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Ionic Liquids for Lanthanide and Actinide Chemistry

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Dedicated to the memory of Professor Dr. Herbert Schumann

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Ionic liquid chemistry has developed into a tremendously popular field of chemistry in the last decade. It has been realized that ionic liquids show features that cannot be realized in conventional molecular solvents. The widely tuneable class of ionic liquids has become important for lanthanide and actinide coordination chemistry, f-element spectroscopy, f-element electrochemistry and electrodeposition, organic synthesis and catalysis as well as inorganic nanomaterial synthesis. For example, ionic liquids offer the possibility to synthesize and crystallize quite uncommon lanthanide compounds. Ionic liquids can also be designed in such a way that they become excellent media to study the optical properties of lanthanide compounds. And even ionic liquids based on f-elements can be made. Hydrophobic ionic liquids may replace organic solvents in liquid/liquid f-element extraction processes, not only as a safer extraction phase but also as a smart extractant. Their wide electrochemical window and large ion conductivity make ionic liquids interesting solvents to study the electrodeposition of the very electropositive lanthanide elements. For f-element-catalyzed reactions, higher reaction rates, enhanced selectivity, better immobilization of the catalyst and an easy product recovery have often been observed in certain ionic liquids.

Introduction

Ionic liquid chemistry has developed into a tremendously popular field of chemistry within the last decade. The amount of literature, both original and review papers as well as patents, still grows extraordinarily. It has been recognized that ionic liquids (ILs) show features that cannot be realized in conventional molecular solvents. The widely tuneable class of ILs has become important for lanthanide and actinide coordination chemistry, f-element spectroscopy, f-element electrochemistry and electrodeposition, organic synthesis and catalysis as well as inorganic nanomaterial synthesis. The extremely fast development in the popular field of IL chemistry gives rise to the need for an

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Prof. Dr. Anja-Verena Mudring studied chemistry at the Rheinische Friedrich Wilhelms-Universität in Bonn. Her thesis, which focussed on the chemistry of anionic gold (2001), was carried out at the Max-Planck-Institute for Solid State Research in Stuttgart. As a Feodor-Lynen fellow of the Alexander-von-Humboldt-Stiftung, she joined between 2001 and 2003 the group of Prof. John Corbett at Iowa State University and the Ames Laboratory, where she investigated chemical bonding in Zintl compounds and reduced rare earth halides. In 2003 she established a young researcher group with a Liebig fellowship at the Universität zu Köln, where she obtained her Habilitation in 2006 on the "Chemistry of 6th Period Elements". In 2006 she became a professor for inorganic and materials chemistry at the Ruhr-Universität Bochum. Between 2005 and 2006, she was also an Iowa State faculty affiliate, and since 2008 she is an adjunct professor at the University of Alabama in Tuscaloosa. She is co-editor of the ACS journal "Crystal Growth & Design". She has authored more than 100 publications and has received numerous awards. Lately she was awarded an ERC starting grant for the exploration of ionic liquids for materials chemistry.

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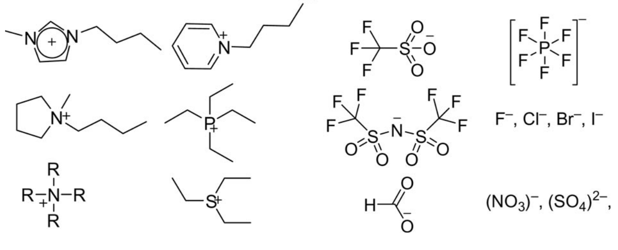
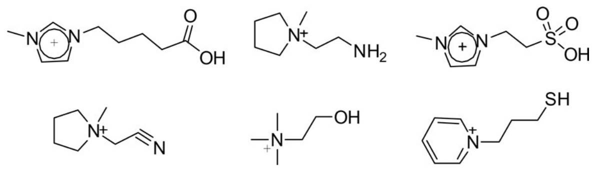
updated review article on lanthanide and actinide chemistry in ILs, although the literature covering the developments until early 2007 have already been reviewed.[1] The current review focuses on solvation and complex formation of lanthanide and actinides in ILs, their luminescence properties, their electrochemistry and the potential of ILs for lanthanide and actinide separation as well as the use of lanthanide and actinide compounds in ILs for catalysis. Literature up to and including the first quarter of 2010 has been taken into account. This review is intended to give a good overview on recent developments. However, lanthanide-based ionic liquid crystals (ILCs) and lanthanide nanoparticles in ILs are not in the focus of this review.

Ionic Liquids

Ionic liquids have become an important class of solvents. According to a commonly accepted definition, ionic liquids are salts with a melting point below 100 °C, many of them are even liquid at room temperature and are built by discrete cations and anions.[2] Most times ILs are composed of organic cations and organic or inorganic anions (see Scheme 1 for typical IL ion representatives). The most prominent IL cations include alkylammonium, alkylphosphonium, *N*,*N′*-dialkylimidazolium as well as *N*-alkylpyridinium cations. The anions may be as simple as chloride, bromide or iodide. Traditionally also tetrahedral and octahedral halido complexes like $[BF_4]^-$, $[AlCl_4]^-$, $[PF_6]^-$ or $[SbF_6]^-$ are employed. Today most times alkylsulfates and alkylsulfonates and even more often perfluorinated anions such as triflate, $[CF_3SO_3]^-$ or bis(trifluoromethylsulfonyl)amide $[(CF_3SO_2)_2N]^-$ are utilized. More sophisticated ions can be found in more recently studied ILs (Scheme 2).



Scheme 1. The ionic liquid toolbox: prominent model cations and anions for ILs.



Scheme 2. Functionalized cations of ILs.

However, ionic liquids are not new materials – they have been known for over a century.[3] Paul Walden's report on ethylammonium nitrate, published in 1914, is viewed as the launch of ionic liquid research. Unfortunately, little attention was paid to it at that time, and it took some twenty more years to realize the power of ionic liquids for technological applications such as cellulose dissolution under mild conditions.[4] This technology was only recently improved so that it might be performed on the industrial level.[5] Roughly some twenty years later, the significance of ILs for electrochemical applications such as electrodeposition of metals like aluminium was recognized.[6] Alas, ionic liquids first used for this kind of application were based on complex metal ions such as $AlCl_4^-$, which easily undergo hydrolysis and are highly corrosive. A significant step forward was the development of a set of ionic liquids that could be handled under ambient conditions.[7] Soon it was realized that such ILs have unique properties as VOCs (volatile organic compounds) as solvent replacements and are materials with new and unique combinations of physical properties. These days it is often the unique materials properties set, neither available in molecular compounds nor in typical crystalline salts, that turn out to be the true advantage of ILs.[8] It is estimated that more than one million simple ionic liquids can be synthesized, each with a different set of chemical and physical properties.[9] The intrinsic nonvolatility, high thermal stability, large liquidus ranges and unique properties possible with many ILs have enhanced the interest in IL chemistry over the years.[8] Thus, ionic liquids truly offer the possibility to design a solvent for a certain application by the right choice of the cation and anion and their combination, which somehow justifies their being promoted as "designer solvents".[10] Even more, the increasing social pressure for new green technologies has led to growing academic and industrial interest in IL technologies. Current research fields include electrochemistry,[11] separation science,[12] chemical synthesis[13] and catalysis.[14] These include breaking azeotropes,[15] thermal fluids,[16] lubricants,[17] paint additives,[18] gas storage applications,[19] processing of cellulose,[20] biphasic chemical processes (e.g., BASF's BASIL®),[21] photovoltaics, fuel cell electrolytes,[22] and "energetic liquids" (nonvolatile liquid high-energy-density materials).[23] Many of these applications have reached the industrial stage.[24] Today, ionic liquids are available commercially from several companies.[25] And no wonder, ionic liquids have also found their entrance into the field of lanthanide and actinide chemistry.

