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Highly Efficient Trivalent Americium/Europium Separation by Phenanthroline-Derived Bis(pyrazole) Ligands

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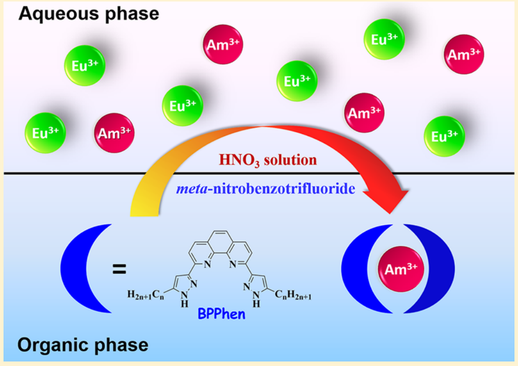
Supporting Information

ABSTRACT: The synthesis, Eu^{3+} complexation, and solvent extraction of Am^{3+} and Eu^{3+} from nitric acid solutions by tetradentate phenanthroline-derived bis(pyrazole) (BPPhen) ligands were described. By using *meta*-nitrobenzotrifluoride as diluent, BPPhen ligands in combination with 2-bromohexanoic acid extracted Am^{3+} and Eu^{3+} with remarkably high efficiency, excellent selectivity, and fast extraction kinetics. Stripping posed no issues. The ligands also showed excellent hydrolytic stability and acid tolerance. 2-Bromohexanoic anion neutralized the charge and increased the lipophilicity of the extracted ion pair. The extraction conformed to a cation exchange model. Slope analysis demonstrated the extraction of 1:2 metal/ligand complexes. Analyses by electrospray ionization mass spectrometry, time-resolved laser-induced fluorescence spectroscopy, Raman, and Fourier transform infrared techniques indicated that the composition of the extracted species is $[Eu(nOct\text{-}BPPhen)_2(H_2O)]^{3+}$. The formation of 1:2 complexes was also confirmed by UV−vis spectroscopic titration and microcalorimetric titration methods. Meanwhile, the stability constants (K) and the thermodynamic parameters (ΔH, ΔS, ΔG) for the complexation of Eu^{3+} with nOct-BPPhen were presented too.



INTRODUCTION

Partitioning and transmutation strategy is very significant for the sustainable development of nuclear energy. As for this strategy, the long-lived radiotoxic minor actinides (An) need to be partitioned from the bulk of lanthanides (Ln) prior to their transmutation, because high neutron absorption cross sections of certain Ln isotopes give rise to great hindrances to the An transmutation.[1] However, owing to the similar chemical properties of An and Ln, their separation is difficult.[2]

It has been shown that the ligands containing soft S- or N-donor atoms are capable of discriminating between An and Ln.[1c,3] The most important characteristics of ligands are the distribution ratios of metal ions defined as the ratio of the concentration of metal ions between organic and aqueous phases ($D_M = [M]_{org}/[M]_{aq}$) and the An/Ln separation factors defined as the ratio of D_{An} to D_{Ln} ($SF_{An/Ln} = D_{An}/D_{Ln}$). The extractability and the selectivity of ligands toward metal ions are usually estimated by D_M and $SF_{Am/Eu}$ values, respectively. The most representative S-donor ligand is bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301), which was able to extract Am^{3+} and Eu^{3+} with an unprecedented $SF_{Am/Eu}$ value of ~5900.[4] Nevertheless, it can only extract from relatively low HNO_3 (pH 3−4) solution owing to nondissociation and oxidative degradation of the ligand at low pH.[4,5] Besides, the phosphorus-based Cyanex 301 would produce large volumes of secondary waste upon incineration at the end its useful life. All of these greatly limit its applications in industrial process. In contrast to S-donor ligands, N-donor ligands not only have better stability against acidity and oxidation but also are composed of the elements C, H, O, and N only (CHON principle), which is beneficial to the waste management, because they are completely incinerable. Thus, more and more attentions have been paid to the research and development of N-donor ligands.

At present, the triazinyl-based N-donor ligands are identified as promising candidates for the An/Ln separation, mainly including 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl) pyridines (BTPs),[6] 6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs),[7] and 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthrolines (BTPhens).[8] These ligands were able to extract Am^{3+} and Eu^{3+} in a wide range of acidity from pH level to molar concentrations of nitric acid solutions with good selectivity ($SF_{Am/Eu} > 100$). However, they suffered from the following defects. First, the D_{An} values were usually so high that it hindered the stripping (e.g., for the extraction from HNO_3 solution into (0.01 mol/L CyMe$_4$-BTPhen in *n*-octanol), $D_{Am} \approx 1300$ for 4.0 mol/L HNO_3; $D_{Am} \approx 17$ for 0.001 mol/L HNO_3), unless it was performed by adding another solvent into organic phase or using water-soluble complexing agents.[8a,7c] Second, extraction kinetics is relatively slow in the absence of a phase-transfer reagent such as *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-

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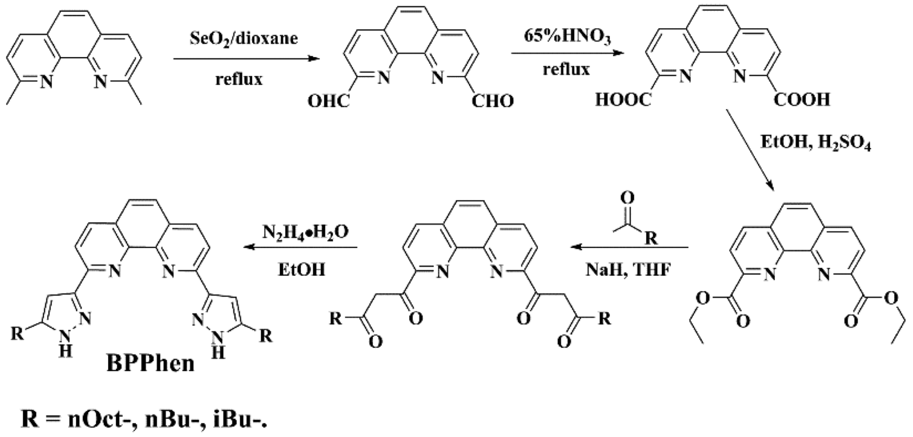
Scheme 1. Synthesis Route of BPPhen Ligands



(2-hexyloxy-ethyl)malonamide (DMDOHEMA) and *N,N,N′,N′*-tetraoctyl-diglycolamide (TODGA).[9] Ultimately, these defects render these ligands unsuitable for use in an industrial process. Accordingly, further great efforts are demanded to find more efficient N-donor ligands.

