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Hydrophilic sulfonated bis-1,2,4-triazine ligands are highly effective reagents for separating actinides(III) from lanthanides(III) *via* selective formation of aqueous actinide complexes†

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We report the first examples of hydrophilic 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) and 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen) ligands, and their applications as actinide(III) selective aqueous complexing agents. The combination of a hydrophobic diamide ligand in the organic phase and a hydrophilic tetrasulfonated bis-triazine ligand in the aqueous phase is able to separate Am(III) from Eu(III) by selective Am(III) complex formation across a range of nitric acid concentrations with very high selectivities, and without the use of buffers. In contrast, disulfonated bis-triazine ligands are unable to separate Am(III) from Eu(III) in this system. The greater ability of the tetrasulfonated ligands to retain Am(III) selectively in the aqueous phase than the corresponding disulfonated ligands appears to be due to the higher aqueous solubilities of the complexes of the tetrasulfonated ligands with Am(III). The selectivities for Am(III) complexation observed with hydrophilic tetrasulfonated bis-triazine ligands are in many cases far higher than those found with the polyaminocarboxylate ligands previously used as actinide-selective complexing agents, and are comparable to those found with the parent hydrophobic bis-triazine ligands. Thus we demonstrate a feasible alternative method to separate actinides from lanthanides than the widely studied approach of selective actinide extraction with hydrophobic bis-1,2,4-triazine ligands such as $CyMe_4$-BTBP and $CyMe_4$-BTPhen.

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Introduction

In recent years there has been a renewed global interest in electricity production through nuclear power as many countries seek to satisfy their future energy needs while reducing their dependence on fossil fuels and their associated greenhouse gas emissions. As a result, nuclear power generation is expected to expand significantly in the next few decades, with several countries announcing plans for new reactor construction.[1] The used nuclear fuel produced by the current light water reactors is comprised mainly of uranium, plutonium, the lanthanides (>98.5 wt%) and less than 1 wt% of the minor actinides Am(III), Cm(III) and Np(III). Currently, the uranium and plutonium are recovered and recycled for re-use as mixed-oxide (MOX) fuel in the PUREX process,[2] but the remaining used fuel still contains the minor actinides, which are responsible for much of the long-term radiotoxicity ($t_{1/2} = 10^3$ to 10^6 years) and heat load of used fuel.

One approach currently being studied for the long-term management of used fuel is the 'partitioning and transmutation' strategy.[3] In this strategy, plutonium and the minor actinides will first be separated from fission products (including the lanthanides) by solvent extraction, and then used as fuel in the next generation of nuclear reactor designs. This separation is essential since some of the fission products and the lanthanides will absorb neutrons instead of the transmutable actinides. The separation of the actinides americium and curium from the lanthanides is considered a key step in increasing the safety and sustainability of nuclear energy,[4] but is nevertheless a challenging goal as the chemical properties of the two groups of elements are very similar.[5]

There is believed to be a more covalent contribution to the metal-ligand bonding with the actinides than with the lanthanides, although the exact origins of this covalency are still not

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fully understood.[6] Recent evidence from structural, spectroscopic and theoretical studies on a range of f-element complexes reinforce this view, although the extent and the nature of this covalent interaction appears to vary across the actinide series.[7,8] Consequently, many soft N- and S-donor ligands have been extensively studied[9] to perform the actinide–lanthanide separation by direct and selective extraction of the actinides from PUREX waste solutions (known as the SANEX process).[10] N-donor ligands containing 1,2,4-triazine[11] moieties have emerged as the most promising class of ligands to perform this separation. The tridentate 2,6-bis(1,2,4-triazin-3-yl)pyridines (BTPs)[12] and the tetradentate 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs)[13] have been extensively studied for this purpose in recent years. It has been shown that the annulated BTBP ligand **1** (Fig. 1) is capable of performing the selective extraction of the minor actinides directly from nitric acid solutions into an organic solvent,[14] and various laboratory demonstrations of this separation have been successfully carried out on both simulated and genuine waste solutions.[15] The more 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**.[16] Very recently, magnetic nanoparticles functionalized with ligand **2** were shown to quantitatively separate Am(III) from Eu(III),[17] paving the way for the application of ligands such as **2** in solid-phase separations. Moreover, it has been shown that two 1,2,4-triazine moieties are required for efficient and selective extractions by polypyridine N-donor ligands.[18]

An alternative method for carrying out the actinide–lanthanide separation has been proposed in several countries. This approach involves the non-selective co-extraction of actinides and lanthanides into an organic phase, followed by selective actinide back-extraction (or stripping) into an aqueous phase using a hydrophilic actinide-selective aqueous complexing agent. This is illustrated by the TALSPEAK process which was developed in the 1960s at Oak Ridge National Laboratory in the USA.[19] In this process, an acidic organophosphorus reagent such as di(2-ethylhexyl)phosphoric acid **3** is employed as the extractant and a polyaminocarboxylate ligand such as diethylenetriaminepentaacetic acid (DTPA) **4** (Fig. 1) is used as the actinide-selective hydrophilic complexing agent.

Unfortunately, this process requires the use of carboxylic acid buffers such as lactic acid or citric acid, which would result in additional secondary waste generation, and only operates within a narrow range of pH (pH 2–3) which is not compatible with that typically found in genuine PUREX waste solutions (pH $\leq$ 0). Despite extensive studies involving different combinations of hydrophobic extractants and hydrophilic aqueous complexant/buffer systems, as well as studies examining the influence of various operational parameters (*e.g.*: nature of the organic diluent, pH, temperature),[20] the TALSPEAK process has not yet reached the level of maturity required for industrial implementation.

