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FULL PAPER

Efficient Separation of Light Lanthanides(III) Using bis-Lactam Phenanthroline Ligands

Mary R. Healy,[a] Alexander S. Ivanov,[a] Yana Karslyan,[b] Vyacheslav S. Bryantsev,[a] Bruce A. Moyer,[a] and Santa Jansone-Popova*[a]

Abstract: Due to the ever-increasing demand for high purity individual rare earth elements, novel and highly selective separation processes are increasingly sought after. Herein, we report a separation protocol that employs shape-persistent 2,9-bis-lactam-1,10-phenanthroline (BLPhen) ligands exhibiting unparalleled selectivity for light trivalent lanthanides. The highly preorganized binding pocket of the ligand allows separation of lanthanides with high fidelity, even in the presence of competing transition metals, in a biphasic separation system. Noteworthy, the selectivity trends of BLPhen ligands toward metal ions across the lanthanide series can be chemically modulated by altering the molecular rigidity of the extractant.

Introduction

Lanthanides, commonly referred to as rare earth elements, are vital for a wide variety of energy technologies and national security applications, including high-performance magnets, electronics, catalysis, to name but a few. The U.S. Department of Energy has deemed many of the rare earth elements as “critical” due to increasing demand and markedly limited supply chain.[1,2] As a result, the evolution of new and better separation processes of lanthanides from rare earth element-bearing minerals and used consumer materials are highly desirable.[3] Owing to the very similar chemical and physical properties of the trivalent lanthanides, their separation into individual elements is known as particularly challenging, however, the slight differences in cationic radii across the lanthanide series can be exploited towards that end. Biphasic separation has been the primary means by which the lanthanides are selectively separated into groups or individual rare earth streams, whereas ion exchange chromatography has predominantly been used to obtain high purity lanthanide products in smaller quantities.[4] Both processes exploit the differences in binding strength of trivalent lanthanides with organic ligands to achieve a separation.

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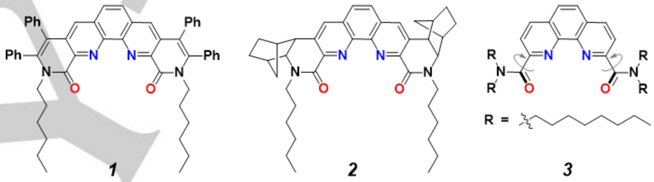
Only a handful of neutral ligands have been previously described that exhibit high selectivity for light lanthanides in solvent extraction systems,[5–8] the majority of the known ligands exhibit the reverse trend, i.e., by being more selective for heavy lanthanides, such as acidic compounds; di-2-ethylhexylphosphoric acid (D2EHPA)[9], a mixture of phosphinic and phosphonic acids (Cyanex 572)[10], di(2-ethylhexyl)phosphinic acid[11], and neutral compounds,[12] such as N,N,N’,N’-tetraoctyl diglycolamide (TODGA),[13-15] trialkylphosphine oxides (e.g., Cyanex 923)[16] and bistriazinylpyridine,[17-19] to mention but a few.



Scheme 1. Chemical structures of rigid BLPhen ligands **1** and **2,** and non-preorganized BAPhen ligand **3**.

The stability constants of complexes formed between trivalent lanthanide ions, Ln(III), and organic ligands containing hard donor atoms generally increase across the lanthanide series as the ionic radius of the element decreases and effective nuclear charge increases.[20] The change in magnitude or steepness of the observed selectivity across the Ln(III) series dictates the efficiency in adjacent lanthanides separation. To the best of our knowledge, no organic extractant has been identified that enables adjacent lanthanide separation in a single step, however, such a process would be highly desirable due to the growing economic and environmental concerns of historical element separations.
Increasingly, the rigidification of the organic ligand used in the extraction processes is gaining attention, not only due to formation of more stable complexes with metal ions in solution,[21] but also because locking the ligand in a specific conformation enforces an apparent size-based selectivity.[21–26] Herein, we exploit the unique shape-persistence of the synthesized[27] 2,9-bis-lactam-1,10-phenanthroline (BLPhen) ligands **1** and **2** (Scheme 1) to achieve an unprecedented selectivity for light lanthanides across the trivalent lanthanide series, even in the presence of transition elements, and rationalize the origin of the observed selectivity using quantum chemical calculations.

