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ARTICLE

# Solvent Extraction of Americium(III) and Europium(III) with Tridentate N,N-dialkyl-1,10-Phenanthroline-2-Amides-Derived Ligands: Extraction, Complexation and Theoretical Study

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The extraction and complexation behavior of soft-hard combined N,N-dialkyl-1,10-phenanthroline-2-amide (PTA) ligands for Am(III) and Eu(III) in $HNO_3$ solution was investigated. The effects of acidity in aqueous, shaking time, concentration of the extractant and the temperature on distribution ratios were studied. The ability for the extraction of both Am(III) and Eu(III) were found to decrease with the increase of the length of substitute alkyl chains, and the highest extractability and selectivity of Am(III) over Eu(III) were found for the diethyl-substituted ligand. The separation factor of Am(III) over Eu(III) reached around 7.6 at low acidity and high salinity. UV-vis titration revealed that the dialkyl-substituted tridentate PTAs all dominantly formed 1:1 complexes with Eu(III), which agreed well with the results of slope analyses in the extraction experiments. The stability constants ($K_{EuL}$) as well as the protonation constants ($K_H$) were also determined by UV-vis titration. Computation chemistry gave a good explanation on the relationship between the alkalinity and the protonation energy of proposed PTA ligands. Density functional theory (DFT) calculations on optimized structures of Am(III) and Eu(III) complexes with C2-PTA showed that the nature of selectivity may originate from the difference of covalency between the metal ion and the donor N atoms, which fits well with the experimental results.

## Introduction

In the spent fuel reprocessing, the high-level liquid waste (HLLW) from PUREX process is the major environmental concern of its high radiotoxicity level. In recent years, remarkable efforts were done in order to achieve safe treatment and disposal of HLLW for the sustainable development of nuclear energy.[1] The partitioning and transmutation (P&T) is one of the most perspective technology to solve this problem. The P&T strategy aims at transforming the minor actinides (MAs) such as Am, Np and Cm into the short-lived or stable isotopes with neutron bombardment, to reduce the burden on geological storage. However, the lanthanides in HLLW have very high neutron capture cross-sections, and need to be removed before the transmutation.[2]
The principal problems in the separation of An(III) from Ln(III) are the same oxidation sate and similar chemical properties. So far, selective extraction with soft or hard ligands (e.g. N, S and O-donor) is the mainstream approach. In the past three decades, some ligands containing soft nitrogen atoms, such as 2,6-bis(5,6-dialkyl-1,2,4-trizain-3-yl)pyridine (R-BTP),[3] 6,6'-bis(5,6-dialkyl-1,2,4-trizain-3-yl)-2,2'-bipyridine (R-BTBP)[4] and 2,9-bis-(5,6-dialkyl-1,2,4-trizain-3-yl)-1,10-phenanthroline (R-BTPhen)[5,6], were exploited as potential extractants, and were proved to have high selectivity on An(III) (Fig. 1, a-c). Several ligands that contain hard oxygen atoms, represent by diglycolamide (DGA) family (Fig. 1d),[7-12] display high affinity on both An(III) and Ln(III). Unfortunately, these ligands are often less selective compared to many ligands containing soft

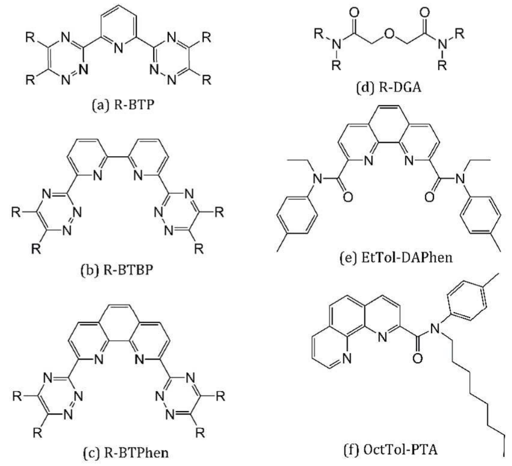

Fig. 1 Structures of extractants discussed in this paper.

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atoms[11,13].

Based on the investigations of these ligands, much effort in improving the extraction ability and selectivity has been done. Earlier G. Modolo *et al*. studied the binary extractants system composed of both soft-donor 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-[1,2,4]trizazin-3-yl)-[2,2']-bipyridine ($CyMe_4BTP$) and hard-donor N,N,N',N'-tetraoctyldiglycolamide (TODGA). This mixture shows better and more efficient extraction than using $CyMe_4BTBP$ alone.[14] However, the binary mixture of extractants make the system much complicated and difficult for further investigation of the extraction mechanics. An ideal solution is to combine both hard and soft donor atoms in one structure simultaneously. Recently, N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (EtTolDAPhen) (Fig. 1e) was developed by Xiao. *et al*., and its extraction behavior for various metal ions such as U(VI), Th(IV), Am(III) and Eu(III) was studied experimentally and theoretically.[15-17] Similar diamide derivations for the separation of An(III) from Ln(III) were studied by M. Yu. Alyapyshev *et al*.[18] These tetradentate ligands contain two O atoms on amide groups and two N atoms on rigidity phenanthroline skeleton. Also, the extraction behavior of mono-substituted phenanthroline derivatives like N-Octyl-N-tolyl-1,10-phenanthroline-2-carboxamide (OcTolPTA) (Fig. 1f) and N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) on Eu(III) was studied by T. Kobayashi *et al*.[19] Synergistic extraction of Ln(III) with MePhPTA and pivaloyltrifluoroacetone (HA) was studied by Y. Hasegawa. *et. al*.[20] Due to the rigid skeleton and hard-soft combined donor atoms, these ligands exhibit fast dynamics and high distribution ratio in solvent extraction of some An(III) and Ln(III). Even so, little attention has been devoted to N,N-dialkyl substituted 2-amide-1,10-phenanthroline-derived ligands for An(III)/Ln(III) extraction and separation by present. As the hard-soft donor combined strategy exhibits such advantages in the designing of novel ligands for separation, further and necessary research should be conducted.

In view of the current situation above, we proposed a series of substituted 1,10-phenanthroline-2-carboxamide ligands with different length of alkyl chains, namely, N,N-diethyl-1,10-phenanthroline-2-carboxamide (C2-PTA), N,N-dibutyl-1,10-phenanthroline-2-carboxamide (C4-PTA) and N,N-dihexyl-1,10-phenanthroline-2-carboxamide (C6-PTA). Their extraction behavior for Am(III) and Eu(III) in $HNO_3$ solution was investigated. The extraction models were studied by slope analysis and the UV-vis titration. DFT calculations were carried out on the basis of the experimental work to provide a better understanding of the bond nature and selectivity of such ligands with metal ions.