In order to overcome the limitations of these processes, we sought to develop water-soluble hydrophilic derivatives of the highly effective bis-1,2,4-triazine N-donor ligands developed to date.[21] Furthermore, it is worth noting that the highly selective BTP and BTBP ligands retain their actinide binding selectivity when dissolved in aqueous solutions.[22] We therefore reasoned that hydrophilic sulfonated bis-1,2,4-triazine ligands would be promising reagents for selective actinide complexation even at the high nitric acid concentrations usually found in genuine waste solutions without the need for additional buffers. Indeed, a sulfonated BTP ligand was found to have excellent selectivity for actinides over lanthanides under these conditions.[23,24] In this article, we report the results of our further studies on sulfonated bis-1,2,4-triazine ligands as highly effective reagents for carrying out actinide–lanthanide separations *via* selective actinide aqueous complex formation.

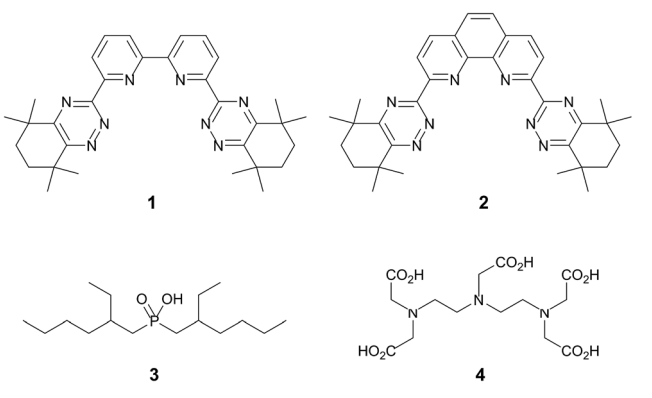
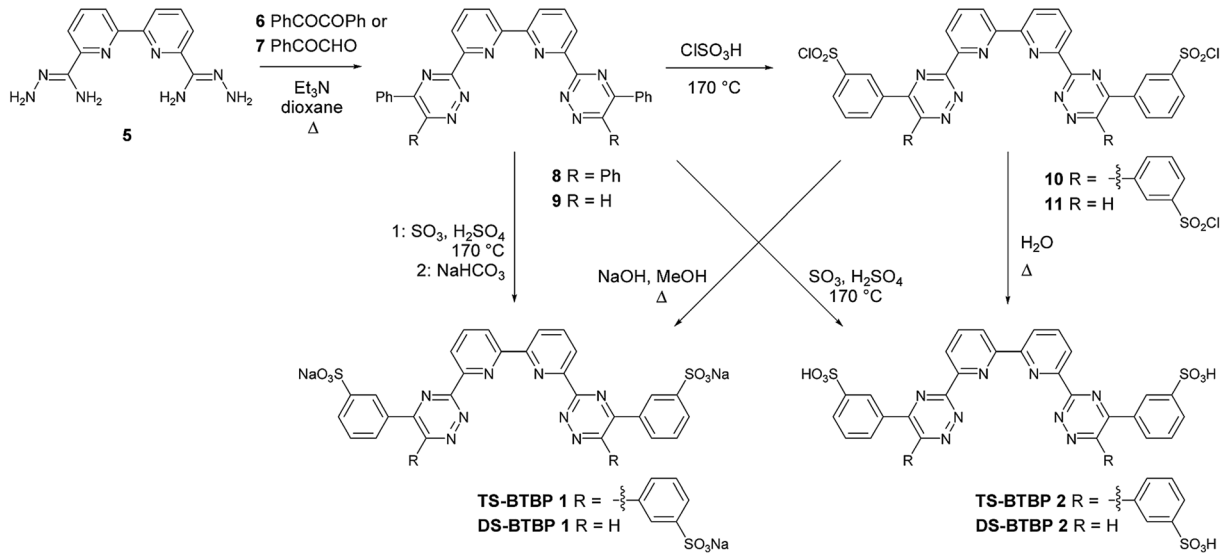


Fig. 1 Structures of the ligands $CyMe_4$-BTBP **1**, $CyMe_4$-BTPhen **2**, di(2-ethylhexyl)phosphoric acid **3** and diethylenetriaminepentaacetic acid (DTPA) **4**.

Results and discussion

Ligand synthesis

The sulfonated bis-triazine ligands were synthesized by the sulfonation of the phenyl rings of both di- and tetraphenyl bis-1,2,4-triazine ligands.[25] The di- and tetraphenyl bis-1,2,4-triazine ligands were obtained by the condensation reactions of diamide dihydrazides with either benzil or phenylglyoxal.[26] The synthesis of disulfonated BTBP ligands (**DS-BTBP**) and tetrasulfonated BTBP ligands (**TS-BTBP**) is shown in Scheme 1. The reactions of diamide dihydrazide **5** with benzil **6** and phenylglyoxal **7** afforded novel BTBPs **8** and **9**, respectively. In the synthesis of **9**, a single regioisomer was obtained, which was assigned as BTBP **9** based on literature precedent.[27] The novel sodium sulfonate BTBPs **TS-BTBP 1** and **DS-BTBP 1** were synthesized using two different approaches. The sulfonation of **8** and **9** with oleum at 170 °C, followed by base treatment ($NaHCO_3$) generated sodium sulfonates **TS-BTBP 1** and **DS-BTBP 1** directly. Alternatively, these ligands were synthesized in a two-step procedure. Treatment of **8** and **9** with chlorosulfonic acid at 170 °C generated the di- and tetrasulfonyl chlorides **10** and **11**, respectively. Hydrolysis of **10** and **11** with sodium hydroxide in refluxing methanol furnished the sodium sulfonates **TS-BTBP 1** and **DS-BTBP 1**, respectively. We found that optimization of this latter two-step route to **TS-BTBP 1** and



Scheme 1 Synthesis of disulfonated BTBP (**DS-BTBP**) ligands **DS-BTBP 1** and **DS-BTBP 2**, and tetrasulfonated BTBP (**TS-BTBP**) ligands **TS-BTBP 1** and **TS-BTBP 2**.

DS-BTBP 1 minimized the contamination of the ligands with inorganic salts.

