Electronic Supporting Information

Chemicals and Materials: Europium(III) acetate hydrate (Eu(OAc)₃·H₂O, 99.9 %, Alfa Aesar), gadolinium (III) acetate tetrahydrate (Gd(OAc)₃·4 H₂O, 99.9 %, ABCR), dichloromethane (99.9 %, Fisher Scientific), ethylene glycol (99 %, J.T. Baker), and ethanol (p.a., Riedel de Hœn) were used as received. 1-Butyl-pyridinium tetrafluoroborate ([C₄mim][BF₄]), (2-hydroxyethyl)-trimethylammonium tetrafluoroborate ([choline][BF₄]), trishexyltetradecylphosphonium tetrafluoroborate ([P₆₆₆₁₄][BF₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) were purchased from Iolitec, Heilbronn, D.

**Preparation of [C₄mim][BF₄]**. The task-specific ionic liquid (TSIL) [C₄mim][BF₄] was prepared according to a common literature procedure.⁸¹ 1-Butyl-3-methylimidazolium chloride (122.1 g, 0.7 mol) was stirred with sodium tetrafluoroborate (76.9 ml, 0.7 mol) in acetonitrile (800 ml) for 72 h at room temperature. After filtration, the mixture was stirred for additional 24 h with 5 g activated carbon. The activated carbon was removed by filtration and acetonitrile was completely removed under vacuum. The residual liquid was mixed with dichloromethane (300 ml) and washed with little amounts of water in order to remove the chloride (silver nitrate test). The colorless liquid was isolated and dried in vacuo. Yield: 134.5 g (85 %). ¹H NMR (250 MHz, CDCl₃): δ 8.64 (s, 1H, imidazole C(2)H), 7.37 (d, 2H, imidazole C=C=CH₂), 4.14 (t, 2H, NC₂H₂), 3.88 (s, 3H, NC₃H₃), 1.80 (quin., NCH₂CH₂n), 1.25 (sext., 2H, NCH₂CH₂n), 0.86 (t, CH₃). ¹³C{¹H} NMR (74.5 MHz, CDCl₃): δ 135.24, 123.04, 121.753, 48.87, 35.30, 31.12, 18.52, 12.54. Anal. Calcd for C₈H₁₅N₂BF₄: C, 42.5; H, 6.7; N, 12.4. Found: C, 42.2; H, 6.6; N, 13.0.

**Tributyltetradecylphosphonium tetrafluoroborate, [P₄₄₄₁₄][BF₄]**. A mixture of 21.76 g (0.05 mol) tributyltetradecylphosphonium chloride (Cytec, Canada Inc.), 5.76 g (0.05 mol) sodium tetrafluoroborate (98%, Aldrich), and 250 ml acetonitrile (99.5%, J. T. Baker) was stirred at room temperature for 72 h. Then, the mixture was filtered and the colorless precipitate was washed with acetone. The solvent was removed in vacuo and the residual liquid was mixed with 300 ml dichloromethane (99.9%, Fisher Scientific). After washing with water until all chloride was removed, the solution was dried over magnesium sulfate (99.9%, Riedel de Hœn), the solvent was removed in vacuo, and the residual liquid was dried at 80 °C for 24 h. Yield: 20.2 g (83 %).

¹H-NMR δH / ppm (298 K, 250 MHz, CDCl₃): 2.26-2.02 (m, 8 H, P-CH₂-(CH₂)x-CH₃), 1.57-1.40 (m, 16 H, P-CH₂-(CH₂)x-CH₃), 1.23 (m, 20 H, P-(CH₂)x-CH₃), 0.95 (t, J=6.8 Hz, 9 H, P-(CH₂)x-CH₃), 0.85 (t, J=6.7 Hz, 3 H, P-(CH₂)x-CH₃).

IR ν / [cm⁻¹]: 2921 (w), 1465 (w), 1048 (m).

Anal. Calcd for C₂₆H₅₆PBF₄: C, 64.2; H, 11.6. Found: C, 63.9; H, 10.7.

Mass spectrometry (FAB) m/z 399.4 ([P₄₄₄₁₄]+), 883.7 (M-[P₄₄₄₁₄]+).

**Synthesis of GdF₃:Eu 5 % with different ionic liquids (LCM1-5):** In a typical synthesis, 150 mg Gd(OAc)₃·4 H₂O (0.4 mmol) and 7 mg Eu(OAc)₃·H₂O (0.02 mmol) were dissolved in 1.5 ml ethylene glycol. Either 5 ml of liquid IL or 2 g of solid IL (~ 0.03 mol) were added to the solution. The reaction mixture was heated in a laboratory microwave (Discover, CEM, Ort, Land) for 10 min at 120 °C. The obtained colloidal solution was centrifuged (2000 rpm), washed several times with dichloromethane and dried at 70 °C.

**Ionothermal synthesis of GdF₃:Eu 5 % via ionothermal method (LCM6):** To a solution of 150 mg Gd(OAc)₃·4 H₂O (0.4 mmol) and 7 mg Eu(OAc)₃·H₂O (0.02 mmol) in 1.5 ml ethylene glycol 5 ml of [C₄mim][BF₄] were added and stirred...
to homogeneity. The reaction mixture was placed in a Teflon-lined autoclave (Anton Parr, Ostfildern, D) and heated for 20 h at 120 °C. The obtained colloidal solution was centrifuged, washed several times with dichloromethane and dried at 70 °C.

