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Highly efficient extraction of actinides with pillar[5]arene-derived diglycolamides in ionic liquids *via* a unique mechanism involving competitive host–guest interactions†

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Actinide partitioning is considered as one of the most challenging issues in nuclear waste remediation. Herein, we unravel a novel extraction mode pertinent to the competitive host–guest interactions for highly efficient actinide extraction. The host–guest recognition event involves binding of a room temperature ionic liquid (RTIL), 1-*n*-octyl-3 methylimidazolium bis(trifluoromethane)sulfonamide (C_8mimNTf$_2$), as both the guest and the solvent by the hosts pillar[5]arene-based diglycolamides (P5DGAs) and the subsequent displacement of the guest by a metal ion. This two-step process suggests a unique competitive ion-mediated displacement mechanism for the metal ion partitioning in the extraction process. The supramolecular extraction system is evaluated for its extraction abilities towards actinide ions such as UO_2^{2+}, PuO_2^{2+}, Pu^{4+}, Am^{3+}, and fission product elements such as Eu^{3+}, Sr^{2+}, Cs^+. The results demonstrate the exceedingly high distribution ratios and favorable separation of Am^{3+} and Pu^{4+} in nitric acid media. All the three P5DGAs form 1 : 1 complexes with Am^{3+}. Time resolved laser fluorescence spectroscopic (TRLFS) studies reveal a strong complexation involving no inner-sphere water molecules in the Eu^{3+}–P5DGA complexes when C_8mimNTf$_2$ is used as the diluent. With high efficiency in the extraction of actinides and a quantitative back extraction outcome, the RTIL-based solvent systems containing pillar[5]arene-DGA ligands developed in this work hold potential as promising candidates for nuclear waste remediation in a more sustainable fashion.

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Introduction

Driven by an ever-increasing concern about the depletion of natural fossil fuels, the development of nuclear energy has become the priority to meet the increasing energy demands in the twenty-first century. Nuclear energy is a cheap, environmentally friendly and clean energy source, which does not generate greenhouse gases and contamination in the atmosphere.[1] However, concomitant with the widespread use of nuclear energy is the inevitable production of high-level radioactive wastes that emanate from the reprocessing of spent fuel in a closed fuel cycle. The safe management of the radioactive wastes constitutes one of the major challenges in the nuclear fuel cycle.[2] Specifically, highly radiotoxic long-lived minor actinides (*e.g.*, isotopes of Am, Cm) have to be separated from the chemically similar but relatively harmless lanthanides in order to satisfactorily accomplish a transmutation process.[3] To this end, tremendous research efforts have been devoted to the development of green processes[4] and organic extractants such as tri-*n*-butyl phosphate (TBP),[5] carbamoylmethylphosphine oxide (CMPO),[6] malonamides,[7] and diglycolamides (DGAs)[8] for the liquid–liquid extraction of actinides, also known as "actinide partitioning" in the spent nuclear fuel. Mounting these ligands onto macrocyclic platforms such as calixarenes[9,31c] preorganized the ligands and greatly improved the extraction of trivalent f-elements, particularly in ionic liquids. The enhanced efficiency is attributed to a co-operative complexation mechanism *via* preorganization of chelating sites on a molecular platform. However, novel macrocyclic frameworks[10] with an ability

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to preorganize the ligating groups for higher separation efficiency and selectivity still remain scarcely reported.

As a new generation of supramolecular macrocyclic hosts, pillar[*n*]arenes have been the focus of considerable research since their first report in 2008.[11] These macrocycles consist of dialkoxybenzene units linked by methylene bridges at 2,5-positions,[12] which render them with a pillar conformation significantly different from their kindred analogues, *i.e.*, well-known calixarenes or resorcinarenes. With easy modifiability on both sides of the pillar and its enclosed hydrophobic cavity, they have found widely varied utilities in molecular machines,[13] artificial transmembrane channel,[14] metal–organic frameworks,[15] controlled drug delivery,[16] sensing,[17] construction of supramolecular polymers,[18] hybrid absorbents,[19] virus inhibitors,[20] *etc*. We have recently reported that pillar[5]arenes functionalized with phosphine oxides (PAPO) are able to differentiate UO_2^{2+} and Th^{4+} more efficiently and selectively than the acyclic analogues in acidic media using molecular solvents.[21] They also exhibited highly selective and sensitive recognition of Th^{4+} and transition metal ions.[22,10*d*] Interestingly, introduction of multiple DGA moieties onto the pillar[5]arene framework led to a significant enhancement in the extraction of Am^{3+} and Eu^{3+} in 1-octanol.[23] The *D* values for these ligands are 10–1000 times larger than that of *N*,*N*,*N*′,*N*′-tetra-i-propyl diglycolamide (TiPrDGA) under comparable conditions. Particularly, an enhanced selectivity was observed upon increasing the spacer length. However, these extraction studies and related reports on pillararenes are reported only with conventional organic solvents as the molecular diluents.

Room temperature ionic liquids (RTILs) are a class of organic salts with negligible vapour pressure, high thermal stability, high ionic conductivity as well as adjustable miscibility and polarity.[24] They are considered as green solvents for organic synthesis,[25] catalysis,[26] absorption,[27] electrochemistry,[28] and solvent extraction.[29] Since the first application of ILs for the extraction of metal ions in 1998,[24*d*] a large number of RTIL-based systems in combination with organic extractants have been reported for the separation of metal ions.[30,31] As reviewed recently, the unique physicochemical properties of RTILs allow for the particular application for actinide extraction and separation as well as back end of the nuclear fuel cycle.[31] Diglycolamides (DGAs),[32] malonamides,[33] trialkyl phosphine oxide (TRPO),[34] and carbamoylmethyl phosphine oxide (CMPO)[35] are typical extractants with high extraction efficiencies for such purposes in RTILs. When diglycolamides were appended to calix[4]arenes (C4DGAs), the resulting extractants in RTILs exhibited a significant enhancement in the extraction efficiency of actinides, particularly with the use of 1-*n*-octyl-3 methylimidazolium hexafluorophosphate (C_8mimPF_6) as the ionic liquid.[36] At the same time, the extraction of UO_2^{2+} and Sr^{2+} was drastically suppressed, indicating the unique separation ability of these solvent systems. Recently, C4DGA ligands modified with alkyl substituents on the nitrogen atom of the DGA units[31*c*,42] demonstrated favourable extraction of the trivalent actinide ions in $C_8mimNTf_2$ under acidic feed conditions, indicating the importance of ionic liquids in the selective recovery of actinides from radioactive wastes. Despite their demerits of aqueous phase solubility losses when RTILs are employed as diluents in some cases for metal ion extraction,[37] they demonstrate intrinsic advantages in terms of enhanced extraction efficiency, reduced volatility and radiochemical stability *vs.* conventional organic solvents.[38] Furthermore, the aqueous solubility of the imidazolium based ionic liquids is mostly seen with the cations containing shorter alkyl chains such as $C_4mimNTf_2$. With longer alkyl chain ionic liquids, such as $C_8mimNTf_2$ and $C_{10}mimNTf_2$, the extraction mechanism resembles that of molecular diluents[39] and the aqueous solubility of the ionic liquids decrease enormously. Similarly, the use of hydrophobic counter ions like NTf_2^- rather than hydrophilic OTf^- could also decrease the loss of ionic liquids.[40]

Inspired by the recent reports on the host–guest complexation between pillar[5]arene and ILs in organic media,[41] we wondered if such a host (ligand)–guest (IL) interaction is involved in the extraction process. Given the observed enhancement in actinide separations by pillar[5]arene-based diglycolamide (P5DGA) ligands in organic solvents,[23] we considered that it would be of interest to examine a novel extraction mode with the P5DGA ligands where host–guest interactions may prevail in ionic liquid-based diluents. Another impetus for the present study stems from the recent findings of an unusually high extraction of the trivalent actinides using the RTIL-based solvent system containing a calix-DGA ligand bearing eight DGA pendant arms.[42] It is expected that the structural difference between these two types of macrocycle-based DGA, where ten DGA groups rather than eight groups are tethered to a pillar[5]arene platform on both rims in pillar conformation, may lead to varying extraction outcomes.

