

Organophosphorus Extractants: A Critical Choice for Actinides/Lanthanides Separation in Nuclear Fuel Cycle

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Abstract: The separation of actinides from lanthanides in spent nuclear fuel reprocessing is a vital step of nuclear fuel cycle process. As one class of mature industrial extractants, the organophosphorus extractants have been widely used for the extraction and separation of actinides and lanthanides in spent fuel reprocessing due to their strong extraction ability and low-cost acquisition. In this concept, the application scope of tributyl phosphate (TBP), bis(2-ethylhexyl) phosphate (HDEHP), octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), trialkyl phosphine oxide (TRPO), and purified Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid, HA301) are introduced, and their extraction

mechanism, as well as structure-function relationships for separation of actinides over lanthanides are also discussed. Furthermore, the design criteria, extraction properties and mechanism of several typical newly developed organophosphorus extractants (CMPO-modified calixarene/pillarene, phenanthroline-derived organophosphorus extractants, and phosphate-modified carborane) based on pre-organized skeletons are briefly reviewed. Finally, the important role played by those organophosphorus extractants is emphasized and potential applications in separation of actinides over lanthanides in future advanced nuclear fuel cycle are identified.

1. Introduction

As an efficient and low-carbon energy source, nuclear energy has been used worldwide on a large scale since the 1950s. One of the biggest obstacles to the safe and effective application of nuclear energy is solving the problem of spent fuel reprocessing for building advanced nuclear fuel cycle systems.^[1] The main components of SNF discharged from the reactor is uranium and plutonium, minor actinides (MAs), and fission products, such as lanthanides, strontium, cesium, and iodine.^[2] Because the chemical properties of the trivalent actinides (An(III)) and trivalent lanthanides (Ln(III)) are very similar, it is very difficult to separate An(III) over Ln(III) by using traditional chemical separation methods.^[3] In order to recover the valuable actinides as target products over the fission products (FPs) of lanthanides, the solvent extraction method has been used in industry to separate actinides from lanthanides.^[4] The solvent extraction method has numerous advantages when used for actinides/lanthanides separation, such as high separation efficiency, low production cost, simple operating procedure and convenience for large-scale industrial applications.^[5] One of the most dominant scientific issues is how to design one highly

efficient extractant with a specific selectivity for target elements from other impurities, high solubility in the organic diluent, strong resistance to acidolysis and radiolysis, and convenience of large-scale synthesis.^[6] At the same time, the selective crystallization to separate lanthanides and actinides is also a hot topic in scientific research.^[7–9]

In order to develop highly efficient extractants and solve the shortcomings of traditional separation processes, researchers have developed a series of organophosphorus extractants in the past few decades and applied them to the separation of actinides over lanthanides in the nuclear fuel cycle.^[10] The molecular structures of several representative organophosphorus extractants discussed in this concept are shown in Figure 1. The traditional organophosphorus extractants reported for actinide separation can be divided into acidic and neutral phosphorus extractants. In recent years, researchers have also grafted traditional neutral and acidic organophosphorus extractants on some pre-organized skeletons to form a series of rigid organophosphorus extractants with excellent extraction ability and high selectivity for actinides. Organophosphorus extractants generally contain phosphorus-oxygen (P=O) or phosphorus-sulfur (P=S) groups with high charge density, which has a strong coordination ability for f-block elements and thus can improve their extraction efficiency.^[11] The side chains of the extractant are basically composed of alkyl or aryl groups, which is helpful to improve the extractant's lipophilicity and solubility in organic solvents, thereby increasing the saturated extraction ability of the extractant towards metal ions. The strong polarity of the P=O/P=S bonds in those organophosphorus extractants results from the high reactivity and strong bond-forming ability of phosphorus atoms, making the steric resistance effect and electronic effect of extractants more adjustable. Therefore, organophosphorus extractants with different structures can be

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designed to achieve the specific extraction selectivity for the desired metal ions.^[12]

Although quantities of organophosphorus extractants have been applied to practical actinide separation processes, there is still a lack of precise studies that reveal the relationships between the profound chemical theory and actual application. Also, there are still lots of unresolved inherent challenges in the

design and building of the advanced solvent extraction separation processes using organophosphorus ligands as extractants. Up to now, the design and synthesis of some novel extractants are still merely based on experience and experimentation. Although quantities of in-depth research have been carried out by various techniques, there is still a lack of a comprehensive summary of the structure-activity relationships between ligand structure and their extraction properties for actinides. Many contribution factors in the complicated extraction system will affect the interaction between the extractant and the metal ions, which leads to an unclear understanding of the extraction mechanism and difficulty in improving the separation efficiency. Due to the lack of accurate in-situ characterization methods, the internal and interfacial behaviors of the two phases in the actual liquid-liquid extraction process are confusing, which makes it impossible to precisely understand the microscopic and mesoscopic molecular reactions and interactions in the extraction process.^[13] Through the combing and summarizing of scientific research achievements in recent decades, this concept aims to point out the key points in the design of highly efficient extractants and clarify the important roles organophosphorus extractants play in the separation of actinides/lanthanides in the nuclear fuel cycle, and meanwhile give some valuable ideas and suggestions for future studies of organophosphorus type ligands.

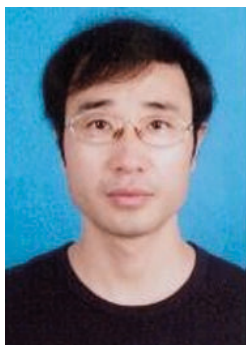
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2. Neutral Organophosphorus Extractants

2.1. Trialkyl phosphate extractant

The trialkyl phosphate extractants represented by tributyl phosphate (TBP) have a strong affinity for high-valent actinides such as U(VI), Th(IV) and Pu(IV), but with weak extraction ability for An(III) and Ln(III).^[14] Therefore, those trialkyl phosphates have been commercially used in the separation of uranium and thorium from natural ores in the hydrometallurgical process and recovery of uranium and plutonium from spent nuclear fuel through the PUREX (Plutonium Uranium Recovery by EXtraction) process.^[15]

The extracted complexes formed between TBP and U(VI)/Pu(IV) are $[\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2]$ and $[\text{Pu}(\text{TBP})_2(\text{NO}_3)_4]$ respectively, and the corresponding complexation modes are shown in Figure 2a. In these structures, the P=O moieties of trialkyl phosphate extractants are the donor groups, which bind to the U(VI) or Pu(IV) by neutral oxygen atoms and give rise to the strong extraction ability even under highly acidic conditions.^[18] Because the extraction ability of TBP for An(III)/Ln(III) is weaker than An(IV) and An(VI), thus uranium and plutonium in spent fuel can be separated by reducing Pu(IV) to Pu(III) using U(IV) or hydroxylamine derivatives as reductants. Notably, although the P=O group has a strong coordination ability for actinides, the oxygen atom in the phosphate group (P–O–R) can weaken this affinity to a certain extent. Therefore, the extraction ability of TBP is weaker than those of its homologs with fewer phosphate ester bonds, such as dibutyl phosphate(HDBP), which helps to

