

Visible and Near-Infrared Emission by Samarium(III)-Containing Ionic Liquid Mixtures

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Highly luminescent anionic samarium(III) β -diketonate and dipicolinate complexes were dissolved in the imidazolium ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6\text{mim}][\text{Tf}_2\text{N}]$. The solubility of the complexes in the ionic liquid was ensured by a careful choice of the counterion of the samarium(III) complex. The samarium(III) complexes that were considered are $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$, where tta is 2-thenoyltrifluoroacetone; $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$, where nta is 2-naphthoyltrifluoroacetone; $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$, where hfa is hexafluoroacetylacetone; and $[\text{choline}]_3^+[\text{Sm}(\text{dpa})_3]$, where dpa is pyridine-2,6-dicarboxylate (dipicolinate) and $[\text{choline}]^+$ is (2-hydroxyethyl)trimethyl ammonium. The crystal structures of the tetrakis samarium(III) β -diketonate complexes revealed a distorted square antiprismatic coordination for the samarium(III) ion in all three cases. Luminescence spectra were recorded for the samarium(III) complexes dissolved in the imidazolium ionic liquid as well as in a conventional solvent, that is, acetonitrile or water for the β -diketonate and dipicolinate complexes, respectively. These experiments demonstrate that $[C_6\text{mim}][\text{Tf}_2\text{N}]$ is a suitable spectroscopic solvent for studying samarium(III) luminescence. High-luminescence quantum yields were observed for the samarium(III) β -diketonate complexes in solution.

Introduction

Ionic liquids are attractive solvents because they exhibit good thermal, chemical, and electrochemical stabilities.^{1–3} They can be used as alternative solvents for organic reactions^{4–6} as well as for studies in catalysis⁷ and electrochemistry.^{8–10} Although less well-known, ionic liquids are also promising spectroscopic solvents, providing media that enable high-luminescence quantum yields (QYs) and enhanced photostabilities.^{11–13}

Thanks to a high-luminescence intensity combined with relatively easy-to-interpret emission spectra, fundamental research in the area of lanthanide luminescence has traditionally been focused on the europium(III) ion. For the same reasons, most of the work related to the spectroscopy of lanthanide-doped ionic liquids was also based on the emission of europium(III).^{13–18} Although less well-studied, samarium(III) is an interesting lanthanide emitter since it shows visible luminescence (red/orange color) at different wavelengths than europium(III) (red color) or terbium(III) (green color). In addition, a large contribution of the samarium(III) luminescence output is situated in the near-infrared region of the electromagnetic spectrum.^{19–23} Ionic liquids are good solvents for the study of the emission properties of lanthanide ions.^{11,24–26} Due to their low vapor

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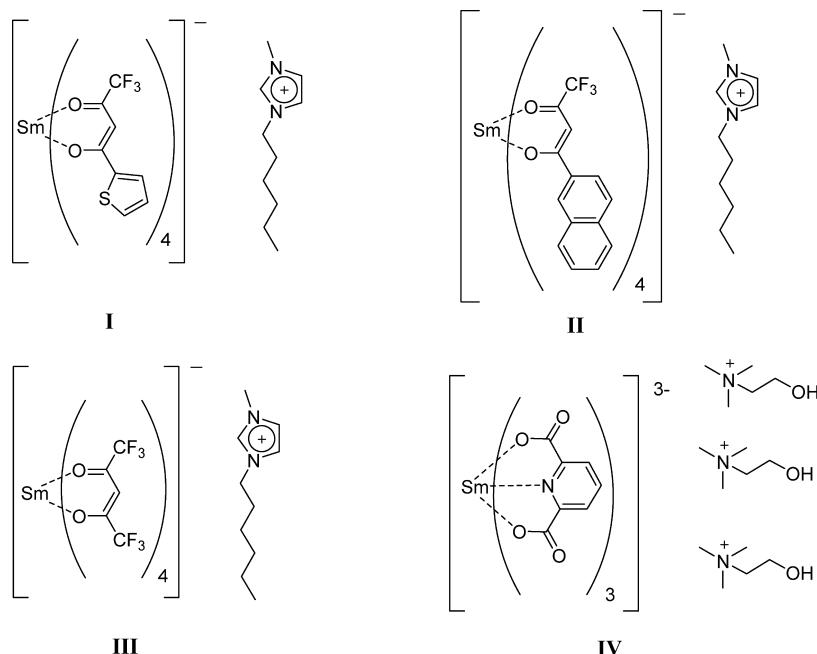


Figure 1. Schematic structure of the samarium(III) complexes $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ (**I**), $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$ (**II**), $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$ (**III**), and $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$ (**IV**).

pressure they can be thoroughly dried, so that the water concentration can be lowered to a very low level. This is an advantage for the lanthanide(III) emission, because water molecules in the neighborhood of the lanthanide ion can quench the excited states.

The inherent weaker luminescence intensity of samarium(III) compounds in comparison to europium(III) compounds is related to a smaller energy gap between the emitting level and the next lower energy level: ca. 7500 cm^{-1} in the case of samarium(III) versus ca. $12\,500\text{ cm}^{-1}$ in the case of europium(III). This results in a more efficient quenching of the excited state in the case of samarium(III).²⁷ The luminescence intensity of samarium(III) is, as for all lanthanide(III) ions, also limited by its poor light-absorbing abilities (typically less than $3\text{ L mol}^{-1}\text{ cm}^{-1}$ for samari-

um(III)). One way to overcome this problem is to form complexes of the ions with organic sensitizers that strongly absorb light and transfer the energy to the metal center (antenna effect). β -Diketone ligands are known to be very efficient sensitizing ligands.^{28–30} A major drawback of these ligands is the limited photostability of the corresponding complexes dissolved in organic solvents. Europium(III) β -diketonate complexes have been reported to show an enhanced photostability when dissolved in an imidazolium ionic liquid.¹³