To probe the effect of the counterion on the selective complexation properties of the sulfonated ligands, we also synthesized the di- and tetrasulfonated BTBPs as their corresponding free acids **TS-BTBP 2** and **DS-BTBP 2** (Scheme 1). These were synthesized either by hydrolysis of the sulfonyl chlorides **10** and **11** with water at reflux, or, more preferably, by direct sulfonation of BTBPs **8** and **9** with oleum and subsequent precipitation of the ligands with acetone.

The regioselectivity of the sulfonation reactions of **8** and **9** was established by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the disulfonated BTBP ligand **DS-BTBP 1** in deuterated DMSO (Fig. 2) shows the expected spin–spin coupling pattern of a *meta*-disubstituted phenyl ring. As well as the expected resonances for the pyridine protons H1–H3, the spectrum displays a triplet for H8 at 8.74 ppm with very weak ($J = 1.4$ Hz) *meta*-coupling to H7/H5. Proton H6 appears as a triplet at 7.67 ppm with strong ($J = 7.7$ Hz) *ortho*-coupling to H7/H5, while protons H7 and H5 appear as a pair of double-triplets. Thus the sulfonation reactions of **8** and **9** occurred in the *meta*-position, as anticipated based on the electronic deactivation of the *ortho*- and *para*-positions of the phenyl rings of **8** and **9** by the electron withdrawing triazine rings. Regioselective *meta*-sulfonation was previously reported in the chlorosulfonation reactions of some 5,6-diphenylpyrazines,[28] which are electronically similar to the 5,6-diphenyl-1,2,4-triazine moiety of ligand **8**.

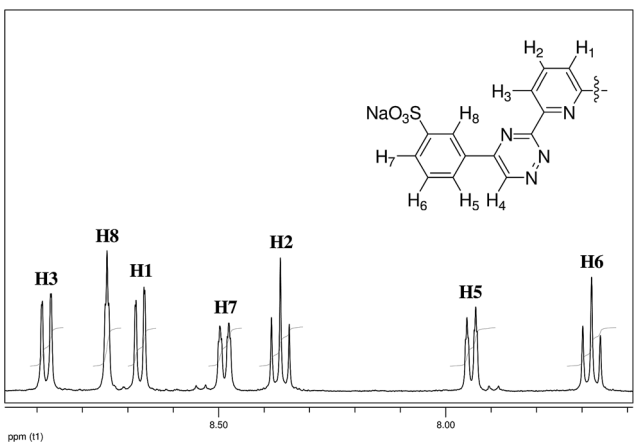
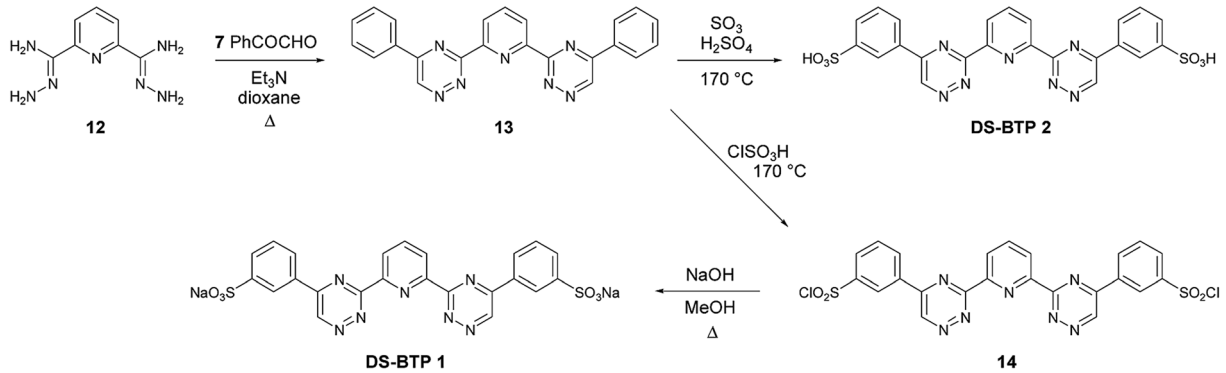


Fig. 2 Aromatic region of the ^{1}H NMR spectrum of disulfonated BTBP ligand **DS-BTBP 1** in deuterated DMSO with peak assignments (H4 appears as a singlet at 10.18 ppm and is omitted for clarity).

We also synthesized the disulfonated BTP (**DS-BTP**) ligands **DS-BTP 1** and **DS-BTP 2** as shown in Scheme 2. These ligands have a lower sulfur content that the previously reported tetrasulfonated BTP,[23,24] and thus would generate less solid waste after incineration of the spent solvent streams from used fuel reprocessing. Diphenyl-BTP **13** was obtained as a single regioisomer by treatment of diamide dihydrazide **12** with phenylglyoxal in hot dioxane. Disodium sulfonate BTP **DS-BTP 1** was synthesized by the chlorosulfonation of **13** with chlorosulfonic acid, followed by hydrolysis of the resulting disulfonyl chloride **14**. Disulfonic acid BTP **DS-BTP 2** was also synthesized by the direct sulfonation of **13** with oleum, followed by precipitation with acetone (Scheme 2).

In order to establish if the point of attachment of the sulfonated phenyl rings on the triazine rings of disulfonated BTPs **DS-BTP 1** and **DS-BTP 2** had any significant influence on its complexation properties, we also synthesized and screened the regioisomeric BTPs **DS-BTP 3** and **DS-BTP 4** in which the sulfonated phenyl rings are attached at C-6 of the triazine ring (Scheme 3). Diphenyl-BTP **15** (the opposite regioisomer of **13**) was thus synthesized from acetophenone as previously described in the literature,[29] and sulfonated as before to yield **DS-BTP 3** and **DS-BTP 4**.



Scheme 2 Synthesis of disulfonated BTP (DS-BTP) ligands DS-BTP 1 and DS-BTP 2.

