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Extraction of minor actinides, lanthanides and other fission products by silica-immobilized BTBP/BTPhen ligands†

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Novel BTBP [bis-(1,2,4-triazin-3-yl)-2,2'-bipyridine] / BTPhen [bis-(1,2,4-triazin-3-yl)-1,10-phenanthroline] functionalized silica gels have been developed to extract minor actinides, lanthanides and other fission products. BTPhen functionalized silica gel is capable of near-quantitative removal of Am(III) in the presence of Eu(III) from aqueous HNO₃, while BTBP functionalized silica gel is able to remove problematic corrosion and fission products that are found in PUREX raffinates.

After the removal of uranium and plutonium in the PUREX (Plutonium and Uranium Redox EXtraction) process, post-PUREX raffinate still contains the lanthanides, other fission products and the minor actinides neptunium, americium and curium; the latter three elements being responsible for a large proportion of the long-term radiotoxicity and heat load of post-PUREX raffinate.^{1,2} One approach currently being studied for the long-term management of irradiated fuel is to separate these minor actinides from the lanthanides; after which they can be transmuted, using high-energy neutrons or fast neutrons in a Generation IV reactor, to short-lived radionuclides or stable non-radioactive elements.^{3–9} Separation of the minor actinides from the chemically similar lanthanides has been achieved by the SANEX solvent extraction process (Selective ActiNide EXtraction) using soft N-donor ligands containing the 1,2,4-triazine moiety (Fig. 1).^{10–15} During this process, the radionuclides and non-radioactive fission products that are in an aqueous nitric acid phase are treated with the extraction reagent dissolved in an organic phase. CyMe₄-BTBP **2** is the current European reference ligand capable of performing the selective extraction of minor actinides directly from nitric acid solutions into an organic solvent and a laboratory demonstration has been successfully carried out on post-PUREX raffinate.¹⁶ However, 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) **2** not only selectively separates the minor actinides from the lanthanides, but it also co-extracts certain corrosion and fission

products such as Ni(II), Pd(II), Ag(I) and Cd(II), complicating the separation of trivalent actinides for transmutation.¹⁷

Although much progress has been made concerning the development of extractants for the liquid-liquid extraction processes that can partition minor actinides from lanthanides, far less effort has been placed on a solid-liquid extraction and separation of the minor actinides from the corrosion and fission products.

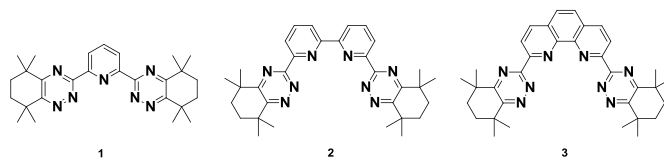


Fig. 1 Structural formulae of CyMe₄-BTP **1**, CyMe₄-BTBP **2** and CyMe₄-BTPhen **3**.

Considering that the minor actinide content in post-PUREX raffinate is smaller than that of U and Pu in the spent fuel, immobilization of actinide-selective ligands onto solid supports could provide an alternative method for carrying out separation and pre-concentration of minor actinides from PUREX raffinates.^{18–20} Further benefits of a system based on a solid phase extractant include no requirement for mixing or phase separation, and possible use of pressure or vacuum to increase flow rate, or use of magnetic separation.^{19,21,22} We have recently demonstrated that, when magnetic nanoparticles (MNPs) are combined with ligands such as 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (CyMe₄-BTPhen) **3**, these functionalized MNPs can be used either to extract both minor actinides and lanthanides at low concentrations of HNO₃ or to extract minor actinides selectively over lanthanides at high (4 M) concentration of HNO₃. These functionalized MNPs can be collected magnetically in preference to centrifugation.²³ In this work, we report an alternative technology for the sequential separation of fission products and then minor actinides from lanthanides using a two-column system, the first packed with BTBP-functionalized SiO₂ gel and the second with BTPhen-functionalized SiO₂ gel.