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Results and Discussion

A nearly quantitative transfer of light lanthanides (La-Nd) into an organic phase was observed when the rigid BLPhen ligands **1** and **2** dissolved in 1,2-dichloroethane were contacted with 0.9 M nitric acid solution containing 14 trivalent lanthanide nitrates (La-Nd, Sm-Lu) for 25 hours[28], indicating that the shape-persistent binding cavity decorated with two nitrogen and two oxygen donor atoms has strong preference for Ln(III) with larger ionic radii. As expected, the non-preorganized 2,9-bis-amide-1,10-phenanthroline (BAPhen) ligand **3** showed poor extractability and no apparent selectivity across the lanthanide series (see the ESI†, Table S1). The results are depicted in Figure 1, where the extraction efficiency of each Ln(III) by the two BLPhen ligands from nitric acid and hydrochloric acid is represented as the distribution (*D*) value that is equal to the metal ion concentration present in the organic phase divided by its concentration in the aqueous phase. Remarkable extraction efficiency across the lanthanide series is observed when using ligand **1** and nitric acid system (Figure 1a). Due to the very steep change across the series, not only the unprecedented selectivity for light versus heavy Ln(III) but also eminent intra-lanthanide selectivity is observed.

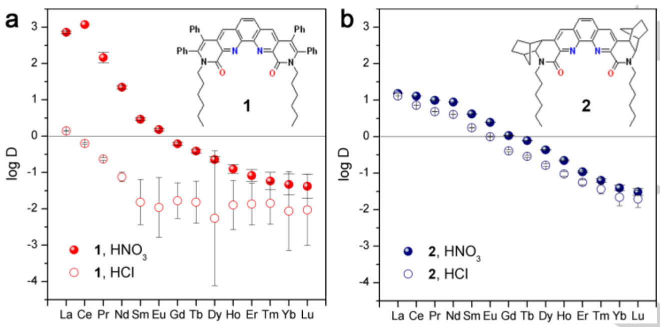

Figure 1. Variation of log D in the extraction of Ln(III), 0.5 mM each, with 7.0 mM ligand (a) **1** and (b) **2** from 0.9 M HNO_3 and 0.9 M HCl media into 1,2-dichloroethane at 25 ^{0}C after 25 hours. Due to 100% extraction of Ce(III) by **1** from HNO_3, log D values are calculated using the limit of detection of the instrument.

In Table 1 the selectivity among lanthanides is expressed as separation factors (*SF*): a ratio between two *D* values, e.g., D_{Pr}/D_{Nd}. As can be seen, the selectivity for La(III) vs. Lu(III) is 1.7x10^4, a value that is higher than previously reported for the most selective neutral 18-crown-6 ether/trichloroacetic acid system,[5] where $SF_{La/Lu}$ approached 1.2x10^4. Especially interesting is the selectivity observed for the adjacent lanthanide pair Nd/Pr of 6.6. The use of didymium, historical name of the Nd and Pr mixture, in permanent magnets makes their separation particularly important for the recycling of metals from used electronic parts to be reblended into new sintered magnets or other materials.

The extraction of Ln(III) from HCl medium by **1** is less efficient compared to HNO_3, with only the first four lanthanides (La-Nd) being partially extracted into the organic phase. This, however, does not hold true for the BLPhen ligand **2**, where the extraction behaviour from the two acids is comparable (Figure 1b). The marked variation in extraction behaviour can be attributed to the differences in complexation strength of these ligands with rare earth elements. Specifically, the oxygens in **2** are stronger donors due to favourable electron-donating effects of lactam nitrogens, resulting in more stable complex formation with Ln(III) nitrates and chlorides in the organic phase, whereas the two-path delocalization of lactam nitrogen lone pair in **1** diminishes the Lewis basicity of the adjacent lactam oxygens, causing weaker complexation with Ln(III) salts. The greater complexation strength of **2** with Ln(III) and lesser preorganization of the four donor atoms (*vide infra*) result in gradual selectivity increase across the Ln(III) series from right to left, in comparison to ligand **1**. Additionally, the variance in speciation of **1** and **2** with Ln(III) nitrates in the organic phase leads to observed difference in distribution values (Figure 1), i.e., **1** predominantly forms 1:1 ligand to metal complexes, whereas, both 1:1 and 2:1 ligand to metal species are present in the organic phase for ligand **2**.[28]

