HETEROCYCLES, Vol. 95, No. 1, 2017, pp. 575-586. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 8th August, 2016, Accepted, 14th November, 2016, Published online, 31st January, 2017
DOI: 10.3987/COM-16-S(S)26

EFFECTIVE SEPARATION OF Am(III) FROM Cm(III) USING MODIFIED BTPHEN LIGANDS

Ashfaq Afsar,[a] Alyn C. Edwards,[b] Andreas Geist,[c] Laurence M. Harwood,*[a] Michael J. Hudson,[a] James Westwood,[a] and Roger C. Whitehead[b]

[a]School of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 6AD, UK. E-mail: l.m.harwood@reading.ac.uk
[b]School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK. E-mail: roger.whitehead@manchester.ac.uk
[c]Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), 76021 Karlsruhe, Germany. E-mail: andreas.geist@kit.edu

Dedicated to Professor Dr. Masakatsu Shibasaki on the occasion of his 70th birthday

Abstract – Electronic modulation of CyMe$_4$-BTPhen with 5-bromo and 5-(4-hydroxyphenyl) substituents leads to enhanced separation of Am(III) from Cm(III) over 0.1 – 3 M HNO_3 ($SF_{Am/Cm}$ = ca. 9 at 0.1 M HNO_3). In addition, substituting bromine atoms at the 5 and 6 positions of the phenanthroline backbone provides a mean of separating Am(III) from Eu(III) ($SF_{Am/Eu}$ = ca. 240 at 3 M HNO_3).

After the removal of plutonium (Pu) and uranium (U) in the PUREX process, the dominant part of the long-term radiotoxicity and heat load of spent fuel arises from minor actinides such as americium (Am) and curium (Cm). Separation of the minor actinides [An(III)] from fission products, particularly the chemically very similar lanthanides [Ln(III)] by solvent extraction has been achieved using soft *N*-donor molecules containing the 1,2,4-triazine moiety.[1-6] Molecules such as the quadridentate ligands CyMe$_4$-BTBP **1** and CyMe$_4$-BTPhen **2** (Figure 1) have so far shown the most promising properties for these separations in liquid-liquid extraction tests. It has been demonstrated on genuine waste solution that CyMe$_4$-BTBP **1** is a suitable ligand for the separation of An(III) from Ln(III) in a laboratory-scale SANEX process, although the phase transfer agent DMDOHEMA (*N*,*N*'-dimethyl-*N*,*N*'-dioctyl[(hexyloxy)ethyl]malonamide) was needed to improve the otherwise slow extraction kinetics.[7-11] The advent of CyMe$_4$-BTPhen **2** improved the

kinetics of complexation without the need for added phase transfer reagent and is a promising alternative to CyMe$_4$-BTBP **1**. This ligand has the specific difference from the BTBPs in that CyMe$_4$-BTPhen **2** is held in the cis conformation required for complexation and is thus more preorganized for complex formation; furthermore it has a dipole moment and is surface active at the hydrophobic-hydrophilic interface.[12-16]

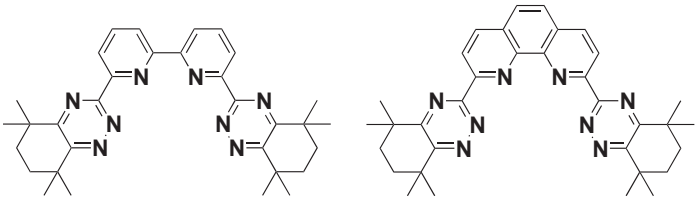


Figure 1. Structural formulae of CyMe$_4$-BTBP **1** and CyMe$_4$-BTPhen **2**

Although much progress has been made concerning the partition of minor actinides from the lanthanides, far less progress has been made on the separation of adjacent minor actinide elements Am and Cm. Separation of Am and Cm is an important concept in advanced nuclear fuel cycles proposed in order to reduce the transuranic content of nulear waste to be placed in geological repositories.[17,18] A fuel containing only Am would ease the demands on a reactor for transmutation. Furthermore, due to the high specific activity and high spontaneous fission in the decay of Cm, any dry or wet fabrication of Cm containing transmutation targets will require special shielding and handling.[19] However, Am(III) and Cm(III) are difficult to separate because both ions are most stable in solution in the trivalent oxidation state, they are nearly the same size, and form chemical bonds with very similar properties.[20,21,14,15] Different approaches have been investigated to carry out the very challenging separation of Am(III) and Cm(III).

The separation of Am(III) from Cm(III) using chromatography, employing organic resins, and selective oxidation of americium to Am(IV) and Am(VI) followed by extraction of the oxidized species have been proposed; however, it is technically challenging to couple chromatographic separations with the continuous liquid-liquid extraction processes favoured for large-scale nuclear separations. Furthermore, the higher valence Am species are potent oxidizers with standard aqueous reduction potentials in excess of + 1.7 V, which makes them difficult to produce and maintain long enough to accomplish a separation.[19,22,23] The drawbacks to the chromatographic and oxidation approaches have spurred efforts to separate Am(III) and Cm(III) directly through solvent extraction. A few solvent extraction systems for separating Am(III) from Cm(III) have been developed, but all have their drawbacks.[24-27,18-21]

Recently, we reported[28] a promising approach to direct separation of Am(III) from Cm(III) using modified bis-(1,2,4-triazin-3-yl)phenanthrolines (Br-CyMe$_4$-BTPhen **3** and 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen **4**, Figure 2), which resulted in an enhancement of the separation selectivity of Am(III) from Cm(III). We also reported[28-30] that the $SF_{Am/Eu}$ increased with bromine substitution at the 5-position of BTPhen.

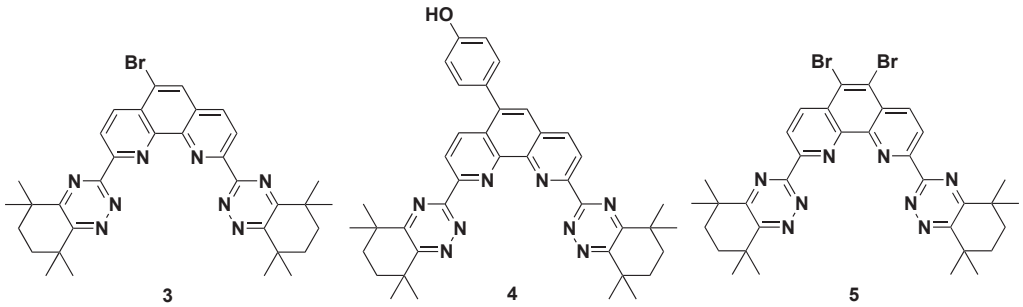
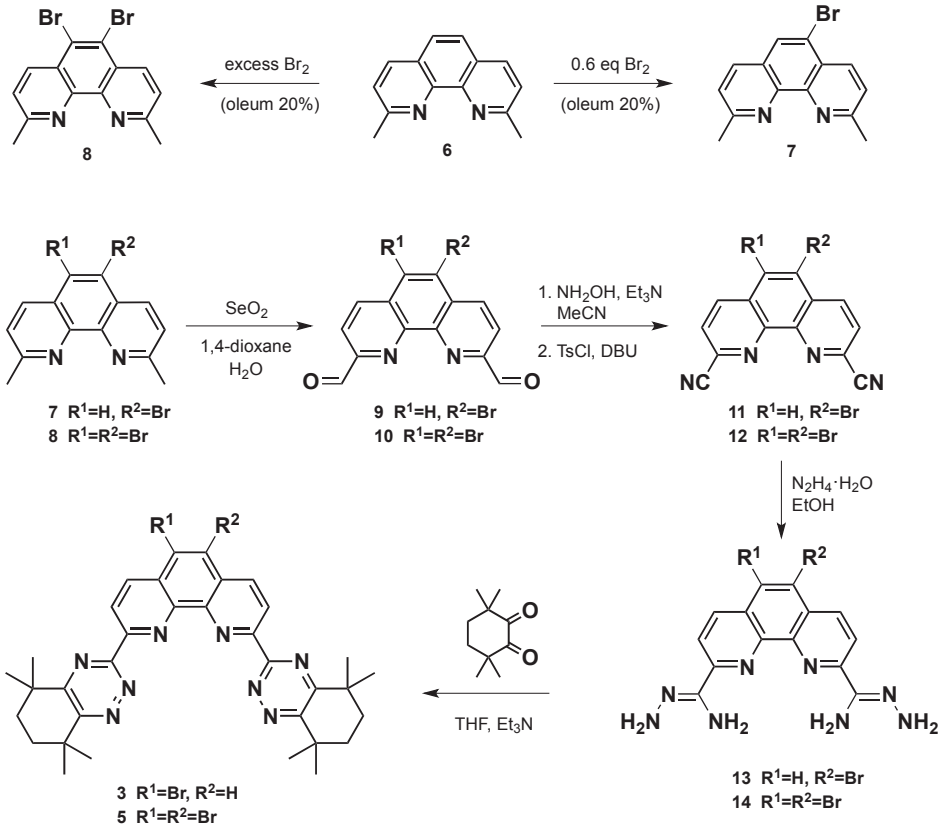
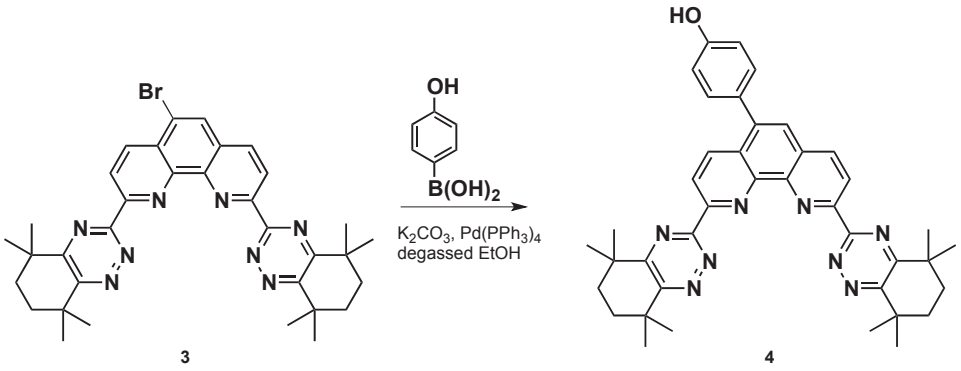


Figure 2. Structural formulae of Br-CyMe$_4$-BTPhen **3**, 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen **4** and Br$_2$-CyMe$_4$-BTPhen **5**

Therefore, with the success of **3** and **4** in the separation of Am(III) from Cm(III) and Eu(III), it was decided to explore further the role of contact time and electronic effects by substituting two bromine atoms at the 5 and 6 positions of CyMe$_4$-BTPhen. It was anticipated that having two bromine atoms at C-5 and C-6 would further depress the extraction of lanthanides by reducing electron density on the phenanthroline nitrogens of BTPhen, due to the cumulative inductive electron-withdrawing effects of the bromine substituents, but the effect on Am(III) – Cm(III) separation selectivity could not be predicted. The modified bis-(1,2,4-triazin-3-yl)phenanthrolines (BTPhen) ligands **3**, **4** and **5** were synthesized following a synthetic protocol previously described (Scheme 1).



Scheme 1. Synthetic protocol for ligands **3-5**



Scheme 1. Synthetic protocol for ligands **3-5** (continued)

Preliminary solvent extraction experiments were then carried out to determine the ability of $CyMe_4$-BTPhen **2**, 5-Br-$CyMe_4$-BTPhen **3**, 5-(4-hydroxyphenyl)-$CyMe_4$-BTPhen **4** and Br_2-$CyMe_4$-BTPhen **5** to extract Am(III) over Cm(III) and Eu(III). Solutions of **2**, **3**, **4** and **5** in 1-octanol (0.01 M) were contacted (30 – 240 min) with nitric acid solutions (0.1 – 3 M) spiked with ^{241}Am, ^{244}Cm and ^{152}Eu radiotracers. New to this study was to vary the contact time as well as the nitric acid concentration.

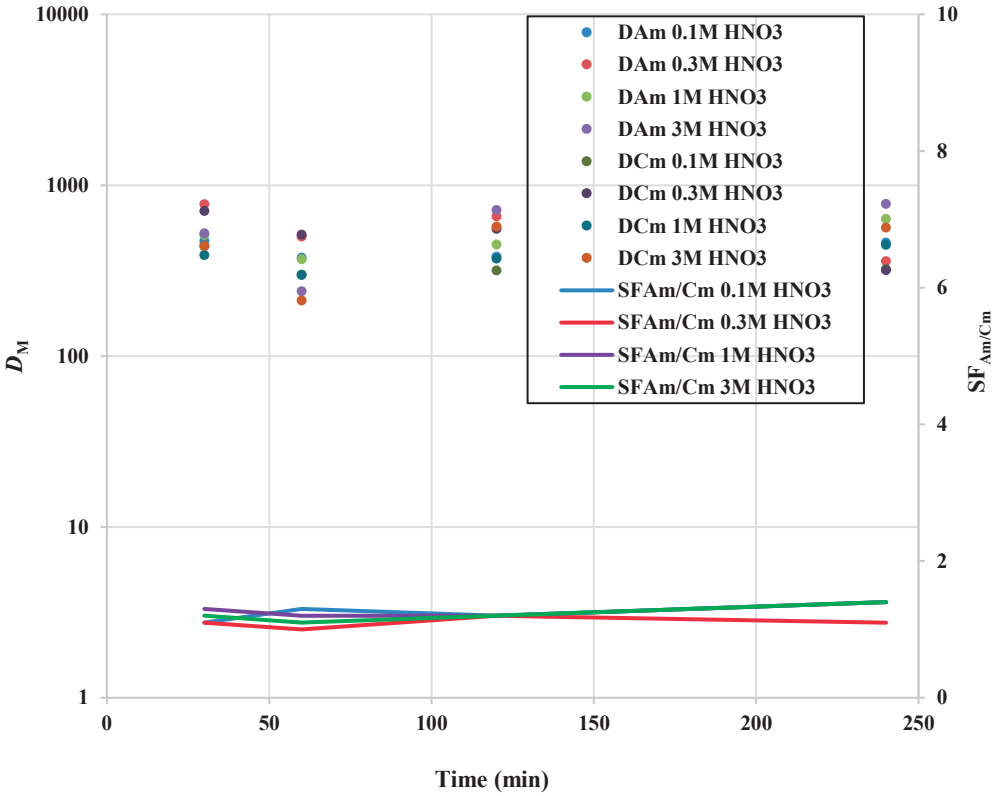


Figure 3. Distribution ratios (*D*) and separation factors (SF) of Am(III) and Cm(III) at varying HNO_3 concentration as a function of time for **2**

The distribution ratios (*D*) and separation factors (SF) of Am(III) and Cm(III) at varying HNO_3 concentration as a function of time for **2** are shown in Figure 3. High distribution ratios (D_{Am} = *ca.* 777 at 3

M HNO_3 and D_{Cm} = *ca.* 706 at 3 M HNO_3) were obtained for both Am(III) and Cm(III) at 0.1 – 3 M HNO_3 solution with no significant selectivity (max. $SF_{Am/Cm}$ = *ca.* 1 at 0.1 – 3 M HNO_3). The extraction of Am(III) and Cm(III) from nitric acid by 5-Br-CyMe$_4$-BTPhen **3** in 1-octanol as a function of time is shown in Figure 4. In this case, increase in *D* values for both Am(III) and Cm(III) and a lowering of selectivity were observed with increasing HNO_3 concentration, resulting in a maximum separation factor ($SF_{Am/Cm}$) of *ca.* 7 at 0.1 and 0.3 M HNO_3 with contact times of 60 and 30 min respectively. At 1 and 3 M HNO_3, higher *D* values for both Am(III) and Cm(III) (D_{Am} = *ca.* 480 and D_{Cm} = *ca.* 260 at 3 M HNO_3) were observed, but the selectivity for Am(III) over Cm(III) was significantly lower resulting in a maximum $SF_{Am/Cm}$ = *ca.* 4 (1 M HNO_3) and $SF_{Am/Cm}$ = *ca.* 2 (3 M HNO_3) with 30 min contact time.

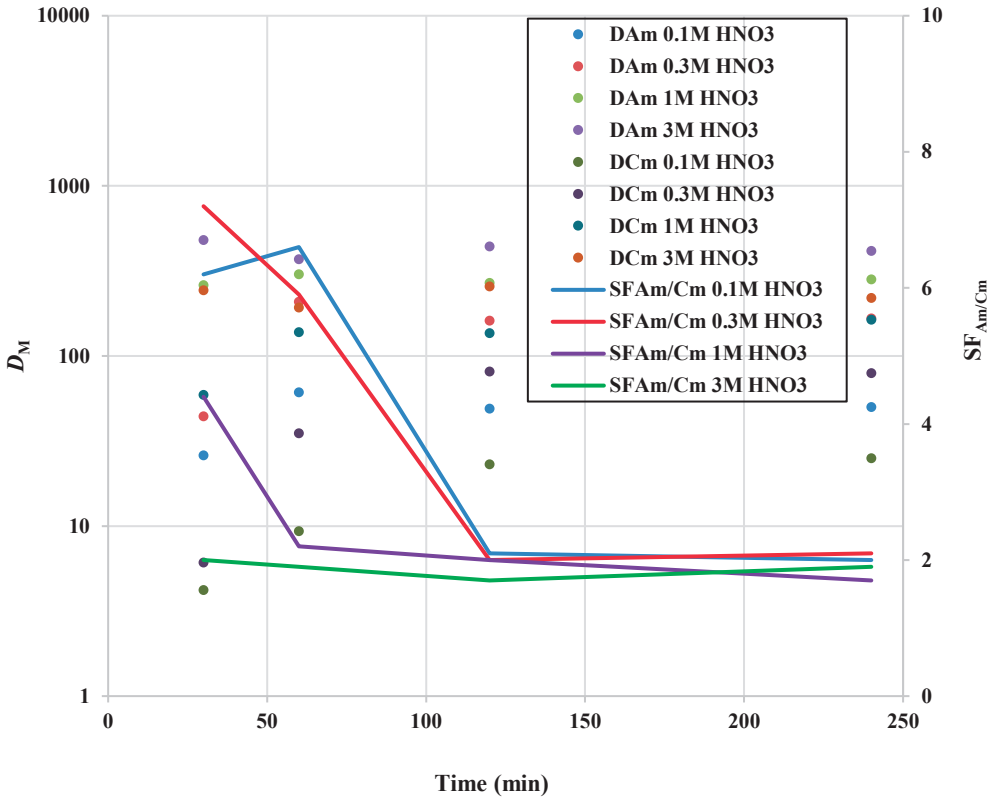


Figure 4. Distribution ratios (*D*) and separation factors (SF) of Am(III) and Cm(III) at varying HNO_3 concentration as a function of time for **3**

The extraction of Am(III) and Cm(III) from nitric acid as a function of time by 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen **4** in 1-octanol was subsequently investigated and compared with the corresponding data for **2** and **3**. Very high *D* values (Figure 5) for both Am(III) and Cm(III) were obtained (D_{Am} and D_{Cm} > 1000 at 3 M HNO_3), indicating that the extraction of Am(III) and Cm(III) by **5** was highly efficient and the resulting separation factor ($SF_{Am/Cm}$) was *ca.* 9 at 0.1 M HNO_3 with contact time of 30 min. An increase in *D* values for both Am(III) and Cm(III) and decrease in selectivity for Am(III) over Cm(III)

were observed with increasing HNO_3 concentration, resulting in a maximum separation factors ($SF_{Am/Cm}$) of *ca.* 7, 5 and 2 at 0.3, 1 and 3 M HNO_3 with contact times of 120, 60 and 60 min, respectively.

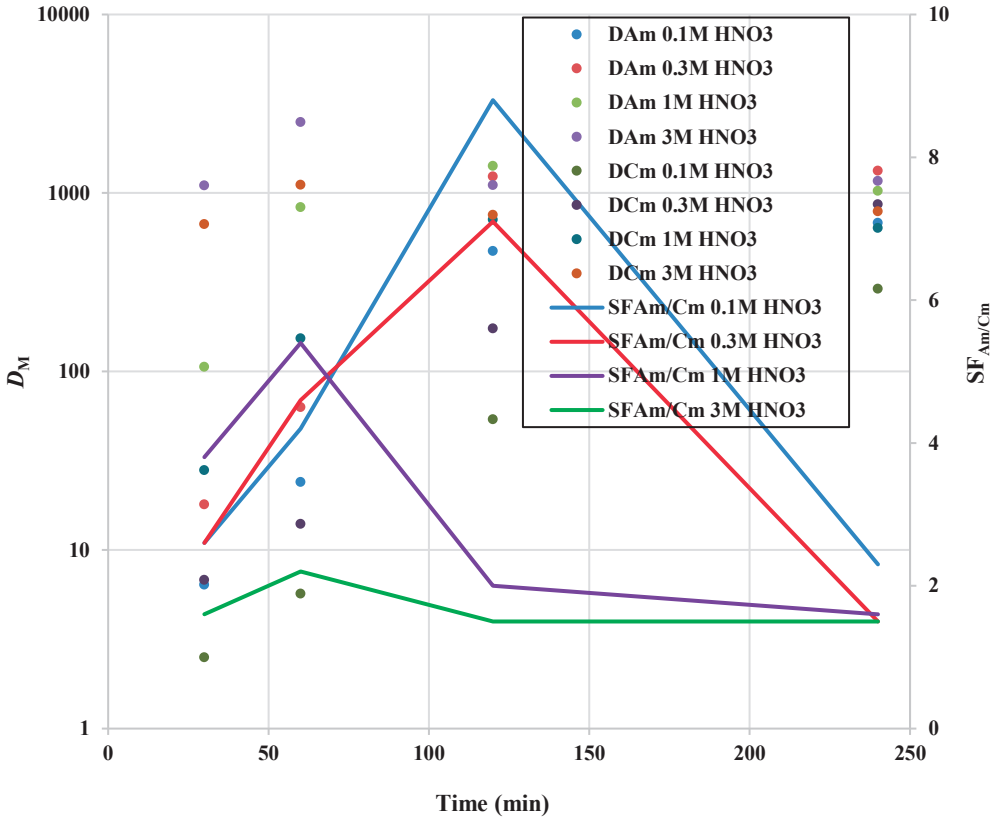


Figure 5. Distribution ratios (*D*) and separation factors (SF) of Am(III) and Cm(III) at varying HNO_3 concentration as a function of time for **4**

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 Br_2-$CyMe_4$-BTPhen **5** in 1-octanol as a function of nitric acid concentration of the aqueous phase are shown in Figure 6. High selectivities were observed for Am(III) over Eu(III) ($SF_{Am/Eu}$ = *ca.* 240 at 3 M HNO_3) with a significant increase in *D* values for Am(III) and Eu(III) with increasing HNO_3 concentration. Figure 6 also shows a very interesting feature; a suppression of the extraction of Eu(III) compared to $CyMe_4$-BTPhen **2** and Br- $CyMe_4$-BTPhen **3** giving *D* values well below 1 over most HNO_3 concentrations. The extraction of Am(III) and Cm(III) from nitric acid by **5** in 1-octanol is shown in Figure 7. The *D* values for both Am(III) and Cm(III) increased with increasing HNO_3 concentration, resulting in a maximum separation factor ($SF_{Am/Cm}$) of *ca.* 2 at 0.1 – 3 M HNO_3.

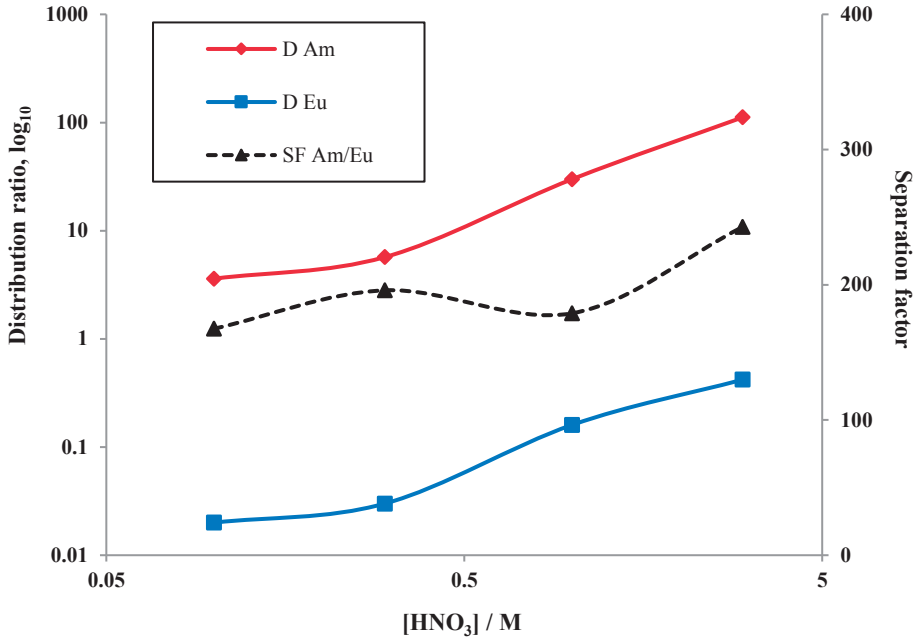


Figure 6. Extraction of Am(III) and Eu(III) by Br_2-$CyMe_4$-BTPhen **5** in 1-octanol as a function of nitric acid concentration (contact time 60 min)

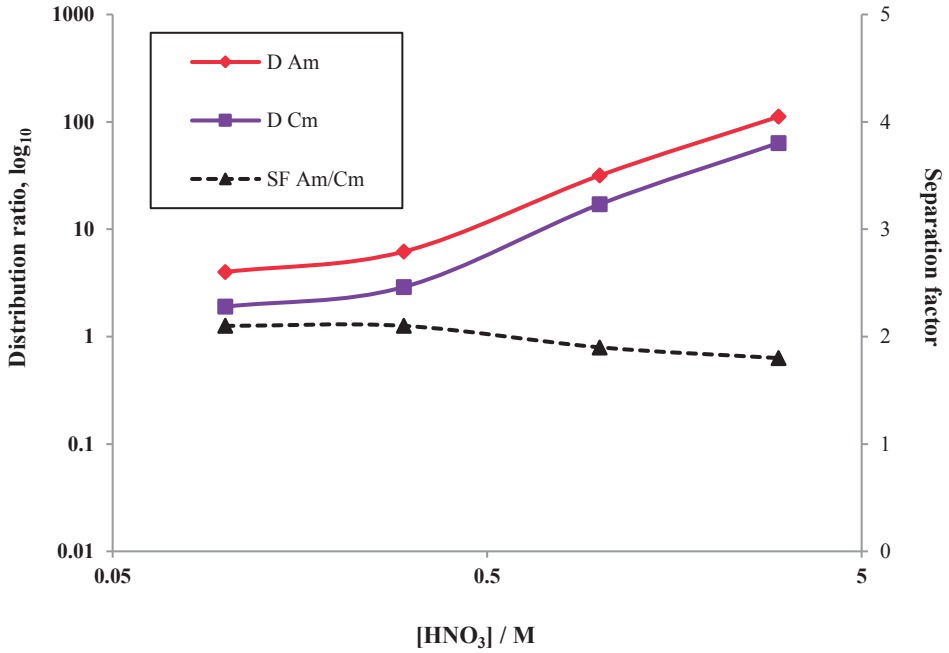


Figure 7. Extraction of Am(III) and Cm(III) by Br_2-$CyMe_4$-BTPhen **5** in 1-octanol as a function of nitric acid concentration (contact time 60 min)

In summary, we have reported a promising approach to the direct separation of Am(III) from Cm(III) via a liquid-liquid separation system that does not require oxidation of Am(III) or resort to chromatographic separations. We have also demonstrated that functionalization of the phenanthroline backbone of

$CyMe_4$-BTPhen with 5-bromo or 5-(4-hydroxyphenyl) substituents makes the ligand more selective for Am(III) over Cm(III). Both 5-Br-$CyMe_4$-BTPhen **3** and 5-(4-hydroxyphenyl)-$CyMe_4$-BTPhen **4** exhibited useful selectivity for Am(III) over Cm(III) with a maximum separation factor of *ca.* 9 at 0.1 M HNO_3 (30 min contact time) and *ca.* 7 at low HNO_3 concentrations (0.1 – 0.3 M) with contact times of 30 and 60 min, respectively. In the case of Br_2-$CyMe_4$-BTPhen it may be that the inductive electron-withdrawing effect of the 5,6-dibromo-substituents can explain why this is a less effective ligand for Eu(III). This has opened up a whole new range of extraction possibilities leading to very high Am(III) – Eu(III) and workable Am(III) – Cm(III) separations that are dependent on HNO_3 concentration and also contact time.

EXPERIMENTAL

General Procedures:

NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform ($CDCl_3$) and Deuterated DMSO (dimethyl sulfoxide-d_6) were used as solvents. Chemical shifts (δ values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublets, doublet of doublets of doublets and broad resonances respectively. Coupling constants (*J*) are quoted in Hertz. IR spectra were recorded as Nujol® mulls (N) on a Perkin Elmer RX1 FT-IR instrument. All the melting points were determined on a Gallenkamp melting point apparatus. Mass spectra (*m/z*) were recorded under conditions of electrospray ionisation (ESI). The ions observed were quasimolecular ions created by the addition of a hydrogen ion denoted as $[MH]^+$ or [M + Na]. The instrument used was Xcalibur Tune 2.1 (SP1).

2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (2).[12] To a suspension of 1,10-phenanthroline-2,9-dicarbohydrazonamide (0.58 g, 2 mmol) in THF (75 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (0.74 g, 4.4 mmol, 2.2 eq). Triethylamine (3.5 mL, 25.3 mmol) was added and the mixture was heated under reflux for 3 days. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with CH_2Cl_2 (25 mL). The filtrate was evaporated and the solid was triturated with Et_2O (100 mL). The insoluble solid was filtered and washed with further Et_2O (100 mL) and allowed to dry in air to afford the ligand **2** as a yellow solid (0.92 g, 83%); Mp 247-250 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.55 (s, 12H), 1.58 (s, 12H), 1.89 (s, 8H), 7.95 (s, 2H), 8.48 (d, *J* = 8.4 Hz, 2H), 8.90 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) = 29.3, 29.9, 33.7, 36.7, 37.6, 123.5, 127.6, 129.9, 137.4, 146.5, 153.9, 161.4, 163.3, 165.1; $C_{68}H_{76}N_{16}$ [2M + Na] requires *m/z* 1139.6331; (FTMS + c ESI) MS found *m/z* 1139.6345; IRν_{max} / cm^{-1} = 3490, 2962, 2931, 2866, 2224, 1622, 1588, 1554, 1516, 1499, 1472.

5-Bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (3).[28] To a suspension of 5-bromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (1.02 g, 2.7 mmol) in THF (75 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (0.96 g, 5.7 mmol, 2.1 eq). Triethylamine (25 mL, 179.4 mmol) was added and the mixture was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with petroleum ether (40-60 °C) (100 mL). The insoluble solid was filtered and washed with petroleum ether (40-60 °C) (100 mL) and allowed to dry in air to afford the **3** as a yellow solid (1.45 g, 84%); Mp 197-200 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.54 (s, 12H), 1.56 (s, 12H), 1.90 (s, 8H), 8.29 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.86 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.95 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) = 29.3, 29.8, 33.6, 33.8, 36.7, 37.5, 122.0, 124.0, 124.1, 128.9, 129.8, 130.6, 136.3, 137.3, 146.0, 146.9, 154.4, 154.7, 161.1, 161.3, 163.3, 163.4, 165.0, 165.1; $C_{34}H_{37}N_8Br$ $[MH]^+$ requires *m/z* 637.2397 and 639.2377; (FTMS + p ESI) MS found *m/z* 637.2392 and 639.2371; IR ν_{max} / cm^{-1} = 3531, 3486, 2959, 2927, 2865, 1644, 1609, 1510, 1475, 1452, 1439.

4-(2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthrolin-5-yl)-phenol (4).[28] A suspension of 5-bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (0.51 g, 0.8 mmol), tetrakis(triphenylphosphane)palladium(0) (0.04 g, 0.04 mmol, 0.05 eq), (4-hydroxyphenyl)boronic acid (0.13 g, 0.9 mmol, 1.1 eq) and potassium carbonate (0.15 g, 1.1 mmol, 1.4 eq) in degassed EtOH (75 mL) was heated to reflux for 18 h under nitrogen. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with EtOH (20 mL). The filtrate was evaporated and the solid residue was taken up in CH_2Cl_2 (150 mL) and water (100 mL) was added. The organic layer was washed with saturated brine (100 mL) and dried over $MgSO_4$. The filtrate was evaporated and the solid was triturated with Et_2O (100 mL). The insoluble solid was filtered and washed with Et_2O (50 mL) and allowed to dry in air to afford **4** as a yellow solid (0.31 g, 59%); Mp 250-252 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.58 (s, 12H), 1.61 (s, 12H), 1.93 (s, 8H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 8.8 Hz, 1H), 8.87 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) = 29.3, 29.9, 33.8, 36.7, 37.6, 115.6, 122.9, 123.7, 127.0, 128.2, 129.5, 129.5, 130.0, 136.3, 137.3, 140.2, 145.3, 146.5, 153.2, 153.3, 157.7, 161.0, 161.3, 163.5, 163.6, 165.2, 165.3; $C_{40}H_{43}N_8O$ $[MH]^+$ requires *m/z* 651.3554; (FTMS + p ESI) MS found *m/z* 651.3553; IR ν_{max} / cm^{-1} = 3399, 2962, 2931, 2865, 1611, 1587, 1514, 1471, 1456, 1389, 1365.

5,6-Dibromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (5). To a suspension of 5,6-dibromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (0.51 g, 1.1 mmol) in pyridine (50 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (0.45 g, 2.7 mmol, 2.5 eq). The suspension was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with petroleum ether (40-60 °C) (50 mL). The insoluble solid was filtered and washed with petroleum ether (40-60 °C) (25 mL) and allowed to dry in air to afford the **5** as a yellow solid (0.04 g, 5%); Mp 142-145 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.54 (s, 12H), 1.55 (s, 12H), 1.90 (s, 8H), 8.90 (d, J = 8.0 Hz, 2H), 8.98 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) = 29.3, 29.8, 33.6, 33.7, 36.7, 37.5, 124.6, 126.3, 129.6, 138.6, 145.9, 154.7, 160.8, 163.6, 165.1; $C_{34}H_{36}N_8Br_2$ $[MH]^+$ requires *m/z* 715.1502, 717.1482 and 719.1462; (FTMS + p ESI) MS found *m/z* 715.1486, 717.1466 and 719.1446; IR ν_{max} / cm^{-1} = 2958, 2930, 2868, 1702, 1584, 1514, 1458, 1363, 1244.

Solvent Extraction Experiments. Experiments were performed extracting ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) from HNO_3 (varied concentration) into 10 mmol/L BTPhen in 1-octanol. Each 500 µL of organic and aqueous phases were contacted on a vortex shaker (40 Hz) equipped with a temperature control unit set to 20 °C. Contacting time was varied. After phase separation by centrifugation, ^{241}Am(III) and ^{152}Eu(III) were determined by gamma counting (Packard Cobra Auto Gamma 5003) in 300 µL aliquots of both phases. ^{241}Am(III) and ^{244}Cm(III) were determined by alpha spectrometry (Canberra 7401) following dilution of aqueous samples or back extraction of organic samples into a 0.5 M ammonium glycolate solution adjusted to pH 4. An uncertainty of 20% was estimated for the distribution ratios measurements, which were not repeated.

ACKNOWLEDGEMENTS

The authors thank the UK Engineering and Physical Sciences Research Council (EPSRC) for funding. Use of the Chemical Analysis Facility (CAF) at the University of Reading is gratefully acknowledged. All data supporting this study are reported in this paper and electronic supplementary information (ESI). Any enquiries about the data should be addressed to the corresponding author.

