²

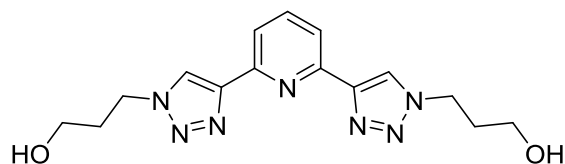


Figure 2 Molecular structure of PTD.

In this paper, the complexation of PTD with Cm(III) and Eu(III) is studied by time-resolved laser fluorescence spectroscopy (TRLFS). Cm(III) and Eu(III) are used as representatives for An(III) and Ln(III) respectively due to their excellent spectroscopic properties. The stoichiometry of the formed complexes is determined and the influence of the solvent on the complexation of M(III) with PTD is investigated. A theoretical Eu(III)/Am(III) separation factor ($SF_{Eu(III)/Am(III)}$) is derived from the $\log\beta_3$ values of $[M(PTD)_3]^{3+}$ ($M = Cm(III), Eu(III)$) obtained by TRLFS and compared to the separation factor observed in extraction experiments³².

Experimental Section

Chemicals

All chemicals used were purchased from Sigma Aldrich or Alfa Aesar and used as received. The concentration of the Cm(III) stock solution was $2.12 \cdot 10^{-5}$ mol/L in 0.017 mol/L HClO₄ (isotopic mass distribution: 89.7% Cm-248, 9.4% Cm-246, $\leq 1\%$ Cm-243, Cm-244, Cm-245 and Cm-247). The Eu(III) stock solution contained 1.07 mmol/L Eu(III) in 0.01 mol/L HClO₄. PTD was synthesized at the University of Parma.³² The ligand stock solutions for titration experiments were prepared by dissolving 13.16 mg of PTD in 500 μ L of the respective medium (10^{-3} mol/L

HClO₄ or 0.44 mol/L HNO₃) yielding a PTD concentration of 80 mmol/L. All solutions were prepared with ultrapure water (Millipore, Billerica, USA; 18.2 MΩ·cm).

TRLFS setup

TRLFS studies were performed using a Nd:YAG laser (Continuum Surelite) -pumped dye laser system (NARROWscan D-R Dye laser) with a repetition rate of 10 Hz. For the excitation of Cm(III) a wavelength of $\lambda = 396.6$ nm was used. For investigations of Eu(III) a wavelength of $\lambda = 394$ nm was applied. After spectral decomposition by a spectrograph (Shamrock 303i) with a 1199 lines mm⁻¹ grating, the spectra were recorded by an ICCD camera (iStar Gen III, ANDOR) with an integrated delay controller. Light scattering and short-lived fluorescence of organic compounds were discriminated by applying 1 μ s delay time between excitation and detection of the fluorescence signal.

TRLFS sample preparation

Samples for TRLFS were prepared by dissolving 2.35 μ L of Cm(III)/Eu(III) stock solutions in 498 μ L of the different media. Consequently, M(III) solutions with 10⁻⁷ mol/L of Cm(III) and 5·10⁻⁶ mol/L of Eu(III) initial concentrations were obtained. For titration experiments, aliquots of PTD solutions (with concentrations between 20 mmol/L and 80 mmol/L in the respective medium) were subsequently added to the sample. After each titration step, samples were allowed to equilibrate for 5 minutes which proved to be sufficient.

Extraction experiments

Aqueous phases consisted of 80 mmol/L PTD dissolved in 0.44 mol/L HNO₃ or with 1 mol/L NaNO₃ in 10⁻³ mol/L HClO₄. These solutions were spiked either with 10⁻⁷ mol/L Cm(III) (for TRLFS) or with 1 kBq of Am-241/Eu-152 each (for determination of $SF_{\text{Eu(III)/Am(III)}}$, [Am-

241] = $3.3 \cdot 10^{-8}$ mol/L, [Eu-152] = $1.0 \cdot 10^{-9}$ mol/L). For all extraction experiments, organic phases consisted of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80.

Extraction experiments were performed by contacting 500 μ L of both phases in a 2 mL vial. The mixing was performed by a shaker at 2500 rpm for 30 min. Aliquots of both phases (300 μ L) were separated following centrifugation. Activities of Am-241/Eu-152 were determined using a gamma counter (Packard Cobra Auto Gamma 5003). For TRLFS analysis, the samples were transferred into quartz cuvettes without further dilution.

Results and Discussion

Complexation of Cm(III) in 10^{-3} mol/L HClO₄

Initial TRLFS experiments with Cm(III) were performed in 10^{-3} mol/L HClO₄. HClO₄ is chosen since ClO₄⁻ is a non-coordinating anion and has a negligible influence on the complexation of Cm(III) with PTD. Figure 3 (left) shows the normalized Cm(III) emission spectra resulting from the ${}^6D'_{7/2} \rightarrow {}^8S'_{7/2}$ transition as a function of the ligand concentration.

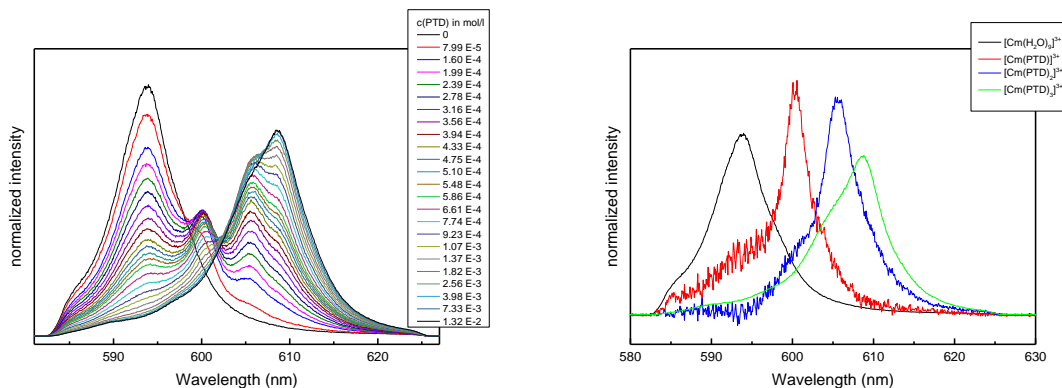


Figure 3 Left: Normalized fluorescence spectra of Cm(III) at increasing PTD concentration in 10^{-3} mol/L HClO₄. [Cm(III)]_{ini} = $1 \cdot 10^{-7}$ mol/L. Right: Normalized emission spectra of the [Cm(PTD)_n]³⁺ (n = 0,1,2,3) complexes in 10^{-3} mol/L HClO₄.

