# Rare Earth Metal Containing Ionic Liquids

**Denis Prodius[a], Anja-Verena Mudring[a, b*]**

[a] *Critical Materials Institute, Ames Laboratory, Iowa State University, Ames, Iowa 50011-3020, USA*

[b] *Department of Materials Sciences and Engineering, Iowa State University, Ames, Iowa, 50011-3111, USA*

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As an innovative tool ionic liquids (ILs) are widely employed as alternative, smart, reaction media (vs. traditional solvents) offering interesting technology solutions for dissolving, processing and recycling of metal containing materials. The costly mining and refining of rare earths (RE) together with the at the same time increasing demand for high-tech and energy-related applications around the world urgently requires effective approaches to improve the efficiency of rare earth separation and recovery. In this context ionic liquids appear as an attractive technology solution. This review addresses the structural and coordination chemistry of rare earth based ionic liquids with the aim to add to an understanding of the potential of ionic liquids in the chemistry of rare earths.

*Keywords: rare earth compounds, ionic liquids, coordination chemistry*

**Highlights**

¤We review the synthesis and structural features of known rare earth based ionic liquids

¤Important characteristics of the rare earth based ionic liquids are described

¤Melting point as well as other properties can be tuned to give desirable features by the choice of the rare earth and, most importantly, the ligands and counterions

**Contents**



## 1. Introduction

Chemistry of the rare earths has developed rapidly during the last 30 years due to an enormous number of diverse applications [1]. The production and application of rare earth compounds constitute an important strategic and dynamic segment of the energy production, electronic and chemical industries (Fig. 1). New markets are developing for individual high-purity rare earths, particularly for neodymium and dysprosium for use in high-performance permanent magnets. A variety of motors and actuators depend on permanent magnets in huge quantities (>$10^8$ kg per year) and averages to more than 9.5 g of rare earth magnet per terrestrial [2].

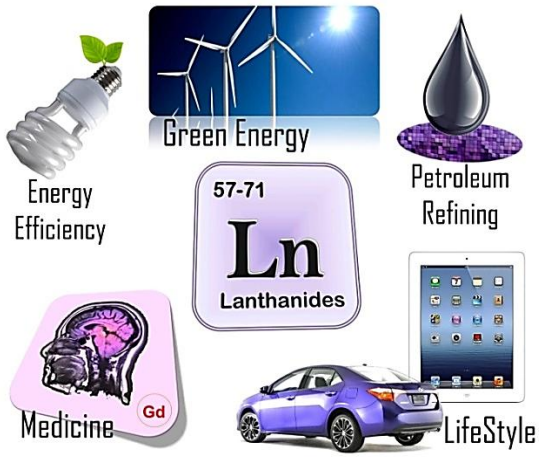



**Fig. 1**: Some applications of rare earths in everyday life.

Most people would be surprised how extensively magnets are used in everyday life. Magnets are being utilized to help us perform certain operations when we drive cars, listen to music, work at our computer or use electrical power from wind farms. Almost 65% of the rare earths used in the United States and Western Europe are consumed in catalysts mainly as FCC catalysts (Fluid Catalytic Cracking) for crude petroleum refining. Contrasting with physical separation processes such as atmospheric or vacuum distillations, the FCC uses the catalyst and heat to break apart the large molecules of gas oil into the smaller molecules comprised of gasoline, distillate, butane/propane and other important products.

*Abbreviations*: ILs, ionic liquids; RE, rare earth; FCC, fluid cracking catalysts; GBCA, Gadolinium Based Contrast Agents; MRI, magnetic resonance imaging; $Tf_2N^-$, bis(trifluoromethanesulfonyl)amide; RTIL, room-temperature ionic liquid; $C_1C_3$pyr, 1-methyl-1-propylpyrrolidinium; $OTf^-$, trifluorosulfonate; CV, cyclic voltammetry; HWP, halfwave potentials; DTSA, ditoluenesulfonylamide; DETCAP, diethyl-2,2,2-trichloroacetylphosphoramidate; $C_2$mim, 1-ethyl-3-methylimidazolium; $C_4$mim, 1-butyl-3-methylimidazolium; $C_6$mim, 1-hexyl-3-methylimidazolium; tta, 2-thenoyltrifluoroacetonate; Hhfacac, hexafluoroacetylacetone; OPC, organic plastic crystal; $C_{12}$mim, 1-dodecyl-3-methylimidazolium cation; $MC_1$mim, 1,2,3-trimethylimidazolium; dca, dicyanamide; tcm, tricyanomethanide; dcnm, dicyanonitrosomethanide; DNtM, dinitromethanide; NtCM, cyanonitromethanide; NtDCM, dicyanonitromethanide; NtNCM, cyanonitronitrosomethanide; $N_{2222}$, tetraethylammonium; CL, cycle; HT, heating transition; CT, cooling transition; Δ*H*, enthalpy of transition; S→L, solid to liquid transition; L→S, liquid to solid transition; G→L, glass to liquid transition; L→G, liquid to glass transition; bet, $Me_3N^+$-$CH_2COO^-$; cmim, N-carboxymethylimidazolium; PMMA, poly(methylmethacrylate.

*Corresponding author. Tel: +515 509 5616; e-mail: *mudring@iastate.edu*

Coordination chelates of gadolinium - Gadolinium-Based Contrast Agents (GBCA) - are intravenous drugs which make certain tissues, abnormalities or disease processes more clearly visible on magnetic resonance imaging (MRI) scans. Also the worldwide need for rare earths has enormously increased due to consumer desire for light weight, compact or super-miniaturized electronic devices such as cell phones, flat panel displays as well as because of an increasing demand for 'green' and energy efficient technologies such as hybrid cars, wind turbines and lighting devices.

The continuous development and improvement of rare earth-based materials for advanced applications together with the fact that rare earths are considered to be critical materials asks for more elaborate non-trivial and advanced synthetic approaches. One of them certainly is the use of ionic liquids (ILs). Ionic liquid chemistry has developed into a tremendously popular field of chemistry over the last decade. The amount of literature, scientific papers as well as patents, still grows exceptionally. It has been recognized that ionic liquids show features that cannot be realized in conventional molecular 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 below. Most times ILs are composed of organic cations and organic or inorganic anions (see Figure 2 for typical IL ion representatives).

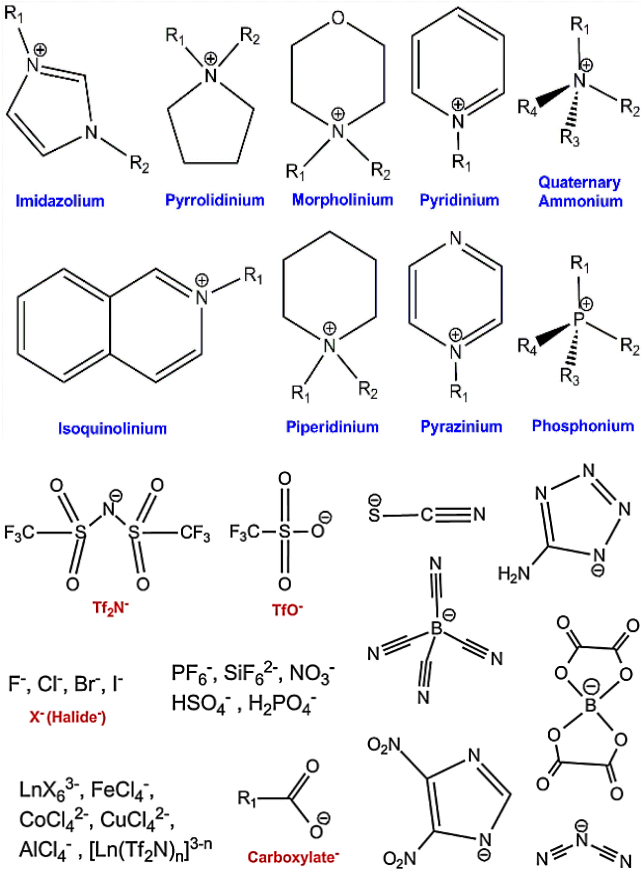



**Fig. 2**: The basic ionic liquid "toolbox": cations (top) and anions (bottom).

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 complexes of high symmetry like $[BF_4]^-$, $[AlCl_4]^-$, $[PF_6]^-$ or $[SbF_6]^-$ are also employed (Figure 2). Today most times alkylsulfates and alkylsulfonates and even more often perfluorinated anions such as triflate, $[CF_3SO_3]^-$ or bis(trifluoromethylsulfonyl)imide $[(CF_3SO_2)_2N]^-$ ($Tf_2N^-$) are utilized. An easy way to incorporate rare earth cations in ionic liquids is by complexation through the above mentioned prominent anions when converting the respective rare earth salt in an appropriate ionic liquid. Examples are the reaction of anhydrous trivalent rare earth iodides with triethylsulfonium iodide or methyl-propylpyrrolidinium iodide [3, 4]. The chlorides can even be obtained from aqueous or alcoholic solutions [4, 5]. Unfortunately, the reaction products have quite high melting points. To lower the melting point of the salt containing the rare earth in the form of a complex anion, it is advisable to switch to large, but unfortunately generally less coordinating anions such as the bis(trifluoromethanesulfonyl)imide, $Tf_2N^-$, anion.

