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Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-triazine Ligand

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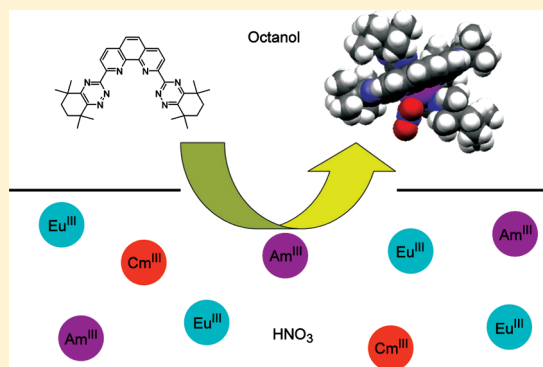
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S Supporting Information

ABSTRACT: The synthesis, lanthanide complexation, and solvent extraction of actinide(III) and lanthanide(III) radiotracers from nitric acid solutions by a phenanthroline-derived quadridentate bis-triazine ligand are described. The ligand separates Am(III) and Cm(III) from the lanthanides with remarkably high efficiency, high selectivity, and fast extraction kinetics compared to its 2,2'-bipyridine counterpart. Structures of the 1:2 bis-complexes of the ligand with Eu(III) and Yb(III) were elucidated by X-ray crystallography and force field calculations, respectively. The Eu(III) bis-complex is the first 1:2 bis-complex of a quadridentate bis-triazine ligand to be characterized by crystallography. The faster rates of extraction were verified by kinetics measurements using the rotating membrane cell technique in several diluents. The improved kinetics of metal ion extraction are related to the higher surface activity of the ligand at the phase interface. The improvement in the ligand's properties on replacing the bipyridine unit with a phenanthroline unit far exceeds what was anticipated based on ligand design alone.



INTRODUCTION

During the production of electricity from nuclear power, a typical 1000 MW(e) light water reactor produces 20–30 t of spent nuclear fuel per annum.¹ This spent fuel consists mainly (>98.5%) of uranium and short-lived fission products, which do not pose a long-term hazard. However, approximately 1 wt % of the spent fuel is composed of plutonium and the minor actinides (Am, Cm, Np), which are highly radiotoxic. Plutonium is the main contributor to the long-term radiotoxicity of spent nuclear fuel. Its separation through the PUREX (plutonium and uranium extraction) process and reuse as fuel (MOX fuel) in nuclear reactors is current industrial practice.² The remaining waste still contains the minor actinides, necessitating the containment and separation of the waste from the biosphere for many thousands of years, a situation that represents a serious environmental concern.

If the minor actinides could be removed, the mandatory storage time of the remaining waste decreases from several thousand years to a few hundred years. One strategy for reducing the radiotoxicity of the waste involves partitioning and transmutation of the long-lived minor actinides into shorter-lived or stable elements by neutron fission.³ However, it is first necessary to separate the actinides from the bulk of the lanthanides and

other fission and corrosion products that are also present in the acidic PUREX waste streams because the lanthanides have high neutron capture cross sections.⁴ The separation of the radioactive minor actinides from the lanthanides is therefore one of the principal current challenges in nuclear waste reprocessing. This separation is made all the more difficult given the chemical similarities between the two groups of elements.⁵ However, it is thought that the greater availability of the valence orbitals in the actinides means that there is a more covalent contribution to metal–ligand bonding than with the lanthanides. The origins of this covalency are still not fully understood and remain the subject of ongoing debate and study.⁶

It has been shown that ligands with soft N-donor atoms can exploit this small but significant difference between the actinides and lanthanides, and many N-heterocyclic ligands have been investigated for their ability to carry out this separation by solvent extraction.⁷ Two ligand classes have emerged as the most promising: the terdentate 2,6-bis(1,2,4-triazin-3-yl)pyridine ligands (BTPs)⁸ and the quadridentate 6,6'-bis(1,2,4-triazin-3-yl)-

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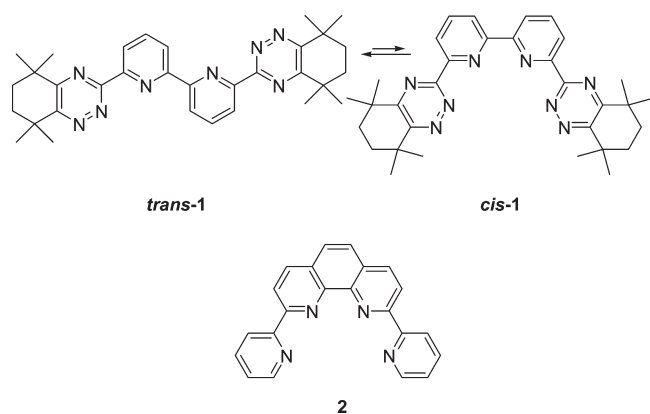


Figure 1. Conformations of the annulated BTBP ligand **1** and structure of 2,9-di(2-pyridyl)-1,10-phenanthroline, **2**.

2,2'-bipyridine ligands (BTBPs). The BTBP ligands are currently the most suitable ligands for these separations.⁹ The annulated BTBP **1** has extraction and back-extraction properties that could be suitable for a continuous separation process (Figure 1).^{10,11} Unlike the BTBPs bearing alkyl side chains on the triazine rings, **1** is stable to hydrolysis and resistant toward radiolysis and degradation by free radicals because the labile benzylic hydrogens have been replaced by methyl groups.¹² Recently, some unusual uranyl (UO_2^{2+}) complexes of **1** have been isolated and characterized.¹³