## Experimental

### Synthesis and characterization of PTA

The synthesis route of N,N-dialkyl-2-amide-1,10-phenanthroline-derived ligands is similar to that of EtTolDAPhen, MePhPTA and C2-PTA, as described elsewhere, and is shown in Fig. 2.[15,19,21] The final crude product was purificated with silica gel column chromatography (methanol/dichloromethane = 1/15), and then recrystallized from ethanol. NMR spectra were measured on a Bruker AVANCE III HD 400 MHz spectrometer. FT-IR spectra were recorded on a Bruker VERTEX 70 instrument. ESI-MS data were obtained on a Bruker microTOF-Q II spectrometer.

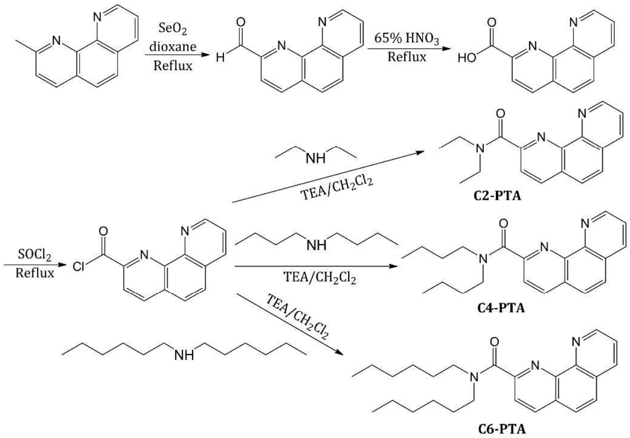

Fig. 2 Synthesis route of C2-, C4- and C6-PTA.

**C2-PTA:** $^1H$ NMR ($CDCl_3$, 400 MHz, ppm): $\delta$ 9.21 (dd, 1H, $J_{7\text{-}9}$ = 1.6 Hz, $J_{8\text{-}9}$ = 3.6 Hz, $H_9$), 8.34(d, 1H, $J$ = 8.2 Hz, $H_4$), 8.27(d, 1H, $J$ = 8.0 Hz, $H_7$), 7.92(d, 1H, $J$ = 8.4 Hz, $H_3$), 7.83(m, 2H, $J$ = 3.6 Hz, $H_5$ and $H_6$), 7.65(dd, 1H, $J_{7\text{-}8}$ = 8.0 Hz and $J_{8\text{-}9}$ = 4.4 Hz, $H_8$), 3.50-3.58, 3.62-3.69(m, 4H, $J$ = 7.1 Hz), 1.23-1.29, 1.32-1.38 (t,6H, $J$ = 7.1 Hz). $^{13}C$ NMR ($CDCl_3$, 100 MHz, ppm): 168.73, 154.89, 150.42, 146.13, 144.66, 136.92, 136.07, 129.03, 128.57, 127.37, 126.25, 123.10, 122.51, 43.52 and 40.61, 14.47 and 12.99. FT-IR: (KBr, $v$/cm$^{-1}$): 3381, 2976, 2936, 2889, 1624, 1460, 1379, 1094, 1049, 881, 758. ESI-MS: 280.1443 (M+H$^+$), 318.0994 (M+K$^+$), 559.2792 (2M+H$^+$), 581.2604 (2M+Na$^+$), 597.2351 (2M+K$^+$). Yield: 66%; pale-pink powder; mp 120-121 $^oC$.

**C4-PTA:** $^1H$ NMR ($CDCl_3$, 400 MHz, ppm): $\delta$ 9.20 (dd, 1H, $J_{7\text{-}9}$ = 1.2 Hz and $J_{8\text{-}9}$ = 4.2 Hz, $H_9$), 8.33(d, 1H, $J$ = 8.2 Hz, $H_4$), 8.26(d, 1H, $J$ = 8.0 Hz, $H_7$), 7.93(d, 1H, $J$ = 8.2 Hz, $H_3$), 7.83(m, 2H, $J$ = 3.6 Hz, $H_5$ and $H_6$), 7.64(dd, 1H, $J$ = 8.0, 4.3 Hz, $H_8$), 3.53-3.60, 3.45-3.52(t, 4H, $J$ = 8.0 Hz), 1.78(m, 4H, $J$ = 8.0 Hz), 1.42-1.62(m,4H, $J$ = 7.6 Hz), 0.91(t, 6H, $J$ = 7.6 Hz). $^{13}C$ NMR (CDCl3, 100 MHz, ppm): 168.74, 154.88, 150.32, 144.55, 136.84, 136.00, 128.99, 128.51, 127.38, 126.23, 123.08, 122.79, 49.29 and 46.47, 31.25 and 29.83, 20.56 and 20.00, 13.97 and 13.66. FT-IR: (KBr, $v$/cm$^{-1}$): 3384, 2958, 2933, 2871, 1625, 1473, 1382, 1120, 1028, 860, 729. ESI-MS: 336.2067 (M+H$^+$), 358.1893 (M+Na$^+$), 374.1624 (M+K$^+$), 671.4015 (2M+H$^+$), 693.3821 (2M+Na$^+$). Yield: 54%; yellow oily liquid at room temperature.

**C6-PTA:** $^1H$ NMR ($CDCl_3$,400 MHz, ppm): $\delta$ 9.21 (dd, 1H, $J$ = 1.6 Hz and 4.0 Hz, $H_9$), 8.34 (d, 1H, $J$ = 8.4 Hz, $H_4$), 8.27 (dd, 1H, $J$ = 1.6, 8.0 Hz, $H_7$), 7.93 (d, 1H, $J$ = 8.0 Hz, $H_3$), 7.83 (m, 2H, $J$ = 3.6 Hz, $H_5$ and $H_6$), 7.65 (m, 1H, $J$ = 8.0 Hz, $H_8$), 3.44-3.60 (t, 4H, $J$ = 8.0 Hz), 1.77 (m, 4H, $J$ = 7.6 Hz), 1.25-1.36 (m, 12H), 0.89 (t, 6H). $^{13}C$ NMR ($CDCl_3$, 100 MHz, ppm): 168.76, 154.92, 150.41, 146.17, 144.65, 136.90, 135.99, 129.02, 128.52, 127.41,

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126.23, 123.14, 122.69, 49.28 and 47.80, 31.80 and 31.69, 29.01 and 28.60, 27.70 and 27.01, 22.71 and 22.65, 14.05 and 13.90. FT-IR: (KBr, *v*/cm$^{-1}$): 3388, 2952, 2931, 2866, 1625, 1458, 1377, 1166, 860, 727. ESI-MS: 392.2690 (M+H$^+$), 414.2505 (M+Na$^+$). Yield: 57%; light-yellow oily liquid at room temperature.

