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EXTRACTION PROPERTIES OF 4-TETRA(HYDROXYPHENYL)BTPHEN IN LIQUID-LIQUID EXTRACTION SYSTEMS WITH CYCLOHEXANONE/OCTANOL OR IN A SOLID-PHASE EXTRACTION SYSTEM

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Dedicated to Professor Kaoru Fuji on the occasion of his 80th birthday

Abstract – The extraction properties of tetra(4-hydroxyphenyl)BTPhen have been investigated. Liquid-liquid extraction studies in proposed SANEX diluents, cyclohexanone and 1-octanol, indicate that actinide-lanthanide separation is superior in cyclohexanone; whereas actinide-actinide separation is more efficient in 1-octanol. Immobilization of the ligand onto a silica support results in the separation factor becoming dependent upon the concentration of nitrate anions in the aqueous phase. The immobilized ligand was also applied to the extraction of transition metals, resulting in >70% uptake of all transition metals examined, in the presence of alkali and alkaline earth metals.

INTRODUCTION

Spent nuclear fuel (SNF) consists largely of uranium (U, 94%), fission and corrosion products (Sr, Cs, I, Tc, Ni, Pd, Ag, Cd, 4-5%) plutonium (Pu, 1%) and minor actinides (Np, Am, Cm, 0.1%). The fission products are responsible for the majority of the radiotoxicity of SNF; however, their short half-lives result in a quick decrease in radiotoxicity. On the other hand, the major long-term radiotoxicity is caused by the minor actinides (Np, Am and Cm), despite contributing only 0.1% to the spent fuel mass.¹⁻³ After removal of U and Pu by the plutonium-uranium reductive extraction process (PUREX), the separation of actinides from fission products, particularly the chemically very similar lanthanides, is crucial to allow

partitioning and transmutation of the actinides to reduce the radiotoxicity of the waste further.⁴ The transmutation process may be carried out in new Generation IV reactors or ADS (Accelerator Driven System) dedicated transmuters where high-energy neutrons are used to convert the actinides into shorter-lived radionuclides or stable elements. In such reactors, the high neutron-capture cross-section of the lanthanides would be a hindrance to the transmutation process.

The selective actinide extraction (SANEX) process currently involves a liquid-liquid extraction process using hydrophobic ligands containing multiple soft *N*-donor atoms to separate actinides from lanthanides selectively.⁵⁻⁷ The SANEX process is typically carried out with an aqueous phase containing nitric acid with a ligand dissolved in the organic phase.⁸ 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-2,2'-bipyridine (CyMe₄BTBP) **1** (Figure 1) is the current European benchmark ligand for the SANEX process. It is capable of performing selective actinide extraction, and a laboratory demonstration has been successfully carried out on post-PUREX raffinate.⁹ Quadridentate ligands such as CyMe₄BTBP **1** exploit the more covalent nature of the metal-ligand bond with actinides, as a result of more diffuse nature of the actinide 5f orbitals that extend further than the 6d orbitals.¹⁰ The more recently developed CyMe₄BTPhen **2** (Figure 1) has improved An/Ln separation performance, at least in part due to being locked into the binding conformation.¹¹⁻¹³ In 1-octanol, CyMe₄BTPhen **2** has an extraction efficiency of 2 orders of magnitude higher than CyMe₄BTBP **1** along with faster extraction kinetics.^{13,14} Different analogues of the BTPhen system have been tested to determine the most effective structure for actinide separation.¹⁵ This paper investigates the extraction efficiency of tetra(4-hydroxyphenyl)BTPhen **3** (Figure 1) in cyclohexanone and octanol at various nitric acid concentrations. Ligand **3** was also immobilized onto functionalized silica via the phenolic groups and we report herein the effect of nitrate ion concentration upon An/Ln separation factor, as well as the uptake of possible fission products.

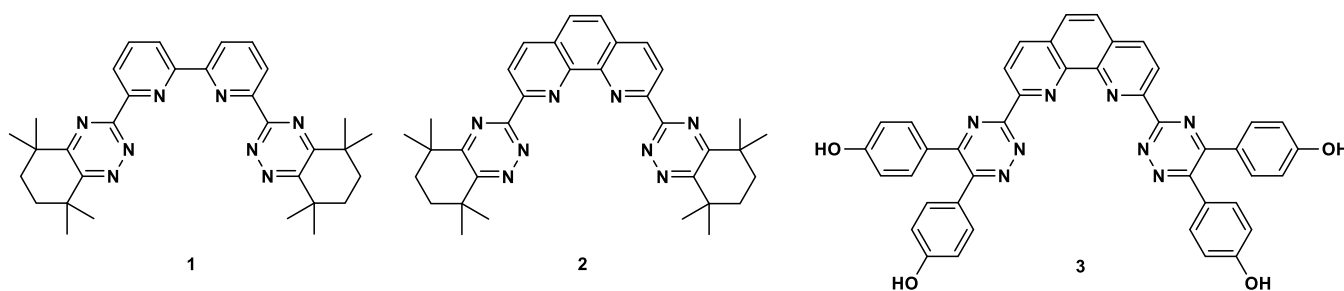


Figure 1. Structures of CyMe₄BTPhen **1**, CyMe₄BTBP **2** and tetra(4-hydroxyphenyl)BTPhen **3**