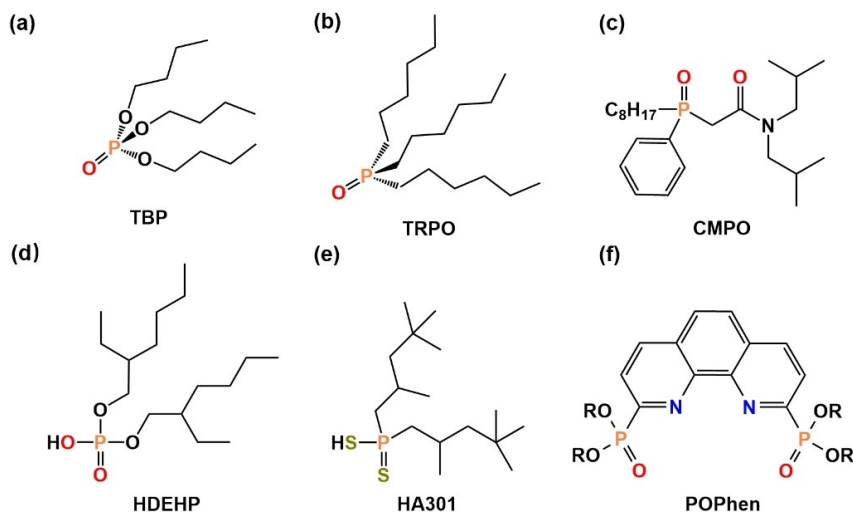


Figure 1. Several representative organophosphorus extractants reviewed in this concept: (a) tributyl phosphate (TBP); (b) trialkyl phosphine oxide (TRPO); (c) octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO); (d) Bis(2-ethylhexyl)phosphate (HDEHP); (e) bis(2,4,4-trimethylpentyl) dithiophosphinic acid (HA 301); (f) phosphonate-phenanthroline (POPhen).

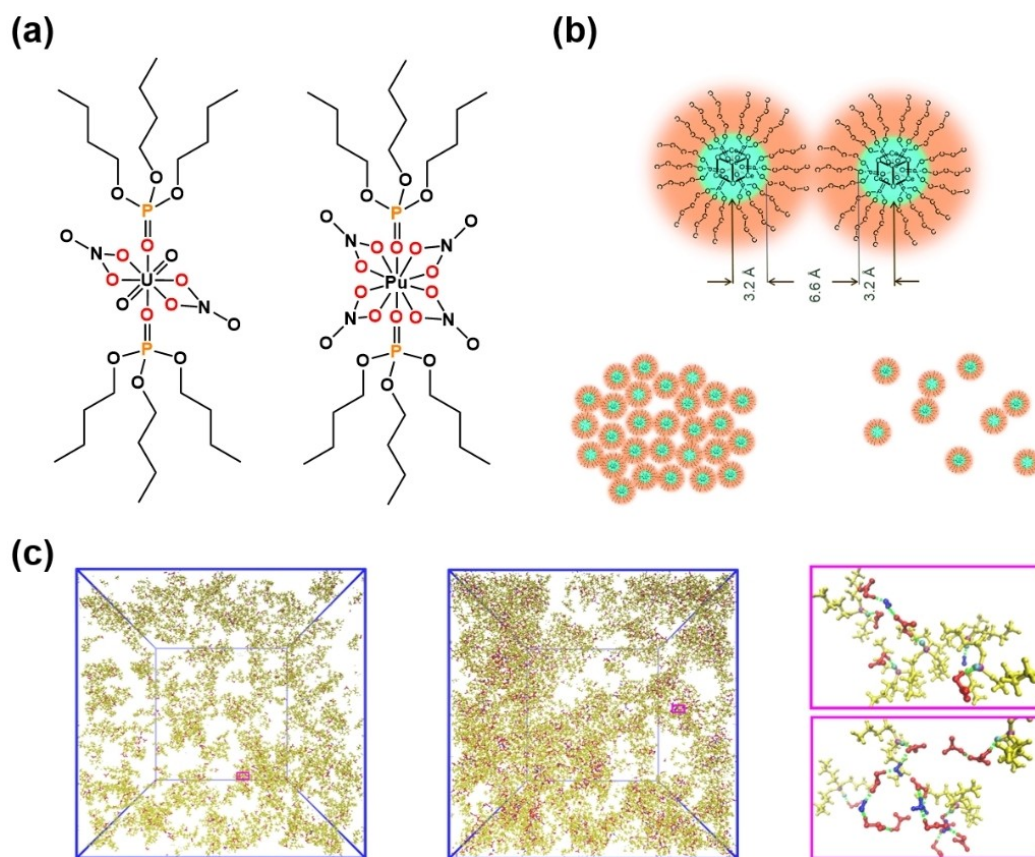


Figure 2. (a) The structure of $[\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2]$ and $[\text{Pu}(\text{TBP})_2(\text{NO}_3)_4]$. The probable mechanism of third-phase formation: (b) reverse micelle (Copyright © 2017 Royal Society of Chemistry.), and (c) micro-emulsion.^[16,17] (Copyright © 2018 American Chemical Society.)

elute the extracted actinides and keep a balance between extraction and stripping effects.^[19,20]

Otherwise, when extraction of high-concentration metal ions by those ligands like TBP in a strong nitric acid system, it

will form a third phase by reverse micelles or micro-emulsions mechanism, which will hinder the extraction process and hamper the subsequent stripping process (Figure 2b and c). This is because with the acidity and concentration of metal ions

in the aqueous phase increase, the extracted complex will be easier to gather and form reversed micelles. In systems with low concentrations of acid and metal ions, thermodynamically stable and evenly dispersed reversed micelle solutions are usually formed. When the concentration of acid or metal ions increases, more polar substances enter the reversed micelle core, increasing the mutual attraction between the micelles to form a third phase.^[21] Some researchers also believe that the extracted complexes may not aggregate as reversed micelle or W/O-type microemulsion, but exist as a continuous phase, whose microstructure is similar to the Winsor III microemulsion formed by surfactants. Both TBP/HNO₃/H₂O in organic phase and third phases can form the extended mesh aggregates through hydrogen bond interaction.^[16,17] The formation of the third phase can be reduced by appropriate adjustment of the alkyl side chains of the extractant to improve the solubility of the extracted complex in the organic phase and thereby promote its further industrial application.^[22]

2.2. Phosphorus oxide extractant

Substitution of the phosphate groups with alkyl moieties in trialkyl phosphate extractants and the trialkyl phosphate oxide (TRPO) extractants are obtained, which hold strong extraction ability for trivalent, tetravalent, hexavalent actinides and lanthanides, but with very weak affinity for cesium (I), strontium

(II) and other fission products in nitric acidic solutions (< 2 mol/L HNO₃).^[23] When using kerosene as the diluent, the mixed TRPO type extractants with different straight carbon chains (C6–C8) have a strong ability to selectively extract different f-elements (Ln(III)/U(VI)/Np(IV)/Pu(IV)/Am(III)/Cm(III)) over other fission products from highly-level liquid waste (HLLW).^[24] Using 5.5 mol/L nitric acid, 0.5 mol/L oxalic acid, and 0.5 mol/L Na₂CO₃ for multi-step stripping, three groups of Am(III)/Cm(III)/Ln(III), Np(IV)/Pu(IV) and U(VI) can be selectively stripped into aqueous phase respectively, so as to achieve the purpose of group separation of f-elements based on their different oxidation states.^[25,26]

The coordination chemistry properties between TRPO with different side chains (such as *i*-Pr and phenyl) and various f-block elements have been investigated.^[27–29] The single-crystal structures of lanthanides/actinides complexes with TRPO-type ligands are shown in Figure 3a. It was found that quite different complexation models were formed between different lanthanides with certain TRPO ligands due to the “lanthanide contraction” effects. Light lanthanides with larger radii can form larger coordination number complexes than those heavy lanthanides (from 9 to 7), and the number of TRPO molecules in the lanthanide complexes was reduced from 3 to 2. Similar to most lanthanide ions, TRPO and Am(III) can also form a 3:1 ligand-to-metal complex. However, for AnO₂²⁺ (An=U, Np) the 2:1 complex species are formed and in these structures two TRPO molecules simultaneously participate in coordination with