This paper is about the luminescence properties of samarium(III) complexes, with special emphasis on the near-infrared spectra and on quantum yield determination. The luminescence properties of the following types of anionic complexes were studied in an imidazolium ionic liquid and in acetonitrile or in water: three β -diketonate complexes, $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$, $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$, and $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$ (where tta is 2-thienyltrifluoroacetone, nta is 2-naphthyltrifluoroacetone, and hfa is hexafluoroacetylacetone), and one dipicolinate complex, $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$ (dpa = pyridine-2,6-dicarboxylate) (Figure 1). The ionic liquid selected as the spectroscopic solvent was the hydrophobic 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6\text{mim}][\text{Tf}_2\text{N}]$. Imidazolium ionic liquids can be prepared with a transparency up to 280 nm (absorbance < 0.2).³¹ In general, some ionic liquids have been reported to be transparent through almost the whole visible and near-infrared spectral regions.^{32,33} The solubility of the samarium(III) complexes in the ionic liquid was ensured by the

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preparation of anionic complexes. This was achieved for the tetrakis β -diketonate complexes by using the 1-hexyl-3-methylimidazolium $[C_6\text{mim}]^+$ cation of the ionic liquid also as the counterion of the anionic tetrakis complexes. For the samarium(III) tris dipicolinate complex, the (2-hydroxyethyl)trimethyl ammonium or choline ion was chosen as the counterion since it was not possible to isolate pure $[C_6\text{mim}]_3[\text{Ln}(\text{dpa})_3]$ complexes.³⁴ $\text{Na}_3[\text{Ln}(\text{dpa})_3]$, which is not soluble in the ionic liquid, was formed instead. $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$ was found to be soluble in the imidazolium ionic liquid but more difficult to dissolve than the corresponding tetrakis β -diketonate complexes.

Experimental Section

General Techniques. Elemental analyses (carbon, hydrogen, nitrogen) were made on a CE Instruments EA-1110 elemental analyzer. ^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz). Photoluminescence spectra in the visible region have been recorded on an Edinburgh Instruments FS900 spectrofluorimeter. This instrument is equipped with a xenon arc lamp, a microsecond flashlamp (450 W; pulse length, 2 μs), and a red-sensitive photomultiplier (300–850 nm). The low-temperature measurements were performed with an optical cryostat from Oxford Instruments, Optistat DN liquid nitrogen, which was placed in the sample compartment of the spectrofluorimeter.

The luminescence spectra in the infrared region were measured on an Edinburgh Instruments FLS920 near-infrared spectrometer, with a xenon arc lamp (450 W), a double excitation monochromator, and a Hamamatsu R5509-72 near-infrared photomultiplier tube (600–1700 nm). The sample compartment can be equipped with an integrating sphere (diameter 15 cm) coated with BaSO_4 for quantum yield measurements.

Quantum Yield Determination. The luminescence quantum yields of the samarium(III) β -diketonate complexes in solution were determined in a regular spectroscopic setup relative to quinine sulfate in 1N H_2SO_4 ($\text{QY} = 54.6\%$)³⁵ and 9,10-diphenylanthracene in cyclohexane ($\text{QY} = 70\%$),³⁶ according to the equation

$$\Phi_x = \left(\frac{1 - 10^{-A_s}}{1 - 10^{-A_x}} \right) \left(\frac{I_{E_x}}{I_{E_s}} \right) \left(\frac{n_x}{n_s} \right)^2 \Phi_s \quad (1)$$

The subscripts x and s stand for sample and standard, respectively. A is the absorbance at the excitation wavelength. I_E is the number of (corrected and integrated) emitted photons. n is the refractive index of the solvent ($n = 1.3384$, 1.4260, 1.3430, and 1.4281 for H_2O , cyclohexane, acetonitrile, and $[C_6\text{mim}][\text{Tf}_2\text{N}]$, respectively). The β -diketonate solutions were prepared with an absorbance A equal to 0.5 in 0.2 cm cells ($\approx 3.5 \times 10^{-5}$ M for $[\text{Sm}(\text{tta})_4]^-$ and $[\text{Sm}(\text{nta})_4]^-$ and $\approx 1.5 \times 10^{-4}$ M for $[\text{Sm}(\text{hfa})_4]^-$) at the excitation wavelength. To avoid dissociation of the complex, we could not dilute the solutions to the ideal absorbance of 0.05 (minimal inner-filter effect). To avoid a large overlap in absorption and emission spectra of the organic standards, the solutions of the standards were

prepared with an absorbance of 0.05 at the excitation wavelength. At low concentrations, the emission intensity is assumed to be proportional to the absorption A , that is, for solutions with an absorbance up to 0.05. At higher concentrations, the factor $1 - 10^{-A}$ has to be used instead of A for the calculation of the luminescence quantum yield of a sample x relative to a standard, as stated in eq 1.³⁷ The excitation wavelengths were kept the same for the standard and sample solutions. The use of two standards allows for an internal control when the quantum yield of one standard is calculated from the experiment relative to the other standard. In this case, the quantum yield measurement was valid if the values found for the quantum yield of the standards did not deviate more than 10% from the theoretical value. Every measurement was repeated three times. Because of the photoinstability of the samarium(III) β -diketonate complexes in organic solvents, the absorbance of the solutions was remeasured before each emission scan.

In addition, the luminescence quantum yield of the samarium(III) complexes in solution were also determined with the use of an *integrating sphere* introduced in the sample compartment of the fluorimeter. The sphere is coated on the inside with a highly scattering material so that the light coming into the sphere will undergo multiple reflections and is directed toward the detector. To avoid errors, the integrating sphere was also calibrated with a standard, that is, $[\text{Eu}(\text{tta})_3\text{phen}]$ in DMF ($\text{QY} = 19.6\%$, for solutions containing 5×10^{-5} M ($A = 0.5$ in 2 mm cells)).

Synthesis of the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)imide, $[C_6\text{mim}][\text{Tf}_2\text{N}]$. 1-Hexyl-3-methylimidazolium bromide $[C_6\text{mim}][\text{Br}]$ was prepared under very mild conditions, as described previously.³¹ 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6\text{mim}][\text{Tf}_2\text{N}]$, was obtained using a metathesis reaction between $[C_6\text{mim}][\text{Br}]$ and lithium bis(trifluoromethylsulfonyl)imide, following a procedure described by Bonhôte et al.³⁸ This involves the addition of an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide to $[C_6\text{mim}][\text{Br}]$. The ionic liquid $[C_6\text{mim}][\text{Tf}_2\text{N}]$ spontaneously separated from the aqueous layer. The resulting ionic liquid was washed several times with small aliquots of water (20 mL) until no longer bromide residues could be detected by the AgNO_3 test. ^1H NMR (300 MHz, CDCl_3 , 20 °C, TMS): δ 8.71 (s, 1H), 7.33 (d, $J = 1.83$ Hz, 1H), 7.32 (d, $J = 1.83$ Hz, 1H), 4.16 (t, $J = 7.74$ Hz, 2H), 3.93 (s, 3H), 1.86 (m, $J = 6.39$ Hz, 2H), 1.31 (m, 6H), 0.88 (t, $J = 6.39$ Hz, 3H).

