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Study on the Extraction and Coordination Properties of U(VI) with Four Asymmetric

Diglycolamides

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Abstract

Diglycolamides, (DGAs) as effective clean ligands capable of extracting trivalent lanthanides and actinides from HLLW, have garnered widespread attention in the research on HLLW separation. In this article, four asymmetric diglycolamides, namely: N,N'-dimethyl-N,N'-di(1-methylheptyl) diglycolamide (DMBMHDGA, L¹), N,N'-dimethyl-N,N'-di(1-ethylhexyl) diglycolamide (DMBEHDGA, L²), N,N'-dimethyl-N,N'-di(2-methylheptyl) diglycolamide (DMB2MHDGA, L³), N,N'-dimethyl-N,N'-di(2-ethylhexyl) diglycolamide (DMB2EHDGA, L⁴), were synthesized using the acyl chlorides method. The extraction performance of U(VI) under different extraction conditions in an HNO₃ system using four ligands was investigated. The structural information of the four ligands and their complexes with U(VI) was analyzed by density functional theory (DFT). The study showed that L¹ exhibited better extraction efficiency for U(VI) compared to the other three ligands, and all four ligands formed 1:1 or 2:1 complexes with U(VI). Furthermore, U(VI) primarily interacted with three oxygen atoms of each ligand through electrostatic interactions and electrostatic interactions with partial

covalent character to form complexes. The results indicated that ligands with shorter alkyl branches and α -positioned alkyl branches demonstrated superior extraction performance.

Key words: Uranium(VI); Liquid-Liquid extraction; Coordination DFT; Asymmetric diglycolamide

Introduction

The global energy landscape is accelerating its transformation, with nuclear power development incorporated into the national energy security strategies of many countries to transition energy systems from high-carbon to low-carbon. However, the long-term management and disposal of spent nuclear fuel will face significant challenges [1, 2]. High-level liquid waste (HLLW) generated during the Purex process contains over 95% of the radioactivity from spent fuel, including trace amounts of unrecovered U and Pu, as well as minor actinides (such as Am, Np, Cm), long-lived fission products (such as Tc, Cs, Sr), and lanthanides [3–5]. One approach to handling HLLW is to adopt Partitioning and Transmutation (P&T) technology [6]. Lanthanide elements have large neutron absorption cross-sections and significant industrial application value. Therefore, proper separation of lanthanide elements not only ensures the smooth progress of transmutation but also benefits the rare earth industry [7–9]. To prevent secondary pollution caused by sulfur- or phosphorus-containing organic ligands used in the process during incineration treatment, diamide podand ethers, which exhibit good extraction performance for lanthanides and actinides and comply with the CHON principle, have attracted extensive attention from scholars at home and abroad [10–12].

Diglycolamides (DGAs) have attracted considerable attention because they not only comply with the CHON principle but also exhibit greater molecular flexibility and more coordination sites than

malonamide-based ligands [13–16]. If two N atoms of DGAs are connected to four identical groups, this DGA is called a symmetric DGA. Sasaki and his colleagues were the first to conduct a comprehensive study on symmetric DGAs [17]. They synthesized and tested DGAs containing straight alkyl chains with different lengths ranging from methyl to decyl, and found that N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) exhibited high distribution ratios for actinides (Am(III), Th(IV), Pu(IV), U(VI), etc.) and lanthanides, while also demonstrating good radiolysis stability [17–19]. During solvent extraction mediated by TODGA, the organic phase may split and form a third phase capable of enriching radioactive nuclides. This poses a nuclear criticality risk, disrupts process operational stability, reduces separation efficiency, and seriously threatens the safety and economy of nuclear facilities [20]. To effectively suppress this organic phase splitting behavior, phase modifiers such as N,N-dihexyloctanamide (DHOA), tributyl phosphate (TBP), n-octanol, and n-decanol are typically introduced into the extraction system [21, 22]. However, the introduction of phase modifiers also gives rise to secondary effects, such as promoting excessive extraction of nitric acid and co-extraction of fission product elements, thereby adversely affecting extraction selectivity [21, 23]. To address the challenge of third-phase formation in solvent extraction, research focus has gradually shifted toward asymmetric diglycolamides bearing different alkyl substituents on the amide nitrogen atoms. Their short-chain substituents alleviate steric hindrance during extraction coordination, while the long-chain substituents reduce the polarity of the metal complexes, thereby enhancing solubility in nonpolar diluents [24–26]. Experiments have shown that these ligands can effectively suppress or even circumvent the third-phase phenomenon, while maintaining efficient extraction of trivalent lanthanide and actinide ions and exhibiting higher extraction capacity.

At present, the asymmetric DGAs investigated in the literature generally fall into two categories:

If the alkyl chains attached to the same N atom are the same, it is referred to as Type I asymmetric DGAs; otherwise, it is Type II asymmetric DGAs. Ravi and Sasaki's team found that asymmetric DGAs of type I and type II (such as N,N,-di-dodecyl- N',N' -di-octyl-3-oxapentane-1,5-diamide(D3DODGA), N,N' -dimethyl-N,N' -dioctyl-3-oxapentane-1,5-diamide (DMDODGA), etc.) exhibit superior extraction capabilities for nuclides such as U(VI) or Ln (III) in HNO₃ systems compared to symmetric DGAs. Moreover, even without the addition of phase modifiers, they are less prone to generating third-phase substances, thereby reducing the generation of hazardous organic waste and secondary waste to a certain extent [18, 27–29]. In addition, Gujar et al. replaced the straight chain of symmetric DGA with a branched alkyl substituent (N,N, N', N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA)). Although T2EHDGA has a relatively low distribution for U(VI), it achieved the separation of Am(III) from other metal ions [30]. Mowafy et al. varied the chain length and degree of branching of the linear alkyl substituents on the nitrogen atoms of diamide podands, and found that in nitric acid media, the distribution ratio of Ln(III) decreases with increasing chain length, while the extraction performance of ligands bearing branched alkyl chains is consistently inferior to that of their corresponding linear-structured counterparts [31].