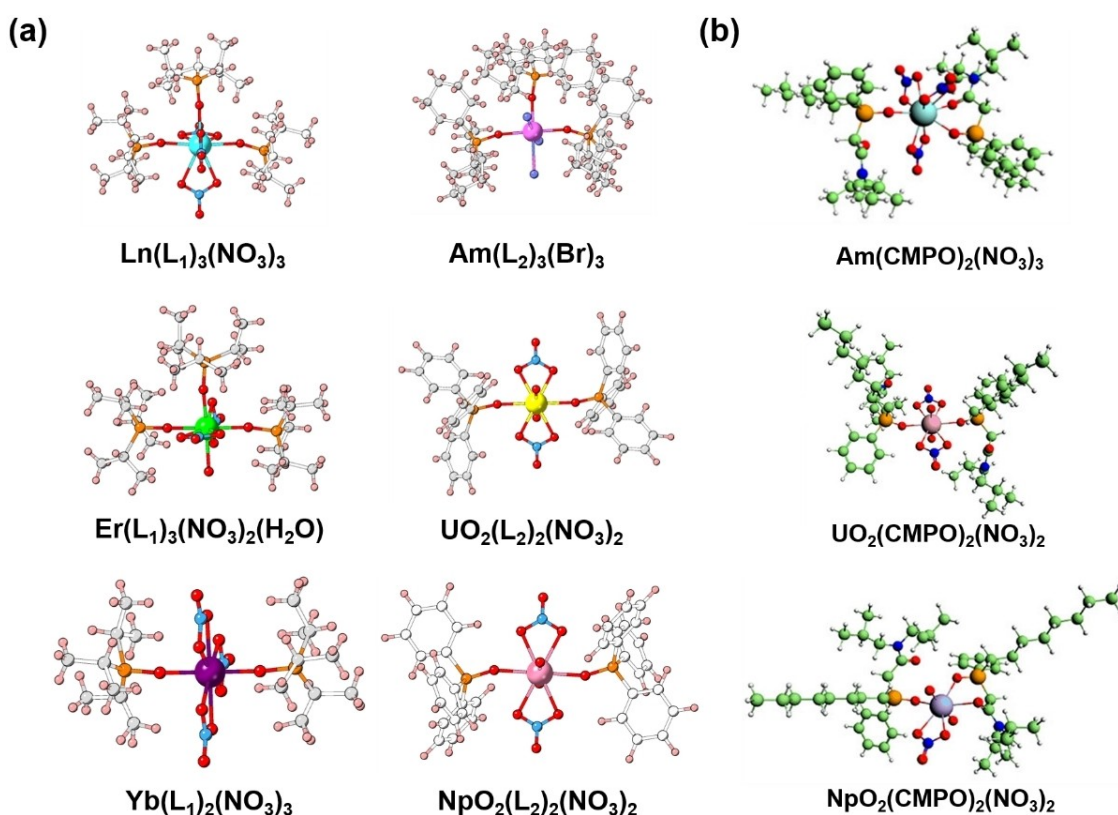


Figure 3. (a) Single-crystal structures of complexes formed between TRPO ($\text{L}_1 = \text{T}(i\text{-Pr})\text{PO}$; $\text{L}_2 = \text{T}(\text{Ph})\text{PO}$) and Ln(III) (La(III)–Pr(III), Er(III), Yb(III)), Am(III), U(VI), and Np(VI).^[27–29] (b) Simulated structures of complexes between CMPO and Am(III), Eu(III), U(VI), and Np(VI).^[30,31] (Copyright © 2013 American Chemical Society.)

actinides ion in the equatorial plane of AnO_2^{2+} . Additionally, two nitrate ions are involved in the coordination and maintain the electrical neutrality of the complex.

Another kind of phosphorus oxide extractant used for actinides/lanthanides separation is a series of bidentate hybrid extractants represented by CMPO, which have both phosphorus oxide and carbonyl as donor groups.^[32] CMPO can form stable complexes with different actinides (Am(III) , U(VI) , Np(VI) , etc.). Because nitrate anions participated in the formation of actinide complexes, so increasing the concentration of nitrate in the aqueous phase can strengthen the extraction ability of CMPO for actinides. The simulated structures of complexes formed between CMPO and Am(III) , U(VI) , and Np(VI) are shown in Figure 3b. In these ligands, the substituents of phosphoryl groups can adjust the extraction ability of extractants, while the substituents on the amide groups can modulate the ligands' selectivity and compatibility with organic solvents. Due to the steric hindrance and entropy effects, the higher degree of branching of the substituents, the lower the extraction ability of the extractants will have. There is an "abnormal aryl substitution effect" in those bidentate and multidentate phosphorus oxide extractants. When the alkyl group linked with a phosphorus atom is replaced by an aryl group, the extraction ability of the extractants will become stronger.^[33] This abnormal phenomenon may result from the aryl group as an electron-rich system, which can offer abundant electron clouds for the P=O bond during the coordination process, thereby can enhance the ligand's extraction ability for metal ions. Therefore, CMPO can effectively extract actinides and lanthanides under a wide range of nitrate acidic conditions. Further studies showed that the extraction ability of CMPO to Am(III) is stronger than that of lanthanide ions in high-acidity nitric or hydrochloric acid systems.^[34] These conclusions are further proved by DFT calculation studies at the theoretical level.^[30,31]

Based on the CMPO ligands, the TRansUranium EXtraction (TRUEX) process has been developed for co-extraction of both lanthanides and actinides in the first step and then followed by the multi-step stripping process using different eluents to achieve the separation of actinides over lanthanides in the second step.^[35] The main disadvantages of CMPO are its small load ability and poor compatibility with alkane diluents. These drawbacks can be resolved by adding synergetic extractants, such as 2,6-bis((diphenylphosphino)methyl)pyridine *N,P,P*-trioxide (NOPOPO), to improve the solubility of the extracted compound in organic solvents and increase the saturated extraction ability.^[36]

3. Acidic Organophosphorus Extractants

3.1. Organophosphorus acid extractant

The organophosphorus acid extractant can ionize protons and exist as hydrogen bond dimers in an aqueous solution. During the extraction process, organophosphorus acid extractant could bond with metal ions to form the stable extracted complex via a cation-exchange mechanism with protons. When lactic acid is

added to the solution, this type of extractant simultaneously coordinates with two metal ions by different donor groups to form a bridged multicore metal-ligand complex as shown in Figure 4a–c.^[37]

The extraction ability of organophosphorus acid type extractants is mainly dependent on the acidity of the phosphonic acid group: the introduction of a strong electronegative substituent directly connected to the P=O group helps to reduce the pK_a value and increase the acidity of the extractant, thereby enhancing its extraction ability.^[41] The structure of the alkyl side chains can also significantly affect the extraction ability: branched chains with large steric hindrances will hinder the occurrence of the extraction reaction, thereby weakening the ligand's extraction ability for metal ions. As a representative of organophosphorus acid extractants, HDEHP has a strong extraction ability for both An(III) and Ln(III) under low acidity conditions (0.01–0.1 mol/L HNO_3), which was selected as the extraction reagent in the Trivalent Actinide Lanthanide Separation with Phosphorus-reagent Extraction from Aquatic Complexes (TALSPEAK) process.^[38] This process uses lactic acid as a buffer reagent to maintain the pH of the solution in the range of 2.5–4.5. The water-soluble diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid (DTPA, Figure 4d) ligand containing soft N donor atoms is employed as an actinide-selective holdback reagent, which can selectively complex with An(III) and prevent them from being co-extracted by HDEHP together with Ln(III) into the organic phase, thereby achieving the purpose of separation An(III) over Ln(III) . The extraction ability of HDEHP toward An(III) and Ln(III) in the absence and attendance of DTPA is shown in Figure 4e. In the absence of DTPA, HDEHP showed similar extraction performance for An(III) and Ln(III) . On the contrary, when adding DTPA into aqueous phase, HDEHP exhibits a much stronger extraction ability for An(III) than Ln(III) . This is because that DTPA can form the water-soluble complex with Ln(III) and effectively inhibit the extraction of An(III) by HDEHP into organic phase. It was also found that with the concentration of DTPA increasing from 0.001 mol/L to around 0.1 mol/L, both the distribution ratios of An(III) and Ln(III) decreased simultaneously with the $SF_{\text{Nd/Am}}$ values maintained around 10 (Figure 4f).^[40,42]