Herein, we report on the novel extraction mode in efficient actinide extraction (UO_2^{2+}, PuO_2^{2+}, Pu^{4+}, Am^{3+}) involving competitive host–guest interaction in the RTIL ($C_8mimNTf_2$) using pillar[5]arene-based diglycolamide (P5DGA), which was synthesized by us in a previous communication[23] (Fig. 1). The

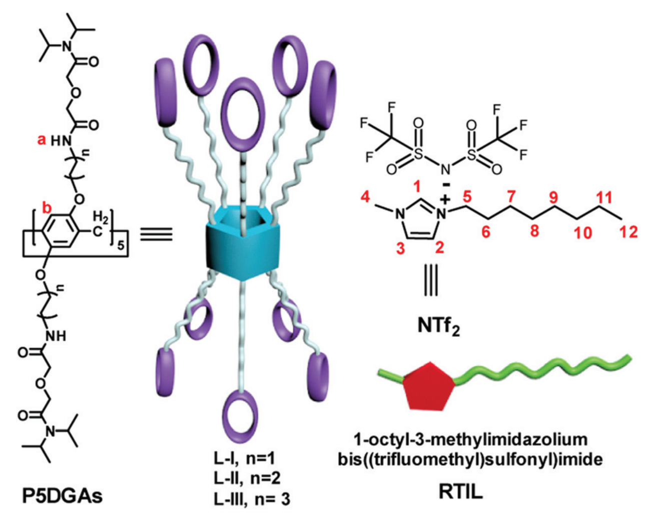

Fig. 1 Molecular structures and schematic representation of the ligands **L-I**, **L-II**, **L-III** and room temperature ionic liquid, $C_8mimNTf_2$.

extraction performance of fission product element ions (Cs^+, Sr^{2+} and Eu^{3+}) was also investigated. Despite the progress made by exploiting the host–guest interactions of pillararenes and metal ions for various purposes,[43] this work represents the first example of this type of macrocyclic receptors with ligating groups utilized as extractants in ILs in separation processes. The unique extraction mechanism was discussed and correlated to the extraction results to disclose the actinide partitioning and separation behaviour. The nature of the extracted species was ascertained from ligand concentration variation studies as well as the high resolution mass spectrometry technique and further investigated by time-resolved laser induced fluorescence. The photo-physical properties provided a better insight for complexation. The stripping studies were carried out to evaluate the reusability and recycling efficiencies of the solvents containing P5DGA in ionic liquids, which demonstrate the sustainability of the solvent system and underline the 'green' nature of the chosen extraction system.

Results and discussion

Host–guest chemistry between P5DGAs and $C_8mimNTf_2$

The complexation of **L-I** with $C_8mimNTf_2$ was first studied by ^1H NMR spectroscopy. As shown in Fig. 2b, when 1.0 equiv. of **L-I** is added into an acetone-d_6 solution of $C_8mimNTf_2$ (2.0 mM), the signals related to the protons H_1 and H_2 on C_8mim^+ of the RTIL not only shift upfield significantly but also become so broadened that they are hardly visible (Fig. 2c).[13d] These changes in the chemical shift and broadened pattern strongly suggest the formation of a complex between **L-I** and C_8min^+, causing protons H_1 and H_2 to be located within the cavity of the pillar[5]arene-based diglycolamide residues and shielded by the electron-rich cyclic framework. Embedding an imidazole moiety in the macrocyclic cavity often leads to an upfield shift of these protons.[44] Such a change in the chemical shift therefore suggests the threading of the C_8mim^+ through the cavity. On the other hand, protons H_a and H_b on **L-I** also experience a slight downfield shift due to the interactions between **L-I** and $C_8mimNTf_2$, corroborating the residing of the ionic liquid in the cavity. In fact, dipropoxypillar[5]arene (DPP5) without DGA groups also showed complexation of a structural analogue of $C_8mimNTf_2$, *i.e.*, 1-butyl-3 methylimidazolium, in the cavity.[45]

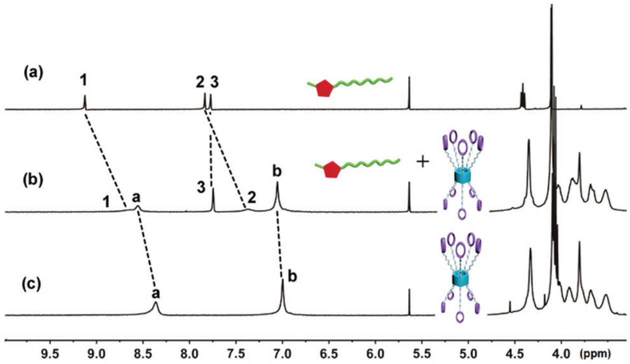

Fig. 2 Stacked partial ^1H NMR spectra (400 MHz, acetone-d_6, 298 K): (a) $C_8mimNTf_2$ (2.0 mM) and (b) **L-I** (2.0 mM) + $C_8mimNTf_2$ (2.0 mM) (c) **L-I** (2.0 mM).

Table 1 Binding constants K_a of P5DGAs with $C_8mimNTf_2$ and $Eu(NO_3)_3 \cdot 6H_2O$ in CH_3CN at 298 K

Binding constants[a] (M^{-1})	$C_8mimNTf_2$	$Eu(NO_3)_3 \cdot 6H_2O$
L-I	$(3.8 \pm 0.3) \times 10^3$	$(5.4 \pm 0.7) \times 10^4$
L-II	$(2.0 \pm 0.4) \times 10^3$	$(2.0 \pm 0.2) \times 10^4$
L-III	$(1.0 \pm 0.2) \times 10^3$	$(1.2 \pm 0.3) \times 10^4$

[a] The binding constants were obtained by UV-vis titration experiments and fitted with the ReactLab EQUILIBRIA software.

To elucidate the binding mode between **L-I** and $C_8mimNTf_2$, a 2D NOESY experiment was carried out in acetone-d_6. From the 2D NOESY spectrum of a solution containing 10.0 mM **L-I** and 10.0 mM $C_8mimNTf_2$ (Fig. S1†), cross-informant correlations are observed between protons H_4 and H_5 of the imidazolium cation and protons H_b on **L-I**, suggesting that C_8mim^+ is accommodated in the cavity of the pillar[5]arene. The fact that the pillararenes with DGA bearing different spacer lengths exhibit similar association affinities towards binding ILs (Table 1) is consistent with the binding of $C_8mimNTf_2$ inside the cavity rather than at the portals.

