Supporting information:

A novel approach to optically active ion doped luminescent materials via electron beam evaporation into ionic liquids

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Experimentals

Physical vapor deposition. In order to prepare the $MgF_2:Eu^{3+}$ colloids a typical SMAD equipment (TVP 800, Torrovap, Canada) was used.[1] In a typical experiment, 40 ml of $[C_1C_4im][BF_4]$ was placed in the reactor glass bulb. A mixture of 1800 mg MgF_2 (ABCR, 99.99 %) and 200 mg EuF_3 (ABCR 99.95 %; REO) optimally yielding a molar concentration of MgF_2:Eu 5.8 % was grinded under inert atmosphere and placed in a Fabmate® crucible (Kurt-Lesker company, England) for evaporation. The setup was pumped with an oil diffusion pump to 3•10-5 Torr. The IL was allowed to degas for 4 hours. The glass bulb was then started to rotate. After a homogeneous film of the ionic liquid formed on the inner glass surface, the fluoride mixture was evaporated with an e-beam gun under dynamic vacuum onto the ionic liquid using a filament current of 36 mA and an acceleration voltage of 4000 V. After evaporation, the as-prepared colloid was then siphoned into a Schlenk tube under argon atmosphere. The particles were precipitated by adding a dichlormethane/ methanol mixture (1:1 by volume) and centrifuged at 2000 rpm. The particles were washed several times to remove the remaining ionic liquid. Finally, the particles were dried at 80 °C under vacuum.

Microwave reaction. For comparison with a typical chemical approach, MgF_2:Eu particles were also synthesized with a microwave-assisted method wherein an ionic liquid is applied as solvent, reagent and stabilizer all-in-one. In a typical reaction, 200 mg magnesium acetate tetrahydrate (Sigma-Aldrich, 99.0 %) and 17.1 mg europium acetate hydrate (ABCR, 99.9 %) were mixed in 1 ml ethylene glycol. The solution was added to 5 mL of $[C_1C_4im][BF_4]$ in a 10 mL glass vessel equipped with a Teflon septum and heated to 120°C by using a single-mode microwave operating at 2455 MHz (CEM Discover, Kamp-Lintfort, Germany). The reaction mixture was kept at this temperature for 10 min while stirring vigorously and controlling temperature, pressure before cooling to room temperature by means of pressurized air. The obtained colloidal solution was centrifuged, and the reaction product was washed several times with an ethanol/dichloromethane mixture (1:1 by volume). Finally, the colorless powder was dried at 70°C.

Powder X-ray diffraction. PXRD measurements were performed by using a G670 diffractometer operating with MoKα radiation and equipped with an image plate-detector (Huber, Rimsting, Germany). The powders were sealed in 0.5 mm Lindemann capillaries under argon.

Transmission electron microscopy. Electron micrographs were obtained on a Tecnai G20 HRTEM transmission electron microscope (Fei, Hillsboro, USA). An acceleration voltage of 200 kV was applied. For sample preparation, a small amount of the sample was dispersed in ethanol and dropped on the TEM-Grid (Mesh 300, Plano®, Wetzlar, Germany).

Energy dispersive X-ray microanalysis. EDX was measured with a JEOL JSM 6510 scanning electron microscope equipped with a Bruker EDX detector.

Inductively coupled plasma optical emission spectrometry. ICP-OES to determine the content of the europium ions in the powdered fluoride sample. After chemical digestion, the obtained solutions are transferred into a high-frequency plasma in the form of an aerosol. Therein, the constituents are atomized and partially ionized at temperatures above 6000 K. Inductively coupled plasma emission spectrometry was carried out on a Unicam PU 7000 spectrometer (Budapest, Hungary).

Luminescence measurements. Luminescence measurements were conducted by using a Fluorolog FL 3–22 spectrophotometer (Horiba JobinYvon, Unterhachingen, Germany) equipped with a continuous xenon lamp for steady-state measurements and a pulsed xenon lamp for obtaining decay curves. Double gratings for the excitation and emission spectrometer were used as monochromators. The signal was detected by using a photomultiplier. For the measurements, powdered samples were filled in silica tubes and carefully positioned in the incoming beam in the sample chamber. As often observed for nanoparticles, the decay curves did not show monoexponential character. Therefore average decay times were calculated according to a common procedure.[2] Quantum yields were determined with an integrating sphere following the procedure of Bünzli et al.

