DOI: 10.1002/anie.200801159

Ionic Liquids (1)

Europium-Based Ionic Liquids as Luminescent Soft Materials**

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As versatile materials, ionic liquids have received substantial attention in recent years. Their inherent properties, such as generally negligible vapor pressures, wide liquid ranges, good thermal stabilities, considerable electric conductivities, and wide electrochemical windows, are advantageous for a large number of applications.[1] Many of these properties are related to the principles of "green" chemistry.[2] As salts, ionic liquids are composed of distinct cations and anions, which renders them tunable. They may be designed for specific applications by incorporation of functionalities in one or both ions as well as by the choice of cation–anion combination.

Metal-containing ionic liquids are auspicious new materials which can favorably combine the properties of ionic liquids with magnetic, photophysical/optical or catalytic properties that originate from the metal incorporated in the complex anion. Recently, it has been shown that solutions of f-element compounds in ionic liquids are promising novel soft luminescent materials for use in photochemistry and spectroscopy.[3] Complex ionic f-element compounds may be advantageous as active materials in organic light-emitting diodes (OLEDS).[4] Special interest for f elements in ionic liquids comes from actinide and lanthanide separation and extraction as well as nuclear fuel reprocessing and waste treatment.[5] Furthermore, ionic liquids offer the possibility of electrodeposition of the electropositive f elements themselves.[6] Thus, the investigation of f-element chemistry in ionic liquids is of relevance for various fields.[7]

Examples of ionic liquids containing f elements are, to date, $Na_{13}[Ln(TiW_{11}O_{39})_2]\cdot x H_2O$ ($x = 27$–44) with f-element polyoxometallates of the Keggin type[8] and complex lanthanide thiocyanates $[C_4mim]_{x-3}[Ln(NCS)_x(H_2O)_y]$ ($x = 6, 7, 8$ (for La), $y = 0$–2, $x + y < 10$).[9] However, all these compounds contain water either as crystal water or even as a coligand. They are similar to compounds like the Glauber salt $Na_2SO_4\cdot 10H_2O$ that melts in its own crystal water at 32 °C[10] or $NaOAc\cdot 3H_2O$ at 58 °C, which is used commercially as a latent heat storage material.[11] Their liquid state is more like a solution than a true melt. Unfortunately, when it comes to optical applications, water efficiently absorbs the energy of the excited state through excitation of O–H vibrations, leading to high radiationless decay rates. In the case of f-element luminescence in the NIR region, this can result in the complete quenching of any emission.[3d] However, water-free compounds could overcome this obstacle.

Herein, we report an unprecedented series of low-melting europium-containing ionic liquids that avoid the use of any neutral coligand such as water and consequently can be regarded as the first true f-element-based ionic liquids. They have the general composition $[R]_x[Eu(Tf_2N)_{3+x}]$ (Tf_2N = bis(trifluoromethanesulfonyl)amide; $x = 1$ for R = 1-propyl-3-methylimidazolium (C_3mim) and 1-butyl-3-methylimidazolium (C_4mim); $x = 2$ for R = 1-butyl-1-methylpyrrolidinium (C_4mpyr)). These compounds are synthesized by metathesis reactions from stoichiometric amounts of europium(III) bis(trifluoromethanesulfonyl)amide salts and the corresponding Tf_2N-based ionic liquids. The melting points (onset of melting) of crystalline material were determined by differential scanning calorimetry (DSC) to be 81.0 °C for $[C_3mim][Eu(Tf_2N)_4]$ (**1**) and 67.9 °C for $[C_4mim][Eu(Tf_2N)_4]$ (**2**). $[C_4mpyr]_2[Eu(Tf_2N)_5]$ (**3**) melts at 92.1 °C; however, before melting to an isotropic liquid, an endothermic thermal event is observed, which could be assigned to a phase transition at 73.9 °C. The lower melting point of **2** than **1** can be understood to originate from a combination of two effects. As C_4mim is larger than C_3mim from the Kapustinskii equation, a lower lattice energy can be estimated for **2**.[12] Furthermore, a C_4 side chain offers more conformational flexibility than a C_3 chain, leading to higher packing frustrations.[13] The high melting point of $[C_4mpyr]_2[Eu(Tf_2N)_5]$ (**3**) compared to the $C_n$mim ($n = 3, 4$) compounds **1** and **2** is expected, as pyrrolidinium salts generally show higher melting points than imidazolium salts. Additionally, the higher charge of the complex anion also contributes to a higher melting point. However, all three compounds show a strong tendency to form supercooled liquids. Compound **1** crystallizes from the melt at about 11 °C, **2** at 10 °C, and **3** at 53 °C (for DSC traces and further information, see the Supporting Information). The crystallization of imidazolium salts is often inhibited because of the high degree of charge delocalization and the large geometrical aniosotropy of the substituted, nearly planar imidazolium cation.[14] A liquid of the composition "$[C_4mim]_2[Eu(Tf_2N)_5]$" showed no tendency to crystallize at all. Instead, a glass transition around −50 °C was found. By applying careful cooling procedures, $[C_4mim][Eu(Tf_2N)_4]$ crystallized from the melt, leaving $[C_4mim][Tf_2N]$ behind. In fact, a solution of 1 mol $[C_4mim][Eu(Tf_2N)_4]$ in 1 mol $[C_4mim][Tf_2N]$ represents the eutectic in the phase diagram. In contrast, **1**–**3** are congruently melting compounds.

