Supporting Information

Ce$^{3+}$ sensitized bright white light emission from colloidal Ln$^{3+}$ doped CaF$_2$
anocrystals for developing transparent nanocomposites
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Experimental Section:

**Materials.** Tm$_2$O$_3$, Tb$_2$O$_3$ (99.99%, from Aldrich), Ce(NO$_3$)$_3$.6H$_2$O, Sm(NO$_3$)$_3$.6H$_2$O (99.9%, from Aldrich), NH$_4$F(98%, from Aldrich) Citric Acid (CA)(99%, from sigma), Ca(NO$_3$)$_2$.4H$_2$O (98%, from Merck), HNO$_3$(1M, 70%, from Merck), and Distilled water were used for the Synthesis. All chemicals were used without further purification.

**Synthesis.** Citric Acid (CA) - coated CaF$_2$:Ce$^{3+}$(x%Tm$^{3+}$(0%or1%))/Tb$^{3+}$(y%)/Sm$^{3+}$(z%)[x = 0.15, 20, 25, y = 0, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.0, z = 0.06, 0.5, 0.4, 0.37, 0.35, 0.3] nano crystals were synthesized using microwave (MW) procedure. Briefly, various stoichiometric amounts of Tm$_2$O$_3$, Tb$_2$O$_3$ were converted to their corresponding nitrates by dissolving in 1N nitric acid whereas Ca(NO$_3$)$_2$.4H$_2$O, Sm(NO$_3$)$_3$.6H$_2$O, Ce(NO$_3$)$_3$.6H$_2$O, citric acid(CA) and ammonium fluoride(NH$_4$F) were used as received. In a typical procedure Ca(NO$_3$)$_2$.4H$_2$O (0.786mmol), Ce(NO$_3$)$_3$.6H$_2$O (0.20mmol), Tm(NO$_3$)$_3$ (0.01mmol), Tb(NO$_3$)$_3$ (0.006mmol), Sm(NO$_3$)$_3$.6 H$_2$O (0.0035mmol) were taken in a 100 ml beaker and dissolved in 15ml of distilled water. Citric acid (4mmol/10ml distilled water) was added slowly to the above nitrate mixture and vigorously stirred at room temperature for 1 hour .Then NH$_4$F (2.5mmol /5ml) taken in excess stoichiometric amount was added drop wise and stirred for 30 minutes. Subsequently, the colloidal solution was transferred into a 30ml glass vial used for microwave synthesis (Anton Parr Monowave 300 microwave reactor under temperature control mode). The vial was tightly sealed with teflon cap and microwave heated at 150°C for 15 minutes. The final product obtained as white precipitate was collected by centrifugation and washed thrice with distilled water, to remove any unreacted reactants, impurities dried under vacuum.

**Characterization techniques:**

**X-Ray diffraction study (XRD):** The XRD patterns were collected using the Rigaku-Smart Lab diffractometer attached with a D/texf ultra-detector and a Cu-K$_\alpha$ source operating at 35 kV and 70 mA. The scan range was set from 10-90$^\circ$ (2θ) with a step size of 0.02$^\circ$ and a count time of 2 sec. The samples were well powdered and spread evenly on a quartz slide.

**Transmission electron microscopy (TEM):** Transmission electron microscopy (TEM) images were taken using ultrahigh resolution FEG-TEM (JEOL JEM 2100F) with a 200 kV electron source and for imaging a drop of the nanocrystals dispersion was taken on a carbon coated 300 mesh Cu grid and dried in air.

**Scanning electron microscopy (SEM):** Field emission scanning electron microscopy (FESEM) images were collected on The SUPRA 55-VP JSM-Through patented GEMINI column technology. Prior to loading the samples into the chamber, they were coated with a thin film of gold in order to avoid charging effects.

**Fourier transform infrared spectroscopy (FTIR):** The FTIR spectra were recorded using Perkin Elmer Spectrometer RX1 spectrophotometer with KBr disk technique in the range of 4000-400 cm$^{-1}$. For recording the FTIR spectra 10 mg of the samples were mixed with 200 mg of KBr to make the pellets.

**Thermogravimetric analysis (TGA):** Thermogravimetric analysis was performed using Mettler Toledo TGA 851 instrument under N$_2$ atmosphere at a heating rate of 10$^\circ$ min$^{-1}$. 
Photoluminescence study (PL): The room temperature photoluminescence spectra were recorded using a Horiba Jobin Yvon Flurolog spectrophotometer equipped with a 450 W Xe lamp. The photoluminescence lifetime measurements were performed with Horiba Jobin Yvon Flurolog machine equipped with a pulsed Xe source operating at a power of 25 W. The absolute quantum yield measurement was performed using the integrating sphere purchased from Edinburgh Instruments. The sphere was placed in Edinburgh Instruments' FLSP 920 system, having a 450 W Xe lamp as excitation source. Red sensitive PMT was used as the detector.