### Solvent Extraction

The stock solution of radioactive $^{241}$Am (3.08 MBq/L) + $^{152}$Eu (1.85 MBq/L) radiotracers containing stable Eu$^{3+}$ carrier (1800 mg/L) was provided by Institute of Modern Physics (IMP), Chinese Academy of Sciences (CAS). All the other chemical reagents were analytical grade, and were used without further purification. The radioactive operations were performed in the lid-shielding glovebox. The organic phases were prepared with stock solution of PTA in the diluent (600 μL). Then the pre-equilibrated organic phases were mixed with equal volume of the aqueous phases containing $HNO_3$ solution and 50 μL radiotracers in 10 mL centrifuge tubes. The mixtures were vigorously shaken for several minutes under constant temperature to reach equilibrium. After shaking and phase separation by centrifugation (3000 rpm), 450 μL of the aqueous phase and the organic phase were transferred separately into fresh tubes. The γ ray counts of the isotopes were measured by an HPGe-γ-detector (EG&G Ortec GEM-30200-P with a relative efficiency of 30%). A DSPEC-502$^{TM}$ Digital Gamma-Ray Spectrometer was employed for data acquisition. The energy resolution (FWHM) was 1.70 keV at 1332.5 keV. The areas of characteristic peaks of $^{241}$Am (59.5 keV) and $^{152}$Eu (121.8 keV) were calculated respectively by Gaussian fitting. The extraction processes were repeated three times and the results were averaged. The errors of the net areas for all peaks were less than 5%.

The distribution ratio of metal ions ($D_M$) is defined as the ratio of analytical concentration in each phase, which is in proportional to the ratio of corresponding peak areas in γ spectra:

$$D_M = [M]_{(org.)}/[M]_{(aq.)} = A_{(org.)}/A_{(aq.)} \tag{1}$$

The separation factor of Am(III) over Eu(III) ($SF_{Am/Eu}$) was determined by the ratio of $D_{Am}$ and $D_{Eu}$.

### UV-vis Titration

The UV-vis titration was carried out in methanol. To determine the composition and the stable constant of EuL complexes ($K_{EuL}$), 0.2 mmol/L $Eu(NO_3)_3{\cdot}6H_2O$ solution was added by aliquot 10 μL to the solution containing 30 μmol/L ligands (C2-, C4- and C6-PTA). To determine the protonation constant of the ligands ($K_H$), 2 mmol/L $HNO_3$ solution was added by aliquot 10 μL to the solution containing 30 μmol/L ligands (C2-, C4-, C6-PTA and non-substituted 1,10-phenanthroline). The mixture was stirred in the quartz cuvette (*b* = 1.0 cm) for 1 min, which was enough to reach the equilibrium. The spectra at 190-360 nm were measured with the UV-vis spectrometer (Thermo Scientific, Evolution 300) at 293 ± 0.1 K. The spectra at the wavelength of from 250 nm to 320 nm representing the superposition of the absorbance of free ligands and the complexes were used for analysis. The obtained data were fitted with the available ThordarsonFittingProgram.[22]

### Theoretical Methods

The theoretical calculations for protonated PTAs were carried out by Density Functional Theory (DFT) with B3LYP[23] correlation function in *Gaussian 09*d software package.[24] The Pople-style double-ζ 6-31G(d) basic sets[25] were used for light CHON atoms. For metal atoms, the quasi-relativistic effective core potentials (RECPs) were adopted: the 60 and 28 electrons were replaced by the employed small-core RECPs for Am and Eu, respectively. The residual 35 electrons were treated with the complementary energy-consistent pseudorelativistic basic sets.[26,27] The calculations for the complexes of Am(III) and Eu(III) were in septet spin multiplicity in ground state, and no symmetry was adopted for constraint. The original geometry structures were optimized under the above-mentioned theoretical level to reach the stationary point. The frequencies were calculated right after the geometry optimization to make sure the obtained structures were the minima on the potential energy surface. The geometry parameters were examined on the optimized structures. The natural population analysis (NPA) was carried out in the NBO 5.0 version.[28] For energy calculations in aqueous phase, the polarizable continuum model (PCM)[29] was used to take into account solvation effect. The protonation energy for a ligand (L) was defined as the energy difference of the following reaction:[30,31]

$$L + H_3O^+ \rightarrow [LH(H_2O)]^+ \tag{2}$$

It was calculated at the same level of theory on the basis of optimized geometry structures.

## Results and discussion

### Solvent Extraction Studies

**Effect of acidity and the substituted alkyl chain.** The extraction behavior of C2-, C4- and C6-PTA was tested in same condition. The effect of acidity in aqueous was examined by varying the initial concentration of nitric acid from 0.0001 to 1.0 mol/L. The influence on *D*(Am) and *D*(Eu) are shown in Fig. 3.

It can be seen that the distribution ratios of both Am(III) and Eu(III) as well as $SF_{Am/Eu}$ decrease with the increase of nitric acid concentration. This is due to the protonation of donor N

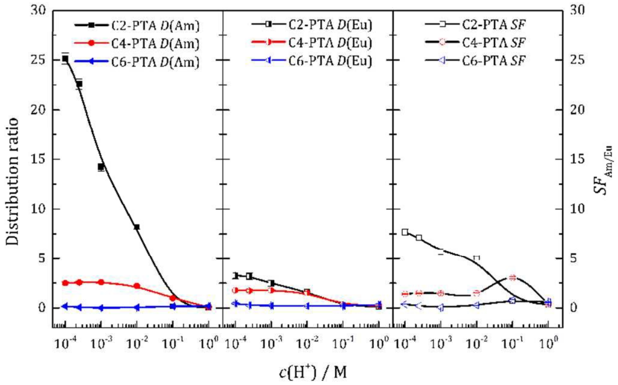

Fig. 3 Effect of initial acidity in aqueous phase by different C2-PTA, C4-PTA and C6-PTA. Organic phase: 0.2 mol/L PTA in chloroform. Aqueous: $HNO_3$ + $^{241}$Am/$^{152}$Eu radiotracers. *T* = 293 K.

