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Journal:	*Dalton Transactions*
Manuscript ID:	DT-ART-02-2015-000679.R2
Article Type:	Paper
Date Submitted by the Author:	01-Apr-2015
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Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Probing the Difference in Covalence by Enthalpy Measurements: A New Heterocyclic N-Donor Ligand for Actinide/Lanthanide Separation

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Complexation of Am(III), Nd(III), and Eu(III) with a new heterocyclic nitrogen-donor ligand, 2,9-di(quinazolin-2-yl)-1,10-phenanthroline (denoted as BQPhen in this paper), was studied by thermodynamic measurements and theoretical computations. The stability constants of two successive complexes in dimethylformamide, ML^{3+} and ML_2^{3+} where M stands for Nd, Eu, or Am while L stands for the BQPhen ligand, were determined by absorption spectrophotometry. The enthalpy of complexation was determined by microcalorimetry. Results show that BQPhen forms ten times stronger complexes with Am(III) than Eu(III) or Nd(III) under identical conditions, suggesting that BQPhen could be used as an efficient extractant for the separations of trivalent actinides from lanthanides. The higher binding strength of BQPhen towards Am(III) than Nd(III) or Eu(III) is mainly due to the more favourable enthalpy of complexation for Am(III)/BQPhen complexes, implying a higher degree of covalence in the Am(III)/BQPhen complexes than the lanthanide(III)/BQPhen complexes. The thermodynamic trend was corroborated with computational results and validated by solvent extraction experiments that demonstrated BQPhen preferably extracted Am(III) more than Eu(III), with a separation factor of about 10. Discussions have been made to compare BQPhen with other phenanthroline derivatives such as CyMe4-BTPhen, a bis-triazine-phenanthroline derivative that was reported in the literature. Data suggest that, under identical conditions, BQPhen would form stronger complexes with Am(III), Eu(III), and Nd(III) than CyMe4-BTPhen.

Introduction

To reduce the long-term heat loading and radiotoxicity in the high level nuclear wastes, a strategy of partitioning and transmutation (P&T) has been proposed for the development of advanced nuclear fuel cycles. With the P&T strategy, the long-lived minor actinides, mainly Am(III) and Cm(III) that are the major contributors to the long-term heat loading and radiotoxicity, are separated from the trivalent lanthanides and transmuted into short-lived or stable isotopes.[1] The separation of trivalent actinides (An(III)) from lanthanides (Ln(III)) is an extremely challenging task due to their similarity in chemical properties.[2] In the past more than 20 years, considerable efforts have been made to develop advanced materials and methodologies to separate An(III) from Ln(III). Among the efforts, use of ligands containing donor atoms “softer” than oxygen, e.g., nitrogen, has received much attention, and a few excellent reviews have been published on this subject.[2-5]

Ligands bearing aromatic N-donors were found to complex An(III) more strongly than Ln(III), supposedly due to a greater covalent character of the An(III)-N bond than the Ln(III)-N bond.[5-7] A number of such aromatic N-donor ligands have been synthesized in the past as the candidate extractants for An(III)/Ln(III) partitioning,[3-5] including derivatives of bis-triazine-pyridine (BTP). The tridentate BTP ligands have shown interesting binding properties and selectivity for An(III) over Ln(III). For example, CyMe4-BTP (Figure 1, a), was found to have high separation factors for Am(III) over Eu(III) (denoted as $SF_{Am/Eu}$, the ratio of the distribution coefficients of Am(III) and Eu(III)) in solvent extraction.[8] The composition of the extracted metal complex species was believed to be $[M(BTP)_3]^{3+}$, similar to that in the solid.[9] Other tridentate pyridine-related ligands have been studied, including C5-hemi-BTP (Figure 1, b),[10] 2,6-bis(6-ethylpyridazin-3-yl)pyridine (Et-BDP, Figure 1, c),[11] and 2,6-bis(6-propyl-1,2,4,5-tetrazin-3-yl)pyridine (nPr-tetrazine, Figure 1, d).[11]

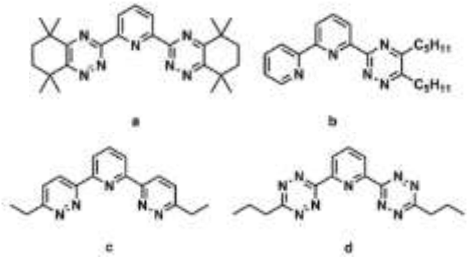


Figure 1. Structures of tridentate N-donor ligands: CyMe4-BTP (a), C5-hemi-BTP (b), Et-BDP (c), and nPr-tetrazine (d).

In contrast to the tridentate BTP ligands, a series of tetradentate N-donor ligands such as the derivatives of bis-triazine-bipyridine (BTBP) have also been studied. For example, CyMe4-BTBP (Figure 2, a) was found to be an effective extractant for the separation of An(III) from Ln(III).[10,12-14] Most recently, a new tetradentate ligand, CyMe4-BTPhen (Figure 2, b), was prepared to use as an extractant for the separation of Am(III) from Ln(III).[15] The phenanthroline framework in CyMe4-BTPhen fixes the pyridine nitrogens in the cis-configuration, resulting in the reduction of the pre-organization energy. It was found to be a highly efficient and selective extractant with fast extraction kinetics in comparison with CyMe4-BTBP.[15] By reviewing the development of various ligands reported in the literature, it can be seen that major efforts in the ligand design have been made in three aspects: (1) increasing ligand denticity, (2) improving the preorganization of the donor atoms in the ligand, and (3) revealing the fundamental principles governing the selectivity. With the objective of understanding the origin of the difference in binding with N-donor ligands between actinides and lanthanides, in the present work, we have designed and prepared a new heterocyclic tetradentate N-donor ligand, 2,9-di(quinazolin-2-yl)-1,10-phenanthroline (BQPhen, Figure 2, c), studied the thermodynamics of its complexation with Am(III), Nd(III) and Eu(III) with spectrophotometry and microcalorimetry in a single phase, determined the distribution coefficients of Am(III) and Eu(III) in solvent extraction using BQPhen as the extractant in nitrobenzene, and corroborated the experimental data with DFT computations. Conducting the thermodynamic studies in a single phase made it feasible to use calorimetric enthalpy measurements to provide insight into the differences between the degree of covalence in the BQPhen complexes with An(III) and those with Ln(III). The thermodynamic trends, corroborated by bond distances obtained by theoretical computations, were validated by the separation of Am(III) from Eu(III) in the solvent extraction experiments.

The new BQPhen ligand differs from CyMe4-BTBP and CyMe4-BTPhen in the number of nitrogen atoms (6 in BQPhen, 8 in CyMe4-BTBP and CyMe4-BTPhen, Figure 2) and the structural moieties (quinazoline in BQPhen, CyMe-4 triazine in CyMe4-BTBP and CyMe4-BTPhen, Figure 2). The BQPhen ligand was designed on the basis of the following considerations: (1) It is interesting to note that, in the complexes of CyMe4-BTBP and CyMe4-BTPhen (Figure 2, a and b), only the two pyridine nitrogens and two of the upper-inward nitrogens on the 1,2,4-triazines coordinate to An(III) or Ln(III), while the two outward nitrogens and the two lower-inward nitrogens do not participate in the complexation.[15-17] Therefore, the smaller number of nitrogen atoms in BQPhen may not weaken its binding ability with An(III) and Ln(III). Besides, the introduction of the quinazoline moieties makes BQPhen a completely aromatic ligand that could have higher chemical and radiological stability than non-aromatic ligands. Also, because BQPhen could have different solubilities in various solvents, adding BQPhen to the families of heterocyclic N-donor ligands such as CyMe4-BTBP and CyMe4-BTPhen broadens the choice of diluents in the applications of solvent extraction.

