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Intense near-infrared luminescence of anhydrous lanthanide(III) iodides in an imidazolium ionic liquid

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Abstract

Anhydrous neodymium(III) iodide and erbium(III) iodide were dissolved in carefully dried batches of the ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim][Tf_2N]. Provided that the ionic liquid had a low water content, intense near-infrared emission could be observed for both the neodymium(III) ion and for the erbium(III) ion. Luminescence lifetimes have been measured, and the quantum yield of the neodymium(III) sample has been measured. Exposure of the hygroscopic samples to atmospheric moisture conditions caused a rapid decrease of the luminescence intensities.

1. Introduction

Just like inorganic ionic compounds (for instance sodium chloride), *ionic liquids* consist entirely of positive and negatively charged ions [1–3]. While the melting point of inorganic salts is typically several hundreds of degrees centigrade, the melting point of ionic liquids is by definition below 100 °C. Several types of ionic liquids are even at room temperature liquid (*room temperature ionic liquids* or RTILs). The cation of an ionic liquid is typically a large organic cation, such as imidazolium, pyridinium or a quaternary ammonium ion. As the anion, often Cl^-, Br^-, BF_4^-, PF_6^- or $CF_3SO_3^-$ is used. The properties of ionic liquids (miscibility with water and other solvents, dissolving ability, polarity, viscosity, density, etc.) can be tuned by an appropriate choice of the anion and the cation. Thus, ionic liquids are often considered as '*designer solvents*' [2]. So far, most studies of ionic liquids have focused mainly on their use as '*green solvents*' for organic reactions including polymerizations, as a catalyst, as an extraction solvent for the separation of metal ions or as an electrolyte in fuel cells. Only a few papers demonstrate the use of ionic liquids as a solvent for spectroscopic or photophysical studies [4–8]. For instance, the solvatochromism of selected dyes and the fine structure in the fluorescence spectra of polycyclic aromatic hydrocarbons have been used to probe the polarity of ionic liquids [9–12]. The solvent properties of ionic liquids can be designed in such a way that a weakly-coordinating solvent is gained. In this respect, ionic liquids become interesting solvents to investigate the spectroscopic behaviour of lanthanide complexes in solution, especially of complexes with weakly binding ligands, which otherwise would be unable to compete with the solvent molecules for a binding site on the lanthanide ion [13–15]. In fact, ionic liquids

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can be excellent solvents to study the near-infrared luminescence of lanthanide complexes in solution, as they not only dissolve organic, but also inorganic lanthanide compounds. So far, only a limited number of papers describe the lanthanide-containing ionic liquids [13–22].

In this Letter, we describe the spectroscopic properties of lanthanide(III) iodide complexes (Ln = Nd, Er) in an anhydrous imidazolium ionic liquid [C_{12}mim][Tf_2N]. Special emphasis is paid to the near-infrared luminescence shown by these complexes and to the importance of using carefully dried ionic liquids.

2. Experimental

All preparations were carried out under an argon atmosphere using a glove-box and standard Schlenk-techniques.

NdI_3 and ErI_3 were synthesized from the elements (30 h/200 °C) in a silica tube and purified by sublimation of the crude product at 800 °C under high vacuum [23,24]. The ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim][Tf_2N], was synthesized following a literature procedure [25]. First, [C_{12}mim]Br was obtained by solvent-free alkylation of *N*-methylimidazole with 1-bromododecane at 80 °C. The crude product was recrystallized from acetonitrile/toluene, dissolved in water and heated to 70 °C. One equivalent of lithium bis(trifluoromethylsulfonyl)imide in water was added dropwise and the mixture was stirred for another 24 h at room temperature. The product, which formed a second phase to water, was purified by addition of activated charcoal and filtration through aluminium oxide. It was washed with small aliquots of water until no halide residues could be detected in the extract ($AgNO_3$ test).