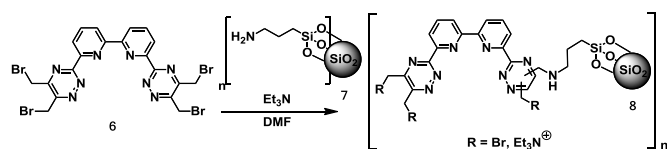
The ligand 6,6'-bis(5,6-bis(bromomethyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine (tetra-bromomethyl-BTBP) **6** was synthesized by our previously reported protocol (ESI†).^{24,25} As a solid support for the BTBP **6**, aminopropyl-functionalized SiO₂ gel **7** was purchased from

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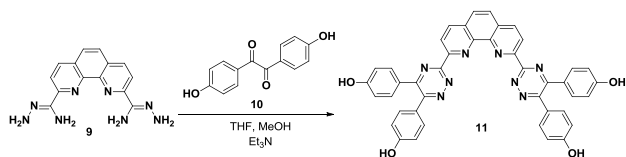
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

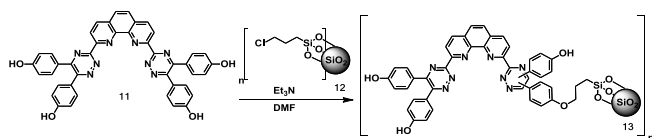
Sigma Aldrich. This BTBP ligand **6** was then directly immobilized onto the SiO₂-gel (Scheme 1). The tetra(4-hydroxyphenyl)BTPhen **11** was synthesized by the condensation reaction of bis(diaminodihydrazide) **9** with 4,4'-dihydroxybenzil **10** as shown in Scheme 2.^{3,26–28} This tetra(4-hydroxyphenyl)-BTPhen ligand **11** was then immobilized onto commercially available chloropropyl-functionalized SiO₂ gel **12** (Scheme 3).



Scheme 1 Immobilization of BTBP **6** on silica gel.



Scheme 2 Synthesis of tetra(4-hydroxyphenyl)BTPhen **11**.



Scheme 3 Immobilization of BTPhen **11** on silica gel.

Several characterization methods were employed to assess the degree of immobilization of BTBP **6** and BTPhen **11** ligands onto the silica surface. The presence of bands at 1500–1600 cm⁻¹ owing to C=C aromatic vibrations were observed in the FT-IR spectra (ESI†) for the BTBP-functionalized SiO₂ gel **8** and BTPhen-functionalized SiO₂ gel **13**. Elemental analysis (ESI†) showing an increase in the content of C, H and N of the functionalized silica and thermogravimetric analysis (ESI†) allowed the determination of the nature and degree of surface modification in each case indicating that the amount of BTBP ligand **6** bound onto the SiO₂ surface was about *ca.* 14%; while the content of BTPhen ligand **11** in the BTPhen-functionalized SiO₂ gel **13** was estimated to be *ca.* 10% (ESI†).

The aqueous solutions for the solid phase extraction experiments were prepared by spiking nitric acid solutions (0.001–4 M) with stock solutions of ²⁴¹Am and ¹⁵²Eu and then adding 1 mL of spiked aqueous solution to 14 mg of BTBP-functionalized SiO₂ gel **8** or 17 mg of BTPhen-functionalized SiO₂ gel **13**. The suspension was 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 is defined as $D_w = (A_0 - A) / A \cdot V/m$, where A_0 and A were initial and final number of counts in the taken standard/aliquot, V is a volume of an aqueous phase shaken and m is a mass of the material **8** or **13**. The separation factor is $SF_{Am/Eu} = D_{wAm} / D_{wEu}$.

