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Unfolding the Extraction and Complexation Behaviors of Trivalent f-Block Elements by a Tetradentate N,O-Hybrid Phenanthroline Derived Phosphine Oxide Ligand

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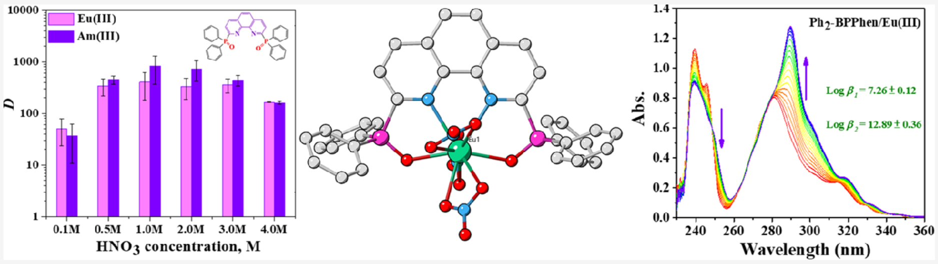

ABSTRACT: In this work, a tetradentate N,O-hybrid 2,9-bis(diphenylphosphine oxide)-1,10-phenanthroline (Ph$_2$-BPPhen) ligand was studied for the coextraction of trivalent f-block elements from nitric acid media. The extraction as well as the complexation behaviors of Ph$_2$-BPPhen with f-block elements were thoroughly investigated using ^{31}P and ^{1}H NMR spectrometry, UV−vis spectrophotometry, single crystal X-ray diffraction, and density functional theoretical (DFT) calculation. Ph$_2$-BPPhen exhibits remarkably extraction ability for both Am(III) and Eu(III) and more than 99.5% of Am(III) and Eu(III) were extracted from 1.0 M HNO$_3$ solution. Slope analysis suggests that both 2:1 and 1:1 ligand/metal complexes were probably formed during the extraction. The 1:1 and 2:1 Ln(III) complexes with Ph$_2$-BPPhen were also identified in CH$_3$OH solution by NMR spectrometry, and the stability constants were determined via UV−vis spectrophotometry. Structures of the 1:1 Eu(Ph$_2$-BPPhen)(NO$_3$)$_3$ and Am(Ph$_2$-BPPhen)(NO$_3$)$_3$ complexes were further elucidated by single X-ray crystallography and DFT calculations. The higher extractability of Ph$_2$-BPPhen toward trivalent Am(III) and Eu(III) compared with the previously reported phenanthroline-derived amide and phosphonate ligands was attributed to the stronger affinity of the −P═O(R)$_2$ group to metal ions. The results from this work indicate that the N,O-hybrid 1,10-phenanthroline derived phosphine oxide ligand can serve as a new and promising candidate for coextraction of trivalent f-block elements in the treatment of nuclear waste.

■ INTRODUCTION

Developing nuclear energy has become an important way to promote energy transformation, reduce greenhouse-gas emissions, and curb global warming worldwide nowadays. However, a significant problem of nuclear power inevitable to face is the disposal of the spent nuclear waste to minimize the long-term radiotoxicity and heat load originated from the long-lived minor actinides (Np, Am, and Cm) and Pu.[1,2] At present, partitioning and transmutation (P&T) is widely accepted as a promising and effective approach to solve this problem,[3,4] namely, the long-lived actinides are separated (partitioning) from spent nuclear waste prior to being transmuted (transmutation) into short-lived or stable isotopes by fast neutron bombardment in the fission reactor.[5,6]

Although most of the neptunium and plutonium could be recycled through the PUREX process,[7−10] to date the industrial separation of trivalent long-lived minor actinides of Am(III) and Cm(III) from PUREX raffinate has not been realized.[11,12] This is because that the PUREX raffinate is a very complex system that contains more than 1500 nuclides with high HNO$_3$ acidity (3.0−4.0M) and strong radioactivity. What's more, the extremely similar chemical properties (such as similar ion radius, ion charge, and coordination number) between trivalent actinide and the neutron poisonous lanthanide elements[13] make the separation of trivalent actinides over lanthanides from PUREX raffinate very challenging.[14−16] To reduce the difficulty of separation of trivalent minor actinides directly from PUREX raffinate, multistep partitioning strategy for separation of actinides were adopted worldwide over the past several

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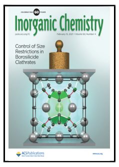

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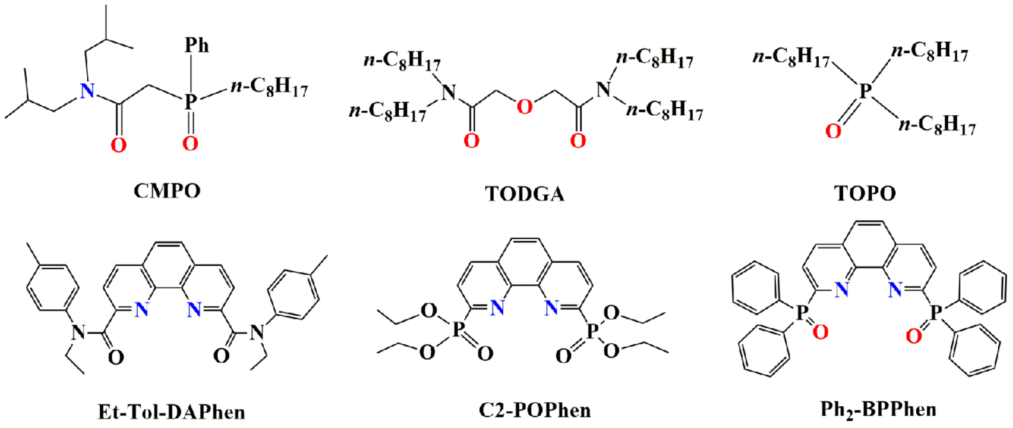

Figure 1. Promising extractants for f-block elements separation involved in this work.

decades.[11,14,17] As one of the key steps, the coseparation of trivalent actinides and lanthanides in these TALSPEAK (Trivalent Actinide and Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Complexes, America),[18,19] ARTIST (Amide-based Radio-resources Treatment with Interim Storage of Transuranics, Japan),[17] DIAMEX (DIAMide Extraction, Europe) processes were achieved using some O-donor ligands such as TODGA[14,15,20,21] or CMPO[15] type extractants (Figure 1). Then the separation of trivalent actinides over lanthanides were further achieved using soft N/S-donor ligands,[12,13,22−34] which exhibit greater affinity for trivalent actinides than lanthanides.