## 2. Rare earth based Ionic Liquids

### 2.1. Perfluorinated complexes and derivatives

The $Tf_2N^-$ ion has gained much attention as an anion in many room-temperature ionic liquids (RTILs), since it has become clear that anions with diffuse charges and negligible capability to form hydrogen-bonding interactions have the highest potential to produce salts that are liquid at room temperature and below [7-10]. Indeed, most crystal structures of ionic liquids with the $Tf_2N^-$ ion revealed no substantial hydrogen bonding between the cation and anion [11-14]. It is, therefore, not surprising that the $Tf_2N^-$ ion has often been considered as weakly or even non-coordinating. Nevertheless, in 2005 Mudring with co-workers successfully realized the synthesis of the first homoleptic $Tf_2N$-complex obtained by interaction of $YbI_2$ with the ionic liquid $[C_1C_3pyr][Tf_2N]$ ($C_1C_3pyr$ = 1-methyl-1-propylpyrrolidinium) [15]. The crystal structure reveals $Yb^{II}$ being coordinated by four $Tf_2N^-$ ions bidentately through their oxygen atoms so that the $Yb^{2+}$ cation is surrounded by eight oxygen atoms in the form of a distorted square antiprism. Two cations of the ionic liquid balance the charge of the complex anion (Figure 3).

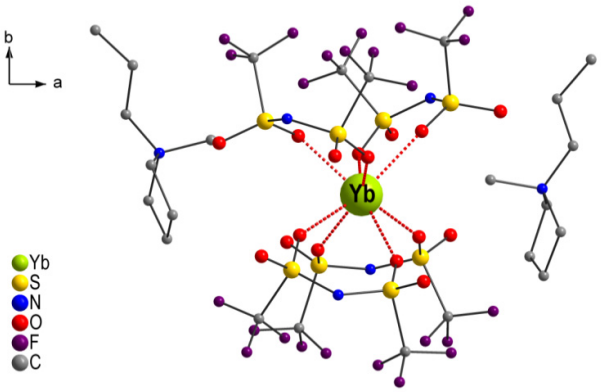



**Fig. 3**: Asymmetric unit of the crystal structure of $[C_1C_3pyr]_2[Yb(Tf_2N)_4]$. Hydrogen atoms are omitted for clarity.

Actually this was the first structure showing the $Tf_2N^-$

ion coordinating in a $\eta^2$-bidentate manner to a metal center to form discrete anionic molecules. Some time later, in the same laboratory, the solvation and ligand exchange reactions of ytterbium(III) were investigated as a model for the late trivalent f-elements [16].

Crystalline $[C_1C_4pyr][Yb(Tf_2N)_4]$ was obtained by carefully cooling a supersaturated solution of $Yb(Tf_2N)_3$ in $[C_1C_4pyr][Tf_2N]$ to room temperature. Structural analysis revealed that the asymmetric unit of $[C_1C_4pyr][Yb(Tf_2N)_4]$ contains two crystallographically independent ytterbium cations both with a trigonal dodecahedral environment of oxygen atoms (Figure 4). This coordination polyhedron is mostly preferred over a cube when ligand–ligand repulsion, like in case of the $Tf_2N^-$ anions, plays a role for the coordination number eight.

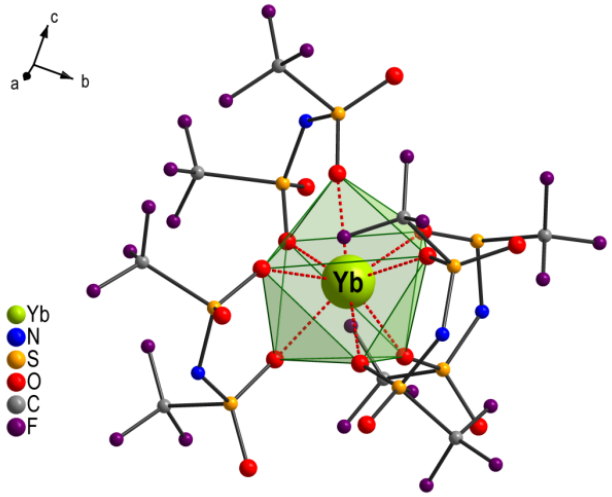
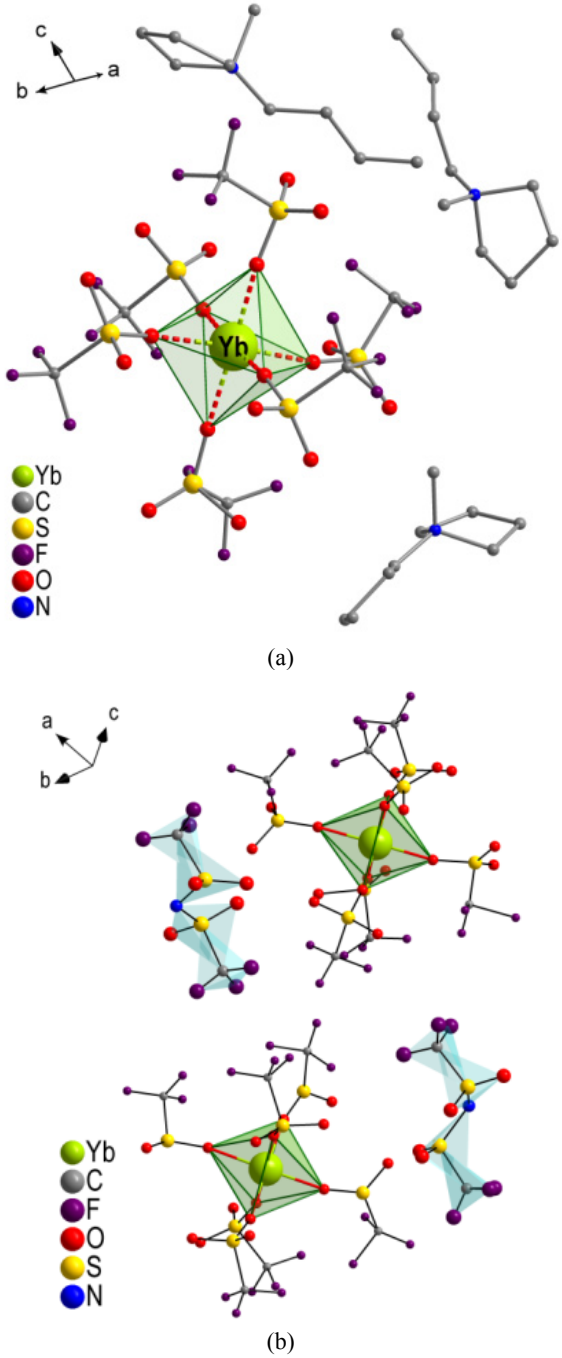



**Fig. 4**: Coordination of Yb(III) in$[C_1C_4pyr][Yb(Tf_2N)_4]$.

Similar to $[C_1C_4pyr][Yb(Tf_2N)_4]$, $[C_1C_4pyr]_3[Yb(OTf)_6]$ could be obtained by reacting $Yb(OTf)_3$ in $[C_1C_4pyr][OTf]$ (OTf = triflate, trifluorosulfonate) [16]. In the complex anion, $[Yb(OTf)_6]^{3-}$, all $OTf^-$ ligands coordinate in a monodentate, nonbridging fashion, which yields isolated octahedral anions embedded in a $[C_1C_4pyr]^+$ matrix (Figure 5). In fact, $[Yb(OTf)_6]^{3-}$ is the first structurally characterized homoleptic triflate complex (Figure 5) and it became clear that ionic liquids with comparatively weakly anions are excellent media to generate unusual coordination environments with weakly coordinating anions which cannot be realized in stronger coordinating, traditional solvents [17].

In order to investigate ligand exchange reactions, $Yb(Tf_2N)_3$ was dissolved in the IL $[C_1C_4pyr][OTf]$. That ligand exchange occurs, becomes evident in the crystalline compound $[C_1C_4pyr]_4[Yb(OTf)_6][Tf_2N]$ (Figure 5b), in which the $Tf_2N^-$ anions are incorporated in the crystal structure only in a noncoordinating fashion.

Thus, the stronger coordinating $OTf^-$ anion is able to completely substitute the less Lewis basic $Tf_2N^-$ anion in the first coordination sphere of the $Yb^{3+}$ ion (Figure 5). The ytterbium cation is surrounded solely by $OTf^-$ anions in an octahedral fashion as in $[C_1C_4pyr]_3[Yb(OTf)_6]$. As expected, such a ligand exchange could not be observed for $Yb(OTf)_3$ in $[C_1C_4pyr][Tf_2N]$. It was also demonstrated that the ion exchange in the rare earth coordination sphere can be efficiently monitored by means of cyclic voltammetry (CV). The measured halfwave potentials (HWP) of the studied systems can be linked to the electron-donor properties of the metal cation. Recently [18], was it was given proof that $Eu(Tf_2N)_3$ can act as both an optical and electrochemical probe for the determination of the Lewis acidity of an ionic liquid anion. The probe technique is based on the assumption that any stronger Lewis basic anion will lead to a replacement of $Tf_2N^-$ in the coordination sphere. The changes can be detected both by cyclic voltammetry and luminescence spectroscopy.




