

1 **Solvent extraction studies for the separation of trivalent actinides from**  
2 **lanthanides with a triazole-functionalized 1,10-phenanthroline**  
3 **extractant**

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16 **Solvent extraction studies for the separation of trivalent actinides**  
17 **from lanthanides with a triazole-functionalized 1,10-phenanthroline**  
18 **extractant**

19

20 A new *N*-atom donor extractant 2,9-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-  
21 1,10-phenanthroline (EH-BTzPhen) was synthesized and used in solvent  
22 extraction studies to separate the trivalent minor actinides americium(III) and  
23 curium(III) from europium(III), representing fission product lanthanides. The  
24 extractant was found to be soluble in 1-octanol and in the Aliquat-336 nitrate  
25 ([A336][NO<sub>3</sub>]) ionic liquid diluent, but insoluble in *n*-dodecane. The  
26 [A336][NO<sub>3</sub>] is a fully incinerable room temperature ionic liquid, and has a  
27 higher flash point than aliphatic diluents such as 1-octanol. The EH-BTzPhen  
28 proved to be effective for selective minor actinide extraction only in combination  
29 with 2-bromohexanoic acid synergist when 1-octanol was used as a diluent  
30 ( $SF_{Am/Eu} > 200$ ). The change of the diluent from 1-octanol to Aliquat-336 nitrate  
31 allowed selective An(III) extraction from low acidity feed solutions without the  
32 need of a synergist ( $SF_{Am/Eu} \sim 70$  and  $SF_{Am/Cm} \sim 1.9-2.2$ ). The phase transfer  
33 kinetics of the ligand-metal complexes is however very slow at 22 °C in the case  
34 of both solvents. With this newly synthesized extractant the achieved  $SF_{Am/Cm}$   
35 were comparable to the values achieved with the established CyMe<sub>4</sub>BTBP and  
36 CyMe<sub>4</sub>BTPPhen extractants.

37 Keywords: Minor actinides, lanthanides, solvent extraction, Aliquat-336, ionic  
38 liquids, 1,2,3-triazole

39 **1. Introduction**

40 Minor actinides (neptunium, americium and curium) are responsible for the  
41 long-term heat emission and radiotoxicity of high level radioactive waste obtained after  
42 nuclear fuel reprocessing. Recycling of uranium and plutonium *via* the Plutonium  
43 Uranium Redox Extraction (PUREX) process is a mature technology applied on an  
44 industrial scale.<sup>1</sup> The separation of neptunium is possible with a modification of the  
45 PUREX flow sheet.<sup>2,3</sup> However, trivalent americium and curium are diverted to the

46 highly active raffinate together with the other fission and corrosion products, because  
47 tri-*n*-butyl phosphate (TBP, the extractant used in the PUREX process), has no affinity  
48 towards the extraction of trivalent metal ions. The separate management or  
49 transmutation of americium and curium could allow for a more dense design of a deep  
50 underground final repository of conditioned high activity waste.<sup>4,5</sup> However, curium  
51 would require excessive shielding and criticality control through all process stages of  
52 transmutation target fabrication due to its intensive neutron emission. Therefore, a  
53 partitioning and transmutation (P&T) scenario would largely benefit from a robust and  
54 efficient chemical separation process to separate americium from curium and the  
55 lanthanides.

56 Soft-donor extractants using nitrogen or sulfur-based donor groups were found to be  
57 suitable for the separation of trivalent minor actinides from lanthanides.<sup>6-8</sup> The  
58 tetradentate *N*-atom donor extractants 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-  
59 1,2,4-benzotriazin-3-yl)-2,2'-bipyridine (CyMe<sub>4</sub>BTBP)<sup>9,10,11-13</sup> and 2,9-bis(5,5,8,8-  
60 tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline  
61 (CyMe<sub>4</sub>BTPPhen)<sup>14,15</sup> are capable of extracting Am(III) and Cm(III) directly from highly  
62 active raffinate solutions. The metal-ligand interaction between the trivalent actinides  
63 An(III) and CyMe<sub>4</sub>BTBP or CyMe<sub>4</sub>BTPPhen is possible due to the presence of four *N*-  
64 atoms each having a lone electron pair in the metal-binding cavity (Figure1). Both  
65 compounds contain the six-membered triazinyl rings, where two of the donor lone  
66 electron pairs are softer nucleophiles than the lone pair of the pyridine-type *N*-atom of  
67 the 1,10-phenanthroline or 2,2'-bipyridine moiety. The increased nucleophilicity of the  
68 *N*-atom in the 2-position in the triazinyl ring is caused by the lone pair of the adjacent  
69 non-coordinating *N*-atom at position 1 (so-called *alpha effect*).<sup>16-19</sup> The excellent Am/Eu  
70 separation factors ( $SF_{Am/Eu} = 140$  and  $SF_{Am/Eu} = 200-400$  for CyMe<sub>4</sub>BTBP and

