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## COMMUNICATION

## Effective separation of the actinides Am(III) and Cm(III) by electronic modulation of Bis-(1,2,4-triazin-3-yl)phenanthrolines†

Ashfaq Afsar,<sup>a</sup> Laurence M. Harwood,<sup>\*a</sup> Michael J. Hudson,<sup>a</sup> James Westwood<sup>a</sup> and Andreas Geist<sup>b</sup>

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It has been shown that modification of the phenanthroline backbone of CyMe<sub>4</sub>-BTPPhen leads to subtle electronic modulation, permitting differential ligation of Am(III) and Cm(III) resulting in separation factors up to 7.

Neptunium (<sup>237</sup>Np), americium (<sup>241</sup>Am, <sup>243</sup>Am) and curium (<sup>244</sup>Cm, <sup>245</sup>Cm) are the principal source of the long-term radiotoxicity of nuclear waste remaining after PUREX reprocessing of uranium and plutonium from spent fuel. These so-called “minor actinides” arise from neutron irradiation of uranium and plutonium occurring within a nuclear reactor. One scheme to reduce further the radiotoxicity of the nuclear waste is to separate these minor actinides from the lanthanides also present in the post-PUREX raffinate; after which they can be transmuted, using high-energy neutrons, to short-lived radionuclides or stable non-radioactive elements.<sup>1</sup>

Whilst the aqueous oxidation state chemistry of neptunium is complex, americium and curium commonly exist as Am(III) and Cm(III) in aqueous solution. It has been shown that heterocycles containing soft *N*-donor atoms are capable of separating trivalent actinide ions [An(III)] from trivalent lanthanide ions [Ln(III)].<sup>2-8</sup> The selectivity of these reagents for An(III) over Ln(III) is believed to arise from a slightly more covalent interaction between the *N*-donor atoms and the 5*f* orbitals of An(III).<sup>2, 9,10</sup> Bis-(1,2,4-triazine) molecules, such as those depicted in Fig. 1, show high selectivities, with CyMe<sub>4</sub>-BTPPhen **3** showing optimum extraction performance to date.<sup>11</sup> The tridentate 2,6-bis(1,2,4-triazin-3-yl)pyridines (BTPs),<sup>12-14</sup> and the quadridentate 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs)<sup>15-17</sup> have been the focus of intensive research. It has been shown that the extraction properties of CyMe<sub>4</sub>-BTBP<sup>18-22</sup> **2** can be markedly improved by pre-organization of the molecule using a 1,10-phenanthroline moiety (BTPPhens).<sup>11, 23-27</sup>

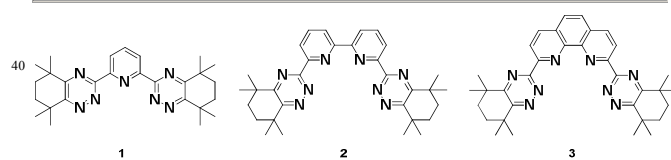
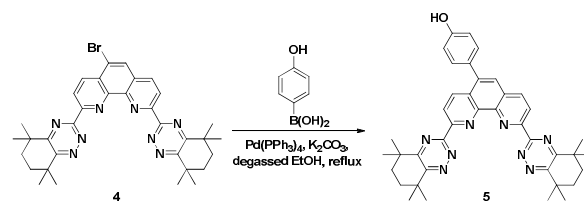


Fig. 1 Structural formulae of CyMe<sub>4</sub>-BTP **1**, CyMe<sub>4</sub>-BTBP **2** and CyMe<sub>4</sub>-BTPPhen **3**.

After separation of Am(III) and Cm(III) from the lanthanides, an additional refinement could be separation of the Am(III) from

