

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Enhanced visible and near infrared emissions via Ce³⁺ to Ln³⁺ energy transfer in Ln³⁺-doped CeF₃ nanocrystals (Ln=Nd and Sm)[†]

99Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Tuhin Samanta^a, Shyam Sarkar^a, Venkata. N. K. B. Adusumalli^a, Athma E. Praveen^a and Venkataramanan Mahalingam^{a*}

We report the enhancement of both visible and near infrared (NIR) emissions from Nd³⁺ ions *via* Ce³⁺ sensitization in colloidal nanocrystals for first time. This is achieved in citrate capped Nd³⁺-doped CeF₃ nanocrystals under ultraviolet (UV) irradiation ($\lambda_{\text{ex}}=282$ nm). The lasing transition (⁴F_{3/2}→⁴I_{11/2}) at 1064 nm from Nd³⁺-doped CeF₃ nanocrystals has much higher emission intensity *via* Ce³⁺ ions sensitization compared to the direct excitation of Nd³⁺ ions. The nanocrystals were prepared using a simple microwave irradiation route. Moreover, the study has been extended to Sm³⁺-doped CeF₃ nanocrystals which show strong characteristic emissions of Sm³⁺ ions *via* energy transfer from Ce³⁺ ions. The energy transfer mechanism from Ce³⁺ to Nd³⁺ and Sm³⁺ ions is proposed.

1. Introduction

There is a surge in the research interest towards developing lanthanide (Ln³⁺)-doped nanomaterials as they possess sharp luminescence signals with longer excited state lifetime (in the range of μs to ms). In addition, Ln³⁺ ions possess luminescent peaks over a wide electromagnetic spectrum. Particularly interesting are those emitting in the near-infrared (NIR) region *i.e.* the spectrum with the wavelength range of 700 to 2100 nm. NIR luminescence of lanthanide ions (Ln³⁺) find applications in NIR LED technology, lasers, solar energy conversion, medical science and telecommunication.¹⁻⁴ For example, Ln³⁺ ions such as Er³⁺, Nd³⁺, Tm³⁺ and Ho³⁺ have characteristic emissions in the NIR region and can be used as active materials for developing optical amplifiers.⁵⁻⁷ In addition, NIR emission is quite valuable for biological applications because of lower scattering from body than visible photons, low auto-fluorescence, deep penetration and transparent to biological tissues.⁸⁻¹¹ However, Ln³⁺ ions in aqueous media possess very weak emission intensities owing to their low molar absorption coefficients ($2\text{-}10\text{ M}^{-1}\text{ cm}^{-1}$), which is attributed to both spin- and parity-forbidden $4f\text{-}4f$ transitions of Ln³⁺ ions.¹²⁻¹⁴ In addition, non radiative transitions are very efficient in aqueous medium leading to further reduction of luminescence efficiency. One way to improve the luminescence efficiency is *via* antenna effect, where typically organic fluorophore possessing high absorption coefficient used as sensitizer for Ln³⁺ ions. The organic fluorophore transfers the absorbed

energy to Ln³⁺ ions leading to enhanced luminescence quantum efficiency of Ln³⁺ ions. However, most of the reports on antenna effect are restricted to Ln³⁺ complexes.¹⁵⁻¹⁶ Moreover, organic molecules generally photobleach and are relatively less stable. On the other hand, Ce³⁺ ions can be used as a sensitizer as they possess high absorbance co-efficient ($\sim 10^{18}\text{ cm}^{-2}$) due to allowed $4f\text{-}5d$ transition.¹⁷⁻²⁰ The optical characteristics of Ce³⁺ ions for efficient energy transfer are mainly attributed to two reasons: broad emission leading to better overlapping with absorption bands of other Ln³⁺ ions and faster luminescence decay.²¹⁻²⁴ However, sensitization of luminescence *via* Ce³⁺ ions is mostly restricted to visible emission of Tb³⁺ ions and to some extent Dy³⁺ ions.²⁵⁻²⁶ Recently, we have used Ce³⁺ ions for sensitizing Tm³⁺ ions to get single band blue emission from NaYF₄ nanocrystals.²⁷

Our objective is to sensitize NIR emissions using Ce³⁺ ions. Among NIR emitting Ln³⁺ ions, Nd³⁺ and Sm³⁺ are interesting for the following reasons. For example, Nd³⁺ ions possess important laser transition at 1064 nm (e.g. Nd³⁺-doped Y₃Al₅O₁₂).²⁸⁻³⁰ In fact the 1064 nm is used in achieving 532 nm *via* second harmonic generation. Furthermore, this emission due to the transition from ⁴F_{3/2}→⁴I_{11/2} energy levels falls well in the second “human optical window” (1000-1350 nm).³¹⁻³⁵ Similarly, Sm³⁺ ions possess two emissions in this optical window (near 1020 and 1150 nm) in addition to a strong emission at 940 nm. Moreover, the emission of Nd³⁺ shows remarkable thermal sensitivity leading to their use as sub-tissue thermal sensors.³⁶⁻³⁸ However, both Nd³⁺ ions and Sm³⁺ ions

possess sharp $f-f$ absorption which are difficult to pump.³⁹⁻⁴¹ Although there are quite a few reports on Ce^{3+} to Nd^{3+} energy transfer, they are mostly restricted to glass matrix.⁴²⁻⁴⁶ In fact, to our knowledge there are no reports on Ce^{3+} sensitized NIR emissions from Nd^{3+} or Sm^{3+} ions in colloidal nanocrystals, particularly in aqueous milieu.⁴⁷⁻⁴⁸ This is important as there is increasing demand for NIR emitting materials for biological imaging application. Furthermore, colloidal nanocrystals can easily coated or incorporated in sol-gel systems which is helpful for thin film device fabrication.