Synthesis of the Samarium(III) β -Diketonate Complexes. The samarium(III) complexes 1-hexyl-3-methylimidazolium tetrakis(thenoyltrifluoroacetonato) samarate(III), $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$; 1-hexyl-3-methylimidazolium tetrakis(naphthoyltrifluoroacetonato) samarate(III), $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$; and 1-hexyl-3-methylimidazolium tetrakis(hexafluoroacetonato) samarate(III), $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$ were prepared by first dissolving 6 equiv of the β -diketone ligand in ethanol and deprotonating it with an aqueous solution of NaOH (6 equiv) at 50 °C, followed by the addition of 1.5 equiv of the ionic liquid $[C_6\text{mim}][\text{Br}]$ in ethanol and the dropwise addition of 1 equiv of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ in water. The solution was left to stir and cool down to room temperature overnight. For $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ and $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$, a yellowish precipitate of the complex was formed. In the case of $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$, the solvent was removed partly under reduced pressure and precipitation was achieved while

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keeping the solution at 6 °C. The products have been filtered and washed with ice-water as well as dried in vacuo at 50 °C. The complexes were characterized by CHN analysis.

[C₆mim][Sm(tta)₄] yield: 64%. Anal. calcd (found) for C₄₂H₃₅N₂O₈F₁₂SSm: C, 41.96% (41.94%); H, 2.93% (3.38%); N, 2.33% (2.36%). [C₆mim][Sm(nta)₄] yield: 77%. Anal. calcd (found) for C₆₆H₅₁N₂O₈F₁₂Sm(H₂O): C, 56.76% (56.30%); H, 3.82% (3.65%); N, 2.01% (1.73%). [C₆mim][Sm(hfa)₄] yield: 20%. Anal. calcd (found) for C₃₀H₂₃N₂O₈F₂₄Sm(H₂O): C, 30.96% (30.78%); H, 2.16% (2.44%); N, 2.41% (2.38%).

Synthesis of the Samarium(III) Dipicolinate Complex: (choline)₃[Sm(dpa)₃]. Pyridine-2,6-dicarboxylic acid (3 equiv) was dissolved in 7 mL of H₂O together with 2.115 mL of a solution of cholineOH, 45 wt % in MeOH (6 equiv). The pH was checked to ensure neutrality, and the solution was heated to 70 °C, followed by the dropwise addition of SmCl₃·6H₂O (1 equiv) in water. The solution was left to stir for 2 h. Water was removed by a rotavap. The product was washed with methanol to remove residues of choline chloride and dried in vacuo at 50 °C. The yield was 61%. Anal. calcd (found) for C₃₆H₅₁N₆O₁₅Sm(H₂O)₂: C, 43.49% (43.67); H, 5.57% (5.80%); N, 8.45% (8.28).

Crystallography. X-ray intensity data were collected on a SMART 6000 diffractometer equipped with a CCD detector using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The images were interpreted and integrated with the program SAINT from Bruker.³⁹ All three structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.⁴⁰ Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC 712706, CCDC 712707, and CCDC 712708 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystallographic Data for [C₆mim][Sm(tta)₄]. C₄₂H₃₅F₁₂N₂O₈S₄-Sm, $M = 1202.36 \text{ g mol}^{-1}$, monoclinic, $P2_1/c$ (14:b2), $a = 12.468(2) \text{ \AA}$, $b = 18.768(3) \text{ \AA}$, $c = 20.616(3) \text{ \AA}$, $\beta = 97.381(9)^\circ$, $V = 4784.2(14) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.669 \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 11.741 \text{ mm}^{-1}$, $F(000) = 2396$, crystal size $0.5 \times 0.1 \times 0.1 \text{ mm}^3$, 8411 independent reflections. Final $R_1 = 0.0909$ for 3425 reflections with $I_0 > 2\sigma(I_0)$ and $wR_2 = 0.1745$ for all data.

Crystallographic Data for [C₆mim][Sm(nta)₄]. C₆₆H₅₁F₁₂N₂O₈-Sm, $M = 1378.45 \text{ g mol}^{-1}$, monoclinic, $P2_1/c$ (14:b2), $a = 16.3645(11) \text{ \AA}$, $b = 17.1989(14) \text{ \AA}$, $c = 23.5340(15) \text{ \AA}$, $\beta = 117.030(4)^\circ$, $V = 5900.2(8) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.552 \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 8.320 \text{ mm}^{-1}$, $F(000) = 2780$, crystal size $0.3 \times 0.3 \times 0.15 \text{ mm}^3$, 9810 independent reflections. Final $R_1 = 0.0703$ for 5906 reflections with $I_0 > 2\sigma(I_0)$ and $wR_2 = 0.1995$ for all data.

Crystallographic Data for [C₆mim][Sm(hfa)₄]. C₃₀H₂₃F₂₄N₂O₈-Sm, $M = 1145.86 \text{ g mol}^{-1}$, monoclinic, $P2_1/n$ (14:b2), $a = 12.9584(2) \text{ \AA}$, $b = 17.8877(2) \text{ \AA}$, $c = 17.3453(2) \text{ \AA}$, $\beta = 90.7880(10)^\circ$, $V = 4020.19(9) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.893 \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 12.481 \text{ mm}^{-1}$, $F(000) = 2236$, crystal size $0.3 \times 0.15 \times 0.15 \text{ mm}^3$, 7637 independent reflections. Final $R_1 = 0.0358$ for 6933 reflections with $I_0 > 2\sigma(I_0)$ and $wR_2 = 0.0956$ for all data.

(39) SAINT Manual Version 5/6.0; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.

(40) SHELXTL-PC Manual Version 5.1; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.

