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A remarkable enhancement in Am^{3+}/Eu^{3+}selectivity by an ionic liquid based solvent containing bis-1,2,4-triazinyl pyridine derivatives: DFT validation of experimental results†

Arunasis Bhattacharyya,*[a] Seraj A. Ansari,[a] Trilochan Gadly,[b] Sunil K. Ghosh,[b] Manoj Mohapatra[a] and P. K. Mohapatra*[a]

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Mutual separation of trivalent actinide (An^{3+}) and lanthanide (Ln^{3+}) using several soft (N) donor ligands (bis-(5,6-dialkyl-1,2,4-triazinyl)pyridine (R-BTP)) is attempted for the first time in room temperature ionic liquid (RTIL) medium. The results indicate a spectacular enhancement in the selectivity as compared to that in molecular diluents with a separation factor (S.F.) of >3000 for Am^{3+} over Eu^{3+} using the methyl derivative (Me-BTP) in RTIL medium using $[C_n mim]\cdot[NTf_2]$ as the diluents (where n = 2, 3, 4, 6 or 8). Such a high S.F. value has never been reported before with any of the R-BTP derivatives in molecular diluents. An opposite trend in the distribution ratio values of both Am^{3+} and Eu^{3+} with the increasing size of the alkyl (R) group is observed in RTIL medium when compared with that in molecular diluents. The differences in the extraction behaviour of R-BTPs in RTILs *vis-à-vis* molecular diluents are explained on the basis of the difference in the nature of complexes extracted in these two distinctly different media as supported by the time resolved fluorescence (TRFS) study. An unusually high extractability and selectivity for Am^{3+} over Eu^{3+} with Me-BTP was attributed to the formation of a 1 : 4 complex for Am^{3+}, which was never reported earlier with any of the R-BTP derivatives in molecular diluents. DFT studies indicated higher metal 'd' and 'f' orbital participation (covalence) in the bonding with R-BTP in the case of Am^{3+} complexes as compared to that in the case of Eu^{3+} complexes, which resulted in the selectivity of these classes of ligands. The observed results may have a great significance in the radioactive waste management involving the partitioning and transmutation strategy.

Introduction

One of the most challenging problems in the back end of the nuclear fuel cycle is the separation of trivalent actinides (An^{3+}) from the lanthanides (Ln^{3+}) as these two classes of 'f' block elements possess very similar complexation behaviour due to their comparable charge to radius ratios.[1,2] Soft (S,N) donor ligands show preference for An^{3+} ions over Ln^{3+} ions due to their ability to form stronger covalent bonds with An^{3+} ions. This has been attributed to the higher spatial distribution of the '5f' orbitals of the actinides as compared to that of the '4f' orbitals of the lanthanides. A large number of literature

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[a] *Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India. E-mail: arunasis12@yahoo.co.in, mpatra@barc.gov.in*

[b] *Bioorganic Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*

† Electronic supplementary information (ESI) available: **Distribution studies**: Fig. S1: Effect of aqueous phase acidity on the extraction of Am^{3+} and Eu^{3+} with 0.01 M MeBTP in different $C_n mim\cdot NTf_2$; Fig. S2: Effect of aqueous phase acidity on the selectivity of Am^{3+} over Eu^{3+} with 0.01 M MeBTP in different $C_n mim\cdot NTf_2$; Fig. S3: Effect of aqueous phase acidity on the extraction of Am^{3+} and Eu^{3+} with 0.01 M EtBTP in different $C_n mim\cdot NTf_2$; Fig. S4: Effect of aqueous phase acidity on the selectivity of Am^{3+} over Eu^{3+} with 0.01 M EtBTP in different $C_n mim\cdot NTf_2$; Fig. S5: Effect of aqueous phase acidity on the extraction of Am^{3+} and Eu^{3+} with 0.01 M n-PrBTP in different $C_n mim\cdot NTf_2$; Fig. S6: Effect of aqueous phase acidity on the selectivity of Am^{3+} over Eu^{3+} with 0.01 M n-PrBTP in different $C_n mim\cdot NTf_2$; Fig. S7: The effect of MeBTP concentration on the Am^{3+} and Eu^{3+} extraction; Org. phase: 0.004–0.02 M MeBTP in C4mim·NTf_2; aq. phase: 0.1 M HNO_3; Fig. S8: Effect of EtBTP concentration on the Am^{3+} and Eu^{3+} extraction; org. phase: 0.004–0.02 M EtBTP in C4mim·NTf_2; aq. phase: 0.1 M HNO_3; Fig. S9: Effect of nPrBTP concentration on the Am^{3+} and Eu^{3+} extraction; org. phase: 0.004–0.02 M nPrBTP in C4mim·NTf_2; aq. phase: 0.1 M HNO_3; **Luminescence studies**: Fig. S10: Decay of Eu^{3+} complexes in the organic extract (λ_{ex} = 327 nm (for Eu-MeBTP), 359 nm (for Eu-EtBTP) and 358 nm (for Eu-nPrBTP) and λ_{em} = 616 nm)): org. phase: 0.01 M RBTP + 1 M 2-bromooctanoic acid in n-dodecane; aq. phase: 0.1 M HNO_3; Fig. S11: Decay of Eu^{3+} complexes in the organic extract (λ_{ex} = 247 nm and λ_{em} = 616 nm): org. phase: 0.01 M RBTP in $C_4 mim\cdot NTf_2$; aq. phase: 0.1 M HNO_3; Table S12: Two center Mayer's bond order in the 'M–N' bonds in different Am^{3+} and Eu^{3+} complexes of Me-BTP. See DOI: 10.1039/c5dt00149h