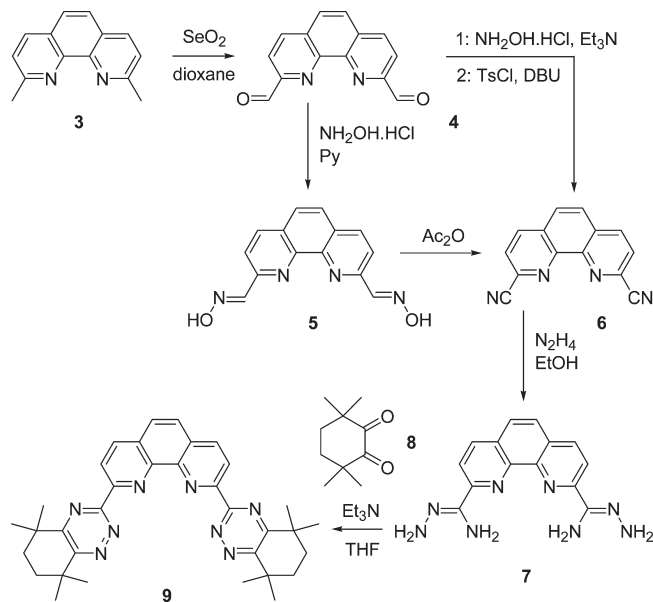
However, the rates of extraction of the actinides by **1** was rather slow, and a phase-transfer agent (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexoxyethyl) malondiamide) was required to improve the kinetics of extraction.¹⁰ This represents a disadvantage for the use of **1** in the proposed generation IV fast reactors. Since a conformational change by **1** from the *trans*-conformation to its less-favored *cis*-conformation is required prior to metal ligation, we hypothesized that this need for molecular reorientation was responsible for the slow rates of extraction by **1**.

The *cis*-locked 1,10-phenanthrolines are versatile ligands in a wide range of applications. Their rigidity and the juxtaposition of their donor atoms means that complex formation is both more rapid and more thermodynamically favored than their 2,2'-bipyridine analogues.¹⁴ For example, it has been reported that the preorganized, phenanthroline-based ligand **2**¹⁵ exhibits higher levels of complex stability and selectivity toward Cd(II) than related ligands such as quaterpyridine.¹⁶ In addition, phenanthrolines have larger dipole moments than the 2,2'-bipyridines¹⁷ and often coordinate strongly to water via hydrogen bonding.¹⁸ These properties could lead to improved extraction kinetics in a separation process since the ligand may interact more favorably with the organic/water interface. On the basis of this, we predicted that a *cis*-locked quadridentate bis-triazine ligand containing a 1,10-phenanthroline moiety would show improved extraction properties compared to its 2,2'-bipyridine counterpart **1**. Herein, we report the synthesis, lanthanide complexation, and solvent extraction chemistry of the first of a new class of bis-triazine ligands in which the 2,2'-bipyridine moiety of **1** has been replaced by a 1,10-phenanthroline moiety.

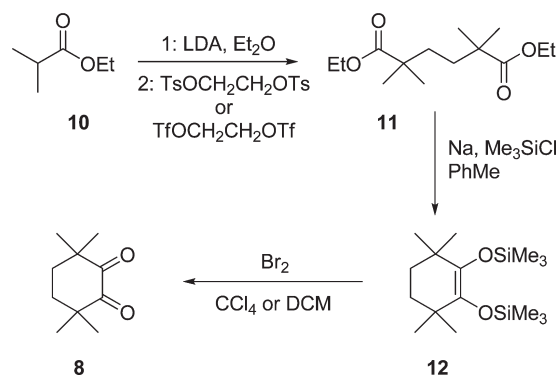
RESULTS AND DISCUSSION

Synthesis and X-ray Crystallography. The new ligand **9** was synthesized as shown in Scheme 1. The dinitrile **6** was synthesized

Scheme 1. Synthesis of the BTPPhen Ligand **9**



Scheme 2. Modified and Improved Synthesis of the Diketone **8**



from 2,9-dimethyl-1,10-phenanthroline **3** following known procedures.¹⁹ The conversion of dioxime **5** to dinitrile **6** gave a low yield (37%) of product in our hands. Consequently, we developed a one-pot method for the synthesis of the dinitrile **6** from the dialdehyde **4**. The reaction of the dinitrile **6** with hydrazine hydrate in EtOH gave the novel diamide dihydrazide **7** in near quantitative yield. The condensation of **7** with diketone **8** in THF at reflux afforded 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPPhen) **9** in 59% yield (see Supporting Information). The ligand **9** was obtained as a stable hydrate, as indicated by its ¹H NMR spectrum, the water remaining bound to the ligand *in vacuo* (0.1 mmHg) and after heating at 120 °C for 24 h.

The known diketone **8**²⁰ was synthesized by a modified procedure (Scheme 2). The diester intermediate **11** proved very difficult to synthesize on a large scale using the literature method (oxidative coupling of pivalic acid using $\text{H}_2\text{O}_2/\text{FeSO}_4$, followed by esterification of the resulting diacid),²¹ but we have since developed a new synthesis of **11** involving the alkylation of ethyl isobutyrate **10** with ethane-1,2-disulfonate esters.²² This

130 procedure gave the diester **11** in 69–70% yield. This contrasts with when 1,2-dihaloethanes were used in attempted alkylation
 131 reactions, where none of the desired diester **11** was formed and the major product was the ethyl α -haloisobutyrate.²³ The diester
 132 **11** was converted to the diketone **8** as previously described (see Supporting Information).^{20a} Using this modified procedure,
 133 diketone **8** was readily synthesized on a multigram scale in much improved overall yield (44% overall compared to <5% using the
 134 previous method).
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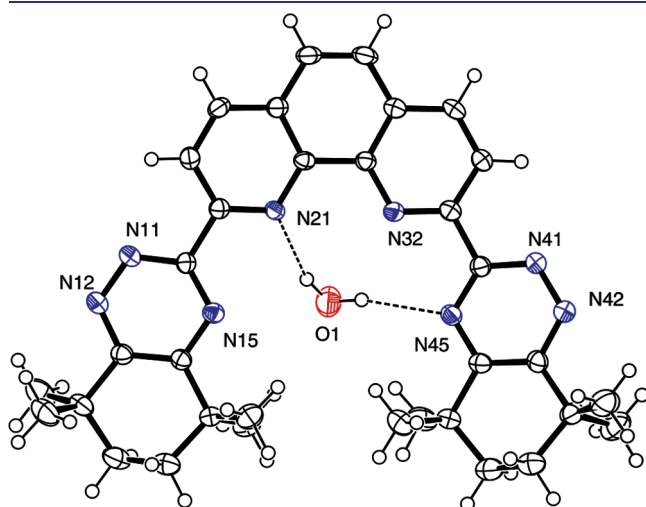


Figure 2. Molecular structure in the crystal of the BTPhen ligand **9**. Thermal ellipsoids are at 30% probability. Hydrogen bonds are shown as dotted lines. Distances are O(1)–N(21) 3.003(2), O(1)–N(45) 3.125(2) Å. Other solvent molecules are omitted for clarity.

