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Ligands for f-element extraction used in the nuclear fuel cycle

Different types of organophosphorus, diamide and N-heterocyclic ligands, and their individual pre-organisation on molecular platforms, are being used for the separation of actinides and lanthanides from nuclear waste.

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## Ligands for f-element extraction used in the nuclear fuel cycle

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Liquid–liquid extraction is the major technique being applied for the partitioning of f-elements from nuclear waste. In this review, the recent developments in ligand design, optimization and extraction properties are summarised for the main classes of extractants (organophosphorus ligands, diamides and N-heterocycles), with a focus on the separation of actinides and lanthanides. Structural modifications, pre-organisation and different solvent systems, as key factors for the fine-tuning of the extraction properties, are discussed. From this review, it appears that small modifications of the structure of the ligand, the pre-organising platform or the solvent can have significant impact on the extraction (and separation) of metal ions. Interest in the combinations of ligands for the extraction processes is growing, since they provide improvements over individual ligands. Similarly, unconventional approaches are being pursued to develop more efficient and greener processes.

### Introduction

A drawback of energy production using nuclear power plants is the disposal of spent nuclear fuel, due to the long-term and high radiotoxicity generated by the minor actinides (An) and plutonium. Partitioning and transmutation (P&T)<sup>1–3</sup> is an approach aimed at the separation (partitioning) of the spent nuclear fuel into its components, followed by transmutation of

An into less hazardous isotopes. However, due to their high neutron-poisoning capacity, the lanthanides (Ln) need to be separated before the transmutation of An, because they prevent the process;<sup>4</sup> this would provide a source of metals of technological interest.<sup>5</sup> Due to their similar physical and chemical properties, the partitioning of An and Ln is the most challenging hydro-metallurgical separation known.<sup>6</sup>

Solvent extraction is a common technique for the separation of An and Ln, and a series of partitioning approaches has been developed.<sup>7–9</sup> These separation processes rely on the use of complexing ligands, organic solvents, ionic liquids (ILs), or a combination thereof, ideally allowing for several parameters to

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be changed to improve the separation efficiency. The use of room temperature ionic liquids (RTILs) is gaining increasing attention because these potentially “green”<sup>10,11</sup> solvents can have beneficial effects on the extraction properties of the ligands. On the other hand, their inherent disadvantages (*i.e.* high viscosity and poor resistance to radiolytic degradation) need careful consideration.<sup>12</sup>

The classes of ligands on which research efforts have been mostly focused in recent years are neutral and acidic organophosphorus compounds (developed initially for the PUREX, TRUEX and TALSPEAK processes),<sup>7</sup> diamides, such as diglycolamides (DGAs)<sup>13</sup> and malonamides (for the DIAMEX process), and N-heterocyclic ligands (for the SANEX process).<sup>14</sup> Several reviews dealing with specific subjects within the nuclear waste remediation have been published in recent years. Heterogeneous materials for the support of ligands<sup>15–17</sup> as well as ionic liquid systems<sup>12,18,19</sup> have received particular attention. To the best of our knowledge, however, an overview comprising the most important classes of ligands of interest, and their recent development, is not available.

In the present review, we focus on the latest advances made in the area of development, modification and application of suitable ligands for liquid–liquid extraction of An and Ln. The discussion is divided into three parts and follows the chronological order of the development of the main classes of ligands (organophosphorus ligands, diamides and N-heterocycles). For each of them, the effect of structural modifications, the platforms for pre-organisation and the effect of different solvent systems, including ionic liquids, are discussed.

Reports regarding analytical techniques, physico-chemical data, computational studies, and extraction chromatography and solid phase extraction<sup>20</sup> have been included only when they contribute to clarity or context.

## Organophosphorus ligands

### Background and synthetic approach

Organophosphorus compounds are among the first classes of compounds that were employed for the reprocessing of spent

nuclear fuel, and generally favour the complexation of An over that of Ln(III). Tributylphosphate (TBP) has been the ligand of choice for the reprocessing industry for a long time, but its relatively high solubility in water/HNO<sub>3</sub> solutions and tendency toward third-phase formation have supported the search for alternatives that are able to overcome these limitations.<sup>21</sup>

In addition to the steric hindrance around the phosphorus atom, the extraction properties of organophosphorus compounds heavily depend on two factors: the presence of OH groups on the phosphorus atom, and the number of OR groups compared to that of the R groups; thus, they can be distinguished in ionophores (organophosphorus organic acids) and non-ionophores (organophosphorus neutral ligands).

The complexation of acidic ligands relies on their deprotonated form. Therefore, the pH window in which the ligands display the desired extraction behaviour can, theoretically, be modulated by functionalisation of the phosphoric/phosphonic/phosphinic acid with electron-withdrawing groups of different strengths.

Neutral ligands preferably complex An, rather than Ln, and their coordinating ability depends on the basicity of the phosphoryl oxygen. In this regard, alkyl groups are more electron-donating than alkoxy groups, and hence the basicity of the oxygen atom increases in the order: phosphates < phosphonates < phosphinates < phosphine oxides.<sup>22</sup>

Several reviews dealing with different aspects of organophosphorus compounds have been published, including fundamental coordination chemistry,<sup>8</sup> combination of acidic and neutral ligands in the same phase,<sup>23</sup> and separation methods and techniques.<sup>9</sup> Most of the published reviews, however, provide a general overview of the most common ligands and focus on their use in the proposed processes.<sup>7,24,25</sup>

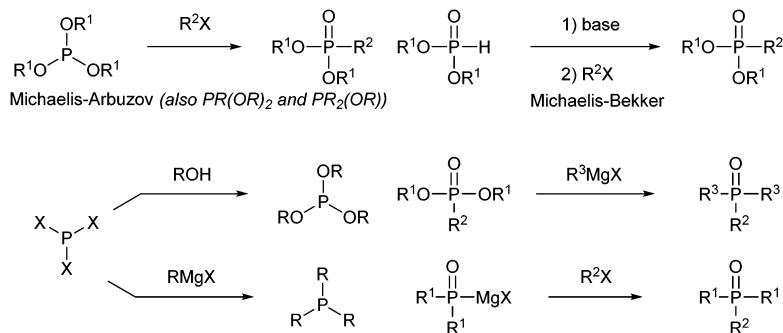
The most common synthetic pathways for the preparation of organophosphorus compounds, summarised in a review,<sup>26</sup> are the Michaelis-Arbuzov and Michaelis-Bekker reactions, the use of organometallic compounds, and phosphoryl halides (Scheme 1). In the Michaelis-Arbuzov reaction, a trialkyl phosphite reacts with an (activated) alkyl halide to yield the corresponding phosphonic ester. Substituting one or two of the alkoxy groups of the starting phosphite with alkyl groups, yields the corresponding phosphinic ester and phosphine oxide. The Michaelis-Bekker reaction starts with the deprotonation of a hydrogen phosphonate, followed by a nucleophilic substitution on an (activated) alkyl halide. This reaction is also used for the first step of the preparation of carbamoylmethylphosphine oxides (CMPOs, *vide infra*), using formaldehyde instead of the alkyl halide. Recently, popular methods include the reaction of phosphoryl mono-, di- and trihalides with alcohols to give the corresponding esters, or with Grignard reagents to form a P–C bond.<sup>27</sup> Conversely, P–C bonds can be formed when phosphoryl esters react with Grignard reagents.<sup>28</sup> Alternatively, magnesium halide dialkylphosphinites can be used as nucleophiles with (activated) alkyl halides.

The following section deals with the developments in the design of neutral and acidic organophosphorus ligands, CMPOs, and hybrid organophosphorus/heterocycle ligands since the publication of recent reviews (*vide supra*).



Willem Verboom

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Scheme 1

### Neutral organophosphorus ligands

Tributyl phosphate (TBP, Chart 1) has been used for decades in the PUREX process, but tends to form a third phase upon complexation of metal ions. Therefore, several alternative ligands have been studied, trying to improve the hydrodynamic and phase separation properties. A series of isomers of triphenyl phosphate (Chart 1) showed that the  $D$  values (distribution ratio, defined as the ratio between the concentration of metal in the organic phase and in the aqueous phase,  $D = [M]_{\text{org}}/[M]_{\text{aq}}$ ) for the extraction of U(vi) and Pu(iv) are comparable to those of TBP, but their aqueous solubility is lower. The alkyl chain, however, affected the radiolytic stability of the compounds. Triamyl phosphate (TAP) was more susceptible than TBP, whereas the radiation stability of tris(isoamyl) phosphate (TiAP) was comparable to that of TBP.<sup>29</sup>

More interesting results were obtained with diamyl amylphosphonate (DAAP, Chart 1). Compared to TBP, the density, viscosity and phase disengagement times of DAAP were lower and the  $D$  values for U(vi), Th(iv) and Pu(iv) were higher ( $D_M = 65, 35$  and  $120$  for DAAP and  $20, 5$  and  $20$  for TBP, for U(vi), Th(iv) and Pu(iv), respectively, at  $4 \text{ M HNO}_3$ ).<sup>30</sup> A variation in the length of the alkyl chain from  $n$ -butyl to  $n$ -octyl did not affect the extraction of An, whereas it caused a decrease in the density and aqueous solubility (from  $692$  to  $0.11 \text{ mg L}^{-1}$  for DBBP and DBOP, respectively, Chart 1), and an increase in the viscosity of DBBP, DBHP and DBOP.<sup>21</sup> On the other hand, the length of the alkoxy chains affected the  $D$  values for the extraction of U(iv) and Th(iv) ( $D_U = 105$  and  $D_{Th} = 55$  for DBHP,  $D_U = 80$  and  $D_{Th} = 35$  for DAHP at  $4 \text{ M HNO}_3$ , Chart 1).<sup>29</sup> This suggested that the basicity of the phosphoryl group is more influenced by the length of the alkoxy chains than that of the alkyl chains.

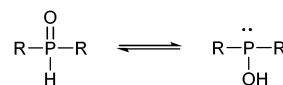


TBP	$R^1, R^2 = O(n\text{-Bu})$	DBHP	$R^1 = n\text{-C}_6\text{H}_{13}, R^2 = O(n\text{-Bu})$
TAP	$R^1, R^2 = O(n\text{-C}_5\text{H}_{11})$	DAHP	$R^1 = n\text{-C}_6\text{H}_{13}, R^2 = O(n\text{-C}_5\text{H}_{11})$
TsAP	$R^1, R^2 = 1\text{-methylbutoxy}$	DBOP	$R^1 = n\text{-C}_8\text{H}_{17}, R^2 = O(n\text{-Bu})$
T2MBP	$R^1, R^2 = 2\text{-methylbutoxy}$	DHePO	$R^1 = \text{H}, R^2 = n\text{-C}_6\text{H}_{13}$
TiAP	$R^1, R^2 = 3\text{-methylbutoxy}$	DHpPO	$R^1 = \text{H}, R^2 = n\text{-C}_7\text{H}_{15}$
DBBP	$R^1 = n\text{-Bu}, R^2 = O(n\text{-Bu})$	DOPO	$R^1 = \text{H}, R^2 = n\text{-C}_8\text{H}_{17}$
DAAP	$R^1 = n\text{-C}_5\text{H}_{11}, R^2 = O(n\text{-C}_5\text{H}_{11})$	DDPO	$R^1 = \text{H}, R^2 = n\text{-C}_{10}\text{H}_{21}$

Chart 1

In the case of dialkylphosphine oxides (DAPOs, Chart 1), ligands bearing longer alkyl chains showed higher  $D_U$  values (at  $0.01 \text{ M HNO}_3$ ,  $39.4 \text{ DHePO} < 41.8 \text{ DHpPO} < 47.4 \text{ DOPO} < 84.6 \text{ DDPO}$ , Chart 1). However, the  $D$  values were higher at lower acidity (*i.e.*  $0.01 \text{ M HNO}_3$ ), as opposed to trialkyl phosphates and phosphonates that exhibited higher extraction at higher  $\text{HNO}_3$  concentrations. With DAPOs, two different extraction mechanisms took place depending on the acidity: a cation exchange mechanism at lower acidity, and a solvation mechanism at higher acidity. DAPOs established a tautomeric equilibrium in solution (Scheme 2) and acidity of which medium controlled form was more abundant, with the P-OH form behaving like an acidic ligand.<sup>28</sup>

A change in extraction mechanism was also observed in the case of phosphoryl task-specific ionic liquids (TSILs) dissolved in 3-alkyl-1-methylimidazolium bis(trifluoro-methanesulfonyl)imide ( $[\text{C}_n\text{mim}][\text{NTf}_2]$ ). In the case of  $[\text{C}_n\text{imPA}][\text{NTf}_2]/[\text{C}_n\text{mim}][\text{NTf}_2]$  (Chart 2), the extraction of Pu(iv) at low acidity occurred through a solvation mechanism, and above  $4 \text{ M HNO}_3$ , an anion exchange mechanism was in operation. Moreover, an increase in chain length (either on the  $[\text{C}_n\text{imPA}]^+$  ion or  $[\text{C}_n\text{mim}]^+$  ion) caused an increase in  $D$  values (at  $4 \text{ M HNO}_3$ ,  $D_{\text{Pu}} = 15, 28$  and  $32$  for  $[\text{C}_n\text{imPA}][\text{NTf}_2]/[\text{C}_4\text{mim}][\text{NTf}_2]$  with  $n = 1, 3$  and  $4$ , respectively) and resulted in a high selectivity (defined by the separation factor S.F., the ratio between the  $D$  values of two metal ions,  $\text{S.F.}_{M1/M2} = D_1/D_2$ ) with respect to U(vi) and Am(III) ( $\text{S.F.}_{\text{Pu/U}} = 10$ ,  $\text{S.F.}_{\text{Pu/Am}} = 1750$  with  $[\text{C}_4\text{imPA}][\text{NTf}_2]/[\text{C}_4\text{mim}][\text{NTf}_2]$  at  $4 \text{ M HNO}_3$ ).<sup>31</sup>  $[\text{C}_1\text{imPO}][\text{NTf}_2]$  (Chart 2) showed different extraction mechanisms with different metal ions. It extracted U(vi) *via* a cation exchange mechanism and Pu(iv) *via* a solvation mechanism. The ligand showed preference for Pu(iv) over U(vi) ( $D_{\text{Pu}} = 30$ ,  $D_U = 6$  at  $2 \text{ M HNO}_3$  using  $[\text{C}_8\text{mim}][\text{NTf}_2]$ ) and negligible extraction of other metal ions. In addition, in this case, an increase in lipophilicity of the RTIL ( $[\text{C}_8\text{mim}]^+$  instead of  $[\text{C}_4\text{mim}]^+$ ) caused an increase of the  $D$  values.<sup>32</sup>



R = alkyl, aryl

Scheme 2



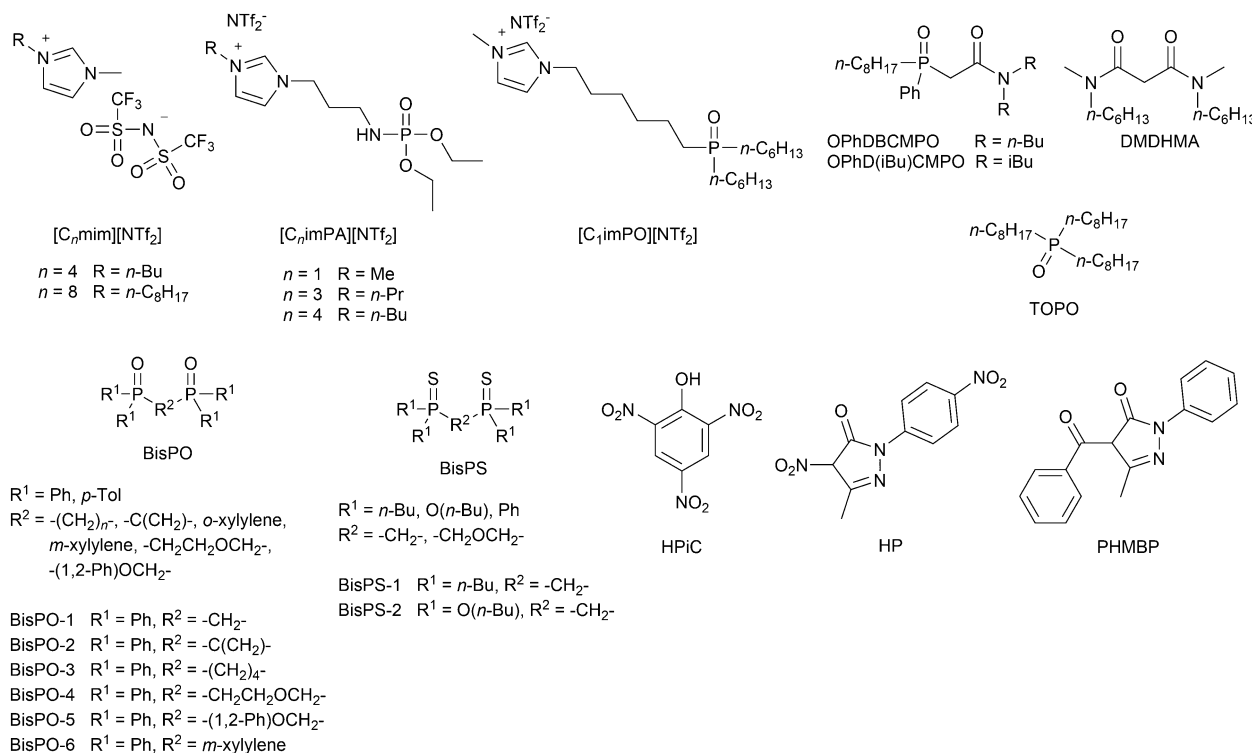


Chart 2

To exploit the chelate effect and to improve the extraction of the metal ion, bidentate organophosphorus compounds were prepared and compared to known ligands such as OPhD(iBu)CMPO and DMDHMA. It was found that the  $D$  values followed the order BisPO-1 > BisPO-2 > OPhD(iBu)CMPO > DMDHMA (Chart 2) for several An and that the extraction of U(vi) was preferred, in this order, over Th(iv), Am(III) and Np(v). These results highlighted that phosphoryl oxygens are stronger donors than the carbonyl ones and that a conjugated planar structure (BisPO-2) decreases the extraction of An.<sup>33</sup> A review discussed the synthetic methods used to obtain bisphosphine oxides and their fundamental extraction and complexing properties.<sup>26</sup>

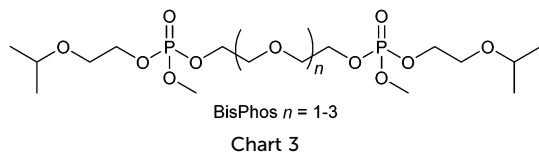
BisPO-1 also exhibited good extraction properties for Ln(III), with preference for the lighter lanthanides over the heavier ones ( $D_{\text{La}} \approx 500$ ,  $D_{\text{Lu}} \approx 25$ ). Modifications of the methylene bridge (Chart 2) led to an inversion of the preference trend, with heavy Ln(III) being extracted better than the lighter ones. Extension of the methylene linker lowered the  $D$  values (for BisPO-3,  $D_{\text{La}} \approx 0.025$ ,  $D_{\text{Lu}} \approx 8$ ). The inclusion of an etheric oxygen (BisPO-4) had little effect on the extraction, while the incorporation of a phenyl ring raised the extraction to  $D$  values comparable to those of BisPO-1 (BisPO-5 and BisPO-6).<sup>34</sup> A decrease in  $D$  values was also observed with diphosphine sulphides (Chart 2). Ligands with a longer spacer and an etheric oxygen did not show any extraction of Am(III) and Eu(III). In this case, however, due to the presence of a sulfur atom, the diphosphonothioate exhibited  $D$  values up to three orders of magnitude higher than that of the diphosphine

sulphide ( $D_{\text{Am}} > 100$  for BisPS-2 and  $D_{\text{Am}} \approx 0.1$  for BisPS-1 in 0.1–1 M HNO<sub>3</sub>), even though there was no discrimination between Am(III) and Eu(III).<sup>27</sup>

The addition of picrolonic acid (HP, Chart 2) as a synergist, allowed for the extraction of Ln ions from hydrochloric acid solutions. This type of extraction is difficult due to the low solubility of Cl<sup>−</sup> in organic solvents. For this purpose, HP showed a higher synergic effect than PHMBP or picric acid (HPiC). The combination of BisPO-1 with HP achieved the extraction of Ln(III) up to three orders of magnitude higher than TOPO + HP in the same conditions ( $D$  values for La–Lu were in the range of 0.003–0.1 for TOPO + HP and 10–300 for BisPO-1 + HP).<sup>35</sup>

Extension of the linker between phosphoryl units in bidentate ligands was also detrimental for the extraction using supercritical CO<sub>2</sub> (sCO<sub>2</sub>). Phosphoric esters separated by various numbers of ethylene glycol units (Chart 3) showed that the extraction efficiency increased in the order BisPhos  $n = 3 < n = 2 < n = 1$  with a range from 55% to 79% and a preference for heavier Ln(III).<sup>36</sup>

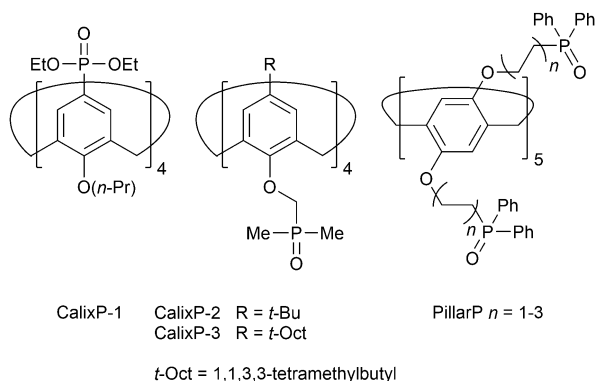
**Neutral organophosphorus ligands on platforms.** Trivalent f-elements have high coordination numbers ( $\geq 6$ ), requiring the binding to the same metal ion of several ligands at the same time.<sup>8</sup> Pre-organisation of ligating sites resulted in better extractants (more favourable entropic changes) with higher metal selectivities. The structure of the platform on which the donor groups are tethered strongly influences the performance of these ligands.<sup>37</sup> In particular, calix[4]arenes have extensively been studied because this platform can be prepared in good



yields and large amounts,<sup>38</sup> and both rims can be functionalised.<sup>37</sup> In an overview about the use of multicoordinate ligands in the extraction of An and Ln(III), several phosphoryl-functionalised calix[4]arenes have been discussed.<sup>37</sup> Higher homologous calix[n]arenes have also been studied for the extraction of other metal ions relevant to nuclear waste processing, like Cs(I) ( $n = 8$ )<sup>39</sup> and U(VI) ( $n = 4-6, 8$ ).<sup>40</sup>

Phosphoryl calix[4]arenes have shown great capability in the extraction of Th(IV). Phosphonate calix[4]arene CalixP-1 (Chart 4) exhibited very high selectivity towards Th(IV) over Ln(III) (La, Gd, Yb) in highly acidic solutions ( $> 2 \text{ M HNO}_3$ ).<sup>41</sup> Similarly, phosphine oxide calix[4]arene CalixP-2 (Chart 4) could selectively extract Th(IV) with negligible extraction of La, Eu and Y.<sup>42</sup> In the case of the corresponding *tert*-octyl derivative CalixP-3 (Chart 4), higher concentrations of actinide salts ( $> 9 \times 10^{-3} \text{ M}$ ) and ligand ( $> 10^{-3} \text{ M}$ ) could be used without the risk of third phase formation; moreover, it showed selectivity towards U(VI) and Th(IV) (58% and 56% of extraction, respectively) over Ln ions that were not extracted. The addition of TBP to CalixP-3 in chloroform resulted in a strong synergic effect in the extraction of U(VI): individual solutions of CalixP-3 and TBP could extract 58% and 11% of U(VI), respectively, but their mixture recovered 96% of the metal ions.<sup>43</sup>

Good separations between U(VI), Th(IV) and the Ln(III) were obtained with diphenylphosphine oxide groups pre-organised on a pillar[5]arene platform (Chart 4). Even though the ligand could host more than one metal ion, the complexes with Th(IV) and U(VI) were formed in a 1 : 1 M : L stoichiometry. The extraction of An and Ln(III) increased with increasing  $\text{HNO}_3$  concentration. An increase in  $\text{NaNO}_3$  concentration also induced a clear preference for the extraction of U(VI) over Th(IV) (up to  $\text{S.F.}_{\text{U/Th}} = 12$  at  $4 \text{ M NaNO}_3$ ). In the presence of the synergist hexabrominated cobalt bis(dicarbollide) anion ( $\text{Br}_6\text{-CCD}$ ), the PillarP ligands showed a preference for Eu(III) over Am(III)



(up to  $\text{S.F.}_{\text{Eu/Am}} = 5$  in *m*-nitrobenzotrifluoride (*m*-NBTF) at  $1 \text{ M HNO}_3$ ).<sup>44</sup>

The arrangement of two methanediphosphonate groups on calix[4]arenes (CalixP-4–6, Chart 5) resulted in ligands able to extract Eu(III) and Am(III) from both alkaline and acidic solutions. Bearing a mixture of phosphonate and phosphine oxide groups, CalixP-4 showed the highest  $D_{\text{Am}}$  values among the ligands investigated ( $D_{\text{Am}} = 2$  at pH 12.6). Bisphosphonate hydroxycalix[4]arenes CalixP-5 and CalixP-6, on the other hand, were able to extract Am(III) and Eu(III) from  $\text{HNO}_3$  solutions with higher extraction efficiency (for CalixP-5,  $D_{\text{Am}} = 30$  at  $1 \text{ M HNO}_3$  and  $D_{\text{Am}} = 0.9$  at pH 12.4), whereas the selectivity was higher from alkaline solutions ( $\text{S.F.}_{\text{Am/Eu}} = 2.5$  and  $1.1$  at pH 12.4 and  $1 \text{ M HNO}_3$ , respectively).<sup>45</sup>

Thiacalix[4]arenes have the same structure as calix[4]arenes, but the methylene bridge between the phenol rings is substituted by a sulfur atom. *tert*-Butylthiacalix[4]arene (SCalixP-1, Chart 5) showed very high extraction and selectivity for Am(III) from alkaline solutions ( $D_{\text{Am}} > 150$ ,  $\text{S.F.}_{\text{Am/Eu}} = 18$  at pH 12). While appropriate functionalisation of calix[4]arenes increased the extraction efficiency and S.F. values, the opposite occurred in the case of thiacalix[4]arenes.<sup>46,47</sup> Among several thiacalix[4]arenes (Chart 5), only bromo-substituted SCalixP-2 showed an improvement in  $\text{S.F.}_{\text{Am/Eu}}$  value with respect to SCalixP-1 ( $D_{\text{Am}} = 30$ ,  $\text{S.F.}_{\text{Am/Eu}} = 30$  at pH 12). In particular, ligands SCalixP-5, SCalixP-6 and SCalixP-9 were poorly soluble in *m*-NBTF, and ligands SCalixP-4 and SCalixP-7 formed a precipitate upon contact with an alkaline solution. Ligand SCalixP-3, on the other hand, exhibited increased solubility in *m*-NBTF and a good extraction performance ( $D_{\text{Am}} = 10$ ,  $\text{S.F.}_{\text{Am/Eu}} = 20$  at pH 11.5), though not as good as ligands SCalixP-1 and SCalixP-2. In general, thiacalix[4]arenes showed a narrow pH window in which they are able to extract metal ions ( $\Delta\text{pH} < 1$  in the range pH 11–13).<sup>48</sup>

Another modification on the calix[4]arene platform involves the functionalisation of one of the methylene bridges with an alkyl chain. Tetraphosphoryl calix[4]arenes CalixP-8 (Chart 5) were compared to the corresponding non-alkylated calix[4]arene (CalixP-2, Chart 4) and only showed a small decrease in the extraction of Eu(III) (65, 55 and 50% extraction of Eu with ligands *t*-BuCalix, CalixP-8  $n = 5$  and 6, respectively). These experiments demonstrated that the presence of an alkyl chain on the methylene bridge of calix[4]arenes did not significantly affect their extraction properties. Therefore, these functionalised calix[4]arenes were proposed as precursors for heterogeneously supported ligands.<sup>49</sup>

An alternative approach to improving the extraction of metal ions was the use of water-soluble phosphoryl calix[4]arenes. Calix[4]arenes CalixP-10 and CalixP-11 (Chart 5) were successfully applied in a micelle-mediated extraction (MME) for the recovery of Am(III) and Eu(III). In this process, the addition of an aqueous solution of ligand CalixP-10 or CalixP-11 to an acidic aqueous solution of metal ions triggered the formation of micelles (due to the high acidity and ionic strength), followed by a second phase that was separated upon centrifugation. Compared to liquid-liquid extraction (LLE) with *m*-NBTF, this method afforded an

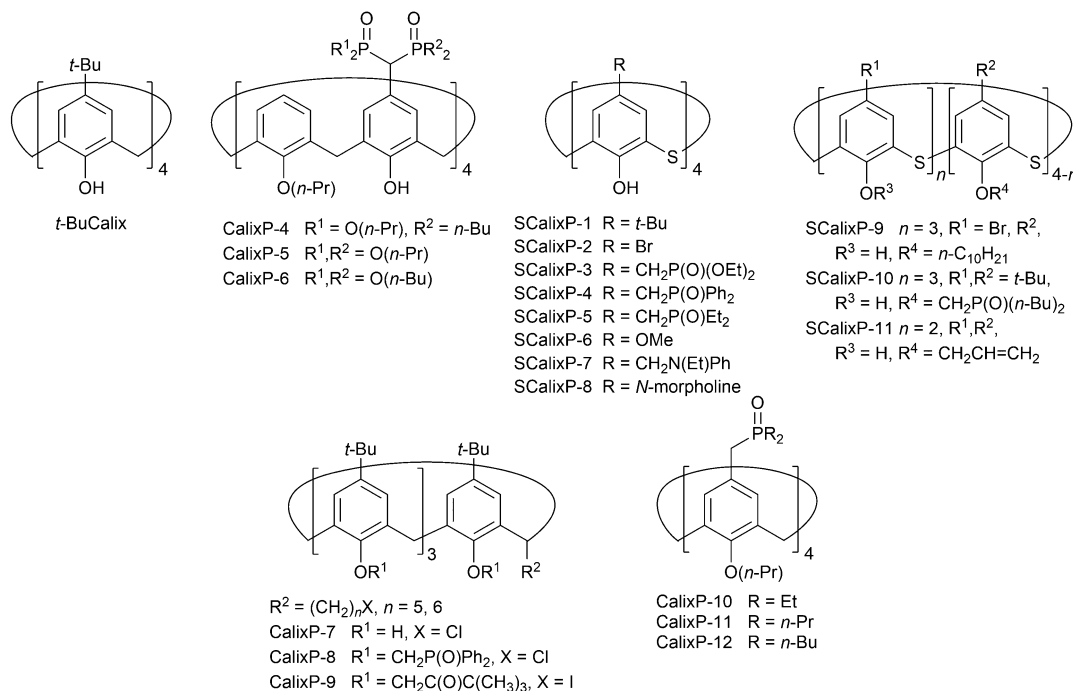


Chart 5

average increase of the  $D$  values of two orders of magnitude ( $D_{\text{Eu}} = 0.01\text{--}2$  in LLE and  $10\text{--}30$  in MME for CalixP-10 at  $0.1\text{--}10$  M  $\text{HNO}_3$ ;  $D_{\text{Eu}} = 0.05\text{--}10$  in LLE and  $10\text{--}1000$  in MME for CalixP-11 at  $0.1\text{--}10$  M  $\text{HNO}_3$ ). However, ultrasonic treatment or electrochemical deposition were needed to recover the ligand after the extraction.<sup>50</sup>

