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Ionic liquid as plasticizer for europium(III)-doped luminescent poly(methyl methacrylate) films†

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Flexible luminescent polymer films were obtained by doping europium(III) complexes in blends of poly(methyl methacrylate) (PMMA) and the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C$_6$mim][Tf$_2$N]. Different europium(III) complexes have been incorporated in the polymer/ionic liquid matrix: [C$_6$mim][Eu(nta)$_4$], [C$_6$mim][Eu(tta)$_4$], [Eu(tta)$_3$(phen)] and [choline]$_3$[Eu(dpa)$_3$], where nta is 2-naphthoyltrifluoroacetonate, tta is 2-thenoyltrifluoroacetonate, phen is 1,10-phenanthroline, dpa is 2,6-pyridinedicarboxylate (dipicolinate) and choline is the 2-hydroxyethyltrimethyl ammonium cation. Bright red photoluminescence was observed for all the films upon irradiation with ultraviolet radiation. The luminescent films have been investigated by high-resolution steady-state luminescence spectroscopy and by time-resolved measurements. The polymer films doped with β-diketonate complexes are characterized by a very intense $^5D_0 \rightarrow {}^7F_2$ transition (up to 15 times more intense than the $^5D_0 \rightarrow {}^7F_1$) transition, whereas a marked feature of the PMMA films doped with [choline]$_3$[Eu(dpa)$_3$] is the long lifetime of the $^5D_0$ excited state (1.8 ms).

Introduction

Lanthanide(III) complexes are interesting luminescent materials for use in molecular devices.[1–7] Processable lanthanide-based luminescent molecular materials can be obtained by doping the lanthanide(III) complex in a polymer matrix.[8,9] Typical applications of such polymer films are in organic light emitting diodes (OLEDs)[10–14] or in active optical polymer fibers for data transmission.[15–17] A popular polymer matrix for use as host for luminescent lanthanide complexes is poly(methyl methacrylate) (PMMA), which is transparent at wavelengths longer than 250 nm.[18] The first experiments on optical materials based on PMMA doped with β-diketonate complexes go back to the 1960's when the lanthanide β-diketonates have been tested as active components in chelate lasers. For instance, Wolff and Pressley (1963) doped europium(III) tris(2-thenoyltrifluoroacetonate) into PMMA and observed laser action in this material.[19] Several other authors have investigated the spectroscopic and photophysical properties of lanthanide(III) complexes in PMMA.[20–25] A disadvantage of PMMA films or sheets is their brittleness, due to the high glass transition temperature of this polymer (around 100 °C). Flexible polymer films can be obtained by blending the polymer with a plasticizer. The most commonly used plasticizer for PMMA and other polymers like PVC is di-(2-ethylhexyl)-phthalate (DEHP, also called DOP after dioctyl phthalate). Because there are concerns about the health and environmental aspects related to the use of DEHP and similar compounds,[26,27] the search for more sustainable plasticizers is an active research field.[28] Imidazolium ionic liquids have been proposed as performant plasticizers for PVC,[29] and especially for PMMA.[30–33]

In this paper, it is shown that highly luminescent flexible films can be obtained by doping europium(III) complexes into a composite material consisting of PMMA and the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, [C$_6$mim][Tf$_2$N], as the plasticizer. Different europium(III) compounds, both ionic and non-ionic complexes, have been selected: [Eu(tta)$_3$(phen)], [C$_6$mim][Eu(tta)$_4$], [C$_6$mim]-[Eu(nta)$_4$], [choline]$_3$[Eu(dpa)$_3$], where tta is 2-thenoyltrifluoroacetonate, phen is 1,10-phenanthroline, nta is 2-naphthoyltrifluoroacetonate, dpa is 2,6-pyridinedicarboxylate (dipicolinate) and choline is the 2-hydroxyethyltrimethyl ammonium cation (Fig. 1).

Results and discussion

The flexible PMMA/ionic liquid films were prepared by dissolving the europium(III) complex first in the pure ionic liquid [C$_6$mim][Tf$_2$N]. In the case of [Eu(tta)$_3$(phen)], [C$_6$mim]-[Eu(tta)$_4$] and [C$_6$mim][Eu(nta)$_4$] the complex was first dissolved in dichloromethane and a specific amount of this solution was added to the ionic liquid. A given amount of the europium(III)/ionic liquid solution was mixed with a solution of PMMA in tetrahydrofuran. The resulting solution was spread on a glass slide and the solvent was allowed to