At present, there are few studies on the extraction performance of the short chain substituents located at the α and β positions of the long chain substituents, so four kinds of asymmetric diglycolamides, namely: N,N'-dimethyl-N,N'-di(1-methylheptyl) diglycolamide (DMBMHDGA, L¹), N,N'-dimethyl-N,N'-di(1-ethylhexyl) diglycolamide (DMBEHDGA, L²), N,N'-dimethyl-N,N'-di(2-methylheptyl) diglycolamide (DMB2MHDGA, L³), N,N'-dimethyl-N,N'-di(2-ethylhexyl) diglycolamide (DMB2EHDGA, L⁴). Their extraction performance for U(VI) was investigated in nitric acid system with 40/60 (V/V)% n-octanol/kerosene as diluent, and the stoichiometric number of ligand

and U(VI) was determined. And based on density functional theory, the structures and coordination properties of ligands and complexes were analyzed by Gaussian 16 and Multiwfn software. The relationships between the structures of four ligands and their extraction properties and coordination properties were discussed and analyzed from two aspects of experiment and theoretical calculation, providing data support for subsequent research.

Experimental section

Equipments and materials

Bromoisooctane (99%), 2-BROMOOCTANE (AR) and uranyl nitrate hexahydrate (99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd; 3-bromooctane (95%) was purchased from Zhengzhou alpha Chemical Co., Ltd; Methylamine (30%~33%) was purchased from Wuhan nalabai Biotechnology Co., Ltd; All other chemical reagents (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

T214 analytical balance, Beijing Saiduolisi Instrument System Co., Ltd; Yre-201d rotary evaporator, Gongyi Yuhua Instrument Co., Ltd; X - II inductively coupled plasma mass spectrometer (ICP-MS), Thermo Fisher, USA; Avance 600MHz nuclear magnetic resonance spectrometer (NMR), Brooke, Germany; S100 centrifuge tube constant temperature oscillator, Jiangsu Kunshan Dianshanhu Instrument Equipment Co., Ltd; QI-861 magnetic stirrer, Beijing Yihua Tongbiao Technology Co., Ltd; Gzx-9070mbe digital display blast drying oven, medical equipment factory of Shanghai Boxun Industrial Co., Ltd.

Ligand synthesis

In this article, the ligand required for the experiment was synthesized by acyl chloride method,

that is, the corresponding bromoalkane reacted with methylamine alcohol to produce secondary amine, and then the secondary amine was acylated to produce the corresponding diamide pods. The synthesis method is shown in Figure 1.

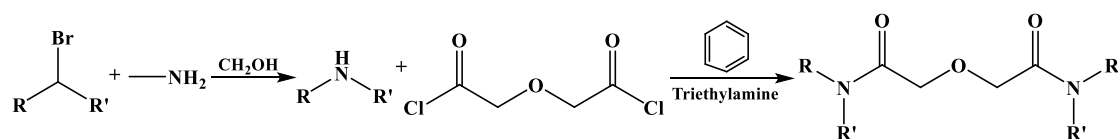


Fig. 1 Synthesis scheme of DGAs

Bromoalkanes and methylamine alcohols were mixed at a molar ratio of 1:8 and reacted at 110 °C for no less than 24 h. Upon completion of the reaction, the mixture was subjected to vacuum distillation to remove excess 2-(methylamino)ethanol, giving a yellowish-brown liquid. An appropriate volume of trichloromethane was added to dissolve the crude product, after which the solution was washed with saturated sodium carbonate solution and the organic phase was separated. The target secondary amine was finally obtained by collecting the fraction distilling at 190–195 °C. The secondary amine prepared in the previous step was mixed with triethylamine at a molar ratio of 1:1 in benzene. The mixture was placed in an ice-water bath with stirring, and diacetyl dichloride was slowly added dropwise. After full reaction, the mixture was filtered and distilled under reduced pressure to remove impurities, and the residue was dissolved in petroleum ether. The solution was then brought into contact with HNO₃ to form a third phase, which was washed and dried under vacuum overnight to afford the product with a yield of approaching 60% 60%, and the purity of the ligand was determined to be >98 mol% by quantitative ¹H-NMR.. The four ligands were characterized by ¹H-NMR: L¹ ¹H NMR (CDCl₃) δ: 0.89 (t, 3H, CH₃^{1-methylheptyl}), 1.16 (q, 1H, CH^{1-methylheptyl}), 1.22 (d, 3H, CH₃^{1-methylheptyl}), 2.79 (s, 3H, CH₃^{dimethyl}), 4.34 (q, 2H, CH₂^{amide}). L² ¹H NMR (CDCl₃) δ: 0.87 (m, 6H, CH₃^{1-ethylhexyl}), 1.47 (m, 10H, CH₂^{1-ethylhexyl}), 2.77 (t, 3H, CH₂^{dimethyl}), 3.48, 4.54 (dp, 1H, CH^{1-ethylhexyl}), 4.38, 4.42 (m, 10H, CH₂^{amide}). L³ ¹H NMR (CDCl₃) δ: 0.91 (m, 6H, CH₃^{2-methylheptyl}), 1.17, 1.30 (m, 8H, CH₂^{2-methylheptyl}), 1.81 (q,

1H, CH²-methylheptyl), 2.98 (t, 3H, CH₃^{dimethyl}), 3.10, 3.26 (m, 2H, CH₂^{2-methylheptyl}), 4.36 (s, 2H, CH₂^{amide}).

L⁴ ¹H NMR (CDCl₃) δ: 0.91 (m, 6H, CH₃^{2-ethylhexyl}), 1.29 (m, 8H, CH₂^{2-ethylhexyl}), 1.65 (q, 1H, CH₂^{2-ethylhexyl}), 2.96 (t, 3H, CH₃^{dimethyl}), 3.28 (m, 2H, CH₂^{2-ethylhexyl}), 4.35 (s, 2H, CH₂^{amide}).