However, in those reported Ln(III)/An(III) coextraction processes,[20,21] in order to improve the extraction efficiency and prevent the formation of third phase, the multicomponent combinations such as TOGDA/TBP,[20] CMPO/TBP[35] (Figure 1), as well as other fission or corrosion products masking agents like oxalic acid and *N*-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA) needed to be added during extraction. The utilization of these multicomponent extractants, phase modifiers, and masking agents would inevitably increase the complexity of the extraction process and cause more secondary wastes.

Therefore, to overcome these drawbacks and simplify the current multiextraction systems, one probable solution is using the N,O-hybrid ligands, which have combined merits of hard O-donor ligands and soft N-donor ligands to simultaneously extract both lanthanide and actinide elements.[36] Recently, one class of N,O-mixed phenanthroline-derived phosphonate ligands[37−39] (like C2-POPhen, Figure 1) were reported for separation of actinide over lanthanide elements. It has been found that C2-POPhen held stronger extraction ability toward trivalent lanthanides and actinides than the previously reported *N*,*N*′-diethyl-*N*,*N*′-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen, Figure 1) ligand under similar experimental conditions,[40−42] but its affinity for trivalent actinides and lanthanides still remained weak. It is well-known that the substitution of phosphonate ($-P{=}O(OR)_2$) with phosphine oxide ($-P{=}O(R)_2$ groups could increase the basicity of O donors.[15,43] Thus, we deduce that the N,O-hybrid 1,10-phenanthroline derived phosphine oxide ligand (Ph_2-BPPhen, Figure 1) will exhibit stronger extraction ability for f-block elements. In this work, the ligand synthesis, solvent extraction as well as the complexation behaviors of Ph_2-BPPhen with trivalent lanthanide and actinide elements were systematically investigated.

■ EXPERIMENTAL SECTION

Chemicals. The trivalent lanthanides nitrates $La(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$, and $Lu(NO_3)_3{\cdot}6H_2O$ as well as Et_4NNO_3 for extraction and complexation studies are analytical grade and were used as received without further purification. Other commercially obtained chemical reagents like Cs_2CO_3, anhydrous diethyl ether, CH_3CN, CH_3OH, dry toluene, $Pd(OAc)_2$, 1,1′-bis(diphenylphosphino)ferrocene (dppf), ethyl-phenylphosphinate, diphenylphosphine oxide, and 2,9-dichloro-1,10-phenanthroline for the synthesis experiments are all analytical grade. Ph_2-BPPhen was synthesized using a palladium-catalyzed C−P cross-coupling reaction between 2,9-dichloro-1,10-phenanthroline and diphenylphosphine oxide according to the reported procedures.[44,45] Ph_2-BPPhen, ^1H NMR (500 MHz, $CD_3OD/CDCl_3$ (10/3, v/v), 295 K): $\delta = 7.30$ ppm (m, 8H, −Ar−*H*), 7.51 ppm (t, 4H, −Ar−*H*), 7.95 ppm (m, 8H, −Ar−*H*), 8.07 ppm (s, 2H, −Phen−*H*), 8.59 ppm (dd, 2H, −Phen-*H*); 8.64 ppm (dd, 2H, −Phen−*H*); ^{31}P NMR (121 MHz, $CD_3OD/CDCl_3$ (10/3, v/v), 295 K): $\delta = 22.55$ ppm (s, 1P).

Solvent Extraction. (Precautions: ^{241}Am and $^{152,154}Eu(III)$ with strong radioactivity could pose serious health threats; thus, all the radioactive experiments were performed in special radiological facilities.) The liquid−liquid solvent extraction of radioactive nuclides $^{241}Am(III)$ and $^{152,154}Eu(III)$ by Ph_2-BPPhen were all performed at 298 ± 1 K with a phase ratio of 1:1. The organic phases of 5.0 mM Ph_2-BPPhen in nitrobenzene used for extraction were acquired by directly dissolving the solid Ph_2-BPPhen in nitrobenzene. The aqueous phases contain different concentrations of HNO_3 varying from 0.1 to 4.0 M spiked with $^{241}Am(III)$ and $^{152,154}Eu(III)$ radiotracers. For a typical extraction experiment, a 0.5 mL of organic phase was added into the 0.5 mL of aqueous phase and then the mixture was thoroughly shaken for 180 min at 298 ± 1 K to reach extraction equilibrium. After centrifugation and phase separation, aliquot of 0.1 mL aqueous phase was added into a plastic scintillation vial to measure the radioactivity counts of $^{241}Am(III)$ and $^{152,154}Eu(III)$ before and after solvent extraction by a Quantulus 1220 Ultra model liquid scintillation spectrometer. The distribution ratios (D) of $^{241}Am(III)$ and $^{152,154}Eu(III)$ were calculated by the ratio between the radioactivity counts of the organic phase and aqueous phase after extraction. The concentrations of the nonradioactive Eu(III) in aqueous phases before and after extraction for slope analysis experiments were determined by ICP-OES (730-ES, Varian Inc., America).

NMR Spectroscopy Titration. The stock solutions of Ph_2-BPPhen, $La(NO_3)_3$, and $Lu(NO_3)_3$ were prepared by directly dissolving the ligand, $La(NO_3)_3{\cdot}6H_2O$ or $Lu(NO_3)_3{\cdot}6H_2O$ in the mixture of $CD_3OD/CDCl_3$, respectively. For a typical $^1H/^{31}P$ NMR titration experiment, an initial 0.5 mL of pure Ph_2-BPPhen dissolving in CD_3OD was added into an NMR tube and its ^1H/NMR and ^{31}P NMR spectra were collected on a Bruker Avance III model 500 MHz instrument, respectively. Then a certain amount of La(III) or Lu(III) in CD_3OD solution was added into the NMR tube. After each addition,

