Check for updates

New synthetic pathway towards BTrzPhen-tetraol: a hydrophilic 2,9-bis-triazolyl-1,10-phenanthroline ligand for selective americium stripping†

P. Troosters, [a,b] T. Opsomer, *[b,c] K. Van Hecke, [a] K. Verguts, [a,c]
F. Reniers, [b] K. Van Hoecke, [a] P. Zsabka, [a,d] T. Cardinaels [a,b] and
W. Dehaen [b]

Selectively separating Am(III) from nuclear waste streams is an extremely challenging task due to the presence of the trivalent lanthanides and Cm(III). 1,10-Phenanthroline ligands decorated with 1,2,4-triazines or 1,2,3-triazoles have emerged as promising extractants for achieving such separation. In this article, a new robust synthetic pathway towards the hydrophilic, CHON compliant bistriazoylphenanthroline ligand BTrzPhen-tetraol is reported. BTrzPhen-tetraol was synthesised both as the hydrochloride and as the free base with overall yields of 66% and 48%, respectively. The ligand demonstrated excellent solubility and stability in dilute nitric acid solutions, with no observable decomposition after three days in 0.5 mol L^{-1} HNO$_3$ at 50 °C. Additionally, it exhibited rapid stripping kinetics for Am(III) and Eu(III). Liquid–liquid extraction experiments conducted with BTrzPhen-tetraol, TODGA, and radiotracers of Am(III), Cm(III), and Eu(III) yielded maximum Eu(III)/Am(III) and Cm(III)/Am(III) separation factors of 84 and 2.4, respectively, at 0.26 mol L^{-1} HNO$_3$. Notably, the separation factors achieved with BTrzPhen-tetraol are comparable to those of existing systems. While only a minor influence of the BTrzPhen concentration on the distribution ratios of Am and Cm was observed under the given conditions, these results highlight the effectiveness of hydrophilic BTrzPhen ligands for selective americium stripping and encourage further optimisation to enhance performance.

Introduction

Proper management of spent nuclear fuel (SNF) is of high importance to reduce its environmental impact.[1] Developing a closed nuclear fuel cycle where the processed SNF can be reused as new fuel can significantly reduce the long-term heat load of the final nuclear waste, which is the limiting factor for the footprint and size of the final geological repositories.[2] The long-term heat load and radiotoxicity of the SNF is dominated by the transuranium (TRU) elements Np, Pu, Am and Cm.[3] Plutonium, and by applying some process modifications also neptunium, can be removed by the well-known Plutonium

Uranium Reduction EXtraction (PUREX) process.[4] Partitioning can be applied to further separate the TRU elements from the PUREX highly active raffinate (HAR). Several partitioning processes have been developed in the past decades under Euratom Framework Programmes, the most recent ones being GENIORS and PATRICIA. One of the well-known former partitioning processes is the DIAMide EXtraction (DIAMEX) process where *N,N′*-dimethyl-*N,N′*-dioctylhexyl-ethoxymalonamide (DMDOHEMA) is used as the extracting agent to separate the minor actinides (MA) and lanthanides (Ln) from other fission and activation products (FP and AP) which will remain in the HAR.[5] Some of the lanthanides are strong neutron absorbers and, moreover, are present in much higher quantities than the MA, which prevent efficient burning of the MA in Gen IV reactors.[6] The Cm isotopes are inducing issues in fuel handling and fabrication due to their high neutron dose.[7,8] Since the half-life of the most abundant ^{244}Cm isotope is relatively short (18 years), it is acceptable to dispose of Cm(III) together with the fission products.[9] Therefore, the selective separation of Am(III) is of high interest to avoid problems related to Cm and the lanthanides. However, a difficulty lies in the similar chemical behaviour of

a Nuclear Energy Technology (NET), Belgian Nuclear Research Centre (SCK CEN), B-2400 Mol, Belgium
b Department of Chemistry, KU Leuven, B-3001 Leuven, Belgium
c Nuclear Medical Applications (NMA), Belgian Nuclear Research Centre (SCK CEN), B-2400 Mol, Belgium. E-mail: tomas.opsomer@sckcen.be
d Studsvik Nuclear AB, 61060 Nyköping, Sweden

†Electronic supplementary information (ESI) available: Experimental details for the synthesis of compounds **8–10**, NMR spectra, and data from the extraction experiments. See DOI: https://doi.org/10.1039/d4dt03399j

trivalent lanthanides and actinides. Moreover, separation of Am(III) and Cm(III) is even more challenging because of both their similar effective nuclear charge and ionic radius.[10–12]

Ligands consisting of soft aromatic nitrogen donors have been studied extensively to separate MA from the lanthanides.[13–15] Soft donors enhance the covalent character of the ligand-actinide bond compared to the ligand-lanthanide bond, and can also induce selectivity for Am(III) over Cm(III).[16,17] CyMe$_4$-BTP, CyMe$_4$-BTBP and CyMe$_4$-BTPhen (Fig. S1, ESI†) are three lipophilic ligands which have shown good actinide/lanthanide separation factors when used in a regular Selective ActiNide EXtraction (SANEX) process.[18–20] The SANEX process is preceded by a DIAMEX-type extraction with DMDOHEMA or the diglycolamide TODGA (Fig. S1, ESI†) which can be used as an alternative to co-separate the MA and lanthanides from the FP.[21,22] After their extraction into the organic phase, the MA and lanthanides must be stripped into an aqueous phase, which is, after adjustment of the acidity, send to a second extraction cycle using one of the bistriazinyl based lipophilic ligands mentioned above, to selectively separate the MA from the lanthanides (= SANEX). This additional extraction cycle results in a larger solvent consumption and a larger footprint of the separation plant.[5] Therefore, the innovative SANEX (i-SANEX) process has gained substantial interest. In the i-SANEX process, all trivalent actinides are directly and selectively stripped from a loaded organic phase to an aqueous phase containing a hydrophilic extractant.[21] An example of such an extractant is SO$_3$-Ph-BTP (Fig. S1, ESI†). SO$_3$-Ph-BTP shows efficient Eu(III)/Am(III) separation with a Eu(III)/Am(III) separation factor up to 1000.[23] Later, the i-SANEX process was adapted to the Americium Selective Extraction (AmSel) process.[6,22,24,25] Unfortunately, SO$_3$-Ph-BTP did not show selectivity for Am(III) over Cm(III).[23] Therefore, the hydrophilic sulfonated counter parts of CyMe$_4$-BTBP and CyMe$_4$-BTPhen were investigated. Eu(III)/Am(III) separation factors of 150–250 and 250–1000 have been obtained for SO$_3$-Ph-BTBP and SO$_3$-Ph-BTPhen (Fig. S1, ESI†), respectively.[6] Moreover, for both ligands Cm(III)/Am(III) separation factors of *ca.* 2.5 have been obtained.[23] Despite the promising extraction results of SO$_3$-Ph-BTP, SO$_3$-Ph-BTBP and SO$_3$-Ph-BTPhen in the i-SANEX and AmSel process, these ligands are not CHON compliant. The sulfur atoms are undesired because of the generation of corrosive residues after incineration.[13,22] Additionally, sulfur might also end up in the Am bearing fuel, where it can affect the properties of the fuel. Therefore, the focus of research in this field nowadays lies on the development of ligands that only consist of the elements C, H, O and N.