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atoms on 1,10-phenanthroline moiety. C2-PTA shows a much higher extraction selectivity of Am(III) over Eu(III). The maximum values of *D*(Am) and *D*(Eu) reach (25.2 ± 0.2) and (3.3 ± 0.1), respectively. As lower acid concentration will cause the hydrolysis of Am(III) and Eu(III) in aqueous, the highest $SF_{\mathrm{Am/Eu}}$ is determined to be (7.6 ± 0.3) at the acidity of around $10^{-4.0}$ mol/L. Similar trends were also observed in the extraction of Eu(III) by some other N-donor ligands like 1,3-bis[3-(2-pyridyl)pyrazol-1-yl]propane (Bibpp), 1,2-bis[3-(2-pyridyl)pyrazyl-1-methyl]benzene (Dbnpp)[31] and OcTolPTA,[19] but *D*(Eu) values by C2-, C4- and C6-PTA are below those of OcTolPTA. Meanwhile, the distribution ratios of Am(III) and Eu(III) by C4-PTA and C6-PTA are all much lower than those by C2-PTA, respectively, while the trend of decrease along with the increase of acidity remains the same. The distribution ratios of the two metal ions by C4-PTA are all below 2.6, and the separation factors are all below 3.0. For C6-PTA, the distribution ratios are even lower than 0.5, showing that hardly can C6-PTA extract trace amount of Am(III) or Eu(III) from $HNO_3$ medium. It suggests that the distribution ratios decrease as the amidic alkyl chains extend, and that the longer alkyl chains suppress the extraction. The phenomena may probably attribute to the following reasons. First, PTAs with longer alkyl chains have higher alkalinity and are easier to be protonated (this will be discussed later in this work), which could inhibit the conversion of the ligands to the tridentate conformation during the extraction. Second, longer alkyl chains may have higher steric hindrance for the coordination, and the long lipophilic alkyl chains may prevent the ligand from cutting into the aqueous phase at the contact surface of the two phases. This finding can also be supported by other amide derivatives.[9,11]

As C2-PTA showed the greatest extraction ability, it was chosen as the representative in subsequent experiments.

**Effect of nitrate ions.** The effect of nitrate ions on the extraction of Am(III) and Eu(III) with 0.2 mol/L C2-PTA was processed, see Fig. 4. Sodium nitrate was chosen as the salting-out agent in the concentration of 0.1-4.0 mol/L, while the acid concentration was fixed at $10^{-3.63}$ mol/L. In Fig. 4, as the concentration of nitrate ions increases, *D*(Am) and *D*(Eu) clearly increase at identical rates, while $SF_{\mathrm{Am/Eu}}$ remains about the same. On the fact of the appearance in the experiment, it can be inferred that nitrate ions promote the formation of the complexes at high concentration, acting as counter-ions or binding ligands of the metal ions[17].

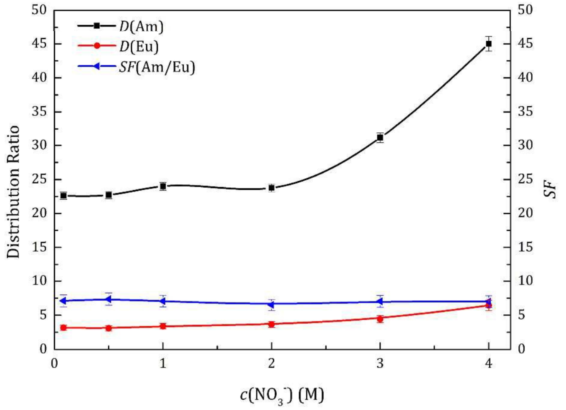

Fig. 4 Effect of nitrate ion concentration. Organic phase: 0.2 mol/L C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ radiotracers + $NaNO_3$. *T* = 293 K.

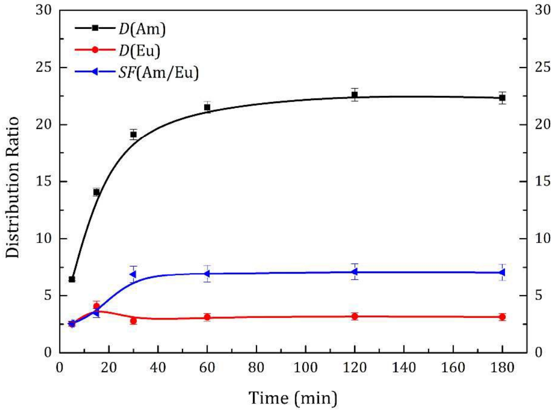

Fig. 5 Effect of shaking time. Organic phase: 0.2 mol/L C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ radiotracers. *T* = 293 K.

**Effect of shaking time.** The equilibrium time in the extraction with 0.2 mol/L C2-PTA in chloroform was examined. As Fig. 5 presents, the extraction process reached equilibrium after shaking for 60 min at 57 rpm, 293 K. It can be seen that PTA ligands exhibit a fast kinetics comparable with BTPs, BTBPs and BTPhens.[3,5] This may probably due to the rigidity skeleton of the two juxtapose nitrogen atoms on the *cis*- conformation, which is favorable for coordination with metal cations. To ensure the complete equilibrium of extraction in such condition, all the mixtures were shaken for 120 min in this work.

**Effect of extractant concentration.** Fig. S13 shows the distribution ratios and separation factors dependence of C2-PTA concentration on Am(III) and Eu(III) extraction. The concentration of the ligand in chloroform ranges from 0.01 to 0.2 mol/L. As is shown in Fig. S13, both *D*(Am) and *D*(Eu) increase with the increase of C2-PTA concentration, and *D*(Am) grows much faster than *D*(Eu), and as a result, the $SF_{\mathrm{Am/Eu}}$ values also increase within the range of the measurement.

The model for the extraction of trivalent metal ions (M) with PTA can be expressed as:[19]

$$\mathrm{M}^{3+}_{(\mathrm{aq.})} + 3\mathrm{NO}_3^-{}_{(\mathrm{aq.})} + x\mathrm{PTA}_{(\mathrm{org.})} = \mathrm{M(PTA)}_x(\mathrm{NO}_3)_{3(\mathrm{org.})} \tag{3}$$

The apparent equilibrium constant ($K_{\mathrm{ex}}$) and distribution ratio (*D*) are defined as

$$K_{\mathrm{ex}} = \frac{[\mathrm{M(PTA)}_x(\mathrm{NO}_3)_3]_{(\mathrm{org.})}}{[\mathrm{M}^{3+}]_{(\mathrm{aq.})}[\mathrm{NO}_3^-]^3_{(\mathrm{aq.})}[\mathrm{PTA}]^x_{(\mathrm{org.})}} \tag{4}$$

$$D = \frac{[\mathrm{M(PTA)}_x(\mathrm{NO}_3)_3]_{(\mathrm{org.})}}{[\mathrm{M}^{3+}]_{(\mathrm{aq.})}} \tag{5}$$