Dissolution, Solvation and Complexation of Lanthanides and Actinides in Ionic Liquids

There are several ways to dissolve lanthanide compounds in ionic liquids. As mentioned above, ionic liquids can be designed for special use and have therefore also been called "task-specific ionic liquids" (TSILs). They can be obtained by introducing organic functional groups into the cation or anion of the familiar ILs. When the functional group has the ability to coordinate to the metal ion (preferably as a bidentate or a polydentate ligand), the dissolution of metal oxides or metal salts in the ionic liquid is facilitated. Among these functional groups, the carboxyl functional group seems to be the most useful and, in consequence, ILs bearing this functionality have been studied quite well. 3-(5-Carboxypropyl)-1-methylimidazolium bromide and 3-(5-carboxypropyl)-1-butylimidazolium bromide in combination with certain neutral ligands such as 1,10-phenanthroline (phen) and 2-thenoyltrifluoroacetone (TTA) turned out to be quite powerful in dissolving europium(III) oxide.[26] Some time ago, it was found that lanthanide oxides can be dissolved in protic betaine ionic liquids provided water is present.[27] Betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf_2N]), for example, bears one carboxyl group in the ammonium cation. The deprotonated betainium (bet) is a zwitterion according to the formula [$^+Me_3N\text{-}CH_2\text{-}COO^-$]. This ionic liquid is able to dissolve stoichiometric amounts of rare-earth and other metal oxides. By mixing lanthanide oxides with [Hbet][Tf_2N] in water and refluxing for 12 hours, [$Eu_2(bet)_8(H_2O)_4$][Tf_2N]$_6$, [$Eu_2(bet)_8(H_2O)_2$][Tf_2N]$_6$·2H_2O and [$Y_2(bet)_6(H_2O)_4$][Tf_2N]$_6$ could be isolated.[28] The metals can be extracted from the ionic liquid by an acidic aqueous solution, and the ionic liquid can be recycled for reuse. Interestingly, [Hbet][Tf_2N] is miscible with water above but not below 55.5 °C, which facilitates the separation procedure. Another way to help the dissolution of 4f- and 5f-element oxides like UO_2, UO_3, Nd_2O_3, Eu_2O_3 and Pr_6O_{11} in ionic liquids like [C_4mim][Tf_2N] (C_4mim = 1-butyl-3-methylimidazolium) is the addition of HNO_3.[29] Other protic acids were less suitable than HNO_3. For the uranium oxides, the existence of [$UO_2(NO_3)_3$]$^-$ could be confirmed (even in the presence of water) by UV/Vis and extended X-ray fine structure (EXAFS) spectroscopy. The formation of complex ion [$UO_2(NO_3)_3$]$^-$ from $UO_2(NO_3)_3$·6H_2O with [N(*n*Bu)$_4$][NO_3] (*n*Bu = *n*-butyl) in [C_4mim][Tf_2N] was studied by absorption, magnetic circular dichroism (MCD) and uranium L_{III} EXAFS spectroscopy.[30] In case of UO_2, the complex anion is probably formed through the oxidation of U^{IV} to U^{VI} by NO_3^-/NO_2^- reduction and a simultaneous complexation with NO_3^-.[29] The kinetics of dissolution and the role of water in the oxidative dissolution process have also been investigated. The first coordination sphere of the uranyl ion when dissolved either as a UO_2X_2 salt (X = nitrate, trifluoromethanesulfonate, perchlorate) or as $UO_2(SO_4)$ in [C_4mim][X] {X = tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)amide} or [N_{441}][Tf_2N] was investigated by combining UV/Vis and EXAFS spectroscopy and molecular dynamic simulation.[31] It was found that the formation of the first coordination sphere results from a competition between the counterions initially bound to the uranyl cation, the IL anions, and, if present, other anions in the solution, such as impurities. The limited solubility of uranyl nitrates and triflates in tetrafluoroborate and hexafluorophosphate ionic liquids can be overcome by addition of Cl^-, which leads to the formation of chlorido complexes. However, UO_2SO_4 seems to be insoluble even when Cl^- is added. The gradual addition of one to four chloride anions to the uranyl cation in [C_4mim][Tf_2N] has also been simulated by molecular dynamics calculations.[32] UO_2^{2+} in neat [C_4mim][Tf_2N] is complexed solely by five Tf_2N^- ions. Upon addition of Cl^-, Tf_2N^- gets replaced by chloride anions, [UO_2Cl_4]$^{2-}$ being the most stable complex uranyl anion. [UO_2Br_4]$^{2-}$ was found to be the dominating species when [C_4mim]$_2$[UO_2Br_4] was dissolved in the ionic liquids [C_4mim][Tf_2N] and [$MeBu_3N$][Tf_2N].[33] Neutral ligands, such as triphenylphosphane oxide ($OPPh_3$), can also enter the first coordination sphere of the uranyl cation, forming stable complexes in ILs that contain weakly coordinating anions. By dissolving uranyl perchlorate in [C_4mim][NfO] (NfO: nonafluorobutanesulfonate), the formation of a fourfold complex of [UO_2]$^{2+}$ and $OPPh_3$ can be detected in the liquid phase by ^{31}P NMR spectroscopy and in the solid by single-crystal X-ray structure analysis.[34] Molecular dynamic studies of homoleptic hexachlorido complexes of U^V, U^{IV} and U^{III} in [C_4mim][Tf_2N] or [N_{1114}][Tf_2N] reveal that [UCl_6]$^{3-}$ is surrounded by a first coordination shell exclusively formed by [C_4mim]$^+$ or [N_{1114}]$^+$, whereas in the cases of [UCl_6]$^{2-}$ and [UCl_6]$^-$, the Tf_2N^- anion is able to enter the first coordination sphere.[35] It is noteworthy that [C_4mim]$^+$ shows a stronger interaction with [UCl_6]$^{3-}$ than [N_{1114}]$^+$ due to its higher hydrogen bonding capability. The UV/Vis absorption spectra of uranyl bis(trifluoromethylsulfonyl)amide, uranyl perchlorate, uranyl nitrate and uranyl acetate as well as that of a 18-crown-6 complex have been studied in the ionic liquids [C_4mpyr][Tf_2N], [C_4mim][Tf_2N], [C_6mim][Tf_2N], [C_6mim]Br and [C_6mim]Cl with the aim to investigate the coordination and ligand sphere of the uranyl cation.[36] It was found that the spectra in the presence of chloride, nitrate and acetate are comparable to those in acetone and acetonitrile. The bis(trifluoromethylsulfonyl)amide anion of the ionic liquid has apparently no influence on the optical spectra of the uranyl anion and, in consequence, was thought to be noncoordinating when stronger competing ligands such as halides are present (see above). In the case of wet ionic liquids, water was found in the first coordination sphere of uranium(VI). The formation of chlorido complexes of Np^{IV} and Pu^{IV} in [C_4mim][Tf_2N] and [C_4mim][Tf_2N]/[C_4mim]Cl mixtures have also been studied.[37] Upon dissolution of [C_4mim]$_2$[$AnCl_6$] (An = Np, Pu) in [C_4mim][Tf_2N], the hexachlorido complex, [$AnCl_6$]$^{2-}$, obviously remains intact, even upon addition of water. Addition of [C_4mim]Cl to these solutions seems to lead to the formation of higher chlorido complexes. It appears that [$AnCl_6$]$^{2-}$ complexes enhance the hydrolysis of [PF_6]$^-$ ionic liquids.[38] Solutions of $Eu(OTf)_3$ and $Cm(ClO_4)_3$,[39] and in addition those of $Eu(ClO_4)_3$ and $Am(ClO_4)_3$,[40] in [C_4mim][Tf_2N] were studied by time-resolved laser fluorescence spectroscopy (TRLFS). The measurements point to two species with similar coordination sphere. The influence of the quencher Cu^{II} on the fluorescence emission behaviour of Eu^{III} and Cm^{III} was studied in [C_4mim][Tf_2N] and for Eu^{III} also in 1-butyl-1-methylpyrrolidinium bis[(trifluoromethylsulfonyl)amide]. Whilst Cu^{II} quenches the emission of Eu^{III}, for Cm^{III} no significant influence on the decay of the excited state could be observed. This circumstance was attributed to a stronger covalent metal–ligand interaction for the actinide cation. TRLFS was also used to study the dissolution and complexation of some Eu^{III}, Cm^{III} and Am^{III} salts by N_3^- in $[C_4mim][Tf_2N]$.[41] Whilst for Eu^{III} a comparatively fast complexation by N_3^- was evidenced, the same process occurs more slowly for the trivalent actinides. This may be of relevance for separation purposes. This ligand exchange can be evidenced not only by X-ray structure analysis but also by cyclic voltammetry.[42] $Yb(OTf)_3$ (OTf = triflate, trifluoromethanesulfonate) dissolves in the triflate ionic liquid $[C_4mpyr][OTf]$ (C_4mpyr = *N*-propyl-*N*-methylpyrrolidinium) upon forming the complex anion $[Yb(OTf)_6]^{3-}$ (Figure 1).[43]

$$Yb(OTf)_3 + 3[C_4mpyr][OTf] \rightarrow [C_4mpyr]_3[Yb(OTf)_6]$$

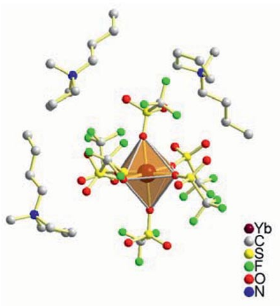


Figure 1. Cut-out of the crystal structure of $[C_4mpyr]_3[Yb(OTf)_6]$.