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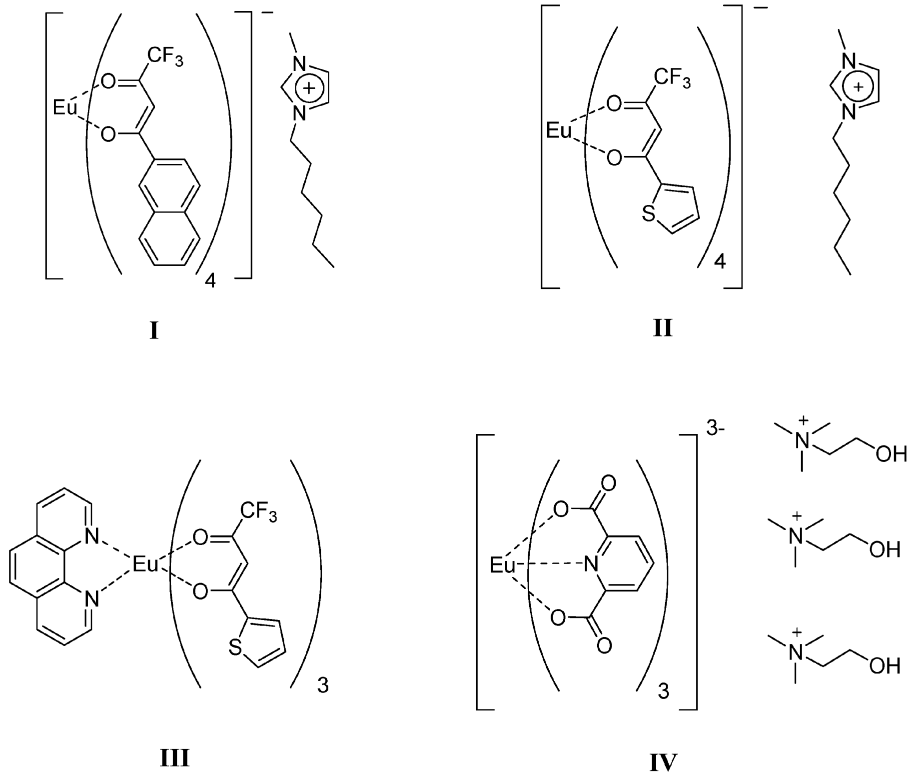

Fig. 1 Structure of the europium(III) complexes used in this study. $[C_6mim][Eu(nta)_4]$ (**I**), $[C_6mim][Eu(tta)_4]$ (**II**), $[Eu(tta)_3(phen)]$ (**III**) and $[choline]_3[Eu(dpa)_3]$ (**IV**).

evaporate. It was found that the processing temperature of the luminescent films is very critical. A first series of films doped with $[C_6mim][Eu(nta)_4]$ was prepared at 60 °C. Although these films were luminescent, the luminescence spectrum differed from what is expected for a tetrakis β-diketonate complex. In particular, the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ ratio was only 6.9, whereas values higher than 10 are expected for a europium(III) β-diketonate complex.[34] Probably, dissociation of the europium(III) tetrakis β-diketonate complex occurred, due to the potentially coordinating carbonyl (C═O) groups of the PMMA matrix or THF molecules which are difficult to entirely remove from the films. The synthetic procedure was slightly adapted after these negative results. A second series of $[C_6mim][Eu(nta)_4]$-doped PMMA/ionic liquid films were therefore prepared at room temperature and in the dark. The films were prepared in the dark, because it is known that the lanthanide β-diketonate complexes have a low photostability in most organic solvents, including in the THF which was used for solvent processing of the thin films.[34] The resulting films are red luminescent under UV irradition (Fig. 2) and show a typical europium(III) β-diketonate emission spectrum (Fig. 3). Although the luminescence spectrum consists of different lines of the $^5D_0 \rightarrow {}^7F_J$ multiplet (J = 0–4 in our experiments), the very intense $^5D_0 \rightarrow {}^7F_2$ line at 16337 cm^{-1} (612 nm) clearly dominates the spectrum. This luminescence line is responsible for the red luminescence color visible by the naked eye upon UV irradiation. The intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ line to that of the $^5D_0 \rightarrow {}^7F_1$ line, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, is 14.1. Although the intensity ratio is high, it is still not as high as the value of 18.6 that was observed for the $[C_6mim][Eu(nta)_4]$ complex dissolved in the ionic liquid $[C_6mim][Tf_2N]$. This could be due to small distortions of the first coordination sphere of the europium(III) ion by the PMMA matrix or remaining THF molecules and these small distortions are clearly reflected in the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$. Another explanation could be that the $[C_6mim][Eu(nta)_4]$ complex partially dissociates in the polymer matrix. This hypothesis is supported by the fact that the luminescence decay curve of the $^5D_0$ excited state is a bi-exponential curve, with the two components being 397 ± 20 μs (58%) and 680 ± 34 μs (42%). The average decay time is 553 μs and this is very similar to the value observed for the $[C_6mim][Eu(nta)_4]$ complex dissolved in the $[C_6mim][Tf_2N]$ ionic liquid (550 μs).[35] Although the $^5D_0 \rightarrow {}^7F_0$ line seems to be at a first glance unsplit, a closer look reveals that the line is broadened and shows a shoulder. This, in combination with the bi-exponential decay, points to the presence of more than one europium(III)-containing species. Gao *et al.* also reported on bi-exponential decay curves found for the luminescent lifetimes of similar samarium(III) and europium(III) tetrakis β-diketonate complexes in lanthanide-doped PMMA polymers.[36] The β-diketonate ligands that they investigated were benzoyltrifluoroacetonate (btfac) and hexafluoroacetylacetonate (hfac). In the case of $[Ln(btfac)_4]^-$ they associated these bi-exponential decay curves with a partial dissociation of the lanthanide complex resulting in the presence of $[Ln(btfac)_3]$ as well as $[Ln(btfac)_4]^-$ species in the doped polymers. The authors pointed to the influence of the solvent on the dissociation of the complexes.

