

Hydrophilic Clicked 2,6-bis-Triazolyl-Pyridines Endowed with High Actinide Selectivity and Radiochemical Stability: towards a Closed Nuclear Fuel Cycle

Elena Macerata,^{*,§} Eros Mossini,[§] Stefano Scaravaggi,[§] Mario Mariani,[§] Andrea Mele,[¶] Walter Panzeri,[¶] Nathalie Boubals,[†] Laurence Berthon,[†] Marie-Christine Charbonnel,[†] Francesco Sansone,[‡] Arturo Arduini,[‡] Alessandro Casnati.^{*,‡}

[§] Nuclear Engineering Division, Department of Energy, Politecnico di Milano, P.zza L. da Vinci 32, I-20133 Milano, Italy

[¶] Department of Chemistry, Materials and Chemical Engineering “G. Natta”, Politecnico di Milano, Piazza L. da Vinci, 32, I-20133 Milano (Italy) and CNR-ICRM, Via L. Mancinelli, 7, I-20131 Milano, Italy

[†] Nuclear Energy Division, RadioChemistry & Processes Department, CEA, 30207 Bagnols-sur-Cèze, France

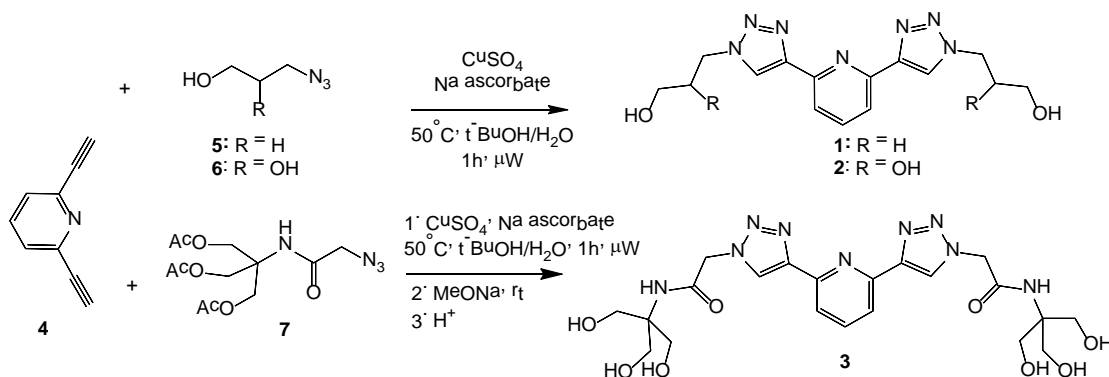
[‡] Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/a, 43124 Parma, Italy

Supporting Information

ABSTRACT: There is still an evident need for selective and stable ligands able to separate Actinide(III) from Lanthanide(III) metal ions in view of the treatment of the accumulated radioactive waste and of the recycling of Minor Actinides. We have herein demonstrated that hydrophilic 2,6-bis-triazolyl-pyridines are able to strip all Actinides in all the different oxidation states from a diglycolamide-containing kerosene solution into an acidic aqueous phase. The ascertained high Actinide selectivity, efficiency, extraction kinetics and chemical/radiolytic stability spotlight this hydrophilic class of ligands as exceptional candidates for advanced separation processes fundamental for closing the nuclear fuel cycle and solving the environmental issues related to the management of existing nuclear waste.

The search for efficient and robust ligands for the selective complexation and extraction of Actinide (An) cations in the presence of large amounts of Lanthanide (Ln) metal ions and other fission products is a topic of high priority not only for a sustainable development and public acceptance of nuclear energy, but also for the treatment of the existing radioactive wastes.¹ Whatever decision the governments will take on the future of nuclear energy, we have the duty versus future generations to ensure a proper and safer management of all the radioactive wastes produced in the latest 75 years for energy and weapon production.² The option of a closed nuclear fuel cycle,³ that is recycling of the reusable components of nuclear waste as new fuel, would allow a significant reduction of the waste volume and a more convenient exploitation of natural resources.⁴ Moreover, it would also reduce the long-term radiotoxicity and decay heat of the final nuclear wastes. In the last decades great efforts have been devoted to this challenging issue and the Partitioning and Transmutation strategy is being considered worldwide a conceivable way to achieve this goal.^{1a,5} Within this approach, several multi-cycle advanced separation processes have been proposed that are mainly based on the combined co-extraction of An and Ln from the PUREX (Plutonium URanium EXtraction