71 CyMe<sub>4</sub>BTPhen, respectively) originate from the stronger covalent character of the  
72 An(III)-N bonds compared to Ln(III)-N bonds.<sup>7</sup> At equilibrium, neither of these  
73 extractants show a high Am/Cm separation factor ( $SF_{Am/Cm} \approx 2.5$  for CyMe<sub>4</sub>BTBP and  
74 CyMe<sub>4</sub>BTPhen).<sup>11, 14</sup> When using the ionic liquid [A336][NO<sub>3</sub>] as diluent in  
75 combination with CyMe<sub>4</sub>BTPhen as extractant similar Am/Cm separation factors were  
76 observed at equilibrium and (much higher) separation factors were observed in non-  
77 equilibrium conditions.<sup>20</sup> The ionic liquid [A336][NO<sub>3</sub>] was recently also tested in  
78 combination with the hard-donor extractant TODGA for the An(III) + Ln(III) co-  
79 extraction from a simulated HAR solution and was found to be an interesting alternative  
80 to molecular diluents like *n*-dodecane.<sup>27</sup> Moreover, TODGA was found to have a higher  
81 radiation stability in [A336][NO<sub>3</sub>] than in aliphatic diluents.<sup>28</sup>

82 The effect of replacing 2 (1,2,4-) triazine moieties by 2 (1,2,3-) triazole moieties in the  
83 case of the BTP complexants for An(III) and Ln(III) separation was demonstrated in the  
84 hydrophilic, tridentate complexant 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine  
85 (PyTri-Diol).<sup>21, 22</sup> It proved to be a viable CHON-compliant alternative for the  
86 previously suggested SO<sub>3</sub>-Ph-BTP molecule in the i-SANEX process.<sup>23, 24</sup> Similarly, a  
87 hydrophilic tetradentate 2,9-bis-(1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline complexant  
88 (BTrzPhen) was developed and tested with the purpose of Am(III)/(Cm(III)+Ln(III))  
89 separation in an i-SANEX type process.<sup>25</sup> The compound allowed a  $SF_{Cm/Am}$  of 2.5 from  
90 a loaded *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA) containing solvent. The  
91 achieved Eu(III)/Am(III) separation factors were lower by a factor of two than those  
92 achieved with PyTri-Diol. With both BTrzPhen and PyTri-Diol molecules, the increase  
93 of aqueous nitric acid concentration resulted in a loss of stripping efficiency,  
94 presumably be due to protonation of the extractants.

95 Recently the synthesis and solvent extraction of the lipophilic, tetradentate 6,6'-bis(1-  
96 (2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-2,2'-bipyridine (EH-BTzBP) was reported.<sup>26</sup> It  
97 was found that the extractant shows promising Am/Eu separation factors when used in  
98 combination with 2-bromohexanoic acid. The extraction properties of the novel  
99 extractant with respect to Cm(III) were not investigated.

100 For the present study, the unprecedented lipophilic 2,9-bis(1-(2-ethylhexyl)-1*H*-1,2,3-  
101 triazol-4-yl)-1,10-phenanthroline (EH-BTzPhen) was synthesized (Figure 1). The  
102 extraction of An(III) and Ln(III) was studied using 1-octanol and Aliquat-336 nitrate  
103 ([A336][NO<sub>3</sub>]) diluents. The purpose of this investigation was to study the extraction  
104 kinetics and selectivity of the extractant regarding Am(III), Cm(III), and Eu(III). The  
105 selectivity in solvent extraction is compared to the extractants with six-membered  
106 heterocycles.

107

## 108 **2. Experimental**

### 109 **2.1 Materials used for solvent extraction**

110 Aliquat® 336 chloride ([A336][Cl], quaternary amine content: 88.2 – 90.6 %) of  
111 which the main component is tri-*n*-octylmethylammonium chloride ([N<sub>1888</sub>][Cl]), 1-  
112 octanol (purity > 99 %), citric acid (purity > 99 %), 2-bromohexanoic acid (purity 97  
113 %), silver(I) nitrate (purity: 99.9 %), ammonium nitrate (purity > 99 %),  
114 Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (purity: 99.9 %) and Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (purity: 99.9 %) were obtained  
115 from Sigma-Aldrich (Steinheim, Germany). Potassium nitrate (purity > 97.0 %), sodium  
116 nitrate (purity > 97.0 %) and sodium hydroxide (Titrisol) were obtained from Merck  
117 KGaA (Darmstadt, Germany). Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (purity: 99.9 %) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O  
118 (purity: 99.99 %) were obtained from Alfa Aesar GmbH (Karlsruhe, Germany).

