

Electronic Supporting Information for Publication

Easy access to ultra long-time stable, luminescent reduced lanthanide(II) fluoride nanoparticles in ionic liquids

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Materials: Europium(II) fluoride (99.9 %) was purchased from ABCR, Germany, and was directly used without further purification. The used ionic liquids were prepared as follows:

1-Butyl-3-methylimidazolium chloride ([C₄mim][Cl]): 1-methylimidazole (36.5 ml, 0.458 mol) and 1-chlorobutane (47.5 ml, 0.458 mol) were heated under reflux in acetonitrile at 80 °C for 72 h. The solvent was evaporated and the resulting liquid was dissolved in dichloromethane and subsequently crystallized from toluene at -50 °C. Afterwards, the white crystalline reaction product was washed in toluene under argon atmosphere and finally dried in vacuo at 60 °C. Yield: 75.84 g, 94.8 %. ¹H-NMR (250 MHz, δ/ppm, CDCl₃): 0.88 (t, 3 H), 1.29 (m, 2 H), 1.83 (m, 2 H), 4.03 (s, 3 H), 4.24 (t, 2 H), 7.59 (s, 1 H), 7.72 (s, 1 H), 10.36 (s, 1 H).

1-Butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]): A solution of [C₄mim][Cl] (75.84 g, 0.434 mol) and sodium tetra-fluoroborate (47.65 g, 0.434 mol) in acetone was reacted at room temperature for 72 h. After removing of the precipitated sodium chloride, the remaining solution was stirred with activated charcoal. Then the solvent was evaporated. The remaining liquid was dissolved in dichloromethane and washed with several amounts of de-ionized water in order to remove any remaining chloride (silver nitrate test). Subsequently, the solvent was boiled off and the obtained colourless liquid was dried in vacuo at 80 °C for 48 h. Yield: 58.4 ml, 75.2 %. Water content: 27 ppm. ¹H-NMR (250 MHz, δ/ppm,

CDCl_3): 0.88 (t, 3 H), 1.30 (m, 2 H), 1.85 (m, 2 H), 4.07 (s, 3 H), 4.29 (t, 2 H), 7.62 (s, 1 H), 7.77 (s, 1 H), 10.46 (s, 1 H).

Trimethylbutylammonium chloride ([N₁₁₁₄][Cl]): In a sealed flask, butyl chloride (38.2 ml, 0.726 mol) was added to trimethylamine (184.2 ml, 25 wt % aqueous solution, 0.726 mol) with acetonitrile and heated to 70 °C for 16 h. After evaporation of the solvent, the obtained liquid was washed with dichloromethane and dried in vacuo at 60 °C for 16 h leading to white crystals. Yield: 48.76 g, 88.6 %. ¹H-NMR (250 MHz, δ /ppm, CDCl_3): 0.91 (t, 3 H), 1.34 (m, 2 H), 1.70 (m, 2 H), 3.17 (s, 9 H), 3.44 (m, 2 H).

Trimethylbutylammonium bis(trifluoromethylsulfonyl)imide ([N₁₁₁₄] [Tf₂N]): [N₁₁₁₄][Cl] (48.76 g, 0.323 mol) in water was added to an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (92.61 g, 0.323 mol) and stirred for 4 h. After filtration, [N₁₁₁₄][Tf₂N] was extracted with dichloromethane and washed with water until no chloride could be detected (silver nitrate test). Subsequently, the solvents were evaporated and the residual viscous liquid was dried in vacuo at 100 °C for 48 h. Yield: 61 ml, 64.4 %. Water content: 46 ppm. ¹H-NMR: (250 MHz, δ /ppm, CDCl_3): 0.92 (t, 3 H), 1.37 (m, 2 H), 1.72 (m, 2 H), 3.37 (s, 9 H), 3.52 (m, 2 H).

1-Butyl-1-methylpyrrolidinium chloride ([C₄C₁pyr] [Cl]): Methyl pyrrolidine (54.6 ml, 0.52 mol) and 1-chlorobutane (54.6 ml, 0.52 mol) were heated under reflux in acetonitrile at 60 °C for 72 h. The solvent was removed and the resulting liquid was dissolved in dichloromethane to crystallize from toluene at -50 °C within 12 h. The slightly yellow product was washed with toluene under argon atmosphere and dried in vacuo at 60 °C until the product turns white. Yield: 76.33 g, 83 %. ¹H-NMR: (250 MHz, δ /ppm, DMSO): 0.97 (t, 3 H), 1.45 (m, 2 H), 1.74 (m, 2 H), 2.28 (m, 4 H), 3.31 (s, 3 H), 3.65 (t, 2 H), 3.84 (m, 4 H).

