2,6-Bis(1-alkyl-1*H*-1,2,3-triazol-4-yl)- pyridines: selective lipophilic chelating ligands for minor actinides

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2,6-Bis(1-alkyl-1*H*-1,2,3-triazol-4-yl)- pyridines: selective lipophilic chelating ligands for minor actinides

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Abstract

Starting from the promising Minor Actinides (MA) affinity showed by the water-soluble ligands (PyTri-polyols) with the *2,6-bis[1H-1,2,3-triazol-4-yl]-pyridine* chelating unit, different attempts were made to functionalize the same N_3-donor set with alkyl chains in the 1- position of triazole nuclei to obtain novel lipophilic extractants endowed with comparable MA selectivity. Solubility in organic diluents was found to be the main limitation to the development of efficient lipophilic ligands, thus resulting in less efficient extractants with respect to their hydrophilic analogues and sometimes impairing the selectivity evaluation. Interestingly, the ethyl hexyl derivative (**PTEH**) showed adequate extraction capability and a MA selectivity comparable to that of the hydrophilic PyTri family.

Keywords

Partitioning, selective MA extraction, nitrogen ligand, PyTri ligand, click chemistry, radioactive waste treatment

Introduction

Energy production by means of nuclear power plants could likely play a central role in satisfying the ever-increasing power demand due to the population growth and the development of the emerging countries, as well as in reducing greenhouse gas (GHG) emissions [1-4]. In this perspective, innovative nuclear fuel cycles should be developed in order to reduce the long-term radiotoxicity and heat generation of Spent Nuclear Fuel (SNF), improve resources exploitation, simplify technical requirements of geological repository and enhance its long-term safety [5]. Nowadays great efforts are constantly dedicated to the development of compact and efficient hydrometallurgical MA partitioning processes based on CHON compliant (completely incinerable compounds containing only C, H, O, N atoms) hydrophilic or lipophilic ligands [6]. Several Joint Research projects have been funded by European Commission in order to accomplish this task [7, 8]. In particular, the *r*-SANEX (*regular*-Selective ActiNide EXtraction), *1c*-SANEX (*1cycle*-SANEX) and *i*-SANEX (*innovative*-SANEX) processes have been developed to separate trivalent MA from the high active raffinate downstream of DIAMEX (DIAMide EXtraction) or PUREX (Plutonium URanium Extraction)-like processes using lipophilic heterocyclic aromatic N-donor BTP (*bis-triazinyl-pyridine*), BTBP (*bis-triazinyl-bipyridine*) and BTPhen (*bis-triazinyl-1,10-phenanthroline*) ligands and their hydrophilic sulfonated versions, respectively [9-12]. Among the hydrophilic complexants considered up to now for implementation in *i*-SANEX process, the PyTri (*2,6-bis(1H-1,2,3-triazol-4-yl)-pyridine*) ligands resulted to be highly selective for actinides ($SF_{Eu/An} \approx 60\text{-}150$) and endowed with an extremely high radiolytical and chemical stability [13, 14]. It is worth noting that PyTri-Diol is the first CHON compliant complexant suitable for industrial implementation, since it proved to be able to achieve the An/Ln separation in centrifugal contactor device [15]. Furthermore, its affinity for all actinides in all the oxidation states has still to be completely investigated to assess its scope and limitations in the GANEX (Group ActiNide EXtraction) process. On the other hand, to date, $CyMe_4$-BTBP is the reference lipophilic ligand of the *r*-SANEX and *1c*-SANEX processes. However, even if it has shown good separation efficiency and satisfactory radiochemical stability in biphasic conditions, its low solubility, loading capability and slow kinetics hinder its application in industrial-like equipment [16, 17].

Taking into account all the remarkable results collected for the hydrophilic PyTri ligands, a lipophilic counterpart, *2,6-bis(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)pyridine* (BTTP), was proposed [18]. Although rather efficient in complexation of trivalent metal ions in homogeneous acetonitrile solution, this novel ligand showed so low extraction efficiencies for both Am(III) and Eu(III) to impair not only the determination of selectivity but also their potential use in the separation processes. It was proposed that the discrepancy between the high stability constants of BTTP in acetonitrile and its extraction behavior in biphasic octanol/water systems was due to the strong solvation of metal ions by water molecules [18].

On the basis of our experience with the hydrophilic derivatives of PyTri ligands, we focused our attention on trying to turn the *2,6-bis(1,2,3-triazolyl)pyridine* chelating unit into an efficient lipophilic ligand able to selectively extract MA into an organic solvent from acidic aqueous phases. This represents an attempt to overcome the above described issues of the reference $CyMe_4$-BTBP ligand and could clearly simplify the MA/Ln separation process. To this purpose, herein, we report the synthesis and extracting behavior of five novel derivatives (see Fig. 1) having the N_3 chelating core of PyTri and functionalized on the 1-position of triazolyl moieties, and Py nucleus in one case, with different alkyl groups.