119  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (purity: 99.0 %) was obtained from Fluka Chemica (Seelze, Germany).  
120  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (purity: 99.9 %),  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (purity: 99.9 %),  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$   
121 (purity: 99.9 %),  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (purity: 99.9 %) and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (purity: 99.9 %)  
122 were obtained from Strem Chemicals (Kehl, Germany). Trace metal grade nitric acid  
123 was obtained from Fischer Scientific Ltd. (Loughborough, UK). MilliQ water was used  
124 for all dilutions (resistivity: minimum 18.2 M $\Omega$  cm).  $^{241}\text{Am}$  tracer in 1 mol L $^{-1}$   $\text{HNO}_3$   
125 solution (radiochemical purity > 99 %) was available from legacy stocks of SCK CEN.  
126  $^{244}\text{Cm}$  (radiochemical purity > 99.902 %) and  $^{152}\text{Eu}$  (radiochemical purity > 99 %)  
127 radiotracers in 1 mol L $^{-1}$   $\text{HNO}_3$  solutions were obtained from Eckert and Ziegler  
128 Nuclitec GmbH (Braunschweig, Germany).

129 The [A336][Cl] ionic liquid was converted into its nitrate form by a metathesis reaction  
130 by stirring 120 mL of [A336][Cl] with 120 mL of an aqueous solution of 2.5 mol L $^{-1}$   
131  $\text{KNO}_3$  for 4 hours, followed by phase separation in a 1 L separation funnel. The  
132 equilibration and separation steps were repeated seven times until no AgCl precipitation  
133 was observed upon addition of drops of  $\text{AgNO}_3$  solution to the aqueous phase. After the  
134 metathesis reaction, the organic phase was washed three times with an equal volume of  
135 MilliQ water. The density of [A336][ $\text{NO}_3$ ] was determined with a density meter (Anton  
136 Paar DMA 4500 M), while the density of nitric acid solutions and nitrate solutions were  
137 taken from density tables.

## 138 **2.2 Synthesis of EH-BTzPhen**

139 All chemicals used for the synthesis of EH-BTzPhen were purchased from Acros  
140 Organics, Sigma Aldrich, Alfa Aesar and TCI Europe and used as received. For column  
141 chromatography, 70-230 mesh silica 60 (Acros) was used as the stationary phase. NMR  
142 spectra were recorded on a Bruker Avance III HD 400 spectrometer and chemical

143 shifts ( $\delta$ ) are reported in parts per million (ppm) referenced to tetramethylsilane ( $^1\text{H}$ ), or  
144 the internal (NMR) solvent signal ( $^{13}\text{C}$ ). The high-resolution mass spectrum was  
145 acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer  
146 (Synapt G2 HDMS, Waters, Milford, MA). The sample was infused at 3  $\mu\text{l}/\text{min}$  and the  
147 spectrum was obtained in positive ionization mode with a resolution of 15000 (FWHM)  
148 using leucine enkephalin as lock mass. The melting point was determined on a Mettler-  
149 Toledo DSC 1 instrument, using a heating rate of 4  $^\circ\text{C min}^{-1}$  and under a helium  
150 atmosphere.

151 The 2,9-diethynyl-1,10-phenanthroline was prepared in two steps from neocuproine, as  
152 described in the literature.<sup>25, 29</sup> EH-BTzPhen was synthesized according to a modified  
153 literature procedure using a copper-catalyzed azide-alkyne cycloaddition reaction  
154 (click-reaction) between the 2,9-diethynyl-1,10-phenanthroline and racemic 3-  
155 (azidomethyl)heptane, dissolved in DCM (Scheme 1).<sup>30</sup> 2,9-Diethynyl-1,10-  
156 phenanthroline (600 mg, 2.63 mmol) and racemic 3-(azidomethyl)heptane (939 mg,  
157 6.05 mmol) were added to a 250 mL round-bottom flask and dissolved in 53 mL of  
158 dichloromethane (DCM). A solution of sodium ascorbate (1.042 g, 5.26 mmol) in  
159 47 mL of water was added as a second phase. While stirring, a solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
160 (13 mg, 0.053 mmol) and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)  
161 (28 mg, 0.053 mmol) in 10.5 mL of  $\text{H}_2\text{O}:\text{DMSO}$  (1:1) was added slowly, followed by  
162 the addition of *N,N*-di-isopropylethylamine (DIPEA) (1.869 g, 14.46 mmol). The  
163 resulting mixture was stirred vigorously at room temperature for two days after which it  
164 was diluted with chloroform and washed with water (3x) and brine (1x). The organic  
165 layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated. Next, the crude product was dissolved in  
166 diethyl ether and filtered. The filtrate was then concentrated and further purified via  
167 column chromatography on silica ( $\text{CHCl}_3:i\text{PrOH}$  with gradient (1:0 to 19:1)) to yield

168 the pure product as an off-white solid (75 % yield, 1.066 g, mixture of stereoisomers).

169  $M_p = 147\text{ }^\circ\text{C}$ .