Dissolution of $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$ yields $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ (Figure 2), where the Tf_2N^- ligand has been replaced by the stronger Lewis basic OTf^- in the coordination sphere of Yb^{3+}.

$$Yb(Tf_2N)_3 + 6[C_4mpyr][OTf] \rightarrow [C_4mpyr]_4[Yb(OTf)_6][Tf_2N] + 2[C_4mpyr][Tf_2N]$$

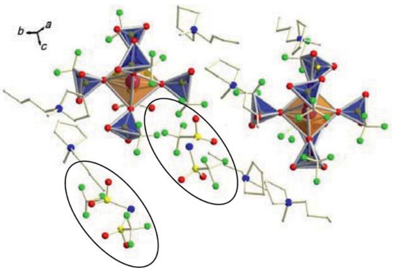


Figure 2. Part of the crystal structure of $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$: noncoordinating Tf_2N encircled, coordinating SO_3R groups shown as tetrahedra.

In compounds crystallized from such solutions, the Tf_2N^- anion is only found as a noncoordinating anion. Similar observations have been made for lanthanide iodides in $[C_4mpyr][Tf_2N]$, where compounds such as $[C_4mpyr]_4[LnI_6][Tf_2N]$ crystallize from LnI_3 solutions.[44] If $[C_3mpyr][Tf_2N]$ is used as the solvent, an extra formula unit of the IL is not included in the crystal structure for packing reasons.[45] In order to elucidate the coordination of trivalent lanthanides in commonly used bis(trifluoromethylsulfonyl)amide-based ionic liquids, lanthanide bis(trifluoromethylsulfonyl)amides $Ln(Tf_2N)_3$ (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Lu) were dissolved in $[C_4mpyr][Tf_2N]$. From such solutions, compounds with a general composition of $[C_4mpyr]_2[Ln(Tf_2N)_5]$ for the larger lanthanides, Ln = Pr–Tb, and $[C_4mpyr][Ln(Tf_2N)_4]$ for the smaller lanthanides, Ln = Dy–Lu, could be crystallized according to

$$Ln(Tf_2N)_3 + 2[C_4mpyr][Tf_2N] \rightarrow [C_4mpyr]_2[Ln(Tf_2N)_5], \ (Ln = La–Tb)$$

$$Ln(Tf_2N)_3 + [C_4mpyr][Tf_2N] \rightarrow [C_4mpyr][Ln(Tf_2N)_4], \ (Ln = Dy–Lu)$$

The larger lanthanides are ninefold coordinated by four bis(trifluoromethylsulfonyl)amide ligands binding in a chelating mode and one additional ligand anion coordinating in a monodentate fashion to the metal (Figure 3).[46] The smaller lanthanides prefer a coordination number of eight, which is realized by four anions binding in a chelating fashion. Such a local surrounding was also found in the solid-state structure of $[C_4mim][Y(Tf_2N)_4]$.[47]

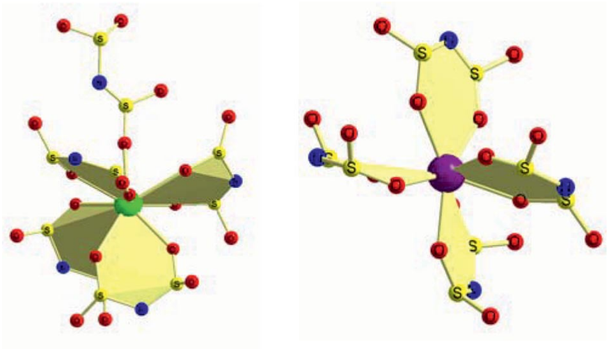


Figure 3. Local lanthanide cation surrounding for the larger (Ln = La–Tb) and smaller (Ln = Dy–Lu) atoms in $[C_4mpyr]_n[Ln(Tf_2N)_{3+n}]$, the CF_3 groups are omitted for clarity.

The compounds $[C_4mpyr]_2[Ln(Tf_2N)_5]$ (Ln = La–Tb) are ionic liquids themselves with melting points below 100 °C (Figure 4 and discussion below).

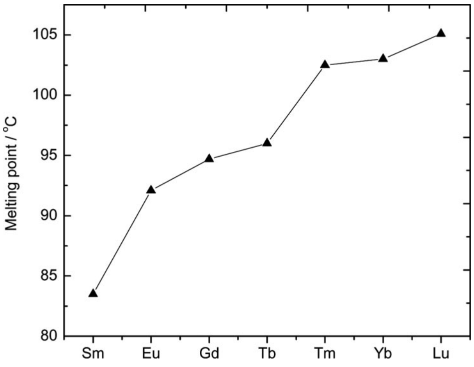


Figure 4. Melting points of $[C_4mpyr]_n[Ln(Tf_2N)_{3+n}]$.

The solvation of La^{3+}, Eu^{3+} and Yb^{3+} as representatives for a large, medium and small trivalent lanthanide cations, respectively, in $[C_4mim][SCN]$ and $[N_{4441}][SCN]$ (N_{4441} = tributylmethylammonium) was studied by molecular dynamics.[48] A force field for SCN^-, representing both SCN^- as a ligand and SCN^- in the ionic liquid, was developed. The first solvation sphere of Ln^{III} is found to be built by 6 to 8 N-coordinated NCS ligands, depending on the respective Ln^{III} and the ionic liquid. The second coordination shell is formed by 13–14 $[C_4mim]^+$ or 8–9 $[N_{4441}]^+$ cations. A given $[Ln(NCS)_n]^{n-3}$ complex is found to be better stabilized by the imidazolium-based than by the ammonium-based IL. From free energy potential of mean force (PMF) calculations, it can be concluded that the imidazolium-based IL favours higher coordination numbers relative to the ammonium-based ionic liquid. Eu^{III} supports the addition of an eighth SCN ligand to $[Eu(NCS)_7]^{4-}$ in $[C_4mim][SCN]$ but not in $[N_{4441}][SCN]$. Yb^{III} favours the addition of a seventh ligand to form $[Yb(NCS)_7]^{4-}$ in $[C_4mim][SCN]$ but not in $[N_{4441}][SCN]$. In case of La^{III}, the formation of $[La(SCN)_8]^{5-}$ is preferred over $[La(SCN)_7]^{4-}$, which is favoured in both ILs, but the energy difference between the two complex anions is found to be larger in the imidazolium-based IL. This effect was attributed to the larger H-bonding capability of the imidazolium cation compared to that of the ammonium cation.

