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Towards understanding the correlation between UO_2^{2+} extraction and substitute groups in 2,9-diamide-1,10-phenanthroline

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2,9-Diamide-1,10-phenanthroline (DAPhen) ligands represent a new family of tetradentate extractants given their strong affinity to actinides and the CHON principle. Among this family, *N*,*N*′-diethyl-*N*,*N*′-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen), initially reported by us, exhibits excellent selectivity towards actinides (U, Th, Am, Pu) over lanthanides and thus can be potentially applied in the group actinide extraction (GANEX) process for the group separation of actinides. In this article, by tailoring the lengths of alkyl chains, we synthesized other four DAPhen ligands with different substitute groups in the diamide moieties, and characterized the relationship between properties and substitute groups of DAPhen ligand. The extraction results show that three of the ligands exhibit high performance in UO_2^{2+} extraction from an acidic solution and the extracted UO_2^{2+} can be easily stripped by only using ultrapure water. Spectrophotometry titration confirms that UO_2^{2+} combined with all the four ligands in 1:1 mode. The extended X-ray absorption finestructure (EXAFS) study shows that six donor atoms comprise the first equatorial shell of the UO_2^{2+} ions bonded by the DAPhen ligands, among which two nitrogen and two oxygen atoms are from the DAPhen ligand, while other two oxygen atoms are from one nitrate ions. This article promises to provide basic data for assessing the feasibility of this kind of DAPhen ligands applied in actinides separation from nuclear wastes.

2,9-diamide-1,10-phenanthroline, UO_2^{2+}, extraction, UV-Vis titration, EXAFS

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1 Introduction

Growing energy demand and continuous environmental issues have led to increasing interest in nuclear energy all over the world [1]. The rapid developments in nuclear energy, however, results in a large quantity of nuclear spent fuel that contains an intense radioactivity and must be managed in time [2]. Uranium (95.5%) and plutonium (0.9%) comprise the major radioactive components in spent nuclear fuel which can be separated by plutonium and uranium extraction (PUREX) process maturely using tri-*n*-buty phosphate (TBP) as extractant [3]. The rest of the wastes are known as the high level liquid waste (HLLW), which contains a slight of minor actinides (such as americium, curium and neptunium) [4]. These minor actinides exhibit a long lasting radiotoxicity, being not only harmful to organism health and environmental protection, but also difficult to be handled in geological repository [5]. Partitioning and transmutation (P&T) process is developed intending to bomb these minor actinides by neutrons and to transform these long-lived elements into short-lived fission products [6,7]. However, an unignorable amount of lanthanides is found to weaken the P&T process severely by absorbing neutrons [8]. Thus, separation of actinides (An) from lanthanides (Ln) before the P&T process is indispensable [9,10]. An/Ln separation is a

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long-standing and challenging problem, a result of the similar chemistries of these elements [11–13]. In the last decades, several ligands have been developed for the An/Ln separation, including DMDOHEMA (developed by CEA in 1980s and used in the DIAMEX process) [14], TODGA (developed by JAEA in 2000s) [15], TOPO (developed by INET and Tsinghua in 1980s and used in TRPO process) [16] and CMPO (developed by ANL in 1980s and used in the TRUEX process) [17]. These ligands always aim at one or several certain actinides extraction but not the group separation of actinides. Recently, we have reported a phenanthroline based tetradentate ligand with hard-soft donors combined in the same molecule, *N*,*N'*-diethyl-*N*,*N'*-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen), for the group separation of actinides over lanthanides [18]. The extraction results show that this ligand is stable and very efficient for the separation of a series of actinides (U, Th, Am, Pu) from the lanthanides. The coordination behaviors of Et-Tol-DAPhen with UO_2^{2+}, Eu^{3+} and Th^{4+} were then studied by UV-Vis titration experiments and single-crystal structure analysis. The results suggest that the chemical stoichiometry of all the test metal complexes with Et-Tol-DAPhen is 1:1. In addition, the coordination mode of Et-Tol-DAPhen with Eu^{3+} and UO_2^{2+} was also studied by electrospray ionization mass spectrometry (ESI-MS) and density functional theory (DFT) study [19], which gives a similar conclusion. These studies highlight vast opportunity of Et-Tol-DAPhen applied in group separation of actinides over lanthanides, and also offer basic data in coordination and extraction of actinides and lanthanides with this new kind of ligands. Up to now, however, the questions of whether or not the peripheral substitute groups of the DAPhen ligand correlates with the binding ability and selectivity of the resultant extractants has not been addressed. Structure optimization by tailoring substitute groups of the DAPhen ligand for the construction of more effective extractant is of great significance [20]. This inspired us to characterize the relationship between properties and substitute groups of DAPhen ligand in the realm of group separation of actinides. To achieve this aim, we modified the structure of DAPhen ligand by varying the substituent group in the diamide moieties and synthesized four DAPhen ligands with different alkyl chains on the diamide. Then, UO_2^{2+} extraction by the four ligands were performed in detail. Considering that spectrometry offers a powerful tool for understanding the coordination behavior of actinides/lanthanides [21], UV-Vis titration as well as the extended X-ray absorption finestructure (EXAFS) measurement were explored to characterize the UO_2^{2+} complex in acetonitrile. The results clearly reveal influence of substituent groups on the properties of the DAPhen ligand.