170  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 9.56$  (br s, 2H), 8.65 (d,  $J = 8.4$  Hz, 2H), 8.43 (d,  $J =$

171 8.4 Hz, 2H), 7.92 (s, 2H), 3.39 – 2.80 (m, 4H), 1.26 – 1.10 (m, 2H), 1.05 – 0.88 (m,

172 4H), 0.83 – 0.29 (m, 24H) (Figure S1).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz):  $\delta = 151.69$ ,

173 147.92, 145.51, 137.24, 128.58, 126.36, 125.34, 120.67, 53.67, 39.23, 29.57, 27.93,

174 22.97, 22.81, 13.98, 9.98 (Figure S2).

175 HRMS (ESI-Q-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{32}\text{H}_{42}\text{N}_8$ : 539.3605; found:

176 539.3601.

### 177 ***2.3 Batch solvent extraction and analytical procedures***

178 Batch extraction studies were performed using 4 mL glass vials that fit into the  
179 boreholes of an in-house fabricated metal block mounted on a TMS-200 Thermoshaker  
180 (Nemus Life, Sweden). The temperature was controlled by the use of a cooling loop  
181 connected to a MC250 Microcool chiller (Lauda-Brinkmann, Germany).

182 A stock solution for the lanthanide-nitrate containing aqueous phases was prepared by  
183 dissolving the calculated amounts of trivalent nitrate salts of La, Ce, Pr, Nd, Sm, Eu,  
184 Gd, Dy, Yb and Y in  $0.1\text{ mol L}^{-1}\text{ HNO}_3$  to obtain a  $10^{-3}\text{ mol L}^{-1}$  initial concentration of  
185 each Ln(III). From this stock solution 1 mL was taken for dilution to 100 mL in the  
186 desired final nitric acid concentration to obtain a final lanthanide concentration of  $10^{-5}$   
187  $\text{mol L}^{-1}$  each. The exact nitric acid concentration of the stock solutions was determined  
188 by titration using an autotitrator (716 MPT Titrino, Metrohm Switzerland) filled with  
189  $0.1\text{ mol L}^{-1}$  or  $0.01\text{ mol L}^{-1}$  NaOH stock solution (Titrisol, Merck) or by measurement  
190 with a pH meter (691 pH meter, Metrohm, Switzerland). Spiked feed solutions were

191 prepared by adding 3 kBq (in 10  $\mu$ L volume) of each of the tracers  $^{241}\text{Am}$ ,  $^{152}\text{Eu}$  and  
192  $^{244}\text{Cm}$  to 1 mL of the initial aqueous feed solution. All tracer-spiked aqueous feed  
193 solutions were prepared in advance and mixed thoroughly before contacting with the  
194 organic phase.

195 In a typical extraction experiment, 1 mL of the aqueous phase was mixed with an equal  
196 volume of pre-equilibrated organic phase and shaken at 22  $^{\circ}\text{C}$  at 2060 rpm in a vial. The  
197 organic phase was pre-equilibrated with a nitric acid solution of the same acid  
198 concentration as used for the feed solution of the extraction step. After the equilibration,  
199 the phase disengagement was enhanced by centrifugation of the vials for 5 min at 4000  
200 rpm using a Heraeus Labofuge 200 centrifuge. After phase separation, 300  $\mu$ L aliquots  
201 of the aqueous and organic phases were collected for gamma activity measurements.

202 Gamma spectrometric analysis of  $^{241}\text{Am}$  (using the 59.5 keV  $\gamma$ -peak) and  $^{152}\text{Eu}$  (using  
203 the 121.8 keV, 344 keV, 778.9 keV, 964 keV, 1112 keV and 1408 keV  $\gamma$ -peaks) was  
204 performed using a HPGe detector (Canberra Semiconductors N. V., Olen, Belgium)  
205 with Genie2000 software. The activities of  $\alpha$ -particle emitting radionuclides in each  
206 separated phase were determined using  $\alpha$  spectroscopy. Weighed amounts of the  
207 organic or aqueous phases were pipetted on a cupped steel planchet, heated under an  
208 infrared lamp (Theratherm 150 W, Osram, Germany) and subsequently burned in using  
209 a gas torch. The  $^{241}\text{Am}$  ( $E_{\alpha} = 5.485$  MeV) and  $^{244}\text{Cm}$  ( $E_{\alpha} = 5.805$  MeV) alpha peaks  
210 were measured using an  $\alpha$  spectrometer (Alpha Analyst, Canberra) equipped with  
211 Passivated Implanted Planar Silicon (PIPS)  $\alpha$  detectors (Canberra Olen N.V., Olen,  
212 Belgium). The spectra were analyzed using Apex Alpha software.

