Supporting information

Ionic Liquid based Approach to High-quality Nanoscale Functional Materials

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Synthesis of materials:

All procedures were performed using standard Schlenk-equipment. All chemicals were used as received from the supplier. $[MeBu_3N][(SO_2CF_3)_2N]$ as ionic liquid was synthesized according to a recipe described elsewhere.

$LaPO_4$:Ce,Tb (45 mol-%, 15 mol-%): 124 mg (0.334 mmol) $LaCl_3$ x $6H_2O$, 140 mg (0.367 mmol) $CeCl_3$ x $7H_2O$ and 47 mg (0.126 mmol) $TbCl_3$ x $6H_2O$ were dissolved in 5 ml ethanol (EtOH) and 10 ml ionic liquid (IL). A solution of 163 mg (1.66 mmol) crystalline H_3PO_4 in 2 ml EtOH and 5 ml IL was added dropwise over a period of 30 minutes under vigorous stirring at a temperature of 70°C. Thereafter, the transparent dispersion had been maintained under reduced pressure while the temperature was raised to 100°C until the gas evolution stopped. The vessel was kept under reduced pressure and placed in a standard laboratory microwave oven (MLS rotaprep). Here, the mixture was heated to 300°C (pyrometric control) by irradiating with 800 W for about 10 s. The transparent dispersion was left to cool down, diluted with 20 ml of EtOH and placed in an ultrasound bath. The nanocrystals were washed and collected by centrifugation and redispersion in EtOH, which is performed trice. After drying under reduced pressure, colourless solids were obtained in yields of 86-92 %. For further analytical characterisation nanocrystals were applied as-prepared or after redispersing in EtOH.

$LaPO_4$:Eu (5 mol-%): 353 mg (0.95 mmol) $LaCl_3$ x $6H_2O$ and 18 mg (0.05 mmol) $EuCl_3$ x $6H_2O$ were dissolved in 5 ml ethanol (EtOH) and 10 ml ionic liquid (IL). A solution of 196 mg (2.00 mmol) crystalline H_3PO_4 in 2 ml EtOH and 5 ml IL was added dropwise over a period of 30 minutes under vigorous stirring at a temperature of 70°C. Thereafter, the synthesis follows the procedure as given in case of $LaPO_4$:Ce,Tb. $LaPO_4$:Eu was obtained with yields of 85-90 %.

In_2O_3:Sn (7 mol-%): 21 mg (0.081 mmol) of $SnCl_4$ and 295 mg (1.008 mmol) of $InCl_3$ x $4H_2O$ were dissolved in 15 ml of $[N(CH_3)(C_4H_9)_3][N(SO_2CF_3)_2]$ as ionic liquid (IL) and 2 ml of DMF (solution A). In addition, $[N(CH_3)_4]OH$ was dissolved in 5 ml of IL and 2 ml of EtOH (solution B). Thereafter, solution A was added drop-wise to solution B under vigorous stirring at a temperature of 70 °C. Subsequently, all volatiles were removed under reduced

pressure while raising the bath temperature to 160 °C. After the gas evolution stopped, the reaction vessel was maintained under reduced pressure of 3 x 10^{-3} mbar and placed in a microwave oven and heated to 300 °C within 15 seconds. The pressure was reduced immediately to 3 x 10^{-3} mbar to remove water stemming from proceeding condensation. Finally, the dispersion was diluted with ethanol, and the blue particles were collected by centrifugation. Redispersion of the particles in ethanol, applying ultrasonic treatment, and centrifugation were repeated three times with the particles finally redispersed in ethanol.

Analytical characterization:

Scanning Electron Microscopy (SEM) was carried out with a Zeiss Supra 40VP. The nanocrystals were deposited on glass from ethanolic dispersions via pipette or on a transparency (HP color laser-jet transparencies) via ink-jet printing and examined without sputtering. Characterization was carried out at room temperature at an acceleration voltage of 10 kV and a working distance of 3 to 10 mm.

Transmission Electron Microscopy (TEM) and electron diffraction were performed on a Philips CM200 FEG/ST operating at 200 kV. Samples were prepared by ultrasonic nebulization of ethanolic dispersions on a Lacey-film copper grid.

X-Ray Powder Diffraction (XRD) was conducted with a Stoe STADI-P operating with Ge-monochromatized Cu-K_α radiation.

Dynamic Light Scattering (DLS) was conducted in polystyrene or quartz cuvettes with a Nanosizer ZS from Malvern Instruments. Prior to the investigation, dry powders were redispersed via ultrasonic treatment in diethylene glycol or ethanol.

Photo luminescence (PL) was recorded with a Jobin Yvon Spex Fluorlog 3 equipped with a 450 nm Xe-lamp and double grating excitation and emission monochromators. $LaPO_4$:Ce,Tb dispersions in ethanol were measured in standard quartz cuvettes at ambient temperature. Emission spectra were corrected for the wavelength-dependent response of the spectrometer. The quantum yield of the dispersion ($\varphi_{PL\text{-}LaPO4}$, λ_{exc} = 273 nm) was determined relative to the quantum yield of Coumarin 307 in methanol ($\varphi_{PL\text{-}Coumarin}$, = 0.95(2), λ_{exc} = 273 nm) with similar optical density.

Layer formation was performed by printing as-prepared In_2O_3:Sn nanocrystals were redispersed in mixtures of ethanol/methanol (1:1) to a concentration of 2.0 wt-%. Layer formation was then performed with a standard ink-jet printer (Lexmark Z735 and HP desk-jet 540). In order to gain a sufficient layer thickness, printing was repeated 10 times as a layer-by-layer process. Thereafter layer densification was performed with standard pressing

equipment (Specac stainless steel pressing tool, 13 mm in diameter; Specac hydraulic laboratory press applied at 80 kN).

Four-point probe measurements were conducted using a Keithley system (485 Autoranging Picoammeter, 199 System DMM/Scanner, 230 Programmable Voltage Source) and an electrode distance of 1.0 mm.