Table 1 summarizes the intensity ratios $I(^5D_0 \rightarrow {}^7F_J)/I(^5D_0 \rightarrow {}^7F_1)$ for $[C_6mim][Eu(nta)_4]$ in PMMA/ionic liquid

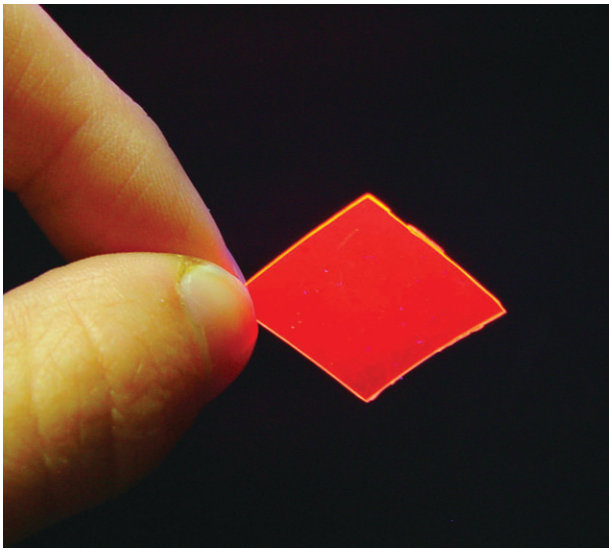

Fig. 2 Luminescent flexible PMMA/[C_6mim][Tf_2N] film doped with the europium(III) complex [C_6mim][Eu(nta)$_4$] (irradiation with UV radiation of 365 nm).

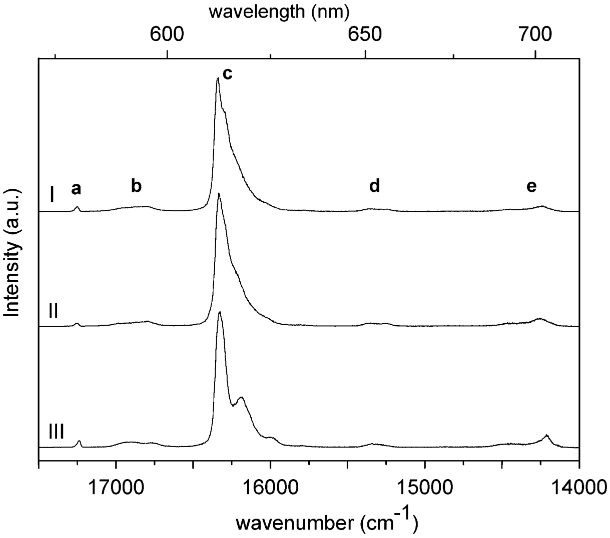

Fig. 3 Luminescence spectra of europium(III)-doped PMMA/[C_6mim][Tf_2N] film recorded at room temperature (excitation wavelength is 340 nm): I: [C_6mim][Eu(nta)$_4$]; II: [C_6mim][Eu(tta)$_4$]; III: [Eu(tta)$_3$(phen)]. The assignment of the lines is: $^5D_0 \rightarrow {}^7F_0$ (a); $^5D_0 \rightarrow {}^7F_1$ (b); $^5D_0 \rightarrow {}^7F_2$ (c); $^5D_0 \rightarrow {}^7F_3$ (d) and $^5D_0 \rightarrow {}^7F_4$ (e).

film, [C_6mim][Tf_2N], THF and as the pure complex in the solid state. All the corresponding emission spectra look very similar. The intensity ratios of the $^5D_0 \rightarrow {}^7F_2$ line and the $^5D_0 \rightarrow {}^7F_4$ line to that of the $^5D_0 \rightarrow {}^7F_1$ line are slightly different. The luminescence spectrum of a [C_6mim][Eu(nta)$_4$]—doped PMMA/ionic liquid films was re-measured two months after the first spectroscopic experiments. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ was found to be 11.9, which is slightly lower than the value of 14.1 observed for the freshly prepared films. Drying the aged films for 48 h *in vacuo* at room temperature had only little effect on the luminescence spectrum. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ was 10.4. However, drying the aged films for 48 h at 50 °C had a very pronounced effect on the luminescence spectra. Not only was a difference in shape for the $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm noticed, but the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ decreased to 8.0. This is a further indication that the europium(III)-doped polymer films are not very resistant to higher temperatures.