Prospective diluents for the SANEX process must display high organic solubility of the ligand and its complexed species, high flashpoint, low water solubility (to avoid formation of emulsions), high stability in acidic media (4 M HNO₃), resistance to radiolysis and be available in industrial quantities at low cost.^{16,17} Both cyclohexanone and 1-octanol fulfil these requirements and have been proposed to be used in model SANEX processes. Tetra(4-hydroxyphenyl)BTPPhen **3** is more soluble in cyclohexanone (higher than 10 mM) than in octanol (5 mM), which raises the possibility for better extraction efficiency. However, 1-octanol is less water-soluble and has been used in other actinide separation processes around the world.^{18,19} Therefore, the comparison between different diluents is crucial to find the optimum solvent for any SANEX process.

An alternative to a liquid-liquid separation is the use of a liquid-solid process where the immobilization of actinide-selective ligands onto a solid support averts the need for phase separation and mixing; removing the requirement for large volumes of solvent that results in the concomitant generation of large amounts of waste.^{20,21} This technique is particularly advantageous for the recovery of small quantities of metals from bulk solution.²² In general, such separation materials can be classified as extraction chromatographic (EXC) resins or solid-phase extractants (SPE) depending on their nature. Extraction chromatographic resins typically comprise a ligand that is impregnated into an inert support. The behavior of such materials can be readily described / predicted using the properties of the ligand in liquid-liquid extraction. Contrary to EXC, solid-phase extractants represent solid supports that have been derivatized by selective ligands that are covalently bound to the support.²³ Extraction chromatographic separation studies of the trivalent actinides and lanthanides have been demonstrated using various *N*-donor ligands (BTP, BTBP and BTPPhen derivatives) on different supports (SiO₂-P, PAN, XAD resin).²⁴⁻³² A recent example of solid-phase extractants developed for actinide–lanthanide separation involves the triazine soft *N*-donor (Me₄BTPPhen) linked covalently with poly(vinylbenzyl) chloride to generate PVB–Me₄BTPPhen.³³ In an earlier study, we have demonstrated that tetra(4-hydroxyphenyl)BTPPhen-functionalized silica gel **4** (Figure 2) was able to extract actinides from lanthanides with a separation factor $SF_{Am/Eu} \approx 140$ in 4 M HNO₃.³²

Much of the focus of fuel reprocessing has been on the separation of actinides from lanthanides and far less has been on the partitioning of adjacent minor actinide elements Am(III) and Cm(III) and no such large-scale process is currently available. Cm(III) produces a lot of heat in the decay process and cannot be transmuted with Am(III) as the excess heat will cause problems in fuel fabrication, requiring additional shielding.³⁴ The separation of Am(III) and Cm(III) is challenging due to their similar ionic radii and bond forming properties and is possibly one of the most difficult separations in the overall partitioning and transmutation process.^{35,36} Many different approaches have been studied including high-pressure ion

exchange, extraction chromatography and solvent extraction using di(2-ethylhexyl)phosphoric acid (HDEHP). More recently, we have demonstrated efficient separation of Am(III) and Cm(III) with $SF_{Am/Cm} = 7.9$.^{21,37-39}

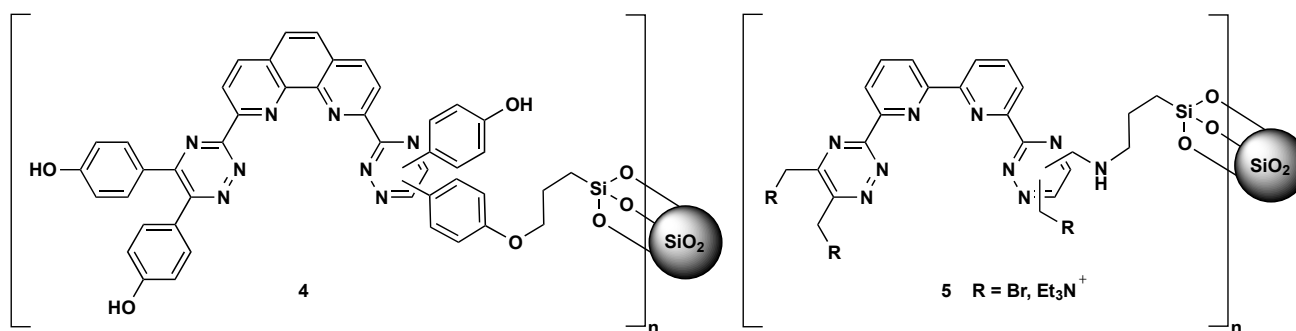


Figure 2. Structures of tetra(4-hydroxyphenyl)BTPhen-functionalized silica gel **4** and tetra-bromomethylBTBP-functionalized silica gel **5**