In recent years, a new kind of pyrazolyl-pyridine-based N-donor ligand, such as 2,6-bis(5-alkyl-1*H*-pyrazol-3-yl)pyridine (C5-BPP),[10] 1,3-bis[3-(2-pyridyl)pyrazol-1-yl]propane (Bippp),[11] and alkyl-substituted pyridylpyrazole (Cn-PypzH)[12] has received increasing attention in An/Ln separation because of high selectivity, fast extraction kinetics, and good chemical stability. In particular, C5-BPP exhibited very good effectiveness. With 2-bromohexanoic acid as lipophilic anion source and kerosene as diluent, C5-BPP can give an $SF_{Am/Eu}$ value of ∼100 at 0.5 mol/L HNO_3.[10] Meanwhile, the extraction kinetics was very fast with equilibrium for Am^{3+} and Eu^{3+} being reached after only 15 min.[10b] Nevertheless, a regular-SANEX process demonstration test using C5-BPP as extractant showed that the stripping of An^{3+} is incomplete by 0.8 mol/L HNO_3.[13] Although increasing the acidity of stripping solution is good for the complete stripping, this way is not feasible because of the formation of precipitate at HNO_3 concentration in excess of 1.0 mol/L.[10,13] Consequently, the water-soluble complexing agents such as (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), citric acid,[14] and glycolic acid[15] must be used, which greatly limit the viability of C5-BPP for process applications.

To perform the efficient stripping under highly acidic conditions, it is necessary to improve the acid stability of ligand. One rational method is to introduce a new moiety, for example, phenanthroline into ligand structure. In fact, it has been clearly shown that phenanthroline-based BTPhens have much better adaptability to acidity than pyridine-based BTPs. For instance, BTPhens can extract Am^{3+} and Eu^{3+} from 4.0 mol/L HNO_3 solution,[8a] whereas BTPs only works from 1.0 mol/L HNO_3 solution.[6a] From this point of view, it could be expected that there is also better tolerance toward acidity by replacing pyridine moiety of alkylated bis-pyrazolylpyridines (BPPs) with a phenanthroline moiety. And the problem troubling the stripping may be overcomed. Moreover, the preorganized structure of phenanthroline moiety in the molecule may improve extraction properties.[8,16]

Our aim is to develop a new kind of phenanthroline-derived bis(pyrazole) ligand. In this work, three novel tetradentate N-donor ligands 2,9-bis(5-alkyl-1*H*-pyrazol-3-yl)-1,10-phenanthroline (BPPhen; Scheme 1) consisting of a phenanthroline moiety and two pyrazol moieties were synthesized and characterized. Their solvent extraction behavior toward Am^{3+} and Eu^{3+} in HNO_3 solutions was investigated. Meanwhile, the complexation behavior of ligand with Eu^{3+} was also examined by electrospray ionization mass spectrometry (ESI-MS), time-resolved laser-induced fluorescence spectroscopy (TRLFS), Raman, Fourier transform infrared (FTIR), UV−vis spectroscopic titration, and microcalorimetric titration methods.

■ EXPERIMENTAL SECTION

General. All reagents supplied by Aladdin were analytical grade or chromatographic grade without purification unless otherwise stated. Solutions of $Eu(NO_3)_3$ or $Eu(ClO_4)_3$ were prepared from Eu_2O_3 (99.99%, Aldrich) in dilute HNO_3 or dilute $HClO_4$, respectively. The trace stock solutions of ^{241}Am or ^{152}Eu in 0.10 mol/L HNO_3 solution were provided by China Institute of Atomic Energy (CIEA).

UV−Vis spectra were performed with a PERSEE TU-1810 spectrophotometer. Microcalorimetric titration was conducted using an isothermal titration calorimeter (MicroCal VP-ITC). TRLFS was performed with an HORIBA TEMPRO-01. Raman spectra were performed with an HORIBA LabRAM HR800. FTIR spectra were recorded on a Nicolet Nexus 670 model instrument. NMR spectra were recorded on a Varian Inova 400 MHz NMR spectrometer using chloroform-*d* as solvent with tetramethylsilane as internal standard. Mass spectra were obtained in the ESI mode using a liquid chromatography−mass spectrometry ion trap time-of-flight (LCMS-IT-TOF) spectrometer.

Synthesis. BPPhen ligands were synthesized according to Scheme 1. 1,10-Phenanthroline-2,9-dicarboxylic acid was prepared referring to the literature.[17]

Synthesis of 1,10-Phenanthroline-2,9-dicarboxylic Acid Diethyl Ester. A 3.9 g amount (15 mmol) of 1,10-phenanthroline-2,9-dicarboxylic acid and concentrated H_2SO_4 (16 mL) were refluxed for 12 h in absolute ethanol (EtOH; 150 mL). Then the solvent was completely removed under reduced pressure, and the brown residue was dissolved in dichloromethane (DCM; 200 mL). Subsequently, the resulting solution was neutralized with 5% $NaHCO_3$ aqueous solution and washed three times with deionized water. Finally, the organic phase was dried with anhydrous Na_2SO_4 overnight. The product was obtained as the pale yellow solid with a pungent odor after distilling off DCM. The pure substance was obtained by recrystallization from ethyl acetate (EtOAc)/DCM/EtOH (v/v, 1:1:1). Yield: 3.5 g (11 mmol, 73%).

Synthesis of 1,1′-(1,10-Phenanthroline-2,6-diyl)bis(5,5-dialkane-1,3-dione). A 7.4 mmol amount of alkan-2-one (iBu-BPPhen: 0.93 mL of methyl isobutyl ketone; nBu-BPPhen: 0.92 mL of hexan-2-one; nOct-BPPhen: 1.4 mL of decan-2-one) was dissolved in freshly distilled tetrahydrofuran (THF, 30 mL), and then NaH (0.60 g, 60%

dispersion in paraffin oil, 15 mmol) was added gradually under an argon atmosphere at room temperature. After 0.50 h, 1,10-phenanthroline-2,9-dicarboxylic acid diethyl ester (1.0 g, 3.1 mmol) was added gradually. The reaction was continued and refluxed for 12 h followed by cooling to room temperature. The solvent was removed under reduced pressure. And then, the 1:5 mixture of glacial acetic acid and water (30 mL) was added to the burgundy viscous residue. After it was filtered, washed to neutral with deionized water, and dried in vacuo, a reddish-brown solid was obtained and used without further purification.