Crystal structure analyses of compounds **1**–**3** reveal ninefold oxygen coordination for the Eu^{3+} center, which can best

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[**] Support from the DFG within the priority program "Lanthanoid specific functionalities" SPP 1191 and from the Fonds der Chemischen Industrie is gratefully acknowledged. A.V.M. thanks the Fonds der Chemischen Industrie for a Chemiedozenten-Stipendium.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801159.

be described as a distorted tricapped trigonal prism (Figure 1). The mean oxygen–europium separations of 244–245 pm are similar to values found for typical organometallic complexes with the same coordination number.[15] The oxygen donors surrounding the Eu^{3+} cation in [C$_4$mpyr]$_2$[Eu(Tf$_2$N)$_5$] come from four bidentate bis(trifluoromethanesulfonyl)amide ligands (bonding mode shown in Scheme 1 a) and one monodentate ligand (Scheme 1 c). The monodentate Tf$_2$N ligand adopts a *transoid* conformation (relative orientation of the CF$_3$ groups with respect to the S-N-S plane), which is also the more stable conformation for the free Tf$_2$N anion.[16] For the bidentate ligands, both conformations are observed. One of the four ligands adopts a *cisoid* conformation and another one a *transoid* conformation, whilst the other two ligand positions show a mixed occupation by ligands in *cisoid* and *transoid* conformations. Whereas in [C$_4$mpyr]$_2$[Eu(Tf$_2$N)$_5$] (**3**) isolated [Eu(Tf$_2$N)$_5$]$^{2-}$ units are present, for [C$_3$mim][Eu(Tf$_2$N)$_4$] (**1**) and [C$_4$mim][Eu(Tf$_2$N)$_4$] (**2**), dimeric europium units of the composition [Eu$_2$(Tf$_2$N)$_8$]$^{2-}$ are formed. In **1** and **2**, one of the Tf$_2$N ligands coordinates not only in a bidentate chelating fashion to one Eu^{3+} center but also forms a bridge to a neighboring Eu^{3+} ion, where it coordinates in a monodentate fashion (Scheme 1 b). Although **1** and **2** have very similar structures, the Tf$_2$N ligands adopt different conformations. In **1**, only one Tf$_2$N ligand does not adopt a *transoid* conformation. On the contrary, in **2**, four of the five Tf$_2$N ligands adopt the *cisoid* conformation. For all compounds **1**–**3**, the S–O interatomic distances on the binding site of the ligand are on average about 0.03 Å larger than those on the non-coordinating site (1.43–1.47 vs. 1.42–1.44 Å). The S–N interatomic distances (d_{mean}(S–N) = 1.56–1.57 Å) and the S-N-S bonding angles ($\angle_{\text{mean}}$(S-N-S) = 125–127°) are comparable to the values found for similar compounds.[17] Furthermore, they match the values found for the free ligand.[18]