### Acidic organophosphorus ligands

Dialkyl organophosphorus acids, such as HEH[EHP] and Cyanex 272 (Chart 6), are being widely used in industrial extractions and separations of rare earths (REs). However, HEH[EHP] shows poor selectivity for heavy Ln(III), high stripping acidity and low S.F. values for several couples of rare earths (Gd/Eu, Er/Y, Lu/Yb). Cyanex 272, despite the lower stripping acidity, exhibits low extraction capacity, easy formation of emulsions and low separation of some rare earth couples.<sup>51</sup> Acidity and steric

hindrance are two of the major factors determining the extraction properties of acidic organophosphorus ligands. Looking for valid alternatives to HEH[EHP] and Cyanex 272, various modifications of the alkyl chains have been investigated. However, a compromise between good extraction ability and low stripping acidity proved to be challenging. For example, PA-1 showed high selectivity for heavy Ln(III), good extraction and separation along the entire Ln series ( $D_{\text{Er-Lu}} = 10^3\text{--}10^4$ ,  $D_{\text{La-Ho}} = 20\text{--}200$ , S.F. values among Ln(III) in the range of  $1.1\text{--}360$ ,  $3$  M  $\text{HNO}_3$ ), but quantitative stripping of the metal ions only occurred at  $7$  M  $\text{H}_2\text{SO}_4$ .<sup>52</sup> The introduction of lactic acid (HLact) and citric acid ( $\text{H}_3\text{cit}$ ) as masking agents in the aqueous phase proved to be an additional parameter able to improve the extraction and S.F. values for HEH[EHP]. The extraction of a  $3:1$  Ce:Pr mixture at pH 3.5 increased from  $<35\%$  (S.F.<sub>Pr/Ce</sub>  $< 2$ ) to  $>90\%$  (S.F.<sub>Pr/Ce</sub> =  $10.5$ ) upon addition of a  $1:10$  HLact: $\text{H}_3\text{cit}$  mixture.<sup>53</sup>

Branching of the alkyl chains of dialkylphosphinic acids (Chart 6) caused a decrease in extraction ability, which was more pronounced the closer the branching was to the phosphorus atom. Acids without branched chains on the  $\alpha$ -C or  $\beta$ -C showed extraction abilities as strong as those of HEH[EHP], whereas acids with branching on those positions (or with cycloalkyl groups) exhibited poor extraction, like Cyanex 272. Diarylphosphinic acids were poorly soluble in apolar solvents.<sup>51</sup> Only ligand PA-2 showed a higher extraction ability than Cyanex 272 and a lower stripping acidity than HEH[EHP]. The separation among Ln(III) also improved, compared to Cyanex 272 (S.F.<sub>Gd/Eu</sub> =  $1.46$  and S.F.<sub>Er/Y</sub> =  $1.47$  for PA-2, compared to S.F.<sub>Gd/Eu</sub> =  $1.16$  and S.F.<sub>Er/Y</sub> =  $1.20$  for Cyanex 272).<sup>54</sup>

Comparison of methyl- and ethyl-branched dialkylphosphinic acids (Chart 6) showed that the steric hindrance at the  $\alpha$ -C was



$R^1, R^2 = n\text{-C}_5\text{H}_{11}, n\text{-C}_6\text{H}_{13}, n\text{-C}_{10}\text{H}_{21}, 1,2\text{-dimethylpropyl}, 1\text{-methylbutyl}, 3\text{-methylbutyl}, 3,3\text{-dimethylbutyl}, \text{cyclopentyl}, \text{Ph}, 2\text{-ethylhexyl}, 1\text{-methylheptyl}, 2\text{-methylheptyl},$

HEH[EHP]  $R^1 = 2\text{-ethylhexyloxy}, R^2 = 2\text{-ethylhexyl}$   
 Cyanex 272  $R^1, R^2 = 2,4,4\text{-trimethylpentyl}$   
 HDEHP  $R^1, R^2 = 2\text{-ethylhexyloxy}$   
 PA-1  $R^1, R^2 = 4\text{-nonylphenyloxy}$   
 PA-2  $R^1, R^2 = 2,3\text{-dimethylbutyl}$   
 PA-3  $R^1, R^2 = \text{cyclohexyl}$   
 PA-4  $R^1, R^2 = 1\text{-ethylhexyl}$

Chart 6

greater than that at the  $\beta$ -C and that an ethyl group had a stronger effect than a methyl group. The cyclohexyl group in PA-3, despite its bulkier size compared to the methyl group of PA-4, resulted in higher extraction. The restricted rotation of the cyclohexyl group was supposed to lead to a lower steric hindrance. These effects were stronger for the extraction of heavier Ln(III) than for lighter ones.<sup>55</sup>

HEH[EHP], in combination with HEDTA (Chart 7), was studied as part of the Advanced TALSPEAK concept. The An(III) ions were preferentially bound by HEDTA in a citrate-buffered aqueous solution, whereas the Ln(III) ions were extracted by HEH[EHP] in the organic phase (*n*-dodecane). As opposed to traditional TALSPEAK, this process showed little dependence upon the pH or the HEH[EHP], HEDTA, and citrate concentrations over the ranges that might be expected in a nuclear fuel recycling plant, and faster extraction kinetics. In flow extraction experiments,  $D_{Ln}$  values in the range of 0.6–17 were observed, with a minimum S.F.<sub>Eu/Am</sub> = 3.24.<sup>56</sup> Changing the buffer system to a malonate buffer improved the extraction kinetics at higher acidity and a low pH dependence when the extraction was performed at pH 2.5–4.0.<sup>57</sup> Gamma irradiation studies showed a decrease in the S.F. values due to degradation of HEDTA and consequent increase in the  $D$  values.<sup>58</sup> Process optimization and a flowsheet test demonstrated that An(III) was separated from Ln(III) with a decontamination factor > 1000.<sup>59,60</sup>

Due to the lower acidity required to strip the metal ions from Cyanex 272 solutions, a mixture of it with HEH[EHP] was used to study whether it would result in improved extraction behaviour. However, the mixed phosphonic/phosphinic acid extractants appeared to have an antagonistic effect. In contrast, the acid consumption in the stripping process would be reduced, and the size of the required equipment would double, due to the lower overall metal loading.<sup>61</sup> On the other hand, a synergistic effect was observed between Cyanex 272 and HDEHP (Chart 6). In the separation of Ln(III), Gd(III), Nd(III) and Dy(III), a 4 : 1 Cyanex 272 : HDEHP mixture showed an increase in S.F. values, compared to similar mixtures including only one of the organophosphorus acids and 8-hydroxyquinoline (HQ). The most favourable results were obtained for the separation of Dy(III) from La(III), Nd(III) and Gd(III) (for example, S.F.<sub>Dy/La</sub> > 3000 with Cyanex 272 + HDEHP and S.F.<sub>Dy/La</sub>  $\approx$  1000 with HQ + HDEHP).<sup>62</sup> The use of HEH[EHP] together with Cyanex 923 (a mixture of  $R^1R^2R^3P=O$ , in which  $R^1$ ,  $R^2$  and  $R^3$  are any combination of  $n$ -C<sub>6</sub>H<sub>13</sub> and  $n$ -C<sub>8</sub>H<sub>17</sub>) for the co-extraction of An(III) and Ln(III), and an aqueous solution of polyaminopolycarboxylate ligands for the selective stripping of An(III) was proposed as an alternative to traditional TALSPEAK. The extractants employed showed very high solubility limits and

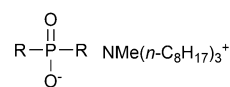
relatively low molar mass, allowing for higher loadings of the organic solution. S.F.<sub>Eu/Am</sub> values up to 60 could be obtained.<sup>63</sup>

Synergic effects were also observed in binary mixtures. For example, comparing mixtures based on carboxylates and dialkylphosphates of secondary and tertiary amines, the effect largely depended on the type of ammonium ion used. The R<sub>2</sub>NH<sub>2</sub>E-H[EHP]–R<sub>2</sub>NH<sub>2</sub>Capr systems showed a synergistic effect, whereas the R<sub>3</sub>NHEH[EHP]–R<sub>3</sub>NHCapr (R = C<sub>8</sub>H<sub>17</sub>, CaprH = caprylic acid) systems had an antagonistic effect.<sup>64</sup>

Binary extractants, such as those depicted in Chart 8, were shown to extract metal ions by a solvation mechanism and that their extraction profile was independent of the aqueous phase acidity. Moreover, the extraction capacity of the binary extractants increased in the series of methyltrioctylammonium salts in the order dialkylmonothiophosphinate < dialkyl phosphate < dialkylphosphinate and exhibited higher  $D$  values than Cyanex 272 ( $D_{Gd} \approx 1$  vs.  $D_{Gd} \approx 1000$  for Cyanex 272 and its methyltrioctylammonium salt, respectively).<sup>65</sup>

Bidentate S-donor dithiophosphinic acids were the first type of ligands to show extremely high separation between An and Ln(III). This class of ligands and their extraction behaviour have been described in a review dealing with the literature up until 2011.<sup>66</sup> Purified ligands PSA-1 and PSA-4 (Chart 9) reached S.F.<sub>Am/Eu</sub> values > 4000,<sup>67</sup> and in the presence of synergists, their performance increased considerably (S.F.<sub>Am/Eu</sub> > 40 000 with ligand PSA-1 in the presence of 2,2'-bipyridine and 1,10-phenanthroline).<sup>68</sup> Ligand PSA-1, however, was found to undergo hydrolysis at pH < 2.5 and was susceptible to radiolysis.<sup>69</sup>

Smaller analogues of the dialkylthiophosphinic acids (ligands PSA-2 and PSA-3, Chart 9) were investigated, because, due to their lower molecular weight (compared to ligand PSA-1), they could afford higher gravimetric loading of An by 53 and 35%, respectively. Ligand PSA-2, however, exhibited low  $D$  values, probably because the short chains reduced its hydrophobicity to a great extent. Ligand PSA-3 was more stable under radiolytic and hydrolytic degradation conditions than ligand PSA-2 and had very good extraction properties.  $D_{Am}$  values increased from 0.5 to > 1000 in the pH range of 2.4–4.1, whereas the  $D_{Eu}$  values remained < 0.7 in the same pH range. The S.F.<sub>Am/Eu</sub> values of ligand PSA-3 were lower than those of PSA-1, but selective



[EH[EHP]][N<sub>1888</sub>] R = 2-ethylhexyloxy  
[Cyanex272][N<sub>1888</sub>] R = 2,4,4-trimethylpentyl  
[N<sub>1888</sub>] = NMe(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub><sup>+</sup>

Chart 8

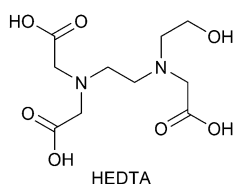


Chart 7

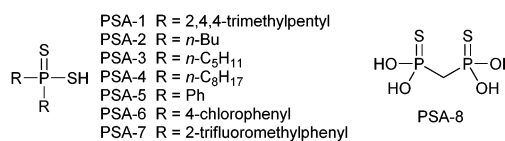


Chart 9



extraction of Am(III) could still be achieved, accompanied by a 35% increase in An loading.<sup>70</sup>

Diaryl dithiophosphinic acids PSA-5 and PSA-6 showed lower extraction ability, but were more resistant to degradation. The presence of a synergist (TBP or a trialkylphosphine oxide) significantly improved the extraction.<sup>71</sup> On the other hand, ligand PSA-6 exhibited preference for tetravalent An giving a good separation of Np and Pu at high HNO<sub>3</sub> concentration (at 4 M HNO<sub>3</sub>,  $D_{\text{Np(IV)}} \approx 3000$ ,  $D_{\text{Pu(IV)}} \approx 30$ ,  $D_{\text{Np(V)}} \approx 0.3$ ,  $D_{\text{Pu(III)}} \approx 0.01$ ).<sup>72</sup>

Ligand PSA-7 reached an extremely high selectivity for Am(III) over Eu(III) ( $\text{S.F.}_{\text{Am/Eu}} > 10^5$ ) in trifluoromethylphenyl sulfone (FS-13) without the need for a synergist.<sup>73</sup> Recently, it was observed that ligand PSA-7 (Chart 9) also selectively extracted Am(III) from toluene solutions, with  $\text{S.F.}_{\text{Am/Eu}}$  values  $> 600$  (at pH 4.2) that increase up to  $> 10^5$  at pH 2. The extraction of Am(III) is lower at lower acidity, but remains around  $D_{\text{Am}} = 100$  at pH  $> 2.5$ .<sup>74</sup> Moreover, the addition of TOPO as a synergist increased the overall extraction of metal ions, improving the  $D$  values also at lower acidity. At 0.1 M HNO<sub>3</sub> (pH 1), addition of 4–100 mM TOPO to the extraction mixture caused an increase of  $D_{\text{Am}}$  from  $\approx 0.5$  to  $\approx 60$ , although with a decrease of the  $\text{S.F.}_{\text{Am/Eu}}$  value from 201 to 10. Low extraction was observed for all the Ln(III) ( $D$  values  $< 0.3$ ), while other An were extracted better than Am(III). The extraction from simulated UREX raffinate using 0.5 M ligand PSA-7, 0.1 M

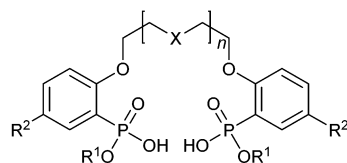
TOPO in toluene at 1 M HNO<sub>3</sub>, showed a preference for Np ( $D_{\text{Np}} = 732$ ), followed by U ( $D_{\text{U}} = 51$ ), Pu ( $D_{\text{Pu}} = 31$ ), Am ( $D_{\text{Am}} = 6$ ) and the Ln(III) ( $D_{\text{Ln}} > 0.2$ ).<sup>75</sup>

Similarly, water-soluble bis-thiophosphonic acid PSA-8 (Chart 9) exhibited a strong complexation ability for Eu(III) and Am(III) in the back-extraction from a TODGA-loaded solution. At 0.1 M ligand concentration, both metal ions were strongly complexed and extraction occurred with no selectivity. Decreasing the concentration of the ligand, the  $D$  values could be adjusted to higher values, but the selectivity was lower than in the case of water-soluble diamide ligands.<sup>76</sup>

Efficient separation among U(VI), Th(IV) and Ln(III) has been achieved with the use of bis-phosphoryl ligands (Chart 10). The influence of different linkers between the two arylphosphoryl units was studied (ligands BisPA-1,2), and the most promising one appeared to be the diethylene glycol chain; ligand BisPA-2 ( $n = 1$ ) showed a high selectivity for Th(IV) towards U(IV) ( $D_{\text{Th}} \approx 60$ ,  $D_{\text{U}} \approx 1.4$  at 3 M HNO<sub>3</sub>).<sup>77</sup> Modification of the substituents on the phenyl rings and on the phosphonic acid (ligands BisPA-3–8) revealed that selective extraction of U(VI) in the presence of Ln(III) from weakly acidic solutions was possible with all the ligands (0.04 M HNO<sub>3</sub>,  $D_{\text{U}} > 40$ ). However, a slight increase in the HNO<sub>3</sub> concentration caused a drop in the  $D$  values (down to 0.3–0.9 at 4 M HNO<sub>3</sub>). The extraction of Th(IV), on the other hand, was extremely efficient only with ligands BisPA-6–8 ( $D_{\text{Th}} > 450$  at 0.04 M HNO<sub>3</sub>). An increase in acidity caused the  $D$  values to drop, but reasonable extraction was achieved also at higher HNO<sub>3</sub> concentrations ( $D_{\text{Th}} > 20$  at 0.74 M HNO<sub>3</sub>,  $D_{\text{Th}} > 2$ , for BisPA-5,7).<sup>78</sup>

**Acidic organophosphorus ligands on platforms.** Pre-organisation of phosphonic acids on a calix[4]arene platform resulted in a very high extraction efficiency at low acidity, with a general preference for heavy Ln(III). Tetraphosphonic acid CalixPA-1 (Chart 11) showed an extraction behaviour and S.F. values similar to those of HEH[EHP] (Chart 6), which is commonly used in industrial applications. However, the acidity required for quantitative stripping was too high ( $> 6$  M HNO<sub>3</sub>).<sup>79</sup>

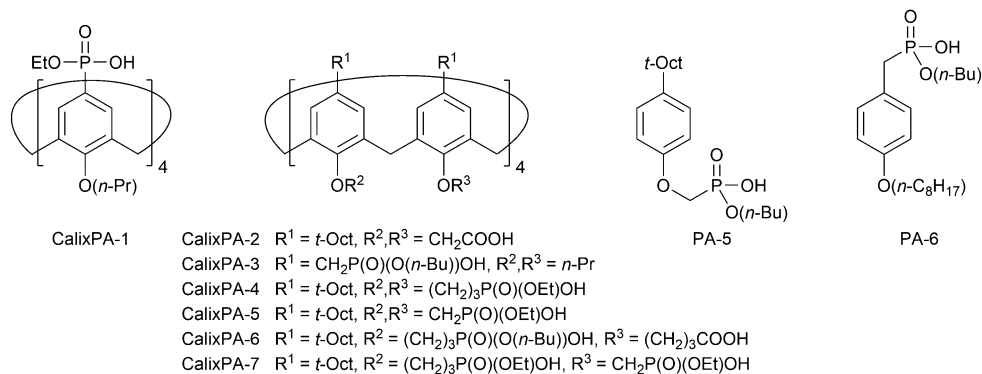
More encouraging results have been obtained combining different complexing groups at alternate positions on the narrow rim of the calix[4]arene platform (Chart 11). Ligand CalixPA-4



BisPA-1 X = CH<sub>2</sub>, R<sup>1</sup> = Et, R<sup>2</sup> = H, n = 1  
BisPA-2 X = O, R<sup>1</sup> = Et, R<sup>2</sup> = H, n = 0-2

X = O, n = 1  
BisPA-3 R<sup>1</sup> = Et, R<sup>2</sup> = H  
BisPA-4 R<sup>1</sup> = n-Bu, R<sup>2</sup> = H  
BisPA-5 R<sup>1</sup>, R<sup>2</sup> = Et  
BisPA-6 R<sup>1</sup> = n-Bu, R<sup>2</sup> = Et  
BisPA-7 R<sup>1</sup> = Et, R<sup>2</sup> = t-Bu  
BisPA-8 R<sup>1</sup> = n-Bu, R<sup>2</sup> = t-Bu

Chart 10



CalixPA-1

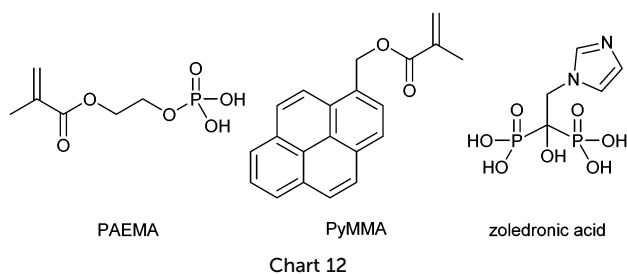
CalixPA-2 R<sup>1</sup> = *t*-Oct, R<sup>2</sup>, R<sup>3</sup> = CH<sub>2</sub>COOHCalixPA-3 R<sup>1</sup> = CH<sub>2</sub>P(O)(O(*n*-Bu))OH, R<sup>2</sup>, R<sup>3</sup> = *n*-PrCalixPA-4 R<sup>1</sup> = *t*-Oct, R<sup>2</sup>, R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>P(O)(OEt)OHCalixPA-5 R<sup>1</sup> = *t*-Oct, R<sup>2</sup>, R<sup>3</sup> = CH<sub>2</sub>P(O)(OEt)OHCalixPA-6 R<sup>1</sup> = *t*-Oct, R<sup>2</sup> = (CH<sub>2</sub>)<sub>3</sub>P(O)(O(*n*-Bu))OH, R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>COOHCalixPA-7 R<sup>1</sup> = *t*-Oct, R<sup>2</sup> = (CH<sub>2</sub>)<sub>3</sub>P(O)(OEt)OH, R<sup>3</sup> = CH<sub>2</sub>P(O)(OEt)OH

*t*-Oct = 1,1,3,3-tetramethylbutyl

Chart 11

gave higher extraction than calix[4]arenes CalixPA-2 and CalixPA-3, with a separation efficiency comparable to that of CalixPA-3. This highlighted the importance of the phosphoryl groups for the selectivity and the narrow rim functionalisation for higher extraction.<sup>80</sup> Calix[4]arene CalixPA-5 exhibited the highest extraction ability among this series of ligands. Using phosphonic acids PA-5 and PA-6 as model compounds, it was demonstrated that the phenoxy oxygen atom participates in the formation of the complex, increasing the *D* values and decreasing the selectivity.<sup>81</sup> The performance of ligand CalixPA-6 was somewhat lower, showing a moderate extraction ability and a poor separation efficiency, due to the synergic effect of phosphonic acids and carboxylic acids.<sup>82</sup> Calix[4]arene CalixPA-7, owing to the different length of the spacer groups, was the best ligand among this series, with performances comparable to those of HEH[EHP] (Chart 6). Ligand CalixPA-7 exhibited an extraction ability similar to that of ligand CalixPA-4 and a selectivity comparable to HEH[EHP]. The extraction ability of these ligands followed the general trend CalixPA-5 >> CalixPA-7 > CalixPA-4 > CalixPA-6 > CalixPA-3 > CalixPA-2 ≈ HEH[EHP], whereas for the selectivity it was HEH[EHP] > CalixPA-7 > CalixPA-4 > CalixPA-3 > CalixPA-2 > CalixPA-5 >> CalixPA-6.<sup>80</sup>

More elaborate approaches have been developed using polymer-based ligands. Carbon nanotubes (CNTs) were dispersed in a copolymer composed of PAEMA, *N*-isopropylacrylamide (NIPAM) and PyMMA (PAEMA/NIPAM/PyMMA, Chart 12). Upon photo-irradiation, the CNTs heated up the copolymer, induced a phase transition and increased the extraction of Ln ions, compared to the non-irradiated system. Moreover, this photo-swing mechanism resulted in an increase in S.F. values for the different couples of metal ions. The photo-swing process could be repeated without loss of extraction capacity or selectivity.<sup>83</sup> Another strategy employed coordination polymer materials based on the complexation of Zr(IV) by 1-hydroxy-2-(1*H*-imidazol-1-yl)ethane-1,1-diyl bisphosphonate (zoledronate, Chart 12). Materials with higher phosphorus mole fractions showed a very high selectivity for the extraction of Ln(III) and Th(IV) with respect to fission product elements. Materials with lower phosphorus mole fractions were selective only for Th(IV). This suggested a separation method in which sorbent materials containing different quantities of phosphorus mole fractions were used in sequence to selectively extract Ln(III) after removal of Th(IV). These Th-saturated materials could be directly transformed into sodium zirconium phosphate (NZP), one of the most stable phosphate ceramic materials.<sup>84</sup>



## CMPOs

Initially, organophosphorus compounds, such as TBP, were used for the extraction of U and Pu from spent nuclear fuel, *via* the PUREX process. Among a series of bidentate ligands developed by Siddall in the early 1960s (BPM, CP and CMP, Chart 13), carbamoylmethylphosphonates (CMPs), combining a phosphonate ester with an amide showed good extraction properties for Ce, Pm and Am.<sup>85,86</sup> The presence of the carbonyl group reduced the competition between HNO<sub>3</sub> and the desired metal ion for the phosphoryl group, thus improving the extraction of Am(III) and Ln(III). However, CMPs are susceptible to radiolytic and hydrolytic degradation, have a tendency for third phase formation, show a low efficiency during the stripping of Pu and U and result in an increased volume of waste due to the need of salting out agents.<sup>25</sup>

A series of modifications of the structure of CMPs (Chart 13), including alkyl and aryl substituents on the amide and phosphoryl groups, alkylation of the methylene bridge and extension of the linker, revealed that the most efficient and selective ligand for Am(III) extraction was *n*-octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide OPhD(iBu)CMPO (Chart 13). Alkyl chains at the phosphoryl atom reduced the tendency for third phase formation, whereas phenyl rings increased the selectivity.<sup>87–89</sup> The alkyl chains on the amide mostly contributed to the solubility of the ligand; however, the highest selectivity was observed with long or branched chains (S.F.<sub>Pu(IV)/Am(III)</sub> and S.F.<sub>U(VI)/Am(III)</sub> with CMPOs with long/branched alkyl chains were an order of magnitude higher than those of other CMPOs, S.F.<sub>Am/Ln</sub> > 2).<sup>90</sup> Conversion of phosphine oxide into the corresponding phosphine sulfide (CMPS, Chart 13) caused a drop in the extraction and selectivity for An over Ln(III).<sup>91</sup> Extension or removal of the methylene bridge caused a decrease in *D* values, whereas its alkylation increased the solubility and selectivity, albeit reducing the extraction capacity.<sup>87–89</sup> The alkyl chains hindered the formation of the chelate complex by limiting the conformational mobility around the central carbon atom.<sup>92</sup>

A mixture of TBP and OPhD(iBu)CMPO was employed in the TRUEX process.<sup>93,94</sup> Addition of TBP to the extracting mixture improved the *D*<sub>Am</sub> values, reduced the tendency for third phase formation and decreased the susceptibility to radiolytic and hydrolytic degradation.<sup>25</sup> A summary about actinide partitioning using CMPOs, with particular focus on the process, was published by Ansari *et al.*<sup>25</sup>

The tendency to third phase formation was exploited for the design of a solvent-less system using DPhDBCMPPO (Chart 13). The ligand is solid at room temperature, but becomes liquid ("liquid reagent", LR) upon contact with solutions of mineral acids, due to the formation of DPhDBCMPPO·HNO<sub>3</sub>·*n*H<sub>2</sub>O (*n* = 2–3) adducts. In the extraction of several An, DPhDBCMPPO showed an increase in the *D* values by one order of magnitude, compared to the ligand dissolved in dichloroethane (DCE), with *D*<sub>Pr(LR)</sub> = 1.6, *D*<sub>Pr(DCE)</sub> = 0.1, *D*<sub>Np(IV)(LR)</sub> = 242, *D*<sub>Np(IV)(DCE)</sub> = 20. Interestingly, the mixture of ligand and HNO<sub>3</sub> had redox properties, the metal ions Pu(III) and Np(V) were oxidised to Pu(IV) and Np(VI), while Am(VI) was reduced to Am(III).<sup>95</sup>

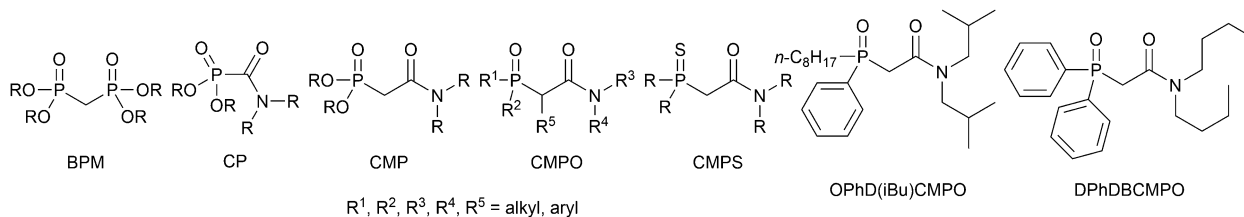


Chart 13

Mixtures of acidic and neutral ligands, aimed at the design of a single process able to perform the separation of An and Ln(III) (rather than a sequence of processes, each devoted at a specific separation), were discussed in a review by Lumetta *et al.*<sup>23</sup> These mixtures have the possibility to tune their properties by adjusting the pH. In the proposed TRUSPEAK process, based on a combination of OPhD(iBu)CMPO and HDEHP (Chart 6), the extraction behaviour of CMPO prevailed at high  $\text{HNO}_3$  concentration and that of HDEHP at a high pH.<sup>96</sup> The extraction of Eu(III) and Am(III) (at 1 M  $\text{HNO}_3$ ) was comparable to that obtained in the TRUEX process (CMPO + TBP) and higher than that of HDEHP alone. S.F.<sub>Eu/Am</sub> values up to 18 were obtained in the stripping step with DTPA (Chart 60). However, an increase in the concentration of  $\text{HNO}_3$  during the extraction step caused a decrease in the  $D$  values. In a highly acidic solution, HDEHP dimers are cleaved and the phosphoric acid interacts with CMPO. The formation of a HDEHP–CMPO adduct at  $[\text{HDEHP}] > [\text{CMPO}]$  significantly lowered the number of CMPO molecules available for complexation with the metal (0.1 M CMPO + 1.0 M HDEHP in  $n$ -dodecane:  $D_{\text{Am}} \approx 200$  at 0.1 M  $\text{HNO}_3$ ,  $D_{\text{Am}} \approx 0.5$  at 5 M  $\text{HNO}_3$ ).<sup>97</sup> Upon substitution of HDEHP with phosphonic acid HEH[EHP] (Chart 6), the extraction and stripping of metal ions were less sensitive to the  $\text{HNO}_3$  concentration (extraction: in the range 0.1–5 M  $\text{HNO}_3$ ,  $D_{\text{Am}} = 3$ –5; stripping: in the pH range 1.5–3.5,  $D_{\text{Am}} = 0.3$ –3, S.F.<sub>Ln/Am</sub> = 5–22), indicating more favourable process conditions.<sup>98</sup>

In the proposed ALSEP concept,<sup>99</sup> the CMPO ligand was replaced by a DGA ligand (*vide infra*). As opposed to the couple HDEHP–DGA, the mixture HEH[EHP]–DGA had a less steep pH profile for the stripping of Am(III)<sup>99</sup> and a higher selectivity in the An/Ln separation.<sup>100</sup> The neutral ligand, on the other hand, affected the recovery of Ln(III) ions, as TEHDGA did not extract light Ln as efficiently as TODGA (Chart 32).<sup>99</sup> In this process, An(III) and Ln(III) ions were co-extracted in the organic phase ( $n$ -dodecane) by TODGA at high  $\text{HNO}_3$  concentration (>3 M  $\text{HNO}_3$ ). Subsequently, the An(III) ions were selectively stripped

using a citrate-buffered DTPA solution at pH 3–4, while HEH[EHP] retained the Ln(III) in the organic phase, reaching S.F.<sub>Ln/Am</sub> values > 20.<sup>101</sup>

Substitution of the amide group with a methylketone (Chart 14) gave ligands with better extraction properties than DPhDBCMPPO, TBP and TOPO. Phosphorylketones BPO-1,2 showed good  $D$  values for U(IV) ( $D_{\text{U}} = 10$ –17 at 4 M  $\text{HNO}_3$  for ligands BPO-1) and preference for heavier Ln(III) ( $D_{\text{Ho}}$  and  $D_{\text{Yb}} = 3$ –7) over lighter ones ( $D_{\text{La}}$  and  $D_{\text{Nd}} = 0.7$ –2). There was no clear distinction between the effects of the linear alkyl chains on the extraction, whereas ligand BPO-2 (with phenyl substituents) always showed lower  $D$  values.<sup>102</sup>

Changing the linear alkyl chains to branched and cyclic ones (Chart 14), however, caused a decrease in the extraction performances of the ligands and a higher dependency of the  $D$  values on the nature of the substituents. Ligands BPO-2–5 were unable to extract Th(IV), and the extraction of U(VI) dropped by an order of magnitude ( $D_{\text{U}} = 0.2$ –1.2 at 4 M  $\text{HNO}_3$ ). The steric hindrance due to the phenyl ring on the linker overwhelmed the influence of the other substituents, and hence it was speculated that the extraction efficiency was independent of the structure of the groups on the phosphorus atom ( $D_{\text{Ho}} \approx 0.7$  at 4 M  $\text{HNO}_3$ ). On the other hand, the selectivity of ligands BPO-2 and BPO-3 for Yb(III) towards the other metal was good ( $D_{\text{Yb}} \approx 4$ ,  $D_{\text{La}}$  and  $D_{\text{Nd}} = 0.4$ –1 for BPO-2 and BPO-3, respectively, at 4 M  $\text{HNO}_3$ ).<sup>103</sup>