The ionic liquid was dried for 120 h in a Schlenk tube at 150 °C under reduced pressure and rigorous stirring. NdI_3 (81.5 mg, 0.155 mmol) and ErI_3 (81.4 mg, 0.148 mmol) were prepared into a silica tube (11 mm in diameter) and [C_{12}mim][Tf_2N] (3.1198 g, 5.86 mmol) was added. The tube was sealed off under dynamic vacuum and put in an ultrasonic bath until dissolution of the rare-earth salts was complete.

The steady-state luminescence spectra and the lifetime measurements were measured on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W Xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm^{-1}), an emission monochromator (600 lines mm^{-1}) and a liquid nitrogen cooled Hamamatsu R5509-72 near infrared photomultiplier tube. For the lifetime measurements we combined the FS-920P spectrofluorimeter with the 532 nm (frequency doubled) line of a Continuum Minilite II Nd:YAG laser. The luminescence lifetime has been determined by measurement of the luminescence decay curve. All photoluminescence spectra were recorded at room temperature. The quantum yield of the neodymium sample was determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) of Edinburgh Instruments. The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The quantum yield can be defined as: the integrated intensity of luminescence signal divided by the integrated intensity of the absorption signal. Only the intense luminescence band around 1054 nm measured by the integrating sphere, but this intensity value was corrected by taking into account the relative intensity of the other transitions (as determined from the steady-state luminescence spectrum). In this way, an intensity value that corresponds to the total luminescence output was obtained. The absorption intensity was calculated by subtracting the integrated intensity of the light source (with the sample in the integrating sphere) from the integrated intensity of the light source (with a blanco sample in the integrating sphere). The blanco sample was a silica measuring cell, filled with the pure ionic liquid [C_{12}mim][Tf_2N].

3. Results and discussion

For this Letter, we have synthesized neodymium(III) iodide (NdI_3) and erbium(III) iodide (ErI_3), and dissolved these compounds in the ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}MIM][Tf_2N]. We chose this ionic liquid because imidazolium is one of the most commonly used cation for ionic liquids, and because the use of a long side chain (dodecyl) results in a good balance between high polarity of the solvent and substantial lipophilicity at the same time. Additionally, the bis(trifluoromethylsulfonyl)imide anion results in very hydrophobic liquids with relatively low viscosity, and it is known to be weakly coordinating. In addition, lanthanide iodides were chosen as they can be reliably obtained as strictly anhydrous samples and iodide is the weakest coordinating ligand among the halides. Efforts have been made to make the ionic liquid as dry as possible, in order to avoid water molecules that can quench the near-infrared luminescence.

Excitation and emission spectra were recorded at room temperature, and the luminescence decay times were measured. Both the neodymium(III) and erbium(III) sample exhibit an intense photoluminescence. The intensity of the near-infrared luminescence strongly depends on the water content of the ionic liquid, in the sense that luminescence could only be observed for neodymium(III) iodide and erbium(III) iodide dissolved in a carefully dried ionic liquid sample. In order to exclude water from the sample, sample preparation had to be done in a glovebox and the ionic liquid solution was sealed in a silica ampoule filled with argon gas. As soon as the seal of the ampoule was broken and the sample was exposed to atmospheric humidity, the luminescence intensity decreased rapidly and substantially. At the same time, the ionic liquid solution turned turbid, although it turned clear again after addition of a drop of water. Finally, no near-infrared luminescence could be measured any longer. These results can be interpreted by the fact that water enters the first coordination sphere of the lanthanide ion, followed by quenching of the excited state of the lanthanide ion by vibronic coupling of the lanthanide electronic states with the vibrational states of the water molecules (*multiphonon relaxation*). It is well known that water molecules can effectively quench near-infrared luminescence of lanthanide ions. The fact that trivalent lanthanide cations prefer water in their first coordination sphere instead of iodide or Tf_2N anions can be explained by the HSAB-theory of Pearson [26]. The trivalent lanthanide ion is a hard Lewis acid and it prefers to bind to the hard Lewis base water, rather than to the soft Lewis base iodide. The cloudiness of the solution was most probably due to the formation of mixed iodide-hydroxy species or hydrated iodo complexes that subsequently dissolve in the ionic liquid. Since the Tf_2N ions are weakly coordinating anions, they cannot compete successfully with water molecules or even with iodo ligands for the lanthanide ion. The strong influence of water molecules on the properties of lanthanide(III) ions dissolved in ionic liquids can also be illustrated by recent literature data. A recent theoretical study by Chaumont and Wipff [20] shows that water molecules in ionic liquids containing europium(III) chloro complexes coordinate directly to the europium(III) ion. In the absence of chloro ligands, an europium(III) aquo complex $[Eu(H_2O)_9]^{3+}$ is formed. Because the iodo ligands bind weaker to the lanthanide(III) ion than chloro ligands, it can be expected that addition water molecules present in the ionic liquid can easier replace iodo ligands than chloro ligands from the first coordination sphere of the lanthanide ion. An experimental spectroscopic study of europium(III) triflate in the ionic liquid $[BMIM][Tf_2N]$ revealed that in the presence of small amounts of water the Eu^{3+} ion is heavily hydrated and that the luminescence properties of Eu^{3+} are strongly influenced [13].