A CHON compliant 1,10-phenanthroline-based ligand was first reported by Edwards *et al.* in 2017.[26] BTrzPhen-tetraol (Fig. S1, ESI†) has two 1,2,3-triazoles instead of 1,2,4-triazines and is functionalised with two dihydroxypropane moieties to improve water solubility. A clear selectivity for Am(III) over Eu(III) was observed from a loaded TODGA containing organic phase, and a separation factor for Eu(III)/Am(III) of 47 was obtained at a HNO$_3$ concentration of 0.33 mol L^{-1}.[26] Additionally, an Cm(III)/Am(III) separation factor of 2.5 was

obtained which is similar to the sulfonated BTBP and BTPhen analogues.[23] BTrzPhen-tetraol was synthesised *via* the well-known copper(I)-catalysed azide–alkyne cycloaddition (CuAAC) reaction in an overall yield of 32%. To prevent copper from binding with the phenanthroline ligand, the copper-coordinating tris((1-benzyl-4-triazolyl)methyl)amine (TBTA) needs to be added.[27] Moreover, the intermediate compounds were purified by column chromatography, making this synthetic strategy unfavourable for an industrial process from both an economical and ecological perspective.[26] Recently, two other bistriazolylphenanthroline ligands were also synthesised using the CuAAC reaction.[28] This article introduces a metal- and chromatography-free synthesis of BTrzPhen-tetraol. To further evaluate the potential of this hydrophilic extractant, we investigated its solubility, stability, and the stripping kinetics and selectivity for americium in solvent extraction experiments.

Experimental

Materials and methods used for ligand synthesis

All the (dry) solvents used for synthesis and purification were ordered from Thermo Fisher Scientific. All the reagents used for synthesis were ordered from Fluorochem, Sigma-Aldrich, ACROS Organics, J&K Scientific, Fisher Scientific or BDH Chemicals and used without further purification. The stationary phase for column chromatography was 70–230 mesh silica 60 (Merck). The nuclear magnetic resonance (NMR) spectra were recorded on a BrukerAvance III HD 400 or a Bruker Avance II + 600. ^{13}C-detected NMR experiments were ^{1}H-decoupled using power-gated decoupling. The chemical shifts (δ, ppm) were determined relative to the internal solvent signal. Coupling constants (J) are reported in Hertz (Hz) and were directly obtained from the spectra. The following abbreviations were used: s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet) and br (broadened) to indicate the multiplicity of the peaks. The high-resolution mass spectra (HRMS) were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at 3 µL min^{-1} and the spectrum was obtained in positive ionisation mode with a resolution of 15 000 (FWHM) using leucine enkephalin as lock mass. Melting points were determined on a Reichert-Jung Thermovar system and are uncorrected. Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer. Attenuated Total Reflectance (ATR) was used for direct examination of the products, utilizing the Bruker ATR 282 platinum setup. OPUS software was used to analyze the recorded spectra. All samples were applied neat.

Synthetic procedures

(1E,1′E)-2,2′-(1,10-Phenanthroline-2,9-diyl)bis(N,N-dimethylethen-1-amine) (2). To a flame-dried Ar-flushed Ace pressure tube equipped with a magnetic stirring bar, neocuproine **1** (1.56 g, 7.50 mmol) and Bredereck's reagent (7.75 mL, 5 equiv.) were added quickly and the tube was sealed with a

PTFE front-seal plug with a silicone O-ring. The mixture was stirred for 4 h at 160 °C. After cooling down to room temperature, the mixture was transferred to a round-bottom flask using diethyl ether and evaporated *in vacuo*. A minimal amount of DCM was then used to rinse the solids from the wall of the flask. Next, diethyl ether (15 mL) was added to obtain a fine yellow suspension, and the mixture was cooled in an ice bath while stirring. Pentane (30 mL) was added slowly. The fine precipitate was allowed to settle, and the supernatant was decanted. The residue was washed with a diethyl ether-pentane mixture (45 mL, 1 : 2) and finally with pure pentane (40 mL). Evaporation of the residual solvents at the rotary evaporator gave pure bisenamine **2** as a yellow-orange powder in a yield of 79% (1.88 g).

MP: 189–192 °C. **HRMS** (ESI-Q-TOF): m/z [M + H]$^+$ calcd for $C_{20}H_{22}N_4$: 319.1917; found: 319.1912.

^{1}**H NMR** (400 MHz, chloroform-*d*) δ 7.87 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 13.4 Hz, 2H), 7.41 (s, 2H), 7.28 (d, J = 8.5 Hz, 2H), 5.57 (d, J = 13.4 Hz, 2H), 2.98 (s, 12H). ^{13}C **NMR** (101 MHz, chloroform-*d*) δ 158.4, 145.5, 145.2, 135.7, 125.8, 123.3, 119.3, 98.5, 40.8.

4-(Azidomethyl)-2,2-dimethyl-1,3-dioxolane (3). To a round-bottom flask were added (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzene-sulfonate **7** (7.80 g, 27.24 mmol), sodium azide (8.86 g, 136.20 mmol) and 30 mL of DMF. The reaction mixture was stirred overnight at 100 °C. After the reaction was cooled down to room temperature, the mixture was diluted with EtOAc (1×) and washed with H$_2$O (3×). The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated *in vacuo* at 35 °C to obtain the product as a yellow oil in 82% yield (3.53 g). The product **4** was stored in the dark. Characterisation data were in accordance with the data reported in the literature.[29]

^{1}**H NMR** (400 MHz, chloroform-*d*) δ 4.29–4.23 (m, 1H), 4.07–4.03 (m, 1H), 3.78–3.75 (m, 1H), 3.41–3.37 (m, 1H), 3.31–3.27 (m, 1H), 1.46 (s, 3H), 1.36 (s, 3H). ^{13}C **NMR** (101 MHz, chloroform-*d*) δ 110.1, 74.7, 66.7, 52.9, 26.7, 25.3. **FTIR** (cm^{-1}): 2100, 1373, 1269, 1213, 1155, 1075, 1052, 908, 836, 728, 649 and 514.