Separation of the minor actinides from the corrosion and fission products such as Ni, Pd, Ag and Cd is crucial to simplify the separation of the trivalent actinides destined for transmutation.⁴⁰ CyMe₄BTBP co-extracts the fission products with the minor actinides, but is a poor extractant of U and Pu, hence our previous publication proposed the use of a two column technique, one for extracting fission and corrosion products, and another for extracting the minor actinides.⁴¹ This technique requires the fabrication and use of two different types of ligand, complicating the process. Production of similar ligands with mostly identical reagents and synthesis steps that produce the ligands that meet the differing specifications would therefore be advantageous.^{42,43}

RESULTS AND DISCUSSION

The distribution ratios D_{Am} and D_{Eu} and separation factors ($SF_{Am/Eu}$) shown in Figure 3 and Figure 4 display the separation for Am(III) over Eu(III) for the tetra(4-hydroxyphenyl)BTPhen ligand **3** in cyclohexanone and in octanol respectively, as a function of nitric acid concentration (0.001 – 4 M). The value of the separation factor close to unity in 0.001 M HNO₃ in cyclohexanone (Figure 3) indicates that, in this diluent, the ligand **3** does not distinguish Am(III) over Eu(III) at low concentrations of nitric acid. However, the overall trend in the separation factors for cyclohexanone shows an increase in separation factor with increasing concentration of nitric acid, with separation factors at 0.5 M and 1 M HNO₃ ($SF_{Am/Eu} = 26.0 \pm 1.5$ for 1 M HNO₃) suggesting either pH or the ligating effect of nitrate ions is affecting the selectivity. Unfortunately, the distribution ratios for Am(III) (D_{Am}) were rather low, with the highest

value being observed in 1 M HNO_3 with $D_{\text{Am}} = 1.7 \pm 0.1$. These data imply that, in cyclohexanone, **3** can differentiate Am(III) over Eu(III) at > 0.5 M HNO_3 but its extraction efficiency is too low.

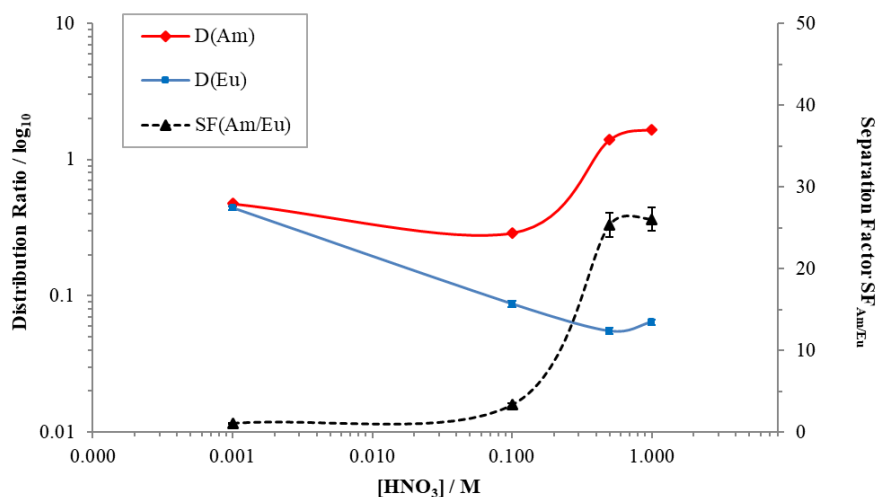


Figure 3. Extraction of Am(III) and Eu(III) by 10 mM tetra(4-hydroxyphenyl)BTPhen **3** in cyclohexanone as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

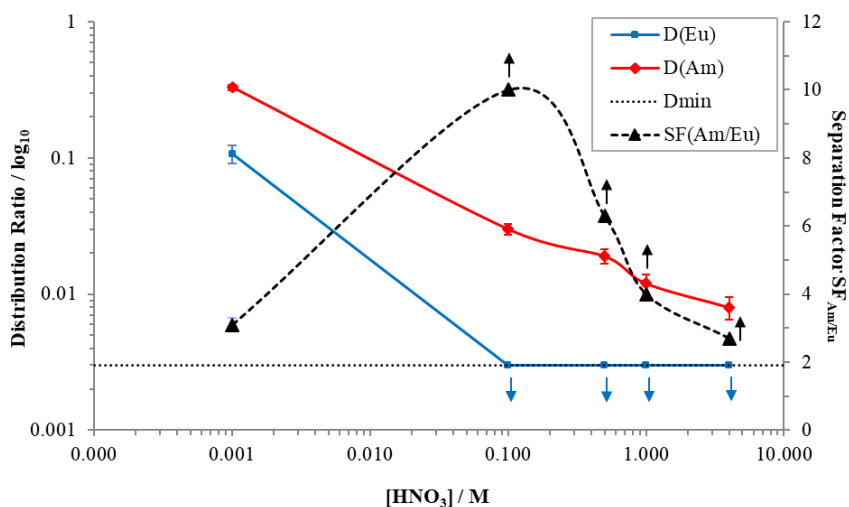


Figure 4. Extraction of Am(III) and Eu(III) by 5 mM tetra(4-hydroxyphenyl)BTPhen **3** in octanol as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

