Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ce^{3+} sensitized bright white light emission from colloidal Ln^{3+} doped CaF_2 nanocrystals for developing transparent nanocomposites

Venkata N. K. B. Adusumalli, Murthy Koppisetti and Venkataramanan Mahalingam*

* mvenkataramanan@yahoo.com

Experimental Section:

Materials. Tm_2O_3, Tb_2O_3 (99.99%,from Aldrich), $Ce(NO_3)_3.6H_2O$, $Sm(NO_3)_3.6H_2O$ (99.9%, from Aldrich), NH_4F(98%,from Aldrich) Citric Acid (CA)(99%,from sigma), $Ca(NO_3)_2.4H_2O$(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 Tm2O3, Tb2O3 were converted to their corresponding nitrates by dissolving in 1N nitric acid whereas $Ca(NO_3)_2.4H_2O$, $Sm(NO_3)_2.6H_2O$, $Ce(NO_3)_3.6H_2O$, citric acid(CA) and ammonium fluoride(NH_4F) were used as received. In a typical procedure $Ca(NO_3)_2.4H_2O$ (0.786mmol), $Ce(NO_3)_3.6H_2O$ (0.20mmol), $Tm(NO_3)_3$ (0.01mmol), $Tb(NO_3)_3$ (0.0006mmol), $Sm(NO_3)_3.6\ H_2O$ (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_4F (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/tex ultra-detector and a Cu-K_α source operating at 35 kV and 70 mA. The scan range was set from 10-90^0 (2θ) with a step size of 0.02^0 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-With 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^o 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 resulation. The excitation source was a 280 nm Nano LED with 500 ps detection time resulation. Fluorescence emission was monitored at λ = 330nm.

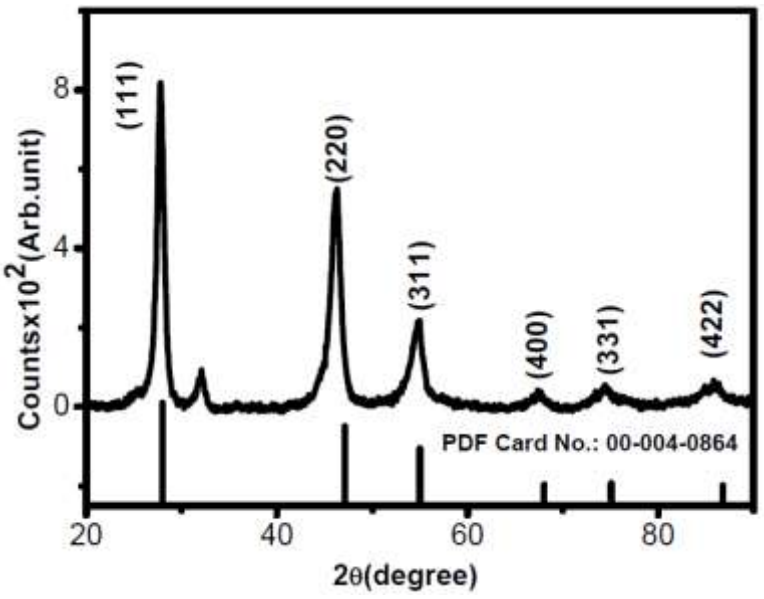

Figure.S1 Power X-Ray diffraction (XRD) patterns of CaF_2:Ce^{3+} (20%)/Tm^{3+} (1%)/Tb^{3+} (0.06%) /Sm^{3+} (0.3%) nanocrystals.