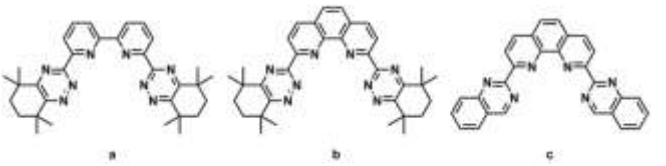


Figure 2. Structures of three heterocyclic tetradentate N-donor ligands. CyMe4-BTBP (a), CyMe4-BTPhen (b), and BQPhen (c).

Results

Complexation of Am(III) with BQPhen in 0.1 M $(CH_3)_4N(ClO_4)$/DMF

The absorption spectrum of Am(III) in DMF, unavailable in the literature, was collected and compared with that of Am(III) in an aqueous solution in Figure 3. The peak of the absorption band of Am(III) in 1 M HClO4 is at 503.0 nm (in agreement with the literature[18]), but it is shifted to 504.7 nm for Am(III) in DMF. This red-shift suggests that DMF solvates Am^{3+} more strongly than water, in consistent with the order of “hard donor strength” of solvents at 25 °C: DMF (34.3) > water (24.7).[19]

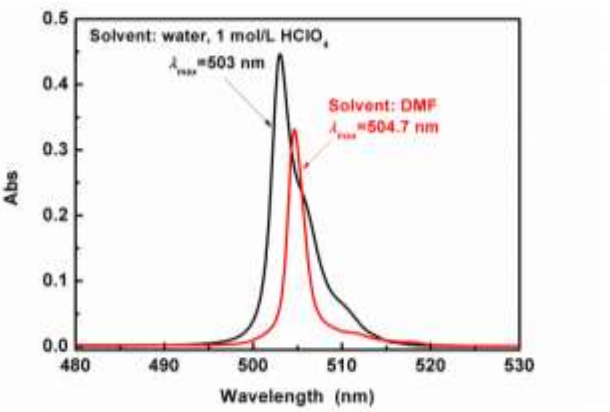


Figure 3. Absorption spectra of Am(III) in 1 M $HClO_4$ (black, $[Am^{3+}] = 1.09\times10^{-3}$ M) and DMF (red, $[Am^{3+}] = 7.81\times10^{-4}$ M).

A representative spectrophotometric titration of Am(III) in DMF with BQPhen is shown in Figure 4. The absorbance of Am^{3+} at 504.7 nm decreased when BQPhen was added, while new bands successively appeared at 509.3 nm and 512.1 nm, suggesting the formation of two successive complexes. Factor analysis of the spectra by the HypSpec2009 program[20] also indicated that there are three absorbing species (including free Am^{3+}). Accordingly, the spectra were fitted with the formation of AmL^{3+} and AmL_2^{3+} as shown by reactions (1) and (2), where M represents Am. The stability constants of the complexes were calculated and summarized in Table 1. The molar absorptivities of the Am(III) species in DMF were also calculated and shown in Figure 4.

$$M^{3+} + L = ML^{3+} \quad (1)$$

$$M^{3+} + 2L = ML_2^{3+} \quad (2)$$

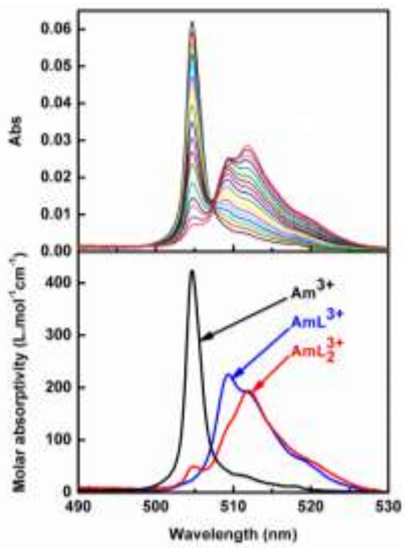


Figure 4. Spectrophotometric titration of Am(III) with BQPhen. t = (25.0 ± 0.1) °C, I = 0.1 M $(CH_3)_4N(ClO_4)$ in DMF. Initial solution in cuvette: V^0 = 0.700 mL, $C_{Am}{}^0$ = 1.45 × 10^{-4} M; Titrant: BQPhen, C_L = 7.20 × 10^{-4} M, total 0.200 mL added. Top: Titration spectra; Bottom: Calculated molar absorptivities of Am(III) species.

Complexation of Nd(III) and Eu(III) with BQPhen in 0.1 M $(CH_3)_4N(ClO_4)$/DMF.

Absorption spectrophotometry. Because the molar absorptivity of Nd(III) is low and Eu(III) does not have proper absorption bands in the UV-Vis region, spectrophotometric studies of the complexation of Nd(III) and Eu(III) were conducted by monitoring the absorption bands of BQPhen in the wavelength range of 200 – 400 nm. The absorption bands in this range are most probably due to the π-π* transitions from the aromatic nature of the BQPhen ligand. A representative titration of Nd(III)/BQPhen was shown in Figure 5. The titration spectra of Eu(III)/BQPhen were similar, provided in Figure S1 of Electronic Supporting Information (ESI). Again, factor analysis by HypSpec2009 indicated there were three absorbing species (including the free L). The spectra were fitted with the model including the formation of two successive complexes shown by reactions (1) and (2), where M stands for Nd or Eu. The overall stability constants and molar absorptivities of the 1:1 (NdL^{3+} and EuL^{3+}) and 1:2 (NdL_2^{3+} and EuL_2^{3+}) complexes were calculated and shown in Table 1, Figure 5 and Figure S1, respectively.

Table 1. Thermodynamic parameters of BQPhen complexation with Ln(III) and Am(III) in 0.1 M $(CH_3)_4N(ClO_4)$/DMF.

Reaction	Metal ion	logβ	ΔH kJ/mol	ΔS J/(mol·K)
$M^{3+} + L = ML^{3+}$	Nd^{3+}	7.11 ± 0.30	-5.41 ± 0.10	118 ± 6
	Eu^{3+}	7.26 ± 0.27	-4.49 ± 0.09	124 ± 5
	Am^{3+}	7.99 ± 0.46	-10.1 ± 0.2	119 ± 9
$M^{3+} + 2L = ML_2^{3+}$	Nd^{3+}	11.9 ± 0.8	-11.3 ± 0.2	190 ± 16
	Eu^{3+}	12.9 ± 0.5	-7.6 ± 0.1	221 ± 10
	Am^{3+}	14.1 ± 0.6	-14.7 ± 0.6	220 ± 18

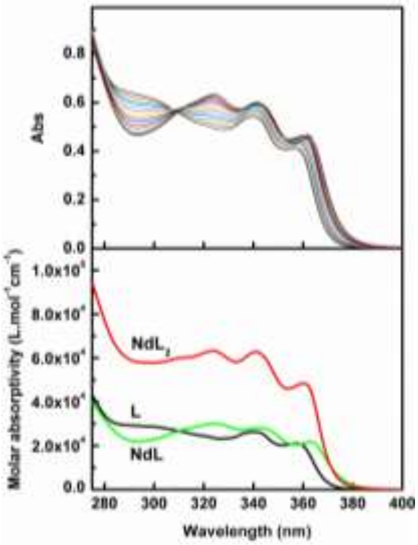


Figure 5. Spectrophotometric titration of BQPhen with Nd(III) perchlorate in DMF (I = 0.1 M $(CH_3)_4N(ClO_4)$) at 25 °C. Top: absorption spectra, V^0 = 2.50 mL, $C_L{}^0$ = 2.02 × 10^{-5} M; Titrant: 5.25 × 10^{-4} M $Nd(ClO_4)_3$. Bottom: calculated molar absorptivities, L (black), NdL^{3+} (green), and NdL_2^{3+} (red).