By introducing Eq. (5) into Eq. (4), and taking logarithm of both sides, the linear equation can be obtained:

$$\lg D = \lg K_{\mathrm{ex}} + 3\lg[\mathrm{NO}_3^-]_{(\mathrm{aq.})} + x\lg[\mathrm{PTA}]_{(\mathrm{org.})} \tag{6}$$

When the composition of aqueous is kept consistent, and $K_{\mathrm{ex}}$ is a constant at a given temperature, all the constants can be merged into C, and the equation can be simplified into:

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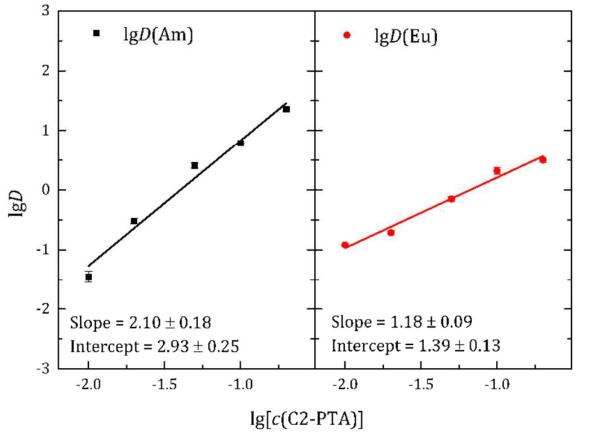

Fig. 6 Ligand concentration dependence of distribution ratios on the extraction of Am(III) and Eu(III) by C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ radiotracers. *T* = 293 K.

$$\lg D = x\lg[\text{PTA}]_{(\text{org.})} + C \qquad (7)$$

According to Eq. (7), plots of lg*D*(Am), lg*D*(Eu) as a function of lg[C2-PTA] give two straight lines, presenting the coordination number of extractant molecules by the value of *x*, see Fig. 6. It elucidates that in such condition, C2-PTA forms 1:1 (*x* = 1.18 ± 0.09) and 2:1 (*x* = 2.10 ± 0.18) species with Eu(III) and Am(III), respectively. Though Eu(III) and Am(III) form different species in such solution, it is still considerable due to the tiny difference between the ion radius and the electron structures of the metal atoms in their complexes, and this difference can usually be observed in the extraction of Am(III) and Eu(III) with many other N-donor ligands.[32-36]

Generally, both lanthanides (III) and actinides (III) mostly form complexes of CN = 8, 9, 10 with such tridentate ligands (such as BTP and PTA), or tetradentate ligands (such as BTBP, BTPhen and DAPhen), as is reported elsewhere.[3,4,15,16] In those 1:1 complexes, one metal ion coordinate with one ligand, together with three bidentate nitrate ions in inner-sphere, constituting neutral $ML(NO_3)_3$ species (CN = 9 or 10). In some 2:1 complexes, however, one metal ion combine with two tridentate or tetradentate ligands as well as one or two nitrate ion(s) in the inner sphere like $ML_2(NO_3)_x^{(3-x)+}$ (*x* = 1, 2), and the nitrate ions in outer sphere can be extracted simultaneously into organic phase (in form of an ionic polymer) to keep the electric neutrality[4]. It is reported by T. Kobayashi *et al*. that the PTAs with benzene ring (MePhPTA and OcTolPTA) mainly form 2:1 complexes with Eu(III).[19] Compared with the conclusion for C2-, C4- and C6-PTA, the difference is likely to be attribute to the steric hindrance. In MePhPTA and OcTolPTA, the large steric hindrance of aromatic rings may prevent the ligand in the stable *trans*- conformation from turning to *cis*-conformation, and this could result in the absence of complexation of carbonyl O atom with metal ion. UV-vis titration of MePhPTA and non-substituted Phen by Eu(III) revealed that their 2:1 complexes are found, suggesting that a similar behavior of both coordinating with the two N atoms on the phenanthroline rings is likely the case.

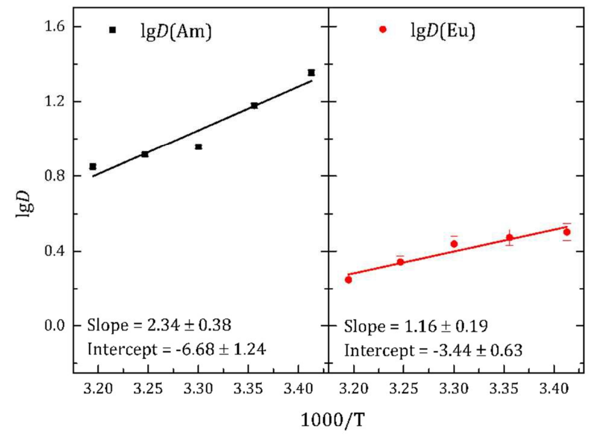

Fig. 7 Effect of temperature. Organic phase: 0.2 mol/L C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ radiotracers.

**Effect of temperature.** According to the Van't Hoff equation, the enthalpy change of the extraction reaction has the relationship with the extraction constant and distribution ratio:

$$\Delta H = -R\frac{\partial \ln K_{ex}}{\partial(1/T)} = -2.303R\frac{\partial \lg D}{\partial(1/T)} \qquad (8)$$

where R is the gas constant. By plotting lg*D* versus 1/T, the straight lines can be obtained, and the values of Δ*H* in the extraction on Am(III) and Eu(III) can simply be estimated from the slope of the corresponding line ((2.34 ± 0.38) and (1.16 ± 0.19), respectively), see Fig. 7. As calculated by Eq. (8), the –Δ*H* values are determined to be (44.8 ± 7.3) kJ/mol for Am(III) and (22.2 ± 3.6) kJ/mol for Eu(III), respectively. This indicates that the extraction processes are exothermic, and higher temperature would restrain the extraction reaction.

### Solution Spectroscopy and Stability Constant Determination

**Eu(III)-PTA complexes.** UV-vis titration was carried out to determine the stable constant of the EuL complexes. The change of absorption during the UV-vis titration of C2-, C4- and C6-PTA by Eu(III) are shown in Fig. 8. It can be seen that a free ligand has a strong absorption peak at 268 nm in methanol solution. With the addition of Eu(III) the absorption at 268 nm gradually decreases, while the new peak at 287 nm corresponding to EuL complexes increases. Only one isosbestic point is found at 276 nm, denoting the 1:1 complexes formed. This is also consistent with the result of slope analysis, and is also similar to the complexation behaviors of EtTolDAPhen.[15] By fitting the data at the wavelength of 287 nm, the stable constants ($K_{EuL}$) were determined, see Table 1.