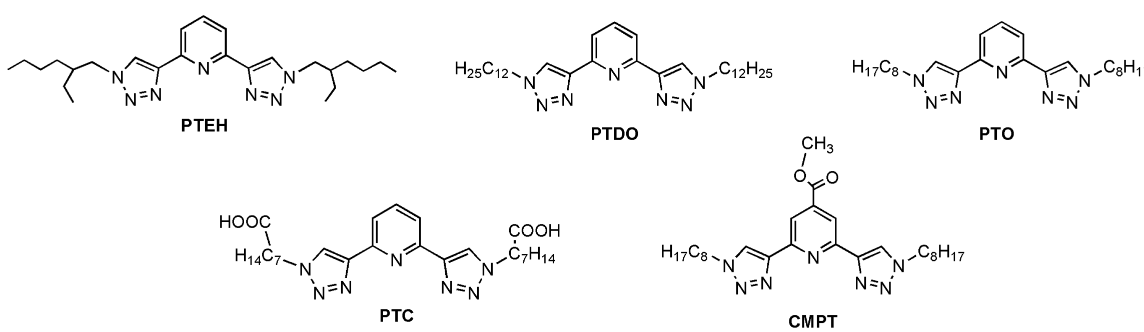


Fig. 1 Molecular structures of **PTEH**, **PTDO**, **PTO**, **PTC** and **CMPT**

Experimental

Reagents and materials

Melting points were measured on an Electrothermal apparatus in capillaries sealed under nitrogen atmosphere. Bruker AV300 and AV400 spectrometers were employed to record ^{1}H and ^{13}C NMR spectra. Coupling constants (J) are given in Hz. As internal standards partially deuterated solvents were used. Waters single quadrupole instrument SQ Detector was employed to record ESI-MS spectra. Merck 60 F254 silica gel was used for TLC analysis, while flash column chromatography was performed by using 230-400 mesh Merck 60 silica gel. The commercially available reagents and chemicals used in this study were analytical reagent grade and used without additional purification. Kerosene (reagent grade, low odor, aliphatic fraction > 95%) and 1-octanol (purity ≥ 99%), both from SIGMA-ALDRICH company, together with dichloromethane (purity > 99%) from Alfa Aesar, were used as diluents. The organic solutions were prepared by dissolving weighed amounts of extractants in the different diluents. Nitric acid solutions were obtained by diluting concentrated nitric acid (from FLUKA, ≥ 65% w/w) with distilled water. The stock solution of ^{241}Am was supplied by Eurostandard CZ (Czech Republic), the radiotracers ^{152}Eu and ^{244}Cm were supplied by CERCA-LEA (France).

Synthesis

2,6-Diethynylpyridine (**1**) [19] and methyl 2,6-diethynylisonicotinate (**2**) [20, 21] were synthetized according to literature procedures starting from 2,6-dibromopyridine or citrazinic acid, respectively.

2-ethylhexyl 4-methylbenzenesulfonate. Prepared according to literature procedure [22]. Pyridine (6 ml, 76 mmol) was added to a solution of 2-ethyl-hexan-1-ol (5 g, 38 mmol) in 25 ml of dry dichloromethane (DCM) under inert conditions. The reaction mixture was cooled to 0 °C and a solution of *p*-toluene sulfonylchloride (7.00 g in 25 ml DCM) was added drop-wise. The reaction mixture was stirred for 48 hours at room temperature then quenched with water and the aqueous layer extracted with DCM (3 x 20 ml). The organic phases were washed with HCl 1 M then dried over anhydrous Na_2SO_4

and the solvents evaporated *under vacuum* to get the final product as a colorless oil. Yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (2H, d, *J* = 8.2 Hz, *H*Ar), 7.36 (2H, d, *J* = 8.2 Hz, *H*Ar), 3.98-3.89 (2H, m, CH_2Ts), 2.47 (3H, s, Ar-CH_3), 1.55 (1H, hept, *J* = 6.1 Hz, C*H*CH_2Ts), 1.38-1.11 (8H, m, CH_2), 0.88-0.78 (6H, m, CH_3).

Synthesis of 3-azidomethyl-heptane. 2-ethylhexyl 4-methylbenzenesulfonate (15.0 g, 52.7 mmol) were dissolved in 70 ml of dry dimethylformamide (DMF) with NaN_3 (6.8 g, 104.6 mmol) under inert conditions. The reaction was stirred for 48 h then quenched with water. The aqueous layer was extracted with DCM (3 x 25 ml), the collected organic phases were washed with water (3 x 50 ml) and then dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure to get the product as a colorless oil. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (2H, d, *J* = 5.8 Hz, CH_2N_3), 1.51 (1H, hept, *J* = 6.1 Hz, C*H*CH_2N_3), 1.42-1.25 (8H, m, CH_2), 0.93-0.89 (6H, m, CH_3). ESI-MS (+): 184.1 $[M+H]^+$.

Synthesis of 1-azidooctane. Prepared according to literature procedure [23] from 1-bromooctane in 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (2H, t, *J* = 7.0 Hz, CH_2N_3), 1.61 (2H, quint, *J* = 7.0 Hz, C$H_2CH_2N_3$), 1.34-1.30 (10H, m, CH_2), 0.90 (3H, t, *J* = 6.6 Hz, CH_3).

Synthesis of 1-azidododecane. Prepared according to literature procedure [23]. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (2H, t, *J* = 6.8 Hz, CH_2N_3,), 1.4 (2H, m, C$H_2CH_2N_3$), 1.18-1.08 (18H, m, CH_2), 0.69 (3H, bs, CH_3).

Synthesis of 8-azidooctanoic acid. Prepared according to literature procedure [24]. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (2H, t, *J* = 7.0 Hz, CH_2N_3,), 2.36 (2H, t, *J* = 7.4 Hz, CH_2COOH), 1.66-1.57 (4H, m, CH_2), 1.40-1.32 (6H, m, CH_2).

General procedure for the synthesis of PTEH, PTO, PTDO, CMPT and PTC

1.00 g of 2,6 diethynylpyridine (**1**) or methyl 2,6-diethynylisonicotinate (**2**) was dissolved in 35 ml of dry DMF under inert conditions. For the synthesis of **PTC**, H_2O was used as solvent. Then, $CuSO_4{\cdot}5H_2O$ (0.02 eq.), Na ascorbate (0.2 eq.) and the appropriate alkyl azide (2.5 eq.) were added to the mixture. The resulting solution was stirred for 24/72 hours at room temperature and then quenched with water. This mixture was extracted with DCM (3 x 15ml). The organic phases were then collected, dried over anhydrous Na_2SO_4 and finally the solvents were evaporated under reduced pressure.

2,6-bis(1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl)pyridine (PTEH): reaction time 72h; eluent for flash chromatography: hexane/ethyl acetate 8:2; yield: 65 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (2H, s, Triaz-*H*), 8.12 (2H, d, *J* = 7.8 Hz, Py$H_{3,5}$), 7.89 (1H, t, *J* = 7.8 Hz, PyH_4), 4.34 (4H, d, *J* = 6.9 Hz, CH_2N), 1.97 (2H, quint, *J* = 6.2 Hz, C*H*CH_2N), 1.41-1.32 (16H, m, CH_2), 0.98-0.92 (12H, t, *J* = 7.4 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 148.2, 137.7, 122.3, 119.3, 53.8, 40.5, 30.4, 28.5, 23.7, 22.9, 14.0, 14.05. ESI-MS (+): 438.7 $[M+H]^+$, 460.6 $[M+Na]^+$, 897.9 $[2M+Na]^+$. mp: 60.3-60.6 °C

