Lanthanide-doped luminescent ionogels†

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Ionogels are solid-oxide host networks confining at a meso-scale ionic liquids, and retaining their liquid nature. Ionogels were obtained by dissolving lanthanide(III) complexes in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide, [C6mim][Tf2N], followed by confinement of the lanthanide-doped ionic liquid mixtures in the pores of a nano-porous silica network, [C6mim][Ln(tta)3], where tta is 2-thienyltrifluoroacetanate and Ln = Nd, Sm, Eu, Ho, Er, Yb, and [choline][Tb(dpa)], where dpa = pyridine-2,6-dicarboxylate (dipicolinate), were chosen as the lanthanide complexes. The ionogels are luminescent, ion-conductive inorganic–organic hybrid materials. Depending on the lanthanide(III) ion, emission in the visible or the near-infrared regions of the electromagnetic spectrum was observed. The work presented herein highlights that the confinement did not disturb the first coordination sphere of the lanthanide ions and also showed the excellent luminescence performance of the lanthanide tetrakis β-diketonate complexes. The crystal structures of the complexes [C6mim][Yb(tta)3] and [choline][Tb(dpa)3] are reported.

Introduction

Lanthanide(III) complexes are interesting luminescent materials for application in molecular devices.1,2 Typical applications are the use of lanthanide(III) compounds as active components in organic light emitting diodes (OLEDs)3 and in optical fibers for data transmission.4 The light emitted by trivalent lanthanide ions has a high color purity because of the narrow emission lines and the emission wavelength can be tuned by a proper choice of the lanthanide ion. The molar absorptivity values of the forbidden intraconfigurational f-f transitions are typically less than 10 L mol⁻¹ cm⁻¹. This weak light absorption is a drawback, because the photoluminescence intensity is proportional to the amount of absorbed light energy. The problem can be partially solved by arranging a shell of strongly absorbing organic ligands around the lanthanide ion, which can transfer the excitation energy to the lanthanide ion, where it is converted into metal-centered luminescence. These organic ligands can also shield the lanthanide ion from molecules with high-energy vibrations, like water molecules, which would otherwise depopulate the excited states of the lanthanide ions by radiationless deactivation.5 β-Diketonates are the most popular ligands for the design of luminescent molecular lanthanide(III) complexes.6,7 Lanthanide(III) β-diketonate complexes have been incorporated in different types of host matrices, e.g. polymers,8,9 sol–gel glasses,9 inorganic–organic hybrid materials,10 liquid crystals11 and ionic liquids.12,13 Recently, we introduced lanthanide-doped ionogels as a new type of luminescent material.14 Ionogels are hybrid materials consisting of an ionic liquid confined inside the nano-sized pores of a silica matrix.15 The ionogels are obtained as monoliths featuring both the transparency of silica and the good ionic conductivity performances of the ionic liquid, despite the nanometer scale of confinement. The conductivity of the ionogel corresponds well to that of the ionic liquid indicating an interconnecting porosity of the silica matrix. They can be made completely stable in water and in several organic solvents, in which they can be immersed without damage for months.16 The mechanical properties of ionogels are also very similar to those of regular sol–gel hybrid materials. The volume of the ionic liquid is more or less three times the volume of the silica matrix. It is noteworthy that ionogels can contain 80 vol% of ionic liquid, which was shown to retain liquid-like dynamics.17 The heat resistance of the ionogel depends also on the type of ionic liquid, typically being in the range of 550–600 K. The ability to easily shape the ionogels provides an attractive versatility to prepare coatings, rods or pellets, making it possible to implement them in optical devices. These ionic conductor materials could be excellent candidates for the design of electroluminescent devices. Ionogels can be considered as a new type of ionic-liquid based material.18 In our previous study, we doped the 1-hexyl-3-methylimidazolium tetrakis(naphthoyltrifluoroacetanato)europate(III) complex in an ionogel consisting of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide, [C6mim][Tf2N], confined into a silica matrix.14

In this paper we generalize our initial results on europium(III)-doped ionogels by extending the work to other ligands and

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lanthanide(III) ions. In a first series of ionogel samples, the lanthanide complex was \([\text{C}_6\text{mim}][\text{Ln(tta)}_4]\), where \(\text{C}_6\text{mim}\) is the 1-hexyl-3-methylimidazolium cation, \(\text{tta}\) is 2-thienyltrifluoroacetone and \(\text{Ln} = \text{Nd, Sm, Eu, Ho, Er, Yb}\) (Fig. 1).