With octanol as diluent (Figure 4), the most surprising finding is the decreasing trend of D_{Am} with increasing nitric acid concentration. This is in contradiction to the behaviour of all the BTPhen- and BTBP-families of ligands studied previously in octanol and may be due to hydrogen bonding interactions between the relatively acidic phenolic groups on the ligand and the octanol solvent. The D_{Am} distribution ratios observed in octanol were even lower than those in cyclohexanone and did not exceed unity under

any conditions. These data indicate that octanol is not an efficient diluent for actinide extraction from lanthanides for ligand **3**.

Table 1. Comparison of distribution weight ratios and separation factors of similar BTPhen ligands in 1-octanol

Entry	Name	$D_{w,Am}$ at 4M HNO ₃	SF _{Am/Eu} at 4M HNO ₃
1	tetra(4-hydroxyphenyl)BTPhen 3	0.008 ± 0.001	>2.7
2	CyMe ₄ BTPhen 2	1314 ⁴¹	398
3	C5BTPhen 6	101 ⁴²	178
4	<i>n</i> -C4BTPhen 7	ca. 50 ⁴³	ca. 125
5	<i>sec</i> -C4BTPhen 8	ca. 100 ⁴³	ca. 210

Surprisingly, unlike other BTPhen ligands **2**, **6**, **7**, **8**, ligand **3** shows very low $D_{w,Am}$ and separation factors (Table 1). This phenomenon may be a result of mesomeric electron donation by the phenolic groups increasing the pK_a of the triazole rings.

Figure 5 shows the distribution ratios of Am(III) and Cm(III) (D_{Am} and D_{Cm}) for tetra(4-hydroxyphenyl)BTPhen **3** in cyclohexanone and the corresponding separation factors. In addition to the $D_{Am-gamma}$ (similar to the case of D_{Eu} measurement), D_{Am} values measured by alpha-spectrometry are shown in the graph. Excellent agreement of the $D_{Am-gamma}$ with the D_{Am} values serves as validation of the experimental procedure. Whilst there is an increasing separation factor as the concentration of nitric acid increases, the maximum value ($SF_{Am/Cm} = 2.1 \pm 0.2$ at 1 M HNO₃) is below the values observed previously for other ligands in this family. As discussed above, the Am(III) distribution ratios are rather low and D_{Am} exceed unity for [HNO₃] ≥ 0.5 M ($D_{Am} = 1.6 \pm 0.1$ for 1 M

HNO₃). The distribution ratios show that, in cyclohexanone, this ligand shows moderate selectivity for Am(III) over Cm(III) at higher concentrations of nitric acid.

The octanol studies of **3**, shown in Figure 6, indicate rather scattered separation factors. At higher concentrations of HNO₃ ([HNO₃] ≥ 0.5 mol/L), both the D_{Am} and D_{Cm} are close to, or even below, the limit of detection. Hence, this system is not a candidate for Am (III) / Cm (III) separation.

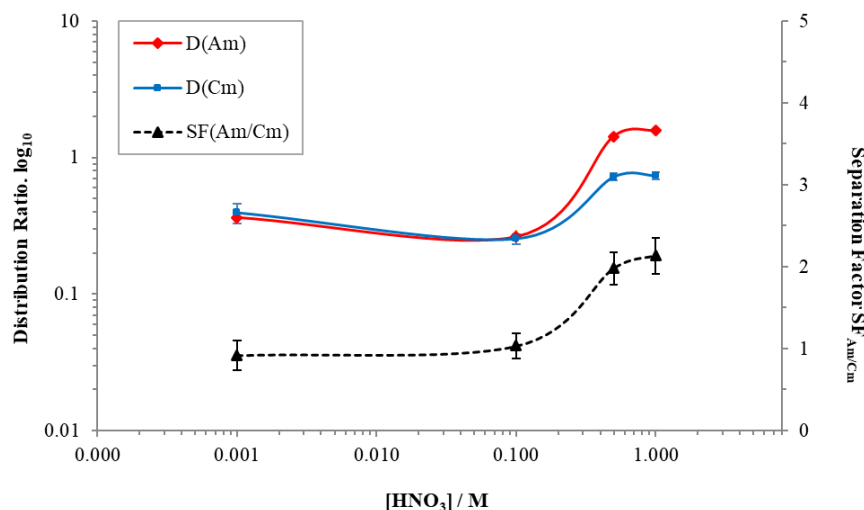


Figure 5. Extraction of Am(III) and Cm(III) by 10 mM tetra(4-hydroxyphenyl)BTPhen **3** in cyclohexanone as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