3.2. Thiophosphonic acid extractant

According to the hard-soft acid-base (HSAB) theory, the An(III) are softer acids than Ln(III) because of the more diffused **5f** electron orbitals than that of **4f** electron orbitals.^[43] As above mentioned, organophosphorus extractants have the P=O groups with a strong electronegative hard O donor atom, which lacks $\text{An(III)}/\text{Ln(III)}$ selectivity. Due to the stronger polarizability, the S atom is a much softer donor atom than O, so it has a stronger affinity for softer An(III) than Ln(III) and holds $\text{An(III)}/\text{Ln(III)}$ selectivity.^[44] Based on this, a typical extraction process for the separation of An(III) over Ln(III) using the S-donor extractant dithiophosphonic acid (Cyanex 301) has been developed by Tsinghua University, whose separation effect has also been evaluated in hot test.^[45]

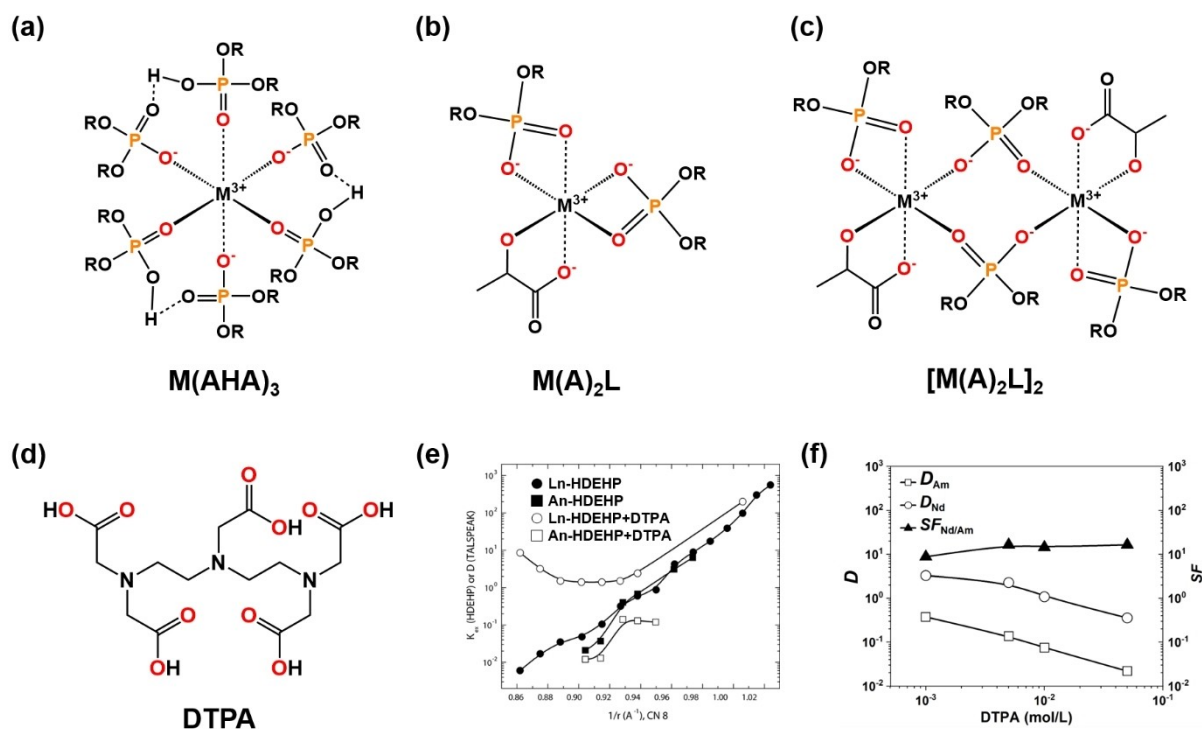


Figure 4. The structures of M-HDEHP complexes ($M = \text{An(III)/Ln(III)}$, $HA = \text{HDEHP}$, $L = \text{lactic acid}$). (a) $M(AHA)_3$, (b) $M(A)_2L$ and (c) $[M(A)_2L]_2$; (d) Molecular structure of DTPA.^[38] (e) The extraction ability of HDEHP on An(III) and Ln(III) with or without DTPA.^[39] (Copyright © 1968 Published by Elsevier Ltd.) (f) Effect of DTPA concentration on the extraction of Am(III) and Nd(III).^[40]

The so-called purified Cyanex 301 is [bis (2,4,4-trimethylpentyl) dithiophosphonic acid (HA301, and its separation factor ($SF_{Am/Eu}$) of HA301 for Am(III) over Eu(III) is up to 5800 ($T = 298 \text{ K}$) (Figure 5a).^[44] Coordination chemistry behaviors studies demonstrate that the extraction mechanism of HA301 for lanthanide series is different due to the lanthanide contraction effect.^[46] The schematic diagram for revealing this mechanism is shown in Figure 5b. All Ln(III) are coordinated with three HA301 molecules to form the 1:3 metal-to-ligand complexes, and HA301 has strong affinity for light lanthanide (La(III)) complex than those of heavy lanthanides. From light lanthanides to heavy lanthanides, the number of sulfur atoms in the inner coordination sphere decreases and the number of oxygen atoms increases. This confirms that during the complexation process, the lighter lanthanides tend to form an inner-sphere complex, while the heavier lanthanides tend to form an outer-sphere complex with HA301.^[50] The DFT calculation and coordination experiments were combined to study the differences in extraction mechanism and coordination strength between HA301 and An(III)/Ln(III): Calculated ML_3 ($M = \text{Eu(III)}$, Am(III) , and Cm(III) ; $L = \text{HA301}$) structure with C_3 symmetry is shown in Figure 5c, which is the most stable complex in gas phase. Theoretical and experimental results proved that the covalency extent of the coordination bond, the degree of desolvation, and the coordination mode all affect the extraction ability of HA301 and An(III)/Ln(III).^[47,51]

Although HA301 has a good An(III)/Ln(III) separation ability, there still exist some problems in practical application: (1) The

operating acidity is much lower than real HLLW (3–4 mol/L HNO_3) with a narrow range ($\text{pH} = 3.5\text{--}4.0$); (2) The structural stability of HA301 is inadequate under irradiation and acid conditions.^[52] To overcome these shortcomings, researchers have synthesized a series of dialkyl and diaryl substituted dithiophosphonic acid extractants (Figure 5d), and studied the relationship between their structures and extraction properties as follows: the dithiophosphonic acid extractants with symmetrical alkyl chains have strong extraction and separation ability toward An(III) over Ln(III), whose extraction ability increases with the decrease of the branching degree of alkyl chains.^[48] The introduction of electron-donating (such as $-\text{CH}_3$) groups can enhance the extraction ability of aryl-armed dithiophosphonic acid ligands, but the introduction of strong electron-withdrawing groups (such as $-\text{CF}_3$) can improve the selectivity between Am(III) and Ln(III).^[49] Adding synergistic extractants such as TBP can also enhance the extraction ability of the HA301 system under the premise of ensuring the Am(III)/Eu(III) separation ability of HA301.^[53]