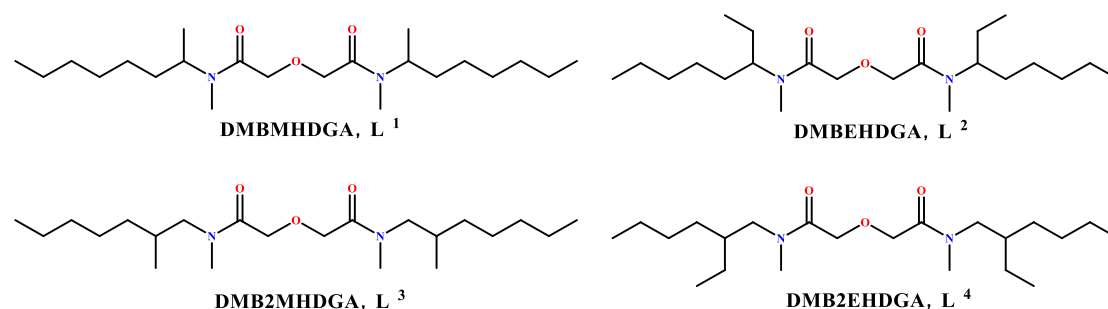


Fig. 2 Schematic diagram of four ligand structures

Solvent extraction

Four ligands were used to extract U (VI). The variables in the extraction experiment include extraction time, HNO₃ concentration in the aqueous phase, ligand concentration and temperature. The concentration of U (VI) in the aqueous phase was 5 mmol/L. The organic phase uses n-octanol/kerosene with a volume ratio of 40/60 (v/v)% as diluent. Due to the addition of n-octanol in the diluent, there was no third phase in the extraction experiment. During the extraction experiment, the aqueous phase with a volume ratio of 1:1 was fully contacted with the organic phase and centrifuged. The aqueous phase was taken out and diluted. The concentration of U (VI) in the aqueous phase was determined by inductively coupled plasma mass spectrometry (ICP-MS). The concentration of U (VI) in the organic phase is obtained by subtracting the initial concentration of U (VI) in the aqueous phase from the concentration of U (VI) in the aqueous phase after extraction. The distribution ratio is calculated according to formula (1):

$$D_U = \frac{c_{org}}{c_{aq}} = \frac{c_{ini} - c_{aq}}{c_{aq}} \quad (1)$$

Where, C_{org} and C_{aq} are the concentrations of U(VI) in the organic phase and aqueous phase,

respectively, at extraction equilibrium, with units of mol/L. C_{ini} is the initial concentration of U (VI) in the aqueous phase, with unit of mol/L. All data were from three parallel experiments, and the relative standard deviation (RSD) was less than $\pm 5\%$.

Theoretical calculations

Density Functional Theory (DFT) is a quantum mechanical calculation method, which is widely used in the fields of material science, chemistry and physics. It is used to study the electronic structure and properties of multi electron systems. It has been widely used in the theoretical study of lanthanide and actinide complexes [32]. In this article, Gaussian 16 is used to optimize the structure of ligands and complexes, and B3LYP hybrid functional, which is widely used in the theoretical study of lanthanide and actinide complexes, is used [33–35]. The ECP28MWB_SEG pseudopotential basis set was used for U(VI), while the 6-311G(d) polarization basis set was applied to C, H, O, and N [36–38]. The complex structures were optimized at the B3LYP/6-311G(d)/RECP level of theory in the gas phase, yielding output files containing their wavefunction information. Based on the output file, an analysis of the ligand's hard and soft acid-base properties was conducted, and the wavefunction file was analyzed using Multiwfn 3.8 software. This led to the acquisition of conclusions regarding the van der Waals electrostatic potential (ESP) contour map of the ligand, as well as the Mayer bond order and topological structure of the complex [39, 40].

Results and discussion

Effect of time on extraction of U(VI)

Firstly, it is necessary to investigate the influence of oscillation time on the extraction rate of

U(VI) to facilitate determining the time required for subsequent extraction experiments to reach extraction equilibrium. Extraction experiments were conducted at oscillation times of 1 min, 3 min, 5 min, 10 min, 15 min, 20 min, 30 min, and 40 min, with the results shown in Figure 3. The results indicate that the extraction rates of U(VI) by the four ligands are high, with L^1 , L^2 , and L^4 reaching equilibrium at around 5 min, and L^3 reaching equilibrium at around 10 min. Considering the influence of various environmental variables on the distribution ratio in subsequent experiments and the interference from other external factors, a 30-min extraction equilibrium time will be adopted to ensure complete extraction equilibrium.