process) raffinate,⁶ followed by the subsequent An/Ln separation, necessary to successfully implement the An transmutation. The European strategy,⁷ initially proposed few decades ago, aims at co-extracting An(III) and Ln(III) in an organic phase with the DIAMEX (DIAMide EXtraction) and DIAMEX-like processes by using malonamides or the highly efficient N,N,N',N'-tetraoctyl diglycolamide (TODGA, *see* Figure S9).⁸ Furthermore, several processes were proposed for the selective An separation from Ln, such as the SANEX (Selective ActiNide EXtraction) process.⁹ Enormous progresses were made in the latest years in the design of selective An ligands. Several soft heterocyclic N-donor ligands showed important An/Ln selectivities.¹⁰ However, due to the basicity of nitrogen atoms involved in cation coordination, only few of them are able to operate under highly acidic conditions. Among these ligands, BTPs (bis-triazinyl pyridine) and BTBPs (bis-triazinyl bipyridine) are characterized by a remarkably interesting selectivity,¹¹ but also by low chemical stability under the typical harsh conditions and, sometimes, by slow kinetics. Recently, it was proposed to combine the unselective An-Ln extraction by TODGA with the selective back-extraction (stripping) into an aqueous layer of the trivalent An cations through the so-called *i*-SANEX (*innovative* SANEX) process or, even better, of all the Actinides in all their possible oxidation states via the GANEX (Group ActiNides EXtraction) process.¹² However, despite of the different ligands proposed for stripping purposes,^{10,12,13} none of them gather all the required characteristics to implement an industrial process, that are i) water solubility, ii) ability to complex hard metal ions such as An iii) An/Ln selectivity, iv) hydrolytic and radiolytic stability, v) high loading capacity, vi) fast kinetics of (de)complexation, vii) complete incinerability (contain only C, H, O, N atoms). We herein propose the use of the pyridine-2,6-bis(1H-1,2,3-triazol-4-yl) (PyTri, Scheme 1) as a proper N₃ chelating moiety for the An/Ln separation which comprises all the requested characteristics. Although this “clickable” binding motif has been intensively studied in the latest fifteen years as terdentate ligating units both in supramolecular and coordination chemistry,^{14a} to the best of our knowledge, there are no example in the literature

Scheme 1. The synthesis of ligands 1-3 used in the present study.

Only very few reports deal with Lanthanide-PyTri complexes in the solid state or in aprotic solvents also as potential bioimaging agents.^{14b} The recent publication by Kiefer et al. on a lipophilic 2,6-bis[1-(*p*-tolyl)-1H-1,2,3-triazol-4-yl]pyridine showing an interesting selectivity in binding Cm(III) over Eu(III) in CH₃CN but unable to extract Am and Eu into an organic phase, prompted us to disclose our results on the class of hydrophilic PyTri ligands.^{14c} We synthesised a series of ligands **1-3** (Scheme 1) based on the PyTri chelating motif and characterized by the presence, at their periphery, of an increasing number of OH groups to ensure solubility in aqueous solutions. Ligand **1**^{14b} and **2** were straightforward prepared by clicking 2,6-diethynyl-pyridine (**4**) with the azides **5** and **6**, respectively, under classical CuAAC conditions. Ligand **3** was, on the other hand, obtained after a similar cycloaddition reaction but starting from the tris-acetylated azide **7**,¹⁵ followed by Zemplen deprotection by MeONa in MeOH and acidification. Ligands **1-3**, characterized by NMR and ESI-MS techniques, are soluble up to 0.15-0.20 M in water and diluted nitric acid solutions (*see SI* for details). Moreover, UV-*vis* measurements showed that the loss of ligands **1-3** from the acidic layer to the organic phase (kerosene/1-octanol 95/5 v/v, both in the absence and in the presence of 0.2 M TODGA) was negligible within the experimental error. The potentiality of this class of ligands in the selective An extraction was obtained by performing liquid-liquid extraction tests and measuring the D_M values of Eu(III), Am(III), Cm(III) and Pu(IV). Two different organic