In this article, we report enhanced visible and NIR luminescence from Nd^{3+} -doped CeF_3 nanocrystals via Ce^{3+} sensitization. The lasing transition ($^4F_{3/2} \rightarrow ^4I_{11/2}$) at 1064 nm from Nd^{3+} -doped CeF_3 nanocrystals has shown emission strength about 3 times higher compared to that of the direct excitation of Nd^{3+} ions. Similarly, strong emissions in the NIR region is observed for Sm^{3+} -doped CeF_3 nanocrystals. We emphasize that all these are achieved from water and DMSO dispersible colloidal nanocrystals which can be useful for bioimaging applications.

2. Experimental Section

2.1. Materials

Cerium nitrate [$Ce(NO_3)_3$, 99.98%], neodymium oxide [Nd_2O_3 , 99.9%], samarium nitrate [$Sm(NO_3)_3$, 99.9%], trisodium citrate (>98%), sodium tetrafluoroborate (98%) and absolute ethanol were purchased from Sigma Aldrich. All chemicals were of analytical grade and used without further purification. Double distilled water was used throughout the synthesis and characterization.

2.2. Synthesis

Citrate functionalized Ln^{3+} -doped CeF_3 nanocrystals were prepared by simple microwave assisted method. Briefly, 0.95 mmol of $Ce(NO_3)_3$ and 0.05 mmol of $Nd(NO_3)_3$ were taken in a 100 ml round bottom flask and completely dissolved in 15 ml of double distilled water. To this clear aqueous solution 1.5 mmol $NaBF_4$ and 4 mmol tri sodium citrate (TSC) were added and stirred until complete dissolution. The mixture was magnetically stirred for 15 minutes at room temperature. Finally the mixture was transferred to a 30 ml vial, used for microwave synthesis. The synthesis was carried out using Anton Parr 300 microwave reactor. The vial was tightly sealed with a teflon cap and the reaction was carried out at 180°C temperature for 10 minutes and then cooled to room temperature. The product was collected by centrifugation and washed trice with absolute ethanol. It should be noted that the microwave experiments were carried out in temperature control mode. Simultaneous gas jet cooling (3-5 bar) during microwave irradiation was performed by using compressed air (6 bar). All microwave experiments were carried out using magnetic stirring at a rate of 600 rpm. The same protocol was used for the synthesis of citrate capped Sm^{3+} -doped CeF_3 nanocrystals.

[0.97 mmol of $Ce(NO_3)_3$ and 0.03 mmol of $Sm(NO_3)_3$ in 15 mL double distilled water.]

2.3. Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku-smartlab diffractometer with Cu $K\alpha$ operating at 70kV and 35 mA at a scanning rate of 1° min^{-1} in the 2θ range from 20° to 80° . The samples were completely powdered and spread evenly on a quartz slide. TEM measurement was carried out using a high resolution FEG transmission electron microscope (JEOL, JEM 2100F) with a 200 KeV electron source. Briefly, a drop of the CeF_3 nanocrystals in water was taken on a strong carbon coated on 300 mesh Cu grid and dried in air. The FT-IR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique in the range of $400\text{-}4000\text{cm}^{-1}$. Thermogravimetric analysis was performed using Mettler Toledo TGA 851 instrument under N_2 atmosphere at a heating rate of $10^\circ \text{ min}^{-1}$. The photoluminescence measurements were done with the Horiba Jobin Yvon Fluorolog. All the emission spectra were recorded using steady state 450 W Xe lamp as the excitation source. The luminescence lifetime measurements were performed in a with the Horiba Jobin Yvon Fluorolog machine with a pulsed Xe source of 150 W.

3. Results and discussion

3.1. Phase and structure

The phase analysis of the Ln^{3+} -doped CeF_3 ($Ln = Nd$ and Sm) nanocrystals were performed using powder X-ray diffraction (XRD) measurements. Fig. 1 shows the XRD pattern of the Nd^{3+} -doped CeF_3 nanocrystals along with that of standard pattern for bulk CeF_3 . All the peaks are matched well with that of standard CeF_3 (ICSD PDF Card No.-00-038-0452) suggesting the formation of pure hexagonal phase. The miller indices for each peak are shown above the corresponding peaks.

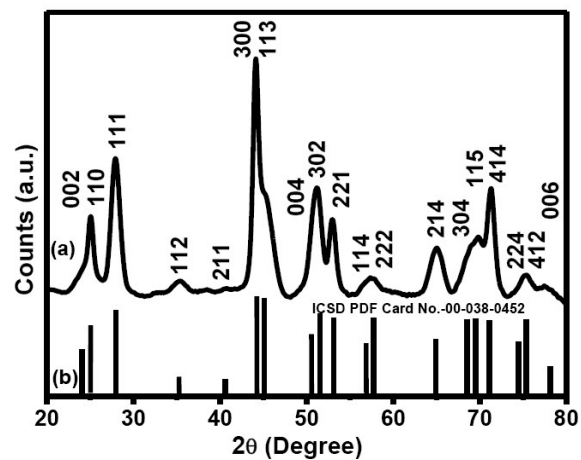


Fig. 1 Powder XRD patterns of (a) Nd^{3+} -doped CeF_3 nanocrystals and (b) standard hexagonal CeF_3 crystals (ICSD PDF Card No.-00-038-0452).