In the second series of ionogels, the lanthanide complex was \([\text{choline}][\text{Tb(dpa)}_3]\), where the \(\text{dpa}\) is the dipicolinate or pyridine-2,6-dicarboxylate ligand (Fig. 2).

**Results**

The tetrakis \(\beta\)-diketonate complexes \([\text{C}_6\text{mim}][\text{Ln(tta)}_4]\) were prepared in ethanol by reaction of the lanthanide salt \(\text{LnCl}_3 \cdot x\text{H}_2\text{O}\) with an excess of the sodium salt of 2-thienyltrifluoroacetone (1 : 6 ratio), in the presence of the ionic liquid \([\text{C}_6\text{mim}]\text{Br}\). However, the same procedure could not be used for the synthesis of the \([\text{C}_6\text{mim}][\text{Tb(dpa)}_3]\) complex: \(\text{Na}_3[\text{Tb(dpa)}_3]\) was obtained instead. The reason for this experimental problem is most probably the strong interaction of the sodium ions (from the base \(\text{NaOH}\) used to deprotonate dipicolinic acid) with the carboxylate functional group of the dipicolinate ligand, favoring the interaction with the sodium ion instead of the \([\text{C}_6\text{mim}]^+\) cation. To avoid the use of any sodium compound, (2-hydroxyethyl)trimethylammonium hydroxide (choline hydroxide, \([\text{choline}]\text{OH}\)) was chosen as the base for deprotonation of dipicolinic acid. As a consequence, the \([\text{C}_6\text{mim}]^+\) cation is replaced by the (2-hydroxyethyl)trimethylammonium (= choline) cation in the resulting compound \([\text{choline}][\text{Tb(dpa)}_3]\), which is soluble (in limited amounts) in the \([\text{C}_6\text{mim}]\text{Br}\) ionic liquid.

From the crystal structure of \([\text{C}_6\text{mim}][\text{Yb(tta)}_4]\), it is evident that no water or other solvent molecules are coordinated to the ytterbium(III) ion (Fig. 3). The crystal structure of \([\text{C}_6\text{mim}][\text{Yb(tta)}_4]\) consists of 1-hexyl-3-methylimidazolium \([\text{C}_6\text{mim}]^+\) cations and \([\text{Yb(tta)}_4]^-\) anions. Two crystallographically independent ytterbium(III) ions are present in the asymmetric unit. The eight-coordinate ytterbium(III) ions are surrounded by four 2-thienyltrifluoroacetate ligands with \(\text{Yb} - \text{O}\) distances ranging from 2.280(4) Å to 2.326(4) Å (Fig. 4). The coordination polyhedron around ytterbium(III) can be described as a distorted square antiprism. The three acidic hydrogens of the imidazolium cations form \(\text{C} - \text{H} \cdots \text{O}\) hydrogen bonds to the oxygens of the coordinating \(\beta\)-diketonate ligands of the two independent ytterbate(III) anions ranging from 2.308 Å to 2.629 Å. In the packing, a disordered ethanol solvent molecule is present.

The crystal structure of \([\text{choline}][\text{Tb(dpa)}_3]\) consists of triply negative charged \([\text{Tb(dpa)}_3]^-\) anions and choline cations (Fig. 5).
and 6). The terbium(III) ions are nine-coordinate by three tridentate, dinegatively-charged dipicolinate ligands with Tb–O and Tb–N distances of 2.403(2) Å and 2.497(2) Å, respectively. The terbium(III) ion is located on the threefold symmetry axis. Each of the three non-coordinating carbonyl oxygens of the dipicolinate ligands form a basket-like environment at opposite sites of the [Tb(dpa)]³⁻ anion. The choline cations are located above these cavities, forming O–H⋯O hydrogen bonds to these carbonyl oxygens (O–O distance of 2.68(1) Å), disordered along a threefold axis. The third choline cation is situated between each three [Tb(dpa)]³⁻ moieties and disordered on six symmetry-equivalent positions because of the combination of a threefold axis and an inversion center. This choline cation forms a hydrogen bond to an adjacent carbonyl oxygen atom of a dpa ligand (O–O distance of 2.73(1) Å). The H(O) hydrogen atoms of the choline cations could be localized from the difference Fourier map. Structures with extensively disordered choline cations have been reported before.¹⁹