Fig. 2 shows the weight distribution ratios for Am(III) and Eu(III) (D_{wAm} and D_{wEu}) and the separation factors for Am(III) over Eu(III) ($SF_{Am/Eu}$) for BTBP-functionalized SiO₂ gel **8** as a function of nitric acid concentration (0.001 M–4 M). The separation factors were calculated as $SF_{Am/Eu} = 32 \pm 17$, 193 ± 171 , 46 ± 45 and 8 ± 7 at 0.001,

0.1, 1 and 4 M HNO₃, respectively. The low separation factor values indicate that BTBP ligand **6** immobilised on SiO₂ gel did not significantly differentiate in the extraction of Am(III) or Eu(III) from HNO₃ solutions. On the other hand, for BTPhen-functionalized SiO₂ gel **13**, high weight distribution ratios ($D_w > 90$) were obtained for both Am(III) and Eu(III) at 0.001 M HNO₃ solution with no selectivity ($SF_{Am/Eu} = 0.69 \pm 0.04$) for Am(III) over Eu(III). At 0.1 M HNO₃, a more significant increase in D_w values was observed for Am(III) ($D_{wAm} = 4883 \pm 974$) than for Eu(III) ($D_{wEu} = 630 \pm 51$) resulting in $SF_{Am/Eu} = 7.7 \pm 1.7$. With increasing HNO₃ concentration (1 M), decreases in the D_w values for both Am(III) and Eu(III) were observed ($D_{wAm} = 250 \pm 12$, $D_{wEu} = 4.2 \pm 0.4$), but a higher separation factor ($SF_{Am/Eu} = 60 \pm 6$) resulted. Interestingly, at 4 M HNO₃ a further decrease in D_w value for Am(III) gave $D_{wAm} = 28 \pm 1$ but, in this case the D_w value observed for Eu(III) of $D_{wEu} \approx 0.2$ and the resulting separation factor ($SF_{Am/Eu} \approx 140$), meant that only Am(III) was retained on the BTPhen-functionalized SiO₂ gel **13**. This effect of HNO₃ concentration on the degree of extraction of Am(III) and Eu(III) mirrors that of CyMe₄-BTPhen functionalized MNPs where we proposed that the shortness of the linking-chain on the MNPs constrains the CyMe₄-BTPhen ligand to form 1:1 complexes with M(III) cations with 3 nitrates ligating for the 10-coordination and so making the complex electronically neutral.^{23,29} Extraction capabilities of aminopropyl-functionalized SiO₂ gel **7** and chloropropyl-functionalized SiO₂ gel **12** were also investigated; however no extraction was observed for Am(III) or Eu(III), over the full range of concentrations of HNO₃.

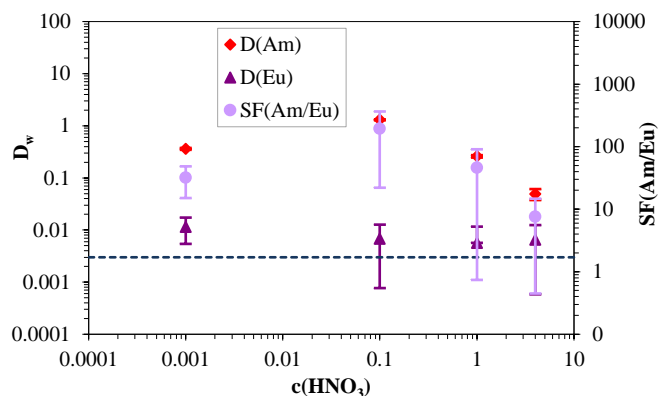


Fig. 2 Extraction of Am(III) and Eu(III) by BTBP-functionalized SiO₂ gel **8** as a function of nitric acid concentration.

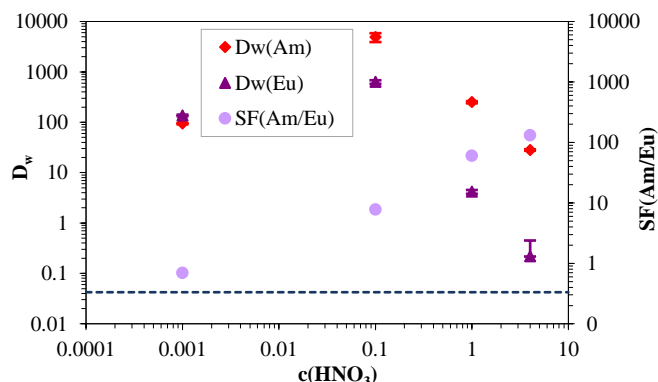


Fig. 3 Extraction of Am(III) and Eu(III) by BTPhen-functionalized SiO₂ gel **13** as a function of nitric acid concentration.