Table 1 Relative intensities of the transitions in the luminescence spectra of [C_6mim][Eu(nta)$_4$] in PMMA/ionic liquid film, in the ionic liquid [C_6mim][Tf_2N], in THF and in the solid state[a]

^7F_J	PMMA/IL film	[C_6mim][Tf_2N]	THF	Solid state
$^7F_0$	10	≈0	10	10
$^7F_1$	100	100	100	100
$^7F_2$	1410	1860	1430	1660
$^7F_3$	40	80	20	50
$^7F_4$	80	190	20	130

[a] The integrated intensities are given in arbitrary units, but normalized so that the intensity of the $^5D_0 \rightarrow {}^7F_1$ line is set equal to 100.

The luminescence spectra of the europium(III) complexes [C_6mim][Eu(tta)$_4$] and [Eu(tta)$_3$(phen)] in the PMMA/ionic liquid films are also shown in Fig. 3. Comparison of these spectra with that of [C_6mim][Eu(nta)$_4$] shows that the luminescence spectra of [C_6mim][Eu(nta)$_4$] and [C_6mim][Eu(tta)$_4$] are very similar, whereas very clear differences are noticed between these spectra and that of [Eu(tta)$_3$(phen)]. This very nicely illustrates that the overall appearance of the luminescence spectrum is more dependent on the class of β-diketonate complex (tetrakis complex or Lewis base adduct of tris complex) than on the nature of the β-diketonate ligand. The $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ ratios are 15.0 and 12.4 for [C_6mim][Eu(tta)$_4$] and [Eu(tta)$_3$(phen)], respectively. As for [C_6mim][Eu(nta)$_4$], the luminescence decay curves of the $^5D_0$ state were found to be bi-exponential for both [C_6mim]-[Eu(tta)$_4$] and [Eu(tta)$_3$(phen)]. The lifetime components were 761 ± 38 μs (36%) μs and 457 ± 23 μs (64%) for [C_6mim][Eu(tta)$_4$]. For [Eu(tta)$_3$(phen)], the respective values are 744 ± 37 μs (69%) and 459 ± 23 μs (31%). Just as in the case of [C_6mim][Eu(nta)$_4$], the $^5D_0 \rightarrow {}^7F_0$ transitions are asymmetrically broadened.

Samples of [C_6mim][Eu(tta)$_4$] in PMMA, but without the ionic liquid plasticizer, were prepared to investigate the influence of the ionic liquid on the spectroscopic properties of the europium(III)-doped polymer films. The luminescence spectra of [C_6mim]Eu(tta)$_4$] in PMMA and of [C_6mim]Eu(tta)$_4$] in PMMA/ionic liquid look very similar. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of [C_6mim][Eu(tta)$_4$] in the PMMA film was found to be 14.5 (compared to 15.0 for [C_6mim][Eu(tta)$_4$] in the PMMA/ionic liquid film). However, the two lifetime components in the luminescence decay curve of [C_6mim][Eu(tta)$_4$] in the PMMA film are 374 ± 19 μs (57.1%) and 671 ± 34 μs (42.9%), which is slightly lower than the values observed for [C_6mim][Eu(tta)$_4$] in the PMMA/ionic liquid film: 457 ± 23 μs (64%) and 761 ± 38 μs (36%). The longer lifetimes of the europium(III) complex PMMA/ionic liquid film can be explained by a dilution effect. The concentration of carbonyl groups is lower in the PMMA/ionic liquid films than in pure PMMA films. Because of the strong infrared absorption by the vibrations of the carbonyl groups, these groups can efficiently contribute to the non-radiative relaxation of the $^5D_0$ state. In the PMMA/ionic liquid films, the non-radiative relaxation of the $^5D_0$ state is less efficient than in PMMA films, leading to longer lifetimes for the excited state. Another possible explanation is that the presence of the ionic liquid ensures a more homogeneous distribution of the ionic europium(III) complexes in the PMMA polymer and therefore to less undissolved aggregates and less quenching of the luminescence.

In order to have an example of a europium(III) complex with ligands other than β-diketonates, the compound $[choline]_3[Eu(dpa)_3]$ was prepared. The 2-hydroxyethyl-trimethyl ammonium (choline) cation was selected instead of the 1-hexyl-3-methylimidazolium cation, because of experimental difficulties experienced when trying to prepare pure samples of $[C_6mim]_3[Eu(dpa)_3]$. Experimental procedures similar to those used for the synthesis of the tetrakis β-diketonate complexes, always lead to the formation of $Na_3[Eu(dpa)_3]$ instead of $[C_6mim]_3[Eu(dpa)_3]$.