Synthesis of 2,9-Bis(5-alkyl-1H-pyrazol-3-yl)-1,10-phenanthroline. The crude product obtained from the previous step reaction and hydrazine hydrate (80% in H_2O, 6.0 mL, a large molar excess) were dissolved in absolute EtOH (25 mL) and refluxed at 70 °C for 5 h. After it cooled, the subsequent mixture was filtered and washed with cold EtOH and then recrystallized from DCM/*n*-hexane (v/v, 5:1).

Characterization Data. **nOct-BPPhen** (0.71 g, 43%) **FT-IR** (KBr, ν/cm^{-1}): 3339, 3204, 2926, 2852, 1589, 1502, 1466, 1148, 994, 857, 799, 542. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.22 (s, 2H, Phen-*H*), 7.93 (s, 2H, Phen-*H*), 7.72 (s, 2H, Phen-*H*), 6.69 (s, 2H, pyrazolyl-*H*), 2.70 (s, 4H, NCH_2), 1.71 (s, 2H, NCH_2CH_2), 1.28 (s, 20H, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 0.90 (s, 6H, CH_3). **ESI-MS** (*m/z*): Found: 559.3577 ([M + Na]$^+$). Calcd: 559.3525 ([M + Na]$^+$). **iBu-BPPhen** (0.80 g, 50%) and **nBu-BPPhen** (0.75 g, 47%). The detailed characterization data are listed in Section S1.

Solvent Extraction. The aqueous phases consisted of trace amounts of ^{152}Eu or ^{241}Am plus a stable $Eu(NO_3)_3$ carrier in different concentrations of HNO_3 solutions. The organic phases were prepared by dissolving the synthesized ligand and 2-bromohexanoic acid in diluent. Equal volumes (1.0 mL) of the organic and aqueous phases were stirred in a 5.0 mL round-bottom flask at 25 ± 0.5 °C for 0.50 h unless otherwise stated. Then the mixture was centrifuged to separate phases. The activity of ^{241}Am or ^{152}Eu in each phase was separately determined with a NaI(Tl) scintillation counter. All the extraction experiments were performed in triplicate.

Hydrolysis Study. A solution of 0.010 mol/L nOct-BBPhen and 1.0 mol/L 2-bromohexanoic acid in *meta*-nitrobenzotrifluoride (F-3) was contacted with an equal volume of 5.0 mol/L HNO_3 over 100 d. The two phases were stirred for 1.0 h, followed by settling for 2.0 h. This cycle was repeated one after another. Samples of the organic phase were withdrawn at regular intervals for the extraction experiments. The next steps were same as the solvent extraction part described above. The resulting *D* and SF values were employed to evaluate the hydrolytic stability of nOct-BPPhen ligand. In addition, the organic phases before and after contacting with 10 mol/L HNO_3 solution over a month were also analyzed by ESI-MS measurements.

UV−Vis Titration. The UV−vis spectroscopic titration was performed at 25 ± 0.2 °C in methanol medium. A 2.0 mL nOct-BPPhen solution with an initial concentration of 2.0×10^{-5} mol/L was added to a quartz cell of 1 cm path length, and an initial spectrum of the ligand was recorded. For each titration, the 4.0×10^{-4} mol/L $Eu(NO_3)_3 \cdot 6H_2O$ solution was added into the cell in 10 μL aliquots and shaken, and spectra from 205 to 400 nm were recorded up to the variation in absorbance became negligible. Spectra obtained were fit with HypSpec program.[18] Spectroscopic experiments were run in triplicate.

Microcalorimetric Titration. The calorimeter cell containing a $Eu(NO_3)_3$ solution at a concentration of 5.0×10^{-5} mol/L was titrated with 1.0×10^{-3} mol/L nOct-BPPhen solution. The heat of titrant dilution ($Q_{dil,j}$) was determined in a separate run. The net reaction heat was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$ ($Q_{ex,j}$ is resultant of heat released or absorbed during the formation of different species involved). Raw data were acquired as a plot of heat rate (μJ/s) versus time (s) and integrated to give a curve of enthalpy change per mole of injected nOct-BPPhen (ΔH, kJ/mol) versus molar ratio of reactants (nOct-BPPhen−$Eu(NO_3)_3$). The stability constants (*K*) were obtained by fitting the data. The experiment was repeated three times. The Gibbs free energy change (ΔG) was evaluated by using the equation $\Delta G = -RT \ln K$, and then the entropy change (ΔS) was calculated from the equation $\Delta S = (\Delta H - \Delta G)/T$.

■ RESULTS AND DISCUSSION

Solvent Extraction. Prior screening tests had shown that alone BPPhen ligands in common diluents such as toluene, *n*-octanol, and F-3, hardly extract Am^{3+} and Eu^{3+} from HNO_3 solution. Nevertheless, fortunately, the extractability can be greatly enhanced in the presence of 2-bromohexanoic acid. Besides, the influence of diluent on the extraction was also evaluated (see Table S1). In F-3, nOct-BPPhen not only has good solubility but also exhibits remarkably high efficiency and selectivity. Consequently, the extraction behaviors of BPPhen ligands toward Am^{3+} and Eu^{3+} were investigated by employing F-3 as diluent and 2-bromohexanoic acid as lipophilic anion source.

Influence of Contact Time. A drawback of many N-donor ligands such as nPr-BTP and $CyMe_4$-BTBP is their slow extraction kinetics.[6c,9a] The extraction kinetics of BPPhen ligands was evaluated with the results shown in Figure S10. The investigation reveals that the extraction kinetics is very fast with equilibrium reached within 15 min for both Am^{3+} and Eu^{3+}. To ensure the complete equilibrium, the following extraction experiments were performed for 0.50 h.