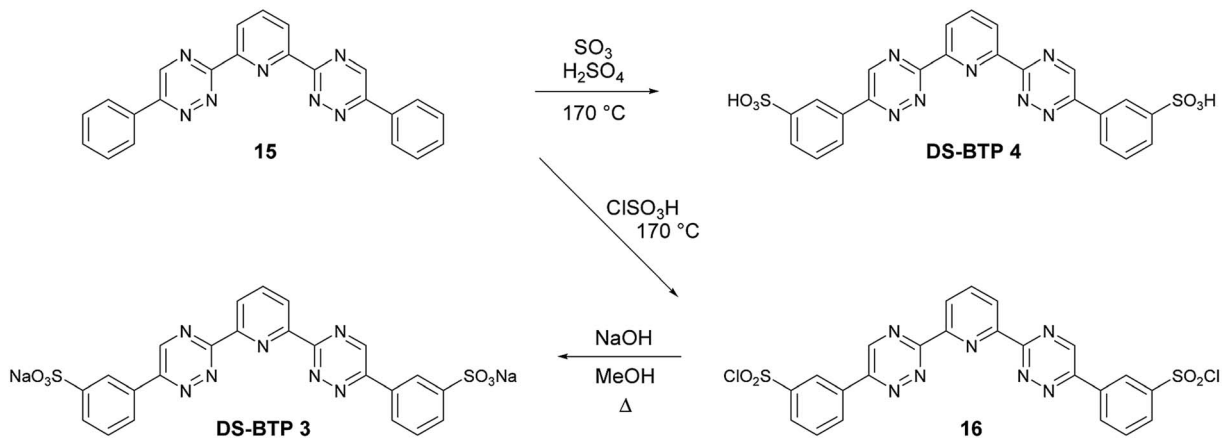
The hydrophobic BTPhen ligand **2** was found to be an improved ligand for the selective extraction of actinide(III) over lanthanide(III) than the related BTBP **1** (Fig. 1).[16] We therefore reasoned that a hydrophilic tetrasulfonated BTPhen ligand might be a more selective actinide(III) aqueous complexant than its BTBP counterparts **TS-BTBP 1** and **TS-BTBP 2** (Scheme 1), and could be capable of preventing the extraction of actinide(s)(III) by the non-selective hydrophobic ligand *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA) at higher nitric acid concentrations. We thus synthesized the tetrasulfonated BTPhen (**TS-BTPhen**) ligands **TS-BTPhen 1** and **TS-BTPhen 2** from the novel tetraphenyl-BTPhen **18** as shown in Scheme 4.

Numerous attempts to grow suitable crystals of the sulfonated ligands **TS-BTBP 1**, **DS-BTBP 1**, **DS-BTP 1** and **TS-BTPhen 1** for X-ray crystallographic analysis by slow evaporation from water or water/methanol mixtures were made without success. In order to aid the isolation of crystals suitable for X-ray analysis, lipophilic derivatives of **TS-BTBP 1** and **DS-BTP 1** were synthesized by cation metathesis reactions of **TS-BTBP 1** and **DS-BTP 1** with tetraphenylphosphonium chloride in water (Scheme 5). The resulting tetraphenylphosphonium salts **20** and **21** were obtained in high yields, and were soluble in most organic solvents. However, our attempts to obtain crystals of **20** and **21** suitable for X-ray analysis by slow evaporation from organic solvents met with no success.

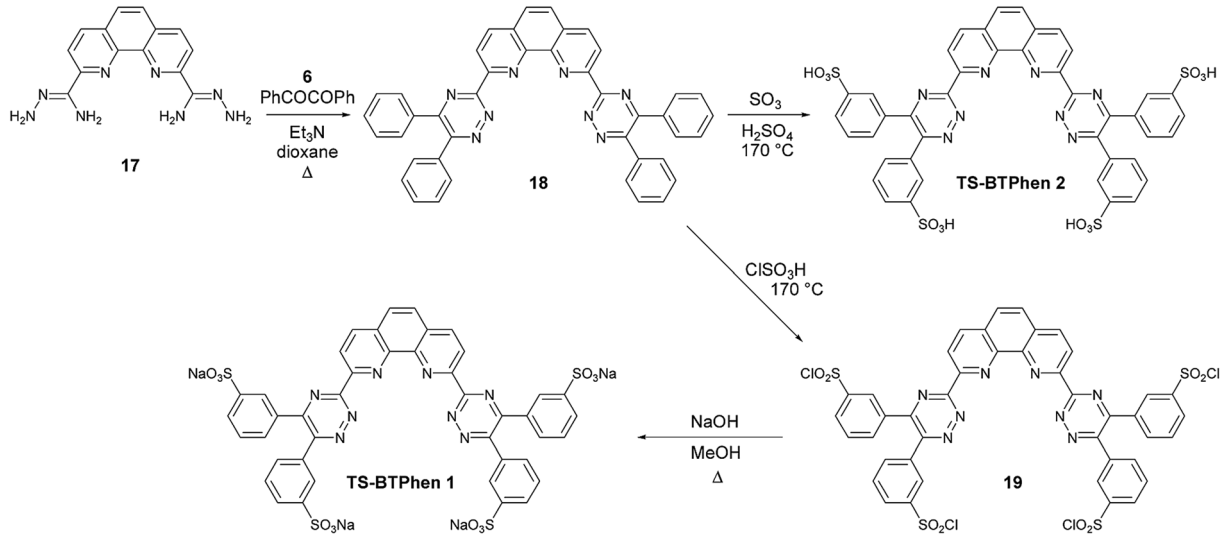
Solvent extraction studies

The solubilities of the sulfonated bis-triazine ligands in 0.5 M nitric acid are presented in the ESI.† The tetrasulfonated ligands **TS-BTBP 1**, **TS-BTBP 2**, **TS-BTPhen 1**, and **TS-BTPhen 2** all showed high aqueous solubilities (>0.11 M). Surprisingly, the solubilities of disulfonated BTPs **DS-BTP 1** and **DS-BTP 2** were similar to those of the tetrasulfonated BTBP and BTPhen ligands, despite only having half the number of sulfonate groups. In contrast, disulfonated BTBPs **DS-BTBP 1** and **DS-BTBP 2** were significantly less soluble in water than their tetrasulfonated counterparts **TS-BTBP 1** and **TS-BTBP 2**, and formed turbid solutions in water and nitric acid. Disulfonated BTP **DS-BTP 4** was significantly less soluble than its regioisomer **DS-BTP 2**, while disodium sulfonate BTP **DS-BTP 3** was not sufficiently soluble to be used in the extraction tests (<0.005 M).