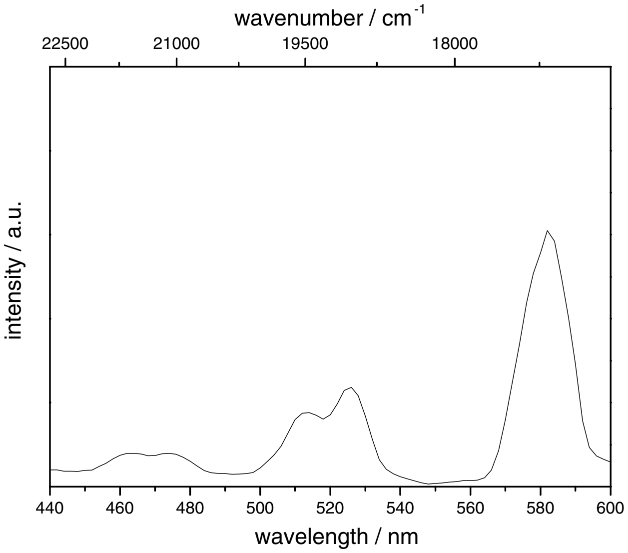

Fig. 1. Excitation spectrum of NdI_3 in $[C_{12}MIM][Tf_2N]$ at room temperature. The luminescence has been monitored at 1054 nm.

The excitation spectrum of NdI_3 in $[C_{12}MIM][Tf_2N]$ is shown in Fig. 1. To record the excitation spectrum, the emission intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition at 1054 nm was monitored while the excitation wavelength was continuously changed between 200 and 600 nm. In the excitation spectrum, the 4f–4f transitions of the Nd^{3+} ion are clearly visible. These transitions are intraconfigurational transitions within the $4f^3$ shell of the Nd^{3+} ion. To record the photoluminescence spectrum, direct excitation in the $^4I_{9/2} \leftarrow {}^4G_{5/2}$ absorption band of Nd^{3+} at 570 nm was chosen. In the photoluminescence spectrum, three transitions can be observed between 750 and 1450 nm (Fig. 2): $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (877 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1054 nm) and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1330 nm). The most intense transition is the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. The luminescence decay curves were measured and a single exponentional function could be fitted to the data. The experimental luminescence lifetime was 15.3 μs. Due to the high intensity of a neodymium emission, the luminescence quantum yield could be determined. By averaging six measurements a value of 1.5 ± 0.2% was obtained for the quantum yield. This value is quite high for a neodymium(III) compound