^1H NMR titration experiments were performed in acetone-d_6 in order to determine the complexation ratio between the ligands and $C_8mimNTf_2$ (Fig. S2–S7†). Mole ratio plots indicate a 1 : 1 stoichiometry for all complexes formed by P5DGA ligands and $C_8mimNTf_2$, which is consistent with the early results on the ethoxy substituted pillararenes.[35a,c] The Job's plot provides another piece of evidence for a 1 : 1 binding mode (Fig. S8†). At the same time, an isobestic point was also observed in the UV-vis titration experiments, indicating the formation of the C_8mim^+–P5DGA complex. Furthermore, density functional theory (DFT) calculations at the M062X/6-31G (d, p) level were performed for a host molecule **L-I** (Fig. S13†) and its model complex comprising **L-I** and 1-ethyl-3 methyl-imidazolium. The energy-minimized structure of the complex reveals an excellent fit of the C_2mim^+ into the cavity of the pillararene with a 1 : 1 binding stoichiometry (Fig. 3 and Table S2†). In this complex, the imidazolium cation inside the cavity engages in seven C–H⋯O H-bonding interactions, six $N^+ \cdots O$ ion-dipole interactions with oxygen atoms on the neighboring benzene rings and two C–H⋯π interactions (Fig. S14†). The C–H⋯π distances are 2.378 Å and 2.347 Å, respectively, shorter than 3.05 Å, indicating the existence of strong C–H⋯π interactions.[46] The DFT calculations reveal that C_2mim^+ could indeed thread into the cavity of the pillar[5]arene, which also provides strong support for the complexation between the host, **L-I**, and the guest, C_8mim^+. The mass spectrum of a 1 : 1 mixture of **L-III** with $C_8mimNTf_2$ uncovered a peak of the highest intensity at m/z = 3789.633, corresponding to the complex [**L-III** + C_8mim]$^+$ with the isotope pattern being consistent with the simulated one (Fig. S12†).

Therefore, it can be inferred that the initial extraction process in the P5DGA system involves the host–guest inter-

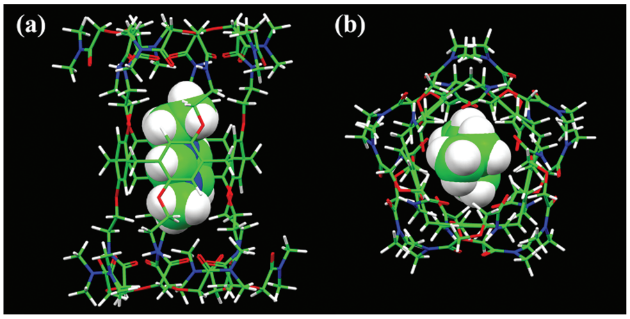

Fig. 3 Side view (a) and top view (b) of the optimized geometry of the host–guest complex of **L-I** and C_2mim^+ at the M062X/6-31G (d, p) level (green = C, white = H, red = O and blue = N, the guest C_2mim^+ is in the space filling model). All terminal isopropyl groups of each chain in the host molecule, **L-I**, are replaced by methyl groups for simplicity.

action between P5DGAs and $C_8mimNTf_2$ as expressed by eqn (1).

$$[\mathrm{P5DGA}]_{\mathrm{IL}} + \mathrm{C_8mim^+}_{\mathrm{IL}} \rightleftharpoons [\mathrm{C_8mim}\cdot\mathrm{P5DGA}]^+{}_{\mathrm{IL}} \qquad (1)$$

where the subscript ‘IL’ refers to the species in the ionic liquid phase.

Extraction of Am^{3+} at different feed acidities by competitive host–guest interactions

Am^{3+} was first selected as the representative of actinides to optimize the extraction conditions before testing many other actinide elements. The influence of the feed acid concentration on the extraction of Am^{3+} was examined in $C_8mimNTf_2$ using three diglycolamide-functionalized pillar[5]arenes, *i.e.*, **L-I, L-II** and **L-III.**

Interestingly, unusually high distribution ratio (*D*) values were obtained with Am^{3+} for all P5DGAs in the acidity range of 0.1–3.0 M (Fig. 4). For example, the D_{Am} values of 728 ± 11, 1164 ± 15 and 4098 ± 13 for **L-I**, **L-II**, **L-III**, respectively, were achieved at 1.0 M HNO_3, which are 121–485 times higher than those in 1-octanol, a molecular diluent used under comparable conditions (Table 2). These results in the ionic liquid at 1.0 M HNO_3 are comparable to those obtained with a both-side DGA functionalized calix[4]arene (C4DGA) at 0.5 M HNO_3. Lowered acidity with P5DGA leads to better extraction than the latter. For example, the D_{Am} value of **L-III** at 0.5 M HNO_3 is 8411 (Table S3†), while it is 5500 for C4DGA at 5.0×10^{-4} M.[42] Meanwhile, **L-III** extracts PuO_2^{2+} 60% more efficiently than C4DGA. In addition, the extraction also operates well with pillararene-based extractants than a tripodal diglycolamide-based extractant (T-DGA). At 1.0×10^{-3} M, the D_{Am} for T-DGA is 3.1, which is in sharp contrast to the D_{Am} values of 5510 ± 25–8411 ± 12 for P5DGA ligands at 5.0×10^{-4} M.[52] Therefore, pillararene-based diglycolamides are superior to the documented calixarene-based diglycolamides and tripodal diglycolamides.

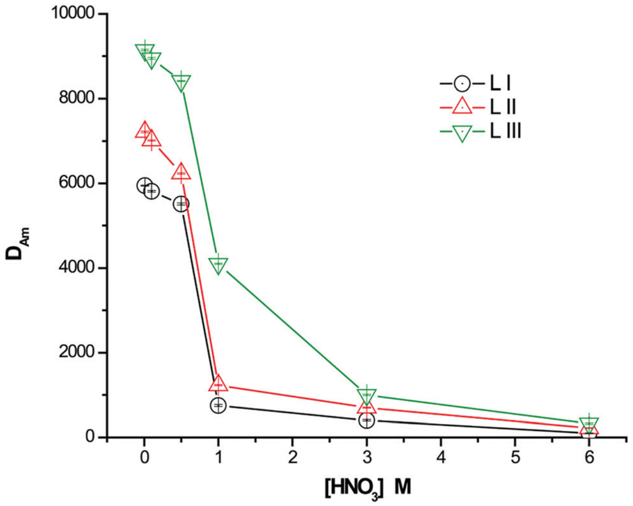

Fig. 4 Acidity-dependant extractions of Am^{3+} from an aqueous phase of various acidities into $C_8mimNTf_2$ at 25 ± 1.0 °C using 5.0×10^{-4} M P5DGAs.

In general, the distribution ratios of Am^{3+} decrease sharply up to 1.0 M HNO_3, followed by an alleviated reduction with increasing HNO_3 concentrations from 1.0 to 4.0 M. The extraction profile resembles diglycolamides like TODGA[47] and one-side DGA functionalized calix[4]arene.[31c] This suggests the operation of a cation-exchange mechanism throughout the acidity range examined using a two-rim DGA functionalized pillar[5]arene, and can be expressed by eqn (2a):

$$\begin{aligned}&\mathrm{Am_{aq}}^{3+} + m\mathrm{NO_{3\,aq}}^- + (2-m)\mathrm{C_8mim_{IL}}^+ \\ &\quad + [\mathrm{C_8mim}\cdot\mathrm{P5DGA}]_{\mathrm{IL}}{}^+ \rightleftharpoons [\mathrm{Am(NO_3)}_m\cdot\mathrm{P5DGA}]_{\mathrm{IL}}{}^{(3-m)+} \\ &\quad + (3-m)\mathrm{C_8mim_{aq}}^+\end{aligned} \qquad (2a)$$

where the subscript ‘aq’ denotes the species present in the aqueous phase, and ‘*m*’ is the number of nitrate anions associated with the extracted complex. It should be noted that a competitive exchange between $Am(NO_3)_3$ in the aqueous phase and complexed C_8mim^+ with P5DGA in the IL phase is assumed to occur. In addition, since P5DGA and $C_8mimNTf_2$ forms a host–guest complex in 1 : 1 stoichiometry as corroborated by the Job's plot, the species is expressed in the equation as $[C_8mim\cdot P5DGA]^+$.