213 The *distribution ratio* ( $D$ ) of a given analyte was calculated as the ratio of the  
214 concentration of the analyte present in the organic phase over the concentration present

215 in the aqueous phase in accordance with Equation (1).

$$216 \quad D_M = \frac{[M_{org.eq.}]}{[M_{aq.eq.}]} \quad (1)$$

217 The highest and lowest distribution ratio limits for  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  determined by the  
218  $\alpha$  spectrometry detection limits in the aqueous or organic phases were 1000 and 0.001,  
219 respectively.  $\gamma$  spectrometry allowed the determination of distribution ratios for  $^{241}\text{Am}$   
220 between 200 and 0.05 and between 1000 and 0.001 for  $^{152}\text{Eu}$ .

221 The *separation factor* ( $SF$ ) of two elements was calculated from the distribution ratios  
222 of the respective elements in accordance with Equation (2):

$$223 \quad SF = \frac{D_{Mx}}{D_{My}} \quad (2)$$

### 224 **3. Results and discussion**

225 Solubility tests were conducted on the freshly synthesized extractant. The  
226 solubility of the extractant was lower than  $0.01 \text{ mol L}^{-1}$  in *n*-dodecane, resulting in a  
227 slurry with most of the compound left undissolved. It also shows to be insoluble in  
228 pentane, hexane and heptane. The  $\pi$ - $\pi$  stacking of the planar phenanthroline groups of  
229 EH-BTzPhen molecules might be a reason for the preferred crystallization over  
230 solubilisation in aliphatic diluents. The extractant proved to be soluble in various polar  
231 diluents; 1-octanol (up to  $0.2 \text{ mol L}^{-1}$ ) and the ionic liquid [A336][NO<sub>3</sub>] (up to  $0.2 \text{ mol}$   
232  $\text{L}^{-1}$ ). The compound showed a high solubility (during the synthesis and purification  
233 steps) in dichloromethane, chloroform and diethylether. In contrast to our EH-BTzPhen,  
234 the tridentate 2,6-Bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl]pyridine (PTEH), carrying  
235 identical moieties was highly soluble both in apolar kerosene as well as polar DCM and  
236 1-octanol.<sup>31</sup> For solvent extraction studies,  $0.01 \text{ mol L}^{-1}$  solutions of the EH-BTZPhen

237 in both 1-octanol and in Aliquat-336 nitrate ionic liquid were used. Scoping studies  
238 were performed to test the compatibility of the extractant in these two diluents with an  
239 acidic aqueous phase. 1 mol L<sup>-1</sup>, 0.75 mol L<sup>-1</sup> and 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> resulted in the  
240 formation of a white precipitate in the case of both solvents, which did not dissolve after  
241 several weeks. With 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> the organic phase remained clear, however a  
242 small amount of opaque layer was formed at the interphase. Protonation of the nitrogen  
243 atoms in the second or third position of triazole rings and subsequent inter-molecular *H*-  
244 bond formation can be a plausible reason for the observed precipitation. The  
245 unsubstituted 1*H*-1,2,3-triazole is a stronger base (pK<sub>a</sub> = 1.17)<sup>32</sup> than the 1,2,4 triazine  
246 (pK<sub>a</sub> < 0). In comparison to EH-BTzPhen, neither CyMe<sub>4</sub>BTBP, nor CyMe<sub>4</sub>BTPhen  
247 (both containing triazines) show acid-induced precipitation when their organic solutions  
248 are contacted with acidic aqueous phases. The acid-induced precipitation of EH-  
249 BTzPhen is a marked contrast with the result of the acid stability test using 1 mol L<sup>-1</sup>  
250 HNO<sub>3</sub> performed by Muller and Nash on EH-BTzBP in toluene.<sup>26</sup> The structural  
251 difference between the two compounds is the *cis*-locked conformation of the 1,10-  
252 phenanthroline moiety compared to the 2,2'-bipyridine unit. Contact of organic  
253 solutions of EH-BTzPhen with aqueous phases at lower acidities (pH 2-3) did not result  
254 in the formation of precipitates. Solvent extraction studies were conducted only at these  
255 pH values to prevent precipitation.

256

257 Since the structurally similar EH-BTzBP molecule was previously tested in a molecular  
258 diluent, we also tested our new *cis*-locked EH-BTzPhen in 1-octanol.<sup>26</sup> This scoping  
259 solvent extraction study did not result in extraction of <sup>241</sup>Am(III), <sup>244</sup>Cm(III) and  
260 <sup>152</sup>Eu(III) from 1 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> aqueous feed solution with 0.01 mol L<sup>-1</sup> EH-  
261 BTzPhen in 1-octanol:  $D_{Am} = (0.25 \pm 0.04)$ ,  $D_{Eu} = (0.094 \pm 0.001)$ . It is known that