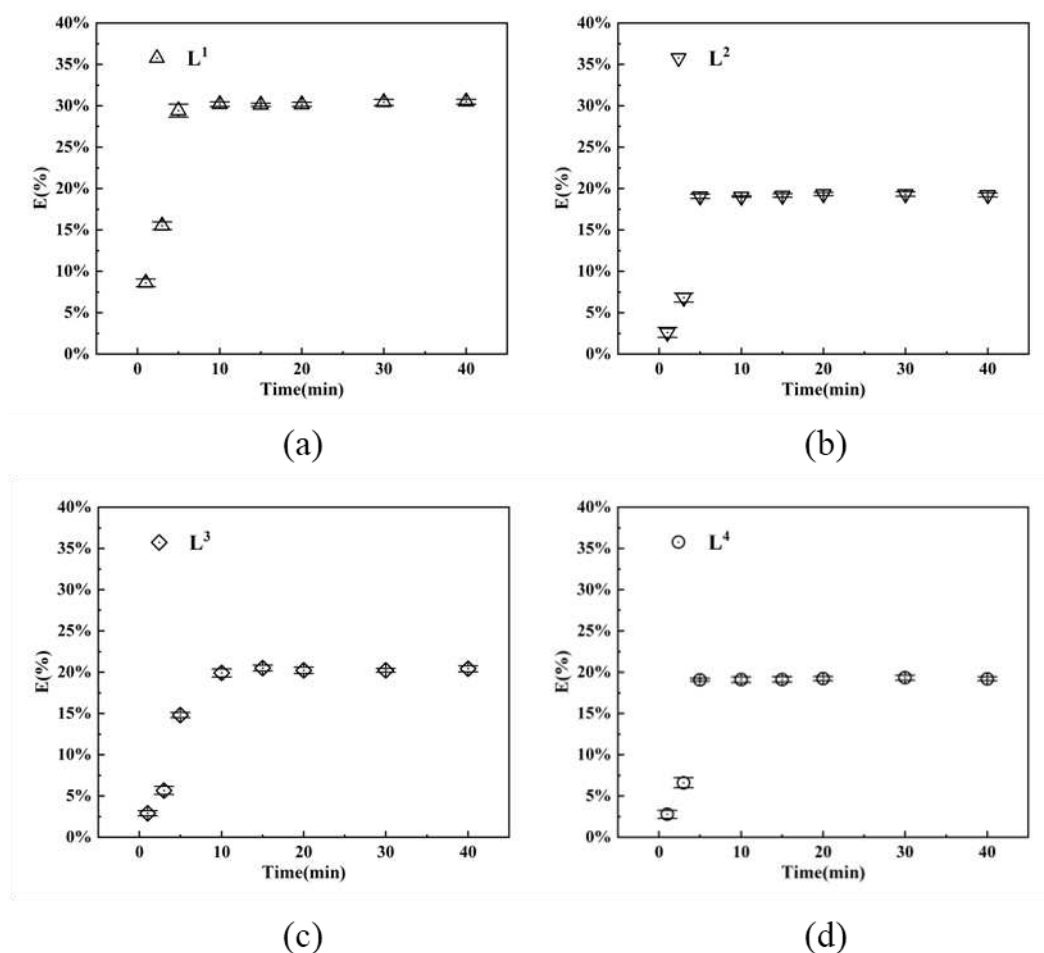


Fig. 3 The variation of U(VI) extraction rate with extraction time
 ($[U(VI)]_{ini}=5$ mmol/L, $[HNO_3]_{ini}=3.0$ mol/L, $[L]_{org}=0.02$ mol/L, O:A=1:1, T=298 K)

Effect of acid concentration on extraction of U(VI)

Some scholars have indicated in previous studies that Diglycolamidess exhibit good extraction performance for lanthanide and actinide elements across a wide range of HNO_3 acidity [41, 42]. Therefore, this article explores the extraction behavior of U(VI) by four ligands in systems with HNO_3 concentrations of 0.5, 1, 2, 3, 4, and 6 mol/L. As shown in Figure 4, the variation of D_U with the concentration of HNO_3 in the aqueous phase under different HNO_3 acidities was obtained. The results indicate that under the same conditions, D_U increases with the increase of the initial concentration of HNO_3 in the aqueous phase for all four ligands, which is mainly due to the common ion effect and salting-out effect of nitrate ions. However, a review of the literature has revealed that, within the same acidity range, the D_U values for Ln(III) reported by Liu et al. exhibited an initial increase and then remained essentially stable at 3–6 mol/L HNO_3 . Moreover, Zhao et al. also observed a similar trend for D_U even when employing the same ligand and extraction conditions with Ln(III) as the target metal ion. Notably, this trend was consistent with the U(VI) extraction results reported by Wei et al., and likewise, neither a maximum value nor an equilibrium point was identified within the experimental range [13, 43, 44].

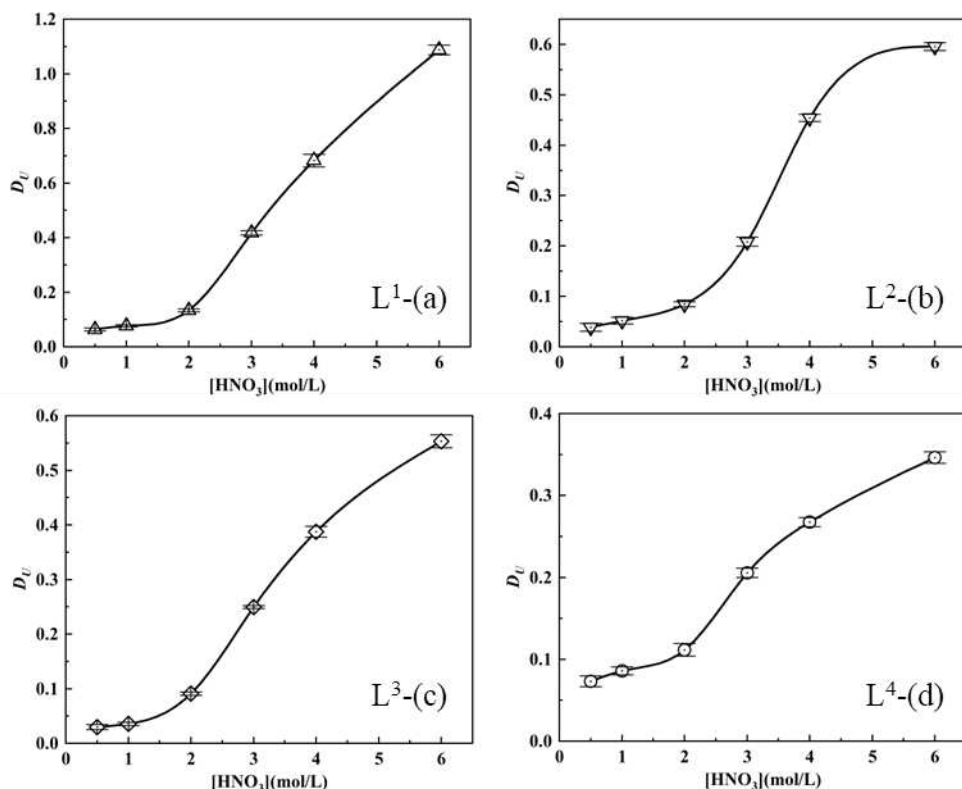
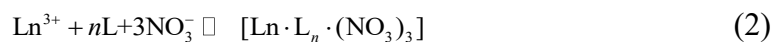


Fig. 4 The variation of U(VI) distribution ratio with initial HNO_3 concentration in aqueous phase ($[\text{U(VI)}]_{\text{ini}}=5 \text{ mmol/L}$, $[\text{L}]_{\text{org}}=0.02 \text{ mol/L}$, $\text{O:A}=1:1$, $T=298 \text{ K}$)

Effect of ligand concentrations on extraction of U(VI)

This article examines the influence of four ligands on the distribution ratio of U(VI) under the conditions of ligand concentrations of 0.02 mol/L, 0.04 mol/L, 0.06 mol/L, 0.08 mol/L, and 0.10 mol/L, as well as a nitric acid concentration of 3 mol/L. Using n to represent the coordination number, the extraction process can be represented as follows.