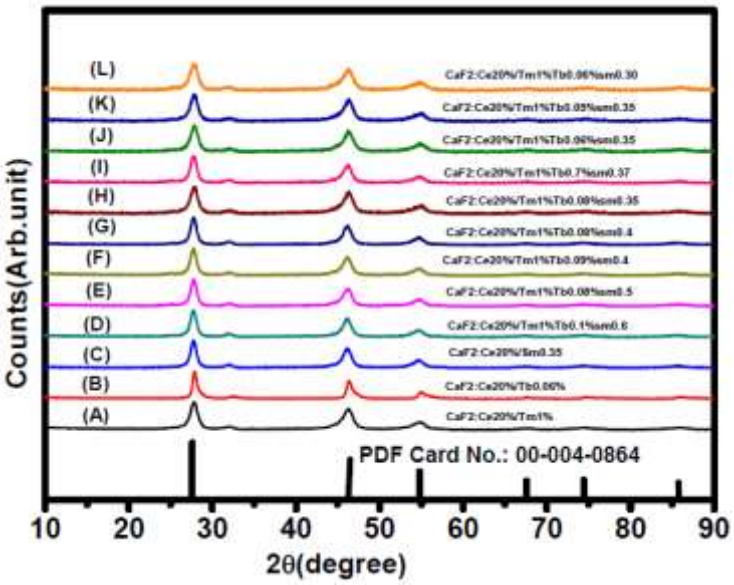

Figure.S2 The XRD pattern for CaF_2:Ce^{3+} (20%)/Tm^{3+}(X %), Tb^{3+} (Y %) and Sm^{3+} (Z %) NCs. [x= 0, 1; y= 0, 0.1, 0.08, 0.09, 0.07, 0.06, 0.05; Z=0, 0.6, 0.5, 0.4, 0.37, 0.35, 0.30].

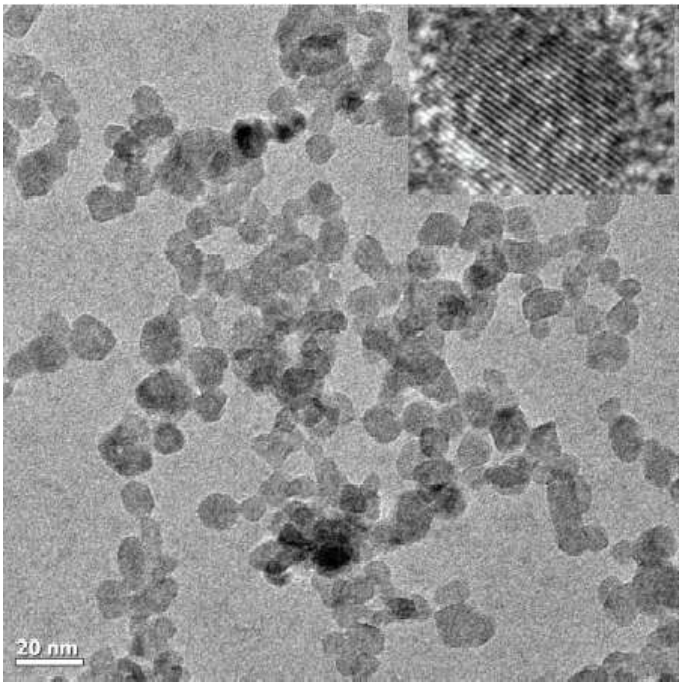

Figure.S3 HRTEM images of CA-capped Ce^{3+}/Tm^{3+}/Tb^{3+}/Sm^{3+}-doped CaF_2 nanocrystals.

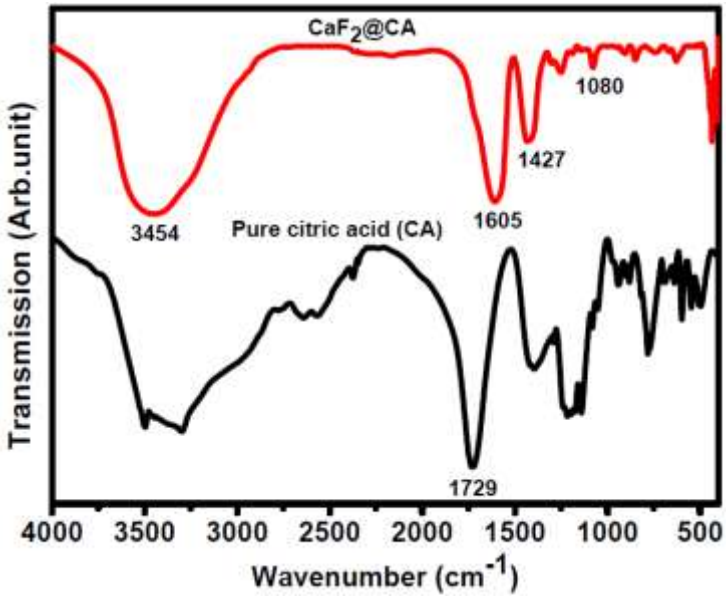

Figure.S4 FTIR spectra of CA alone and the same coated over CaF_2 nanocrystals.