2,6-bis(1-dodecyl-1H-1,2,3-triazol-4-yl)pyridine (PTDO): reaction time 48h; yield: 50 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (2H, bs, Py$H_{3,5}$), 8.09 (2H, bs, Py$H_{3,5}$), 7.86 (1H, bs, PyH_4), 4.42 (4H, bs, CH_2N), 1.97 (4H, bs, C$H_2$$CH_2$N), 1.37-1.27 (36H, bs, CH_2), 1.97 (6H, bs, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 148.3, 137.6, 121.8, 119.3, 50.6, 31.9, 30.4, 29.6, 29.4, 29.3, 29.0, 26.5, 22.7, 14.1. ESI-MS (+): 572.7 $[M+Na]^+$, 1122.1 $[2M+Na]^+$. mp: 125.0-125.3 °C

2,6-bis(1-octyl-1H-1,2,3-triazol-4-yl)pyridine (PTO): reaction time 48h; yield: 55 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (2H, s, Triaz-*H*), 8.12 (2H, d, *J* = 7.7 Hz, Py$H_{3,5}$), 7.88 (1H, t, *J* = 7.7 Hz, PyH_4), 4.45 (4H, t, *J* = 7.2 Hz, CH_2N), 1.99 (4H, quint, *J* = 6.9 Hz, C$H_2$$CH_2$N), 1.38-1.29 (10H, m, C$H_2$), 0.89 (6H, t, *J* = 6.8 Hz, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 148.3, 137.7, 121.9, 119.2, 50.5, 31.7, 30.3, 29.02, 28.94, 26.5, 22.6, 14.0. ESI-MS (+): 460.2 $[M+Na]^+$, 897.5 $[2M+Na]^+$. mp: 117.0-117.6 °C

methyl 2,6-bis(1-octyl-1H-1,2,3-triazol-4-yl)isonicotinate (CMPT): reaction time 72h; yield: 90 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (2H, bs, Triaz-*H*), 8.24 (2H, bs, Py$H_{3,5}$), 4.44 (4H, bs, CH_2N), 4.00 (3H, bs, OCH_3), 1.98 (4H, bs, NCH_2CH_2), 1.35-1.66 (10H, bs, CH_2), 0.89-0.85 (6H, t, *J* = 6.1 Hz, CH_2CH_3).

8,8'-(4,4'-(pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))dioctanoic acid (PTC): reaction time 24h; yield: 40 %. ^{1}H NMR (400 MHz, CD_3OD): δ 8.61 (2H, s, Triaz-*H*), 7.94 (3H, m, $PyH_{3,4,5}$), 4.49 (4H, t, *J* = 7.0 Hz, CH_2N), 2.25 (4H, t, *J* = 7.3 Hz, CH_2CO), 1.99 (4H, quint, *J* = 6.9 Hz, $CH_2CH_2N_3$), 1.60 (4H, quint, J = 7.0 Hz, CH_2CH_2COOH), 1.38-1.27 (12H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 176.3, 163.5, 137.7, 137.6, 127.3, 123.3, 78.9, 33.5, 29.7, 28.8, 28.7, 28.6, 28.3, 25.9, 24.7, 24.5. ESI-MS: 498.60 $[M+H]^+$, 520.70 $[M+Na]^+$, 536.61 $[M+K]^+$.

