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Synthesis of Novel BTPhen-functionalized Silica-coated Magnetic Nanoparticles for Separating Trivalent Actinides and Lanthanides

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Dedicated to Professor Victor Snieckus on the occasion of his 80th birthday

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Abstract   BTPhen [bis-(1,2,4-triazin-3-yl)-1,10-phenanthroline] functionalized magnetic nanoparticles (MNPs), which selectively extract Am(III) over Eu(III) from 0.1 M HNO₃ with fast kinetics and a separation factor of 30 have been synthesized. These MNPs also show a small but significant selectivity for Am(III) over Cm(III) with a separation factor of around 3 in 0.1 M HNO₃. We report also the synthesis of these BTPhen and related ligands via an improved synthetic route by-passing the problematic benzyl oxidation with stoichiometric SeO₂.

Key words  Spent nuclear fuel, BTPhen ligand, magnetic nanoparticles, solid phase extraction, benzyl halogenation.

Spent nuclear fuel produced by current nuclear reactors is comprised mainly of uranium, plutonium, the lanthanides (98.5%) and approximately 0.1 wt% of the minor actinides [Am(II), Cm(III) and Np(III)]. Despite only accounting for approximately 1 wt% of spent fuel, Pu and the minor actinides are the main contributors to the long-term radioactivity (τ1/2 = 10⁵ to 10¹³ years) and heat load in spent nuclear fuel. Currently, uranium and plutonium are separated industrially by solvent extraction process (PUREX) and recycled after their conversion to produce new fuel. One proposed approach currently being studied is the partitioning and transmutation of minor actinides to short-lived radionuclides or stable non-radioactive elements using high-energy neutrons in dedicated ADS (accelerator driven systems) transmuters or fast neutrons in a Generation IV reactor. However, to achieve this, selective extraction of minor actinides from neutron absorbing poisons (lanthanides) is required.

Separation of trivalent actinides from trivalent lanthanides is a challenging goal as the physicochemical properties of the two groups of elements are very similar. This renders their chemical separation a challenging task, particularly given the high radioactivity of the waste necessitating the need for remote handling. Fortunately, previous studies have shown that separation of the minor actinides from lanthanides can be achieved by the SANEX solvent extraction process (Selective Actinide EXtraction) using soft N-donor ligands containing the 1,2,4-triazine moiety (Figure 1). It has been postulated that one of the major contributors to this selectivity is the more radially extended nature of the 5f-actinide orbitals versus the 4f-lanthanide orbitals. Consequently, it is believed that the metal-ligand bonding interaction in actinide complexes is more covalent in nature than in lanthanide complexes. CyMe₄BTBP 1 is the current European reference ligand capable of performing such extractions and a laboratory demonstration has been successfully carried out on post-PUREX raffinate. The more recently pre-organized 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen) ligand 2 was recently reported as a highly efficient and selective minor actinide extraction agent with greatly improved properties compared to 1.

Figure 1 CyMe₄BTBP 1 and CyMe₄BTPhen 2

Previous work on the minor actinide-lanthanide separations has focused on solvent extraction processes (e.g. SANEX process) but these processes come with other disadvantages, such as the requirement for substantial liquid storage and containment and generation of additional secondary waste. 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 emphasized on the alternative approaches such as solid-liquid extraction. Replacing the current liquid-liquid extraction methods with a system based on a solid phase extractant could eliminate the large volumes of secondary organic waste generated during separation. To overcome the limitations of liquid-liquid extraction process, we previously demonstrated that when magnetic nanoparticles (MNPs) are combined with ligands such as CyMe₄BTPhen, these functionalized MNPs could be used to extract the minor actinides and the radioactive material could then be collected magnetically in preference to centrifugation. In the present study, we report an alternative route for the synthesis of tetra(4-hydroxyphenyl)BTPhen 10 as a highly effective reagent for carrying out actinide-lanthanide separations and investigate its extraction capabilities when immobilised on MNPs.

The first challenge in this work was to develop a fast and efficient route to produce target BTPhen ligand 10. Until recently, all reported syntheses of BTPhen ligands and analogues have involved the benzylic oxidation of commercially

N N CHCl₃
NCS, m-CPBA
N N
Cl₃C CCl₃

N N
O O
2. TsCl, pyridine
1. NH₂OH.HCl
Et₃N, MeCN

Old Route
New Route

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available neocuproine 3 using stoichiometric equivalents of SeO₂ which leads to the formation of enormous amounts of toxic selenium metal rendering this route unsuitable.³⁷ In addition, the reaction to form bisaminohydrazide 8 required 6 days to go to completion. Therefore, a new synthetic route recently developed by our group in collaboration with Whitehead et. al.³⁷ that negated the need for toxic selenium dioxide, was adapted to our needs (Scheme 1).

Several characterization methods were employed to assess the degree of immobilization of BTPhen ligand 10 onto the surface of MNPs. In the FT-IR spectra of iodoalkyl-functionalized SiO₂-coated MNPs 11 and BTPhen-functionalized SiO₂-coated MNPs 12, strong absorption bands centred at 1050 cm⁻¹ owing to Si-O-Si stretching were observed for both samples. However, the absorptions at 1500–1600 cm⁻¹ owing to C=C aromatic vibrations were only observed for the BTPhen-functionalized SiO₂-coated MNPs 12 (See supporting information).