Influence of HNO_3 Concentration. The influence of HNO_3 concentration on the extraction is shown in Figure 1. In the range of HNO_3 concentrations examined (0.50−3.0 mol/L), both D_{Am} and D_{Eu} decrease with increasing acidity. This can be mainly ascribed to the following two factors. On the one hand, the ligands are likely to be protonated in contact with aqueous phase of increasing acidity, resulting in the decrease of available ligand concentration. On the other hand, the dissociation of 2-bromohexanoic acid is suppressed under high acidity conditions, leading to a weakening of synergistic effect.[12] In addition, the $SF_{Am/Eu}$ values decrease with increasing acidity, which can be explained as that the slight difference in properties between Am^{3+} and Eu^{3+} results in that D_{Am} declines slightly faster than D_{Eu}. Thus, $SF_{Am/Eu}$ values show a downward trend.

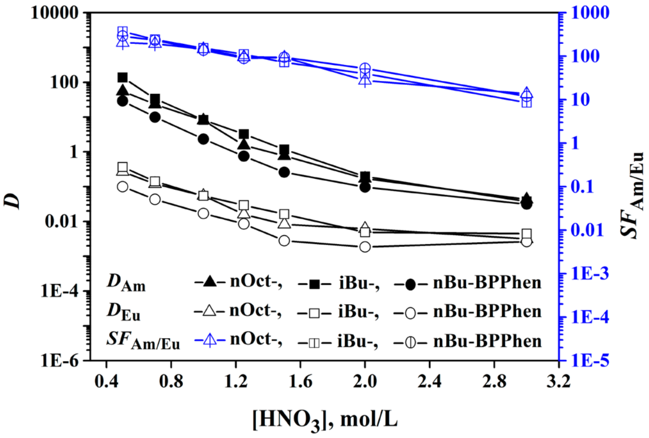


Figure 1. Influence of HNO_3 concentration on the extraction of Am^{3+} and Eu^{3+}. Organic phase: 0.010 mol/L ligand and 1.0 mol/L 2-bromohexanoic acid in F-3; aqueous phase: 1.0 mmol/L $Eu(NO_3)_3$ spiked with trace amount of ^{241}Am or ^{152}Eu in HNO_3 solution.

Furthermore, from Figure 1, it also can be observed that the extractabilities of iBu- and nOct-BPPhen are very close and slightly stronger than that of nBu-BPPhen under the same experimental conditions. This phenomenon can be explained as follows. On the one hand, iBu-BPPhen might have a little lower steric hindrance than nBu-BPPhen, resulting in a favorable extraction. Similar result is also observed for BTP derivatives.[6a] On the other hand, nOct-BPPhen, in which the steric hindrance of *n*-octyl radical is obviously larger than that of *n*-butyl radical, does not show a lower extractability than nBu-BPPhen. It is likely that the greater lipophilic capacity of nOct-BPPhen promotes extracted species into organic phase.[19]

For the An/Ln separation, the acidity of feed liquid issued from the stripping after the coextraction of An and Ln by CMPO, TODGA, or TRPO, etc.,[20] is often in the range of 0.1−0.5 mol/L HNO_3.[21] As a result, the influence of HNO_3 concentration within this range on the extraction was investigated particularly as shown in Figure S11. Very high D_{Am} values up to 1000 are observed, demonstrating that the extraction of Am^{3+} by BPPhen ligands is very efficient. D_{Eu} values are less than 10, resulting in high $SF_{Am/Eu}$ values with the magnitude of 1×10^2. The extraction performances of BPPhen ligands exhibited are better than most of other N-donor ligands such as C5-BPP,[10] BTBP,[7a] and BTPhen,[8a] suggesting that BPPhens have a good application prospect in the An/Ln separation.

In consideration of the solubility of ligand in organic phase as well as the ligand loss in aqueous phase, nOct-BPPhen was employed as an optimal ligand in the following extraction experiments.

Influence of Ligand Concentration. Slope analysis was employed to determine the number of nOct-BPPhen molecules involved in the extracted metallic complexes. Figure 2 shows the influence of ligand concentration on the extraction of Am^{3+} and Eu^{3+}. The plot of log D_M versus log[nOct-BPPhen] gives two straight lines with slope values of ∼2, indicating the formation of 1:2 metal/ligand extracted complexes.

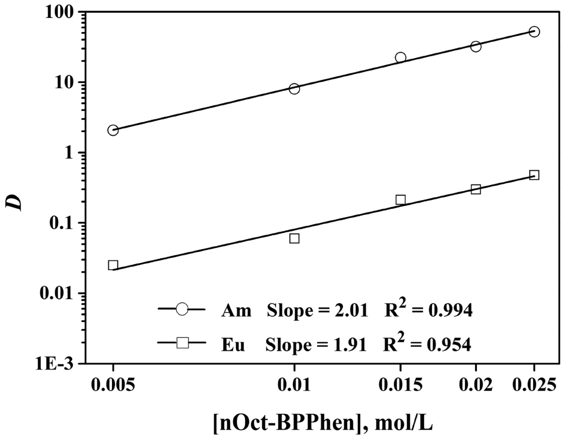


Figure 2. Influence of ligand concentration on the extraction of Am^{3+} and Eu^{3+}. Organic phase: different concentrations of nOct-BPPhen and 1.0 mol/L 2-bromohexanoic acid in F-3; aqueous phase: 1.0 mmol/L $Eu(NO_3)_3$ spiked with trace amount of ^{241}Am or ^{152}Eu in 1.0 mol/L HNO_3 solution.

Influence of 2-Bromohexanoic Acid Concentration. As lipophilic anion source, 2-bromohexanoic acid plays an important role in the synergistic extraction process for many neutral N-donor ligands.[10,22] For a deeper understanding of its role, the influence of 2-bromohexanoic acid concentration on the extraction was also investigated. Considering that the dissociation of 2-bromoalkanoic acids ($pK_a \approx 2.5$) may be suppressed under high acidity conditions, the extraction experiment was performed at a low acidity of 0.01 mol/L HNO_3.[12,22a,c] The results are demonstrated in Figure 3. The plot of log D_M versus log[2-bromohexanoic acid] gives two straight lines with slope values of ∼3, suggesting that three 2-bromohexanoic acid molecules are involved in the extraction. On the basis of the above results of slope analysis, the extraction equilibrium equation can be expressed as follows:

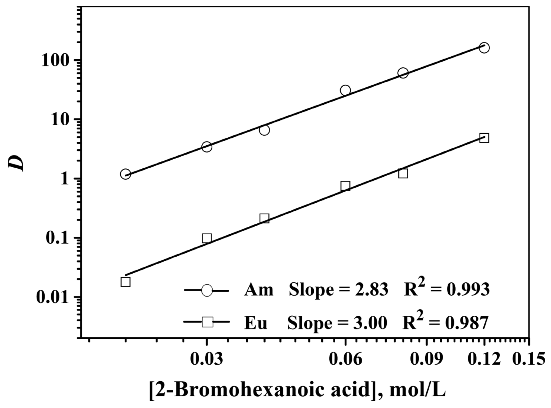


Figure 3. Influence of 2-bromohexanoic acid concentration on the extraction of Am^{3+} and Eu^{3+}. Organic phase: 3.0 mmol/L nOct-BPPhen and different concentrations of 2-bromohexanoic acid in F-3; aqueous phase: 15 ppm $Eu(NO_3)_3$ spiked with trace amount of ^{241}Am or ^{152}Eu in 0.01 mol/L HNO_3 solution.

$$2L_{org} + 3HA_{org} + M^{3+}_{aq} \rightleftharpoons [ML_2]A_{3org} + 3H^{+}_{aq} \qquad (1)$$

where L, HA, and M denote ligand, 2-bromohexanoic acid, and metal ions, respectively. The subscripts (org) and (aq) represent organic phase and aqueous phase, severally. The extraction conforms to a cation exchange model.

Stripping. Besides the excellent extraction properties, the good stripping performances are also essential for a promising extraction system. For this reason, stripping was investigated by oxalic acid and nitric acid solutions, which are common stripping agents.[23] Results are listed in Table 1. It can be seen that the stripping efficiency of nitric acid is far superior to that of oxalic acid. And furthermore, the stripping percentage increases with increasing HNO_3 concentration, which agrees with the influence of acidity on the extraction as shown in Figure 1. Almost quantitative stripping of Am^{3+} and Eu^{3+} can be achieved at 3−4 stages and at single stage, respectively, by 3.0 mol/L HNO_3. It completely avoids employing water-soluble complexing agents.

Table 1. Stripping of Am^{3+} and Eu^{3+} from the Loaded Organic Phase

	stripping percentage, %							
			HNO_3, mol/L					
	0.01 mol/L oxalic acid		1.0		2.0		3.0	
stripping stage	Am^{3+}	Eu^{3+}	Am^{3+}	Eu^{3+}	Am^{3+}	Eu^{3+}	Am^{3+}	Eu^{3+}
I	0.12	4.4	7.8	79	68	100	84	100
II	0.20	6.7	15	97	93	100	95	[a]
III	0.31	10	21	100	98	[a]	99	[a]
IV	0.40	13	27	100	100	[a]	100	[a]

[a] No metal ions detected in organic phase.

Hydrolysis Stability and Acid Tolerance. A recycling option in process applications for acidic waste treatment

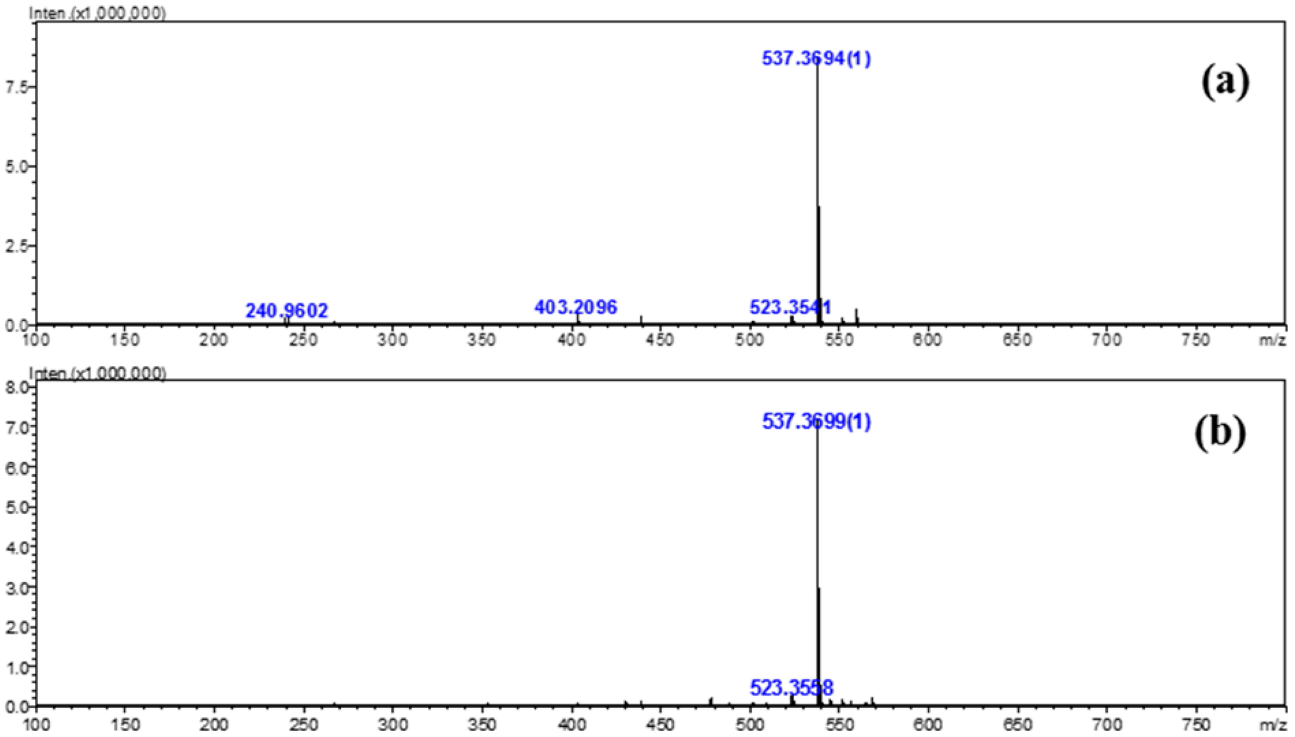


Figure 4. ESI-MS spectra of the organic phases before (a) and after (b) contacting with 10 mol/L HNO_3 solution over a month in the range of m/z = 100−800.