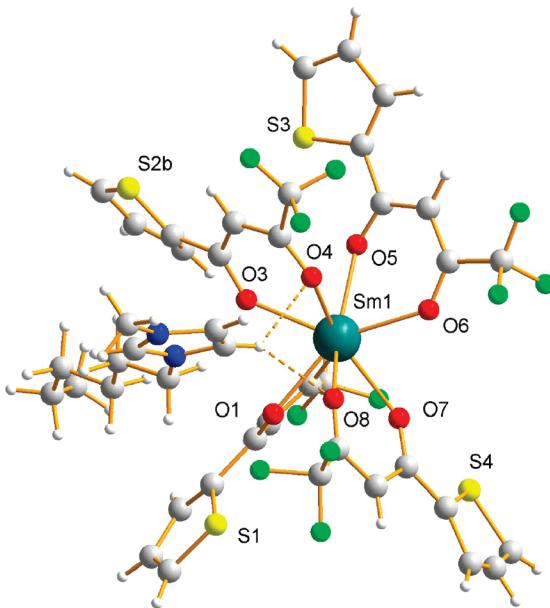


Figure 2. Molecular structure of [C₆mim][Sm(tta)₄]. The hydrogen bonding between the [C₆mim]⁺ cations and [Sm(tta)₄]⁻ anions is illustrated for one of the acidic hydrogen atoms of the imidazolium cation.

Results and Discussion

The crystal structure of [C₆mim][Sm(tta)₄] consists of [C₆mim]⁺ cations and [Sm(tta)₄]⁻ anions. The samarium(III) ion is surrounded by four thenoyltrifluoroacetone ligands. The coordination number of the samarium(III) ion is eight, and the coordination polyhedron can be described as a distorted square antiprism. There is no solvent molecule coordinating to the samarium(III) ion. Two of the three acidic hydrogens of the imidazolium cation form hydrogen bonds in a range from 2.43 to 2.63 Å to the oxygens of the coordinating thenoyltrifluoroacetone ligands. This is illustrated in Figure 2.

The crystal structure of [C₆mim][Sm(nta)₄] exhibits a similar coordination to that observed for [C₆mim][Sm(tta)₄] (Figure 3). Two of the three acidic hydrogens of the imidazolium cation form hydrogen bonds in a range from 2.33 to 2.54 Å to the oxygens of the coordinating naphthoyltrifluoroacetone ligands. Additionally, $\pi-\pi$ -stacking interactions between the imidazolium cation and one of the naphthoyl rings of the naphthoyltrifluoroacetone ligand can be observed within a centroid-to-centroid distance of 3.89 Å.

The crystal structure of [C₆mim][Sm(hfa)₄] is analogous to the two previously described structures, but with four hexafluoroacetylacetone ligands, forming a distorted square antiprismatic surrounding of the samarium(III) ion (Figure 4). The three acidic hydrogens of the imidazolium cation form hydrogen bonds in a range from 2.63 to 2.67 Å to the oxygens of the coordinating hexafluoroacetylacetone ligands. This type of hydrogen-bonding interaction, which also occurs for the complexes [C₆mim][Sm(tta)₄] and [C₆mim][Sm(nta)₄], is exemplarily shown for the surroundings of an imidazolium cation in Figure 5.

The luminescence spectra of [C₆mim][Sm(tta)₄], [C₆mim][Sm(nta)₄], and [C₆mim][Sm(hfa)₄] dissolved in the ionic liquid

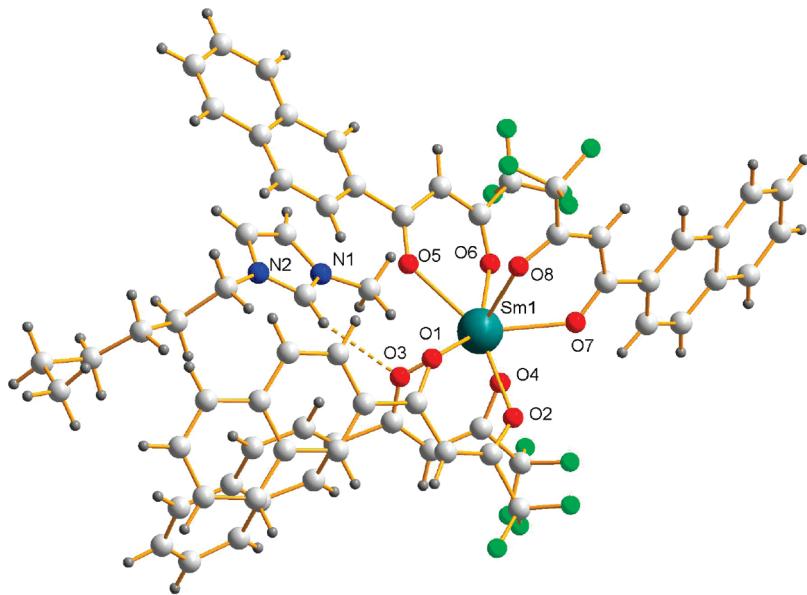


Figure 3. Molecular structure of $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$. The hydrogen bonding between the $[C_6\text{mim}]^+$ cations and $[\text{Sm}(\text{nta})_4]^-$ anions is illustrated for one of the acidic hydrogen atoms of the imidazolium cation.

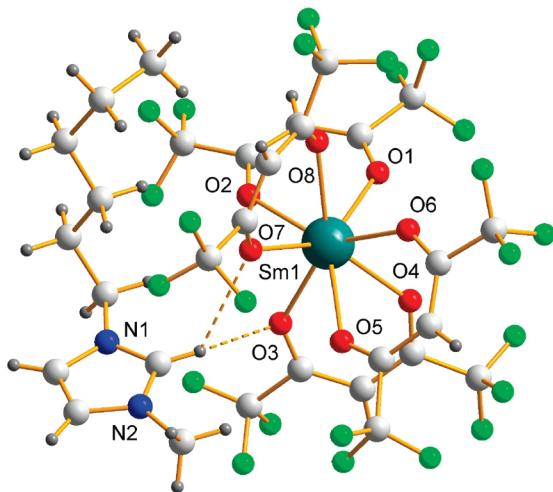


Figure 4. Molecular structure of $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$. The hydrogen bonding between the $[C_6\text{mim}]^+$ cations and $[\text{Sm}(\text{hfa})_4]^-$ anions is illustrated for one of the acidic hydrogen atoms of the imidazolium cation.