To provide atomic-scale insight into the unique separation ability and complexation behaviour of ligands **1** and **2** with Ln(III), first-principles calculations based on density functional theory (DFT) were performed. The approach we adopt here aims at predicting how the selectivity of one reference ligand changes with respect to another one in aqueous environment. We note that the current computational methods based on DFT are at best able to reproduce the trend in selectivity, but not the absolute values from extraction experiments. Herein, we present the results for model reactions that only reflect the effects of inner-sphere coordination on selectivity in the homogeneous aqueous media. Furthermore, in the absence of direct structural information in solution, the calculations were carried out on the experimentally obtained solid-state structures of 1:1 Ln(III) complexes[27] with model ligands (Figure 2a), in which the structural integrity is retained with the exception of long *n*-hexyl chains at the amide nitrogens that were replaced by methyl groups. Acknowledging a possibility of forming more complex extraction species possessing different stoichiometry in the organic phase, computational results for the 1:1 complexes could nevertheless be helpful in understanding how a complete preorganization of BLPhen ligands can be used to achieve an unprecedented control of selectivity for lighter rare earth elements. In the first step of computational investigation, it is

Table 1. Separation factors for Ln(III) using 7 mM ligand **1** and **2**/ 0.9 M HCl and HNO_3/ 1,2-dichloroethane system at 25 °C after 25 hours.

Ligand [a]	Acid	$SF_{La/Ce}$ [a]	$SF_{Ce/Pr}$[a]	$SF_{Pr/Nd}$	$SF_{Nd/Sm}$	$SF_{Sm/Eu}$	$SF_{Eu/Gd}$	$SF_{Gd/Tb}$	$SF_{Tb/Dy}$	$SF_{La/Lu}$
1	HNO_3	0.6	8.1	**6.6**	7.5	1.9	2.5	1.6	1.7	**17326**
1	HCl	2.2	2.7	3.1	4.9	1.4	0.7	1.1	2.8	149
2	HNO_3	1.2	1.3	1.1	2.1	1.7	2.3	1.4	1.8	495
2	HCl	1.8	1.5	1.2	2.3	1.8	2.4	1.4	1.8	660

[a] Due to 100% extraction of Ce by **1**, log D values are calculated using the limit of detection of the ICP-OES instrument.

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important to test whether the applied level of theory can reasonably reproduce the experimental values of the Gibbs free energy change, ΔG_{aq}, for the Ln(III) complexation in aqueous solution with the related non-preorganized ligand, 2,9-bis-amide-1,10-phenanthroline (BAPhen).[29] Despite some similarities in the dependencies of the predicted and experimental selectivities, theoretical results show some difficulty in reproducing them, which are overestimated by 1.25-2.31 kcal/mol (Figure S1 and Table S2). Therefore, rather than predicting absolute values of selectivities, it would be more meaningful to trace the differences in lanthanide selectivity between the highly preorganized BLPhen ligands **1a**, **2a** and the reference, non-preorganized BAPhen ligand. Following our previous work,[30] relative aqueous selectivities for La(III) over the other Ln(III) ions were computed according to the following ligand exchange reaction:

$$La(BAPhen)(NO_3)_{3(aq)} + Ln(BLPhen)(NO_3)_{3(aq)} \rightleftharpoons La(BLPhen)(NO_3)_{3(aq)} + Ln(BAPhen)(NO_3)_{3(aq)} \quad (1)$$

The results for BLPhen ligands **1a** and **2a** (Figure 2b) confirm much higher selectivity of the preorganized ligands for light lanthanides, with ligand **1a** exhibiting greater separation of the adjacent light lanthanide pairs, as observed experimentally.

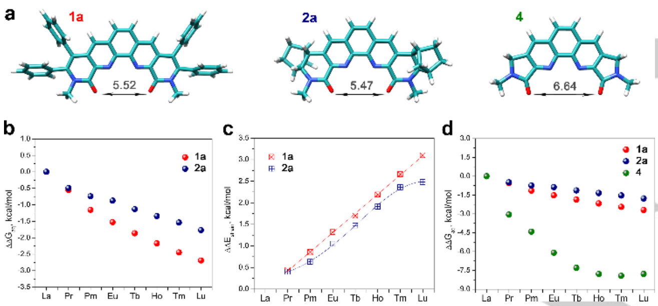

Figure 2. (a) Optimized geometries (M06/6-31+G(d)) of ligands **1a**, **2a**, and **4** (computationally designed ligand) with bond distances (Å) between the two oxygen donor atoms. (b) DFT (M06/LC/6-31+G(d)) calculated relative aqueous phase selectivities, $\Delta\Delta G_{aq}$ (La/Ln), kcal/mol, for the preorganized ligands **1a** and **2a** with respect to the non-preorganized ligand, 2,9-bis-amide-1,10-phenanthroline (BAPhen). (c) Ligands strain energy, $\Delta\Delta E_{strain}$, kcal/mol upon complexation with Ln(III) relative to complexation with La(III). (d) DFT calculated relative aqueous phase selectivities, $\Delta\Delta G_{aq}$ (La/Ln), kcal/mol, for the computationally designed ligand **4** with respect to the non-preorganized ligand BAPhen in comparison with **1a** and **2a**.