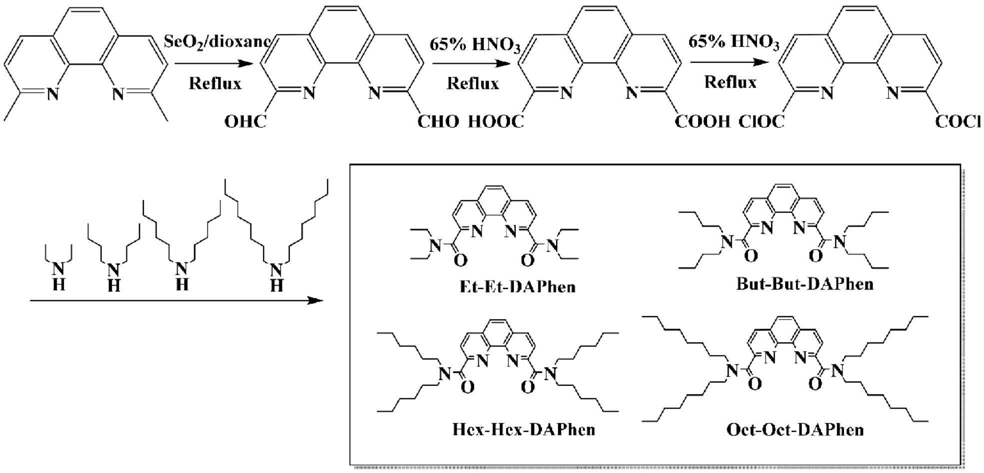
2 Experimental

2.1 Synthesis of the ligands

The four DAPhen ligands used in this study were prepared by tailoring the substituent group in the diamide moieties of Et-Tol-DAPhen reported in our previous work [18]. The synthesis procedure is given in Scheme 1 and the details were described as follows.

2.1.1 2,9-Dicarboxylic acid-1,10-phenanthroline

Selenium oxide (13.5 g, 0.12 mol) and 2,9-dimethyl-1,10-phenanthroline (5 g, 0.02 mol) were added into a mixture of 1,4-dioxane (320 mL) and ultra-pure water (50 mL) in a 500 mL of round-bottom flask. The reaction remained under reflux for 3 h and filtered while hot, then the filtrate was left to cool. Golden product, 2,9-dicarbaldehyde-1,10-phenanthroline (4.62 g, 80.56%), was obtained after another filtration. Then, 2,9-dicarbaldehyde-1,10-phenanthroline (3 g, 0.013 mol) was added into concentrated nitric acid (65%, 60 mL). After refluxing for 3 h, the solution was cooled by



Scheme 1 Synthesis route of DAPhen ligands.

poured onto the solid ice and the crude product was separated out gradually. The crude product was filtered to get the solid product and dried before the next step [18].

2.1.2 N,N′-Diethyl-N,N′-diethyl-2,9-diamide-1,10-phenanthroline (Et-Et-DAPhen)

2,9-Diacyl chloride-1,10-phenanthroline was synthesized by adding 2.9-dicarboxylic acid-1,10-phenanthroline (2.86 g, 10.68 mmol) into the thionyl chloride (70 mL) and refluxing under 85 °C for 3 h. After removal of the thionyl chloride by reduced pressure distillation, dichloromethane (70 mL) was added as the solvent, and diethylamine (1.72 g, 23.51 mmol) and triethylamine (4.76 g, 47.00 mmol) were added slowly into the mixture. After 3 h refluxing under nitrogen atmosphere, the solvent was removed by reduced pressure distillation. The residue was purified with silica gel column chromatography (eluent: $CH_3OH/CHCl_3=1/50$), yielding white powders of ligand a (3.16 g, 78.08%). ESI-MS: *m/z* $(M+H)^+$ 379.2. ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.64$ (d, $J=8.0$ Hz, 2H), 8.12 (s, 2H), 7.95 (d, $J=8.0$ Hz, 2H), 3.55 (q, $J=8.0$ Hz, 4H), 3.41 (q, $J=8.0$ Hz, 4H), 1.22 (t, $J=8.0$ Hz, 12H).