Time resolved fluorescence study: The time resolved fluorescence studies were performed using Horiba Jobin Yvon time correlated single photon counting (TCSPC) set up with picoseconds resolution. The excitation source was a 280 nm Nano LED with 500 ps detection time resolution. Fluorescence emission was monitored at \( \lambda = 330 \text{nm} \).

Figure.S1 Power X-Ray diffraction (XRD) patterns of CaF\(_2\):Ce\(^{3+}\) (20%)/Tm\(^{3+}\) (1%)/Tb\(^{3+}\) (0.06%)/Sm\(^{3+}\) (0.3%) nanocrystals.
Figure S2 The XRD pattern for CaF$_2$:Ce$^{3+}$ (20%)/Tm$^{3+}$ (X %), Tb$^{3+}$ (Y %) and Sm$^{3+}$ (Z %) NCs. [x= 0, 1; y= 0, 0.1, 0.08, 0.09, 0.07, 0.06, 0.05; Z=0, 0.6, 0.5, 0.4, 0.37, 0.35, 0.30].

Figure S3 HRTEM images of CA-capped Ce$^{3+}$/Tm$^{3+}$/Tb$^{3+}$/Sm$^{3+}$-doped CaF$_2$ nanocrystals.
Figure S4 FTIR spectra of CA alone and the same coated over CaF$_2$ nanocrystals.

Figure S5 Digital image of Ce$^{3+}$/Tm$^{3+}$/Tb$^{3+}$/Sm$^{3+}$-doped CaF$_2$ nanocrystals (A) with CA capping and (B) without capping agent.
Figure S6 Thermo gravimetric analysis (TGA) curves of CA (solid trace) and CA-coated Ce\(^{3+}\)/Tm\(^{3+}\)/Tb\(^{3+}\)/Sm\(^{3+}\)-CaF\(_2\) (dotted trace) nanocrystals.

Figure S7 PL spectra of CaF\(_2\)-Ce\(^{3+}\) (20%)/Tm\(^{3+}\) (1%) (blue trace), CaF\(_2\) -Ce\(^{3+}\) (20%) Tb\(^{3+}\) 0.06%) (green trace) CaF\(_2\)-Ce\(^{3+}\) (20%) Sm\(^{3+}\) (0.3%) (red trace), nanocrystals.
Figure S8 Photoluminescence decay curves of Ce\(^{3+}/(20\%)/\)Tm\(^{3+}/(1\%)/\)Tb\(^{3+}/0.06\%)/\)Sm\(^{3+}-\)CaF\(_2\) nanocrystals measured after exciting at 280 nm. The emission collected for Tm\(^{3+}\) 450nm (A), for Tb\(^{3+}\) 542nm (B) and for Sm\(^{3+}\) 594nm emissions.

Figure S9 Excitation (A) and emission spectra (B) of Ce\(^{3+}/(20\%)/\)Tm\(^{3+}/(1\%)/\)Tb\(^{3+}/0.06\%)/\)Sm\(^{3+}-\)CaF\(_2\) nanocrystals measured in the integrating sphere.
**Figure S10** Emission spectra of CaF$_2$-Ce$^{3+}$ 20% and different concentration of Tm$^{3+}$ (x %) / Tb$^{3+}$ (y %) / Sm$^{3+}$ (z %) doped nanocrystals. The $\lambda_{ex}$ is 280 nm.

**Figure S11.** Photoluminescence decay curves of Ce$^{3+}$/ (20%)/Tm$^{3+}$ (1%)/Tb$^{3+}$0.06%/Sm$^{3+}$-CaF$_2$ nanocomposite film measured after exciting at 280 nm. The emission peaks collected for Tm$^{3+}$ is 450nm (A), for Tb$^{3+}$ is 542nm (B) and for Sm$^{3+}$ is 594nm (C).
**Figure S12** Transmittance spectra of pure PVA film and PVA nanocomposite film.

**Figure S13** PL spectra of CaF$_2$-Ce$^{3+}$/Tm$^{3+}$/Tb$^{3+}$/Sm$^{3+}$ nanocrystals measured using RGB colour filters. (A) spectrum with blue filter (500 nm short pass filter), (B) spectrum with green filter (530 nm-570nm band pass filter) and (C) spectrum with red filter (570 nm long pass filter).