Photostability of a highly luminescent europium β-diketonate complex in imidazolium ionic liquids†

Peter Nockemann, Eva Beurer, Kris Driesen, Rik Van Deun, Kristof Van Hecke, Luc Van Meervelt and Koen Binnemans*

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A high quantum yield and an enhanced photostability was found for a europium(III) tetrakis(2-thenoyltrifluoroacetonate) complex after dissolving the complex in a weakly-coordinating imidazolium ionic liquid.

Lanthanide(III) β-diketonate complexes are widely exploited for applications such as materials for flat-panel displays, luminescent probes in bioassays, UV sensors and as laser materials.[1] This type of complex exhibits a high quantum efficiency in combination with narrow band emission and a high color purity.[2] Contrary to solid inorganic lanthanide compounds, coordination compounds with organic ligands are well processable and compatible with polymeric host matrices, so that they are of interest as active materials in new types of OLEDs.[3]

A well known example of a highly efficient red-emitting europium(III) complex is [Eu(tta)$_3$(phen)] (tta = 2-thenoyltrifluoroacetonate) which has a quantum yield of 36.5%.[4] The photochemical stability is an important factor to consider when the application of lanthanide(III) β-diketonates in luminescent devices is assessed. It has been reported that lanthanide(III) β-diketonate complexes can be unstable towards long-term UV irradiation.[5]

Ionic liquids are a new class of solvents which have attracted the attention of academic as well as industrial researchers during the last few years.[6] Ionic liquids exhibit useful properties such as electric conductivity, a negligible vapour pressure and a high thermal and electrochemical stability.[7] Some recent studies demonstrate the use of room-temperature ionic liquids (RTILs) in photochemistry and spectroscopy.[8] Lanthanide-doped ionic liquids can be regarded as new luminescent 'soft' materials.

Our approach was to find a complex that combines a good shielding of the lanthanide ion with photosensitization by an efficient light-harvesting antenna like 2-thenoyltrifluoroacetonate, and which is soluble in an ionic liquid. We have selected the 1-hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoroacetonato)europate(III) complex, [HMIM][Eu(tta)$_4$] (**1**), wherein the coordination sphere of the lanthanide ion is saturated and thus no solvent coordination occurs (Fig. 1). By introducing the 1-hexyl-3-methylimidazolium ([HMIM]$^+$) cation in the ionic complex, the solubility in the corresponding ionic liquid, [HMIM][Tf$_2$N] (Tf$_2$N = bis(trifluoromethanesulfonyl)imide) was enhanced in comparison with alkali counter ions. Moreover, the potential influence of different cations on the spectroscopic properties was avoided.

Compound **1** has been prepared by deprotonating four equivalents of the ligand 2-thenoyltrifluoroacetone in ethanol with an aqueous solution of NaOH, followed by addition of one equivalent of [HMIM][Br] in ethanol and the dropwise addition of one equivalent of EuCl$_3$·6H$_2$O in ethanol. The solution was left to stir overnight, after which a yellow precipitation of **1** had been formed. Crystals suitable for X-ray diffraction were obtained after slow evaporation from an ethanolic solution of the complex at room temperature.‡ The ionic liquid was prepared following modified standard literature procedures for the synthesis of spectroscopic grade ionic liquids.[8]

The crystal structure of **1** (see Fig. 2) shows that the europium(III) ion is surrounded by four 2-thenoyltrifluoroacetonate ligands. The coordination number of the europium(III) ion is eight, and the coordination polyhedron can be described as a distorted square antiprism. No solvent molecules are coordinated to the europium(III) ion. The acidic H(C2)-hydrogen of the imidazolium cation forms strong hydrogen bonds in a range from 2.336(6) Å to 2.689(7) Å to the oxygens of the [Eu(tta)$_4$]$^-$ moieties; that is in analogy with the C–H···X hydrogen bonding in imidazolium ionic liquids.[9]

Dissolving [HMIM][Eu(tta)$_4$] in the ionic liquid [HMIM][Tf$_2$N] does not affect the spectroscopic fine structure of the emission spectrum of the compound compared to a solution of the same compound in acetonitrile (Fig. 3). The Tf$_2$N$^-$ anions are known to coordinate very weakly to lanthanide ions.[10] Apart from the fine structure, a slightly lower absolute quantum yield Φ was measured for the complex in the ionic liquid (54%) compared to a fresh solution in acetonitrile (61%).