N,*N*′-Dibutyl-*N*,*N*′-dibutyl-2,9-diamide-1,10-phenanthroline (But-But-DAPhen), *N*,*N*′-dihexyl-*N*,*N*′-dihexyl-2,9-diamide-1,10-phenanthroline (Hex-Hex-DAPhen) and *N*,*N*′-dioctyl-*N*,*N*′-dioctyl-2,9-diamide-1,10-phenanthro-line (Oct-Oct-DAPhen), were synthesized following the same procedure as that used for *N*,*N*′-diethyl-*N*,*N*′-diethyl-2,9-diamide-1,10-phenanthroline except that dibutylamine, dihexylamine and diotcylamine instead of diethylamine were used, respectively. All the ligands were characterized by ESI-MS and NMR, as shown as follows: *N*,*N*′-Dibutyl-*N*,*N*′-dibutyl-2,9-diamide-1,10-phenanthroline (yield 66.1%), ESI-MS: *m/z* $(M+H)^+$ 491.4. ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.63$ (d, $J=8.3$ Hz, 2H), 8.11 (s, 2H), 7.92 (d, $J=8.3$ Hz, 2H), 3.51 (q, $J=7.5$ Hz, 4H), 3.40 (q, $J=7.5$ Hz, 4H), 1.70–1.64 (m, 8H), 1.44–1.39 (m, 4H), 0.99–0.96 (m, 10H), 1.55 (t, $J=7.5$ Hz, 6H). *N*,*N*′-Dihexyl-*N*,*N*′-dihexyl-2,9-diamide-1,10-phenanthroline (yield 37.8%), ESI-MS: *m/z* $(M+H)^+$ 603.5. ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.63$ (d, $J=8.0$ Hz, 2H), 8.11 (s, 2H), 7.92 (d, $J=8.0$ Hz, 2H), 3.51–3.44 (m, 8H), 1.68–1.62 (m, 8H), 1.35 (m, 12H), 0.91 (m, 18H), 0.49 (m, 4H). *N*,*N*′-Dioctyl-*N*,*N*′-dioctyl-2,9-diamide-1,10-phenanthroline (yield 22.2%), ESI-MS: *m/z* $(M+H)^+$ 735.2. ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.63$ (d, $J=8.0$ Hz, 2H), 8.12 (s, 2H), 7.93 (d, $J=8.0$ Hz, 2H), 3.50 (q, $J=8.0$ Hz, 8H), 1.61 (m, 8H), 1.37–1.30 (m, 20H), 0.93–0.88 (m, 26H), 0.67 (m, 6H).

2.2 Solvent extraction experiments

A stock solution of UO_2^{2+} was prepared by dissolving the $UO_2(NO_3)_3\cdot 6H_2O$ solid with ultrapure water in a volumetric flask. A 2 mL aqueous phase consisting of 0.5 mM UO_2^{2+} in nitric acid solutions was contacted with a 1 mL organic phase containing 1.0 mM Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene, respectively. A phase ratio of 2:1 aqueous: organic phase was used here to reduce the usage of organic diluents and achieve a higher extraction capacity. 1-(Trifluoromethyl)-3-nitrobenzene was used as a diluent in view of its good dissolving capacity towards DAPhen ligands, strong hydrophobicity, and suitable density. Prior to extraction, the organic phase was pre-equilibrated with the aqueous phase of the same composition as the extraction experiment except being void of uranium. The kinetics data indicated that 20 min is enough to reach extraction equilibrium for all the four ligands. Thus all the extraction experiments were carried out for 30 min with the aid of a vortex shaker. After 2 min of centrifugation at 6000 r/min, the concentration of UO_2^{2+} in the aqueous phase was determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Horiba JY2000-2, Japan). For ICP-OES measurement (the detection limit is below 0.01 ppm), the supernatant was diluted 25–100 times to make sure that the UO_2^{2+} concentration in the dilution is 1–5 μg/mL. The distribution ratio (*D*) was calculated as follows:

$$D=\frac{(C_\mathrm{i}-C_\mathrm{f})}{2C_\mathrm{f}}, \tag{1}$$

where C_i and C_f represent the initial and final concentrations of U(VI) in the aqueous phase, respectively; 2 designates the volume ratio of organic phase and aqueous phase during the extraction. Above equations for calculation of the *D* value made a convenience that only the aqueous phase was measured. All values were measured in duplicate with uncertainty within 5%.