The X-ray crystal structure of the ligand **9** (Figure 2)²⁴ shows one of the bound water molecules located in the coordination cavity of the ligand. The two outer triazine rings of BTPhen **9** are twisted away from the conformation required for metal ligation such that the N(11)–C–C–N(21) and N(32)–C–C–N(41) torsion angles are $-159.0(2)^\circ$ and $-159.0(2)^\circ$, respectively. The central N(21)–C–C–N(32) torsion angle is $-8.6(3)^\circ$. The Eu(III) complex of BTPhen **9** was synthesized (see Supporting Information) and structurally characterized by X-ray diffraction.²⁵ We were surprised to find that the bis-complex of stoichiometry $[\text{Eu}(\mathbf{9})_2\text{NO}_3]^{2+}$ had been formed (Figure 3), even though a single equivalent of **9** was used in the crystal growing experiment.

This is the first time that a 1:2 lanthanide complex with any quadridentate bis-triazine ligands has been isolated and structurally characterized. Although it is known that the BTBP ligands can form both 1:1 and 1:2 complexes in solution, only 1:1 complexes have been previously characterized by X-ray diffraction.²⁶ The metal is 10-coordinate, being fully enclosed by two molecules of **9** in addition to a single bidentate nitrate ion. The geometry can best be considered as a capped square antiprism with the bidentate nitrate group occupying the capping site. The bond lengths from the metal to the outer triazine nitrogen atoms are equivalent, with a range of 2.546(6)–2.616(5) Å to those to the inner phenanthroline nitrogen atoms with a range of 2.561(6)–2.598(5) Å. Indeed the mean bond lengths are 2.587 and 2.582 Å, respectively. These metal–nitrogen bond lengths are very similar to those found in the 1:1 complexes formed by the BTBP ligands.²⁶ By contrast to the ligand conformation, now the outer torsion angles N(11)–C–C–N(21) and N(32)–C–C–N(41) are $6.0(10)^\circ$ and $-6.0(10)^\circ$ with the central torsion angle being $-0.6(8)^\circ$. The corresponding angles in the second ligand are $4.6(11)^\circ$, $10.6(10)^\circ$, and

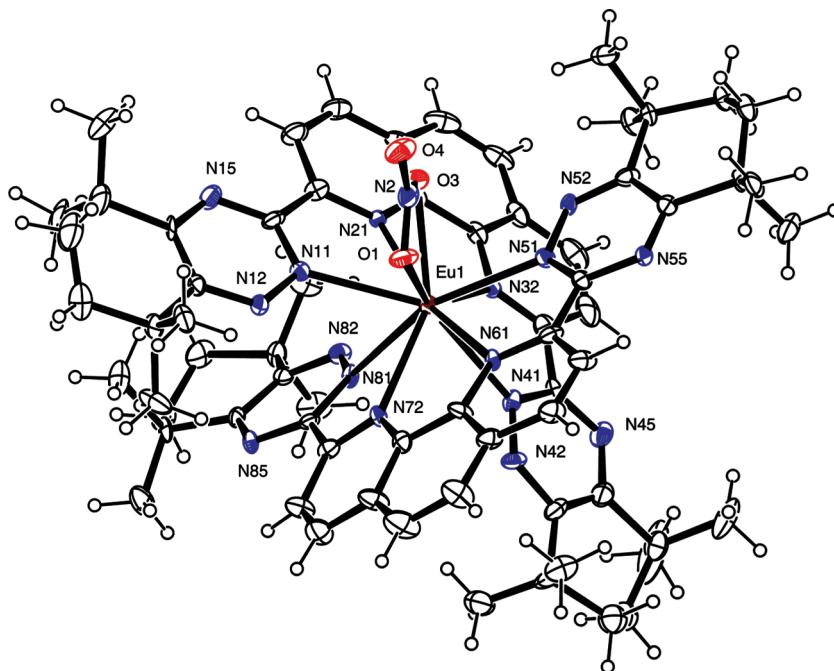


Figure 3. Molecular structure in the crystal of the $[\text{Eu}(\mathbf{9})_2\text{NO}_3]^{2+}$ cation. Thermal ellipsoids are at 30% probability. The $[\text{Eu}(\text{NO}_3)_5]^{2-}$ counterions and solvent molecules have been omitted for clarity. Selected bond lengths [Å]: Eu(1)–N(51) 2.546(6), Eu(1)–N(72) 2.561(6), Eu(1)–N(32) 2.571(7), Eu(1)–N(21) 2.598(5), Eu(1)–N(81) 2.572(6), Eu(1)–N(61) 2.598(5), Eu(1)–N(11) 2.615(7), Eu(1)–N(41) 2.616(5), Eu(1)–O(1) 2.540(6), Eu(1)–O(3) 2.593(5).

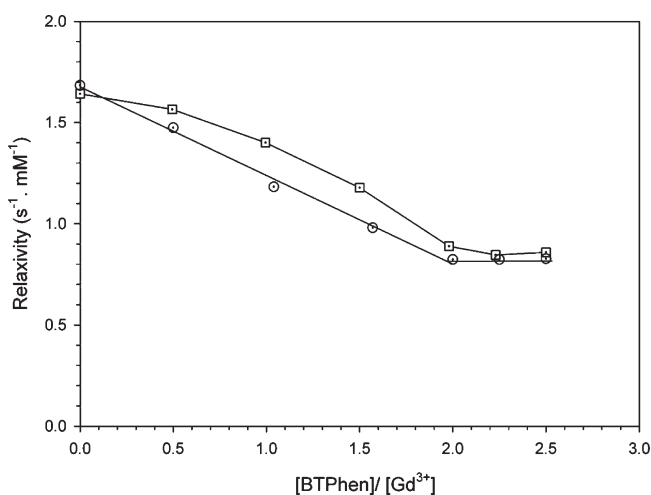


Figure 4. Nuclear magnetic relaxation dispersion (NMRD) titration curve of an anhydrous CD₃CN solution of Gd(ClO₄)₃ (○) and Gd(NO₃)₃ (□) by BTPhen 9.