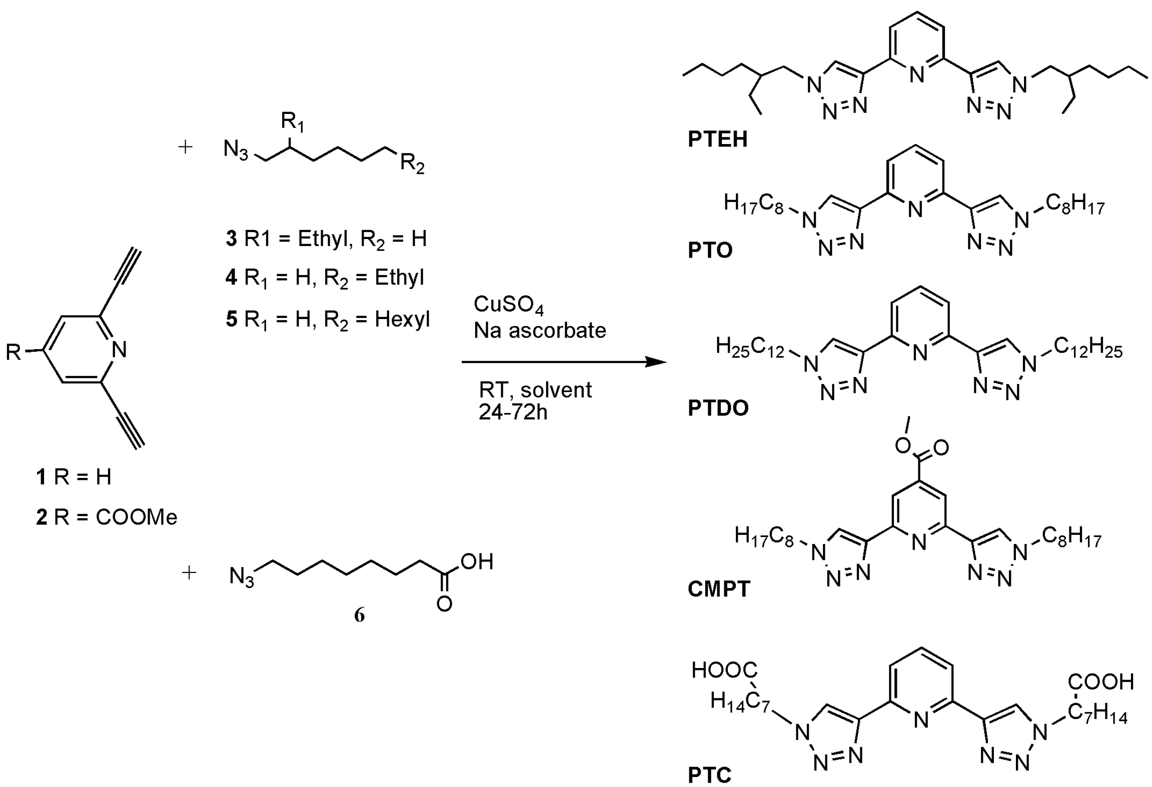
Experimental conditions

Solubility of extractants was evaluated by dissolving a weighed amount of compound in the chosen diluent at 22 ± 1 °C and by stepwise addition of a weighed amount of diluent until the solutions became clear. Sonication and heating were exploited to facilitate ligand dissolution only if necessary. Only the organic phases containing 1-octanol were pre-equilibrated with an equal volume of nitric acid of suitable concentration, before performing the liquid-liquid extraction tests, in order to ensure that the aqueous phase acidity did not change during the tests. The concentration of HNO_3 in the aqueous phase was checked by titration with NaOH before and after the extraction experiments. Besides that, all the extraction tests were carried out following a standard protocol. The organic phases were contacted in closed single-use Eppendorf microtubes with an equal volume of the aqueous phases containing the cations to be extracted and vigorously shaken at room temperature (22 ± 1 °C) with a mixer for 1 hour, which proved to be sufficient to achieve the chemical equilibrium. An aliquot of 200 µL of each phase was sampled after centrifugation. The activity concentrations of ^{241}Am and ^{152}Eu in each phase were measured by γ-spectrometry (2″ × 2″ NaI(Tl), Silena SNIP N MCA) exploiting the γ-lines at 59.5 keV and 121.8 keV, respectively. Following sample preparation by diluent evaporation to dryness on steel planchet, the activity concentrations of ^{241}Am and ^{244}Cm were checked by α-spectrometry (ORTEC Octête PLUS) by exploiting the α-lines at about 5.4 MeV and 5.8 MeV, respectively. The result of ^{244}Cm was normalized on the activity concentration of ^{241}Am obtained from γ and α spectrometries. Each test was performed in duplicate. Extraction tests were performed only with the organic phases in which no precipitate or third phase formation were observed. Extraction data were considered reliable only if no third phase was observed during the tests and the mass balance was 100 ± 5%. Distribution ratios, D_M, were then calculated as the ratio between the activity concentration of the radiotracers (or the concentration of the stable elements) in the organic phase and that in the aqueous phase. The error related to distribution ratios between 0.01 and 100 is around ± 5%, while it extends to ±20% for smaller and larger values. The selectivity is expressed by the Separation Factor, $SF_{MA/Ln}$, which is the ratio of D_{MA} over D_{Ln}. In order to assess the extracting properties of the ligands, solvent extraction tests were performed with aqueous phases at different HNO_3 concentrations spiked with a total activity of about 8000 Bq of ^{241}Am, ^{152}Eu and, in some cases, ^{244}Cm.

Results and discussion

Synthesis

The syntheses of the lipophilic ligands used in this work (Scheme 1) were accomplished by directly clicking the appropriate alkyl azide derivative **3-6** onto the 2,6-dialkynyl-pyridine **1-2**. The reactions proceeded smoothly at room temperature in a mixture of DMF/H_2O (only water in the case of the azide **6**). After 24-72 hours, the ligands were extracted in the organic phase and purified by column chromatography, resulting in yields of 40-90%. The structure of all the final ligands were properly confirmed by NMR and MS spectroscopy.



Scheme 1 Synthesis of the lipophilic PyTri derivatives used in this work

Solubility

The ligands under study are characterized by a common pyridine bis-triazolyl chelating unit adorned with chains at 1-position of the triazole unit having different length, polarity and structures. **PTDO** contains two n-dodecyl chains, **PTO** and **PTEH** have two octyl chains but while these units are linear for the former, they are branched for the latter one (*2-ethyl-hexyl*). In **PTC** the triazole units are functionalized with an ω-caprylic acid moiety. **CMPT** has a similar structure to **PTO** but in the former ligand the pyridine unit was functionalized with a *carboxymethyl* unit in 4 position. All these modifications should not significantly affect the efficiency and selectivity of binding and extraction of these ligands, with the exception of **CMPT** for which the addition of the ester group could change its basicity and thus its extraction properties. On the other hand, they might play a role in determining their solubility in diluents. In the preliminary stage of this study, a comparison of the solubility of the ligands in different diluents was attempted. Kerosene was chosen as main diluent, due to its widespread use in industrial separation processes. It was used alone or in addition with 1-octanol, because this alcohol prevents the formation of problematic third phases and has already been used in other separation processes with good performances [25]. Data reported in Table 1 clearly indicate that **PTEH** resulted to be the most soluble ligand, even if in pure kerosene the formation of third phase was observed during liquid-liquid extraction tests. **PTDO** is soluble in kerosene at a concentration of 0.01 M and at lower values in 1-octanol and kerosene/1-octanol mixtures. In the case of **PTDO**, the use of dichloromethane and a mixture of dichloromethane/1-octanol 50/50% v/v enabled to increase the ligand solubility, while no significant effects were obtained for **PTEH**.

Table 1 Solubility limits for ligands **PTEH, PTDO**, **PTO** and **CMPT** in different diluents (T = 22 ± 1 °C)

	Concentration, [M]			
Diluent	**PTEH**	**PTDO**	**PTO**	**CMPT**
Kerosene (K)	0.2*	0.01	≤ 0.01	0.025
Kerosene/1-octanol 95/5% v/v	0.2	≤ 0.009	n.p.	n.p.
Kerosene/1-octanol 90/10% v/v	0.2	≤ 0.0085	n.p.	n.p.
Kerosene/1-octanol 80/20% v/v	0.2	≤ 0.0075	n.p.	n.p.
Kerosene/1-octanol 70/30% v/v	0.2	≤ 0.0066	n.p.	n.p.
Kerosene/1-octanol 50/50% v/v	0.2	≤ 0.01	n.p.	n.p.
1-octanol (O)	0.2	≤ 0.0075	0.05	0.1*
Dichloromethane (DCM)	0.2	0.1	n.p.	0.01
Dichloromethane/1-octanol 50/50% v/v	0.2	0.05	n.p.	n.p.

* third phase formation during liquid-liquid extraction test, n.p.: not performed

Contrarily, the solubility for **PTO** and **CMPT** ligands are quite low and also the use of dichloromethane, pure or mixed with 1-octanol, did not help neither to improve solubility, nor to avoid third phase formation during the extraction test. In detail, regarding **PTO** ligand, the maximum solubility was found to be 0.05 M in pure 1-octanol. Lower values were found for **CMPT** ligand with a maximum of 0.025 M in pure kerosene, suggesting that the addition of a carboxylate group gives some aid to the solubility properties only when 1-octanol is used. Regarding **PTC** ligand, several attempts were made in order to find the best testing conditions (see Table SI 1) but the solubility resulted very low in any cases. Summarizing, it is possible to infer that the introduction of branched alkyl side chains (*cf*. **PTEH** *vs.* **PTO**) results to be extremely effective to significantly increase the ligand solubility compared to the introduction of longer but linear alkyl chain (*cf*. **PTDO** *vs.* **PTO**). Moreover, the results are encouraging since the considered ligands exhibit higher solubility limit values with respect to those reported in literature for the lipophilic BTTP, that exhibits a solubility limit of 0.001 M in pure 1-octanol, even after the addition of 0.5 M 2-bromodecanoic acid [18].