Luminescence spectra and lifetime of Eu(III)/BQPhen in DMF. Figure 6 shows the luminescence emission spectra of Eu(III) in DMF at 25 °C. The spectra contain the emission bands of the excited state $^5D_0$ to the sublevels of the ground state, ^7F_j, where j = 0, 1, 2, 3, and 4. Among these, the emission band of $^5D_0 \rightarrow {}^7F_2$ (around 613.8 nm) is most sensitive to the coordination environment of Eu(III). As BQPhen was added, the intensity of this band increased substantially with slight red-shift from 613.8 nm to 615.2 nm, indicating the complexation of BQPhen with Eu(III). Meanwhile, the shape of the $^5D_0 \rightarrow {}^7F_2$ band also changes, from a broad branched band at low L/M ratios (0.3 – 0.9) to a sharp single peak at high L/M ratios (> 2). Because the shape and branching of the bands are probably related to the symmetry of the species in solution, the change in the shape of the $^5D_0 \rightarrow {}^7F_2$ band could imply that the higher complex (e.g., ML_2) has higher symmetry than the lower complex (e.g., ML).

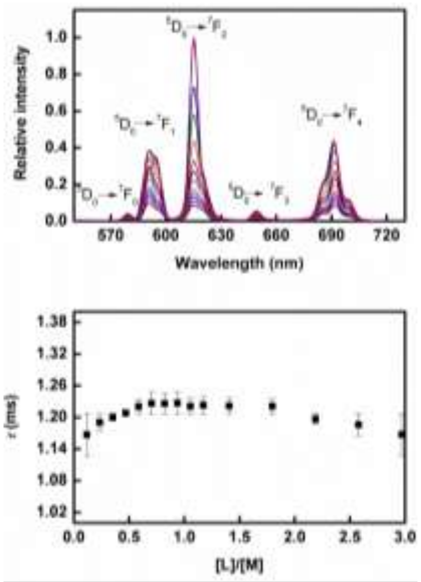


Figure 6. Luminescence titration of Eu(III) with BQPhen (I = 0.1 M $(CH_3)_4N(ClO_4)$) at 25°C. Top: emission spectra of Eu(III), Excitation wavelength = 395 nm. Initial solution: V^0 = 1.00 mL, $C_{Eu}{}^0$ = 5.30 × 10^{-5} M; Titrant: 4.08 × 10^{-4} M BQPhen. Bottom: Calculated luminescence life time of Eu(III). Initial solution: V^0 = 2.00 mL, $C_{Eu}{}^0$ = 4.25 × 10^{-4} M; Titrant: 3.32 × 10^{-3} M BQPhen.

Usually the emission band of $^5D_0 \rightarrow {}^7F_1$ (around 590 nm) is not sensitive to the coordination environment of Eu(III) in solution because it originates from a magnetic dipole transition. However, significant changes in the intensity and shape of this band were observed as BQPhen was added into the Eu(III) solution. Such phenomena were also observed in some other systems with strong complexing ligands such as diethylenetriaminepentaacetic acid (DTPA)[21] and bis-triazine-pyridine (BTP) ligands.[4,22,23] Usually, a "transition ratio", i.e., the ratio of the intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ bands, reflects the changes in the inner coordination sphere of Eu(III).[4] In DMF, the transition ratio was found to increase as BQPhen was added into the Eu(III) solution due to the replacement of DMF by BQPhen to form the Eu(III)/BQPhen complexes. Attempts to calculate the stability constants of the Eu/BQPhen complexes by fitting the luminescence data were not successful, probably because of the fact that, unlike the optical absorption, luminescence emission intensities are not always quantitatively proportional to the concentrations of the emitting species. As a result, the stability constants of the Eu(III)/BQPhen complexes listed in Table 1 were solely calculated with the optical absorption spectra.

The luminescence decay patterns of the Eu(III)/BQPhen/DMF solutions were fitted with single-exponential functions to calculate the luminescence lifetime (τ). For the solution in the absence of BQPhen ([L]/[M] = 0 in Figure 6), τ was found to be 0.8 ms. Using the correlation between the lifetime and the hydration number,[24] $n_{H2O} = 1.05/\tau - 0.70$, the hydration number of Eu(III) in this solution was calculated to be 0.6, comparable to the experimental uncertainty of n_{H2O} (i.e., ±0.5). This means that the water content in the primary solvation sphere of Eu(III) in the working DMF solutions was negligible. The Eu(III) in the DMF solution was probably present as the $[Eu(DMF)_8]^{3+}$ species, similar to a previous observation that Eu^{3+} was surrounded by a well-ordered solvation sphere containing eight DMF molecules with C_{2v} symmetry.[25] For all solutions in the presence of BQPhen ([BQPhen]/[Eu(III)] = 0.1 - 3.0), τ was (1.21 ± 0.04) ms, indicating the absence of water in the primary solvation sphere of Eu(III). The observed changes in the emission spectra were due to the replacement of DMF by BQPhen. In this sense, the stability constants of the BQPhen complexes in DMF obtained in this study should be considered "conditional" stability constants, better described by reactions (3) and (4).

$$M(DMF)_8{}^{3+} + L = ML(DMF)_4{}^{3+} + 4\ DMF \qquad (3)$$
$$M(DMF)_8{}^{3+} + 2\ L = ML_2{}^{3+} + 8\ DMF \qquad (4)$$

Enthalpy of complexation

Figures 7 and 8 show the representative data from calorimetric titrations of Am(III) and Eu(III) with BQPhen. The calorimetric titration of Nd(III) with the ligand was similar and is shown in Figure S2 of ESI. Multiple Titrations were performed with different concentrations of $C_M{}^0$ (M = Am, Eu, or Nd). Using the calorimetric data in conjunction with the stability constants obtained by spectrophotometry, the enthalpies of complexation at 25 °C were calculated. The enthalpies, as well as the entropies of complexation calculated accordingly, are summarized in Table 1.

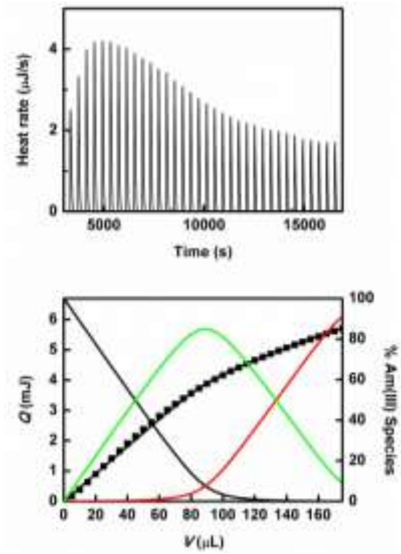


Figure 7. Microcalorimetric titration of Am(III)/BQPhen complexation (t = 25 °C, I = 0.1 M $(CH_3)_4N(ClO_4)$ in DMF). Titrant: 4.49 × 10^{-3} M BQPhen, 0.005 mL × 34 additions. Initial solution: V^0 = 0.900 mL, $C_{Am}{}^0$ = 4.43 × 10^{-4} M. Top: thermogram. Bottom: total heat (left y axis; closed symbol - experimental; line - calculated) and speciation of Am(III) (right y axis, lines - Am^{3+} (black), AmL^{3+} (green), $AmL_2{}^{3+}$ (red)) versus the volume of the titrant.

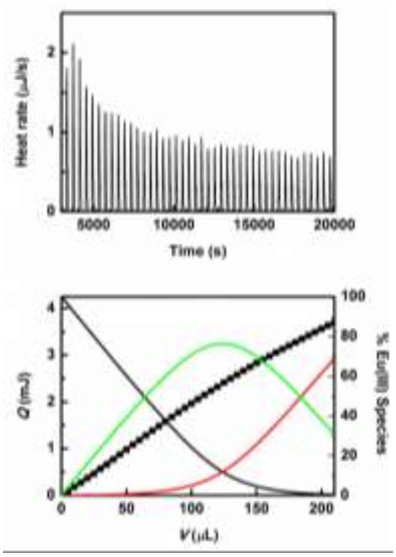


Figure 8. Microcalorimetric titration of Eu(III)/BQPhen complexation (t = 25.0°C, I = 0.1 M ($(CH_3)_4N(ClO_4)$) in DMF). Titrant: 4.49 × 10^{-3} M BQPhen, 0.005 mL × 42 additions. Initial solution: V^0 = 0.900 mL, $C_{Eu}{}^0$ = 6.17 × 10^{-4} M. Top: thermogram. Bottom: total heat (left y axis; closed symbol - experimental; line - calculated) and speciation of Eu(III) (right y axis, lines - Eu^{3+} (black), EuL^{3+} (green), $EuL_2{}^{3+}$ (red)) versus the volume of the titrant.