For UO_2^{2+} stripping, the organic phase loaded with UO_2^{2+} was contacted with an equal volume of ultrapure water during 30 min at room temperature with the aid of a vortex shaker. The resulting mixture was centrifuged at 6000 r/min for 2 min and the organic phase was separated completely from the aqueous phase. The concentration of UO_2^{2+} in the aqueous phase was determined by the ICP-OES method.

2.3 UV-Vis titration

The absorption spectroscopy was measured by a HITACHI U-3600 (Japan). Stoke solutions of 0.002 M UO_2^{2+} in acetonitrile were prepared by dissolving the $UO_2(NO_3)_3\cdot 6H_2O$ solid into HPLC grade acetonitrile; The concentration of ligands in acetonitrile was 2.0×10^{-5} M. And 0.01 M tetraethylammonium nitrate (Et_4NNO_3) was added into the ligand solutions to control the ionic strength. Each 10 μL of the UO_2^{2+} solutions were titrated into 5 mL of the ligand solution. After mixing for 15 min, the absorption spectroscopy of the solution was measured with a 1.0 cm quartz cell. The recorded wavelength range was 250–400 nm with a bandwidth of 1 nm. The stability constants were calculated with the HypSpec program [22,23].

2.4 EXAFS measurement

The samples for EXAFS studies were prepared by liquid-liquid extraction method at room temperature. Specially, 2 mL of 3 M nitric acid aqueous phase containing 17.5 mM UO_2^{2+} and 2 mL of 1-(trifluoromethyl)-3-nitrobenzene with 17.5 mM ligands were mixed in a stoppered test tube and vigorously shaken by a vortex mixer for 30 min. Before the extraction process, the organic phase was pre-equilibrated with 3 M HNO_3 for 10 min at room temperature. An aliquot of the organic phase was transferred to the EXAFS sample holder and sealed with Kapton tape.

The EXAFS spectra at the U-L_{III} edge (17166 eV) were recorded in fluorescence mode in the range of 17.0–17.9 keV [24], using synchrotron radiation at the beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF). A silicon (111) double-crystal monochromator was used to tune the incident X-ray beam to the desired energies. An yttrium foil (K-edge 17038 eV) was simultaneously measured in transmission mode for energy calibration of the monochromator. The data processing was analyzed with the ATHENA code [23]. The E_0 energy was set at the maximum of the absorption edge. The maximum energy of the absorption edge confirms the redox states of +VI for uranium (17173.6 eV). The linear pre-edge background was subtracted and normalized to extract the EXAFS signal. Pseudoradial distribution functions (PRDF) were acquired by Fourier transform in $k^3x(k)$ with the ATHENA code between 2.5 and 13.5 Å^{-1}. Using ARTEMIS code, the R factor (%) and the quality factor (QF, reduced chi-square) of the fits were obtained. For EXAFS data analysis, the theoretical phase shift and amplitude functions for single and double scattering paths are calculated by the program FEFF6 and optimized as implemented in the FEFFIT code using the model structure of U-Et-Tol-DAPhen complex reported in our previous work [18]. Experimental data were then fitted using four individual single scattering paths. Fitting procedure was performed on the k^3-weighted FT-EXAFS from 1.0 to ~3.0 Å. The amplitude reduction factor S_0^2 was fixed at 1.0, and the shifts in the threshold energy ΔE_0 were linked to all the paths.

3 Results and discussion

3.1 Solvent extraction studies

The effects of HNO_3 concentration on UO_2^{2+} extraction by Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene solvent were investigated. As shown in Figure 1, almost no UO_2^{2+} extraction occurred for Et-Et-DAPhen, whereas the other three DAPhen ligands exhibit a strong extraction ability toward UO_2^{2+}. Under the test conditions in 3 M HNO_3 solution, the distribution ratios by But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen were determined to be 118, 92 and 90, respectively. Although these values are lower than that for Et-Tol-DAPhen [25], these ligands represent highly efficient UO_2^{2+} extractants. With regard to Et-Et-DAPhen, the poor extraction ability probably results from the fact that the short alkyl chain in diamide moieties make the ligand hard to dissolve in organic solvent but prefer to transfer into the aqueous phase during the extraction. Besides, it is notable that among these DAPhen ligands, But-But-DAPhen shows the highest extraction ability towards UO_2^{2+} regardless of the concentrations of HNO_3 and the Hex-Hex-DAPhen and Oct-Oct-DAPhen were slightly worse, indicating that the long alkyl chain has the steric effect thus weaken the coordination of UO_2^{2+} with the donor atoms. The results here clearly reveal the important roles of alkyl chain in diamide moieties for determing the extraction ability of DAPhen ligand.