In the absence of PTD, the Cm(III) emission spectrum displays an emission band at 593.8 nm. This corresponds to the Cm(III) aqua ion.³³ With increasing ligand concentration, three additional emission bands are observed at $\lambda = 600.1$ nm, 605.5 nm and 608.6 nm. These emission bands show a bathochromic shift compared to the Cm(III) aqua ion. This results from an increased splitting of the ${}^6D_{7/2}$ state of Cm(III) and is consistent with the stepwise complexation of Cm(III) with PTD. The spectra of the different Cm(III) species ($[\text{Cm}(\text{PTD})_n]^{3+}$, $n = 0 - 3$) (Figure 3, *right*) were determined by peak deconvolution. Using the spectra of the pure components, the normalized spectra of the titration experiment were analysed yielding the fractions of the formed species. Upon complexation the fluorescence intensity (FI) increases. The FI factors of the formed complexes relative to the Cm(III) aqua ion are determined to be $\text{FI}([\text{Cm}(\text{PTD})]^{3+}) = 1$, $\text{FI}([\text{Cm}(\text{PTD})_2]^{3+}) = 1.1$, $\text{FI}([\text{Cm}(\text{PTD})_3]^{3+}) = 2$, according to the method described in ref.²⁵. Taking into account these FI factors, the concentrations of the $[\text{Cm}(\text{PTD})_n]^{3+}$ ($n = 0 - 3$) species are calculated. The obtained species distribution at increasing ligand concentration is shown in Figure 4.

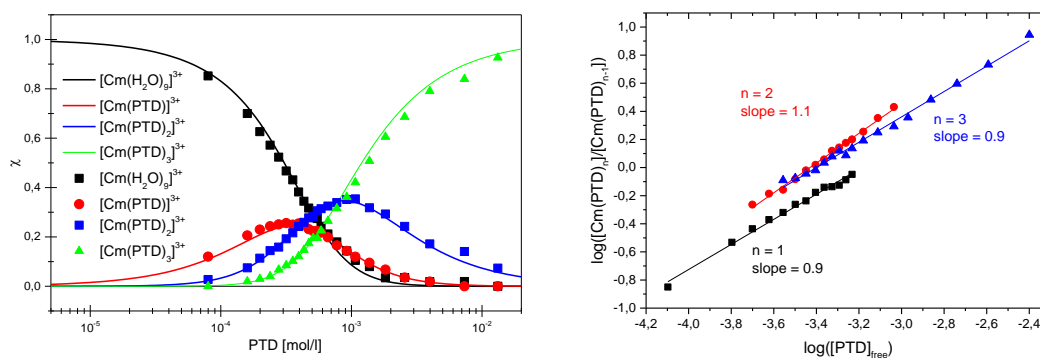
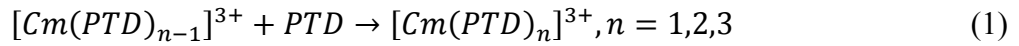


Figure 4 Left: Species distribution of Cm(III) in 10^{-3} mol/L HClO_4 as a function of the PTD concentration. Symbols, experimental data. Lines, calculated with $\log\beta_1 = 3.2$, $\log\beta_2 = 6.6$ and

$\log\beta_3 = 9.7$. Right: Double logarithmic plot of ($[Cm(PTD)_n]/[Cm(PTD)_{n-1}]$) vs. the free PTD concentration.

At low ligand concentration, the Cm(III) aqua ion is the main species. With increasing ligand concentration the amount of $[Cm(PTD)]^{3+}$ complex increases with a maximum fraction of 25% at $3.7 \cdot 10^{-4}$ mol/L of PTD. At ligand concentrations larger than $5 \cdot 10^{-4}$ mol/L, $[Cm(PTD)_2]^{3+}$ is the predominant species with a maximum fraction of 35% at $8.8 \cdot 10^{-4}$ mol/L of PTD. At higher ligand concentrations ($\geq 8 \cdot 10^{-4}$ mol/L), $[Cm(PTD)_3]^{3+}$ becomes the main component in solution.

The stepwise formation of Cm(III)-PTD complexes is described by the following reaction:



The stepwise and cumulative conditional stability constants for the formation of Cm(III)-PTD complexes are calculated respectively according to:

$$K = \frac{[Cm(PTD)_n]^{3+}}{[Cm(PTD)_{n-1}]^{3+} \cdot [PTD]_{free}} \quad (2)$$

$$\beta_n = \frac{[Cm(PTD)_n]^{3+}}{[Cm]^{3+} \cdot [PTD]_{free}^n} \quad (3)$$

From equation 2, equation 4 is derived:

$$\log \frac{[Cm(PTD)_n]^{3+}}{[Cm(PTD)_{n-1}]^{3+}} = n \cdot \log[PTD]_{free} + \log K \quad (4)$$

According to equation 4, a double logarithmic plot of the concentration ratio $\frac{[Cm(PTD)_n]^{3+}}{[Cm(PTD)_{n-1}]^{3+}}$ vs. the free ligand concentration is expected to yield a slope of 1 for the stepwise complexation of Cm(III) with PTD (eq 1). The derived slopes are between 0.9 and 1.1 (Figure 4, *right*), thus they are in excellent agreement with the hypothesized stepwise Cm(III)-PTD complexation model. This confirms the correct assignment of the Cm(III)-PTD complex species to the emission bands

at $\lambda = 600.1$ nm, 605.5 nm, and 608.6 nm. Using equation 2, the conditional stability constants for the formation of $[\text{Cm}(\text{PTD})_n]^{3+}$ complexes ($n = 1,2,3$) are calculated to be $\log\beta_1 = 3.2 \pm 0.2$, $\log\beta_2 = 6.6 \pm 0.2$ and $\log\beta_3 = 9.7 \pm 0.3$. The value for $\log\beta_3$ obtained for PTD is significantly lower than the one derived for the water-soluble BTP at the same conditions ($\text{SO}_3\text{-Ph-BTP}$, $\log\beta_3 = 12.2$).³⁴ This result is in agreement with the higher concentration of PTD required for the efficient and selective stripping of An(III) in biphasic extraction experiments compared to $\text{SO}_3\text{-Ph-BTP}$.^{19, 32}