To understand the origin of selectivity, we analyzed the degree of ligand preorganization for larger vs. smaller Ln(III) ions and the induced ligand strain, associated with structural reorganization upon binding with metal ions. The DFT optimized structures of the ligands in a free form (Figure 2a) indicate that **1a** is evidently more preorganized for the complexation with light lanthanides, because of a larger bite (5.52 Å), (the distance between the oxygen donor atoms), compared to that of ligand **2a** (5.47 Å). Analysis of the ligand strain energy, ΔE_{strain}, in Figure 2c further emphasizes differential behaviour of **1a** and **2a** in the complexation across the Ln(III) series. Ligand **1a** with unsaturated lactam rings is more rigid than ligand **2a** and exhibits larger reorganization energy upon complexation with Lu(III) relative to complexation with La(III), enabling effective discrimination between light and heavy lanthanides. These results indicate that the BLPhen selectivity can be modulated by fine-tuning the rigidity of the ligand architectures, providing a viable strategy for efficient separation of adjacent Ln(III) ions. As a proof of concept, we computationally designed a more rigid ligand **4** (Figure 2a) via replacement of fused six-membered lactam rings by five-membered lactams in BLPhen, resulting in a structure with an even larger bite size (6.64 Å). Consequently, this ligand is predicted to exhibit dramatically enhanced selectivity toward Ln(III) with larger ionic radii (Figure 2d), but at the expense of having reduced binding strength (Table S3).

One extremely important feature of any extraction system is the ability to recover (strip) the metal ions from the formed complexes in organic phase, ideally, by using mild aqueous solution that does not contain large excess of acid or base. To assess the recovery of metal ions, the 1,2-dichloroethane solutions saturated with metal-ligand complexes were contacted with deionized water at 25 °C for 66 hours. Despite the very similar extraction profile from HCl and HNO_3 media by **2**, significant differences are evident in the stripping behaviour (Figure 3a). A better recovery of Ln(III) is seen from the organic solutions containing chloride as a counterion, indicating the formation of weaker complexes between **2** and trivalent lanthanide chlorides in an organic phase. The concentration of metal ions that were initially present in the stock solution prior to the extraction and that is now recovered after a single extraction-stripping sequence can also be calculated. Almost 50% of Pr^{3+}, Nd^{3+}, Sm^{3+}, and Eu^{3+} chloride can be transferred into an aqueous solution using ligand **2**—HCl system, with similar recovery of Pr-Eu nitrates using ligand **1** and HNO_3 system (Figure 3b). On the other hand, the recovery of Ln(III) from the organic phase loaded with ligand **2** and lanthanide nitrate complexes is poor due to very strong metal—ligand coordination.

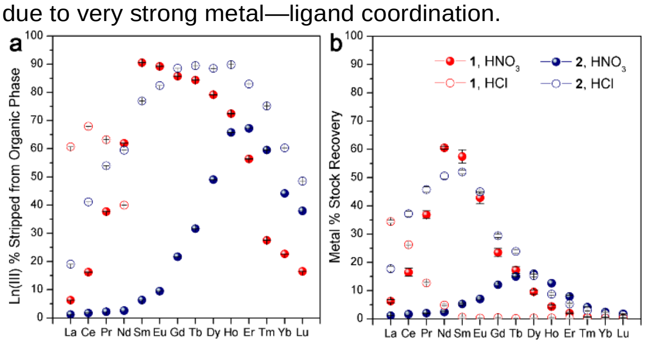

Figure 3. (a) Percentage of Ln(III) recovered from 1,2-dichloroethane solution loaded with Ln(III)-**1** and Ln(III)-**2** chloride and nitrate complexes after contact with water at 25 °C for 66 hours; (b) Overall percentage of Ln(III) recovered from the initial stock solution (0.9 M HCl and HNO_3) in a single extraction and water stripping sequence using ligands **1** and **2**.