In addition, stripping experiments were also carried out given continuous operation of the extraction systems and cyclic utilization of the extractants, in which the extracted UO_2^{2+} in the organic phase containing But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen ligands, respectively, were simply back-extracted into ultra-pure water. As shown in Figure 2, the stripping percentage for the ultrapure water in one stage is more than 90%, and following four stages of stripping experiments, an almost complete stripping (~100%) of UO_2^{2+} can be achieved. Thus, from the point of easy recycling view, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene are potentially suitable to be applied in real UO_2^{2+} separation.

3.2 UV-Vis titration of the UO_2^{2+} complexes

To further understand the coordination of UO_2^{2+} with Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen, UV-Vis titration was explored here to determine the stoichiometry and stability constant of the UO_2^{2+} complexes in acetonitrile. Figure 3 shows the UV-Vis absorption spectra of UO_2^{2+} with Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen at various UO_2^{2+} concentrations. As can be seen, with the increasing of UO_2^{2+} concentration, the UV-Vis spectra for the four ligands exhibit a similar variation trend. Specifically, the distinct absorption band for ligands at 273 nm gradually decreases and a new absorption band assigned to UO_2^{2+} complexes appears at 301 nm. No obvious band shift and shape variations of the spectra were observed for all the four ligands. We thus assume that a similar UO_2^{2+} complex with the same stoichiometry and the similar structure formed when changed the

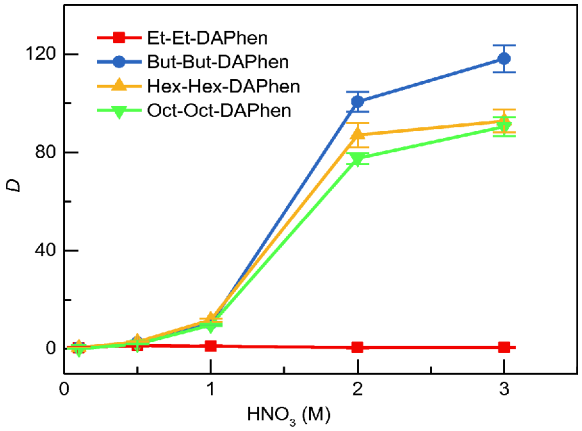


Figure 1 UO_2^{2+} extraction by 1.0 mM Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene as a function of HNO_3 concentration at room temperature (color online).

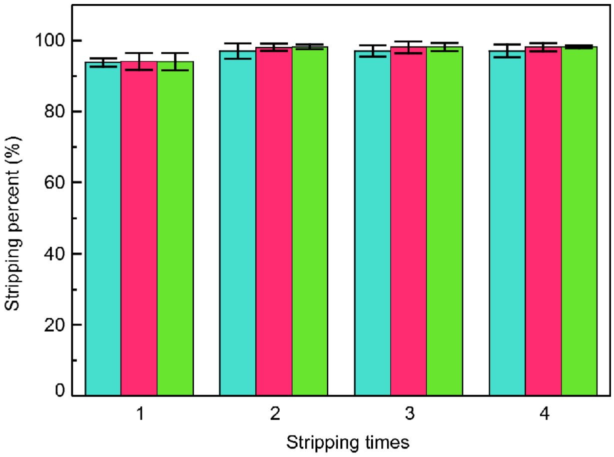


Figure 2 UO^{2+} stripping from UO_2^{2+}-loaded organic phases containing DAPhen ligands using the same volume of ultra-pure water. Red, green and blue color represent But-But-DAPhen, Hex-Hex-DAPhen, and Oct-Oct-DAPhen, respectively (color online).