To determine the number of cations and anions involved in the extraction process as depicted in eqn (2a), the extraction of Am^{3+} by 10^{-4} M **L-III** in $[C_8mim][NTf_2]$ was carried out by varying the concentration of C_8mim^+ (used in the form of C_8mimCl) in the aqueous phase. The distribution ratios decrease gradually with the increasing concentration of the ionic liquid cation in the aqueous phase (Fig. S15†). The dependence of $\log[C_8mim^+]$ as a function of $\log[D_{Am}]$ provides a linear relationship with the negative slope of *ca.* −1, from which the “*m*” value is calculated to be 2 (Fig. S16†). Therefore, the eqn (2a) is simplified as eqn (2b):

$$\begin{aligned}&\mathrm{Am_{aq}}^{3+} + 2\mathrm{NO_{3\,aq}}^- + [\mathrm{C_8mim}\cdot\mathrm{P5DGA}]_{\mathrm{IL}}{}^+ \\ &\quad \rightleftharpoons [\mathrm{Am(NO_3)_2}\cdot\mathrm{P5DGA}]_{\mathrm{IL}} + \mathrm{C_8mim_{aq}}^+\end{aligned} \qquad (2b)$$

This indicates that only the bound cation $[C_8mim]^+$ in the host–guest complex participates in the transfer of the ionic

Table 2 Comparative extraction data of actinides and fission product elements using 5.0×10^{-4} M P5DGAs in $C_8mimNTf_2$ and 1-octanol; feed: 1.0 M HNO_3; equilibration time: 3.0 h

Metal ions	$C_8mimNTf_2$						1-Octanol					
	L-I	**L-II**	**L-III**	$SF_{\mathbf{L\text{-}I}}$[a]	$SF_{\mathbf{L\text{-}II}}$[a]	$SF_{\mathbf{L\text{-}III}}$[a]	**L-I**	**L-II**	**L-III**	$SF_{\mathbf{L\text{-}I}}$[a]	$SF_{\mathbf{L\text{-}II}}$[a]	$SF_{\mathbf{L\text{-}III}}$[a]
$D_{Am(III)}$	728 ± 11	1164 ± 15	4098 ± 13	—	—	—	1.5 ± 0.1	9.6 ± 0.2	15 ± 1	—	—	—
$D_{Cs(I)}$	0.01 ± 0.001	0.03 ± 0.001	0.03 ± 0.001	7.3×10^4	3.9×10^4	1.4×10^5	0.008 ± 0.0002	0.02 ± 0.001	0.01 ± 0.001	1.88×10^2	4.80×10^2	1.50×10^3
$D_{Sr(II)}$	0.07 ± 0.002	0.04 ± 0.001	0.03 ± 0.001	1.0×10^4	2.9×10^4	1.4×10^5	0.05 ± 0.001	0.03 ± 0.001	0.02 ± 0.001	3.0×10^1	3.20×10^2	7.50×10^2
$D_{Pu(IV)}$	93 ± 4	52 ± 2	41 ± 2	7.8	22	1.0×10^2	0.41 ± 0.02	1.02 ± 0.05	1.1 ± 0.1	3.66	9.41	1.36×10^1
$D_{Pu(VI)}$	0.31 ± 0.01	0.22 ± 0.01	0.19 ± 0.01	2.4×10^3	5.3×10^3	2.2×10^4	0.12 ± 0.01	0.29 ± 0.01	0.47 ± 0.02	1.25×10^1	3.31×10^1	3.19×10^1
$D_{U(VI)}$	0.16 ± 0.01	0.38 ± 0.01	0.5 ± 0.02	4.6×10^3	3.1×10^3	8.2×10^3	0.07 ± 0.002	0.09 ± 0.002	0.1 ± 0.01	2.14×10^1	1.07×10^2	1.50×10^2
$D_{Eu(III)}$	865 ± 14	1731 ± 17	7803 ± 21	0.8	0.7	0.5	12.4 ± 0.9	63 ± 3	52 ± 3	0.12	0.15	0.29

[a] SF means the separation factor values of Am^{3+} with respect to other metal ions using ligands **L-I**, **L-II** and **L-III**, *i.e.*, $SF_{\mathbf{L\text{-}I}} = D_{Am(III)}/D_M$.

liquid into the aqueous phase, and that Am^{3+} gets extracted to the ionic liquid phase at the expense of $[C_8mim]^+$ cations. Experiments with varying nitrate concentrations in the aqueous phase (Fig. S17†) suggest that nitrate ions are involved in the extraction process. We speculate that neutral P5DGA molecules form a host–guest complex with $C_8mimNTf_2$ first, which enhances the hydrophilicity of the host molecule. As a result, the more hydrophilic pillararenes easily approach the interface of the organic and aqueous layers and exchange the encapsulated imidazolium ions with the metal ions in the aqueous phase. Different from the conventional ion exchange mechanism where the cation alone of a diluent shifts to the aqueous phase, the extraction process observed here is associated with host–guest complex formation first, followed by an exchange process.

The D_{Am} values were found to be especially lower from 1.0 to 4.0 M HNO_3 than those from 0.01 to 1.0 M, indicating that the proton exerts a great impact on the Am^{3+} extraction at higher acidity. This can be rationalized on the basis of a competing equilibrium reaction (3) as follows:

$$\begin{aligned} &{H_{aq}}^+ + {[C_8mim \cdot P5DGA]_{IL}}^+ \\ &\quad \rightleftharpoons {[H \cdot P5DGA]_{IL}}^+ + {C_8mim_{aq}}^+ \end{aligned} \tag{3}$$

To prove evidence for the competitive binding of H^+ ions by replacing Am^{3+} in the complex, the ^1H NMR experiment was carried out by adding 40.0 equiv. of trifluoroacetic acid (TFA) into the **L-I**-C_8mim^+ complex in $CDCl_3/CD_3CN$ (1 : 1, v/v). A dramatic downfield shift of C_8mim^+ protons going back to its original resonance was observed (Fig. S18†), strongly suggesting that C_8mim^+ is dethreaded from the cavity of **L-I**. At the same time, the protonation of the macrocycle **L-I**, *i.e.*, the formation of $[H{\cdot}P5DGA]^+$ was confirmed by a downfield shift (0.38 ppm) of amide protons. These results corroborate the assumption that decreased *D* values at a higher acid concentration could be due to the increased protonation of amide oxygen atoms, which significantly decrease the binding ability of the ligands towards Am^{3+} in the aqueous phase.