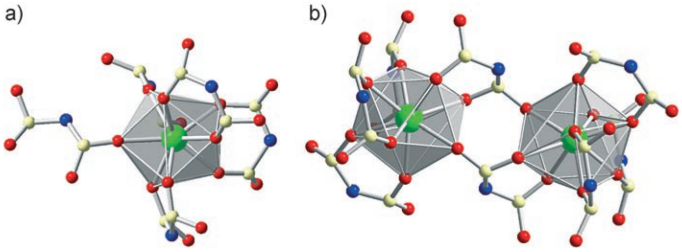
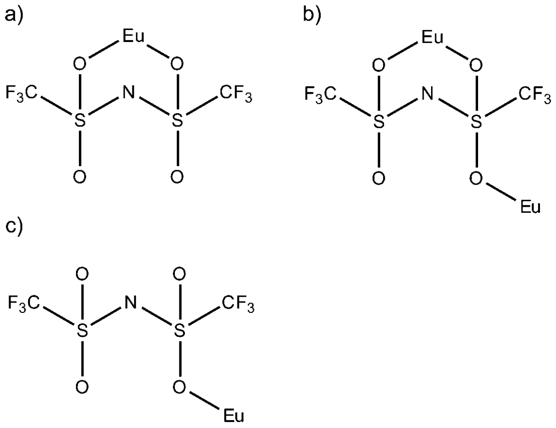


Figure 1. Local environment of Eu^{3+} in a) [C$_4$mpyr]$_2$[Eu(Tf$_2$N)$_5$] and b) [C$_3$mim][Eu(Tf$_2$N)$_4$]. CF$_3$ groups are omitted for clarity. S yellow, O red, N blue, Eu green.



Scheme 1. Coordination modes of Tf$_2$N ligand in compounds **1**–**3**.

Raman spectroscopy has proven to be a valuable tool to monitor the complexation of metal cations by the Tf$_2$N ligand.[19] The ν_s(SNS) bands of **1** and **2** are found at 754 and 752 cm^{-1}, respectively. For uncomplexed Tf$_2$N$^-$ in the ionic liquids [C$_3$mim][Tf$_2$N] and [C$_4$mim][Tf$_2$N], the ν_s(SNS) band is found at much lower wavenumber (741 cm^{-1}, see the Supporting Information). The ν_s(SO$_2$) bands should be even more sensitive to complex formation, and indeed for **1** and **2**, the bands are split into two peaks at 1115 and 1150 cm^{-1}, whereas in the ionic liquids [C$_3$mim][Tf$_2$N] and [C$_4$mim][Tf$_2$N] the vibrations occur at 1113 and 1136 cm^{-1} and 1115 and 1136 cm^{-1}, respectively.

The excitation and emission spectra of **1**–**3** show the characteristic transitions for Eu^{3+} ions (Figure 2). Interestingly, the emission spectra of compounds **1**–**3** look alike. However, the spectra of solid samples are distinctly different from those of the liquid ones. Whereas in the emission spectra

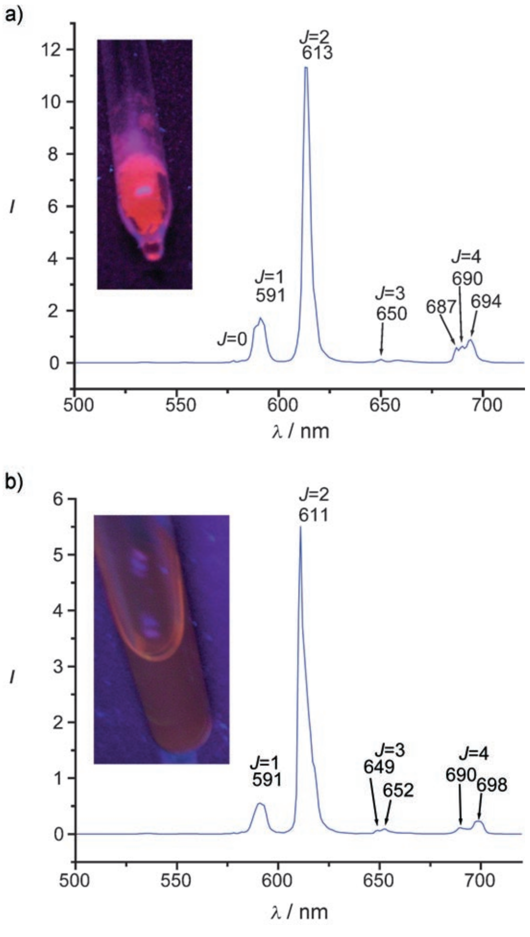


Figure 2. Emission spectrum of [C$_3$mim][Eu(Tf$_2$N)$_4$] in the a) solid and b) metastable liquid state. Insets: Sample under UV radiation.