The average crystallite size is found to be 8.5 nm as calculated using the Debye-Scherrer equation, $t = (0.9\lambda/\beta\cos\theta)$, where, t stands for average crystallite size, λ denotes the wavelength ($\lambda = 1.5418 \text{ \AA}$) of incident X-ray, β denotes the corrected full width at half maximum (FWHM) and θ denotes the diffraction angle. Lattice parameters of Nd^{3+} -doped CeF_3 nanocrystals from XRD are found to be $a=b=7.1024$, $c=7.2612$ and $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. The hexagonal phase CeF_3 nanocrystals adopt the same structure as LaF_3 , and the space group of these two crystals is $P3C1$. The highest point group of this structure is D_{3d} . In this structure, the anion ligand number is 12, *i.e.* each cation is surrounded by 12 anions. The cation sits at the center of an icosahedron. Twelve fluorides are close: four at the bottom corners of the icosahedron, four in the faces of the icosahedron, and four at top corners of the icosahedron. The cation can be considered as 12 coordinate. The schematic of the unit cell crystal structure of hexagonal CeF_3 obtained using the visualization for electronic and structural analysis (VESTA) program is shown in Fig. 2. The atomic coordinates (x , y and z) used for the calculations are used from the reported literature⁴⁹ and shown in Table S1 (see ESI).

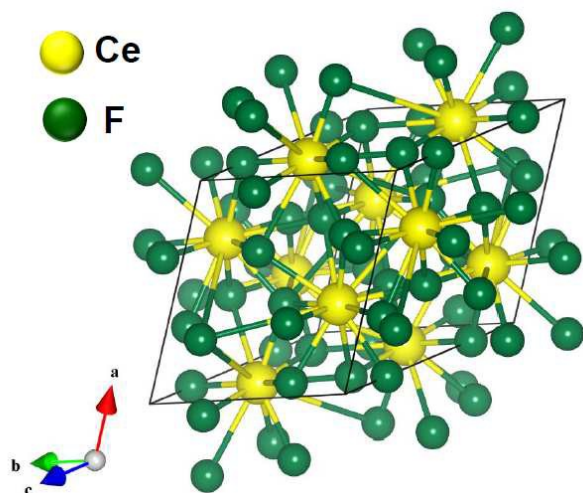


Fig. 2 Schematic presentation of the unit cell structure of CeF_3 nanocrystals.

3.2. Morphology analysis

The morphology of the citrate-functionalized Nd^{3+} -doped CeF_3 nanocrystals is obtained by transmission electron microscopy (TEM) as shown in Fig. 3. From the TEM images the formation of oval shaped nanocrystals is clear. The average aspect ratio of the Nd^{3+} -doped CeF_3 nanocrystals is found to be approximately 0.8 (length=20 nm and breadth=16 nm). For the semi-quantitative analysis of the elements present in the Nd^{3+} -doped CeF_3 nanocrystals energy-dispersive X-ray (EDX) analysis was performed. The EDX analysis spectra of Nd^{3+} -doped CeF_3 microcrystals is shown in Fig. S1 (see ESI[†]). It confirms the presence of Ce, F, and Nd in the sample.

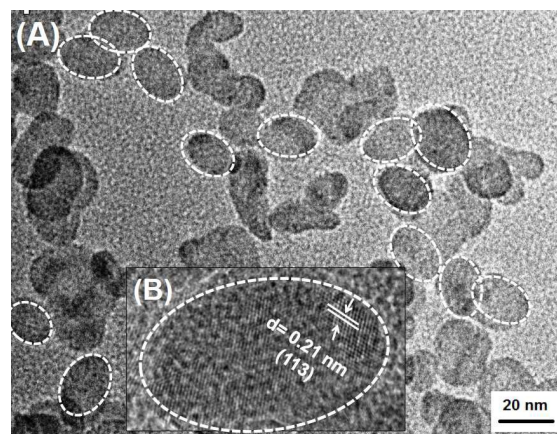


Fig. 3 TEM image of Nd^{3+} -doped CeF_3 nanocrystals and the inset shows HR image of a nanocrystal. White color circles are indicating the boundary of the nanocrystals.

3.3. Surface functionalization

The high dispersibility of the citrate functionalized CeF_3 nanocrystals in water suggests the binding of citrate ions to the surface of the nanocrystals which is supported by the FTIR analysis. The FTIR spectra of citrate capped CeF_3 nanocrystals along with pure trisodium citrate molecules are shown in Fig. 4. For the free TSC, major peaks are observed near 3453 , 2985 , 1600 and 1399 cm^{-1} . The strong and broad stretching vibration band centered at 3448 cm^{-1} is assigned to O–H in TSC and the peak at 2952 cm^{-1} is attributed to the methylene (CH_2) stretching vibrations of the alkyl chains of TSC. The band at 1600 cm^{-1} is assigned to the C=O asymmetric stretching vibration of the $-\text{COO}^-$ group, and the band at 1399 cm^{-1} is due to symmetric stretching vibrations of C–O in $-\text{COO}^-$ group of the TSC.⁵⁰ In case of citrate capped Nd^{3+} doped CeF_3 nanocrystals, all the characteristic peaks for TSC molecule are observed, however the C=O stretching frequency is shifted towards lower wavenumber (at 1590 cm^{-1}) which clearly indicates the binding of the TSC ligand onto the surface of the Nd^{3+} doped CeF_3 nanocrystals.

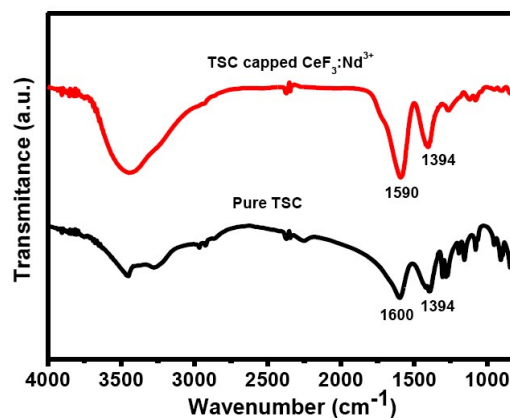


Fig. 4 FTIR spectra of citrate capped Nd^{3+} -doped CeF_3 nanocrystals and pure TSC molecules.

To further confirm the citrate functionalization onto the surface of CeF_3 nanocrystals, TGA analysis was conducted. The TGA curves for both citrate capped CeF_3 nanocrystals and pure TSC are shown in Fig. S2, (see ESI†). For the free TSC the major weight loss is noted from 250°C due to the decomposition of TSC molecules. For the citrate functionalized CeF_3 nanocrystal, the onset of decomposition is shifted to the higher temperature (~275°C) which further confirms that the citrate molecules are strongly attached to the surface of CeF_3 nanocrystals. The wt% of citrate molecules attached to the CeF_3 is close to 3.12% as calculated from the weight loss from the TGA analysis. Further confirmation for the attachment of the citrate ligands to the nanocrystals comes from the high stability of the nanocrystals in water. The dispersion of the nanocrystals was relatively stable in water for more than 10 hours. The photoluminescence study suggests that the luminescence intensity of Nd^{3+} ions reduced by only ~30% after 10 hours. The digital images of the colloidal dispersion along with the corresponding emission spectra are shown Fig. S3.

3.4. Optical properties

Photoluminescence (PL) studies have been carried out for the colloidal 0.1 wt(%) Nd^{3+} -doped CeF_3 nanocrystals in water. Upon excitation at 282 nm, the nanocrystals dispersion shows visible and NIR emissions as shown in Fig. 5. The prominent band in the visible region is at 693 nm, which is assigned to the $^2I_{15/2} \rightarrow ^4F_{7/2}$ transition. In addition, the nanocrystals dispersion shows characteristic NIR bands of Nd^{3+} ions at 1062 and 1339 nm in water, which are assigned to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$ transitions, respectively. The most intense band at 1062 nm is potentially suitable for application in laser emission and telecommunication. The inset of Fig. 5 displays the excitation spectrum which shows intense broad peak at 282 nm by monitoring the emission at 1062 nm. This peak is due to $4d5f \rightarrow 5f$ electronic transition of Ce^{3+} ions. This confirms the energy transfer from Ce^{3+} to Nd^{3+} ions. To further verify the

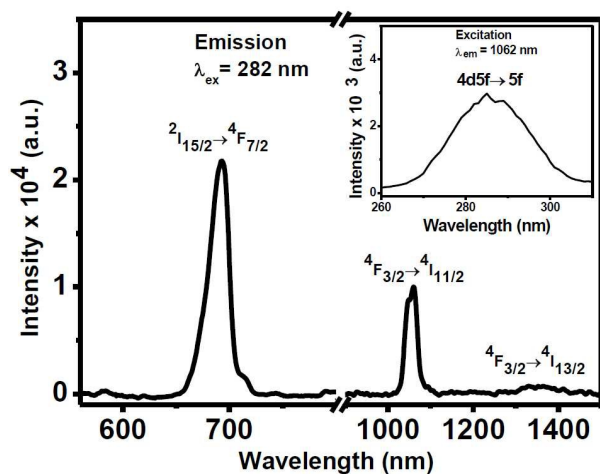


Fig. 5 PL emission spectrum of 5 mol(%) Nd^{3+} -doped CeF_3 nanocrystals in water covering visible to NIR region ($\lambda_{\text{exc}} = 282$ nm). Inset shows excitation spectrum for the same nanocrystals ($\lambda_{\text{em}} = 1062$ nm).

occurrence of energy transfer, we prepared Nd^{3+} -doped (5 mol%) LaF_3 nanocrystals using the same synthesis protocol. Upon excitation at 280 nm, no characteristic emission from Nd^{3+} ions is observed confirming the energy transfer from Ce^{3+} to Nd^{3+} in Nd^{3+} -doped CeF_3 nanocrystals (see Fig. S4). To understand the energy transfer efficiency, PL spectra of Nd^{3+} -doped CeF_3 nanocrystals were collected at direct excitation (514 nm) and 282 nm excitation. From Fig. 6, it is clear that upon 282 nm excitation the visible emission and NIR emission intensity increases by two and three times, respectively, compared to that of direct excitation. These results strongly suggest that efficient energy transfer is occurring from Ce^{3+} to Nd^{3+} ions.

