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Luminescent Ionogels Based on Europium-Doped Ionic Liquids Confined within Silica-Derived Networks

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Luminescent ionogels were prepared by doping an europium(III) tetrakis β-diketonate complex into an imidazolium ionic liquid, followed by immobilization of the ionic liquid by confinement in a silica network. The ionogels were obtained by a non-hydrolytic method as perfect monoliths featuring both the transparency of silica and the ionic conductivity performances of ionic liquids. The ionogels contain 80 vol % of ionic liquid. The organic−inorganic hybrid materials showed a very intense red photoluminescence under ultraviolet irradiation. The red emission has a very high coloric purity.

Introduction

The current strong research interest in room-temperature ionic liquids is related to their tunable properties, as the choice of the cation−anion combination permits the ionic liquid to be suitably tailored for one specific task. Particularly, ionic liquids can be made, nonflammable, stable at temperatures higher than 300 °C, miscible or not with water or other solvents, thus forming a new class of "green" solvents, which considerably broadens the range of biphasic systems available in catalysis (especially transition metal catalysis).[1−7]

Ionic liquids are also known as high performance electrolytes (in relation to their high ionic conductivity and wide electrochemical stability window), widely used in electrochemical devices as solar cells.[8,9] Some recent studies have highlighted the interest of ionic liquids in photochemistry and spectroscopy.[10−12] However, the development of ionic liquids as advanced materials is in most cases hampered by their liquid state. Accordingly, besides studies on ionic liquid crystals,[13,14] much research is currently devoted to immobilizing ionic liquids. Immobilization of ionic liquids by an organogelator could offer a solution, but these physical *ionogels* suffer from poor mechanical strength.[15−17] Another strategy involves the immobilization of the ionic liquid within polymer membranes, by polymerization of monomers in the ionic liquid,[18] cross-linking of a polymer dissolved in the ionic liquid,[19] or swelling a polymer with the ionic liquid.[20] Other ways consist of immobilizing ionic liquids as adsorbed films on porous solids, as silica particles,[21−23] or in confining ionic liquids within silica matrices via sol−gel processing.[24,25] The latter way has the advantage of immobilizing a larger amount of ionic liquid and meeting the transparency required for optical applications. Unfortunately hydrolytic sol−gel methods failed in producing reproducible monoliths. Composite ionic liquid based materials were prepared by coupling a trimethoxysilane group via a covalent linker to an imida-

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zolium ring, followed by hydrolysis in an acidic aqueous solution.[26,27]

Recently, new *ionogels* have been obtained by a non-hydrolytic method as perfect monoliths featuring both the transparency of silica and the outstanding ionic conductivity performances of the ionic liquid, despite the nanometer scale of confinement.[28−30] They could be made completely stable in water and in numerous organic solvents, in which they could be immersed without damage for months.[31] Moreover the ability to easily shape the ionogels provides an attractive versatility to prepare coatings, rods or pellets, making it possible to implement optical devices. Particularly these ionic conductor materials are excellent candidates for the design of electroluminescent devices.

In this paper, we report on the luminescent ionogels based on an immobilized imidazolium ionic liquid doped with a europium(III) β-diketonate complex. This type of luminophore was chosen because europium(III) β-diketonates are excellent luminescent materials.[32−37] To the best of our knowledge, this is the first time that luminophores were incorporated into inorganic-organic hybrid materials containing large quantities of ionic liquids. Luminescence spectra of ruthenium complexes in ionic liquids confined within a silica network have been reported, but these ruthenium-doped materials have been developed as solid electrolytes for dye-sensitized solar cells and not as luminescent hybrid materials.[38]

Results and Discussion

The ionic liquid used to prepare the ionogel was 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6mim][Tf_2N]. In order to have a europium(III) β-diketonate complex with a good solubility in the ionic liquid matrix, we designed a new anionic europium(III) complex with the same cation as the ionic liquid: 1-hexyl-3-methylimidazolium tetrakis(naphthoyltrifluoroacetonato)europate(III) (Figure 1). In principle other 1-alkyl-3-methylimidazolium ions could have been used without altering the properties of the system drastically. The naphthoyltrifluoroacetonate ligand is known to be a very efficient sensitizer of europium(III)-centered luminescence.[32]

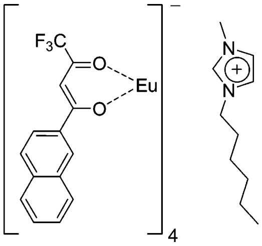

Figure 1. Molecular structure of the luminescent europium(III) complex 1-hexyl-3-methylimidazolium tetrakis(naphthoyltrifluoroacetonato)europate(III).