Distribution ratios and the separation factor for Am(III) and Eu(III) in solvent extraction

Figure 9 shows the distribution ratios of Am(III) and Eu(III), D_{Am} and D_{Eu}, as a function of the concentration of BQPhen in the organic phase ($[\overline{\mathrm{L}}]$). Over a range of BQPhen concentrations (from $10^{-4.3}$ to $10^{-3.2}$ M), D_{Am} was found to be always higher than D_{Eu} by one order of magnitude. Very good linear relationships between log$D$ and log $[\overline{\mathrm{L}}]$ were observed for both Am(III) and Eu(III):

$$\log D_{Am} = 1.84 \log[\overline{\mathrm{L}}] + 8.27 \quad (5)$$
$$\log D_{Eu} = 1.83 \log[\overline{\mathrm{L}}] + 7.22 \quad (6)$$

The nearly identical slopes of 1.84 and 1.83 for Am(III) and Eu(III) suggest that the stoichiometry of the extracted species is the same and it is mainly the ML_2 complexes that were extracted for both Am(III) and Eu(III) under the experimental conditions. The intercept of the linear correlation (8.27 for Am(III) and 7.22 for Eu(III)) represents a composite quantity including two terms including the extraction equilibrium constant (logK_{ex}) and a term related to the concentrations of the proton and nitrate in aqueous phase and the concentration of 2-bromohexanoic acid (HA) (see description of the extraction reaction in ESI). Because an identical aqueous phase (0.01 M HNO_3) and the same concentration of HA were used in the extraction experiments for both Am(III) and Eu(III), the difference in the intercepts between Am(III) and Eu(III) (8.27 – 7.22 = 1.05) represents the difference in the extraction equilibrium constant (logK_{ex}) between Am(III) and Eu(III), i.e., logK_{ex}(Am) - logK_{ex}(Eu) = (8.27 – 7.22) = 1.05, or K_{ex}(Am)/K_{ex}(Eu) = 11.

By definition, the separation factor, $SF_{Am/Eu}$, is the ratio of K_{ex}(Am)/K_{ex}(Eu) or D_{Am}/D_{Eu}.[26] From the numerical values of D_{Am} and D_{Eu} in Table S1 of ESI, a non-weighted average value of D_{Am}/D_{Eu} was calculated to be (10.0 ± 1.7), essentially the same as the value of K_{ex}(Am)/K_{ex}(Eu). In fact, the value of K_{ex}(Am)/K_{ex}(Eu) represents the "fitted" value of D_{Am}/D_{Eu} in the BQPhen concentration range from $10^{-4.3}$ to $10^{-3.2}$ M. In brief, BQPhen has a separation factor of 10 – 11 for Am(III) over Eu(III) in the solvent extraction of this study.

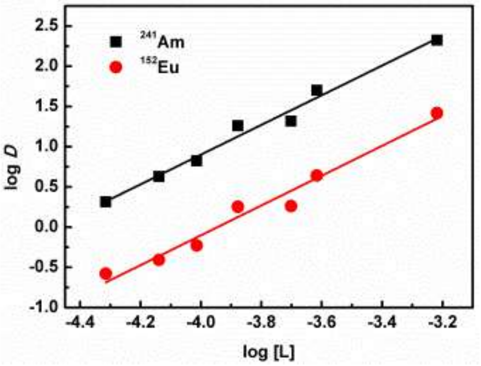


Figure 9. The dependency of the distribution coefficients of Am(III) and Eu(III) (D_{Am} and D_{Eu}) on the concentration of BQPhen in solvent extraction. Organic phase: different concentration of BQPhen and 0.2 M 2-bromohexanoic acid in nitrobenzene; aqueous phase: 0.01 M HNO_3 with trace ^{241}Am or ^{152}Eu; t = 25 °C.

DFT computational results

Optimization of the geometry of BQPhen and CyMe4-BTPhen ligands. BQPhen could have two conformational isomers (a and b, shown in Figure S3 of ESI). DFT calculations showed that the two isomers have nearly identical energy (-1405.17087898 a.u. for a, and -1405.17106489 a.u. for b). For CyMe4-BTPhen, data in the literature showed that the 'inward-inward" isomer is the more favorable conformation.[27] As a result, isomer a of BQPhen and the 'inward-inward" isomer of CyMe4-BTPhen were geometrically optimized at the B3LYP level in this work. The geometries are shown in Figure 10, and the calculated natural charge on the nitrogen atoms in the two ligands are summarized in Table 2.

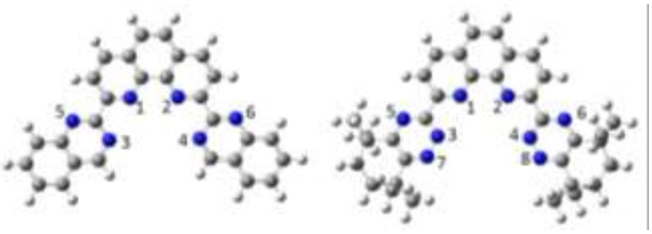


Figure 10. Optimized geometries of BQPhen (left) and CyMe4-BTPhen (right) in the gas phase. N (blue), C (grey), H (white).

Table 2. Natural charges of the nitrogen atoms in BQPhen and CyMe4-BTPhen and their complexes with Am(III) and Eu(III) (the numbering of N is shown in Figure 10).

Donor atom	BQPhen			CyMe4-BTPhen		
	L	$Am(NO_3)L_2^{2+}$	$Eu(NO_3)L_2^{3+}$	L	$Am(NO_3)L_2^{2+}$	$Eu(NO_3)L_2^{3+}$
N1	-0.381	-0.590	-0.586	-0.377	-0.593	-0.597
N2	-0.381	-0.575	-0.577	-0.377	-0.568	-0.591
N3	-0.436	-0.525	-0.533	-0.204	-0.403	-0.413
N4	-0.436	-0.501	-0.514	-0.204	-0.437	-0.417
N5	-0.475	-0.370	-0.373	-0.466	-0.330	-0.339
N6	-0.475	-0.363	-0.369	-0.467	-0.332	-0.340
N7				-0.201	-0.156	-0.162
N8				-0.202	-0.143	-0.147

Optimization of the geometry of the Am(III) and Eu(III) complexes with BQPhen and CyMe4-BTPhen and calculation of energy. To understand the difference in the binding strength between BQPhen and CyMe4-BTPhen with An(III) and Ln(III) and help interpret their behavior in separation processes, the structures of two hypothetical complexes, $[M(BQPhen)_2NO_3]^{2+}$ and $[M(CyMe4\text{-}BTPhen)_2NO_3]^{2+}$, where M = Am or Eu, were optimized at the B3LYP/6-31G(d,p)/RECP level, and shown in Figure 11. These hypothetical complexes were selected for calculation and comparison because they could probably represent the extracted Am or Eu species in the solvent extraction from nitric acid media using BQPhen or CyMe4-BTPhen as the extractant. The calculated natural charge on the nitrogens in the Am(III)/Eu(III) complexes, and the Am-N and Eu-N bond distances are summarized in Table 2 and Table 3, respectively.

Table 3. Bond distances in the complexes of BQPhen and CyMe4-BTPhen with Am(III) and Eu(III).