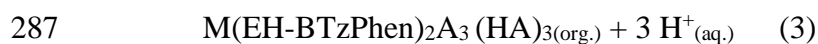
262 some soft *N*-atom donor extractants are able to extract the metal nitrates directly from  
263 acidic feed solutions without the need for a synergist. The formerly mentioned  
264 CyMe<sub>4</sub>BTBP and CyMe<sub>4</sub>BTPhen are examples of such tetradentate extractants. The  
265 tridentate 2,6-bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4yl]pyridine (PTEH) (in a solution  
266 of 0.2 mol L<sup>-1</sup> in kerosene/1-octanol mixture) was able to extract Am(III) selectively  
267 (*SF*<sub>Am/Eu</sub> ~ 80) without the addition of a synergist.<sup>31</sup>

268 However, some other *N*-atom donor extractants, like the tetradentate EH-BTzBP  
269 are not able to stabilize the metal nitrates in an aliphatic organic phase, but extraction is  
270 possible with the use of a lipophilic anion source.<sup>26</sup> Therefore, the addition of 2-  
271 bromohexanoic acid as a lipophilic anion source was tested with the present EH-  
272 BTzPhen extractant (Figure 2). Speciation studies of Eu(III) complexes with EH-  
273 BTzBP using time-resolved laser-fluorescence spectroscopy (TRLFS) did not show the  
274 presence of bromohexanoate anions in the first coordination sphere.<sup>35</sup> Therefore, it is  
275 assumed that bromohexanoate anions act as outer-sphere anions for charge  
276 compensation in the organic phase. Figure 2 shows that the extraction kinetics of  
277 0.01 mol L<sup>-1</sup> EH-BTzPhen + 1 mol L<sup>-1</sup> 2-bromohexanoic acid in 1-octanol is slow. The  
278 equilibrium distribution ratios were reached in 24 h for <sup>241</sup>Am(III) and <sup>244</sup>Cm(III) and  
279 within 12 h for <sup>152</sup>Eu(III). Equilibrium distribution ratios were (400 ± 100) for  
280 <sup>241</sup>Am(III), (190 ± 50) for <sup>244</sup>Cm(III) and (1.7 ± 0.2) for <sup>152</sup>Eu(III).

281

282 The solvent extraction mechanism for the EH-BTzBP/bromohexanoic acid/toluene  
283 solvent was suggested to be best described as a cation exchange between the acidic  
284 protons of 2-bromohexanoic acid and the trivalent metal ions and we assume a similar  
285 mechanism for the EH-BTzPhen analogue (Equation (3)).<sup>26</sup>





288 Where HA represents 2-bromohexanoic acid.

289 The use of 2-bromohexanoic acid would be difficult in nuclear fuel cycle applications as  
290 the introduction of high concentrations of bromine in the organic solvent is a  
291 disadvantage from the point of view of secondary waste treatment. Furthermore,  
292 radiation induced degradation would most probably liberate highly corrosive bromine  
293 from such a solvent.

294 Figure 3 shows the distribution ratios of  $^{241}\text{Am(III)}$ ,  $^{244}\text{Cm(III)}$  and  $^{152}\text{Eu(III)}$  for batch  
295 liquid-liquid extraction experiments using feed solutions with  $[\text{Ln(III)}] = 10^{-5} \text{ mol L}^{-1}$ ,  
296  $\text{pH} = 3$  and  $1 \text{ mol L}^{-1} \text{NH}_4\text{NO}_3$  and an organic phase composed of  $0.01 \text{ mol L}^{-1} \text{EH-}$   
297  $\text{BTzPhen}$  in  $[\text{A336}][\text{NO}_3]$  as a function of equilibration time. Kinetic experiments were  
298 conducted until 110 h, after which the  $\text{Am(III)}$  distribution values reached equilibrium,  
299 while distribution ratios of  $^{244}\text{Cm(III)}$  and  $^{152}\text{Eu(III)}$  still slightly increased. Such an  
300 extremely slow extraction is not advantageous in a continuous solvent extraction  
301 process, as it would require the design of a plant with large footprint and cost. The  
302 solvent radiolysis and equipment wear would also be more important in case of very  
303 long contact times. However, it is shown in our recent study using the  $\text{CyMe}_4\text{BTPPhen}$   
304 complexant in  $[\text{A336}][\text{NO}_3]$  that the slow kinetics can be significantly improved by  
305 increasing the temperature.<sup>20</sup> The time needed to reach the equilibrium is more  
306 dependent on factors affecting diffusion of species to and from the interphase. By  
307 comparing the kinetics of  $\text{CyMe}_4\text{BTPPhen}$  in  $[\text{A336}][\text{NO}_3]$  under comparable conditions  
308 as used in this study, we hypothesize that the high viscosity of the ionic liquid cannot be  
309 alone the reason.