**Instrumentation:** Elemental analysis was obtained on a Vario EL (Elementar Analysensysteme GmbH, Hanau, D). Nuclear Magnetic Resonance (NMR) spectra were measured on a Bruker Advance DPX 200 or a Bruker Advance DPX 250 spectrometer (Bruker Germany GmbH, D). The peaks corresponding to the residual protons of the deuterated solvents were used as an internal reference. Attenuated total reflection (ATR) spectroscopy was carried out on an Alpha P ATR spectrometer, which is equipped with a diamond crystal (Bruker, Karlsruhe, D). Solid samples were pressed on the crystal; liquid samples were dropped onto the crystal. Powder X-ray diffraction (PXRD) measurements were carried out on a Huber G670 diffractometer with image plate detector (MoKα, λ = 0.70107nm; Huber, Rimsting, Germany).

Transmission electron microscopy (TEM) measurements were undertaken on a Tecnai G² 20 X-Twin TEM (Fei, Hillsboro, USA) or a Hitachi H-8100 transmission electron microscope (for sample LCM 1). An acceleration voltage of 200 kV was applied. Energy-dispersive X-ray (EDX) spectra were recorded with an EDAX detector (Fei, Hillsboro, USA) or an Oxford EDX detector Penta FET. For the measurement a suspension of the samples in ethanol (prepared in an ultrasonic bath) was dropped onto a copper or gold grid coated with carbon and then allowed to dry in air. In the EDX spectra carbon, copper and gold are grid specific lines. Silica and copper lines origin from the sample holder. The particle size distribution was obtained by measuring the size of the synthesized particles on different overview TEM images with the program ES Vision (Fei, samples LCM2-7) or iTEM (Olympus Soft Imaging System, sample LCM1). In images with agglomeration, only particles at the border were considered. The averaged particle size and the standard deviation were calculated from the data.

Fluorescence and phosphorescence measurements were measured on a Fluorolog FL 3-22 spectrometer (Horiba Jobin Yvon (Unterhaching, D). A choice between a continuous xenon lamp with 450 W for fluorescence and a pulsed xenon lamp for phosphorescence measurements is possible. Double gratings for the excitation and emission spectrometer are applied as monochromators. The signal is detected by a photomultiplier. For measurement, powdered samples were filled in silica tubes and carefully positioned in the incoming beam in the sample chamber. Synchrotron radiation measurements have been carried out at the beamlin I (SUPERLUMI) at Hasylab, DESY, Germany. On SUPERLUMI station, time and energy resolved luminescence spectroscopy exciting in the VUV region is possible. The samples are stored in ultra-high vacuum (10⁻⁹ – 10⁻¹⁰ mbar). At first, the synchrotron radiation is focused on the entrance slit of the primary monochromator by means of mirrors. There are two holographic concave gratings (1200 grooves/mm), a grating coated with aluminium and MgF₂ or a grating coated with platinum, which are optimized for different ranges in the spectrum. The resulting resolution interval range is in between 0.02 and 0.3 nm. After having passed the gratings, the beam goes through a mechanical chopper which allows to remove some pulses of the radiation in order to enlarge the interval of these. Finally, the beam is focused on the sample which is kept on a special holder. The emitted light passes the secondary grating and is detected by either a conventional photomultiplier or a CCD camera. The principal setup of the SUPERLUMI station and further information can be obtained from the HASYLAB homepage: http://hasylab.desy.de/facilities/doris_iii/beamlines/i_superlumi/index_eng.htm
At least 100 particles were considered for each particle size distribution.

**SI-Figure 1.** Particle size distribution (left, 100 particles were considered) and representative EDX spectrum (right) of GdF$_3$:Eu 5% prepared from [C$_4$mim][PF$_6$].

**SI-Figure 2.** Particle size distribution (left, 170 particles were considered) and representative EDX spectrum (right) of GdF$_3$:Eu$^{3+}$ 5% prepared from [C$_4$Py][BF$_4$].

**SI-Figure 3.** Particle size distribution (left, 100 particles were considered) and representative EDX spectrum (right) of GdF$_3$:Eu$^{3+}$ 5% prepared from [P$_{66614}$][BF$_4$].
SI-Figure 4. Particle size distribution (left, 115 particles were considered) and representative EDX spectrum (right) of GdF₃:Eu³⁺ 5% prepared from [choline][BF₄].

SI-Figure 5. Particle size distribution (left, 100 particles were considered) and representative EDX spectrum (right) of GdF₃:Eu³⁺ 5% prepared from [C₄mim][BF₄] via ionothermal route.

SI-Figure 6. Room temperature VUV excitation spectra of GdF₃:Eu³⁺ 5% particles synthesized from different ionic liquids.
SI-Figure 7. Schematic illustration of the quantum cutting mechanism of the Gd$^{3+}$-Eu$^{3+}$ ion couple.