The reduction of the ketone to an alcohol led to a reversal of the selectivity, compared to phosphorylketones. Ligands BPO-6–8 (Chart 14) showed a preference for light Ln(III) over heavier ones, followed by U(VI). The presence of the hydroxy group caused a decrease in the  $D$  values for U(VI) ( $D_{\text{U}} \approx 0.4$  at 4 M  $\text{HNO}_3$  for BPO-6) and an increase in the  $D$  values for light Ln(III), following the order TOPO < TBP < BPO-9 < BPO-8 < BPO-7 < BPO-6 ( $D_{\text{La}} = 2.3$  and 1 for BPO-6 and TOPO, respectively, at 4 M  $\text{HNO}_3$ ).<sup>104</sup>

Substitution of the central methylene bridge by a nitrogen atom (Chart 14) slightly changed the extraction properties with respect to DPhDBCMPPO. The  $D$  values for phosphorylureas

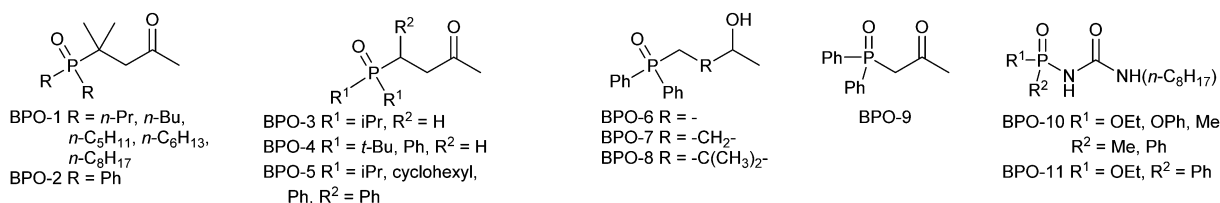


Chart 14

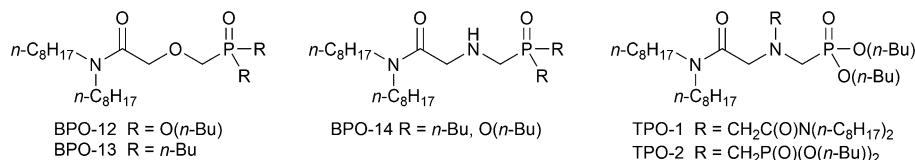


Chart 15

BPO-10,11 increased with increasing HNO<sub>3</sub> concentration and were in the same range as DPhDBCMPPO (Chart 13). Only BPO-11 showed an improved selectivity. The *D* values for heavier Ln(III) (*D*<sub>Ho</sub> = 1.07, *D*<sub>Yb</sub> = 0.88 at 3.75 M HNO<sub>3</sub>) were higher than those of lighter Ln(III) (*D*<sub>La</sub> = 0.46, *D*<sub>Nd</sub> = 0.48), allowing for group separation.<sup>105</sup>

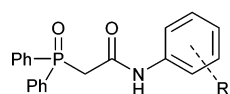
In the case of BPO-14 (Chart 15), the combined presence of a nitrogen atom and an extended bridge caused a decrease in the extraction as the HNO<sub>3</sub> concentration increased, without distinction between phosphonate and phosphine oxide groups (*D*<sub>Am</sub> ≈ 0.01, *D*<sub>Eu</sub> ≈ 0.1 at 4 M HNO<sub>3</sub>). Substitution of the nitrogen by an oxygen atom (BPO-12,13) or addition of a third *O*-donor group (TPO-1,2) improved the extraction behaviour. The behaviour of BPO-12,13 depended on the nature of the substituents at the phosphorus atom, but in both cases Eu(III) was preferred over Am(III). Phosphonyl ligand BPO-12 showed a lower extraction, but a better selectivity than OPhD(iBu)CMPO (*D*<sub>Am</sub> ≈ 0.7, *D*<sub>Eu</sub> ≈ 4, S.F.<sub>Eu/Am</sub> = 5.5 at 4 M HNO<sub>3</sub>), whereas the phosphine oxide ligand BPO-13 exhibited extraction as high as OPhD(iBu)CMPO at low HNO<sub>3</sub> concentration (*D*<sub>Am</sub> ≈ 1, *D*<sub>Eu</sub> ≈ 0.1 at 0.1 M HNO<sub>3</sub>) and intermediate response (between OPhD(iBu)CMPO and BPO-12) at higher acidity (*D*<sub>Am</sub> ≈ 4, *D*<sub>Eu</sub> ≈ 10, S.F.<sub>Eu/Am</sub> = 2.5 at 4 M HNO<sub>3</sub>). Ligands TPO-1,2 preferentially extracted Am(III) over Eu(III), as other CMPOs, but the *D* values were low (0.01 < *D* < 0.5 in the range 0.01–4 M HNO<sub>3</sub>). However, in the presence of two

phosphonate groups (TPO-2), Am(III) was extracted somewhat better than Eu(III), and maximum selectivity was reached at 1 M HNO<sub>3</sub> (*D*<sub>Am</sub> ≈ 0.5, *D*<sub>Eu</sub> ≈ 0.1, S.F.<sub>Eu/Am</sub> ≈ 5).<sup>27</sup>

Using a phenyl ring to introduce an additional phosphine oxide group (Chart 16) caused an increase in the extraction efficiency, as compared to the tripodant amine (TPO-1–2). The ligands containing a *meta*-substituted phenyl ring showed higher *D* values than the corresponding *ortho*-substituted ones (CMPO-4 vs. CMPO-2), and better results were obtained when the additional phosphine oxide was separated from the phenyl ring by a methylene group. CMPO-5 showed the highest *D* values among these ligands and showed a strong preference for Th(IV) over U(VI) and for lighter Ln(III) over heavier ones (at 3 M HNO<sub>3</sub>, *D*<sub>Th</sub> ≈ 150, *D*<sub>U</sub> ≈ 13, *D*<sub>Eu</sub> ≈ 2.5, *D*<sub>Lu</sub> ≈ 0.1). Interestingly, at higher HNO<sub>3</sub> concentration, the *D* values for the Ln ions converged to ≈ 0.3, whereas those for Th(IV) and U(VI) increased.<sup>106</sup> This behaviour was observed for several neutral organophosphorus compounds and has been explained as a combination of the salting out effect of HNO<sub>3</sub> and the competition between HNO<sub>3</sub> and the metal ions for the binding sites of the molecule.<sup>107</sup>

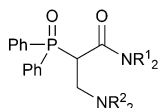
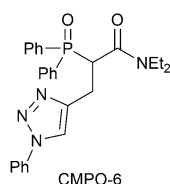
Alkylation of the CMPO central methylene group with amino- and triazolyl-containing chains had different effects, depending on the metal ion extracted. The presence of the amine (CMPO-7) caused a decrease in the extraction of U(VI), Th(IV) and Ln(III) and an increase in the extraction of Pd(II), a fission product that can interfere with the extraction of An and Ln(III).<sup>108</sup> The selectivity for Pd(II) was more pronounced with a triazolyl chain (*D*<sub>Pd</sub> = 21 with CMPO-6 and *D*<sub>Pd</sub> = 0.05 with DPhDBCMPPO), whereas the extraction of U(VI) and Ln(III) was only slightly affected, but the ligand was unable to extract Th(IV).<sup>109</sup>

Pre-organisation of two triazolylCMPO units on a benzene platform (Chart 17) increased the selectivity for Pd(II) even more, with *D*<sub>Pd</sub> values up to 62 at 3 M HNO<sub>3</sub>. On the other hand, all the ligands, except BisCMPO-2, also showed an increase in the extraction of U(VI), Th(IV) and the Ln(III) (for BisCMPO-3 and

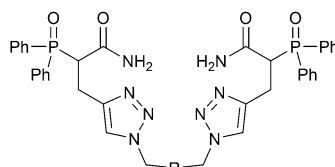


CMPO-1 R = H  
CMPO-2 R = *o*-P(O)Ph<sub>2</sub>  
CMPO-3 R = *o*-CH<sub>2</sub>P(O)Ph<sub>2</sub>  
CMPO-4 R = *m*-P(O)Ph<sub>2</sub>  
CMPO-5 R = *m*-CH<sub>2</sub>P(O)Ph<sub>2</sub>

Chart 16



R<sup>1</sup> = Et, iBu, *n*-C<sub>6</sub>H<sub>13</sub>  
R<sup>2</sup> = Et, *n*-Bu



BisCMPO-1 R = 1,2-phenylene, 1,3-phenylene, 1,4-phenylene,  
2,4,6-trimethyl-1,3-phenylene  
BisCMPO-2 R = 4,4'-(1,1'-biphenyl)ylene  
BisCMPO-3 R = 2,3,5,6-tetramethyl-1,4-phenylene

Chart 17



CMPO-6,  $D_U = 165$  and  $18$ ,  $D_{Th} = 10$  and  $1$ ,  $D_{Eu} = 0.11$  and  $0.01$ , respectively, at  $3\text{ M HNO}_3$ ).<sup>110,111</sup> An account about the improvement of the extraction performances upon pre-organisation of the ligands on molecular platforms was reported in a review including CMPOs, as well as diamides and N-heterocyclic donors.<sup>37</sup>

A comparison of several CMPOs and  $\beta$ -aminophosphine oxide (bAPO) derivatives (Chart 18) demonstrated the positive effect of preorganisation on the extraction of metal ions. Increasing the number of CMPO units increased the  $D$  values in the extraction of Ln(III) from acidic medium (the  $D_{Eu}$  values for DPhDBCMPPO, BisCMPO-4,5 and TrisCMPO-1 were  $0.03$ ,  $1$ ,  $1$ ,  $1.6$ ,  $4$  and  $10$ , respectively, from  $3\text{ M HNO}_3$ ). A similar trend was also observed for bAPO derivatives.<sup>112</sup> However, the extraction properties of the ligand were highly influenced by the platform used for preorganisation and not only by the number of CMPO units.

Connecting two CMPO units with a pentyl spacer *via* the methylene groups (BisCMPO-8, Chart 18) did not affect the extraction of Ln(III), but increased the extraction of U(VI) and lowered that of Th(IV), leading to an improved U/Th separation, compared to DPhDBCMPPO ( $D_U = 10$ ,  $D_{Th} = 0.4$ , S.F.<sub>Th/U</sub> =  $0.04$  for BisCMPO-8,  $D_U = 2$ ,  $D_{Th} = 50$ , S.F.<sub>Th/U</sub> =  $25$  for DPhDBCMPPO, at  $3\text{ M HNO}_3$ ).<sup>113</sup> In contrast, bisCMPOs with an alkyl linker connecting the amidic nitrogens (BisCMPO-6<sub>n</sub>) showed an increase in the extraction of Ln(III) compared to BisCMPO-8. BisCMPO-6<sub>5</sub>, with a pentyl linker, gave a better extraction than BisCMPO-6<sub>3</sub>, followed by CMPO-8 and BisCMPO-6<sub>3</sub>, indicating

that a certain distance and flexibility between the two CMPO units is required to achieve good extraction. Compared to BisCMPO-7, a structural analogue with a diethylene glycol spacer, BisCMPO-6<sub>5</sub> showed higher  $D$  values, apparently due to an increased hydrophobicity.<sup>114</sup>

Increasing the length of the spacer to acquire triethylene glycol (BisCMPO-9, Chart 19) had almost no effect on the extraction ability of the ligand, whereas a further increase in tetraethylene glycol (BisCMPO-10) caused an increase in the extraction of Ln(III) by an order of magnitude (for BisCMPO-7, BisCMPO-9 and BisCMPO-10, respectively,  $D_{Eu} = 1$ ,  $2$ ,  $50$ , at  $3\text{ M HNO}_3$ ), with good separation among the Ln ( $D_{La} = 100$ ,  $D_{Lu} = 10$  for BisCMPO-10). The results were also better than those of BisCMPO-8 ( $D_{Eu} = 0.3$ ), the monoCMPO analogue CMPO-8 ( $D_{Eu} = 0.5$ ) and tripodal CMPO TrisCMPO-1 ( $D_{Eu} = 25$ ) and TrisCMPO-4 ( $D_{Eu} = 0.26$ ). The extraction of U(VI) and Th(IV) benefitted as well from the tetraethylene glycol spacer, with higher  $D$  values than BisCMPO-8 and DPhDBCMPPO ( $D_U = 25$ ,  $D_{Th} = 794$ , S.F.<sub>U/Th</sub> =  $32$  for BisCMPO-10, at  $3\text{ M HNO}_3$ ).<sup>115</sup> Even lower extraction for Ln(III), Th(IV) and U(VI) was obtained with TrisCMPO-3 and TrisCMPO-2 ( $D_{Eu} = 0.09$  for both ligands,  $D_U = D_{Th} = 0.08$  for TrisCMPO-3,  $D_U = D_{Th} = 0.8$  for TrisCMPO-2 at  $1\text{ M HNO}_3$ ), whereas at  $5\text{ M HNO}_3$ , TrisCMPO-2 showed a good extraction efficiency for the An ( $99$  and  $98\%$ , corresponding to  $D_U \sim 100$ ,  $D_{Th} \sim 50$ , respectively). The lower performance of TrisCMPO-3 could be attributed to the phosphonate groups that are weaker donors than the phosphine

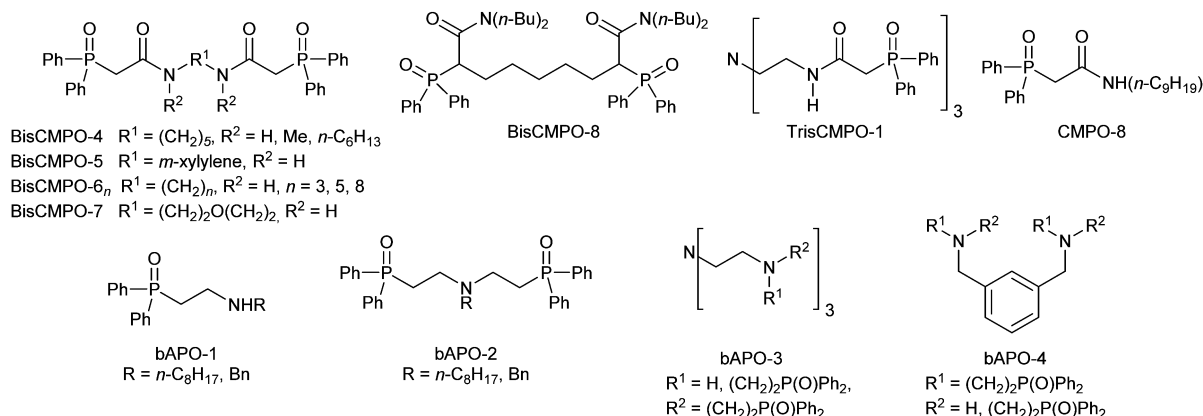


Chart 18

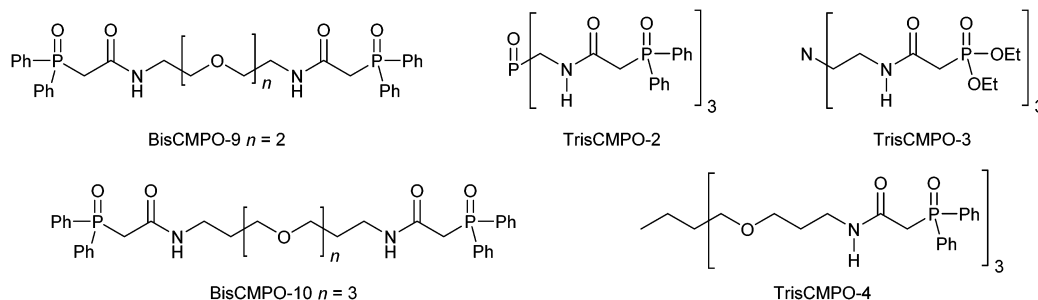


Chart 19

oxides used in TrisCMPO-1. The behaviour of TrisCMPO-2 was attributed to the capping phosphine oxide group and the shorter linker, that forced the ligating sites to spread and form a larger pocket, resulting in a preference for U(vi) and Th(iv) over the Ln(III).<sup>116,117</sup>

**CMPOs on platforms.** The extraction properties of appropriately functionalised calix[4]arenes depend on the interplay between various elements (substituents on the complexing units, linkers with the calix[4]arene platform, substituents on the opposite rim, presence of other heteroatoms, steric hindrance, hydrophobicity, *etc.*). Hence, it is difficult to make predictions of the outcome that structural changes may have on the performance of the ligand.<sup>37</sup> The extraction behaviour of wide-rim CMPO-calix[4]arenes, (Chart 20) having adamantyl groups as linkers between the CMPO units and the platform, resembles that of the narrow-rim derivative CalixCMPO-2. The best results were obtained with CalixCMPO-5<sub>1</sub>, as it seemed that without spacer (CalixCMPO-5<sub>0</sub>), steric hindrance among adamantyl groups obstructed the formation of the complexes, whereas the ethylene linkers (CalixCMPO-5<sub>2</sub>) loosened the pre-organisation of the CMPO units ( $D_{Eu} = 0.25, 1.17$  and  $0.18$  for CalixCMPO-5<sub>m</sub> with  $m = 0, 1, 2$ , respectively, at  $1\text{ M HNO}_3$ ). Wide-rim adamantyl-calix[4]arene CalixCMPO-5<sub>1</sub> exhibited good extraction for Am(III) and Eu(III), but low selectivity ( $S.F._{Am/Eu} = 1.2$  at  $3\text{ M HNO}_3$ ), while wide-rim calix[4]arene CalixCMPO-1 showed lower  $D$  values and higher selectivity ( $S.F._{Am/Eu} = 4.9$  at  $3\text{ M HNO}_3$ ). Conversely, CalixCMPO-5<sub>1</sub> behaved similar to narrow-rim derivative CalixCMPO-2 ( $S.F._{Am/Eu} = 1.3$  at  $3\text{ M HNO}_3$ ).<sup>118</sup>

Functionalising *p*-adamantylcalix[4]arene with CMPOs at the narrow rim resulted in an increase in the extraction performance, compared to *p*-alkylcalix[4]arenes (Chart 20). In the extraction of Ln, ligands CalixCMPO-7,8 showed higher  $D$  values than the corresponding *p*-H, *p*-*tert*-Bu and *p*-*tert*-octyl derivatives CalixCMPO-2–4, following the order  $D_{Ln}(\text{CalixCMPO-7}_4) > D_{Ln}(\text{CalixCMPO-7}_3) > D_{Ln}(\text{CalixCMPO-7}_2)$ , whereas the extraction of Th(iv) was lower. Among the calix[4]arenes bearing CMPOs with linkers of different lengths, CalixCMPO-8<sub>34</sub> exhibited  $D$  values comparable with those of CalixCMPO-7<sub>4</sub>. All the

ligands (CalixCMPO-2–8) extracted Th(iv) very well, but high selectivity was obtained with ligands bearing short alkyl linkers, namely CalixCMPO-2–4 ( $S.F._{Th/Ln}(\text{CalixCMPO-4}) > 34$ ,  $S.F._{Th/Ln}(\text{CalixCMPO-3}) > 30$ ,  $S.F._{Th/Ln}(\text{CalixCMPO-2}) > 28$ ,  $S.F._{Th/Ln}(\text{CalixCMPO-7}_3) > 19$ ). There is generally a preference for lighter Ln over heavier ones (with the highest value being  $S.F._{La/Yb}(\text{CalixCMPO-8}_{34}) = 10.4$ ), but the  $S.F.$  values are negligible if compared to CalixCMPO-1, which reached  $S.F._{La/Yb} > 1600$ .<sup>119</sup>

The effect of the rigidity of the spacer was also investigated, comparing spacers able to form one or two intramolecular H-bonds. Ligands CalixCMPO-10,11 (Chart 20), with a spacer containing one hydrogen bond, extracted La(III) better than CalixCMPO-9 that has two such bonds ( $D_{La} = 0.27, 3.39, 2.28$  for CalixCMPO-9–11, respectively, at  $1\text{ M HNO}_3$ ). Despite ligands CalixCMPO-9–11 exhibiting poor extraction for Ln(III) and a preference for Th(iv) ( $D_{Th}$  in the range of  $5.4\text{--}20$  at  $1\text{ M HNO}_3$ ), they highlighted the importance of spacer rigidity for the tuning of the extraction properties.<sup>120</sup>

Pillar[5]arene is a molecular platform based on a macrocycle composed of five benzene rings resembling a cylinder more than a cone (as the calix[4]arenes). Up to five complexing units can be attached to each side of the molecule.<sup>121</sup> Functionalisation of a pillar[5]arene with CMPOs on both sides (PillarCMPO, Chart 21) revealed that the  $D_{Am}$  and  $D_{Eu}$  values were somewhat lower than those of CMPO-calix[4]arenes studied previously (CalixCMPO-1, CalixCMPO-12–15),<sup>122,123</sup> but the dependence of the extraction on the concentration of  $\text{HNO}_3$  was different. Upon increasing the acidity, the extraction increased; however, at  $>1\text{ M HNO}_3$ , a sudden drop in the extraction occurred. Due to the relatively large number of CMPO units on the molecule, the competition between  $\text{H}^+$  and metal ions was stronger than with other ligands. Only PillarCMPO ( $n = 3$ ) showed selectivity for Am(III) over Eu(III) ( $D_{Am} = 171$ ,  $D_{Eu} = 13$ ,  $S.F._{Am/Eu} = 13$ , at  $1\text{ M HNO}_3$ ), whereas PillarCMPO ( $n = 1, 2$ ) extracted the two metal ions to the same extent; on the other hand it could form  $2:1\text{ M:L}$  complexes in a stepwise manner to form a bimetallic complex.<sup>124</sup>

Extremely high  $D$  values with pre-organised CMPOs were obtained with ionic calix[4]arenes bearing cobalt bis(dicarbollide)

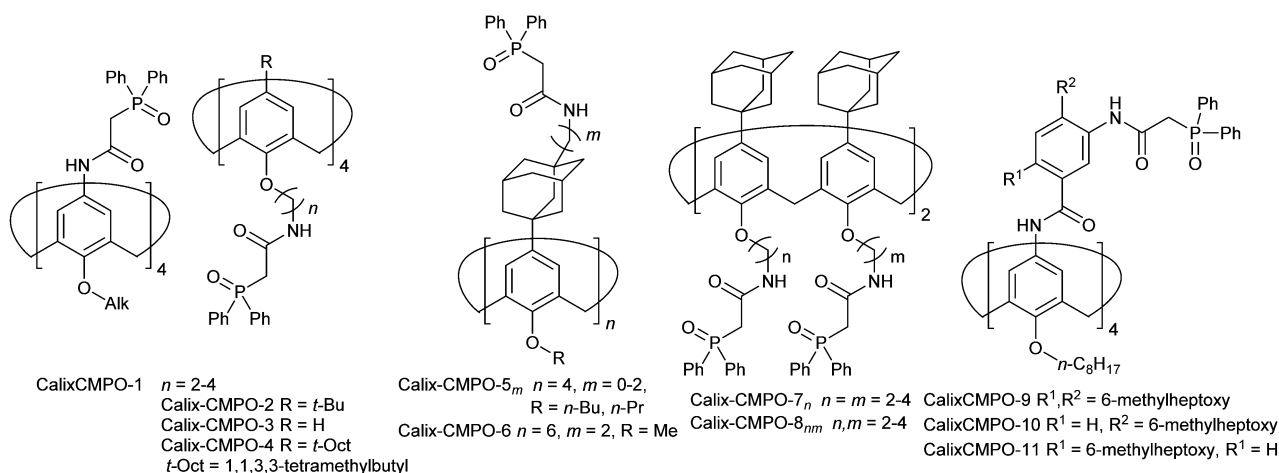


Chart 20

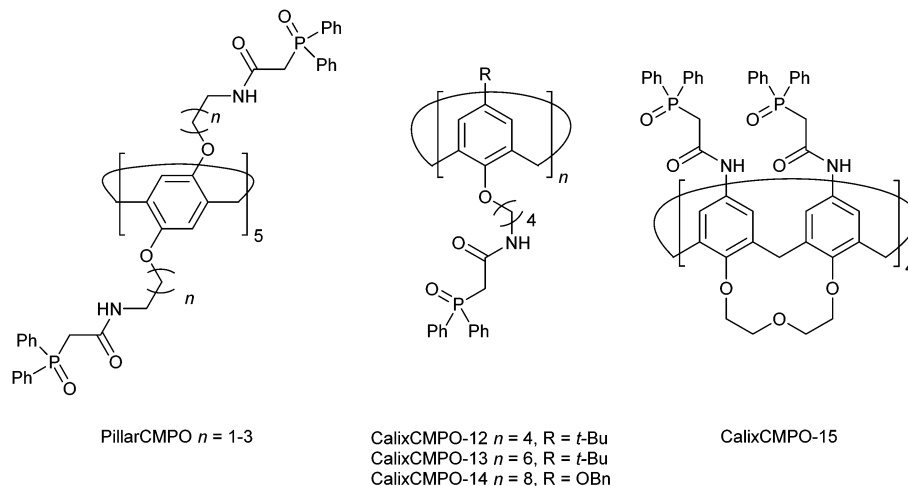


Chart 21

anions (CCD, A in Chart 22). CMPO and CCD were arranged on the narrow rim of calix[4]arenes in different combinations (1 : 3, 2 : 2 and 3 : 1 ratios) and configurations (1,2- or 1,3-positions) and were tested in the extraction of Ln(III) and An. The extraction efficiency decreased with increasing  $\text{HNO}_3$  concentration and followed the order CCDCMPO-4 > CCDCMPO-1 > CCDCMPO-3 >> CCDCMPO-2. Due to the presence of three CCD anions, ligand CCDCMPO-2 ( $D_{\text{Am}}$ ,  $D_{\text{Eu}} < 0.01$  at 2 M  $\text{HNO}_3$ ) could provide charge neutralisation, but the single CMPO unit was not able to fully saturate the coordination sites of the metal. Conversely, CCDCMPO-1 ( $D_{\text{Am}} = 41$ ,  $D_{\text{Eu}} = 27$ ,  $\text{S.F.}_{\text{Am/Eu}} = 1.55$ , at 2 M  $\text{HNO}_3$ ) with three CMPO groups, could complete the coordination of the metal. CCDCMPO-4 ( $D_{\text{Am}}$ ,  $D_{\text{Eu}} > 100$ , at 2 M  $\text{HNO}_3$ ) provided higher  $D$  values due to the balance between charge neutralisation and complete coordination. The vicinal positioning of the CMPO units of CCDCMPO-3 ( $D_{\text{Am}} = 27$ ,  $D_{\text{Eu}} = 16$ ,  $\text{S.F.}_{\text{Am/Eu}} = 1.7$ , at 2 M  $\text{HNO}_3$ ) resulted in lower  $D$  values compared to CCDCMPO-4, suggesting that the alternate disposition offered stronger complexation. Pre-organisation of the CMPO moieties at the wide rim (CCDCMPO-6) resulted in  $D$  values lower than those of the related compounds CCDCMPO-4 and CCDCMPO-5, probably because of the poor flexibility of the CMPO units that were connected directly at the *ipso*-positions. However, the extraction efficiency was generally so high that it prevented the stripping of metal ions, unless it was performed at high

acidity in the presence of strong complexing agents (like DTPA).<sup>125</sup>

CCD-functionalised ionic CMPO ligands (Chart 23) showed very high extraction efficiencies from highly acidic solutions. In the extraction of Eu(III) and Am(III), CCDCMPO-7a showed  $D$  values ( $D_{\text{Eu}} = 66$  at 3 M  $\text{HNO}_3$  in nitrophenyl hexyl ether (NPHE)) up to four orders of magnitude higher compared conventional CMPO ligands ( $D_{\text{Eu}} = 0.1$  at 3 M  $\text{HNO}_3$  in NPHE with  $\text{OPhD(iBu)CMPO}$ ). The ionic ligand also exhibited better extraction than a synergic mixture of CMPO and CCD ( $D_{\text{Eu}} = 7$  at 3 M  $\text{HNO}_3$  in NPHE with  $\text{OPhD(iBu)CMPO} + \text{Br}_6\text{CCD}$ ). Due to the low separation between An and Ln(III) ( $\text{S.F.}_{\text{Am/Eu}} \approx 1$ ), these compounds were proposed for the removal of the whole group of M(III) ions from highly acidic waste.<sup>126</sup> Alkyl chains on the nitrogen atom increased the extraction properties, probably because they increased the hydrophobicity of the ligand, whereas the presence of an *n*-octyl chain on the phosphine oxide improved the solubility in less polar solvent mixtures, without too much effect on the extraction. Eu(III) could be back-extracted from the organic phase by dilution of the extraction mixture with *n*-propanol, or using complexing agents (DTPA).<sup>127</sup> Halogenation of the CCD anion (CCDCMPO-8) improved the hydrolytic stability of the ligands in apolar solvents. After 30 days, there was no sign of hydrolysis for the halogenated compounds, whereas control CCDCMPO-7b had already showed decomposition after 10 days.<sup>128</sup>

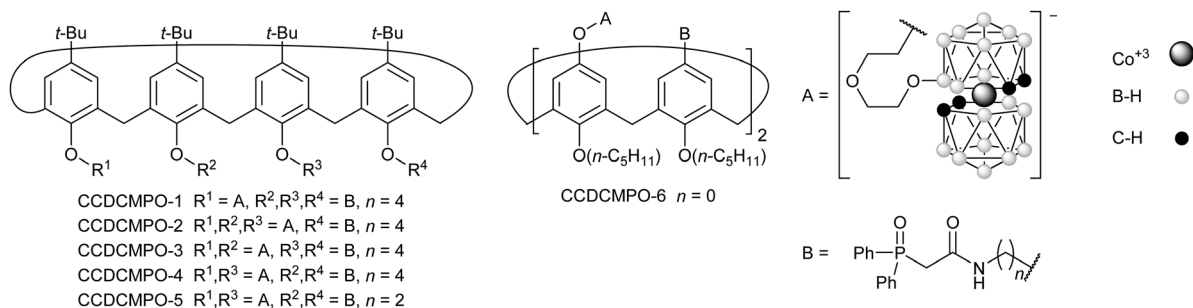


Chart 22

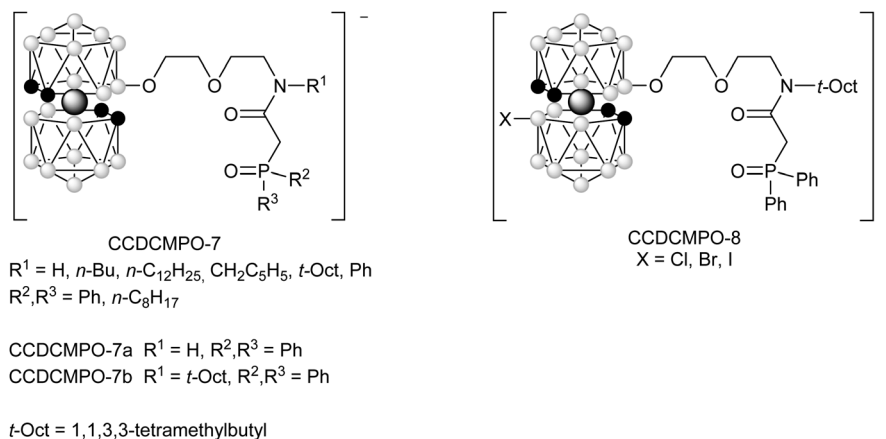


Chart 23

Attachment of a 3-alkylimidazolium-1-yl unit to the CMPO skeleton led to TSILs as depicted in Chart 24 that could be used without any diluent, or within a RTIL. In these systems, the extraction of metal ions depends on the metal ion extracted and on the contraposing effects of the alkyl chain on the imidazolium and the RTIL anions. For ligands  $[\text{C}_6\text{imCMPO}][\text{X}]$  ( $X = \text{Cl}, \text{Br}, \text{PF}_6$ ), with a short *n*-hexyl chain, the *D* values were higher with the hydrophobic hexafluorophosphate anion than with halides. In the case of ligands with an *n*-octyl chain ( $[\text{C}_8\text{imCMPO}][\text{X}]$ ,  $X = \text{Cl}, \text{Br}, \text{PF}_6$ ), the efficiency followed the reverse order ( $\text{Cl} > \text{Br} > \text{PF}_6$ ), whereas for ligands with a long hexadecyl chain ( $[\text{C}_{16}\text{imCMPO}][\text{X}]$ ,  $X = \text{Cl}, \text{Br}, \text{PF}_6$ ) the extraction was not affected by the nature of the anion.<sup>129</sup> Substituting the hexafluorophosphate anion for a bis(triflimide) anion ( $[\text{C}_n\text{imCMPO}][\text{NTf}_2]$ ,  $n = 12, 14$ ), increased the extraction performance, which, however, remained lower than that of CMPO diluted in the same RTIL ( $D_{\text{Am}} = 0.16$  for  $[\text{C}_{12}\text{imCMPO}][\text{PF}_6]$  in  $[\text{C}_8\text{mim}][\text{PF}_6]$ ,  $D_{\text{Am}} = 16$  for  $[\text{C}_{12}\text{imCMPO}][\text{NTf}_2]$  in  $[\text{C}_8\text{mim}][\text{NTf}_2]$  at 3 M  $\text{HNO}_3$ ).<sup>130,131</sup> Although in the extraction of U(vi) the *D* values decreased in the order  $[\text{C}_4\text{mim}][\text{NTf}_2] > [\text{C}_6\text{mim}][\text{NTf}_2] > [\text{C}_8\text{mim}][\text{NTf}_2]$  ( $D_{\text{Am}} = 42, 26, 17$  for  $[\text{C}_{12}\text{imCMPO}][\text{NTf}_2]$  in  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with  $n = 4, 6, 8$ , respectively, from 3 M  $\text{HNO}_3$ ), there was little change upon an increase in  $\text{HNO}_3$  concentration. Ligand  $[\text{C}_{12}\text{imCMPO}][\text{NTf}_2]$  showed a remarkable increase in the extraction of Pu(iv) when  $[\text{C}_4\text{mim}][\text{NTf}_2]$  was used as a diluent ( $D_{\text{Am}} = 3550$  for  $[\text{C}_{12}\text{imCMPO}][\text{NTf}_2]$  in  $[\text{C}_4\text{mim}][\text{NTf}_2]$ ,  $D_{\text{Am}} = 1384$  for  $\text{OPhD}(\text{iBu})\text{CMPO}$  in  $[\text{C}_4\text{mim}][\text{NTf}_2]$ ), whereas the other two TSILs caused a decrease in the *D* values ( $D_{\text{Am}} = 2217$  and  $852$  for  $[\text{C}_{12}\text{imCMPO}][\text{NTf}_2]$  in  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with  $n = 6, 8$ ;  $D_{\text{Am}} = 2834$  and  $2827$  for  $\text{OPhD}(\text{iBu})\text{CMPO}$  in  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with  $n = 6, 8$ ).<sup>130</sup> In the

extraction of Np ions by  $[\text{C}_{12}\text{imCMPO}][\text{PF}_6]$ , very high *D* values were obtained, with a difference between Np(iv) and Np(vi) of almost an order of magnitude.<sup>132</sup>

### Hybrid organophosphorus/heterocycle ligands

Hybrid organophosphorus/heterocycle ligands aim at the modulation of the extraction behaviour of the phosphoryl group, by coupling it with “soft” heterocyclic N-, O- and S-donors, to achieve better selectivity.