(a)

(b)

**Fig. 5**: (a) The asymmetric unit of $[C_1C_4pyr]_3[Yb(OTf)_6]$; (b) Part of the crystal structure of $[C_1C_4pyr]_4[Yb(OTf)_6][Tf_2N]$ where two noncoordinating $Tf_2N$-ligands are encircled with blue background. $[C_1C_4pyr]^+$ cations and hydrogen atoms are omitted for clarity.

In order to elucidate the coordination of trivalent rare earths in commonly used bis(trifluoromethylsulfonyl)amide-based ionic liquids, rare earth bis(trifluoromethylsulfonyl)amides $RE(Tf_2N)_3$ (RE = Pr, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Lu) were dissolved in $[C_1C_4pyr][Tf_2N]$. From such solutions, compounds with a general composition of $[C_1C_4pyr]_2[RE(Tf_2N)_5]$ for the larger radius rare earths (RE = Pr–Tb) and $[C_1C_4pyr][RE(Tf_2N)_4]$ for the smaller rare earths (RE = Dy–Lu), could be crystallized. The larger rare earths 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 6) [19, 20].

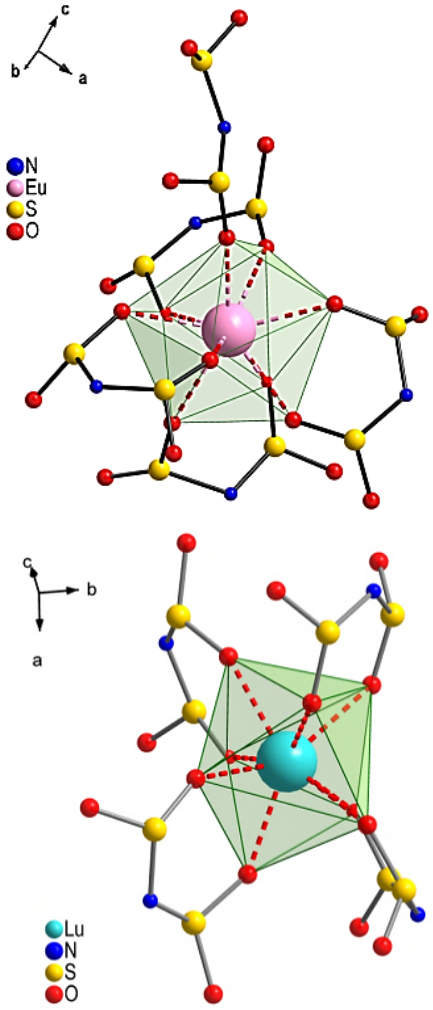



**Fig. 6**: Local rare earth cation coordination environment for the larger (RE = La–Tb; C.N. = 9) (top) and smaller (RE = Dy–Lu; C.N. = 8) (bottom) trivalent cations in $[C_1C_4pyr]_n[RE(Tf_2N)_{3+n}]$, $CF_3$-groups are omitted for clarity.

The smaller rare earths 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 crystal structure of $[C_4mim][Y(Tf_2N)_4]$ (1-methyl-3-butylimidazolium) [21]. The series of compounds $[C_1C_4pyr]_2[RE(Tf_2N)_5]$ (RE = La–Tb) qualify as ionic liquids as they show melting points below 100 °C (Figure 7). The europium compound shows strong luminescence. Changing to imidazolium based cations, a set of highly luminescent ionic liquids were developed (Figure 7b, insert) [22]. All, $[C_3mim][Eu(Tf_2N)_4]$ (1-methyl-3-propyl), $[C_4mim][Eu(Tf_2N)_4]$, and $[C_1C_4pyr]_2[Eu(Tf_2N)_5]$ show excellent photophysical properties, such as long lifetimes of luminescence even at the large $Eu^{III}$ concentration, small line width, and high color purity.

To improve the photophysical properties, Mudring and co-workers continued their research by replacing the $CF_3$ groups of the $Tf_2N$ anion with toluene groups in the ligand (DTSA ≡ ditoluenesulfonylamide) in the hope that the toluene group can serve as a better light–absorbing chromophore (antenna). As the result two new Eu-based ionic liquid systems, $[C_4mim][Eu(DTSA)_4]$ and $[C_4mim]_2[Eu(DTSA)_5]$ were synthesized at 120°C under inert conditions using 1-butyl-1-methylimidazolium as cation [23].

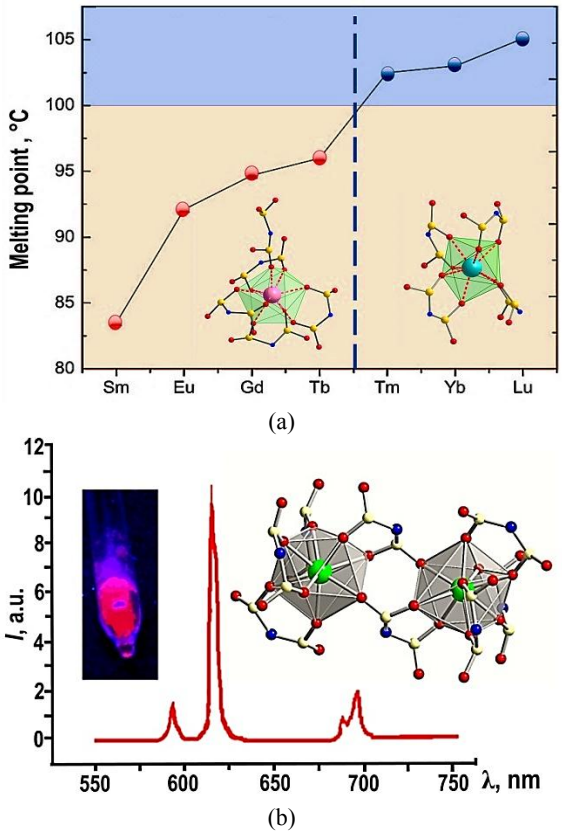



**Fig. 7**: (a) Melting points of $[C_1C_4pyr]_n[RE(Tf_2N)_{3+n}]$; (b) Emission spectrum and structure (as insert, right side) of $[C_3mim][Eu(Tf_2N)_4]$ with photograph of a sample under UV light (insert, left side).

As these compounds solidify below 100°C as glasses they qualify as ionic liquids. Fluorescence measurements show that the materials exhibit a strong red luminescence of high color purity. An easy access to a similar set of compounds was achieved by reacting water/ethanol solutions of 1-ethyl-3-methylimidazolium chloride ($C_2mim$), or 1-butyl-3-methylimidazolium chloride ($C_4mim$), rare earth trichloride and diethyl-2,2,2-trichloroacetylphosphoramidate (DETCAP). The resulting compounds have a common formula of [R][RE(DETCAP)$_4$] (R = 1-ethyl-3-methylimidazolium, RE = Eu (**1**) and Tb (**2**); R = 1-butyl-3-methylimidazolium ($C_4mim$), RE = Eu (**3**), and Tb(**4**)), in which the rare earth

centers are chelated by four chelating pseudo-betadiketonate ligands $(DETCAP)^-$, forming the respective complex anions. Fluorescence measurements at both room and liquid nitrogen temperatures, respectively, show that these materials show intense characteristic Eu(III) or Tb(III) emissions and have long decay times. Their overall quantum yields were determined to be in the range of 30-49% [24].

## 2.2. β-Diketonates

1,3-Diketone based ligands are very popular in the coordination chemistry of rare earths because they can form stable rare earth complexes with a variety of interesting, especially optical and magnetic, properties [25, 26]. However, in the field of ionic liquids, only a very few attempts have been made to introduce 1,3-diketones into ionic liquids for the reason that some 1,3-diketonates can decompose in water. The europium β-diketonate complex [27], 1-hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoroacetonato)europate(III), $[C_6mim][Eu(tta)_4]$ ($C_6mim$ = 1-hexyl-3-methylimidazolium), containing deprotonated 2-thenoyltrifluoroacetonate (tta) as the coordinating ligand proved to be stable in ethanol/water mixtures. This compound exhibits excellent photophysical properties such as a high quantum yield [28].

In 2009 Tang and Mudring prepared two new terbium complexes with hexafluoroacetylacetone (Hhfacac) as the ligand [29]. Reaction of Hhfacac with $[C_4mim]Cl$ or $[C_4mpyr]Br$ and terbium(III) chloride in basic ethanol/water solutions yielded the new compounds $[C_4mim][Tb(hfacac)_4]$ and $[C_4mpyr][Tb(hfacac)_4]$. Crystal structure analysis of $[C_4mim][Tb(hfacac)_4]$ shows that each $Tb^{III}$ ion is eight-coordinated by oxygen atoms from four chelating (hexafluoroacetyl)acetonate anions (Figure 8).