The ionogels were obtained following a non-hydrolytic sol–gel processing route. The silicon-containing precursors tetra-methoxysilane (TMOS) and methyltrimethoxysilane (MTMS), 50% of each, were mixed with formic acid (FA) and the pure ionic liquid (IL, [C₆mim][Tf₂N]) in a molar ratio FA:Si:IL 7.8: 1:0.5. The mixture was stirred for about 15 min. After this, gelation occurred within 36 h. Complete aging of the ionogel was obtained after 8 days. The aging process can be followed by monitoring the weight loss. In a second step, the [C₆mim][Tf₂N] ionic liquid was removed from the silica matrix by Soxhlet extraction with acetonitrile for 24 h. At this point a lanthanide(III)-doped ionic liquid was prepared by mixing an appropriate amount of a solution of the lanthanide(III) complex in dichloromethane with the [C₆mim][Tf₂N] ionic liquid followed by evaporation of dichloromethane. The lanthanide(III)-doped ionic liquid was absorbed by the porous silica matrix obtained after the Soxhlet extraction by dipping the wet gels into the lanthanide(III)-complex/ionic liquid solution. This three-step procedure had to be used because of the instability of the lanthanide(III) β-diketonate and dipicolinate complexes towards acids (formic acid catalyst used for the sol–gel synthesis). The ionogels were obtained as monolithic samples.
The ionogels doped with [C₆mim][Sm(tta)₄], [C₆mim][Eu(tta)₄] and [choline][Tb(dpa)₃] show a strong photoluminescence when irradiated with ultraviolet light (Fig. 7). The samarium(III) compound exhibits orange-red luminescence, the europium(III) compound intense bright red luminescence and terbium(III) a vivid green luminescence. The luminescence of the other samples could not be observed by the naked eye, because these ionogels emit in the near-infrared region.

Fig. 7 Luminescence of the monolithic ionogel samples doped with the samarium(III), europium(III) and the terbium(III) complexes (λexc = 365 nm).

The luminescence spectrum of the [C₆mim][Eu(tta)₄]-doped ionogel is shown in Fig. 8. The spectrum is typical for a europium(III) β-diketonate complex featuring a very intense 5D₀ → 7F₂ transition at 16330 cm⁻¹ (612 nm). The assignment of the transitions and the relative intensities of the emission bands are summarized in Table 1. Only one symmetric line is observed for the 1D₁ → 3F₀ transition. The narrow peaks observed in the luminescence spectra of samarium(III) (Fig. 9) are transitions between the 1G₅/₂ excited state and the different J-levels of the 6H term (1Hₓ, J = 5/2–15/2) and the 4F term (4Fₓ, J = 1/2–9/2). The most intense transitions are the 2G₅/₂ → 2H₀/₂ line at 15475 cm⁻¹ (646 nm) in the visible region and the 3G₅/₂ → 4F₅/₂ line at 10510 cm⁻¹ (950 nm) in the near-infrared region.

The emission peaks in the neodymium(III)-doped ionogel correspond to transitions between the 6F₃/₂ level and the different J levels of the ground state 7I term (7Iₓ, J = 9/2–13/2), with the 6F₃/₂ → 1I₁/₂ line at 9447 cm⁻¹ (1058 nm) being the most intense transition (Fig. 10). The luminescence spectrum of the ytterbium(III)-doped ionogel consists of only one relatively broad emission peak, with its maximum at 10256 cm⁻¹ (975 nm) and corresponding to the transition between the 2F₅/₂ excited state and the 2F₅/₁ ground state (Fig. 11). Luminescence could be detected for the erbium(III)-containing ionogel (Fig. 12) as well as for the holmium(III)-containing ionogels (Fig. 13), although the luminescence is quite weak. The emission spectrum of the ionogel doped with the terbium(III) complex [choline][Tb(dpa)₃] is very similar to the emission spectrum obtained for [choline][Tb(dpa)₃] dissolved in the [C₆mim][Tf₂N] ionic liquid as well as to the spectrum of [choline][Tb(dpa)₃] in the solid state (Fig. 14). Confinement of the terbium(III)-doped ionic liquid in the porous silica host did not change the fine structure in the luminescence spectra of the [Tb(dpa)₃]³⁻ complex.