Complexation of Cm(III) with PTD in 0.44 mol/L HNO_3

Biphasic extraction experiments showed the promising properties of PTD as a selective An(III) stripping agent.³² The optimal nitric acid concentration for an aqueous phase containing PTD was found to be 0.44 mol/L HNO_3 for process application.³² Therefore, the complexation of Cm(III) with PTD was investigated at these conditions. Figure 5 (*left*) shows the normalized Cm(III) fluorescence emission spectra as a function of PTD concentration in 0.44 mol/L HNO_3 .

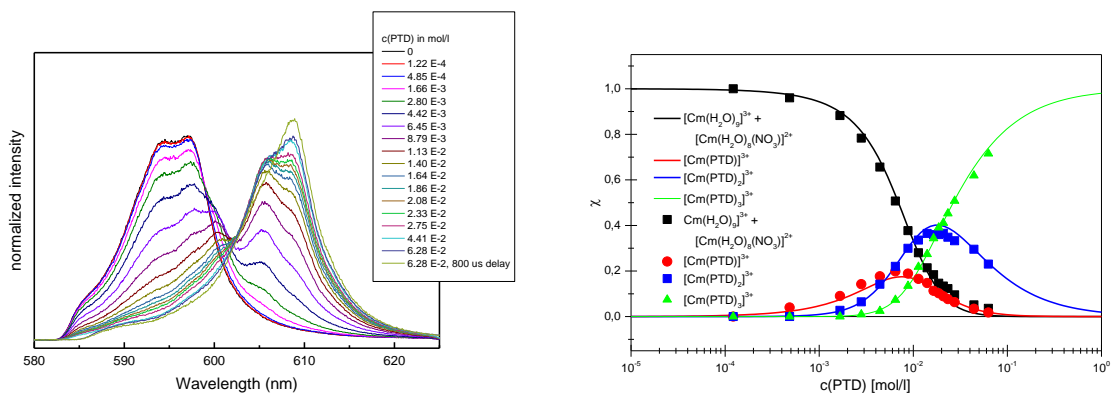


Figure 5 *Left*: Normalized fluorescence spectra of Cm(III) at increasing concentration of PTD in 0.44 mol/L HNO_3 . $[\text{Cm}(\text{III})]_{\text{ini}} = 1 \cdot 10^{-7}$ mol/L. *Right*: Species distribution of Cm(III) in 0.44 mol/L HNO_3 as a function of the PTD concentration. Symbols, experimental data. Lines, calculated with $\log\beta_1 = 1.7$, $\log\beta_2 = 4.0$ and $\log\beta_3 = 5.7$.

Without addition of ligand, the emission spectrum displays two emission maxima at $\lambda = 594.4$ nm and $\lambda = 597.1$ nm. In agreement with the literature, these emission bands are referred to the Cm(III) aqua ion and the Cm(III) mononitrate complex ($[\text{Cm}(\text{NO}_3)(\text{H}_2\text{O})_8]^{2+}$) formed by interaction with nitrate anions.³⁵ At increasing ligand concentration, three additional emission bands occur at $\lambda = 600.2$ nm, $\lambda = 605.5$ nm and $\lambda = 608.7$ nm. The positions of these emission bands are in excellent agreement with those of the $[\text{Cm}(\text{PTD})_n]^{3+}$ ($n = 1,2,3$) complexes observed in 10^{-3} mol/L HClO_4 . For this reason, the pure component spectra obtained in 10^{-3} mol/L HClO_4 (Figure 3, right) are used for the peak deconvolution. In addition, identical FI factors are determined in both media. Figure 5 (*right*) shows the obtained species distribution at increasing ligand concentration.

The complexation of Cm(III) starts at a ligand concentration of $4.85 \cdot 10^{-4}$ mol/L. Initially the $[\text{Cm}(\text{PTD})]^{3+}$ complex forms with a maximum fraction of 18% at $7.56 \cdot 10^{-3}$ mol/L. The formation of the $[\text{Cm}(\text{PTD})_2]^{3+}$ complex starts at a ligand concentration of $1.66 \cdot 10^{-3}$ mol/L and exhibits the maximum fraction of 40% at $1.86 \cdot 10^{-2}$ mol/L. When the ligand concentration is above $2.0 \cdot 10^{-2}$ mol/L, $[\text{Cm}(\text{PTD})_3]^{3+}$ becomes the main complex species in solution. Utilizing the obtained species distribution (Figure 5, *right*), slope analyses were performed (cf. supporting information) proving the accurate deconvolution and assignment of the observed emission bands. The conditional stability constants of the formed Cm-PTD complexes (in 0.44 mol/L HNO_3) are calculated to be $\log\beta_1 = 1.7 \pm 0.2$, $\log\beta_2 = 4.0 \pm 0.2$ and $\log\beta_3 = 5.7 \pm 0.3$.

The species distributions obtained in 0.44 mol/L HNO_3 and 10^{-3} mol/L HClO_4 exhibit similar maximum fractions of the formed $[\text{Cm}(\text{PTD})_n]^{3+}$ complexes. This is evident when comparing the maximum fractions of the 1:1 complex (18% in 0.44 mol/L HNO_3 and 25% in 10^{-3} mol/L HClO_4) and the 1:2 complex (40% in 0.44 mol/L HNO_3 and 35% in 10^{-3} mol/L HClO_4).