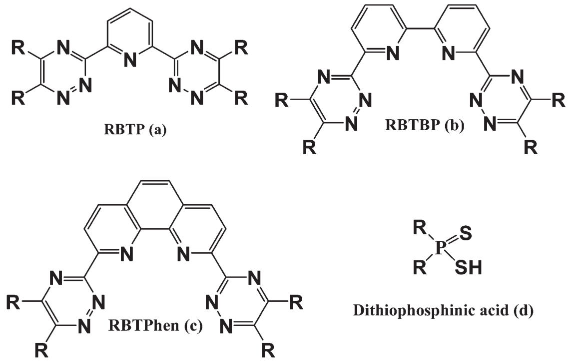

Fig. 1 Promising soft (S, N) donor ligands for the selective extraction of An^{3+} over Ln^{3+}.

reports are available on the Ln^{3+}/An^{3+} separation using various 'S' and 'N' donor ligands.[3–9] Alkyl substituted bis-triazinyl pyridine (R-BTP), bis-triazinyl bipyridine (R-BTBP) and bis-triazinyl phenanthroline (R-BTPhen) (Fig. 1) ligands are found to be quite promising in this regard showing high selectivity for An^{3+} over Ln^{3+} ions.[6] The major drawbacks of these 'N' donor heteropolycyclic ligands include their poor solubility in suitable organic long-chain hydrocarbon solvents, *viz*. *n*-dodecane, kerosene *etc*. In all the cases, a long chain alcohol, *viz*. *n*-octanol, was required along with *n*-dodecane.[3,5,6]

Room temperature ionic liquid (RTIL) based solvent systems are being extensively investigated for the recovery of actinides and fission products from feeds relevant in the nuclear fuel cycle due to many of their advantages over the molecular organic solvents which include (i) low volatility, (ii) non-flammability and (iii) high thermal stability, resulting in a higher safety in the processes employing the RTILs, *etc*.[10–12] RTILs display higher stability under α and γ radiation.[13] Moreover, it has been, recently, reported that the R-BTP based extraction system is more radiation resistant in RTIL medium as compared to that in molecular solvents.[14] It is, therefore, important to explore the use of RTILs for process applications using radioactive elements with better recycling possibilities. Cocalia *et al.*[15] have observed similar extraction and complexation behaviour of various actinide and lanthanide ions with dialkyl phosphoric and phosphinic acids in RTIL and molecular diluents. On the other hand, a number of literature reports are available where a differential complexation and extraction behaviour is noticed in RTIL and molecular solvents.[16] A significant enhancement in the extraction of trivalent lanthanide ions using *N*,*N*,*N*′,*N*′-tetra-*n*-octyl diglycolamide (TODGA) was reported in $[C_2mim][NTf_2]$ as compared to that in molecular solvents, *viz*. iso-octane medium and mutual selectivity among the lanthanide ions was also found to be altered in the RTIL medium.[17] The different extraction behaviour in molecular solvents and RTIL media was explained on the basis of different extraction mechanisms in these two kinds of solvents. In the RTIL media, the lanthanide ions are extracted following the cation exchange mechanism, where the extraction of metal ions resulted in the simultaneous transfer of an equivalent amount of the cationic part of the RTIL (C_2mim^+) to the aqueous phase. Sun *et al.*[18] reported an enhancement in the selective extraction among the Ln^{3+} ions using a TALSPEAK type solvent where the di-2-ethylhexyl phosphoric acid (HDEHP) was taken in RTIL in place of di-isopropyl benzene (DIPB) in the presence of a buffering agent (glycolic acid or citric acid) in the aqueous phase. Stumpf *et al.* have studied the coordination chemistry of An^{3+} and Ln^{3+} in RTIL medium which indicated differential coordination behaviour of these two classes of 'f block' elements in RTIL medium unlike that in the aqueous medium.[19] They have also studied the azide complexation of An^{3+} and Ln^{3+} ions in RTIL medium and observed slower complexation in the case of the former.[20] From the observed differential behavior between An^{3+} and Ln^{3+} towards the N_3^- complexation in RTIL, they mentioned the possibility of using RTIL media for Ln^{3+}/An^{3+} separation using the selective extractants for An^{3+}. However, to the best of our knowledge, only one literature report is available where the mutual separation of trivalent actinides and lanthanides has been carried out in RTIL medium[21] where a task specific ionic liquid (TSIL) containing the DTPA moiety was used to enhance the selectivity in a TALSPEAK type separation scheme. However, no literature report is available on the selective extraction of An^{3+} in RTIL media using any of the well known 'N' and 'S' donor extractants (Fig. 1) mentioned above. The evaluation of RTILs in the Ln^{3+}/An^{3+} separation using BTP based 'N' donor ligands is of particular interest due to two main reasons, *viz*. (i) to avoid the use of toxic and hazardous long chain alcoholic solvents to solubilize the BTP derivatives in molecular solvents, *viz*. *n*-dodecane or kerosene and (ii) to explore the possibility of improvements in the separation behaviour of An^{3+} and Ln^{3+} ions using the BTP – RTIL solvent system as differential coordination behaviour of these two classes of 'f' block elements is noticed in RTIL medium.

In the present paper, a systematic study on the separation of Am^{3+} and Eu^{3+} ions has been carried out using several substituted BTP ligands *viz*., Me-BTP, Et-BTP and *n*-Pr-BTP in $[C_n mim][NTf_2]$ (where $n = 2, 3, 4, 6, 8$). Time resolved fluorescence spectroscopy (TRFS) studies have also been carried out with the organic extract of the Eu^{3+} ion in order to understand the difference in its extraction behaviour in the ionic liquid *vis-à-vis* molecular diluent (*n*-dodecane) based solvent systems. Computational studies were also carried out on the Am^{3+} and Eu^{3+} complexes in order to find out the differences in the metal–ligand orbital overlap and bond distances in these two metal complexes.