Extracting properties

Several liquid-liquid extraction tests were performed in order to gain indications concerning the extracting properties of the novel ligands. Solubility constraints strongly limit a detailed evaluation of the extracting performances and in particular the possibility to compare all the ligands in the same diluent. It is in fact well known how even small changes in the diluent may strongly influence the extracting properties of an organic ligand [26, 27]. However, some interesting considerations can be drawn from the reported data.

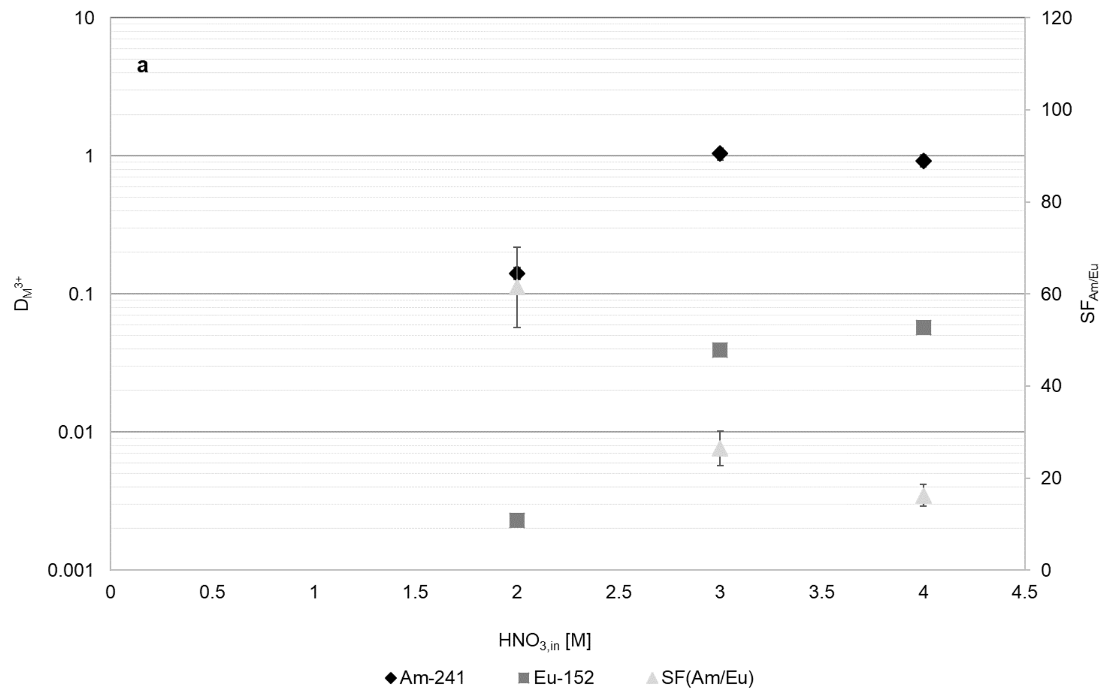
PTDO ligand showed very low extraction efficiency for both Am(III) and Eu(III) (D_M < 0.001) in the mixtures of kerosene and 1-octanol (see Table SI 2), similarly to what already reported for BTTP in 1-octanol. Interestingly, when dissolved in dichloromethane and in a mixture dichloromethane/1-octanol (Table 2), a higher ligand concentration could be used and a significant increase in the sole Am(III) extraction was observed, if compared to the kerosene/1-octanol mixtures. In particular, in dichloromethane and at the highest nitric acid concentrations (3-4 M), distribution ratios for both Am(III) and Eu(III) could be calculated and, even if they are still below the unit, indicate that the ligand exhibited a rather interesting selectivity ($SF_{Am/Eu}$ = 41-56).

Table 2 Distribution ratios and separation factors for **PTDO** ligand as a function of the diluent mixture composition and of the ligand concentration in the organic phase. Aqueous phase: trivalent ^{241}Am and ^{152}Eu in HNO_3 solutions.

[L], M	Diluent	$[HNO_3]_{in}$, M	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.075	DCM	1	0.0014 ± 0.0001	<<0.001	>>1
		2.25	0.018 ± 0.002	<<0.001	>>18
		3	0.074 ± 0.007	0.0013 ± 0.0001	56 ± 7.9
		4	0.059 ± 0.006	0.001 ± 0.0001	41 ± 5.9
0.05	DCM/O 50/50% v/v	1	0.003 ± 0.0003	<<0.001	>>3
		3	0.027 ± 0.003	<<0.001	>>27

Ligands **PTO** and **CMPT** were tested in 1-octanol, where they showed the highest solubility. However, the extraction efficiencies for both Am(III) and Eu(III) are very low and no selectivity for Am over Eu could be found (see Table SI 3-4). Interestingly, **CMPT** in dichloromethane (Table SI 4) disclosed a selectivity close to that already observed for **PTDO** in the same diluent (Table 2). Furthermore, such selectivity is comparable to that displayed by the hydrophilic PyTri-hexaol derivative reported in the literature [13]. Due to its very limited solubility, the behavior of ligand **PTC** was investigated only in few extracting conditions resulting in a very low extraction efficiency, as reported in Table SI 5.

Contrary to the results collected with sparingly soluble **PTDO**, **PTO**, **PTC** and **CMPT** ligands, **PTEH** gave remarkably interesting results by exhibiting high separation efficiency in almost all the mixtures tested, as shown in Fig. 2-4 (see Table SI 6-9 for numerical results). In dichloromethane the distribution ratios of Am(III) are close to 1 at $[HNO_3] \geq 3$ M, D_{Eu} lower than 0.1 and the separation factor around 16-25 (Fig. 2*a*). The efficiency further increases in the other diluents. In 1-octanol, the D-values for Am(III) are above 1 for nitric acid concentration ranging from 1 to 4 M with a separation factor ranging from 90 to 70 (Fig. 2*b*) and D_{Eu} values well below the unit.