−4.9(11)°, respectively. The four donor nitrogen atoms in each ligand are approximately planar (rms deviations 0.01, 0.07 Å) with the metal 0.729(3) and 0.585(4) Å, respectively, from each N4 plane. These two N4 planes intersect at 69.8(2)°. The bond lengths to the two nitrate oxygen atoms are 2.540(6) and 2.593(5) Å.

pK_a Determination and NMR Studies of Lanthanide Complexes. It is rather paradoxical that metal ions are so well extracted from concentrated acid aqueous solutions by ligands such as **1** and **9** despite their easily protonatable central bipyridine or phenanthroline units. The basicity of these ligands must be strongly decreased by the electron-withdrawing triazine substituents, but little or no information on the pK_a of these ligands is yet available to substantiate this hypothesis. The pK_a of the ligand **9** was thus determined by ¹H NMR spectroscopy.²⁷ The dependence of the NMR shifts of BTPhen **9** upon the DCl concentration in deuterated methanol (10⁻⁷–3 M, > 99% methanol) was recorded (see Supporting Information). The NMR titration curves display a well-defined shift jump between −log[DCl] = 4 and 2 followed by a smooth shift increase at higher acid concentrations. The first protonation pK_a of **9** (3.1 ± 0.1) is assigned to the protonation of the phenanthroline ring; it is close to the value reported for the BTP ligands in 76% methanol (pK_a = 3.3)^{7c} and is much lower than the pK_a of phenanthroline itself in water (4.92). The electron-withdrawing effect of the triazine rings of **9** is also responsible for the low value of the second pK_a (0.3 ± 0.1, 0.2 ± 0.1, and 0.03 ± 0.03 for phenanthroline protons 3, 4, and 5, respectively), which is tentatively assigned to the second protonation of phenanthroline.

Using lanthanides as actinide surrogates, the complexation behavior of BTPhen **9** toward the lanthanides was studied by NMR spectroscopy to gain an understanding of the species likely to be involved in the extraction of the trivalent actinides.

As shown earlier,^{11a} the maximum stoichiometry of lanthanide complexes in an organic solvent can be deduced from a nuclear magnetic relaxation dispersion (NMRD) titration in which the relaxation rate of a Gd³⁺ solution is measured for different metal:ligand ratios. The progressive formation of a metal complex is accompanied by the removal of solvent molecules. Consequently,

the ¹H relaxation time of these molecules increases as the latter are no longer in the immediate vicinity of the paramagnetic centers. The relaxation rate thus decreases and a plateau is reached when the metal complex is fully formed. NMRD titrations are presented in Figure 4 for Gd³⁺ perchlorate and nitrate salts to which BTPhen **9** is progressively added in anhydrous acetonitrile. The clear breaks in the titration curves for a 1:2 ratio indicate that stable bis-complexes are formed in both cases. However, the curvature in the NMRD titration plot of the nitrate salt indicates that the nitrate ion is better able to compete with the BTPhen ligand **9** than the perchlorate ion. In keeping with these data, NMR peaks due to the free ligand are observed as soon as 1:2 metal:ligand ratios are exceeded. The number of resonances and their shifts in all the NMR spectra discussed below remain identical whether this ratio is 1:1 or 1:2, and the bis-complex is thus the major solution component in these conditions.

The NMR spectrum of the diamagnetic bis-complex formed between anhydrous Lu(ClO₄)₃ and BTPhen **9** in acetonitrile displays two methyl peaks, three aromatic peaks, and a multiplet between 1.45 and 1.65 ppm that originates from the rapidly inverting cyclohexenyl groups (see Supporting Information). These peaks broaden somewhat at lower temperatures, but the changes are insufficient for a quantitative analysis that would lead to an estimation of the activation energy. Attempts in chloroform/acetonitrile mixtures at 223 K were also unsuccessful and were not pursued, as the rigidification of cyclohexene itself is reached only at 109 K.²⁸ A NOESY spectrum was recorded to verify the assignments (see Supporting Information). Cross-peaks were observed between the cyclohexenyl protons and between the aromatic protons but not between these two groups. No cross-peaks were observed between two different protons on separate ligands. The spectrum of Lu(BTPhen)₂³⁺ was used as a reference for deducing the paramagnetic shifts induced by the Yb³⁺ ion. The latter is known to induce essentially pure dipolar shifts from which solution structures can be inferred.²⁹

The ¹H NMR spectrum of a 1:2 mixture of Yb(ClO₄)₃ and BTPhen **9** in anhydrous acetonitrile is shown in Figure 5. All resonances are easily assigned from their respective areas and from COSY spectra. Three aromatic protons resonate at high and low fields, and the cyclohexenyl substituents give rise to two methyl peaks and two methylene peaks. The aliphatic substituents are thus rapidly inverting their conformation on the NMR time scale (over a 17 ppm shift range). This remains true between 298 and 230 K.

A molecular modeling calculation was made following the procedure used for a related bis-triazine ligand derived from 2,2':6',2''-terpyridine (force-field approach with parameters published for lanthanide complexes).^{11b} The optimized structure of the 1:2 bis-complex of **9** with Yb³⁺ is shown in Figure 6. As expected, the most stable conformation is an arrangement in which the two ligands are perpendicular to each other. All cyclohexenyl groups in the modeled structure are in the half-chair conformation, in agreement with molecular calculations performed for cyclohexene.²⁸ The red arrows in Figure 6 indicate the smaller interatomic distances found between two ligands in the bis-complex. All these distances are larger than the sum of the van der Waals radii. The structure is thus not sterically crowded, and there is ample room for additional coordinating anions or solvent molecules. The full dipolar