ligand from Et-Et-DAPhen to Oct-Oct-DAPhen. Then, the stoichiometries of the complexes were determined by fitting the experimental data using the HypSpec program [17]. The results suggest that 1:1 stoichiometry well matches the experimental data for all the four ligands. That is, one UO_2^{2+} ion bonds one ligand even at a low UO_2^{2+} concentration. This is consistent with that for previously reported Et-Tol-DAPhen [25], giving an indication that tailoring the substituent group in the diamide of DAPhen ligand from ethyl to octyl and even to tolyl does not change the stoichiometry of UO_2^{2+} complex. The stability constants ($\log\beta$) of the UO_2^{2+} complexes were also calculated as listed in Table 1. The stability constants of Et-Tol-DAPhen is given for comparison. The results show that all of the four ligands have comparable complexation ability towards UO_2^{2+} in acetonitrile with $\log\beta$ ranged from 4.0 to 4.5. The stability constants, i.e., the binding affinity between UO_2^{2+} and these ligands follows the trend Et-Et-DAPhen≈Oct-Oct-DAPhen<Hex-Hex-DAPhen<But-But-DAPhen (Table 1), paralleling to the trend in the extraction results (Figure 1). When the length of alkyl chain becomes longer, the stability constant becomes smaller, which probably attributed to the steric effect on the complexation as mentioned above. Although different solvents were used in this article and that for Et-Tol-DAPhen, the larger stability constant of Et-Tol-DAPhen denotes a better binding affinity between UO_2^{2+} and Et-Tol-DAPhen, which are in good agreement with the fact that Et-Tol-DAPhen shows better UO_2^{2+} extraction under the same condition. These results indicated that the substituent group in the diamide of DAPhen may tailor the extraction ability of this ligand by affecting its binding affinity with UO_2^{2+}.

3.3 EXAFS analysis of the UO_2^{2+} complexes

EXAFS spectra at the U-L$_{III}$ edge were recorded to further characterize the UO_2^{2+} coordination structure in organic phase. Given the poor signal-to-noise ratio of the spectra for the UO_2^{2+} complex with Oct-Oct-DAPhen, we here only collected the EXAFS spectra of the UO_2^{2+} complexes with Et-Et-DAPhen, But-But-DAPhen and Hex-Hex-DAPhen (see experimental section for the details). Figure 4 shows the comparison of the k^3-weighted EXFAS spectra and the FT magnitude of the three solution samples (A, B and C). Also shown in Figure 4 is the spectra of crystalline UO_2^{2+} complex with Et-Tol-DAPhen for reference (D). It can be seen that both the oscillation mode and intense FT peaks at the range of 1–4 Å (not phase correction) for spectrum A, B and C are in good agreement with each other as well as with that of crystalline UO_2^{2+} complex with Et-Tol-DAPhen. Specifically in the FT magnitude (Figure 4(b)), the EXAFS spectra are dominated by the two axial Oyl contributions (peak 1). Contributions at $R+\Delta R<1.0$ Å are low frequencies spline removal artifacts. Equatorial coordination is split into two distinct contributions (Figure 4, peaks 2 and 3). In crystalline UO_2^{2+} complex with Et-Tol-DAPhe, the equatorial split from the DAPhen ligand. The similar EXAFS spectra for ions coordinate DAPhen ligands in a similar mode regardless of the substituent group in the diamide. After reasonable fittings of the spectra, the metric parameters including coordination number (*CN*), interatomic distance (*R*), Debye-Waller factor (σ^2), energy shift (ΔE), and *R*-factor were extracted, as presented in Table 2. It is clear parameters, which further confirm a similar type of the UO_2^{2+} coordination in the UO_2^{2+} complexes with all the test DAPhen ligands including reported Et-Tol-DAPhen. Detailedly, U–O$_{ax}$ distances of ~1.77 Å obtained are typical of UO_2^{2+} compounds [26,27], and the U–O$_{ax}$ σ^2 value (0.001–0.002 Å^2) are consistent with the reported value for UO_2^{2+} (0.001–0.003 Å^2) [28,29]. There are two O atoms at a distance of ~2.36 Å and four O/N atoms at a distance of ~2.53 Å, comprising the first equatorial shell