Experimental

Reagents and chemicals

The ligands (Me-BTP, Et-BTP and *n*-Pr-BTP) were synthesized following the procedure described elsewhere[22] and characterized by elemental analysis, melting point and NMR (^1H as well as ^{13}C) spectral analysis. ^{241}Am was purified by a method reported earlier[23] and the purity was checked by alpha spectrometry. ^{152,154}Eu was procured from the Board of Radiation and Isotope Technology (BRIT), Mumbai, India and was used after ascertaining its radiochemical purity. Suprapur nitric acid (Merck) and MilliQ water (Millipore) were used for preparing the tracer solutions. High purity crystals (99.99%) of $Eu(NO_3)_3 \cdot 5H_2O$ (Sigma-Aldrich) were used to prepare the organic extract of the Eu^{3+} ion for luminescence studies.

Distribution studies

Distribution studies were carried out with ^{241}Am and ^{152,154}Eu as the tracers spiked in aqueous solutions containing varying nitric acid concentrations from 0.1 to 1.0 M. The strip solution from the 'actinide partitioning' step which is usually at ~0.2 M HNO_3 when the diglycolamides are used as extractants for actinide partitioning[24] is proposed to be used as the feed for the lanthanide–actinide separation. It was, therefore, thought of interest to limit the HNO_3 concentration in the range of 0.1 M–1.0 M in the present studies. The ionic liquid solvents were prepared using 0.01 M solutions of Me-BTP, Et-BTP or *n*-Pr-BTP in $[C_n mim][NTf_2]$ (where n = 2, 3, 4, 6, 8). Equal volumes (0.25 mL) of the organic and the aqueous phases were taken in a leak-tight stoppered tube and agitated in a thermostated water bath at 25 ± 0.1 °C for 2 hours. The two phases were then centrifuged and assayed by taking suitable aliquots (0.1 mL) from both the phases followed by their radiometric assay by gamma ray counting using a NaI(Tl) scintillation detector. In the cases of mixture of radiotracers, an HPGe detector was used. The distribution ratio for a given metal ion (D_M) was calculated as the ratio of counts per minute of the corresponding radiotracer per unit volume in the organic phase to that in the aqueous phase. The separation factor (S.F.) is defined as D_{Am}/D_{Eu}. Material balance was within the error limits of ±5%.

Luminescence study

The luminescence studies of the organic extracts of the Eu^{3+} ions by Me-BTP, Et-BTP and *n*-Pr-BTP in 2-bromooctanoic acid/*n*-dodecane and in $[C_4mim] \cdot [NTf_2]$ were performed using an Edinburgh FLS 900 unit provided with a CD-920 controller and micro sec (Xe) flash lap. The data acquisition and analysis were done using the F-900 software provided by Edinburgh Analytical Instruments, UK. The fluorescence decay curves for all the samples were recorded on a 12 ms scale and fitted *via* an iterative method.

Computational study

Gas phase geometries of the Am^{3+} and Eu^{3+} complexes of Me-BTP were optimized at the GGA level of density functional theory (DFT) by using Becke's exchange functional[25] in conjunction with Perdew's correlation functional[26] (BP86) with generalized gradient approximation (GGA) where 28 and 60 electron core pseudopotentials (ECPs) along with the corresponding def-SV(P) basis set were selected for the Eu^{3+} and Am^{3+} ions, respectively. All other lighter atoms were treated at the all electron (AE) level. All the calculations were performed using the TURBOMOLE program package.[27,30]

Results and discussion

Distribution studies in $[C_n mim] \cdot [NTf_2]$

Distribution studies of Am^{3+} and Eu^{3+} were carried out using the R-BTP derivatives (R = Me, Et and *n*-Pr) in $[C_n mim][NTf_2]$ media (n = 2, 3, 4, 6 and 8) from 0.1, 0.5 and 1.0 M HNO_3 medium (Fig. S1–S6 in ESI†).

Am^{3+} selectivity of Me-BTP over Eu^{3+} was found to be enormously high in $[C_n mim][NTf_2]$ media, which is clearly shown in Fig. 2 and Table 1.

The S.F. values were found to be in the range of several thousands using Me-BTP even with 0.1 M HNO_3 and as shown from Table 1, such a high S.F. value for Am^{3+} over Eu^{3+} is unprecedented with any of the BTP derivatives in molecular diluents. Carbamoylmethylenephosphine oxide (CMPO), an extensively studied ligand for the actinide partitioning, does not show any selectivity between trivalent actinides and lanthanides.[1] However, Naganawa *et al.* reported an S.F. value of 30 for Am^{3+} over Eu^{3+} with CMPO in the presence of the weakly complexing hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate ($TFPB^-$).[31] In a previous study, we reported an enhancement in the selectivity (S.F. = ~500) for Am^{3+} over Eu^{3+} using Et-BTP in the presence of a hydrophobic weak anion, chlorinated cobalt dicarbollide (HCCD). Et-BTP, otherwise, showed an S.F. value of <100 in the presence of 2-bromocarboxylic acid.[32] The results from the aqueous phase nitric concentration variation studies (Fig. 3) indicated a decrease in the D_M and a concomitant decrease in the S.F. values with increasing HNO_3 concentration. The decrease in D_M with increasing HNO_3 concentration agreed with our previous results in molecular diluents with the difference that the metal ion extraction was much higher even with a significantly lower ligand concentration. The difference in complexation behaviour of An^{3+} and Ln^{3+} with the azide ion was reported to be higher in $[C_4mim][NTf_2]$ as compared to that in the aqueous medium.[20] Furthermore, an increase in metal ion extraction with increasing alkyl functionality in the ionic liquids in the case of Me-BTP did not support the conventional ion-exchange mechanism and an ion-pair mechanism may be proposed as given below:

$$M_{aq}{}^{3+} + nL_{IL} + 3NTf_{2IL}{}^{-} = [M(L)_n]^{3+}[NTf_2]_{3IL}{}^{-}$$

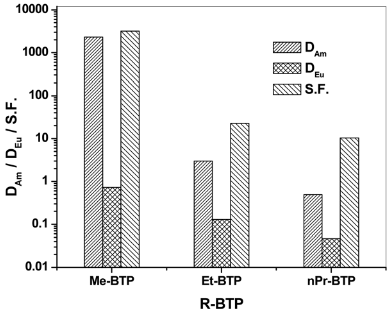

Fig. 2 Extraction and separation behaviour of Am^{3+} and Eu^{3+} from 0.1 M HNO_3 medium using 0.01 M R-BTP in $[C_8mim] \cdot [NTf_2]$.