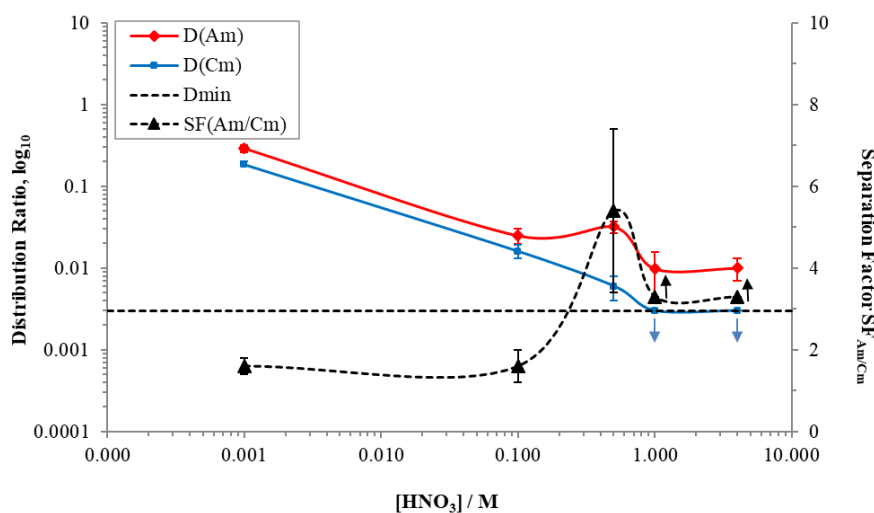


Figure 6. Extraction of Am(III) and Cm(III) by 5 mM tetra(4-hydroxyphenyl)BTPhen **3** in octanol as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

Subsequently, the ligand was immobilized onto silica gel and the resulting functionalized silica gel **4** was used in a solid-liquid extraction system. Our previous work with this silica-immobilized extractant

showed high weight distribution ratios across a range of nitric acid concentrations ($D_{w,Am} = 28 - 4883 \text{ mL g}^{-1}$, $D_{w,Eu} = 0.2 - 630 \text{ mL g}^{-1}$ from 0.001 – 4 M HNO_3) for Am(III) and Eu(III) and the highest separation factor value was calculated to be $SF_{Am/Eu} \approx 140$ at 4 M HNO_3 .³² Herein, we report the effect of the concentration of perchloric acid on the extraction of Am(III), Eu(III), and Cm(III) (Figure 7) to test the effect of pH vs anion concentration on extraction selectivity because ClO_4^- is a non-chelating counterion, unlike the coordinating nitrate ion. When comparing these data, it can be seen that, similar to the nitric acid case reported previously,³² the separation factor $SF_{Am/Eu}$ initially increases with increasing HClO_4 concentration but then decreases sharply with perchloric acid concentrations higher than 0.1 M.

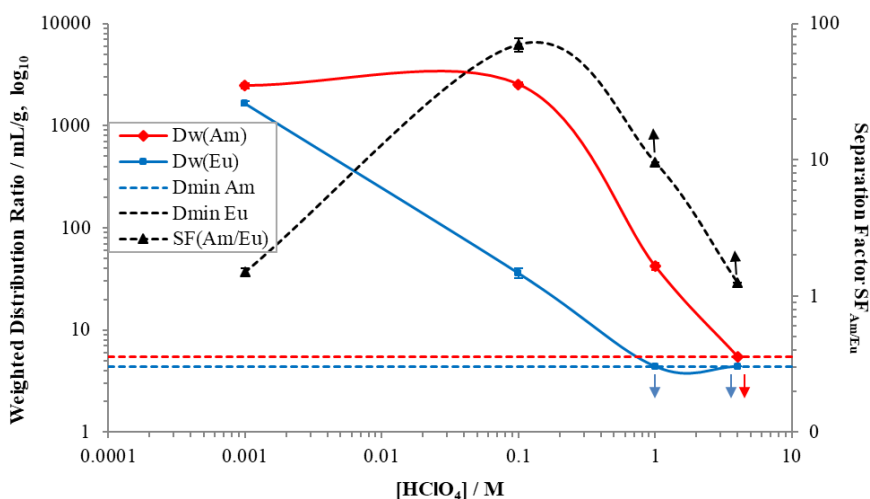


Figure 7. Extraction of Am(III) from Eu(III) by 6.4 mg of silica immobilized tetra(4-hydroxyphenyl)BTPhen **4** as a function of perchloric acid concentration. $V/m = 143 \text{ mLg}^{-1}$. The system was shaken for 90 mins at 1800 rpm.

Therefore, upon comparing the extraction data, the immobilized tetra(4-hydroxyphenyl)BTPhen **4** does not extract at higher concentrations of perchloric acid. However, the decrease of extraction efficiency with increasing acid concentration is much lower in nitric acid. Interestingly, the extraction data are not too dissimilar at lower concentrations of the acids. This would support the conclusion that pH is more important than the concentration of nitrate ions at $\text{pH} < 0.1 \text{ M}$ and the concentration of nitrate ions becomes more prevalent at concentrations $> 0.1 \text{ M}$.