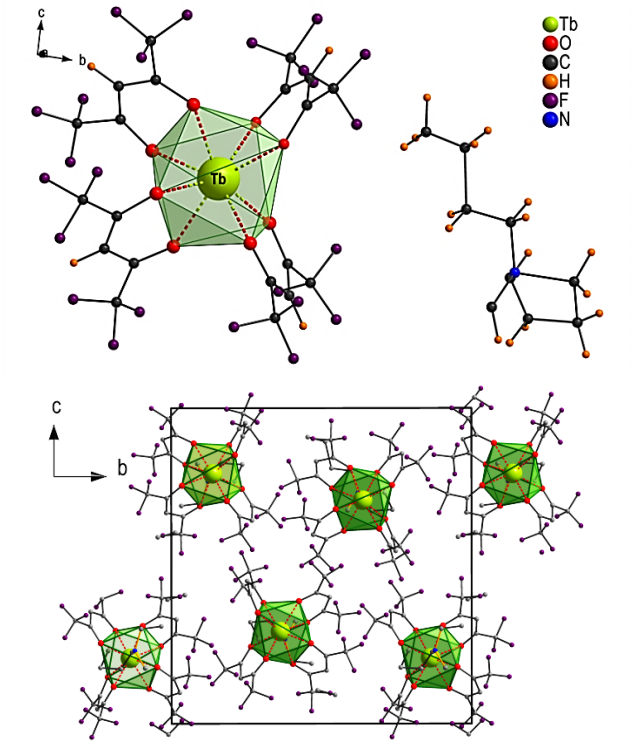



**Fig. 8**: Asymmetric unit of $[C_4mim][Tb(hfacac)_4]$ (top) and 2D layer of $[C_4mim][Tb(hfacac)_4]$ in the *bc* plane (bottom).

The coordination polyhedron around Tb(III) can be best described as a square antiprism. A large amount of C–H···F hydrogen bonds can be found within the $[Tb(hfacac)_4]^-$ anion as well as between the $[C_4mim]^+$ cations and $[Tb(hfacac)_4]^-$ anions. They play a very important role in assembling the structure: through the linkage of intra- and intermolecular C–H···F interactions, they form a 2D layer in the *bc* plane (Figure 8, bottom) which further build a 3D construction. The structure of $[C_4mpyr][Tb(hfacac)_4]$ is very similar and extensive intra- and intermolecular hydrogen bonding was also found in this compound. However, thermal investigations reveal quite different thermal behaviour. Whilst $[C_4mim][Tb(hfacac)_4]$ melts at 116.2 °C and crystallizes at 102.3 °C upon cooling the thermal behavior of $[C_4mpyr][Tb(hfacac)_4]$ indicates the formation of an organic plastic crystal (OPC). In the range of 20 to 150 °C, there are overall four distinct endothermic solid→solid phase transitions which are observed at 38.0, 57.7, 85.8 and 98.4 °C before finally melting occurs at 111.4 °C. The magnitude of the thermal changes of the solid-solid phase transitions can be associated with the rotation of the $[C_4mim]^+$ cation about the molecular axis during the heating process and points to a progressive transformation from a fully ordered crystalline state to an increasingly disordered phase. Both compounds show very strong emission in the visible region of light which are characteristic for the terbium(III) ion.

Incorporation of such rare earth β-diketonates in the ionic liquid component of solid-state ionogels can lead to a novel family of luminescent organic-inorganic hybrid materials. This concept has been proven by Binnemans et al. on the luminescent ionogels based on an immobilized imidazolium ionic liquid doped with a tetrakis-(naphthoyltrifluoroacetonato)-europate(III) complex (Figure 9) [30].

**Fig. 9**: Luminescent organic-inorganic hybrid ionogel with Eu(III)-doped complex under ultraviolet irradiation. Adapted with permission from [30]. Copyright 2006 American Chemical Society.

These materials contain about 80 vol % of ionic liquid and show a very intense, high color purity red photoluminescence under ultraviolet irradiation.

Another interesting photoluminescent ionic liquid ($T_m$ = 63 °C) based on the europium(III) tetrakis(β-diketonate) complex with a tetraalkylphosphonium as counterion was synthesized by Pereira, Laia and co-workers [31]. It was

concluded that basicity enhances the coordination of solvent molecules with Eu(III), while acidity/proticity gives rise to interactions between the solvent molecules and naphthoyltrifluoroacetone.

## 2.3. Thiocyanates

In 2006 Nockemann and co-authors reported on rare earth containing ionic liquids based on the 1-butyl-3-methylimidazolium ($C_4$mim) cation and rare earth thiocyanate anions of the general formula $[RE(NCS)_x(H_2O)_y]_{3-x}$, where x = 6-8; y = 0-2 [32]. The compounds were synthesized by a metathesis procedure starting from stoichiometric amounts of rare earth(III) perchlorate, $NH_4NCS$, and a thiocyanate ionic liquid with the corresponding imidazolium cation. Most of these ionic liquids are found to be liquids or supercooled liquids at room temperature and tend to form glasses rather than crystals upon cooling. A few of the compounds of the type $[C_4mim]_{x-3}[RE(NCS)_x(H_2O)_y]$ (where x = 6 (Y) or 7 forPr, La, Nd, and y = 1 for Pr, La, Nd or 2 (Y)) were crystallized at about 16 °C from the molten state while other representatives are liquids even below room temperature. The crystal structure of $[C_4mim]_4[La(NCS)_7(H_2O)]$ (Figure 10) shows that the coordination polyhedron of the lanthanum(III) ion can be described as a slightly distorted square antiprism and which is completed by seven isothiocyanate anions and one water molecule.

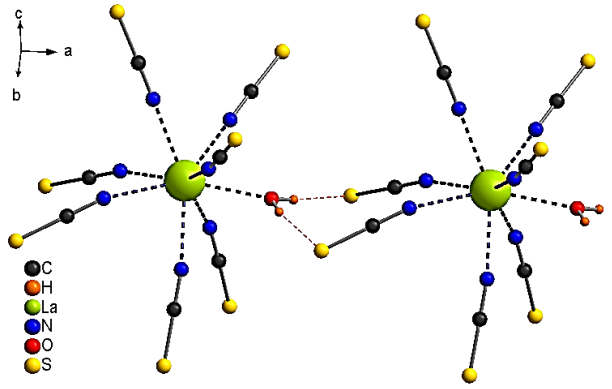



**Fig. 10**: Molecular structure of the anionic unit $[La(NCS)_7(H_2O)]^{4-}$ showing hydrogen bonding from coordinated water molecules to the isothiocyanate anions. The $[C_4mim]^+$ cations were omitted for clarity.

The coordinated water molecule forms strong hydrogen bonds to the isothiocyanate anion of the neighbouring $[La(NCS)_7(H_2O)]^{4-}$ unit resulting in a polymeric stacking of the anions.

This might explain their higher tendency to crystallize. All the compounds exhibit a complete miscibility with other imidazolium-based ionic liquids, including hydrophobic ionic liquids, and in some cases (x = 7 and 8) even in apolar solvents such as dichloromethane. They are also soluble in water, but undergo a complete hydrolysis.

The incorporation of rare earth ions into ionic liquids offers the advantage of a metal ion that has a considerably higher effective magnetic moment than any known transition metal, and thus would give the best response to an external magnetic field. It has been shown that not only the liquid itself can be manipulated by a magnetic field, but also that nonmagnetic (diamagnetic) materials can be transported and separated according to their density and magnetic susceptibility in these liquids [33]. In this context, the new ionic liquids $[C_6mim]_{5-x}[Dy(SCN)_{8-x}(H_2O)_x]$ (x = 0–2, $C_6$mim = 1-hexyl-3-methylimidazolium) were synthesized from $[C_6mim]SCN$, KSCN, and $Dy(ClO_4)_3 \cdot 6H_2O$ according to a slightly modified procedure for similar rare earth based ionic liquids. All reported dysprosium based liquids $[C_6mim]_3[Dy(SCN)_6(H_2O)_2]$, $[C_6mim]_4[Dy(SCN)_7(H_2O)]$, and $[C_6mim]_5[Dy(SCN)_8]$ contain dysprosium(III) as the magnetically active ion with a $4f^9$ electron configuration and show strong response to conventional neodymium magnets (Figure 11) [34].

**Fig. 11:** Response of the orange-colored ionic liquid $[C_6mim]_3[Dy(SCN)_6(H_2O)_2]$ to a neodymium magnet (artistic interpretation).

These dysprosium based room-temperature ionic liquids cannot only be manipulated by a magnet but also exhibit an intense yellow emission of high color purity under UV light excitation, which is characteristic for dysprosium(III). For all the samples, a monoexponential intensity decay was detected, indicating that only one dysprosium(III) species is present.

Using (1*R*,2*S*)-(−)-*N*-methylephedrine ((−)MeEph), a ligand containing a chiral center, a series of multifunctional ionic liquid crystals $[(-)MeEphC_nH_{2n+1}]_5[Dy(SCN)_8]$ (n = 14, 16, 18) have recently been synthesised by Warner and co-workers [35]. A complex counteranion $[Dy(SCN)_8]^{5-}$ is employed, where $Dy^{III}$ provides fluorescent and magnetic properties. These compounds exhibit two characteristic emission peaks ($^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$) in $CH_3CN$ solution and the solid state ($\lambda_{ex}$ = 366 nm). The emission intensities of these compounds were found to be very sensitive to the phase.

## 2.4. Halides and nitrate anions as ligands

An alternative approach for creating new magnetic liquids and magnetorheological fluids is the use of organic cations which lack acidic protons, preventing the establishment of hydrogen bonded networks as seen in the imidazolium salts, for example $(C_2mim)[LaCl_6]$ [36]. It decomposes without melting around 600 K ($C_2$mim ≡ 1-ethyl-3-methylimidazolium). The large trihexyl(tetradecyl)phosphonium cation is a good candidate for formation of metal ion containing RTILs (room temperature ionic liquid), as the massive cation inhibits crystallization. In addition, the trihexyl(tetradecyl)phosphonium cation does not have an acidic proton which can form hydrogen bonds that would facilitate crystallization. Thus, reaction of trihexyl(tetradecyl)phosphonium chloride, $[PR_4]Cl$, with gadolinium trichloride yield the corresponding

paramagnetic $[PR_4]_3[GdCl_6]$ ionic liquid with a $\chi T$ value equal to 7.72 emu·mol$^{-1}$·K (measured at 300 K and H = 0.1 T) [37].