4. Pre-Organized Organophosphorus Extractants

The degree of the skeleton pre-organized of one extractant can significantly affect its extraction performances toward metal

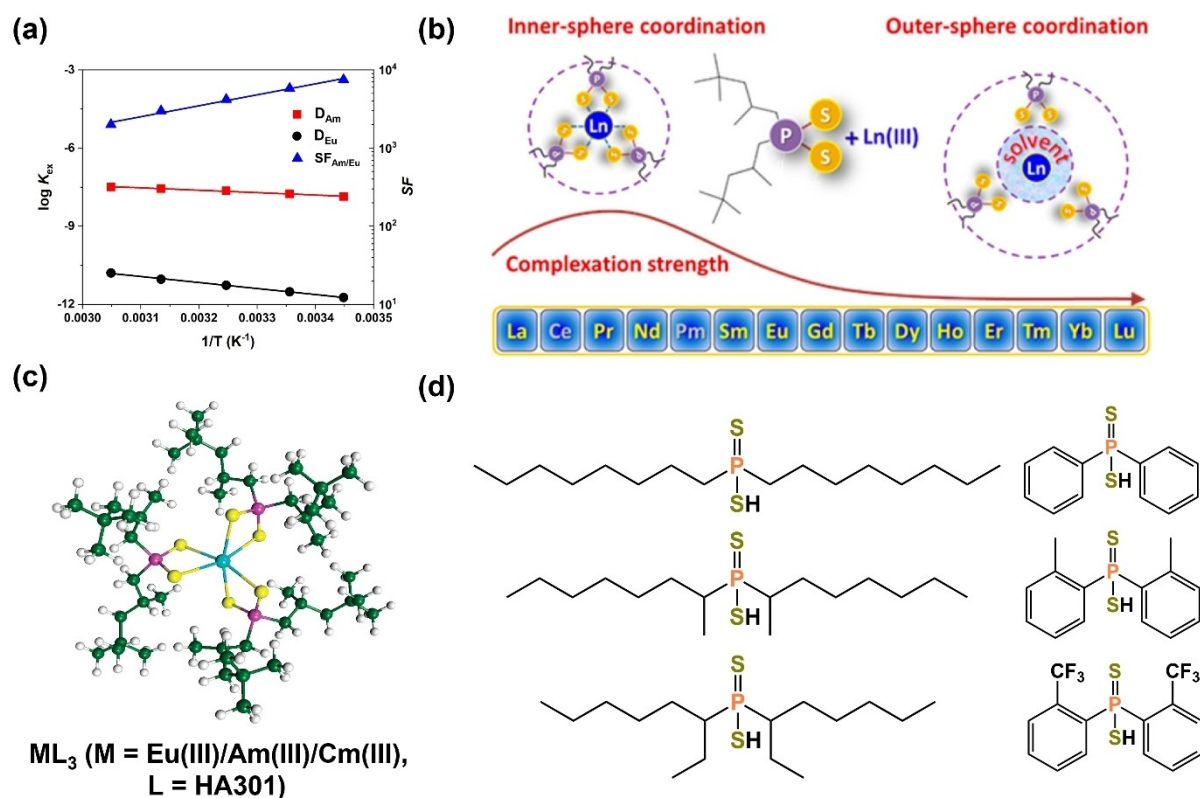


Figure 5. (a) The effect of temperature on the extraction of Am(III) and Eu(III) by HA301.^[44] (b) Schematic diagram of the transition of coordination mode between HA301 and lanthanides.^[46] (Copyright © 2017 American Chemical Society.) (c) Calculated ML_3 ($M=Eu(III)$, $Am(III)$, and $Cm(III)$; $L=HA301$) structure with C_3 symmetry.^[47] (Copyright © 2010 American Chemical Society.) (d) The layout diagram of the demonstration platform.^[48,49]

ions including extraction ability, extraction rates and selectivity. The reasons can be divided into the following two parts:

- (1) The rigid structure of the extractant will reduce both the required energy to twist into a complex conformation and the energy threshold of the extraction reaction. Meanwhile, the pre-organized skeleton is conducive to increasing the entropy of the coordination reaction, which improves the complex stability and the ion-recognition ability of ligands.^[54]
- (2) Because lanthanides and actinides are high coordination number ions with f-orbitals, which can chelate with multiple functional groups simultaneously. Some pre-organized extractant skeletons can provide additional donor atoms, which have a great promotion on the chelation and extraction ability of f-element.^[55]

Therefore, grafting organophosphorus extractants on some pre-organized skeletons to develop some novel extractants can improve their extraction ability and selectivity for actinides over lanthanides.^[56]

4.1. Supramolecular-based organophosphorus extractant

There are a variety of excellent advantages of macrocycle supramolecular compounds represented by calixarene and pillararene, such as easy synthesis, strong thermal and chemical

stability, and high radiation resistance.^[57,58] By modifying different edges of the benzene ring, adjusting the bridge chain between structural units, and regulating the size of the skeleton cavity, the calixarene, pillararene and their derivatives can form stable complexes with different metal cations.^[59] At the same time, the special structural characteristics of calixarene provide an ideal rigid or semi-rigid platform for coordination with actinides, whose pre-organized skeleton plays an important role in improving the extraction ability and selectivity of the extractant (Figure 6a).^[60]

CMPO is introduced on the upper and lower edges of the calixarenes, which are more conducive to selectively binding with An(III) and Th(IV) respectively due to their different sizes of coordination cavity built by the constrained CMPO-calixarenes groups.^[63] The structures of CMPO-modified calixarene extractants are shown in Figure 6b. This functionalization of calixarenes increases the extraction selectivity for Am(III) over Eu(III) but has little effect on its extraction ability. As shown in Figure 6c, CMPO-calix[4]arenes extractants have stronger extraction ability for Am(III) and Cm(III) and hold larger $SF_{Am/Eu}$ values than initial CMPO ligand under the same conditions. Meanwhile, the introduction of calixarene can also strengthen the chemical stability and radiation resistance of extractants.^[61] Further studies showed that the local chelation environment of CMPO-calixarene can also be adjusted by changing the structure of the intramolecular hydrogen bond, thereby changing its