Many lanthanide compounds have interesting photophysical properties. It is well known that lanthanide(III) luminescence features generally narrow emission bands, long decay times, and a large Stokes shift. Lanthanide compounds have gained enormous attention for their potential use as materials in light-emitting diodes, medical and biological applications. Typical properties of ILs are such that many of them are colourless (or slightly yellowish) and transparent through almost the whole visible and near-infrared spectral region. This makes them very interesting as optical solvents. In fact, most of the studies on the luminescence of lanthanides in ionic liquids are carried out on Eu^{III} because of its superior physico-optical properties. However, by a suitable choice of the coordinating ligands, other Ln^{III} ions can also show good luminescence in ionic liquids. Sm^{III} shows a red luminescence similar to that of Eu^{III}. However, because of the smaller energy gap between the excited level and the next lower energy level, radiationless decay is more likely to occur in Sm^{III} samples. In addition the low absorption coefficients of Sm^{III} hamper an effective excitation and hence strong luminescence. However, when ligands that can act as sensitizers can be used in such a way that they absorb light and then efficiently transfer this energy to Sm^{III}, a strongly enhanced Sm^{III} luminescence can be observed. Indeed, it was found that ligands such as 2-thenoyltrifluoroacetylacetonate, 2-naphtoyltrifluoroacetylacetonate and bis(trifluoromethylsulfonyl)amide are suitable ligands for this purpose, and the luminescence spectra of the respective compounds together with the decay times in $[C_6mim][Tf_2N]$ have been reported.[49] The emission and excitation spectra of anhydrous NdI_3, DyI_3 and TbI_3 in the ionic liquid $[C_{12}mim][Tf_2N]$ were reported. It was found that this ionic liquid is an excellent medium to study the optical properties of lanthanides. However, as soon as water (from the atmosphere) comes into the system, the lifetime is reduced dramatically.[50] It is thought that, if water enters the coordination sphere of the oxophilic lanthanide, efficient vibronic coupling leads to high radiationless decay rates. In case of NIR-emitting lanthanides, only a few O–H vibrations have to be excited to bridge the comparatively small energy gap between the excited state and the ground state of the lanthanide ion. In consequence, radiationless decay is highly likely. Improved photophysical properties, such as a high quantum yield and enhanced photostability are observed when hydrophobic ionic liquids are used and strongly coordinating ligands are present, as was shown for a solution of 1-hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoroacetonate)europate(III) in $[C_6mim][Tf_2N]$.[51] A europium-based luminescent ionogel with good performance could be obtained by first doping an ionic liquid $[C_6mim][Tf_2N]$ with the strongly emissive 1-hexyl-3-methylimidazolium tetrakis(naphthoyltrifluroacetonate)europate(III) and subsequent immobilization within a silica network.[52] The physico-optical properties of $LnCl_3L_2(H_2O)$ and $LnCl_3L(H_2O)_2$ with L = 1,10-phenanthroline and 2,2′-bipyridine were studied in $[C_{12}mim]Cl$.[53] It was confirmed that coordinating chloride ligands increase the energy of the LMCT (ligand to metal charge transfer) state. The influence of water on the luminescence of Eu^{III} in $[C_4mim]Cl$ has been studied.[54] It was shown that in case of moderate (substoichiometric) water content of $[C_4mim]Cl$, no significant amounts of water enter the coordination sphere of Eu^{III}, which would result in diminished luminescence. This is also supported by the formation of $[C_2mim]_3[LnCl_6]$ (Ln = La, Pr, Nd, Sm, Eu, Gd, and Er) from $LnCl_3\cdot xH_2O$ in $[C_2mim]Cl$.[55]

For a few years, ionic liquids have been used as media to trap atypical and unusual f-element salts. By dissolution of f-element metal salts in a variety of ionic liquids, f-element-containing compounds, which often exhibit unusual coordination numbers, modes or geometries in the solid state, can be obtained. For example, the structure of $UO_2(OAc)_2$(meimid) is the first representative compound in which a methylimidazole (meimid) coordinates to an uranyl unit, UO_2^{2+}. If methylimidazole is viewed as a histidine analogue, some interesting information for the behaviour of uranyl salts in biological systems can be derived.[56] By reacting hydrated lanthanide(III) chlorides with 1-ethyl-3-methylimidazolium chloride at different conditions [with or without the addition of HCl (aq), in an open or sealed vial], Rogers and co-workers successfully isolated two crystalline forms of compounds: $LnCl_3(OH_2)_4\cdot2([C_2mim]Cl)$ (Ln = Gd and Er)[57] and $[C_2mim]_3[LnCl_6]$ (Ln = La, Pr, Nd, Sm, Eu, Gd, and Er).[55] The isolation of the mixed-valent neptunium compound $[C_4mim]_5[Np(NpO_2)_3(H_2O)_6Cl_{12}]$ from wet $[C_4mim]_2[NpCl_6]$ in the presence of oxygen is yet another proof of the usefulness of ionic liquids as crystallization media.[58] Heptaaqua(*p*-toluenesulfonato-O)europium(III) bis(*p*-toluenesulfonate) dihydrate, $[Eu(p\mathrm{Tos})(H_2O)_7][p\mathrm{Tos}]_2(H_2O)_2$, could be crystallized from a solution of $Eu(p\mathrm{Tos})_3$ in 1-ethyl-3-methylimidazolium tosylate, $[C_2mim](p\mathrm{Tos})$.[59] The compound signifies the structural link between the long-known lanthanide tosylate hydrates $[Ln(H_2O)_9](p\mathrm{Tos})_3(H_2O)$ with noncoordinating tosylate and $[Ln(H_2O)_6(p\mathrm{Tos})_2](p\mathrm{Tos})_2(H_2O)_3$ in which two tosylate groups coordinate to the lanthanide cation. The octanuclear europium cluster $[C_4mpyr]_6[Eu_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(\mu_2\text{-}OTf)_{14}(OTf)_2](HOTf)_{1.5}$ could be obtained from wet $[C_4mpyr][OTf]$.[60] The oxygen-centred Eu_8-cluster polyhedron can be described as a bicapped octahedron or a triangulated dodecahedron. Each of the triangular faces of the cluster is capped by one μ_3-hydroxo group. Fourteen μ_2-triflate ($CF_3SO_3^-$) anions bridge the cluster edges via oxygen atoms. Together with two terminally coordinating triflate anions, they complete the cluster unit.

Lanthanide-Containing ILs

[C_3mim][Eu(Tf_2N)$_4$], [C_4mim][Eu(Tf_2N)$_4$] and [C_4mpyr]$_2$[Eu(Tf_2N)$_5$] represent the first f-element ionic liquids in which the lanthanide cation is not surrounded by additional, neutral co-ligands. These ionic liquids show a strong red luminescence typical for Eu^{III}. The decay times of luminescence of about 2 ms in the liquid state together with a small emission line width and high colour purity of emission renders them interesting for certain applications.[61] Similarly, the optical properties of [C_4mpyr]$_2$[Pr(Tf_2N)$_5$], which has a melting point just above 100 °C, have been studied by luminescence spectroscopy.[62] All of the liquid state spectra show not only an astonishingly well-resolved but also strong emission from the ^3P_J (J = 0,1) levels. Ionic liquids like [C_4mim][Tb(hfacac)$_4$] (Figure 5) or [C_4mpyr][Tb(hfacac)$_4$] (hfacac = hexafluoroacetylacetonate) can be obtained by replacing the comparatively weakly coordinating Tf_2N^- with hfacac.[63] These show the typical strong green emission of terbium. Also the neodymium compound [C_4mim][Nd(hfacac)$_4$] was described.[64]

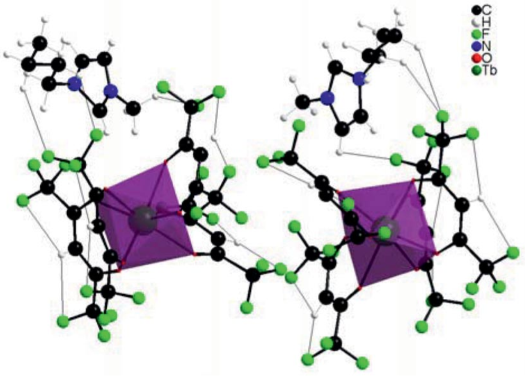


Figure 5. Asymmetric unit of [C_4mim][Tb(hfacac)$_4$] (**1**). C-H···F hydrogen bonds are presented by dotted grey lines.