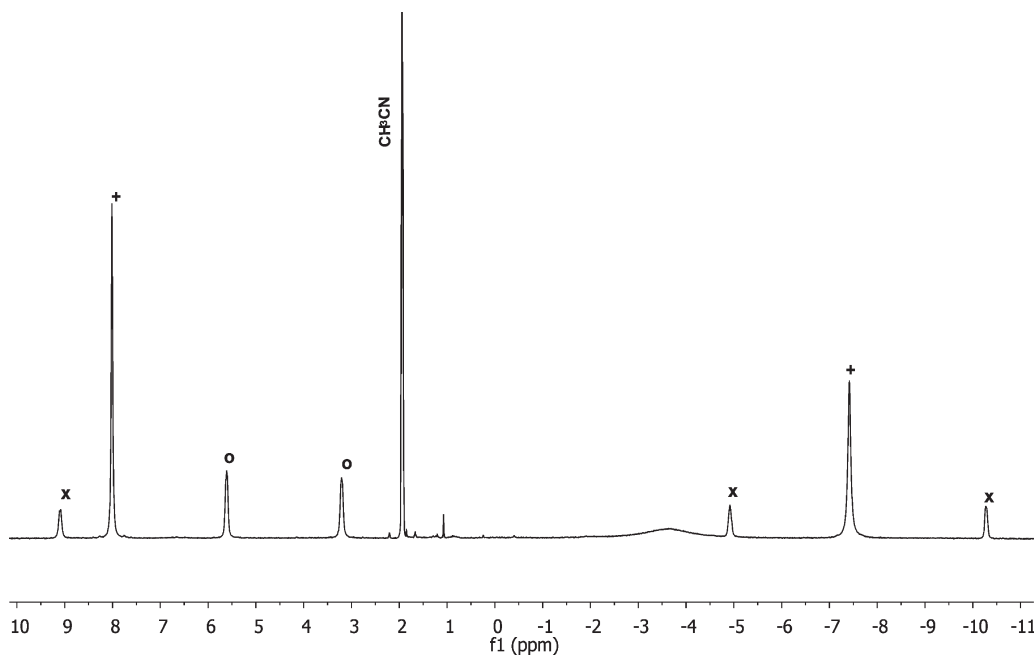


Figure 5. ^1H NMR spectrum of a 1:2 $\text{Yb}(\text{ClO}_4)_3/\text{BTPhen } 9$ mixture in anhydrous CD_3CN at 263 K. Assignments: (+) methyl protons, (O) methylene protons, (x) aromatic protons (broad peak at -3.7 ppm: traces of water).

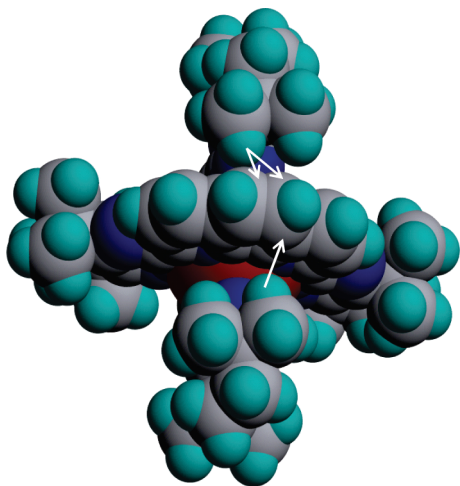


Figure 6. Force field simulation of the optimized structure of the 1:2 bis-complex of BTPhen 9 with Yb^{3+} . The arrows show the shortest interatomic distances in the metal complexes. These distances are larger than the sum of the van der Waals radii. See Supporting Information for a list of structural parameters.

274 equation 1 was used to unravel the solution structure of the
275 Yb^{3+} BTPhen 9 bis-complex.

$$\delta_i = \frac{1}{12\pi} \left[\left(\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \right) \frac{\langle 3 \cos^2 \theta_i - 1 \rangle}{r_i^3} + (\chi_{xx} - \chi_{yy}) \frac{\langle \sin^2 \theta_i \cos 2\psi_i \rangle}{r_i^3} \right] \quad (1)$$

276 In this equation,²⁹ the paramagnetic shifts depend on mag-
277 netic susceptibility terms that are identical for all nuclei and on
278 geometric terms that are different for each nucleus and are easily

279 computed from a molecular model. The factors θ_i , ψ_i and r_i are
280 the polar coordinates of proton i in the set of axes of the magnetic
281 susceptibility tensor with the metal ion at its origin. This equation
282 has been used successfully for obtaining the solution structure of
283 lanthanide chelates²⁹ or of proteins modified by grafting a
284 paramagnetic metal complex.³⁰ In the latter case, the spectra
285 display so many shifted resonances that the orientation of the
286 susceptibility axes can be included in a fit between the experi-
287 mental and calculated paramagnetic shifts. This is not the case for
288 the BTPhen complex that exhibits only seven NMR resonances,
289 but this complex features symmetry elements with which the axes
290 of the magnetic susceptibility tensor must coincide. The z axis
291 was thus oriented with the C_2 axis that bisects the two phenan-
292 throline groups. In addition to this axis, there are two symmetry
293 planes, either through the phenanthroline rings or between these
294 rings (i.e., at 45°). The x and y axes can be located in either plane.
295 For symmetry reasons, the same correlation between experi-
296 mental and calculated paramagnetic shifts will be obtained, but
297 the sign of the magnetic susceptibility terms will change. This is
298 also true if the x (or y) axis is exchanged with the z axis (see
299 Supporting Information). As shown in Figure 7, there is a very
300 good correlation between the calculated and experimental para-
301 magnetic shifts based on the dipolar eq 1. The correlation is
302 especially good if one takes into account that the cyclohexenyl
303 rings are rapidly inverting. The geometric factors of each ex-
304 changing group were obtained by computing the mean of the
305 factors for two proton sets exchanging their positions during the
306 ring inversion process. No account was taken of the transition
307 states nor of the fact that cyclohexene adopts various less stable
308 geometries in addition to the half-chair conformation.²⁸ Not
309 surprisingly, the datum point that is the most removed from the
310 correlation line in Figure 7 originates from one of the methyl
311 proton sets undergoing rapid inversion. The geometric factors of
312 the exchanging protons are very different in this particular case,
313 and larger errors are thus expected.