The sulfonated ligands were tested for their ability to suppress selectively (or mask) the extraction of Am(III) from nitric acid solutions by the hydrophobic O-donor ligand *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA). This ligand is the preferred ligand for the non-selective co-extraction of An(III) and Ln(III) from high level waste solutions; the essential first step in the reprocessing of used nuclear fuel (known in Europe as the DIAMEX process).[30] Each of the sulfonated ligands (0.01 M) was added to 0.5 M HNO_3 spiked with Am(III) and Eu(III) tracers, and the distribution ratios and separation factors were measured



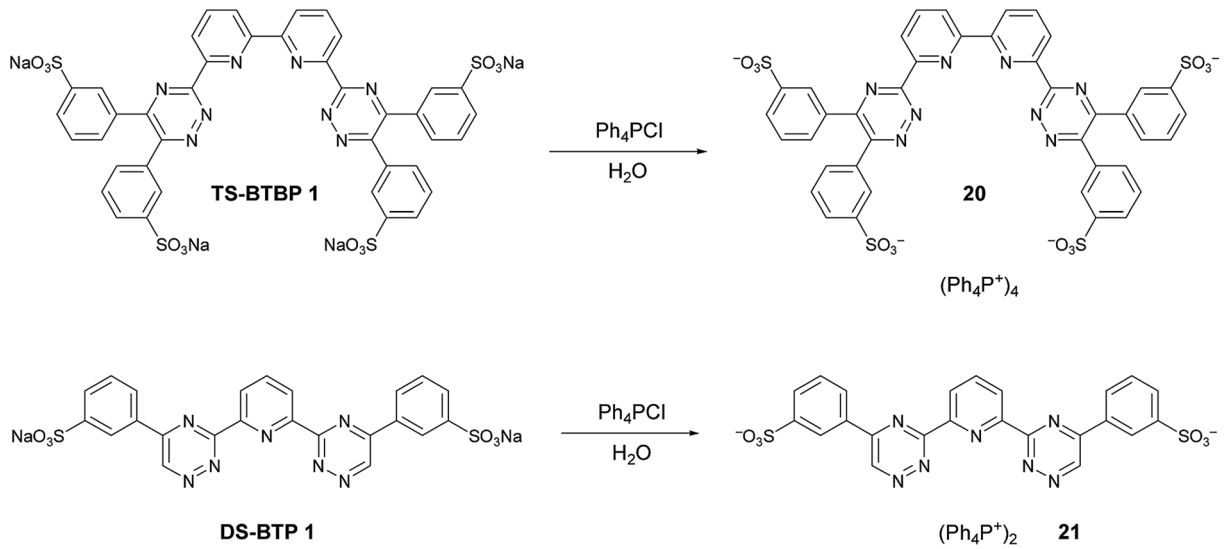
Scheme 3 Synthesis of disulfonated BTP (DS-BTP) ligands DS-BTP 3 and DS-BTP 4.



Scheme 4 Synthesis of tetrasulfonated BTPhen (**TS-BTPhen**) ligands **TS-BTPhen 1** and **TS-BTPhen 2**.

after contacting these aqueous phases with organic solutions containing TODGA (0.2 M) in kerosene/octanol (volume ratio 95 : 5). These results were compared to that of a blank sample, which did not contain any sulfonated ligand in the aqueous phase. The results for the tetrasulfonated bis-triazine ligands **TS-BTBP 1**, **TS-BTBP 2**, **TS-BTPhen 1** and **TS-BTPhen 2** are shown in Fig. 3.

As shown, all the tetrasulfonated ligands are able to suppress the extraction of Am(III) from the aqueous phase by TODGA, while the extraction of Eu(III) by TODGA is far less suppressed. The net result is that Eu(III) is selectively extracted. In the case of **TS-BTBP 1**, the distribution ratio for Am(III) decreases from 46.0 ± 4 in the absence of **TS-BTBP 1** in the aqueous phase to 0.121 ± 0.009 in the presence of **TS-BTBP 1** in the aqueous phase. The resulting separation factor for Eu(III) over Am(III) increases from 3.5 ± 0.9 in the absence of **TS-BTBP 1** to 616 ± 178 in the presence of **TS-BTBP 1** in the aqueous phase. When any of the four tetrasulfonated BTBP or BTPhen ligands are used, the distribution ratios for Am(III) are below 1, while those for Eu(III) remain above 50. The separation factors for Eu(III) over Am(III) ($SF_{Eu/Am}$) for all four ligands are in the range 256–616. The decrease in D_{Am} and increase in $SF_{Eu/Am}$ on adding a tetrasulfonated bis-triazine ligand to the aqueous phase is an indication that these sulfonated ligands are complexing Am(III) over Eu(III) in a highly selective manner. The results for the free acids **TS-BTBP 2** and **TS-BTPhen 2** are comparable to those for the corresponding sodium salts **TS-BTBP 1** and **TS-BTPhen 1**, indicating that the counterions play very little role in the selective complexation of Am(III) as expected. Interestingly, the results for the tetrasulfonated BTBPs are comparable to those of



Scheme 5 Synthesis of tetraphenylphosphonium sulfonate ligands **20** and **21** *via* cation metathesis reactions of ligands **TS-BTBP 1** and **DS-BTP 1**.