Thus, it is obvious that size and shape of cations as well as their tendency for secondary interactions such as hydrogen bonding are vital in defining the melting points of the salts. Combining the rod-shaped 1-dodecyl-3-methylimidazolium cation, ($C_{12}$mim), with the $[DyBr_6]^{3-}$ complex anion, yielded a material, $[C_{12}mim]_3[DyBr_6]$ (Figure 12), which has not only interesting optical and magnetic properties but also is mesomorphic [38].

The reaction of $DyBr_3$ with $[C_{12}mim]Br$ at 120 °C produces a yellowish highly viscous bulk product which after recrystallization from MeCN (cooling to 5°C) results in a single crystalline product, $[C_{12}mim]_3[DyBr_6]\cdot 2CH_3CN$, as colorless needles. Single crystal X-ray structure analysis reveals the asymmetric unit to contain three crystallographically independent $[C_{12}mim]^+$ cations, one unique $[DyBr_6]^{3-}$ unit and two acetonitrile molecules. The dysprosium ion is 6-fold coordinated by bromide ions in the form of a nearly ideal octahedron (Figure 12, left bottom). Two of the dodecyl chains (cations 1 and 2) adopt all-trans conformations (Figure 12, left top), while the third (cation 3) reveals a gauche conformation ("crank-handle"-like arrangement) around the C7-C8 bond with a torsion angle of 54°. The compound was found to show thermotropic liquid crystalline behavior and forms smectic mesophases which were investigated by hot-stage polarizing optical microscopy and differential scanning calorimetry. Magnetic measurements show for Dy(III) in $[C_{12}mim]_3[DyBr_6]$ an effective magnetic moment of $\mu_{eff}$ = 9.6 μB at room temperature.

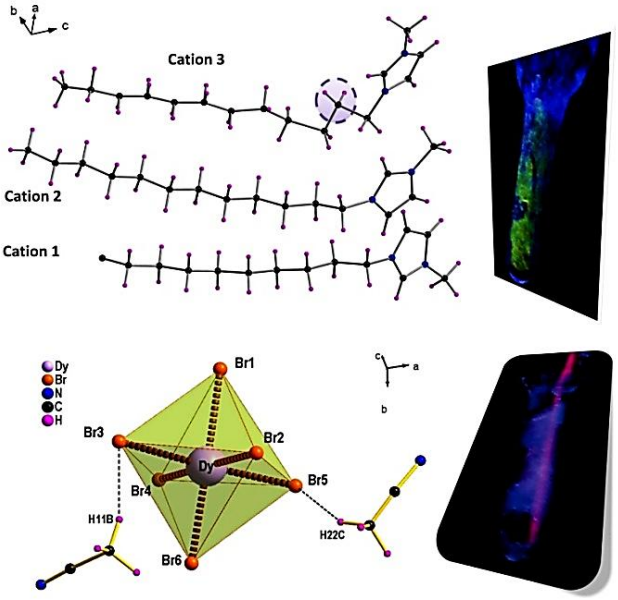



**Fig. 12**: Components of the asymmetric unit in the crystal structure of $[C_{12}mim]_3[DyBr_6]\cdot 2CH_3CN$: three unique $[C_{12}mim]^+$ cations (left top); $[DyBr_6]^{3-}$ octahedron with hydrogen bonded acetonitrile molecules, viewed along the *b* axis (left bottom). Luminescence of liquid crystalline $[C_{12}mim]_3[DyBr_6]$ at room temperature under excitation of a conventional UV lamp: $\lambda_{ex}$ = 254 nm (right top) and 366 nm (right bottom).

The sample shows superparamagnetism and can be manipulated by an external magnetic field. The emission color of $[C_{12}mim]_3[DyBr_6]$ can be tuned from white to orange-yellow by the choice of the excitation wavelength (Figure 12, right). With $\lambda_{ex}$ = 254 nm the common Dy(III) emission is observed which mainly arises from the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition and, in consequence, the sample appears orange (Figure 12, right top). Sample excitation with $\lambda_{ex}$ = 366 nm leads to the blue-whitish luminescence from the imidazolium cation itself.

In the analogous terbium compound the emission color can be switched between white and green [39]. Doping the ionic liquid crystal $C_{12}$mimBr (ILC) with $EuBr_2$, $SmBr_3$, $TbBr_3$ and $DyBr_3$ ILC materials were obtained that show luminescence in the three basic colors [40]. In case of the terbium and dysprosium materials it was possible to tune the emission color by a mere change of the excitation light wavelength.

By reacting europium bromide with $[C_{12}mim]Br$ (1-dodecyl-3-methylimidazolium bromide) in acetonitrile $[C_{12}mim]_4[EuBr_6]Br\cdot CH_3CN$ could be obtained at –15 °C. Its structure is characterized by double layers of $[C_{12}mim]^+$ cations with interdigitated alkyl chains which are separated by anion layers formed by $[EuBr_6]^{3-}$ octahedral and $Br\cdots CH_3CN$ units (Figure 13) [41]. Upon warming to room temperature the compound loses acetonitrile to form the room temperature ionic liquid crystal $[C_{12}mim]_4[EuBr_6]Br$. The temperature dependent structural behavior has been characterized by differential scanning calorimetry and hot-stage polarizing optical microscopy. In the temperature range of –3 to 98 °C this compound adopts a smectic liquid crystal phase. At 77 K it shows a strong red emission with a lifetime of 2.6 ms.

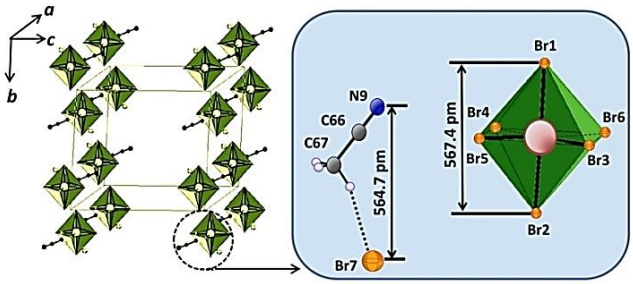



**Fig. 13**: Anion packing in the unit cell of $[C_{12}mim]_4[EuBr_6]Br\cdot CH_3CN$ (left) and comparison of the space requirements of a $Br\cdots CH_3CN$ moiety and a $[EuBr_6]$ octahedron (right). $[EuBr_6]^{3-}$ octahedra are shaded in green with front faces open.

In 2008 Shreeve and co-workers have demonstrated the synthesis and characterization of energetic ionic liquids based on anionic rare earth nitrate complexes [42]. Stoichiometric amounts of various nitrogen containing organic cations (Figure 14), iodide salts, $AgNO_3$, and $La(NO_3)_3\cdot 6H_2O$ were heated under reflux in acetonitrile in the absence of light.


**Fig. 14**: Nitrogen containing ionic liquid cations used for La(III)

and Ce(III) based energetic ionic liquids.

After AgI and the solvent were removed, viscous liquids remained. All these salts have the characteristics of room-temperature ionic liquids and are thermally stable over the range of 185 to 235 °C in a nitrogen atmosphere. According to theoretical calculations, these new compounds potentially can be used as propellants.

Later Tao and co-authors have presented the synthesis and characterization of eleven new water-free lanthanum ionic liquids/ionic liquid crystals $[C_nmim]_3[La(NO_3)_6]$, where (n = 1 to 18) (Table 1 and Figure 15) [43].

Table 1. Physicochemical properties of complexes, from [43].

| *n* | $T_m$ [°C] | $T_d$ [°C] | $\rho$ [g·cm$^{-3}$] |
|---|---|---|---|
| $[C_1mim]_3[La(NO_3)_6]$ | 115 | 303 | 1.74 |
| $[C_2mim]_3[La(NO_3)_6]$ | 51 | 319 | 1.70 |
| $[C_{n\text{-}4}mim]_3[La(NO_3)_6]$ | 29 | 304 | 1.67 |
| $[C_{iso4}mim]_3[La(NO_3)_6]$ | -28 | 310 | 1.62 |
| $[C_{iso5}mim]_3[La(NO_3)_6]$ | 84 | 316 | 1.54 |
| $[C_6mim]_3[La(NO_3)_6]$ | 68 | 315 | 1.55 |
| $[C_8mim]_3[La(NO_3)_6]$ | 57 | 318 | 1.46 |
| $[C_{12}mim]_3[La(NO_3)_6]$ | <RT | 320 | 1.40 |
| $[C_{14}mim]_3[La(NO_3)_6]$ | 36 | 322 | 1.25 |
| $[C_{16}mim]_3[La(NO_3)_6]$ | 51 | 324 | 1.23 |
| $[C_{18}mim]_3[La(NO_3)_6]$ | 63 | 322 | 1.20 |

$T_m$ = melting point; $T_d$ = decomposition temperature; $\rho$ = density at 25 °C

It was possible to crystallize the $[C_1mim]^+$ compound. From its crystal structure (Fig. 15) it becomes clear that the coordination polyhedron around the lanthanum ion is formed by six bidentately coordinating nitrate anions.