Cm(III). However separation of these two closely related minor actinides is even more challenging than that of Am(III)/Eu(III). Separation of the adjacent actinide elements Am(III) and Cm(III) is an important concept in advanced nuclear fuel cycles proposed in order to reduce the transuranic content of nuclear waste to be placed in geological repositories.<sup>28, 29</sup> A fuel containing only Am(III) would ease the demands on a reactor for transmutation. Furthermore, removal of Cm(III) would reduce difficulties in fuel fabrication. However, Am(III) and Cm(III) are difficult to separate because they both possess the same charge, and are nearly the same size<sup>30</sup> resulting in very similar chemical properties.<sup>31</sup> The separation of Am(III) from Cm(III) using chromatography employing organic resins has been proposed,<sup>32</sup> however, it is technically challenging to couple chromatographic separations with the continuous liquid-liquid extraction processes favoured for large-scale nuclear separations.<sup>31</sup> A molecule that selectively binds either Am(III) or Cm(III) could offer substantial advantages for transmutation.<sup>31</sup> A few solvent extraction systems for separating Am(III) from Cm(III) have been developed,<sup>32-34</sup> but all have their drawbacks. Therefore, with the success of CyMe<sub>4</sub>-BTPPhen **3** in the separation of Am(III) and Eu(III), it was decided to apply this *N*-heterocyclic system to attempt separation of Am(III) and Cm(III).

In our previous studies,<sup>24</sup> we reported the effects of bromine substitution at the 5 and 5,6-positions of the 1,10-phenanthroline nucleus of C5-BTPPhen<sup>26</sup> which resulted in an enhancement of the separation selectivity of Am(III) from Eu(III). In this study, we have demonstrated that CyMe<sub>4</sub>-BTPPhen ligands with a bromo or 4-hydroxyphenyl substituent at the 5-position exhibit substantial selectivity for Am(III) over Cm(III). These molecules provide a means of amplifying the very small differences in the covalent interactions of Am(III) and Cm(III) with ligands.



Scheme 1 Synthesis of 5-phenol-CyMe<sub>4</sub>-BTPPhen **5**.

The 5-BrCyMe<sub>4</sub>-BTPPhen ligand **4** was synthesized following a synthetic protocol previously described.<sup>11, 24, 26, 35</sup> Replacement

of the bromine with a 4-hydroxyphenyl substituent was successfully achieved by Suzuki coupling<sup>36</sup> with 4-hydroxyphenylboronic acid to give 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPPhen **5** (Scheme 1).

Preliminary solvent extraction experiments were then carried out to determine the ability of CyMe<sub>4</sub>-BTPPhen **3**, 5-Br-CyMe<sub>4</sub>-BTPPhen **4** and 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPPhen **5** to extract Am(III) over Cm(III) and Ln(III). Solutions of **3**, **4** and **5** in 1-octanol (0.03 M) were contacted with nitric acid solutions spiked with <sup>241</sup>Am, <sup>244</sup>Cm and <sup>152</sup>Eu radiotracers and 20 mg/L of each lanthanide and yttrium.

The distribution ratios for Am(III) and Eu(III) ( $D_{Am}$  and  $D_{Eu}$ ) and the separation factors for Am(III) over Eu(III) ( $SF_{Am/Eu}$ ) for CyMe<sub>4</sub>-BTPPhen **3** in 1-octanol as a function of nitric acid concentration of the aqueous phase are shown in Fig. 2. High selectivities were observed for Am(III) over Eu(III) ( $SF_{Am/Eu} = ca. 70$  at 3 M HNO<sub>3</sub>) with a significant decrease in  $D$  values for Am(III) with increasing HNO<sub>3</sub> concentration.

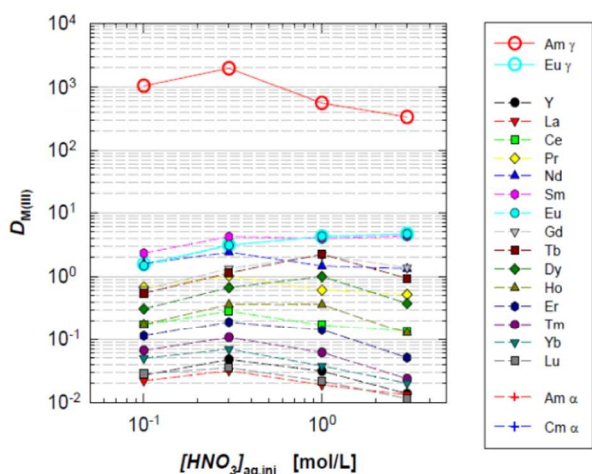


Fig. 2 Extraction of Am(III), Ln(III) and Y(III) by CyMe<sub>4</sub>-BTPPhen **3** in 1-octanol as a function of nitric acid concentration.