The experimental results of the influence of ligand concentration on the distribution ratio are shown in Figure 5. The horizontal axis of the graph represents the logarithm of the ligand concentration, and the vertical axis represents the logarithm of the distribution ratio of the ligand to U(VI). The results indicate that as the concentration of the ligand increases, the distribution ratio of the ligand to U(VI) also increases. According to the slope method, an image of $\lg D_U - \lg [\text{L}]_{\text{org}}$ needs to be

plotted. The slope n of the fitted straight line obtained from the graph is the stoichiometric ratio of U(VI) to the ligand molecules. The slopes in the figure indicate that U(VI) forms extracted complexes with all four ligands in both 1:1 and 1:2 stoichiometries. However, Boltoeva et al. and Wei et al. reported that U(VI) exhibits a 1:2 stoichiometry with DGA only when ionic liquids serve as the solvent, whereas in organic solvents a 1:1 coordination predominates, with 1:2 coordination of U(VI) with TODGA observed only at low acidity (1.2 mol/L HNO_3) [44–46]. The acidity employed in this work is 3 mol/L HNO_3 , which may offer more promising prospects for HLLW treatment applications.

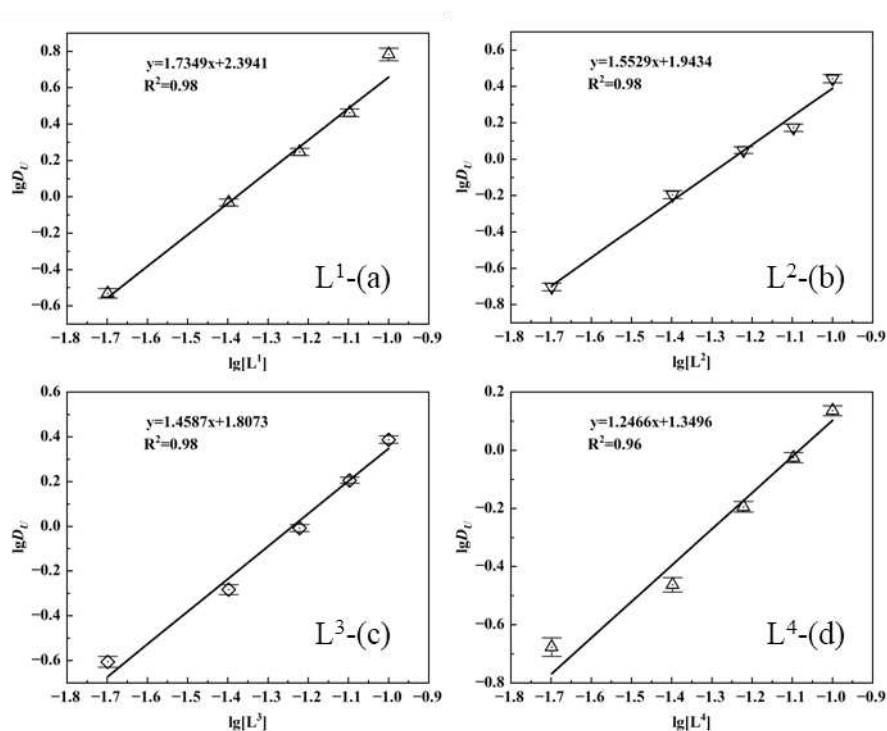


Fig. 5 The variation of U(VI) distribution ratio with the concentration of ligand ($[\text{HNO}_3]_{\text{ini}} = 3.0$ mol/L, $[\text{U(VI)}]_{\text{ini}} = 5$ mmol/L, O:A=1:1, $T = 298$ K)

Effect of temperature on extraction of U(VI)

In the experiment, the extraction behavior of U(VI) by four ligands in 3 mol/L HNO_3 at temperatures of 25°C, 30°C, 35°C, and 40°C was investigated. The experimental results, as shown in Figure 6, indicate that the distribution ratio (D_U) decreases with increasing temperature within the experimental range, suggesting that the extraction process is exothermic. Furthermore, an increase in

temperature is detrimental to the extraction process.

By fitting the straight lines in the figure, the reaction enthalpy changes ΔH for the extraction of U(VI) by the extractants L^1 , L^2 , L^3 , and L^4 can be determined, as shown in Table 1. The absolute value of the reaction enthalpy for ligand L^4 is the smallest, while that for ligand L^3 is the largest. Therefore, temperature changes have the least impact on the extraction performance of ligand L^4 and the most significant impact on ligand L^3 .

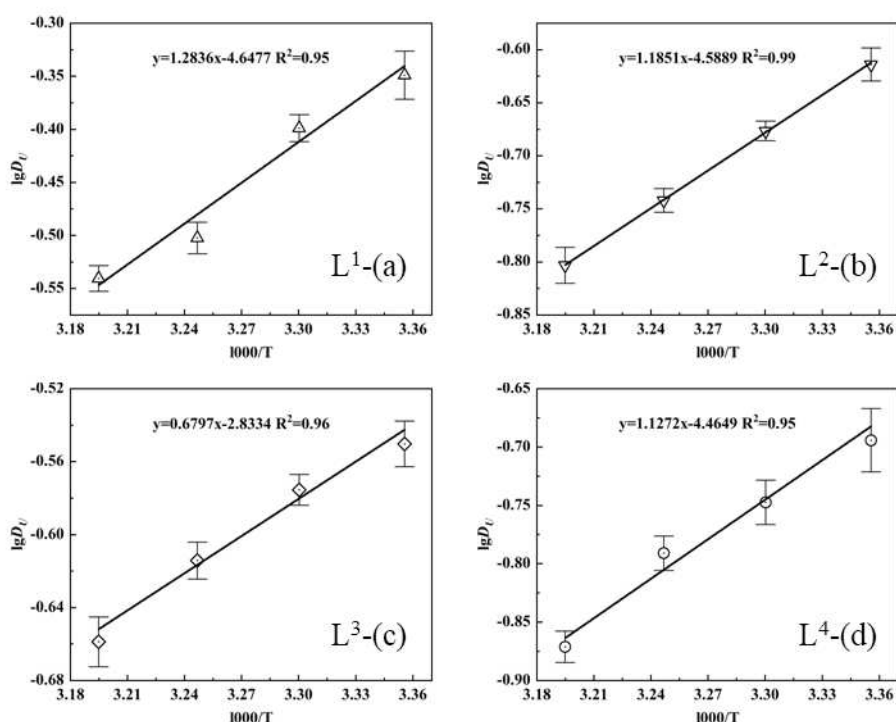


Fig. 6 The variation of U(VI) distribution ratio with extraction temperature ($[U(VI)]_{ini}=5$ mmol/L, $[HNO_3]_{ini}=3.0$ mol/L, $[L]_{org}=0.02$ mol/L, O:A=1:1).