As previously reported, tetra-bromomethylBTBP-immobilized on silica as its tetra-ammonium salt **5** demonstrated excellent extraction capacities for transition metals.³² Silica-immobilized tetra(4-hydroxyphenyl)BTPhen **4** was also tested for transition metal extraction. The immobilized ligand (1 g, ~9.8% BTPhen loading) was packed into a glass column (internal diameter = 13 mm), and washed

with 2% HNO₃ solution (10 mL). Stock solutions (10 mL, 100 ppb) in 2% HNO₃ were passed through the column at rate of 1 mL per minute. The filtrate was collected and analysed by ICP-MS, indicating >70% uptake of Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mo⁴⁺, Ag⁺, Cd²⁺, Pb²⁺, Pd²⁺, Os⁴⁺, Pt⁴⁺, Au³⁺, Zr⁴⁺, Nb⁵⁺, Hf⁴⁺, Ta⁵⁺, and W⁶⁺ at pH 0.5. Re⁴⁺, Ir³⁺ and Sb⁵⁺ showed lower uptakes at 68, 40, 50% respectively (Figure 8). More significantly, Ni²⁺, Pd²⁺, Ag⁺ and Cd³⁺, significant corrosion and fission products in PUREX raffinates, were found to be near quantitatively extracted. Like its BTBP counterpart, the ligand did not extract Group I, II or III metals (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺).

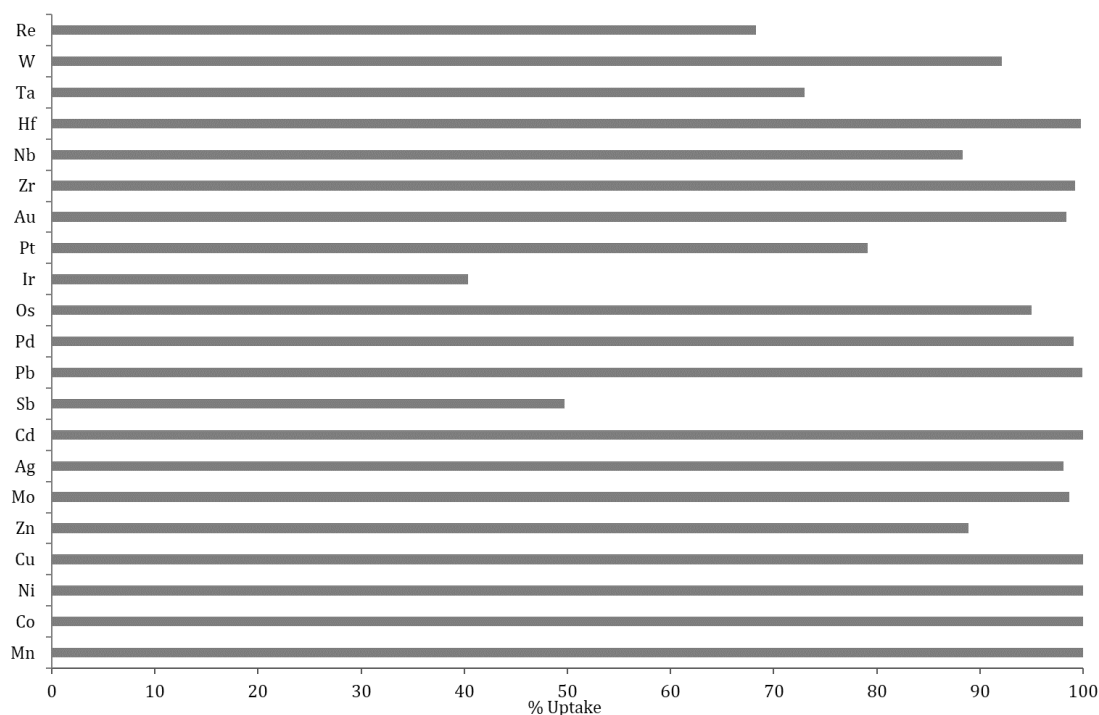


Figure 8. Percentage uptake of metal ions (10 ppb) from aqueous solution at pH 0.5 (HNO₃) by tetra(4-hydroxyphenyl)BTPhen functionalized silica **4**

In conclusion, we report the effect of diluent on the liquid-liquid extraction properties of tetra(4-hydroxyphenyl)BTPhen **3**. Cyclohexanone offers higher solubility and greater separation factors for actinide–lanthanide extraction over octanol; whereas, with octanol, the *D*-values were too low for practical application. The ligand **3** was also immobilized onto silica gel and the effects of a non-ligating acid (perchloric acid) versus a ligating acid (nitric acid) were examined. Extraction of both actinides and lanthanides was seen at lower concentrations of perchloric acid (up to 0.1 M HClO₄) but not at higher concentration as had previously been observed with nitric acid. These findings support the conclusion that the extraction ability of a ligand is strongly correlated with the complexation of the acid anions to the metal(III) ion and is only pH dependent at very low acid concentrations. The immobilized ligand system **4**

was also tested for extraction of transition metals, showing >70% uptake of most with particular affinity for Ni²⁺, Pd²⁺, Ag⁺ and Cd²⁺, the corrosion and fission products from PUREX raffinates.