The luminescence spectrum of $[choline]_3[Eu(dpa)_3]$ in a PMMA/ionic liquid film is quite different from those of the films containing europium(III) β-diketonate complexes (Fig. 4). First of all, the $^5D_0 \rightarrow {}^7F_2$ line of $[choline]_3[Eu(dpa)_3]$ is much narrower than that of the β-diketonate complexes, indicating the presence of only one crystal-field component. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 3.1, which is much lower than the value of the β-diketonates. Two crystal field components are visible for the $^5D_0 \rightarrow {}^7F_1$ transition, which indicates that the $^7F_1$ multiplet is split into two crystal-field levels. The $^5D_0 \rightarrow {}^7F_0$ line is very weak and barely visible, but zooming in on the transition reveals that, in contrast to this line in the β-diketonate complexes, the line has a symmetrical shape. In Table 2, an overview of the relative intensities of the transitions in the luminescence spectra of $[choline]_3[Eu(dpa)_3]$ in the PMMA/IL films, in the ionic liquid and in THF are compared. The luminescence decay curve is monoexponential and the lifetime of the $^5D_0$ excited state is exceptionally long for a molecular europium(III) complex: 1803 ± 90 μs. These spectroscopic and photophysical data indicate that the europium(III) ion is at a site of rather high symmetry. The weakness of the $^5D_0 \rightarrow {}^7F_0$ line and the splitting patterns of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions support the view that the europium(III) ion is located at a site of approximately D_{3h} symmetry.[37,38] D_{3h} is the symmetry of an undistorted tricapped trigonal prism. The very long lifetime of the $^5D_0$ excited state is an indication of poorly efficient non-radiative relaxation processes due to the good shielding of the Eu^{3+} by the 2,6-pyridinedicarboxylate (dipicolinate) ligands from the environment. In addition, $[choline]_3[Eu(dpa)_3]$ is found to be stable in the PMMA/ionic liquid films. The emission spectrum of $[Eu(dpa)_3]^{3-}$-doped composite PMMA/ionic liquid film was also recorded two months later and after drying *in vacuo* for 48 h at 50 °C. The spectrum was very similar to the previously recorded emission of the $[Eu(dpa)_3]^{3-}$-doped composite PMMA/ionic liquid film and the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ line to that of the $^5D_0 \rightarrow {}^7F_1$ line, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, remained constant (3.0 compared to 3.1 for the europium(III)-doped film recorded for the first time). The europium(III) ions are very well shielded in the dipicolinate complex due to a rigid nine-coordinating structure. Perhaps this can explain the better luminescence properties for $[choline]_3[Eu(dpa)_3]$ in the composite PMMA/ionic liquid films compared to the europium(III) β-diketonate complexes.

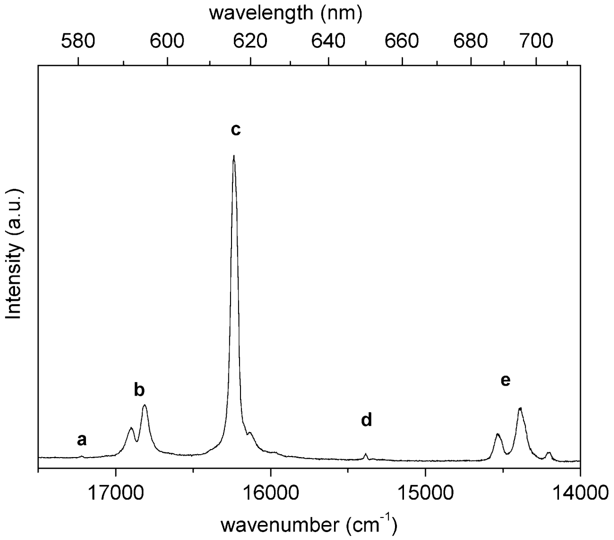

Fig. 4 Luminescence spectrum of $[choline]_3[Eu(dpa)_3]$-doped PMMA/$[C_6mim][Tf_2N]$ film. Emission is recorded at room temperature. Excitation wavelength was set at 280 nm. The assignment of the lines is: $^5D_0 \rightarrow {}^7F_0$ (a); $^5D_0 \rightarrow {}^7F_1$ (b); $^5D_0 \rightarrow {}^7F_2$ (c); $^5D_0 \rightarrow {}^7F_3$ (d) and $^5D_0 \rightarrow {}^7F_4$ (e).