2,9-Bis(1-((2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1H-1,2,3-triazol-4-yl)-1,10- phenanthroline (4). To a flame-dried, Ar-flushed reaction tube, 4-(azidomethyl)-2,2-dimethyl-1,3-dioxolane **3** (1.97 g, 12.56 mmol), 1,10-phenanthroline-2,9-bisenamine **2** (1.00 g, 3.14 mmol) and 6 mL of dry 1,4-dioxane were added quickly. The mixture was stirred for 20 h at 120 °C. After finishing of the reaction, the mixture was allowed to cool down to room temperature resulting in the formation of an orange precipitate. Next, 20 mL of water was added resulting in the complete precipitation of the product. The solid was then filtered and 4 times 20 mL of a 30% isopropanol in water solution was used to rinse the reaction tube and to wash the residue. The product **4** was obtained as an orange solid in a yield of 87% (1.48 g).

MP: 133–135 °C. **HRMS** (ESI-Q-TOF): m/z [M + H]$^+$ calcd for $C_{28}H_{30}N_8O_4$: 543.2468; found: 543.2460.

^{1}**H NMR** (400 MHz, chloroform-*d*) δ 9.39 (s, 2H), 8.59 (d, J = 8.3 Hz, 2H), 8.41 (d, J = 8.4 Hz, 2H), 7.89 (s, 2H), 3.95–3.65 (m,

8H), 3.51 (br s, 2H), 1.17 (s, 12H). ^{13}C **NMR** (101 MHz, chloroform-*d*) δ 150.9, 148.5, 145.5, 137.5, 128.8, 126.6, 125.3, 120.7, 110.1, 73.8, 67.2, 52.3, 26.8, 25.2.

3,3′-((1,10-Phenanthroline-2,9-diyl)bis(1H-1,2,3-triazole-4,1-diyl)) bis(propane-1,2-diol) hydrochloride (BTrzPhen-tetraol 5). In a reaction tube, 0.60 g (1.11 mmol) of 2,9-bis(1-((2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline **4** was dissolved in 11 mL of 1,4-dioxane. Next, 15 mL of a 1 mol L^{-1} HCl solution was added and the reaction mixture was stirred at 50 °C overnight. Afterwards, the mixture was concentrated *in vacuo* to obtain the product as a dark brown solid in quantitative yield (0.51 g).

MP: 238–241 °C. **HRMS** (ESI-Q-TOF): m/z [M + H]$^+$ calcd for $C_{22}H_{22}N_8O_4$: 463.1842; found: 463.1840.

^{1}**H NMR** (400 MHz, DMSO-*d*$_6$) δ 9.11 (s, 2H), 8.73 (d, J = 8.5 Hz, 2H), 8.53 (d, J = 8.4 Hz, 2H), 8.07 (s, 2H), 4.75–4.68 (m, 2H), 4.54–4.45 (m, 2H), 3.97 (br s, 2H), 3.55–3.47 (m, 2H), 3.44–3.36 (m, 2H). ^{13}C **NMR** (101 MHz, DMSO-d6) δ 149.3, 145.7, 142.6, 138.9, 128.3, 126.5, 126.3, 120.4, 70.6, 63.3, 53.3.

3,3′-((1,10-Phenanthroline-2,9-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(propane-1,2-diol) (BTrzPhen-tetraol 6). In a reaction tube, 0.40 g (0.74 mmol) of 2,9-bis(1-((2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline **4** was dissolved in 6 mL of a 1 mol L^{-1} HCl solution and the reaction mixture was stirred at 50 °C overnight. After cooling down to room temperature, NaOH (2 mol L^{-1}) was added until a pH of 10 was reached. Next, 15 mL of chloroform was added and the mixture was shaken and sonicated, resulting in the formation of an oily substance which was suspended in the chloroform phase. The mixture was left to settle overnight, allowing the oil to solidify. The precipitate was filtered and washed 3 times with 10 mL of water to remove residual salts. Next, the solid was dried in the vacuum oven at 50 °C overnight. The product was obtained as a brown-orange solid in a yield of 72% (0.25 g).

MP: 148–150 °C. **HRMS** (ESI-Q-TOF): m/z [M + H]$^+$ calcd for $C_{22}H_{22}N_8O_4$: 463.1842; found: 463.1840.

^{1}**H NMR** (400 MHz, DMSO-d6) δ 8.91 (s, 2H), 8.60 (d, J = 8.4 Hz, 2H), 8.47 (d, J = 8.4 Hz, 2H), 8.00 (s, 2H), 5.28–5.20 (m, 2H), 4.91 (t, J = 5.5 Hz, 2H), 4.64–4.53 (m, 2H), 4.42–4.32 (m, 2H), 3.94 (br s, 2H), 3.48–3.36 (m, 4H). ^{13}C **NMR** (101 MHz, DMSO-d6) δ 150.0, 147.2, 145.1, 137.5, 128.2, 126.3, 125.3, 119.6, 70.4, 63.4, 53.3.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate (7). (2,2-Dimethyl-1,3-dioxolan-4-yl)methanol (5.00 g, 37.83 mmol) was added to a flame-dried round-bottom flask and dissolved in 20 mL of dry pyridine. The mixture was cooled in an ice-bath and stirred for 20 minutes. *p*-Toluenesulfonyl chloride (10.82 g, 56.75 mmol) was dissolved in 4 mL of dry DCM and added dropwise to the cooled reaction mixture. Subsequently, the mixture was stirred for 2 h at 0 °C. The reaction was monitored by TLC using EtOAc/petroleum ether (PE) (1 : 4) as the eluent. After the reaction was finished, the mixture was diluted with DCM and the pyridine was extracted with 1 mol L^{-1} HCl (3×). The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated *in*

vacuo. Next, the reaction mixture was purified *via* column chromatography using EtOAc/PE (1 : 4) as the eluent. The product **7** was obtained as a white solid in 79% yield (8.55 g). Characterisation data were in accordance with the data reported in literature.[29]

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.80 (d, 2H), 7.35 (d, 2H), 4.30–4.24 (m, 1H), 4.05–3.95 (m, 3H), 3.75 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.45 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (101 MHz, chloroform-*d*) δ 145.1, 132.6, 129.9, 128.0, 110.0, 72.9, 69.6, 66.1, 26.6, 25.1, 21.6.

Spectrophotometric evaluation of BTrzPhen-tetraol transfer to the organic phase

Extraction of BTrzPhen-tetraol into the organic phase (5 vol% 1-octanol in *n*-dodecane pre-equilibrated with 3.15 mol L^{-1} HNO_3) during a stripping experiment was investigated using UV-VIS spectrometry. Samples were prepared by contacting 1 mL of a 0.05 mol L^{-1} HNO_3 solution containing 10 mmol L^{-1} of ligand **6** with the pre-equilibrated organic phase (1 mL) during 30 minutes. After phase separation by centrifugation, 500 μL of the organic phase was combined with 19.3 μL of DMSO and 100 μL of EtOH (this experiment was performed in triplicate). Reference samples (100, 50, 10 and 1 μmol L^{-1}) were prepared by mixing 19.3 μL of a solution of ligand **6** in DMSO (2.6, 1.3, 0.26 and 0.026 mmol L^{-1}), 100 μL of EtOH and 500 μL of the pre-equilibrated organic phase. A blank solution was prepared by adding 19.3 μL of DMSO without ligand **6** and 100 μL of EtOH to 500 μL of the pre-equilibrated organic phase. To mimic the stripping experiments, the pre-equilibrated organic phase added to the reference samples and blank solution was initially contacted with a 0.05 mol L^{-1} HNO_3 solution. Spectra were recorded with a Shimadzu UV-1800 spectrophotometer, in HELLMA precision SUPRASIL® quartz cells with a path length of 10 mm. The spectrum of the blank solution was recorded and subtracted from the sample spectra to correct for background contributions. The obtained data were analysed with Shimadzu UVProbe software. The results of the experiment are illustrated in Fig. S23 (ESI†).

