Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Enhanced quantum efficiency for Dy^{3+} emissions in water dispersible PbF_2 Nanocrystals

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Experimental section:

Synthesis of PAA-coated PbF_2:Dy^{3+}nanocrystals. Poly(acrylic acid)(PAA) coated PbF_2:Dy^{3+}(x%) nanoparticles [x= 0, 0.5, 1, 2, 5 and 8] were prepared using lead nitrate and sodium fluoride as precursors in a mixture of ethylene glycol and ethanol with PAA as the surfactant. Briefly, aqueous solutions of $Pb(NO_3)_2$ and $Dy(NO_3)_3$ were added to a mixture of ethanol (20 mL) and ethylene glycol (10 mL) under magnetic stirring. The sodium fluoride solution (2mmol) was then added, and the solution was vigorously stirred for about 30 min. To this mixture PAA (0.1 g) was added and the stirring was maintained for another 30 min. Subsequently the milky colloidal solution was transferred to a 100-mL Teflon lined autoclave. The autoclave was tightly sealed and then heated at 200 °C for 24 h before cooled down to room temperature naturally. The final product was collected by centrifugation, and washed twice with ethanol, followed by deionized water to remove any remaining reactants.

Instrumentation:

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku-smartlab diffractometer with Cu Kα operating at 200kV and 45mA at a scanning rate of 1º min^{-1} in the 2θ range from 15º to 90º. The samples were completely powdered and spread evenly on a quartz slide. TEM measurement was carried out using an FEI (Czech Republic), type FP5018/40 TECHNAI G^2 SPIRIT BioTWIN transmission electron microscope. Briefly, a drop of the PbF2 nanoparticles in water was taken on a strong carbon coated on 300 mesh Cu grid and dried in air. Field emission scanning electron microscopy (FESEM) images were taken on the JEOL, JSM-6700F, Japan. Prior to loading of the samples into the chamber, they were coated with a thin film

of platinum in order to avoid charging effects. The FT-IR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique in the range of 400-4000cm^{-1}. Thermogravimetric analysis was performed using Mettler Toledo TGA 851 instrument under N_2 atmosphere at a heating rate of 10^{o} min^{-1}. The photoluminescence measurements were done with the Horiba Jobin Yvon Fluoromax-3. All the emission spectra were recorded using steady state 450 W Xe lamp as the excitation source and were measured by exciting the sample in UV region at 350 nm. The luminescence lifetime measurements were performed in a with the Horiba Jobin Yvon Fluoromax-4CP machine with a pulsed Xe source of 25 W.