Insight into the extraction mechanism

To provide evidence for the hypothetical mechanism in the presence of metal ions, ^1H NMR experiments were carried out at room temperature. $La(OTf)_3$ was used to replace radioactive Am^{3+} for the ^1H NMR experiments since it is diamagnetic. The triflate OTf^- was selected as the counter anion for its weak coordinating ability towards the lanthanides in solution. First, the threading of C_8mim^+ into the cavity of the pillararene is indicated by the drastic upfield shifts of protons H_1 and H_2 of the imidazolium ion with an equimolar mixing of **L-I** and $C_8mimNTf_2$ (Fig. 5a and b). Upon addition of 1.0 equiv. of La^{3+} to the solution of **L-I** and C_8mim^+, protons H_1 and H_2 are shifted downfield, strongly suggesting the dethreading of the C_8mim^+ from the cavity of **L-I** (Fig. 5c). The marginal change in the chemical shift of protons H_a and H_b before and after the complexation of La^{3+} (Fig. 5d and e) is ascribed to the fact that the binding site for La^{3+} is located too far away from H_a

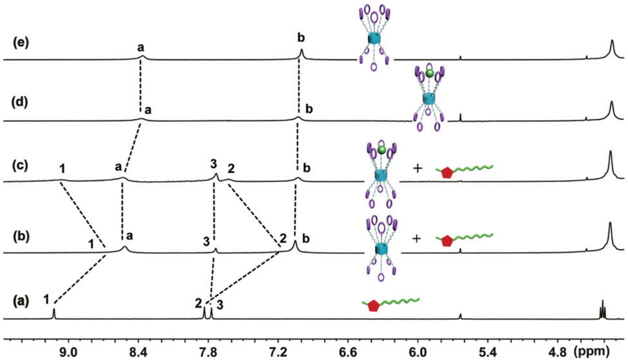

Fig. 5 Stacked ^{1}H NMR spectra of (a) C_8mimNTf$_2$ (b) **L-I** + C_8mimNTf$_2$, (c) **L-I** + C_8mimNTf$_2$ + La(OTf)$_3$, (d) **L-I** + La(OTf)$_3$ and (e) **L-I**, each at 2.0 mM in acetone-d$_6$.

and H_b, and thus the binding of La^{3+} exerts little influence on their chemical shifts. High resolution ESI-MS experiments were carried out to further corroborate the formation of the metal complex. Non-radioactive Eu^{3+} having chemical properties similar to Am^{3+} was used. The mass spectrum of a 1 : 1 mixture of ligand **L-I** with Eu(NO$_3$)$_3$·6H$_2$O shows a peak of high intensity at m/z 1074.1683, corresponding to the complex [**L-I** + Eu + CH$_3$OH]$^{3+}$ with the isotope pattern being consistent with the simulated one (Fig. S9†). For **L-II** and **L-III**, 1 : 1 complexes were also observed under identical conditions (Fig. S10 and S11†). These results clearly demonstrate the occurrence of weakened host (pillararene)–guest (C_8mim$^+$) interaction in the presence of La^{3+}, *i.e.*, **L-I** prefers to complex with the metal ion over C_8mim$^+$. The above competitive recognition process may be driven by the greater binding ability of the ligand toward the metal ion. Severe aggregation often hampers the accurate determination of the association constant (K_a).[48,49] Fortunately in our case, when **L-III** (0.5 mmol) was mixed with the ionic liquid (C_8mim$^+$), the dynamic light scattering (DLS) experiment showed the presence of particles of sizes of less than 3 nm in diameter, indicating no apparent aggregation for the complex formed between the P5DGA ligand and the ionic liquid. Then the UV-vis titration experiments (Table 1 and Fig. S19–S24†) were performed in CH$_3$CN with titration curves fitted with ReactLab EQUILIBRIA software to yield a binding affinity of *ca.* 10^4 M^{-1} for the Eu^{3+} ion, which is an order of magnitude larger than the determined 10^3 M^{-1} for the imidazolium ion.[50] Additionally, the steric effect may also play a role in facilitating the displacement. Thus, a competitive displacement-based mechanism pertinent to the extraction process could be proposed as shown in Fig. 6.

When P5DGA ligands are dissolved in C_8mimNTf$_2$, they form complexes with the C_8mim$^+$ ions. The larger binding affinities of the P5DGA macrocycle toward metal ions facilitate the metal ion-mediated displacement of C_8min$^+$ in the cavity, leading to the formation of extractable complexing species and partially accounting for the unusually high distribution ratios observed. It is necessary to point out that the extraction process involving the competitive host–guest interactions to increase the distribution ratio value is different from the synergistic separation process that mainly stems from the enhanced solubility of the extracted species in the ionic liquid.[51] To the best of our knowledge, the extraction mechanism based on host (pillararene)–guest (C_8mim$^+$) chemistry, specifically, the displacement of the entrapped ionic liquid molecules by metal ions to effect a separation process has never been reported before.

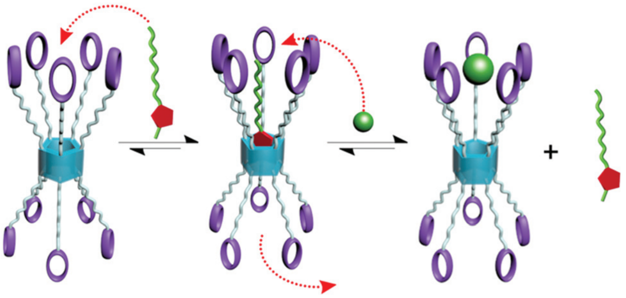

Fig. 6 Schematic representation of the ionic liquid-based solvent extraction mechanism involving competitive host–guest interactions. (Metal ion is represented as a green ball while other symbols are in accordance with Fig. 1.)

Extraction kinetics

The kinetics on the Eu^{3+} extraction was then carried out using C_8mimNTf$_2$ as the diluent (Fig. 7). In principle, the equilibrium with RTILs should be attained at a relatively longer time than those with conventional molecular diluents due to the slow rate of mass transfer arising from the high viscosity of the ionic liquids.[31a,c] As expected, slow extraction kinetics were found for the extraction of Eu^{3+} into C_8mimNTf$_2$ using all the three ligands, **L-I**, **L-II** and **L-III**. The distribution ratios of Eu^{3+} increase with increasing equilibration times of up to 120 min, and then level off beyond 120 min in all cases (Fig. 7). This

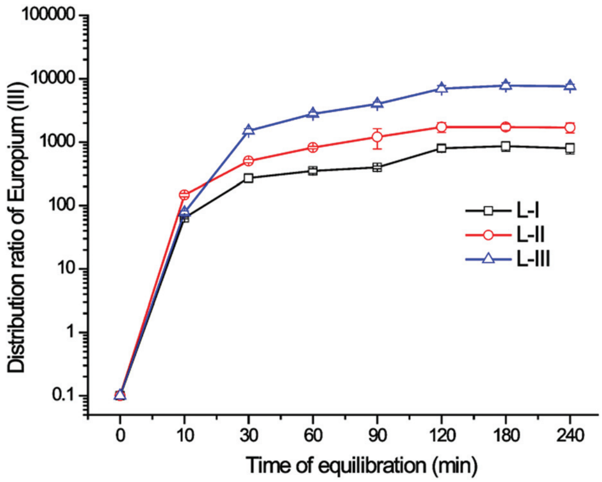

Fig. 7 Kinetics of Eu^{3+} extraction at different equilibration times into the RTIL phase. Aqueous phase: 1.0 M HNO$_3$; organic phase: 5.0×10^{-4} M P5DGAs in C_8mimNTf$_2$.

trend agrees well with those from our previous findings where the kinetics of Am^{3+} extraction was slow in $C_8mimNTf_2$ with either diglycolamide-functionalized calix[4]arenes (C4DGA)[31c] or a tripodal diglycolamide (T-DGA)[52] used as the extractants.