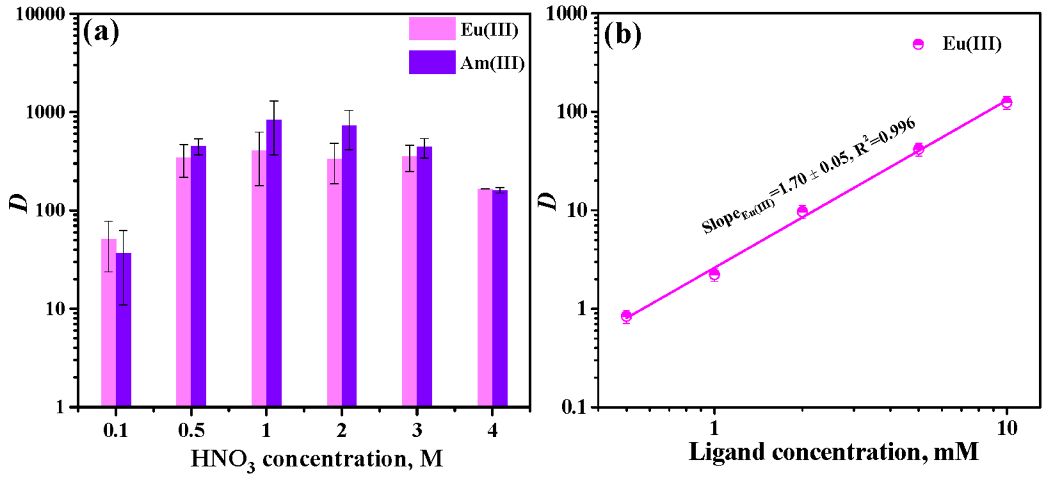

Figure 2. (a) Extraction results of tracer amount of radioactive ^{241}Am(III) and ^{152,154}Eu(III) by Ph_2-BPPhen (5.0 mM) in nitrobenzene as a function of HNO_3 concentration; (b) effect of ligand concentration on the extraction of Eu(III) from 1.0 M HNO_3 solution (D = distribution ratio; contact time, 180 min; temperature, 295 ± 1 K).

the resulting solution was vigorously mixed for 3 min to reach the complexation equilibrium and then the ^{1}H and ^{31}P NMR spectra of the samples were recorded. The NMR titrations were stopped until no further changes were observed in the NMR spectra.

UV−vis Spectrophotometry Titration. All spectrophotometric titrations were carried on a Hitachi UH-5300 model spectrophotometer (Japan) at 298 ± 1 K to determine the stability constants of typical lanthanide metal ions complexing with Ph_2-BPPhen. Absorption spectra were recorded in the wavelength range of 230−370 nm (with an interval of 0.2 nm), where the ligand and its complexes with lanthanide metal ions exhibit characteristic absorption peaks. Stock solutions of $Ln(NO)_3$ (Ln = La, Nd, Eu, and Lu) were obtained by dissolving solid lanthanide nitrates in CH_3OH, and the concentrations of lanthanide ions in CH_3OH were analyzed by ICP-OES after diluted with deionized water. The concentrations of ligands were calculated from the weighted solid ligands dissolving in CH_3OH. The ionic strength of all the stock solutions were kept at 0.01 M by adding a certain amount of tetraethylammonium nitrate as the background electrolyte. In a typical titration, an initial 2.2 mL of the ligand solution was added into a quartz cell with 10 mm optical path. After collecting the initial spectra of ligand, certain amounts of lanthanide metal ions solution were added into the cell and then the mixture was mixed thoroughly for 3 min to reach complexation equilibrium before the absorption spectra were collected. In general, 16−20 additions were performed and thus a series of 17−21 spectra were obtained for each titration. Similar to NMR titration, the spectrophotometric titration was stopped until no obvious changes were observed in the titration spectra. The stability constants of lanthanide metal ions complexation with Ph_2-BPPhen were calculated from the resulting titration data using the nonlinear regression method on the HypSpec program.[46]

Single-Crystal X-ray Diffractometry. Single crystals of 1:1 Eu(III) complexes with Ph_2-BPPhen suitable for X-ray diffraction were successfully obtained by slowly diffusing the diethyl ether into the solution of $Eu(NO_3)_3{\cdot}6H_2O$ (3.0 mg) and Ph_2-BPPhen (2.4 mg) dissolving in the mixture of dichloromethane, methanol, and acetonitrile with the volume ratio of 10:1:1. X-ray crystallographic data of Eu(III) complexes were collected with a Photon II detector Mo−Kα radiation (λ = 0.71073 Å) at 170 K on a Bruker D8 Venture I diffractometer.

Computational Details. Quantum mechanical calculations were performed with density functional theory (DFT) using the B3LYP method based on the Gaussian 09 package.[47] For structure optimization, the energy-consistent scalar-relativistic WB-adjusted 52-electron−core or 84-electron−core ECPs were selected for Eu or Am, respectively.[48−50] Usually, the geometry structure is not sensitive to the basis sets. Limited by our computational resources, the 1:1 Ph_2-BPPhen/Am(III) or Ph_2-BPPhen/Eu(III) complexes with 81 atoms can hardly be dealt with small core effective potential for geometry optimization. Therefore, the ECP52MWB and ECP84MWB ECPs were used for geometry optimization. The corresponding (7s6p5d2f1g)/[6s5p4d2f1g] basis sets were used for Am and (6s6p5d)/[4s4p4d] + 2s1p1d basis sets were used for Eu.[48,49,51,52] All the other C, H, O, N, and P atoms were treated at the AE level with 6-31G* basis sets as implemented in the Gaussian 09 package.[47] For analyzing the bonding character, a single point calculation with the optimized structure was taken with more accurate ECP and related basis sets. The ECP60MWB and ECP28MWB were used for Am and Eu, respectively.[52−55] Meanwhile, the associated (14s13p10d8f6g)/[6s6p5d4f3g] and (14s13p10d8f6g)/[6s6p5d4f3g] basis sets were used for Am and Eu, respectively.[55,56] The optimized structures of Am(III) and Eu(III) complexes were built by the Gauss View 5.0 program. The Wiberg bond indices of Am(III) and Eu(III) complexes were calculated with Multiwfn 3.3.9. program.[57]

RESULTS AND DISCUSSION

Solvent Extraction Study. To test the feasibility of using Ph_2-BPPhen as an extractant for coextraction of trivalent minor actinides and lanthanides from highly active liquid waste (HLW), the extraction of Am(III) and Eu(III) under HNO_3 concentrations that varied from 0.1 to 4.0 M by Ph_2-BPPhen was performed. As presented in Figure 2a, very high distribution ratio (D) values were obtained for both Am(III) (D > 800) and Eu(III) (D > 400), suggesting that Ph_2-BPPhen held strong extraction ability for both Am(III) and Eu(III) in a highly acidic HNO_3 solution. Even at 4.0 M HNO_3, more than 99.3% of Am(III) and Eu(III) ($D_{Am(III)}$ > 160, $D_{Eu(III)}$ > 160) were removed from the aqueous phase. However, the extraction separation factors of Am(III) over Eu(III) ($D_{Am(III)}/D_{Eu(III)}$ values) is very low (ranging from 0.5−2.1) within the entire HNO_3 concentrations tested. These results demonstrate that Ph_2-BPPhen is a very promising extractant for efficient coseparation of An(III) and Ln(III) from HLW. Additionally, it was also observed that the D values of both Am(III) and Eu(III) increased significantly with HNO_3 concentration increasing from 0.1 to 1.0 M and then decreased gradually when further increasing the HNO_3 concentration from 2.0 to 4.0 M, which probably resulted from the competitive reactions of metal ions and the protons binding with the Ph_2-BPPhen molecules as shown in the following three equations:

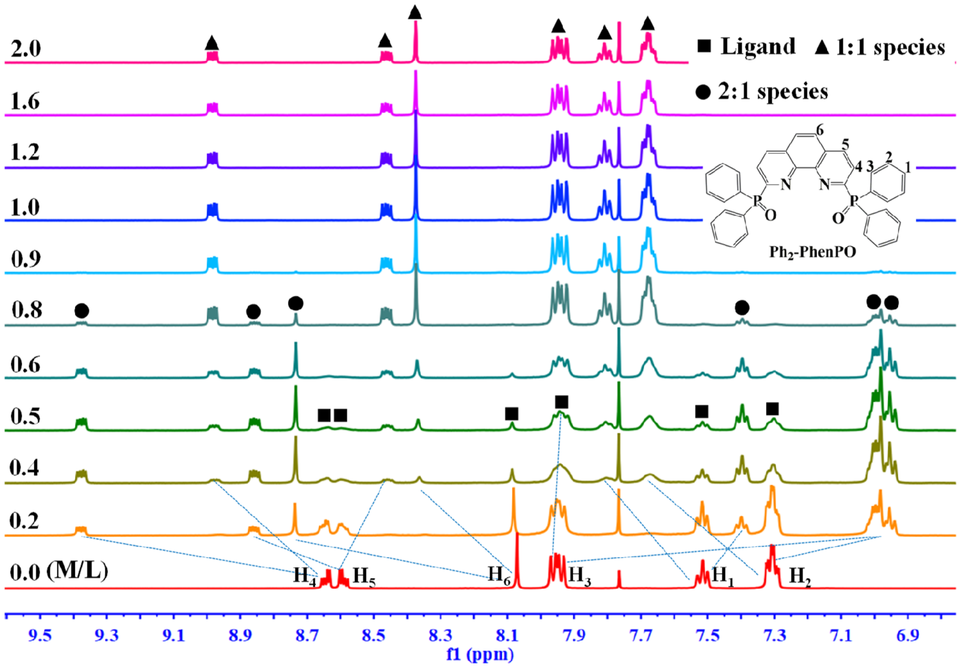

Figure 3. Stacked ^{1}H NMR spectra (6.7−9.7 ppm) of Ph_2-BPPhen (10.0 mM) titrated with $Lu(NO)_3$ in the mixture of $CD_3OD/CDCl_3$ (v/v, 10/3) at 295 K. M/L denotes the molar ratio of Lu(III) with Ph_2-BPPhen in tested samples.

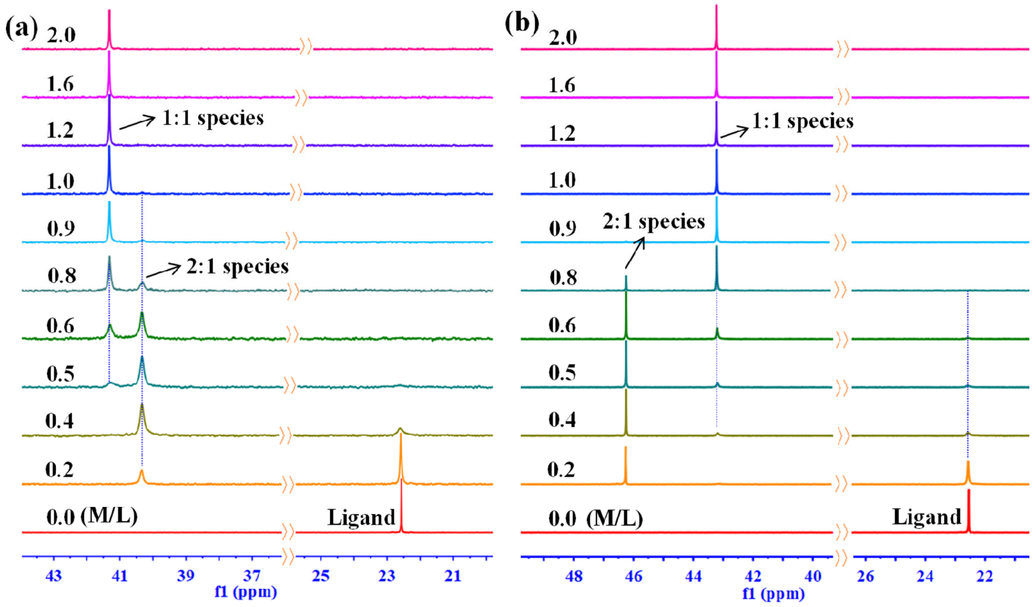

Figure 4. Stacked ^{31}P NMR spectra of Ph_2-BPPhen (15.0 mM) titrated with (a) $La(NO_3)_3$ and (b) $Lu(NO)_3$ in the mixture of $CD_3OD/CDCl_3$ (v/v, 10/3) at 295 K. M/L denotes the molar ratio of Ln(III) with Ph_2-BPPhen in tested samples.

$$3NO_3^{-} + Am^{3+} + Ph_2\text{−}BPPhen \leftrightarrow Am(NO_3)_3(Ph_2\text{−}BPPhen) \qquad (1)$$

$$3NO_3^{-} + Am^{3+} + 2Ph_2\text{−}BPPhen \leftrightarrow Am(NO_3)_3(Ph_2\text{−}BPPhen)_2 \qquad (2)$$

$$n HNO_3 + Ph_2\text{−}BPPhen \leftrightarrow [H_n{\cdot}Ph_2\text{−}BPPhen]{\cdot}(NO_3)_n \qquad (3)$$

Initially, at low HNO_3 acidity conditions (0.1−1.0 M), the extraction reaction 1 was dominant. With further increasing the HNO_3 concentration, the protonation reaction 3 gradually held the advantage and thus the metal ions extraction decreased. Similar extraction behaviors toward metal ions as a function of HNO_3 concentration have also been found with other N-donor ligands.[37,40]

To probe the extraction mechanism, the extraction of nonradioactive lanthanide ion of Eu(III) from 1.0 M HNO_3 solution as a function of ligand concentration was performed and the results are presented in Figure 2b. The slope of log $D_{Eu(III)}$ versus log[Ph_2-BPPhen] was 1.70, which indicates that both 1:1 and 2:1 complexes were the extracted species in the organic phase. It can be reasonable to deduce that Am(III) could also form these two type of complexes during the extraction