Although the freshly prepared solution in acetonitrile exhibited the highest quantum yield Φ, after 10 days of exposure to daylight

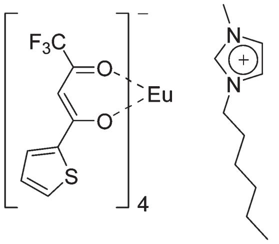

Fig. 1 1-Hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoro-acetonato)europate(III) complex.

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200 F, B-3001, Leuven, Belgium.
E-mail: koen.binnemans@chem.kuleuven.be; Fax: +32 16 32 79 92;
Tel: +32 16 32 74 46

† Electronic supplementary information (ESI) available: Experimental details, characterization details of the complexes, table of lifetimes and absolute quantum yields, synthesis of spectrograde ionic liquids. See http://dx.doi.org/10.1039/b506915g

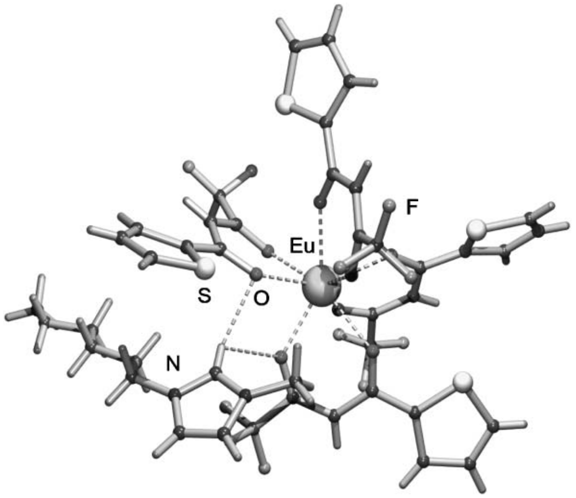

Fig. 2 Part of the crystal structure of **1**, showing the coordination sphere around the europium(III) ion.

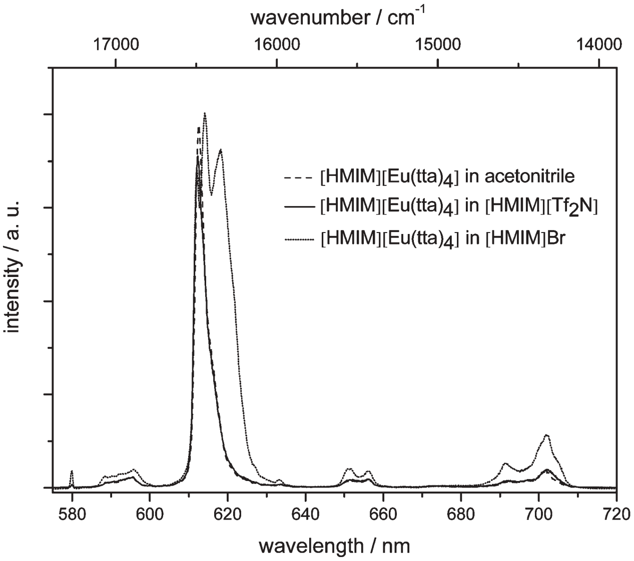

Fig. 3 High resolution photoluminescence spectra of a solution of [HMIM][Eu(tta)$_4$] in acetonitrile and in the ionic liquids [HMIM][Tf$_2$N] and [HMIM]Br.

in a quartz cuvette, a decrease in the quantum yield to $\Phi = 51\%$ was observed (see Fig. 4).§ A decrease in quantum yield was also observed for some reference europium(III) 2-thenoyltrifluoroacetonate complexes [Eu(tta)$_3$(H$_2$O)$_2$], [Eu(tta)$_3$(phen)] and [(CH$_2$)$_5$NH$_2$][Eu(tta)$_4$] ([(CH$_2$)$_5$NH$_2$]$^+$ = piperidinium cation) in acetonitrile. All samples were measured intermittently during a time period of 10 days and stored under the same conditions at room temperature.

A much faster decrease of the quantum yield of **1** in acetonitrile after UV irradiation points to photochemical degradation of the β-diketonate complex. This instability of europium(III) β-diketonate complexes towards light exposure has already been reported.[5,11–13] For instance, for a similar europium(III) tetrakis(2-thenoyl-trifluoroacetonate) complex with a different cation a half-life (decay to 50% of the initial value of luminescence intensity under UV irradiation) of 36 hours for the pure complex has been reported by Xu *et al.*[12] The mechanism of the decay has been proposed to be associated with a photodegradation of the β-diketonate ligand, but no detailed mechanism has been reported until now.[13] Preliminary monitoring of the photochemical reaction by NMR spectroscopy, that has been performed on the corresponding lanthanum(III) complex in deuterated acetonitrile, also indicates a decomposition of the β-diketonate ligands in organic solvents. The long-term changes could also be followed by UV/Vis absorption spectroscopy. The detailed mechanism of degradation is not fully clarified yet and is still under investigation. The luminescence lifetimes of the complexes are not significantly affected by the degradation process.

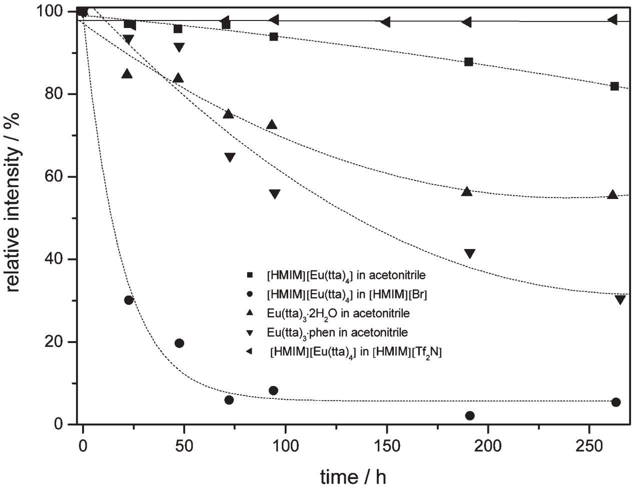

Fig. 4 Comparison of the long-term photostability (exposure to daylight) of europium(III) β-diketonate complexes in acetonitrile and in ionic liquids.

Contrary to this photochemical instability, for a solution of **1** in the ionic liquid [HMIM][Tf$_2$N], no significant decrease of the quantum yield could be observed after 10 days of exposure to daylight (see Fig. 5). The stability in the ionic liquid was also monitored by exposing a fresh sample of **1** dissolved in [HMIM][Tf$_2$N] to 8 periods of 1 hour (with periods of 5 min

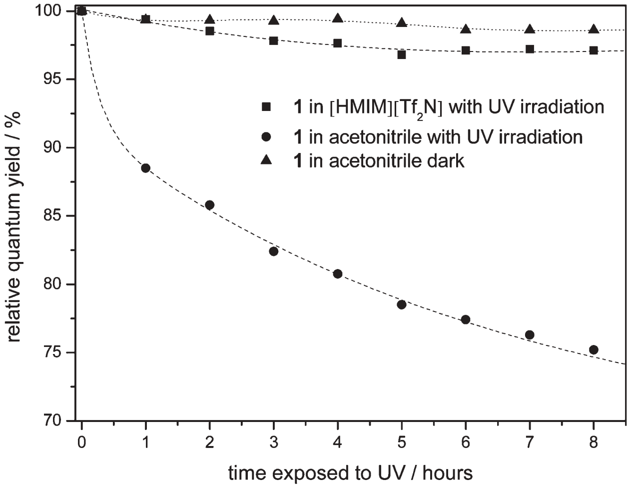

Fig. 5 Relative decrease of quantum yield under UV exposure in an acetonitrile solution compared to a solution in a [HMIM][Tf$_2$N] ionic liquid and to a sample not exposed to UV radiation.