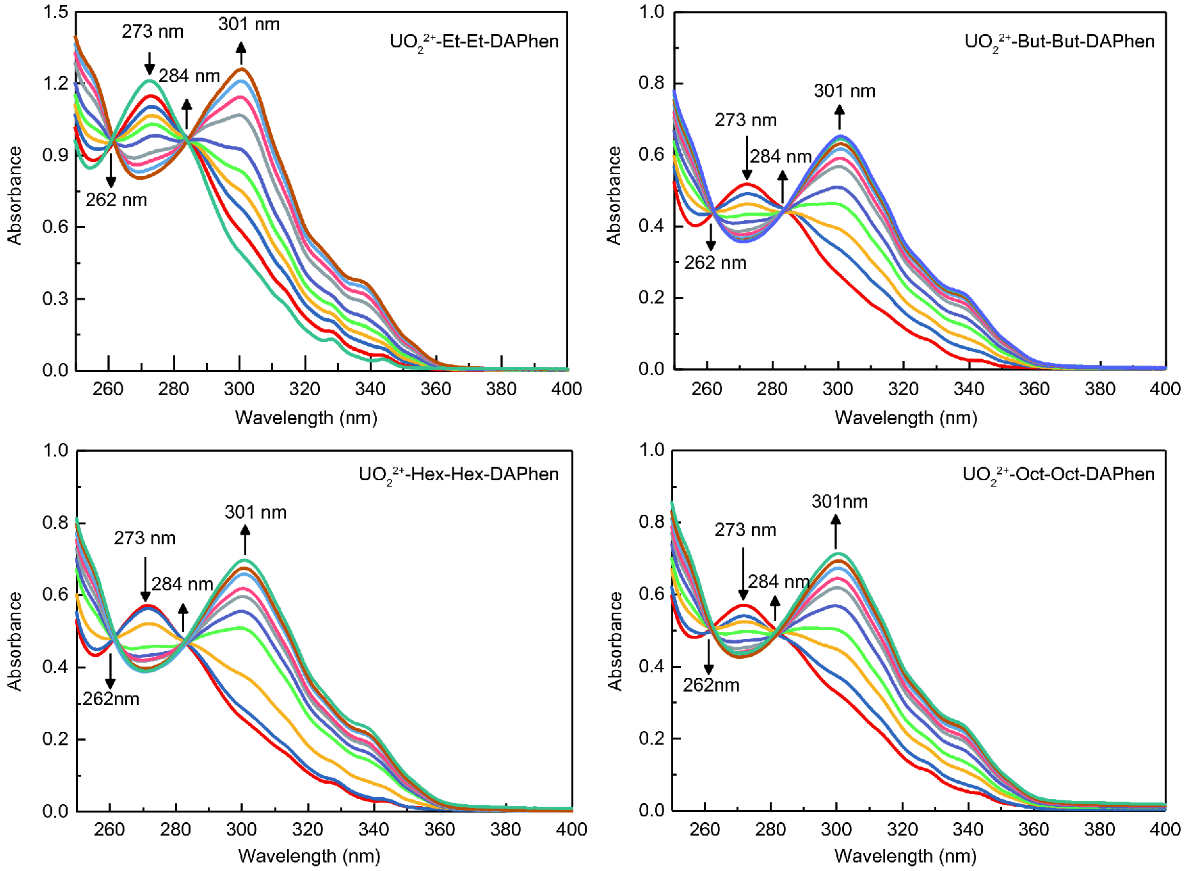


Figure 3 Spectrophotometric titration of Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen (C_L=2×10^{-5} M) with $UO_2(NO_3)_2$ in acetonitrile (C_M=0–3.0×10^{-5} M), *T*=25 °C, *I*=0.01 M Et_4NNO_3 (color online).

Table 1 Stability constants (log*β*) for UO_2^{2+} complexes with Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen and Oct-Oct-DAPhen in acetonitrile determined by UV-Vis spectrometry

Ligand	complexation reaction	log*β*
Et-Et-DAPhen	UO_2^{2+}+L=UO_2L^{2+}	4.07
But-But-DAPhen		4.51
Hex-Hex-DAPhen		4.32
Oct-Oct-DAPhen		4.02
Et-Tol-DAPhen		4.68 [18]

of UO_2^{2+} ions. One N atom at ~2.9 Å was fitted as the second equatorial shell, and the U–N distance is well consistent with that in reported crystalline UO_2^{2+} complex with Et-Tol-DAPhen, in which one nitrate ion binds one UO_2^{2+} ion in bidentate fashion. All the above results clearly suggest that the UO_2^{2+} complexes with Et-Et-DAPhen, But-But-DAPhen and Hex-Hex-DAPhen have the similar coordination structure with that of crystalline UO_2^{2+} complex with Et-Tol-DAPhen. That is, one DAPhen ligand bonds one UO_2^{2+} ion in tetradentate mode through two amide oxygen atoms and two pyridine nitrogen atom, while nitrate oxygen atoms bridge one nitrate ion and one UO_2^{2+} ions in bidentate mode. The same structure also indicates that tailoring the substituent group in the diamide of DAPhen from ethyl to octyl and even to tolyl does not change the coordination behavior of this ligand with UO_2^{2+}.