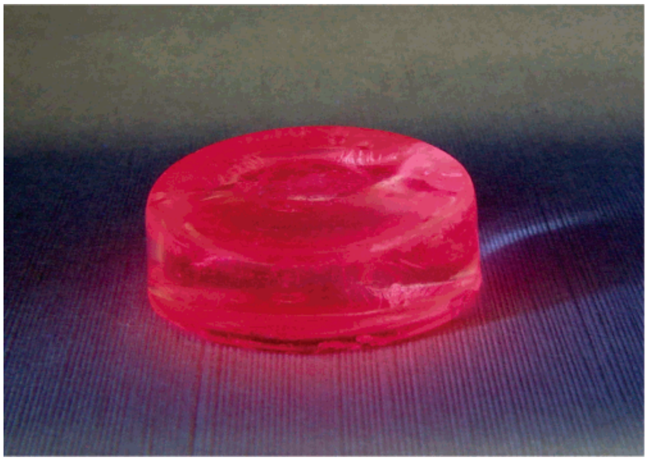

Figure 2. Luminescence of europium(III)-doped ionogel under ultraviolet irradiation.

In order to avoid decomposition of the europium(III) complex during the non-hydrolytic sol−gel processing, which involves the use of formic acid, a three-step workup was carried out. First a monolith ionogel was prepared from the undoped [C_6mim][Tf_2N] ionic liquid. In a second step, the ionic liquid was replaced in the ionogel by acetonitrile, and finally the acetonitrile contained in the porous network was replaced by the europium(III)-doped ionic liquid. The resulting material was crack-free, fully transparent, and colorless, quite similar to the initial ionogel. It is noteworthy that this solid contained 80 vol % of ionic liquid.

The europium(III)-doped ionogel showed an intense red photoluminescence when irradiated with UV radiation (Figure 2). In Table 1, an overview of the different transitions observed in the luminescence spectrum of the europium(III)-doped ionogel are summarized.[39−41] Although the luminescence spectrum consists of different lines of the $^5D_0 \rightarrow {}^7F_J$ multiplet ($J = 0{-}6$), the very intense $^5D_0 \rightarrow {}^7F_2$ line at 16 353 cm^{-1} (611.5 nm) dominates the spectrum, and this luminescence line is responsible for the red luminescence color (Figure 3). The intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ line to that

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Table 1. Summary of the Lines Observed in the Luminescence Spectrum of the Europium(III)-Doped Ionogel

line assignment	transition mechanism[a]	wave-number (cm^{-1})	wave-length (nm)	intensity (a.u.)[b]	branching ratio (%)[c]
$^5D_0 \rightarrow {}^7F_0$	ED	17256	579.5	5	≈0
$^5D_0 \rightarrow {}^7F_1$	MD	16849	593.5	100	4
$^5D_0 \rightarrow {}^7F_2$	ED	16353	611.5	2155	87
$^5D_0 \rightarrow {}^7F_3$	ED	15349	651.5	60	3
$^5D_0 \rightarrow {}^7F_4$	ED	14235	702.5	135	5
$^5D_0 \rightarrow {}^7F_5$	ED	13324	750.5	5	≈0
$^5D_0 \rightarrow {}^7F_6$	ED	12338	810.5	20	1

[a] ED = forced electric dipole transition; MD = magnetic dipole transition. [b] Integrated intensities in arbitrary units, but normalized so that the intensity of the $^5D_0 \rightarrow {}^7F_1$ line is set equal to 100. [c] The branching ratio gives the contribution (in %) of a given line to the total luminescence intensity. The sum of the branching ratios is 100%.