**Naphthyridine.** Phosphoryl naphthyridines are potentially tridentate ligands. Extraction of metal ions from alkaline carbonate solutions is expected to be more efficient, because the extractable neutral complexes contain twice as many lanthanide ions than from nitrate solutions.<sup>133</sup> Naphthyridine NaphP-1 (Chart 25) showed rather poor extraction of Ln(III), but there was selectivity between light and heavy Ln(III), and the *D* values were virtually independent of the pH ( $D_{\text{La}}, D_{\text{Nd}} \approx 0.22$ ,  $D_{\text{Ho}}, D_{\text{Yb}} \approx 0.10$  at 0.355 M  $\text{Na}_2\text{CO}_3$ ). In the case of NaphP-8 (Chart 25) the *D* values were two orders of magnitude higher than those of NaphP-1, showing good selectivity for light Ln(III) ( $\text{S.F.}_{\text{La/Ho}} \approx 12$  at 0.355 M  $\text{Na}_2\text{CO}_3$ ). Interestingly, the extraction of Nd(III) was very high at low  $\text{Na}_2\text{CO}_3$  concentration (similar to Ln(III),  $D_{\text{Nd}} = 18$  at 0.078 M  $\text{Na}_2\text{CO}_3$ ) and lower upon an increase in basicity (similar to Ho(III) and Yb(III),  $D_{\text{Nd}} = 5$  at 0.355 M  $\text{Na}_2\text{CO}_3$ ). Moreover, the ligands did not extract any Na(I), and back-extraction of the metal ions could be achieved with 0.05 M  $\text{HNO}_3$ .<sup>133</sup>

Naphthyridines with a  $\text{C}_2$  alkyl spacer between the heterocycle and the phosphine oxide group (Chart 25) gave good results in the extraction of U(vi), with high selectivity with respect to Ln(III) and *D* values up to 436 ( $\text{S.F.}_{\text{U/Eu}} = 242$ , from 1 M  $\text{NH}_4\text{ClO}_4$ ). The presence of a double bond in the linker or a 1,6-naphthyridine group prevented the formation of a tridentate ligand. Introduction of a substituent at the  $\alpha$ -position of the phosphoryl group had a substantial influence on the extraction properties. Electron-withdrawing groups reduced the basicity of the phosphoryl group, whereas electron-donating substituents improved the extraction of metal ions because of the increased basicity of the oxygen atom, strengthening the O–M bond.

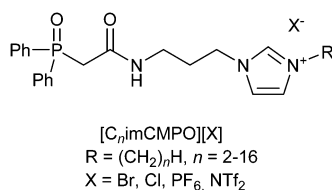


Chart 24



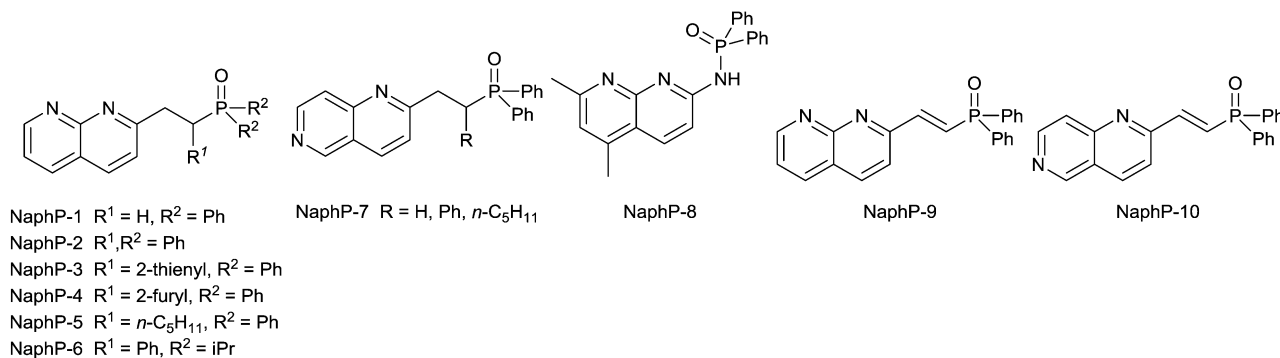


Chart 25

Phenyl or thienyl groups caused a decrease in the  $D$  values (NaphP-1,  $D_U = 125$ , NaphP-2,3,  $D_U = 5.8$  and  $1.5$ , respectively), whereas an  $n$ -pentyl chain increased the extraction of U(VI) (NaphP-5,  $D_U = 186$ ). Likewise, replacement of the phenyl substituents at the phosphorus atom with the more electron-donating isopropyl groups induced better  $D$  values (NaphP-6,  $D_U = 436$ ).<sup>134</sup>

**Pyrazine.** The nitrogen atoms on pyrazines are less basic ( $pK_b = 13.8$ ) than those on pyridines ( $pK_b = 8.8$ ); hence, pyrazine-based ligands are expected to perform better at higher acidity than pyridine-based ones. In addition, the introduction of phosphonates and phosphine oxides would further decrease the nucleophilicity of the nitrogen atom, hence further increasing the affinity towards An over Ln(III). However, these combined effects resulted in very poor extraction of metal ions in the case of ligands Pyraz-1,2 and Pyraz-4,5 (Chart 26). Only Pyraz-1, bearing two phosphine oxide groups, was able to recover Am(III) and Eu(III), but the  $D$  values were  $<1$  in the range  $0.01\text{--}4\text{ M HNO}_3$ .<sup>135</sup>

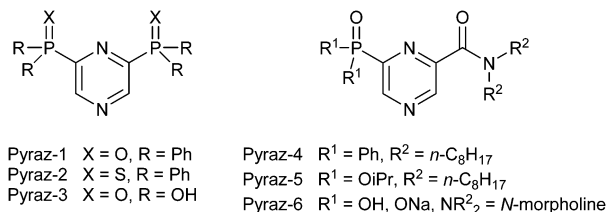


Chart 26

On the other hand, hydrophilic Pyraz-3 and Pyraz-6 (Chart 26) exhibited interesting properties for the back-extraction of An and Ln(III). At a concentration of  $0.1\text{ M}$ , nearly 100% of the metal ions were extracted in the aqueous phase. Upon reduction of the ligand concentration, the  $D$  values of Am(III) and Eu(III) increased, and those of Eu(III) were even faster ( $D_{Eu} = 0.002$  and  $0.6$  at  $0.1$  and  $0.01\text{ M}$  ligands, respectively at pH 1), leading to an increase of  $S.F._{Eu/Am}$  values ( $S.F._{Eu/Am} = 4.6$  and  $40$  at  $0.1$  and  $0.01\text{ M}$  ligands, respectively, at pH 1). However, a further decrease in the ligand concentration was sensitive to the loading of the metal. Pyraz-6 showed a behaviour similar to that of Pyraz-3, but a good separation between Eu(III) and Am(III) was achieved at a ligand concentration of  $0.1\text{ M}$  and higher pH values ( $D_{Eu} = 1.84$ ,  $D_{Am} = 0.15$  at pH 3). Although the  $S.F._{Eu/Am}$  values were lower ( $S.F._{Eu/Am} \sim 10\text{--}14$ ), higher pH values and higher concentrations are more favourable conditions for the back-extraction process (lower amount of acid needed, less sensitive to metal loading).<sup>135</sup>

Hydrophobic pyrazine ligands pre-organised on a calix[4]arene platform<sup>136</sup> (Chart 27) showed an increase in extraction performance of  $10^4$  to  $10^5$  times compared to the monovalent ligands. CalixPyr-6, with four pyrazines, each bearing an amide and a phosphine oxide group, exhibited higher  $D$  values ( $D_{Am} = 13.5$ ,  $D_{Eu} = 14.0$  at  $3\text{ M HNO}_3$ ) than other ligands with fewer pyrazine units, or substituted with moieties other than the phosphine oxide ( $D < 0.19$  for all other ligands at  $3\text{ M HNO}_3$ ). Addition of  $1\text{ mM CCD}^-$  anion as a synergist caused an increase in the extraction of Am(III) and Eu(III), but the effect was dependent on the pH and the ligand employed. At both  $0.01$  and  $3\text{ M HNO}_3$ , there was a levelling of the extraction

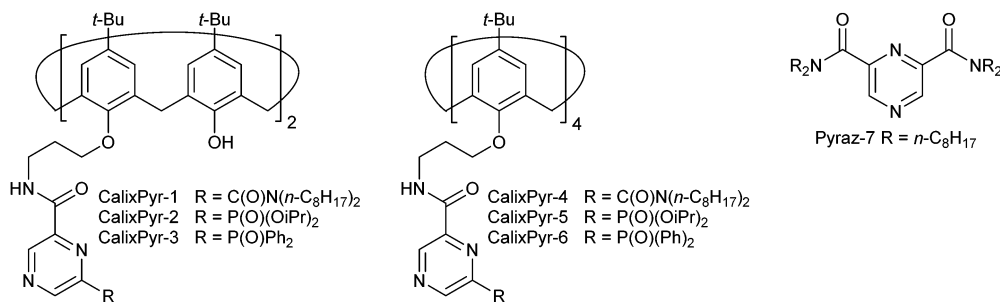


Chart 27

performance among ligands CalixPyr-4–6 and Pyraz-7: high extraction at low acidity ( $D_{\text{Am}} = 280\text{--}450$  at  $0.01\text{ M HNO}_3$ ) and low extraction at high acidity ( $D_{\text{Am}} \sim 10^{-3}$  at  $3\text{ M HNO}_3$ ), except for CalixPyr-6 ( $D_{\text{Am}} = 40$ ). At pH 1 ( $0.1\text{ M HNO}_3$ ), there was differentiation in the  $D$  values of ligands CalixPyr-4–6 ( $D_{\text{Am}} = 0.5, 173, 794$ , respectively) and their behaviour with increasing the concentration of synergist from  $1\text{ mM}$  to  $5\text{ mM}$ . Ligands CalixPyr-5,6 exhibited an increase in the  $D$  values by an order of magnitude and stable or decreasing S.F.<sub>Am/Eu</sub> values (between 1 and 3 for both ligands). Increasing the  $\text{CCD}^-$  concentration, CalixPyr-4 spanned a wider range of  $D$  values ( $D_{\text{Am}} = 0.5$  and  $\sim 500$  at  $1$  and  $5\text{ mM CCD}^-$ , respectively) and the separation between the two metal ions improved (up to S.F.<sub>Am/Eu</sub>  $\approx 7$ ).<sup>137</sup> In this case, pyrazine diamide CalixPyr-4 benefitted the most from the addition of the synergist, because the  $D$  values remained lower. On the other hand, the extraction of metal ions by CalixPyr-6 was so high that the selectivity was lost.

A strong enhancement in the extraction of Am(III) and Eu(III) was also observed when the calix[4]arene pyrazines CalixPyr-5,6 were used in RTILs ( $D_{\text{Am}} = 62$  and  $850$ , respectively, at  $3\text{ M HNO}_3$ ), whereas the extraction with diamide ligands CalixPyr-1 and CalixPyr-4 and bipodal ligands CalixPyr-2,3 remained unaffected. Increasing the chain length of  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 4, 6$  and  $8$ ) resulted in a decrease in the  $D$  values ( $D_{\text{Am}} = 850, 395, 241$  for CalixPyr-6 and  $n = 4, 6$  and  $8$ , respectively, at  $3\text{ M HNO}_3$ ) and a change in the extraction mechanism (ion-exchange for  $n = 4$  and  $6$ , solvation extraction for  $n = 8$ ). Interestingly, ligands CalixPyr-5,6 showed lower extraction for U(VI), Pu(IV) and fission products than Am(III), suggesting that this extraction system could be used for the extraction of trivalent An from bulk uranium.<sup>138</sup>

**NOPO/CMPO.** Pyridine *N*-oxide is being studied as a mono- and bifunctional platform for the complexation of f-metal ions. The studies mainly focused on the preparation of phosphorylated derivatives that could act as bi- or tridentate ligands (Chart 28). According to crystallographic data, the compounds with a methylene bridge between the phosphine oxide groups and the carbon atoms at the 2- and 6-positions of the pyridine *N*-oxide were best suited for the complexation of Ln. Moreover, in the crystalline state, NOPO derivatives (NOPO-6–8) act as tridentate ligands for Ln(III), Am(III), Pu(IV) and Th(IV). Crystal structures of the tetraphenyl derivative NOPO-6 (Chart 28) have been extensively studied, but due to the poor solubility of the ligand in solvents suited for large-scale operations (tends to be

soluble only in polar, volatile solvents like chloroform), extraction experiments were limited.<sup>139,140</sup>

For this reason, derivatives bearing long alkyl chains were studied for the liquid–liquid extraction of Am(III) and Eu(III) from apolar solvents. Bis-2-ethylhexyl derivative NOPO-3 (Chart 28) is soluble in toluene but not in *n*-dodecane, and it showed weak extraction of Am(III) and Eu(III) ( $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values between  $0.0003$  and  $0.02$  at  $0.01\text{--}2\text{ M HNO}_3$ ). The related tetraalkyl derivative NOPO-7 (Chart 28), is soluble in both toluene and *n*-dodecane, exhibiting better results in the latter. The  $D$  values increased with increasing  $\text{HNO}_3$  concentration ( $D_{\text{Am}} \sim 0.07$  at  $0.01\text{ M HNO}_3$ ) reaching a maximum at  $0.8\text{ M HNO}_3$  ( $D_{\text{Am}} \sim 50$ ) and lowering upon further increase in acidity ( $D_{\text{Am}} \sim 8$  at  $3\text{ M HNO}_3$ ). The extraction of Eu(III) followed a similar pattern, but the selectivity for Am(III) increased at higher acidity (S.F.<sub>Am/Eu</sub>  $\approx 10$  at  $3\text{ M HNO}_3$ ).<sup>139</sup> Tetraoctyl ligand NOPO-8 (Chart 28) showed good extraction for tri-, tetra-, penta- and hexavalent An, with results comparable to those of OPhD(iBu)CMPO and NOPO-7. The stripping of the metal ions was possible at lower acidities, but An(IV) and An(VI) required the use of an additional complexant (oxalic acid or sodium carbonate) in the aqueous phase.<sup>141</sup>

Investigation of the effect of structural modification on the extraction properties revealed that the presence of additional pyridine *N*-oxide functionalities (NOPO-5, Chart 28) was detrimental, yielding  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values one to four orders of magnitude lower than those of the parent NOPO-4 ligand. The attachment of a third pyridine ring (NOPO-2, Chart 28) only slightly affected the extraction of metal ions and also prevented the complete oxidation of the pyridine rings during the synthesis of the ligand.<sup>140</sup> Pre-organisation of the meNOPO moieties on a cyclic diamine (NOPO-9, Chart 28) caused a decrease in the  $D$  values for the extraction of Am(III) and Eu(III), compared to the parent meNOPO ligand (NOPO-4). However, the dependence of the extraction on the acidity of the aqueous phase changed. At  $>2\text{ M HNO}_3$ , the  $D$  values for Am(III) and Eu(III) with NOPO-9 were higher than those of NOPO-4, encouraging additional research on more organophilic derivatives.<sup>142</sup>

CMPO-functionalised pyridine *N*-oxides (Chart 29), despite their low solubility in *n*-dodecane, showed good results in 1,2-dichloroethane. Crystal structures revealed that NOPO-10 formed tridentate complexes with a single Ln(III) ion, whereas NOPO-11 formed a one-dimensional polymer with the CMPO unit complexing one metal ion in a bidentate fashion and the *N*-oxide complexing a different metal ion. Ligands NOPO-13

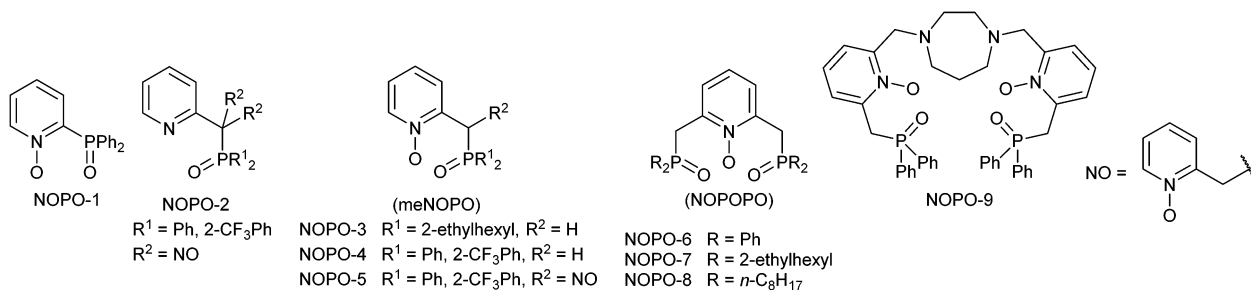
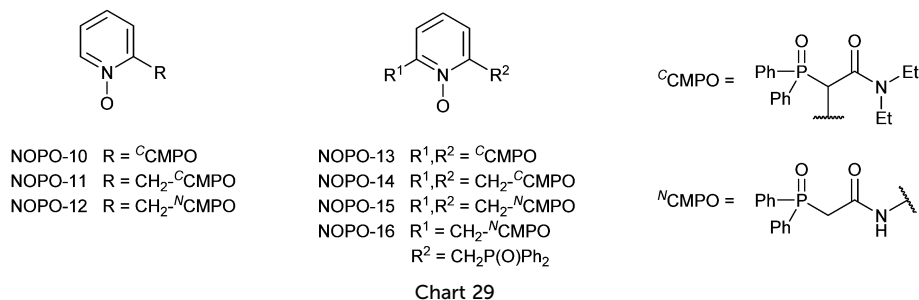


Chart 28



and NOPO-14 showed a mixture of tri-, tetra- and pentadentate binding. In the extraction of Am(III) and Eu(III), these ligands exhibited better performances than OPhD(iBu)CMPO and NOPO-8. The presence of the *N*-oxide group in NOPO-10, resulted in increased extraction and selectivity for Am(III) over most of the HNO<sub>3</sub> concentration range tested (0.01–4 M HNO<sub>3</sub>), reaching a maximum at 1 M HNO<sub>3</sub> ( $D_{\text{Am}} \approx 0.1$ , S.F.<sub>Am/Eu</sub>  $\approx 7$  for NOPO-10;  $D_{\text{Am}} \approx 0.02$ , S.F.<sub>Am/Eu</sub>  $\approx 1$  for OPhD(iBu)CMPO). NOPO-13 and NOPO-14 showed a continuous increase in the  $D$  values, as opposed to OPhD(iBu)CMPO and NOPO-8, which at >1 M HNO<sub>3</sub> displayed a decreasing trend. Moreover, NOPO-13 exhibited higher extraction and separation (S.F.<sub>Am/Eu</sub>  $\approx 10$  over the entire range of acidity) of Am(III) and Eu(III) than the reference ligands already at 1 M HNO<sub>3</sub> ( $D_{\text{Am}} \approx 0.2$ , 100 and 1000 for NOPO-13 at 0.01, 1 and 4 M HNO<sub>3</sub>, respectively).<sup>143</sup>

Attaching CMPO units *via* the nitrogen atom of the amide, on the other hand, resulted in lower extraction of metal ions ( $D_{\text{Am}}$  and  $D_{\text{Eu}}$  for NOPO-12 were between 10<sup>−5</sup> and 10<sup>−4</sup>), or low solubility (NOPO-14). NOPO-15 gave results similar to NOPO-4 (Chart 28).<sup>144</sup>

**Dibenzothiophene.** Bisphosphorylated dibenzofuran (DBF) derivatives (Chart 30) have been proposed as an alternative platform to pyridine *N*-oxide, due to the similar relative position and distance of the donor atoms. Crystallographic data showed that the DBF oxygen is not a sufficiently strong donor to offset the structural strain and to form a tridentate ligand. However, DBT-1 showed  $D$  values comparable to those of OPhD(iBu)CMPO, whereas the extraction with DBT-3 was one order of magnitude lower. Nevertheless, DBF ligands preferentially extracted Eu(III) over Am(III), as opposed to CMPOs and related ligands.<sup>145</sup>

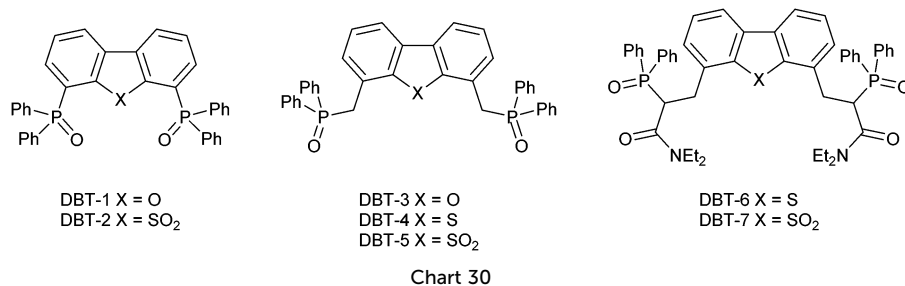
Substitution of the DBF oxygen atom with sulfur, followed by oxidation to dibenzothiofene sulfone (DBT, Chart 30), drastically changed the extraction behaviour of the ligands. DBT-4 displayed poor stability in acidic solution, and its oxidised form DBT-5

showed poor extraction of Am(III) and Eu(III), with  $D$  values similar to those of DBT-3 (Chart 30). On the other hand, DBT-2 exhibited stronger extraction than OPhD(iBu)CMPO at <1 M HNO<sub>3</sub>. Moreover, the  $D_{\text{Am}}$  values were higher at lower acidity, decreasing as the HNO<sub>3</sub> concentration increased ( $D_{\text{Am}} \approx 0.3$  and 0.001 at 0.01 and 5 M HNO<sub>3</sub>, respectively).<sup>146</sup>

Functionalisation of the dibenzothiophene platform with CMPO units (DBT-6 and DBT-7, Chart 30) did not cause an improvement in the extraction of metal ions, but changed the extraction profile back to resemble that of other CMPOs and NOPO-14 (low  $D$  values at low acidity, maximum values close to 1 M HNO<sub>3</sub>, decreasing values at higher acidity).<sup>147</sup> DBT-6 and DBT-7 showed  $D$  values comparable to those of DBT-2 (Chart 29). Interestingly, DBT-6 was stable towards air oxidation, but underwent partial oxidation once coordinated with Ln(III) ions.<sup>148</sup>

## Conclusions

The effect that the substituents attached to the phosphorus atom of neutral and acidic organophosphorus ligands and of CMPOs have on the extraction properties can be as strong as that of a pre-organising platform. The presence of a P–H bond in phosphine oxides caused two distinct extraction mechanisms (solvation and ion-exchange mechanism) to take place, dependent on the pH. The length of the spacer between the bonding sites in bidentate ligands determined the metal ions to be preferentially extracted, in the same way as the functionalisation of the narrow- or wide-rim of calix[4]arenes. Using binary mixtures of acidic ligands, it was possible to increase the  $D$  values, maintaining a low stripping acidity. Acidic ligands have also been used as anionic components of TSILs and they showed promising results when combined with ammonium cations to form non-fluorinated ILs. Modification of the CMPO skeleton generally had adverse effects on the extraction properties of metal ions, whereas pre-organization of the CMPO moieties was



successful to give improved  $D$  and S.F. values. Hybrid organo-phosphorus/heterocycle ligands, on the other hand, showed better extraction than CMPOs.

## Diamides

### Malonamides

One of the reasons for the introduction of the DIAMEX process (based on malonamides) was that phosphorus-based systems produced large volumes of secondary waste upon incineration of the used solvent.<sup>25</sup> Pentalkyl malonamides, on the other hand, give less waste upon incineration and are relatively simple to prepare. The simplest route involves the amidation of a malonic ester or malonyl chloride, followed by alkylation of the central methylene (Scheme 3).<sup>149</sup> The  $D$  values obtained in the extraction of An(III) and Ln(III) are generally lower than those of other ligands like CMP(O), DGAs and trialkyl phosphine oxide (TRPO), but these diamides do not need the addition of phase modifiers to avoid third phase formation in most of the solvents, and the stripping of metal ions from malonamide solutions is easier than with other ligands.<sup>150</sup>

A comparison of a series of related pentalkyl malonamides showed that the introduction of an oxygen atom into the central alkyl chain decreased the tendency for third phase formation at high  $\text{HNO}_3$  concentration and slightly increased the extraction of An, but this was countered by steric hindrance (1 M ligand in  $n$ -dodecane, 3 M  $\text{HNO}_3$ ; DMBTDMA:  $D_{\text{Am}} = 9$ ; DMDOHEMA:  $D_{\text{Am}} = 9$ ; DMDCDEMA:  $D_{\text{Am}} = 9$ ). However, in the extraction of the An Pu(IV), Pu(VI), Np(IV), Np(V), Np(VI) and U(VI), the  $D$  values were comparable. On the other hand, the steric hindrance provided by the cyclohexyl groups only allowed the formation of 1:2 M:L complexes, whereas for the other ligands the stoichiometry was either 1:2 or 1:3, depending on the metal and the oxidation state. Though this property decreased the performance in the extraction studies, it proved advantageous in a supported liquid membrane (SLM) system, since it

reduced the aggregation of malonamides in the pores of the membrane.<sup>149,151</sup>

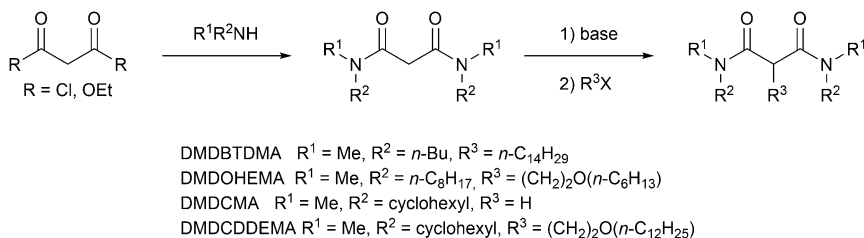
The removal of the central alkyl chain from DMDCDEMA simplified the synthesis, since the product could be purified by crystallisation, but proved to be detrimental to the extraction properties. DMDCMA (Scheme 3) was not soluble in  $n$ -dodecane, showed poor extraction in paraffinic alcohols and had third phase formation at low acidity, even in PTMS.<sup>152</sup>

The functionalisation of malonamides with additional amide groups (Chart 31) decreased the solubility in apolar solvents, like kerosene, and increased the tendency for third phase formation. More polar solvents (nitrobenzene and 1,2-dichloroethane) were necessary to achieve good solubility and prevent third phase formation. However, only the ligand bearing two malonamide units (TMA-1) could extract Ln(III) from  $\text{HNO}_3$  solutions ( $D_{\text{Eu}} = 15$ , 0.5 M  $\text{HNO}_3$ ).<sup>153</sup>

The use of RTILs as solvents for the extraction with malonamides changed their extraction behaviour in a way similar to that of DGAs (*vide infra*). The  $D$  values were significantly enhanced compared to those observed in less polar solvents, such as  $n$ -dodecane, and a lower ligand concentration was required. However, DMBTDMA showed higher  $D$  values than DMDOHEMA in RTIL medium. The  $D$  values decreased as the  $\text{HNO}_3$  concentration increased for Am(III), U(VI) and Np(IV), but the effect on Pu depended on the oxidation state of the metal ion. However, in the case of malonamides, only  $[\text{C}_4\text{mim}][\text{NTf}_2]$  showed good  $D$  values, while those in  $[\text{C}_6\text{mim}][\text{NTf}_2]$  and  $[\text{C}_8\text{mim}][\text{NTf}_2]$  were very low.<sup>154</sup>

Better results were obtained when tetra(2-ethylhexyl)malonamide was used to prepare the TSIL  $[\text{P}_{66614}][\text{MA}]$  (Chart 31). A  $[\text{P}_{66614}][\text{MA}]$  concentration of 0.05 M in  $[\text{P}_{66614}][\text{NO}_3]$  was sufficient to achieve good separation of Ln from RE ( $D_{\text{Ln}} 30\text{--}1000$ ,  $D_{\text{RE}} < 3$ ). The TSIL showed preference for heavier Ln, and stripping and regeneration of the extractant could be achieved just by washing with a 0.5 M NaOH solution.<sup>155</sup>

Substituting the central methylene bridge of a malonamide with a nitrogen atom completely changed the selectivity of the molecule (Biuret(C8), Chart 31). In this case, several transition



Scheme 3

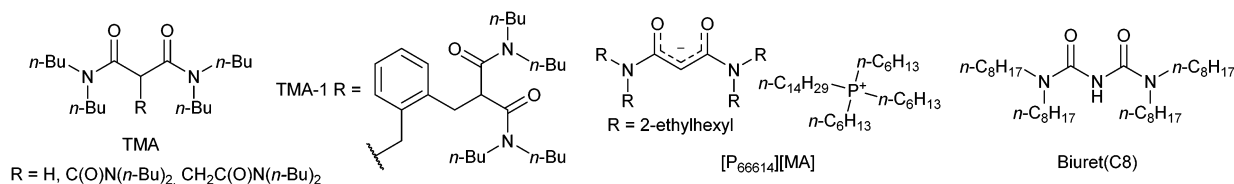


Chart 31



metals (Au, Pd, Pt, Hg, Re, Zr) could be extracted at low  $\text{HNO}_3$  concentration. Pu and U were extracted with  $D$  values of 100 or higher, while Am(III) was not extracted at all.<sup>156</sup>