4 Conclusions

We report here a detail investigation on UO_2^{2+} extraction and coordination with four tetradentate ligands, *N*,*N*′-diethyl-*N*,*N*′-diethyl-2,9-diamide-1,10-phenanthroline (Et-Et-DAPhen), *N*,*N*′-dibutyl-*N*,*N*′-dibutyl-2,9-diamide-1,10-phenanthroline (But-But-DAPhen), *N*,*N*′-Dihexyl-*N*,*N*′-dihexyl-2,9-diamide-1,10-phenanthroline (Hex-Hex-DAPhen) and *N*,*N*′-dioctyl-*N*,*N*′-dioctyl-2,9-diamide-1,10-phenanthroline (Oct-Oct-DAPhen), aiming to characterize the relationship between properties and substitute groups of DAPhen ligands. The results suggest that tailoring the substituent group in the diamide of DAPhen from ethyl to octyl and even to tolyl does not change the coordination structure of the UO_2^{2+} complexes, but affects the extraction ability of the ligands in the following two ways: (1) a short alkyl chain in diamide moieties make the ligand hard to dissolve in organic solvent but prefer to transfer into the aqueous phase during the extraction, thus leading to a poor UO_2^{2+} extraction. (2) A long alkyl chain or a bulky substituent group exhibits clear steric

Table 2 Metric parameters obtained by fitting of the EXAFS spectra

Sample	Shell	*CN*[a]	*R* (Å)[b]	s^2 (Å^2)[c]	*DE* (eV)[d]	*R*-factor[e]
UO_2^{2+}-EED	U–O$_{ax}$	2[f]	1.77	0.002	9.0	0.013
	U–O$_1$	2.1	2.37	0.007	9.0	–
	U–O$_2$/N$_1$	3.8	2.52	0.007	9.0	–
	U–N$_2$	1.2	2.94	0.002	9.0	–
UO_2^{2+}-BBD	U–O$_{ax}$	2[f]	1.77	0.002	9.7	0.008
	U–O$_1$	2.2	2.41	0.008	9.7	–
	U–O$_2$/N$_1$	4.4	2.53	0.008	9.7	–
	U–N$_2$	0.8	2.94	0.001	9.7	–
UO_2^{2+}-HHD	U–O$_{ax}$	2[f]	1.79	0.001	8.2	0.006
	U–O$_1$	2.3	2.42	0.006	8.2	–
	U–O$_2$/N$_1$	3.9	2.52	0.006	8.2	–
	U–N$_2$	1.0	2.95	0.001	8.2	–
UO_2^{2+}-ETD	U–O$_{ax}$	2[f]	1.78	0.002	7.2	0.012
	U–O$_1$	2.1	2.41	0.006	7.2	–
	U–O$_2$/N$_1$	3.8	2.52	0.007	7.2	–
	U–N$_2$	1.2	2.94	0.001	7.2	–

a) Coordination number, *N*±~20%; b) interatomic distance, *R*±~0.03 Å;c) Debye-Waller factor; d) energy shift linked for all the paths; e) goodness of fit parameter; f) fixed parameter; UO_2^{2+}-EED, UO_2^{2+}-BBD, UO_2^{2+}-HHD and UO_2^{2+}-ETD denote the UO_2^{2+} complexes with Et-Et-DAPhen, But-But-DAPhen, Hex-Hex-DAPhen, and Et-Tol-DAPhen, respectively.

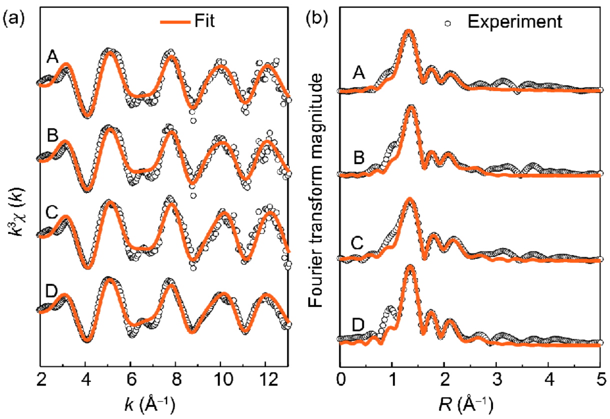


Figure 4 (a) Raw U L$_{III}$-edge k^3 weighted EXAFS spectra of the UO_2^{2+} complex with Et-Et-DAPhen (A), But-But-DAPhen (B), and Hex-Hex-DAPhen (C) including the best theoretical fits and crystalline UO_2^{2+} complex with Et-Tol-DAPhen (D) as reference. (b) Corresponding Fourier transforms. The FT spectra are not corrected for phase shift (color online).

effect thus weaken the extraction ability of DAPhen ligand by reducing its binding affinity (positively correlated to the stability constants) with UO_2^{2+}. The findings of this article offer basic data for U(VI) complexation with DAPhen ligands and thus helping to establish a structure-property relationship that benefits designing more efficient ligands for actinide separation. Further work is in progress to further optimize structure of the DAPhen ligand by varying more substituent groups, and also to assess radiation stability of these ligands for applications under irradiation as in treatment of high-level radioactive waste liquid.

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Conflict of interest The authors declare that they have no conflict of interest.

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