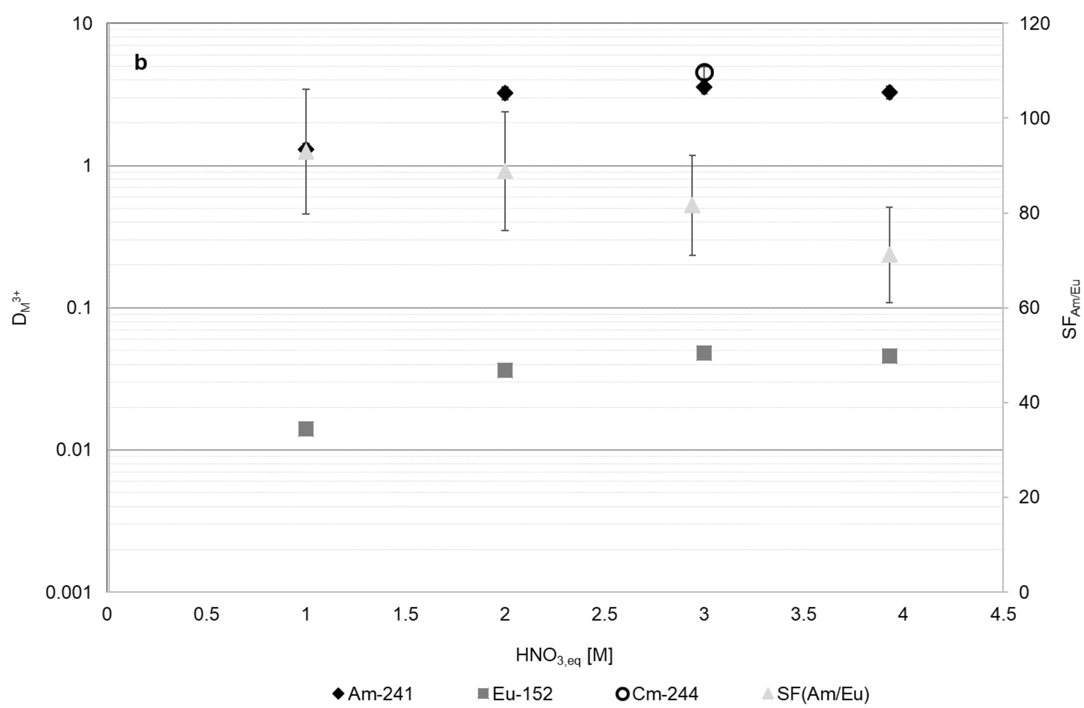


Fig. 2 Distribution ratios (whose error bars are within the marker size) and separation factors as a function of the nitric acid concentration of the aqueous phase at equilibrium. Organic phase: 0.2 M of **PTEH** ligand in dichloromethane (*a*) and in 1-octanol (*b*). Aqueous phase: HNO_3 solutions spiked with trivalent ^{241}Am and ^{152}Eu, in one test also ^{244}Cm

As shown in Fig. 3, when contacted with a spiked 3 M HNO_3 aqueous phase, the ligand exhibits good extracting performances in all the kerosene/1-octanol mixtures considered, in particular in the range of 1-octanol percentage from 10 % to 30 %. In such conditions the separation factor even reaches values around 80-82.