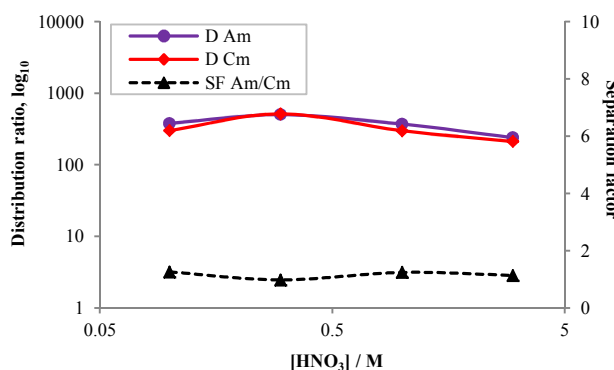


Fig. 3 Extraction of Am(III) and Cm(III) by CyMe<sub>4</sub>-BTPPhen **3** in 1-octanol as a function of nitric acid concentration.

Distribution ratios for Am(III) and Cm(III), and the separation factors at different nitric acid concentrations for **3** were also examined (Fig. 3). However, no selectivity was observed for Am(III) over Cm(III), over the range of concentrations of HNO<sub>3</sub>.

The extraction of Am(III), Ln(III) and Y(III) from nitric acid by 5-Br-CyMe<sub>4</sub>-BTPPhen **4** in 1-octanol is shown in Fig. 4. In this

case, the  $D$  values for Am(III) increased with increasing nitric acid concentration in the aqueous phase. The  $D$  values for Eu(III) and the other trivalent lanthanides [Ln(III)] and Y(III) were approximately one order of magnitude lower than with **3**, and the resulting separation factor ( $SF_{Am/Eu} = ca. 680$  at 3 M HNO<sub>3</sub>) was superior to that of **3**. In this instance, all the Ln(III) showed  $D$  values less than 1 over most HNO<sub>3</sub> concentrations.

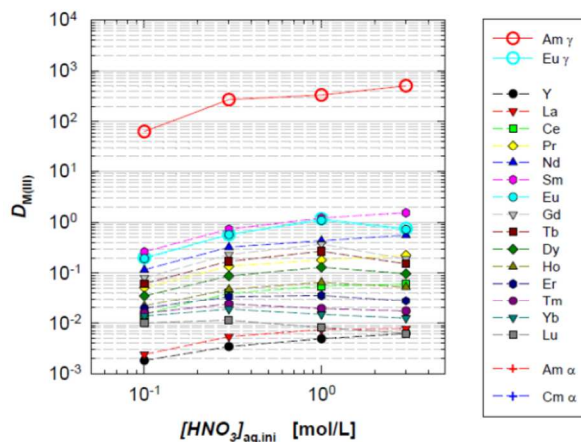


Fig. 4 Extraction of Am(III), Ln(III) and Y(III) by 5-Br-CyMe<sub>4</sub>-BTPPhen **4** in 1-octanol as a function of nitric acid concentration.

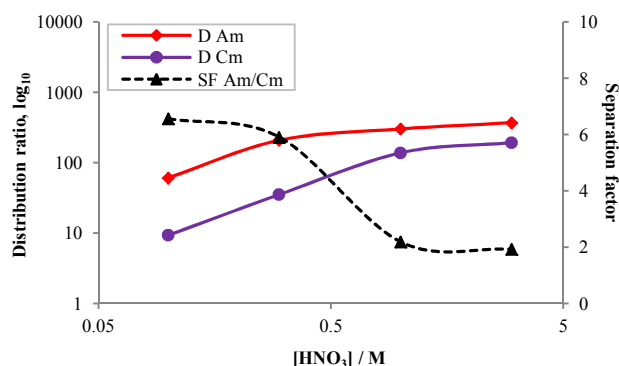


Fig. 5 Extraction of Am(III) and Cm(III) by 5-Br-CyMe<sub>4</sub>-BTPPhen **4** in 1-octanol as a function of nitric acid concentration.