Phenanthroline- and 2,2'-bipyridine-based ligands are known to form strong complexes with a variety of metal ions, especially d-block elements: Pd, Cu, Fe, Ag etc.,[29–32] which pose a major problem in selective recovery of f-block elements: trivalent lanthanides from rare earth element-bearing minerals and used electronic parts, and actinides from used nuclear fuel.[33] Since phenanthroline-based ligands **1** and **2** exhibit strong preference for Ln(III) with larger ionic radii, the extraction of the following interfering d-block metal ions: Ag^{+}, Pd^{2+}, Fe^{3+} and Cu^{2+}, in addition to four different Ln(III), were tested. The results presented in Figure 3a, show that both ligands **1** and **2** still maintain unprecedented selectivity for early Ln(III) over Fe(III) and Cu(II) in 1,2-dichloroethane/nitric acid system but, unsurprisingly, both also co-extract Pd(II), while Ag(I) gets extracted predominantly by ligand **1**. Furthermore, as shown in Figure 3b, it is possible to selectively recover trivalent lanthanides from the organic phase saturated with ligand **1**-metal nitrate complexes. More than 35% of each Ce^{3+}, Pr^{3+} and Nd^{3+} can be recovered in pure water in a single extraction-stripping sequence with very limited release of Ag(I) and no release of Pd(II). It is important to note that with each continues extraction BLPhen ligand **1** will accumulate Pd(II) and Ag(I), limiting the capacity for Ln(III) salts. Therefore, occasional regeneration of the ligand loaded with Ag(I) and Pd(II) would be necessary to achieve the separation of valuable Ln(III) and transition metal ions.

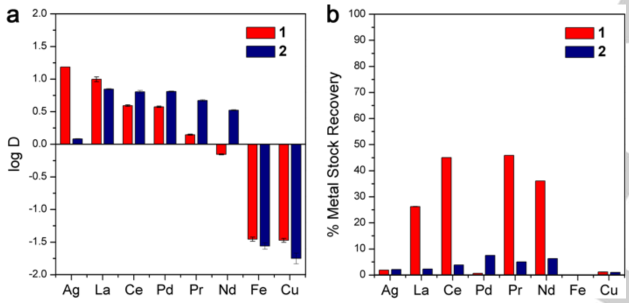

Figure 3. Performance of BLPhen ligands in the presence of transition metals in solution: (a) Change of log D in the extraction of lanthanides (La-Nd) and transition metals (Ag, Pd, Fe and Cu), 0.5 mM each, with 4.0 mM ligand **1** and **2** from 0.9 M HNO_3 media into 1,2-dichloroethane at 25 °C after 25 hours. (b) Overall percentage of Ln(III) and transition metals recovered from the initial stock solution in a single extraction and water stripping sequence.

Conclusions

In summary, we have demonstrated a remarkable single-step separation of light rare earth elements using shape-persistent BLPhen ligands. This is achieved by the unique ligand pre-organisation and rigidification, resulting in low strain energies upon complexation with large metal ions. The quantum chemical calculations point to the importance of substituents at the phenanthroline core of BLPhen ligand, which control the rigidity of the ligands and consequently impact their selectivity towards lanthanide ions. Our findings indicate that the separation ability and extraction strength exhibited by BLPhen ligands can be further modulated, enabling a new rare earth separation strategy.

Experimental Section

General: Ligands **1** and **2** were synthesized using experimental procedures described in reference 22. Organic solutions were prepared by dissolving ligand **1** or **2** in 1,2-dichloroethane (HPLC grade, >99.8% purity, Sigma-Aldrich). Aqueous solutions of Ln(III) were prepared from Single Element standards (High-Purity Standards). The hydrochloric (TraceMetal Grade from Fisher chemical) and nitric (ULTREX II from J.T. Baker) acids were used to adjust acid concentration in metal-containing aqueous solutions. All aqueous solutions were diluted to the desired volume with deionized water (Milli-Q, 18.2MΩ-cm). All reagents were of analytical grade and used as received.

General procedure for the separation of Ln(III) salts using BLPhen ligands: 750 µL aqueous phase consisting of 7 mM Ln(III) (0.5 mM of each Ln(III)) in 0.9 M HNO_3 or 0.9 M HCl was contacted with an equal volume of an organic phase containing 7 mM of either ligand **1** or **2** in 1,2-dichloroethane that was pre-equilibrated with 0.9 M of the respective acid. The two phases were contacted by end-over-end rotation in individual 1.8 mL capacity snap-top Eppendorf tubes using a rotating wheel in an air box set at 25.5 °C ± 0.5 °C. Contacts were performed in triplicate with a contact time of 25 hours. Following contacting, the triplicate samples were subjected to centrifugation at 1,811 × g for two minutes at 20 °C to separate the phases. Each triplicate was then subsampled, with 500 µL aliquots of the aqueous phases transferred to individual polypropylene tubes containing 2.5 mL of 4% HNO_3 for analysis using ICP-OES. Similarly, two samples of the initial Ln(III) solution in 0.9 M acid were also prepared for the analysis. The areas found under the observed peaks were used for determining distribution (*D*) values.