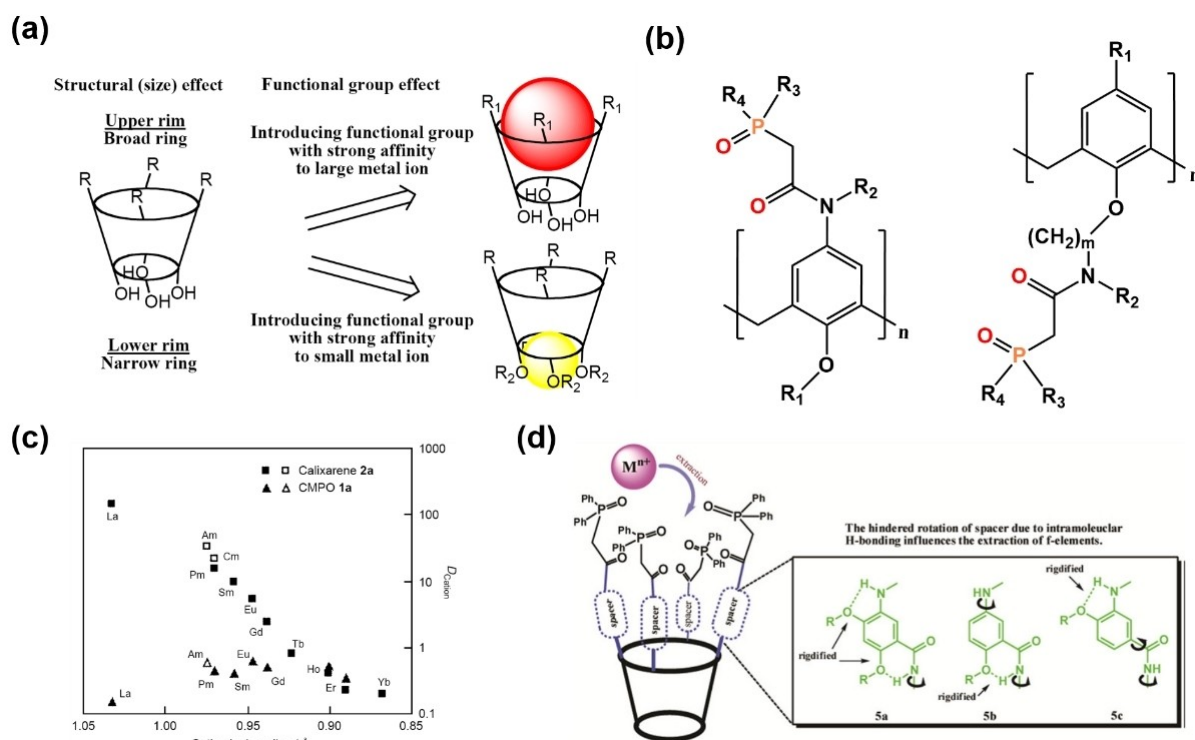


Figure 6. (a) Multiple affinity effects of cyclic structure and functional group.^[60] (Copyright © 2010 Japan Association of Solvent Extraction.) (b) The structures of CMPO-calixarene extractants. (c) The difference between the extraction ability of CMPO-calixarene and CMPO.^[61] (Copyright © 1998 Royal Society of Chemistry) (d) Intramolecular hydrogen bonding affects the extraction ability of CMPO-calixarene on f-element.^[62] (Copyright © 2014 Published by Elsevier Ltd.)

extraction ability on lanthanides/actinides (Figure 6d).^[62] How to increase the solubility of the CMPO-calixarenes extractant in the organic phase to a higher level (such as 0.1 mol/L) is the key problem that needs to be solved. Through structural modification, using some new organic phases may be an effective way to solve this problem, which is very important for designing highly efficient CMPO-calixarenes derivatives for the separation of actinides from HLLW.^[64]

Compared with traditional organophosphorus extractants, pillararene-based organophosphorus extractants exhibit higher extraction efficiency, better separation performance and stronger irradiation stability, when they are used for separation of actinides by solvent extraction.^[70] The functional side chains (phosphorus oxide, CMPO, etc.) that serve as chelating agents are symmetrically anchored at the edges of the highly organized pillararene skeleton (Figure 7a).^[65] The phosphorus oxide functionalized pillararenes exhibit stronger extraction ability for actinides (U(VI), Am(III), and Pu(IV)) in ionic liquid (RTIL) than that in dichloromethane (DCM) at room temperature. As shown in Figure 7b, it was found that the distribution ratios of actinides are greatly affected by acidity in aqueous phase, and the $D_{\text{Pu(IV)}}$ shows an opposite trend to $D_{\text{Am(III)}}$ and $D_{\text{U(VI)}}$.^[66] The extractants could be protonated under high acidity conditions, which produces electrostatic repulsive interactions with metal cations, thereby reducing the extraction ability. However, the Pu(IV) will generate $[\text{Pu}(\text{NO}_3)_6]^{2-}$ anion in a high-concentration nitric acid system, which can be more easily

combined with the protonated extractant, thereby improving its extraction.^[66] The unique host–guest interaction between the supramolecular and metal ions are proved by MS, NMR, fluorescence and IR techniques, which contributes to a stepwise extraction mechanism of competitive substitution in RTIL extraction systems (Figure 7c).^[68] During this coordination process, the shorter side chains with stronger rigidity can hinder the extractant to transform into a suitable conformation for binding with metal ions. However, the longer side chains allow the chelating group to rotate flexibly and freely, which is conducive to binding with metal ions. In conclusion, the solvent extraction and DFT calculation confirm that the CMPO-functionalized pillararenes in RTIL system have good potential application in selectively separate actinides from other fission products (Cs(I), Sr(II)) (Figure 7d).^[69]

4.2. Phenanthroline-based extractant

More recently, in our group, another class of pre-organized phenanthroline-derived organophosphorus extractants (phosphonate, phosphorus-oxide, and phosphinate) were designed based on the “soft-hard donor combined” strategy, which contains both the soft N atoms and hard O atoms for separation of actinides over lanthanides.^[71] According to the differences between organophosphorus functional groups, organophosphorus-phenanthroline extractants can be divided into phos-

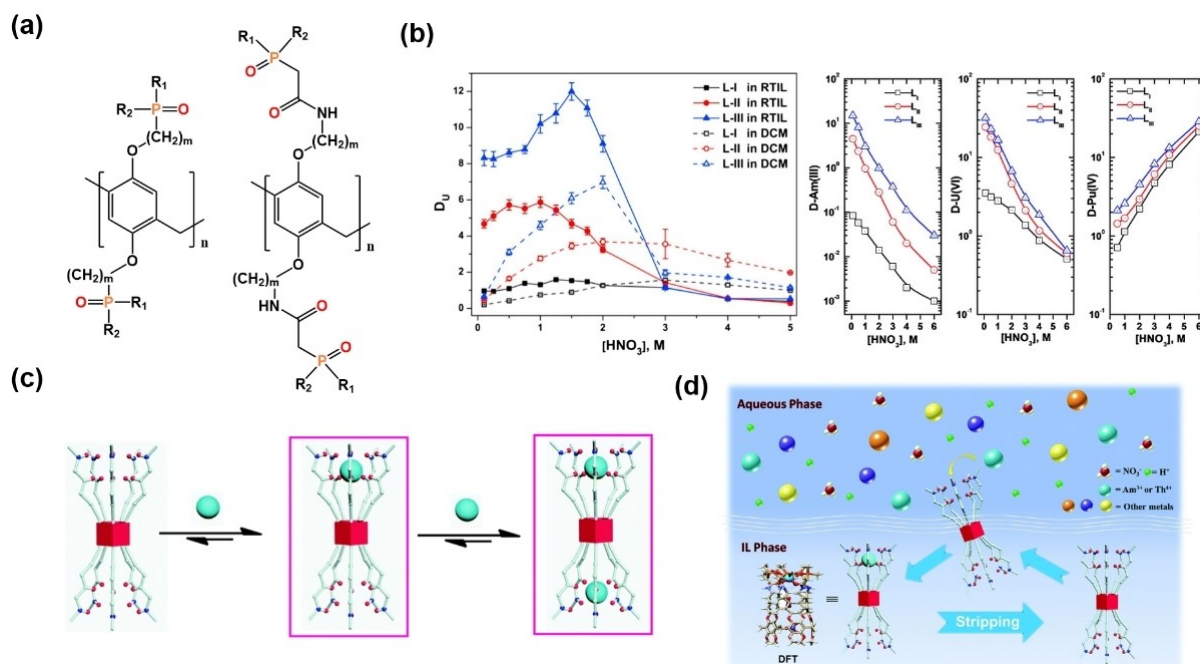


Figure 7. (a) The structures of phosphorus oxide and CMPO modified pillararene extractants.^[65] (b) The extraction of phosphorus oxide pillararene toward actinides in DCM and RTIL.^[66,67] (Copyright © 2017 Published by Elsevier Ltd.; Copyright ©2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) (c) The unique stepwise binding mechanism of the CMPO-functionalized pillararenes with Am(III).^[68] (Copyright © 2014 Royal Society of Chemistry) (d) Extraction and complexation process of some actinides with CMPO-functionalized pillararenes in RTIL.^[69] (Copyright ©2017 Elsevier B.V. All rights reserved.)