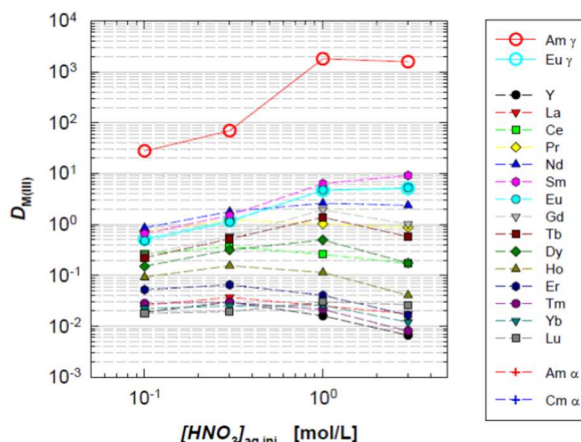


Fig. 6 Extraction of Am(III), Ln(III) and Y(III) by 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPPhen **5** in 1-octanol as a function of nitric acid concentration.

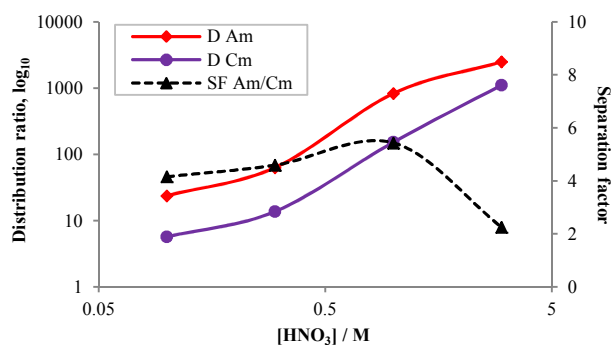


Fig. 7 Extraction of Am(III) and Cm(III) by 5-(4-hydroxyphenyl)CyMe<sub>4</sub>-BTPPhen **5** in 1-octanol as a function of nitric acid concentration.

Gratifyingly, **4** showed a significant selectivity for Am(III) over Cm(III), with an increase in  $D$  values for both Am(III) and Cm(III) and a lowering of selectivity being observed with increasing HNO<sub>3</sub> concentration, resulting in a maximum separation factor ( $SF_{Am/Cm}$ ) of ca. 7 at 0.1 M HNO<sub>3</sub> (Fig. 5).

The extraction of Am(III), Ln(III) and Y(III) from nitric acid by 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPPhen **5** in 1-octanol was subsequently investigated and compared with the corresponding data for **3** and **4**. Very high  $D$  values (Fig. 6) for Am(III) were obtained ( $D_{Am} > 1000$  at 3 M HNO<sub>3</sub>), indicating that the extraction of Am(III) by **5** was highly efficient. The  $D$  values for Ln(III) and Y(III) were somewhere between those obtained for **3** and **4**, and the resulting separation factor ( $SF_{Am/Eu}$ ) was ca. 320 at 3 M HNO<sub>3</sub>. The extraction of Am(III) and Cm(III) from nitric acid by **5** in 1-octanol is shown in Fig. 7. The  $D$  values for Am(III) and Cm(III) again increased with increasing HNO<sub>3</sub> concentration, this time resulting in a maximum separation factor ( $SF_{Am/Cm}$ ) of ca. 5 at 1 M HNO<sub>3</sub>.

In summary, we have demonstrated that functionalization of the phenanthroline backbone of CyMe<sub>4</sub>-BTPPhen **3** with 5-bromo or 5-(4-hydroxyphenyl) substituents makes the ligand more selective for Am(III) over Ln(III). More significantly, both 5-Br-CyMe<sub>4</sub>-BTPPhen **4** and 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPPhen **5** exhibit useful selectivity for Am(III) over Cm(III) with a maximum separation factor of ca. 7 at 0.1 M HNO<sub>3</sub> and ca. 5 at 1 M HNO<sub>3</sub>, respectively. In the case of **4** it may be that the inductive electron-withdrawing effect of the 5-bromo- substituent can explain why this is a less effective ligand for Ln(III) than CyMe<sub>4</sub>-BTPPhen **3**. Conversely, the mesomeric electron donating properties of the 5-(4-hydroxyphenyl)- substituent in **5** may explain why lanthanides such as samarium, europium and neodymium show increased  $D$  values at higher nitric acid concentrations. Given the relative distance of these substituents from the donor nitrogens of the triazine rings, any such effects are necessarily subtle but both systems provide notable differentiation between Am(III) and Cm(III).

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## Notes and references

<sup>a</sup> School of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 6AD, UK. E-mail: l.m.harwood@reading.ac.uk

<sup>b</sup> Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), 76021 Karlsruhe, Germany

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