

Electronic supplementary information

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*

1. Characterization of the complexes

Table 1: CHN-results for the complexes.

Complex	CHN-results measured % (calculated %)	Yield [%]
HMIM[Eu(tta) ₄]	C: 42.2 (41.9), H: 3.0 (2.9), N: 2.6 (2.3)	86
[Eu(tta) ₃ (phen)]·H ₂ O	C: 42.6 (42.7), H: 2.1% (2.2), N: 2.5 (2.8)	35
[Eu(dbm) ₃ (phen)]	C: 68.4 (68.2), H: 4.4% (4.0), N: 2.7 (2.8)	89
[Eu(tta) ₃ (H ₂ O) ₂]	C: 34.0 (33.9), H: 1.8% (1.9)	45
[Eu(tta) ₃ (bipy)]	C: 41.8 (42.0), H: 2.4% (2.1), N: 2.4 (2.9)	26

Abbreviation used in the table above are the following:

bipy	2,2'-bipyridine
Hdbm	dibenzoylmethane
HMIM	1-hexyl-3-methylimidazolium
Htta	2-thenoyltrifluoroacetate
phen	1,10-phenanthroline

2. Experimental details of the synthesis of HMIM[Eu(tta)₄]

1.5 mmol of [HMIM]Br, 6 mmol of 2-thenoyltrifluoroacetone and 6 mmol of NaOH in an aqueous solution (1 M) were dissolved in 9 ml ethanol. The solution was heated up to 50 °C and stirred until the ligand was completely dissolved. A solution of 1 mmol Europium(III)chloride (EuCl₃·6H₂O) was dissolved in 2 ml of water and dropwise added to the ligand solution. A precipitation was formed while the solution was cooled down to room temperature. The solution was filtered and carefully washed with ice-cooled water. The formed complex was recrystallized from a small amount of ethanol and was dried in a vacuum oven at 50 °C.

3. Instrumentation

The steady-state luminescence spectra and the lifetime measurements were measured on an *Edinburgh Instruments* FS-900 spectrofluorimeter. This UV/VIS instrument is equipped with a xenon arc lamp, a microsecond flashlamp and a red-sensitive photomultiplier (300-850 nm). The luminescence lifetime has been determined by measurement of the luminescence decay curve. All photoluminescence spectra were recorded at room temperature. The quantum yields of the samples were determined using an integrating sphere (150 mm diameter, BaSO₄ coating) of *Edinburgh Instruments*. The spectra were corrected for variations in the output of the excitation source and for variations in the detector response.

Elemental analysis (Carbon-Hydrogen-Nitrogen) were performed on a CE-instrument EA-1110 elemental analyser. UV/VIS absorption spectra were recorded on a Cary 5000e spectrophotometer. Water contents of the ionic liquids were checked with a coulometric Karl-Fischer-titrator DL-39 (*Mettler-Toledo*).

4. Lifetimes and quantum yields

Table 1: Lifetimes and quantum yields of fresh solutions

Complex	Solvent	Lifetime / μs	Quantum yield %
HMIM[Eu(tta) ₄]	MeCN	615	61.3%
HMIM[Eu(tta) ₄]	HMIMBr	445	14.3%
HMIM[Eu(tta) ₄]	[HMIM][Tf ₂ N]	572	52.7%
[Eu(tta) ₃ (phen)]*	DMF	186	36.5%
[Eu(dbm) ₃ (phen)]*	MeCN	183	4.9%
[Eu(tta) ₄ (C ₅ H ₁₂ N)]*	MeCN	603	63.3%

*also used for calibration of integrating sphere

5. Synthesis of 'spectrograde' ionic liquids

1-Hexyl-3-methylimidazolium bromide, [HMIM][Br]_{colorless}

1-Methylimidazole (99%, purchased from ACROS) was freshly distilled from potassium hydroxide under reduced pressure. 400 ml of 1-bromohexane (99%, purchased from ACROS) was first distilled and extracted with four times 20 ml of concentrated sulfuric acid until no longer brownish discoloration of the acid phase appeared. Then, 1-bromohexane was washed with water, neutralized with a concentrated NaHCO₃-solution and washed with water again. Drying with MgSO₄ followed, and after filtration, the organic phase was distilled over P₂O₅ under reduced pressure.

Into a round-bottom flask equipped with a magnetic stirrer, a septum under argon atmosphere and cooled in an ice bath, were placed 0.25 mol (21.1 ml) of 1-methylimidazole and 60 ml of anhydrous toluene. This mixture was stirred for a half hour. An excess of 1-bromohexane (0.35 mol, 67.6 ml) was very slowly added dropwise by a syringe to the vigorously stirred mixture. The reaction mixture was protected from light by wrapping the flask in aluminum foil. After the reaction mixture had been stirred for 62 hours, the mixture was allowed to warm to room temperature. The slightly viscous, colorless product was separated from the toluene phase and washed two times with 50 ml of toluene and then two times with 50 ml of ethyl acetate. The ionic liquid was thereafter dried for 5 hours on a rotavap under reduced pressure at 70 °C. Yield: 82%. The product is an oily liquid at RT. ¹H-NMR (DMSO-d₆, δ/ppm relative to TMS): 10.23 (s, 1H), 7.46 (t, 1H), 7.64 (t, 1H), 4.23 (t, 2H), 3.99 (s, 3H), 1.81 (m, 2H), 1.23 (m, 6H), 0.76 (t, 3H).

1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [HMIM][NTf₂]

1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [HMIM][NTf₂], was synthesized by a metathesis reaction, following a procedure described by Bonhôte *et al.* [1] An aqueous solution of lithium bis(trifluoromethanesulfonyl)imide was added to [HMIM][Br]. 35 g of the ionic liquid were washed several times with small aliquots of water (20 ml) until no longer bromide residues were detected by the AgNO₃ test. Yield: 95%. The product is an oily liquid at RT. ¹H-NMR (acetone-d₆, δ/ppm relative to TMS): 9.02 (s, 1H), 7.76 (t, 1H), 7.71 (t, 1H), 4.37 (t, 2H), 4.07 (s, 3H), 2.0-1.8 (m, 6H), 1.39 (m, 2H), 0.95 (t, 3H).

[1] P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* 35 (1996) 1168.