Table 1 Comparison of two phase extraction and separation behaviour of Am^{3+} and Eu^{3+} using R-BTP in molecular solvents and RTIL media[a]

Ligand (L)	Org. phase	Aq. phase	D_{Am}	S.F.	Ref.
Me-BTP	0.004 M L+1 M BDA/TCE	0.013 M HNO_3	213	24	4
	0.02 M L+1 M BOA/*n*-dodecane	0.4 M HNO_3	0.15	41	32
	0.01 M L in $[C_4mim]\cdot[NTf_2]$	0.1 M HNO_3	231	412	PW
	0.01 M L in $[C_8mim]\cdot[NTf_2]$	0.1 M HNO_3	>2000	>3000	PW
Et-BTP	0.004 M L+1 M BDA in TCE	0.013 M HNO_3	420	26	4
	0.02 M L+1 M BOA/*n*-dodecane	0.4 M HNO_3	7.31	66	32
	0.01 M L in $[C_4mim]\cdot[NTf_2]$	0.1 M HNO_3	2.9	14.5	PW
	0.01 M L in $[C_8mim]\cdot[NTf_2]$	0.1 M HNO_3	2.97	23	PW
*n*Pr-BTP	0.0344 M L in TPH/EhOH (4/1)	0.3 M HNO_3 + 1.6 M NH_4NO_3	45.3	143	4
	0.01 M L in $[C_4mim]\cdot[NTf_2]$	0.1 M HNO_3	0.67	9	PW
	0.01 M L in $[C_8mim]\cdot[NTf_2]$	0.1 M HNO_3	0.49	10.4	PW

[a] BDA: 2-bromo decanoic acid; BOA: 2-bromo octanoic acid; EhOH: 2-ethyl-hexanol; TCE: 1,1,2,2-tetrachloroethane; PW: present work; S.F. = D_{Am}/D_{Eu}.

The lower extraction with ionic liquids having smaller alkyl groups may be attributed to a lower solubility of the bulky metal ligand ion-pair complexes containing 3 extractant molecules in the ionic liquid phase. On the other hand, in most of the other cases involving Et-BTP or *n*-Pr-BTP for the extraction of either Am^{3+} or Eu^{3+}, the extraction with $[C_n mim][NTf_2]$ was higher with n = 2 or 3 and lower extraction was seen with higher alkyl chains (n = 4, 6 or 8) suggesting the scope for the cation-exchange mechanism of the type:

$$M_{aq}^{3+} + nL_{IL} + 3C_n mim_{IL}^{+} = [M(L)_n]_{IL}^{3+} + 3C_n mim_{aq}^{+}$$

Though both extraction mechanisms can be conveniently suggested based on the dependence of metal ion extraction with HNO_3 concentration in a particular RTIL, the higher concentration of nitric acid is likely to decrease metal ion extraction due to protonation and subsequent aqueous partitioning of the extractant. Furthermore, as the acidity of the aqueous phase increases, the nitrate ion activity increases and due to the higher complexing nature of the nitrate ion as compared to the weakly coordinating NTf_2^- ion of RTIL, metal ion interaction with R-BTP ligands decreases, which results in a concomitant decrease in the selectivity.

An interesting difference in the trends of the D_M and S.F. values was observed when the R-BTP ligands with varying 'R' groups are compared in molecular diluents and RTIL (Table 1). An increase in the D_M values with an increase in the size of the 'R' group from methyl (Me) to ethyl (Et) in *n*-dodecane medium was reported in the presence of 2-bromo-octanoic acid.[4,32] In the present work, however, we observe a significant decrease in the D_M values with an increase in the size of the 'R' group from methyl to ethyl and from ethyl to *n*-propyl which is in sharp contrast to the previously reported trend. This has been largely attributed to the differences in the extracted complex stoichiometry. It was interesting to note that while 1 : 1 (M : L) species were found to be extracted in molecular diluent systems, 1 : 3 (M : L) species were extracted in ionic liquids. In molecular diluents, the increasing hydrophobicity of the ligand with increasing alkyl chain length favours the partitioning of the metal–ligand complex in the organic phase resulting in the enhancement in D_M values. This has been corroborated by luminescence studies which indicated 1 : 1 stoichiometry of the extracted complex (*vide supra*), where the role of increasing steric hindrance with increasing size of the alkyl substituent is expected to be less pronounced. On the other hand, in the RTIL medium, the partitioning of the metal–R-BTP complex in the organic phase is facilitated by the presence of bulk concentration of the hydrophobic anion, NTf_2^-. Moreover, the luminescence studies showed the formation of the D_3 symmetric 1 : 3 Eu^{3+} complex and, therefore, the increasing alkyl chain length hinders the approach of three such bulky ligands resulting in a sterically strained geometry which in turn is reflected in lower D_M values. In order to further understand the unusually high selectivity of Me-BTP as compared to Et-BTP and *n*-Pr-BTP in RTIL medium, Am^{3+} and Eu^{3+} extraction studies were carried out by varying the ligand (RBTP) concentration in $[C_4mim][NTf_2]$ medium to identify the nature of the extracted species (Fig. S7–S9 in ESI†). The results indicated that Eu^{3+} was extracted as their respective 1 : 2 complexes with all the three ligands studied. Am^{3+} was, however, extracted as the 1 : 3 complex with Et-BTP and *n*-Pr-BTP. In the case of Me-BTP, on the other hand, it is extracted as an unusual 1 : 4 complex, which resulted in unusually high selectivity of Me-BTP for Am^{3+} over Eu^{3+} in RTIL medium due to the extraction of a significantly more hydrophobic complex of Am^{3+} (compared to the respective Eu^{3+} complex). Formation of the 1 : 4 complex for the Am^{3+} extraction with Me-BTP, however, could not be explained on the basis of well known facts as it required an Am^{3+} coordination number of 12 for binding of all the four Me-BTP ligands in a tridentate manner. Am^{3+} extraction in the $[C_n mim][NTf_2]$ medium was, therefore, more favoured with respect to the Eu^{3+} extraction as the hydrophobic chain length (n) increased. The weakly coordinating NTf_2^- ion of RTIL cannot compete with the R-BTP ligands for the metal ion coordination and hence, due to more affinity of the R-BTP ligands for Am^{3+} over Eu^{3+} ion a higher metal–ligand stoichiometry in the case of Am^{3+} (1 : 4 for Me-BTP) as compared to the Eu^{3+} (1 : 2 for Me-BTP) ion was observed which resulted in improved selectivity for Am^{3+} over Eu^{3+} in $C_n mim\cdot NTf_2$ medium.