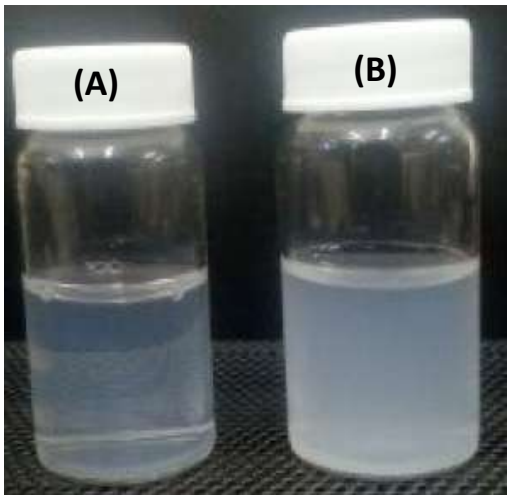

Figure.S5 Digital image of $Ce^{3+}/Tm^{3+}/Tb^{3+}/Sm^{3+}$-doped CaF_2 nanocrystals (A) with CA capping and (B) without capping agent.

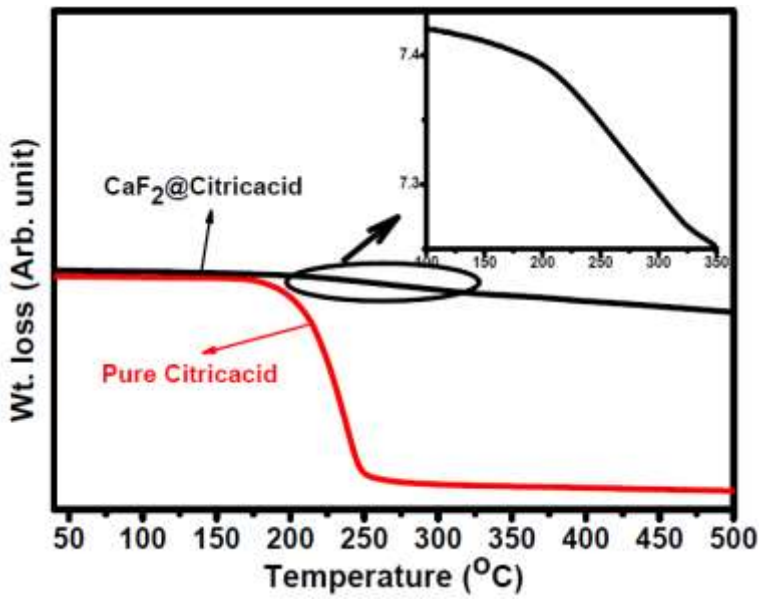

Figure.S6 Thermo gravimetric analysis (TGA) curves of CA (solid trace) and CA-coated Ce^{3+}/ Tm^{3+}/ Tb^{3+}/Sm^{3+}-CaF_2 (dotted trace) nanocrystals.

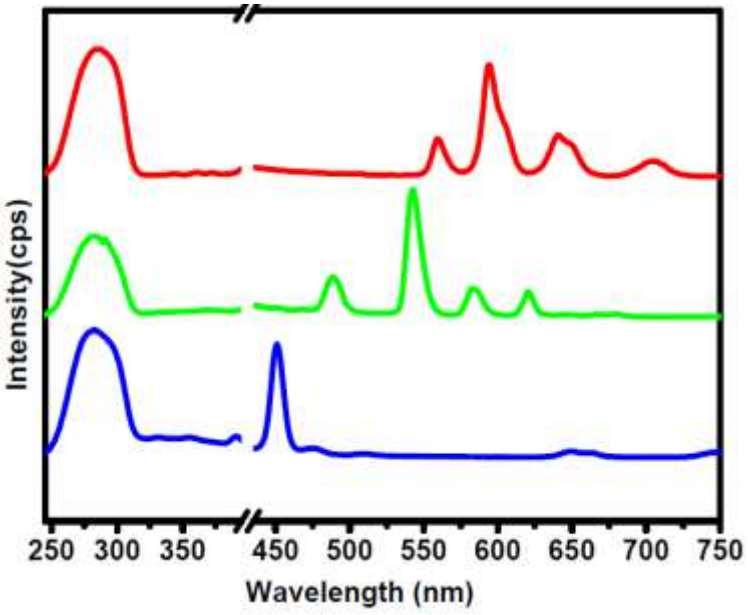

Figure.S7 PL spectra of CaF_2-Ce^{3+} (20%)/ Tm^{3+} (1%) (blue trace), CaF_2 -Ce^{3+} (20%) Tb^{3+} 0.06%) (green trace) CaF_2-Ce^{3+} (20%) Sm^{3+} (0.3%) (red trace), nanocrystals.