Donor atom	BQPhen		CyMe4-BTPhen	
	$R_{Am\text{-}N}$, Å	$R_{Eu\text{-}N}$, Å	$R_{Am\text{-}N}$, Å	$R_{Eu\text{-}N}$, Å
N1	2.65	2.66	2.64	2.66
N2	2.64	2.65	2.62	2.65
N3	2.71	2.72	2.73	2.71
N4	2.67	2.69	2.61	2.69

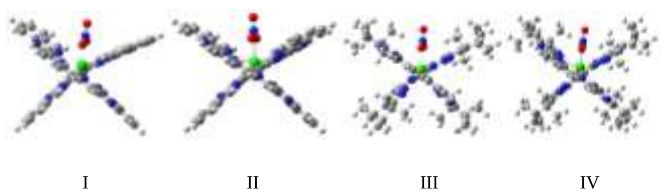


Figure 11. Optimized structures of $[ML_2(NO_3)]^{2+}$ (M = Am^{3+}, Eu^{3+}; L = BQPhen, CyMe4-BTPhen) in the gas phase. Green, blue, red, grey and white color denote M, N, O, C and H atoms, respectively. I: $[Am(BQPhen)_2(NO_3)]^{2+}$, II: $[Eu(BQPhen)_2(NO_3)]^{2+}$, III: $[Am(CyMe4\text{-}BTPhen)_2(NO_3)]^{2+}$, IV: $[Eu(CyMe4\text{-}BTPhen)_2(NO_3)]^{2+}$.

Discussion

Comparison between Am(III) and Ln(III)

Difference in the stability constants between Am(III)/BQPhen and Ln(III)/BQphen and implications in separations. Data in Table 1 show that BQPhen forms stronger complexes with Am(III) than Eu(III) and Nd(III) in DMF. The stability constant of the $[Am(BQPhen)_2]^{3+}$ complex is about ten times and a hundred times higher than those of $[Eu(BQPhen)_2]^{3+}$ and $[Nd(BQPhen)_2]^{3+}$ complexes, respectively.

It is known that the complex formation is only one of several processes that contribute to the distribution behaviour of metal ions in a two-phase extraction system, including the desolvation of participating species, complex formation, and interfacial material transfer. Therefore, it remains a question whether the higher binding strength of BQPhen with Am(III) than Ln(III) could be directly translated into higher extractability of Am(III) than Ln(III) by BQPhen in solvent extraction. However, a previous DFT study suggested that the extraction efficiency is mainly due to the binding free energy of the ligands to the metals,[28] and the metal/ligand complexation could play a dominant or critically important role in determining the distribution behaviour. In such cases, a prediction can be made, based on the higher binding ability of BQPhen with Am(III) than Eu(III), that BQPhen would have higher extractability for Am(III) than Eu(III) in two-phase solvent extraction. This prediction was validated in the present work by the results of solvent extraction discussed below.

Selectivity of BQPhen for Am(III) over Eu(III) in solvent extraction. Solvent extraction data in this work (Figure 9) showed that the extracted species are the 1:2 complexes of Am(III) (or Eu(III)) with BQPhen, and that the separation factor for Am(III) over Eu(III) was 10 - 11, which is in excellent agreement with the difference in the binding strength of BQPhen (10 times stronger for $[Am(BQPhen)_2]^{3+}$ than $[Eu(BQPhen)_2]^{3+}$) (Table 1). The agreement implies that the difference in the binding strength with BQPhen between Am(III) and Ln(III) is the dominant driving force for the separation of Am(III) from Eu(III) by BQPhen extraction. The solvent extraction data, while demonstrating that BQPhen is a highly selective ligand with the potential in the applications of An(III)/Ln(III) separation processes, validate the prediction of the selectivity of BQPhen based on thermodynamic measurements in a single phase.

Gibbs free energy of a hypothetical reaction. With the theoretically calculated Gibbs free energies in the gas phase (ΔG_g), and "relative" free energies for solvation ($\Delta\Delta G_{solv}$) of all species (Table S2 in ESI), it is possible to calculate the free energies for a hypothetical reaction below,

$$[M(NO_3)(H_2O)_7]^{2+} + 2L \rightarrow [M(L)_2(NO_3)]^{2+} + 7\ H_2O \qquad (7)$$

This hypothetical reaction was selected for calculation because it could, to some extent, represent reactions involved in a solvent extraction process (see the description of extraction experiments in ESI). The free energy of reaction in the gas phase ($\Delta G_{g,r}$) and in water ($\Delta G_{solv,r}$), is shown in Table 4. These values indicate that, for both BQPhen and CyMe4-BTPhen, the free energy of reaction is lower for Eu(III) than Am(III) in the gas phase. However, after the correction of the free energy of solvation ($\Delta\Delta G_{solv,r}$), the free energy of reaction ($\Delta G_{solv,r}$) of Am(III) is lower than that of Eu(III) by 1.63 kJ/mol for BQPhen and by 5.24 kJ/mol for CyMe4-BTPhen, respectively. This means that $[Am(L)_2(NO_3)]^{2+}$ will form more favorably than $[Eu(L)_2(NO_3)]^{2+}$ in water. For the BQPhen system, a difference of 1.63 kJ/mol in the free energy of reaction corresponds to a difference in the equilibrium constant of reaction (7) for Am(III) and Eu(III) as $\Delta\log K(\mathrm{Am/Eu}) = 0.66$, suggesting that the separation factor for Am(III) over Eu(III) could be about 5. This factor predicted by the DFT calculations of reaction (7) is lower than the separation factor predicted by the difference in thermodynamic binding strength and observed by solvent extraction experiments ($SF_{\mathrm{Am/Eu}} \approx 10$). However, we consider the agreement between the values is quite satisfying, noting that reaction (7) does not exactly represent the extraction reaction (see description of extraction in ESI).

Table 4. Gibbs free energy of complexation for the reaction (7), calculated at the B3LYP/6-311G(d,p)/RECP level of theory.

Ligand	M	$\Delta G_{g,r}$ kJ/mol	$\Delta\Delta G_{solv,r}$ kJ/mol	$\Delta G_{solv,r}$ kJ/mol
BQPhen	Am	-425.93	296.91	-129.02
	Eu	-436.42	309.03	-127.39
CyMe4-BTPhen	Am	-538.11	395.72	-142.39
	Eu	-553.02	415.87	-137.15

Enthalpy of complexation and difference in covalence. The selectivity for An(III) over Ln(III) by ligands with soft donor atoms (e.g., N) is usually assumed to originate from higher covalence in the An(III)-ligand bonds due to the larger extension and more participation of 5f orbitals in bonding in actinide complexes.[7,29] From a thermodynamic point of view, such greater covalence should be manifested by a more exothermic enthalpy of complexation.[30] The results of a few thermodynamic studies where the enthalpy of complexation was directly determined by calorimetry in a homogeneous phase seem to support such argument. For example, the enthalpies of complexation of Cm(III) with a few aminocarboxylic acids (nitrilotriacetic acid, trans-1,2-cyclohexanedinitrilotetraacetic acid, and ethylene-dinitrilotetraacetic acid) were found to be 5 - 6 $\mathrm{kJ \cdot mol^{-1}}$ more exothermic than those of Eu(III) in 0.5 M $NaClO_4$ aqueous solutions,[31,32] which could probably be attributed to higher covalence in the Cm-N bond than the Eu-N bond. In a comparative study of the complexation of Am(III) and Eu(III) with 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ) in 75/25 (volume %) methanol/water, the enthalpy of complexation for Am(III)/ADPTZ was found to be about 7 $\mathrm{kJ \cdot mol^{-1}}$ more exothermic than that for Eu(III)/ADPTZ.[33] A more recent study showed that, under identical conditions in 1% v/v ethanol/water, the 1:1 complex of bis(2,4,4-trimethylpentyl)dithiophosphinate with Cm^{3+} was about ten times stronger than that with Nd(III), mainly because the enthalpy of complexation for CmL^{2+} is 3.5 $\mathrm{kJ \cdot mol^{-1}}$ less endothermic than that of NdL^{2+}, implying stronger covalent interaction in CmL^{2+} than NdL^{2+}.[34]

Data from the present study (Table 1) show that the enthalpies of complexation for the BQPhen complexes with Am(III), Nd(III) and Eu(III) are all exothermic, favourable to the complexation. More importantly, the enthalpy of complexation for the AmL^{3+} complex is 4.5 – 5.5 $\mathrm{kJ \cdot mol^{-1}}$ more exothermic than those of NdL^{3+} and EuL^{3+}, and the enthalpy of complexation for the AmL_2^{3+} complex is 3.4 – 7.1 $\mathrm{kJ \cdot mol^{-1}}$ more exothermic than those of NdL_2^{3+} and EuL_2^{3+}, while the entropies of complexation are nearly the same within experimental uncertainties. Obviously, it is the difference in the enthalpy of complexation between the Am(III) and Ln(III) systems that results in stronger (by 1 -2 orders of magnitude) complexation of the former than the latter. This observation, in line with those observed for the complexation of An(III) and Ln(III) with other N-donor ligands[31-33] and S-donor ligand,[34] supports the argument that there is higher covalence in the complexes of soft donor atoms (e.g., N, S) with An(III) than Ln(III).