Luminescence study

In molecular diluents. Luminescence studies were carried out with the Eu^{3+} extract in the organic phase containing 0.01 M R-BTP + 1 M 2-bromo-octanoic acid in *n*-dodecane. Fig. 4 shows the excitation spectra of the Eu^{3+}-R-BTP complexes.

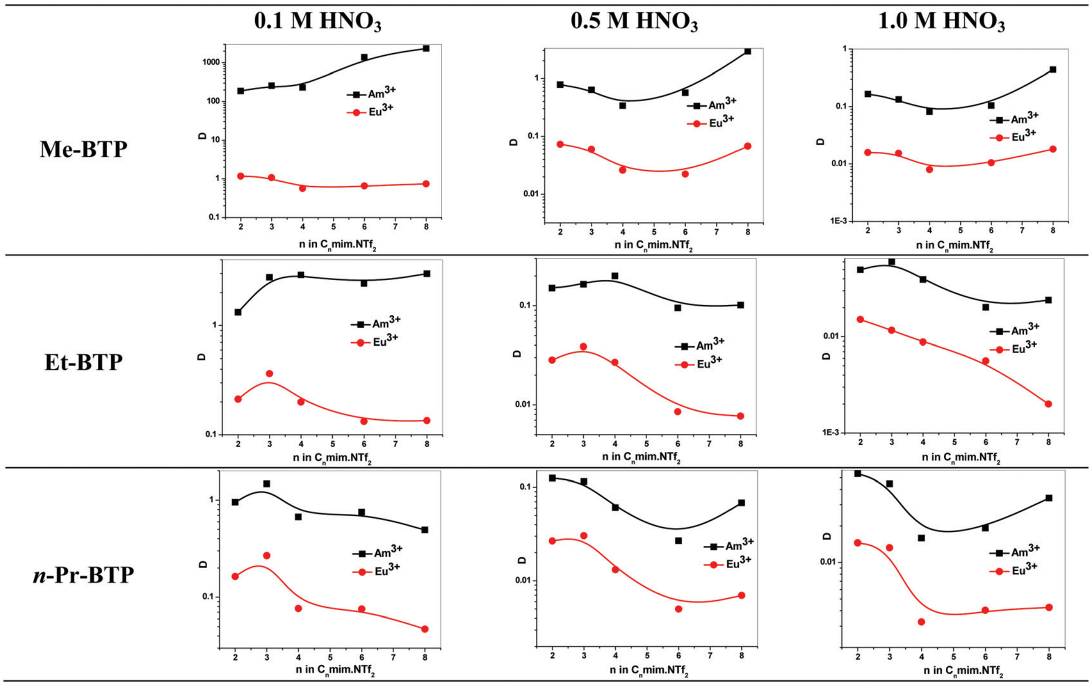

Fig. 3 Effect of alkyl chain length (n) in the $C_n$mim·NTf$_2$ on the extraction of Am^{3+} and Eu^{3+} using RBTP at different HNO_3 concentrations.

The relative intensities of various f → f transitions alter in these complexes. In the case of Eu^{3+}-Me-BTP complex, λ_{max} is at 326 nm whereas in the cases of Eu^{3+}-Et-BTP and Eu^{3+}-*n*-Pr-BTP complexes, the λ_{max} values are at 359 and 358 nm, respectively. The emission spectra of these complexes are shown in Fig. 5, which indicates similar spectra for the Eu^{3+} complexes with all the three ligands. The asymmetry ratio (A.R. > 2) values are quite high indicating the formation of asymmetric complexes. In order to gain more insight into the stoichiometry of the complexes, their lifetimes were measured by recording the decay profiles (Fig. S10†) of the Eu^{3+}-R-BTP complexes which are extracted in the *n*-dodecane phase in the presence of 2-bromooctanoic acid, which fitted to a single exponential decay pattern indicating the formation of 1 : 1 complexes similar to those reported in the literature.[33] 2-bromooctanoic acid, being a stronger anion, can compete with the R-BTP ligands. The presence of more than one unit of the R-BTP molecule in the inner sphere of the Eu^{3+} ion is, therefore, not observed in the present case.

In [C$_4$mim][NTf$_2$]. The results of the luminescence studies carried out using the Eu^{3+} extract in ionic liquid based solvents (R-BTP in [C$_4$mim]·[NTf$_2$]) are entirely different from that observed in the *n*-dodecane medium.