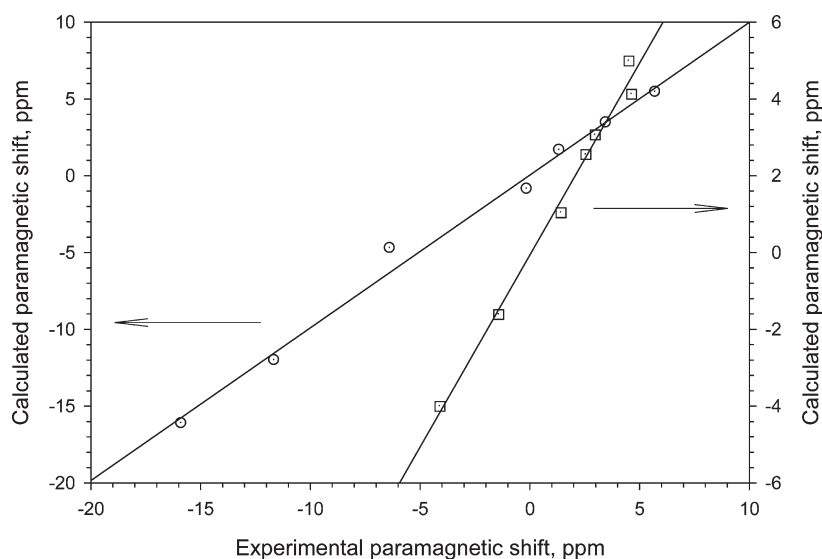


Figure 7. Correlation between the calculated and experimental paramagnetic shifts of the bis-complexes of BTPPhen **9** with Yb³⁺ perchlorate (○) or nitrate (□); y axis on left: perchlorate, y axis on right: nitrate.

314 There is one feature worthy of note in these calculations that
 315 has not been mentioned in the literature so far. As the two ligands
 316 are planar in an environment of 2-fold symmetry, an agreement
 317 indistinguishable from the one presented in Figure 7 is obtained
 318 if the angle between the two ligands is increased or decreased.
 319 The geometric factors are of course modified, but the magnetic
 320 susceptibility terms are also changing and the correlation between
 321 calculated and experimental paramagnetic shifts remains
 322 unaltered. (For instance, if the angle between the two BTPPhen
 323 ligands is 90°, 75°, 60°, and 45°, the magnetic susceptibility
 324 factors in eq 1 become 1392 and -4038, 1804 and -3600, 1617
 325 and -3788, and 1543 and -3863 Å⁻³, respectively.) We are
 326 confronted here with a limit of the dipolar shift analysis method
 327 that does not arise with nonplanar ligands such as one based on 2,
 328 2':6',2''-terpyridine^{11b} or other complexes investigated so far.²⁹ A
 329 consequence of this is that a good correlation will still be
 330 obtained if the structure of the complex becomes flatter to allow
 331 for the entrance of an anion or a solvent molecule in the first
 332 coordination sphere. A good correlation between experimental
 333 and calculated shifts is thus still expected for the bis-BTPPhen
 334 nitrate complex depicted in Figure 3, as it features a pseudo-2-
 335 fold symmetry axis and a larger opening for accommodating
 336 an anion.

337 A similar analysis was carried out for the 1:2 bis-complex of
 338 BTPPhen **9** with Eu shown in Figure 3. The ¹H NMR spectrum of
 339 a 1:2 mixture of **9** and Eu(ClO₄)₃ was recorded, and the analysis
 340 of the induced paramagnetic shifts was performed as for the
 341 Yb(III) bis-complex (see Supporting Information). However,
 342 unlike Yb(III), the contact paramagnetic shifts for Eu(III) are
 343 larger than the dipolar paramagnetic shifts, and thus the dipolar
 344 eq 1 cannot be used as reliably for solution structure deter-
 345 minations.^{29d,31} Only a qualitative agreement was obtained, from
 346 which the solution structure of the complex could not be reliably
 347 established.

348 In the ¹H NMR spectrum of a 1:2 mixture of Yb(NO₃)₃ and
 349 BTPPhen **9** in acetonitrile (see Supporting Information), the
 350 entrance of a nitrate ion into the first coordination sphere is
 351 clearly indicated by paramagnetic shifts that are totally different
 352 from those observed in the perchlorate case. The magnetic

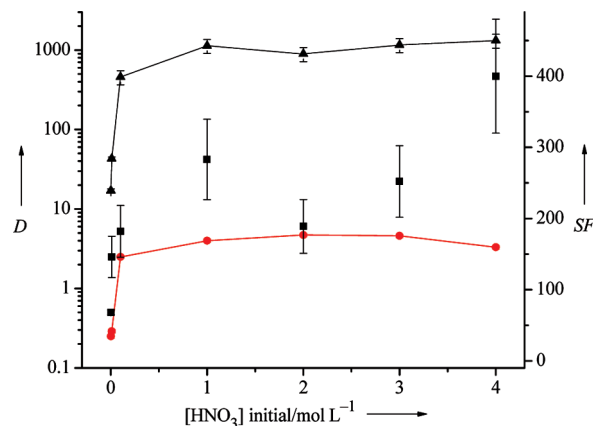


Figure 8. Extraction of Am(III) and Eu(III) by BTPPhen **9** in octanol (0.01 M) as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, \blacktriangle = D_{Am} , \bullet = D_{Eu} , \blacksquare = $SF_{Am/Eu}$, mixing time: 60 min, temperature: 22 ± 1 °C).

353 susceptibility terms should indeed be totally different because
 354 of the presence of a charged species directly coordinated to the
 355 metal ion. However, the molecular model remains valid, as
 356 shown by the good correlation between experimental and
 357 calculated shifts presented in Figure 7. Nevertheless, the degree
 358 of opening of the bis-complex to accommodate the nitrate ion
 359 remains unknown, and it appears that NMR spectroscopy is of no
 360 help in solving this particular problem.