In order to establish the efficiency of the luminescent materials, the quantum yield (quantum efficiency) of the europium(III) luminescence was determined using the formula:[39]

$$\Phi_{Eu} = \frac{\tau_{obs}}{\tau_R} \qquad (1)$$

where τ_{obs} is the observed luminescence lifetime of the $^5D_0$ excited state and τ_R is the radiative lifetime (*i.e.* the lifetime of the excited state in the absence of non-radiative processes). τ_{obs} was evaluated using the luminescence decay curves and taking the average lifetime in the case of bi-exponential decay. The radiative lifetime τ_R of the $^5D_0$ excited state was calculated using the formula:[39]

$$\frac{1}{\tau_R} = A_{MD}\, n^3 \left(\frac{I_{tot}}{I_{MD}}\right) \qquad (2)$$

where n is the refractive index of the medium, A_{MD} is the Einstein coefficient for spontaneous emission for the $^5D_0 \rightarrow {}^7F_1$ transition

Table 2 Relative intensities of the transitions in the luminescence spectra of $[choline]_3[Eu(dpa)_3]$ in PMMA/ionic liquid film, in the ionic liquid $[C_6mim][Tf_2N]$, and in THF[a]

^7F_J	PMMA/IL film	$[C_6mim][Tf_2N]$	THF
$^7F_0$	≈0	≈0	≈0
$^7F_1$	100	100	100
$^7F_2$	330	420	430
$^7F_3$	5	10	5
$^7F_4$	100	150	170

[a] The integrated intensities are given in arbitrary units, but normalized so that the intensity of the $^5D_0 \rightarrow {}^7F_1$ line is set equal to 100.

in vacuo and I_{tot}/I_{MD} is the ratio of the total intensity of the emission spectrum (integrated area) to the intensity of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$. The intensity of this magnetic dipole transition is insensitive to the ligand environment of the Eu^{3+} ion and it can be shown that A_{MD} equals 14.65 s^{-1}. For the refractive index n, it was assumed that the refractive index of the films is in a good approximation the same as that of pure PMMA (n = 1.49). No dispersion is taken into account. It should be noted that the $^5D_0 \rightarrow {}^7F_5$ and the $^5D_0 \rightarrow {}^7F_6$ transitions were lying outside the wavelength range of our spectroscopic setup, but it is known that in general these transitions contribute less than 5% to the total luminescence output.[39] The quantum yields for the different luminescent films are listed in Table 3. It can be noticed that there is only a slight variation in the quantum yield for the different complexes (between 41 and 48%). At first sight, it may not seem logic that [choline]$_3$[Eu(dpa)$_3$] with a much longer observed lifetime has a quantum yield that is very comparable with those of the β-diketonate complexes, but the radiative lifetime of [choline]$_3$[Eu(dpa)$_3$] (3.85 ms) is also much longer than that of the β-diketonate complexes (between 1.19 and 1.41 ms). It should also be noted that the intensity of the emitted light is not only dependent on the quantum efficiency or quantum yield but also on the amount of light that is absorbed by the complex.

A current trend in ionic liquid research is the broadening towards applications which are less obvious than the use of ionic liquids as non-volatile solvents for organic reactions.[40] Ionic liquids offer a great potential in materials sciences and technology.[41–46] In this work we take advantage of the property of the ionic liquid to act as a plasticizer for polymeric materials. A major benefit of the ionic liquid plasticizer in the PMMA polymer matrix is without doubt the possibility to obtain flexible luminescent films. It has also been reported in the literature that the ionic liquid plasticizer leads to polymers with higher thermal stability.[32] This is not a great advantage for present luminescent materials, because the limiting factor for their use is the low thermal stability of the europium(III) β-diketonate complexes. The ionic liquid acts not only as a plasticizer, but also reduces the quenching of the $^5D_0$ excited state, leading to longer lifetimes of this excited state. This can probably be attributed to a better dissolution or dispersion of the europium(III) complexes in the polymer matrix (avoiding cluster formation) or to a dilution effect which moderates the contribution of the carbonyl groups of the PMMA matrix to the non-radiative deactivation of the $^5D_0$ state. In Table 3, an overview of the intensity ratios $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ and the luminescence decay times of the different europium(III) complexes in the PMMA/ionic liquid matrix are given. The similarities between the β-diketonate complexes and the different behavior of the films doped with [choline]$_3$[Eu(dpa)$_3$] are evident.

Recently, some of us introduced lanthanide-doped ionogels as a new type of luminescent material.[35,47] *Ionogels* are hybrid materials consisting of an ionic liquid confined inside the nano-sized pores of a silica matrix.[48–50] The ionogels are obtained as perfect monoliths featuring both the transparency of silica and the outstanding ionic conductivity performances of the ionic liquid, despite the nanometre scale of confinement. The conductivity of the ionogel corresponded well to that of the ionic liquid indicating an interconnecting porosity of the silica matrix. The volume of the ionic liquid was 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.[51] In the ionogel, the ionic liquid is the major component. In contrast, in the PMMA/ionic liquid films, the major component is still the polymer. The ionic liquid is in these materials more or less an additive, albeit an important one. Both PMMA/ionic liquid composite materials and ionogels can be processed into monolithic bulk samples, but for the preparation of lanthanide-doped thin films are PMMA/ionic liquid composites easier to work with. It should be noted that our PMMA/IL composites are structurally related to the PMMA/[C$_2$mim][Tf$_2$N] polymer electrolytes reported by Watanabe and coworkers.[52]