The excitation spectra (Fig. 6) indicate that the ligand to metal charge transfer band at 247 nm is much stronger as compared to the f → f transition bands. This clearly indicates a strong ligand sensitized luminescence of Eu^{3+} in its R-BTP complexes in the RTIL medium. Such a strong ligand sensitization was not observed in molecular diluents (*vide supra*). The emission spectra (Fig. 7) of all the three Eu^{3+}-RBTP complexes are similar to A.R. values of ~1 where the peak at ~580 nm due to the $^5D_0 \rightarrow {}^7F_0$ transition is completely absent. This is indicative of D_n, D_{nd} or D_{nh} site symmetry around the Eu^{3+} ion.[34,35] The doublet at ~593 nm due to the $^5D_0 \rightarrow {}^7F_0$ transition and singlet at ~616 nm due to the $^5D_0 \rightarrow {}^7F_0$ transition is the signature of D_3 symmetric 1 : 3 complexes.[36,37] The anion present in bulk (NTf_2^-) in the RTIL medium is a weak anion and, therefore, cannot compete with the R-BTP ligands. The metal coordination is, therefore, saturated by three R-BTP ligands resulting in nine coordination numbers around the Eu^{3+} ion. This is supported by very high τ values (~2 ms or higher). Similar high τ values suggesting complete dehydration of the inner coordination sphere has been previously reported.[36,37] This was, however, not consistent with the results of distribution studies, which indicated the presence of 1 : 2 complex of Eu^{3+}.

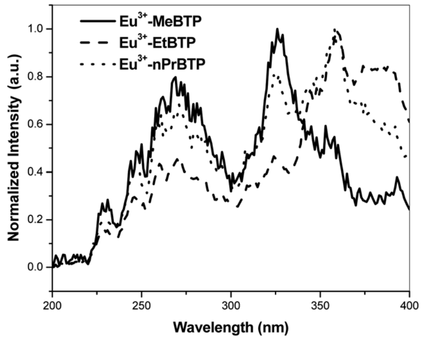

Fig. 4 Excitation spectra of Eu^{3+} complexes in the organic extract (λ_{em} = 616 nm): org. phase: 0.01 M RBTP + 1 M 2-bromooctanoic acid in *n*-dodecane; Aq. phase: 0.1 M HNO_3.

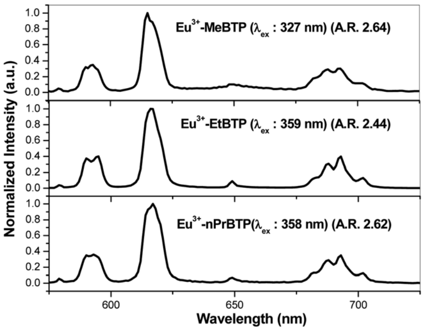

Fig. 5 Emission spectra of Eu^{3+} complexes in the organic extract: org. phase: 0.01 M RBTP + 1 M 2-bromooctanoic acid in *n*-dodecane; aq. phase: 0.1 M HNO_3.

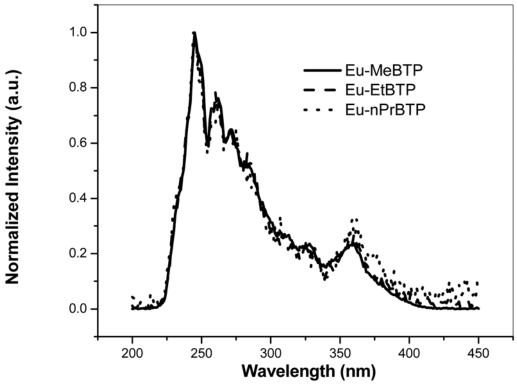

Fig. 6 Excitation spectra of Eu^{3+} complexes in the organic extract (λ_{em} = 616 nm): org. phase: 0.01 M RBTP in $[C_4mim][NTf_2]$; aq. phase: 0.1 M HNO_3.

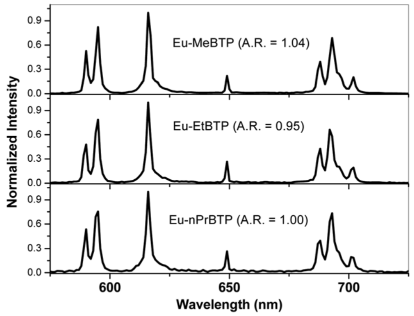

Fig. 7 Emission spectra of Eu^{3+} complexes in the organic extract (λ_{ex} = 247 nm): org. phase: 0.01 M RBTP in $C_4mim{\cdot}NTf_2$; aq. phase: 0.1 M HNO_3.

The lifetime spectra of all the three Eu^{3+} complexes are given in Fig. S11† and large lifetime values (Table 2) for all the three R-BTP complexes conform to such high stoichiometric (1 : 3) complexes[33] in the RTIL medium. This unusual behaviour could be rationalized based on the assumption that due to the high ligand sensitization, the fluorescence yield of the 1 : 3 complex was much higher as compared to the 1 : 2 complex. The 1 : 3 complex, in spite of its negligible concentration, was, therefore, dominated in the fluorescence spectra of the Eu^{3+} complexes of the R-BTP ligands in its organic extract in RTIL media.