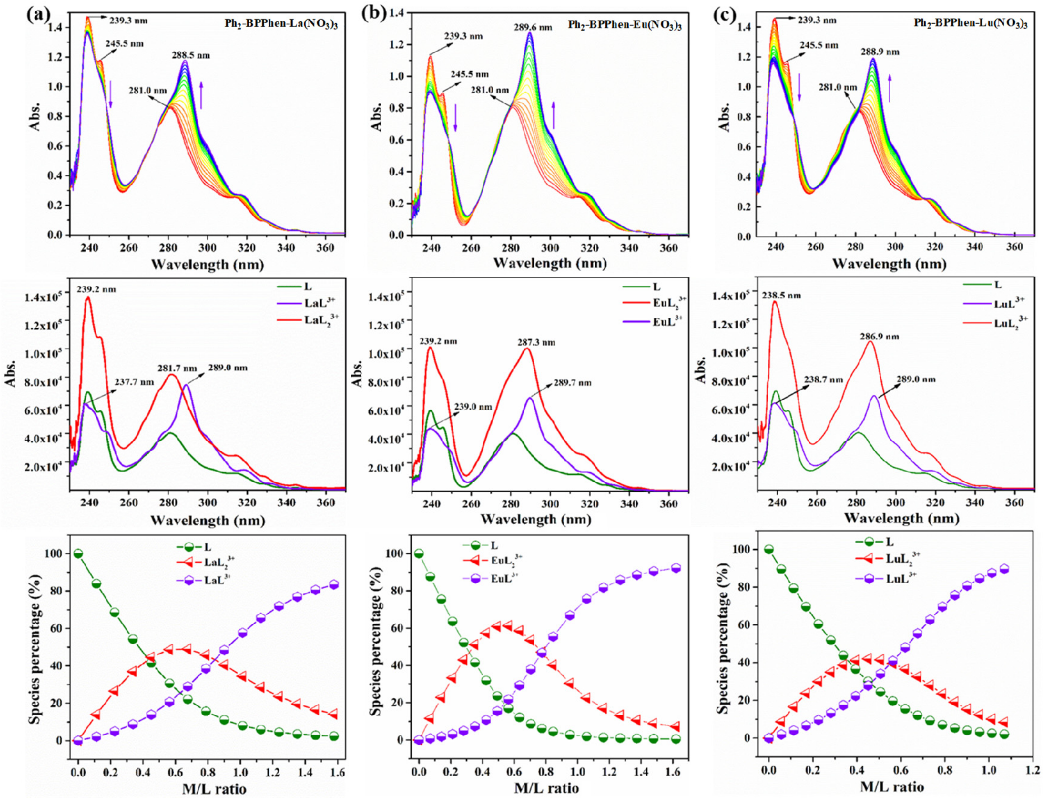

Figure 5. Spectrophotometric titrations of Ph_2-BPPhen complexing with typical lanthanide metal ions in CH_3OH solution ($T = 298 \pm 1$ K, $I = 0.01$ M Et_4NNO_3, $V_0 = 2.20$ mL). Top row: the normalized absorption spectra collected during titration. Middle row: the molar absorptivities of lanthanide complexes calculated from spectral deconvolution. Bottom row: the species distribution curves as a function of the M/L ratio during titration. Experimental conditions: left (a) $La(NO_3)_3$, $C_L/C_{La(III)} = 0.023$ mM/0.38 mM, a total of 0.22 mL $La(NO_3)_3$ solution was added; (b) $Eu(NO_3)_3$, $C_L/C_{Eu(III)} = 0.02$ mM/0.31 mM, a total of 0.235 mL of $Eu(NO_3)_3$ solution was added; (c) $Lu(NO_3)_3$: $C_L/C_{Lu(III)} = 0.023$ mM/0.19 mM, a total of 0.22 mL of $Eu(NO_3)_3$ solution was added.

process[28,37] due to the chemical similarities between trivalent lanthanide and actinide ions.

NMR Titration Analysis. NMR spectroscopic titration is a very sensitive and effective approach to determine the speciation as well the structure of organic ligands with diamagnetic metal ions in solution.[1,26,33,58−61] Therefore, NMR titrations of Ph_2-BPPhen with two typical diamagnetic lanthanides, La(III) and Lu(III), were conducted to identify the species formed in solution. As shown in Figure 3, the NMR titration results suggest that the 2:1 ligand-Lu(III) complex was initially formed, since the intensity of one new group of six NMR peaks (labeled with black circles) corresponding to the six aromatic protons of Ph_2-BPPhen increased to the maximum at M/L = 0.5, and meanwhile the initial appeared six peaks related to the free ligand (labeled with black square) almost disappeared at M/L = 0.5−0.6.[37,38,59] Those NMR signals related to the 2:1 species decreased gradually, and another new group of peaks (labeled with black triangle) emerged and intensified at M/L ≥ 0.2 and then became constant at M/L > 1.0, suggesting the formation of the 1:1 ligand-metal species. The above trend in the ^1H NMR titration spectra agrees well with the successive formation of the 2:1 and 1:1 Ph_2-BPPhen/Ln(III) complexes[37,59] in solution. Similar changes were also found in the titration of Ph_2-BPPhen with $La(NO_3)_3$ under identical conditions (Figure S3).

The formation of both 2:1 and 1:1 species was also demonstrated by the ^{31}P NMR spectra of Ph_2-BPPhen titrated with La(III) and Lu(III) nitrates. As presented in Figure 4, two new sets of clearly resolved peaks locating at 40.3 and 41.3 ppm corresponding to the 2:1 and 1:1 species, respectively, for La(III) complexes (Figure 4a), and at 46.3 and 43.2 ppm corresponding to the 2:1 and 1:1 species, respectively, for Lu(III) complexes (Figure 4b) were observed with the M/L ratio increasing from 0.2 to 2.0. These results were in perfect agreement with the above ^1H NMR titration results. What's more, the greater changes found in the chemical shifts of phosphorus for Lu(III) complexes as compared to the corresponding La(III) complexes indicate that the complexation strength of Ph_2-BPPhen with Lu(III) might be stronger than that of La(III). Notably, the complete transformation of the 2:1 species into the 1:1 species when M/L ≥ 1.0 indicated that the 1:1 La(III) or Lu(III) complexes with Ph_2-BPPhen were more thermodynamically stable than those of 2:1 complexes in nitrate medium.[59] It was quite different from that of Ln(III)/R-BTPhen complexes, of which the 2:1 complex was the predominant species in solution,[13,59] but this is similar to that of 2,9-diamide-1,10-phenanthroline DAPhen/Ln(III) complexes.[40]