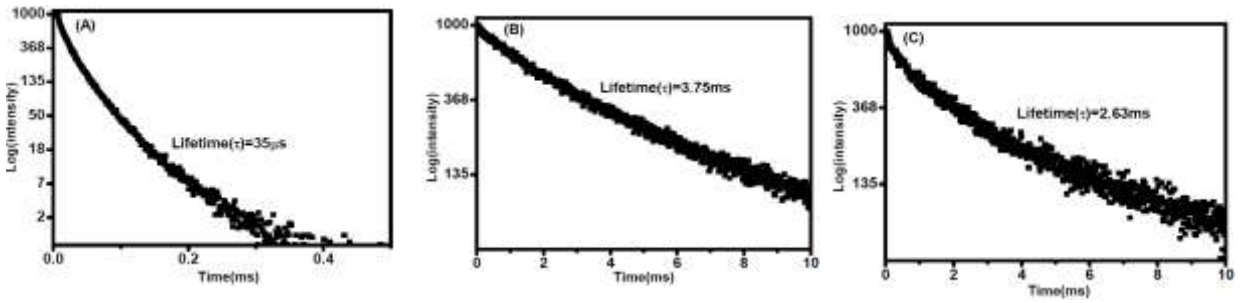

Figure.S8 Photoluminescence decay curves of Ce^{3+}/(20%)/Tm^{3+}(1%)/Tb^{3+}0.06%/Sm^{3+}-CaF_2 nanocrystals measured after exciting at 280 nm. The emission collected for Tm^{3+} 450nm (A), for Tb^{3+} 542nm (B) and for Sm^{3+} 594nm emissions.

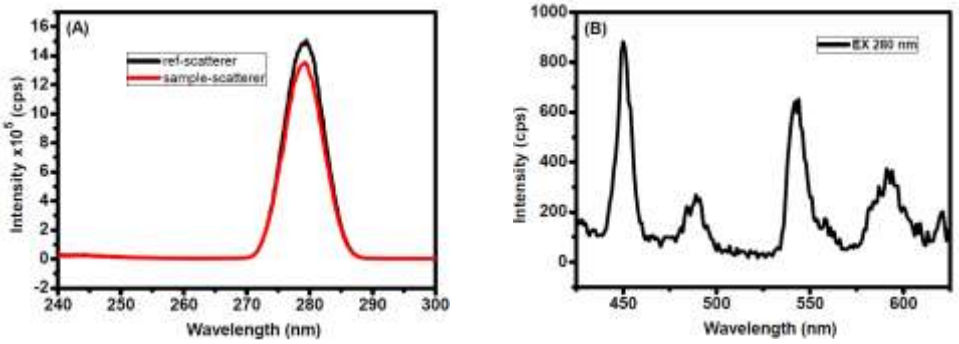

Figure .S9 Excitation (A) and emission spectra (B) of Ce^{3+}/ (20%)/Tm^{3+} (1%)/Tb^{3+}0.06%/Sm^{3+}-CaF2 nanocrystals measured in the integrating sphere.

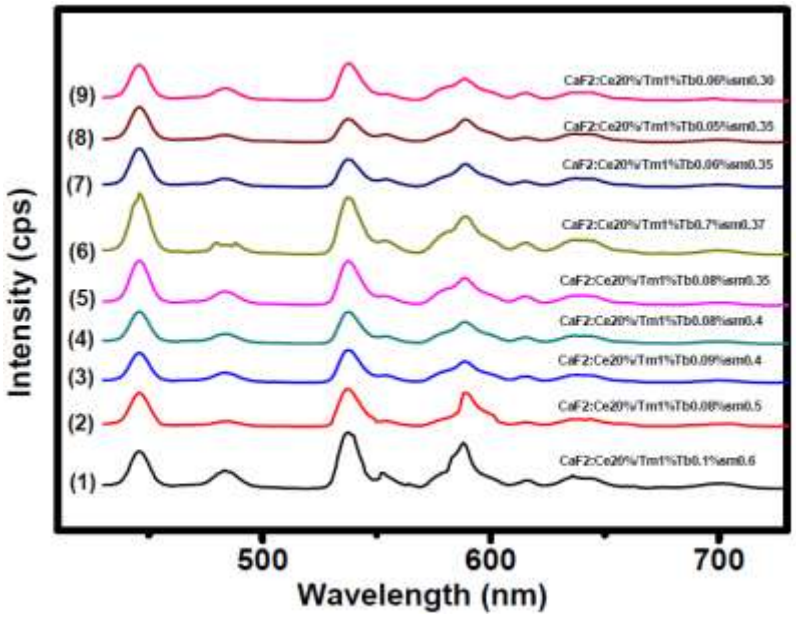

Figure.S10 Emission spectra of CaF_2-Ce^{3+} 20% and different concentration of Tm^{3+} (x %) /Tb^{3+} (y %) / Sm^{3+} (z %) doped nanocrystals. The λ_{ex} is 280 nm.