Comparison of M-N bond distances and electronegativities on N. The stronger binding strength of BQPhen with Am(III) than Eu(III) and the higher covalence in the Am(III)/BQPhen complexes than the Eu(III)/BQPhen complexes can be further discussed based on the electronegativities and bond distances obtained by DFT computation.

As shown in Table 2, for the BQPhen complexes of Am(III) and Eu(III), the natural negative charges of the N donors in $EuL_2(NO_3)^{2+}$ are all, except for N1, higher than those in $AmL_2(NO_3)^{2+}$. This indicates that more electron density is donated from the N donors to Am(III) than Eu(III), implying a higher degree of orbital overlapping between the N donors and Am(III) than that between the N donors and Eu(III). Such difference is manifested by the bond distances shown in Table 3. In the BQPhen complexes with Am(III) and Eu(III), the bond distances of Am-N (for N1, N2, N3, and N4) are all shorter by 0.01 – 0.02 Å than those of Eu-N (Table 3). Taking into consideration that the ionic radius (for the coordination number of 8) of Am^{3+} (1.108 Å)[35] is longer by 0.042 Å than that of Eu^{3+} (1.066 Å),[36] the Am-N bonds are indeed stronger than the Eu-N bonds, reflecting a higher degree of covalence in the Am(III)/BQPhen complexes.

Comparison between BQPhen and CyMe4-BTBP/CyMe4-BTPhen

Direct comparison of the thermodynamic data of BQPhen from the present study and those of CyMe4-BTBP and CyMe4-BTPhen in the literature is difficult because of several reasons: (1) different solvents were used in these studies; (2) no enthalpy data for the complexation of CyMe4-BTBP and CyMe4-BTPhen with An(III) or Ln(III) were available in the literature.

However, according to the difference in the "hard donor strength" of different solvents and the DFT computational results, comparisons between the BQPhen system and those of CyMe4-BTBP and CyMe4-BTPhen can be made on a qualitative basis. Pertinent data for comparison are summarized in Table 5.

Table 5. Comparison of stability constants of the An(III) and Ln(III) complexes with different ligands (BQPhen, CyMe4-BTPhen, and CyMe4-BTBP)

Ligand	logβ ($M^{3+} + 2L = ML_2^{3+}$) M = Cm(III)	M = Am(III)	M = Eu(III)	Solvent	Method	Ref.
BQPhen		14.1(6)	12.9(5)	DMF (I = 0.1M)	UV-Vis	p.w.
CyMe4-TPhen	13.8(2)		11.6(4)	Methanol (3.3 mol% water)	TRLFS	37
CyMe4-BTBP	12.4(3)		11.3(3)	Methanol (3.3 mol% water)	TRLFS	37
			11.9(5)	Methanol (I = 0.01M)	UV-Vis	10

Two trends are shown by the data in Table 5: (1) for each ligand (BQPhen, CyMe4-BTPhen, or CyMe4-BTBP), the An(III) complexes are about 1-2 orders of magnitude stronger than the Eu(III) complexes; (2) the stability constants of the BQPhen complexes (in DMF) are higher than those of corresponding CyMe4-BTPhen or CyMe4-BTBP complexes (in methanol with or without small quantities of water). The first trend indicates that all three ligands favor the complexation with An(III) over Ln(III), suggesting they could be potential extractants with selectivity for An(III) over Ln(III) in separation processes. Similar to BQPhen, the selectivity of CyMe4-BTPhen for An(III) could also be attributed to the stronger interactions of its N donors with Am(III) than Eu(III) based on the calculated natural charges on the N donors and the bond distances for the CyMe4-BTPhen complexes (Table 2 and Table 3). As the computational data in Table 2 show, the natural negative charges on most of the N donors in the Am(III)/CyMe4-BTPhen complexes are lower than those in the Eu(III)/CyMe4-BTPhen complexes. Also, the calculated bond distances of Am-N in the Am(III)/CyMe4-BTPhen complexes are shorter than those of Eu-N in the Eu(III)/CyMe4-BTPhen complexes (Table 3).

The second trend, though based on the data obtained in different media, could suggest that BQPhen is a stronger complexant than CyMe4-BTPhen or CyMe4-BTBP. The very low solubility of BQPhen in methanol precludes the experimental studies of its complexation with Am(III) or Eu(III) in methanol that could allow direct comparison with CyMe4-BTPhen and CyMe4-BTBP in the same solvent. However, it is known that DMF has a higher hard donor strength (34.3) than methanol (16.7) and water (24.7),[19] meaning that DMF solvates the metal ions more strongly than water or methanol.[38-40] In other words, the complexation of BQPhen with Am(III) or Eu(III) in methanol/water would be even stronger than that in DMF. It is reasonable to conclude, therefore, that BQPhen is a stronger ligand than CyMe4-BTPhen and CyMe4-BTBP.

The stronger binding strength of BQPhen could be explained by the higher electronegativity of the N donor atoms in BQPhen than those in CyMe4-BTPhen, as the DFT computations show. Results in Table 2 show that, between BQPhen and CyMe4-BTPhen, the natural charges of the N atoms in the phenanthroline framework (N1/N2) are nearly identical (-0.381/-0.381 for BQPhen and -0.377/-0.377 for CyMe4-BTPhen), but the natural charges of other nitrogen atoms are different: the natural charges of the inward quinazolin-nitrogens in BQPhen (N3/N4, -0.436/-0.436) are substantially more negative than those of the inward triazine nitrogens in CyMe4-BTPhen (N3/N4, -0.204/-0.204). The natural charges of the outward quinazolin-nitrogens in BQPhen are also higher (N5/N6, -0.475/-0.475) than those in CyMe4-BTPhen (N5/N6, -0.466/-0.467). The higher electronegativity on the quinazolin-nitrogens in BQPhen results in the higher binding strength of BQPhen than that of CyMe4-BTPhen.

Conclusions

A new heterocyclic tetradentate N-donor ligand, 2,9-di(quinazolin-2-yl)-1,10-phenanthroline (BQPhen), was designed and synthesized. Thermodynamic measurements indicate that BQPhen has strong binding ability with trivalent actinides and lanthanides and, more importantly, the stability constants of Am(III)/BQPhen complexes are about 10 times stronger than those of Nd(III)/BQPhen or Eu(III)/BQPhen complexes under identical experimental conditions, predicting that BQPhen could have high selectivity for Am(III) over Ln(III). Experimental solvent extraction data in this work have validated this prediction. DFT computational results help to interpret the strong binding ability and the selectivity of BQPhen for An(III) over Ln(III).

Calorimetric data indicate that the enthalpy of complexation of BQPhen with An(III) is more exothermic than Ln(III) while the entropy of complexation is similar for An(III) and Ln(III). Therefore, the difference in the binding ability between An(III) and Ln(III) was soley due to a more favorable enthalpy of complexation for An(III). A higher degree of covalence in the An(III)/BQPhen complexes is presumably the origin of stronger binding between An(III) and BQPhen.

As CyMe4-BTBP and CyMe4-BTPhen that have been reported in the literature, BQPhen could be an efficient and selective extractant for the separation of trivalent actinides from high level nuclear wastes. Addition of the new BQPhen ligand to the family of heterocyclic N-donor ligands broadens the choice of diluents in solvent extraction, and improves the chemical and radiological stability of the extractants.