Spectrophotometric Titration Analysis. To further identify the stability constants of lanthanides complexes with Ph_2-BPPhen, the UV−vis spectrophotometric titration of Ph_2-BPPhen with four representative lanthanides La(III), Eu(III), Nd(III), and Lu(III) were performed in nitrate/CH_3OH solution ($I = 0.01$ M Et_4NNO_3). As presented in Figure 5, the absorption band of Ph_2-BPPhen in the range of 220 to 370 nm was very sensitive to its coordination environment and thus these spectral changes could be used to determine the complexation speciation and the corresponding stability

Table 1. Stability Constants (log β) of Typical Lanthanides La(III), Nd(III), Eu(III), and Lu(III) Complexation with Ph_2-BPPhen[a]

ligand	lanthanides	reaction	log β	I	ref
Ph_2-BPPhen	La^{3+}	$L + La^{3+} = LaL^{3+}$	5.34 ± 0.03	0.01 M Et_4NNO_3	p.w.
		$2L + La^{3+} = LaL_2^{3+}$	10.42 ± 0.15		p.w.
	Nd^{3+}	$L + Nd^{3+} = NdL^{3+}$	6.10 ± 0.06	0.01 M Et_4NNO_3	p.w.
		$2L + Nd^{3+} = NdL_2^{3+}$	10.77 ± 0.24		
	Eu^{3+}	$L + Eu^{3+} = EuL^{3+}$	7.26 ± 0.12	0.01 M Et_4NNO_3	p.w.
		$2L + Eu^{3+} = EuL_2^{3+}$	12.89 ± 0.36		
	Lu^{3+}	$L + Lu^{3+} = LuL^{3+}$	7.01 ± 0.18	0.01 M Et_4NNO_3	p.w.
		$2L + Lu^{3+} = LuL_2^{3+}$	12.11 ± 0.40		
Et-Tol-DAPhen	Eu^{3+}	$L + Eu^{3+} = EuL^{3+}$	3.81	0.01 M Et_4NNO_3	40
C2-POPhen	Eu^{3+}	$L + Eu^{3+} = EuL^{3+}$	4.92 ± 0.03	0.01 M Et_4NNO_3	38
C4-POPhen	Eu^{3+}	$L + Eu^{3+} = EuL^{3+}$	5.03 ± 0.03	0.01 M Et_4NNO_3	37

[a] In CH_3OH media at 298 ± 1 K determined using the spectrophotometry method and comparison with other typical tetradentate N,O-mixed phenanthroline-derived ligands. I is the ionic strength and p.w. means present work.

constants. All three groups of titration spectra corresponding to the Ph_2-BPPhen complexation with La(III), Eu(III), and Lu(III) exhibited similar spectral changes. Upon addition of these lanthanide metal ions, the absorption peak of ligand at 239.3 nm gradually decreased and another peak at 281.0 nm was enhanced and red-shifted. For each titration spectra, obvious isosbestic points were found, which suggested that one more complex species was formed during titration. After further analysis with the HypSpec program,[46] it was found the titration spectral data could be best fitted with the successive formation of 1:1 and 2:1 Ph_2-BPPhen/Ln(III) complexes. These results were in good agreement with the above NMR titration results. The calculated molar absorptivities and the species distribution curves are shown in Figure 5 (middle and bottom row). The obtained stability constants of the Ph_2-BPPhen/Ln(III) complexes are listed in Table 1, which were compared with the lanthanides complexes with other previously reported hard—soft donors combined ligands. The titration of Ph_2-BPPhen with another lanthanide Nd(III), which has the most similar ionic radii with Am(III) among all the lanthanide ions,[62,63] was also conducted in CH_3OH, and the titration results are presented in Figure S4.

Ph_2-BPPhen exhibited relatively stronger complexation ability with lanthanide ions than other structurally similar N,O-hybrid phenanthroline derived ligands such as Et-Tol-DAPhen,[40] C4-POPhen,[37] and C2-POPhen[38] in Et_4NNO_3/CH_3OH media. The stability constants (log β_1) for the 1:1 complexes of LaL^{3+}, NdL^{3+}, EuL^{3+}, and LuL^{3+} (L = Ph_2-BPPhen) were 5.34 ± 0.03, 6.10 ± 0.06, 7.26 ± 0.12, and 7.01 ± 0.18, respectively. The stability of the 1:1 Eu(III) complex was 1—3 orders magnitude larger than those of the 1:1 Eu(III) complexes of C2-POPhen (log $\beta_1 = 4.93 \pm 0.03$), C4-POPhen (log $\beta_1 = 5.03 \pm 0.03$), and Et-Tol-DAPhen (log $\beta_1 = 3.81$) under identical conditions. This result indicates that substitution of the phosphonates or amide groups with phosphine oxides on the phenanthroline framework could significantly strengthen the coordinating ability toward trivalent lanthanide elements.[15] Given the similar extraction properties of Ph_2-BPPhen for both Am(III) and Eu(III), it is reasonable to conclude that those —P═O groups functionalized phenanthroline ligands also should have strong affinity to minor trivalent actinides. The stronger basicity of the oxygen atom in the Ph_2-BPPhen compared with other ligands might be the main reason.[43] The remarkable enhanced complexation ability of Ph_2-BPPhen toward Am(III) and Eu(III) compared with other reported N,O-hybrid phenanthroline derived ligands also implies that Ph_2-BPPhen has good potential in coseparation of trivalent f-block elements from HLW.

Additionally, it has been found that the stability constants of both 1:1 and 2:1 complexes formed between Ph_2-BPPhen and trivalent lanthanide ions increased from La(III), Nd(III) to Eu(III) and then decreased from Eu(III) to Lu(III). This trend in the complexation strength agrees well the extraction properties of Ph_2-BPPhen for La(III), Eu(III), and Lu(III) as shown in Figure S5. The stability constants of the 2:1 species of Ph_2-BPPhen with La(III), Nd(III), Eu(III), and Lu(III) were determined to be 10.42 ± 0.15, 10.77 ± 0.24, 12.89 ± 0.36, and 12.11 ± 0.40, respectively. The similar increasing and then decreasing trend in lanthanide series complexation was also reported in other N,O-mixed ligands such as *N*-octyl-*N*-tolyl-1,10-phenanthroline-carboxamide (OcTolPTA)[64] and 1,10-phenanthroline-2,9-dicarboxamide (PDAM).[65] This might be attributed to the best size match of the coordination cavity constructed by a Ph_2-BPPhen molecule with Eu(III) among the four lanthanide ions tested.

