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Separation of americium from complex radioactive mixtures using a BTPhen extraction chromatography resin

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ABSTRACT

Extraction chromatography (EC) resins are widely used in analytical radiochemical separations, in particular for actinide separation. However, there is currently limited choice for separation of americium using EC, with DGA (N,N,N′,N′-tetra-n-octyldiglycolamide) resin being the preferred option. Here, we describe preparation and testing of a covalently-linked EC resin utilising a triazine soft N-donor (Me_4BTPhen) extractant for americium extraction. The resin was generated by conjugation of a Me_4BTPhen derivative with poly(vinylbenzyl) chloride to generate PVB–Me_4BTPhen. PVB–Me_4BTPhen was shown to extract americium from a complex matrix simulating nuclear forensic samples, and containing lanthanides, actinides and matrix elements with high Am (III) recovery (>90%) and low extraction of other elements, and provides an alternative to the currently used BTPhen liquid–liquid separation process for Am (III) extraction.

1. Introduction

Soft N-donor ligands based on 1,2,4-triazines have shown selectivity for trivalent actinides (such as Am (III) and Cm) over other actinides and lanthanides [1]. Such ligands have high Am (III)/Eu (III) selectivity factors and are applicable to both the proposed n-SANEX (N-donor Selective Actinide Extraction) industrial reprocessing methodology and to complex mixtures typically expected in nuclear forensic investigations [2]. Nuclear forensic techniques aim to characterise unknown radioactive materials to provide evidence for use in legal cases, for example in seizures of illicit nuclear material. The collection of data must be performed in a timely manner and analytical techniques must be strategically applied to minimise sample loss/damage [2]. Previously, we reported use of the ligand $CyMe_4$BTPhen **1** (SF Am/Eu > 250; Fig. 1) to achieve americium separation from simulated nuclear forensic matrices containing actinides, lanthanides and matrix elements (*e.g.* d-block metals, Fe (III), Ca (II)) [3]. This process and similar separations using soft N-donor ligands on Am (III)/Eu (III) mixtures [4] employ liquid–liquid organic/aqueous extraction. However, this technique has limitations arising from poor ligand solubility, [5] variation in extraction capabilities with mixing type [3], volatile organic compounds, acidic/radiolytic stability and slow phase transfer [1]. Immobilisation of the ligand to generate an extraction chromatography (EC) resin could therefore offer advantages over the current liquid–liquid process. Other actinide-selective ligands such as diamyl amine phosphonate (DAAP) have been immobilised to generate EC resins (*e.g.* Amberlite XAD-7 (UTEVA®)). The ability to recondition the resin and vary elution methods allows extensive use in radiochemical analysis [6]. Further benefits over liquid–liquid extraction include no requirement for mixing or phase separation, and possible use of a vacuum system to increase flow rate. There are numerous EC resin methods for separation of U, Pu, Th and Np (*e.g.* TRU, TEVA®, UTEVA®). However, the only methods for Am extraction on EC resins utilise DGA or LN resin, and these methods cannot typically achieve Am (III)/ Ln (III) separations without additional purification [7]. Also, most EC resins are generated by encapsulation of a ligand into a polymeric support such as Amberlite, rather than covalent linkage between ligand and support, as has been shown for the soft N-donor ligand *iso*-propyl BTP [8]. Therefore, we surmised that a covalently-linked, soft N-donor ligand based EC resin for Am (III) (and/or Cm) could offer new benefits over the current resins for Am (III) separation in radiochemical analysis, especially in nuclear forensic investigations where a rapid result for americium is desired.

Here, we report synthesis of a Me_4BTPhen–polyvinyl benzyl (PVB) cross-linked polymer **2** (hereafter referred to as PVB–Me_4BTPhen, Fig. 1) and modification of our previously reported Am (III) extraction method. Initial experiments showed

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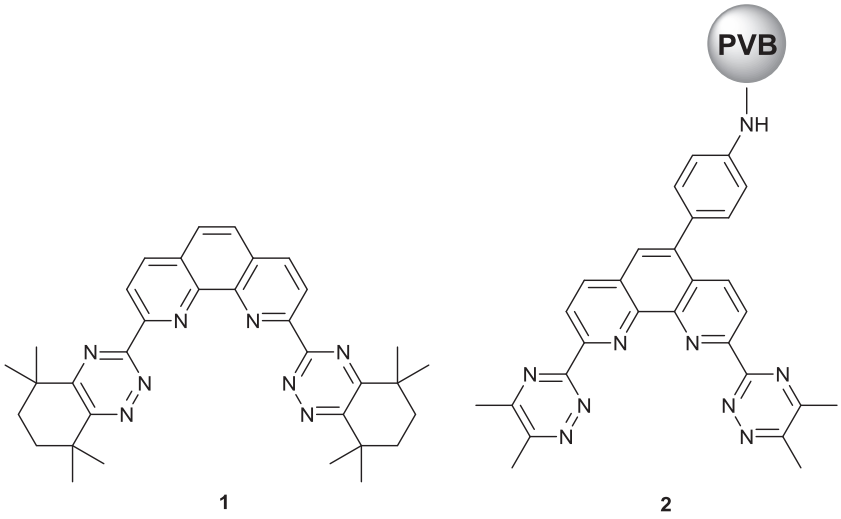