Table 1 Thermodynamic parameters of the extraction reaction between the ligands and Ln^{3+} .

Ligands	L^1	L^2	L^3	L^4
$\Delta H(kJ/mol)$	-21.58	-22.69	-24.58	-13.01

Theory calculations

Based on the results of the extraction experiment, this article decides to adopt an M:L = 1:2 ratio to construct initial models of the complexes between the ligands L^n ($n = 1, 2, 3, 4$) and U(VI). Figure 7

displays the electrostatic potential (ESP) diagrams for L^n ligands. Their molecular geometries were optimized using the gas-phase B3LYP/6-311G(d) theoretical level. The red area in the figure represents the region with lower electron density, corresponding to the local maximum positive potential region. And the blue area represents the region with higher electron density (electron-rich region), corresponding to the local minimum negative potential region. The electron-rich region generally contains lonepair electrons and π electron clouds of some high electronegativity atoms, making it more likely to coordinate with positively charged metal ions that can provide electron binding sites [47, 48].

For the four ligands L^1 , L^2 , L^3 , and L^4 , each possesses three minimal electrostatic potential (ESP) points, located near the oxygen atom (O_{ether}) of one ether oxygen bond and two amide oxygen atoms (O_{amide1} and O_{amide2}) respectively. The ESP values in the vicinity of O_{amide1} and O_{amide2} are lower than those around O_{ether} , indicating that the coordination ability of the two amide oxygen atoms with the metal ion is stronger than that of the oxygen atom in the ether oxygen bond. For ligands L^1 and L^2 , where the methyl and ethyl substituents are located at the α -position, the ESP values of O_{amide1} and O_{amide2} are lower than those of ligands L^3 and L^4 , where the substituents are located at the β -position. This suggests that alkyl substituents at the α -position have a stronger electron-inducing effect, resulting in a stronger coordination bond with the metal ion.

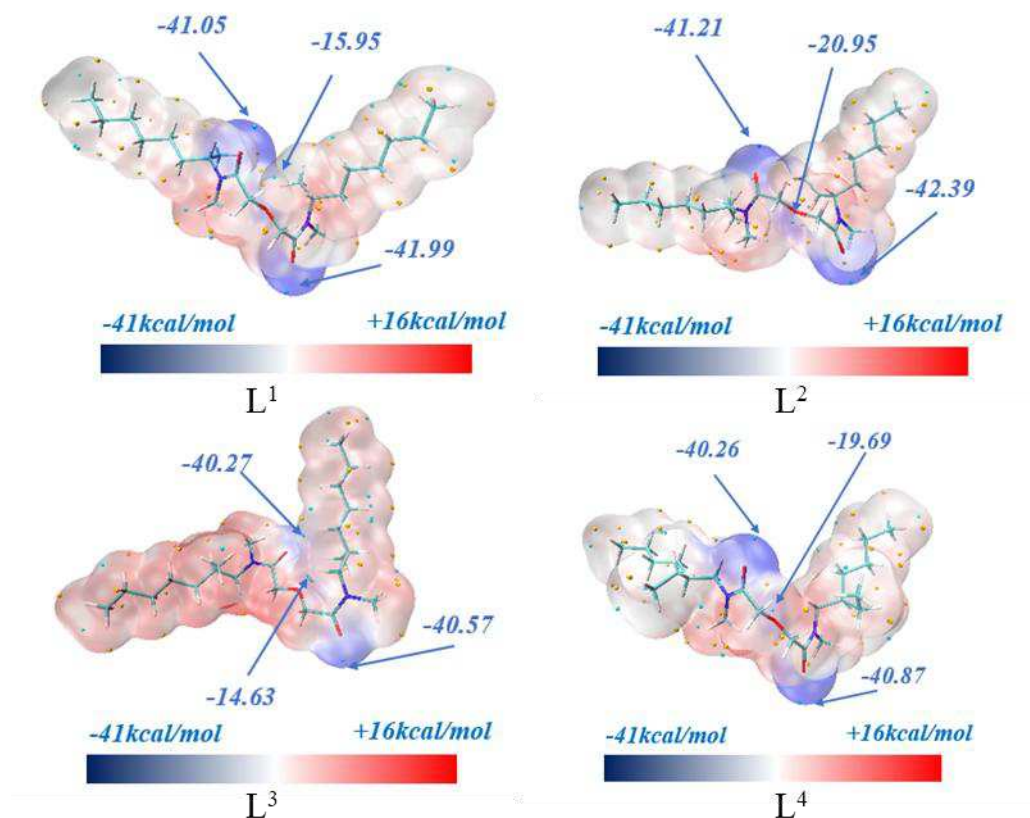


Fig. 7 Van der Waals surface ESP contour map of four ligands

In addition, Mulliken charge population analysis was conducted on four ligands to calculate the local charges of atoms. As shown in Table 2, the Mulliken charges of the O_{ether} in the four ligands are relatively close, and all are smaller than those of O_{amidel1} and O_{amidel2}, consistent with the ESP analysis.

Table 2 Mulliken charge (eV) population of four ligands: O_{ether}, O_{amidel1}, and O_{amidel2}

Ligands	Q-O _{ether}	Q- O _{amidel1}	Q- O _{amidel2}
L ¹	-0.455	-0.510	-0.520
L ²	-0.457	-0.504	-0.523
L ³	-0.454	-0.498	-0.520
L ⁴	-0.456	-0.501	-0.526

Based on the Lewis acid-base theory, an analysis of the hardness and softness of four ligands was conducted, and the results are presented in Table 3 [49, 50]. According to the hard-soft acid-base theory, the acid-base properties of a ligand can be quantified by its hardness (η), which is defined as half the difference between the vertical ionization potential (IP) and the vertical electron affinity (EA), i.e., $\eta = (IP - EA)/2$ [48]. The data in the table indicate that the ligand L³ exhibits strong hard-base

characteristics. For lanthanide elements, electrons are successively filled into the 4f orbitals. However, as the atomic number increases, the shielding effect of the 4f electrons on the atomic nucleus gradually weakens, leading to an increase in the effective nuclear charge number. Therefore, the hardness of heavy lanthanide elements is higher than that of light lanthanide elements. Since hard bases tend to combine with hard acids, the L^1 ligand may exhibit stronger coordination selectivity towards heavy lanthanide ions with high atomic numbers.