phases were obtained by contacting a 0.2 M TODGA solution in kerosene/1-octanol 95/5 v/v with an equal volume of 3 M nitric acid feeds similar in composition to the raffinate coming from the PUREX process. Two synthetic aqueous feeds were considered containing only trivalent An (*i*-SANEX feed) or tri- and tetravalent An (GANEX feed), in addition to inactive Y and Ln (from La to Gd) (*see Tables S1*). The TODGA-based solutions were able to co-extract 99.9% of An and Ln present in the aqueous phases as determined by ICP-MS, α and γ spectrometry. Subsequently, these TODGA-based loaded organic solutions were contacted with the acidic stripping phases containing ligands **1-3**. HNO₃ concentration was monitored after each step (*see SI*). As shown in Table 1, the results of a blank experiment (0.25 M HNO₃ stripping solution with no hydrophilic ligand) indicate that, apart from the lighter La ion, only a small percentage of the other cations is back extracted in the acidic aqueous phase. Less than 1% of Eu and 6% of Am are released under these conditions, in agreement with the already known poor Ln/An selectivity of TODGA.^{8b} The introduction of the hydrophilic PyTri-ligands in the aqueous layer considerably increases the Am extraction in water by competing with TODGA. This results in a decrease of the D_{Am} values by nearly two orders of magnitude, while those of Eu are decreased to a much lower extent. In the case of **1**, for instance, the Am concentration in the organic phase is reduced from 94% to 14%, while the Eu concentration only from 99% to 96%.

Table 1. D_M and SF values for the stripping of Am³⁺ from a TODGA-based organic phase into a PyTri-based aqueous solution.

Stripping phase ^a	Blank		0.1 M Ligand 1		0.15 M Ligand 2		0.15 M Ligand 3	
	[HNO ₃] = 0.25 M		[HNO ₃] = 0.25 M		[HNO ₃] = 0.25 M		[HNO ₃] = 0.25 M	
Element	D_M^b	% in org	D_M^b	% in org	D_M^b	% in org	D_M^b	% in org
²⁴¹ Am	16.3	94.2	0.17	14.5	0.27	21.2	0.77	37.7
¹⁵² Eu	113	99.1	24.5	96.1	27.0	96.4	44	97.8
La	1.29	56.3	1.34	57.3	1.06	51.5	1.12	52.8
SF _{Eu/Am} ^c	6.93		144.35		99.96		57.14	
SF _{La/Am} ^c	0.08		7.88		3.92		1.45	

^aOrganic phase in the stripping tests: 0.2 M TODGA in kerosene/1-octanol (95/5 v/v) loaded with *i*-SANEX feed. ^b D_M is defined as the ratio between the concentration/activity of the metal (M) in organic phase over that in aqueous phase. ^cSF_{Ln/An} is defined as the ratio between D_{Ln} and D_{An} .