### Diglycolamides

Diglycolamides<sup>13</sup> constitute an important class of ligands for actinide partitioning first introduced in the early 1990s as a substitute for malonamides.<sup>157</sup> They form weaker complexes with acids<sup>158</sup> and are tridentate ligands, rather than the bidentate malonamides, which effectively reduce the amount of ligand required for extraction.<sup>25</sup> DGA ligands are commonly prepared by reaction of diglycolic anhydride or diglycolic acid with two equivalents of amine in the presence of dicyclohexylcarbodiimide (DCC). Alternatively, simpler methods involving diglycolyl chloride and an amine in organic solvents<sup>13</sup> or under Schotten-Baumann conditions have been used.<sup>159</sup> The preparation of asymmetrical DGAs was performed in two steps reacting diglycolic anhydride with two different amines, promoted by DCC. The use of *p*-nitrophenyl-activated DGA gave better results than DCC coupling in the synthesis of multipodal DGAs.<sup>160</sup>

DGA ligands extract Ln better than An and show a preference for trivalent An over tetra- and hexavalent An. In general, their extraction behaviour is highly influenced by the alkyl chains on the amide groups. Complexation constants increase upon going from methyl to *n*-pentyl substituted DGAs (Chart 32). They decrease significantly for DGAs containing alkyl substituents beyond the *n*-pentyl group. This reduction becomes even more prominent in the case of the branched alkyl (2-ethylhexyl) substituted DGA (e.g., for Nd(III)  $\log \beta_{2(\text{TMDGA})} = 6.66$ ,  $\log \beta_{2(\text{TPDGA})} = 9.59$ ,  $\log \beta_{2(\text{TEHDGA})} = 7.04$ ).<sup>161</sup> DGA derivatives with short alkyl chains (Me, Et) are very soluble in water, while derivatives with long alkyl chains (*n*-octyl, *n*-dodecyl, 2-ethylhexyl) are moderately soluble in *n*-dodecane. The presence of aryl substituents decreases the solubility in both aqueous and organic solvents;<sup>162</sup> therefore, a decrease in the extraction of Ln(III) was observed when the linear alkyl chains increased from *n*-butyl ( $D_{\text{Eu}} = 3.01$ ) to *n*-dodecyl ( $D_{\text{Eu}} = 2.26$ ). At the same time, substituting an alkyl chain (*n*-octyl) with an aryl substituent gave an increase in  $D$  value ( $D_{\text{Eu}}$  from 1.92 for DMDODGA to 2.13 for DMDPhDGA). In general, steric hindrance caused by bulky

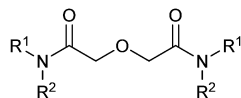
substituents is considered the main reason for the decrease in complexing ability.<sup>163</sup>

In the extraction of hexavalent An, TPDGA, THDGA, TODGA and TDDGA did not show any regular trend, but the extractability of the metal ions could be modified by adjusting their oxidation states.<sup>164</sup> The presence of a methyl and a *n*-dodecyl group on each amide gave D<sup>3</sup>DMDGA (Chart 32) a high extraction ability for uranium nitrate ( $D_{\text{U}} > 25$  at 4.5 M  $\text{HNO}_3$ ). The methyl substituents in D<sup>3</sup>DMDGA markedly reduced the steric hindrance around the metal ion, and the extraction capacity significantly increased compared to that of other DGAs. The two *n*-dodecyl chains of D<sup>3</sup>DMDGA improved the organic solubility of extracted species and prevented third phase formation.<sup>165</sup>

The preparation of asymmetrical DGAs showed that even the increase in length of only one side of the ligand causes a decrease in  $D$  values ( $D_{\text{Eu}} = 165$ , 158 and 23 for DHDODGA, D<sup>2</sup>DODGA and D<sup>3</sup>DODGA, respectively, at 0.1 M DGA and 1 M  $\text{HNO}_3$ ).<sup>166</sup> On the other hand, different combinations of amines allowed for an increase in the loading of metals in aqueous and organic phases (D<sup>3</sup>DEHDGA)<sup>167</sup> and improved separation from other rare earth elements (REEs) (D<sup>2</sup>DHDGA).<sup>168</sup>

A problem often encountered with DGAs in *n*-dodecane is the formation of a third phase upon complexation of the metal ions. Branching alkyl groups increased the third-phase formation tendency, as well as an increase in aqueous phase acidity, irrespective of the nature of the DGA and the diluent used.<sup>169</sup> On the other hand, increasing the chain length of the alkyl groups reduced the third phase formation, but only the presence of *n*-dodecyl chains decreased the tendency of third phase formation to a significant extent so that no phase modifier was required.<sup>170</sup> In particular, D<sup>3</sup>DODGA (Chart 32) was found to be a good compromise, having a high distribution ratio of trivalent Ln(III) and An(III) ( $D_{\text{Eu}} > 100$ ,  $D_{\text{Am}} > 10$  at 2 M  $\text{HNO}_3$ )<sup>170</sup> from  $\text{HNO}_3$  medium and low  $D_{\text{Sr}}$  values, and performed well from the hydrodynamic point of view under severe radioactive environment conditions up to 1000 kGy, while not requiring a phase modifier.<sup>171</sup>

A series of modifications of the backbone of TODGA revealed that rigidification increased the  $D$  values for the extraction of Am(III) and Eu(III), but provided no differentiation between the two metal ions ( $D$  values between 5 and 10 at 2 M  $\text{HNO}_3$ ).<sup>172</sup> A different arrangement of the structural elements of DGAs



$\text{R}^1, \text{R}^2 = (\text{CH}_2)_n\text{H}$ , Ph, *i*Pr, *i*Bu, 2-ethylhexyl,  $n = 1-12$

TMDGA	$\text{R}^1, \text{R}^2 = \text{Me}$	DMDODGA	$\text{R}^1 = \text{Me}, \text{R}^2 = n\text{-C}_8\text{H}_{17}$
TPDGA	$\text{R}^1, \text{R}^2 = n\text{-Pr}$	DHDODGA	$\text{R}^1 = n\text{-C}_6\text{H}_{13}, \text{R}^2 = n\text{-C}_8\text{H}_{17}$
TiPrDGA	$\text{R}^1, \text{R}^2 = i\text{Pr}$	D <sup>2</sup> DHDGA	$\text{R}^1 = n\text{-C}_{10}\text{H}_{21}, \text{R}^2 = n\text{-C}_6\text{H}_{13}$
THDGA	$\text{R}^1, \text{R}^2 = n\text{-C}_6\text{H}_{13}$	D <sup>2</sup> DODGA	$\text{R}^1 = n\text{-C}_{10}\text{H}_{21}, \text{R}^2 = n\text{-C}_8\text{H}_{17}$
TODGA	$\text{R}^1, \text{R}^2 = n\text{-C}_8\text{H}_{17}$	D <sup>3</sup> DMDGA	$\text{R}^1 = n\text{-C}_{12}\text{H}_{25}, \text{R}^2 = \text{Me}$
TEHDGA	$\text{R}^1, \text{R}^2 = 2\text{-ethylhexyl}$	D <sup>3</sup> DODGA	$\text{R}^1 = n\text{-C}_{12}\text{H}_{25}, \text{R}^2 = n\text{-C}_8\text{H}_{17}$
TDDGA	$\text{R}^1, \text{R}^2 = n\text{-C}_{10}\text{H}_{21}$	D <sup>3</sup> DEHDGA	$\text{R}^1 = n\text{-C}_{12}\text{H}_{25}, \text{R}^2 = 2\text{-ethylhexyl}$
DMDPhDGA	$\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$		

Chart 32

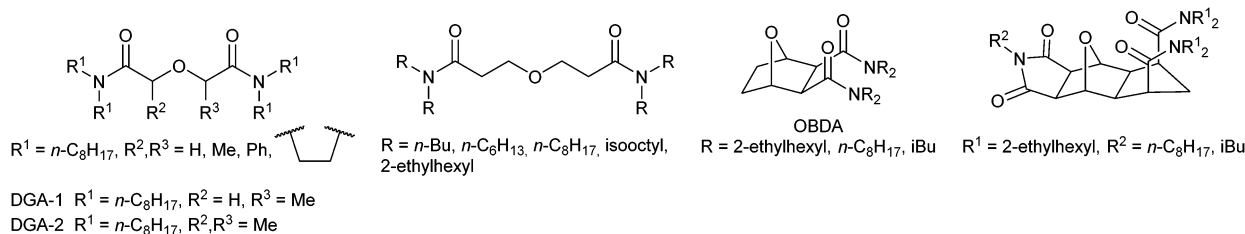


Chart 33

(two tertiary amides and an ether group) on a conformationally constrained structure led to the synthesis of 7-oxabicyclo[2.2.1]-heptane-2,3-dicarboxamides (OBDA, Chart 33). These ligands showed a strong preference for Am(III) over Pu(IV), followed by Eu(III), with  $D_{\text{Pu}}$  values up to 10 times higher than those for TEHDGA. Beyond 3 M  $\text{HNO}_3$ , the ligand underwent hydrolysis and the  $D$  values dropped rapidly.<sup>173</sup> A modification of the backbone structure that reduced the electron density on the etheric oxygen atom, managed to prevent the hydrolysis and provided a  $D_{\text{Pu}}$  up to 60 at 6 M  $\text{HNO}_3$ . However, the synthesis of this ligand was quite laborious.<sup>174</sup>

The inclusion of an additional carbon atom between the etheric oxygen and the carbonyls drastically reduced the extraction of Am(III) and Eu(III) ions,<sup>172</sup> but allowed for a good separation in  $n$ -octane between U(VI) and Th(IV) ions ( $D_{\text{U}} = 3$ ,  $D_{\text{Th}} = 0.12$  at 2 M  $\text{HNO}_3$ ), which are usually poorly extracted by DGAs. In this case, the ligand probably acted as a planar tridentate ligand, fitting better than other DGAs around the metal ion.<sup>175</sup>

The addition of one or two methyl groups to the central methylene carbon atoms of TODGA induced a reduction of the extraction efficiency for An(III) and Ln(III) and overall reduced  $D$  values, including those for Sr(II) ( $D_{\text{Eu}} = 20$  and 5,  $D_{\text{Am}} = 0.1$  and 0.05 at 2 M  $\text{HNO}_3$  for DGA-1 and DGA-2, respectively, Chart 33). On the other hand, this might be beneficial as the stripping behaviour could be improved, even at moderate  $\text{HNO}_3$  concentrations.<sup>176</sup> DGA-2 proved to be more resistant to radiolytic degradation than DGA-1 and TODGA.<sup>177</sup>

The extraction behaviour of DGA ligands also depends on the nature of solvent used. A comparison of the performance of some DGAs dissolved in several solvents showed that non-chlorinated organic solvents (nitrobenzene, 1-octanol,  $n$ -dodecane) give rise to higher  $D$  values than chlorinated ones and toluene, following the general order: nitrobenzene > 1-octanol >  $n$ -dodecane  $\approx$  1,2-dichloroethane > chloroform  $\approx$  toluene.<sup>162</sup>  $n$ -Dodecane is among the preferred solvents for solvent extraction studies, because more polar solvents are either more viscous, more toxic, more volatile and/or have significant aqueous solubility. Recently, the interest in room temperature ionic liquids (RTILs) has been growing because of their properties (*i.e.* they are virtually non-volatile and non-flammable solvents) and because the extraction behaviour of DGAs changed when RTILs were used as solvents or additives.<sup>19</sup> For example, in the case of TEHDGA, a 3–10 times increase in the  $D_{\text{Am}}$  value was observed when the ionic liquid  $[\text{N}_{1888}][\text{DEHP}]$  (Charts 6 and 9) was added to  $n$ -dodecane.<sup>178</sup>

The extraction of An with TODGA dissolved in RTILs of general formula  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 4, 6, 8$ ) followed a cation exchange mechanism: extraction was higher at low  $\text{HNO}_3$  concentration and decreased at higher acidity. An increase in the length of the carbon chain attached to the RTIL increased the hydrophobicity of the imidazolium cation, hampering the cation exchange and further decreasing the  $D$  values. It should be noted that for quantitative extraction of Am(III) from 1 M  $\text{HNO}_3$ , 0.1 M TODGA in  $n$ -dodecane was required, while 0.01 M TODGA was enough in  $[\text{C}_8\text{mim}][\text{NTf}_2]$ .<sup>179</sup> Even though  $[\text{C}_4\text{mim}][\text{NTf}_2]$  showed higher extraction of actinide and lanthanide ions than  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , the aqueous solubility of the former led to the degradation of the RTIL system by slow leaching of the cation, thus favouring the use of the latter. In  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , the general trend in the extraction behaviour with DGAs was similar to that observed in  $n$ -dodecane, where longer chains on the DGA induced lower  $D$  values, but the kinetics of the process was considerably slowed down.<sup>180</sup> The extraction kinetics was also affected by the metal ion involved; for example, Am(III) required only 10 min to reach equilibrium extraction, while Pu(IV) and U(VI) needed 30 min (1 M TODGA in  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , 1 M  $\text{HNO}_3$ ).<sup>179</sup>  $[\text{C}_4\text{mim}][\text{NTf}_2]$  has also been used to support DGAs (Chart 32; with  $R^1 = R^2 = (\text{CH}_2)_n\text{H}$ ,  $n = 1\text{--}12$ ) on diatomaceous silica for chromatography extraction by impregnation, obtaining  $D_{\text{Am}}$  values up to 3000, but low S.F. values ( $\text{S.F.}_{\text{Am/Cm}} = 1.0\text{--}2.5$  at 0.1–6 M  $\text{HNO}_3$ ).<sup>181</sup>

Changing the ions constituting a RTIL also affected the formed complex and the extraction mechanism. Th(IV) formed 1:2 complexes with TBDGA in  $[\text{C}_4\text{mim}][\text{PF}_6]$  and  $[\text{C}_6\text{mim}][\text{PF}_6]$ , but the stoichiometry changed to 1:1 in  $[\text{C}_8\text{mim}][\text{PF}_6]$ . At the same time, TBDGA in the former two RTILs extracted Th(IV) *via* a cation exchange mechanism, while in the less hydrophilic  $[\text{C}_8\text{mim}][\text{PF}_6]$ , the extraction proceeded by solvation of neutral complexes.<sup>182</sup> Similarly, the extraction of metal ions with TEHDGA in methyltriocylammonium nitrate ( $[\text{N}_{1888}][\text{NO}_3]$ ) followed the solvation mechanism, due to the very high hydrophobicity of the  $[\text{N}_{1888}]^+$  cation.<sup>183</sup>

An alternative approach to reducing the dissolution of the cation of the RTIL in the aqueous phase is the preparation of functionalised ionic liquids (or task-specific ionic liquids, TSILs). In the case of a DGA-containing TSIL (Chart 34), it was found that in this system also the extraction of Eu(III) was higher than that of Am(III) and that An(III) was extracted better than An(IV), while An(VI) ions were extracted to a lower extent. However, the  $D$  values decreased at higher aqueous phase acidity ( $D_{\text{Am}}$  from 400 to 5 between 0.1 M and 6 M  $\text{HNO}_3$ ).<sup>184</sup>

Dilution of the DGA-TSIL in  $[C_4mim][NTf_2]$  increased the mass transfer, the efficiency of the stripping and the radiolytic stability of the system. Using  $[PF_6]^-$  as IL counterion provided better separation factors, but reduced the radiolytic stability, while with  $[NTf_2]^-$ , a better decontamination of  $^{137}Cs$  and  $^{90}Sr$  was achieved.<sup>185</sup> Although these properties made DGA-TSIL a very promising ligand for nuclear remediation, the  $D$  values decreased for all the metals tested when a simulated high level waste (SHLW) was used. In addition, the ligand showed a high extraction ability for many other metal ions present in the SHLW besides An and Ln, thus reducing its effectiveness.<sup>186</sup>

The functionalisation of one DGA unit with two alkylimidazolium groups proved to be detrimental for the extraction of Ln. No extraction was observed at any acidity because this TSIL forms water-soluble complexes with Ln. On the other hand, it exhibited very good stripping properties from a TODGA-containing aqueous phase.<sup>187</sup>

Water-soluble DGAs, aimed at selective stripping of An(III) and Ln(III), were prepared by tethering carboxylate salts or varying lengths of ethylene glycol chains to the DGA backbone. While the structure of DGA-4 (Chart 34) resembles that of EDTA, its solubility was poor and the complexes were not strong enough to strip metal ions from TODGA solutions. Among the other ligands, only DGA-3 ( $n = 0$ ) showed very strong stripping abilities for Eu(III) and Am(III), which increased with increasing pH and ligand concentration ( $D_{Am}$  10–1 at 0.01 M DGA and 0.1–0.001 at 0.1 M DGA and 1–4 M  $HNO_3$ ).<sup>76</sup>

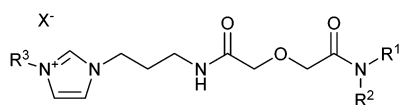
**DGA-analogues and DGA acid.** The search for an acidic ligand with a DGA backbone to be used for lanthanide extraction instead of commercial organophosphorus compounds led to the use of suitable diglycolamic acids.<sup>188</sup> While DGAs usually exhibit increasing  $D$  values with an increase in aqueous phase acidity,

diglycolamic acids show an opposite trend, with higher  $D$  values at high pH. DODGAA (Chart 35) quantitatively extracted all the Ln, but had a higher selectivity for heavier Ln<sup>189</sup> independent of the molecular solvent used.<sup>190</sup>  $C_{12}DGA$  (Chart 35) clearly highlighted that the basicity of the amide oxygen has great influence on the extraction performance and separation ability for RE cations: these values were more than ten times lower than those of DODGAA.<sup>191</sup>

In the case of DODGAA-TSIL  $[N_{1888}][DODGAA]$ , it was shown that the deprotonation of the ligand also has a crucial role in the complexation of metal ions. The  $D_{Nd}$  values for  $[N_{1888}][DODGAA]$  in  $[N_{1888}][NO_3]$  were higher than those for HDGA in  $[N_{1888}][NO_3]$  ( $D_{Nd} = 22$  in the former case,  $D_{Nd} = 6$  in the latter, 4 M  $HNO_3$ ).<sup>192</sup> The same trend was also observed for the 2-hydroxyacids Hhmo and Hhfo (Chart 35). For the extraction of Am(III) and Eu(III), the  $D$  values for Hhfo were higher than those for Hhmo at the same pH, because of the electron-withdrawing effect of the trifluoromethyl group, which increased the fraction of deprotonated species.<sup>193</sup>

The non-fluorinated  $[N_{1888}][DODGAA]$  TSIL is fully miscible with paraffinic solvents and extracts Eu(III) and Am(III) as neutral metal nitrate complexes. The extraction of the metal ions decreased as the length of the paraffinic solvent increased and the two metal ions could be separated just after the addition of DTPA (between  $10^{-5}$  and  $10^{-3}$  M) to the aqueous phase. The main drawback was that after extraction, the ionic liquid was converted into its precursor  $[N_{1888}][NO_3]$  and needed treatment prior to recycling.<sup>194</sup>

The substitution of the etheric oxygen with a nitrogen atom changed the size recognition of the ligand, making DGA-5 (Chart 35) very selective for the mutual separation of Sc(III), Co(II), Ni(II) and Mn(II) at pH 2–6, while DODGAA showed very little selectivity against RE metal ions.<sup>195,196</sup>



DGA-TSIL

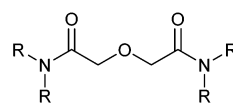
 $R^1 = n\text{-C}_8\text{H}_{17}$  $R^2 = \text{H}, n\text{-C}_8\text{H}_{17}$  $R^3 = \text{Et}, n\text{-Bu}, n\text{-C}_6\text{H}_{13}$  $X = PF_6, NTf_2, N(CF_3CF_2SO_2)_2, SO_3(CF_2)_3CF_3$ DGA-3  $R = (CH_2)_2(OCH_2CH_2)_nOH, n = 0-2$ DGA-4  $R = CH_2C(O)ONa$ 

Chart 34

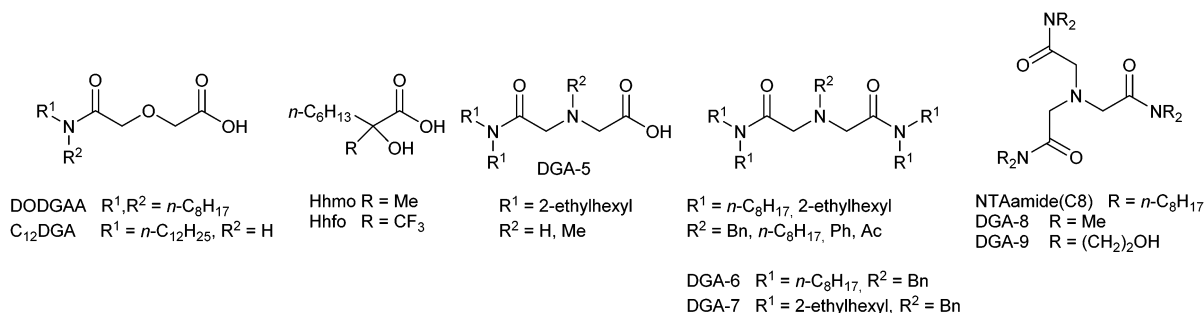


Chart 35

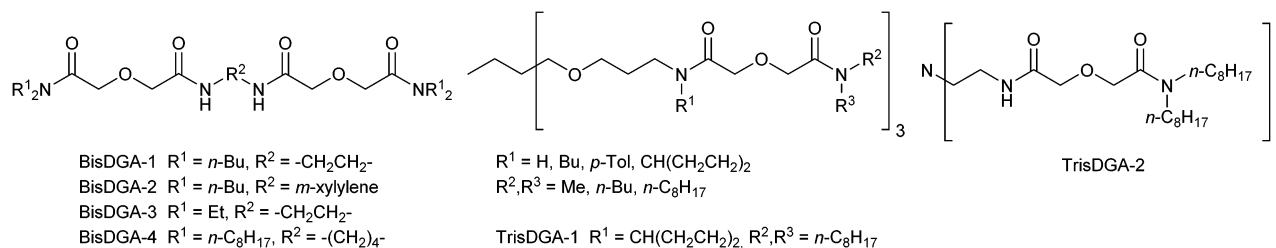


Chart 36

The same substitution performed on DGAs made the ligands unable to extract Am(III) and Eu(III), unless a third amide group was also introduced, as in NTA-amide ligands. DGA-6 and DGA-7 exhibited reverse extraction properties compared to TODGA: they both extracted Am(III) better than Eu(III) and the efficiency was higher at low  $\text{HNO}_3$  concentration.<sup>172</sup> In the case of NTA-amide(C8) (Chart 35), the  $\text{S.F.}_{\text{Am/Ln}}$  values were  $>23$ , using 0.5 M NTA-amide/*n*-dodecane and 0.2 M  $\text{HNO}_3$ . The addition of TEDGA to the aqueous solution as masking agent also allowed for the separation of Am(III) from Cm(III).<sup>197,198</sup> On the other hand, NTA-amide(C8) exhibited a very high selectivity for Th(IV) over the other An, with  $\text{S.F.}_{\text{Th/M}}$  values between  $10^2$  and  $10^4$  in the entire range of  $\text{HNO}_3$  concentrations tested. This was due to the backbone of the ligand being an almost perfect match to Th(IV).<sup>199</sup>

The water-soluble versions of NTA-amide, DGA-8 and DGA-9 (Chart 35), proved to be good stripping agents from TODGA solutions. The first one showed a good selectivity for Am(III) ( $\text{S.F.}_{\text{Am/Eu}} = 11.1$ ) and the second was more efficient in the extraction of both Eu(III) and Am(III), but less selective.<sup>76</sup> The difference in selectivity between TODGA and DGA-8 was supported by DFT calculations.<sup>200</sup>

**DGAs on platforms.** To mimic the formation of DGA reverse micelles in solution and the organisation of the ligands around the metal centres, DGA moieties have been pre-organised on chemical platforms, bearing different numbers of DGA units, with the expectation to form assemblies having a better affinity towards f-elements than the single ligands.

A simple way to prepare pre-organised DGAs is to link them by a bridge (Chart 36). Comparison of a more flexible bridge, BisDGA-1, and a more rigid one, BisDGA-2, showed that both have a strong preference for Eu(III) rather than Am(III) ( $D_{\text{Eu}} = 83.9$  and  $280.0$ ,  $D_{\text{Am}} = 12.1$  and  $35.2$  for BisDGA-1 and BisDGA-2, respectively, in *n*-octanol at 3 M  $\text{HNO}_3$ ). Compared to TODGA, both ligands had six times higher  $\text{S.F.}_{\text{Eu/Am}}$  values. However, when the extractions were performed in toluene, the selectivity of BisDGA-1 for Eu over Am increased ( $\text{S.F.}_{\text{Eu/Am}} = 7$  and  $76$  in *n*-octanol and toluene, respectively).<sup>201</sup> The flexible bridge structure was also used to prepare the water-soluble ligand BisDGA-3, which was used as masking agent in the extraction of Am(III) and Eu(III) from acidic solutions using NTA-amide(C8). It allowed for  $\text{S.F.}$  values that could be better modulated than in the case of TEDGA, providing a better masking efficiency ( $\text{S.F.}_{\text{Am/Eu}} = 26$  with 0.01 M BisDGA-3).<sup>202</sup>

The pre-organisation of the DGA moieties on a tripodal structure provides an arrangement that closely resembles that

of the ligands in the metal complex, and it was shown that alkylation of the amidic nitrogens for tripodal DGAs gave rise to a 1000 times increase in the  $D$  values compared to those of the non-alkylated ligand.<sup>203</sup>

Tripodal diglycolamide TrisDGA-1 (Chart 36) exhibited high  $D$  values for Am(III) (215), Pu(IV) (145) and Np(IV) (77), while the extraction of  $\text{UO}_2^{2+}$  was negligible. SLM studies showed that quantitative transport of Am(III) could be achieved, while TODGA could only afford 15% Am transport.<sup>204</sup> TrisDGA-1 had a clear advantage over TODGA, also in ionic liquid  $[\text{C}_4\text{mim}][\text{NTf}_2]$  at low  $\text{HNO}_3$  concentrations.<sup>160</sup> TrisDGA-2 (Chart 36) showed competitive properties for extraction of Ln(III) and An using ionic liquids from 3 M  $\text{HNO}_3$  solutions ( $D_{\text{Am}} = 161$ ,  $D_{\text{Eu}} = 126$ ). The ligand showed a reversal in selectivity in Am(III)–Eu(III) extraction when  $[\text{C}_4\text{mim}][\text{NTf}_2]$  was used instead of apolar solvents, while this was not observed for TrisDGA-1. Moreover, the extraction of Eu(III) using the ionic liquid was acidity independent.<sup>205</sup>

In the case of DGA-functionalized poly(propylene imine) diaminobutane dendrimers (BisDGA-4, DendrDGA-1,2, Chart 37), an increase in the chelating units (and octyl chains) corresponded to an increase in  $D_{\text{Am}}$  values. The increase in extraction efficiency, however, led to a decrease in selectivity ( $D_{\text{Am}} = 104$ ,  $D_{\text{Eu}} = 300$ ,  $\text{S.F.}_{\text{Eu/Am}} = 3$  for DendrDGA-2;  $\text{S.F.}_{\text{Eu/Am}} = 9$  for TODGA). Even though DendrDGA-1 and DendrDGA-2 may be able to form complexes with more than one metal ion simultaneously, only complexes with 1:1 M:L stoichiometry were found in apolar solvents.<sup>206</sup> SLM studies showed that quantitative mass transfer of Am(III), Eu(III) and Pu(IV) from 3 M  $\text{HNO}_3$  could be achieved in 5 h.<sup>207</sup>

Tripodal DGAs pre-organized on a 1,3,5-substituted benzene platform (Chart 38), showed great affinity for Pu(IV). TrisDGA-5 achieved good separation of the metal, exhibiting  $\text{S.F.}_{\text{Pu/Eu}} = 3.5$  and  $\text{S.F.}_{\text{Pu/Am}} = 28$ . Oxidation of the metal ion to  $\text{PuO}_2^{2+}$  completely inhibited the extraction. TrisDGA-3, based on the

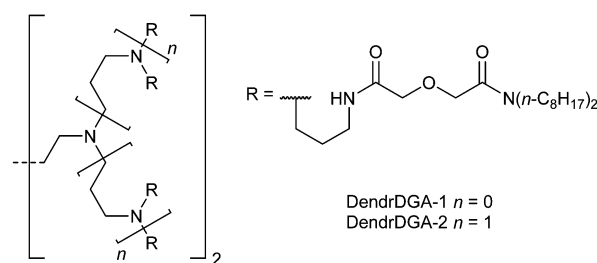


Chart 37



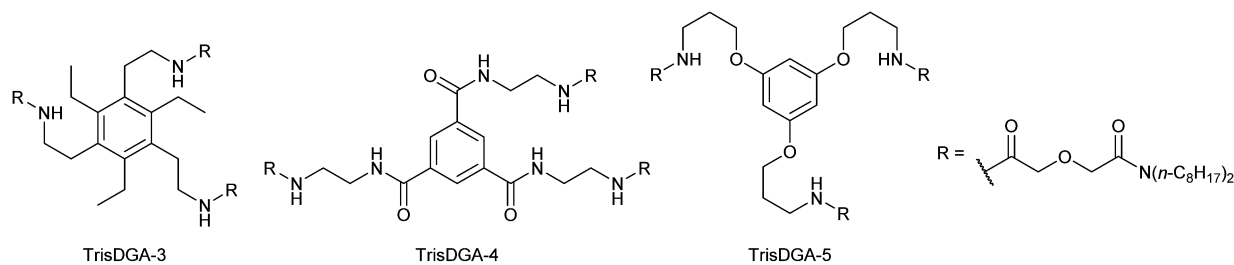


Chart 38

efficiently pre-organising 1,3,5-triethylbenzene platform,<sup>208,209</sup> showed the highest  $D$  and lowest  $S.F._{Eu/Am}$  values at high  $HNO_3$  concentration, followed by TrisDGA-4 and TrisDGA-5, when the extraction was performed in apolar solvents ( $D_{Eu} = 390, 110, 33$  for TrisDGA-3, TrisDGA-4 and TrisDGA-5, respectively at 3 M  $HNO_3$ ).<sup>210</sup> Carrying out the extraction using  $[C_4mim][NTf_2]$ , on the other hand, caused TrisDGA-5 to show the highest  $D$  values, followed by TrisDGA-4 and TrisDGA-3 ( $D_{Eu} = 10, 30, 93$  for TrisDGA-3, TrisDGA-4 and TrisDGA-5, respectively at 1 M  $HNO_3$ ).<sup>211</sup>

The following step is the pre-organisation of the ligand on calix[4]arenes, which gave increased  $D$  values in the case of CMPO and malonamides (*vide supra*).<sup>37</sup> The support of DGAs on calix[4]arenes gave insights on how the arrangement of the DGA units on the platform affects the extraction behaviour. Tetra-DGA-substituted calix[4]arenes, as CalixDGA-1 (Chart 39), formed 1:1 M:L complexes and showed higher  $D$  values than TODGA and 1,3-di-DGA-substituted calix[4]arenes. The latter both formed 1:2 M:L complexes. The presence of alkoxy groups, such as in CalixDGA-3, made the ligand more organophilic, but reduced the extraction ability, compared to those without alkoxy groups (CalixDGA-2), because of steric hindrance during the formation of the complex.<sup>212</sup> The stoichiometry of the complex was influenced by the polarity of the solvent, as demonstrated by CalixDGA-1 that forms 1:2 M:L complexes in nitrobenzene.<sup>213</sup>

Narrow rim DGA-functionalised derivatives showed high extraction efficiency, while wide rim DGA-functionalised derivatives exhibited almost no extraction, probably because of the wider pocket and the lower flexibility of the pendant arm.