phonate-phenanthroline (POPhen), bis(phosphine-oxide)-phenanthroline (BPPhen), and phosphinate-phenanthroline (PIPhen).^[73,74] The structures of these three kinds of phenanthroline-based extractants are shown in Figure 8a–c. Of which, the C4-POPhen ligand has a significant extraction selectivity for

Am(III) over Eu(III) ($D_{Am(III)} > 100$, $SF_{Am/Eu} > 7$) under high acidic conditions (2 mol/L HNO_3).^[75] The increase in the length of the carbon chain from ethyl to n-butyl improves the solubility of the extracted compound in the organic phase and thus promotes the metal ions extraction.^[76] It was found that the

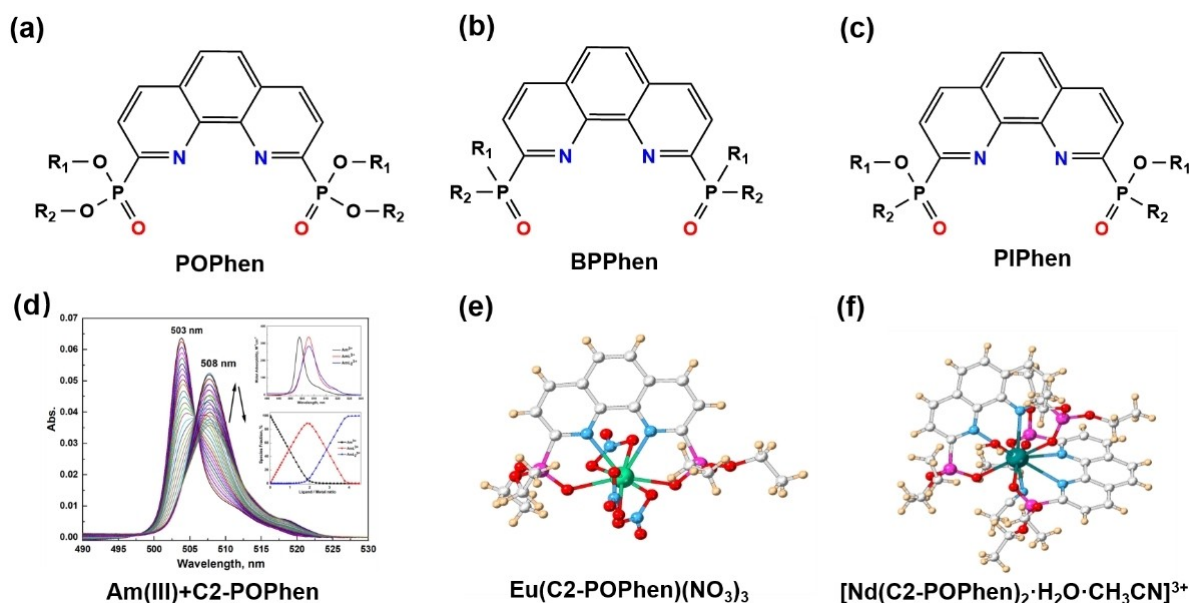


Figure 8. Molecular structures of (a) POPhen, (b) BPPhen, and (c) PIPhen. (d) UV-vis titration of Am(III) and C2-POPhen.^[71] (Copyright © 2019 American Chemical Society.) Single-crystal structures of (e) Eu(C2-POPhen)(NO₃)₃ and (f) [Nd(C2-POPhen)₂·H₂O·CH₃CN]³⁺ complexes.^[72]

extraction selectivity of Am(III)/Eu(III) can be further improved by using isopropyl or cyclohexyl substituted *i*Pr-POPPhen and cHex-POPPhen extractants as a result of the steric hindrance of these two substituents ($D_{\text{Am(III)}/\text{Eu(III)}} > 100$, $SF_{\text{Am(III)}/\text{Eu(III)}} > 10$, 2 mol/L HNO_3).^[73]

Otherwise, the introduction of phenyl-armed phosphorus oxide groups as side chains into the phenanthroline skeleton can significantly enhance the extraction ability of the extractant but weaken its Am(III)/Eu(III) separation factor ($D_{\text{Am(III)}/\text{Eu(III)}} > 500$, $SF_{\text{Am(III)}/\text{Eu(III)}} < 5$, 2 mol/L HNO_3).^[77] Results of spectroscopy, single-crystal diffraction and theoretical calculations studies show that organophosphorus-phenanthroline extractants could form two complexes species ($M:L = 1:1$ and $1:2$) with An(III)/Ln(III) (Figure 8d–f). Further studies showed that POPPhen has a stronger affinity for heavy lanthanides than light lanthanides ($\text{Lu(III)} > \text{Eu(III)} > \text{La(III)}$), which may be a result that the heavier lanthanides with smaller radii match well with the cavity size of the structure of extractant. What's more, different counter anions also have a significant impact on the coordination ability of POPPhen ($\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^-$), which may be caused by the different competition coordination abilities between extractants and counter anions with metal ions.^[72] Compared with BPPhen, PIPhen with two phosphinate groups has a higher Am(III)/Eu(III) extraction and separation ability, but its separation factor is still lower than that of POPPhen ($D_{\text{Am(III)}/\text{Eu(III)}} > 700$, $SF_{\text{Am(III)}/\text{Eu(III)}} < 5$, 2 mol/L HNO_3).^[78] Therefore, how to modify the structure of phenanthroline-derived organophosphorus extractants and improve their separation ability for Am(III) over Eu(III) still needs to be further studied.

4.3. Carborane-based extractant

In addition to using the usual organic-phase extraction and aqueous-phase stripping in traditional liquid-liquid solvent extraction method, other separation methods by regulating the inherent properties of the extractant to change its affinity for the target metal ions, so as to selectively capture-release the target metal ions and achieve the purpose of separation. Ménard's group has designed and synthesized an ortho-substituted nido-carborane anion, $[1,2-(\text{Ph}_2\text{PO})_2-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ ($^{\text{PO}}\text{Cb}^{2-}$), which contains two phosphate groups as donor groups.^[79] The conformation of $^{\text{PO}}\text{Cb}^{2-}$ could be elegantly adjusted by the electrochemical oxidation-reduction method, which can be used to adjust the angle between the carbon borane and the phosphate groups in the ligand (Figure 9a). When closo-carborane is reduced to nido-carborane, it breaks the C–C bond and opens the cage and thus $^{\text{PO}}\text{Cb}^{2-}$ can form a $[\text{UO}_2\text{X}_n(^{\text{PO}}\text{Cb})_{(2-n/2)}]^{2-}$ ($n=0, 2$; $\text{X}=\text{Cl}^-, \text{OAc}^-$) complex with UO_2^{2+} ions. When oxidized by the electrochemical method, $^{\text{PO}}\text{Cb}^{2-}$ will change to the closo-conformation and lose the ability to coordinate with UO_2^{2+} ions. Figure 9b confirms that the $^{\text{PO}}\text{Cb}/^{\text{PO}}\text{Cb}^{2-}$ system has a strong ability to extract UO_2^{2+} , a weak ability to extract Th(IV) ($SF_{\text{U/Th}} = 25$), and no extraction for Nd(III), Sm(III), and Cs(I). As shown in Figure 9c, these capture and release processes make this system the ability to selectively extract UO_2^{2+} ions over other interfering metal ions like Cs(I), Th(IV), Sm(III) and Nd(III) from aqueous phases.^[80]