However, the obtained $\log\beta_3$ values differ by 4 orders of magnitude ($\log\beta_3 = 5.7 \pm 0.3$ in 0.44 mol/L HNO_3 and 9.7 ± 0.3 in 10^{-3} mol/L HClO_4), revealing an important impact of the applied medium on the conditional stability constants. Therefore, the influence of protonation and ionic strength on the complexation of Cm(III) with PTD was investigated in detail.

Influence of ionic strength on the complexation of Cm(III) with PTD

In order to investigate the impact of ionic strength on the complexation of Cm(III) with PTD, samples were prepared containing 10^{-7} mol/L of Cm(III) and $5.56 \cdot 10^{-4}$ mol/L of PTD in 10^{-3} mol/L HClO_4 . The ionic strength was increased by subsequent additions of NaClO_4 in 10^{-3} mol/L HClO_4 . Figure 6 (*left*) shows the evolution of the Cm(III) emission spectra at increasing ionic strength.

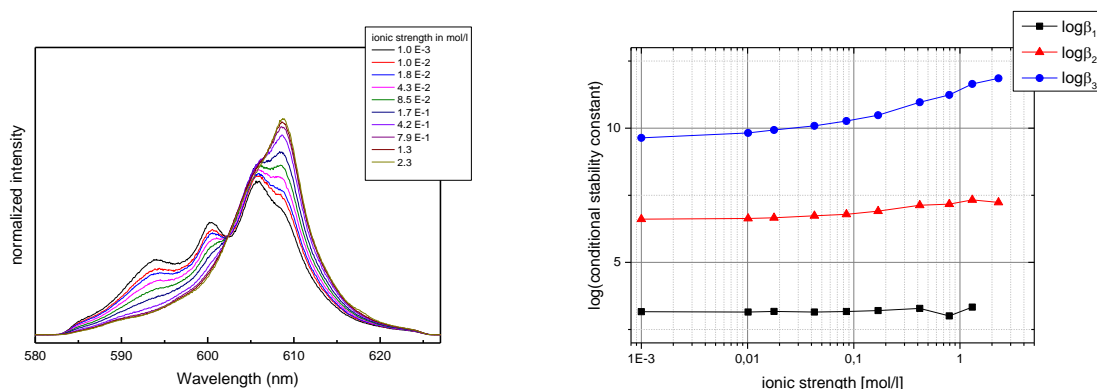


Figure 6 *Left*: Normalized fluorescence spectra of Cm(III) with PTD at increasing NaClO_4 concentration (0 to 2.3 mol/L) in 10^{-3} mol/L HClO_4 . $[\text{Cm(III)}]_{\text{ini}} = 1 \cdot 10^{-7}$ mol/L, $[\text{PTD}]_{\text{ini}} = 5.56 \cdot 10^{-4}$ mol/L. *Right*: Double logarithmic plot of the conditional stability constants of $[\text{Cm(PTD)}_n]^{3+}$ species, ($n = 1,2,3$) as a function of ionic strength.

The emission spectra show an increased formation of species containing an higher number of PTD molecules with increasing ionic strength. The fractions of the Cm(III) aqua ion and the 1:1 complex (initially both fractions greater than 20%) decrease below 5% with increasing ionic

strength. The formation of the 1:2 complex is also repressed, resulting in a decrease of the fraction of 1:2 complex from 33% at 10^{-3} mol/L to 9% at 2.3 mol/L NaClO_4 . In contrast, the fraction of the 1:3 complex increases from 20% in 10^{-3} mol/L HClO_4 up to 87% at 2.3 mol/L ionic strength. The stronger complexation of Cm(III) with PTD at higher ionic strength results in the increase of the conditional stability constant β_3 by two orders of magnitude revealing a stabilization of $[\text{Cm}(\text{PTD})_3]^{3+}$ at higher ionic strength (see Figure 6 *right*).

Influence of H^+ concentration on the complexation of Cm(III) with PTD

The 4 orders of magnitude decrease of $\log\beta_3$ value observed in 0.44 mol/L HNO_3 with respect to 10^{-3} mol/L HClO_4 cannot be explained by the influence of the higher ionic strength, since the latter one proved to have a stabilizing effect. Furthermore, the concurring reaction of Cm(III) with nitrate is known to have only a minor influence on Cm(III) complexation in presence of strong complexing ligands.²² Hence, further titration experiments were performed investigating the influence of the H^+ concentration on the complexation of Cm(III) with PTD. Figure 7 (*left*) shows the normalized Cm(III)-PTD emission spectra ($5.56 \cdot 10^{-4}$ mol/L of ligand in 10^{-3} mol/L HClO_4) at increasing HClO_4 concentration. HClO_4 is used due to the non-coordinating properties of the ClO_4^- anion. Therefore, the influence of the increasing H^+ concentration can be observed exclusively in the titration experiment.

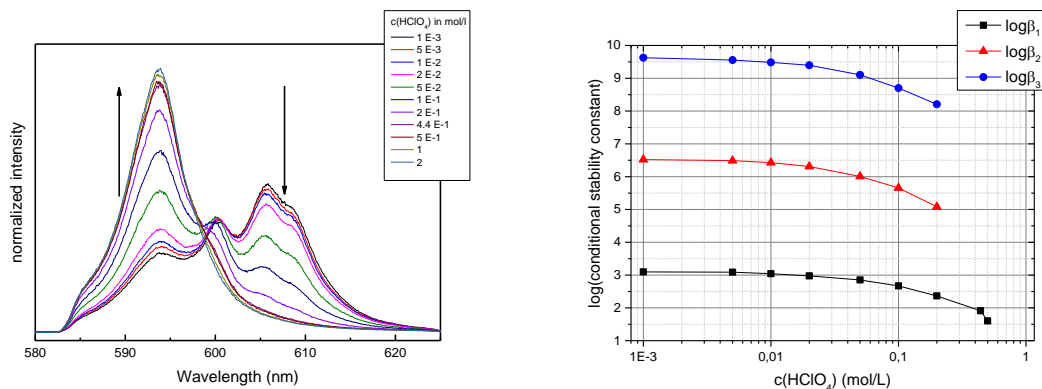


Figure 7 *Left*: Normalized fluorescence spectra of Cm(III) with PTD at increasing HClO₄ concentration. [Cm(III)]_{ini} = 1·10⁻⁷ mol/L, [PTD]_{ini} = 5.56·10⁻⁴ mol/L. *Right*: Double logarithmic plot of the conditional stability constants of [Cm(PTD)_n]³⁺, (n = 1,2,3) as a function of proton concentration. At HClO₄ concentrations greater than 0.2 mol/L no [Cm(PTD)₂]³⁺ or [Cm(PTD)₃]³⁺ complexes and at HClO₄ concentrations greater than 0.5 mol/L no [Cm(PTD)]³⁺ was observed. Hence no logβ_n could be obtained for the respective complexes at higher acid concentration.