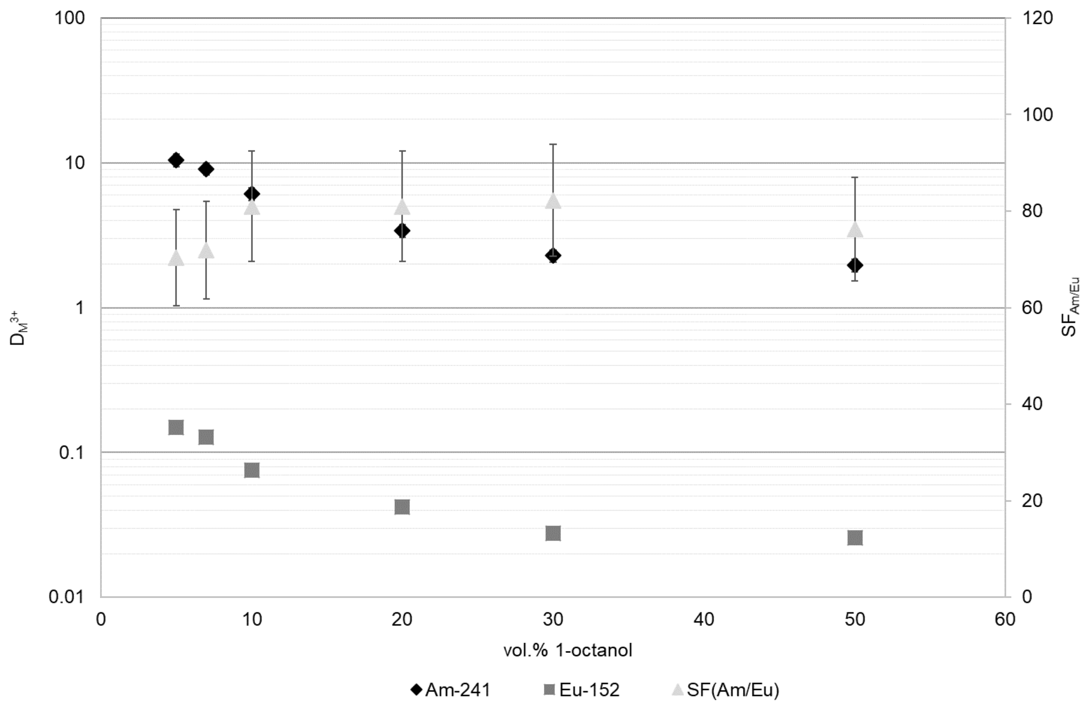
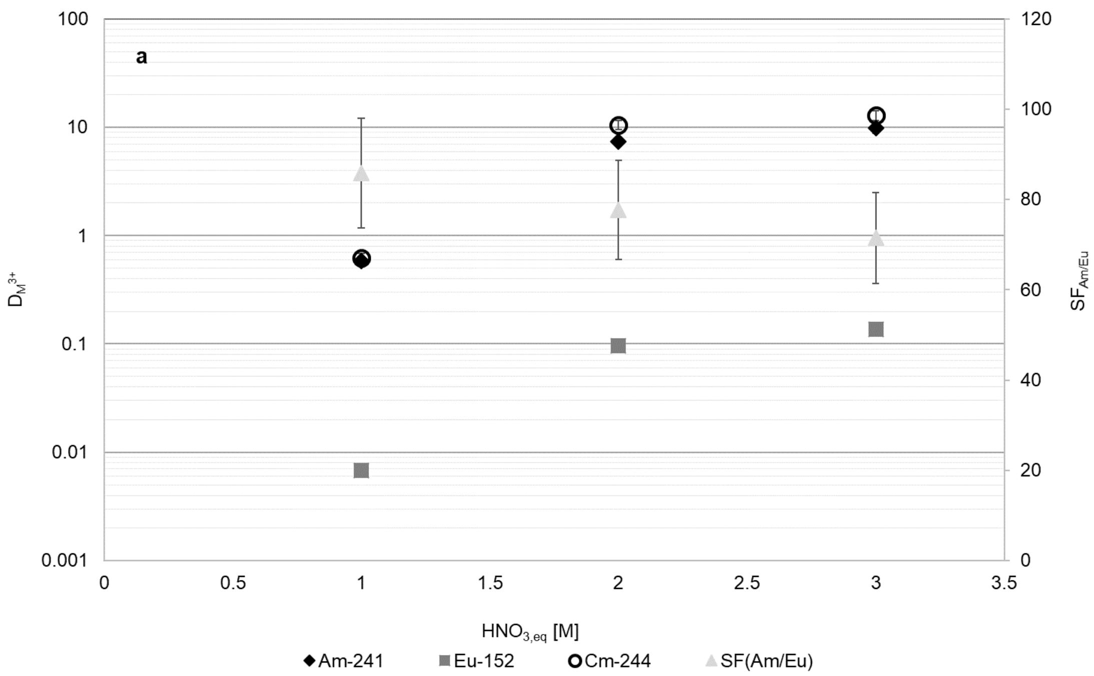
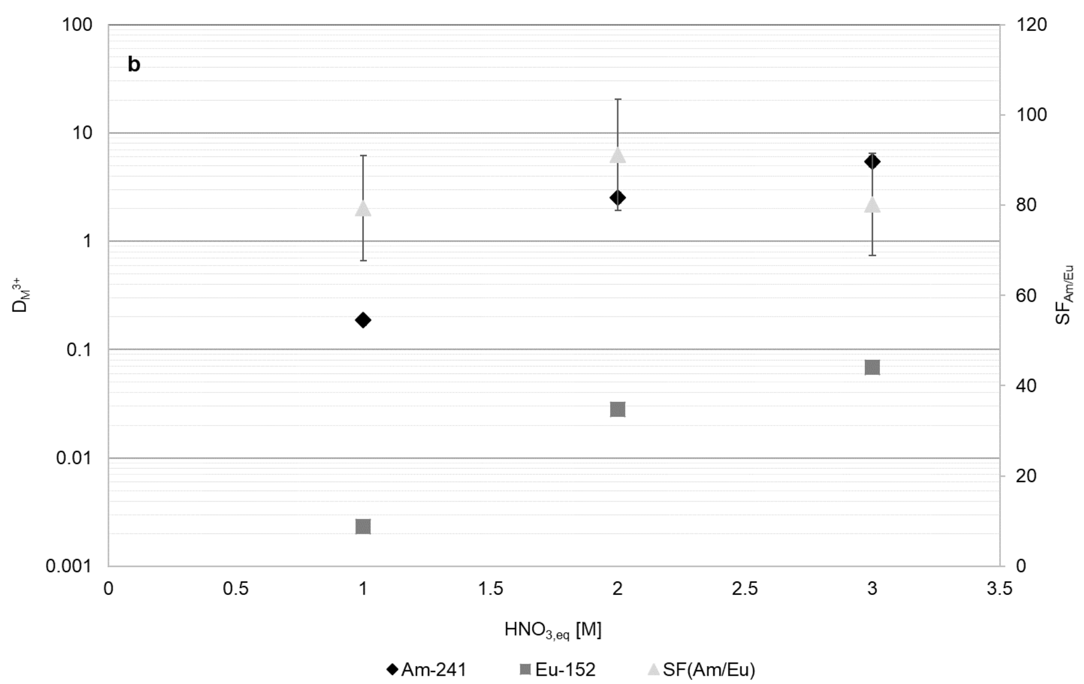


Fig. 3 Distribution ratios (whose error bars are within the marker size) and separation factors as a function of the diluent mixture composition (% of 1-octanol in the 1-octanol/kerosene v/v mixture). Organic phase: 0.2 M of **PTEH** ligand. Aqueous phase: 3 M HNO_3 solutions spiked with trivalent ^{241}Am and ^{152}Eu

Furthermore, Fig. 4 reports the distribution ratios and the separation factors for the **PTEH** ligand in three kerosene mixtures containing 5, 10 and 20 % of 1-octanol (v/v) as a function of the nitric acid concentration of the aqueous phase.


a
100
10
1
0.1
0.01
0.001
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
$D_{M^{3+}}$
$SF_{Am/Eu}$
$HNO_{3,eq}$ [M]
Am-241
Eu-152
Cm-244
SF(Am/Eu)


b
100
10
1
0.1
0.01
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120
100
80
60
40
20
0
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0.5
1
1.5
2
2.5
3
3.5
$D_{M^{3+}}$
$SF_{Am/Eu}$
$HNO_{3,eq}$ [M]
Am-241
Eu-152
SF(Am/Eu)