$[C_6\text{mim}][\text{Tf}_2\text{N}]$ are presented in Figure 6, and the assignments of the emission lines are given in Table 1. The spectra were recorded at room temperature, and the emission range covers the visible as well as the near-infrared part of the electromagnetic spectrum. The excitation wavelength was set at 372 nm ($26\ 882\ \text{cm}^{-1}$) for $[\text{Sm}(\text{tta})_4]^-$ and $[\text{Sm}(\text{nta})_4]^-$ and at 334 nm ($29\ 940\ \text{cm}^{-1}$) for $[\text{Sm}(\text{hfa})_4]^-$. The excitation energy is absorbed by the ligands and transferred to the samarium(III) emitting center in a subsequent step (antenna effect). The three β -diketonate complexes show similar spectra. The emitting level for the visible and the near-infrared transitions is the ${}^4G_{5/2}$ level. The emission peaks correspond to transitions from the ${}^4G_{5/2}$ level to the different J levels of the ${}^6\text{H}$ term (${}^6\text{H}_J$, $J = 5/2-15/2$) and the ${}^4\text{F}$ term (${}^4\text{F}_J$, $J = 5/2-11/2$).²³ The most intense transition in the visible region is the hypersensitive ${}^4G_{5/2} \rightarrow {}^6\text{H}_{9/2}$ (c) transition. In the near-infrared area, the most intense transition is the ${}^4G_{5/2} \rightarrow {}^4\text{F}_{5/2}$ (g) transition. The transition located at 560 nm ($17\ 850\ \text{cm}^{-1}$), ${}^4G_{5/2} \rightarrow {}^6\text{H}_{5/2}$ (line a), has a

predominant magnetic dipole character, whereas the transition at 645 nm ($15\ 500\ \text{cm}^{-1}$), ${}^4G_{5/2} \rightarrow {}^6\text{H}_{9/2}$ (line c), is a hypersensitive transition. The intensity ratio $I({}^4G_{5/2} \rightarrow {}^6\text{H}_{9/2})/I({}^4G_{5/2} \rightarrow {}^6\text{H}_{5/2})$ can be calculated and used as a measure for the polarizability of the chemical environment of the samarium(III) ion.⁴¹ As is usually the case for europium(III) β -diketonate complexes, this value is relatively high for samarium(III) β -diketonate complexes in comparison to, for example, samarium(III) dipicolinate complexes. The calculated intensity ratios for the different samarium(III) complexes are summarized in Table 2. In Figure 7, a cuvette with a luminescent solution of $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$ dissolved in the ionic liquid $[C_6\text{mim}][\text{Tf}_2\text{N}]$ is shown.

Ionic liquids are glass-forming liquids when cooled down to liquid-nitrogen temperatures, making them even more suitable as spectroscopic solvents. The emission spectrum of $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ in $[C_6\text{mim}][\text{Tf}_2\text{N}]$ recorded at 77 K shows a better resolution of the crystal-field fine structure but is essentially very similar to the spectrum recorded at room temperature (see the Supporting Information). It is noteworthy that a comparison of the spectra at 77 K and at room temperature reveals one extra peak at 530 nm ($18\ 850\ \text{cm}^{-1}$) in the room-temperature emission spectrum that disappears when the solution is cooled down to liquid-nitrogen temperatures. This phenomenon has been demonstrated before in samarium(III) luminescence spectra and is assigned to the ${}^4F_{3/2} \rightarrow {}^6\text{H}_{5/2}$ transition.²⁷ The ${}^4F_{3/2}$ level is situated at approximately $1100\ \text{cm}^{-1}$ above the highly emitting ${}^4G_{5/2}$ level and can be thermally populated at room temperature. The emission spectra of the samarium(III) β -diketonate complexes were also recorded in the solid state as well as in acetonitrile. The emission spectra of $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ are very similar in the solid state, in acetonitrile solution, as well as in the ionic liquid,

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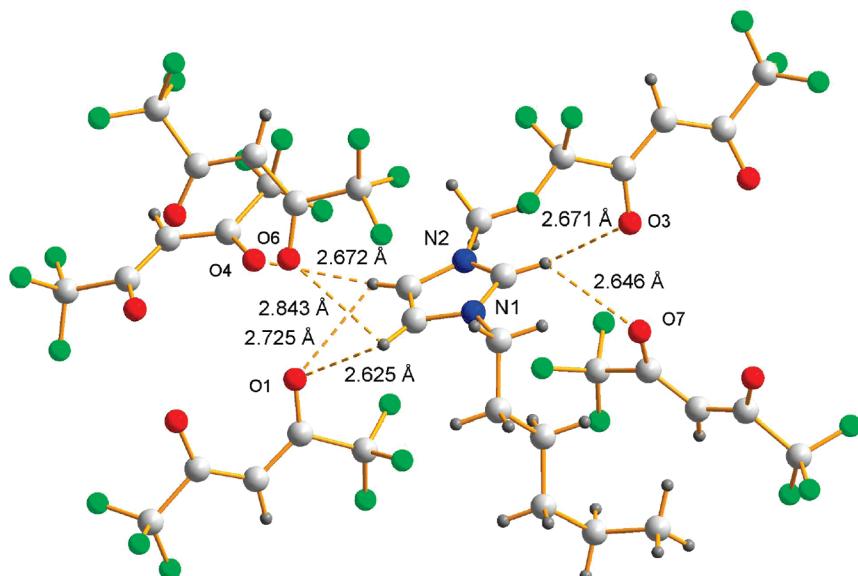


Figure 5. Surrounding of an imidazolium cation with the hydrogen-bonding interactions from the acidic imidazolium hydrogens to the surrounding hexafluoroacetylacetone ligands in the crystal structure of $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$.