At a HClO₄ concentration of 10⁻³ mol/L, all three [Cm(PTD)_n]³⁺ (n = 1,2,3) complex species are observed. By increasing the HClO₄ concentration, the Cm(III) emission spectra shown in Figure 7 (*left*) display a strong decrease of the complexed Cm(III) species. At HClO₄ concentrations greater than 0.5 mol/L, the Cm(III) aqua ion is the only observed species. Even though the simultaneously increasing ionic strength should stabilize the formed complexes, these experimental results show that the increase of the H⁺ concentration in the applied medium leads to a decrease of the conditional stability constants (see Figure 7, *right*). This decline of Cm complexation with PTD is consistent with the difference of the conditional stability constants observed in 10⁻³ mol/L HClO₄ and 0.44 mol/L HNO₃ and emphasizes the strong influence of H⁺ concentration on the complexation behavior of the ligand.

Complexation of Eu(III) with PTD in 10^{-3} mol/L HClO₄

Further experiments were performed to investigate the complexation of Eu(III), as a representative of the trivalent lanthanides, with PTD. Initial studies on Eu(III)-PTD complexation were performed in 10^{-3} mol/L HClO₄ to prevent the impact of both H⁺ concentration and ionic strength on the complexation reaction. Figure 8 (*left*) displays the normalized Eu(III) emission spectra at increasing ligand concentration.

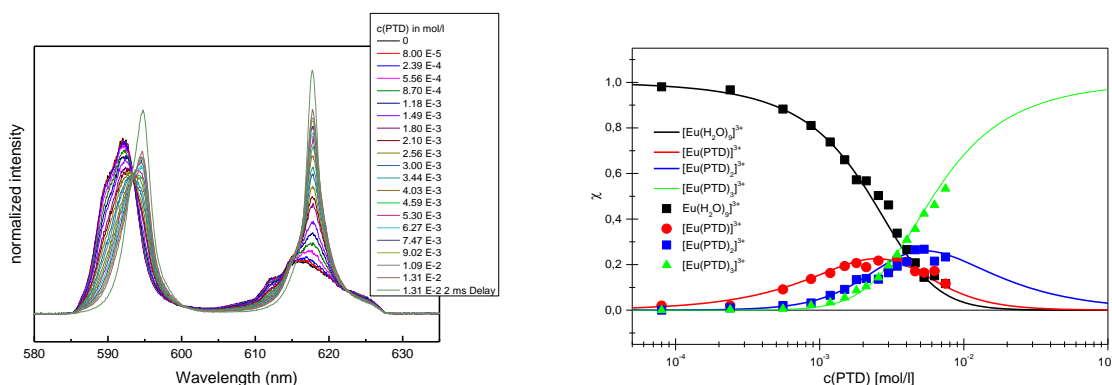


Figure 8 *Left*: Normalized fluorescence spectra of Eu(III) at increasing PTD concentration in 10^{-3} mol/L HClO₄. $[\text{Eu(III)}]_{\text{ini}} = 5 \cdot 10^{-6}$ mol/L. *Right*: Species distribution of Eu(III) as a function of PTD concentration in 10^{-3} mol/L HClO₄. Symbols experimental data, lines calculated with $\log\beta_1 = 2.3$, $\log\beta_2 = 4.8$ and $\log\beta_3 = 7.3$.

With increasing ligand concentration, three Eu(III)-PTD complex species are formed. The spectra of the pure components are displayed in the supporting information. The FI factors of the Eu(III) complex species are determined to be $[\text{Eu(PTD)}]^{3+} = 1$, $[\text{Eu(PTD)}_2]^{3+} = 1$, $[\text{Eu(PTD)}_3]^{3+} = 3.5$. Figure 8 (*right*) shows the obtained species distribution. Using this speciation, the slope analyses were performed confirming the hypothesized $[\text{Eu(PTD)}_n]^{3+}$ ($n = 1,2,3$) species (*cf.* supporting information).

The formation of $[\text{Eu}(\text{PTD})]^{3+}$ starts at a ligand concentration of $8 \cdot 10^{-5}$ mol/L and exhibits a maximum of 23% at $2.5 \cdot 10^{-3}$ mol/L PTD. At ligand concentration greater than $5.56 \cdot 10^{-4}$ mol/L, $[\text{Eu}(\text{PTD})_2]^{3+}$ is formed. This species has a maximum fraction of 27% at $5.3 \cdot 10^{-3}$ mol/L PTD. At ligand concentration above $3.7 \cdot 10^{-3}$ mol/L, $[\text{Eu}(\text{PTD})_3]^{3+}$ is the predominant species in solution.

The conditional stability constants were determined ($\log\beta_1 = 2.3 \pm 0.3$; $\log\beta_2 = 4.8 \pm 0.3$; $\log\beta_3 = 7.3 \pm 0.4$). In particular, the $\log\beta_3$ value is approximately two orders of magnitude lower than the value of the corresponding Cm(III) complex (9.7 ± 0.3), confirming the An(III)/Ln(III) selectivity observed in extraction experiments.³² This difference between Cm(III) and Eu(III) complexation is comparable to that observed for both lipophilic and hydrophilic BTPs.⁸

Complexation of Eu(III) with PTD in 0.44 mol/L HNO₃

In addition, the complexation of Eu(III) with PTD was studied at the same HNO₃ concentration (0.44 mol/L) used in the extraction. Figure 9 (*left*) shows the normalized Eu(III) emission spectra at increasing ligand concentration.