The compounds contain no water and all hexanitratolanthanate ionic liquids were found to be stable against moisture and decomposed only at temperatures above 300 °C. Compounds with n = 8, 12, 14, 16, 18 were found to be ionic liquid crystals (DSC, POM) forming a smectic A phase.

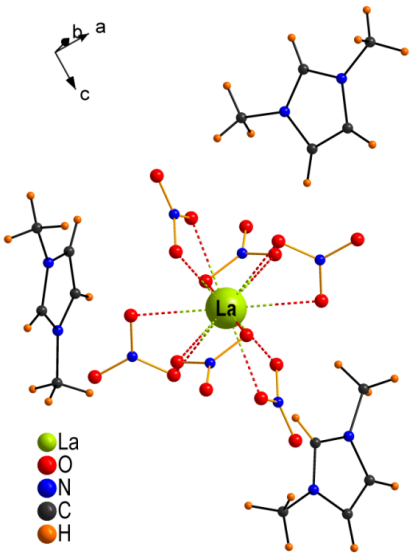



**Fig. 15**: Part of the crystal structure of $[C_1mim]_3[La(NO_3)_6]$.

Using a straightforward reaction beetween 1-alkyl-3-methylimidazolium nitrate and $RE(NO_3)_3{\cdot}6H_2O$ (RE = Nd, Eu) in acetonitrile, sixteen new anhydrous RE-based complexes have been synthesized by Guo-Hong Tao and co-workers (Figure 16) [44-46]. Complexes $[C_nmim]_3[Nd(NO_3)_6]$ (n = 4, 6, 8) are found to be room temperature liquids and display intense near-infrared (NIR) luminescence emission. A series of thermally stable luminescent ionic liquids, $[MC_1mim]_2[Eu(NO_3)_5]$ and $[C_nmim]_3[Eu(NO_3)_5]$ (n = 1, 2, 4, 6, 8), show bright red luminescence of high color purity. Sm(III)-based ionic liquids incorporating hexanitratosamarate(III) anions, $[MC_1mim]_2[Sm(NO_3)_6]$ and $[C_nmim]_3[Sm(NO_3)_6]$ (n = 2, 4, 6, 8), emit orange photoluminescence under ultraviolet (UV) lamp irradiation (Figure 16) and exhibit high stability to heat (decompose in the range of 287–313 °C).

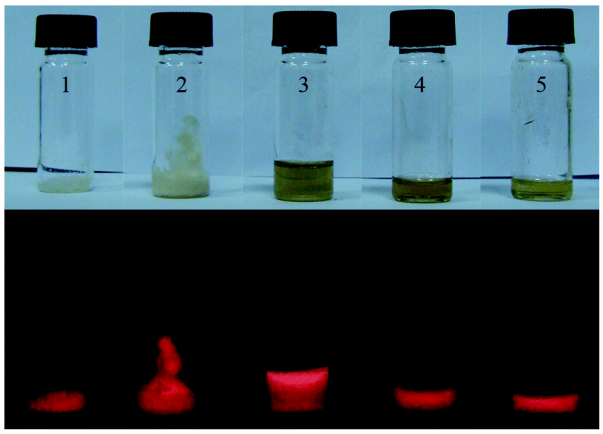



**Fig. 16:** Images of $[MC_1mim]_2[Sm(NO_3)_6]$ and $[C_nmim]_3[Sm(NO_3)_6]$ (n = 2, 4, 6, 8) complexes (from left to right) under daylight (top) and under ultraviolet irradiation (bottom). Reproduced with permission from [46].

## 2.5. Polynitrile compounds

Nitrogen/oxygen rich anions as for example nitrile-/nitroso-/nitro-containing molecules can not only be used for creating energetic ILs. The polynitrile anions, dicyanamide (dca) and tricyanomethanide (tcm), have been integrated into a number of ILs which already found application in organic chemistry and solar cell technology. Their low point symmetry and high charge delocalization make these anions ideal for the design of new ILs. Primary examinations of ligand systems related to pseudohalides, the dicyanonitrosomethanide (dcnm) anion (Figure 17) has been shown to readily coordinate to lanthanoid(III) cations via $\eta^2$-nitroso groups, to form the 12-coordinate homoleptic complexes $[RE(dcnm)_6]^{3-}$ (RE = La–Gd) [47, 48].

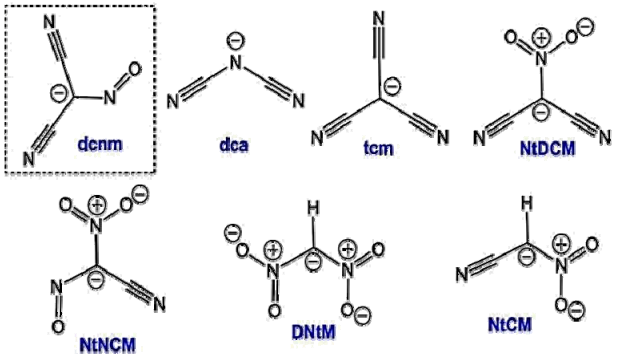



**Fig. 17**: Nitrile-/nitroso-/nitro-containing molecules that have acted as anions in ionic liquids; DNtM=dinitromethanide, NtCM=cyanonitromethanide, NtDCM=dicyanonitromethanide, NtNCM=cyanonitronitrosomethanide.

The melting point (126 °C) of $(N_{2222})_3[La(dcnm)_6]$ ($N_{2222}$ = tetraethylammonium) suggested that an analogue with a larger cation would have a lower melting point, leading to new rare earth based ILs. This hypothesis was indeed confirmed by the synthesis of the first series of lanthanoid-based ILs to contain the dicyanonitrosomethanide ligand, $(N_{4444})_3[RE(dcnm)_6]$ (RE=La, Ce, Pr, Nd) (Figure 18), which displayed polymorph-dependent melting points [49, 50].

This phenomenon was proven by a temperature-dependent in situ synchrotron-based X-ray powder diffraction. An extension of the family of ionic liquids with the $[RE(dcnm)_6]^{3-}$ anion and a variety of cations could be realized via a metathesis reaction between the silver salt of dicyanonitrosomethanide, the respective $RECl_3 \cdot xH_2O$, and a halide salt of the desired counter cation in an alcoholic solution (Eq. 1):

$$\mathbf{6\ Ag(dcnm) + 3(cat)X + RECl_3 \cdot xH_2O \rightarrow}$$
$$\mathbf{\rightarrow (cat)_3[RE(dcnm)_6] + 3AgX\downarrow + 3AgCl\downarrow + xH_2O} \quad \mathbf{(1)}$$

This results in the formation of an insoluble precipitate of silver halide, which is removed from the reaction solution by filtration, leaving the target complex in solution.

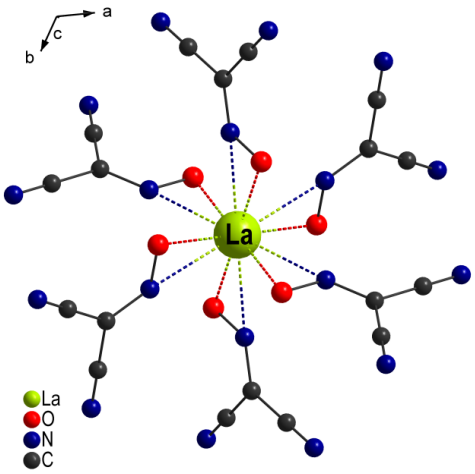



**Fig. 18**: The $[La(dcnm)_6]^{3-}$ anion from the crystal structure of $(C_2mim)_3[La(dcnm)_6]$, and the dicyanonitrosomethanide (dcnm) anion [50].

Rapid crystallization of the product was observed by cooling in conjunction with reducing the volume of the solution under vacuum. The aforesaid method yielded a range of ILs with imidazolium ($C_2mim$), pyridinium ($C_4C_1py$), and ammonium ($N_{1114}$, $N_{1112OH}$) based counter cations. Attempts to synthesise complexes containing lanthanoids heavier than gadolinium proved problematic, presumably due to the smaller radii of these lanthanoids inhibiting the formation of 12-coordinate complexes. This difficulty was encountered in previous attempts to synthesise $[RE(dcnm)_6]^{3-}$ complexes with the smaller tetramethylammonium and tetraethylammonium cations. Measurements of the thermal properties of complexes indicated that they all have melting points below 100 °C and can therefore be classified as ILs. The melting points and enthalpies of the phase transitions are given in Table 2. $(C_4C_1py)_3[Ce(dcnm)_6]$ was found to melt at 38.1 °C, the lowest melting point of all the complexes containing the $[RE(dcnm)_6]^{3-}$ trianion. The melt did not recrystallize upon cooling and formed a supercooled glass at -28.7 °C (Table 2). As expected, the use of ammonium-based counter cations gave complexes with higher melting points than those containing the imidazolium and pyridinium counter cations. While $(N_{1114})_3[RE(dcnm)_6]$ (RE = Sm, Gd) are ILs, the analogues containing lighter lanthanoids melt above 100 °C. The complex $(N_{1112OH})_3[Ce(dcnm)_6]$ was not observed to melt below 160 °C due to the presence of stronger intermolecular hydrogen bonds, as seen in the crystal structure.