Evaluation of actinide extraction and separation behaviour

Isolation of the long-lived radiotoxic actinides is the key step for the strategy of partitioning and transmutation (P&T).[53] So the ability to extract and separate actinides constitutes an utmost important parameter for the extractants.[54] The extraction of several important actinide ions including UO_2^{2+}, PuO_2^{2+}, Pu^{4+}, Am^{3+} was investigated along with fission products such as Eu^{3+}, Sr^{2+}, Cs^+ under identical conditions. For comparison purpose, the extraction experiments were conducted using 1.0 M nitrate acid as the aqueous feed and 5.0×10^{-4} M **L-I**, **L-II** and **L-III** in $C_8mimNTf_2$ as the organic phase. In parallel with the use of ionic liquids is the employment of *n*-octanol as the organic diluent in extraction experiments. The results of the distribution ratio and separation factors are listed in Table 2. In terms of distribution ratios, these values decrease in the order of $Eu^{3+} \sim Am^{3+} > Pu^{4+} \gg PuO_2^{2+} \sim UO_2^{2+} > Sr^{2+} \sim Cs^+$ in $C_8mimNTf_2$, a trend which is similar to that observed with 1-octanol. Nevertheless, observations of high distribution ratios for both Eu^{3+} and Am^{3+} are quite unusual compared with those data obtained in 1-octanol. For example, the $D_{Am(III)}$ drops sharply from 728 ± 11 in $C_8mimNTf_2$ to 1.5 ± 0.1 in 1-octanol with **L-I**. In the ionic liquid, the separation factors (SF) for Am^{3+} with respect to other actinides (UO_2^{2+}, PuO_2^{2+}, Pu^{4+}) and fission products (Sr^{2+}, Cs^+) are found to be superior compared to those reported in organic diluents for all the three ligands. A dramatic decrease of separation factors by *ca.* two to three orders of magnitude in 1-octanol is observed in the case of Am^{3+} against Cs^+, Sr^{2+}, PuO_2^{2+} and UO_2^{2+}. It is noteworthy that a longer spacer length tends to enhance the extraction selectivity in both the ionic liquid and organic diluent. This can be seen from ligand **L-III** bearing a more extended spacer compared to the other two ligands. This ligand with superior performances in terms of both extraction efficiency and separation selectivity towards Am^{3+} (except for Eu^{3+}) may find applications in the selective separation of actinide in the nuclear waste remediation through the "P&T" strategy.[53] In addition, the SF values for Pu^{4+} with respect to UO_2^{2+} and PuO_2^{2+}, as well as lower oxidation state fission product ions such as Sr^{2+} and Cs^+ were also found to be very high with P5DGA ligands in the RTIL system as compared to 1-octanol (Tables S4 and S5†). All these results indicate that the solvent systems containing the P5DGA ligands and the $C_8mimNTf_2$ diluents show much better extraction efficiency than molecular organic solvent systems, thereby holding potential in remediation of actinides (Am^{3+} or Pu^{4+}) for the high level wastes.

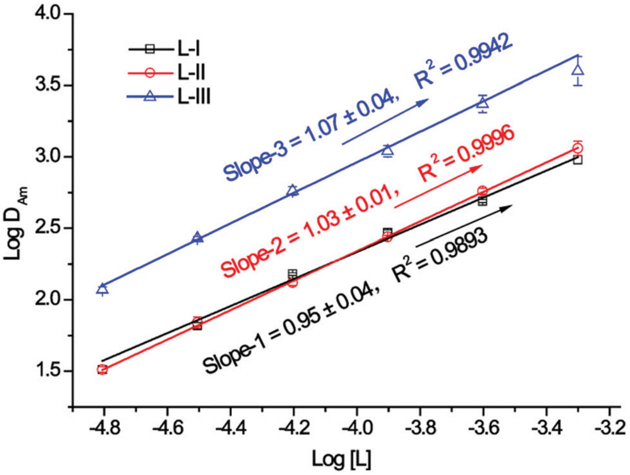

Fig. 8 Plots of log D_{Am} *versus* log[L] for the extraction of Am^{3+} by P5DGAs from 1.0 M HNO_3 aqueous solution into $C_8mimNTf_2$ at 25 ± 1.0 °C.

Speciation studies

To gain further insights into complexes formed between Am^{3+} and P5DGA ligands, variations in the distribution ratio as a function of ligand concentration were investigated. For all the three extractants **L-I**, **L-II** and **L-III**, plotting the distribution ratio of the Am^{3+} (log D_{Am}) as a function of the concentration of the ligand (log[L]) yields the linear plots, the slopes of which suggest 1 : 1 rather than 2 : 1 stoichiometry for all the three complexes (Fig. 8). This 1 : 1 stoichiometry was further confirmed by using either MS soft ionization (Fig. S9–S11†) or the Job's plot method carried out in acetonitrile (Fig. S25†). Even in the presence of two or more equiv. of Eu^{3+}, results from NMR and MS spectra still point to the binding of only one metal ion by the ligands. Complex formation with a 1 : 1 instead of 2 : 1 stoichiometry is quite unusual for P5DGAs carrying two identical binding sites, which nevertheless was similarly observed previously for a diglycolamide-functionalized calix[4]arene[31c] and often involves a complicated process.[9]

In addition, the FT-IR experiments reveal a shift of C═O stretching frequency from 1643 cm^{-1} to 1625 cm^{-1} upon addition of Eu^{3+} ions to the solution of ligand **L-I** (Fig. S26†), suggesting the coordination of Eu^{3+} to the P5DGA ligands.

Time resolved fluorescence spectroscopic study of the complexation of Eu^{3+} with P5DGA ligands

It has been established that time-resolved laser fluorescence spectroscopy (TRLFS) is a convenient technique for probing the nature of the coordination of Eu^{3+}.[31c] With this technique, it is possible to provide information on whether the metal ion is bound to the P5DGA ligands through outer-sphere or inner-sphere complexation, going beyond the simple stoichiometry information provided by methods such as slope analysis. Thus, TRLFS experiments were performed to obtain information on the symmetry of the complexes and the number of inner-sphere water molecules. Considering the difficulty in detection of Am^{3+} due to its very low fluorescence intensity, the studies were performed using Eu^{3+} with similar properties as a surrogate for Am^{3+}. As shown in Fig. 9, compared to the fluorescence spectra of the Eu^{3+} aqueous complex in dilute

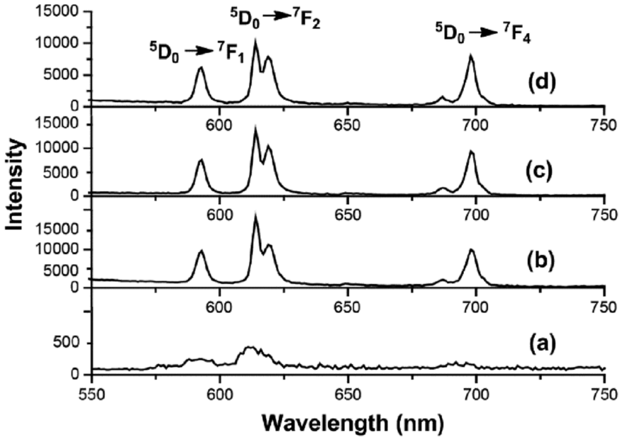

Fig. 9 Emission spectra of (a) Eu^{3+}-aquo, (b) Eu^{3+}–**L-I**, (c) Eu^{3+}–**L-II** and (d) Eu^{3+}–**L-III** complexes in C$_8$mimNTf$_2$ obtained by time-resolved fluorescence spectroscopy.