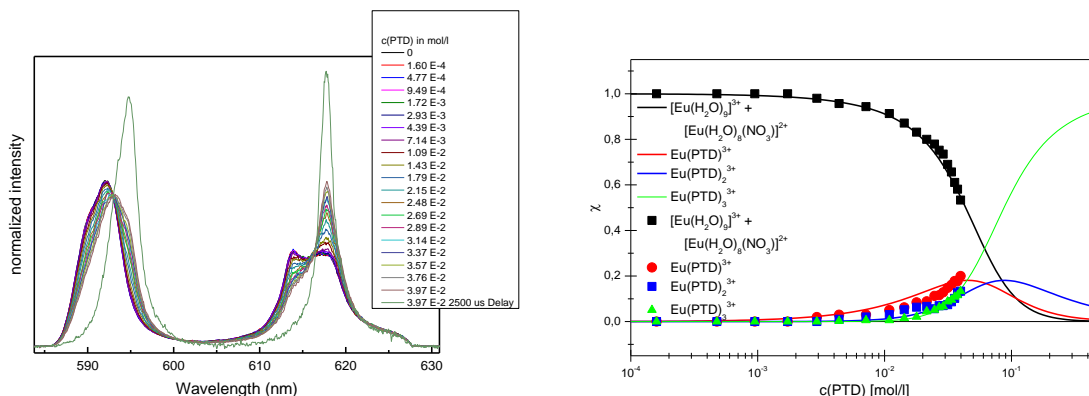


Figure 9 *Left*: Normalized fluorescence spectra of Eu(III) at increasing PTD concentration in 0.44 mol/L HNO₃. $[\text{Eu}(\text{III})]_{\text{ini}} = 5 \cdot 10^{-5}$ mol/L. *Right*: Species distribution of Eu(III) in 0.44 mol/L HNO₃ as a function of PTD concentration. Symbols represent experimental data, lines designate calculations with $\log\beta_1 = 0.9$, $\log\beta_2 = 2.1$ and $\log\beta_3 = 3.7$.

Besides the Eu(III) aqua ion and the mono-nitrate complex, three $[\text{Eu}(\text{PTD})_n]^{3+}$ ($n = 1,2,3$) complex species are formed. However, the conditional stability constants for the complexation of Eu(III) with PTD are very low under these conditions. As a result, a quantitative formation of the $[\text{Eu}(\text{PTD})_3]^{3+}$ species is not achieved. The spectrum of the $[\text{Eu}(\text{PTD})_3]^{3+}$ complex was obtained by measurements performed after a 2.5 ms delay between the laser excitation and the optical detection. After the long delay time, the fluorescence of all species containing water in the first coordination sphere is decayed and the spectrum of the 1:3 complex is recorded exclusively. Pure component spectra for the $[\text{Eu}(\text{PTD})]^{3+}$ and the $[\text{Eu}(\text{PTD})_2]^{3+}$ complexes were taken from the titration experiments in 10^{-3} mol/L HClO_4 . Taking into account the above defined FI factors, the species distribution is obtained as a function of the ligand concentration (Figure 9, *right*).

The complexation of Eu(III) with PTD in 0.44 mol/L HNO_3 starts at a ligand concentration of $2.93 \cdot 10^{-3}$ mol/L. At PTD concentrations above $6.2 \cdot 10^{-2}$ mol/L, the 1:3 complex becomes the major species in solution. The 1:1 and the 1:2 complexes exhibit only very low intensities in the investigated concentration range. Hence, the determined values for $\log\beta_1$ and $\log\beta_2$ are affected by large errors ($\log\beta_1 = 0.9 \pm 0.4$; $\log\beta_2 = 2.1 \pm 0.5$) due to the low fractions of complex species. Furthermore, slope analyses could not be performed for the stepwise complexation of Eu(III) with PTD. Only for the formation of $[\text{Eu}(\text{PTD})_3]^{3+}$ from the solvated Eu(III), a linear slope of 2.8 was obtained corresponding to the coordination of 3 ligand molecules (*cf.* supporting information). The $\log\beta_3 = 3.7 \pm 0.3$ is 2 orders of magnitude lower than the value obtained for Cm(III) at the same conditions (5.7 ± 0.3). This difference again confirms the excellent selectivity of PTD for An(III) over Ln(III).

A summary of the herein obtained conditional stability constants and a comparison with SO_3^- -Ph-BTP (until now the reference molecule for the *i*-SANEX process) are given in Table 1.

Table 1 Summary of conditional stability constants of $[M(\text{PTD})_3]^{3+}$ complexes in comparison with analogous $[M(\text{SO}_3\text{-Ph-BTP})_3]^{9-}$ complexes, (M = Cm(III), Eu(III)).^{20, 36}

medium		$\log\beta_3$ ($[\text{Cm}(\text{PTD})_3]^{3+}$)	$\log\beta_3$ ($[\text{Eu}(\text{PTD})_3]^{3+}$)	$\log\beta_3$ ($[\text{Cm}(\text{SO}_3\text{-Ph-BTP})_3]^{9-}$)	$\log\beta_3$ ($[\text{Eu}(\text{SO}_3\text{-Ph-BTP})_3]^{9-}$)
10^{-3} HClO ₄	mol/L	9.7 ± 0.3	7.3 ± 0.4	12.2 ± 0.3	10.2 ± 0.3
0.44 HNO ₃ PTD)/0.5 HNO ₃ (for Ph-BTP)	mol/L (for mol/L SO ₃ - Ph-BTP)	5.7 ± 0.3	3.7 ± 0.3	10.6 ± 0.3	8.5 ± 0.3

Fluorescence lifetimes of Cm(III) and Eu(III) complexes

The fluorescence lifetimes of Cm(III) and Eu(III) 1:3 complexes with PTD were determined in the different media. Table 2 and Table 3 report the measured lifetimes and the number of water molecules in the first coordination sphere calculated according to the Kimura equation³⁷ for Cm(III) and the Horrocks equation³⁸ for Eu(III), respectively.

Table 2 Fluorescence lifetimes of $[\text{Cm}(\text{PTD})_3]^{3+}$ complexes in the different media and number of inner sphere water molecules.