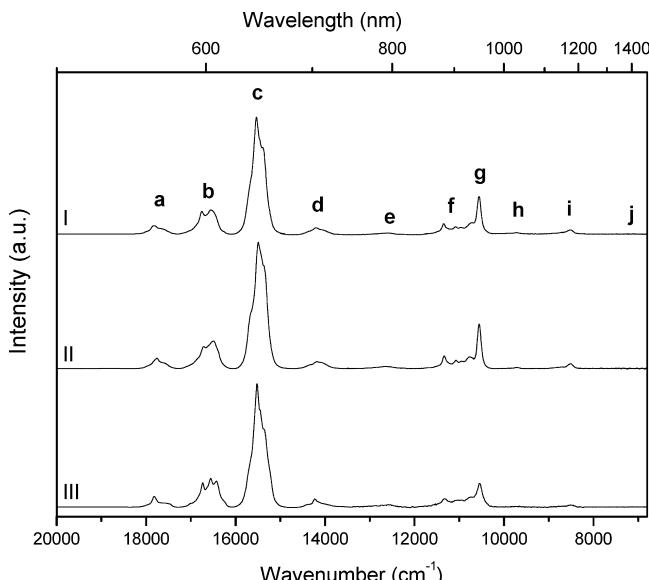


Figure 6. Room-temperature luminescence spectra of the samarium(III) β -diketonate complexes dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$: I, $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$; II, $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$; III, $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$. The excitation wavelength was set at 372 nm for $[\text{Sm}(\text{tta})_4]^-$ and $[\text{Sm}(\text{nta})_4]^-$ and at 334 nm for $[\text{Sm}(\text{hfa})_4]^-$. The assignment of the lines is given in Table 1.

$[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ (see the Supporting Information). This indicates that the first coordination sphere of $[\text{Sm}(\text{tta})_4]^-$ remains essentially intact upon dissolution of the complex in the ionic liquid. Similar results were found for $[\text{C}_6\text{mim}][\text{Eu}(\text{tta})_4]$; that is, the spectroscopic fine structure of the emission spectrum was not affected when the complex was dissolved in $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ compared to a solution of the same compound in acetonitrile.¹³

Although β -diketonates are well-known as very efficient energy donors, one of their major drawbacks is their often limited photostability in conventional organic solvents. The photostability of a europium(III) β -diketonate complex has been reported to be enhanced by the use of an ionic liquid.¹³ This was observed and demonstrated for the samarium(III)

Table 1. Summary of the Lines Observed in the Luminescence Spectrum of the Samarium(III) β -Diketonate Complexes Dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$

line ^a	line assignment	wavenumber (cm^{-1})	wavelength (nm)
a	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$	17850	560
b	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$	16610	602
c	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$	15500	645
d	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$	14140	707
e	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{13/2}$	12630	792
f	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{1/2}$	11400	877
	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{3/2}$	10710	934
	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{15/2}$		
g	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{5/2}$	10560	947
h	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{7/2}$	9710	1030
i	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{9/2}$	8570	1167
j	$^4\text{G}_{5/2} \rightarrow ^4\text{F}_{11/2}$	7250	1379

^a The letters correspond to those in Figure 6.

Table 2. Ratio of the Integrated Intensities $I(^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2})/I(^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2})$ and Luminescence Decay Times τ of the Samarium(III) Complexes Dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$, Acetonitrile, or Water

Sample	Solvent	$I(^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2})/I(^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2})$	τ (μs)
$[\text{C}_6\text{mim}][\text{Sm}(\text{tta})_4]$	$[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$	11.7	78 ± 4
	<i>MeCN</i>	13.5	106 ± 5
$[\text{C}_6\text{mim}][\text{Sm}(\text{nta})_4]$	$[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$	11.7	66 ± 3
	<i>MeCN</i>	11.2	76 ± 4
$[\text{C}_6\text{mim}][\text{Sm}(\text{hfa})_4]$	$[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$	10.6	72 ± 4
	<i>MeCN</i>	9.6	83 ± 4
	$[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$	5.4	61 ± 3
	$[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$		
	<i>H₂O</i>	4.9	21 ± 1

complex $[\text{C}_6\text{mim}][\text{Sm}(\text{tta})_4]$. For this experiment, $[\text{C}_6\text{mim}][\text{Sm}(\text{tta})_4]$ was dissolved in the ionic liquid $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ as well as in acetonitrile, dichloromethane, chloroform, ethanol, and N,N-dimethylformamide. The absorbance of the different solutions was followed as a function of their exposure to UV-light in a regular setup of the spectrofluorimeter (excitation source: xenon arc lamp, 450 W). The radiation wavelength was set at 340 nm, as this wavelength was used for the quantum yield determination of $[\text{C}_6\text{mim}][\text{Sm}(\text{tta})_4]$. The solutions were prepared with an absorbance of about 0.5 in 0.2 cm cells (before exposure to UV-light);

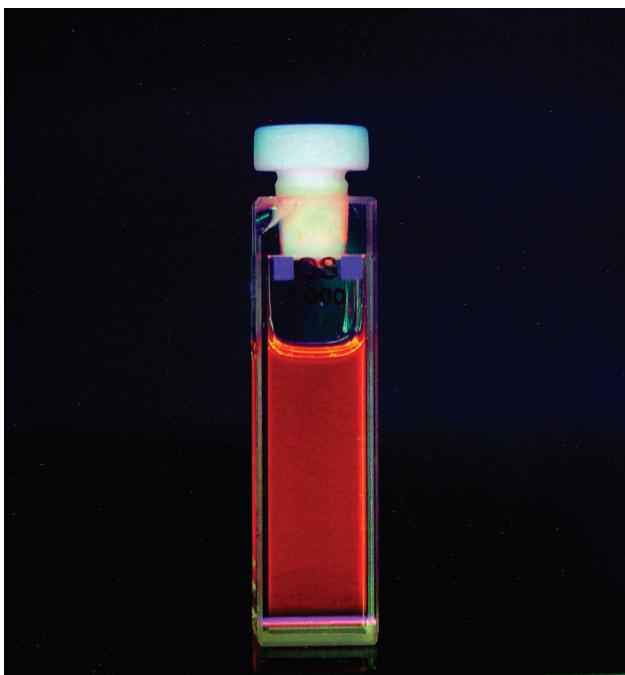


Figure 7. Luminescence of $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$ dissolved in the ionic liquid $[C_6\text{mim}][\text{Tf}_2\text{N}]$. The sample was irradiated with UV light ($\lambda = 365 \text{ nm}$).