Table 3 Emission lifetimes of the complexes of Eu^{3+} with the three P5DGA ligands as well as the photo-physical properties obtained from luminescence investigation

System	Eu^{3+}–**L-I**	Eu^{3+}–**L-II**	Eu^{3+}–**L-II**
Number of species	1	1	1
Lifetime (μs)	1292	1230	1400
Number of H$_2$O molecules	0	0	0
Asymmetric factor	2.50	2.71	2.43
Ω_2	4.10×10^{-20}	4.46×10^{-20}	4.01×10^{-20}
Ω_4	4.40×10^{-20}	5.10×10^{-20}	4.89×10^{-20}
$A_{2\text{ed}}$	1.07×10^2	1.16×10^2	1.04×10^2
$A_{4\text{ed}}$	5.68×10^1	6.62×10^1	6.38×10^1
A_{md}	4.26×10^1	4.27×10^1	4.27×10^1
τ_R (s)	4.67×10^{-3}	4.26×10^{-3}	4.50×10^{-3}
τ_{NR} (s)	1.74×10^{-3}	1.69×10^{-3}	2.03×10^{-3}
η (quantum yield)	0.28	0.28	0.31
β_1 (branch ratio)	0.20	0.18	0.19
β_2 (branch ratio)	0.50	0.49	0.47
β_4 (branch ratio)	0.27	0.28	0.29

nitric acid (1.0 M HNO$_3$) those from the Eu^{3+}–P5DGA complexes in C$_8$mimNTf$_2$ display markedly increased intensities at the three characteristic peaks *i.e.*, 617 nm ($^5D_0 \rightarrow {}^7F_2$ hypersensitive transition, electric dipole), 592 nm ($^5D_0 \rightarrow {}^7F_1$ transition, magnetic dipole), and 690 nm ($^5D_0 \rightarrow {}^7F_4$ transition, electric dipole, sensitive to the Eu^{3+} environment about 20–40 times larger in relative intensity than those at 617 nm). Similar changes at these three wavelengths were also reported for other DGA-derived ligands including C4DGA,[31c] T-DGA-RTIL[52] and P5DGA in 1-octanol,[23] and suggest a strong interaction of the metal ion with the DGA moieties on the pillararene. It was documented that the luminescence lifetime depends on several radiation and radiation-less decay processes and that the number of inner-sphere water molecules (N_{H_2O}) could be determined by the lifetime of the $^5D_0$ emitting level (τ) of Eu^{3+}. The two parameters, N_{H_2O} and τ follow an empirical relationship in eqn (4):[55]

$$N_{H_2O} = (1.06/\tau) - 0.19 \qquad (4)$$

It is well-known that the Eu^{3+}-aquo ion complexes contain nine water molecules in their primary coordination′ sphere.[52] Given the presence of large amounts of the nitric acid in the aqueous phase, the nitrate ion would interact with ligands pre-occupied by the coordinated water molecules due to the competing effect. This leads to removal of some or all water molecules from the primary hydration sphere, causing an increase in the emission lifetime. Indeed, the lifetime data obtained from the decay curves of Eu^{3+}–P5DGA (Table 3) revealed prolonged lifetimes of 1.292, 1.230 and 1.400 ms for **L-I**, **L-II** and **L-III**, respectively, suggesting a complete replacement of the nine inner-sphere water molecules by the donor atoms of P5DGA. Detailed analyses of the luminescence spectra provide more insights suggesting a complete replacement of the nine inner-sphere water molecules by the donor atoms of P5DGA. Detailed analyses of the luminescence spectra provide more insights into the Eu^{3+}–P5DGA complexes in C$_8$mimNTf$_2$. Absorption bands in the UV-vis range are assigned as $^7F_0 \rightarrow {}^5D_2$, $^5G_{2,3,4}$ and $^5L_6$ transitions (Fig. S27†), which are in accordance with the assignments of lanthanide spectra by Dieke[56] and Carnall *et al.*[57] $^7F_0 \rightarrow {}^5L_6$ transition band was found to be the most intense among all absorption bands as also observed in the case of Al(NO$_3$)$_3$–SiO$_2$ sol–gel glass.[58] The transitions in the emission spectra of the above complexes (Fig. 9) are assigned as $^5D_0 \rightarrow {}^7F_n$ transitions (where n = 0, 1, 2, 3, 4).[52] The high intensity of $^5D_0 \rightarrow {}^7F_2$ transition indicates that the Eu^{3+} ions reside in an asymmetric environment, and the asymmetric factor, a measure of asymmetry[59] establishes the most asymmetric nature for the **L-II**–Eu^{3+} complex, while the asymmetry in other two complexes is comparable. The mono exponential lifetime of the complexes (Fig. S28–S30†) suggests the existence of single species while the lifetime values reveal that there is no water molecule in the primary coordination sphere of Eu^{3+}.[60] The deconvolution of each transition line of the emission spectra reveals one peak for $^5D_0 \rightarrow {}^7F_0$ transition, two peaks for $^5D_0 \rightarrow {}^7F_1$ transition, two peaks for $^5D_0 \rightarrow {}^7F_2$ transition and four peaks for $^5D_0 \rightarrow {}^7F_4$ transition (Fig. S31–S33†). The splitting pattern suggests the C_{4v} local symmetry around Eu^{3+} to be similar to some of the Eu^{3+} complexes of diglycolamide functionalized calixarenes in C$_8$mimNTf$_2$.[61] The Judd–Ofelt parameters were evaluated from the emission spectra,[62] demonstrating that the covalency of the metal oxygen bond in different ligands follows the order of Eu^{3+}–**L-II** > Eu^{3+}–**L-I** > Eu^{3+}–**L-III** (Table 3). The magnetic dipole transition probability of all the complexes is found to be the same, indicating that the perturbation due to the ligand field could hardly influence the magnetic dipole moment transition. The maximum transition probability is found for electric dipole $^5D_0 \rightarrow {}^7F_2$ transition. The more substituted ligand molecules might provide additional non-radioactive pathways for de-excitation, which is likely to be responsible for the maximum lifetime in the case of the Eu^{3+}–**L-III** complex. The branching ratios of all the complexes are found to follow the trend: $\beta_2 > \beta_4 > \beta_1$.