Medium	Lifetime [μs]	$n(\text{H}_2\text{O}) \pm 0.5$
10^{-3} mol/L HClO ₄	546 ± 27	0.4
0.44 mol/L HNO ₃	498 ± 25	0.5

Table 3 Fluorescence lifetimes of $[\text{Eu}(\text{PTD})_3]^{3+}$ complexes in the different media and number of inner sphere water molecules.

Medium	Lifetime [μs]	$n(\text{H}_2\text{O}) \pm 0.5$
10^{-3} mol/L HClO_4	2446 ± 122	-0.2
0.44 mol/L HNO_3	2532 ± 127	-0.2

The fluorescence lifetimes of Cm(III) and Eu(III) indicate that no water molecules are present in the first coordination sphere of the respective M(III). This is consistent with the formation of $[\text{M}(\text{PTD})_3]^{3+}$ complexes as shown by slope analyses. Furthermore, these lifetimes reveal a significant difference between PTD and BTP ligands. The former is a non-quenching ligand while BTP ligands exhibit strong quenching effects on the fluorescence of Cm(III), resulting in fairly short fluorescence lifetimes in the range of 200 - 350 μs .^{34,39}

TRLFS studies in extraction experiments

According to the speciation results obtained for Cm(III) and Eu(III) with PTD in 0.44 mol/L HNO_3 , a mixture of different $[\text{M}(\text{PTD})_n]^{3+}$ ($n = 2,3$) species is observed at 80 mmol/L of PTD. To confirm the results of the homogeneous phase TRLFS experiments, a liquid-liquid extraction experiment was performed by contacting an aqueous phase consisting of 10^{-7} mol/L Cm(III) and 80 mmol/L PTD in 0.44 mol/L HNO_3 with an organic phase consisting of 0.2 mol/L TODGA + 5%vol. 1-octanol in Exxsol D80. Following phase separation, both aqueous and organic phases are separately investigated by TRLFS.

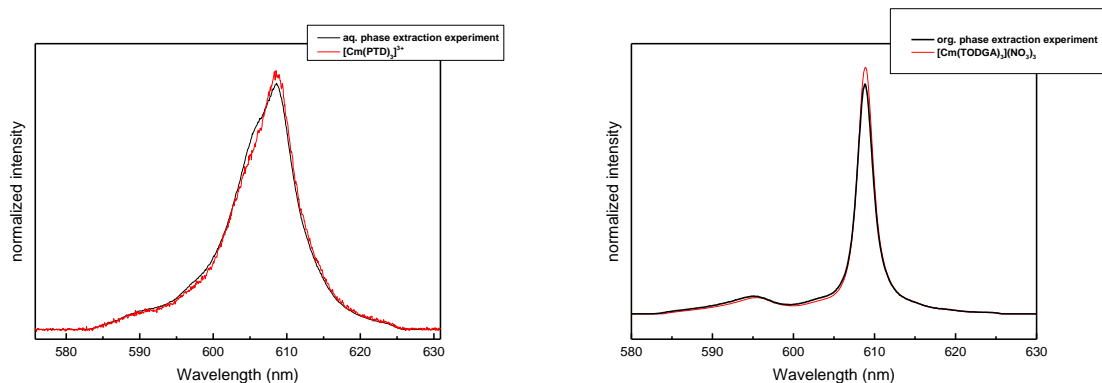


Figure 10 *Left*: Normalized Cm(III) emission spectrum of the aqueous phase after extraction and comparison with the $[\text{Cm}(\text{PTD})_3]^{3+}$ spectrum. *Right*: Normalized Cm(III) emission spectrum of the organic phase and comparison to the $[\text{Cm}(\text{TODGA})_3](\text{NO}_3)_3$ spectrum.⁴⁰ Extraction experiments: aq. phase: 10^{-7} mol/L Cm(III), 80 mmol/L PTD in 0.44 mol/L HNO_3 , org. phase 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80.

The deconvolution of the aqueous phase Cm(III) spectrum (Figure 10, *left*) reveals the presence of a mixture of $[\text{Cm}(\text{PTD})_2]^{3+}$ and $[\text{Cm}(\text{PTD})_3]^{3+}$ species with fractions of 22% and 78%, respectively. This is in excellent agreement with the speciation obtained in monophasic titration experiments, where 20% of $[\text{Cm}(\text{PTD})_2]^{3+}$ and 80% of $[\text{Cm}(\text{PTD})_3]^{3+}$ complexes are observed (Figure 5, *right*). In the organic phase the $[\text{Cm}(\text{TODGA})_3](\text{NO}_3)_3$ complex is observed exclusively (Figure 10, *right*). As the distribution ratios and separation factors for Cm(III) and Am(III) are identical within the error range³² these results provide a strong indication that the lower separation factor achieved with PTD ($SF_{\text{Eu(III)/Am(III)}} \approx 150\text{--}200$)³² compared to $\text{SO}_3\text{-Ph-BTP}$ ($SF_{\text{Eu(III)/Am(III)}} \approx 1000$)¹⁹ might be due to the formation of $[\text{Cm}(\text{PTD})_2]^{3+}$ along with $[\text{Cm}(\text{PTD})_3]^{3+}$ in the aqueous phase. Further extraction experiments with a modified aqueous phase were performed to confirm this hypothesis. As the conditional stability constant for the complexation of M(III) with PTD is strongly dependent on the H^+

concentration of the applied medium, further extraction experiments were performed at a proton concentration of 10^{-3} mol/L to ensure quantitative formation of $[\text{Cm}(\text{PTD})_3]^{3+}$. Moreover, since TODGA requires nitrate anions in the aqueous phase, 1 mol/L NaNO_3 was added to the solution. Two experiments were performed, one after spiking the aqueous phase with a Cm-248 concentration suitable for TRLFS to reveal the formed $[\text{M}(\text{PTD})_n]^{3+}$ ($n = 1-3$) species, the other after adding 1 kBq of Am-241 and Eu-152 to determine the $SF_{\text{Eu(III)/Am(III)}}$.