EXPERIMENTAL

Tetra(4-hydroxyphenyl)BTPhen **3** and tetra(4-hydroxyphenyl)BTPhen functionalized silica gel **4** were synthesized according to our previously reported procedure.³² ¹H NMR spectra were recorded on Bruker DPX-400 (400 MHz) or Bruker Nanobay (400 MHz) spectrometers using the central resonance of DMSO-*d*₆ (DMSO, δ_H = 2.50 ppm) as internal reference. ¹³C NMR spectra were recorded on Bruker DPX-400 (101 MHz) or Bruker Nanobay (101 MHz) spectrometers using the central resonance of DMSO-*d*₆ as the internal reference. All chemical shifts are quoted in parts per million (ppm), measured from the centre of the signal, except in the case of multiplets of more than one proton, which are quoted as a range. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), multiplet (m), (ap.) apparent, (br) broad and combinations thereof. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer as a thin film. Accurate mass data were recorded on a V.G. Micromass 70-70 F machine under chemical ionisation (CI) or under electrospray conditions on a Thermo Scientific LTQ Orbitrap XL instrument. All other reagents were used as obtained from commercial sources, unless otherwise stated. ICP-MS analysis was carried out using a Thermo-Fisher iCAP Q ICP-MS with Rh as the internal standard.

Synthesis of Tetra(4-hydroxyphenyl)BTPhen **3**³²

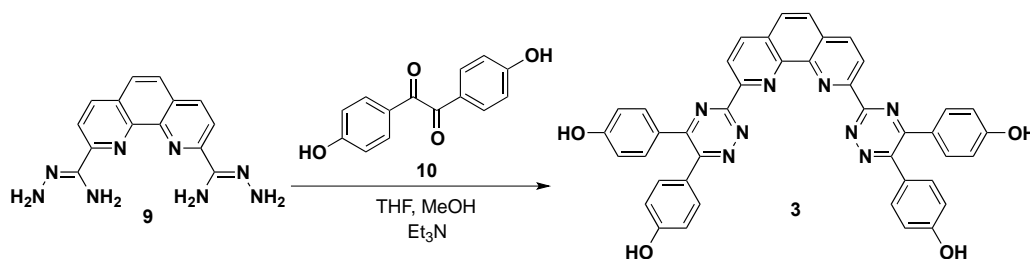


Figure 9. Synthesis of tetra(4-hydroxyphenyl)BTPhen **3**

To a suspension of 1,10-phenanthroline-2,9-dicarbohydrazonamide **9** (0.60 g, 2 mmol) in THF (100 mL) and MeOH (100 mL) was added 4,4'-dihydroxybenzil **10** (1.10 g, 4.6 mmol, 2.3 eq). Triethylamine (50 mL, 356.2 mmol) was added and the mixture was heated at 80 °C for 3 days. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with DCM (25 mL). The filtrate was evaporated and the solid was triturated with MeOH (100 mL). The insoluble solid was filtered and washed with further MeOH (50 mL) and Et₂O (50 mL) and allowed to dry in air to afford the ligand as a yellow solid (0.99 g, 69%); Mp 280–282 °C (decomp.); ¹H NMR (400.1 MHz, DMSO-*d*₆) δ_H

(ppm) = 6.78-6.93 (m, 8H), 7.51-7.71 (m, 8H), 8.11 (s, 2H), 8.58 (d, $J = 8.0$ Hz, 2H), 8.61 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$) δ_{C} (ppm) = 115.4, 122.9, 125.5, 126.1, 127.7, 129.5, 130.7, 131.6, 137.7, 145.5, 152.6, 154.6, 155.3, 159.0, 159.6, 160.5; $\text{C}_{42}\text{H}_{27}\text{O}_4\text{N}_8$ $[\text{M}+\text{H}]^+$ requires m/z 707.2150; (FTMS + P ESI) MS found m/z 707.2153; IR ν_{max} / cm^{-1} = 3206, 1608, 1590, 1483, 1442, 1377, 1276, 1240, 1169.