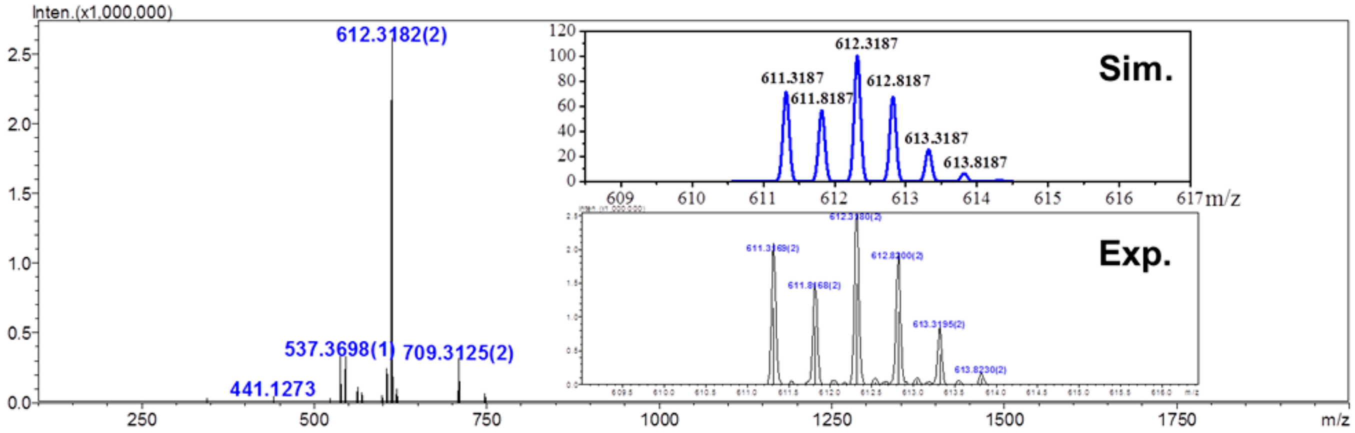


Figure 5. Positive ESI mass spectrum of the Eu-loaded organic phase, where 5.0 mmol/L nOct-BPPhen and 1.0 mol/L 2-bromohexanoic acid in F-3 was contacted with 1.0 mmol/L $Eu(NO_3)_3$ dissolved in 0.10 mol/L HNO_3. (inset) Computer simulation of the isotope distribution pattern of $[Eu(nOct\text{-}BPPhen)_2H_{-1}]^{2+}$.

requires that the ligands should have an adequate hydrolytic stability and good acid tolerance. Thereby, the stability of nOct-BPPhen was studied. The results are shown in Figure S12. It is found that the D_{Am}, D_{Eu}, and $SF_{Am/Eu}$ values remain at the initial level with no observable changes, suggesting excellent hydrolytic stability of nOct-BPPhen on long-term (100 d) exposure to 5.0 mol/L HNO_3.

In general, the N-donor ligands such as *n*-alkylated BTPs and C5-BPP have an unsatisfactory resistance against nitric acid.[24,10] To estimate well nOct-BPPhen's acid tolerance, the acidity of aqueous phase was elevated to 10 mol/L, which is high enough for an An/Ln separation process. The ESI-MS spectra of the organic phases before and after contacting with HNO_3 solution are displayed in Figure 4. The peak at m/z = 537.3670 observed in the spectra is attributed to nOct-BBPhen associated with H^+. The intensity of this peak is thought to be unchanged after 10 mol/L HNO_3 treatment over a month. It is quite different from *n*-alkylated bis(triazine) ligands such as n-Pr-BTP that are almost completely destroyed in contact with 1.0 mol/L HNO_3 over several days.[25] In addition, no precipitate formed in the sample under this condition. These results indicate that nOct-BPPhen is robust resisting degradation resulting from acidic conditions.

Complexation of Eu^{3+} with nOct-BPPhen. The complexation behavior of nOct-BPPhen with Eu^{3+} was investigated in biphasic and monophasic systems, respectively. In view of the similarities in the chemical properties of An and Ln, Eu^{3+} was taken as the surrogate of Am^{3+}, and the results of the Eu^{3+} subsequent complexation studies can be extended for the Am^{3+} system as well.

ESI-MS Analysis. To further identify the extracted species, ESI-MS analysis of the Eu-loaded organic phase was performed. Figure 5 shows the positive ESI spectrum of the Eu-loaded organic phase. The peak at m/z 612.3180 is assigned to the 1:2 complexes $[Eu(nOct\text{-}BPPhen)_2H_{-1}]^{2+}$, as confirmed by the simulation of the corresponding isotopic clusters. This result is in good agreement with that of slope analysis.

Generally speaking, trivalent f-elements in their complexes with tri- or tetradentate N-donor ligands exhibit coordination numbers of 8, 9, or 10.[6b,7d,8a] According to the aforesaid results of ESI-MS and slope analyses, the formation of 1:2 Eu^{3+}/nOct-BPPhen complexes means that two tetradentate ligands bind one Eu^{3+} through eight nitrogen atoms, leaving the coordination site to be occupied with either H_2O or NO_3^-.[26] To confirm whether there is H_2O or NO_3^- taking part in the coordination, Raman, FTIR, and TRLFS analyses were performed. Meanwhile, the comparison between nitrate and perchlorate systems was also made, because perchlorate ions have lower affinity for Eu^{3+} than nitrate ions.[27]

Raman and FTIR Spectra Analyses. The Raman and FTIR spectra of organic phases (pristine, after contacting with HNO_3 or $HClO_4$ solution, and Eu-loaded organic phases) are shown in Figure S14 and Figure 6, respectively. The Raman spectra show obvious differences between the Eu-loaded organic phases and the Eu-unloaded organic phases, indicating that Eu^{3+} is extracted into organic phase. Meanwhile, the shape of the Raman spectrum of the Eu-loaded organic phase prepared from nitrate system is almost the same as that prepared from perchlorate system. And the characteristic band of NO_3^- in the range of 1480−1650 cm^{-1} was not observed, suggesting that NO_3^- might not appear in the extracted species. Moreover, if there were a NO_3^- in the inner coordination sphere, the peak assigned to $[Eu(nOct\text{-}BPPhen)_2(NO_3)]^{2+}$ should appear at m/z = 643.8165 (calculated from molecular weight calculator program, http://www.alchemistmatt.com) in the ESI-MS spectrum (Figure 5) due to a strong coordination ability of NO_3^- with Eu^{3+}.[21] But in fact, there is no the peak corresponding to this m/z value. All of this leads to the conclusion that NO_3^- is absent from the inner sphere of the central Eu^{3+} in the complex.