1-Butyl-1-methylpyrrolidinium dicyanamide ([C₄C₁pyr] [DCA]): [C₄C₁pyr][Cl] (61.18 g, 0.22 mol) and sodium dicyanamide (31.15 g, 0.24 mol) were stirred for 12 h in dichloromethane. After filtration, [C₄C₁pyr][DCA] was washed with 10 ml of water three times and the solvent was evaporated. Subsequently, the residual viscous liquid was dried in vacuo at 100 °C for 48 h. Yield: 31 ml, 66.4 %. Water content: 46 ppm. ¹H-NMR: (250 MHz, δ /ppm, DMSO): 0.49 (t, 3 H), 0.92 (m, 2 H), 1.29 (m, 2 H), 1.78 (m, 4 H), 2.60 (s, 3 H), 2.89 (t, 2 H), 3.07 (m, 4 H).

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄C₁pyr] [Tf₂N]):

Lithium bis(trifluoromethylsulfonyl)imide (161.63 g, 0.525 mol) was added to [C₄C₁pyr][Cl] (76.64 g, 0.518 mol) in dichloromethane and stirred for 12 h. After filtration, [C₄C₁pyr][BTA] was washed with water until no chloride could be detected (silver nitrate test). Subsequently, the solvent was evaporated and the residual viscous liquid was dried in vacuo at 100 °C for 48 h. Yield: 98 ml, 62.7 %. Water content: 24 ppm. ¹H-NMR: (250 MHz, δ/ppm, DMSO): 0.93 (t, 3 H), 1.31 (m, 2 H), 1.69 (m, 2 H), 2.09 (m, 4 H), 2.98 (s, 3 H), 3.29 (t, 2 H), 3.44 (m, 4 H).

Preparation of EuF₂ nanoparticles: The preparation of the colloidal EuF₂ solutions were carried out in a rotary metal vapour synthesis reactor (TVP 800, Torrovap, Canada) based upon the design of Timms (K. J. Klabunde, P. L. Timms, P. S. Skell, S. Ittel, *Inorg. Synth.* **1979**, *19*, 59). In a typical experiment, a graphite lined tungsten box heater (Kurt J. Lesker Company, USA) containing 40 mg of europium(II) fluoride was placed between the water-cooled electrodes, whereupon 40 ml of the dried ionic liquid was placed in the flask, which then was started to rotate in order to form a film on the glass surface. The ionic liquid was degassed by pumping the setup with a mechanical pump and an oil diffusion pump to 10⁻⁶ Torr. While the crucible was heated by resistive heating to evaporate the metal in dynamic vacuum, the rotating flask was water-cooled and the ionic liquid was stirred to facilitate the diffusion of EuF₂ into the solvent and to avoid particle agglomeration. After all EuF₂ has been evaporated, the prepared colloidal solution was transferred under argon atmosphere to a Schlenk flask for further analysis.

Instrumentation: TEM images were recorded on an H-8100 microscope of Hitachi, Japan with an enclosed Oxford EDX detector Penta FET system. All samples were directly measured in the ionic liquid by diluting the sample with acetonitrile and placing a drop on a carbon-coated copper grid on an aluminum support. Fluorescence measurements were carried out on a Fluorolog FL3-22 spectrometer obtained by Horiba Jobin Yvon, Germany. All samples were prepared in small quartz ampoules. NMR spectra were recorded in deuterated chloroform on an Advance DPX 250 spectrometer (Bruker, Germany). UV-Vis measurements were carried out on a Cary 5000 UV-Vis-NIR spectrophotometer (Varian, Germany). All spectra were measured in quartz cuvettes with an empty cuvette as reference. IR measurements were carried out with an attenuated total reflection Alpha P ATR including a diamond crystal (Bruker, Germany). Powder X-ray diffraction were accomplished by a XRD

Huber G670 (Rimsting, Germany) with a molybdenum cathode. The used Guinier geometry features a focal radius of 90 mm with steps of 0.005 °. For the measurement EuF_2 was first calcined at 500 °C for 4 h and then measured in a 0.3 mm Lindeman capillary under argon atmosphere.