Thermogravimetric analysis indicated that the amount of BTPhen ligand 10 bound onto the MNPs was about ca. 25% (See Supporting Information). Surface morphology and structural features of BTPhen-functionalized SiO₂-coated MNPs 12 were studied by TEM and SEM analysis (See Supporting Information). Besides the spherical core structure, a more disordered organic moiety layer could be seen in which the thickness of the outer layer was determined to be ca. 10 nm. Furthermore, elemental analysis found a decrease in the iodine content from 38.9 % in 11 to 1.4 % in 12 and the presence of 0.9 % nitrogen confirming the modification of MNPs with the BTPhen ligand 10 (See supporting information).

The extraction data are summarized in Tables 1 and 2. Figure 2 shows the weight distribution ratios for Am(III) (D_wAm) and Eu(III) (D_wEu) and the separation factors for Am(III) over Eu(III) (SF_{Am/Eu}) for BTPhen-functionalized SiO₂-coated MNPs 12 as a function of nitric acid concentration (0.001 M – 4 M). The MNPs 12 exhibited high extraction ability for both Am(III) and Eu(III) (D_w > 600) at 0.001 M HNO₃ solution with no selectivity (SF_{Am/Eu} = 0.73 ± 0.04) for Am(III) over Eu(III). At 0.1 M HNO₃, the D_w for Am(III) is larger than 450 indicating that an effective extraction can still be achieved at 0.1 M HNO₃ solution. However, the D_w for Eu(III) falls from 858 ± 24 to 15 ± 1 resulting in a high SF_{Am/Eu} = 30 ± 2. With increasing HNO₃ concentration (1 M), decreases in the D_w values for both Am(III) and Eu(III) were observed (D_wAm = 25 ± 1, D_wEu was under the detection limit, i.e. $D_wEu < 3.0$), resulting in separation factor SF_{Am/Eu} > 8. At 4 M HNO₃, a further decrease in value for Am (III) gave D_wAm = 10 ± 1; D_w value observed for Eu(III) was again < 3.0 and the resulting separation factor was SF_{Am/Eu} > 3.

### Table 1. Extraction of Am(III) and Eu(III) by BTPhen-functionalized SiO₂-coated MNPs 12 as a function of nitric acid concentration.

<table>
<thead>
<tr>
<th>c(HNO₃)</th>
<th>D_wAm</th>
<th>D_wEu</th>
<th>SF_{Am/Eu}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>625</td>
<td>+/-</td>
<td>24</td>
</tr>
<tr>
<td>0.1</td>
<td>456</td>
<td>+/-</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>+/-</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>+/-</td>
<td>&lt;3.0</td>
</tr>
</tbody>
</table>

Figure 2. Extraction of Am(III) and Eu(III) by BTPhen-functionalized SiO₂-coated MNPs 12 as a function of nitric acid concentration.

These results are very similar to those of our previous work where BTPhen ligand 10 immobilized on SiO₂ gel extracted both minor actinides and lanthanides at low concentrations of HNO₃ yet exhibited very high selectivity for minor actinides over...
lanthanides at 4 M HNO₃ (SF₃m/Sm = 140). Weight distribution ratios for Am(III) and Cm(III), and the separation factors at different nitric acid concentrations were also examined (Figure 3). The Dₚ values for both Am(III) and Cm(III) decreased with increasing nitric acid concentration, in agreement with earlier results, resulting in a small but significant SF₃m/Cm = 3.0 ± 0.5 at 0.1 M HNO₃.

![Figure 3](image_url)

Table 2 Extraction of Am(III) and Cm(III) by BTPhen-functionalized SiO₂-coated MNPs 12 as a function of nitric acid concentration.

<table>
<thead>
<tr>
<th>[HNO₃] M</th>
<th>Dₚ Am</th>
<th>Dₚ Cm</th>
<th>SF₃m/Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>613</td>
<td>92</td>
<td>1.2</td>
</tr>
<tr>
<td>0.1</td>
<td>500</td>
<td>61</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

In summary, we report a modified route for synthesis of BTPhen ligand 10 avoiding the use of toxic SeO₂ and immobilisation of BTPhen ligand 10 on SiO₂-coated MNPs. These functionalized MNPs 12 exhibited good selectivity for Am(III) over Eu(III) at 0.1 M HNO₃ (with a separation factor of 30) and showed a small but significant selectivity for Am(III) over Cm(III) with a nominal separation factor of around 3 in 1 M HNO₃. Furthermore, both Am(III) and Eu(III) can be co-extracted at low concentrations of HNO₃ (0.001 M) if required. The uptake behavior of Am(III) and Eu(III) by MNPs 12 at different molarities of HNO₃ demonstrates that the extraction process is highly dependent on HNO₃ concentration and these results represent a substantial breakthrough in the development of solid-phase materials for the important and challenging minor actinide-lanthanide separation.

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**Supporting Information**

YES (this text will be updated with links prior to publication)

**Primary Data**

N0 (this text will be deleted prior to publication)

**References and Notes**

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