All the ligands **1-3** show an impressive selectivity for Am, since the Eu over Am separation factors ($SF_{Eu/Am}$) increase from 7, the typical value for TODGA observed in the blank tests, to 144 for ligand **1**, 100 for **2** and 57 for **3** (Table 1). This indicates that a clear separation between Eu, bound to TODGA in the organic phase, and Am, better coordinated to PyTri-ligands in the aqueous layer than to TODGA in the organic phase, is taking place. The observed Am/La selectivity is consistently lower than that the Am/Eu selectivity and results from a known inability of TODGA to tightly bind lighter Ln ions rather than from an intrinsic affinity of PyTri-ligands for La(III) ion. The D_{La} values, in fact, remain practically constant in the absence or presence of the hydrophilic ligands. However, the Am/La selectivity displayed is certainly high enough to implement an effective separation process. The same ligands were also tested in the stripping conditions simulating the GANEX process (Figure 1 and Table S2). The data nicely point out the ability of these ligands to co-extract An in different oxidation states, even if with different extraction efficiencies. Remarkably, these preliminary tests outlined that ligands **1** and **2** have a quite similar behavior with $D_{Am(III)}$, $D_{Cm(III)}$ and $D_{Pu(IV)}$ close to 0.1, while D_{Eu} is around 14. Both the ligands showed a $SF_{Eu/Am}$ around 240 and a percentage of Am recovery close to 95% in one step. Ligand **2** seems to be slightly more selective for Pu ($SF_{Eu/Pu} = 280$) compared to ligand **1** ($SF_{Eu/Pu} = 180$). Despite of its higher water solubility, ligand **3** always shows lower selectivity for An both in *i*-SANEX and GANEX conditions, indicating that the presence of the hard amide carbonyl groups might interfere with the separation process (Table S3). For this reason, further studies were limited to ligands **1** and **2**.

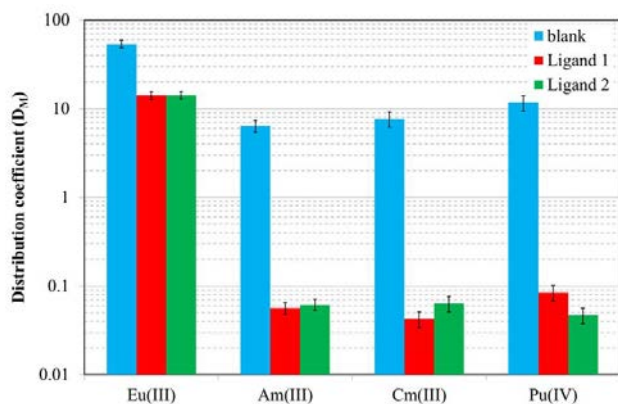


Figure 1. D_M values for the stripping of Am^{3+} , Cm^{3+} and Pu^{4+} from a TODGA-based organic phase into a PyTri-based aqueous solution, in comparison with the blank experiment.

An important aspect to be considered in nuclear reprocessing involving high radiation fields is the kinetic issue. The cation complexation equilibria should take place with fast kinetics in order to ensure that extraction reaches the equilibrium within the very short residence time of the phases in the centrifugal contactors, devices typically used in industrial applications. For this aim, the organic phases loaded with an *i*-SANEX feed and the PyTri-based stripping phases were shaken with a benchtop shaker for different time periods ranging from 5 to 60 minutes. The D_M values of both ligands **1** and **2** reach their maximum within 5 minutes indicating that the equilibrium is achieved very fast and there are no kinetics limitations (*see SI*). A further demanding requirement to be satisfied for a successful ligand is its chemical stability under the harsh process conditions. Ligands in fact

should be hydrolytically stable at the low pH conditions and at the high temperatures arising, as well as radiolytically resistant under the intense radiation fields, mainly due to the α -emitters present in the radioactive solutions to be decontaminated. Aggressive hydroxyl radicals are formed under these conditions so that a strong and radical resistant organic structure is required. Although the annual doses to which extractants are exposed may change consistently depending on fuel type and burn-up, a value of 100 kGy is often considered as a realistic average annual absorbed dose.¹⁶ For these reasons stripping experiments were carried out with **1** and **2** solutions irradiated up to 200 kGy with a ^{60}Co source (2.5 kGy/h) and fresh TODGA-based organic phases loaded from *i*-SANEX feed (for details *see SI*).