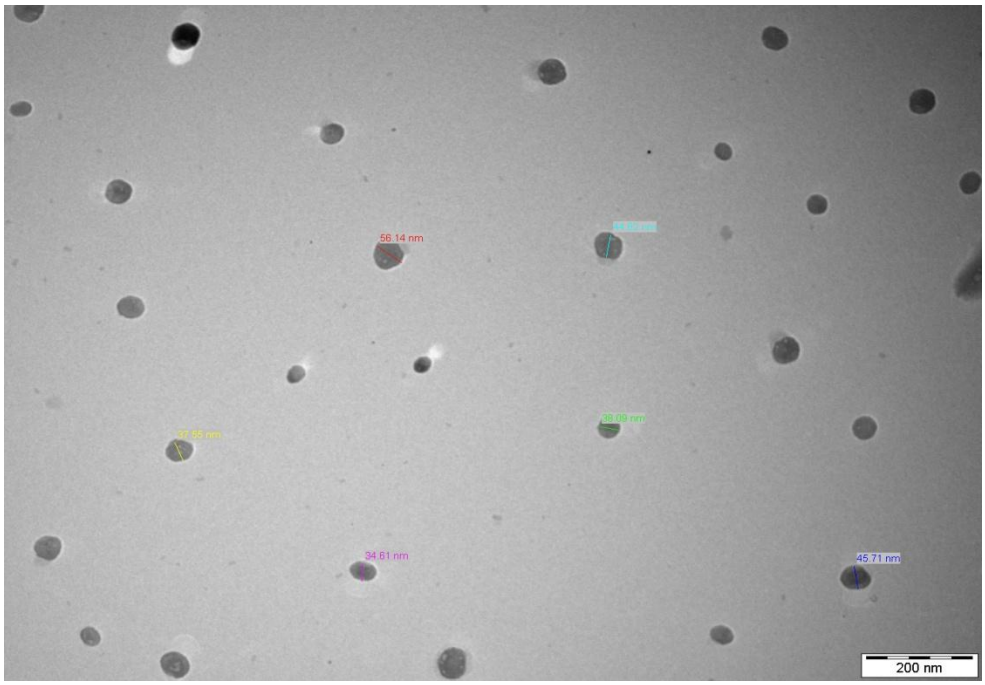

Fig. S1 Transmission electron microscopy (TEM) image of Dy^{3+}-doped PbF_2 nanocrystals.

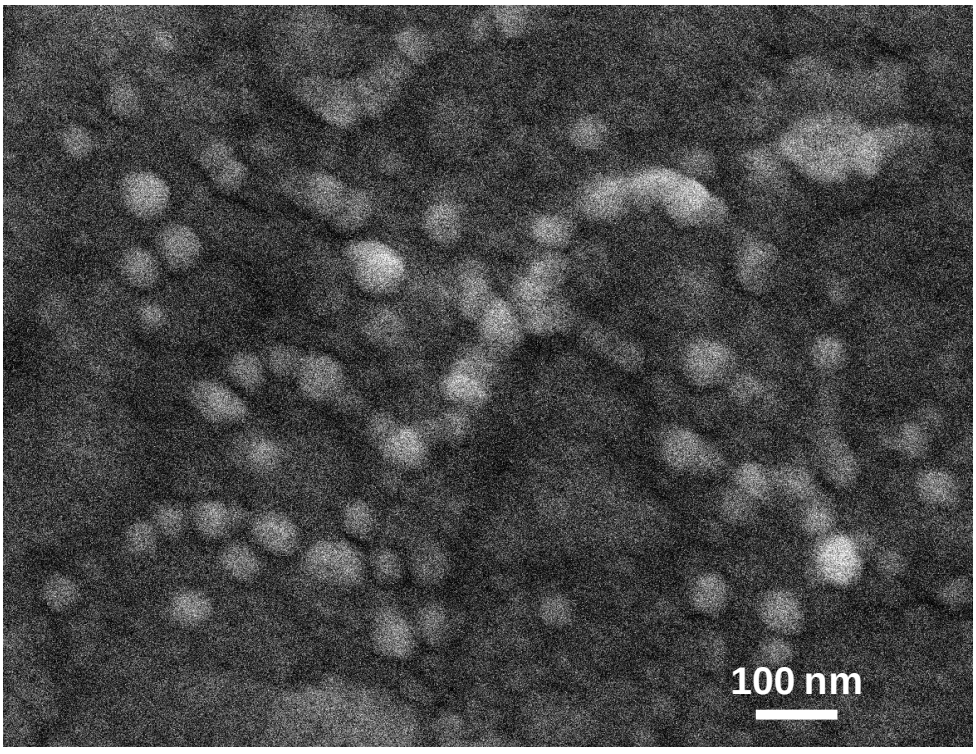

Fig. S2 Scanning electron microscopy (SEM) image of Dy^{3+}-doped PbF_2 nanocrystals.