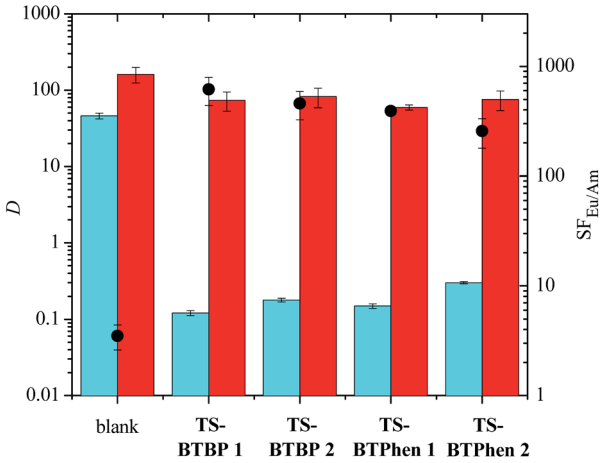


Fig. 3 Extraction of Am(III) and Eu(III) from 0.5 M nitric acid by TODGA (0.2 M dissolved in 5 vol% octanol in kerosene) in the absence and presence of tetrasulfonated BTBP and BTPhen ligands (0.01 M) in the aqueous phase (D = distribution ratio, SF = separation factor, blue bar = D_{Am}, red bar = D_{Eu}, ● = $SF_{Eu/Am}$, mixing time: 360 min, temperature: 22 °C ± 1 °C).

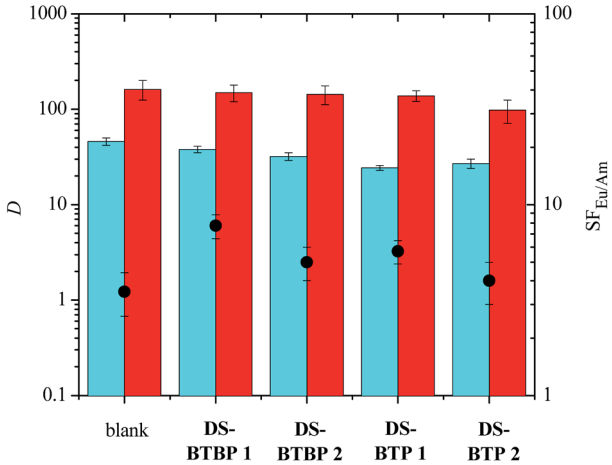


Fig. 4 Extraction of Am(III) and Eu(III) from 0.5 M nitric acid by TODGA (0.2 M dissolved in 5 vol% octanol in kerosene) in the absence and presence of disulfonated BTBP and BTP ligands (0.01 M) in the aqueous phase (D = distribution ratio, SF = separation factor, blue bar = D_{Am}, red bar = D_{Eu}, ● = $SF_{Eu/Am}$, mixing time: 360 min, temperature: 22 °C ± 1 °C).

the corresponding BTPhens, with the $SF_{Eu/Am}$ values for the tetrasulfonated BTPhens **TS-BTPhen 1** and **TS-BTPhen 2** being slightly lower than those of the corresponding BTBPs **TS-BTBP 1** and **TS-BTBP 2**.

Thus, in contrast to ligands **3** and **4** employed in the TALSPEAK process, the combination of a tetrasulfonated bis-1,2,4-triazine ligand **TS-BTBP 1**, **TS-BTBP 2**, **TS-BTPhen 1** or **TS-BTPhen 2** in the aqueous phase and TODGA in the organic phase is able to separate An(III) from Ln(III) in nitric acid solutions of low pH (0.5 M HNO_3) with very high selectivity. It should also be emphasized that, in contrast to the TALSPEAK process, there is no need for additional buffers or salting out agents when one of these tetrasulfonated bis-triazine ligands is used.

The disulfonated ligands **DS-BTBP 1**, **DS-BTBP 2**, **DS-BTP 1** and **DS-BTP 2** were tested under identical conditions to those of the tetrasulfonated BTBP and BTPhen ligands, and the results are presented in Fig. 4. In these cases, the extraction of Am(III) from the aqueous phase by TODGA is only slightly suppressed, and the separation factor for Eu(III) over Am(III) increases only slightly. The highest separation factor was found with disulfonated BTBP **DS-BTBP 1** ($SF_{Eu/Am}$ = 7.75 ± 1.1). Clearly, these disulfonated ligands are less able to suppress the extraction of Am(III) from the aqueous phase by TODGA. In the case of disulfonated BTBPs **DS-BTBP 1** and **DS-BTBP 2**, this could be due to their low aqueous solubilities. However, the results are no better for disulfonated BTPs **DS-BTP 1** and **DS-BTP 2** despite their higher aqueous solubilities (see ESI†). These ligands also fail to suppress the extraction of Am(III) by TODGA. The results for ligands **DS-BTP 1** and **DS-BTP 2** are inferior to those of their tetrasulfonated BTP counterpart.[24] Likewise, 5 mM solutions of disulfonated BTP **DS-BTP 4** were unable to suppress Am(III) extraction by TODGA, and showed similar extraction results to its regioisomeric BTP **DS-BTP 2** (see ESI†). These results demonstrate that four sulfonate groups are required for the highly selective complexation of Am(III) over Eu(III) by bis-triazine ligands in these TALSPEAK-type separation processes.