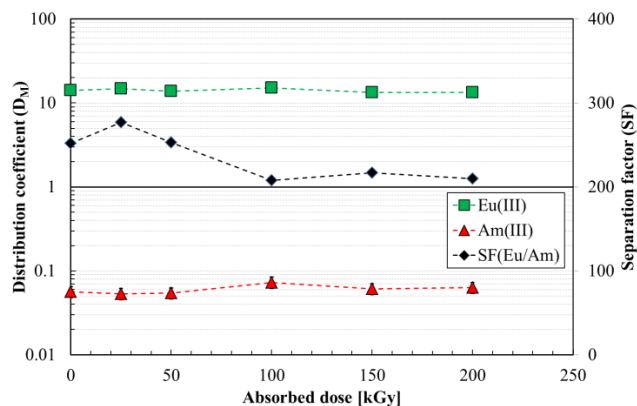


Figure 2. Distribution coefficients for ligand **1** stripping solutions as a function of the absorbed dose. Organic phase: 0.2 M TODGA in kerosene/1-octanol (95/5 v/v) loaded with *i*-SANEX feed; Aqueous phase: irradiated 0.08 M of ligand **1**, $[HNO_3] = 0.44$ M (2.5 kGy/h).

For ligand **1** the distribution coefficients (Figure 2) and the $SF_{Eu/Am}$ values remain almost constant in the whole absorbed dose range considered, consistently with a high radiolytic stability of this ligand. A slight decrease of D_M values was observed for both Am and Eu in the case of ligand **2** for absorbed doses higher than 100 kGy (Figure S10). The radiolytic stability of **1** solutions was further studied by means of several analytical techniques. HPLC-DAD analyses showed that the ligand concentration decreases by 4% and 9% in samples irradiated at 100 kGy (2.5 and 0.14 kGy/h) and at 200 kGy (2.5 kGy/h) respectively, as also confirmed by direct UV-*vis* measurements at $\lambda = 300$ nm. Possible structures of the main radiolytic by-products observed in the HPLC chromatograms (*see SI*) were proposed on the basis of ESI-MS and tandem MS analyses. The proposed degradation paths entail with the oxidation of the alkyl lateral chains by reaction with radical species (presumably OH radicals) coming from diluent radiolysis, while the chelating PyTri structure seems to be unaffected, in complete agreement with the retention of the extracting capability after irradiation. In view of using such stripping solutions in multi-cycle processes, a viable recycling step was devised. ^{241}Am and ^{152}Eu spiked batch experiments showed that the cations complexed by PyTri-ligands could be removed by re-extraction with a fresh TODGA-based solution in the amount of 97% for Am and 100% for Eu in a single stage (*see SI*). In order to shed a light on the reason of the observed selectivity, the stoichiometry and stability of the Metal:Ligand complexes were studied. Higher stoichiometry was observed for Am:1 complexes than for Eu:1 complexes, as shown by liquid-liquid extraction tests at different ligand concentrations (*see*

Figure S12) as well as by ESI-MS experiments in homogeneous solutions (see SI-Section 2.7). Stability constants for the formation of Am(III), Pu(IV) and Eu(III) complexes with ligands **1** and **2** were determined by UV-vis titrations. The spectra were fitted with the 1:1 (and 1:2) complexes giving the apparent $\log\beta'_{1:1}$ (and $\log\beta'_{1:2}$) values (Table 2). For ligand **1** the stability constant for Pu(IV) is two orders of magnitude higher than that of Eu(III). The higher affinity of ligands **1** and **2** for Am compared to Eu also results in the formation of 1:2 complexes as also supported by ESI-MS data and stripping tests with high Cl/CM ratios (Figure S12). Interestingly, the preference of ligands **1** and **2** for An over Ln is consistent with the selectivity for An found in extraction tests.