Stability test

The stability of BTrzPhen-tetraol **6** was investigated by dissolving 10 mmol L^{-1} of ligand in 0.5 mol L^{-1} HNO_3, and heating this solution to 50 °C, up to 3 days. Samples were analysed on a Waters Acquity Arc HPLC system equipped with a Waters 2489 dual wavelength UV/Vis detector. Peaks in the chromatograms were integrated using the Waters® Empower® 3 Software ApexTrack Integration Algorithm. HPLC Method: Column: Waters XBridge® Peptide BEH (C18, 5 μm, 4.6 × 150 mm). Mobile phase: 0.1% (v/v) TFA in Milli-Q water (A) and 0.1% (v/v) TFA in acetonitrile (B). Flow rate: 1 mL min^{-1}. Gradient: 0–1 min (5% B), 1–13.5 min (5–95% B), 13.5–16.5 min (95% B), 16.5–17 min (95–5% B), 17–20 min (5% B). A peak of compound **6** was observed after 7.4 minutes by the UV/Vis-detector at a wavelength of 254 nm and 360 nm.

Materials used for solvent extraction

TODGA was acquired from Technocomm Limited (Edinburgh, UK). 1-Octanol, *n*-dodecane, $Dy(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%), $Ho(NO_3)_3 \cdot 5H_2O$ (purity: 99.9%), $Yb(NO_3)_3 \cdot 5H_2O$ (purity: 99.9%) and $Lu(NO_3)_3 \cdot xH_2O$ (purity: 99.9%) were obtained from Sigma-Aldrich (Steinheim, Germany). $Gd(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%) and $Eu(NO_3)_3 \cdot 6H_2O$ (purity: 99.99%) were obtained from Alfa Aesar GmbH (Karlsruhe, Germany). $La(NO_3)_3 \cdot 6H_2O$ (purity: 99.0%) was obtained from Fluka Chemica (Seelze, Germany). $Pr(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%), $Nd(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%), $Sm(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%), $Y(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%) and $Ce(NO_3)_3 \cdot 6H_2O$ (purity: 99.9%) were obtained from Strem Chemicals (Kehl, Germany). HNO_3 solutions were prepared from 69% trace metal grade HNO_3, acquired from Fisher Scientific Ltd (Loughborough, UK). Milli-Q® grade water was used for all dilutions. [241]Am tracer in 1 mol L^{-1} HNO_3 solution (radiochemical purity >99%) was available from legacy stocks of SCK CEN. [244]Cm (radiochemical purity >99%) and [152]Eu (radiochemical purity >99%) radiotracers in 1 mol L^{-1} HNO_3 solutions were obtained from Eckert and Ziegler Nuclitec GmbH (Braunschweig, Germany). The spiked feed solution was prepared by adding 1 mL of a 300 kBq mL^{-1} in 0.5 mol L^{-1} HNO_3 solution of each radiotracer ([241]Am, [244]Cm and [152]Eu) to a 4 mL glass vial. This resulted in a spiked stock solution of 3 mL containing 100 kBq mL^{-1} of each radiotracer ([241]Am, [244]Cm and [152]Eu) in 0.5 mol L^{-1} HNO_3 which was used for every experiment. The lanthanide stock solution was prepared by dissolving an exact weighed amount of each nitrate salt of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb and Lu in 3.15 mol L^{-1} HNO_3 to obtain a 10^{-5} mol L^{-1} concentration for each of the elements. The exact HNO_3 concentration of the stock solutions was determined through titration using a Mettler Toledo Titration Excellence T5 autotitrator filled with a 0.0180 mol L^{-1} or 0.0195 mol L^{-1} NaOH stock solution.

Gamma spectrometry

All the samples (organic and aqueous phase) were analysed by gamma spectrometry to quantify the present [241]Am using the 59.5 keV γ-peak and [152]Eu using the 121.8 keV γ-peak. The detection was performed using a p-type coaxial HPGe detector (Canberra Semiconductors NV, Olen, Belgium). A DSA-LX multi-channel analyser (MCA) with 8000 channels was used. The detector efficiency was determined specifically for [241]Am and [152]Eu through gravimetric preparation of mixed [241]Am and [152]Eu efficiency calibration solutions from mononuclidic reference solutions with certified activity concentration (PTB, Germany). The spectra were analysed with Genie2000 software.

Alpha spectrometry

Thin layer alpha samples were prepared from the aqueous phases. These were prepared on 20 mm diameter C-1S cupped stainless steel planchets acquired from GA-MA and Associates, Inc., Florida, USA. Of the aqueous samples *ca.* 10 μL was pipetted into the middle of the planchet and the exact mass of

the sample was determined by weighing on an analytical balance. One drop of both a 1 mol L^{-1} HNO$_3$ solution and a 25% NH$_4$OH solution were then added to obtain a smoother distribution. The planchets were then dried under an infrared lamp and subsequently burned with a gas torch to fix the sample. The samples were measured by alpha spectrometry using a Canberra Alpha Analyst spectrometer, equipped with Passivated Implanted Planar Silicon (PIPS) alpha detectors, and analysed with Canberra Apex Alpha software. The alpha spectra were analysed by measuring the area of the ^{241}Am peak at 5.5 MeV and the ^{244}Cm peak at 5.8 MeV. Organic samples were not analysed with alpha spectrometry. Instead, the starting solution (aqueous phase before extraction) was used to determine the amount of ^{241}Am and ^{244}Cm which was left in the organic phase. A method intercomparison between alpha and gamma spectrometry was made for the ^{241}Am activity results.

Inductively coupled plasma mass spectrometry (ICP-MS)

Aqueous samples of the non-radioactive lanthanides were analysed using ICP-MS, on a ThermoFisher Scientific X2 series II ICP-MS instrument with QTEGRA software. The distribution ratios for Dy, Ho, Yb and Lu could not be determined because the concentration of these elements was below the limit of detection.