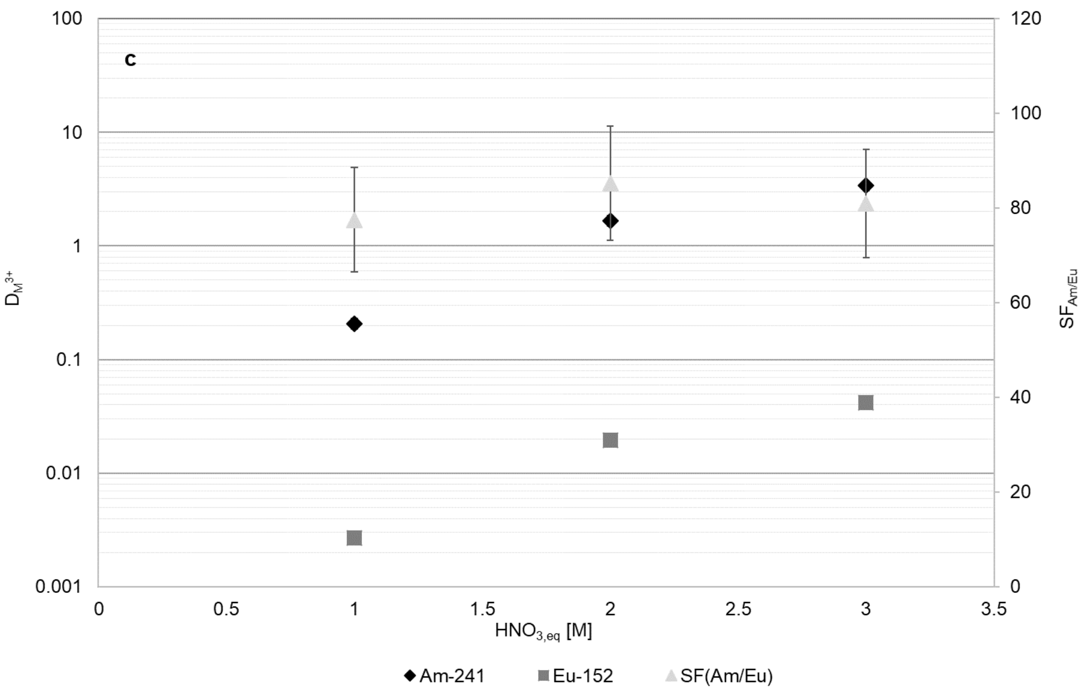

Fig. 4 Distribution ratios (whose error bars are within the marker size) and separation factors as a function of the nitric acid concentration of the aqueous phase at equilibrium. Organic phase: 0.2 M of **PTEH** ligand in kerosene/1-octanol 95/5% v/v (*a*), kerosene/1-octanol 90/10% v/v (*b*) and kerosene/1-octanol 80/20% v/v (*c*). Aqueous phase: HNO_3 solutions spiked with trivalent ^{241}Am, in some cases ^{244}Cm, and ^{152}Eu

Regarding the results in kerosene/1-octanol 95/5% v/v mixture (see Fig. 4*a*), D_{Am} and D_{Eu} slightly increase with increasing the nitric acid concentration of the aqueous phase, while the separation factor slightly decreases from 85 to 70. A similar increase of the D-values was highlighted in the case of kerosene/1-octanol 90/10 and 80/20% v/v mixtures (see Fig.4*b* and 4*c*), while the separation factors oscillate around 80. In particular, concerning D_{Eu}, it remains well below 1 in all the conditions investigated. On the other hand, D_{Am} is under the unit at 1 M nitric acid concentration of the aqueous phase for all the mixtures considered and increases up to 9.8, 5.5 and 3.4, at 3 M nitric acid concentration of the aqueous phase for the mixture with 5, 10 and 20 % of 1-octanol, respectively. Considering the significant advantages deriving from the separation of Cm(III) from Am(III) in the fuel fabrication step, due to the high decay heat produced by Cm and its neutron emission [28], some attempts were performed with an aqueous phase spiked with ^{244}Cm, besides ^{241}Am and ^{152}Eu. As the corresponding hydrophilic derivatives [13], **PTEH** ligand is not able to separate Am(III) from Cm(III), as clearly shown in Fig. 2*b*, Fig. 4*a*, Table SI 7 and Table SI 9. However, an additional process, able to perform Am/Cm separation, could be foreseen downstream from a **PTEH-**based *r*-SANEX or *1c*-SANEX process. Considering the trend against HNO_3 reported in Fig. 4*b*, cations release is foreseeable when the **PTEH** loaded solution is contacted with diluted nitric acid (such as 0.1 M HNO_3). This diluted aqueous phase or directly the **PTEH** organic phase, both loaded with ^{241}Am and ^{244}Cm, could be used as feed in the processes for Am/Cm separation recently developed. In particular, the aqueous solution coming from the back-extraction of the loaded **PTEH** organic phase could be used as aqueous feed in the LUCA (*Lanthaniden Und Curium Americum Trennung*) process [29]. Otherwise, the loaded **PTEH** organic phase could be directly treated in the EXAm (EXtraction of Americium) process [30].

Taking into consideration the information reported in Fig. 3 and Fig. 4, the mixture containing 10 % of 1-octanol should be chosen as reference working diluent. It would allow to limit the 1-octanol concentration in the organic mixture and to obtain satisfactory performance in terms of MA selectivity and extraction efficiency.

Conclusions

Five novel N_3-donor ligands were studied for the selective actinide extraction in SANEX-like processes. They are compliant with the CHON principle. They were tested for the selective MA extraction from a simplified synthetic aqueous feed containing trivalent Am, Cm and Eu. Unfortunately, in the four cases of **PTDO**, **PTO**, **PTC** and **CMPT**, solubility was found to be the main constrain, similarly to that already reported in literature by Kiefer et al. for BTTP ligand. The low ligand concentration used for these four ligands, causes a rather low efficiency of extraction for both Am(III) and Eu(III), that makes the selectivity evaluation quite unreliable, even if in few conditions a promising MA/Ln selectivity was deduced.

On the other hand, **PTEH** was found to be by far more soluble and efficient in extractions with a selectivity that resembles that found in the case of the promising hydrophilic PyTri compounds. It is worth noting that the Am(III) over Eu(III) selectivity observed for **PTEH** in kerosene/1-octanol mixtures is close to and in some cases even higher than 80. These results also demonstrated that branched alkyl chains are much more efficient in enhancing ligand solubility into the organic diluents compared to linear alkyl chains.

Thanks to these promising extracting properties, the novel **PTEH** ligand is worth to be further investigated in order to gain more information about its extraction properties, such as extraction kinetics and speciation, and its radiochemical stability for the possible industrial application of **PTEH** in a SANEX process. The results herein collected will also be of help to modify the structure of this lipophilic class of compounds in order to develop other possible Am/Eu selective ligands.

Acknowledgements

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Supplementary Information

The ^{1}H and ^{13}C NMR spectra of the synthetized ligands, as well as the extraction data, are reported in the Supplementary Information.

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