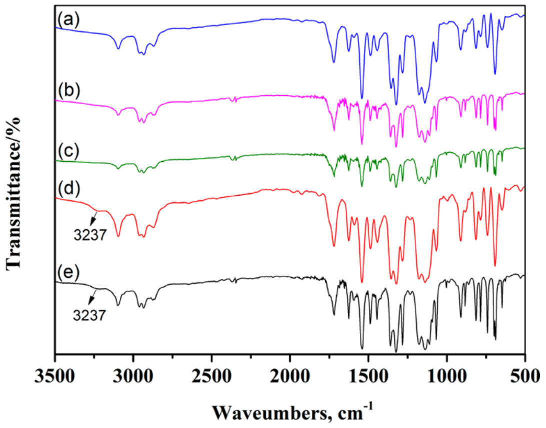


Figure 6. FTIR spectra of the various organic phases containing nOct-BPPhen and 2-bromohexanoic acid in F-3 (initial conditions, organic phase: 0.10 mol/L nOct-BBPhen and 1.0 mol/L 2-bromohexanoic acid in F-3; aqueous phase: 0.05 mol/L Eu^{3+} in the solution of 0.1 mol/L HNO_3 or $HClO_4$). Pristine organic phase (a); organic phase after contacting with 0.10 mol/L HNO_3 (b); organic phase after contacting with 0.10 mol/L $HClO_4$ (c); Eu-loaded organic phase prepared from nitrate system (d); Eu-loaded organic phase prepared from perchlorate system (e).

Because of the complexity of these organic phases, it is difficult to discriminate their FTIR spectra. But fortunately there is a new absorption peak at ~3237 cm^{-1} in the spectra of the Eu-loaded organic phases. It can be assigned to the stretching vibration of coordinated H_2O (the absorption peak of free H_2O at 1730 cm^{-1}), suggesting that H_2O might appear in the inner coordination sphere of the central Eu^{3+} in the complex.[28]

TRLFS Analysis. Further investigation was performed to determine the number of H_2O molecules in the inner sphere of Eu^{3+} by TRLFS analysis method. On the basis of a linear correlation between fluorescence lifetime and number of H_2O molecules in the inner coordination sphere existing (eq 2), the hydration number can be calculated from the fluorescence lifetime with an experimental uncertainty of ±0.5.[29]

$$n(H_2O) = 1.05/\tau - 0.70 \qquad (2)$$

The fluorescence decay curves for the Eu-loaded organic phases prepared from nitrate and perchlorate systems are shown in Figure 7. The decay curves were fitted with single-exponential functions to obtain the fluorescence lifetime (τ, in ms). τ was found to be 0.565 ms for nitrate system and 0.572 ms for perchlorate system. According to eq 2, the hydration numbers were calculated to be 1.2 and 1.1, respectively, indicating the existence of a H_2O molecule in the inner sphere of the central Eu^{3+} in the complex. However, the aforementioned result of ESI-MS analysis indicates that there is no H_2O in the extracted species responding to the molecular ion peak at m/z 612.3180 for Eu^{3+}. This might be explained by a loss of the coordinated H_2O in the process of ionization during MS measurement due to the very weak coordination bond between the central Eu^{3+} and H_2O in the extracted complexes.[28]

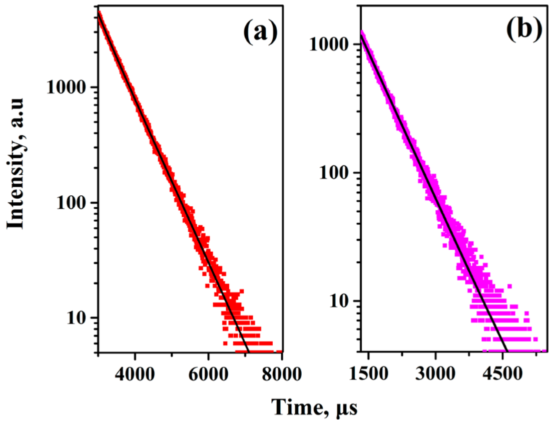


Figure 7. Fluorescence decay curves of Eu^{3+} after extraction to an organic phase of 5.0 mmol/L nOct-BPPhen and 1.0 mol/L 2-bromohexanoic acid in F-3 from an aqueous phase of 0.10 mol/L HNO_3 (a) or $HClO_4$ (b).

On the basis of the above results, it is inferred that the inner-coordination sphere of the extracted 1:2 complexes of Eu^{3+} may comprise two nOct-BPPhen ligands and a H_2O molecule.

UV−Vis Titration. For a deep insight into the complexation behavior of nOct-BPPhen with $Eu(NO_3)_3$, UV−vis spectroscopic titration was performed in methanol medium (see Figure 8). With the addition of $Eu(NO_3)_3$, the absorption at 313 nm

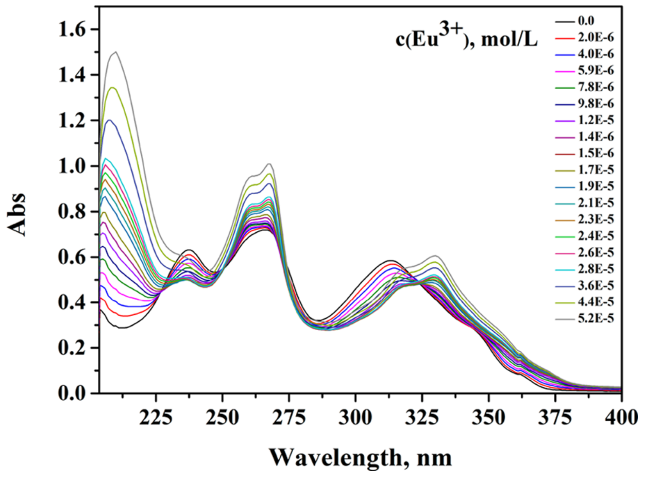


Figure 8. UV−Vis spectroscopic titration of nOct-BPPhen with $Eu(NO_3)_3 \cdot 6H_2O$ in CH_3OH (initial conditions, [ligand] = 2.0×10^{-5} mol/L, volume = 2.0 mL; titration conditions, [$Eu(NO_3)_3 \cdot 6H_2O$] = 4.0×10^{-4} mol/L).