310 We assume the reason for significantly slower kinetics of An(III) extraction by EH-  
311 BTzPhen as compared to CyMe<sub>4</sub>BTPhen is linked to the higher basicity of the 1,2,3-  
312 triazole rings compared to 1,2,4 triazines. Even when the acid concentration in the  
313 organic phase is not sufficient to cause a complete aggregation of the protonated EH-  
314 BTzPhen molecules (manifesting in visible precipitation) there might be a lower degree  
315 of association/supramolecular organization caused by an intermolecular *H*-bond  
316 network. In that case, not the single EH-BTzPhen molecules are the diffusing entities,  
317 but larger number of them, held together by a *H*-bond network. In liquids, according to  
318 the Stokes-Einstein equation the radius of the diffusing entity is inversely proportional  
319 to the diffusion coefficient. Thus the increase of diffusion coefficient of the extractant,  
320 caused by association via *H*-bonds can be the reason for the observed slow extraction  
321 kinetics.

322

323 The distribution ratios for <sup>241</sup>Am(III) and <sup>244</sup>Cm(III) reached values up to  $D_{Am} = (20 \pm 3)$ ,  
324  $D_{Cm} = (8 \pm 1)$ , respectively, while <sup>152</sup>Eu(III) distribution ratios reached values up to  $D_{Eu} =$   
325  $(0.307 \pm 0.003)$ . This is a factor of about 20 lower for An(III) and a factor of 6 lower for  
326 <sup>152</sup>Eu(III) compared to the 1-octanol diluent. In addition, the <sup>241</sup>Am(III)/<sup>152</sup>Eu(III)  
327 separation factors were lower in the case of the ionic liquid based solvent ( $SF_{Am/Eu} \sim 70$   
328 compared to  $SF_{Am/Eu} \sim 200$  in 1-octanol). These separation factors are similar to the one  
329 reported by Muller and Nash using EH-BTzBP in combination with 2-bromohexanoic  
330 acid in toluene.<sup>26</sup>

331 The equilibrium <sup>241</sup>Am(III)/<sup>152</sup>Eu(III) separation factor of  $SF_{Am/Eu} \approx (70 \pm 20)$  reached  
332 promising values for a minor actinide separation process. These distribution ratios are  
333 significantly lower, compared to those obtained with 0.01 mol L<sup>-1</sup> CyMe<sub>4</sub>BTPhen in

334 [A336][NO<sub>3</sub>]:  $D_{Am}$  (1000±250),  $D_{Cm} \sim$  (670±160),  $D_{Eu} =$  (9.9±0.2), while the Am/Eu  
335 separation factor is similar:  $SF_{Am/Eu} =$  (100±30). The lower distribution ratios in general  
336 might be an advantage for back-extraction of the An(III) from the loaded organic phase.  
337 The <sup>241</sup>Am(III)/<sup>244</sup>Cm(III) separation factor was between 2.1 – 3.5 throughout the  
338 investigated contact time (Figure 3), thus slightly higher than in the case of the first  
339 solvent (0.01 mol L<sup>-1</sup> EH-BTzPhen and 1 mol L<sup>-1</sup> 2-bromohexanoic acid in 1-octanol).  
340 The change of the triazinyl rings to 1,2,3-triazolyl rings thus lead to a slight increase of  
341 Am(III)/Cm(III) separation factors compared to CyMe<sub>4</sub>BTPPhen extractant in  
342 [A336][NO<sub>3</sub>] which typically shows a  $SF_{Am/Cm}$  1.4 – 1.8 at equilibrium and higher  
343 values under non-equilibrium conditions. In the case of EH-BTzPhen, it seems no such  
344 difference exists between the  $SF_{Am/Cm}$  at shorter or longer extraction times. From this it  
345 is hypothesized, that the higher  $SF_{Am/Cm}$  are related to the slightly stronger interaction  
346 between the triazole donating *N*-atoms and Am(III) as compared to the interaction with  
347 Cm(III).  
348 The effect of NH<sub>4</sub>NO<sub>3</sub> concentration on the distribution ratios of <sup>241</sup>Am(III), <sup>244</sup>Cm(III)  
349 and <sup>152</sup>Eu(III) was tested at 110 h equilibration time (Figure 4). The distribution ratios  
350 increased with increasing NH<sub>4</sub>NO<sub>3</sub> concentration. In general, the <sup>241</sup>Am(III)/(III) and  
351 Am(III)/Cm(III) selectivity remained constant over the range of NH<sub>4</sub>NO<sub>3</sub> concentration  
352 (disregarding some fluctuations that are presumably caused by measurement  
353 uncertainties). The increase of distribution ratios as a function of the nitrate  
354 concentration suggests that nitrate ions are serving as counter ions in the extracted  
355 complex. The exact extraction mechanism cannot be determined solely on the basis of  
356 solvent extraction experiments.  
357

358 In our efforts to develop a new, more performant tetradentate *N*-donor extractant  
359 molecule, the EH-BTzPhen was synthesized and subject to basic solvent extraction  
360 screening. During these screening studies the molecule displayed unfortunately  
361 important disadvantages, such as incompatibility with higher nitric acid concentrations  
362 and very slow extraction kinetics, indicating that its application in continuous processes  
363 will not be feasible using the investigated solvent composition and extraction  
364 parameters. Therefore, more advanced extractions studies (e.g. effect of acidity,  
365 temperature, ligand concentration) were not relevant and thus not performed.  
366 Notwithstanding these disadvantages, the interesting Am/Cm and Am/Eu separation  
367 factors supports further work on triazole-modified phenanthrolines to overcome the  
368 current issues.