From the table we can see that there is a slight increasing trend of the lg$K_{EuL}$ values in order of C2-, C4- and C6-PTA. Still, such small discrepancies reveal that the differences between the stabilities of Eu(III) with the three ligands may seem dramatic but not enormous, whereas the distribution ratios of C4-PTA and C6-PTA display much lower than those of C2-PTA. Thus the reasons are brought to the steric hindrance and the protonation of ligands in acid solutions, which will be discussed later in this article.

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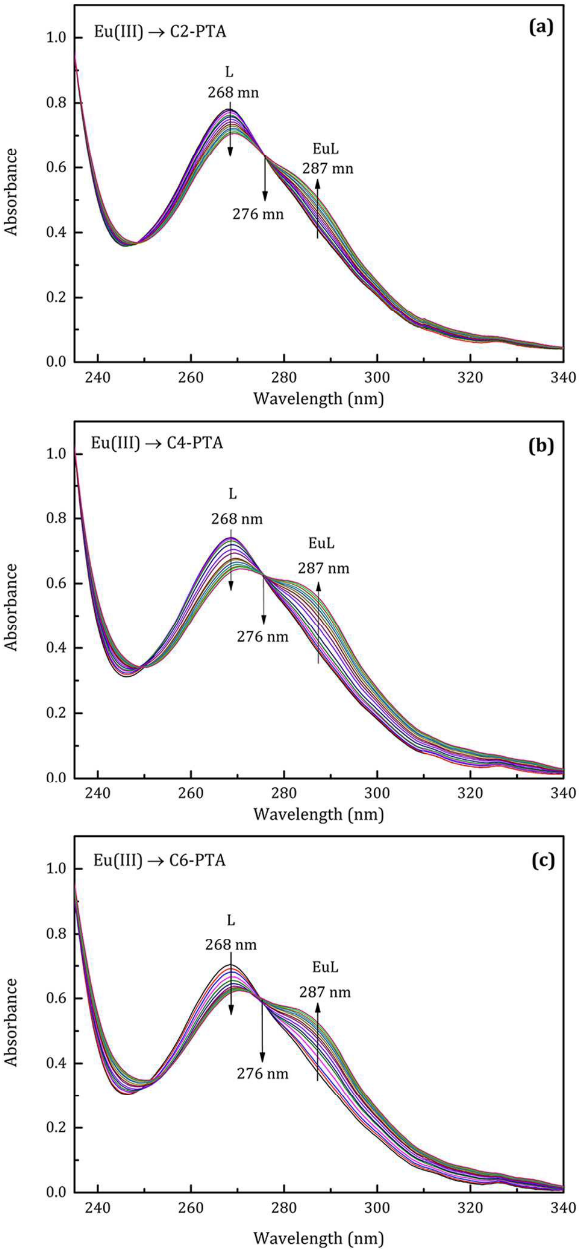

Fig. 8 The UV-vis titration of C2-PTA (a), C4-PTA (b) and C6-PTA (c) by Eu(III) in methanol medium. $c_L = 3.0\times10^{-5}$ mol/L, $c_M = 0–3.7\times10^{-5}$ mol/L, $T$ = 293 K.

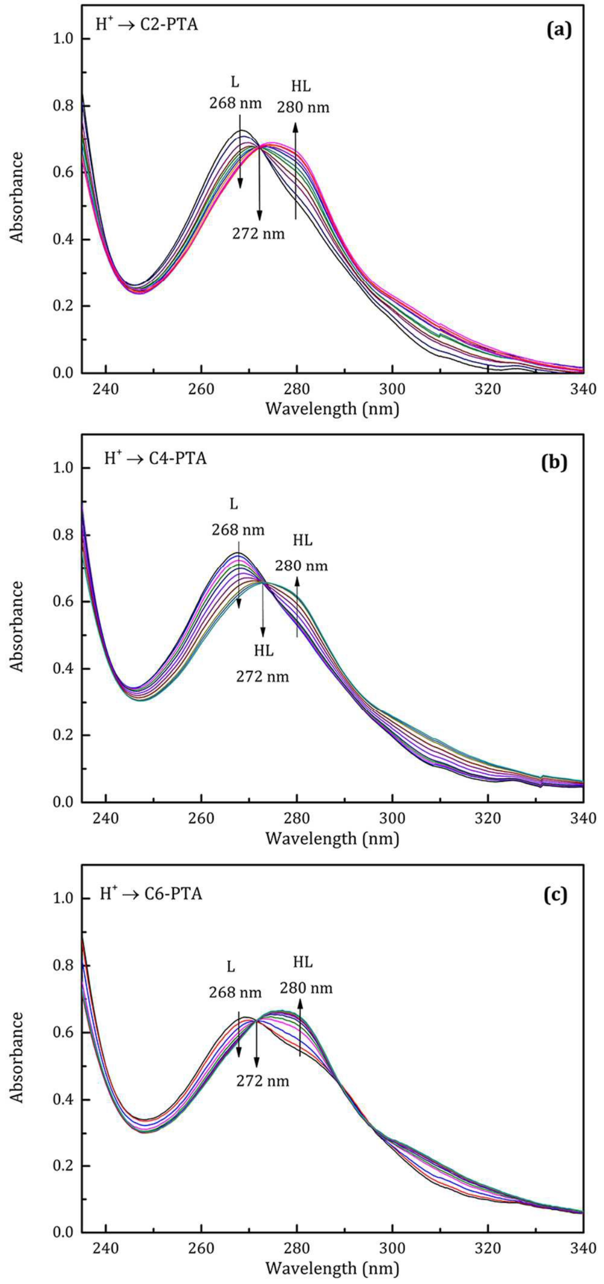

Fig. 9 The UV-vis titration of C2-PTA (a), C4-PTA (b) and C6-PTA (c) by $H^+$ in methanol medium. $c_L = 3.0\times10^{-5}$ mol/L, $c_{H+} = 0–9.3\times10^{-5}$ mol/L, $T$ = 293 K.