Experimental

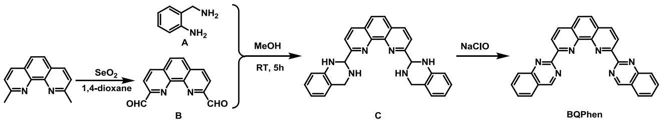
Chemicals

Reagent grade N,N-dimethylformamide (DMF, anhydrous, 99.8%) was purchased from Sigma-Aldrich and used without further purification. The supporting electrolyte, tetramethylammonium perchlorate, $(CH_3)_4N(ClO_4)$ (99%, from

Acros), was dried under vacuum for 24 h at room temperature prior to use. A 0.1 M $(CH_3)_4N(ClO_4)$ solution in DMF was prepared as the ionic medium for coordination experiments. All chemicals used in the ligand synthesis are of reagent grade.

Synthesis of BQPhen

BQPhen was synthesized in a few steps as shown in Scheme 1 and described as follows.



Scheme 1. Synthesis of BQPhen

Preparation of 1,10-phenanthroline-2,9-dicarbaldehyde (B). Selenium dioxide (11.29 g, 101.79 mmol, 2.12 eq) was dissolved in dioxane (250 mL) and water (6 mL) and heated to reflux. To this solution was added a solution of 2,9-dimethyl-1,10-phenanthroline (10.0 g, 48.014 mmol) in dioxane (200 mL) dropwise over 10 min. The mixture was heated under reflux for 30 min. The precipitated selenium metal was filtered (while still being hot). The filtrate was allowed to cool to 0 ^oC and new solid precipitates were obtained. The precipitated solid was filtered and washed with dioxane (50 mL). The solid was triturated with chloroform (500 mL) and filtered. The filtrate was evaporated to obtain 1,10-phenanthroline-2,9-dicarbaldehyde (B) as a light brown solid (4.42 g). The trituration/filtration process was repeated twice (each with 250 mL and 100 mL chloroform, respectively), additional quantities of B (2.81 g and 0.90 g) were obtained. The total yield was 8.13 g (72 %).

Preparation of 2,9-bis(1,2,3,4-tetrahydroquinazolin-2-yl)-1,10-phenanthroline (C). 1.18 g (5 mmol) 1,10-phenanthroline-2,9-dicarbaldehyde (B) and 1.22 g (10 mmol, 2eq) 2-(aminomethyl)aniline (A) were dissolved in 30 ml methanol, and stirred 7 hours at room temperature. After the reaction completed, 2 g of pale yellow solid was obtained by filtration and washed with a small amount of methanol. The yield was 92%. 1H NMR (400 MHz, DMSO-d6), δ 8.55 (d, 1H, J = 11.2 Hz), 8.03 - 7.99 (m, 2H), 6.99 - 6.91 (m, 2H), 6.68 (t, 1H, J = 8.2 Hz), 6.57 (t, 1H, J = 7.2 Hz), 6.43 (d, 1H, J = 11.2 Hz), 5.49 (d, 1H, J = 3.6 Hz), 4.17 - 4.10 (m, 1H), 3.95 - 3.90 (m, 1H), 3.17 (d, 1H, J = 5.2 Hz). HRMS (ESI): m/z [M + Na]+, calcd for $C_{28}H_{24}N_6Na$: 467.1955; found 467.1963.

Preparation of 2,9-di(quinazolin-2-yl)-1,10-phenanthroline (BQPhen). 1.18 g (5 mmol) 1,10-phenanthroline-2,9-dicarbaldehyde (B) and 1.22 g (10 mmol, 2 eq) 2-(aminomethyl)aniline (A) were dissolved in 30 ml methanol, and stirred 7 hours at room temperature. Then 60 ml 7.5% NaClO water solution were added and further stirred for 20 hours at room temperature. The precipitated solid was filtered and washed with methanol (30 ml), distilled water (30 ml) and methanol (15 ml), and then dried under vacuum for 24 hours to obtain 1.7 g white solid (80% yield). 1H NMR (400 MHz, DMSO-d6), δ 10.08 (s, 1H), 9.10 (d, 1H, J = 8.4 Hz), 8.89 (d, 1H, J = 8.4 Hz), 8.43 - 8.37 (m, 2H), 8.28 - 8.20 (m, 2H), 7.91 (t, 1H, J = 7.4 Hz). HRMS (ESI): m/z [M + Na]+ calcd for $C_{28}H_{16}N_6Na$: 459.1329; found 459.1335. NMR and HRMS data are provided in ESI (Figure S4 and S5 respectively).

Preparation of stock solutions for coordination experiments

$Nd(ClO_4)_3$ and $Eu(ClO_4)_3$ solutions. $Nd_2O_3(s)$ and $Eu_2O_3(s)$ were dissolved in 1 M $HClO_4$. The excess oxides were removed by filtration. The obtained aqueous solutions were slowly heated to evaporate until dryness. The solid residue was dried under vacuum for 24 h at 120°C, and then dissolved in DMF. The concentrations of Eu(III) and Nd(III) in the stock solutions were determined by complexometric titrations with EDTA.[41] Luminescence lifetime of Eu(III) was determined to verify that the water content in the DMF solution was negligible (see the luminescence data in the "Results" section).

$Am(ClO_4)_3$ solution. An ^{243}Am(III) solution in HCl was obtained from the laboratory stock (*Caution: due to the high specific α-radioactivity and limited availability of ^{243}Am, extreme precautions must be taken in handling the material*). The solution was slowly dried to remove water and excessive HCl. The residue was dissolved in 1 M $HClO_4$, and the concentration of Am(III) was determined by the optical absorbance at 503.0 nm, using the molar absorptivity of Am(III) as ε_{503} = 410 $cm^{-1}\cdot M^{-1}$.[18] To convert the aqueous Am(III) solution into the DMF solution, the Am(III) solution of accurate volume was slowly dried, and gently heated up to 350 ^oC to remove excess $HClO_4$ (*Caution: extreme precautions must be taken to assure the absence of any organic matter in the container before performing the fuming process. The presence of organic matter in the $HClO_4$ fuming process could lead to explosion*). The residue was quantitatively dissolved in DMF of known volume. Working solutions were prepared by quantitative dilution of the stock solutions.

BQPhen solution. 2,9-di(quinazolin-2-yl)-1,10-phenanthroline (BQPhen, denoted by L in this paper) was dried under vacuum for 24 h at 40 ^oC prior to use. A stock solution ([L] = 3.32 × 10^{-3} M) was prepared by dissolving 7.25 mg BQPhen with 0.1 M $(CH_3)_4N(ClO_4)$/DMF in a 5 mL volume flask. Working solutions of BQPhen were prepared by quantitative dilution of the stock solution with 0.1 M $(CH_3)_4N(ClO_4)$/DMF. The concentrations f the working solutions were determined and verified by the optical absorbance at two different wavelengths ($\varepsilon_{340.0\ nm}$ = 26250 $cm^{-1}\cdot M^{-1}$ and $\varepsilon_{357.5\ nm}$ = 20870 $cm^{-1}\cdot M^{-1}$), which are determined in this work (shown in the supporting information).