X-ray Crystallographic Structure of Eu(III) Complexes. To get more insights into the structural information of Ph_2-BPPhen complexes with trivalent lanthanide and actinide and help understand the coordination behaviors as well as extraction mechanisms in the nitrate media, single crystals of the Eu(Ph_2-BPPhen)$(NO_3)_3$ complex were prepared and structurally characterized by the X-ray diffraction technique, and the structural refinement parameters were summarized in Table 2. Although both 1:1 and 2:1 complexes of Ph_2-BPPhen with lanthanides were found in solution as demonstrated by the foregoing NMR and spectrophotometric titration studies, only the 1:1 type complexes were successfully crystallized.

As presented in Figure 6a, the central Eu(III) metal was 10-coordinated with two nitrogen atoms from phenanthroline framework and two oxygen atoms from two —P═O arms as well as another six oxygen atoms from three bidentate nitrate anions. It is quite different from the 8-coordinated Eu(III) in the previously reported PnPPOEu$(TFA)_3 \cdot H_2O$ complex (where TFA = trifluoroacetate),[66] demonstrating that the counteranion has a significant effect on the structure of these complexes. The mean bond length of Eu—N was 2.630(3) Å, shorter than the corresponding bond length of 2.650(7) Å in PnPPOEu$(TFA)_3 \cdot H_2O$ complex,[66] 2.633(15) Å in Eu(C2-POPhen)$(NO_3)_3$ complex[67] and slightly longer than that (2.628(9) Å) in Eu(BLPhen)$(NO_3)_3$[68] complex. Notably, the mean bond length Eu(III) to the O atoms of Ph_2-BPPhen was also obviously

Table 2. Structural Refinement Parameters for the 1:1 Eu(III) Complex

name	Eu(Ph_2−BPPhen)$(NO_3)_3$
empirical formula	$C_{36}H_{26}EuN_5O_{11}P_2$
CCDC number	2027099
formula weight	918.52
temperature/K	170.0
crystal system	orthorhombic
space group	$Pna2_1$
a/Å	30.5990(6)
b/Å	12.2693(2)
c/Å	10.3127(2)
α/°	90
β/°	90
γ/°	90
volume/Å^3	3871.68(12)
Z	4
ρ_{calc} g/cm^3	1.576
μ/mm^{-1}	1.767
F(000)	1832.0
crystal size/mm^3	0.18 × 0.09 × 0.03
radiation	Mo K_α (λ = 0.71073)
2Θ range for data collection/°	4.764−61.012
index ranges	$-43 \leq h \leq 41$, $-15 \leq k \leq 17$, $-14 \leq l \leq 14$
reflections collected	35979
independent reflections	11640 [R_{int} = 0.0326, R_{sigma} = 0.0457]
data/restraints/parameters	11640/1/496
goodness-of-fit on F_2	1.028
final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0262, wR_2 = 0.0484
largest diff. peak/hole/e Å^{-3}	0.49/−0.63

shorter than that (2.353(13) Å) in the crystal of Eu(C2-POPhen)$(NO_3)_3$ complex and that (2.432(8) Å) in Eu(BLPhen)$(NO_3)_3$. These results suggest that Ph_2-BPPhen has stronger complexation ability with trivalent f-block elements than those phenanthroline derived phosphonate and amide ligands, which agrees well with the trend of stability constants.

Moreover, a closer view from the bottom (Figure 6b) revealed that the central metal ion is located almost in the same plane with the phenanthroline framework along with four phenyl groups symmetrically arranged at both sides of the central coordination plane leading to a highly symmetric molecule of Eu(III) complex. That is why we observed only one single peak signal in the ^{31}P NMR spectra of the 1:1 Eu(III) complex. This symmetric nature might decrease the tension in the coordination bonds of Eu(III) and make the complex more stable. The strong hydrogen bonding interactions with H···O bond distance ranging from 2.410 to 2.695 Å between the oxygen atoms of nitrate and the protons of ligands (Figure 6c) could further help stabilize the complex.

DFT Calculations of Am(III) and Eu(III) Complexes with Ph_2-BPPhen. To obtain the complexation nature of Ph_2-BPPhen (denotes as L) with trivalent lanthanides and actinides, the structures of 1:1 complexes of AmL$(NO_3)_3$ and EuL$(NO_3)_3$ were optimized by B3LYP method. As depicted in Figure 7, similar to other typical tetradentate bipyridine or phenanthroline derivatives,[40,42,67,69] the central metal ions were bound to the ligand by two N atoms of the phenanthroline framework and two O atoms of the P═O groups as well as another six O atoms from three nitrate anions in the structure of 1:1 Am(III)/Eu(III) complexes with Ph_2-BPPhen. The calculated average Am−N bond distance is 2.898 Å, slightly shorter than that of Eu−N (3.002 Å) in the 1:1 complexes despite of the larger ionic radius of Am(III) (1.070 Å) than that of Eu(III) (0.995 Å). By contrast, the Am−O_p bond length (2.463 Å) is longer than that of Eu−O_P (2.397 Å). These results suggest that a bit stronger extraction ability of Ph_2-BPPhen toward Am(III) than Eu(III) as observed in the solvent extraction experiment is probably caused by the stronger interaction between Am(III) and soft nitrogen atoms rather than hard oxygen atoms. Typical molecular orbitals (MOs) (Figure 7) of the 1:1 Am(III) and Eu(III) complexes were calculated, which clearly shows the orbital interaction between f orbitals of metals and 2p orbitals of N and O atoms. Both the 5f orbital (for Am) and the 4f orbital (for Eu) are localized on the metal, indicative of the dominated ionic