Table 2: Thermal behaviour of complexes containing the $[RE(dcnm)_6]^{3-}$ anion [a]

| $Cation^+$, $Ln^{3+}$ | *CL* | HT | T [°C] | $\Delta H$ [kJ·mol$^{-1}$] | CT | T [°C] | $\Delta H$ [kJ·mol$^{-1}$] |
|---|---|---|---|---|---|---|---|
| $C_2mim$, La | 1 | A | 57.7 | 72.92 | B (P) | 6.4 | -20.56 |
| | 2 | B (P) | -7.4 | -38.08 | | | |
| | 2 | A | 59.2 | 71.15 | | | |
| $C_2mim$, Ce | 1 | A | 43.4 | 60.79 | D | -30.6 | |
| | 2 | C | -31.9 | | | | |
| $C_2mim$, Pr | 1 | A | 64.7 | 83.01 | D | -43.4 | |
| | 2 | C | -47.4 | | | | |
| | 2 | B (P) | -6.0 | -34.16 | | | |
| | 2 | B (P) | 15.6 | -25.23 | | | |
| | 2 | A | 62.4 | 83.24 | | | |
| $C_2mim$, Nd | 1 | A | 60.9 | 74.89 | B | 23.1 | -38.95 |
| | 2 | - | 13.9 | 0.82 | | | |
| | 2 | A | 40.1 | 37.82 | B | 20.3 | -39.24 |
| $C_2C_1mim$, Pr | 1 | A | 62.9 | 60.79 | D | -32.0 | |
| | 2 | C | -33.5 | | | | |
| | 2 | B | 5.1 | -41.81 | | | |
| | 2 | A | 61.4 | 63.83 | | | |
| $C_4C_1py$, Ce | 1 | A | 38.1 | 44.16 | D | -28.7 | |
| | 2 | C | -29.8 | | | | |
| $N_{1114}$, La | 2 | A | 109.1 | 68.67 | B | 105.2 | -68.2 |
| $N_{1114}$, Ce | 2 | A | 106.3 | 55.63 | B | 93.8 | -46.72 |
| $N_{1114}$, Pr | 2 | A | 104.8 | 69.72 | B | 96.9 | -65.54 |
| $N_{1114}$, Nd | 2 | A | 102.5 | 74.28 | B | 90.6 | -71.71 |
| $N_{1114}$, Sm | 2 | A | 83.7 | 47.31 | B | 75.4 | -50.33 |
| $N_{1114}$, Gd | 2 | A | 74.8 | 45.02 | B | 55.8 | -44.68 |
| $N_{1114OH}$, Ce | 1 | no transition observed | | | | | |

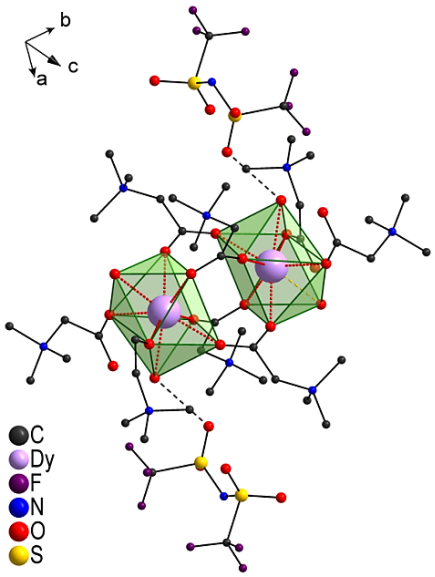
[a] T, onset temperature of transition; CL = cycle; HT = heating transition; CT = cooling transition; $\Delta H$, enthalpy of transition; S→L, solid to liquid transition (**A**); L→S, liquid to solid transition (**B**); G→L, glass to liquid transition (**C**); L→G, liquid to glass transition (**D**); (**P**) denotes partial transition.

## 2.6. Carboxylates

Because of its strong coordination ability carboxylic ligands seem to be the most powerful for the generation of rare earth ionic liquids. In 1998 Xiao-Ming Chen and co-workers reported the first synthesis and structural characterization of homodinuclear europium or terbium(III)-betaine (bet ≡ $Me_3N^+$-$CH_2COO^-$) complexes in which the carboxylate unit coordinates to metal ions in three different fashions [51]. In both isostructural dimeric compounds, $[Eu_2(bet)_8(H_2O)_4](ClO_4)_6$ and $[Tb_2(bet)_8(H_2O)_4](ClO_4)_6$, the metallic cores are connected by quadruply bridging carboxylate functionalities ($\eta^1 : \eta^1 : \mu_2$). Each rare earth ion is further coordinated by two terminal aqua ligands and two monodentate betaine-carboxylates to form a distorted square-antiprismatic coordination geometry. The compound $[Eu_2(bet)_4(H_2O)_8]Cl_6 \cdot 6H_2O$ features a similar dimeric complex cation, in which two bet ligands act as $\eta^1 : \eta^1 : \mu_2$-bidentate ligands, and the other two in the less common

$\eta^2 : \eta^1 : \mu_2$-chelate bridging mode. Unfortunately no thermal characterization was carried out for the compounds.

In 2006 the ability of protonated betaine bis(trifluoromethylsulfonyl)imide ionic liquids to dissolve large quantities of metal oxides with selective metal-solubilizing power was detected [52]. Among the metal oxides used was $Dy_2O_3$, which after solubilization in [Hbet][$Tf_2N$] and slow evaporation of water at room temperature yielded single crystals of $[Dy_2(bet)_8(H_2O)_4][Tf_2N]_6$ (Figure 19a).




| RE | M (°C) |
|---|---|
| Y | 109 |
| La | 78 |
| Pr | 86 |
| Nd | 90 |
| Sm | 88 |
| Eu | 95 |
| Gd | 94 |
| Tb | 88 |
| Dy | 88 |
| Ho | 80 |
| Er | 94 |
| Tm | 97 |
| Yb | 89 |
| Lu | 88 |

(a) (b)

**Fig. 19**: (a) Cationic dimer $[Dy_2(bet)_8(H_2O)_4]^{6+}$ in the structure of $[Dy_2(bet)_8(H_2O)_4][Tf_2N]_6$ with hydrogen bonding from coordinated water molecules to two bis(trifluoromethylsulfonyl)imide anions; (b) Melting points (**M**) for the rare earth complexes $[RE_2(bet)_8(H_2O)_2][Tf_2N]_6$ and $[Nd_2(bet)_8(H_2O)_4][Tf_2N]_6$ [53].

Its structure consists of dimeric $[Dy_2(bet)_8(H_2O)_4]^{6+}$ cations and bis(trifluoromethylsulfonyl)imide anions. Each dysprosium(III) ion is surrounded by six monodentately coordinating betaine zwitterions; four of them are $\mu_2$-bridging so that dysprosium(III) ions occur as dimers (Figure 19a). This group of authors continued further their research on new carboxyl-functionalized task-specific ionic liquids for solubilizing metal oxides. In another work a series of investigations on yttrium and europium compounds with the general formula $[RE_2(RCOO)_6(H_2O)_4]^{6+}$ and $Tf_2N^-$ as anion were reported (where RCOO ≡ betainium and N-carboxymethylmorpholinium) [54, 55]. Unfortunately the thermal behaviour of these compounds was not investigated and it is not clear whether they can be considered as ionic liquids representatives.

Recently Powell and co-workers have demonstrated [56] the synthesis and structural characterization of three dysprosium-containing ionic liquids with the N-carboxymethyl(or ethyl)imidazolium moiety (Figure 20). These compounds represent the first examples of catalytically active ionic liquids in the three-component synthesis of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1H-3-indolyl)-5-phenyl-1H-3-pyrrolecarboxylate which also show single ion magnet behaviour at low temperatures. As single crystal needles of $\{[Dy(cmim)_3(H_2O)_2](Tf_2N)_3\}_n$ and $\{[Dy(cmim)_4(H_2O)_2](PF_6)_3 \cdot 2H_2O\}_n$ (where cmim ≡ N-carboxymethylimidazolium) were very thin, synchrotron radiation was required to elucidate their crystal structures. Adjacent pairs of $Dy^{III}$ cations within the polymeric chains are bridged by two carboxylate groups such that the Dy centres within a chain are related by a c-glide plane.

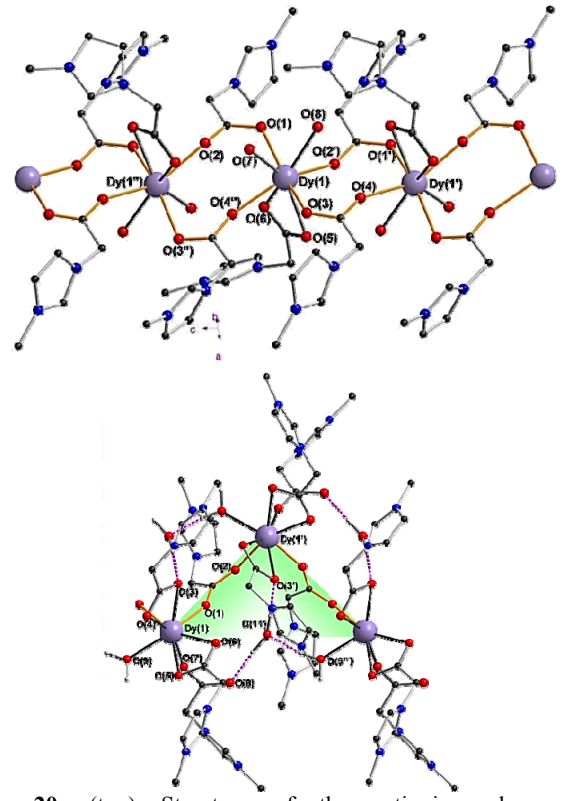



**Fig. 20**: (top) Structure of the cationic polymer in $\{[Dy(cmim)_3(H_2O)_2](Tf_2N)_3\}_n$ (carboxylate bridges in orange); (bottom) A fragment of the cationic polymer in $\{[Dy(cmim)_4(H_2O)_2](PF_6)_3 \cdot 2H_2O\}_n$ (carboxylate bridges in orange, hydrogen bonds as pink dotted lines). Reproduced with permission from [56].