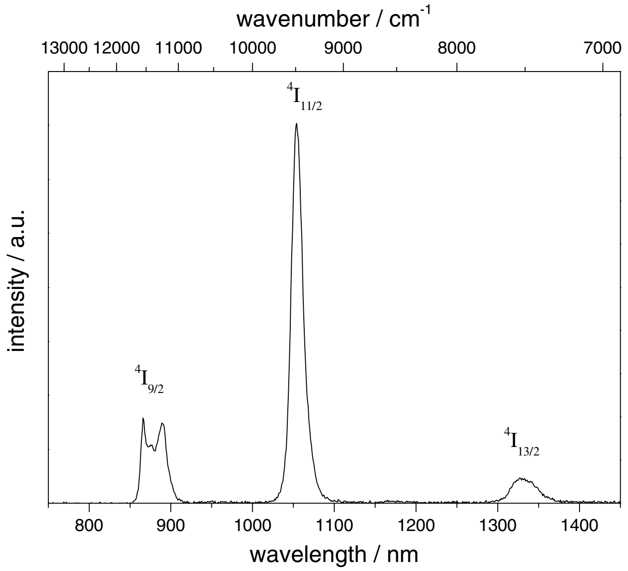

Fig. 2. Emission spectrum of NdI_3 in $[C_{12}MIM][Tf_2N]$ at room temperature. The excitation wavelength was 570 nm. All transitions start from the $^4F_{3/2}$ level.

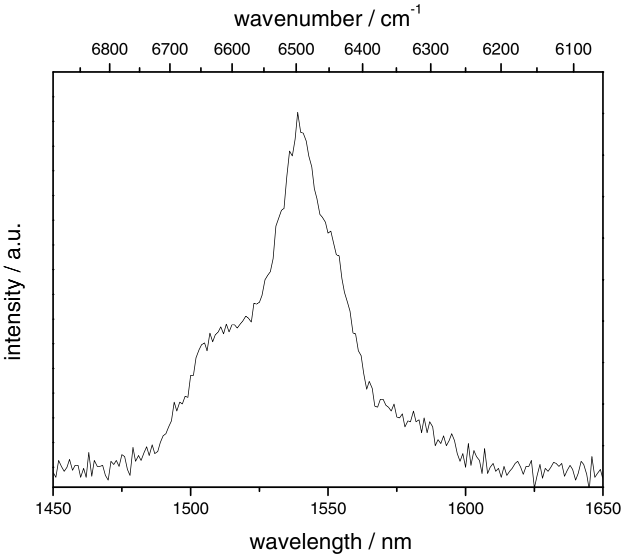

Fig. 3. Emission spectrum of ErI_3 in $[C_{12}MIM][Tf_2N]$ at room temperature. The excitation wavelength was 520 nm. The emission band corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

dissolved in an organic solvent. In fact, it is even higher than the values obtained for many neodymium(III) complexes in deuterated solvents [27,28].

Except for the differences in the positions and intensities of the 4f–4f transitions, the excitation spectrum of ErI_3 in $[C_{12}MIM][Tf_2N]$ is similar to that observed for NdI_3. The 4f–4f transitions are intraconfigurational transitions within the $4f^{11}$ electronic configuration of the Er^{3+} ion. The luminescence spectrum was measured by exciting the sample directly in the $^2H_{11/2} \leftarrow {}^4I_{15/2}$ absorption band of Er^{3+} at 520 nm. It consists of one emission band centered at 1540 nm which corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition (see Fig. 3). The luminescence intensity of the ErI_3 sample is weaker than that of the NdI_3 sample. Because of the presence of a smaller energy gap between the excited state and the ground state in Er^{3+}, the excited state of Er^{3+} can be more efficiently quenched by nonradiative processes than the excited state of Nd^{3+}. This is also reflected by the shorter experimental luminescence lifetime for ErI_3 (10.4 μs) than for NdI_3 (15.3 μs). Nevertheless, these values for the lifetimes are very long compared to literature values of erbium or neodymium compounds in solution. Compared to the neodymium sample, the intensity of the erbium sample was too low to obtain a reliable value for the quantum yield.

4. Conclusions

In conclusion, we have observed an intense near-infrared luminescence for neodymium(III) iodide and erbium(III) iodide dissolved in the ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, $[C_{12}MIM][Tf_2N]$. Special precautions were taken to obtain a very dry ionic liquid. Near-infrared luminescence could only be observed for anhydrous samples, and the luminescence intensity fell back to zero when atmospheric moisture was allowed to enter the solution. Ionic liquids provide a unique environment to study the luminescence properties of complexes of lanthanide ions, because ionic liquids are polar, but weakly coordinating solvents.

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