Functionalisation of the calix[4]arene platform using spacers of different length pointed out that a certain degree of movement is required to properly complex the metal ion. *N*-Alkylation has a strong influence on the extraction, increasing the  $D$  values but reducing the selectivity.<sup>214</sup>

The use of  $[C_8mim][PF_6]$  as solvent allowed CalixDGA-3 to extract Am(III) selectively from a mixture containing U(VI), Pu(IV) and Pu(VI).<sup>215</sup> The ionic liquid was also used to test the behaviour of the calix[4]arenes with SHLW, showing promising results.<sup>216</sup> Further study of the ionic liquid system revealed that better extractions were obtained at low  $HNO_3$  concentrations, reverting the usual trend observed in apolar solvents,<sup>217</sup> and the Am(III) extraction profile of both-side DGA-functionalised calixarene CalixDGA-5 was independent of the acidity of the aqueous phase.<sup>218</sup>

Resorcinarenes (also called cavitands) are platforms related to calix[4]arenes, but with a more rigid skeleton due to the additional bridges. In this context, ResorDGA-1<sup>219</sup> and ResorDGA-2<sup>220</sup> (Chart 40) were prepared and they both showed a higher affinity for heavy Ln (Yb(III)) over lighter Ln (La(III) and Eu(III)). However, in both cases the extractions were poor ( $D$  values < 10), and the selectivities were similar ( $S.F._{Yb/La}$  and  $S.F._{Yb/Eu}$  had values around 100 and 10, respectively).

A higher number of DGA moieties on a cyclic polyaromatic platform can be positioned on pillar[5]arenes. The pre-organisation of five neighbouring DGAs gave  $D$  values 10–1000 times higher than those of TiPrDGA (Chart 32), that was used as a reference, and good  $S.F.$  values were obtained at low acidity. As opposed to the general behaviour of DGAs, after reaching a maximum at 1 M  $HNO_3$ , the increase in acidity caused a decrease in  $D$  values, probably due to a

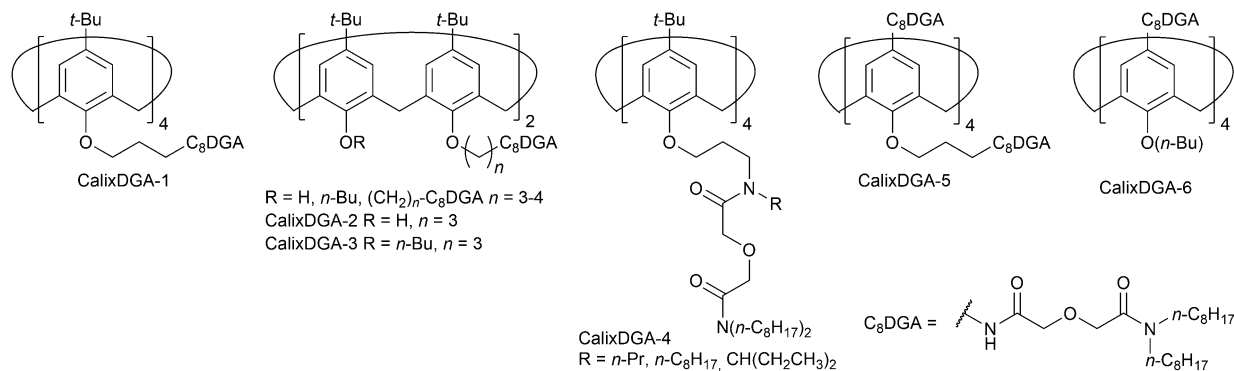


Chart 39

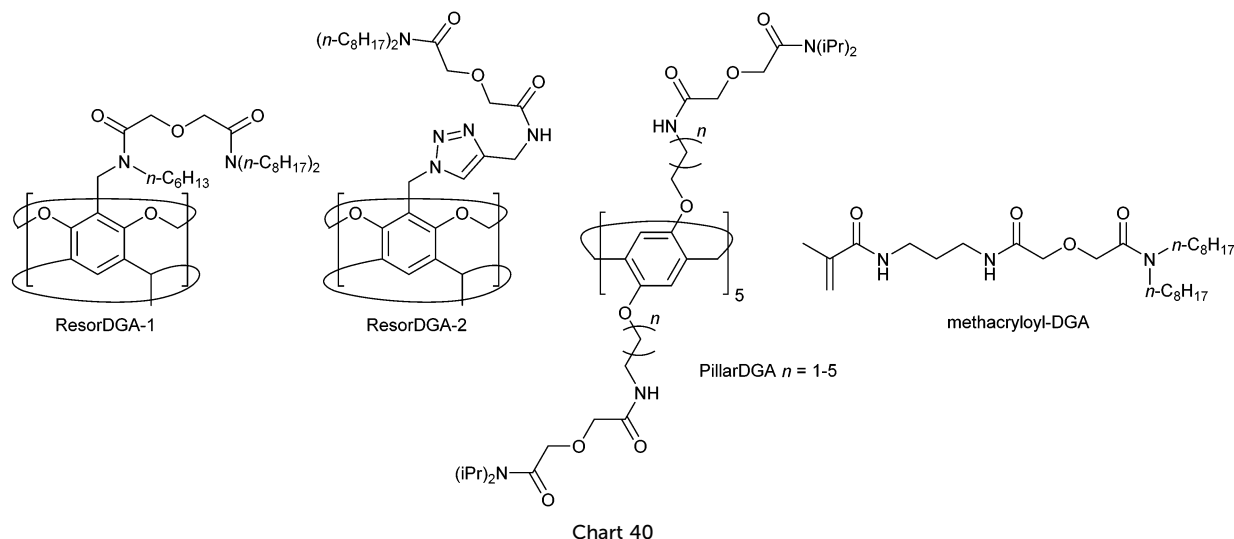


Chart 40

high competition between  $\text{H}^+$  ions and metal ions.<sup>221</sup> When  $[\text{C}_8\text{mim}][\text{NTf}_2]$  was used, a competitive ion-mediated displacement mechanism took place, resulting in 121–485 times higher  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values than those with  $n$ -octanol. At low acidity in ionic liquid, this PillarDGA (Chart 40) exhibited  $D_{\text{Am}}$  values 50% higher than that of the both-side functionalised calix[4]arene CalixDGA-5 (Chart 39) and three orders of magnitude higher than that of T-DGA (Chart 36). This, however, resulted in very low S.F. values. Moreover, these ligands allowed for the separation of  $\text{PuO}_2^{2+}$  from fission products and other An.<sup>222</sup>

Finally, a strategy to pre-organise as many DGA moieties as possible is by the synthesis of a DGA-containing polymer. DGA-bearing methacrylic monomer (Chart 40) and the corresponding polymer showed higher  $D$  values than TODGA for the extraction of Am(III), Eu(III), Pu(IV) and U(VI). Am(III) had a 96% recovery from solutions containing methacryloyl-DGA or from DGA-coated nanoparticles, while recovery from poly(methacryloyl-DGA) was less efficient.<sup>223</sup> Preorganisation of DGA units due to  $\text{HNO}_3$  induced a drastic change in the behaviour and structure of DGA assemblies by promoting the formation of hydrogen bonds among secondary amides.<sup>224</sup>

### Other carbonyls

While diamides such as DGAs and malonamides preferentially extract trivalent An and Ln, long-chain alkyl amides have high

solubility and low third phase formation in  $n$ -dodecane. They also show very good extraction properties for U(VI) and Pu(IV) and are proposed as a substitute for TBP in PUREX processes. A review was published discussing their properties in the Pu/U/Th separation.<sup>158</sup>

Monoamides with similar structures, however, are also produced as degradation products of other ligands; it is therefore very worthwhile to study their extraction properties.<sup>177</sup> For example,  $N,N$ -dioctyl-2-hydroxyacetamide (DOHyA, Chart 41) is a degradation product of TODGA and related DGAs, which shows very high  $D$  values for An and Ln ( $D_{\text{Pu(IV)}} \approx 1000 > D_{\text{Am}} > D_{\text{Eu}} \approx 200$ ,  $D_{\text{U(VI)}} \approx 20$  at  $> 5 \text{ M HNO}_3$ ), but poor extraction of Sr(II), Ru(III) and other fission products.<sup>225</sup> In addition, a synergistic effect in the extraction of Am(III) and Eu(III) was observed for the binary mixture composed of DOHyA and HDEHP (Chart 6) in  $n$ -dodecane, allowing for  $\text{S.F.}_{\text{Am/Eu}} = 10$ .<sup>226</sup> The selectivity for Pu(IV) over U(VI) and Am(III) reached values between 40 and 3400 (depending on the acidity of the aqueous phase), when a TSIL solution of  $[\text{DOAIm}][\text{NTf}_2]$  in  $[\text{C}_4\text{mim}][\text{NTf}_2]$  was used. This increase, however, was observed only upon functionalisation of the TSIL and not by just dissolving a closely related amide ( $N,N$ -dioctylbutyramide) in the RTIL.<sup>227</sup>

A reversal in Pu/U selectivity was observed in tetraalkyl urea, as DRU-2 (Chart 41), which exhibited a  $\text{S.F.}_{\text{U/Pu}}$  value up to 14 ( $D_{\text{U(VI)}} = 1.4$  and  $D_{\text{Pu(IV)}} = 0.1$  at  $5 \text{ M HNO}_3$ ), and ligand DRU-1, which upon addition to an aqueous solution containing U(VI),

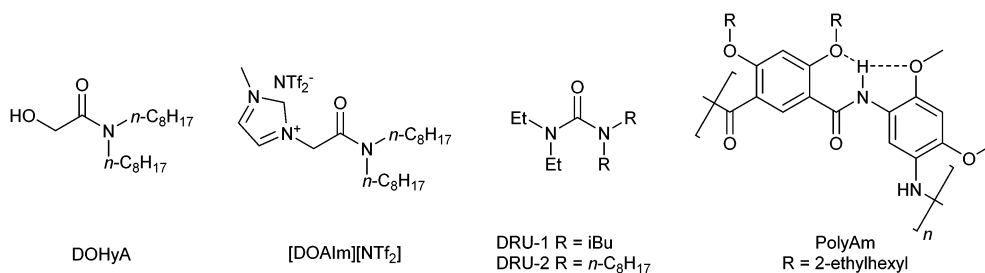


Chart 41

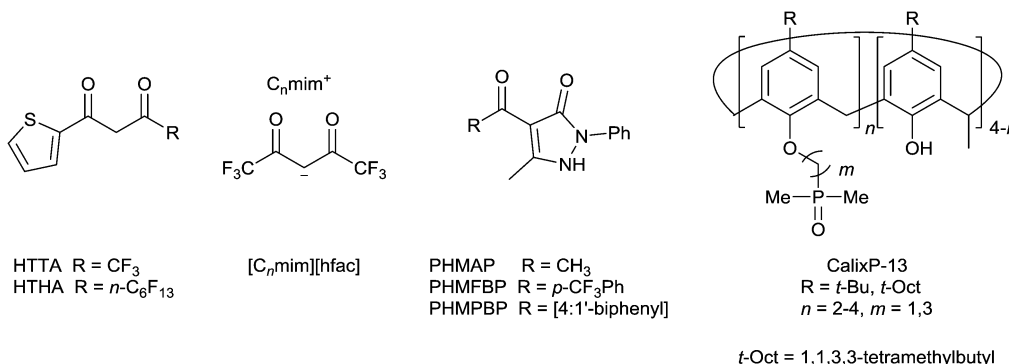


Chart 42

a large excess of Th(IV) and other Ln, caused the selective precipitation of [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2(DRU-1)] crystals.<sup>228</sup> Selectivity for Th(IV) over Ln was exhibited by a polyamide with intramolecular hydrogen bonds (Chart 41). The selectivity increased in the presence of salting-out agents.<sup>229</sup>

Another group of carbonyl ligands that is of interest for nuclear waste partitioning is 1,3-diketones, like thenoyltrifluoroacetone (HTTA, Chart 42), the extraction ability of which is dependent on their deprotonated form: higher *D* values are expected for more acidic ligands and at higher pH.<sup>230</sup> Attempts to improve their performance include the use of fluoruous solvents and the use of ionic liquids. Fluoruous solvents are nontoxic, non-flammable, chemically stable, and immiscible with water. On the other hand, they dissolve only fluorine-tagged compounds.<sup>231</sup> HTHA (Chart 42) was dissolved in *n*-C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub> and exhibited higher *D* and S.F. values than conventional non-fluorinated systems (HTTA in CHCl<sub>3</sub>) and a preference for heavier Ln ions (Lu, Yb, Tm, Er and Ho). However, lighter Ln were hardly extracted.<sup>232</sup> The electron-withdrawing effect of the two trifluoromethyl groups of hexafluoroacetylacetone (Chart 42) was exploited for the preparation of a diketone TSIL, that showed low S.F. values but very high *D* values (*D*<sub>Eu</sub> and *D*<sub>Am</sub> > 100 at 3 M HNO<sub>3</sub>). With the addition of very small amounts of DTPA, good S.F. values could be achieved (from S.F.<sub>Eu/Am</sub> = 0.52 to 25 with 10<sup>-6</sup> M DTPA).<sup>233</sup>

The main advantage provided by HTTA in metal ion extractions was obtained in RTILs. In [C<sub>4</sub>mim][NTf<sub>2</sub>], the extraction proceeded by an anionic exchange mechanism, in which Ln(TTA)<sub>4</sub><sup>-</sup> ions were exchanged for [NTf<sub>2</sub>]<sup>-</sup> ions from the ionic liquid. Despite the degradation of the ionic liquid *via* the loss of the [NTf<sub>2</sub>]<sup>-</sup> anion, the steep acid dependence of the Ln(TTA)<sub>4</sub><sup>-</sup> partitioning made the recovery of the metal ion very simple.<sup>234</sup>

Pyrazolone-based 1,3-diketones derivatives (Chart 42), as PHMBP (Chart 2), have been prepared as alternatives to HTTA because of their lower p*K*<sub>a</sub>. The extraction of An and Ln using PHMBP in [C<sub>8</sub>mim][NTf<sub>2</sub>] showed very high *D* values (*D*<sub>M</sub> > 500), but with no distinction between Am(III) and Eu(III).<sup>235</sup>

More interesting results have been obtained in the presence of binary mixtures, due to synergism between the pyrazolone and the other component of the mixture. When PHMAP (Chart 42) was mixed with TOPO, the *D* values for Am(III) and Eu(III) increased by three orders of magnitude in xylene (from *D*<sub>M</sub> < 0.01 to ~7) and five in [C<sub>8</sub>mim][NTf<sub>2</sub>] (up to *D*<sub>Eu</sub> = 214).<sup>236</sup>

The importance of a phosphine oxide moiety in the synergist molecule was highlighted when the amide groups of a series of DGAs and malonamides were subsequently substituted with this group. Each successive substitution led to an increase in the extraction efficiency of Ln(III).<sup>237</sup>

The effect of synergism in the extraction of An and Ln using pyrazolone derivatives was studied more in depth with phosphorylcalix[4]arenes (CalixP-13, Chart 42). The synergism was stronger in RTILs than in molecular solvents, but its effect did not vary significantly along the lanthanide series.<sup>238</sup> The use of a RTIL increased the *D* values, but it also levelled off the selectivity. On the other hand, the addition of a phosphorylcalix[4]arene increased the *D* values and a more hydrophobic calix[4]arene had a stronger effect.<sup>239</sup> In general the substituent on the benzoyl ring in pyrazolone derivatives had low influence on the extraction efficiency (only 4-trifluoromethyl had a noticeable impact on the *D* values, Chart 42).<sup>240</sup> This topic has also been discussed in a recent review.<sup>241</sup>

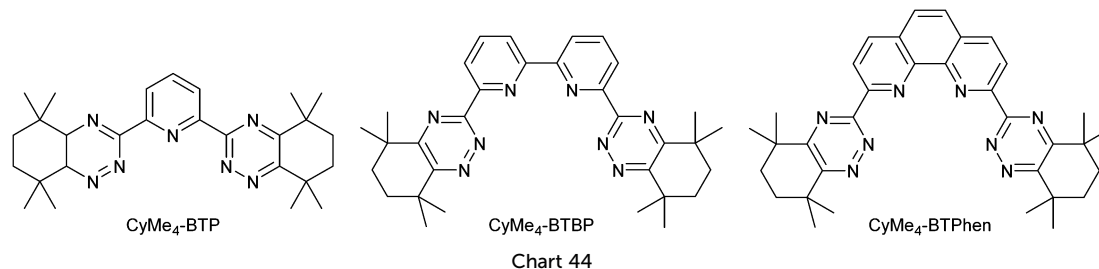
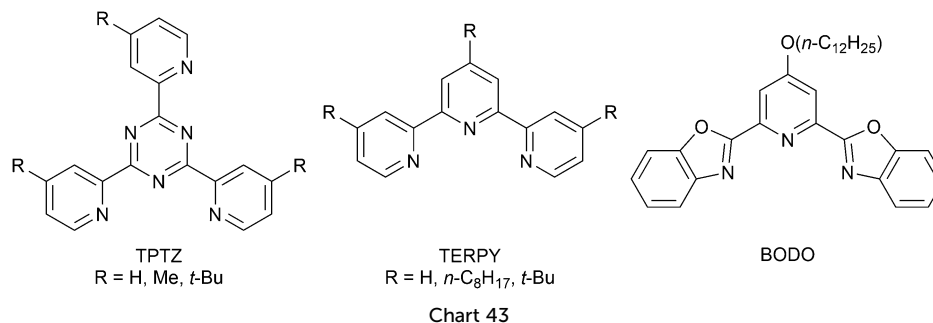
## Conclusions

The length of the alkyl chains of DGAs could be used to balance the strength of the metal complex (short chains) and the solubility in apolar solvents (long chains). Two *n*-dodecyl chains, despite showing lower *D* values than DGAs with shorter groups, were necessary to prevent the formation of a third phase. Moreover, the remaining chains could be changed to tune the extraction properties of the ligand. Diglycolamic acids exhibited preference for heavier Ln and good extraction properties, particularly when used as constituents of IL systems. Pre-organization of the DGA units on flexible tripodal platforms or macrocyclic polyarenes gave rise to increased *D* and S.F. values and showed that functionalisation of the platform has great influence on the extraction properties. RTILs used as diluents and synergic mixtures proved to be effective methods to increase the extraction of metal ions from acidic solutions.

## N-Heterocyclic ligands

### Background and synthetic approach

The initial approach developed for actinide partitioning consisted of a two-step procedure, starting with the co-extraction of An and Ln from PUREX waste solutions, using diamides as extractants



(DIAMEX process). In a second step, called SANEX, the selective extraction of An would be performed in 1–4 M HNO<sub>3</sub> solutions using soft N-donor ligands.<sup>242</sup> These were expected to form complexes with more covalent bond character with An, rather than with Ln (because the external d and f orbitals of An are more diffuse than those of Ln),<sup>243</sup> as supported by computational studies.<sup>244</sup> Recent reviews have described the structural evolution of N-donor ligands from TPTZ (Chart 43) to BTPhen (Chart 44), of which a brief summary is given here.<sup>14,66</sup>

The first class of ligands developed for the SANEX process was derivatives of 2,4,6-trisubstituted-1,3,5-triazine (TPTZ, Chart 43). No extraction of Am(III) or Eu(III) was observed below pH 1 with these ligands, due to the strong competition between H<sup>+</sup> and metal ions.<sup>245</sup> Similar results were obtained with 2,2':6',2''-terpyridines (TERPYs, Chart 43),<sup>245</sup> 2,6-bis(benzoxazol-2-yl)-4-dodecyloxyphenyl (BODO, Chart 43), and its benzimidazole and benzothiazole counterparts.<sup>246</sup>

Subsequent improvements were made by the group of Harwood,<sup>66</sup> using 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP, Chart 44) derivatives that were able to extract Am(III) and Eu(III) from concentrated (1–4 M) HNO<sub>3</sub> with good selectivity without the need of a synergist (S.F.<sub>Am/Eu</sub> > 100); however, stripping of the metal ion was not possible.<sup>247,248</sup> In particular, CyMe<sub>4</sub>-BTP (Chart 44) had good solubility, resistance to radiolysis and hydrolysis, and exceptional extraction properties (*D*<sub>Am</sub> up to 500, S.F.<sub>Am/Eu</sub> up to 5000).<sup>249</sup> The extension of the aromatic system to the tetradentate ligand CyMe<sub>4</sub>-BTBP (Chart 44) allowed for good stripping properties at the cost of very slow extraction kinetics, without losing selectivity.<sup>250</sup>

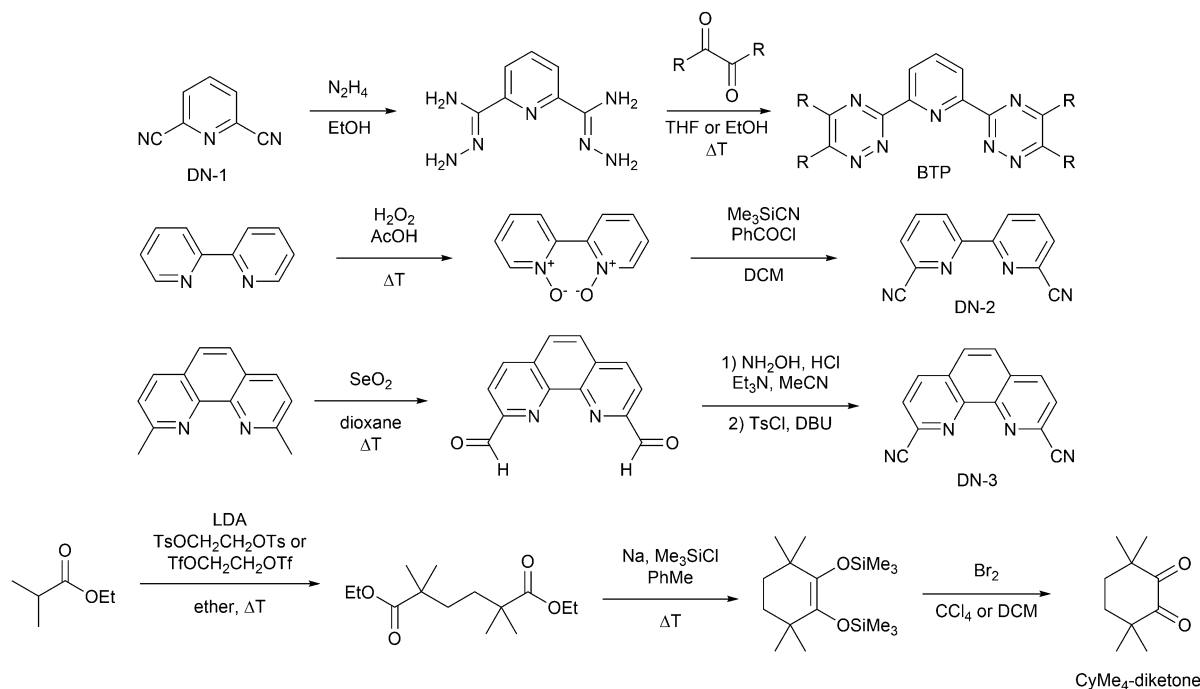
The rates of extraction were significantly faster when the 2,2'-bipyridine system was locked in the *cis*-conformation by the development of 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen) derivatives. Extraction of Am(III) and Eu(III) with

CyMe<sub>4</sub>-BTPhen (Chart 44) was higher than with CyMe<sub>4</sub>-BTBP (*D*<sub>Am</sub> ≤ 1000), with similar selectivity (S.F.<sub>Am/Eu</sub> ≤ 400) and equilibrium could be reached within 15 min of phase mixing (compared to *ca.* 1 h for CyMe<sub>4</sub>-BTBP).<sup>251</sup>

The synthesis of bis-triazinyl ligands is based on the preparation of dinitrile compounds (DN-1–3, Scheme 4) of the corresponding core structure. A specific dinitrile was treated with hydrazine in ethanol, to form the corresponding diamide dihydrazide, and then condensed with a diketone in refluxing THF or ethanol to form the final 1,2,4-triazinyl ring. Bipyridine dinitrile was prepared by oxidation of 2,2'-bipyridine with hydrogen peroxide in acetic acid, followed by a Reissert–Henze cyanation reaction with trimethylsilyl cyanide and benzoyl chloride. Furthermore, 2,9-dimethyl-9,10-phenanthroline was oxidised using selenium dioxide to form the corresponding dialdehyde, which was converted into the dinitrile, by a one-pot transformation into the dioxime, followed by dehydration *in situ* using tosyl chloride and DBU. The synthesis of “CyMe<sub>4</sub>-diketone” (Scheme 4) was carried out by alkylation of the enolate of ethyl isobutyrate with ethylene glycol disulfonate, cyclisation *via* an intramolecular acyloin reaction in the presence of trimethylchlorosilane and final oxidation with bromine.<sup>243</sup>

Even though the improved extraction properties of CyMe<sub>4</sub>-BTPhen over CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-BTP clearly indicate the main structural elements favouring high extraction and selectivity, stability, good stripping, and fast rates of extraction, further studies have been performed to fully understand the relationship between their structure and their properties. This is particularly true if the studies involve new extraction systems (*e.g.* different solvent, ionic liquids, hydrophilic ligands), or if the results have an impact on the economy of the extraction process.<sup>243</sup> These recent developments are described in this review.





### Bis-triazinyl and related ligands

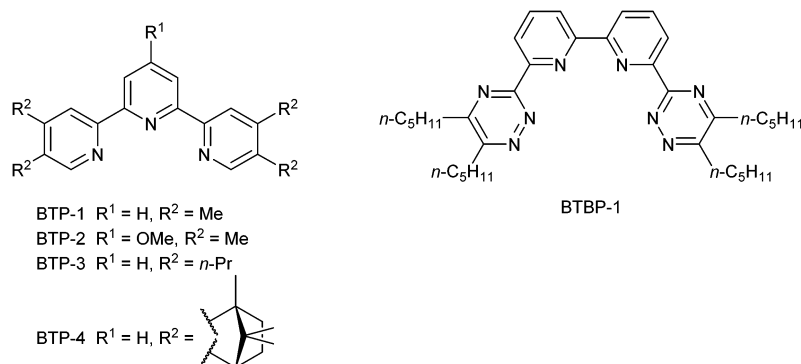
The generally high affinity of BTPs for An was combined with the hydrophilicity of the ligands BTP-1 and BTP-2 (Chart 45), that were tested for the back extraction of An(III) and Ln(III) from TODGA solutions. It was observed that the *O*-alkyl group lowers the selectivity towards Am(III) and that 0.1 M BTP-1 could selectively strip An.<sup>252</sup> BTP-2 showed selectivity for Am(III) also when supported on titania particles or hierarchically porous beads.<sup>253</sup>

Furthermore, 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)-pyridine (BTP-3, Chart 45), which is easier to synthesise than CyMe<sub>4</sub>-BTP, was used to perform extraction studies with the entire series of Ln and several An. The *D* values increased along the lanthanide series and slowly decreased past Ho(III) (from  $D_{La} < 10^{-4}$  to  $D_{Ho} \approx 1$ ). For the An tested (Np, Pu, Am, Cm, Cf), the effect of the decreasing ionic radius was less pronounced (from  $D_{Np} \approx 5$  to  $D_{Cm} \approx 20$ ).<sup>254</sup>

The relatively easy synthesis of BTPs (Scheme 4) is also beneficial when aimed at screening new diketones to be used in

the last step of the synthesis of these ligands. ( $\pm$ )-Camphorquinone, a commercially available diketone, was used as a cheaper alternative to “CyMe<sub>4</sub>-ketone” to prepare BTP-4 (Chart 45), resulting in faster kinetics, good stability ( $> 100$  days in 1 M HNO<sub>3</sub>) and selectivity. In THP/1-octanol (7:3 vol), equilibrium was reached in  $\sim 10$  min and S.F.<sub>Am/Eu</sub> values  $\leq 100$  (0.5 M HNO<sub>3</sub>) were obtained.<sup>255</sup> On changing the solvent system to PTMS, the solubility as well as the resistance to third-phase formation increased (the highest HNO<sub>3</sub> concentration usable increased from 1 M to 2 M). Moreover, since camphorquinone exists in two enantiomers, BTP-4 can be prepared in different diastereomeric forms. When pure *R*- or *S*-camphorquinone was used, a slight increase in the *D* values was observed over those for the racemic camphorquinone.<sup>256</sup>

The use of PTMS with CyMe<sub>4</sub>-BTBP and TBP resulted in a behaviour not previously observed for BTBPs. CyMe<sub>4</sub>-BTBP was dissolved in four mixtures containing different ratios of PTMS and TBP and tested for the extraction of several metal ions



(U, Np, Pu, Am, Cm, Eu). When both CyMe<sub>4</sub>-BTBP and TBP were present, all An were separated from the Ln. However, in the case of the individual ligands, mainly U and Pu were extracted. Since CyMe<sub>4</sub>-BTBP preferentially extracts trivalent An, the extraction of tetra- and hexavalent An was due to an interaction with the diluent.<sup>257</sup>

The solvent used for the extraction with CyMe<sub>4</sub>-BTBP also affected the selectivity towards transition metals. For example, with CyMe<sub>4</sub>-BTBP in TBP and cyclohexanone, several fission products (Pd, Ag, Cd) were co-extracted together with the An. However, CyMe<sub>4</sub>-BTBP in cyclohexanone formed Pd complexes that were soluble both in the organic and the aqueous phase, effectively reducing the selectivity of the extraction and causing loss of ligand; however, higher HNO<sub>3</sub> concentrations limited this effect.<sup>258</sup>

The choice of the diluent used in extractions with BTBP not only had an influence on the preference of metal ions that were extracted and their *D* values, but also the rates of extraction. The extraction of Am(III) with BTBP-1 (Chart 45) showed that higher *D* values are obtained in alcohols with shorter chains, such as hexanol (*D*<sub>Am</sub> ≈ 1) and heptanol as opposed to nonanol and decanol (*D*<sub>Am</sub> ≈ 0.04).<sup>259</sup> In addition, longer chain alcohols also required longer time to reach equilibrium.<sup>260</sup>

The use of RTILs, [C<sub>*n*</sub>mim][NTf<sub>2</sub>] (*n* = 2, 4, 8), changed the extraction mechanism of Eu(III) by CyMe<sub>4</sub>BTPhen (Chart 44) depending on the HNO<sub>3</sub> concentration. The BTPhen/[C<sub>2</sub>mim][NTf<sub>2</sub>] system extracted Eu(III) by a cation exchange mechanism with good *D* values at 0.1 M HNO<sub>3</sub> (*D*<sub>Eu</sub> ≈ 40), which decreased at higher acidity (*D*<sub>Eu</sub> ≈ 0.5 at 3 M HNO<sub>3</sub>). An increase of the length of the alkyl chain on the RTIL also led to a decrease in the *D* values. Both the longer alkyl chain and the higher acidity induced a change in the solvation mechanism.<sup>261</sup>

Another aspect having great impact on the extraction properties of this type of ligands is immobilisation on silica gel. BTBP and BTPhen were immobilised on SiO<sub>2</sub> (Chart 46) and tested for the separation of An, Ln and fission products in a column-based process. BTPhen-1, as it occurs in solution, extracted both minor An and Ln at low HNO<sub>3</sub> concentrations, but displayed a high selectivity (S.F.<sub>Am/Eu</sub> = 140) at 4 M HNO<sub>3</sub>. BTBP-2, on the other hand, could extract corrosion and fission products that are found in the PUREX raffinate.<sup>262</sup>