The coordination sphere around Dy(1) is completed by a chelating carboxylate group from a third $(cmmim)^-$ ligand, and two aqua ligands. The coordination geometry is closest to a bicapped trigonal prism. Within the crystal structure of $\{[Dy(cmim)_3(H_2O)_2](Tf_2N)_3\}_n$ (Figure 19, top), the 1D chains are well separated by the $Tf_2N^-$ anions. Interactions between the chains and the anions are mediated by hydrogen bonding between C–H bonds of the positively charged organic ligands to either O or F atoms of the anions. The structure of the related compound $\{[Dy(cmim)_4(H_2O)_2](PF_6)_3 \cdot 2H_2O\}_n$ also features polymeric chains. However, the linkages are very different and the polymer has a *zig-zag* structure (Figure 20, bottom). The coordination sphere around Dy(1) is completed by two chelating carboxylate groups, an additional unidentate carboxylate ligand and an aqua ligand. The lattice water resides within a triangle formed by the zig-zag chain and interacts with three different $Dy^{III}$ cations (Figure 20, bottom). The temperature

dependence of dc magnetic susceptibility for these compounds shows almost the same thermal evolution with a room temperature $\chi T$ slightly lower than the expected value for one isolated Dy(III) ($S = {}^5/_2$, $L = 5$, $g = {}^4/_3$, $C =$ 14.17 cm$^3$·K/mol). With decreasing temperature the complex has $\chi T$ products that decrease gradually from 300 K, reaching a minimum at 1.8 K. This type of behavior is subjected to strong spin orbital contributions of the strongly anisotropic $Dy^{III}$ ions which can be associated with small magnetic interaction. In order to investigate the dynamic magnetic properties of the complexes, corresponding ac susceptibility measurements in the presence of a weak dc field were performed (Figure 21).

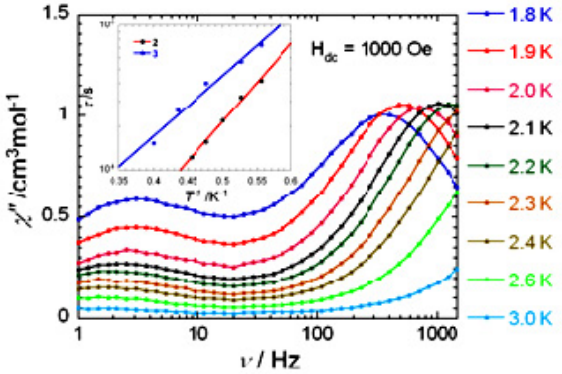



**Fig.21**: Frequency dependence of ac magnetic susceptibility of the complex $\{[Dy(cmim)_3(H_2O)_2](Tf_2N)_3\}_n$ at indicated temperatures under a dc field of 1000 Oe. Inset: Arrhenius semilog plots of the relaxation time, τ vs 1/T of both complexes from ac susceptibility measurements under a static field. Reproduced with permission from [56].

It was demonstrated that the strength of the out-of-phase component of ac susceptibility is dramatically enhanced with the application of a dc field, confirming the presence of slow magnetic relaxation behaviour combined with rapid quantum tunnelling. It was concluded that due to the variability of N-substituted task-specific carboxyalkyl quaternized salts the similar synthetic strategy can be applied for the decrease of melting points of metal-containing ionic liquids.

But not only mono-functionalized carboxylate-ligands can be used. Recently Li and co-workers described novel luminescent soft materials via reaction of $Eu^{3+}$-coordinated carboxyl functionalized ionic liquids with terpyridine functionalized imidazolium salts (Figure 22).

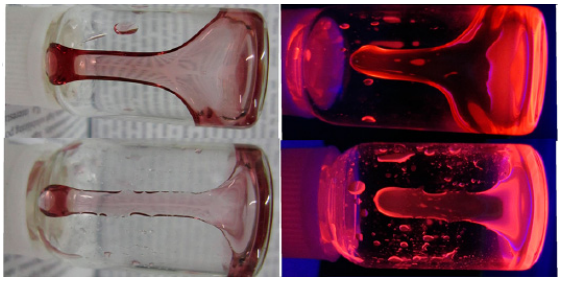


**Fig. 22**: Digital photos of the soft materials: {Eu-[Carb-$C_1$mim]$Tf_2$N-[$C_4$terpyim]Br} (up) and {Eu-[Carb-$C_1$mim]$Tf_2$N-[$C_4$terpyim]$Tf_2$N} (bottom) at day (left) and UV (right) lights. Adapted with permission from [57]. Copyright 2013 American Chemical Society.

These ligands are built from an imidazolium ring substituted on one side with a terpyridine derivative and, on the opposite side, a paraffin chain of various lengths [57].

The obtained materials are either paste-like substances or viscous fluids, depending on the anions of these carboxyl functionalized ionic liquids. The soft materials show bright red emission irradiated with UV light drawing its power from an efficient energy transfer from the terpyridine-functionalized imidazolium salts to the $Eu^{3+}$ ions. Such an energy transfer from an imdazolium cation to $Eu^{3+}$ has been previously reported for $[C_{12}mim]Cl$ doped with $Eu^{3+}$ [58].

Recently Wang et al. reported a simple and environmentally friendly procedure for preparing transparent and luminescent ionogels that consist of ionic ternary Eu(III) complexes incorporated in poly(methylmethacrylate) (PMMA). Such Eu(III)-containing luminescent ionogels are able to emit bright red luminescence due to the dominant emission band peaking at 617 nm ($^5D_0 \rightarrow {}^7F_2$ transition of $Eu^{3+}$) under near-UV light irradiation.

## 3. Conclusions

The multitude of uses of ionic liquids warrants an analogy with the chemist's equivalent of the iPhone [60] and metal containing ionic liquids are upcoming as powerful platforms for applications in numerous hi-tech processes. Here we presented a complete view of the chemistry of rare earth-based ionic liquids and an argumentation of exponential growth of interest in these materials. By creating complicated structures which migrate between liquid and solid phases, the preparative chemist can rely on an existing understanding of the principles and rules of the classical coordination chemistry. However it is necessary to make allowance for the chemical nature of the rare earth ions and their preferences in ability to coordinate with different ligands. For example, in comparison with carboxylates of 3d metals, where the carboxylate group usually acts as a monodentate ($\eta^1$ or $\eta^2$) or bidentate ($\eta^1 : \eta^1 : \mu_2$) ligand, the coordination modes in rare earth carboxylates are more flexible (Figure 23).

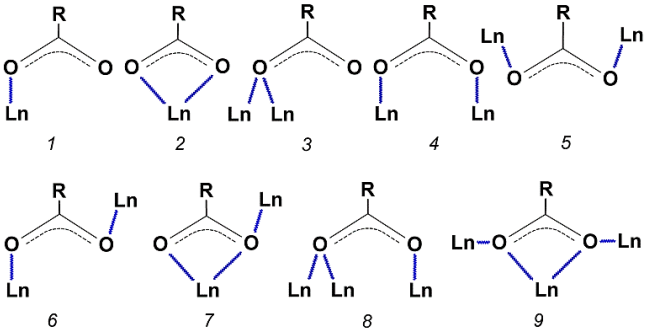



**Fig. 23**: Common coordination modes of the carboxylate group found in rare earth carboxylates: $\eta^1$ (1); $\eta^2$ (2); $\eta^2 : \mu_2$ (3); $\eta^1 : \eta^1 : \mu_2$-*ZZ* (4); $\eta^1 : \eta^1 : \mu_2$-*EE* (5); $\eta^1 : \eta^1 : \mu_2$-*ZE* (6); $\eta^2 : \eta^1 : \mu_2$ (7); $\eta^2 : \eta^1 : \mu_3$ (8); $\eta^2 : \eta^2 : \mu_3$ (9) [61].

Due to the large size of rare earth(III) ions and the ionic nature of the RE-O bonds, the carboxylato-groups can coordinate with rare earth ions without any geometrical limit thus making polydentate or chelating coordination modes possible in the structures. As shown in Figure 23,

nine typical coordination modes of the carboxylate group in rare earth carboxylates are found.

The wide variability of carboxylate derivatives in combination with different co-ligands and anions should provide the scientists a boundless field of work for creativity and the design of new innovative rare earth based hybrid materials. We can summarize that despite of many research activities in the field of ionic liquids, the chemistry of rare earths based ionic liquids is still widely underexplored. It can be anticipated that with ongoing and future research in this area new eco-friendly systems with amazing properties will be found.

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**Graphical Abstract**

# Rare Earth Metal-Containing Ionic Liquids

*Authors*: Denis Prodius, Anja-Verena Mudring*