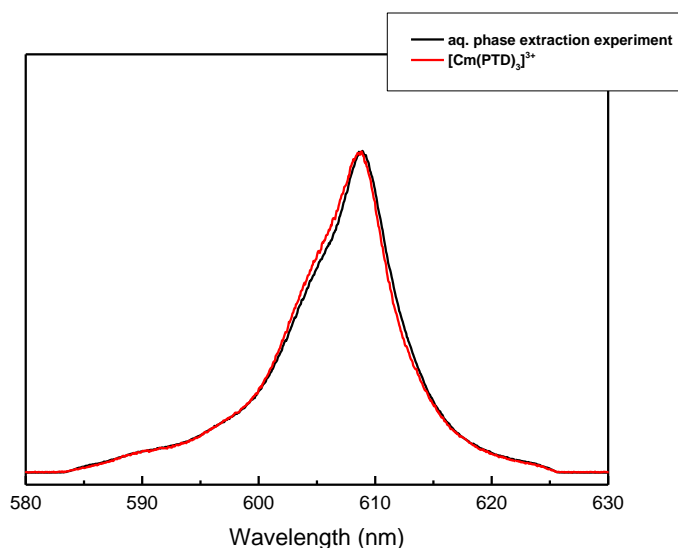


Figure 11 Cm(III) emission spectrum of the aqueous phase after extraction at pH 3 and comparison with the spectrum of $[\text{Cm}(\text{PTD})_3]^{3+}$ species. Aq. phase: 10^{-7} mol/L Cm(III), 80 mmol/L PTD and 1 mol/L NaNO_3 in 10^{-3} mol/L HClO_4 , org. phase: 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80.

The TRLFS spectrum (Figure 11) obtained at lower H^+ concentration (1 mol/L NaNO_3) exhibits the exclusive formation of $[\text{Cm}(\text{PTD})_3]^{3+}$. Furthermore, the observed $SF_{\text{Eu(III)/Am(III)}}$ increases from $\approx 150-200$ (0.44 mol/L HNO_3) to ≈ 600 . This confirms that the incomplete complexation of M(III) with the ligand at 0.44 mol/L HNO_3 results in a decrease of the

$SF_{\text{Eu(III)/Am(III)}}$. Hence, when comparing PTD with $\text{SO}_3\text{-Ph-BTP}$, PTD is not a distinctly less selective complexing agent, but rather a weaker ligand resulting in the formation of lower stoichiometry complexes strongly depending on the H^+ concentration.

Conclusion

In this work, the complexation of Cm(III) and Eu(III) with PTD has been investigated in detail by monophasic TRLFS experiments. The formed $[\text{M(PTD)}_n]^{3+}$ ($n = 1,2,3$) complexes in 1 mmol/L HClO_4 have been identified and characterized and the corresponding $\log\beta_n$ have been determined. By changing the conditions closer to those used in extraction experiments (0.44 mol/L HNO_3), a decrease of the conditional stability constants of four orders of magnitude is observed. To shed light on the role of the medium composition on complexation, the influence of ionic strength and H^+ concentration on the stability constants of Cm(III) with PTD have been investigated. An increase of ionic strength results in the stabilization of the $[\text{M(PTD)}_3]^{3+}$ complex, while an increase of the H^+ concentration causes a significant decomplexation of Cm(III). The results show that in particular the H^+ concentration of the applied medium has a major influence on the stability of the formed complexes.

In addition, speciation studies on Cm(III) with PTD in biphasic liquid-liquid extraction experiments have been performed by TRLFS. The formation of a mixture of $[\text{M(PTD)}_n]^{3+}$ ($n = 2,3$) complex species during the extraction is outlined and is in good agreement with the monophasic titration experiments. To ensure the exclusive formation of $[\text{Cm(PTD)}_3]^{3+}$ during the extraction, focused experiments at lower H^+ concentration (10^{-3} mol/L HClO_4) have been performed. This resulted in an increase of the Eu(III)/Am(III) separation factor from $\approx 150\text{--}200$ (in 0.44 mol/L HNO_3) to ≈ 600 , confirming the hypothesis that the formation of 1:2 besides the 1:3 complexes at 0.44 mol/L HNO_3 reduces the $SF_{\text{Eu(III)/Am(III)}}$ observed for PTD. Hence, the

separation factor of PTD is not a consequence of a poor selectivity, but rather of the experimental conditions used in the extraction conditions and particularly of the high HNO₃ concentration imposed by the process.

Further efforts will be aimed at investigating (1,2,3-triazol-4-yl)pyridine derivatives in order to obtain more stable complexes, thus achieving higher separation factors at extraction conditions. In any case, the relevant coordination properties and the high radio- and hydrolytical stability³³ exhibited by this class of ligands augur well for their application in the separation of Actinides from Lanthanides by using *i*-SANEX processes.

Supporting Information.

The following files are available free of charge.

Further pure component spectra and slope analyses for the complexation of Cm(III)/Eu(III) with PTD not shown in the text, as well as the complete data on the fluorescence lifetime measurements of Cm(III) and Eu(III) -PTD complexes.

Corresponding Author

* Corresponding author: christoph.wagner@kit.edu

Author Contributions

All authors have given approval to the final version of the manuscript. All authors contributed equally.

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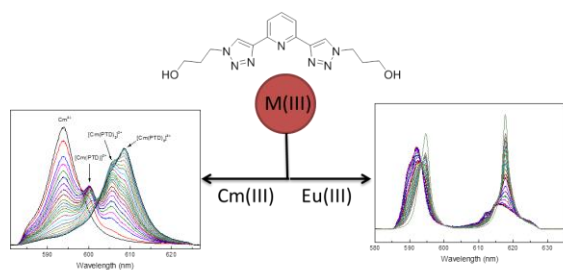
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Synopsis

The complexation of trivalent actinides and lanthanides with the novel CHON compatible, N-donor complexing agent 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine (PTD) is studied by time resolved laser fluorescence spectroscopy and liquid-liquid extraction. The spectroscopic results provide new insights into the complexation mechanism during an extraction process, allowing to improve the separation of trivalent actinides and lanthanides.