Table 2. Apparent stability constants ($\log\beta'$ _{Metal:Ligand}) for Am(III), Pu(IV) and Eu(III) complexes with ligand **1 and **2** obtained by UV-vis titration in methanol/water (75/25 v/v) at 25 °C.**

Metal ion	Ligand	$\log\beta'_{1:1}$	$\log\beta'_{1:2}$	Counterion
Am(III) ^a	1	3.2 ± 0.3	6.2 ± 0.3	Cl ⁻
Am(III) ^b	1	3.5 ± 0.3	6.8 ± 0.3	NO ₃ ⁻
Am(III) ^a	2	3.1 ± 0.3	5.5 ± 0.3	Cl ⁻
Pu(IV) ^c	1	4.3 ± 0.3	-	NO ₃ ⁻
Eu(III)	1	2.4 ± 0.1	-	Cl ⁻
Eu(III)	2	3.0 ± 0.1	-	Cl ⁻

^a pH = 4; ^b in 0.44M HNO₃; the Am $\log\beta'$ values take into account the ligand protonation ($pK_a = 2.1$); ^c with addition of HNO₃ ($\approx 0.6M$ to avoid the hydrolysis of Pu); the Pu $\log\beta'_{1:1}$ values take into account the ligand protonation ($pK_a = 2.1$).

In summary, we have demonstrated the possibility to successfully use hydrophilic PyTri-ligands for the selective stripping of Actinide ions having different oxidation states into a water solution. The competitive TODGA-PyTri system used, takes advantage not only of a lower affinity of TODGA for Actinides but also of a higher affinity of the clicked triazole derivatives for Am(III) and Pu(IV), as demonstrated by the stability constants in homogeneous methanol/water solutions. We believe that this extracting system, when applied to the treatment of radioactive waste, will lead to paramount breakthrough in the development of advanced separation processes towards the closure of the nuclear fuel cycle.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ... <http://pubs.acs.org>. Synthetic procedures and spectroscopic data, experimental details of the extraction experiments, complexation studies, radiolytic stability tests and stripping phase recycling (PDF).

AUTHOR INFORMATION

Corresponding Authors

* elena.macerata@polimi.it

* casnati@unipr.it

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by EU-FP7 ACSEPT (Grant n. 211267) and SACSESS (Grant n. 323282) projects. We thank the Centro Interdipartimentale Misura “G. Casnati” of Parma University for the NMR and MS facilities. We also thank ACTINET and TALISMAN projects for funding Stefano Scaravaggi (five months) and Eros Mossini (three months) for abroad research periods in CEA Marcoule.