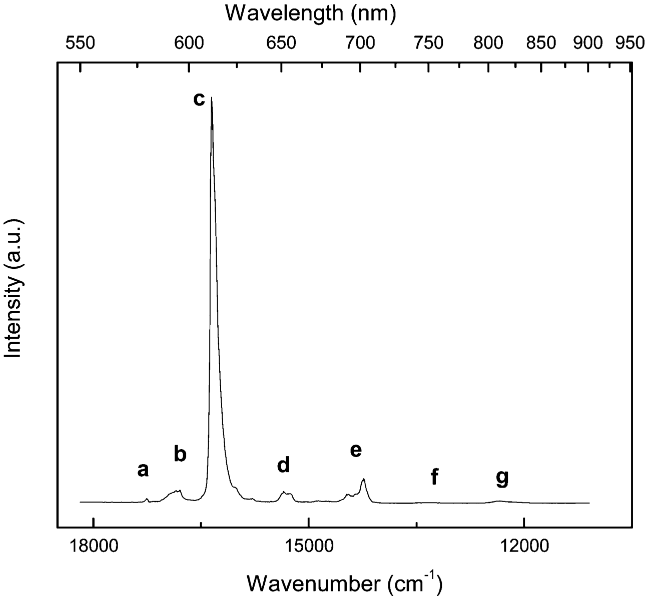

Figure 3. Luminescence spectrum of the europium(III)-doped ionogel at room temperature. The excitation wavelength was 360 nm. The assignment of the lines is as follows: (a) $^5D_0 \rightarrow {}^7F_0$; (b) $^5D_0 \rightarrow {}^7F_1$; (c) $^5D_0 \rightarrow {}^7F_2$; (d) $^5D_0 \rightarrow {}^7F_3$; (e) $^5D_0 \rightarrow {}^7F_4$; (f) $^5D_0 \rightarrow {}^7F_5$ and (g) $^5D_0 \rightarrow {}^7F_6$.

of the $^5D_0 \rightarrow {}^7F_1$ line, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, is 21.6. Moreover, 87% of the luminescence light output is emitted via the $^5D_0 \rightarrow {}^7F_2$ line. These results show that the luminescence light of the europium(III)-doped ionogel is of a high monochromatic purity. An intense $^5D_0 \rightarrow {}^7F_2$ line is typical for europium(III) β-diketonate complexes, but an $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ intensity ratio of more than 20 is exceptional.[32] Notice that the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is taken as a standard transition, because the intensity of a magnetic dipole is to a large extent independent of the local environment of the europium(III) ion.[42,43] On the other hand, the $^5D_0 \rightarrow {}^7F_2$ line is a so-called "hypersensitive transition".[44] Hypersensitive transitions are forced electric dipole transitions that follow the selection rules of electric quadrupole transitions and that are very sensitive to even small changes in the local environment of the lanthanide(III) ion. Although no crystal structure is available for the eight-coordinate europium(III) compound considered in this study, the high intensity of the $^5D_0 \rightarrow {}^7F_2$ line indicates that the actual coordination polyhedron will be closer to a dodecahedron or a bicapped trigonal prism than to a square antiprism (these three are the ideal coordination polyhedra for coordination number eight).[41] Indeed, it can be theoretically shown that no $^5D_0 \rightarrow {}^7F_2$ lines are expected for a europium(III) ion in a square antiprismatic environment (D_{4d} symmetry) or only weak lines in a distorted square antiprismatic environment (D_4 symmetry), whereas the $^5D_0 \rightarrow {}^7F_2$ line will be much more intense for a europium(III) ion in a dodecahedral environment (D_{2d} symmetry) or in a bicapped trigonal prismatic environment (C_{2v}).[45,46] The luminescence decay time of the $^5D_0$ level is 0.52 ms. The decay curve was found to be mono-exponential. These data, in combination with the observation of only one major component for the $^5D_0 \rightarrow {}^7F_0$ line, are evidence for a single, rather well-defined europium(III) site in the ionogel. Next in intensity to the $^5D_0 \rightarrow {}^7F_2$ line is the $^5D_0 \rightarrow {}^7F_4$ line. This line does not significantly contribute to the observed luminescence color, because it is much weaker than the $^5D_0 \rightarrow {}^7F_2$ line and because this line is lying at the border of the visible spectral region. The $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_5$ lines are very weak because they are forbidden by the selection rules of forced electric dipole transitions. The $^5D_0 \rightarrow {}^7F_6$ line is weak, and moreover it is situated in the near-infrared region.