**H-PTA complexes.** The UV-vis titration graphs of C2-, C4- and C6-PTA as well as non-substituted 1,10-phenanthroline (Phen) by $H^+$ in methanol medium are shown in Fig. 9 and Fig. S14. It can be found that with the addition of $H^+$ the absorption at 268 nm gradually decreases, while that at 280 nm corresponding to protonated PTA increases. Only one isosbestic point is found at 272 nm (Fig. 9). The absorption of Phen, protonated Phen and the corresponding isosbestic point appear at 263, 271 and 266 nm (Fig. S14). It can be deduced from the results that the 1:1 protonated HL is formed for each ligand. The protonation constants ($K_H$) are also calculated by fitting the obtained spectra data at the wavelength of 280 nm, and are listed in Table 1. Obviously, there is an increasing trend of the lg$K_H$ values with the increase of alkyl chain length. All the ligands are alkaline, which are easily to be protonated in the presence of $HNO_3$. This can explain why the distribution

**Table 1 Fitting result of UV-vis titration at 287 nm ($Eu^{3+}$ → L) and 280 nm ($H^+$ → L).**

| L | lg$K_{EuL}$ | lg$K_H$ |
|---|---|---|
| C2-PTA | 4.00 ± 0.01 | 3.77 ± 0.03 |
| C4-PTA | 4.10 ± 0.06 | 4.13 ± 0.01 |
| C6-PTA | 4.19 ± 0.02 | 4.22 ± 0.04 |
| Phen | - | 5.39 ± 0.01 |

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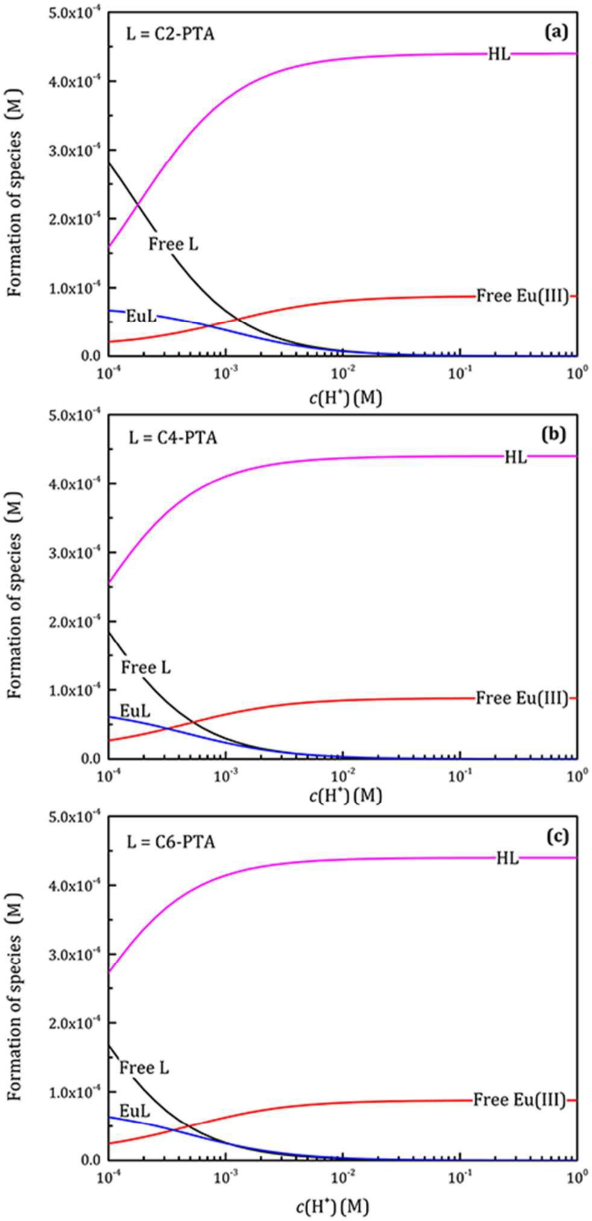

Fig. 10 The species diagrams of Eu(III) complexes with C2-PTA (a), C4-PTA (b) and C6-PTA (c) as a function of $HNO_3$ concentration.

ratios remarkably decrease with the increase of $HNO_3$ concentrations.

Fig. 10 shows the species diagrams as a function of $HNO_3$ concentration from 0.0001 to 1.0 mol/L for the Eu(III)-PTA system. The analytical concentration of the ligands and Eu(III) are set to be $4.4\times10^{-4}$ and $8.8\times10^{-5}$ mol/L, respectively. As the $HNO_3$ concentration increases, the concentration of EuL species as well as free L drastically decreases, and that of HL species increases. The protonation constants are comparable in order of magnitudes to those of the stable constant of Eu(III) with each PTA ligand (Table 1), so the protonation may become the significant side-reaction that compete with the formation of Eu(III)-PTA, and the coordination reaction would be masked in high acidic solution. As a matter of fact, hardly can the EuL species be found ([EuL] < $10^{-7}$ mol/L) according to the calculation, and almost all the ligand molecules are protonated when the $HNO_3$ concentration is higher than $10^{-1.5}$ mol/L. This is well agreed with the conclusion of solvent extraction experiment (Fig. 3).

**DFT Calculations**

**Protonation energies of the ligands.** To explore the relationship between the protonation constant and the molecular structures, the protonation energy values of C2-, C4-, C6-PTA and Phen were calculated at the B3LYP/6-31G(d) level. The calculated protonation energy, as well as the experimental lg$K_H$ values of the ligands are listed in Table 2.

As is shown, all ligands in the table exhibit large negative values of protonation energies, indicating that they are easily to be protonated in the presence of $HNO_3$ solution. The alkalinity of the ligands increases in order of C2-PTA < C4-PTA < C6-PTA < Phen. This should be attributed to the difference of electron density of the delocalized π-electrons on N1 (N(1) atom of the heterocycle) and N2 (N(10) atom of the heterocycle) atoms in PTA and Phen molecules, which is induced by the conjugated effect of electron-withdrawing (–C) of amide groups and the inductive effect of electron-donating (+I) of the alkyl chains. As a consequence, when the substituted alkyl chain increases, the protonation energy become more negative, and the structure turn out to be more difficult to deprotonate. This is consistent with the trend of the experimental lg$K_H$ values. However, the high deprotonation energy could significantly inhibit their conversion to the tridentate conformation during the extraction process, and could be regarded as one of the major reasons why C4-PTA and C6-PTA have much lower distribution ratios on metal ions than C2-PTA.

Additionally, as the protonation energy on N2 showed more negative values than N1 for each PTA ligand, N2 is considered to be the preferential protonation site with smaller steric hindrance compared to N1, according to the calculations.

**Geometry, Natural charge and WBI of $ML(NO_3)_3$ species.** In order to investigate the origin of selectivity of PTA ligands on Am(III) and Eu(III), the models for the 1:1 neutral analogues $ML(NO_3)_3$ (M = Am, Eu; L = C2-PTA) (CN = 9) in gas-phase were studied at the B3LYP/6-31G(d)/RECP level. The 2:1 structure ($ML_2(NO_3)_x^{(3-x)+}$) was not taken into consideration due to the concern of time-consuming calculations.