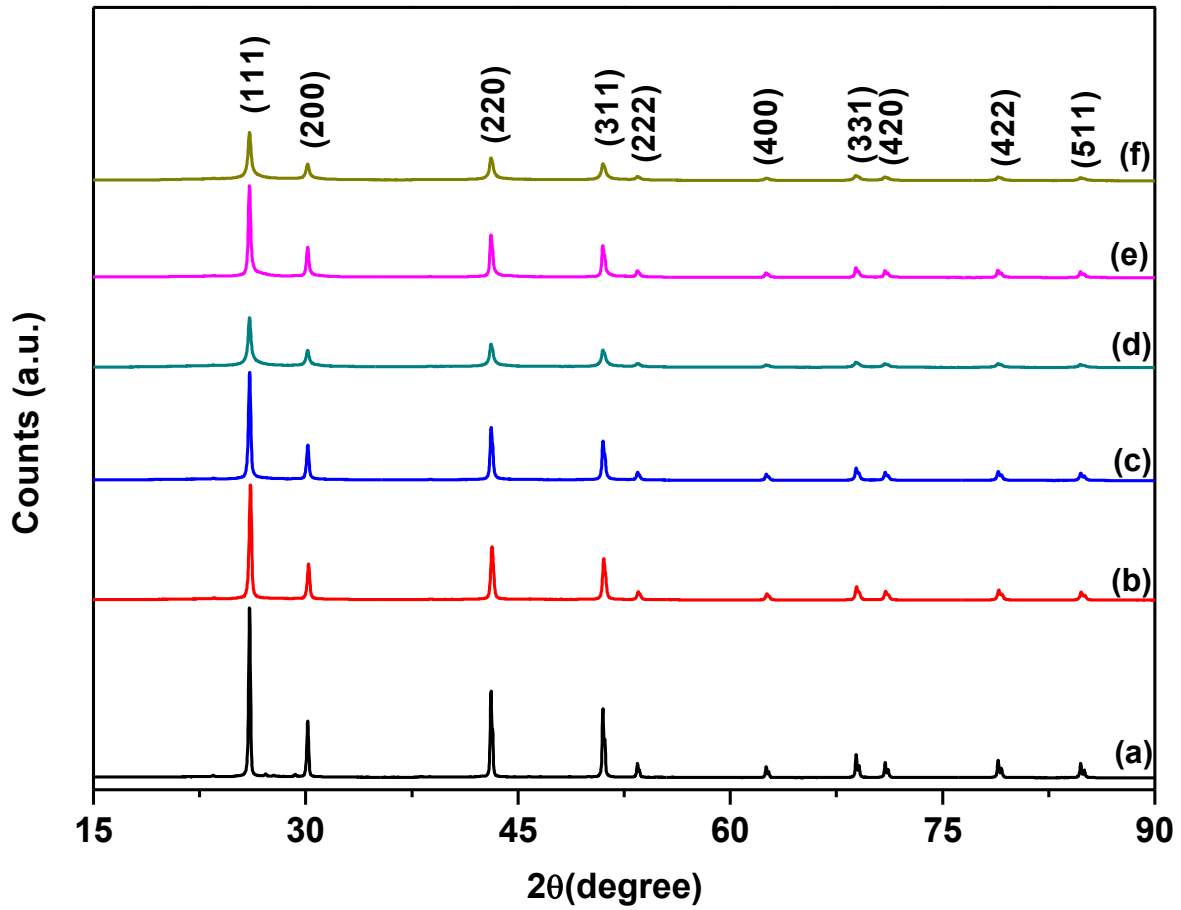

Fig. S3 Powder X-ray diffraction (PXRD) pattern of (a) un-doped PbF_2, (b) $PbF_2:Dy^{3+}$ (0.5%), (c) $PbF_2:Dy^{3+}$ (1%), (d) $PbF_2:Dy^{3+}$ (2%), (e) $PbF_2:Dy^{3+}$ (5%) and (f) $PbF_2:Dy^{3+}$ (8%) nanocrystals.