361 **Solvent Extraction Studies with Am(III), Cm(III), and Eu(III)**
 362 **Radionuclides.** Preliminary solvent extraction experiments were
 363 then carried out to determine the ability of **9** to selectively extract
 364 An(III) over Ln(III). Solutions of the ligand **9** in octanol (0.01
 365 M) were contacted with nitric acid solutions containing ²⁴¹Am
 366 and ¹⁵²Eu radiotracers. The distribution ratios (D) for Am(III)
 367 and Eu(III) and the separation factors ($SF_{Am/Eu}$) at different
 368 nitric acid concentrations are shown in Figure 8. Very high D
 369 values for Am(III) were observed ($D_{Am} > 1000$), indicating that
 370 the extraction of Am(III) by **9** is very efficient. The D values for
 371 Eu(III) were approximately 2 orders of magnitude lower than

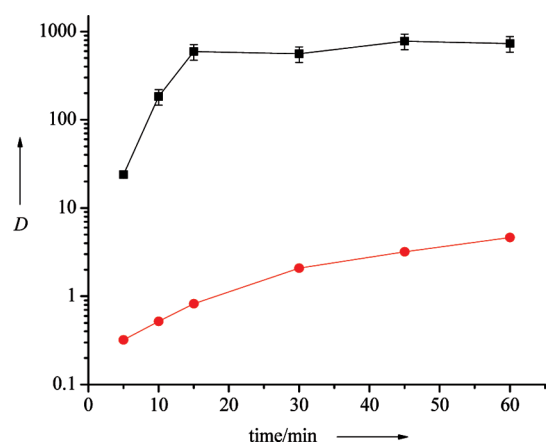


Figure 9. Extraction of Am(III) and Eu(III) from 1 M HNO₃ by BTPhen 9 in octanol (0.01 M) as a function of time (■ = D_{Am} , ● = D_{Eu} ; temperature: 22 ± 1 °C).

those of Am(III) ($D_{Eu} < 10$), and the resulting separation factors were in the range 68–400. These results show that 9 is able to extract Am(III) in preference to Eu(III) with very high selectivity. The formation of stable 1:2 bis-complexes by 9 certainly contributes to the higher D values observed for Am(III) compared to previous N -donor ligands.^{7c} The distribution ratios for Am(III) for 9 are about 2 orders of magnitude higher than those for the related BTBP ligand 1.^{10a} The considerable improvement in the extraction of Am(III) by 9 compared to 1 far exceeds what was anticipated on the basis of molecular design. The high D values observed for 9 make it especially suitable even for low-level waste decontamination where only trace levels of radionuclides are present.

In common with other bis-triazine ligands, BTPhen 9 is able to extract Am(III) from nitric acid solutions of high acidity (1–4 M HNO₃). Thus, although the ligand is likely to be protonated in contact with HNO₃ solutions ($pK_a = 3.1–3.2$), proton competition does not prevent metal ion extraction. This is in contrast with other N -donor ligands based on 2,2':6',2''-terpyridine, which can extract Am(III) only from weakly acidic (<0.1 M HNO₃) solutions.³² The precise reasons for this extraction ability are unclear at this point. It should be noted that, although the competition between protonation and extraction leads to a decrease in D values, an increase in acidity is also an increase in the nitrate ion concentration that favors the extraction. The formation of highly thermodynamically stable 1:2 bis-complexes by BTPhen 9, coupled with the high hydrophobicity of the ligand, could also explain the observed extraction results. In addition, a very low pK_a value of -1.77 has been estimated for 1,2,4-triazine from a correlation between pK_a 's and ionization energies,³³ and the triazine rings of 9 are thus believed to remain unprotonated even at very high acidities. The extraction of lanthanide and actinide salts from concentrated HNO₃ solutions by 9 is thus less thwarted by protonation than for other N -donor ligands.

Figure 9 shows the kinetics of extraction of Am(III) and Eu(III) by BTPhen 9 from 1 M HNO₃ into octanol. For Am(III), relatively fast extraction kinetics are observed even in the absence of a phase-transfer agent, and distribution ratios close to the equilibrium value are reached within 15 min of phase contact time. Thus the kinetics of extraction by the BTPhen ligand 9 are significantly faster than the BTBP ligand 1, which requires up to

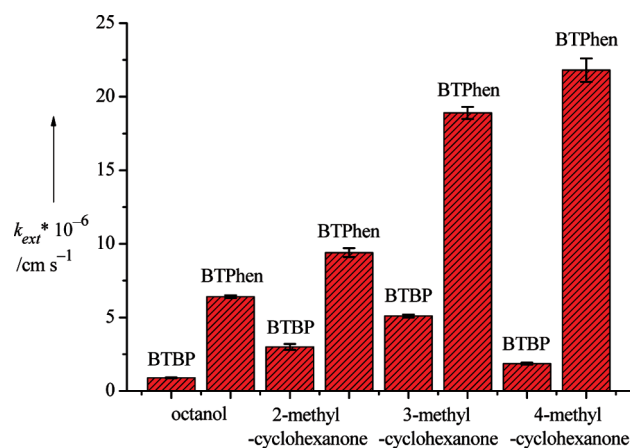


Figure 10. Extraction rate constants (k_{ext}) in different diluents for 0.01 M solutions of BTBP 1 and BTPhen 9 (aqueous phase: 2 M HNO₃).

60 min of contact time to reach its equilibrium D_{Am} value of approximately 4.5.^{10a} The faster rates of extraction by BTPhen 9 mean that the use of a phase-transfer agent such as N,N' -dimethyl- N,N' -dioctyl-2-(2-hexoxyethyl) malondiamide,³⁴ which is needed to improve the extraction kinetics of BTBP 1,¹⁰ is not necessary. Furthermore, as D_{Am} is greater than 10 even after 5 min of contact, an efficient extraction can still take place using shorter contact times if desired.

In a separation process, it is desirable to back-extract (strip) the actinides from the loaded organic phase after the extraction has taken place so that the ligand can be reused in further extraction cycles. Ideally this requires D_{Am} values < 1 for efficient stripping. Figure 8 shows that for 9 the distribution ratios for Am(III) are lowest at low acidity but still exceed 1. The effect of the less polar diluents toluene and hydrogenated tetrapropene (TPH, a dodecane-like diluent) as co-diluents was then studied in order to reduce the D values for Am(III) at low acidities (see Supporting Information). With toluene as the co-diluent, the distribution ratios for Am(III) and Eu(III) both decreased as the volume fraction of toluene increased. This effect was most pronounced at low acidities. With 0.001 M HNO₃ as the aqueous phase, D_{Am} decreased from 1.57 in octanol/toluene (80:20) to 0.11 in octanol/toluene (20:80). When toluene was the sole diluent, a D_{Am} value of 0.02 was observed (aqueous phase: 0.01 M HNO₃). With TPH as the co-diluent, D_{Am} values of 0.48 and 0.45 were observed in the extraction from 0.001 M HNO₃ into octanol/TPH mixtures (60:40 and 50:50), respectively.