Table 3 The vertical electron ionization potential (IP , eV), vertical electron affinity (EA , eV), and hardness (η) of four ligands

Ligands	IP	EA	η
L^1	7.803	0.521	3.641
L^2	7.738	0.574	3.582
L^3	7.596	0.515	3.540
L^4	7.781	0.562	3.610

An initial model of the heavy U(VI) complex was constructed with a $U:L^n$ ratio of 1:2, and geometric optimization was performed at the B3LYP/6-311G(d)/RECP level. The structure of the complex is depicted in Figure 8. The figure shows that both the O atom of the amide group and the ether oxygen atom in the ligand coordinate with U(VI).

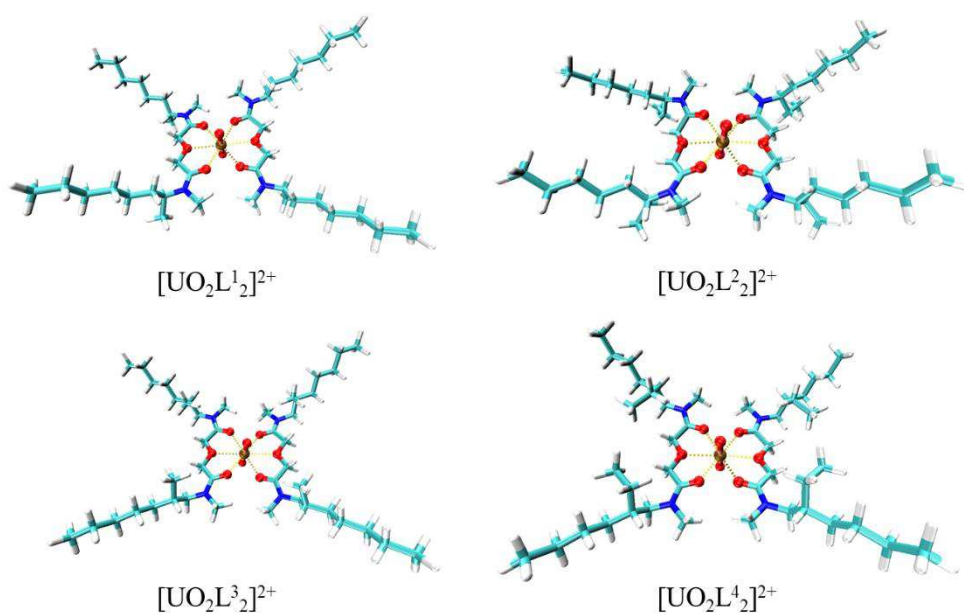


Fig. 8 The optimized structures of $[\text{UO}_2\text{L}_2]^{2+}$ at the B3LYP/6-311G(d)/RECP level of theory (cyan: C, white: H, blue: N, red: O, pink:U).

As shown in Table 4, the bond lengths of the coordination bonds of the four optimized complexes were obtained. The data in the table indicate that the bond length of $\text{U-O}_{\text{ether}}$ is significantly longer than that of $\text{U-O}_{\text{amide1}}$ and $\text{U-O}_{\text{amide2}}$. This phenomenon may be attributed to the relatively lower electron cloud density of the ether oxygen atom, whereas the two amide oxygen atoms possess higher charge density, making U(VI) more inclined to form coordination bonds with the amide oxygen atoms. Additionally, the bond lengths of $\text{U-O}_{\text{amide11}}$ and $\text{U-O}_{\text{amide12}}$, where the methyl substituent is located at the α -position of the L_1 ligand and the ethyl substituent is located at the α -position of the L_2 , are shorter than those of L_3 and L_4 , where the substituent is located at the β -position. This indicates that the alkyl substituent at the α -position has a stronger electron-inducing effect, resulting in a stronger coordination bond with the metal ion, validating the aforementioned analysis of ESP.

Table 4 The average bond lengths of $[\text{UO}_2\text{L}_2]^{2+}$ in $\text{U-O}_{\text{ether}}$, $\text{U-O}_{\text{amide11}}$, and $\text{U-O}_{\text{amide12}}$ after optimization (unit:Å)

Ligands	$\text{U-O}_{\text{ether}}$	Average	$\text{U-O}_{\text{amide11}}$	Average	$\text{U-O}_{\text{amide12}}$	Average
L^1	2.678	2.678	2.417	2.418	2.416	2.417
	2.678		2.418		2.418	
L^2	2.731	2.742	2.438	2.424	2.438	2.424
	2.753		2.410		2.410	
L^3	2.738	2.745	2.435	2.429	2.435	2.429
	2.752		2.423		2.423	
L^4	2.744	2.743	2.434	2.433	2.435	2.434
	2.742		2.432		2.432	

In molecular orbital theory, bond order is used to quantify the strength of chemical bonds between adjacent atoms, effectively reflecting the characteristics of interatomic bonding. This concept occupies a central position in molecular orbital theory, and it is not only used to measure the stability of molecules but also to determine whether molecules have already formed bonds. Mayer bond order (MBO) can be used to quantify the strength of interatomic bonding and is commonly used to judge the

existence and strength of chemical bonds. In this article, Mutiwfn 3.8 was used to perform MBO analysis of the bonding between the ether oxygen atom, two amide oxygen atoms, and metal ions. The results are shown in Table 5 [24, 51, 52].

According to the data in the table, the MBO values for U-O range from 0.170 to 0.375, indicating that the interaction between the ligand and the metal ion exhibits weaker covalency. The average MBO values for bonding of U-O_{amide1} and U-O_{amide2}, which are both amide ligands, are higher than that of U-O_{ether}, suggesting that the charge density of the two amide oxygen atoms is higher than that of the ether oxygen atom, making them more prone to bonding with metal ions. This is consistent with the previous analysis of surface electrostatic potential. The MBO values for U-O in ligands L¹ and L² are higher than those in ligands L³ and L⁴, indicating that ligands with alkyl substituents at the α -position form stronger coordination bonds with metal ions.