We next examined the ability of each sulfonated bis-triazine ligand to suppress the extraction of Am(III) at different nitric acid concentrations to probe the effect of pH on the separation process. Each of the sulfonated bis-triazine ligands followed a trend of increasing distribution ratios for Am(III) and decreasing separation factors of Eu(III) over Am(III) with increasing nitric acid concentration of the aqueous phase (see ESI†). The results for **TS-BTBP 1** are shown in Fig. 5. For the tetrasulfonated BTBP **TS-BTBP 1**, $SF_{Eu/Am}$ decreases from 707 ± 312 in 0.28 M HNO_3 to 127 ± 73 in 1.04 M HNO_3, and the D values for both Am(III) and

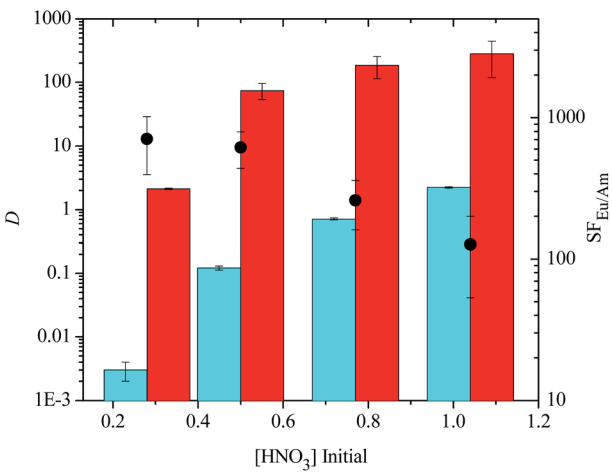


Fig. 5 Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol% octanol in kerosene) in the presence of tetrasulfonated BTBP ligand **TS-BTBP 1** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, blue bars = D_{Am}, red bars = D_{Eu}, ● = $SF_{Eu/Am}$, mixing time: 360 min, temperature: 22 °C ± 1 °C).

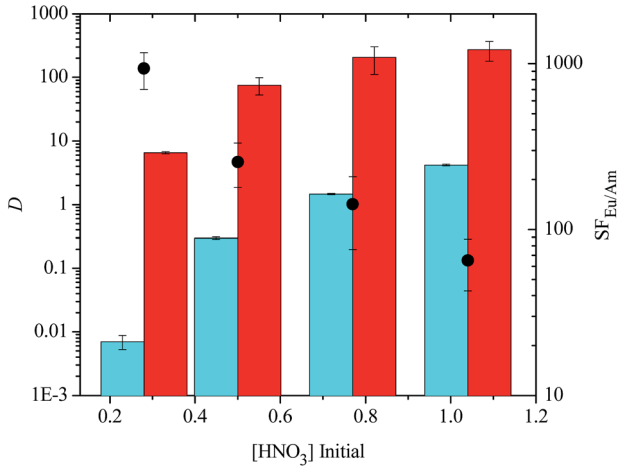


Fig. 6 Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol% octanol in kerosene) in the presence of tetrasulfonated BTPhen ligand **TS-BTPhen 2** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, blue bars = D_{Am}, red bars = D_{Eu}, ● = $SF_{Eu/Am}$, mixing time: 360 min, temperature: 22 °C ± 1 °C).

Eu(III) increase as the nitric acid concentration increases. However, D_{Am} increases somewhat more rapidly than D_{Eu} as $[HNO_3]$ increases, leading to lower selectivities for Eu(III) over Am(III) at higher acid concentrations. However, **TS-BTBP 1** still complexes Am(III) in a selective manner ($SF_{Eu/Am} = 127 \pm 73$) even in 1.04 M HNO_3 (Fig. 5), indicating that effective separations of Eu(III) over Am(III) are possible across a wide pH range.

Similar results were observed for **TS-BTPhen 2** (Fig. 6). For this ligand, $SF_{Eu/Am}$ decreased from 934 ± 233 in 0.28 M HNO_3 to 65 ± 22 in 1.04 M HNO_3. For all the tetrasulfonated ligands, good separations ($D_{Am} < 1$, $D_{Eu} > 1$) of Eu(III) over Am(III) were observed at $[HNO_3] \leq 0.5$ M. In the case of **TS-BTBP 1** and **TS-BTBP 2**, the distribution ratios for Am(III) remained below 1 even in 0.77 M HNO_3. However, at higher nitric acid concentrations, Am(III) extraction by TODGA was no longer suppressed by the sulfonated ligand, and both elements were extracted from the aqueous phase. This is consistent with the observation that the D values for the extraction of Am(III) and Eu(III) by TODGA increase as $[HNO_3]$ increases.[30] These results show that the tetrasulfonated bis-triazine ligands can selectively complex Am(III) and prevent its extraction by TODGA across a wide range of nitric acid concentrations without the need for additional buffers such as lactic acid or citric acid. This is in contrast to the TALSPEAK process which operates within a very restricted pH range (pH = 2–3) that has to be maintained with the aid of buffers. None of the disulfonated BTBP or BTP ligands were able to complex Am(III) selectively and suppress its extraction by TODGA regardless of the nitric acid concentration of the aqueous phase (*i.e.*: $D_{Am} > 1$, see ESI†).

The selectivities of the tetrasulfonated bis-triazine ligands for Am(III) complexation are in general higher than those observed with the polyaminocarboxylate ligands used in the TALSPEAK process. The separation factors for Eu(III) over Am(III) observed with the polyaminocarboxylate ligands used in the TALSPEAK process are shown below in Table 1. Diethylenetriaminepentaacetic acid (DTPA) **4** generally gives the highest selectivities for the complexation of Am(III) over Eu(III), with a maximum separation factor for Eu(III) over Am(III) ($SF_{Eu/Am}$) of 105 being observed in a 1 M citric acid-buffered aqueous phase at pH 3. Other polyaminocarboxylates such as hydroxyethylethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA) and *trans*-1,2-diaminocyclohexanetetraacetic acid (DCTA) give lower separation factors for Eu(III) over Am(III).