Table 2 Lifetime values (in μs) of Eu^{3+} complexes of R-BTP observed in the organic extract of molecular diluent and RTIL

Ligand	0.02 M Ligand + 1 M 2-bromo-octanoic acid in *n*-dodecane	0.02 M Ligand in $[C_4mim]{\cdot}[NTf_2]$
Me-BTP	419 ± 2	2154 ± 2
Et-BTP	692 ± 1	2576 ± 5
*n*Pr-BTP	625 ± 1	1947 ± 3

Computational study

Geometry optimization

The "M–N" bond distances calculated for the $Am(Me\text{-}BTP)_3{}^{3+}$ complex in the present study were found to be very close to those obtained for the $Am(n\text{-}Pr\text{-}BTP)_3{}^{3+}$ complex from the EXAFS study[33] and the $Cm(H\text{-}BTP)_3{}^{3+}$ complex obtained from DFT calculations.[38] The alkyl (R) groups, therefore, have very little effect on the structure and bonding of the Am^{3+} and Eu^{3+} complexes of R-BTP. Me-BTP can, therefore, be considered a good model compound for the other R-BTP (Et-BTP and *n*-Pr-BTP) derivatives studied in the present work.

In the present work, all the computational studies were, therefore, carried out on the Am^{3+} and Eu^{3+} complexes of Me-BTP. Optimized geometries of various Am^{3+} and Eu^{3+} complexes of Me-BTP with different stoichiometries (1 : 1 as obtained in the molecular solvent (*n*-dodecane and 2-bromo-octanoic acid), 1 : 2 and 1 : 3 as obtained in RTIL medium) were shown in Fig. 8. The bond distances between the Am^{3+}/Eu^{3+} ion and coordinating 'N' atoms (central pyridinyl 'N' atom (N_c) and lateral triazinyl 'N' atoms (N_l)) were listed in Table 3. It is to be noted here that 'M–N_c' distances were found to be decreasing as we go from 1 : 1 to 1 : 3 complex. This was because of the fact that the 1 : 1 complex contained three anionic (2-bromo-octanoic acid) ligands, which lowered the charge on the central metal ion, thereby lowering its interaction with the electron donor 'N_c' atom of the ligand.

In the 1 : 2 complex, two anionic ($NO_3{}^-$) ligands are present and therefore metal ion interacts with 'N_c' more strongly as compared to the 1 : 1 complex. In the 1 : 3 complex, no anionic ligand is present in the inner coordination sphere of the metal ion. The interaction of the metal ion with the ligand's electron donor (N_c) atom is, therefore, strongest in the tri-positive 1 : 3 complex with the shortest 'M–N_c' bond distances amongst all the three possible complexes studied in spite of the presence of the three bulky Me-BTP ligands. Shorter 'Am–N' bonds as compared to the 'Eu–N' bonds were observed in all the cases.

Molecular orbitals analysis

Shorter 'Am–N' bonds as compared to the 'Eu–N' bonds in all the three kinds (1 : 1, 1 : 2 and 1 : 3) of complexes could be understood by analyzing the frontier orbitals of those Am^{3+}

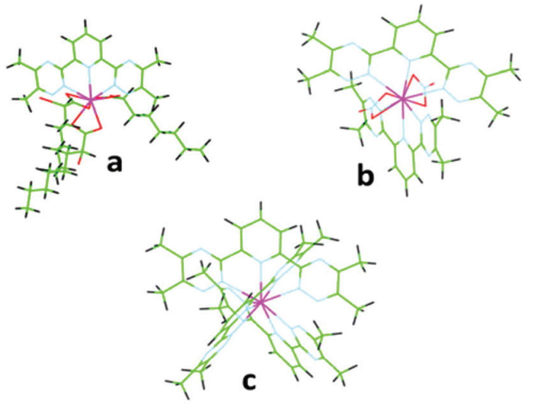

Fig. 8 Optimized geometries of different Am^{3+}/Eu^{3+} complexes of MeBTP.

Table 3 'M–N' bond distances in the optimized geometries of different Am^{3+} and Eu^{3+} complexes of MeBTP[a]

M^{3+}	$M(L)(BOA)_3$	$[M(L)_2(NO_3)_2]^+$	$[M(L)_3]^{3+}$
Am^{3+}	$Am–N_c = 2.676$	$Am–N_c = 2.624(0)$	$Am–N_c = 2.595(3)$
	$Am–N_l = 2.59(3)$	$Am–N_l = 2.575(4)$	$Am–N_l = 2.60(1)$
Eu^{3+}	$Eu–N_c = 2.737$	$Eu–N_c = 2.667(2)$	$Eu–N_c = 2.629(8)$
	$Eu–N_l = 2.629(5)$	$Eu–N_l = 2.629(5)$	$Eu–N_l = 2.63(1)$

[a] L: Me-BTP; BOA: 2-bromo octanoic acid.

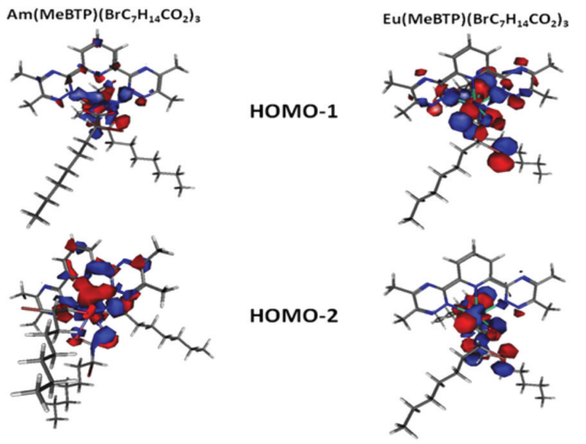

Fig. 9 Frontier orbitals of Am^{3+} and Eu^{3+} complexes of MeBTP and 2-bromo-octanoic acid with 1 : 1 stoichiometry as obtained in *n*-dodecane medium showing the difference in metal–ligand orbital overlap.