In Table 2, the luminescence decay times of the different lanthanide(III) ions doped in the ionogel samples are compared with those of the same lanthanide(III) complex dissolved in the ionic liquid [C₆mim][Tf₂N], i.e. the ionic liquid which is also present in the ionogels. In order to test the stability of the ionogel against water, an ionogel sample containing [C₆mim][Eu(tta)₄] was immersed in water for a period of 1 h. No differences were noticed for the fine structure in the luminescence spectra of the sample before and after immersion in water. Within the limits of the measurement error, the luminescence decay time of the sample before immersion (529 μs) is identical to that of the sample after immersion (532 μs).

![Luminescence spectrum of the [C₆mim][Eu(tta)₄]-doped ionogel (room temperature, λexc = 340 nm).](image)

**Fig. 8** Luminescence spectrum of the [C₆mim][Eu(tta)₄]-doped ionogel (room temperature, λexc = 340 nm). The assignment of the lines is: (a) 5D₀ → 7F₆; (b) 5D₀ → 7F₅; (c) 5D₀ → 7F₄; (d) 5D₀ → 7F₃; (e) 5D₀ → 7F₂; (f) 5D₀ → 7F₁; and (g) 5D₀ → 7F₀.

**Table 1** Summary of the transitions observed in the luminescence spectrum of the europium(III)-doped ionogel

<table>
<thead>
<tr>
<th>Line assignment</th>
<th>Transition mechanism⁴</th>
<th>Wavenumber/cm⁻¹</th>
<th>Wavelength/nm</th>
<th>Intensity (a.u.)⁹</th>
<th>Branching ratio (%)⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D₁ → 3F₀</td>
<td>MD</td>
<td>17244</td>
<td>580.0</td>
<td>5</td>
<td>= 0</td>
</tr>
<tr>
<td>1D₁ → 3F₁</td>
<td>ED</td>
<td>16849</td>
<td>593.5</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
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<td>ED</td>
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<td>612.0</td>
<td>1635</td>
<td>83</td>
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<tr>
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<td>ED</td>
<td>15300</td>
<td>653.5</td>
<td>60</td>
<td>3</td>
</tr>
<tr>
<td>1D₁ → 3F₄</td>
<td>ED</td>
<td>14250</td>
<td>702.0</td>
<td>130</td>
<td>7</td>
</tr>
<tr>
<td>1D₁ → 3F₅</td>
<td>ED</td>
<td>13324</td>
<td>750.5</td>
<td>5</td>
<td>= 0</td>
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<tr>
<td>1D₁ → 3F₆</td>
<td>ED</td>
<td>12326</td>
<td>811.0</td>
<td>25</td>
<td>1</td>
</tr>
</tbody>
</table>

⁴ ED = forced electric dipole transition; MD = magnetic dipole transition. ⁹ Integrated intensities in arbitrary units, but normalized so that I(5D₀ → 7F₁) = 100. The branching ratio gives the contribution (in %) of a given line to the total luminescence intensity.
Fig. 9 Luminescence spectrum of the [C₆mim][Sm(tta)₄]-doped ionogel (room temperature, λₑₜ = 340 nm). The assignment of the lines is: (a) ⁴G₅/₂ → ⁶H₅/₂; (b) ⁴G₅/₂ → ⁶H₇/₂; (c) ⁴G₅/₂ → ⁶H₉/₂; (d) ⁴G₅/₂ → ⁶H₁₁/₂; (e) ⁴G₅/₂ → ⁶H₁₃/₂; (f) ⁴G₅/₂ → ⁶F₁/₂, ⁴G₅/₂ → ⁶F₃/₂, and (g) ⁴G₅/₂ → ⁶H₁₅/₂; (h) ⁴G₅/₂ → ⁶F₅/₂; (i) ⁴G₅/₂ → ⁶F₇/₂ and (j) ⁴G₅/₂ → ⁶F₉/₂.

Fig. 10 Luminescence spectrum of the [C₆mim][Nd(tta)₄]-doped ionogel (room temperature, λₑₜ = 340 nm). The assignment of the lines is: (a) ⁴F₃/₂ → ⁴I₉/₂; (b) ⁴F₃/₂ → ⁴I₁₁/₂ and (c) ⁴F₃/₂ → ⁴I₁₃/₂.

Fig. 11 Luminescence spectrum of the [C₆mim][Yb(tta)₄]-doped ionogel (room temperature, λₑₜ = 340 nm). The assignment of the line is ⁵F₇/₂ → ⁵F₇/₂.