The optimized structures are shown in Fig. S15 and Fig. S16. As

**Table 2 Calculated protonation energy (kJ/mol) values of the ligands. The energy is calculated at the B3LYP/6-31G(d) level, with the ZPE and thermal corrections at 298.15 K, 1.0 atm.**

| L | $\Delta E_1{}^a$ | $\Delta E_2{}^b$ |
|---|---|---|
| C2-PTA | -175.1 | -186.0 |
| C4-PTA | -177.9 | -188.4 |
| C6-PTA | -178.2 | -188.7 |
| Phen | -194.3 | -194.3 |

***a*: the protonation energy on N1 atoms.**
***b*: the protonation energy on N2 atoms.**

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**Table 3 Calculated bond length, natural charges and the Wiberg bond indices (WBI) of optimized structures of $ML(NO_3)_3$ (M = Am, Eu; L = C2-PTA).**

| Complex | | $AmL(NO_3)_3$ | $EuL(NO_3)_3$ |
|---|---|---|---|
| Bond Length (Å) | M-N1 | 2.678 | 2.649 |
| | M-N2 | 2.719 | 2.707 |
| | M-O | 2.486 | 2.441 |
| Natural Charges (e) | M | 1.439 | 1.391 |
| | L | 0.395 | 0.410 |
| | N1 | -0.443 | -0.435 |
| | N2 | -0.462 | -0.449 |
| | O | -0.620 | -0.616 |
| WBI | M-N1 | 0.218 | 0.209 |
| | M-N2 | 0.218 | 0.196 |
| | M-O | 0.292 | 0.308 |

listed in Table 3, the bond lengths of Am-N1 (2.678 Å) and Am-N2 (2.719 Å) are longer than those of Eu-N1 (2.649 Å) and Eu-N2 (2.707 Å) in optimized $ML(NO_3)_3$ complexes, respectively, but the differences between M-N1 and M-N2 bonds are smaller than 0.03 Å. Taking into account that the ionic radii[32] of $Am^{3+}$ (0.98 Å) is larger than that of $Eu^{3+}$ (0.95 Å), the bond distances of Am-N are comparable to or even shorter than those of Eu-N. This trend is also consistent with the M-N bond in BTBP, BTPhen, TPEN, NTAamide, as well as the M-S bond in Cyanex 301.[6,36-39] The length of Am-O bond (2.486 Å) is about 0.045 Å longer than that of Eu-O bond (2.441 Å), showing that hard O atom has comparable or even more affinity towards Eu(III) than Am(III), which is similar to some O-donor ligands, such as Syanex-272 and DGAs.[7,9,37]

The small values of calculated Wiberg bond indices (WBIs) of M-N and M-O, in the range of 0.196–0.308, indicate that the ionic and the electrostatic interaction play the dominant role between M-N and M-O bonds. The WBIs also suggest that Am-N bonds have a little more covalency than Eu-N bonds, while Am-O bond is less covalent than Eu-O bond. The difference of these covalency between the metal and the donor atoms determines the selectivity in Am(III) and Eu(III) ions by ligands.[37,38] The natural charges of Am (1.439 e) are greater than those of Eu (1.391 e). This may originated from the stronger electron affinity of Eu, which may be caused by the well-known lanthanide contraction and the weaker nucleus-screening ability of the 4*f* shell.[36] Furthermore, the natural charge values of N (especially N2) atoms in $AmL(NO_3)_3$ is more negative than those in $EuL(NO_3)_3$ complexes, and the absolute charge difference of Am-L bonds seems to be larger than those of Eu-L bonds.

The calculated results may indicate that PTA has a stronger coordinating ability to Am(III) than Eu(III), and the selectivity of PTA of Am(III) over Eu(III) may be attributed to the bonding nature between the metal and the soft N atoms in phenanthroline rings rather than hard O atoms in amides.[37] This result fits on well with the experiment, and the same conclusion as in some other literatures[4,6,15,16,31,36] can be drawn.

## Conclusions

The extractability of Am(III) and Eu(III) with tridentate N,N-dialkyl-1,10-phenanthroline-2-amide (PTA) ligands, which combine hard-soft donors in single molecule, were investigated. The distribution ratios decrease with the increase of the length of substituted alkyl chains, and C2-PTA was proved to have the best performance in extraction at low acidity among all the three ligands investigated in this work. The dominant 2:1 and 1:1 complexes of Am(III) and Eu(III) with C2-PTA were identified by slope analysis, respectively. The stable constants of the Eu(III)-PTA complexes and the protonation constants of the ligands were determined by UV-vis titration. The species diagrams showed that the protonation was the major reason to reduce the distribution ratios of metal ions in highly acidic nitric solution. DFT calculations also revealed that the protonation energy on N2 side directly influenced the alkalinity of the ligands, which can be modified by the substitute on phenanthroline ring. From a theoretical point of view, the differences of geometry and the electron structures in Am(III) and Eu(III) complexes suggested that the selectivity of PTA ligands might originate from the discrepancies of covalency in Am-N and Eu-N bonds, and all the calculation results are in good accordance with the solvent extraction and UV-vis titration results. With the view of improving the extraction performance to meet the practical needs for actinides/lanthanides separation, the electronic properties of both N atoms should be finely tuned by introducing electron donating groups (EDG) or electron withdrawing groups (EWG) onto the aromatic rings.

The conclusions may shed light on the research of the designing of improved PTA ligands, and contribute to the improvement of structural modifications to develop novel extractants for the separations of actinides from lanthanides in the treatment and disposal of HLLW.

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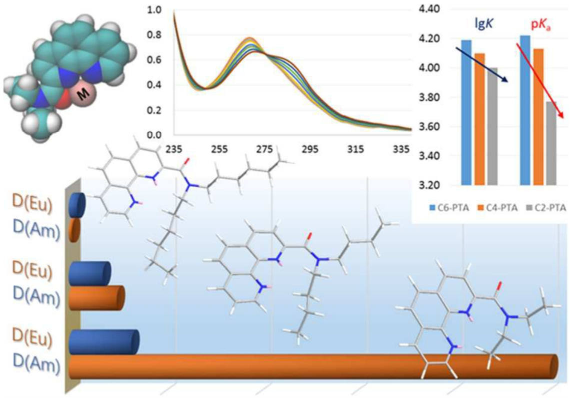

The extraction and complexation of Americium (III) and Europium (III) with three N,N-dialkyl-1,10-Phenanthroline-2-Amides analogues were investigated with theoretical calculations herein.