In contrast, the separation factors for Eu(III) over Am(III) observed with the tetrasulfonated ligands **TS-BTBP 1** and **TS-BTPhen 2** shown in Table 2 are in many cases significantly higher than those found with the polyaminocarboxylate ligands used in TALSPEAK separations. For **TS-BTBP 1**, higher separation factors ($SF_{Eu/Am}$) are found in nitric acid concentrations ranging from 0.28 M to 1.04 M, with a maximum separation factor of 707 ± 312 in 0.28 M HNO_3. For **TS-BTPhen 2**, higher separation factors ($SF_{Eu/Am}$) are found between 0.28 and 0.77 M HNO_3, and the highest separation factor ($SF_{Eu/Am}$) is 934 ± 233 in 0.28 M HNO_3. Only in the case of **TS-BTPhen 2** and **TS-BTPhen 1** in 1.04 M HNO_3 are lower separation factors for Eu(III) over Am(III) found than with DTPA **4** in the TALSPEAK system ($SF_{Eu/Am} = 65 \pm 22$ and 31 ± 13, respectively).

The selectivities of the tetrasulfonated ligands **TS-BTBP 1**, **TS-BTBP 2**, **TS-BTPhen 1** and **TS-BTPhen 2** for Am(III) complexation over Eu(III) are also similar to those of the parent

Table 1 Separation factors for Eu(III) over Am(III) ($SF_{Eu/Am}$) observed in the TALSPEAK system[a]

Hydrophilic ligand	$SF_{Eu/Am}$	Aqueous phase	Organic phase	Ref.
DTPA **4** (0.05 M)	84	Glycolic acid,[b] pH 3	**3** In DIPB[c]	19c,20a
DTPA **4** (0.05 M)	91	Lactic acid,[b] pH 3	**3** In DIPB[c]	19c,20a
DTPA **4** (0.05 M)	105	Citric acid,[b] pH 3	**3** In DIPB[c]	19c,20a
DTPA **4** (0.05 M)	100	Lactic acid,[b] Na^+,[b] pH 4.27	**3** In DIPB[d]	20b
DTPA **4** (0.05 M)	84	Lactic acid,[b] Na^+,[b] pH 2.48	**3** In DIPB[d]	20b
HEDTA (0.005 M)	62	Lactic acid,[b] pH 3	**3** In DIPB[c]	19c
EDTA (0.005 M)	59	Lactic acid,[b] pH 3	**3** In DIPB[c]	19c
DCTA (0.005 M)	32	Lactic acid,[b] pH 3	**3** In DIPB[c]	19c

[a] HEDTA = hydroxyethylethylenediaminetriacetic acid, EDTA = ethylenediaminetetraacetic acid, DCTA = *trans*-1,2-diaminocyclohexanetetraacetic acid, DIPB = 1,4-diisopropylbenzene. [b] 1 M. [c] 0.2 M. [d] 0.5 M.

Table 2 Separation factors for Eu(III) over Am(III) ($SF_{Eu/Am}$) observed with the tetrasulfonated BTBP and BTPhen ligands[a]

Hydrophilic ligand	$SF_{Eu/Am}$	Aqueous phase	Organic phase
TS-BTBP 1	707 ± 312	0.28 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTBP 1	616 ± 178	0.5 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTBP 1	260 ± 99	0.77 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTBP 1	127 ± 73	1.04 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTPhen 2	934 ± 233	0.28 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTPhen 2	256 ± 77	0.5 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTPhen 2	142 ± 66	0.77 M HNO_3	TODGA[b] in 5% octanol in kerosene
TS-BTPhen 2	65 ± 22	1.04 M HNO_3	TODGA[b] in 5% octanol in kerosene

[a] TODGA = *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide. [b] 0.2 M.

hydrophobic ligands BTBP **1** and BTPhen **2** (Fig. 1). The overall separation factor for Eu(III) over Am(III) observed herein with the combination of TODGA in the organic phase and a tetrasulfonated bis-triazine ligand in the aqueous phase is approximately equal to the product of that found for TODGA and a typical hydrophobic BTBP or BTPhen ligand such as BTBP **1** or BTPhen **2**. Thus, in the case of **TS-BTBP 1**, the overall $SF_{Eu/Am}$ of 707 ± 312 in 0.28 M HNO_3 is comparable to the product of that typically found with TODGA ($SF_{Eu/Am}$ = 6.2, see ESI†) and BTBP **1** ($SF_{Am/Eu}$ = approx. 150).[14] Similarly, with **TS-BTPhen 2**, the overall $SF_{Eu/Am}$ of 934 ± 233 is comparable to the product of that found with TODGA ($SF_{Eu/Am}$ = 6.2) and BTPhen **2** ($SF_{Am/Eu}$ = approx. 150–200).[16] This shows that the selectivities of the parent hydrophobic ligands **1** and **2** for Am(III) complexation over Eu(III) are largely preserved when they are made water-soluble by sulfonation.

Conclusions

In summary, we report that tetrasulfonated bis-triazine ligands are highly promising reagents for the separation of trivalent actinides from trivalent lanthanides *via* selective aqueous complexation of actinides in new actinide–lanthanide separation processes based on the TALSPEAK system. Tetrasulfonated bis-triazine ligands are able to selectively complex Am(III) over Eu(III) across a range of nitric acid concentrations (0.28–0.77 M HNO_3) with very high selectivities ($SF_{Eu/Am}$ = 138–934) and without the use of buffers. The selectivities of the tetrasulfonated ligands for Am(III) complexation over Eu(III) are in many cases far higher than those found with the polyaminocarboxylate ligands used in TALSPEAK separations, and are comparable to those of the parent hydrophobic BTBP and BTPhen ligands being studied for selective actinide extraction. Tetrasulfonated bis-triazine ligands thus represent a considerable improvement over the hydrophilic ligands used in the TALSPEAK process. In contrast, disulfonated bis-triazine ligands are unable to selectively complex Am(III) in nitric acid, indicating that four sulfonate groups are required for selective Am(III) complex formation in nitric acid. The number of sulfonate groups was found to be more important for the separation of Am(III) from Eu(III) than the type of ligand used (BTP/BTBP/BTPhen), the location of the sulfonated phenyl ring(s) in the molecule (attached to C-5 or C-6 of the triazine rings) or the counterion used (H^+/Na^+).

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