General procedure for solvent extraction studies

In a typical stripping experiment, 0.2 mol L^{-1} of TODGA was dissolved in a 95/5 vol% n-dodecane/1-octanol diluent. The organic phase was pre-equilibrated twice with a 3.15 mol L^{-1} HNO$_3$ solution and used as such for the stripping experiments. Next, the aqueous phase was prepared by adding 10 µL (1 kBq of each of the tracers ^{241}Am, ^{244}Cm and ^{152}Eu) of the prepared radiotracer stock solution to 590 µL of a 3.15 mol L^{-1} HNO$_3$ solution (for the experiments with the lanthanides, 590 µL of the lanthanide stock solution was used) in a 1.5 mL glass vial. To this vial 600 µL of the pre-equilibrated organic phase was added and the vial was shaken by a TMS-200 Thermoshaker (Nemus Life, Sweden) at 1900 rpm during 30 minutes at ±25 °C (= extraction). Afterwards, phase separation was enhanced by centrifugation for 5 minutes at 4000 rpm using a Heraeus Labofuge 200 centrifuge. After phase separation, 500 µL of the loaded organic phase was transferred to a new 1.5 mL vial and contacted with 500 µL of a 10 mmol L^{-1} BTrzPhen-tetraol solution with the desired HNO$_3$ concentration. This vial was again shaken at 1900 rpm during 30 minutes at ±25 °C by the TMS-200 Thermoshaker, followed by centrifugation (= stripping). After phase separation, 300 µL aliquots of the aqueous and organic phases were collected for analysis.

Safety notice

The stripping experiments were performed with trace amounts of ^{241}Am, ^{244}Cm and ^{152}Eu (about 1 kBq each). Since these are radioactive elements, specific caution is needed to perform the stripping experiments. The experiments were performed in a protected environment: in this case in a fume hood in the supervised area. A lab coat, safety goggles and two pair of gloves were always worn during the experiments. Samples and equipment which got in contact with radioactive material or suspected of contamination are repeatedly wipe-tested to exclude contamination outside the fume hood.

^{241}Am and ^{244}Cm are both alpha-emitters and therefore the largest hazard is when these nuclides are inhaled or digested. Therefore, the nuclides will always be kept in a closed vial when they are transported outside the fume hood. ^{152}Eu is a gamma emitter but due to the low activity which is used, no additional lead shielding is needed for protection.

Results and discussion

Synthesis

In this work, BTrzPhen-tetraol **5,6** was synthesised *via* an alternative synthetic pathway (Scheme 1). An important strategy for the synthesis of 1,2,3-triazoles is the eliminative azide-enamine cycloaddition reaction, and was envisioned as a valuable alternative to the CuAAC reaction.[30–32] The condensation of neocuproine **1** and Bredereck's reagent was proposed for the preparation of the starting bisenamine **2**. Initial attempts were carried out in a microwave setup at a fixed temperature. The progression of the reaction was monitored by means of ^{1}H NMR analysis of the dried crude mixtures. At 100 °C and in the presence of 4 equivalents of Bredereck's reagent, a mixture of starting material, monoenamine and the desired bisenamine was still observed after more than 24 h. However, with 5 equivalents of Bredereck's reagent and at 150 °C, full conversion towards the bisenamine was achieved after 4 hours. The same result was obtained when the reaction was performed using conventional heating (160 °C). Starting from 7.5 mmol of neocuproine, the bisenamine was isolated by precipitation with a yield of 79%. It should however be noted that the enamine is sensitive to hydrolysis. A small amount of decomposition was already observed after a few hours in deuterated chloroform. Next, 4-(azidomethyl)-2,2-dimethyl-1,3-dioxolane **3** was synthesised over two steps according to literature.[29] It was chosen to use the acetonide protected hydroxyl groups to simplify the purification of the cycloaddition product. Azide **3** was reacted in a 1,3-dipolar cycloaddition with the bisenamine **2**. Numerous examples of azide-enamine cycloadditions have been described in the literature in different solvents.[30–32] For this reaction 1,4-dioxane was chosen for the sake of solubility, its favourable boiling point and compatibility with the following precipitation protocol. In this way, bistriazolylphenanthroline **4** was obtained in a yield of 87% (1.48 g). Two hydrophobic derivatives, including the earlier studied EH-BTzPhen,[33] were also successfully synthesised *via* this method using toluene or dioxane as the reaction solvent (**8** and **9**, ESI†). The cycloaddition with tosyl azide gave a hexaaza[5]helicene **10** instead of the intended bis(*NH*-triazol-4-yl)phenanthroline (Scheme S1, ESI†). A major benefit of the cycloaddition towards intermediate **4** is the sustainable
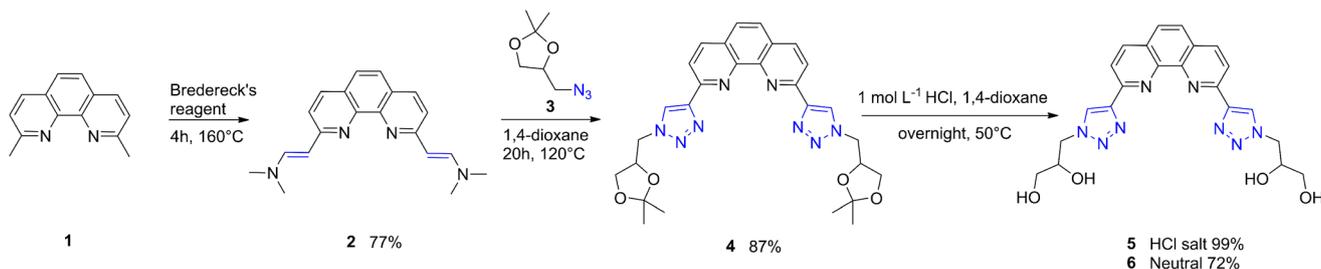
Scheme 1 Synthesis of BTrzPhen-tetraol **5**/**6**.

work-up. Intermediate **4** was precipitated with water and further purified by washing with a 30 : 70 iPrOH/water mixture. The iPrOH/water ratio had to be optimised since the present impurities showed to be insoluble when iPrOH concentrations below 30% were used. On the other hand, iPrOH concentrations above 30% resulted in a decrease of the yield because the product is slightly soluble in iPrOH. Since precipitation was easier on a larger scale, the yield of the reaction significantly increased when the reaction was performed on 1 gram scale (87%) instead of a 500 mg scale (59%). In the final step, the acetals of intermediate **4** were hydrolysed with 1 mol L^{-1} HCl resulting in the formation of BTrzPhen-tetraol **5** in quantitative yield. This resulted in an overall yield of 66%. Since **5** is an HCl adduct, the amount of HCl present was estimated *via* titration with sodium hydroxide, and turned out to be approximately 1.6 equivalents. To obtain the free base, neutralisation with NaOH was performed to afford BTrzPhen-tetraol **6** in 72% yield. This resulted in an overall yield of 48% which is higher compared to the 32% overall yield obtained with the CuAAC route.[26]

Solubility and stability

The solubility of BTrzPhen **5** and **6** was tested by attempting to prepare 10 mmol L^{-1} solutions in aqueous HNO$_3$ (0–3 mol L^{-1}). Ligand **5** was soluble in water without and with HNO$_3$. The free base **6** (10 mmol L^{-1}) was only soluble in aqueous HNO$_3$ solutions with [HNO$_3$] ≥ 0.02 mol L^{-1} after heating to 50 °C. After cooling down to room temperature the ligand remained in solution.