In order to investigate the influence of the confinement of the ionic liquid in the pores of the silica host matrix on the structure of the europium(III) complex, the high-resolution luminescence spectrum of the europium(III) complex in the ionogel was compared to the high luminescence spectra of the europium(III) complex dissolved in the ionic liquid and of the europium(III) complex in powder form (Figure 4). No differences in crystal-field fine structure or in relative intensities could be observed for the spectra recorded on the ionogel or on the ionic liquid. This indicates that confinement of the europium(III)-doped ionic liquid in the silica network has negligible influence on the structure of the europium(III) complex. Comparison of the luminescence spectra of the solid europium(III) complex and of the europium(III) complex dissolved in the ionic liquid shows that the coordination sphere of the europium(III) remains intact upon dissolving it in the ionic liquid. However, differences were observed for the luminescence decay time of the $^5D_0$ excited-state of europium(III). The decay time is appreciably shorter in the solid sample (bi-exponential decay with an average decay time of 0.35 ms) than in the ionic liquid (mono-exponential decay 0.55 ms) or in the ionogel (mono-exponential decay, 0.52 ms). The smaller intermetallic distances leading to interaction between two close europium(III) sites are a possible explanation for the different behavior in the solid state. The concentration of europium(III) in the samples was varied, but this variation had only a minor effect on the luminescence intensity. Although the lanthanide β-diketonates suffer from a poor photostability in solution,[32]

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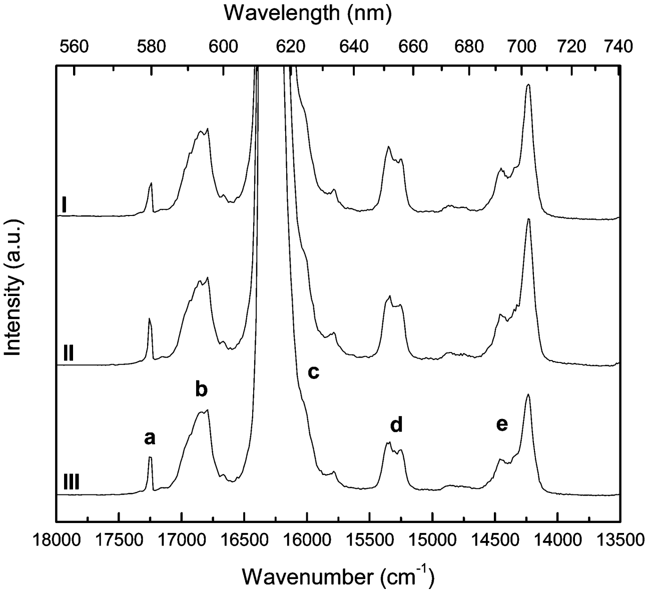

Figure 4. Comparison of the high-resolution luminescence spectra of the europium(III) complex in different matrices at room temperature (excitation wavelength is 360 nm): I : ionogel; II: dissolved in ionic liquid; III: solid compound.

no deterioration of the europium(III) complex in the ionogels when exposed to daylight was detected. This is in agreement with our earlier observation that lanthanide β-diketonate complexes dissolved in an ionic liquid have an improved photostability in comparison with the same complexes dissolved in conventional molecular solvents.[47] The quantum yield (i.e., the ratio between the number of photons emitted and the number of photons absorbed) of the complex dissolved in the ionic liquid was determined relative to 1,10-phenanthroline tris(2-thenoyltrifluoroacetonate) europium(III) dissolved in *N*,*N*-dimethylformamide. The absolute quantum yield of this reference complex is 36.5%.[48] The absorbance of our reference solution (at 340 nm, being the excitation wavelength) was adjusted by dilution to the same absorbance as our samples, and the differences in refractive indices were taken into account. The absolute quantum yield of 1-hexyl-3-methylimidazolium tetrakis-(naphthoyltrifluoroacetonato)europate(III) in both the pure [C_6mim][Tf_2N] and the ionogel was determined to be 53 ± 5%. A direct measurement of the quantum yield in the ionogel was not possible because our integrating sphere was not adapted to the size of the sample and because the shape of the sample was very different from the shape of the cuvette with the reference solution. This might introduce large differences in the absorption, emission, and scattering making the measurement erroneous. However, the quantum yield can also be defined as $\phi = \tau_{\mathrm{exp}}/\tau_{\mathrm{rad}}$, the ratio between the luminescence decay time τ_{exp} and the radiative (or natural) lifetime τ_{rad}. Given the fact that the high-resolution luminescence spectra indicate that the environment around the europium(III) complex in the ionogel is similar to that in the ionic liquid (see Figure 4) and given the fact that the luminescence decay times are similar in the ionogel and in the ionic liquid, it can be expected that the quantum yield of the europium(III)-doped ionogel is similar to that of the europium(III)-doped ionic liquid. This approximation is justified since more than 80% of the ionogel consists of ionic liquid.