Table 3 Experimental intensity ratio parameter η, observed luminescence lifetimes τ_{obs} and quantum yield Φ_{Eu} of the europium(III)-doped PMMA/[C$_6$mim][Tf$_2$N] films

		$\tau_{obs}/\mu s^b$		
Complex	η^a	Component 1	Component 2	Φ_{Eu}
[C$_6$mim][Eu(nta)$_4$]	14.1	680 ± 34 (42%)	397 ± 20 (58%)	0.41
[C$_6$mim][Eu(tta)$_4$]	15.0	761 ± 38 (36%)	457 ± 23 (64%)	0.48
Eu(tta)$_3$phen	12.4	744 ± 37 (69%)	459 ± 23 (31%)	0.46
[choline]$_3$[Eu(dpa)$_3$]	3.1	1803 ± 90	—	0.47

[a] Ratio of integrated intensities given by $\eta = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$. [b] The decay curves were found to be bi-exponential for the β-diketonate complexes and mono-exponential for the [choline]$_3$-[Eu(dpa)$_3$] complex. For the bi-exponential decay curves, the percentage contributions of the two components are given.

Experimental

General

Photoluminescence spectra have been recorded on an Edinburgh Instruments FS900 spectrofluorimeter. This instrument is equipped with a xenon arc lamp, a microsecond flashlamp (2 μs FWHW, repetition rate: 50 Hz) and a red-sensitive photomultiplier (Hamamatsu R-928). All photoluminescence spectra have been recorded at room temperature. The excitation wavelength was set at 340 nm for the β-diketonate complexes and 280 nm for the [choline]$_3$[Eu(dpa)$_3$] complex. A filter with a cutoff wavelength of 390 nm was placed between the sample and the excitation monochromator to reduce stray radiation reaching the detector. The spectral bandwidth was 0.2 nm. The spectra were corrected for the wavelength-dependent sensitivity of the detector. The observed luminescence lifetime of the $^5D_0$ excited state (τ_{obs}) was measured by monitoring the luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition as a function of time after excitation with a microsecond flash lamp. Elemental analyses (CHN) were obtained on a CE Instruments EA-1110 elemental analyzer. ^1H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer.

Synthesis of ionic liquids

The ionic liquid 1-hexyl-3-methylimidazolium bromide, [C$_6$mim][Br], was prepared in spectrograde purity by a reaction between 1-methylimidazole and 1-bromohexane, by a method previously developed by some of us.[53] It is of prime importance to perform the quaternization step at room temperature or lower temperatures, and to prevent heating of the reaction mixture. Also 1-ethylimidazole and 1-bromohexane were carefully purified before use. It should be noted that colorless [C_6mim][Br] can also be obtained by treating a colored sample with charcoal, but the preparative method we used gives an ionic liquid with improved UV transparency in comparison with the charcoal-treated sample. The ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6mim][Tf_2N], was synthesized from [C_6mim][Br] by a metathesis reaction between lithium bis(trifluoromethylsulfonyl)-imide and [C_6mim][Br].[54] The resulting ionic liquid was washed several times with aliquots of water (20 mL) until bromide residues could no longer be detected by the $AgNO_3$ test. This is an indication that the residual bromide concentration is below 200 ppm. The ionic liquid was dried for several hours on a rotavap, at a pressure of 10^{-2} mbar. Heating of the ionic liquid above 40 °C during the drying step was avoided. The water content in the dried [C_6mim][Tf_2N] ionic liquid was about 100 ppm (determined by coulometric Karl Fischer titration). δ_H (300 MHz, $CDCl_3$, 20 °C, Me_4Si): 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). It should be stressed that, for this study, the optical purity of the ionic liquid is of much higher importance than the water, the halide and lithium content. The ionic liquid [C_6mim][Tf_2N] showed no significant light absorption at wavelengths longer than 300 nm, so that it had a good UV transparency and it was totally colorless. Drying the ionic liquid to a very low water content did not make sense, because water is also introduced to the system *via* the THF solvent used for the preparation of the thin PMMA/IL films. The authors are convinced that the low remaining bromide and lithium ion concentrations in the ionic liquid samples do not significantly influence the mechanical and photoluminescence properties of the PMMA/IL composite films.