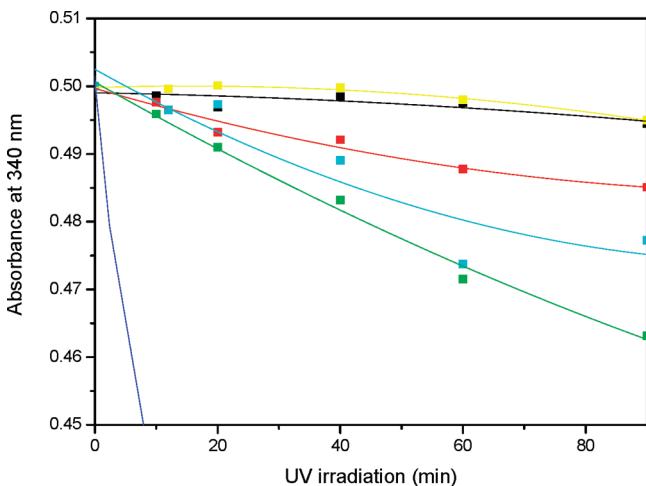


Figure 8. Absorbance of $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ dissolved in the ionic liquid, $[C_6\text{mim}][\text{Tf}_2\text{N}]$ (black), acetonitrile (red), dichloromethane (yellow), chloroform (green), ethanol (light blue), and $N,N\text{-dimethylformamide}$ (dark blue), as a function of the minutes of exposure to UV radiation (340 nm, xenon arc lamp 450W). The absorbance was measured in 0.2 cm cells.

this corresponds to a concentration of approximately $3.5 \times 10^{-5} \text{ M}$, which is also the concentration at which the luminescence quantum yield was measured. In Figure 8, the absorbance at $t = 0$ was normalized to 0.5 exactly for $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ dissolved in the different solvents. From Figure 8, it can be seen that the absorbance of the complex dissolved in acetonitrile, $N,N\text{-dimethylformamide}$, ethanol, and chloroform decreased upon UV-irradiation (340 nm), whereas the absorbance of this complex remains more or less constant when it is dissolved in an ionic liquid or in dichloromethane. Therefore, $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$ dissolved in an ionic liquid exhibits an enhanced photostability compared to acetonitrile, $N,N\text{-dimethylformamide}$, ethanol, and chloroform.

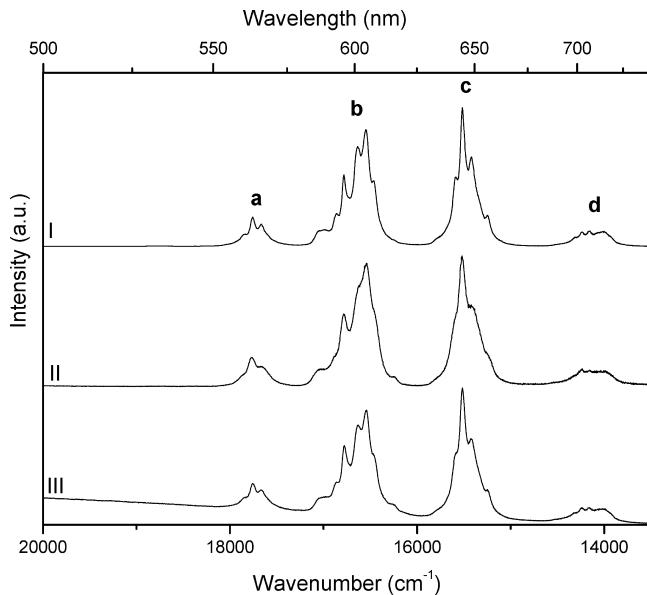


Figure 9. Room-temperature luminescence spectrum of $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$: I, in the solid state; II, dissolved in water; III, dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$. The excitation wavelength was set at 270 nm. The assignment of the lines is (a) $^4G_{5/2} \rightarrow ^6H_{5/2}$, (b) $^4G_{5/2} \rightarrow ^6H_{7/2}$, (c) $^4G_{5/2} \rightarrow ^6H_{9/2}$, and (d) $^4G_{5/2} \rightarrow ^6H_{11/2}$.

In order to extend the scope of this study, a samarium(III) complex with ligands other than β -diketonates was investigated, namely the samarium(III) tris dipicolinate complex, $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$. The luminescence was recorded at room temperature in the solid state, dissolved in water, and dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$ (Figure 9). This complex was not soluble in acetonitrile. From the spectra in Figures 6 and 9 and the values tabulated in Table 2, it can be noticed that the intensity ratio $I(^4G_{5/2} \rightarrow ^6H_{9/2})/I(^4G_{5/2} \rightarrow ^6H_{5/2})$ is smaller for $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$ than for the β -diketonate complexes. The surrounding of the samarium(III) ion does not change upon dissolving of the dipicolinate complex in water or in the ionic liquid.

The luminescence decay times for $[C_6\text{mim}][\text{Sm}(\text{tta})_4]$, $[C_6\text{mim}][\text{Sm}(\text{nta})_4]$, $[C_6\text{mim}][\text{Sm}(\text{hfa})_4]$, and $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$, dissolved in $[C_6\text{mim}][\text{Tf}_2\text{N}]$, are tabulated in Table 2 together with the luminescence lifetimes of the corresponding complexes in acetonitrile or water. The luminescence lifetimes were derived from the luminescence decay curves. For all samarium(III) complexes, the decay curves were found to be monoexponential. The values found for the luminescence quantum yield of the samarium(III) complexes in acetonitrile and in the ionic liquid, $[C_6\text{mim}][\text{Tf}_2\text{N}]$, are given in Table 3. It was not possible to determine the quantum yield of $[\text{choline}]_3[\text{Sm}(\text{dpa})_3]$ because of a strong absorption of the ionic liquid at the absorption range of the dipicolinate ligand, that is, around 270 nm. The errors for the quantum yield values as tabulated in Table 3 correspond to the experimentally found standard deviation from the mean value of a set of data. The values of the quantum yields found by the comparative method and with the use of an integrating sphere are very similar. The quantum yield of the samarium(III) β -diketonate complexes is slightly higher in acetonitrile than in the ionic liquid. This is in agreement with the