Additionally, the extraction of ligand **6** into the organic phase during a stripping experiment was investigated. For this purpose, the organic phase was analysed using UV-VIS spectrophotometry and compared to a dilution series of ligand **6** (Fig. S23, ESI†). While a clear absorbance peak was obtained at 312 nm for a 10 μmol L^{-1} reference solution of ligand **6**, no such peak was present in the spectrum of the organic phase after stripping. This led to the conclusion that less than 0.1% of the extractant was transferred into the organic phase.

The stability of ligand **6** was assessed by HPLC, revealing very slow decomposition in 0.5 mol L^{-1} HNO$_3$. Over 72 hours, the purity steadily decreased by 4% (see Fig. S24 in ESI†).

Stripping kinetics

The stripping experiments were carried out as described in the general procedure for solvent extraction studies. The kinetics

of Am(III) and Eu(III) stripping by BTrzPhen-tetraol **5** and **6** were analysed (Fig. 1 and Fig. S19, ESI†). The distribution ratios remained stable across the investigated time points, indicating that a 5 minute contact time was sufficient to achieve equilibrium. Consequently, the 12 hour contact time used by Edwards *et al.* appears to be unnecessary.[26] Similar kinetics were also observed for SO$_3$-Ph-BTPhen, the benchmark ligand used in the AmSel process.[6]

Influence of HNO$_3$ concentration on stripping behaviour

The influence of HNO$_3$ concentration on the stripping behavior of Am(III), Cm(III), and Eu(III) was investigated (Fig. 2). A clear separation between Am(III) and Eu(III) was observed across the tested HNO$_3$ concentration range. With decreasing HNO$_3$ concentrations, the Eu(III)/Am(III) separation factor (SF$_{Eu/Am}$) increased, likely due to reduced ligand protonation, reaching a maximum of 50 ± 13 (k = 3) at 0.26 mol L^{-1} HNO$_3$. This value aligns well with the separation factor of 47 reported by Edwards *et al.* at 0.33 mol L^{-1} HNO$_3$.[26] Distribution ratios (D) of 0.45 for Am(III) and 1.03 for Cm(III) yielded a Cm(III)/Am
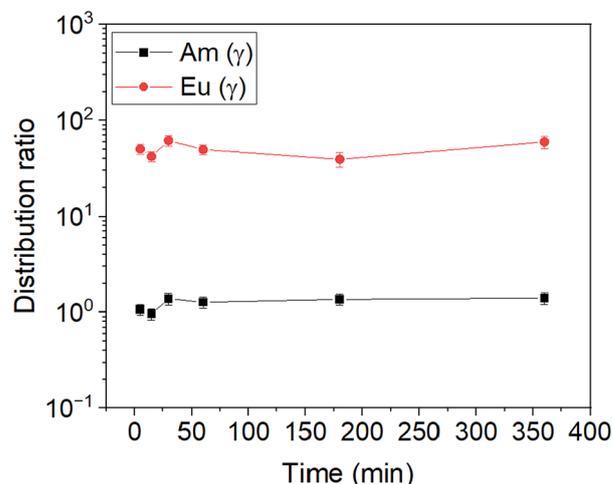

Fig. 1 Distribution ratios of Am(III) and Eu(III) as a function of time. Pre-equilibrated and loaded organic phase (without other lanthanides): 0.2 mol L^{-1} TODGA in 5 vol% 1-octanol in *n*-dodecane. Aqueous phase: 0.26 mol L^{-1} HNO$_3$ and 10 mmol L^{-1} BTrzPhen-tetraol **6**. The measurement uncertainties were calculated for a confidence interval of 99% (k = 3) and are reported in the ESI Table 2.†
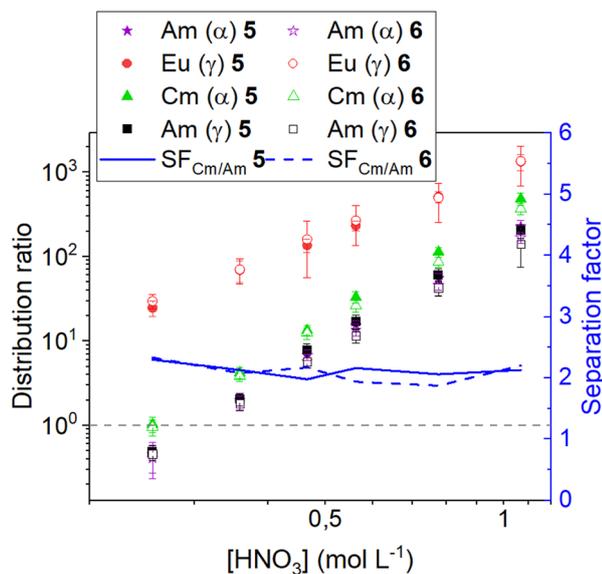
Fig. 2 Distribution ratios ($D_{M(III)}$) of Am(III), Eu(III) and Cm(III) and Cm(III)/Am(III) separation factors ($SF_{Cm/Am}$) as a function of the HNO$_3$ concentration in the stripping with BTrzPhen-tetraol **5** and BTrzPhen-tetraol **6**. Pre-equilibrated and loaded organic phase (without other lanthanides): TODGA (0.2 mol L^{-1}) and 5 vol% 1-octanol in n-dodecane. Aqueous phase: HNO$_3$ (0.26–1.07 mol L^{-1}) and BTrzPhen-tetraol **5** or **6** (10 mmol L^{-1}). The gamma (black squares) and alpha (purple stars) distribution ratios of Am(III) are overlapping. All measurement uncertainties were calculated for a confidence interval of 99% (k = 3) and are reported in the ESI Tables 4–7.†

(III) separation factor ($SF_{Cm/Am}$) of 2.3 ± 0.6 (k = 3), also consistent with Edwards *et al.* ($SF_{Cm/Am}$ = 2.5).[26] Process-suitable distribution values (D_{Am} < 1, D_{Cm} > 1, and D_{Eu} > 10) were achieved at an HNO$_3$ concentration of 0.26 mol L^{-1}, which was therefore chosen for further experiments.[22]

Stripping experiment with varying nitric acid concentrations were performed with both BTrzPhen-tetraol hydrochloride (**5**) and its free base (**6**) under identical conditions (Fig. 2), revealing no significant differences in the distribution ratios of Am(III), Cm(III) and Eu(III). While the HCl salt (**5**) is easier to isolate and dissolves more readily, it is not CHON-compliant. Consequently, the free base (**6**) is preferred, particularly in scenarios where the formation of corrosive combustion products poses challenges for waste management, storage, or fuel manufacturing.[34]