Preparation of [C_1C_4im][Cl]:

In 250 ml acetonitrile, 136 ml 1-methylimidazolium and 180 ml of chlorobutane was dissolved and stirred for 3 days at 85 °C. After that the solvent was removed under vacuum until a viscous oil was obtained. The product was crystallized by dropping this oil into cold ethylacetate. After washing with 20 ml of cold ethyl acetate, the [C_1C_4im][Cl] was dried unter vacuum at 30 °C for one day.

<u>EA:</u> Calulated (Measured): C 55.01 (53.68), N 16.04 (16.32), H 8.66 (7.17) %.

NMR: ^{1}H-NMR (250 MHz, DMSO-d_6), δ_H/ppm 0.90 [t, 3H], 1.28 [m, 2H], 1.77 [m, 2H], 3.84 [s, 3H], 4.16 [t, 2H], 7.68 [d, 1H], 7.75 [d, 1H], 9.07 [s, 1H];

Preparation of [C_1C_4im][BF_4]:

In a 1 l round bottom flask 92,02 g 1-butyl-3-methylimidazolium chloride was dissolved into 550 ml of dried acetonitrile and 57,96g sodium tetrafluoroborat (ABCR) was added. The dispersion was stirred at room temperature for 72 h. Then 5 g of activated charcoal was added and stirred for additional 24 h. After that, the acetonitrile was removed under vacuum and the remaining ionic liquid was dissolved in 300 ml dichloromethane. In order to remove halides, the dichloromethane phase was washed several times with water until no chloride was detected ($AgNO_3$). The solvent was removed in vacuum and the IL was dried with an oil diffusion pump for 24 h at 80 °C. The rest water content in the ionic liquid was confimed by coloumbetric Karl-Fischer titration to be below 20 ppm.

EA: calculated (measured) C 42.51 (42.21), N 12.39 (13.04), H 6.69 (5.87) %.

NMR: ^{1}H-NMR (250 MHz, $CDCl_3$), δ_H/ppm 0,95 [t, 3H], 1,35 [m, 2H], 1,86 [m, 2H], 3,96 [s, 3H], 4,18 [t, 2H], 7,27 [d, 1H], 7,33 [d, 1H], 8,82 [s, 1H]

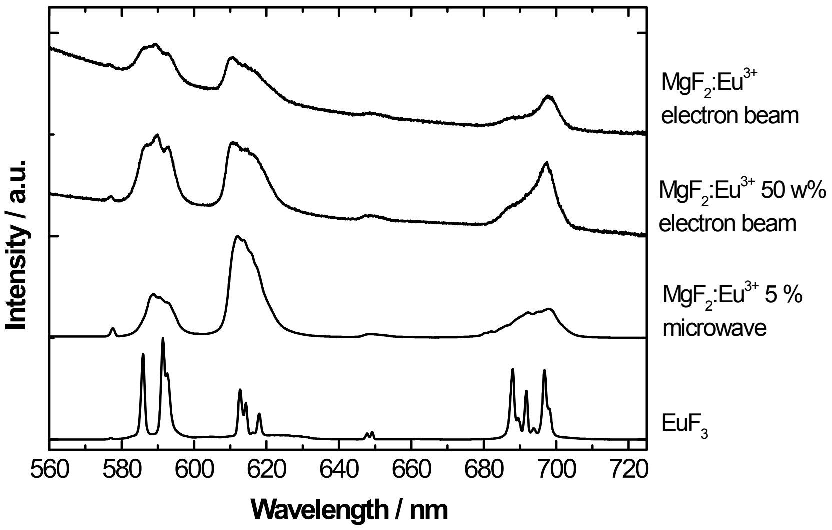

Figure S1. Room temperature emission spectra (λ_{ex}= 393 nm) of the synthesized MgF_2:Eu particles and the starting material EuF_3 for comparison. In addition, a 50 w% sample is added to prove that the broad band or strong signal around 560 nm is not due to a real emission, but more likely to be the result of poor photomultiplier detector correction at low intensities. In case of emission from potentially remaining IL or eventually forming Eu^{2+}, the signal intensity of the strong signal at 560 nm would either stay as intense as in the lower concentrated sample or even increase.

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