

# *Separation of minor actinides from lanthanides using immobilized ligand systems: the role of the counterion*

Article

Accepted Version

Afsar, A., Distler, P., Harwood, L. ORCID: <https://orcid.org/0000-0002-8442-7380>, John, J., Babra, J. S., Selfe, Z., Cowell, J. and Westwood, J. (2019) Separation of minor actinides from lanthanides using immobilized ligand systems: the role of the counterion. *Heterocycles*, 99 (2). pp. 825-833. ISSN 1881-0942 doi: 10.3987/COM-18-S(F)71 Available at <https://centaur.reading.ac.uk/80779/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: [http://dx.doi.org/10.3987/COM-18-S\(F\)71](http://dx.doi.org/10.3987/COM-18-S(F)71)

Publisher: The Japan Institute of Heterocyclic Chemistry

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

[www.reading.ac.uk/centaur](http://www.reading.ac.uk/centaur)

**CentAUR**

Central Archive at the University of Reading

Reading's research outputs online

## SEPARATION OF MINOR ACTINIDES FROM LANTHANIDES USING IMMOBILIZED LIGAND SYSTEMS: THE ROLE OF THE COUNTERION

**Ashfaq Afsar,<sup>a</sup> Petr Distler,<sup>b</sup> Laurence M. Harwood,<sup>a\*</sup> Jan John,<sup>b</sup> Jasraj S.  
Babra,<sup>a</sup> Zoe Y. Selfe,<sup>a</sup> Joeseeph Cowell,<sup>a</sup> and James Westwood<sup>a</sup>**

a. Chemical Sciences Division, University of Reading, Whiteknights, Reading,  
Berkshire RG6 6AD, UK. E-mail: l.m.harwood@reading.ac.uk

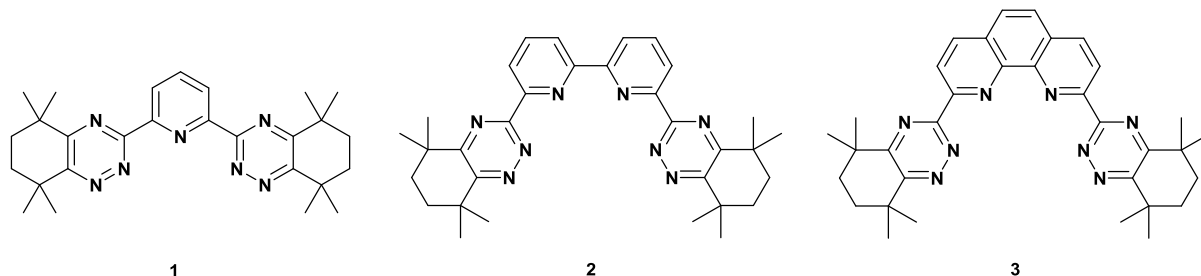
b. Department of Nuclear Chemistry, Czech Technical University in Prague,  
Břehová 7, 11519 Prague 1, Czech Republic. E-mail: jan.john@fjfi.cvut.cz

**Abstract** – A CyMe<sub>4</sub>-BTPhen functionalized silica gel that selectively extracts Am(III) over Eu(III) from 4 M HNO<sub>3</sub> with a separation factor > 154 has been developed. Evidence is presented that the counterion surrounding the M(III) in the proposed 1:1 [BTPhen:M(III)] complex plays an important role in the complexation of Am(III) and Eu(III).

Separation of minor actinides (Am/Cm) from lanthanides is a key step in the reduction of radiotoxicity and thermal emission of nuclear waste.<sup>1</sup> The removal of these elements, which account for ~ 0.1% by mass but for ~ 90% long-lived radiotoxicity of the waste could reduce both the duration of the radiological hazard and the volumes of high-level waste.<sup>2,3</sup> One proposed approach currently being studied for the long-term management of high-level waste after PUREX (plutonium and uranium redox extraction) reprocessing currently used in Europe is to separate the minor actinides (An) from the lanthanides (Ln); after which an can be transmuted into short-lived radionuclides or stable non-radioactive elements using high-energy neutrons in a generation iv reactor.<sup>4-9</sup> However, this separation is very difficult given the similar chemical properties of the Am(iii), Cm(iii) and Ln(iii).<sup>10</sup>

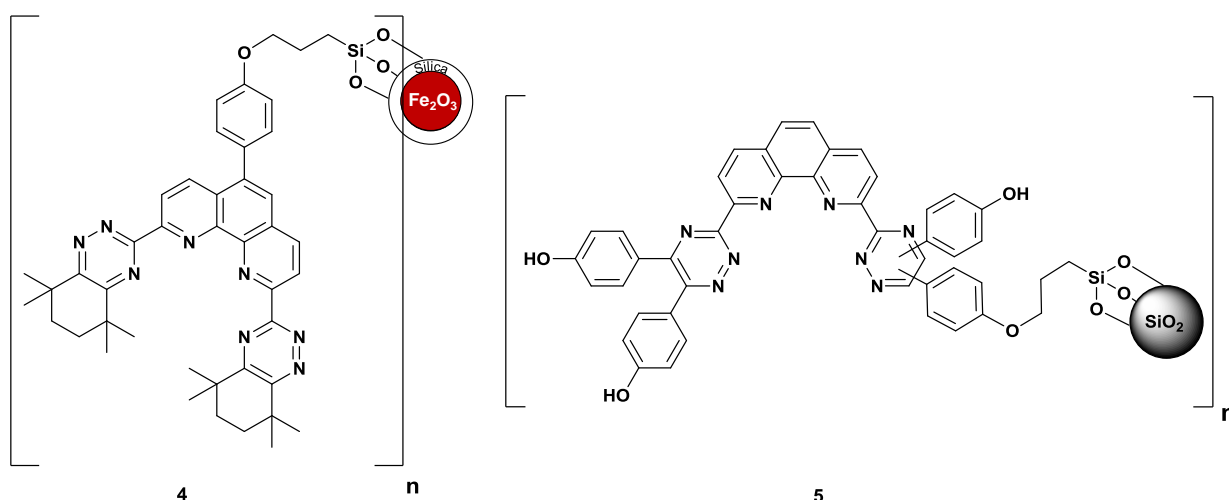
Nevertheless, previous studies have shown that soft *N*-donor ligands containing the 1,2,4-triazine moiety (Figure. 1) are capable of separating An(III) from Ln(III) in a solvent-based SANEX (Selective ActiNide EXtraction) process.<sup>11-13</sup> The selectivity of these reagents for An(III) over Ln(III) is believed to arise from a larger degree of covalency in the An(III)-*N* bond.<sup>14-16</sup> Bis-(1,2,4-triazine) molecules, such as the tridentate 2,6-bis(1,2,4-triazine-3-yl)pyridines (BTPs), and the quadridentate 6,6'-bis(1,2,4-triazin-3-yl)-

2,2'-bipyridines (BTBPs) depicted in Figure. 1, show high selectivities, with 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (CyMe<sub>4</sub>-BTPhen 3) showing optimum extraction performance in the laboratory to date.<sup>17–20</sup>



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

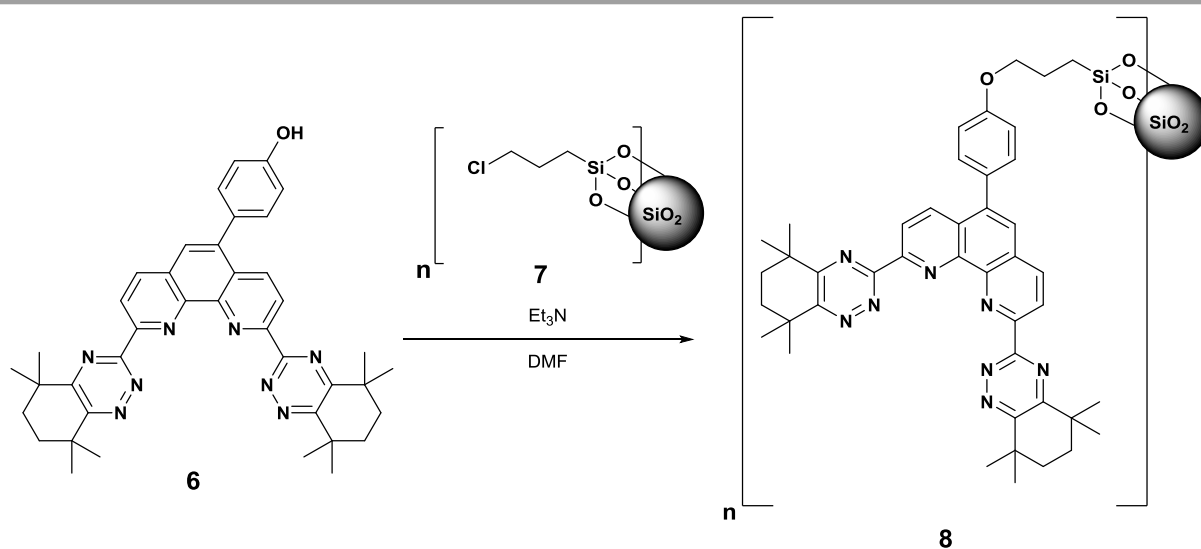
Although several other partitioning processes<sup>21</sup> have also been proposed and studied to separate An(III) from Ln(III), most of these processes utilize liquid-liquid extraction technology that brings certain disadvantages, in particular requiring large volumes of organic solvents, which can become degraded, reducing performance and needing to be disposed as secondary waste.<sup>22–25</sup> Furthermore, liquid-liquid extraction processes often require phase modifiers and can encounter problems with third phase formation.<sup>26</sup> To overcome the disadvantages of liquid-liquid extraction, systems based on solid phase extractants have been proposed.<sup>23–28</sup> We have recently developed and reported magnetic nanoparticle (MNP) and silica gel-based solid phase extractants (Figure. 2), where we have demonstrated that immobilized BTPhen type ligands could be used either to extract both An(III) and Ln(III) at low concentrations of HNO<sub>3</sub> or to extract An(III) selectively over Ln(III) at high concentrations of HNO<sub>3</sub>.<sup>29,30</sup>



**Figure 2.** Structural formulae of CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub>-coated MNP **4** and tetra(4-hydroxyphenyl)-BTPhen-functionalized SiO<sub>2</sub> gel **5**

Previously, we reported a partitioning process for minor actinides and lanthanides based on a column separation technique using the novel tetra(4-hydroxyphenyl)-BTPhen-functionalized SiO<sub>2</sub> gel **5**.<sup>29</sup> Herein, we report the synthesis and extraction properties of a new CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** and investigations into the nature of the counterion influence on extraction efficiency.

The (4-hydroxyphenyl) functionalized CyMe<sub>4</sub>-BTPhen ligand **6** was synthesized following a previously described protocol and was then immobilized onto commercially available chloropropyl-functionalized SiO<sub>2</sub> gel **7** as shown in Scheme 1.<sup>30</sup>



**Scheme 1.** Immobilization of (4-hydroxyphenyl) functionalized CyMe<sub>4</sub>-BTPhen **6** on silica gel

Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA) and thermogravimetric analysis (TGA) were used to assess the degree of incorporation of ligand **6** onto the silica surface. The presence of absorption bands at 1500–1600 cm<sup>-1</sup> assigned to C=C aromatic vibrations in the FT-IR spectrum (ESI†) for **8** provided evidence of the covalent functionalization of **6** onto the SiO<sub>2</sub> surface. EA (ESI†) showed an increase in the content of CHN compared to chloropropyl-functionalized SiO<sub>2</sub> gel **7** and TGA (ESI†) allowed the determination of the degree of surface modification through comparison of the relative mass loss compared to **7** indicating that the content of **6** in the CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** was ~ 25% w/w.

In the initial investigations, the aqueous solutions for the immobilized ligand extraction experiments were prepared by spiking nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>) solutions (0.001 – 4 M) with stock

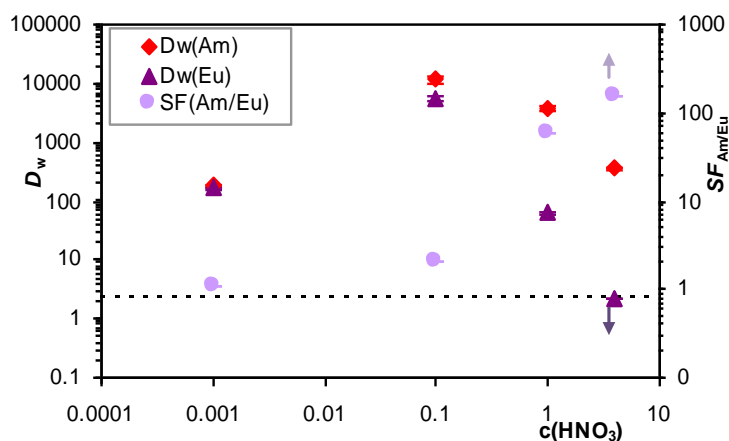
solutions of  $^{241}\text{Am}$  and  $^{152}\text{Eu}$  and then adding 1 mL of the spiked aqueous solution to an accurately weighed amount of CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** or CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub>-coated MNPs **4**. The suspensions were sonicated for 10 min and shaken at 1800 rpm for 90 min. After centrifuging for 10 min, aliquots of the supernatant were separated and taken for gamma measurements. The weight distribution ratios are defined as  $D_w = (I_0 - I)/I \cdot V/m$ , where  $I_0$  and  $I$  were initial and final count rates in the taken standard/aliquot,  $V$  is a volume of an aqueous phase shaken and  $m$  is a mass of the material **8** or **4**. The separation factor is  $SF_{\text{Am/Eu}} = D_{w\text{Am}} / D_{w\text{Eu}}$ .

Extractions were studied at HNO<sub>3</sub> and HClO<sub>4</sub> concentrations of 0.001 M, 0.1 M, 1 M and 4 M. The weight distribution ratios ( $D_{w\text{Am}}$  and  $D_{w\text{Eu}}$ ) and separation factors for Am(III) over Eu(III) ( $SF_{\text{Am/Eu}}$ ) for CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** as a function of HNO<sub>3</sub> concentration are shown in Figure. 3. High weight distribution ratios ( $D_w > 160$ ) were obtained for both Am(III) and Eu(III) at 0.001 M HNO<sub>3</sub> solution with no significant selectivity ( $SF_{\text{Am/Eu}} = 1.1 \pm 0.1$ ) for Am(III) over Eu(III). At 0.1 M HNO<sub>3</sub>, there was an increase in  $D_w$  values for both Am(III) ( $D_{w\text{Am}} = 11630 \pm 2033$ ) and Eu(III) ( $D_{w\text{Eu}} = 5618 \pm 720$ ) resulting in  $SF_{\text{Am/Eu}} = 2.1 \pm 0.4$ . Subsequently, decreases in the  $D_w$  values for both Am(III) and Eu(III) were observed ( $D_{w\text{Am}} = 3813 \pm 384$ ,  $D_{w\text{Eu}} = 63.9 \pm 2.3$ ) at 1 M HNO<sub>3</sub> solution, but now a higher separation factor ( $SF_{\text{Am/Eu}} = 60 \pm 6$ ) resulted. Finally, at 4 M HNO<sub>3</sub>, although a decrease in  $D_w$  value for Am (III) gave  $D_{w\text{Am}} = 354 \pm 12$ ; the  $D_w$  value observed for Eu(III) was  $< 2.3$  and the resulting separation factor was  $SF_{\text{Am/Eu}} > 154$ .

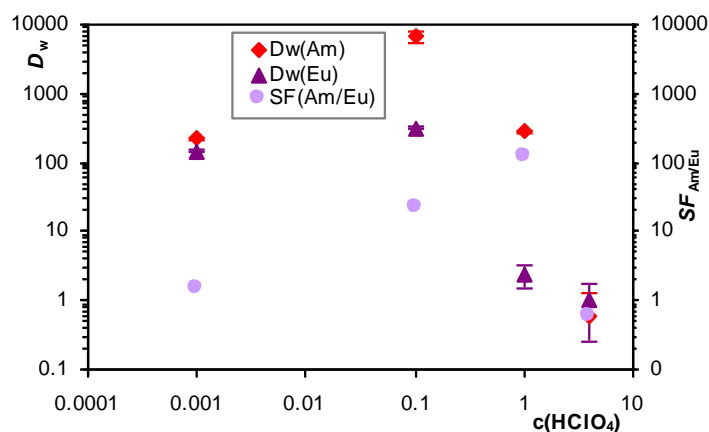
The reduction in  $D_w$  with increasing [HNO<sub>3</sub>] for CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** was also previously observed for **4** and **5** and may, to some extent, be attributed to the increased degree of ligand protonation and thus decreased free ligand concentration.<sup>29,30</sup> The effect of HNO<sub>3</sub> concentration on the degree of extraction of Am(III) and Eu(III) also mirrors that of **4** and **5**, where it was concluded that the limited length of the linking-chain on the MNP/silica gel forced the quadridentate BTPhen ligand to form a 1:1 complex with 10-coordinate M(III) cations.<sup>29,30</sup> Thus, whilst the decreasing pH affected the extraction of both Am(III) and Eu(III), we were intrigued by the possibility that it might be the nature of the counterion surrounding the M(III) species in the 1:1 complex that was leading to the increasing distinction between Am(III) from Eu(III) at increasing HNO<sub>3</sub> concentration.

The effect of HNO<sub>3</sub> concentration on the degree of extraction of Am(III) and Eu(III) also mirrors that of **4** and **5**, where it was concluded that the limited length of the linking-chain on the MNP/silica gel forced the quadridentate BTPhen ligand to form a 1:1 complex with 10-coordinate M(III) cations.<sup>29,30</sup> Thus, whilst the decreasing pH affected the extraction of both Am(III) and Eu(III), we were intrigued by the possibility that it might be the nature of the counterion surrounding the M(III) species in the 1:1 complex

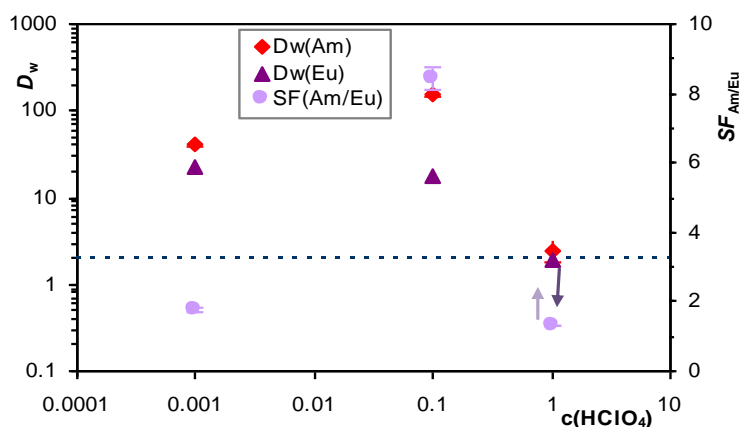
that was leading to the increasing distinction between Am(III) from Eu(III) at increasing  $\text{HNO}_3$  concentration.



**Figure 3.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPPhen-functionalized SiO<sub>2</sub> gel **8** as a function of  $\text{HNO}_3$  concentration. Mass of sorbent: approximately 16 mg, phase volume: 1 mL, V/m ratio:  $\sim 60 \text{ mL g}^{-1}$

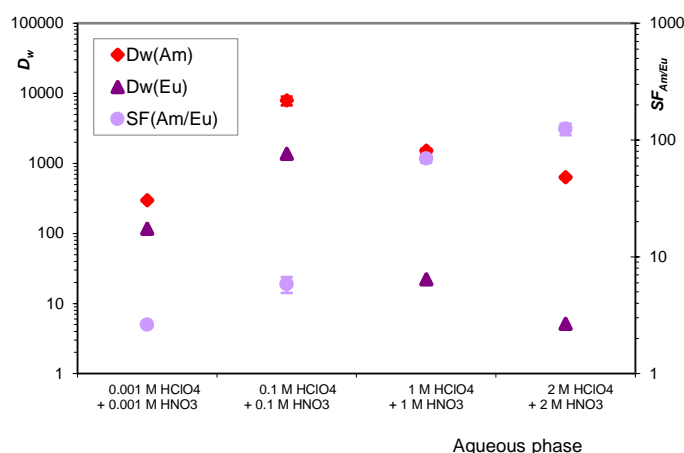


**Figure 4.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPPhen-functionalized SiO<sub>2</sub> gel **8** as a function of  $\text{HClO}_4$  concentration. Mass of sorbent: approximately 15 mg, phase volume: 0.6 mL, V/m ratio:  $\sim 40 \text{ mL g}^{-1}$



**Figure 5.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPPhen-functionalized SiO<sub>2</sub>-coated MNPs **4** as a

function of  $\text{HClO}_4$  concentration. Mass of sorbent: approximately 18 mg, phase volume: 0.6 mL, V/m ratio:  $\sim 33 \text{ mL g}^{-1}$



**Figure 6.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** as a function of  $\text{HClO}_4$  /  $\text{HNO}_3$  concentration. Mass of sorbent: approximately 15 mg, phase volume: 0.6 mL, V/m ratio:  $\sim 40 \text{ mL g}^{-1}$

In order to probe whether the counterion exerts an influence on extraction efficiency, the extraction experiments were repeated, but replacing  $\text{HNO}_3$  with  $\text{HClO}_4$ . Figure. 4 and Figure. 5 show weight distribution ratios for Am(III) and Eu(III) ( $D_{w\text{Am}}$  and  $D_{w\text{Eu}}$ ) and separation factors for Am(III) over Eu(III) ( $SF_{\text{Am/Eu}}$ ) for CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** and CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub>-coated MNPs **4** as a function of  $\text{HClO}_4$  concentration (0.001 M – 4 M), respectively. Similarly, to its behaviour in  $\text{HNO}_3$ , for CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** (Figure. 4), the  $D_w$  values for both Am(III) and Eu(III) initially increased, achieving maximum values at 0.1 M  $\text{HClO}_4$ , and then decreased with increasing  $\text{HClO}_4$  concentration, in agreement with the earlier results. Even though high  $D_w$  values were obtained for both Am(III) ( $D_{w\text{Am}} = 221 \pm 9$  and  $D_{w\text{Am}} = 6864 \pm 1298$ ) and Eu(III) ( $D_{w\text{Eu}} = 145 \pm 5$  and  $D_{w\text{Eu}} = 312 \pm 14$ ) at 0.001 M and 0.1 M  $\text{HClO}_4$  concentrations, all the values (except for those at 0.001 M  $\text{HClO}_4$ ) are significantly lower than those measured in  $\text{HNO}_3$ . In this case the separation factors were calculated as  $SF_{\text{Am/Eu}} = 1.5 \pm 0.1$ ,  $22.0 \pm 2.6$ ,  $119 \pm 27$  and  $\sim 1$  at 0.001, 0.1, 1 and 4 M  $\text{HClO}_4$ , respectively. When comparing **8** in  $\text{HNO}_3$  and  $\text{HClO}_4$ , the absence of the  $\text{NO}_3^-$  counterion decreases the values of  $D_w$ , especially at higher acid concentrations. This can be taken as support for the proposal that the bidentate properties of the nitrate ion play an important role in Am(III) and Eu(III) separation. The separation factors  $SF_{\text{Am/Eu}}$  are similar in nitric and perchloric acids except for the case of 4 mol/L concentration where the substitution of  $\text{HNO}_3$  with  $\text{HClO}_4$  results in a dramatic drop of  $SF_{\text{Am/Eu}}$  from  $> 154$  in  $\text{HNO}_3$  down to  $\sim 1$  in  $\text{HClO}_4$ .

As anticipated, CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub>-coated MNPs **4** exhibited similar extraction



behaviour (Figure. 5) to **8** in HClO<sub>4</sub> solutions showing highest  $D_w$  values for both Am(III) ( $D_{wAm} = 40 \pm 1$  and  $D_{wAm} = 153 \pm 6$ ) and Eu(III) ( $D_{wEu} = 23 \pm 1$  and  $D_{wEu} = 18 \pm 1$ ) at 0.001 M and 0.1 M HClO<sub>4</sub> concentrations and low  $D_w < 2.5$  at 1 M HClO<sub>4</sub> with no extraction observed for Am(III) or Eu(III) at 4 M HClO<sub>4</sub>. When compared with its behaviour in HNO<sub>3</sub> presented in our earlier paper<sup>31</sup> (ESI†), the general trend – decrease of  $D_w$  values with increasing acid concentration – is maintained for **4** in perchloric acid, too. However, in addition to generally lower values of  $D_w$  with increasing acid concentration, a significant difference in values of  $SF_{Am/Eu}$ , especially at higher concentrations, was observed. While the values of separation factor for **4** in HNO<sub>3</sub> were  $SF_{Am/Eu} = 65 \pm 5$  and  $SF_{Am/Eu} > 1300$  at 1 M and 4 M HNO<sub>3</sub>, respectively, no significant Am/Eu separation is observed in HClO<sub>4</sub> at these concentrations. This may again be associated with the bidentate properties of the nitrate anion.

To investigate the effect of [HNO<sub>3</sub>] on extraction efficiency further, experiments were conducted at combined [HNO<sub>3</sub> + HClO<sub>4</sub>] of 0.001 M, 0.1 M, 1 M and 2 M. Figure. 6 shows weight distribution ratios for Am(III) and Eu(III) ( $D_{wAm}$  and  $D_{wEu}$ ) and separation factors for Am(III) over Eu(III) ( $SF_{Am/Eu}$ ) for CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** as a function of [HNO<sub>3</sub> + HClO<sub>4</sub>] (0.001 M – 2 M). Similarly, to the behaviour in HNO<sub>3</sub> alone (Figure. 4), the  $D_w$  values for both Am(III) and Eu(III) initially increased, achieving maximum values at 0.1 M [HNO<sub>3</sub> + HClO<sub>4</sub>], and then decreased with increasing [HNO<sub>3</sub> + HClO<sub>4</sub>], confirming significant role of NO<sub>3</sub><sup>−</sup> in Am(III) and Eu(III) separation with immobilized BTPhen ligands.

In conclusion, we report a remarkable capability of CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel **8** that achieves highly efficient extraction of both minor actinides and lanthanides at low concentrations of HNO<sub>3</sub> yet exhibits high selectivity for minor actinides over lanthanides at 4 M HNO<sub>3</sub> ( $SF_{Am/Eu} > 154$ ). This constitutes the most efficient partitioning process for minor actinides and lanthanides based on an immobilized ligand system thus far. We conclude that the three bidentate nitrate ions surrounding the M(III) in the 1:1 complex play an important role in the distinction between the minor actinides and lanthanides and it is the NO<sub>3</sub><sup>−</sup> concentration that is responsible for the selective separation of minor actinides from lanthanides at high HNO<sub>3</sub> concentrations.<sup>32</sup> An interesting finding is the significant difference between the extraction properties of the new CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub> gel and the CyMe<sub>4</sub>-BTPhen-functionalized SiO<sub>2</sub>-coated MNPs. Even though both systems involve the same ligand grafted onto the support in an identical manner, their behaviour is markedly different.

## ACKNOWLEDGEMENTS

The authors acknowledge the UK Engineering and Physical Sciences Research Council (EPSRC) and the Grant Agency of the Czech Technical University in Prague (grant No. SGS15/216/OHK4/3T/14) for

financial support (A.A. and P.D., respectively). Use of the Chemical Analysis Facility (CAF) and Electron Microscopy Laboratory (EMLab) at the University of Reading is gratefully acknowledged.

## REFERENCES

1. J.-H. Lan, W.-Q. Shi, L.-Y. Yuan, J. Li, Y.-L. Zhao, and Z.-F. Chai, *Coord. Chem. Rev.*, 2012, **256**, 1406.
2. P. J. Panak, and A. Geist, *Chem. Rev.*, 2013, **113**, 1199.
3. A. Leoncini, J. Huskens, and W. Verboom, *Chem. Soc. Rev.*, 2017, **46**, 7229.
4. 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.
5. L. Xu, A. Zhang, Y. Lu, H. Yang, and Z. Liu, *RSC Adv.*, 2016, **6**, 99859.
6. C.-L. Xiao, C.-Z. Wang, L. Mei, X.-R. Zhang, N. Wall, Y.-L. Zhao, Z.-F. Chai, and W.-Q. Shi, *Dalt. Trans.*, 2015, **44**, 14376.
7. Q.-R. Huang, J. R. Kingham, and N. Kaltsoyannis, *Dalt. Trans.*, 2015, **44**, 2554.
8. J. Veliscek-Carolan, *J. Hazard. Mater.*, 2016, **318**, 266.
9. M. Houas, N. Amrani and A. Boucenna, *Ann. Nucl. Energy*, 2016, **97**, 198.
10. M. J. Hudson, L. M. Harwood, D. M. Laventine, and F. W. Lewis, *Inorg. Chem.*, 2013, **52**, 3414.
11. J. Bisson, J. Dehaut, M.-C. Charbonnel, D. Guillaneux, M. Miguirditchian, C. Marie, N. Boubals, G. Dutech, M. Pipelier, V. Blot, and D. Dubreuil, *Chem. – A Eur. J.*, 2014, **20**, 7819.
12. M. M. Maiwald, A. T. Wagner, J. Kratsch, A. Skerencak-Frech, M. Trumm, A. Geist, P. W. Roesky, and P. J. Panak, *Dalt. Trans.*, 2017, **46**, 9981.
13. 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.
14. A. Afsar, D. M. Laventine, L. M. Harwood, M. J. Hudson, and A. Geist, *Chem. Commun.*, 2013, **49**, 8534.
15. G. R. Choppin, *J. Alloys Compd.*, 1995, **223**, 174.
16. M. Kaneko, S. Miyashita, and S. Nakashima, *Inorg. Chem.*, 2015, **54**, 7103.
17. E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.-C. Charbonnel, F. Sansone, A. Arduini, and A. Casnati, *J. Am. Chem. Soc.*, 2016, **138**, 7232.
18. N. J. Williams, J. Dehaut, V. S. Bryantsev, H. Luo, C. W. Abney, and S. Dai, *Chem. Commun.*, 2017, **53**, 2744.
19. 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.

20. 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.
21. A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden, and T. Zevaco, *Solvent Extr. Ion Exch.*, 2012, **30**, 433.
22. R. Liu, Y. Wei, Y. Xu, S. Usuda, S. Kim, H. Yamazaki, and K. Ishii, *J. Radioanal. Nucl. Chem.*, 2012, **292**, 537.
23. Y. Wei, R. Liu, Y. Wu, J. Zu, X. Wang, and Z. Chen, *Energy Procedia*, 2013, **39**, 110.
24. N. Wang, Y. Guo, L. Wang, X. Liang, S. Liu, and S. Jiang, *Analyst*, 2014, **139**, 2531.
25. M. A. Higginson, O. J. Marsden, P. Thompson, F. R. Livens, and S. L. Heath, *React. Funct. Polym.*, 2015, **91–92**, 93.
26. J. Veliscek-Carolan, K. A. Jolliffe, and T. L. Hanley, *Chem. Commun.*, 2015, **51**, 11433.
27. M. Kaur, H. Zhang, L. Martin, T. Todd, and Y. Qiang, *Environ. Sci. Technol.*, 2013, **47**, 11942.
28. S. Ning, Q. Zou, X. Wang, R. Liu, Y. Wei, Y. Zhao, and Y. Ding, *J. Radioanal. Nucl. Chem.*, 2016, **307**, 993.
29. A. Afsar, L. M. Harwood, M. J. Hudson, P. Distler, and J. John, *Chem. Commun.*, 2014, **50**, 15082.
30. A. Afsar, P. Distler, L. M. Harwood, J. John, and J. Westwood, *Chem. Commun.*, 2017, **53**, 4010.
31. A. Afsar, L. M. Harwood, M. J. Hudson, P. Distler, and J. John, *Chem. Commun.*, 2014, **50**, 15082.
32. 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.