Synthesis of europium(III) complexes. The europium(III) tetrakis β-diketonate complexes, [C_6mim][Eu(nta)$_4$] and [C_6mim]-[Eu(tta)$_4$], have been prepared by first dissolving 6 equivalents of 2-naphthoyltrifluoroacetone or 2-thenoyltrifluoroacetone in ethanol and deprotonating the β-diketone with an aqueous solution of NaOH at 50 °C, followed by the addition of 1.5 equivalents of the ionic liquid [C_6mim][Br] in ethanol and by the dropwise addition of $EuCl_3{\cdot}6H_2O$ (1 eq.) in water. The solution was left to stir and cool down to room temperature overnight. A yellowish precipitate of the complex was formed. The product was filtered and washed with ice-water as well as dried *in vacuo* at 50 °C. [C_6mim][Eu(nta)$_4$]: Found: C, 56.65; H, 3.7; N, 1.5 $C_{66}H_{51}N_2O_8F_{12}Eu(H_2O)$ requires C, 56.7; H, 3.8; N, 2.0%. [C_6mim][Eu(tta)$_4$]: Found, C, 41.65; H, 3.0; N, 2.3 $C_{42}H_{35}N_2O_8F_{12}S_4Eu$ requires C, 41.9; H, 2.95; N, 2.35%).

In the case of [Eu(tta)$_3$(phen)], the complex was formed by adding 3 equivalents of 2-thenoyltrifluoroacetone and 1 equivalent of 1,10-phenanthroline in ethanol and deprotonating the β-diketonate ligand with an aqueous solution of NaOH at 50 °C, followed by the dropwise addition of 1 equivalent of $EuCl_3{\cdot}xH_2O$ in water. The solution was left to stir and cooled down to room temperature overnight. A precipitate of the complex was formed. The product has been filtered and washed with ice-water as well as dried *in vacuo* at 50 °C. Found: C, 42.5; H, 2.1; N, 2.6 $C_{36}H_{20}N_2O_6F_9S_3Eu(H_2O)$ requires C, 42.65; H, 2.2; N, 2.8%.

For the synthesis of (choline)$_3$[Eu(dpa)$_3$], 2,6-pyridinedicarboxylic acid (3 eq.) was dissolved in 7 mL of water together with 2.115 mL of a solution of choline hydroxide, 45 wt% in methanol (6 eq.). The pH was checked to be neutral and the solution was heated to 70 °C followed by the dropwise addition of $EuCl_3{\cdot}xH_2O$ (1 eq.) in water. The solution was left to stir for 2 h. Water was removed on 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. Found: C, 43.65; H, 5.45; N, 8.05 $C_{36}H_{51}N_6O_{15}Eu\ (H_2O)_2$ requires C, 43.2; H, 5.6; N, 8.45%.

Synthesis of the PMMA films. PMMA (2 g) was dissolved in 17 mL of THF and stirred overnight. In the case of [C_6mim]-[Eu(nta)$_4$], [C_6mim][Eu(tta)$_4$] and [Eu(tta)$_3$(phen)] a solution of the europium(III) complex in CH_2Cl_2 was prepared. A specific amount of this solution ($n_{\text{complex}} = 1 \times 10^{-6}$ moles) was dissolved in [C_6mim][Tf_2N] (V = 0.3 mL) and added to the PMMA solution. [choline]$_3$[Eu(dpa)$_3$] was dissolved directly in [C_6mim][Tf_2N]. After 10 min the reaction mixture was poured on a glass slide. The films were dried in open air and in the dark for three days. The concentrations of the europium(III)-doped [C_6mim][Tf_2N] solutions were 3.3×10^{-3} mol L^{-1} for [C_6mim][Eu(nta)$_4$], [C_6mim][Eu(tta)$_4$] and [Eu(tta)$_3$(phen)] and 5.9×10^{-4} mol L^{-1} for [choline]$_3$[Eu(dpa)$_3$]. The thickness of the resulting films was about 0.2 mm.

It is important not to heat the solutions containing the europium(III) complex and the films, because otherwise problems with the stability of the β-diketonate complexes will be noticed, as was observed by experiments performed at 60 °C.

Conclusions

In this paper we presented a new type of luminescent hybrid material, which is prepared by doping europium(III) complexes in a matrix consisting of a blend of poly(methyl methacrylate) (PMMA) and the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The ionic liquid acts as a plasticizer. However, it is evident that toxicological tests are necessary before a statement can be made about the toxicity of this ionic liquid in comparison to di-(2-ethylhexyl)-phthalate (DEHP). Nevertheless, it can be anticipated that ionic liquids with a low toxicity and good platisticizing properties can be designed. The ionic liquid also enhances the solubility of the europium(III) complexes in the PMMA matrix. Although we have illustrated here the performance of PMMA/ionic liquid films doped with europium(III) β-diketonate complexes and [choline]$_3$[Eu(dpa)$_3$], the applicability of our system is of course not limited to europium(III) or to these types of ligands. The luminescence color of the flexible PMMA films can be tuned by a suitable choice of the lanthanide ion, ranging from blue for Tm^{3+}, over green for Tb^{3+} and near infrared emission for ions such as Nd^{3+}, Er^{3+} and Yb^{3+}.

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