Even though different diluents, or combinations with co-solvents, were able to modify the extraction behaviour of these ligands, only modifications of their structures could allow more opportunities for fine-tuning the extraction properties. Introduction of substituents on the phenanthroline backbone affected the complexation mostly by modulation of the electronic properties of the ligand. The presence of bromine at the 5- and 5,6-positions of the 1,10-phenanthroline core of the ligand (BTPhen-3 and BTPhen-4, Chart 46) increased the selectivity for Am(III) over Eu(III) with respect to BTPhen-2 (Chart 46). The *D*<sub>Am</sub> values were ~100 for all three ligands, but the subsequent introduction of bromine decreased the extraction of Eu(III) at 4 M HNO<sub>3</sub> (from *D*<sub>Eu</sub> ≈ 1 for BTPhen-2 to *D*<sub>Eu</sub> ≈ 0.1 for BTPhen-4).<sup>263</sup> Similarly, BTPhen-5 (Chart 46) exhibited selectivity for Am(III) over Cm(III) (S.F.<sub>Am/Cm</sub> = 7 at 0.1 M HNO<sub>3</sub>, S.F.<sub>Am/Cm</sub> = 5 and S.F.<sub>Am/Eu</sub> = 100 at 1 M HNO<sub>3</sub>).<sup>264</sup> On the other hand, 5-(4-hydroxyphenyl)-CyMe<sub>4</sub>-BTPhen (BTPhen-6, Chart 46) showed increased *D* values for Ln. In the case of brominated BTPhens, the inductive electron-withdrawing effect could account for the lower extraction of Ln(III), whereas in the case of the 5-(4-hydroxyphenyl) substituent, the mesomeric electron-donating effect could explain the increased *D* values of the Ln(III).<sup>265</sup>

Several modifications on the 1,2,4-triazinyl groups of BTPhen showed that the use of isatin as diketone (Chart 47) is not viable because the resulting ligands co-extract Eu(III) together with Am(III), removing an advantageous aspect of this class of ligands. Aliphatic chains (Chart 47) showed a decrease in *D* values with increasing chain length and lower S.F. values were obtained when asymmetrical ketones were used instead of symmetrical ones. Benzyl-BTPhens (Chart 47) exhibited the highest S.F.<sub>Am/Eu</sub> values (up to 284 for 4,4-(MeO)<sub>2</sub>-benzyl-BTPhen, compared to 350 for CyMe<sub>4</sub>-BTPhen), but they all co-extracted 10–15% of Ln. Overall, a valid alternative to “CyMe<sub>4</sub>-ketone” could not be identified.<sup>266</sup>

On the other hand, encouraging results were obtained with the exploration of hydrophilic N-heterocyclic ligands, which were used in conjunction with TODGA as an alternative to the TALSPEAK process.<sup>7</sup> Tetrasulfonated bis-triazinyl ligands (Chart 48) increased the separation of Am(III) and Eu(III), selectively forming Am(III) complexes in the aqueous phase. Across a range of HNO<sub>3</sub> concentrations (0.28–0.77 M HNO<sub>3</sub>), S.F.<sub>Eu/Am</sub> values of

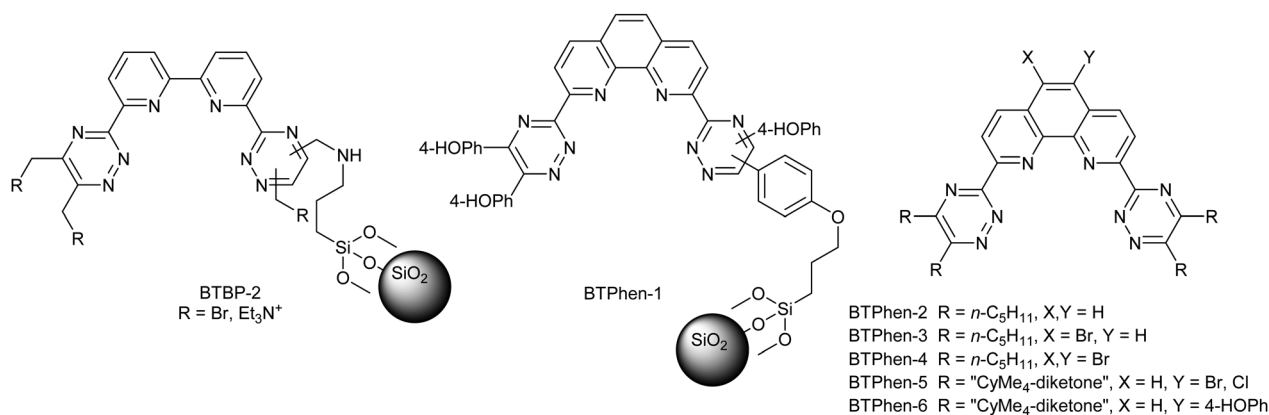


Chart 46

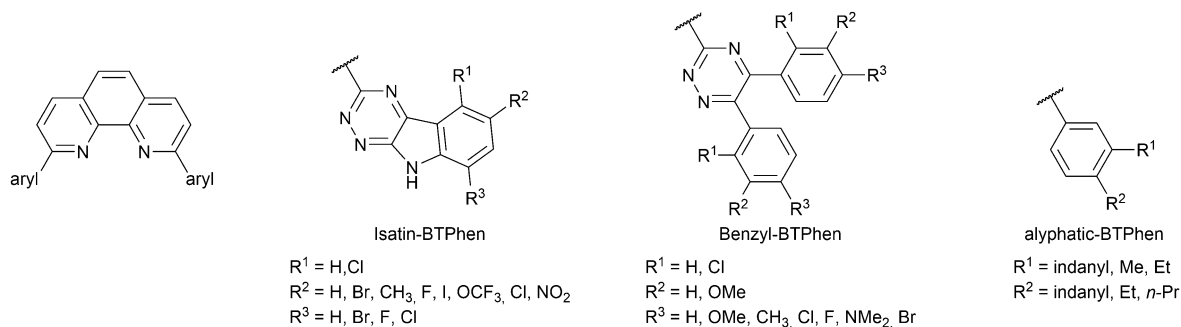


Chart 47

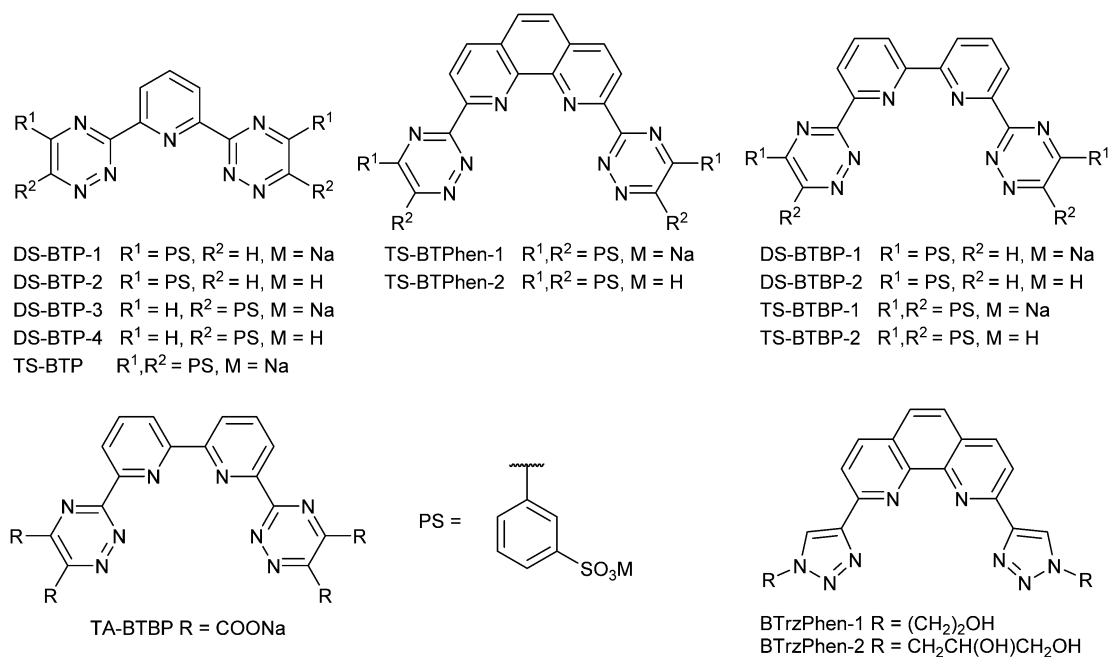


Chart 48

138–934 were obtained, much higher than those obtained with polyaminocarboxylate ligands used in TALSPEAK. Disulfonated bis-triazine ligands (Chart 48) did not contribute to the extraction. The number of sulfonate units was found to be the most relevant parameter, outweighing the type of ligand used (BTP, BTBP, BTPhen), the position of the sulfonate group at the phenyl ring on the molecule, and the sulfonate counterion.<sup>267</sup>

On top of being used as masking agents during the extraction of metal ions from aqueous waste raffinates, hydrophilic ligands can be used in the following step when the metal ions are stripped from the organic phase. TS-BTP (Chart 48) showed a very high selectivity for the stripping of Am(III) over Ln(III) at low  $\text{HNO}_3$  concentration (0.2–0.8 M  $\text{HNO}_3$ ) with the least efficient separation being that between La(III) and Am(III) ( $\text{S.F.}_{\text{La/Am}} \approx 50$ ).<sup>268</sup> TS-BTPhen (Chart 48), on the other hand, exhibited a lower selectivity for Ln(III)/Am(III) separation ( $\text{S.F.}_{\text{La/Am}} = 20$ ), but an increased separation efficiency between Am(III) and Cm(III) ( $D_{\text{Cm}} > 1$ ;  $D_{\text{Am}} < 1$ ;  $\text{S.F.}_{\text{Cm/Am}} = 3.6$ ) within the stripping step, opening up the possibility for a selective Am(III) separation process.<sup>269</sup>

The importance of the presence of sulfonated phenyl units was also supported by stripping experiments performed with TA-BTBP (Chart 48), which bears four carboxylate groups on the triazinyl rings. It showed a lower selectivity for the separation of Am(III) and Eu(III) ( $\text{S.F.}_{\text{Eu/Am}} < 20$ ) than tetrasulfonated bis-triazinyl ligands ( $\text{S.F.}_{\text{Eu/Am}} > 50$ ) in similar conditions. TA-BTBP, conversely, exhibited very good stripping behaviour in alkaline solution (0.2 M NaOH,  $\text{S.F.}_{\text{Eu/Am}} > 27$ ).<sup>270</sup>

The decrease in selectivity with respect to tetrasulfonated bis-triazinyl ligands was attributed to the mesomeric effect of the electron-withdrawing carboxylate groups, which reduced the electron density on the N2 triazine nitrogens (and consequently reduced the covalent character of the M–L bond), as also observed for BTPs.<sup>271</sup> However, similar studies on the electronic effects of substituents on BTPhens led to conclusions contrasting those on BTPs.<sup>263,265</sup> This in turn suggests that inductive and mesomeric effects on BTPhens may have a different influence than on BTPs and BTBPs.

The introduction of hydrophilic moieties *via* triazolyl rings instead of triazinyl (BTrzPhen-1,2, Chart 48) resulted in

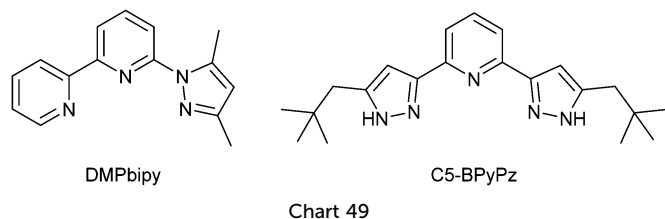


Chart 49

phenanthroline derivatives compliant to the CHON principle with good solubility in  $\text{HNO}_3$  solutions. In the extraction of  $\text{Am(III)}$  and  $\text{Eu(III)}$  from TODGA-loaded organic solutions into acidic aqueous solutions, BTRzPhen-1,2 reached  $\text{S.F.}_{\text{Eu/Am}}$  values up to 50 at 0.3 M  $\text{HNO}_3$ .<sup>272</sup>

Although bis-triazinyl ligands gave rise to exceptional extraction results and solutions to their practical disadvantages (poor chemical and radiolytic stability, slow extraction kinetics, difficult stripping) have been proposed, the difficulties in their synthesis still limit their widespread use. With the intention to better understand the reasons behind the selectivity of BTPs, DMPbipy (Chart 49) was synthesised. Despite its poor extraction and selectivity,<sup>273</sup> it stimulated the development of pyridylpyrazole ligands such as C5-BPyPz (Chart 49). C5-BPyPz alone is not able to extract  $\text{Am(III)}$  and  $\text{Eu(III)}$  from  $\text{HNO}_3$  via a solvation mechanism, but the addition of 2-bromohexanoic acid to the organic phase promoted the extraction by cation exchange, giving  $\text{S.F.}_{\text{Am/Eu}} \approx 100$  from 0.5 M  $\text{HNO}_3$  ( $D_{\text{Am}} \approx 10$ ,  $D_{\text{Eu}} \approx 0.1$ ).<sup>274</sup>

The synthesis of these ligands exploited the cyclisation of 1,3-diketones with hydrazine (Scheme 5). For the preparation of 3-substituted pyridylpyrazoles ( $\text{C}_n\text{PyPzH}$ ), picolinic acid (or dipicolinic acid to prepare bis-pyridylpyrazoles) was transformed into the corresponding ethyl ester. Subsequently, a Claisen condensation with an alkylmethylketone (whose alkyl chain is also the substituent of the pyridylpyrazole) formed the 1,3-diketone system, followed by cyclisation with hydrazine to give the pyrazole ring. For the synthesis of 2-substituted pyridylpyrazoles ( $\text{C}_n\text{PyPz}$ ), acetylpyridine (or diacetylpyridine) was used in an aldol reaction with dimethylformamide dimethyl acetal to form the conjugated enamine-ketone, which acted as a “masked” 1,3-diketone. Cyclisation with hydrazine and alkylation with an alkyl bromide concluded the synthesis.<sup>275</sup>

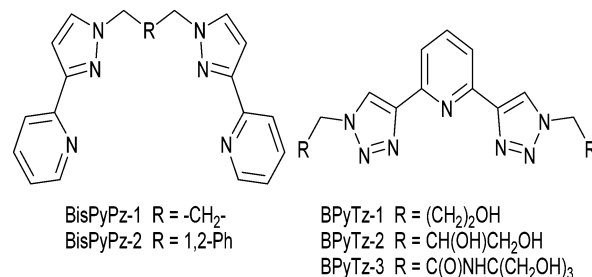
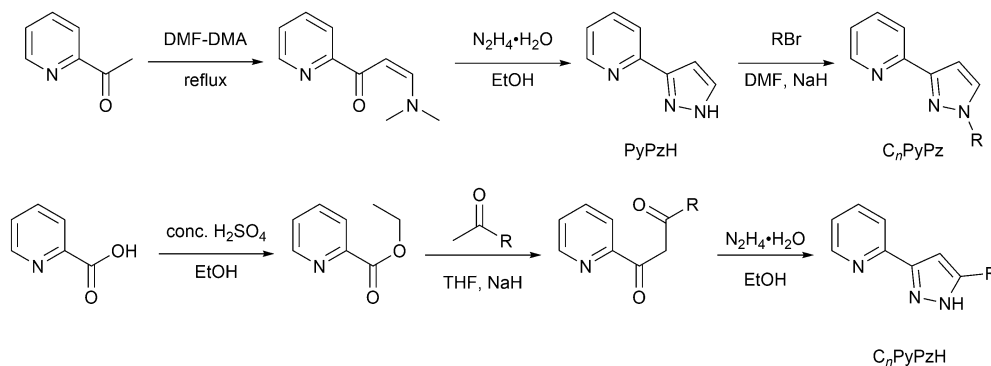


Chart 50

With the intention of pre-organising the pyridylpyrazole units and to mimic the tetradentate structure of BTBPs, BisPyPz-1 and BisPyPz-2 (Chart 50) were prepared and tested for the extraction of  $\text{Am(III)}$  and  $\text{Ln(III)}$  from  $\text{HNO}_3$  solutions. As C5-BPyPz, these ligands required the presence of 2-bromohexanoic acid as synergist and the extraction of metal ions decreased with increasing  $\text{HNO}_3$  concentration. Moreover, these ligands displayed lower selectivity than C5-BPyPz, even at lower  $\text{HNO}_3$  concentration ( $\text{S.F.}_{\text{Am/Ln}} = 15\text{--}60$  at 0.001 M  $\text{HNO}_3$ ).<sup>276</sup> This decrease in performance was attributed to the functionalisation of the N2 on the pyrazole ring. Using simple model ligands  $\text{C}_n\text{PyPz}$  and  $\text{C}_n\text{PyPzH}$  (Scheme 5), it was observed that an alkyl group at the 2-position, instead of the 3-position, reduced the  $D$  values by an order of magnitude. The presence of an alkyl chain at the 3-position, in addition, promoted the selectivity ( $\text{S.F.}_{\text{Am/Eu}} \leq 120$  for  $\text{C}_n\text{PyPzH}$  as opposed to  $\text{S.F.}_{\text{Am/Eu}} \leq 17$  for  $\text{C}_n\text{PyPz}$ ). This could indicate that the 2-position is involved in the formation of the complex and its alkylation blocks the ligating site.<sup>275</sup>

The preparation of pyridyltriazolyl ligands (BPyTz-1–3, Chart 50) could be simply achieved by a copper-catalysed cycloaddition between 2,6-diethynylpyridine and hydrophilic azides. Despite the structural similarity to bis-pyridylpyrazole ligands, these ligands were successfully used as stripping agents from TODGA solutions. Starting from a  $\text{S.F.}_{\text{Eu/Am}} = 7$  (obtained during blank tests of stripping), an increase in selectivity was observed for all three ligands, to 144 for BPyTz-1, 100 for BPyTz-2 and 57 for BPyTz-3. Despite the higher solubility of BPyTz-3, the selectivity was lower, indicating that the amide groups might interfere with the separation process.<sup>277</sup>



Scheme 5



## Amides of heterocyclic carboxylic acids and related compounds

Most bis-triazinyl ligands achieve very high S.F. values, at the expense of the  $D$  values and their applicability being limited to weakly acidic solutions. Diamide-based ligands exhibit high  $D$  values in very acidic solution, but their selectivity is limited. Ligands with both oxygen (amides) and nitrogen (bis-triazinyl) donor atoms have been developed with the aim of combining the advantages of both classes of ligands. An overview about the amides of heterocyclic carboxylic acids was published, discussing them from the perspective of practical use and emphasising advantages and drawbacks.<sup>278</sup>

The oxygen atoms of the amides provide general affinity for An and Ln, allowing for high  $D$  values. The nitrogen atoms of the heterocycles form stronger complexes with An, providing the selectivity. The selectivity can be modulated by changing the number of heterocycles at the cost of shifting the maximum of the extraction ability to higher pH. On the other hand, the alkyl chains on the amides can be modified to regulate the extraction properties of the carbonyl moiety.<sup>279</sup>

With the addition of an amide to BizPy (Chart 51), the carbonyl promoted the coordination with Eu(III) over the protonation of the ligand. The extraction of the metal ion decreased as the  $\text{HNO}_3$  concentration increased (as for N-heterocyclic ligands), but the  $D_{\text{Eu}}$  values for MPhBIZA decreased less than those of BizPy (from 20 to 2, for MPhBIZA, from 0.2 to 0.01 for BizPy).<sup>280</sup>

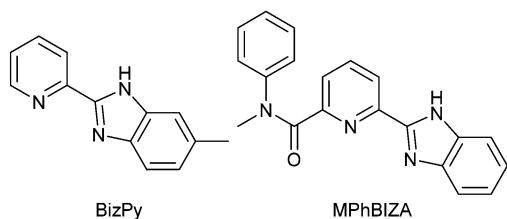


Chart 51

A series of  $N,N'$ -diethyl- $N,N'$ -diphenyl-2,2'-bipyridine-6,6'-dicarboxylic diamides (BPDA, Chart 52) illustrated how even small changes on the phenyl ring can affect the properties of the ligand as a whole. With the ligands dissolved in  $m$ -nitrobenzotrifluoride and the extractions performed from 5 M  $\text{HNO}_3$ , the  $D_{\text{Am}}$  values ranged between 0.1 and 50 and the S.F.<sub>Am/Eu</sub> values between 1 and 19. Better results were obtained with ligands having substituents at the *meta*- and *para*-positions, because of their higher lipophilicity and the electron-donating effect of the substituents. On the other hand, groups at the *ortho*-position decreased the extraction due to steric hindrance.<sup>279</sup>

Similar studies on the effect of alkyl groups on the extraction properties of phenanthroline amides (Chart 52) revealed that an increase in the length of the aliphatic chains led to a decrease in the  $D$  values ( $D_{\text{Am}}$  values were  $\approx 25$  for PhenA-2,  $\approx 3$  for PhenA-4,  $\approx 0$  for PhenA-6 in chloroform at  $10^{-4}$  M  $\text{HNO}_3$ ) and that the absence of one of the amide groups was detrimental to the extraction properties.<sup>281</sup> The introduction of branched chains (PhenDA-2,  $\text{R}^1, \text{R}^2 = \text{iBu}$ ) resulted in even lower  $D$  values than in the absence of alkyl chains (PhenDA-1), although both required the presence of 2-bromooctanoic acid or CCD (for PhenDA-2,  $\text{R}^1, \text{R}^2 = n\text{-Bu}$ )<sup>282</sup> as the synergist ( $D_{\text{Am}} = 21.4$  for PhenDA-1 and 4.6 for PhenDA-2), and the use of a salting out agent could substitute for the 2-bromocarboxylic acid synergist (for PhenDA-3,  $D_{\text{Am}} = 0.5$  in 1 M  $\text{LiClO}_4$  and  $D_{\text{Am}} = 10$  in 2 M  $\text{LiClO}_4$ ).<sup>283</sup> Overall, however, the best results were obtained with PhenDA-4, in line with the results obtained with bipyridine amides. PhenDA-4 showed very high  $D$  values for actinide ions, with a higher preference for Th(IV) ( $D_{\text{Th}} = 205$ ) than U(VI) and Am(III) ( $D_{\text{U}} = 25$ ,  $D_{\text{Am}} = 6$ ). Additionally, the S.F. values of Th(IV), U(VI), and Am(III) toward Eu(III) were 2277, 277, and 67 in 1.0 M  $\text{HNO}_3$ , respectively.<sup>284</sup>

Functionalisation of 1,10-phenanthroline with di(thio)amide, diester or diketone groups showed that the carboxylic acid derivatives PhenDA-5–6 were more selective than diketone PhenDA-7, whereas dithioamide PhenDA-8 suffered from

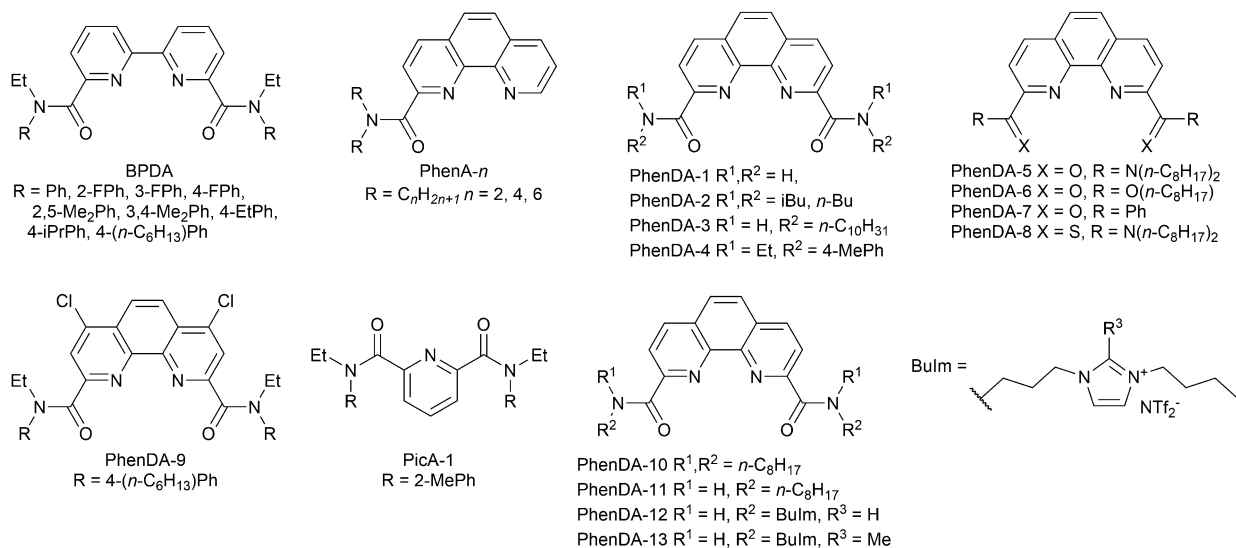


Chart 52

desulfuration at high  $\text{HNO}_3$  concentration (Chart 52).<sup>285</sup> The preferential binding of different metals, however, is also influenced by the structure of the N-heterocycle (picolinamide, bipyridine, phenanthroline, *etc.*). Comparing PicA-1, BPDA and PhenDA-9 (Chart 52) in the extraction of the entire series of Ln at  $\geq 3 \text{ M HNO}_3$ , it was observed that the  $D$  values depended on the size of the cavity and the flexibility of the ligand. PicA-1 preferentially extracts heavier Ln because of the small chelating cavity ( $D_{\text{La}} \approx 1$ ,  $D_{\text{Lu}} \approx 100$ ). The distance between the donor centres in BPDA ( $R = \text{Ph}$ ) is bigger than in PicA-1, but it is also more flexible due to rotation around the C2–C2' bond. Therefore, it can complex both lighter and heavier Ln, but less efficiently ( $D_{\text{La}} \approx 1$ ,  $D_{\text{Lu}} \approx 0.1$ ). PhenDA-9, on the other hand, is more rigid and not able to bind to heavy Ln, that have a smaller ionic radius ( $D_{\text{La}} \approx 500$ ,  $D_{\text{Lu}} \approx 0.1$ ).<sup>286</sup>

However, if the extraction was performed in ionic liquids RTILs, the trend for phenanthroline diamides would change depending on the substituents. PhenDA-10 (Chart 52) in  $[\text{C}_6\text{mim}][\text{NTf}_2]$  showed a very strong preference for the extraction of heavier Ln ( $D_{\text{La}} \approx 10$ ,  $D_{\text{Lu}} \approx 3000$ ). The corresponding dicationic ligand (PhenDA-12) showed higher  $D$  values for lighter Ln (decreasing from  $D_{\text{Ce}} \approx 3000$  to  $D_{\text{Dy}} \approx 10$  and rising again to  $D_{\text{Lu}} \approx 200$ ). The complex behaviour of the  $D$  values in the case of PhenDA-12 was attributed to a change in the composition and conformation of the complex, which was supported computationally.<sup>287</sup>

Picolinamides showed that an increase in the length of the alkyl chains had little effect on the  $D$  values ( $D_{\text{Am}} = 1.86$ , 3.22 and 0.74 for PicA-2–4, respectively, from 5 M  $\text{LiNO}_3$ ), due to two opposing effects: longer alkyl chains decreased the extracting ability of the ligand, but at the same time they increased the solubility of the metal complex. In addition, good S.F. values were observed regardless of the length of the alkyl chain ( $\text{S.F.}_{\text{Am/Eu}} = 5$  for PicA-2–4).<sup>288</sup> At lower  $\text{LiNO}_3$  concentrations, however, picolinamides showed higher selectivity for Am(III)

over Eu(III) ( $D_{\text{Eu}} = 0.4$ ,  $D_{\text{Am}} = 4.2$ ,  $\text{S.F.}_{\text{Am/Eu}} = 10$  at 3 M  $\text{LiNO}_3$ ).<sup>289</sup> Picolindiamides, on the other hand, exhibited poor separation ( $D_{\text{Am}} = 8.82$ ,  $D_{\text{Eu}} = 6.39$ ,  $\text{S.F.}_{\text{Am/Eu}} = 1.4$ ).<sup>288</sup>

Pre-organisation of picolinamide ligands on calix[ $n$ ]arene ( $n = 4, 6$  and 8, CalixPicA-1–11, Chart 53) showed an increase in the extraction efficiency ( $D_{\text{Am}} > 300$ ), but the ligands were limited to weakly acidic conditions ( $< 0.01 \text{ M HNO}_3$ ). Calix[8]-arenes exhibited higher  $D$  values than calix[6]- and calix[4]arene, whereas the highest S.F. values were observed for upper-rim-substituted calix[4]arene CalixPicA-11 ( $\text{S.F.}_{\text{Am/Eu}} = 13.8$ ). Thio-picolinamides CalixPicA-4 were not able to significantly extract An(III) or Ln(III) ions.<sup>290</sup> Decreasing the basicity of the pyridine N atoms (CalixPicA-13 and CalixPicA-15) also allowed for an increase in the  $D$  values at higher  $\text{HNO}_3$  concentration, whereas the addition of electron-donating groups to the pyridine ring (CalixPicA-16) strongly decreased  $D$  values at any acidity.<sup>136</sup> Picolindiamides CalixPicA-17–22 displayed further increase in the  $D$  values due to the cooperation between tridentate ligands and the decrease of pyridine N atom basicity. CalixPicA-19 and CalixPicA-21 showed higher extraction, whereas CalixPicA-17–18 were more selective.<sup>291</sup>

Another class of related ligands is based on modifications of terpyridine diamide (Chart 54). The central pyridine rings were substituted with phenanthroline units to simulate the cavity of a BTPhen ligand, or with triazine rings to lower the affinity towards protons. For solubility reasons, only ligands PhenPDA-1, PhenPDA-2, TPDA-1 and TPDA-2 could be used for extraction experiments. The phenanthroline-based ligands showed better extraction properties. They could extract An with different oxidation states ( $\text{Pu(IV)} > \text{Am(III)} > \text{Cm(III)}$ ) from 3 M  $\text{HNO}_3$ , whereas Eu(III) remained in the aqueous phase. The introduction of phenyl rings on the amide functions led to a better extraction performance, but reduced solubility.<sup>292</sup>

Preparing hydrophilic phenanthroline diamides (Chart 54) did not lead to practically useful ligands, as in the case of