UV-Vis Spectrophotometry

The stability constants of the BQPhen complexes with Nd(III) and Am(III) were determined by UV-Vis spectrophotometry in DMF at (25.0 ± 0.1)^{o}C and a constant ionic strength (0.1 M $(CH_3)_4N(ClO_4)$). Quartz cells of 1 cm path length but different volumes were used on the Cary 6000i (Varian) spectrophotometer. For the studies of Nd(III)/BQPhen, 2.0 mL BQPhen (1 × 10^{-5} M to 5 × 10^{-5} M) initial solution was titrated with Nd(III) solution. The spectra of the ligand in the range of 400 nm to 275 nm were collected with 0.5 nm interval. For the Am(III)/BQPhen studies, 0.7 mL Am(III) solution (1×10^{-4} M to 5×10^{-4} M) was placed in a small cuvette as the initial solution, which was titrated with BQPhen. The spectra were collected in the range from 550 nm to 450 nm. After each addition of the titrant, the solution was thoroughly mixed by stirring for five minutes before the spectra were taken. The mixing time was sufficient because preliminary kinetic experiments indicated that the spectra became stable 3 minutes after the addition of the titrants. The stability constants were calculated by the nonlinear regression program HypSpec 2009.[20]

Luminescence measurements

Luminescence emission spectra and lifetime of Eu(III) in DMF solutions ([Eu(III)] = $(0.5 – 4) \times 10^{-4}$ M; [BQPhen] = $(0.4 - 3) \times 10^{-3}$ M) were acquired on a HORIBA Jobin Yvon IBH FluoroLog-3 fluorometer adapted for time-resolved measurements. 1.0 cm quartz cells were used. A sub-microsecond Xenon flash lamp (Jobin Yvon, 5000XeF) was the light source and coupled to a double grating excitation monochromator for spectral selection. The input pulse energy (100 nF discharge capacitance) was about 50 mJ and the optical pulse duration was less than 300 ns at fwhm. A thermoelectrically cooled single photon detection module (HORIBA Jobin Yvon IBH, TBX-04-D) that incorporates a fast risetime PMT, a wide bandwidth preamplifier, and a picosecond constant fraction discriminator was used as the detector. Signals were acquired using an IBH Data Station Hub and data were analyzed using the commercially available DAS 6 decay analysis software package from HORIBA Jobin Yvon IBH. The goodness of fit was assessed by minimizing the reduced function, χ^2, and visually inspecting the weighted residuals.

Microcalorimetry

Calorimetric titrations were conducted at 25°C with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp., USA) to determine the enthalpy of complexation. Details of the calorimeter and its calibration were provided elsewhere.[42] 0.900 mL solution containing the metal ion ($4.0 - 8.0 \times 10^{-4}$ M) was placed in the calorimetric cell, and titrated with a solution of BQPhen. Multiple titrations with different concentrations of the reagents were performed to reduce the uncertainty. In a typical titration, n additions of 0.005 mL titrant were made (n = 40 - 50) through a 0.250 mL syringe, resulting in n experimental values of the heat generated in the titration cell ($Q_{\mathrm{ex,j}}$, j = 1- n). These values were corrected for the heats of titrant dilution ($Q_{\mathrm{dil,j}}$) that were measured in a separate run. The net reaction heat at the j^{th} point ($Q_{\mathrm{r,j}}$) was obtained from the difference: $Q_{\mathrm{r,j}} = Q_{\mathrm{ex,j}} - Q_{\mathrm{dil,j}}$. The value of $Q_{\mathrm{r,j}}$ is a function of the concentrations of the reactants (C_{M} and C_{L}), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. A least-squares minimization program, HypDeltaH,[43] was used to calculate the reaction enthalpies (ΔH). The corresponding entropies of complexation (ΔS) were calculated from the expression $\Delta G = \Delta H - T\Delta S$, knowing that $\Delta G = -RT \ln\beta$.

Solvent extraction of Am(III) and Eu(III)

Solvent extraction experiments were conducted to measure the distribution ratios of Am(III) and Eu(III) with BQPhen as the extractant. The organic phase contains BQPhen in varied concentrations and 0.2 M 2-bromohexanoic acid in nitrobenzene. The aqueous phase contains trace concentrations of ^{241}Am or ^{152}Eu (about 300 Bq) in 0.01 M HNO_3.

The organic and aqueous phases (400 μL each) were contacted in 2 mL polyethylene Eppendorf micro-tubes and shaken on a constant-temperature water bath shaker (BV330-BN300, Yamato) at 25 °C for 60 minutes (previous experiments showed that this time interval was sufficient for the distribution equilibrium to be achieved). Then the mixture was centrifuged under 10000 g at the same temperature for 5 minutes. Aliquots of 100 μL were withdrawn from each phase and placed in glass scintillation vials for measuring the α-activity by using a Liquid Scintillation Analyzer (Tri-Carb 3100TR, PerkinElmer). To avoid the α-quenching effect by the organic chemicals in the organic phase samples, the 100 μL organic phase sample was pre-treated by repeated drying and heating with concentrated HNO_3 to destroy the organics. Finally, the scintillation vial was heated slowly to 300 °C to vaporize excessive HNO_3. After it was cooled down to the room temperature, 5 mL scintillation liquid was added and mixed thoroughly under ultrasonic oscillation before the liquid scintillation counting. The aqueous phase sample was just mixed with the scintillation liquid without the pre-treatment. The distribution ratio (D_{Am} or D_{Eu}) was calculated from the α-activities of the samples of organic and aqueous phases.

DFT calculations

All the theoretical calculations were carried out by the density functional theory (DFT) method with the Gaussian 09 package[44] and the hybrid B3LYP function.[45,46] For geometry optimizations, the quasi-relativistic effective core potentials (RECP) and the corresponding valence basis sets [47,48] are used for Eu and Am atoms, including 28 and 60 electrons in the core, respectively, while the 6-31G(d) basis sets were adopted for the other atoms including C, H, O, and N.

At the B3LYP/6-311G(d,p)/RECP level of theory, the harmonic vibrational frequencies were calculated on the basis of the optimized structures. The natural atomic charges were determined by natural bond orbital (NBO) analysis[49,50] at the same level of theory. The frequencies of all the chemical species were calculated at the same level of theory on the basis of the optimized geometries. The gas-phase Gibbs free energies (ΔG_{g}/Hartree) were obtained, including the zero-point energy (ZPE) and thermal corrections. At the same level of theory, the "relative" Gibbs free energies of solvation ($\Delta\Delta G_{\mathrm{solv}}$) for the complexes in water were calculated by the Conductor-like Polarizable Continuum Model (CPCM)[51,52] with the default atomic radii based on the optimized structures in the gas phase.

The Gibbs free energy in solvent (ΔG_{solv}) was obtained from ΔG_{g} and $\Delta\Delta G_{\mathrm{solv}}$, according to equation (8):

$$\Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{g}} + \Delta\Delta G_{\mathrm{solv}} \qquad (8)$$

where the "relative" free energies of solvation, $\Delta\Delta G_{\mathrm{solv}}$, include the electrostatic and non-electrostatic components, are described by equation (9):

$$\Delta\Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{non}} = \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{cav}} + \Delta G_{\mathrm{dis}} + \Delta G_{\mathrm{rep}} \qquad (9)$$

The terms ΔG_{el}, ΔG_{non}, ΔG_{cav}, ΔG_{dis}, and ΔG_{rep} are the total electrostatic free energies, the total non-electrostatic free energies, the cavitation energy, the dispersion energy, and the repulsion energy, respectively.

Acknowledgements

The spectrophotometric and calorimetric experiments were conducted at Lawrence Berkeley National Laboratory (LBNL) and were supported by the Director, Office of Science, Office of Basic Energy Science of the U.S. Department of Energy (DOE), under contract No. DE-AC02-05CH11231 at LBNL. Y. Yang thanks for the support from the National Science Foundation of China (Grant No. 91026022). The organic synthesis of the ligand and the DFT computation were conducted, respectively, at Sichuan University and Beijing Normal University.

Keywords: Covalence • Enthalpy of complexation • Trivalent actinides • Lanthanides • Separation

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†Electronic Supplementary Information (ESI) available: [Ligand analysis; Spectrophotometric titration of Eu/BQPhen; Calorimetric titration of Nd/BQPhen; Isomers of BQPhen; Calculated Free Energy of species; Solvent extraction of ^{241}Am and ^{152}Eu]. See DOI: 10.1039/b000000x/

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Graphical Abstract

BQPhen, a new tetra-dentate nitrogen-donor ligand, forms stronger complexes with Am^{3+} than Eu^{3+} or Nd^{3+}, due to a higher degree of covalence in the Am^{3+} complexes. The difference in covalence is reflected in the enthalpy of complexation and bond distances investigated by thermodynamic measurements and DFT computation.