Extraction experiments were then carried out using ²⁴¹Am and ²⁴⁴Cm radiotracers in order to probe the co-extraction of both Am(III) and Cm(III) by BTPhen 9 (see Supporting Information). Both Am(III) and Cm(III) were efficiently co-extracted into octanol/toluene (40:60) solutions by 9 with virtually no selectivity between the two actinides ($SF_{Am/Cm} = 0.7–4$). In the extraction of both Am(III) and Cm(III) from 0.001 M HNO₃ into octanol/toluene mixtures, the D values for both metals decreased as the volume fraction of toluene increased, and D values below 1 were observed for both metals in 40:60, 20:80, and 0:100 octanol/toluene mixtures. These results indicate that the stripping of both Am(III) and Cm(III) from a loaded organic phase is feasible at lower acidities.

The waste streams produced in the PUREX process contain high concentrations of Y(III) and all the trivalent lanthanides in addition to the minor actinides. Information is therefore needed

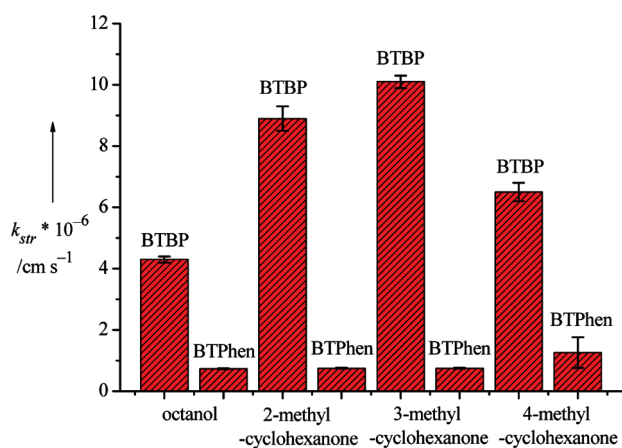


Figure 11. Back-extraction rate constants (k_{str}) in different diluents for 0.01 M solutions of BTBP 1 and BTPhen 9 (aqueous phase: 2 M HNO_3).

on the extraction of the lanthanides as well as the actinides. The extraction of the lanthanides by octanol solutions of BTPhen 9 at several different acidities showed a profile across the lanthanide series of first increasing, then decreasing D values, with the maximum D value being observed for Sm(III) (see Supporting Information). A similar trend was reported for the BTBP ligand 1.^{10a} Thus BTPhen 9 efficiently separates both Am(III) and Cm(III) from the entire lanthanide series.

Kinetics and Surface Tension Measurements. In order to uncover the reasons for the faster extraction kinetics observed with 9 compared to its nonrigidified analogue 1, a comparison of the extraction kinetics of ^{152}Eu by BTBP 1 and BTPhen 9 in different diluents was carried out using the rotating membrane cell technique.³⁵ With octanol, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone as the diluents, the calculated extraction rate constants (k_{ext}) for BTPhen 9 are substantially larger than those for BTBP 1 in each of these diluents (Figure 10). Conversely, the back-extraction (stripping) rate constants (k_{str}) for BTBP 1 are larger than for BTPhen 9 in these diluents (Figure 11). These results suggest that BTPhen 9 will have a faster rate of extraction, but a slower rate of stripping compared to BTBP 1. The fastest extraction kinetics for both ligands were observed in cyclohexanone ($k_{ext} = 121 \times 10^{-6} \text{ cm s}^{-1}$ for 0.01 M BTBP 1 from 2 M HNO_3 ; $k_{ext} = 74.8 \times 10^{-6} \text{ cm s}^{-1}$ for 0.01 M BTPhen 9 from 1 M HNO_3), which is known to improve significantly the kinetics of extraction by the BTBPs.³⁶ Using N,N,N',N' -tetraoctyl diglycolamide^{34,37} as additive also accelerated the extraction kinetics of BTBP 1 in octanol, but was less effective in accelerating the extraction kinetics of BTPhen 9 in octanol (see Supporting Information).

The interfacial tensions between aqueous phases of 1 M HNO_3 and organic phases of BTBP 1 and BTPhen 9 diluted in octanol, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone were then measured using the du Noüy ring method.³⁸ In the case of BTBP 1, surface activity was observed only when the ligand was diluted in 3-methylcyclohexanone and was not observed in the other diluents. In the case of BTPhen 9, surface activity was observed in all four diluents (see Supporting Information). The sharpest decrease in surface tension was observed in octanol. The faster extraction kinetics observed with BTPhen 9 compared to BTBP 1 thus appears to be related to the greater surface concentration of the BTPhen ligand

9 at the interface. Hence BTPhen 9, which exhibits surface activity in all diluents, gives extraction kinetics that are faster than BTBP 1, which is surface active in only one diluent (3-methylcyclohexanone). The greater surface activity observed for BTPhen 9 compared to 1 is in keeping with what was predicted based on ligand design. The higher polarity of 9 and its ability to strongly coordinate to water are probably responsible for its ability to interact favorably with the interface.

CONCLUSIONS

In summary, we have reported the first example of a promising new class of highly selective solvent extraction reagents for the partitioning of trivalent actinides from trivalent lanthanides in nuclear waste streams and have demonstrated that preorganization of the donor atoms for metal ligation with a rigid *cis*-locked 1,10-phenanthroline motif leads to a rapid and highly efficient separation of actinides from lanthanides. Interfacial tension measurements suggest that the improved extraction kinetics of the ligand relative to its 2,2'-bipyridine counterpart are related to higher concentrations of the ligand at the interface. The first X-ray crystal structure of a 1:2 bis-complex of a quadridentate bis-triazine ligand with Eu(III) has been determined. Lanthanide NMR complexation studies allowed the solution structure of the 1:2 bis-complex with Yb(III) to be deduced from the induced paramagnetic shifts. The aliphatic diketone precursor to the ligand has been synthesized by an improved procedure that, for the first time, allows the straightforward synthesis of BTPhen 9 and related ligands on at least a multigram scale. Further applications of the ligand in coordination chemistry are anticipated.

ASSOCIATED CONTENT

Supporting Information. Procedures and characterization data for all compounds. Tables and graphs of solvent extraction data. Figures of optimized structures and NMR spectra of lanthanide complexes. Procedure for pK_a determination. X-ray crystallographic cif files for ligand 9 and its Eu complex. Tables and graphs of kinetic data and interfacial tension measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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