General procedure for the recovery of Ln(III) salts: 600 µL of the organic phase loaded with Ln(III)-ligand complexes was contacted with an equal volume of deionized water. The two phases were contacted by end-over-end rotation in individual 1.8 mL capacity snap-top Eppendorf tubes using a rotating wheel in an air box set at 25.5 °C ± 0.5 °C. Contacts were performed in triplicate for a contact time of 66 hours. Following contacting, the two phases were separated, and an aliquot of the aqueous phase was analysed following general procedure described above.

Computational details: Calculations were carried out with the Gaussian 16, revision B.01 program package.[34] The computational method was density functional theory (DFT) using B3LYP[35,36] and M06[37] functionals. Standard 6-31+G(d) basis set was adopted for the main group elements and hydrogen for geometry optimization. 4f-Elements (La, Pr, Pm, Eu, Tb, Ho, Tm, Lu) were modeled using the large-core (LC) relativistic effective core potentials (RECP) and the corresponding basis sets.[38] The 4f shell was treated as a part of the core, leading to modeling lanthanide ion complexes in a pseudo singlet state configuration. Frequency calculations were performed to ensure real vibrational modes for the minimum ground state structures and to provide zero-point energies (ZPE). ZPE and thermal corrections (T = 298.15 K) calculated at B3LYP/LC/6-31+G(d) were added to the total energy to obtain the Gibbs free energy. Thermal contributions to the gas-phase Gibbs free energies were calculated using standard molecular thermodynamic approximations.[39]
To correct for the well-known breakdown of the harmonic oscillator model for the free energies of low-frequency vibrational modes, frequencies lower than 60 cm^{-1} were raised to 60 cm^{-1} following the so-called quasiharmonic approximation.[40]

Computations taking into account bulk solvent effects were carried out using the IEF-PCM (IEF) implicit solvation model with default settings.[41] All DFT optimizations were conducted on the 1:1 ligand:metal complexes, starting with the experimental crystal structures of the corresponding Ln(III) complexes. The hydrophobic n-hexyl substituents present in experimental extractants (BLPhen) were replaced by the methyl groups. This is fully justified, since recent theoretical studies show that the chain length of hydrocarbon substituents has a little impact on the relative stability of actinide and lanthanide complexes.[42]

The Gibbs free energy change, $\Delta\Delta G_{aq}$(La/Ln), for the competitive complexation of La(III) over Ln(III) was calculated using the approach described in our previous work on predicting stability trends along the Ln(III) series that was capable of reproducing aqueous selectivities arising from the variation in the size of the trivalent f-block metal ions.[43] The relative Ln(III) selectivities for the preorganized ligands **1a**, **2a**, and **4** with respect to the non-preorganized ligand BAPhen were calculated according to reaction (1). Ligand strain energies, $\Delta\Delta E_{strain}$, associated with structural reorganization upon binding with metal ions, were calculated at the M06/LC/6-31+G(d) level of theory.

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Keywords: lanthanide • N ligand • separation • transition metal • phenanthroline

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[28] Timed extraction experiments show that the system reaches equilibrium in 20 hours at 25 °C, see Figure S3 and S4 in Supporting Information. Due to limited solubility of **1** and **2** in non-polar solvents (e.g., Isopar L), 1,2-dichloroethane was used as an

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organic diluent. Slope analysis results are depicted in Figure S5 and S6 in Supporting Information.

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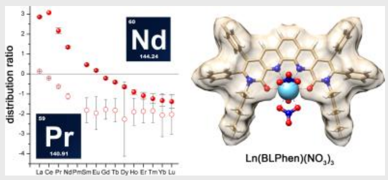
The preorganization of the four donor atoms as well as the size of the binding cavity in a highly rigid 2,9-bis-lactam-1,10-phenanthroline (BLPhen) ligand are key elements controlling the efficient and highly selective coordination with trivalent lanthanide ions, especially cations with larger ionic radii. Moreover, these rigid complexants show extraordinarily high selectivity for light REEs even in the presence of the competing d-block metal ions, such as Cu^{2+} and Fe^{3+}.



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