Immobilization of tetra(4-hydroxyphenyl)BTPPhen **3** on silica gel³²

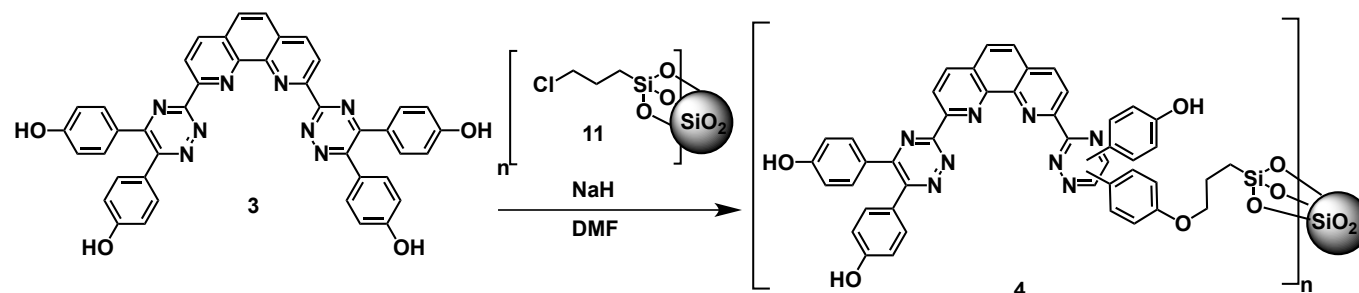


Figure 10. Immobilization of tetra(4-hydroxyphenyl)BTPPhen **3** on silica gel

Sodium hydride (60% dispersion in mineral oil, 0.24 g, 6 mmol, 2 eq) was added to a solution of tetra(4-hydroxyphenyl)BTPPhen **3** (2.11 g, 3.0 mmol) in DMF (100 mL) at 120 °C and the mixture stirred for 30 min. Chloropropyl-functionalized silica gel **11** (4.04 g, ~ 2.5 mmol/g loading) was slowly added and the reaction mixture was stirred at 120 °C overnight. The BTPPhen-functionalized SiO_2 gel **4** was collected by filtration and was thoroughly washed with water (100 mL) and EtOH (100 mL). Finally, the product (3.95 g) was allowed to dry at 120 °C.

Thermogravimetric analysis of this material showed the degree of surface modification and the quantity of loading onto the gel to be *ca.* 10%. FT-IR bands at 1500-1600 cm^{-1} suggested the presence of aromatic C=C vibrations in **4**.

Liquid-liquid and solid phase extraction testing

The aqueous solutions were prepared by spiking acid solutions (0.001 – 4 M HNO_3 or HClO_4) with ^{152}Eu , ^{241}Am , and ^{244}Cm tracers. After spiking, standards for alpha (10 μL) and gamma (200 μL) measurements were taken. In the case of solvent extraction experiments, the organic phase contains extractant **3** in octanol or cyclohexanone. Each organic phase (1 mL) was shaken separately with each (1 mL) of the aqueous phases for 90 min, to ensure equilibrium was reached, using a Heidolph Multi Reax Shaker (1,800 min^{-1}). In the case of solid phase extraction, the requisite amount of **4** was added to the spiked aqueous phase (1 mL) and the mixture shaken for 90 min to ensure equilibrium was reached, using a Heidolph Multi Reax Shaker (1,800 min^{-1}). Both experiments were non-thermostated, the temperature in

the laboratory was approximately 23 °C. After phase separation by centrifugation, two parallel 10 µL aliquots for alpha measurements and 200 µL aliquots for gamma measurements were withdrawn. Activity measurements of ^{241}Am and ^{244}Cm were performed with an ORTEC® OCTETE Plus Integrated Alpha-Spectrometry System equipped with an ion-implanted-silicon ULTRA Alpha Detector, Model BU-020-450-AS. Gamma activity measurements of ^{152}Eu and ^{241}Am were performed with a EG&G Ortec (USA) γ -ray spectrometer using a PGT (USA) HPGe detector.

The distribution ratios were calculated as $D = I_{\text{Org}}/I_{\text{Aq}}$, where the I_{org} and I_{aq} are the count rates in the organic or aqueous phase aliquots respectively. The weight distribution ratios were calculated as $D_w = (I_o - I_{\text{aq}})/I_{\text{aq}} \cdot V/m$, where I_o and I_{aq} were the initial and final counts in the taken standard/aqueous aliquot, V is the volume of the aqueous phase shaken and m is the mass of the material **4**. The separation factors are $SF_{\text{Am/Eu}} = D_{\text{Am}}/D_{\text{Eu}}$ and $SF_{\text{Am/Cm}} = D_{\text{Am}}/D_{\text{Cm}}$, or $SF_{\text{Am/Eu}} = D_{w,\text{Am}}/D_{w,\text{Eu}}$ and $SF_{\text{Am/Cm}} = D_{w,\text{Am}}/D_{w,\text{Cm}}$.

Uptake of Transition Metals using Silica Immobilized Tetra(4-hydroxyphenyl)BTPPhen

A stock solution of 2% HNO_3 spiked with 5 ppb Rh was prepared using ultra-pure water and HNO_3 (70%, purified by redistillation, $\geq 99.999\%$ trace metals basis). All standard solutions were prepared using the stock solution of 2% HNO_3 spiked with 5 ppb Rh. Standards were prepared using metal mixes purchased from Sigma-Aldrich as TraceCERT (Traceable Certified Reference Materials). Standards used to calibrate the ICP-MS were at concentrations of 5, 10, 25, 50 and 100 ppb.

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