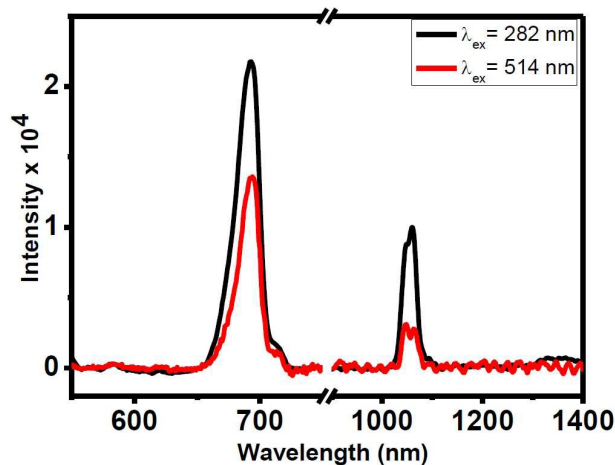


Fig. 6 PL spectra in the visible and NIR regions from Nd^{3+} -doped CeF_3 nanocrystals via Ce^{3+} ions excitation (282 nm) and direct excitation (512 nm).

We have extended our study to check whether energy transfer from Ce^{3+} ion to Sm^{3+} ions is possible. The 3 mol (%) Sm^{3+} -doped CeF_3 nanocrystals were prepared using identical reaction conditions and characterized by XRD analysis. The XRD pattern suggests the formation of pure hexagonal phase CeF_3 nanocrystals as shown in Fig. S5. The PL and excitation spectra of Sm^{3+} (3%)-doped CeF_3 nanocrystals are shown in Fig. 7. Upon 280 nm excitation the dispersion of Sm^{3+} -doped magnetic dipole character.⁵¹ The intensity ratio of $I(^4G_{5/2} \rightarrow ^6H_{9/2})/I(^4G_{5/2} \rightarrow ^6H_{5/2})$ is 1.05 which indicate less polarizability of the chemical environment around the Sm^{3+} ions.⁵² In addition, the nanocrystals show strong NIR emission peaks at 939 nm, 1017 nm and 1152 nm which are ascribed to the $^4G_{5/2} \rightarrow ^6F_{5/2}$, $^4G_{5/2} \rightarrow ^6F_{7/2}$, and $^4G_{5/2} \rightarrow ^6F_{9/2}$ transitions, respectively. These transitions are characteristics of Sm^{3+} ions. CeF_3 nanocrystals in DMSO shows intense peaks at 559, 593, 639 and 702 nm which are assigned to $^4G_{5/2} \rightarrow ^6F_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transitions, respectively. Among these peaks, 939 peaks are quite intense and it falls in the first “human optical window”. It is quite clear Fig. S6, that upon 280 nm excitation, both visible and NIR emission intensity increases by two times compared to that of

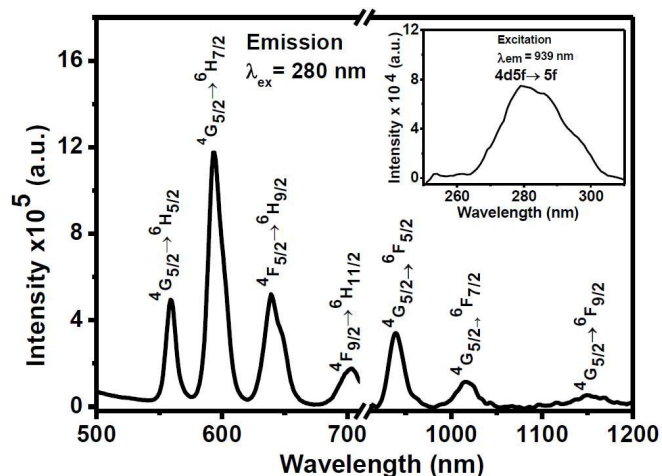


Fig. 7 PL spectrum of 3 mol (%) Sm^{3+} -doped CeF_3 nanocrystals in DMSO covering visible to NIR region ($\lambda_{\text{ex}} = 280$ nm). Inset shown excitation spectrum for the same nanocrystals ($\lambda_{\text{em}} = 939$ nm).

direct excitation (400 nm). We have performed some control experiments to test the effect of the concentrations of Nd^{3+} and Ce^{3+} ions on the emission intensity of the nanocrystals. There is an increase in the emission intensity upto 5 mol% doping for the Nd^{3+} ions and there upon a decrease is noted. Similarly, the optimum doping concentration for Sm^{3+} -doped CeF_3 is found to be 3 mol% (see Fig. S7).

Enhancement of visible and NIR emissions for both Nd^{3+} and Sm^{3+} ions are achieved *via* energy transfer from Ce^{3+} ions. This is supported by the overlap between the emission spectrum of Ce^{3+} ions with the absorbance of Sm^{3+} and Nd^{3+} ions. The results are shown in Fig. S8. The energy transfer efficiency between donor (Ce^{3+}) and acceptor ($\text{Nd}^{3+}/\text{Sm}^{3+}$) is evaluated using the equation $\eta = 1 - \tau_d/\tau_{d0}$. The average terms τ_d , and τ_{d0} are denoted for the excited state lifetimes of the sensitizer in presence and absence of the activator, respectively. The lifetimes of sensitizer Ce^{3+} ions in the presence and absence of

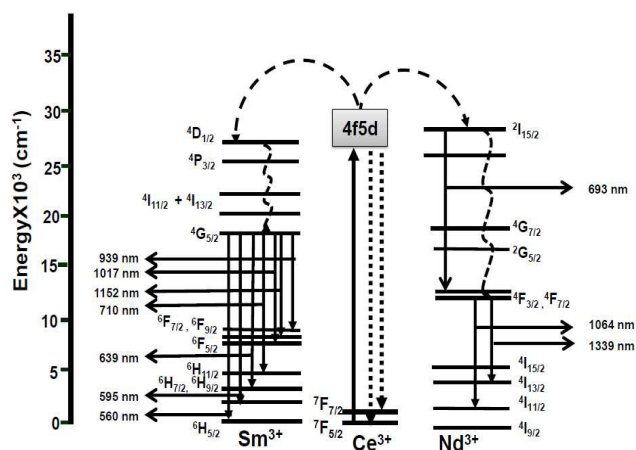


Fig. 8 Schematic of the proposed energy transfer mechanism from Ce^{3+} ions to Nd^{3+} and Sm^{3+} ions.

emitter (i.e. $\text{Nd}^{3+}/\text{Sm}^{3+}$ ions) using Time Correlated Single Photon Counting (TCSPC). The lifetime values of Ce^{3+} ions in CeF_3 , $\text{CeF}_3:\text{Nd}^{3+}$ (5%) and $\text{CeF}_3:\text{Sm}^{3+}$ (3%) nanocrystals are found to be 23 ns, 9.7 ns and 12 ns, respectively.⁵³ Lifetime decay curves are shown in Fig. S9 (see ESI†). The calculated energy transfer efficiency from Ce^{3+} to Nd^{3+} and Sm^{3+} are close to 57% and 48%, respectively. To understand the effect of Nd^{3+} concentration in CeF_3 on the energy transfer efficiency between Ce^{3+} and Nd^{3+} , we have calculated the corresponding lifetimes of Ce^{3+} emissions. It is interesting to note that the energy transfer efficiency increases with the increase in the ND concentration. The values are 53%, 55%, 57% and ~80% respectively, for 1, 3, 5 and 8 mol% Nd^{3+} doping in CeF_3 nanocrystals. Please note that the optimum luminescence efficiency of Nd^{3+} is 5 mol%. This suggests that though there is higher energy transfer probability between Ce^{3+} to Nd^{3+} at higher doping concentration, the cross relaxation between Nd^{3+} - Nd^{3+} is higher leading to self quenching of the luminescence. The lifetime decay curves are shown in Fig. S10. Furthermore, we have measured the lifetimes of Sm^{3+} and Nd^{3+} ions in Sm^{3+} and Nd^{3+} doped CeF_3 nanocrystals, respectively. Lifetimes of Sm^{3+} ions is 741 μs when excited at 282 nm and emission was monitored at 599 nm. Lifetimes of Nd^{3+} ions is 8 μs when excited at 282 nm and emission was monitored at 693 nm. It is shown in Fig. S11.⁵³

3.5. Energy transfer mechanism

The proposed energy transfer mechanism between Ce^{3+} to Nd^{3+} ions and Sm^{3+} ions is schematically shown in Fig. 8. Upon 282 nm excitation, Ce^{3+} ions get excited from $4f^1$ to $4f^05d^1$ levels. A radiative energy transfer occurs from the relaxed lowest $4d5f$ energy level of Ce^{3+} ions to the $^2I_{15/2}$ energy level of Nd^{3+} ions followed by radiative transfer to the low lying $^4F_{7/2}$ level of Nd^{3+} ions. Subsequently, energy transfer from $^4F_{7/2}$ to $^4F_{3/2}$ occurs nonradiatively. Radiative relaxation from $^4F_{3/2}$ levels to the $^4I_{11/2}$ and $^4I_{13/2}$ energy levels of Nd^{3+} ions, lead to the 1064 nm and 1339 nm NIR emissions, respectively. Similarly, for Sm^{3+} -doped CeF_3 nanocrystals, upon 280 nm excitation, Ce^{3+} ions are excited from $4f^05d^1 \rightarrow 4f^1$ level. A radiative energy transfer occurs from the lowest $4d5f$ energy band of Ce^{3+} ions to the $^4D_{1/2}$ energy level of Sm^{3+} ions followed by nonradiative transfer to the low lying $^4G_{5/2}$ level of Sm^{3+} ions. Subsequent decay from $^4G_{5/2}$ levels and $^6F_{9/2}$ levels to the $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$, $^6F_{5/2}$, $^6F_{7/2}$ and $^6F_{9/2}$ Sm^{3+} ions, result in emissions in the visible and NIR regions.

4. Conclusions

In conclusion, we have successfully synthesized hexagonal phase Ln^{3+} doped CeF_3 nanocrystals via microwave assisted method. The morphology of the nanocrystals was oval shaped with an average aspect ratio of ~0.8. The nanocrystals are functionalized with citrate molecules which render them highly water dispersible. In Nd^{3+} and Sm^{3+} -doped CeF_3 nanocrystals, enhanced visible and near infrared (NIR) emissions were observed *via* Ce^{3+} ions sensitization upon

ultraviolet (UV) irradiation ($\lambda_{\text{exc}} = 280$ nm). The energy transfer mechanism from Ce^{3+} to Nd^{3+} and Sm^{3+} ions is proposed. The strong NIR emissions from water dispersible nanocrystals are advantageous for bioimaging application. In addition, they can easily be incorporated into polymer and other sol-gel matrices for the fabrication of devices for telecommunications.

Acknowledgements

VM thanks the Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST), India and IISER-Kolkata for funding. TS, SS and AVNK thank University Grand Commission (UGC), India for the scholarship.

Notes and references

^a Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Kolkata, Mohanpur, West Bengal 741252, India. Fax: 91-33-25873020; Tel: +91(0)9007603474; E-mail: mvenkataramanan@yahoo.com

†Electronic Supplementary Information (ESI) available SEM, EDAX, TGA, PL spectra and digital images of water dispersion of Nd^{3+} doped CeF_3 nanocrystals. Lifetimes, XRD and energy transfer mechanism of Ce^{3+} to Sm^{3+} of Sm^{3+} doped CeF_3 nanocrystals also available.

- S. Mishra, E. Jeanneau, A.-L. Bulin, G. Ledoux, B. Jouguet, D. Amans, A. Belsky, S. Danieleb and C. Dujardin, *Dalton Trans.*, 2013, **42**, 12633.
- S. K. Singh, *RSC Adv.*, 2014, **4**, 58674.
- M. Balestrieri, S. Colis, M. Gallart, G. Ferblantier, D. Muller, P. Gilliot, P. Bazylewski, G. S. Chang, A. Slaouib and A. Diniaia *J. Mater. Chem. C*, 2014, **2**, 9182.
- (a) P. Liu, J. Liu, X. Zheng, H. Luo, X. Li, Z. Yao, X. Yu, X. Shi, B. Hou and Y. Xia *J. Mater. Chem. C*, 2014, **2**, 5769. (b) C. Hazra, T. Samanta, A. V. Asaithambi and V. Mahalingam, *Dalton Trans.*, 2014, **43**, 6623.
- G. Gao, M. Peng and L. Wondraczek *J. Mater. Chem. C*, 2014, **2**, 8083.
- Z.-P. Zheng, X.-X. Zhang, T. Li, J. Yang, L.-M. Wei, L.-G. Zhang, X.-M. Lina and Y.-P. Cai, *Dalton Trans.*, 2014, **43**, 14009.
- J. Zhang and S. Petoud, *Chem.–Eur. J.*, 2008, **14**, 1264.
- D. Wang, B. Xue, X. Kong, L. Tu, X. Liu, Y. Zhang, Y. Chang, Y. Luo, H. Zhao and H. Zhang, *Nanoscale*, 2015, **7**, 190.
- D. Tu, L. Liu, Q. Ju, Y. Liu, H. Zhu, R. Li and X. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 6306.
- E. Hemmer, N. Venkatachalam, H. Hyodo, A. Hattori, Y. Ebina, H. Kishimoto and K. Soga, *Nanoscale*, 2013, **5**, 11339.
- (a) A. F. Collet, K. A. Gogick, K. A. White, S. Villette, A. Pallier, G. Collet, C. Kieda, T. Lib, S. J. Geib, N. L. Rosi, and S. Petoud, *PNAS*, 2013, **113**, 17199. (b) M. Pedroni, F. Piccinelli, T. Passuello, M. Giarola, G. Mariotto, S. Polizzi, M. Bettinella and A. Speghini, *Nanoscale*, 2011, **3**, 1456.
- Y. Liu, D. Tu, H. Zhu, R. Li, W. Luo and X. Chen, *Adv. Mater.*, 2010, **22**, 3266.
- L. Li, Y. Su and G. Li, *J. Mater. Chem.*, 2010, **20**, 459.
- Z. Zhang, H. Feng, L. Liu, C. Yu, X. Lü, X. Zhu, W.-K. Wong, R. A. Jones, M. Pand and C. Su, *Dalton Trans.*, 2015, **44**, 6229.
- J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.
- (a) O. A. Blackburn, M. Tropiano, T. J. Sørensen, J. Thom, A. Beeby, L. M. Bushby, D. Parker, L. S. Natrajan and S. Faulkner, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13378. (b) T. Samanta, C. Hazra and V. Mahalingam, *New J. Chem.*, 2015, **39**, 106.
- S. Wu, C. Li, W. Wei, H. Wang, Y. Song, Y. Zhu and L. Lu, *J. Rare Earths*, 2010, **28**, 171.
- Z. Fang, R. Cao, F. Zhang, Z. Ma, G. Donga and J. Qiu, *J. Mater. Chem. C*, 2014, **2**, 2204.
- B. Gao, Q. Yan, Y. Tong, X. Zhang, H. Ma b, J.-I. Adam, J. Ren, G. Chen, *J. Lumin.*, 2013, **143**, 181.
- D. Chen, Y. Wang, Y. Yu, P. Huang and F. Weng, *J. Appl. Phys.*, 2008, **104**, 116105.
- M. C. Tan, G. A. Kumar, R. E. Riman, *Opt. Express*, 2009, **17**, 15904.
- Y. V. Orlovskii, T. T. Basiev, E.O. Orlovskaya, Y. S. Privisa, V.V. Fedorov, S.B. Mirov, *J. Lumin.*, 2003, **101**, 211.
- J. Mares, B. Jacquier, C. P'edrini, G. Boulon, *Rev. Phys. Appl.* 1987, **22**, 145.
- J. Ueda, P. Dorenbos, A. J. J. Bos, K. Kuroishia and S. Tanabea, *J. Mater. Chem. C*, 2015, **3**, 5642.
- K. Li, M. Shang, D. Geng, H. Lian, Y. Zhang, J. Fan, and J. Lin, *Inorg. Chem.* 2014, **53**, 6743.
- G. V. L. Reddy, L. R. Moorthy, T. Chengaiah, B.C. Jamalaiah, *Adv. Mat. Lett.* 2013, **4**, 841.
- V.N.K.B Adusumalli, S. Sarkar and V. Mahalingam, *chemphyschem*, 2015, **16**, 2313
- L. Tong, J. Lou, Y. Xu, Q. Luo, N. Shen and E. Mazur, *Appl Opt.*, 2002, **41**, 4008.
- S. Satapathy, A. Ahlawat, A. Paliwal, R. Singh, M. K. Singh and P. K. Gupta, *CrystEngComm*, 2014, **16**, 2723.
- P. Samuel, G.A. Kumar, T. Yanagitani, H. Yagi, K. I. Ueda, S. M. Babu, *Opt. Mater.*, 2011, **34**, 303.
- A. M. Smith, M. C. Mancini, and S. Nie, *Nat Nanotechnol.*, 2009, **4**, 710.
- (a) R. Wang and F. Zhang, *J. Mater. Chem. B*, 2014, **2**, 2422. (b) N. Bogdan, F. Vetrone, G. A. Ozin, J. A. Capobianco, *Nano Lett.* 2011, **11**, 835.
- N. Won, S. Jeong, K. Kim, J. Kwag, J. Park, S. G. Kim, and S.Kim, *Mol. Imaging*, 2012, **11**, 338.
- G. Hong, Y. Zou, A. L. Antaris, S. Diao, D. Wu, K. Cheng, X. Zhang, C. Chen, B. Liu, Y. He, J. Z. Wu, J. Yuan, B. Zhang, Z. Tao, C. Fukunaga and H. Dai, *Nature Comm*, 2014, **5**, 4206.
- U. Rocha, K. U. Kumar, C. Jacinto, I. Villa, F. S.-Rodríguez, M. d.l. C. I. d. l. Cruz, A. Juarranz, E. Carrasco, F. C. J. M. van Veggel, E. Bovero, J. G. Solé, and D. Jaque, *small*, 2014, **10**, 1141.
- U. Rocha, C. Jacinto, W. F. Silva, I. Guedes, A. Benayas, L. M. Maestro, M. A. Elias, E. Bovero, F. C. J. M. van Veggel, J. G. Solé, D. Jaque, *ACS Nano*, 2013, **7**, 1188.
- K. Binnemans, *Chem. Rev.* 2009, **109**, 4283.
- (a) A. S. Chauvin, F. Gumy, D. Imbert, J.-C. G. Bünzli, *Spectrosc. Lett.* 2004, **37**, 517. (b) A. J. Steckl, M. Garter, D. S. Lee, J. Heikenfeld and R. Birkhahn, *Appl. Phys. Lett.*, 1999, **75**, 2184.
- J. H. Kim and P. H. Holloway, *Adv. Mater.*, 2005, **17**, 91.

Journal Name

40. A. Bednarkiewicz, D. Wawrzynczyk, M. Nyk, W. Strek, *Opt. Mater.*, **33**, 1481.
41. K. Lunstroot, L. Baeten, P. Nockemann, J. Martens, P. Verlooy, X. Ye, C. G.-Walrand, K. Binnemans, and K. Driesen, *J. Phys. Chem. C*, 2009, **113**, 13532.
42. S. Moeller, A. Hoffmann, D. Knaut, J. Flottmann, T. Juestel, *J. Lumin.* 2015, **158**, 365.
43. B. M. Brewer and M. Nicol, *J. Lumin.*, **23**, 269.
44. H. Dong, L.-D. Sun and C.-H. Yan, *Chem. Soc. Rev.*, 2015, **44**, 1608
45. P. Samuel, T. Yanagitani, H. Yagi, H. Nakao, K. I. Ueda, S. M. Babu, *J. Alloys Compd.* 2010, **507**, 475.
46. F. N. Sayed, V. Grover, S. V. Godbole and A. K. Tyagi, *RSC Advances*, 2012, **2**, 1161.
47. Q. Xiao, Q. Zhou, M. Li, *J. Lumin.*, 2010, **130**, 1092.
48. J. L. Ferrari, K. de O. Lima, E. Pecoraro, R. A. S. Ferreira, L. D. Carlos and R. R. Goncalves, *J. Mater. Chem.*, 2012, **22**, 9901.
49. Pierre Villars, Material Phases Data System (MPDS), CH-6354 Vitznau, Switzerland; SpringerMaterials; sd_1622044 (Springer-Verlag GmbH, Heidelberg, 2014), http://materials.springer.com/isp/crystallographic/docs/sd_1622044; accessed: 13-06-2015.
50. M. Pedroni, F. Piccinelli, T. Passuello, S. Polizzi, J. Ueda, P. Haro-González, L. Martínez Maestro, D. Jaque, J. García-Solé, M. Bettinelli, and A. Speghini, *Cryst. Growth Des.* 2013, **13**, 4906.
51. (a) K. Lunstroot, P. Nockemann, K. Van Hecke, L. Van Meervelt, C. Görrler-Walrand, K. Binnemans and K. Driesen, *Inorg. Chem.*, 2009, **48**, 3018. (b) H. F. Brito, O. L. Malta, M. C. F. C. Felinto, E. E. S. Teotonio, J. F. S. Menezes, C. F. B. Silva, C. S. Tomiyama and C. A. A. Carvalho, *J. Alloys Compd.*, 2002, **344**, 293.
52. L. Sun, Y. Qiu, T. Liu, H. Peng, W. Deng, Z. Wang and L. Shi, *RSC Adv.*, 2013, **3**, 26367.
53. R. L. Nigro, G. Malandrino, I. L. Fragala, M. Bettinelli and A. Speghini, *J. Mater. Chem.*, 2002, **12**, 2816.