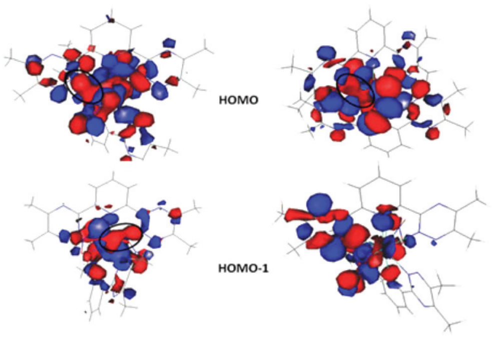

Fig. 10 Frontier orbitals of Am^{3+} and Eu^{3+} complexes of MeBTP with 1 : 2 stoichiometry ($M(MeBTP)_2(NO_3)_2^+$) as obtained in RTIL medium showing the difference in metal–ligand orbital overlap.

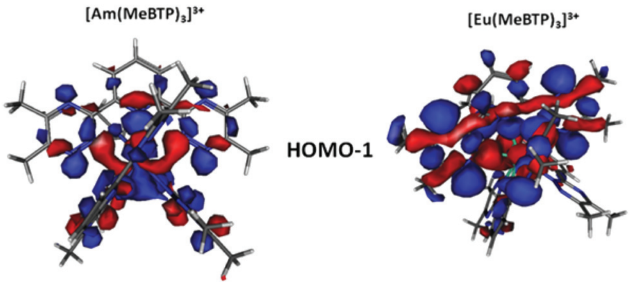

Fig. 11 Frontier orbitals of Am^{3+} and Eu^{3+} complexes of MeBTP with 1 : 3 stoichiometry as obtained in RTIL medium showing the difference in metal–ligand orbital overlap.

Table 4 Total contribution of metal 'd' and 'f' orbitals in the frontier molecular orbitals of different Am^{3+} and Eu^{3+} complexes of MeBTP calculated using the c^2 population analysis (SCPA) method[40]

Complex	Frontier MO	d% (Am/Eu)	f% (Am/Eu)
$M(L)(BOA)_3$	HOMO−1	1.1/0.5	27.3/15.0
	HOMO−2	0.8/0.4	35.7/29.7
$[M(L)_2(NO_3)_2]^+$	HOMO	2.5/0.7	23.2/16.0
	HOMO−1	2.4/0.8	35.6/24.4
$[M(L)_3]^{3+}$	HOMO−1	2.4/0.2	25.2/1.1

and Eu^{3+} complexes (Fig. 9–11). In the M(Me-BTP)(2-$BrC_7H_{14}CO_2)_3$ complex, the bonding interactions of metal ions with Me-BTP was mainly observed in the frontier molecular orbitals (HOMO−1 and HOMO−2) as shown in Fig. 9. These orbitals showed a higher metal–ligand (Me-BTP) overlap in the Am^{3+} complex as compared to that in the Eu^{3+} complex. This was also reflected in the contributions of metal 'd' and 'f' orbitals in those frontier molecular orbitals (Table 4), which showed higher 'd' and 'f' orbital contributions for Am^{3+} as compared to that for Eu^{3+}. Zaiter *et al.* have also reported higher orbital interaction in the Am^{3+} complex of pyrazine as compared to that in the Eu^{3+} complex showing higher Am^{3+}–ligand back bonding.[39] Similar features were also observed for the frontier molecular orbitals of $M(Me\text{-}BTP)_2(NO_3)_2^+$ (HOMO, HOMO−1) and $M(Me\text{-}BTP)_3^{3+}$ (HOMO−1), which mainly participated in the bonding with Me-BTP.

In the $Eu(Me\text{-}BTP)_3^{3+}$ complex, both the 'd' and 'f' orbital contributions of Eu^{3+} were found to be lower as compared to that of Am^{3+} in the $Am(Me\text{-}BTP)_3^{3+}$ complex.

In order to have a quantitative idea about the comparative 'M–N' bond strength for Am^{3+} and Eu^{3+} complexes the molecular orbitals were analysed to calculate the two center Mayer's bond order using the AOMix program[28,29] (Table S12 in the

ESI†), which showed higher bond orders in 'Am–N' bonds as compared to those in 'Eu–N' bonds in the cases of all the complexes studied.

The molecular orbital analysis, therefore, clearly showed the preference of this class of ligands towards An^{3+} over Ln^{3+}. This could be the reason for the tendency of Am^{3+} to form higher stoichiometric complexes with R-BTP as compared to Eu^{3+}.[36] This has been reflected in the present work, where Am^{3+} is extracted as the 1 : 3 complex for Et-BTP and *n*-Pr-BTP, whereas Eu^{3+} is extracted as the 1 : 2 complex only. Me-BTP, moreover, forms extraordinarily high stoichiometric and unusual (1 : 4) complex with Am^{3+}. Further studies are required to investigate the structure of this Am^{3+} complex in detail.

Conclusions

The role of RTIL as a diluent for N-donor ligands (R-BTPs) for the mutual separation of An^{3+} and Ln^{3+} ions is explored from the nitric acid medium for the first time. Significant enhancement in theselectivity is observed as compared to that in molecular diluents with an S.F. value as high as >3000 using Me-BTP as the extractant. The enhanced selectivity in RTIL medium is explained on the basis of the formation of extractable species with a higher metal–ligand stoichiometry in the case of Am^{3+} as compared to that in the case of Eu^{3+}. The nature of the complexes extracted in RTIL *vis-à-vis n*-dodecane media is characterized by the TRFS technique. Computational studies showed higher 'd' and 'f' orbital participation with higher metal–ligand orbital overlap for Am^{3+} complex as compared to that for Eu^{3+} complex in the bonding with Me-BTP. The results of the present work show the possibility of application of RTIL as the promising diluent for the Ln^{3+}/An^{3+} separation using 'N' donor heteropolycyclic ligands, which are otherwise not soluble in hydrocarbon based suitable molecular solvents, *viz*. *n*-dodecane. It will, therefore, be of interest to explore the selective extraction of An^{3+} over Ln^{3+} using soft donor ligands (R-BTBP, R-BTPhen and dithiophosphinic acids) which are known to be more selective than R-BTP derivatives studied in the present work.

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