Table 3. Summary of the Luminescence Quantum Yield Values Found for the Samarium(III) β -Diketonate Complexes in Solution^a

sample	solvent	Φ^b comparative method	Φ^c integrating sphere
[C ₆ mim][Sm(tta) ₄]	[C ₆ mim][Tf ₂ N]	1.60 ± 0.29%	1.85 ± 0.08%
	MeCN	2.84 ± 0.73%	2.70 ± 0.82%
[C ₆ mim][Sm(nta) ₄]	[C ₆ mim][Tf ₂ N]	1.37 ± 0.39%	1.58 ± 0.16%
	MeCN	1.91 ± 0.28%	1.88 ± 0.07%
[C ₆ mim][Sm(hfa) ₄]	[C ₆ mim][Tf ₂ N]	1.06 ± 0.07%	1.45 ± 0.26%
	MeCN	1.59 ± 0.36%	1.34 ± 0.12%

^a The excitation wavelength was 340 nm for [C₆mim][Sm(tta)₄] and [C₆mim][Sm(nta)₄] and 330 nm for [C₆mim][Sm(hfa)₄]. ^b The quantum yield was determined relative to the organic standards: quinine sulfate in 1N H₂SO₄ (QY = 54.6%)³⁵ above and 9,10-diphenylanthracene in cyclohexane (QY = 70%)³⁶ in the case of [C₆mim][Sm(tta)₄] and [C₆mim][Sm(nta)₄] and quinine sulfate in 1N H₂SO₄ (QY = 54.6%)³⁵ in the case of [C₆mim][Sm(hfa)₄]. ^c The quantum yield was determined relative to [Eu(tta)₃phen] in DMF (QY = 19.6%).

values found for the luminescence lifetimes of the samarium(III) β -diketonate complexes in the ionic liquid compared to the compounds in acetonitrile (Table 2). In other words, the emission of samarium(III) is slightly more quenched in the ionic liquid than in acetonitrile. A possible explanation is the quenching of the luminescence in the ionic liquid by the O \cdots H hydrogen bonds that are present between the imidazolium cations and the oxygen atoms of the β -diketonate ligands. These hydrogen bonds are very likely to disappear when the complex is dissolved in a polar solvent such as acetonitrile, where solvation of the anion will increase the distance between the imidazolium cation and the anionic samarium(III) complex. On average, the luminescence quantum yields of [C₆mim][Sm(tta)₄], [C₆mim][Sm(nta)₄], and [C₆mim][Sm(hfa)₄] in [C₆mim][Tf₂N] were found to be 1.7%, 1.5%, and 1.3%, respectively. The values are similar for the three complexes. On the basis of the molecular structure of the Hhfa ligand, we would expect the quantum yield of [C₆mim][Sm(hfa)₄] to be lower compared to that of [C₆mim][Sm(tta)₄] and [C₆mim][Sm(nta)₄]. Because there is no aromatic group present in Hhfa, the position of the triplet excited state of this organic ligand is higher than in the case of Htta and Hnta. The quantum yield found for [C₆mim][Sm(hfa)₄] in [C₆mim][Tf₂N] is indeed slightly lower compared to that for [C₆mim][Sm(tta)₄] and [C₆mim][Sm(nta)₄] (1.3% versus 1.7% and 1.5%), whereas this is not the case for the luminescence lifetimes (72 μ s versus 78 and 66 μ s). As the overall quantum yield is the product of the efficiency of the sensitization process (η_{sens}) and the intrinsic quantum yield of the lanthanide ion (which is related to the luminescence lifetime), this could indicate that the efficiency of the sensitization (η_{sens}) is smaller for [C₆mim][Sm(hfa)₄]. The differences are however small. These quantum yield values are high compared to other quantum yields reported for samarium(III) complexes in solution but can be rationalized by the fact that for most quantum yield determinations the near-infrared contribution of the samarium(III) luminescence has not been taken into account. In the case of samarium(III) β -diketonates, around 20% of the luminescence output is situated in the near-infrared part of the electromagnetic spectrum. The tetrakis β -diketonate complexes are also expected to be among the highest luminescent complexes as a result of the highly efficient antenna effect

of the β -diketonate ligands. Voloshin et al. reported a quantum yield of 0.95% for [Sm(tta)₃(H₂O)₂] in acetonitrile (10⁻³ M solution).⁴² This value is significantly lower, which can be explained by the presence of two water molecules in the first coordination sphere. The luminescence quantum yield of [Sm(hfa)₃(phen)₂] (phen = 1,10-phenanthroline) in acetone (2 × 10⁻² M) was found to be 0.36% for ligand-sensitized samarium(III) visible emission.⁴³ A quantum yield of 2% has been previously reported for another samarium(III) β -diketonate micellar system containing 1,1,1-trifluoro-4-(2-naphthyl)-butane-2,4-dione, trioctylphosphine oxide, and Triton X-100.⁴⁴ An average value for the luminescence quantum yield of samarium(III) complexes in solution is 0.2%.^{45–49}

Conclusion

In conclusion, the imidazolium ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₆mim][Tf₂N], was found to be a suitable spectroscopic solvent for the study of visible and near-infrared luminescence of samarium(III) complexes. The ionic liquid improves the photostability of the samarium(III) β -diketonate complex [C₆mim][Sm(tta)₄] upon UV irradiation, and it allows experiments at liquid-nitrogen temperatures thanks to its glass-forming properties. The luminescence quantum yields of the β -diketonate complexes were high in acetonitrile and in the ionic liquid in comparison to the values earlier reported for samarium(III) complexes in solution. This study also points to the difficulties associated with the determination of luminescence quantum yields for lanthanide complexes. It is advised that the values be determined by two or more independent methods, for instance via a comparative method using standards and via an integrating sphere, in order to obtain reliable quantum yield values. Finally, this work contributes to our further understanding of the structural chemistry of lanthanide β -diketonate complexes. The tetrakis β -diketonate complexes are intriguing compounds because their anionic nature requires strong interactions with the counterions in the crystal structure. Interestingly, we detected strong hydrogen bonding between the imidazolium cations and the β -diketonate ligands in the solid state.

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Supporting Information Available: Table with summary of the crystallographic data. Additional luminescence spectra. CIF files of the crystal structures. This material is free of charge via the Internet at <http://pubs.acs.org>.

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