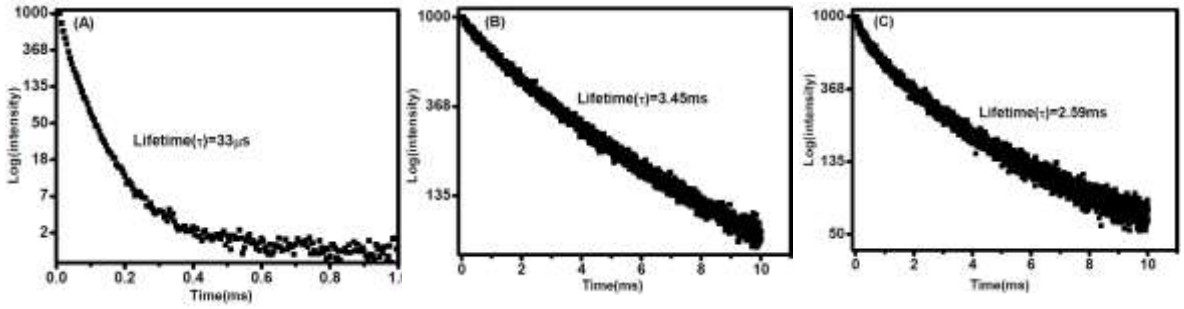

Figure S11. Photoluminescence decay curves of Ce^{3+}/ (20%)/Tm^{3+} (1%)/Tb^{3+}0.06%/Sm^{3+}-CaF2 nanocomposite film measured after exciting at 280 nm. The emission peaks collected for Tm^{3+} is 450nm (A), for Tb^{3+} is 542nm (B) and for Sm^{3+} is 594nm (C).

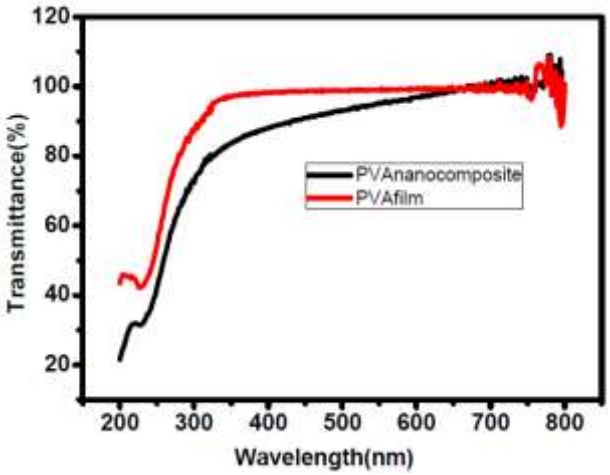

Figure.S12 Transmittance spectra of pure PVA film and PVA nanocomposite film.

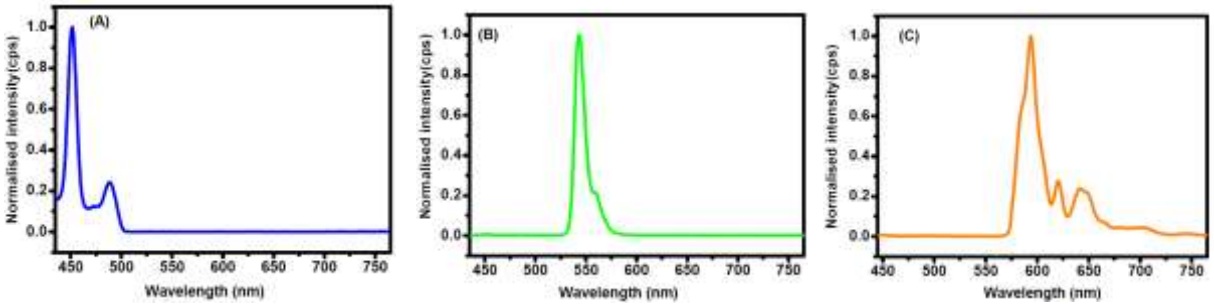

Figure.S13 PL spectra of CaF_2-Ce^{3+}/Tm^{3+}/Tb^{3+}/Sm^{3+} nanocrystals measured using RGB colour filters. (A) spectrum with blue filter (500 nm short pass filter), (B) spectrum with green filter (530 nm-570nm band pass filter) and (C) spectrum with red filter (570 nm long pass filter).