#### 369 **4. Conclusions**

370 As conclusion, the newly synthesized lipophilic tetradentate, CHON-compliant  
371 soft-donor extractant EH-BTzPhen was found to provide interesting selectivity for  
372 An(III) over Eu(III) at low acidities. The compound is soluble in both 1-octanol and  
373 [A336][NO<sub>3</sub>]. The extraction of Am(III) and Cm(III) was possible in 1-octanol with the  
374 combined use of 2-bromohexanoic acid synergist. When [A336][NO<sub>3</sub>] is used as  
375 diluent, extraction of An(III) is feasible without the presence of synergist, although with  
376 slow extraction kinetics at 22 °C. The extractant formed a precipitate in contact with  
377 highly acidic feed solutions. The modulation of the electron density on two of the  
378 nitrogen atoms in the complexing cavity (e.g. by replacing 1,2,4-triazinyl with 1,2,3-  
379 triazol moieties) of CyMe<sub>4</sub>BTPhen retained the Am/Cm and Am/Eu selectivities, but at  
380 lower distribution ratios (beneficial for back-extraction), which might be exploited in  
381 further work involving modified 5-membered heterocycle moieties crafted on bipyridine  
382 or phenanthroline backbone. The use of CHON-compatible, non-flammable

383 [A336][NO<sub>3</sub>] as a diluent for the EH-BTzPhen allowed the extraction of An(III) ions  
384 without the addition of a synergist. This latter finding might be of interest for further  
385 research on complexants that proved to be effective only in the presence of 2-  
386 bromohexanoic acid or similar synergists.

387

388

389

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### 399 **Supplemental online material**

400 Supplementary data [<sup>1</sup>H and <sup>13</sup>C-NMR spectra of the EH-BTzPhen] are available  
401 online.

402

403

404 Figure 1. Chemical structures of the copounds used in this study. [A336][NO<sub>3</sub>] is  
405 represented by its main component, tri-n-octylmethylammonium nitrate ([N<sub>1888</sub>][NO<sub>3</sub>]).  
406 Two additional soft donor extractants, CyMe<sub>4</sub>BTPPhen and CyMe<sub>4</sub>BTBP are represented

407 to facilitate comparison of the structures. The numbering of nitrogen atoms in the  
408 triazynil rings are indicated for the sake of ease.

409 Figure 2. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm  
410 separation factors as a function of equilibration time. Extraction conditions:  $T = 22 \pm 1$   
411  $^{\circ}\text{C}$ ; 2060 rpm; a/o = 1/1; organic phase  $0.01 \text{ mol L}^{-1}$  EH-BTzPhen +  $1 \text{ mol L}^{-1}$   
412 2-bromohexanoic acid in 1-octanol, Aqueous phase: pH = 3;  $1 \text{ mol L}^{-1}$   $\text{NH}_4\text{NO}_3$ ,  
413  $[\text{Ln(III)}] = 10^{-5} \text{ mol L}^{-1}$  each.

414 Figure 3. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm  
415 separation factors as a function of equilibration time. Extraction conditions:  $T = 22 \pm 1$   
416  $^{\circ}\text{C}$ ; 2060 rpm; a/o = 1/1; organic phase  $0.01 \text{ mol L}^{-1}$  EH-BTzPhen in  $[\text{A336}][\text{NO}_3]$ ,  
417 Aqueous phase: pH = 3;  $1 \text{ mol L}^{-1}$   $\text{NH}_4\text{NO}_3$ ,  $[\text{Ln(III)}] = 10^{-5} \text{ mol L}^{-1}$  each.

418 Figure 4. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm  
419 separation factors as a function of nitrate ion concentration. Extraction conditions:  $T =$   
420  $22 \pm 1 \text{ }^{\circ}\text{C}$ ; 2060 rpm;  $t = 110 \text{ h}$ ; a/o = 1/1; organic phase  $0.01 \text{ mol L}^{-1}$  EH-BTzPhen in  
421  $[\text{A336}][\text{NO}_3]$ , Aqueous phase: pH = 3; various concentration of  $\text{NH}_4\text{NO}_3$ ,  $[\text{Ln(III)}] =$   
422  $10^{-5} \text{ mol L}^{-1}$  each.

423 Scheme 1. Synthetic pathway towards EH-BTzPhen.

424

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