Fig. 12 Luminescence spectrum of the [C₆mim][Er(tta)₄]-doped ionogel (room temperature, λₑₜ = 340 nm). The assignment of the line is ⁴I₁₃/₂ → ⁴I₁₅/₂.

Discussion

Lanthanide β-diketonate complexes are very often used as luminescent dopands in inorganic–organic hybrid materials. Different stoichiometries are possible for these complexes: tris complexes, Lewis-base adducts of tris complexes and the tetrakis complexes. The most popular lanthanide β-diketonate complexes are the Lewis-base adducts of tris complexes, like [Ln(tta)₃(phen)]. Although these complexes have successfully been used as luminophores in ionic liquids, we preferred the ionic tetrakis complexes for incorporation in the ionogels. First of all, it can be expected that anionic complexes are less prone to leaching from the ionic liquid host than a neutral complex. Secondly, by choosing the same cation for the counter ion of the tetrakis complex as that of the ionic liquid, the solubility of the lanthanide complex in the ionic liquid can be increased. Moreover, neutral complexes can also be dissolved in the silica part of the ionogel, whereas an ionic complex can be expected to have a much higher affinity for the ionic liquid. Thirdly, the europium(III) tetrakis complexes exhibit a very intense hypersensitive transition ⁵D₀ → ⁷F₂, so that the resulting luminescent light has a high coloric purity. The [C₆mim][Ln(tta)₄] complexes...
are therefore a good choice as luminescent lanthanide-containing dopant, except for terbium(III). Earlier work has shown that the 2-thienyltrifluoroacetinate (tta) ligand is not very suited as sensitizer for terbium(III), because of the low energetic position of the triplet state of the 2-thienyltrifluoroacetinate ligand.\(^{24}\) In fact, the emitting \(^1\text{D}_4\) level of terbium(III) is at a higher energy than the triplet level of most \(\beta\)-diketone ligands.\(^{7}\) Therefore the energy transfer from the \(\beta\)-diketone ligand is not efficient and there will also be a back transfer of the energy from the \(^1\text{D}_4\) level to the \(\beta\)-diketone triplet level. However, the dipicolinate (pyridine-2,6-dicarboxylate, dpa) ligand is an efficient sensitizer of terbium(III) luminescence.\(^{22}\) Our approach was to follow the same strategy as for the tetrakis \(\beta\)-diketone complexes, \textit{i.e.} designing a new complex with a constituent ion of the ionic liquid as counter ion in order to improve the solubility properties of the complex in the ionic liquid. Unfortunately, the \([\text{C}_6\text{mim}]\text{[Tb(dpa)\textsubscript{3}]}\) could not be prepared by the method used for the synthesis of the \([\text{C}_6\text{mim}]\text{[Ln(tta)\textsubscript{4}]}\) complexes, because after all trials the \([\text{Na}\text{[Tb(dpa)\textsubscript{3}]}\) complex was obtained. Therefore, we switched to the \([\text{choline}]\text{[Tb(dpa)\textsubscript{3}]}\) complex. The choline cation can also be an ionic liquid component.\(^{21}\) Recently, D’Ale\(\text{\text{\textae}}\) et al. proposed the use of the guanidinium cation as counter ion in \([\text{Ln(dpa)\textsubscript{3}}]^{-}\) complexes.\(^{29}\)

The emission color of the ionogel can be tuned by a proper choice of the lanthanide ion (Fig. 7). The red emission by europium(III) and the green emission by terbium(III) are well known, but the luminescence properties of samarium(III) are much less documented. Although the red emission by samarium(III) is less intense than that of europium(III) and shifted further to the near-infrared, the samarium(III) ion is of interest because it is emitting both in the red and in the near-infrared spectral region. However, most luminescence studies on samarium(III) complexes neglect the near-infrared emission of this ion. Only recently, near-infrared emission by samarium(III) in molecular complexes is receiving more attention.\(^{8,25}\) The lanthanide ions that are typically used for near-infrared emission are neodymium(III), erbium(III) and ytterbium(III). Holmium(III) exhibits near-infrared luminescence in spectral regions that are complementary to neodymium(III), erbium(III) and ytterbium(III), with an emission band around 1450 nm. However, holmium(III) luminescence has attracted much less attention than luminescence of the other three lanthanide(III) ions. Much of the holmium-related studies have been performed in inorganic matrices,\(^{26}\) and examples of infrared-emission by molecular lanthanide complexes are rare.\(^{27}\)

The tetrakis \(\beta\)-diketone complex creates a very well defined environment for the lanthanide ions. This can be deduced from the high resolution emission spectra of the europium(III) complex in the ionogel (Fig. 8). Only one line is observed for the \(^1\text{D}_4\) → \(^7\text{F}_0\) transition. Moreover, the emission band of this (very weak) transition is symmetrical. This indicates that the tetrakis complex does not dissociate in the ionic liquid matrix. Dissociation would lead to the observation of different species in solution.

Because the ionogels consist of two structurally quite different components, the ionic liquid and the silica matrix, one could raise the question whether the lanthanide complex remains dissolved
in the ionic liquid or whether it will be transferred to the silica network. All experimental data point to incorporation of the tetrakis β-diketone complex in the ionic liquid matrix. First of all, no significant difference in the fine structure of the emission spectra could be observed for the lanthanide(III) complexes dissolved in the ionic liquid and in the ionogel (see for instance Fig. 14). High resolution luminescence spectra would reveal small differences in the coordination environment of the lanthanide ion. The fact that the spectra in the ionic liquid and in the ionogel are very similar also means that the nanoconfinement of the ionic liquid in the silica matrix does not disturb the first coordination sphere of the lanthanide ion. Secondly, the luminescence decay times of the lanthanide complexes dissolved in the ionic liquid and in the ionogel are similar (Table 2). The confinement of the lanthanide-doped ionic liquid in the silica matrix has thus only a limited or no influence on the luminescence decay times.

**Experimental**

**General**

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 (pulse length: 2 μs) and a red-sensitive photomultiplier (300–850 nm). The luminescence spectra in the infrared region were measured on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W xenon lamp as the 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. All photoluminescence spectra have been recorded at room temperature. The sample compartment can be equipped with an integrating sphere coated with BaSO₄ for quantum yield measurements.

**Synthesis of ionic liquids**

The ionic liquid 1-hexyl-3-methylimidazolium bromide, [C₆mim][Br], has been prepared as previously described.²⁴ The ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)), [C₆mim][Tf₂N], was synthesized from [C₆mim][Br] by a metathesis reaction between lithium bis(trifluoromethylsulfonylimide)imide and [C₆mim][Br].²⁵ The resulting ionic liquid was washed several times with aliquots of water (20 ml) until bromide residues could no longer be detected by the AgNO₃ test. δᵣ (300 MHz, CDCl₃, 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 lanthanide(III) complexes**

The lanthanide(III) complexes were synthesized by a method previously described by us.²² The lanthanide(III) β-diketone complexes were prepared by first dissolving 2-thenoyltrifluoroacetone (6 eq.) in ethanol and deprotonating this ligand with an aqueous solution of NaOH at 50 °C, followed by the addition of 1.5 equivalents of the ionic liquid [C₆mim][Br] in ethanol and by the dropwise addition of 1 equivalent of LnCl₃·xH₂O in water. The solution was left to stir and cool down to room temperature overnight. A precipitate of the complex was formed. The product was filtered and washed with ice-water as well as dried in vacuo at 50 °C. The yield of the reaction was on average 30%. Eu complex: Found: C, 41.7; H, 3.0; N, 2.3. Calc. for C₂₉H₂₉N₆O₁₅F₁₄Eu (Mₑ₄ = 1203.94): C, 41.9; H, 2.9; N, 2.3%. Sm-complex: Found: C, 41.9; H, 3.4; N, 2.4. Calc. for C₃₀H₂₉N₆O₁₅F₁₄Sm (Mₑ₄ = 1202.34): C, 42.0; H, 2.9; N, 2.3%. Nd-complex: Found: C, 41.75; H, 3.1; N, 2.3. Calc. for C₃₀H₂₉N₆O₁₅F₁₄Nd (Mₑ₄ = 1196.22): C, 42.2; H, 2.95; N, 2.3%. Yb-complex: Found: C, 41.3; H, 2.9; N, 2.3. Calc. for C₃₀H₂₉N₆O₁₅F₁₄Yb (Mₑ₄ = 1225.02): C, 41.2; H, 2.9; N, 2.3%. Er-complex: Found: C, 41.1; H, 2.8; N, 2.3. Calc. for C₃₀H₂₉N₆O₁₅F₁₄Er (Mₑ₄ = 1219.24): C, 41.4; H, 2.9; N, 2.3%. Ho-complex: Found: C, 41.3; H, 2.8; N, 2.3. Calc. for C₃₀H₂₉N₆O₁₅F₁₄Ho (Mₑ₄ = 1216.91): C, 41.45; H, 2.9; N, 2.3%.

For the synthesis of [choline][Tb(dpa)], pyridine-2,6-dicarboxylic acid (3 eq.) was dissolved in 7 mL of H₂O together with 2.115 ml of a solution of choline hydroxide, 45 wt% in MeOH (6 eq.). The pH is checked to be neutral and the solution is heated to 70 °C followed by the dropwise addition of TbCl₃·xH₂O (1 eq.) in water. The solution was left to stir for 2 h. Water was removed by a rotavap. The product had a white color and was washed with methanol to remove residues of choline chloride and dried in vacuo at 50 °C. Yield: 50%. Found: C, 43.05; H, 5.5; N, 7.9 Calc. for C₂₉H₂₉N₆O₁₄Tb (H₂O): (Mₑ₄ = 1002.78): C, 43.1; H, 5.5, N, 8.4%.

**Synthesis of the ionogels**

Lanthanide(III)-doped [C₆mim][Tf₂N] ionic liquid samples were prepared as follows: an appropriate amount of the lanthanide(III) complex was mixed with dichloromethane. An exact volume of this solution was then diluted into 1.52 ml of a solution of choline hydroxide, 45 wt% in MeOH (6 eq.). The pH is checked to be neutral and the solution is heated to 70 °C followed by the dropwise addition of TbCl₃·xH₂O (1 eq.) in water. The solution was left to stir for 2 h. Water was removed by a rotavap. The product had a white color and was washed with methanol to remove residues of choline chloride and dried in vacuo at 50 °C. Yield: 50%. Found: C, 43.05; H, 5.5; N, 7.9 Calc. for C₂₉H₂₉N₆O₁₄Tb (H₂O): (Mₑ₄ = 1002.78): C, 43.1; H, 5.5, N, 8.4%.

Ionogels were prepared as previously described for [C₆mim][Eu(nta)], [C₆mim][Eu(taa)], [C₆mim][Yb(tta)], [C₆mim][Nd(tta)] 0.0026 mol L⁻¹; [C₆mim][Nd(tta)] 0.0026 mol L⁻¹; [C₆mim][Er(tta)] 0.0033 mol L⁻¹; [C₆mim][Ho(tta)] 0.0015 mol L⁻¹; [choline][Tb(dpa)], 0.0027 mol L⁻¹.

Ionogels were prepared as previously described for [C₆mim][Eu(nta)], doped ionogel i.e. by a non-hydrolytic sol-gel route.¹⁴ Tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS, 50% of each) purchased from Fluka and Alfa Aesar were mixed with formic acid and [C₆mim][Tf₂N] (molar ratio 7.8 : 1 : 0.5). Gelation occurred within 36 h. After complete maturation of the ionogels (8 days aging), [C₆mim][Tf₂N] was removed by Soxhlet extraction with acetonitrile for 24 h. After extraction the wet gels were immediately dipped into lanthanide(III)-doped [C₆mim][Tf₂N] solutions. Complete absorption of Ln(III)-doped [C₆mim][Tf₂N] ionic liquid occurred at room temperature within 48 h. Dichloromethane evaporated from the ionogel samples by exposure to the air.

**Crystallography**

Crystals of the complexes [C₆mim][Yb(tta)], 0.04 CH₃OH and [choline][Tb(dpa)], suitable for X-ray crystallography were crystallized by slowly evaporating an ethanolic and a water solution of the respective compounds. X-ray intensity data were collected.
formulations containing the luminophor can be optimized prior to those in the ionic liquid solvent. This observation is convenient as the lifetimes of the lanthanide complexes in the ionogel are similar to those in the ionic liquid and are not significantly changed upon confinement of the ionic liquid. The coordination sphere of the lanthanide ion is not significantly changed upon confinement of the ionic liquid within the silica matrix of the ionogel. Also the luminescence lifetimes of the lanthanide complexes in the ionogel are similar to those in the ionic liquid solvent. This observation is convenient for the design of luminescent ionogels because the ionic liquid formulations containing the luminophor can be optimized prior to incorporation in the ionogel. Present paper shows that it is possible to prepare monolithic samples of ionogels doped with different lanthanide(III) ions. The next challenge is to prepare stable thin films of these hybrid materials, because this is a prerequisite for the design of luminescent devices.

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