Effect of ligand concentration on stripping behaviour

Further experiments examined the effect of ligand concentration on the distribution ratios of Am(III), Cm(III), and Eu(III) (Fig. 3). In the absence of ligand **6**, the Eu(III)/Am(III) separation factor was 7.3, and the Cm(III)/Am(III) separation factor was 1.6, consistent with the values reported for TODGA ($SF_{Eu/Am}$ = 7, $SF_{Cm/Am}$ = 1.6). The addition of BTrzPhen-tetraol **6** significantly reduced the distribution ratios of Am(III) and Cm(III), but further increasing the ligand concentration from 5 mmol L^{-1} to 50 mmol L^{-1} caused only a minor additional decrease, with no effect on the distribution ratios of Eu(III). A possible expla-
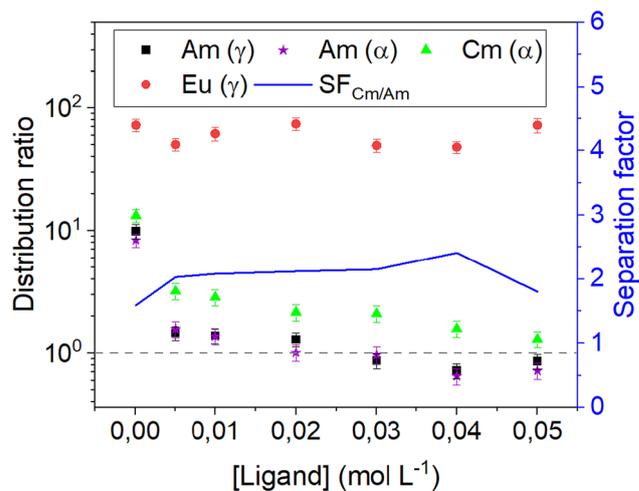

Fig. 3 Influence of the BTrzPhen-tetraol **6** concentration on the distribution ratios of Eu(III), Am(III) and Cm(III). Pre-equilibrated and loaded organic phase (with other lanthanides): TODGA (0.2 mol L^{-1}) and 5 vol% 1-octanol in n-dodecane. Aqueous phase: 0.26 mol L^{-1} HNO$_3$ and 0–50 mmol L^{-1} BTrzPhen-tetraol **6**. The measurement uncertainties were calculated for a confidence interval of 99% (k = 3) and are reported in the ESI Tables 8 and 9.†

nation for these observations is that the nitrate concentration was too low to enable TODGA and BTrzPhen to function optimally. In the presence of higher nitrate concentration, Wan *et al.* observed a subtle decrease in the Am(III) and Eu(III) distribution ratios as the concentration of BTrzPhen ligands increased.[28,35] An increased nitrate concentration could enhance ligand performance, revealing a more pronounced effect of ligand concentration. However, the addition of nitrate salts is undesirable in industrial processes due to their oxidizing properties and the generation of additional waste. Additionally, it also complicates the conversion of Am(III) into Am(III)-bearing fuel.[36] For these reasons, no nitrate salts were used in this study.

At the highest tested ligand concentration (50 mmol L^{-1}), the Eu(III)/Am(III) separation factor reached 84 ± 15 (k = 3). Am(III) stripping was observed at ligand concentrations above 0.03 mol L^{-1}, while the Cm(III) distribution ratios (D_{Cm}) remained above 1 over the entire concentration range. The Cm(III)/Am(III) separation factor ($SF_{Cm/Am}$) was relatively constant, with a value of 2.4 ± 0.5 (k = 3) at a ligand concentration of 0.04 mol L^{-1}. Unfortunately, no linear trend was observed in the distribution ratios of Am(III) or Cm(III), precluding stoichiometric analysis of the metal complexes. This non-linear behavior might be attributed to the formation of mixed complexes. Advanced techniques, such as time-resolved laser fluorescence spectroscopy (TRLFS), could provide further insights into the stoichiometry of these complexes.[37]

Experiments with ligand **5** revealed a less pronounced effect of the ligand concentration on the Am(III) distribution ratios (Fig. S20, ESI†). This could be explained by the presence of HCl in ligand **5**, which slightly increases the acidity of the solution and may increase the Am(III) distribution ratio. This

effect likely counterbalances the reduction in Am(III) distribution ratios caused by increasing ligand concentration, resulting in a negligible net effect.

The distribution ratios of the trivalent lanthanides (La, Ce, Pr, Nd, Sm, Eu and Gd) as a function of the BTrzPhen-tetraol (5 and 6) concentration are reported in the ESI (Fig. S21 and S22†). Interestingly, increasing the ligand concentration had no observable effect on the distribution ratios of the lanthanides at a nitric acid concentration of 0.26 mol L^{-1}. This could somewhat be expected, as BTrzPhen ligands are anticipated to show weaker interactions with lanthanides due to its soft-donor character. Moreover, co-stripping of the larger lanthanides was observed, which must be avoided to achieve selective americium separation. Again, these observations suggest that the TODGA and BTrzPhen ligands do not perform optimally under the conditions tested.

Conclusions

To summarise, a new synthetic pathway for BTrzPhen-tetraol, a CHON-compliant alternative to SO$_3$-Ph-BTBP/Phen, was developed. The enamine-azide cycloaddition reaction proved to be a more effective method compared to CuAAC, offering a robust and scalable synthesis route. The new pathway allows for the production of BTrzPhen on a gram scale with high yields, avoiding column chromatography for purification.

A 10 mmol L^{-1} solution of BTrzPhen-tetraol could be easily prepared in aqueous HNO$_3$ solutions ([HNO$_3$] $\geq$ 0.02 mol L^{-1}), no extraction of the ligand to the organic was detected, and no decomposition was observed after 3 days of exposure to a 0.5 mol L^{-1} HNO$_3$ solution at 50 °C. Stripping experiments using both the HCl salt (5) and free base form (6) of BTrzPhen demonstrated fast stripping kinetics. The Eu(III)/Am(III) and Cm(III)/Am(III) separation factors obtained, 84 ± 15 ($k = 3$) and 2.4 ± 0.5 ($k = 3$) respectively, were in line with earlier reported values.

The effect of ligand concentration on the distribution ratios of Am(III), Cm(III), and lanthanides was investigated. For both the BTrzPhen hydrochloride and the free base, no significant impact of ligand concentration was observed on the distribution ratios of the lanthanides and Y(III). However, the distribution ratio of Am(III) and Cm(III) showed a slight decrease with increasing ligand concentration. The absence of a more pronounced concentration-dependent effect may be due to the low nitrate concentration, which likely prevented optimal ligand performance.

Given its CHON compatibility, BTrzPhen 6 is recommended for further studies. Future research should focus on optimizing the stripping performance of this ligand and mitigating co-stripping of the larger lanthanides.