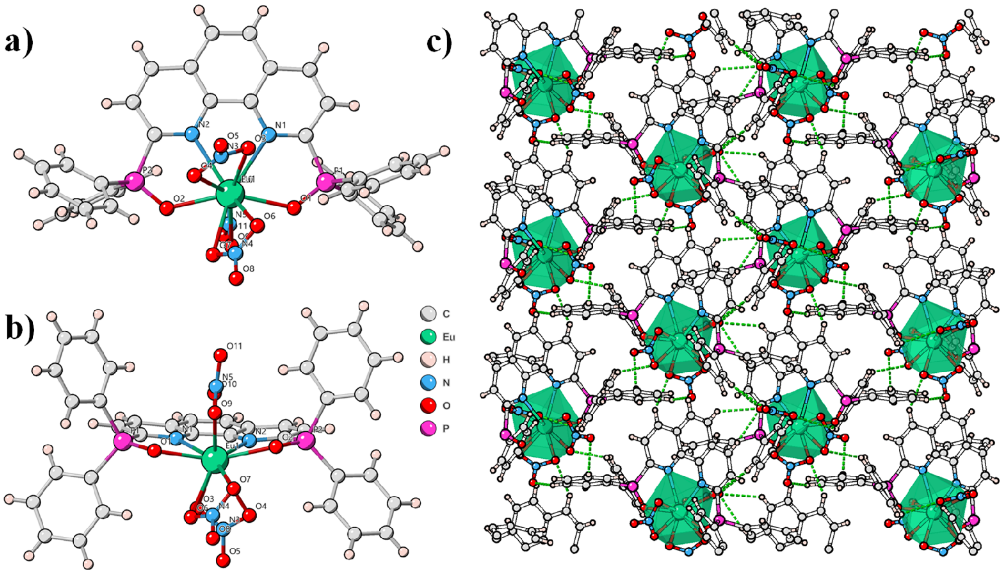

Figure 6. X-ray crystal structure of Eu(Ph_2-BPPhen)$(NO_3)_3$ complex. (a) A front view, (b) a bottom view, and (c) Packing patterns viewed along the b-axis (green dashed line denotes the hydrogen bonds). Selected bond distances (Å): Eu1−O1 2.351(3), Eu1−O2 2.355(2), Eu1−N1 2.642(3), Eu1−N2, 2.618(3), Eu1−O3, 2.501(3), Eu1−O4, 2.528(3), Eu1−O6, 2.596(3), Eu1−O7 2.499(3), Eu1−O9 2.547(3), Eu1−O10, 2.473(3).

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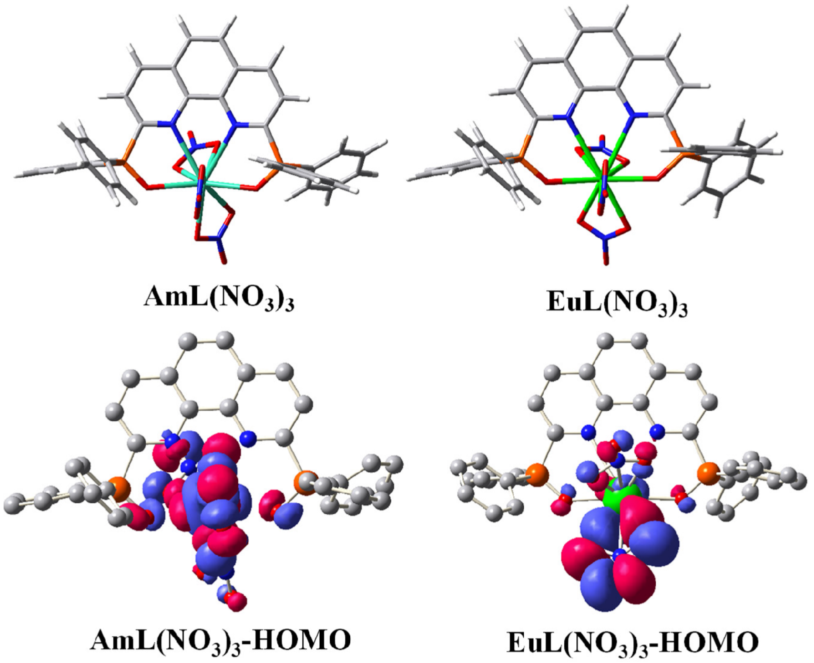
$AmL(NO_3)_3$

$EuL(NO_3)_3$

$AmL(NO_3)_3$-HOMO

$EuL(NO_3)_3$-HOMO

Figure 7. Optimized structures and typical frontier molecular orbitals (MO) of the 1:1 Am(III) and Eu(III) complexes with Ph_2-BPPhen. Cyan, green, orange, red, blue, light gray, and white colors denote Am, Eu, P, O, N, C, and H elements, respectively. The hydrogen atoms were omitted for clarity in the HOMO orbitals of Am(III) and Eu(III) complexes.

character of these coordination bonds. However, the overlap between the 5f and 2p orbitals in the Am complex is more evident than the overlap between the 4f and 2p orbitals in the Eu complex, suggesting more covalency in the coordination bond for the Am complex.

What's more, the bond natures of Am(III) and Eu(III) coordinating with O and N atoms of Ph_2-BPPhen were further elucidated by the Mulliken atomic charges and Wiberg bond indices, which are usually accepted as important parameters to evaluate the complexation strength and characterize the covalency.[37,40,70,71] It was found that the natural charges (Table S1) of Am, nitrogen atoms of phenanthroline (Q_N), and oxygen atoms of phosphine oxide groups in Am(III) complexes are slightly larger than those on the Eu(III) complexes, which also suggests that Ph_2-BPPhen has a slightly stronger affinity to Am(III) over Eu(III). The larger Wiberg bond indices (WBIs) of the Am−N bonds than those of the Eu−N bonds indicate that a more covalent nature is presented in the Am−N bonds. In addition, the WBIs values of Am−O (0.666) and Eu−O (0.669) in the 1:1 complexes are significantly higher than those of previously reported WBIs values of Am−O (0.618−0.622) and Eu−O (0.635−0.636) in 1:1 Am(III) and Eu(III) complexes with POPhen ligands.[37,38] These results agree well with the stronger complexation ability of Ph_2-BPPhen toward Am(III) and Eu(III) than those phenanthroline-derived phosphonate type ligands.

■ CONCLUSIONS

In summary, a novel N,O-hybrid tetradentate phenanthroline-derived phosphine oxide (Ph_2-BPPhen) for the coseparation of trivalent actinides and lanthanides from highly acidic HNO_3 solutions of PUREX raffinate was reported. Ph_2-BPPhen exhibits strong extraction ability toward trivalent f-block elements, and even in 4.0 M HNO_3 media more than 99.3% of Am(III) and Eu(III) could be coextracted. The formation of both 1:1 and 2:1 (ligand/metal) complexes species was identified between Ph_2-BPPhen and f-block elements, of which the 1:1 type is the more stable species. The solvent extraction, stability constants of lanthanide complexes with Ph_2-BPPhen, as well as the single crystal characterization and the DFT calculation results demonstrate that substitution of the phosphonate ($-P{=}O(OR)_2$) with phosphine oxide ($-P{=}O(R)_2$) of the phenanthroline framework could substantially enhance the ligand's affinity with f-block elements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03727.

> $^1H/^{31}P$ NMR spectra of ligand, additional spectrophotometric titration data, extraction experiments, DFT calculation data, as well as the coordinates of the calculated Am(III) and Eu(III) complexes (PDF)

Accession Codes

CCDC 2027099 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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