[C_4mim][Eu(DTSA)$_4$] and [C_4mim]$_2$[Eu(DTSA)$_5$] are analogues of the lanthanide–Tf_2N ionic liquids where the bis(trifluoromethylsulfonyl)amide ligand is replaced by ditoluenesulfonylamide (DTSA).[65] Fluorescence measurements reveal that the materials exhibit a strong red luminescence of high colour purity. The room-temperature ionic liquids [C_6mim]$_{5-x}$[Dy(SCN)$_{8-x}$(H_2O)$_x$] (x = 0–2) also show excellent photophysical properties.[66] They exhibit a bright yellow luminescence. However, the luminescence lifetimes depend on the number of water molecules in the coordination sphere of the trivalent lanthanide ion. The Dy ($^4F_{9/2}$) lifetime of [C_6mim]$_3$[Dy(SCN)$_6$(H_2O)$_2$] at room temperature is 23.8 µs. For [C_6mim]$_4$[Dy(SCN)$_7$(H_2O)], the lifetime is 40.34 µs. As expected, the anhydrous compound [C_6mim]$_5$[Dy(SCN)$_8$] shows the longest lifetime of the excited state with 48.4 µs. Additionally, these dysprosium ionic liquids show a strong response to externally applied magnetic fields and are far superior to the known transition metal ionic liquids because of the extremely high effective moment of Dy^{III} (Figure 6). In consequence, they represent the first examples of room-temperature ionic liquids that combine magnetic and luminescence properties.

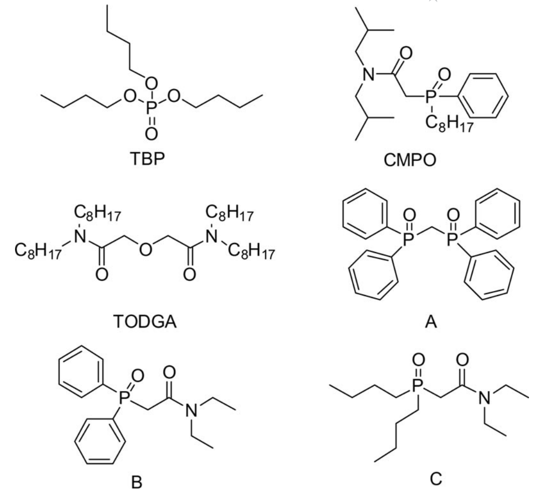
Figure 6. Response of the ionic liquid [C_6mim]$_3$[Dy(SCN)$_6$(H_2O)$_2$] to a neodymium magnet.

Molecular dynamic studies show that in these liquids the coordination numbers of Ln^{III} are the same as in diluted lanthanide salt solution. The fluid behaviour apparently mainly arises from a diffusion of the [C_4mim]$^+$ cations around a quasi-frozen network of anionic complexes.[48]

Extraction

IL/aqueous biphasic separation/extraction is an important process for the purification of lanthanides and treatment of radioactive waste. Removal of actinides from solution and separation from lanthanides are commonly carried out with dodecane, kerosene and chlorinated solvents as the extracting phase. However, safety and human health concerns arise from their low flash points. Substituting the volatile organic compounds (VOCs) by ILs as the extracting phase would minimize the potential hazards. Studies have shown that hydrophobic ionic liquids show better performance than hydrophilic ones and can be used as an alternative for the organic phase in liquid/liquid solvent extraction systems. ILs as the extracting phase have some significant advantages over the conventional VOCs, such as kerosene; for example, they may have low vapour pressure and are usually nonflammable. Low vapour pressure means less loss by evaporation of mixtures.[9a] The enormous quantity provides a large reservoir during the extraction process, whereas nonflammability indicates that ILs are safer than normal organic solvents. These are indeed important factors for both industrial production and scientific research in the field. It was proposed that more than 10^{18} simple organic salts might be potential ILs, which could be prepared by varying the substitution patterns and anion choices as well as using binary, ternary and higher-order suitable ILs that can be used in the separation/extraction of lanthanide and actinide ions. It is also important to note that ILs were shown to be able to withstand α and γ radiation.[67]

It was observed that the extraction yields of lanthanides such as La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+} and Y^{3+} from aqueous HNO_3 solutions with CMPO [*n*-octyl(phenyl)-*N*,*N*-diisobutylcarbonoylmethylphosphane oxide] in [C_4mim][PF_6] were higher than those in dodecane.[68] In total, lower CMPO concentrations could be used, and at the same time an enhanced selectivity was achieved. Stripping of the metal ions from the IL solution was accomplished by using aqueous solutions of acetohydroxamic acid and guanidine carbonate or diethylenetriamine pentaacetic acid and guanidine carbonate or ethylenediamine tetraacetic acid and guanidine carbonate. The most suitable medium for stripping turned out to be a mixture of citric acid, formic acid and hydrazine hydrate in water. A similar investigation was also carried out for the extraction of americium(III) from a nitric acid medium by a solution of TBP (tri-*n*-butylphosphate) and CMPO in [C_4mim][Tf_2N]. The effect of the concentration of nitric acid, CMPO, [C_4mim][NO_3], $NaNO_3$ and TBP and temperature on the distribution ratio of americium(III) was studied. By carrying out the extraction in [C_4mim][Tf_2N], the amount of CMPO needed can be minimized by a factor of four. The distribution of americium(III) decreases with the increase in temperature. And importantly, more than 95% of americium could be stripped by using 1.0 M oxalic acid in ten stages.[69] The extraction of Eu^{3+} from an aqueous nitrate solution with *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine is better when using [C_6mim][Tf_2N] as the extracting phase than with trichloromethane.[70] Recovery of the metal ion from the IL solution could be achieved by simply lowering the pH. Extraction of Sm^{3+}, Eu^{3+}, Gd^{3+} and Dy^{3+} from their acidic nitrate solutions by 1-hydroxy-2,5-pyrrolidinedione was successful with [C_4mim][Tf_2N] or even better with [C_6mim][Tf_2N] as the extracting solvent.[71] A superior liquid/liquid extraction behaviour of *N*,*N*,*N*′,*N*′-tetra(*n*-octyl)diglycolamide (TODGA, Scheme 3) in [$C_n$mim][Tf_2N] was observed for trivalent lanthanides such as La^{3+}, Eu^{3+} and Lu^{3+} (n = 2,4,6) relative to isooctane.



Scheme 3. TBP, CMPO, TODGA, A: tetraphenylmethylenediphosphane dioxide, B: diphenyl(diethylcarbamoylmethyl)phosphane oxide and C: dibutyl(diethylcarbamoylmethyl)phosphane oxide.

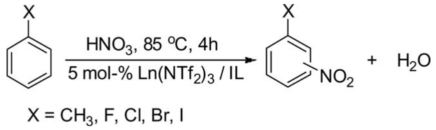
Whilst addition of nitrate in the form of HNO_3 facilitated the extraction into octane by complex formation, the extraction efficiency was increased when using ILs as the extracting phase. Also the extraction selectivity is reversed between the IL and isooctane. In [C_2mim][Tf_2N] the selectivity was Eu^{3+} over La^{3+} over Lu^{3+}. It was shown that TODGA forms a 3:1 complex with La^{3+}, Eu^{3+} and Lu^{3+} in [C_2mim][Tf_2N], whereas in isooctane a 3:1 complex for $La^{3+}$and 4:1 complex for Eu^{3+} and Lu^{3+} were observed. The extraction of La^{3+}, Ce^{3+}, Eu^{3+} and Y^{3+} from their aqueous nitrate solutions with PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) into [C_8mim][Tf_2N] and [C_{12}mim][Tf_2N] was studied.[72] Tf_2N-based ionic liquids with shorter alkyl chains on the imidazolium group showed a solubility of PC-88A that was too low to be useful. [C_8mim][Tf_2N] has a better extraction performance than [C_{12}mim][Tf_2N] and shows the same performance as that of dodecane. Stripping of the lanthanide from the IL solution could be achieved by adding HNO_3. The stripping degree was lower for [C_8mim][Tf_2N] than for [C_{12}mim][Tf_2N]. A three-step process for the extraction of trivalent lanthanides from aqueous solutions involving ionic liquids and supercritical carbon dioxide was developed.[73] It was possible to extract Eu^{3+} and La^{3+} (as analogous for Am^{3+} and Cm^{3+}) from dilute HNO_3 solutions by bringing them into contact with [C_4mim][Tf_2N] containing hexafluoroacetylacetone or, alternatively, tri(*n*-butyl)phosphate. Subsequently, the IL phase containing the lanthanide ion is extracted by supercritical CO_2.[74] The separation of Sc^{3+} from aqueous HNO_3 solutions containing Sc^{3+}, La^{3+}, Y^{3+} and Yb^{3+} could be achieved by extraction with Cyanex 925 (a mixture of branched chain alkyl phosphane oxides) into [C_8mim][PF_6].[75] Pure ionic liquids can also be used for extraction and separation: Ce^{4+} could be separated from nitric acid solutions containing Th^{4+} and Ce^{3+}, Gd^{3+} and Yb^{3+} as representatives for large, medium and small trivalent lanthanide ions by the ionic liquid [C_8mim][PF_6] when the pH was carefully tuned.[76] Ce^{4+} could be quantitatively stripped from [C_8mim][PF_6] by water. The use of ILs may substitute the organic phase, and they are the extracting agent at the same time.[77] Task-specific ionic liquids tris(octylmethylammonium) thiosalicylate, tris(octylmethylammonium) thiocyanate and tris(octylmethylammonium) methionate were used for extracting the uranyl ion from aqueous nitrate solutions.[78] It was found that tris(octylmethylammonium) thiosalicylate and tris(octylmethylammonium) thiocyanate were able to extract uranium almost quantitatively. Back extraction was successful through addition of HNO_3. Also the extraction of Ln (Ln = La–Nd, Sm–Lu, Y) by *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-3-oxapentanediamide without the presence of [C_4mim][Tf_2N] and [C_4mim][PF_6] from aqueous HNO_3 acidic solutions to dichloromethane was studied.[79] When the ILs were added to the extracting phase, a better extraction of the trivalent lanthanide ion from the aqueous to the organic phase was observed. This effect has been ascribed to the hydrophobic nature of the IL anion. The [C_4mim][Tf_2N] showed a performance superior to that of [C_4mim][PF_6]. A similar study was performed by using tetraphenylmethylenediphosphane dioxide, diphenyl(diethylcarbamoylmethyl)phosphane oxide and dibutyl(diethylcarbamoylmethyl)phosphane oxide as the extractants.[80]

Electrochemistry

It has been shown that the extraction of UO_2^{2+} to an ionic liquid can also be combined with an electrochemical recovery. It is possible to electrodeposit uranium oxide (possibly UO_2) from UO_2^{2+} in [C_4mim]Cl.[81] The electrochemical behaviour of 25 mmol/L uranyl nitrate in [C_4mim]Cl was investigated under atmospheric conditions with a glassy carbon working electrode and a platinum quasi-reference electrode at temperatures of 343–373 K by using cyclic voltammetry, chronopotentiometry and square waves.[82] At high temperatures, the cathodic peak potential shifts for the reduction of U^{VI} to U^{IV} towards more negative potentials. Also, higher uranyl nitrate concentrations are observed at more negative the cathodic peak potentials. UO_2 is found to form irreversibly at the glassy carbon working electrode. Investigations of the electrochemistry of $Cs_2UO_2Cl_4$ and $UO_2Cl_2 \cdot nH_2O$ in [C_4mim]Cl by cyclic voltammetry at 80 °C in argon by using a glassy carbon working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode with a liquid junction with [C_4mim][BF_4] show a quasi-reversible reduction of $[UO_2Cl_4]^{2-}$ to $[UO_2Cl_2]^{3-}$ with a redox potential of –0.690 V vs. Ag/AgCl.[83] The electrochemical behaviour of Eu(Tf_2N)$_3$ and Sm(Tf_2N)$_3$ in the ionic liquids [N_{2225}][Tf_2N] (N_{2225} = triethylpentylammonium), [N_{2228}][Tf_2N] (N_{2228} = triethyloctylammonium), [$N_{222(12)}$][Tf_2N] (triethyldodecylammonium) and [P_{2225}][Tf_2N] (N_{2225} = triethylpentylphosphonium), [P_{2228}][Tf_2N] (N_{2228} = triethyloctylphosphonium), [$P_{222(12)}$][Tf_2N] (triethyldodecylphosphonium) as well as [P_{4441}][Tf_2N] (P_{4441} = tributylmethylphosphonium), [P_{4448}][Tf_2N] (P_{4448} = tributyloctylphosphonium) and [$P_{444(12)}$][Tf_2N] (tributyltetradecylphosphonium) was studied.[84] The difference between the cathodic and anodic peak potentials for Eu^{III}/Eu^{II} in [P_{2225}][Tf_2N] was only slightly larger than expected for an ideal reversible reaction. The redox potential for Eu^{III}/Eu^{II} was determined to be –0.15 V vs. Fc/Fc^+; for Sm it was –1.4 V vs. Fc/Fc^+. Electrodeposition of thin layers (40–700 nm) of samarium and cobalt/samarium could successfully be achieved from solutions of Co(Tf_2N)$_2$ and Sm(Tf_2N)$_3$.[85] The deposition potential strongly influences the morphology of the deposits. Increasing the temperature yielded deposited layers of better quality.

Lanthanide-Mediated Catalysis in ILs

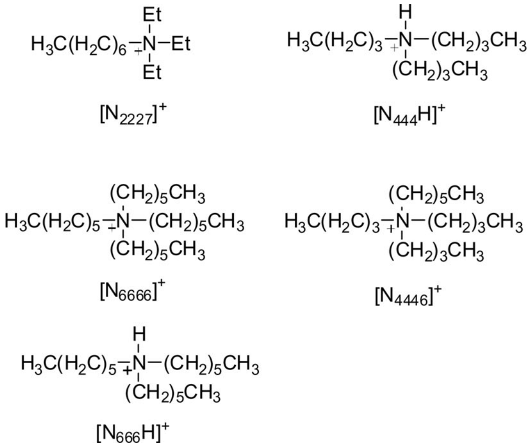
Nitration of aromatic compounds is one of the most important fundamental reactions in the chemical industry, providing very important intermediates for the preparation of various compounds (Scheme 4).



Scheme 4. Nitration of substituted benzenes.

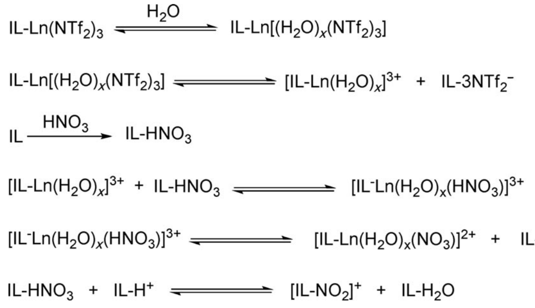
Recently, the use of lanthanide bis[(trifluoromethyl)-sulfonyl]amides {Ln(Tf_2N)$_3$, Ln = La, Sm and Yb} as effective catalysts in quaternary ammonium ionic liquids ([N_{444}H][Tf_2N], [N_{666}H][Tf_2N], [N_{2227}][Tf_2N], [N_{4446}][Tf_2N] and [N_{6666}][Tf_2N]) for the nitration of substituted benzenes was established.[86] Nitric acid with a concentration of 95% turns out to be the best nitrating agent.

The structure and chemical nature of the IL cation has a great effect on the nitration of aromatic compounds. Approximately, the yield of nitrotoluene increases with the decrease in the value of the Kamlet–Taft parameter, β, of the respective ILs (Scheme 5). The highest product yield (24 h, 75.9%) was observed in [N_{444}H][Tf_2N], which had the smallest β value. This might be ascribed to the higher Brønsted acidity and polarity of [N_{444}H][Tf_2N]. When compared with the influence of different concentrations of nitric acid and different structures of IL cations, changing the metal cations has a small effect on the product yield. All the lanthanide bis[(trifluoromethyl)sulfonyl]amides {Ln(Tf_2N)$_3$, Ln = La, Sm and Yb} show catalytic activity in the nitration reaction and achieve nearly the same level of equilibrium in different ILs. It is worthy to note that this catalyst/ionic liquid system could be recovered by simple procedures and recycled for at least five times.[86]



Scheme 5. Quaternary ammonium ILs.

Ceric ammonium nitrate (CAN) is an important reagent for organic oxidizing and nitrating reactions. A series of reactions between naphthalene or 2-methylnaphthalene and CAN in [C_2mim][OTf] was studied at various water contents and different reaction temperatures. A competition between oxidization and nitration was observed. The nitration reaction is favoured at elevated temperature, whereas the oxidization reaction proceeds better in the presence of water. The cerium can be electrochemically oxidized in the IL to the tetravalent state and reused (Scheme 6).[87]



Scheme 6. Proposed mechanism for the formation of NO^{2+}.

In the past few years, thorough investigations in the field of Friedel–Crafts reactions with Sc(OTf)$_3$ as catalyst in ILs have been undertaken.[88] A series of alkenylation reactions of arenes with terminal and internal alkynes with Sc(OTf)$_3$ as catalyst in ionic liquid [C$_4$mim][SbF$_6$] were tested (Table 1 and Scheme 7). Some reactions that are not possible or proceed very slowly in conventional organic solvents can proceed smoothly or better in ionic liquids. Without an IL, the alkenylation of benzene with 1-phenyl-1-propyne in the presence of Sc(OTf)$_3$ proceeds very slowly. A longer time is needed to complete the reaction, but extended reaction times also lead to the formation of undesired side products. The reaction of benzene with phenylacetylene can be completed within 4 h, affording the desired product, 1,1-diphenylethene (see Table 1, entry 5), but when this reaction is carried out in nitromethane, it takes 186 h.[89] Some cationic Pd and Pt catalysts are only effective on electron-rich arenes, whereas Au catalysts cannot catalyze the reaction with internal alkynes. In contrast to these, Sc(OTf)$_3$ in IL can be employed in a wider scope. In the presence of 10 mol-% Sc(OTf)$_3$, the reactions of chlorobenzene with 1-phenyl-1-propyne or diphenylacetylene proceeded very well and were finished in a few hours with satisfying yields, affording the corresponding products as a mixture of *o*-, *m*- and *p*-regioisomers. Moreover, the ionic liquid and the catalyst could be simply separated by decantation of the organic layer and could be reused for subsequent runs without significant loss in activity.

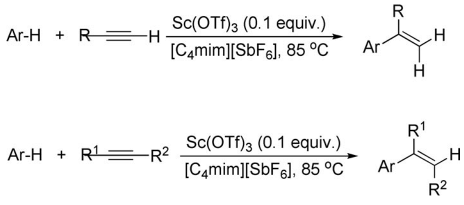
The employment of an ionic liquid in the metal-triflate-catalyzed Friedel–Crafts alkenylation of arenes with alkynes does not only dramatically enhance the catalytic activities, leading to good yields and high regio- and stereoselectivity, but it also makes the recycling of IL and catalyst easier.

Lanthanide triflates not only serve as efficient catalysts for nitration of aromatic compounds and Friedel–Crafts reactions in room-temperature ionic liquids (RTILs), but they are also known to be highly active as hydrofunctionalization catalysts. For Ln(OTf)$_3$-mediated intramolecular HO/cyclization of alkenols, RTILs based on weakly coordinating anions might provide increased Ln^{3+} Lewis acidity due to the minimal coordination of solvent to the Ln^{3+} cation.

Table 1. Metal-triflate-catalyzed Friedel–Crafts alkenylation of arenes with terminal and internal alkynes in [C$_4$mim][SbF$_6$].

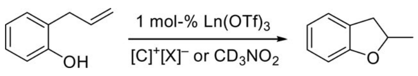
Entry	Ar	R		Time /h	% yield[a]
1	benzene	Ph		4	70
2	*p*-xylene	Ph		4	70
3	*p*-xylene	*p*-CF$_3$–C$_6$H$_4$		22	73
4	*p*-xylene	*p*-Cl–C$_6$H$_4$		12	63
Entry	**Ar–H**	**R^1**	**R^2**	**Time /h**	**% yield[a]**
5	benzene	Ph	Me	4	91
6	benzene	Ph	Ph	2	79
7	*p*-xylene	Ph	Me	4	96
8	*p*-xylene	Ph	Ph	4	80
9	chlorobenzene	Ph	Ph	6	44

[a] Based on alkyne.



Scheme 7. Metal-triflate-catalyzed Friedel–Crafts alkenylation of arenes with terminal and internal alkynes in [C$_4$mim][SbF$_6$].

The intramolecular hydroaloxylation/cyclization of the non-activated alkenols was investigated in different solvents with different lanthanide triflates as catalysts (Scheme 8).[90]



Scheme 8. Intramolecular hydroalkoxylation/cyclization of nonactivated alkenols mediated by lanthanide triflates in ionic liquids.

To investigate the effect of solvent on catalytic activity, CD$_3$NO$_2$ and RTILs were used as solvent separately. In nitromethane, only modest catalytic activity was observed for ytterbium(III), samarium(III) and lanthanum(III) triflates (Table 2, entries 1–3) with a catalytic activity decreasing from Yb^{3+} over Sm^{3+} to La^{3+}. In marked contrast, when the catalytic conversion was carried out in RTILs based on [OTf]$^-$ and [Tf$_2$N]$^-$, the turnover frequency could be enhanced by roughly a factor of 70 (Table 2, entries 6–11), and the reaction time was reduced dramatically. The marked influence of solvent on the reaction rate could be attributed to differences in the Ln^{3+} Lewis acidity in solvents that differ in cation-coordinating strength.[91]

In a large scope of Ln(OTf)$_3$-catalyzed HO/cyclization of primary/secondary aliphatic/aromatic alkenols (Table 3), this synthesis protocol also turns out to be effective for the formation of five- and six-membered oxygen heterocycles. The cyclizations of different alkenyl alcohols [1 mol-% Ln(OTf)$_3$] proceed well with excellent conversions and reasonably large turnover frequencies in 1–24 h at 60–120 °C. The final product can be isolated easily either by extraction with diethyl ether or by vacuum transfer, which avoid the wasting of catalyst and IL and improve the efficiency of recycling. It was also found that the turnover frequencies of

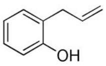
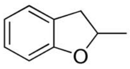
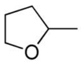
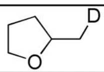
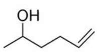
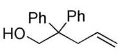
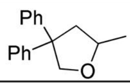
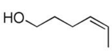
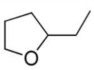
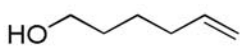
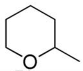
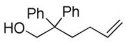
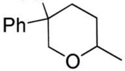
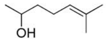
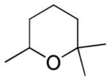
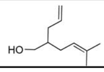
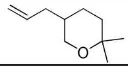
Table 2. Screening of Ln(OTf)$_3$ complexes and reaction media for intramolecular hydroalkoxylation/cyclization.

Entry	Ln^{3+} /mol-%	M^{3+} /Å	Solvent	Time /h	N_t /h^{-1} (°C, %)[a,b]
1	La (5)	1.172	CD_3NO_2	18	0.01 (100, 1)[c]
2	Sm (5)	1.098	CD_3NO_2	18	0.04 (100, 2)[c]
3	Yb (5)	1.008	CD_3NO_2	18	0.10 (100, 9)[c]
4	–	–	[C_2mim][OTf]	18	– (120, –)
5	–	–	[C_1dbu][OTf][d]	18	– (120, –)
6	La (1)	1.172	[C_1dbu][OTf]	3	0.67 (120, 48)
7	Yb (1)	1.008	[C_1dbu][OTf]	3	5.37 (120, 88)
8	Yb (1)	1.008	[C_2mim][OTf]	3	6.37 (129, 93)
9	Yb (1)	1.008	[C_4mim][OTf]	3	6.01 (120, 86)
10	Yb (1)	1.008	[C_2mim][Tf_2N]	3	1.18 (120, 59)
11	Yb (1)	1.008	[C_4mim][Tf_2N]	3	1.07 (120, 52)

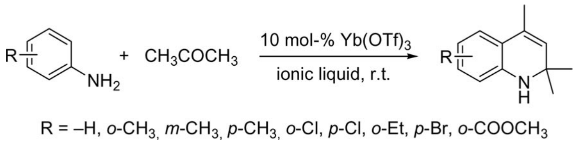
[a] Turnover frequencies determined by ^{1}H NMR spectroscopy by using 1,1,2,2-tetrachloroethane as internal standard. [b] Isolated yield of the purified product. [c] Percent formation of the final product was determined by ^{1}H NMR integration relative to the internal standard because of the low product formation observed. [d] C_1dbu = 1-methyl-1,3-diazabicyclo[5.4.0]undec-7-enium.

the aliphatic/aromatic hydroxyalkene cyclization varies with the Ln^{3+} ionic radius, following the lanthanide contraction[92] (Table 3, entries 4–22), the smallest and most Lewis acidic Ln^{3+} centre being the most efficient.

Table 3. Catalytic alkenol hydroalkoxylation/cyclization mediated by Ln(OTf)$_3$ complexes (1 mol-%) in [C_2mim][OTf].

Entry	Ln^{3+}	Substrate	Product	N_t h^{-1} (°C, yield %)
1 2 3	La Sm Yb			0.82(120,62) 1.58(120,80) 6.37(120,93)
4 5 6	La Sm Yb			0.12(120,⁻) 0.52(120,53) 4.78(120,78)
7	Yb			1.92(120,49)
8 9 10	La Sm Yb			0.51(120,40) 1.14(120,67) 9.24(120,89)
11 12 13	La Sm Yb			0.57(120,61) 1.37(120,82) 46.97(120,95)
14 15 16	La Sm Yb			0.012(90,2) 0.019(90,3) 0.023(90,8)
17 18 19	La Sm Yb			0.36(120,⁻) 0.62(120,73) 1.89(120,88)
20 21 22	La Sm Yb			0.09(120,⁻) 0.24(120,⁻) 9.52(120,90)
23 24 25	La Sm Yb			4.88(90,98) 2.97(90,89) 0.52(90,55)
26 27	La Yb			6.48(60,98) 3.25(60,80)

2,2,4-Trimethyl-1,2-dihydroquinolines are usually used as antioxidants for rubber and polyolefins, food additives, dyes and pharmaceuticals. They can be synthesized either by the Skraup reaction (Scheme 9) or by some violent reactions that require a large amount of strong acid like hydrochloric acid, sulfuric acid or hydrogen fluoride, a Lewis acid like aluminium trichloride or boron trifluoride and temperatures generally above 150 °C. Except for the harsh reaction conditions, another main disadvantage of these synthesis protocols is that the catalyst is destroyed in the workup procedure and cannot be recovered and reused, causing enormous waste.



Scheme 9. Skraup reaction in ILs.

Recently, a new synthesis method allowing for milder reaction conditions was developed with RTILs as the solvent.[93] Anilines were treated with acetone in acetone or some RTILs in the presence of 20%, 10%, 5% or no Yb(OTf)$_3$. In the absence of Yb(OTf)$_3$, this reaction is not possible (Table 4, Entries 1, 5). With Yb(OTf)$_3$ as the catalyst, but with acetone as solvent, the reaction takes place but the yield is very low (40%, even under reflux for 10 h). However, if this reaction is carried out in ILs, the reaction rate and yield are quite obviously improved. The highest yield (81%) can be achieved in [C_4mim][BF_4], in which the reaction only takes 30 min at room temperature.

Table 4. Results of the modified Skraup reaction under different conditions.[a]

Entry	Catalyst (equiv.)	Solvent	Time /min	Reaction temp. /°C	% yield[b]
1	None	[C_4mim][BF_4]	30	room temp.	ND[c]
2	Yb(OTf)$_3$ (0.05)	[C_4mim][BF_4]	30	room temp.	70
3	Yb(OTf)$_3$ (0.1)	[C_4mim][BF_4]	30	room temp.	81
4	Yb(OTf)$_3$ (0.2)	[C_4mim][BF_4]	30	room temp.	81
5	None	Acetone	600	reflux	ND[c]
6	Yb(OTf)$_3$ (0.1)	Acetone	600	reflux	40
7	Yb(OTf)$_3$ (0.1)	[C_4py][BF_4]	30	room temp.	67
8	Yb(OTf)$_3$ (0.1)	[C_4mim][PF_6]	30	room temp.	63
9	Yb(OTf)$_3$ (0.1)	[C_4mim][BF_4]	30	room temp.	81[d]

[a] Entries 1–4 and 5–9 were run with aniline (1 mmol), acetone (3 mmol) and IL (2 mL), and acetone (50 mmol) was used for entries 5 and 6. [b] Isolated yield based on aniline. [c] Not detected. [d] Yb(OTf)$_3$ and [C_4mim][BF_4] were reused five times, and the yields were 79%, 78%, 76%, 70% and 59% in order from the first to the fifth time.

Relative to Sc(OTf)$_3$, Y(OTf)$_3$ and Yb(OTf)$_3$, which are probably the most extensively studied catalysts in lanthanide-mediated catalysis in ILs, Er(OTf)$_3$ is unfrequented. The efficiency of Er(OTf)$_3$ in promoting Diels–Alder reactions between different dienes and dienophiles in ILs was investigated. In most cases, the enhancement of regio- and *endo*/*exo*-selectivity can be observed. An optimized input of catalyst was found to be 10 mol-%.[94] Additionally, the use of ionic liquids as solvents and catalysts for the thia-Michael addition reaction was studied. By employing $Yb(OTf)_3$ as the catalyst (20 mol-%) and $[C_4mim][BF_4]$ as the solvent, the reaction of chalcone with thiophenol can be finished in a shorter time and with a higher product yield relative to parallel reactions carried out in polar or nonpolar organic molecular solvents.[95]

The combination of lanthanide triflate with ionic liquids is sometimes thought as a dream combination for catalysis. S. G. Lee and co-workers screened the catalytic activity of different lanthanide triflates for the cyanosilylation of a variety of aldehydes and ketones in $[C_4mim]$-based ILs with BF_4, SbF_6 and PF_6 as the counteranion. From their results, it is obvious that most lanthanide triflates show significant activity for this kind of reactions (Figure 7), with conversions higher than 86% except for $Pr(OTf)_3$, $Nd(OTf)_3$ and $Dy(OTf)_3$. Among the $[C_4mim]$-based ILs, $[C_4mim][PF_6]$ showed the best performance, which has been ascribed to the in situ anion exchange of OTf with SbF_6 resulting in a more Lewis acidic catalyst.[96]

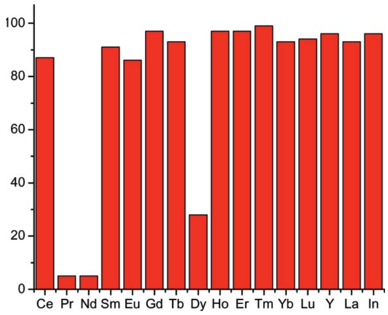


Figure 7. Yields obtained with different lanthanide triflates for cyanosilylation. The conversion was determined by ^1H NMR spectroscopy from the average of three reactions.

Conclusions

The use of ionic liquids in lanthanide and actinide chemistry has led to a number of interesting results in various fields of chemistry. Once a basic understanding of the dissolution and solvation of 4f- and 5f-element compounds in ionic liquids had been established, the benefit of ionic liquids for f-element chemistry could be realized. Ionic liquids offer the possibility to synthesize and crystallize quite uncommon lanthanide compounds. Ionic liquids can be designed in such a way that they become excellent media to study the optical properties of lanthanide compounds. Not only do they show good transparency over a wide range of the optical spectrum, but they can also be made in such a way that radiationless decay by energy transfer from the lanthanide to solvent is far less than in conventional solvents like water or organic solvents such as methanol or tetrahydrofuran. Hydrophobic ionic liquids may replace organic solvents in liquid/liquid f-element extraction processes. Their advantage is not only that they can be made to have a negligible vapour pressure and flammability, which results in a reduced safety hazard, but they can also be tailored to be active extractants. Their wide electrochemical window and large ion conductivity make ionic liquids interesting solvents to study the electrodeposition of even the highly electropositive lanthanide elements. For f-element-catalyzed reactions, higher reaction rates, enhanced selectivity, better immobilization of the catalyst and an easy product recovery have often been observed. Altogether, exciting f-element chemistry has been made accessible by ionic liquids, and many more interesting results can be expected in the future as the field develops.

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