To investigate whether the BTBP-functionalized SiO₂ gel **8** had any potential applications in the removal of fission and corrosion

products such as Ni(II), Pd(II), Ag(I) and Cd(II), extraction experiments were performed to extract metal ions from 2% HNO₃ solution (pH = 0.5) using a column technique. Functionalized SiO₂ gel **8** (10 g, ~1.4 g BTBP **6** loading) packed into a glass column (diameter 3.8 cm, bed volume ~35 mL) was washed with 2% HNO₃ solution (100 mL). Standard solutions at pH 0.5 containing a range of metals, each at 100 ppb concentration (100 mL) were then passed through the column at a rate of 10 mL per minute. The filtrate was collected and analysed by ICP-MS. The uptake of various metal ions – Sc(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Mo(IV), Ag(I), Cd(II), Sb(V), Pb(II), Pd(II), Os(IV), Ir(III), Pt(IV), Au(III), Zr(IV), Nb(V), Hf(IV), Ta(V), W(VI) and Re(IV) at pH 0.5, by BTBP-functionalized SiO₂ gel **8** shows > 80% of uptake efficiency for all the metals except Sb(V) in Fig. 4. Importantly near quantitative extraction of certain problematic corrosion and fission products [Ni(II), Pd(II), Ag(I) and Cd(II)] that are found in the nitric solutions of PUREX raffinates was observed. Significantly, the BTBP-functionalized SiO₂ gel **8** did not show any affinity towards alkali metals or alkaline earth metals such as Na⁺, K⁺, Mg²⁺ and Ca²⁺ or Al³⁺.

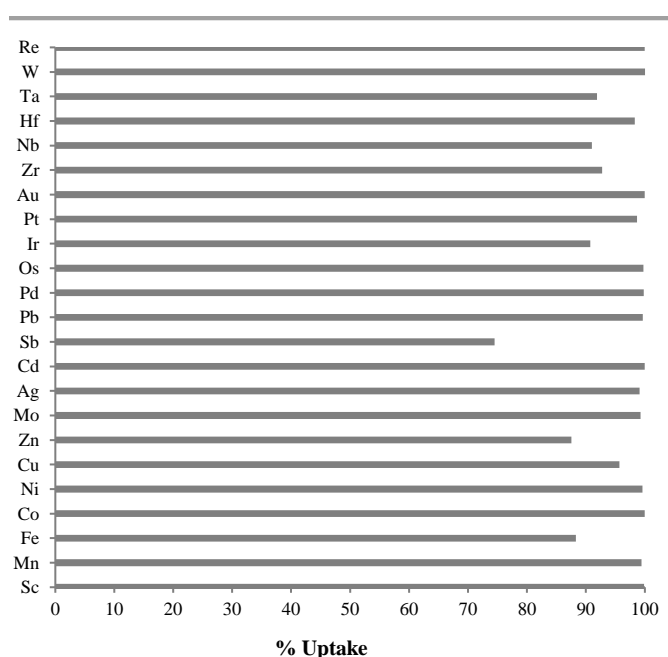


Fig. 4 Percentage uptake of metal ions (100 ppb) from aqueous solution at pH 0.5 by BTBP-functionalized SiO₂ gel **8**.

In summary, we report a promising partitioning process for minor actinides, lanthanides and other fission products based on a column separation technique using novel BTBP/BTPhen immobilized silica gels. The BTBP-functionalized SiO₂ gel can be used to remove problematic corrosion and fission products without extracting alkali or alkaline earth metal cations: while the BTPhen-functionalized SiO₂ gel extracts both minor actinides and lanthanides at low concentrations of HNO₃ yet exhibits very high selectivity for minor actinides over lanthanides at 4 M HNO₃ ($SF_{Am/Eu} = 140$). We propose that this technology could pave the way for the design of an advanced partitioning process for PUREX raffinate consisting of an initial clean-up to remove *d*-block metals and a second stage to remove the minor actinides from the lanthanides. Vitrification and stripping of metals from loaded SiO₂ gel will be the subject of further studies in our laboratory.

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