The emission color of the ionogel can be tuned by a proper choice of the trivalent lanthanide ion.[35] In this study, the emission color was red due to the europium(III) ion. Green emission colors can be expected for terbium(III) complexes, although β-diketonates are not the best choice of ligands to sensitize terbium(III) luminescence and carboxylate ligands will be preferable. In principle, thulium(III) should emit blue light, but here one should also realize that the imidazolium cation can also show blue fluorescence. Luminescence by the lanthanide(III) ions is not restricted to visible light emission, since lanthanide(III) ions like neodymium(III), erbium(III), or ytterbium(III) are well-known for their near-infrared emission. It was shown by some of us that ionic liquids are an excellent solvent for near-infrared emitting lanthanide complexes, so one can expect that ionogels could exhibit near-infrared luminescence by doping with a suitable lanthanide(III) complex.[49−52]

Experimental Section

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 flash lamp (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 $BaSO_4$ for quantum yield measurements.

The ionic liquid 1-hexyl-3-methylimidazolium bromide, [C_6mim][Br], has been prepared as described previously.[53] 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. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 8.71$ (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).

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The europium(III) complex has been prepared by first dissolving 0.72 g of 2-naphthoyltrifluoroacetone (6 equiv) in ethanol and deprotonating this with an aqueous solution of NaOH at 50 °C, followed by the addition of 0.17 g of the ionic liquid [C_6mim][Br] (1.5 equiv) in ethanol and by the dropwise addition of 0.16 g of $EuCl_3 \cdot 6H_2O$ (1 equiv) 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 has been filtered and washed with ice water as well as dried in a vacuum at 50 °C. Anal. Calcd. for $C_{66}H_{51}N_2O_8F_{12}Eu(H_2O)$: C, 56.70; H 3.82; N, 2.00. Found: C, 56.64; H, 3.68; N, 1.48.

Europium(III)-doped [C_6mim][Tf_2N] ionic liquid samples were prepared as followed: 0.0069 g of the europium(III) complex was mixed with 25 mL of dichloromethane. Then, three solutions, with different concentrations in the europium(III) complex (0.0004, 0.00025, and 0.00015 mol/L), were made by dilution into 1.52 g of [C_6mim][Tf_2N].

Ionogels were prepared as previously published by Vioux et al.[28] using a non-hydrolytic sol−gel route. Tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS; 50% of each) purchased from Fluka and Alfa Aesar were mixed with formic acid and pure [C_6mim][Tf_2N] (molar ratio 7.8:1:0.5). Gelation occurred within 36 h. After complete maturation of the ionogels (8 days aging), [C_6mim][Tf_2N] was removed by Soxhlet extraction with acetonitrile for 24 h. After extraction the wet gels were immediately dipped into europium(III) complex/[C_6mim][Tf_2N] solutions. Complete absorption of europium(III)-doped [C_6mim][Tf_2N] ionic liquid occurred at room temperature within 48 h. Dichloromethane evaporated from the ionogel samples by exposure to the air.

Conclusions

We have shown that lanthanide(III) complexes can be efficiently confined in the ionic liquid component of solid-state ionogels, which leads to a completely novel family and concept of luminescent organic−inorganic hybrid materials. This method of immobilization of luminescent complexes in hybrid materials is a general powerful alternative to immobilization of the complexes by covalent linking to the silica network,[55−62] and it expands the types of known functional hybrid organic−inorganic nanocomposites.[63−65] The luminescent ionogels offer the advantages over other luminescent organic−inorganic hybrid materials that these solids are made of 80 vol % of ionic liquid and exhibit a high ionic conductivity.[28−31] The combination of luminescence and ionic conductivity properties of these materials deserves further exploration.

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