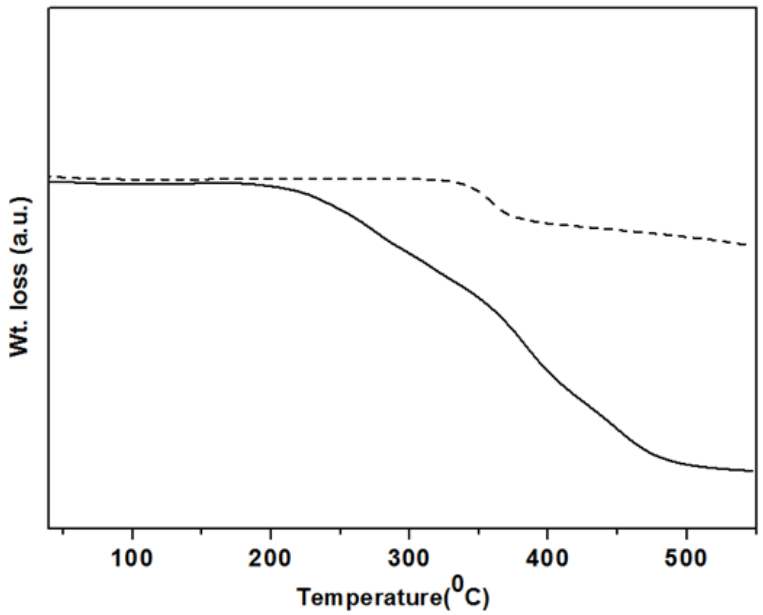

Fig. S4 Thermogravimetric analysis (TGA) curves of PAA (solid trace) and PAA-coated PbF_2:Dy^{3+} (dotted trace) nanocrystals.

Quantum Yield Calculation:

The quantum yield wasdetermined by comparing the luminescence with quinine-sulphate. The quantum yield of the for Dy^{3+}-doped PbF_2 nanocrystals was calculated from the following equation-

$Q_{sample} = Q_{ref} (A/A_{ref}) (I_{ref}/I) (n^2/n_{ref}^2)$

where, Q_{sample} and Q_{ref} are the quantum yields of the nanocrystals and quinine-sulphate respectively, A is the absorbance, I is the integrated area of photoluminescence spectra, and n is the refractive index of the solution.

The quantum yield of Quinine sulphate as the reference is 0.546. The quantum yield of the Dy^{3+}-doped PbF_2 nanocrystalswas estimated by comparing the integrated emission spectra of the aqueous solution with that of Quinine sulphate solution. The sample and the reference have the identical optical density at the excitation wavelength. The calculated quantum yield was

0.068(6.8 %) for Dy^{3+}-doped PbF_2 nanocrystals. For Eu^{3+}-doped PbF_2 nanocrystals quantum yield was 16.21%.

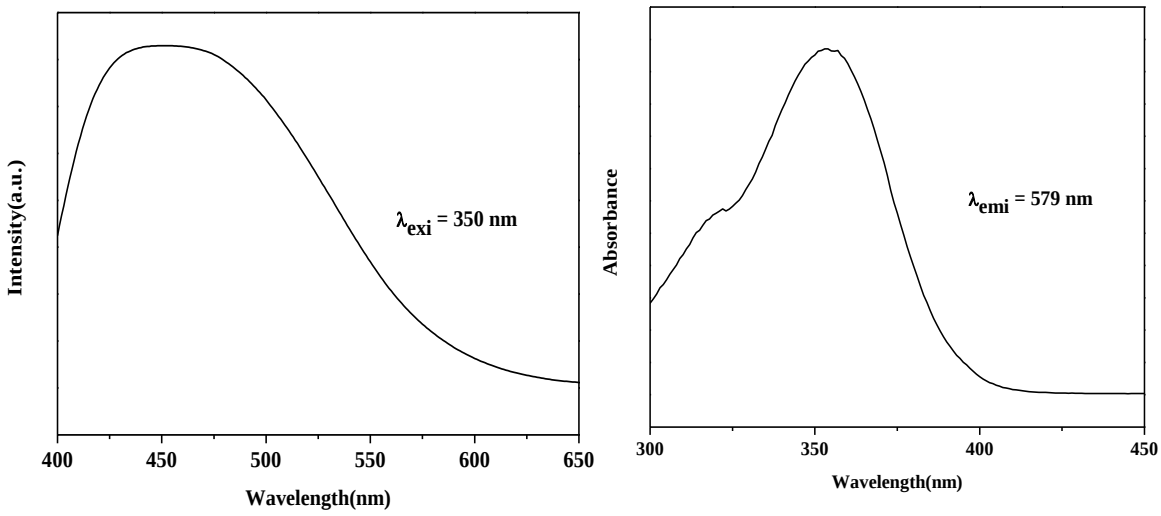

Fig. S5 Excitation and emission spectra of Quinine sulphate.