Data availability

Experimental details for the synthesis of compounds 8–10, NMR spectra, and data from the extraction experiments are available in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 P. A. Baisden and G. R. Choppin, in *Radiochemistry and Nuclear Chemistry*, ed. S. Nagy, Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford, UK, 2007.
2 M. Salvatores and G. Palmiotti, *Prog. Part. Nucl. Phys.*, 2011, **66**, 144–166.
3 F. W. Lewis, L. M. Harwood, M. J. Hudson, A. Geist, V. N. Kozhevnikov, P. Distler and J. John, *Chem. Sci.*, 2015, **6**, 4812–4821.
4 R. J. Taylor, C. R. Gregson, M. J. Carrott, C. Mason and M. J. Sarsfield, *Solvent Extr. Ion Exch.*, 2013, **31**, 442–462.
5 G. Modolo, A. Wilden, A. Geist, D. Magnusson and R. Malmbeck, *Radiochim. Acta*, 2012, **100**, 715–725.
6 P. Kaufholz, F. Sadowski, A. Wilden, G. Modolo, F. W. Lewis, A. W. Smith and L. M. Harwood, *Nukleonika*, 2015, **60**, 815–820.
7 S. Pillon, in *Comprehensive Nuclear Materials*, ed. R. J. M. Konings, Elsevier, 2012, vol. 3, pp. 109–141.
8 C. F. Poole, in *Handbooks in Separation Science*, ed. C. F. Poole, Elsevier, 2020, pp. 45–89.
9 C. Poinssot, C. Rostaing, P. Baron, D. Warin and B. Boullis, *Procedia Chem.*, 2012, **7**, 358–366.
10 C. Ebenezer and R. Vijay Solomon, *Inorg. Chem. Front.*, 2021, **8**, 3012–3024.
11 M. P. Jensen, R. Chiarizia, J. S. Ulicki, B. D. Spindler, D. J. Murphy, M. M. Hossain, A. Roca-Sabio, A. de Blas and T. Rodríguez-Blas, *Solvent Extr. Ion Exch.*, 2015, **33**, 329–345.
12 J. D. Burns, T. C. Shehee, A. Clearfield and D. T. Hobbs, *Anal. Chem.*, 2012, **84**, 6930–6932.
13 Z. Kolarik, *Chem. Rev.*, 2008, **108**, 4208–4252.
14 P. J. Panak and A. Geist, *Chem. Rev.*, 2013, **113**, 1199–1236.

15 F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, A. Wilden, M. Sypula, G. Modolo, T.-H. Vu, J.-P. Simonin, G. Vidick, N. Bouslimani and J. F. Desreux, *Procedia Chem.*, 2012, **7**, 231–238.

16 F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.-H. Vu and J.-P. Simonin, *J. Am. Chem. Soc.*, 2011, **133**, 13093–13102.

17 H. H. Dam, D. N. Reinhoudt and W. Verboom, *Chem. Soc. Rev.*, 2007, **36**, 367–377.

18 M. R. S. J. Foreman, M. J. Hudson, A. Geist, C. Madic and M. Weigl, *Solvent Extr. Ion Exch.*, 2005, **23**, 645–662.

19 M. J. Hudson, L. M. Harwood, D. M. Laventine and F. W. Lewis, *Inorg. Chem.*, 2013, **52**, 3414–3428.

20 S. Trumm, A. Geist, P. J. Panak and T. Fanghänel, *Solvent Extr. Ion Exch.*, 2011, **29**, 213–229.

21 A. Wilden, M. Sypula, C. Schreinemachers, P. Kluxen and G. Modolo, *1-cycle SANEX process development studies performed at Forschungszentrum Jülich*, 2010.

22 P. Zsabka, A. Wilden, K. Van Hecke, G. Modolo, M. Verwerft and T. Cardinaels, *J. Nucl. Mater.*, 2023, **581**, 154445.

23 A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden and T. Zevaco, *Solvent Extr. Ion Exch.*, 2012, **30**, 433–444.

24 P. Kaufholz, G. Modolo, A. Wilden, F. Sadowski, D. Bosbach, C. Wagner, A. Geist, P. J. Panak, F. W. Lewis and L. M. Harwood, *Solvent Extr. Ion Exch.*, 2016, **34**, 126–140.

25 C. Wagner, U. Müllich, A. Geist and P. J. Panak, *Solvent Extr. Ion Exch.*, 2016, **34**, 103–113.

26 A. C. Edwards, P. Mocilac, A. Geist, L. M. Harwood, C. A. Sharrad, N. A. Burton, R. C. Whitehead and M. A. Denecke, *Chem. Commun.*, 2017, **53**, 5001–5004.

27 M. C. Nielsen, A. F. Larsen, F. H. Abdikadir and T. Ulven, *Eur. J. Med. Chem.*, 2014, **72**, 119–126.

28 Y. Q. Wan, H. Hao, L. Yu, Z. P. Wang and P. Mocilac, *RSC Adv.*, 2023, **13**, 21982–21990.

29 A. V. Costa, L. C. Moreira, R. T. Pinto, T. A. Alves, V. V. Schwan, V. T. de Queiroz, M. M. Praça-Fontes, R. R. Teixeira, P. A. B. Morais and W. C. de Jesus, *J. Braz. Chem. Soc.*, 2020, **31**, 821–832.

30 J. John, J. Thomas and W. Dehaen, *Chem. Commun.*, 2015, **51**, 10797–10806.

31 T. Opsomer and W. Dehaen, *Chem. Commun.*, 2021, **57**, 1568–1590.

32 V. A. Bakulev, T. Beryozkina, J. Thomas and W. Dehaen, *Eur. J. Org.*, 2018, **2018**, 262–294.

33 P. Zsabka, T. Opsomer, K. Van Hecke, W. Dehaen, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans and T. Cardinaels, *Solvent Extr. Ion Exch.*, 2020, 719–734.

34 J. Magill, V. Berthout, D. Haas, J. Galy, R. Schenkel, H. Wiese, G. Heusener, J. Tommasi and G. Youinou, *Nucl. Energy*, 2003, **42**, 263–277.

35 P. Ren, P. Huang, X. Yang, Y. Zou, W. Tao, S. Yang, Y. Liu, Q. Wu, L. Yuan, Z. Chai and W. Shi, *Inorg. Chem.*, 2021, **60**, 357–365.

36 L. Luzzi, A. Magni, S. Billiet, M. Di Gennaro, G. Leinders, L. Mariano, D. Pizzocri, M. Zanetti and G. Zullo, *Nucl. Eng. Des.*, 2024, **420**, 113048.

37 P. Weßling, M. Maag, G. Baruth, T. Sittel, F. Sauerwein, A. Wilden, G. Modolo, A. Geist and P. Panak, *Inorg. Chem.*, 2022, **61**, 17719–17729.