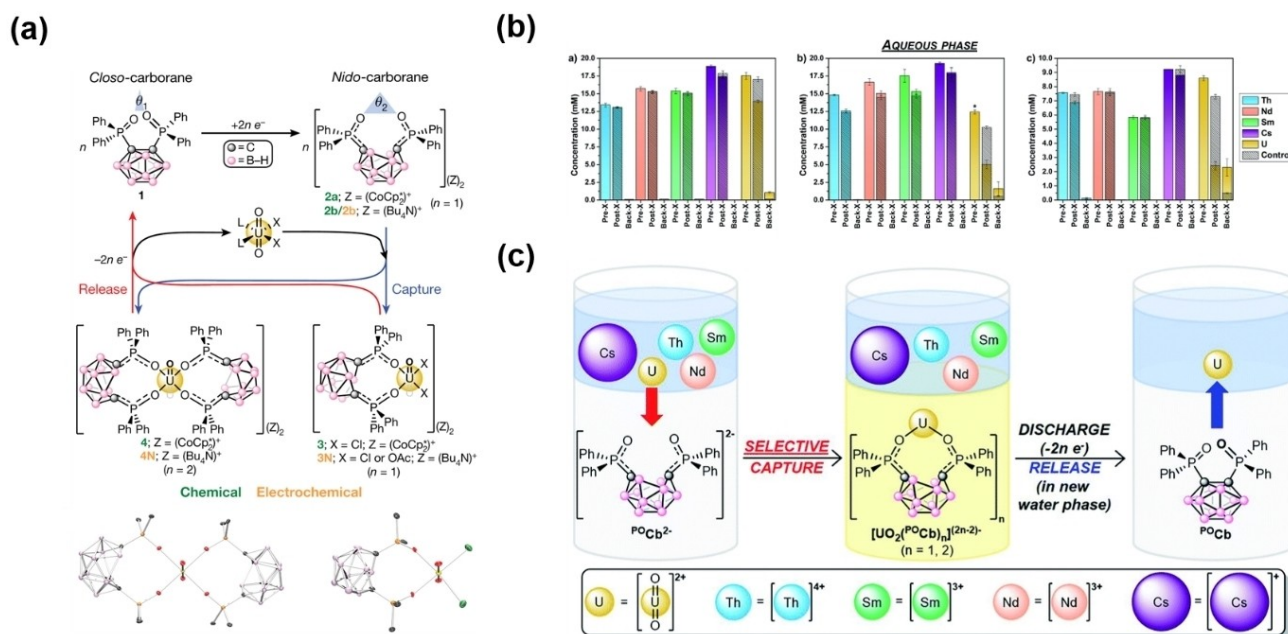


Figure 9. (a) Mechanism of the chemical or electrochemical capture and release of UO_2^{2+} with closo-carborane/nido-carborane system.^[79] (Copyright © 2020, The Author(s), under exclusive licence to Springer Nature Limited) (b) The selective electrochemical capture and release effect of UO_2^{2+} using the $^{\text{PO}}\text{Cb}/^{\text{PO}}\text{Cb}^{2-}$ system in DCE. (c) Selective capture and release of UO_2^{2+} from aqueous solutions containing alkali, lanthanide, and actinide metals by using the $^{\text{PO}}\text{Cb}^{2-}/^{\text{PO}}\text{Cb}$ system.^[80] (Copyright © CC BY-NC 3.0)

5. Conclusion and Perspective

In recent decades, a series of in-depth research has been conducted on the application of various acidic and neutral organophosphorus extractants for the separation of actinides over lanthanides in spent nuclear fuel. TBP has a good affinity for tetravalent and hexavalent actinides, which are used in the extraction and separation of uranium and plutonium in the PUREX process. TRPO and CMPO contain phosphorus oxide groups with high coordination capabilities and thus they have strong extraction capabilities for both actinides and lanthanides. The purpose of separating actinides from lanthanides can be achieved through different stripping methods. HDEHP is also an extractant with a strong extraction ability to f-block elements. After combining with the masking agent DTPA in the aqueous phase, An(III) and Ln(III) can be efficiently separated by HDEHP. The soft S donor ligand Cyanex 301 brings to a high Am(III)/Eu(III) selectivity. However, the weak stability and separation ability under high acidity constrain the practical application of Cyanex 301. Combining the pre-organized calixarene and pillararene skeletons with organophosphorus extractant can improve their extraction selectivity for target ions. But their solubility in conventional organic solvents (such as kerosene and n-dodecane) is insufficient. The phenanthroline organophosphorus extractants have a high extraction ability for lanthanides and actinides, but their separation ability still needs to be improved. These organophosphorus extractants have been considered a class of very promising extractants for actinides/lanthanides separation in practical applications due to their strong extraction ability, high selectivity, strong lipophilicity, and convenience for stripping. Therefore, exploring the extraction mechanism at the microcosmic level, proposing a design strategy from the perspective of molecular structure, and developing some new high-efficient extractants have both scientific research value and practical significance.

The inter-group and intra-group separation of actinides/lanthanides with extremely similar ion radii and chemical properties is a challenging scientific problem and it is difficult to obtain satisfactory extraction and separation performance by various commercialized organophosphorus extractants. At the same time, the research on the coordination chemistry and extraction mechanism between extractant and metal ions are still relatively shallow. Therefore, we believe that the researchers should mainly focus on the following areas in future:

- (1) Most of the non-polar groups in the molecules of organophosphorus extractants are linear-chain typed alkyl or aryl groups. There are barely substituent groups with different functional effects on these side chains. These structural characteristics limit the wide-ranged regulation of the electronic and steric hindrance effects in organophosphorus extractant molecules. Therefore, to reveal the structure-activity relationships between ligand structure and its extraction performance, to design and synthesize the organophosphorus extractants with new kinds of side chains may become one of the future research directions. Such as asymmetric structures with different non-polar substituent groups; cyclic structures with cyclic substituent

groups or ring-forming substituent groups on phosphorus atoms; complex structures with different functional groups such as hydroxyl groups and halogens on the side chains high-stability structures combined with pre-organized skeletons (rigid or semi-rigid).

- (2) The radioactive and chemical toxic actinides are usually replaced by non-radioactive lanthanides in coordination mode and extraction mechanism studies. This kind of approximate replacement method could not accurately verify the actual coordination/extraction mechanism, nor differentiate the minute chemical properties between the actinides/lanthanides. Therefore, based on the radioactive spectroscopy experimental platform, it is of great significance to explore the coordination mode and extraction mechanism between radioactive actinides and organophosphorus extractants by UV-vis titration, single-crystal structure diffraction, extended X-ray absorption fine structure (EXAFS), and other direct experimental methods.
- (3) During the extraction and separation process, the dynamic chemical reaction and the complex reaction system synergistically result in the inconspicuous visualized phenomenon. Some advanced high-precision in-situ characterization methods such as graze incident X-ray diffraction (GIXRD), graze incident small-angle X-ray scattering (GISAXS), X-ray absorption near edge structure (XANES), neutron diffusion and neutron depth profiling (NDP) should be used to explore the extraction dynamic reaction process and material transfer mechanism inside and between the two phases in future studies.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: actinides/lanthanides separation • coordination chemistry • organophosphorus extractant • pre-organization • solvent extraction

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