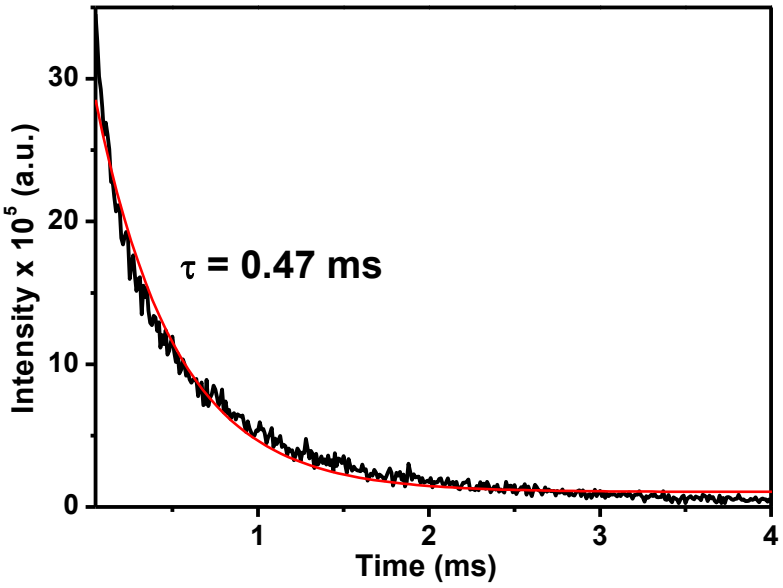

Fig. S6 Photoluminescence decay curve for Dy^{3+} ion in PbF_2 nanocrystals without PAA coating sample. The red trace is the fitted curve.

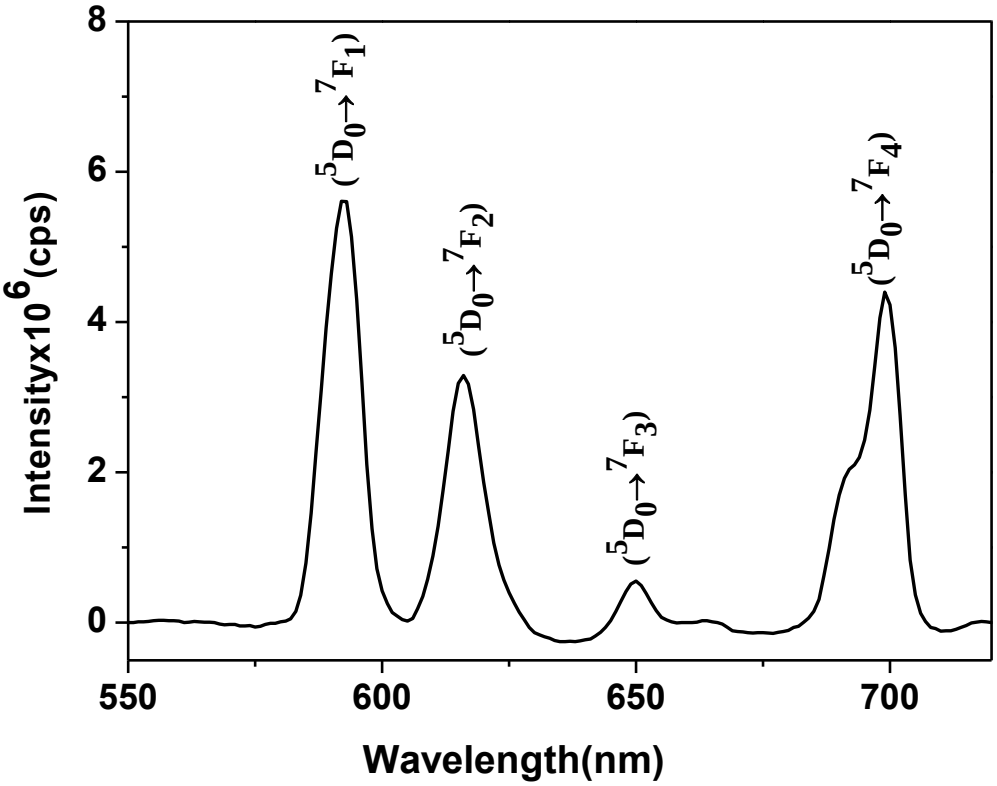

Fig. S7 The emission spectrum collected from PAA coated 5 mol% Eu^{3+}-doped PbF_2 nanocrystals dispersed in water.

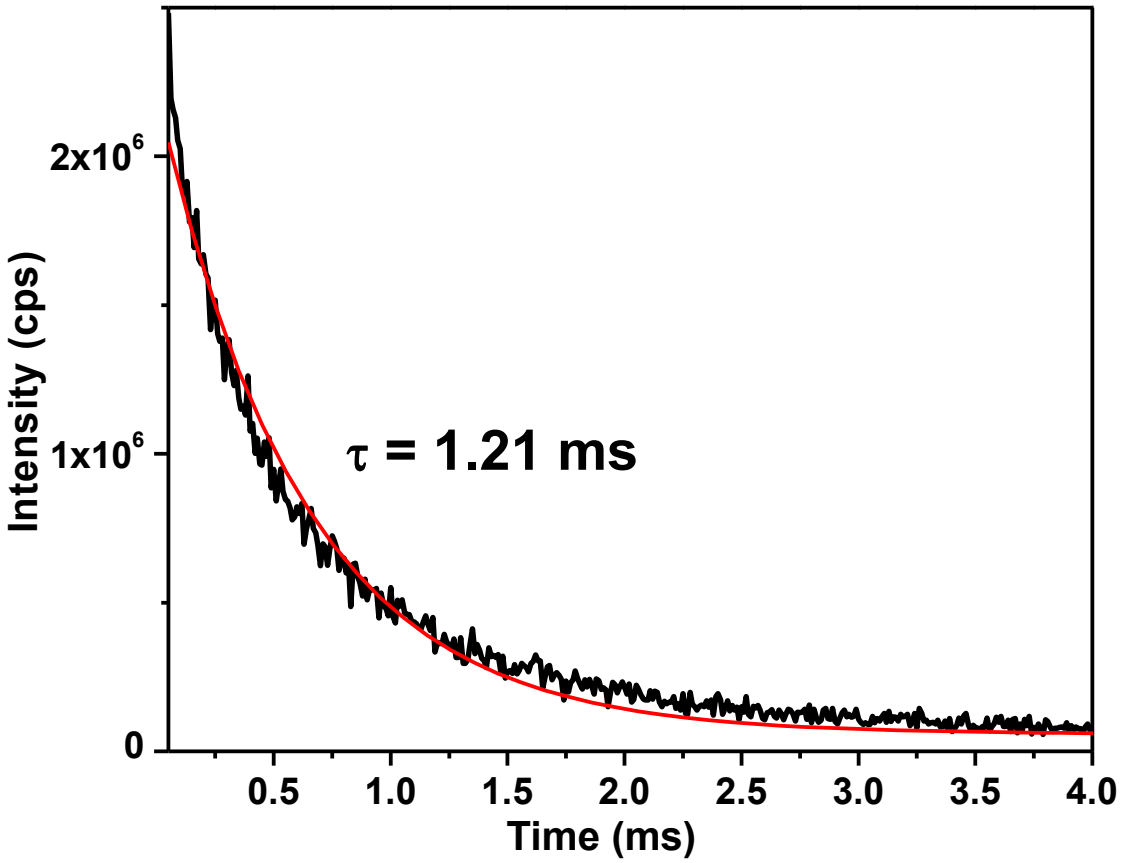

Fig. S8 Photoluminescence decay curve for 5 mol % Eu^{3+} ion in PbF_2 nanocrystals. The red trace is the fitted curve.