Stripping studies

Efficient stripping of a metal ion from an ionic liquid phase is an important feature for evaluating an extraction system.[31c] It

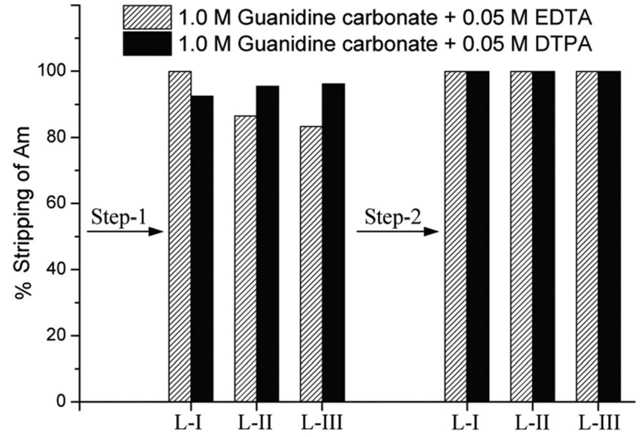

Fig. 10 Stripping studies using buffered complexing agents of EDTA and DTPA.

still represents a challenging task for achieving high extraction and separation efficiencies at both lower and higher acidities. Despite the large difference in distribution ratios with varied HNO_3 concentrations, especially at higher acidities such as 4.0 M, the back extraction is still poor. Our prior studies showed that complexing agents such as DTPA and EDTA in a buffered medium are able to quantitatively back-extract Am^{3+}.[31c] Therefore, we tried two complexing agents, *i.e.*, (i) 1.0 M guanidine carbonate + 0.05 M EDTA and (ii) 1.0 M guanidine carbonate + 0.05 M DTPA, to improve the back extraction efficiency of our system. The stripping results are presented in Fig. 10. Remarkably, almost quantitative stripping takes place using the stripping agents (i) in a single contact at a volume ratio of 1 : 1 for **L-I**, and >83% for **L-II** and **L-III**. The stripping percentage for Am^{3+} is more than 92% for all ligands using the back extractants (ii). In particular, near quantitative stripping is achieved using both (i) and (ii) by simply doubling the contact time during the back extraction for all the ligands. The stripping data suggest that the solvent system containing pillararene-based diglycolamides can be regenerated and reused for further metal ion extraction. In this context, the results implicate an option of sustainability for the extractants.

Conclusions

In summary, we have demonstrated the use of RTIL for the DGA-functionalized pillar[5]arene-based separation process. A novel extraction mode operates in the extraction process, which involves the metal ion-mediated competitive displacement of the guest molecule, *i.e.*, the bound ionic liquid molecule *via* host–guest interactions. The superior performance observed in the ionic liquid to the organic diluent highlights the advantage of the RTIL-based solvent system. Highly selective separation of Am^{3+} and Pu^{4+} has been achieved from the fission products Cs^+ and Sr^{2+} and other actinides UO_2^{2+} and PuO_2^{2+}. Stripping of the minor actinide elements can be easily and quantitatively achieved by back extraction using buffered complexing agents, such as EDTA and DTPA. Time-resolved fluorescence studies confirm the strong interaction of the metal ion with the P5DGA ligands in $C_8mimNTf_2$ and the formation of 1 : 1 complexes where the metal ion contains no inner sphere water molecules. All these results suggest a fairly high recycling possibility of the novel extraction systems and its utility as a sustainable green method for "actinide partitioning" by incorporating supramolecular chemistry into the extraction process.

Experimental

General

The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE AV II-400 MHz (^1H: 400 MHz; ^{13}C: 100 MHz). Acetone-d_6, CD_3CN and $CDCl_3$ were purchased from Cambridge Isotope Laboratories.

Materials

The pillar[5]arene-based diglycolamide ligands were prepared according to the method previously reported by us.[23] $^{85,89}Sr$, ^{137}Cs, Pu (mainly ^{239}Pu),[23] ^{241}Am and $^{152,154}Eu$ tracers were obtained from the Institute of Nuclear Science and Technology and Bhabha Atomic Research Centre. Diethylenetriamide-*N*,*N*,*N′*,*N″*,*N′*-pentaacetic (DTPA, ≥99%) and ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA, ≥99%) were purchased from Aladdin Industrial Corporation, Shanghai, while 1-*n*-octyl-3 methylimidazolium bis(trifluoromethane)sulfonamide ($C_8mimNTf_2$, ≥99%) and 1-*n*-octyl-3 methylimidazolium chloride (C_8mimCl, ≥99%) were procured from Cheng Jie Chemical Co. Ltd, Shanghai, and were used as received. Suprapur nitric acid and ultrapure water were used for preparing nitric acid solutions. All other reagents were of AR grade.

Synthesis of pillararene-based diglycolamide

The P5DGA ligands were prepared as previously reported. The structures were confirmed by ^1H NMR, ^{13}C NMR and HR-MS spectrometry. The purity of the compounds was checked by standard physicochemical methods.

Distribution studies

Typically, the ionic liquid (1.0 mL) containing 5.0×10^{-4} M P5DGAs was added into a polystyrene plastic equilibration tube (10 mL capacity) with an equal volume of an aqueous phase containing the required radiotracer at the required HNO_3 concentration in a thermostated water bath (25 ± 1.0 °C) for about 3 h. After the extraction, equilibration was reached, the experimental tube was centrifuged for 5 min, 0.5 mL of the aqueous phase was transferred into the test tube using micro syringe and the concentration was determined by gamma counting (NaI(Tl) well detector). As for Pu^{4+} distribution detection, a Pu tracer exists in five different oxidation states (Pu^{3+}, Pu^{4+}, Pu^{5+} and PuO_2^{2+}) in a laboratory stock solution. 50 μL of 0.01 M $NaNO_2$ solution (in water) was added to the stock solution of the Pu tracer to convert most of the Pu to Pu^{4+}. Then the feed acidity was adjusted to 1.0 M HNO_3 and was brought into contact with freshly prepared 0.5 M TTA solution in xylene. As a result, only Pu^{4+} will be extracted into the organic phase leaving trace amounts of unconverted Pu in other oxidation states in the aqueous phase. Then the Pu^{4+}-containing organic phase was brought into contact with 8.0 M HNO_3 to strip back the Pu^{4+} into the aqueous phase. After this back extraction, 8.0 M HNO_3 aqueous phase containing plutonium only in its +4 oxidation state was adjusted to 1.0 M HNO_3 and used for the extraction with 5×10^{-4} M P5DGA ligands in $C_8mimNTf_2$. All the extractions were carried out with a biphasic solution (aq : org = 1 : 1, v : v) for 2 h at 300 K in triplicate. A pinch of Ag_2O was added to the Pu tracer solution in 1.0 M HNO_3, followed by heating it for 5 min at 60–70 °C. Different oxidation states of Pu will be converted to PuO_2^{2+} and again the feed was adjusted to 1.0 M HNO_3 (if changed slightly due to heating). Then the solvent extraction study was carried out using pillararene in 1.0 M HNO_3 with phase ratio of 1 at 300 K for 2 h in triplicate.

According to the reported method,[63] liquid–liquid extraction experiments were performed by shaking 1.0 mL of $C_8mimNTf_2$ containing 5.0×10^{-4} M P5DGA ligands and 1.0 mL of the aqueous phase containing 1.0×10^{-4} M UO_2^{2+} in a stoppered tube immersed in a thermostatic bath at 25 ± 1.0 °C for 3 h. Then, 0.5 mL aqueous of the extracted mixture was diluted to 10 mL and measured by ICP-AES.

Fluorescence studies

Emission spectroscopy of the Eu^{3+} complexes was carried out in the IL extracts, by using a spectrometer (Edinburgh Analytical Instruments, UK) that was controlled by a CD 920 controller and equipped with an OPO laser. Excitation of the samples was performed at 395 nm, while the emission spectra were recorded in the range of 575–750 nm. The emission–decay curves were fitted to an exponential function to obtain the lifetimes/decay-rates of the excited states by using inbuilt software GEM/3 (Edinburgh) with a reproducibility of the lifetimes of the excited states of within ±3 μs.

Acknowledgements

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