between measurements) to a 12 mW UV-lamp (324 nm). This photostability test was carried out in comparison with a solution in acetonitrile and a sample of the latter without UV irradiation (except for excitation during measurements). The quantum yield of the solution of **1** in the ionic liquid [HMIM][Tf_2N] stabilized at about 98% of the initial value for the fresh sample—the slight decay is probably due to traces of water in the ionic liquid, which could be introduced by handling the sample and which quenches luminescence. The dry [HMIM][Tf_2N] ionic liquid is hygroscopic, but due to the absence of vapour pressure water can efficiently be removed.

In the ionic liquid [HMIM][Br], significant changes in the fine structure of the emission of [HMIM][$Eu(tta)_4$] can be observed. The $^5D_0 \rightarrow {}^7F_2$ emission at 615 nm is a hypersensitive transition that reveals changes of the coordination sphere of the europium(III) ion. This can be seen in Fig. 3. Changes are also indicated by the dramatic decrease of the quantum yield down to 14% for the fresh solution in the [HMIM][Br] ionic liquid, compared to 61% in an acetonitrile solution. The most probable explanation for this behaviour is a partial exchange of the β-diketonate ligands by bromide anions, thus resulting in a less efficient energy transfer.

The reason for the improved photochemical stabilization of [HMIM][$Eu(tta)_4$] in the ionic liquid [HMIM][Tf_2N] is still not understood, but the crystal structure of [HMIM][$Eu(tta)_4$] leads to the assumption that hydrogen bonding between cation and ligands could play a significant role, since it encapsulates the complex. A strong interaction between host medium and guest is known to remarkably influence the photophysical and photochemical processes of a guest molecule.[12] Therefore computational molecular modelling of the complex in an ionic liquid has to be performed (similar to the studies by Chaumont *et al.*).[14] Nevertheless, along with the versatile properties of ionic liquids, this system appears to have the potential to be developed to a new class of luminescent 'soft' materials.

In summary, we found that the 1-hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoroacetonato)europate(III) complex is photochemically stabilized in a weakly-coordinating imidazolium-based ionic liquid. The tunable properties of ionic liquids together with the stabilization of β-diketonate complexes can open up new potential applications for these materials, *e.g.* as laser dyes or as materials for emissive displays. Currently we expand our research on the stability of tetrakis(β-diketonate) complexes in ionic liquids towards other lanthanides emitting in the visible region like Tb^{3+} and Sm^{3+}, as well as towards the lanthanides emitting in the near-infrared region (Er^{3+}, Nd^{3+}, Yb^{3+}). The preliminary results are very promising.

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Notes and references

‡ *Crystal data for compound* **1**: crystals were grown from ethanol, intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu-Kα radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker,[15] $C_{42}H_{35}EuF_{12}N_2O_8S_4$, M = 1203.92, monoclinic, $P2_1/c$, a = 12.4045(8), b = 18.6683(16), c = 20.5603(14) Å, β = 97.167(5)°, V = 4724.0(6) $Å^3$, T = 100(2) K, Z = 4, D_c = 1.693 g cm^{-3}, μ(Cu-Kα) = 12.060 mm^{-1}, $F(000)$ = 2400, crystal size 0.5 × 0.2 × 0.1 mm, 8007 independent reflections (R_{int} = 0.1816). Final R = 0.0843 for 4845 reflections with $I > 2\sigma(I)$ and $wR2$ = 0.2185 for all data. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[16] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC 271619. See http://dx.doi.org/10.1039/b506915g for crystallographic data in CIF or other electronic format.

§ The quantum yield measurements were performed by means of an integrating sphere. The absolute error on the quantum yield values is about ±0.5%. The tetrakis(2-thenoyltrifluoro-acetonato)europate(III) complex was excited at a wavelength of 340 nm.

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