REFERENCES

- (1) (a) Magill, J.; Berthou, V.; Haas, D.; Galy, J.; Schenkel, R.; Wiese, H. W.; Heusener, G.; Tommasi, J.; Youinou, G. *Nucl. Energ. - J. Br. Nucl.* **2003**, *42*, 263-277. (b) Baisden, P. A.; Choppin, G. R. Nuclear waste management and the nuclear fuel cycle, Encyclopedia of Life Support Systems (EOLSS); EOLSS Publishers: Oxford, U.K., 2007. In Radiochemistry and Nuclear Chemistry, Nagyl, S., Ed.; EOLSS, [http://www.eolss.net]: Oxford, 2007. (c) Reprocessing and recycling of spent nuclear fuel; Woodhead Publishing: Oxford, 2015.
- (2) Brook, B. W.; Alonso, A.; Meneley, D. A.; Misak, J.; Bles, T.; van Erp, J. B. *Sust. Mat. Techn.* **2014**, *1-2*, 8-16.
- (3) Lake, J. A.; Bennett, R. G.; Kotek, J. F. *Sci. Am.* **2002**, *286*, 72-81.
- (4) Salvatores, M.; Palmiotti, G. *Progr. Part. Nucl. Phys.* **2011**, *66*, 144-166.
- (5) (a) Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. in The Chemistry of the Actinide and Transactinide Elements; Morss, L. R.; Edelstein, N. M.; Fuger, J., Springer: Dordrecht, The Netherlands, 2006; Vol. 4, Chapter 24, pp 2622-2798. (b) Nash, K. L.; Lumetta, G. J.; Clark, S. B.; Friese, J. I., Significance of the Nuclear Fuel Cycle in the 21st Century in Separations for the Nuclear Fuel Cycle in the 21st Century, ACS Symposium Series, vol. 933; Lumetta, G. J.; Nash, K.L.; Clark, S. B.; Friese, J. I.; ACS, Washington, DC (USA), 2006, cap.1, p. 3-20.
- (6) Science and technology of tributyl phosphate; CRC Press Inc.: Boca Raton (FL), USA, 1990; Vol. III.
- (7) (a) Bourg, S.; Hill, C.; Caravaca, C.; Rhodes, C.; Ekberg, C.; Taylor, R.; Geist, A.; Modolo, G.; Cassayre, L.; Malmbeck, R.; Harrison, M.; De Angelis, G.; Espartero, A.; Bouvet, S.; Ouvrier, N. *Nucl. Eng. Des.* **2011**, *241*, 3427-3435. (b) Modolo, G.; Geist, A.; Miguiditchian, M. 10 - Minor actinide separations in the reprocessing of spent nuclear fuels: recent advances in Europe A2 - Taylor, Robin. In Ref. 1c; pp 245-287.
- (8) (a) Modolo, G.; Vijgen, H.; Serrano-Purroy, D.; Christiansen, B.; Malmbeck, R.; Sorel, C.; Baron, P. *Sep. Sci. Technol.* **2007**, *42*, 439-452. (b) Ansari, S. A.; Pathak, P.; Mohapatra, P. K.; Manchanda, V. K. *Chem. Rev.* **2012**, *112*, 1751-1772. (c) Galan, H.; Zarzana, C.A.; Wilden, A.; Nunez, A.; Schmidt, H.; Egberink, R.J.M.; Leoncini, A.; Cobos, J.; Verboom, W.; Modolo, G.; Groenewold, G.S.; Mincher, B.J. *Dalton Trans.*, **2015**, *44*, 18049-18056.
- (9) Madic, C.; Hudson, M. J.; Liljenzin, J. O.; Glatz, J. P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. *Prog. Nucl. Energ.* **2002**, *40*, 523-526.
- (10) Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. *Inorg. Chem.* **2013**, *52*, 3414-3428.
- (11) Panak, P. J.; Geist, A. *Chem. Rev.* **2013**, *113*, 1199-1236.
- (12) Geist, A.; Mullich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T. *Solvent Extr. Ion Exch.* **2012**, *30*, 433-444.
- (13) Kolarik, Z. *Chem. Rev.* **2008**, *108*, 4208-4252.
- (14) (a) Byrne, J. P.; Kitchen, J. A.; Gunlaugsson, T. *Chem. Soc. Rev.* **2014**, *43*, 5302-5325. (b) Li, Y.; Huffman, J. C.; Flood, A. H. *Chem. Commun.* **2007**, 2692-2694. (c) Kiefer, C.; Wagner, A.; Beele, B. B.; Geist, A.; Panak, P. J.; Roesky, P. W. *Inorg. Chem.* **2015**, *54*, 7301-7308.
- (15) Scaravaggi, S.; Macerata, E.; Galletta, M.; Mossini, E.; Casnati, A.; Anselmi, M.; Sansone, F.; Mariani, M. *J. Radioanal. Nucl. Chem.* **2015**, *303*, 1811-1820.
- (16) (a) Fermvik, A.; Berthon, L.; Ekberg, C.; Englund, S.; Retegan, T.; Zorz, N. *Dalton Trans.* **2009**, 6421-6430. (b) Magnusson, D.; Christiansen, B.; Malmbeck, R.; Glatz, J. *Radiochim. Acta* **2009**, *97*, 497-502. (c) Mincher, B. J.; Modolo, G.; Mezyk, S. P. *Solvent Extr. Ion Exch.* **2009**, *27*, 1-25. (d) Fermvik, A. *J. Radioanal. Nucl. Chem.* **2011**, *289*, 811-817.