REFERENCES

1. J.-H. Lan, W.-Q. Shi, L.-Y. Yuan, Y.-L. Zhao, J. Li, and Z.-F. Chai, *Inorg. Chem.*, 2011, **50**, 9230.
2. C.-L. Xiao, C.-Z. Wang, L.-Y. Yuan, B. Li, H. He, S. Wang, Y.-L. Zhao, Z.-F. Chai, and W.-Q. Shi, *Inorg. Chem.*, 2014, **53**, 1712.
3. F. W. Lewis, M. J. Hudson, and L. M. Harwood, *Synlett*, 2011, 2609.

4. M. J. Hudson, L. M. Harwood, D. M. Laventine, and F. W. Lewis, *Inorg. Chem.*, 2012, **52**, 3414.
5. F. W. Lewis, L. M. Harwood, M. J. Hudson, U. Mullich, and A. Geist, *Chem. Commun.*, 2015, **51**, 9189.
6. P. J. Panak and A. Geist, *Chem. Rev.*, 2013, **113**, 1199.
7. M. R. S. J. Foreman, M. J. Hudson, A. Geist, C. Madic, and M. Weigl, *Solvent Extr. Ion Exch.*, 2005, **23**, 645.
8. M. Nilsson, C. Ekberg, M. Foreman, M. Hudson, J. O. Liljenzin, G. Modolo, and G. Skarnemark, *Solvent Extr. Ion Exch.*, 2006, **24**, 823.
9. M. G. B. Drew, M. R. S. J. Foreman, C. Hill, M. J. Hudson, and C. Madic, *Inorg. Chem. Commun.*, 2005, **8**, 239.
10. D. Magnusson, B. Christiansen, M. R. S. Foreman, A. Geist, J. P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, and C. Sorel, *Solvent Extr. Ion Exch.*, 2009, **27**, 97.
11. T. Retegan, M. Drew, C. Ekberg, E. L. Engdahl, M. J. Hudson, A. Fermvik, M. R. S. Foreman, G. Modolo, and A. Geist, *Solvent Extr. Ion Exch.*, 2014, **32**, 720.
12. F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. 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.
13. F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, V. Hubscher-Bruder, V. Videva, F. Arnaud-Neu, K. Stamberg, and S. Vyas, *Inorg. Chem.*, 2013, **52**, 4993.
14. J.-H. Lan, W.-Q. Shi, L.-Y. Yuan, J. Li, Y.-L. Zhao, and Z.-F. Chai, *Coord. Chem. Rev.*, 2012, **256**, 1406.
15. N. T. Coogan, M. A. Chimes, J. Raftery, P. Mocilac, and M. A. Denecke, *J. Org. Chem.*, 2015, **80**, 8684.
16. D. M. Whittaker, T. L. Griffiths, M. Helliwell, A. N. Swinburne, L. S. Natrajan, F. W. Lewis, L. M. Harwood, S. A. Parry, and C. A. Sharrad, *Inorg. Chem.*, 2013, **52**, 3429.
17. S. Pillon, J. Somers, S. Grandjean, and J. Lacquement, *J. Nucl. Mater.*, 2003, **320**, 36.
18. F. Lebreton, D. Prieur, D. Horlait, T. Delahaye, A. Jankowiak, C. Léorier, F. Jorion, E. Gavilan, and F. Desmoulière, *J. Nucl. Mater.*, 2013, **438**, 99.
19. 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.
20. F. David, *J. Less Common Met.*, 1986, **121**, 27.
21. M. P. Jensen, R. Chiarizia, I. A. Shkrob, J. S. Ulicki, B. D. Spindler, D. J. Murphy, M. Hossain, A. Roca-Sabio, C. Platas-Iglesias, A. de Blas, and T. Rodríguez-Blas, *Inorg. Chem.*, 2014, **53**, 6003.
22. G. Modolo, P. Kluxen, and A. Geist, *Radiochim. Acta*, 2010, **98**, 193.

23. B. J. Mincher, N. C. Schmitt, B. K. Schuetz, T. C. Shehee, and D. T. Hobbs, *RSC Adv.*, 2015, **5**, 27205.
24. S. Chapron, C. Marie, G. Arrachart, M. Miguirditchian, and S. Pellet-Rostaing, *Solvent Extr. Ion Exch.*, 2015, 1.
25. C. Rostaing, C. Poinssot, D. Warin, P. Baron, and B. Lorraina, *Procedia Chem.*, 2012, **7**, 367.
26. Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, and Y. Morita, *Solvent Extr. Ion Exch.*, 2014, **32**, 179.
27. J. Borrini, A. Favre-Reguillon, M. Lemaire, S. Gracia, G. Arrachart, G. Bernier, X. Hérès, C. Hill, and S. Pellet-Rostaing, *Solvent Extr. Ion Exch.*, 2015, **33**, 224.
28. A. Afsar, L. M. Harwood, M. J. Hudson, J. Westwood, and A. Geist, *Chem. Commun.*, 2015, **51**, 5860.
29. A. Afsar, D. M. Laventine, L. M. Harwood, M. J. Hudson, and A. Geist, *Chem. Commun.*, 2013, **49**, 8534.
30. A. Afsar, L. M. Harwood, M. J. Hudson, P. Distler, and J. John, *Chem. Commun.*, 2014, **50**, 15082.