Fig. 1. Structures of CyMe$_4$BTPhen **1** and PVB–Me$_4$BTPhen **2**.

selective recovery of Am (III) over Eu (III); application of PVB–Me$_4$BTPhen to simulated nuclear forensic samples showed extraction of Am (III) with low levels of co-extraction of matrix elements and other actinides (>90% recovery of Am (III) and low (<10%) extraction of U (VI), Np (IV), Pu (IV) and all stable matrix elements with the exception of Cd (II) and Pr (III) (>20%)). We propose that the EC resin PVB–Me$_4$BTPhen **2** offers a new medium for the separation of americium from complex radioactive mixtures, in particular the lanthanides and early actinides to Pu. Our method removes the need for liquid–liquid separation and, unlike conventional Am (III) EC resins, does not require the use of thiocyanate for elution (using 0.1 M HCl).

2. Experimental

2.1. General experimental detail

All radionuclides used were provided from calibrated stocks in the School of Chemistry, University of Manchester. Micropipettes of 100 μL, 0.1–1 mL and 2–10 μL were calibrated on a 4 decimal place balance with >18 MΩ deionised water in the temperature range 18–22 °C and were found to be within their stated range (±1% RSD). All acid solutions were made from analytical grade concentrated solutions and were diluted with >18 MΩ deionised water. All solutions were considered to have expired within one month of preparation. Gamma counting was performed using a Canberra 2020 coaxial HPGe gamma spectrometer with an Ortec 919E multi-channel analyser. Alpha spectroscopy was performed on a Canberra model 7401VR detector with multi-channel analyser. ICP–MS analysis was performed on an Agilent 7500cx spectrometer. Multiple standards for each element in the range 1–100 ppb were used for ICP–MS quantification. Percentage recoveries of metal ions are calculated relative to initial amounts from the nuclear forensic matrix. All reagents and solvents used were of standard analytical grade unless otherwise stated. Melting points were determined using a Stuart Scientific SMP10 apparatus and are uncorrected. IR spectra were recorded for solid samples using a Bruker Alpha-P ATR spectrometer. NMR spectra were recorded for solutions in $CDCl_3$ or d_6-DMSO on a Bruker Avance III instrument (400 MHz) and were referenced to the residual solvent signal. Assignments were determined using COSY and HMQC experiments. Coupling constants (J values) are quoted to the nearest 0.1 Hz. Low resolution mass spectra were measured on a Micromass Platform II instrument with electrospray ionisation. Accurate mass measurements were obtained using a Micromass Q-TOF instrument with electrospray ionisation. Preparative column chromatography was performed using Sigma–Aldrich silica gel (technical grade, 60 Å, 220–240 mesh, 35–75 μm) and the flash technique [9]. All solvents used were of standard laboratory grade unless otherwise specified. Compositions of solvent mixtures are quoted as ratios of volume. Organic solutions were dried with anhydrous magnesium sulfate.

2.2. Synthesis of PVB–Me$_4$BTPhen 2

2.2.1. 5-bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline 8

Diacetal (800 mg, 4.73 mmol) and triethylamine (2.0 mL, 14.2 mmol) were added to a suspension of amidrazone **7** (890 mg, 2.38 mmol) in 1,4-dioxane (75 mL) and the mixture was stirred at reflux for 3 d. After cooling to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with ice-cold Et_2O (30 mL). The insoluble solid was filtered and washed with further ice-cold Et_2O (30 mL), then purified by column chromatography (CH_2Cl_2/MeOH gradient) to afford the *title compound* **8** as a yellow solid (330 mg, 0.70 mmol, 21%; m.p. 130–133 °C); HRMS found 473.1114, $C_{22}H_{18}BrN_8$ $(M + H)^+$ requires 473.0810; δ_H (400 MHz, $CDCl_3$) 9.01 (d, J = 8.6 Hz, 1 H), 8.93 (d, J = 8.4 Hz, 1 H), 8.88 (d, J = 8.6 Hz, 1 H), 8.39 (d, J = 8.4 Hz, 1 H), 8.30 (s, 1 H); δ_C (100 MHz, $CDCl_3$): 162.6, 161.3, 161.1, 160.3, 160.1, 154.2, 154.0, 146.9, 146.0, 137.3, 136.3, 130.6, 129.8, 129.0, 123.8, 123.7, 122.0.

2.2.2. 4-(2,9-bis(5,6-dimethyl-1,2,4-triazin-3-yl)-1,10-phenanthrolin-5-yl)aniline 9

BTPhen derivative **8** (500 mg, 1.06 mmol), 4-aminophenylboronic acid pinacol ester (257 mg, 1.17 mmol), $Pd(PPh_3)_4$ (61.5 mg, 53 μmol), and K_2CO_3 (0.59 g, 4.27 mmol) were suspended under N_2. After addition of N_2-purged THF (25 mL), methanol (7.5 mL) and water (7.5 mL), the mixture was stirred at 70 °C for 24 h. The solvents were removed *in vacuo*. The resulting crude solid was then dissolved in CH_2Cl_2 (100 mL) and washed successively with aq. KOH (100 mL, 25% w/v) and water (100 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified using column chromatography (CH_2Cl_2/MeOH 96:4) to give the *title compound* **9** (200 mg, 0.41 mmol, 39%); HRMS found 486.2110,