of the solid samples all $^5D_0 \rightarrow ^7F_J$ ($J = 0$–4) transitions are visible, in the liquid state the $^5D_0 \rightarrow ^7F_0$ transition is absent. According to the crystal structure, in the solid state the Eu^{3+} center in **1**–**3** is surrounded by oxygen atoms in a slightly distorted tricapped triangular prism of approximate D_{3h} symmetry. For ideal symmetry, it is expected that the $^5D_0 \rightarrow ^7F_0$ transition would not be observed. However, in the solid, the transition occurs with weak intensity owing to deviations from the ideal point symmetry. In the liquid, the transition becomes even less intense, indicating a change of the coordination environment. The most obvious difference between the emission spectra measured for solid and liquid samples is observed for the $^5D_0 \rightarrow ^7F_4$ transition. In the liquid state, the signal consists of two overlapping peaks around 690 and 698 nm. In the solid state, the peak splits into three transitions at 687, 690, and 694 nm. One possible explanation of this difference could be that a higher coordination number of 10 is adopted in the liquid state. In the case of **3**, this situation could be easily achieved if the monodentate ligand flips to the metal center and coordinates in a chelating mode. For **1** and **2**, one possibility is that the "free" oxygen atom in the chelating bridging ligand binds to a neighboring Eu^{3+} center, turning the ligand from tridentate to tetradentate. A coordination number of 10 would be in agreement with X-ray absorption fine structure (XAFS) studies of similar solutions of Eu^{3+} in Tf_2N-based ionic liquids.[20] The $^5D_0 \rightarrow ^7F_2$ transition is the most intense for all samples; its lineshape is extremely sharp for solid and liquid samples, and the intensity ratios of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions are high. Both facts lead to a good color purity of the emission. The intensity ratios of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions in the emission spectra can be taken as a measure of the asymmetry of the Eu^{3+} site.[21]

It is generally accepted that the asymmetry parameter becomes larger as the interaction of europium with its neighbors becomes stronger and the Eu^{3+} site symmetry becomes lower. The values of 9.94 and 6.56 for solid and liquid **1** and 8.36 and 3.49 for solid and liquid **2** can be compared to values found for Eu^{3+} in different coordination environments[22] and suggest a lower site symmetry and larger europium–ligand interaction in the solid compounds than in the liquids. For a hydrated Eu^{3+} species, an even lower intensity ratio and an asymmetry factor of approximately 0.63 would be expected.[23] Water entering the coordination sphere of the oxophilic lanthanide center has long been noted to have a strong influence on the luminescent properties of lanthanides in ionic liquids. It typically leads to reduced lifetimes for the excited state and eventually to total quenching of any emission.[24,3c,d] For all samples, a monoexponential intensity decay was detected, indicating that just one Eu^{3+} species is present. The Eu ($^5D_0$) lifetime of **1** for $\lambda_{ex,em} = 394$, 613 nm in the solid state is about 2.15 ms; in the (metastable) liquid state it is 1.66 ms (for $\lambda_{ex,em} = 393$, 611 nm). For **2** the respective lifetimes are about 2.21 (for $\lambda_{ex,em} = 394$, 613 nm) and 1.91 ms (for $\lambda_{ex,em} = 393$, 611 nm). The shorter lifetimes for the liquid state can be well understood, as it is easier to excite vibrations in the liquid than in the solid state. Lifetimes of 0.4 ms have been reported for water-free solutions of Eu^{3+} in Tf_2N ionic liquids.[25] However, the lifetimes of **1**–**3** in the liquid state are quite high and seem not to be significantly influenced by the nature of the cation, regardless of the state of mater. The lifetimes are astonishing, especially when the high europium concentrations (100% Eu-doped) are taken into account. At such concentrations, radiationless decay by concentration quenching usually becomes important.

With $[C_3mim][Eu(Tf_2N)_4]$, $[C_4mim][Eu(Tf_2N)_4]$, and $[C_4mpyr]_2[Eu(Tf_2N)_5]$ we present the first f-element ionic liquids that do not need stabilization of the liquid state by neutral coligands. Their crystallization is strongly inhibited such that **1** and **2** form metastable liquids even below room temperature. Compounds **1**–**3** illustrate how the cation of an ionic liquid determines its structure and the overall composition. All compounds possess excellent photophysical properties (high lifetimes at high Eu^{III} concentration, small linewidth, and high color purity), which might render them extremely valuable for various optical applications.

Experimental Section

Experimental details can be found in the Supporting Information.

Received: March 10, 2008
Revised: July 7, 2008

Keywords: europium · ionic liquids · lanthanoids · luminescence · X-ray diffraction

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