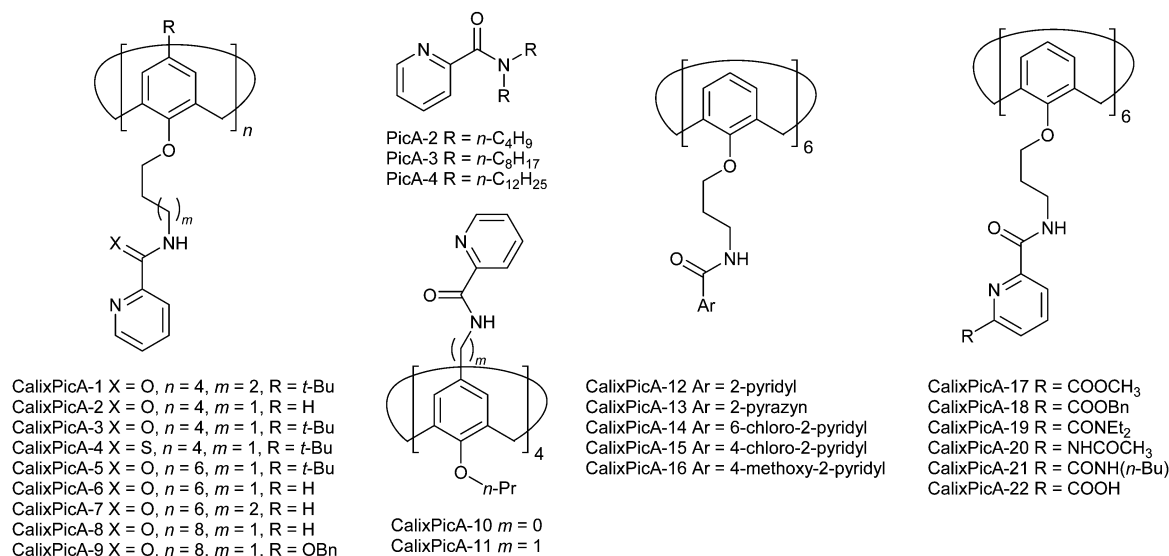


Chart 53

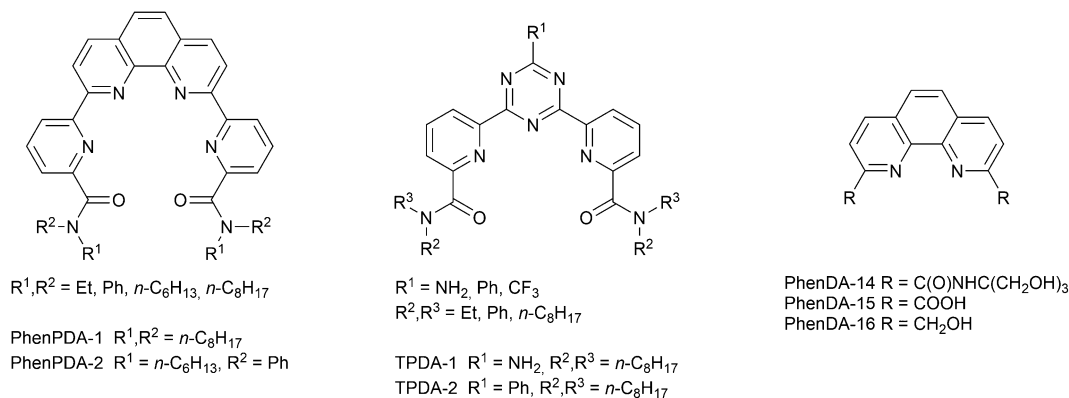


Chart 54

pyridyltriazolyl ligands (Chart 50). PhenDA-14 showed encouraging results in the back-extraction of Am(III) from TODGA-loaded solutions, since upon stripping the  $D_{\text{Am}}$  values decreased by a factor of about 15 (from  $D_{\text{Am}} = 5.42$  to 0.36), while the  $\text{S.F.}_{\text{Eu/Am}}$  increased from 7 to about 30 (at 1 M  $\text{HNO}_3$ ). However, all three ligands were limited by a very low solubility in the aqueous phase. Moreover, the efficiency of the system was severely reduced when tested with a simplified HAR (High Active Raffinate) at 3 M  $\text{HNO}_3$ .<sup>293</sup>

As an alternative way to obtain hydrophilic N-heterocyclic ligands as masking or stripping agents, TPEN derivatives (Chart 55) were prepared; their properties have been recently summarised.<sup>294</sup> With the intention of modulating their properties with the introduction of oxygen donors, the corresponding picolinic acids ( $\text{H}_4\text{TPAEN}$ , Chart 55), as well as variations of the structure of the platform, were studied. Various modifications of dipicolinic acid (PDCA) showed that the selectivity in the back-extraction of Am(III) and Eu(III) from a TODGA-loaded solution was not substantially affected by the addition of various substituents to PDCA ( $3 < D_{\text{Eu}} < 7, 0.5 < D_{\text{Am}} < 1, 7.8 < \text{S.F.}_{\text{Eu/Am}} < 9.8$ ). On the other hand, with  $\text{H}_4\text{TPAEN}$   $\text{S.F.}_{\text{Eu/Am}}$  values as high as 768 could be obtained ( $D_{\text{Am}} = 0.09, D_{\text{Eu}} = 69.10, 0.655$  M ligand, 0.023 M  $\text{HNO}_3, 3$  M  $\text{NaNO}_3$ ).<sup>295</sup>

$\text{H}_4\text{TPAEN}$ , however, has a low solubility in the acidic phase used for stripping. To improve its solubility, and at the same time its Cm(III)/Am(III) selectivity, a series of derivatives (Chart 56) was investigated for the stripping from a 0.2 M TODGA/0.5 M TBP (in TPH) into an acidic aqueous solution (pH 1). All the ligands

tested, except TPAEN-9, showed improved solubility, accompanied by a general decrease in selectivity. The flexibility and the size of the platform appeared to be important for good extraction. Because of the increased rigidity, ligands TPAEN-7–9 poorly extracted both An and Ln, and better results were obtained with ligands with an ethylene diamine bridge. The introduction of chelating spacers, such as azamacrocycles, EDTA and DTPA derivatives (TPAEN-1–4) caused a decrease in selectivity, even if they increased the extraction efficiency. Only the presence of a methoxy group increased the solubility maintaining the Cm/Am selectivity (TPAEN-6,  $\text{S.F.}_{\text{Cm/Am}} = 3.2$ ).<sup>296</sup>

## Conclusions

CyMe<sub>4</sub>-functionalised bis-triazinyl ligands remain the benchmark for N-heterocyclic ligands, since a suitable candidate to substitute CyMe<sub>4</sub>-ketone has not yet been identified. Different modifications of the heterocycles have been investigated in order to tune the properties of these ligands. Water-soluble analogues were efficiently used as holdback ligands. Pyridyl-pyrazoles have been developed as simple alternatives to bis-triazinyl ligands and have shown promising results. Amides of heterocyclic carboxylic acids proved to be a promising compromise between diamide and bis-triazinyl ligands. Compared to the latter, their solubility in organic solvents is higher and they are relatively simple to prepare. In addition, it was possible to change their extraction properties changing the alkyl groups on the amide or by functionalisation of the heterocyclic skeleton.

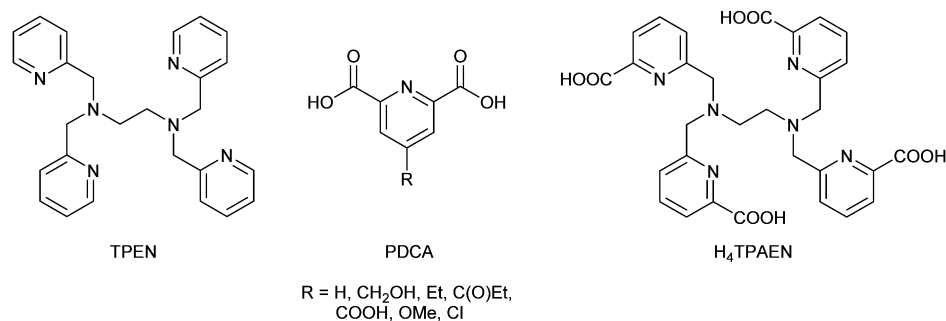


Chart 55

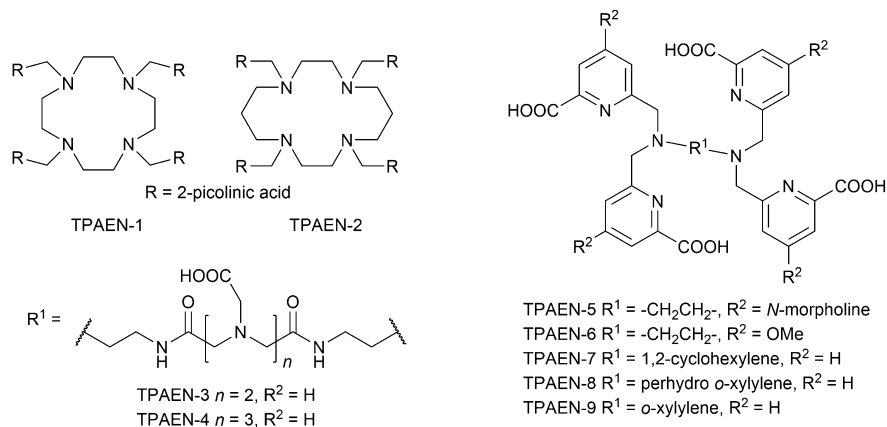


Chart 56

## Miscellaneous

### Other ligands

Functionalised crown ethers (18C6, DB18C6, DBP18C6, DCH18C6) have been studied as synergists with 8-hydroxyquinoline (HQ) for the extraction of Ln(III). The  $D$  values increased with increasing lipophilicity of the ligand and increasing  $HNO_3$  concentration. Despite the HQ/DCH18C6 system providing higher extraction and Ce/La separation than the mixtures with the other synergists, the  $D$  values were very low ( $D_{Ln} \leq 0.07$  at 0–1 M  $HNO_3$  with the four crown ethers).<sup>297</sup>

Compounds based on 15-crown-5, in combination with HPBI (Chart 57) showed interesting results for the extraction of Ln(III), mostly due to a better match between the cavity of these crown ethers and the ionic radii of the metal ions. The inclusion of a phenyl ring on the macrocycle (B15C5) led to lower extraction properties than the parent 15C5 ( $D_{Eu} \approx 1$  and 0.5 for 15C5 and B15C5, respectively, at pH 2.4), probably due to an increase in the rigidity of the macrocycle. On the other hand, substitution of one of the oxygens for a nitrogen atom (BA15C5), caused an increase in the extraction ( $D_{Eu} \approx 2.5$  at pH 2.4). This increase was enhanced by the inclusion of a bulky lipophilic group (PDN1A15C5) bearing an additional donor oxygen ( $D_{Eu} \approx 8$  and 0.4 for PDN1A15C5 and BA15C5, respectively, at pH 2.1). Even though the addition of aza-15-crown-5 derivatives to HPBI afforded higher extraction, a mixture with 15C5 displayed higher selectivity for the mutual separation of Ln(III) ( $S.F._{Eu/La} = 25.5$ , 52.4, for HBPI, and its mixture with 15C5, respectively).<sup>298</sup>

Functionalisation of diaza-18-crown-6 with picolinic acid groups (H<sub>2</sub>BP18C6, Chart 57) resulted in a hydrophilic ligand that showed enhanced Am/Cm separation ( $S.F._{Am/Cm} = 6.5$  with 0.05 M HDEHP in *o*-xylene/0.001 M H<sub>2</sub>BP18C6 in 1 M NaNO<sub>3</sub>, 0.05 M lactate at pH 3). The ligand formed stronger complexes with larger metal ions, thus favouring the extraction of smaller ions into the organic phase. This extraction system, based on competitive complexation, also exhibited good separation among the Ln(III): the series of La–Gd metal ions showed  $D_{Ln}$  values almost evenly spread between 0.005 and 200 (0.05 M HDEHP in *o*-xylene/0.001 M H<sub>2</sub>BP18C6 in 1 M NaNO<sub>3</sub>, 0.05 M lactate at pH 3). However, the separation of Am(III) from light Ln(III) was poor ( $D_{Am} \approx 0.2$ ,  $D_{Cm} \approx 0.6$ ,  $D_{Pr} \approx 0.3$ ,  $D_{Nd} \approx 1.5$ ).<sup>299</sup> Changing the composition of the organic phase to a mixture of 0.05 M TEHDGA (Charts 32) and 0.3 M HEH[EHP] (Chart 6) caused a decrease in the  $D$  values of the lighter Ln(III). This prevented the extraction of La–Nd into the organic phase and allowed the separation of Am(III) and Cm(III) from the Ln(III) in the stripping step.<sup>300</sup>

Separation of An and Ln(III) was also achieved with the water-soluble tetradentate Schiff base H<sub>2</sub>salen-SO<sub>3</sub> (Chart 58). In the extraction of metal ions with HDEHP (Chart 6), the  $D$  values followed the order Np(V) < Cm(III) < Eu(III) < U(VI) ( $D_M = 4.7$ , 10, 19.9 and 98, respectively). However, H<sub>2</sub>salen-SO<sub>3</sub> formed stronger complexes with An(VI) than with trivalent metal ions. Upon addition of H<sub>2</sub>salen-SO<sub>3</sub> to the aqueous phase as the holdback ligand, the extraction of penta- and hexavalent metal ions was reduced by three orders of magnitude, whereas

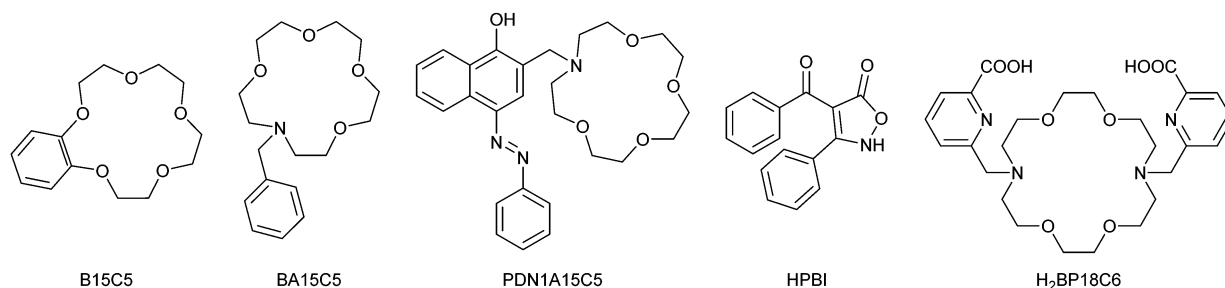


Chart 57



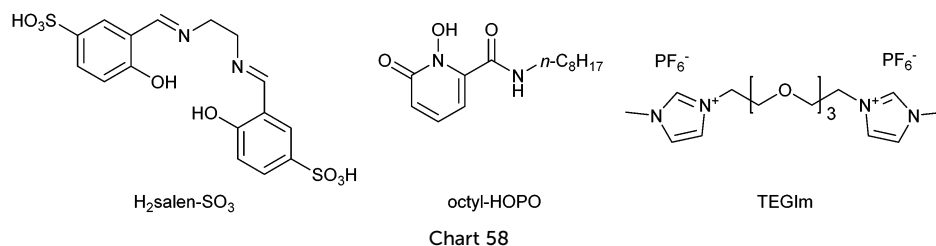


Chart 58

that of trivalent ions decreased by one, changing the order of extraction to  $\text{Np(V)} < \text{U(VI)} < \text{Eu(III)} < \text{Cm(III)}$  ( $D_M = 0.017, 0.13, 3.9$  and  $89$ , respectively).<sup>301,302</sup>

The combination of HDEHP and a holdback ligand (DTPA) is also used in the TALSPEAK<sup>7</sup> process and is aimed at preferably extracting Ln over An. This process, however, has some interconnected disadvantages: because of the low extraction efficiency, a high concentration of HDEHP is required, in turn increasing the susceptibility to third-phase formation and loss of buffering reagents in the organic phase. Octyl-HOPO (Chart 58) has been proposed as a substitute of HDEHP, because of its strong complexing ability for An and Ln(III). In the absence of a holdback ligand, it displayed a strong preference for heavy Ln(III) ( $D_{\text{La-Gd}} \sim 1000$ ,  $D_{\text{Tb-Lu}} \sim 4000\text{--}14\,000$ , citric acid buffer). When the extraction was performed under TALSPEAK conditions, the  $D$  values decreased noticeably and the metals that were better extracted were light and heavy Ln(III) ( $D_{\text{Ce-Nd}} = 152\text{--}440$ ,  $D_{\text{Dy-Lu}} = 120\text{--}1600$ ) over middle Ln(III) ( $D_{\text{Sm-Tb}} = 45\text{--}65$ ). Upon increasing the DTPA concentration (from  $0.005\text{ M}$  to  $0.1\text{ M}$ ), up to forty-fold decrease in the extraction of Am(III) was observed (from  $D_{\text{Am}} \approx 500$  to  $13$ ). The reduction was less pronounced for Eu(III) (from  $D_{\text{Eu}} \approx 4300$  to  $300$ ), leading to an increase in the S.F.<sub>Eu/Am</sub> value (from S.F.<sub>Eu/Am</sub>  $\approx 8.5$  to  $23.5$ ).<sup>303</sup>

An open-chain polyether functionalised with two methylimidazolium groups (TEGIm, Chart 58) displayed good extraction ability in RTILs. The  $D$  values depended on the RTIL used as diluent, with two orders of magnitude between [C<sub>4</sub>mim][NTf<sub>2</sub>] and [C<sub>4</sub>mim][PF<sub>6</sub>] ( $D_{\text{Eu}} \approx 170$  and  $2$ , respectively) and heavier Ln(III) were extracted preferentially over lighter ones ( $D_{\text{La}} \approx 12$ ,  $D_{\text{Lu}} \approx 400$  from [C<sub>4</sub>mim][NTf<sub>2</sub>]). The extraction efficiency decreased as the HNO<sub>3</sub> concentration increased, allowing for selective stripping of the metal ions from the loaded organic phase.<sup>304</sup>

### Alternative approaches for metal ion separation systems

**Homogeneous liquid-liquid extraction.** Betainium bis(trifluoromethylsulfonyl)imide [Hbet][NTf<sub>2</sub>] (Chart 59) is a TSIL able to dissolve large quantities of several metal oxides (including

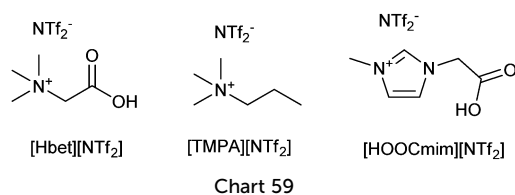


Chart 59

Ln(III) and An), and it is immiscible with water at room temperature. However, it shows thermomorphic behaviour, becoming soluble in water at temperatures  $> 55\text{ }^{\circ}\text{C}$  and at high pH (increasing the metal loading lowers the transition temperature).<sup>305,306</sup> [Hbet][NTf<sub>2</sub>] proved to be a good ligand for U(VI), extracting  $62\%$  ( $D_U \approx 2$ ) of the metal ions from  $0.01\text{ M HNO}_3$  (at room temperature). No extraction was observed with [TMPA][NTf<sub>2</sub>], supporting the idea that the carboxylate group was necessary for the formation of the complex.<sup>307</sup> The thermomorphic properties of the TSIL were exploited for a homogeneous liquid-liquid extraction: the biphasic water/TSIL mixture was heated at  $60\text{ }^{\circ}\text{C}$ , gently shaken, and the phase separation was induced by cooling the mixture. The  $D$  values obtained were the same as in the conventional extraction method, but the extraction time was reduced to  $10\text{ min}$  as opposed to  $1\text{ h}$ . Moreover, U(VI) could be recovered quantitatively from the TSIL by precipitation upon addition of H<sub>2</sub>O<sub>2</sub>.<sup>308</sup> Using a methylimidazolium carboxylic acid RTIL [HOOCmim][NTf<sub>2</sub>] (Chart 59) allowed a reduction in the extraction time to just  $1\text{ min}$  with high extraction efficiency ( $87\%$  U(VI)), although the homogenisation temperature increased to  $75\text{ }^{\circ}\text{C}$ .<sup>309</sup>

**Extraction systems with multiple organic phases.** TSIL systems have also been investigated as an alternative to the TALSPEAK process. The extraction was performed with HDEHP in cumene from an immiscible TSIL in which DTPA was integrated. Cyclic DTPA dianhydride (cDTPA) was dissolved in bistriflimide TSILs based on betaine, carnitine or choline, that reacted with the ligand forming mixed dianhydrides or diesters (Chart 60). This approach avoided the usually laborious synthesis and purification of a TSIL by an *in situ* addition reaction. The extraction of Ln(III) ions with cDTPA showed  $D$  values ranging over three orders of magnitude ( $D_{\text{La}} \approx 0.2$ ,  $D_{\text{Er}} \approx 200$  using [Hbet][NTf<sub>2</sub>] and HDEHP in cumene), with good selectivity for the separation of Am(III) (S.F.<sub>Eu/Am</sub>  $\approx 135$  and  $260$  for [Hbet][NTf<sub>2</sub>] and [chol][NTf<sub>2</sub>]).<sup>310</sup>

Two immiscible non-fluorinated RTILs ([C<sub>2</sub>mim][Cl] and [P<sub>66614</sub>][R<sub>2</sub>POO], Chart 60) have been employed for the separation of Ln(III) from Ni(II). [C<sub>2</sub>mim][Cl] containing small amounts of HCl was used to directly dissolve the metal oxides. Contact of the loaded mixture with [P<sub>66614</sub>][R<sub>2</sub>POO] allowed for quantitative transfer of the Ln ions, whereas Ni(II) was not extracted by this solvent. Stripping with  $2\text{ M HNO}_3$  afforded an aqueous solution of Ln(III) that could be used for further processing.<sup>311</sup> More promising results were obtained with two non-ionic solvent systems. Ethylene glycol was used as a solvent for metal nitrates in a solvent extraction process between two immiscible organic phases. The extraction with TOPO dissolved in *n*-dodecane showed that heavy and light Ln(III) can be separated more

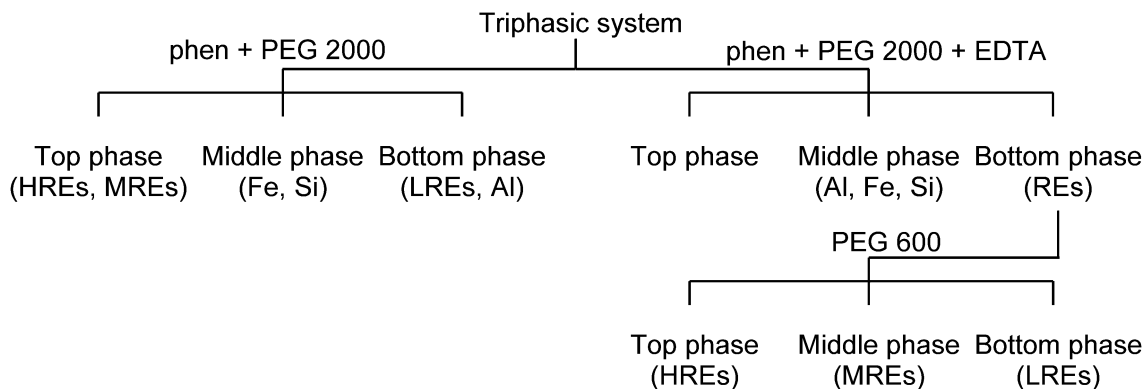
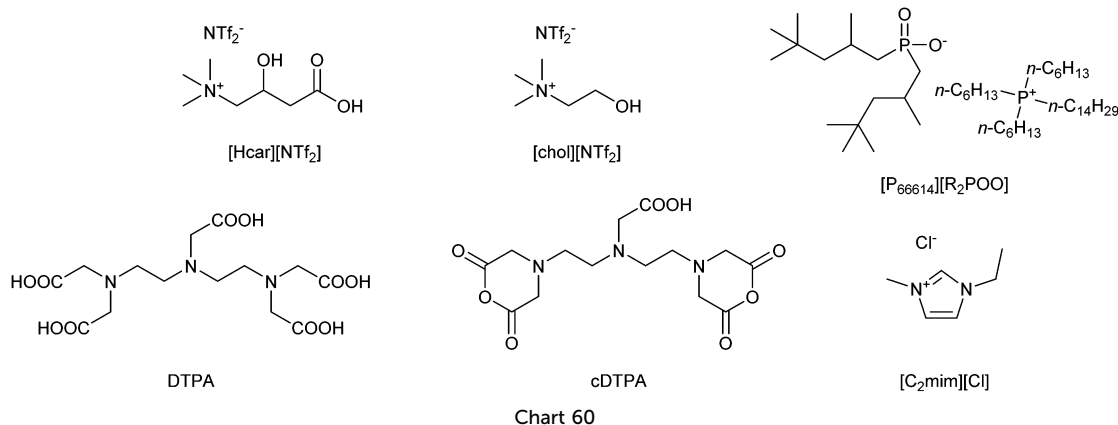


Fig. 1 Schematic representation of the two-step three-liquid-phase system for the separation of REs.

efficiently from this system ( $D_{La-Nd} = 0.05-0.45$ ,  $D_{Gd-Yb} = 4-20$ ) than from aqueous solutions ( $D_{La} = 0.4$ ,  $D_{Ce-Yb} = 1-2$ ).<sup>312</sup>

A two-step three-liquid-phase system composed of Cyanex 272/PEG 2000/ $(NH_4)_2SO_4-H_2O$  (Fig. 1) was described for the separation of Ln(III) into light, middle and heavy ions and for the decontamination from Al, Fe and Si. When 1,10-phenanthroline and PEG 2000 were used, the PEG middle phase was enriched with Fe and Si, whereas Al and light Ln(III) remained in the aqueous phase. Addition of EDTA and 1,10-phenanthroline to the system caused all the Ln(III) to remain in the aqueous phase and the contaminants Al, Fe and Si to be transferred to the PEG phase. Subsequently, using another triphasic system including PEG 600, the three groups of Ln(III) ions could be separated in the three different phases (light Ln in the bottom aqueous phase, middle Ln in the PEG 600 middle phase, heavy Ln in the Cyanex 272 top phase).<sup>313</sup>

**sc-CO<sub>2</sub> as a tunable solvent for metal ion extraction.** TBP dissolved in supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) has been investigated for the extraction of An and Ln(III) from aqueous HNO<sub>3</sub> solutions. The extraction of U(VI), Np, Pu and Am(III) showed that high selectivity can be achieved. The separation of U and Pu was possible at HNO<sub>3</sub> concentrations < 3 M and in the presence of acetohydroxamic acid (AHA) or oxalic acid (OA) to mitigate the extraction of Pu. HNO<sub>3</sub> concentrations < 1 M and the presence of AHA, OA or sodium nitrite suppressed the extraction of Np. Am(III) was not extracted under any condition, whereas the extraction of U(VI) was not affected

by changes in the experimental conditions.<sup>314</sup> The separation between light and heavy Ln(III) with sc-CO<sub>2</sub> could be adjusted by modifying the temperature, pressure and the amount of TBP. Between a couple of light-heavy Ln(III) ions, when the amount of TBP was insufficient to completely extract both metal ions, the lighter one was preferred. On the other hand, an increase of temperature and pressure favoured the extraction of heavier metal ions. Interestingly, the loading capacity of the sc-CO<sub>2</sub> system was higher for mixtures of Ln(III) than for single elements.<sup>315</sup>

An adduct of formula  $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$  was formed when TBP and concentrated HNO<sub>3</sub> were mixed. In this system, TBP acted as a carrier for HNO<sub>3</sub> into sc-CO<sub>2</sub> with a very small amount of water. The TBP-HNO<sub>3</sub> complex was very effective in directly dissolving Ln and An oxides in sc-CO<sub>2</sub>. This opportunity offered several advantages compared to conventional systems, since lower amounts of mineral acid and solvents were required, sc-CO<sub>2</sub> is relatively cheap and non-toxic, and the technology is already well-developed in industry.<sup>316</sup> The performance of the TBP-HNO<sub>3</sub> complex, however, was negatively affected by the increasing amount of water and acid.<sup>317</sup>

## Conclusions and outlook

The challenges of the separation of An and Ln(III) are not easy to overcome; the number of metal ions for which separation is

desired and the similarities between them make the development of a single all-purpose process very difficult. Therefore, the idea of more efficient systems, though more limited in scope, should not be set aside. Indeed, ligands that distinguish An of different oxidation states, and ligands able to differentiate among groups of Ln were generally emphasised as opposed to whole-group extractants. For instance, the extension of the linker between bidentate ligands,<sup>175</sup> functionalisation of the wide rim instead of the narrow one of calix[4]arenes, or changing the backbone of amides of heterocyclic carboxylic acid,<sup>286</sup> changed the preference of the ligand towards heavy Ln, light Ln or actinides. D<sup>3</sup>DMDGA,<sup>165</sup> and other ligands that could form a planar complex with UO<sub>2</sub><sup>2+</sup>, showed an increase in selectivity for An.

Recently, the relationship between ligand structure and extraction properties has been studied more systematically, providing valuable information for the design of new ligands. Ligands following the “CHON principle” are favoured because they are completely incinerable. On the other hand, organophosphorus ligands are either commercially available or offer a simple set of options to change their properties. In view of the large-scale use, ligand cost, radiolytic stability and disposal might be weighted at the same level as extraction and separation efficiency.

Studies on DGAs and N-heterocyclic ligands were recently focused on small modifications for the (successful) fine-tuning of the extraction properties. This showed that even the presence of one or two methyl groups on the DGA backbone has a drastic effect on the extraction,<sup>176</sup> whereas only substituents that induce subtle changes (like a halogen atom) can be used to modify bis-triazinyl ligands without compromising the extraction efficiency.<sup>263,265</sup> On the other hand, amides of heterocyclic carboxylic acids, despite their lower *D* and S.F. values than bis-triazinyl ligands, are potential alternatives because they allow the exploration of more variety in the substituents. Acidic ligands often show a linear dependence of the extraction on the pH, allowing for easier stripping than several strong neutral ligands.<sup>189</sup>

Attention has also been paid to the simplification of the synthesis, in view of large-scale use. Alternatively, simplified versions of known ligands have been attempted. Approaches that provided encouraging results involved the combination of ligands with different properties (hydrophilic/hydrophobic or acidic/neutral, for example) or synergic mixtures (both intra- and intermolecular). In addition, mixtures of acidic ligands (with either acidic or neutral ligands) showed the possibility to exploit the characteristics of the constituents at different pH.<sup>52,53</sup> Synergic and antagonistic mixtures, on the other hand, displayed that it is important to study the interactions among constituents of mixtures and not just assume that a “sum” of their properties is obtained.<sup>64</sup> Hydrophobic/hydrophilic ligand systems have great potential of improvement because they allow for more “knobs to be adjusted” by design. The holdback/extracting/stripping ligand combinations can mutually enhance the ligands’ selectivities, and each of them can be modified independently.

RTIL systems manage to drastically alter the properties of the ligands, but suffer from drawbacks such as leaching of IL cations into the aqueous phase and slow kinetics. The recently

studied more hydrophilic RTILs bearing long alkyl chains have extracted metal ions by a solvation mechanism and may offer an interesting solution.<sup>261</sup> Non-fluorinated TSILs have presented a greener alternative to common NTf<sub>2</sub><sup>−</sup>-based systems, displaying interesting extraction properties.<sup>194,311</sup>

Unless new breakthrough classes of ligands are discovered, from the results reported so far, it appears that extracting systems based on an individual ligand are limited to giving coarse separations among light Ln, heavy Ln, An and other REEs, whereas combinations of ligands would be able to afford the fine separation of individual metal ions. Additionally, new strategies involving water-free extraction systems, multiple organic phases and sc-CO<sub>2</sub> might provide an edge in the development of more efficient extraction processes.

## Abbreviations

ALSEP	Actinide–lanthanide separation
An	Actinide
BODO	Bis(benzoxazol)dodecyloxyppyridine
BTBP	Bis-triazinylbipyridine
BTP	Bis-triazinylpyridine
BTPhen	Bis-triazinylphenanthroline
CCD	Cobalt bis(dicarbollide)
CMP	Carbamoylmethylphosphonate
CMPO	Carbamoylmethylphosphine oxide
D	Distribution ratio
DCC	Dicyclohexylcarbodiimide
DCE	Dichloroethane
DGA	Diglycolamide
DIAMEX	Diamide extraction process
DTPA	Diethylenetriaminopentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
FS-13	Phenyltrifluoromethylsulfone (= PTMS)
HDEHP	Di(2-ethylhexyl) phosphoric acid
IL	Ionic liquid
Ln	Lanthanide
<i>m</i> -NBTF	<i>meta</i> -Nitrobenzotrifluoride
NPHE	Nitrophenyl hexyl ether
<i>t</i> -Oct	1,1,3,3-Tetramethylbutyl
P&T	Partitioning and transmutation
PTMS	Phenyltrifluoromethylsulfone (= FS-13)
PUREX	Plutonium uranium extraction
RE/REE	Rare earth/rare earth element
RTIL	Room temperature ionic liquid
S.F.	Separation factor
SANEX	Selective actinide extraction
SHLW	Simulated high-level waste
SLM	Supported liquid membrane
TALSPEAK	Trivalent actinide–lanthanide separation by phosphorus reagent extraction from aqueous complex
TBP	Tributylphosphate
TEHDGA	Tetra(2-ethylhexyl)diglycolamide
TERPY	Terpyridine
TODGA	Tetraoctyldiglycolamide

TOPO	Trioctylphosphine oxide
TPH	Hydrogenated tetrapropene
TPTZ	Tripyridinetriazine
TRPO	Trialkylphosphine oxide
TRUEX	Transuranic extraction
TRUSPEAK	Transuranic separation by phosphorus reagent extraction from aqueous complex
TSIL	Task-specific ionic liquid

## Conflicts of interest

There are no conflicts to declare.

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