Table 5 The average MBO of bonding for U-O_{ether}, U-O_{amide1}, and U-O_{amide2} in the optimized complex [UO₂L₂]²⁺

Ligands	U-O _{ether}	Average	U-O _{amide1}	Average	U-O _{amide2}	Average
L ¹	0.181	0.181	0.374	0.371	0.368	0.371
	0.181		0.368		0.374	
L ²	0.183	0.178	0.362	0.3615	0.362	0.3615
	0.171		0.361		0.361	
L ³	0.168	0.170	0.359	0.357	0.359	0.357
	0.172		0.355		0.355	
L ⁴	0.173	0.173	0.359	0.359	0.359	0.359
	0.173		0.359		0.359	

Based on the Atomic and Molecular Theory (AIM) proposed by Bader, the Quantum Theory Atom (QTAIM) method has been developed [24, 34, 53]. This method systematically studies the correlation between molecular electron density distribution and traditional chemical properties by integrating density functional theory. Through topological analysis of the (3×3) Hessian matrix of real-

space functions, critical points and topological paths connecting these points can be obtained. The critical points include bond critical points, ring critical points, and cage critical points.

In this article, Multiwfn 3.8 was used to analyze the bond critical points (BCP) of the coordination bonds in the electronic wave function of the complex. The results are presented in Table 6 [54, 55]. Here, $\rho(\mathbf{r})$ represents the electron density at the bond critical point of the coordination bond formed between the O atom of the four ligands and the metal ion, $\nabla^2\rho(\mathbf{r})$ represents the Laplacian operator of electron density (the second derivative of electron density distribution), H represents the total energy density, V represents the potential energy density, and G represents the Lagrangian kinetic energy.

Generally, $\rho(\mathbf{r}) < 0.1 \text{ a.u.}$ and $\nabla^2\rho(\mathbf{r}) > 0$ are considered to represent electrostatic, hydrogen bonding, and van der Waals interactions, while $\rho(\mathbf{r}) > 0.2 \text{ a.u.}$ and $\nabla^2\rho(\mathbf{r}) < 0$ indicate covalent interactions. From the data in the table, it can be seen that the electron density $\rho(\mathbf{r})$ at the bond critical points of U-O_{ether} in the four complexes is less than that of U-O_{amide1} and U-O_{amide2}, indicating that the bonding strength between amide oxygen atoms and metal ions is higher than that of ether oxygen atoms, which is consistent with the previous conclusion. In addition, both U-O_{amide} and U-O_{ether} exhibit $\rho(\mathbf{r}) < 0.1 \text{ a.u.}$ and $\nabla^2\rho(\mathbf{r}) > 0$ at their bond critical points, indicating that electrostatic interactions are primarily present between U-O_{ether}, U-O_{amide1}, and U-O_{amide2}. Studies have shown that $|V|/G < 1$ typically indicates electrostatic, hydrogen bonding, and van der Waals interactions, while $1 < |V|/G < 2$ indicates a certain degree of covalent interaction, and $|V|/G < 2$ indicates covalent interaction. When $H > 0$, bonding is usually non-covalent, and when $H < 0$, it is covalent. For the four ligand-complex pairs, the bond critical points of U-O_{amide} exhibit $1 < |V|/G < 2$ and $H < 0$, indicating that the electrostatic interactions between U-O_{amide1} and U-O_{amide2} mainly exhibit covalent characteristics. The bond critical points of U-O_{ether} exhibit

$|V|/G < 1$, indicating that the main interaction between the ether oxygen atom and the metal ion is electrostatic.

Table 6 QTAIM analysis results of the complex $[\text{UO}_2\text{L}_2]^{2+}$

Species	Bonds	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H	$ V /G$
U-L ¹	U-O _{ether}	0.03091	0.12350	0.00119	0.95991
	U-O _{amidel1}	0.05838	0.22840	-0.00098	1.01690
	U-O _{amidel2}	0.05808	0.22153	-0.00099	1.01759
U-L ²	U-O _{ether}	0.02947	0.10608	0.00012	0.99484
	U-O _{amidel1}	0.05621	0.21168	-0.00077	1.01435
	U-O _{amidel2}	0.05620	0.21165	-0.00077	1.01434
U-L ³	U-O _{ether}	0.02660	0.10191	0.00081	0.96735
	U-O _{amidel1}	0.05735	0.22153	0.00062	1.01109
	U-O _{amidel2}	0.05735	0.22152	0.00062	1.01106
U-L ⁴	U-O _{ether}	0.02688	0.10412	0.00094	0.96241
	U-O _{amidel1}	0.05597	0.21454	-0.00045	1.00837
	U-O _{amidel2}	0.05612	0.21645	-0.00041	1.00753

Conclusion

In this article, four branched asymmetric diamide podands were synthesized in this work, and their extraction performance for U(VI) in nitric acid medium was investigated. The results show that within the experimental range, D_U increases with increasing concentrations of HNO_3 and ligand, and decreases with rising temperature. The slope method indicates that the four ligands form 1:1 and 2:1 complexes with U(VI), and the extraction performance follows the order: $\text{L}^1 > \text{L}^2 \approx \text{L}^3 > \text{L}^4$.

DFT calculations reveal that all four ligands possess three local minima in electrostatic potential near the oxygen atoms, and the coordination ability of O_{amide} is stronger than that of O_{ether} . The Mulliken charges of O_{ether} in the four ligands are relatively close to each other and are all smaller than

those of O_{amide} . The $U-O_{\text{ether}}$ bond lengths in coordination bonds are all longer than the $U-O_{\text{amide}}$ bond lengths. The ligands exhibit weak covalent character when coordinating with U(VI). MBO and QTAIM analyses of the complexes indicate that the interactions between the four ligands and U(VI) exhibit weak covalent character. Furthermore, O_{amide} is more liable to form bonds with metal ions than O_{ether} . The MBO values of ligands L^1 and L^2 are both higher than those of ligands L^3 and L^4 . Ligands with alkyl substituents at the α -position form stronger coordination bonds with metal ions, which is in agreement with the results of extraction experiments.

This article investigates the extraction and coordination properties of asymmetric bis-amide calixarenes with different branching positions toward U(VI) through extraction experiments and DFT calculations. It reveals that the low steric hindrance of short alkyl chains and the electron-donating effect of α -positioned alkyl groups jointly influence the ligand's performance in extracting and coordinating U(VI). The findings provide a theoretical foundation and data support for summarizing structure-activity relationships among ligands with varying chain lengths and branching positions, as well as for developing novel ligands.

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