shifts to ~330 nm. Isosbestic point is observed at 274 nm, revealing the presence of at least two species in solution. However, with further additions of $Eu(NO_3)_3$, to give a stoichiometric excess of $Eu(NO_3)_3$, there is no significant change in the shape of the spectral profile, suggesting an equilibrium being established between two possible species of 1:1 and 1:2 metal/ligand. HypSpec program was used to model the spectra. The best fits were given with consideration of the formation of both 1:1 and 1:2 metal/ligand species, confirming that [Eu(nOct-BPPhen)]$^{3+}$ and [Eu(nOct-BPPhen)$_2$]$^{3+}$ occur over the conditions used in the titrations. This result is in good accordance with that of experimental observations regarding the extracted species. In solvent extraction experiment, nOct-BPPhen was in excess. Nevertheless, the 1:1 species is likely to be forced to form with excess Eu^{3+} present. Similar behavior has been observed by Whittaker.[30]

Microcalorimetric Titration. Calorimetry titration is the technique that can not only be used to directly measure the enthalpy of complexation but also can determine the stability constants. The complexation of Eu^{3+} with nOct-BPPhen was studied in methanol medium using microcalorimetry. Figure 9 shows the data from microcalorimetric titration of $Eu(NO_3)_3$ with nOct-BPPhen. The upper panel exhibits the microcalorimetric heat flow trace. With additional nOct-BPPhen injections into the $Eu(NO_3)_3$ solution, the concentration of free Eu^{3+} decreases, and the reaction gives a smooth exothermic decrease. The lower panel shows that the titration plot can be fitted well.

Thermodynamic parameters and the stability constants are listed in Table 2. In the case of ML$_1$, both ΔH and ΔS are positive, while ΔG is negative, indicating that the complexation process is driven by relatively large entropy changes. This large positive entropy of complexation is likely to arise from the release of solvent molecules from the inner coordination sphere of Eu^{3+} and the ligand during the complexation. Besides, high endothermic enthalpy and large positive entropy change indicate a poor stereochemical conformation of the ML$_1$ complexes, which ultimately gives relatively weak complexation with Eu^{3+}. However, the reaction for ML$_2$ was characterized by strongly negative and favorable ΔH overcoming negative unfavorable entropy term ($T\Delta S < 0$). In other words, it is favorable to form ML$_2$ species in the view of complexation energetics. This could be attributed to the fact that the rigidity and the juxtaposition of donor atoms are benefit for metal ligation.[31,32] Similar phenomena have also been observed on the microcalorimetric titration of CyMe$_4$-BTPhen with $Eu(NO_3)_3$.[32]

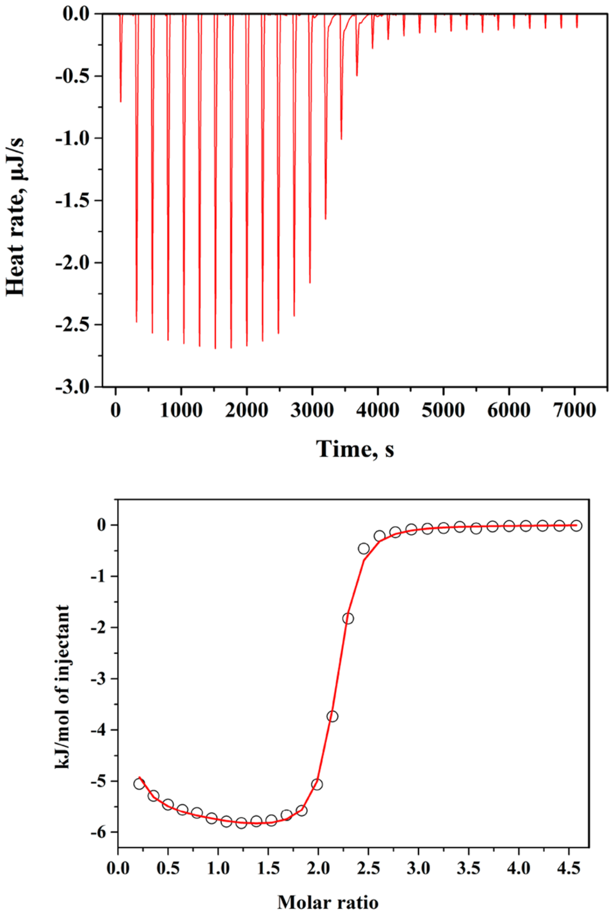


Figure 9. Microcalorimetric titration of nOct-BPPhen with $Eu(NO_3)_3$ in methanol. (initial conditions, [$Eu(NO_3)_3 \cdot 6H_2O$] = 5.0×10^{-5} mol/L; titration conditions, [ligand] = 1.0×10^{-3} mol/L). (upper) Microcalorimetric trace. (lower) Integrated enthalpy value (round) and fitted result (line) of the reaction.

Table 2. Stability Constants and Thermodynamic Parameters for the Complexation of Eu^{3+} with nOct-BPPhen[a]

metal ion	species	log *K*	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
Eu^{3+}	ML$_1$	4.52 ± 0.02	−25.8	57.2 ± 5.36	278
	ML$_2$	7.10 ± 0.01	−40.1	−107 ± 5.36	−224

[a] In methanol at 25 °C.

■ CONCLUSIONS

BPPhen ligands were designed to combine high selectivity for complexation of Am^{3+} over Eu^{3+}, fast extraction kinetics, easy stripping, good hydrolytic stability, and acid-tolerance properties. Slope analysis indicated the formation of 1:2 metal/ligand extracted species, which is consistent with the conclusion drawn from ESI-MS analysis, and this result was also confirmed by UV−vis spectroscopic titration and microcalorimetric titration. Besides, TRLFS analysis indicated the presence of a H_2O

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molecule in the inner coordination sphere of the central Eu cation in the complex. Furthermore, the large exothermic enthalpy and the significant decrease in the degree of disorder for 1:2 metal/ligand species suggested a stronger complex formation due to a favorable preorganized structure of phenanthroline moiety in the molecule. Although 2-bromohexanoic acid complicates the extraction system and makes problems with managing the secondary waste as being not the CHON compound, this work provides significant information on the extraction performances and the species relating to the extraction process. The obtained results contribute to a better understanding of the model of extraction at molecular level and are also of major importance for designing new and more efficient ligands derived from BPPhens for An/Ln separation in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00074.

Characterization data of all compounds, additional extraction experiments, as well as ESI-MS analysis of complexes (PDF)

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Notes

The authors declare no competing financial interest.

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