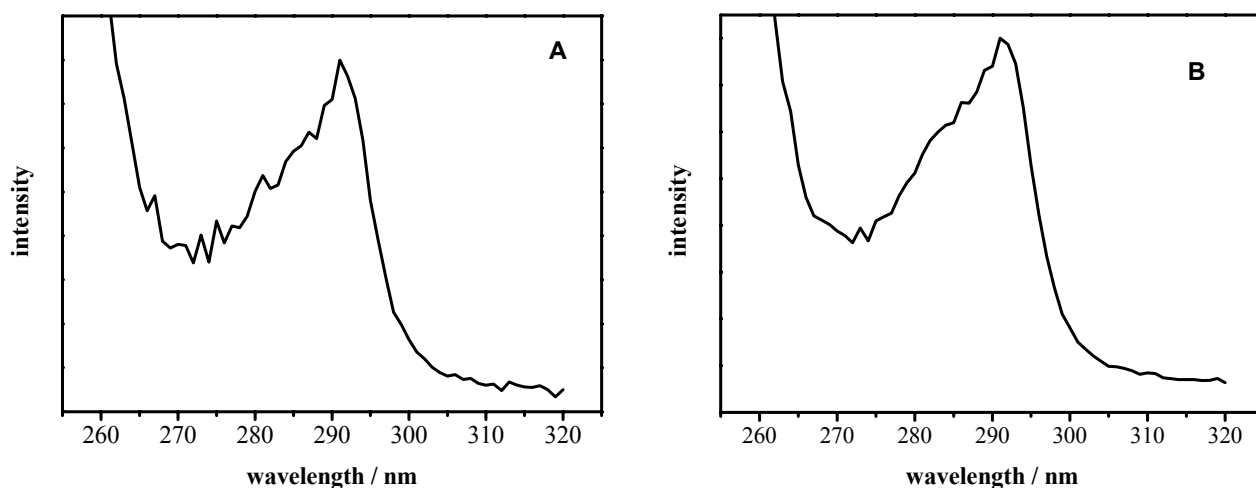


Figure SI-1: The excitation spectra of EuF_2 A) in IL $[\text{C}_4\text{mim}][\text{BF}_4]$ and B) in $[\text{N}_{1114}][\text{Tf}_2\text{N}]$. The emission is recorded at 350 nm at room temperature.

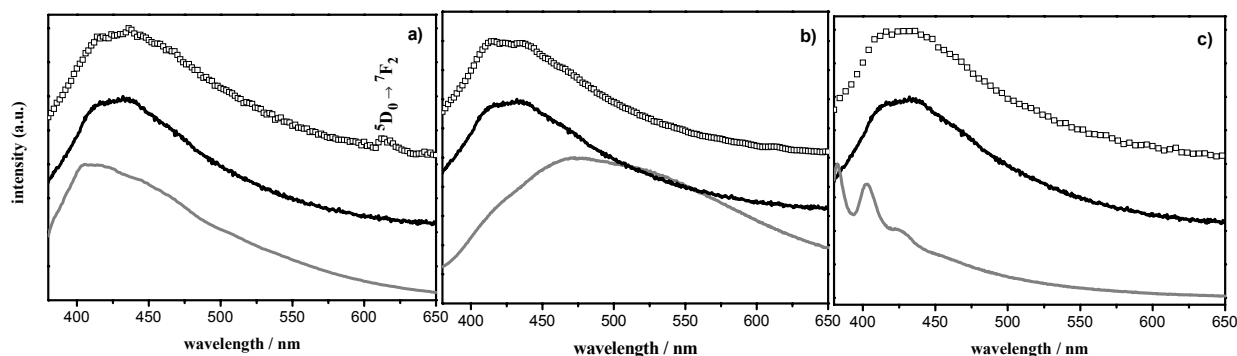


Figure SI-2: Room temperature emission spectra (excited at 350 nm) of the nano- EuF_2 colloid in the respective ionic liquids (black squares) in comparison with the emission spectra of bulk EuF_2 (open circles) as well as of the pure ILs (gray lines) in a) $[\text{C}_4\text{C}_1\text{pyr}][\text{DCA}]$, b) $[\text{C}_4\text{C}_1\text{pyr}][\text{Tf}_2\text{N}]$ and c) $[\text{N}_{1114}][\text{Tf}_2\text{N}]$. All spectra of nano- EuF_2 in IL show a broad band at 430 nm due to the 5d-4f transition of Eu^{2+} . Small amounts of Eu^{3+} are spectroscopically detected at 611 nm in case of $[\text{C}_4\text{C}_1\text{pyr}][\text{DCA}]$, by the notable $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition.