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## Europium-doped LaF<sub>3</sub> nanocrystals with organic 9-oxidophenalenone capping ligands that display visible light excitable steady-state blue and time-delayed red emission†

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Visible light excitable and color tunable ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> nanocrystals (NCs), containing 9-oxidophenalenone ligands bound to the surface as visible light sensitizers for Eu<sup>3+</sup> dopants, have been synthesized by a facile solution-based method. The crystalline phase structure, size, composition, morphology and luminescence properties of the NCs are characterized using X-ray diffraction, high-resolution transmission electron microscopy, energy dispersive X-ray spectroscopy, and steady-state and time-resolved emission spectroscopy. The results show that these NCs are very small in size (<10 nm), display high degree of crystallinity and have pure tysonite structure of LaF<sub>3</sub> with  $P\bar{3}c1$  space group. The visible light excitation of the capping ligands triggers an alternate display of steady-state, short-lived blue emission ( $\tau < 1$  ns) and time-delayed, long-lived sensitized red Eu<sup>3+</sup> emission ( $\tau = 0.41$  ms), allowing photoluminescence chromacity tuning as a function of delay time within a specific inorganic composition. The visible light sensitization of the dopant Eu<sup>3+</sup> sites proves more efficient than direct excitation of 5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs capped by citrate ligands. The dopant Eu<sup>3+</sup> ions are well protected from non-radiative deactivation through high-energy vibrations of the organic capping ligands which is proved by the long lifetime of the sensitized Eu<sup>3+</sup> emission. The time-resolved emission spectra collected over a period of several milliseconds reveal that the dopant Eu<sup>3+</sup> ions occupy at least three different sites in the NC host. It is further inferred that the sensitized Eu<sup>3+</sup> emission primarily comes from surface dopant sites and sites just underneath the surface of the NCs. We propose that some of the interior Eu<sup>3+</sup> sites also display sensitized emission, which are indirectly populated via Eu<sup>3+</sup> → Eu<sup>3+</sup> energy migration from surface-sensitized Eu<sup>3+</sup> sites of the NCs.

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## Introduction

Luminescent europium-based materials have received considerable attention over the past several decades for applications in optoelectronic devices,<sup>1</sup> sensors,<sup>2</sup> spectral converters for solar cells,<sup>3</sup> biological imaging<sup>4</sup> etc. These materials mostly display sharp emission bands of Eu<sup>3+</sup> that correspond

to f-f transitions and are known to exhibit pure red emission with long lifetimes (micro- to milliseconds).<sup>5</sup> The long emission lifetimes of these materials are especially advantageous for biological imaging because the emission can be easily separated from short-lived fluorescence of the background and biological samples by time-resolved imaging.<sup>6</sup> However, lanthanide (Ln<sup>3+</sup>) ions in general are characterized by very low absorption coefficients ( $\epsilon \leq 1 \text{ M}^{-1} \text{ cm}^{-1}$ ) due to the Laporte-forbidden nature of f-f transitions which makes the photoluminescence (PL) process by direct excitation very inefficient. To overcome this limitation, organic ligands containing suitable chromophores with very high absorption coefficients ( $\epsilon \approx 10^4\text{--}10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) are attached to the metal ion which can then act as sensitizers for efficient Eu<sup>3+</sup> luminescence.<sup>7</sup> However, Eu<sup>3+</sup> luminescence due to sensitization by organic ligands is susceptible to quenching when the ion is in close proximity to the energy matched -OH, -CH and -NH oscillators present in the sensitizing ligand and/or solvent.<sup>8</sup> Sensi-

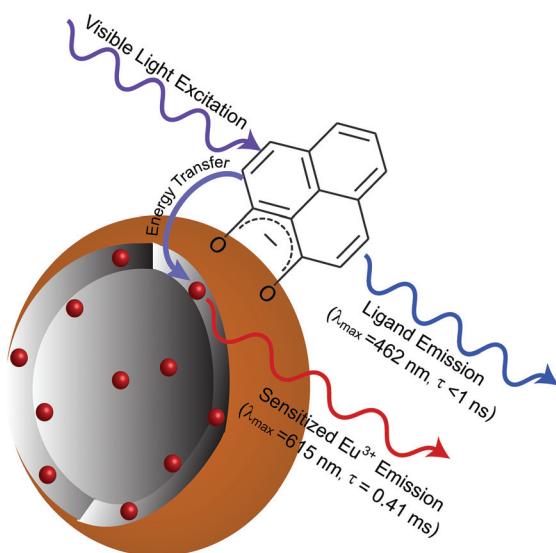
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† Electronic supplementary information (ESI) available: Powder X-ray diffraction (XRD), transmission electron microscopy (TEM) images and TEM size analysis of citrate capped 5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs. Characterization data (HRMS and <sup>1</sup>H NMR) of 9-hydroxyphenalenone ligand. TEM size analysis, <sup>1</sup>H NMR in DMSO-d<sub>6</sub> and time-delayed emission spectrum of a solid sample of 9-oxidophenalenone capped ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs. The comparative absorption and emission spectra of 9-hydroxyphenalenone and 9-oxidophenalenone capped ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs in THF. See DOI: 10.1039/c4dt03249g

tized luminescence from  $\text{Eu}^{3+}$  ions can also be obtained by doping into semiconductor nanocrystals (NCs).<sup>9</sup> However, through this approach, the dopant  $\text{Eu}^{3+}$  ions are not always sensitized with the efficiency of organic sensitizers. The mismatch in the size of cations of semiconductor NC and dopant  $\text{Eu}^{3+}$  ions results in a partial energy transfer from the host to  $\text{Eu}^{3+}$  ions, and often mixed emission from the host NC and  $\text{Eu}^{3+}$  dopants is observed.

A new strategy to boost the luminescence efficiency of dopant  $\text{Ln}^{3+}$  ions inside NC hosts was recently introduced by Petoud and co-workers wherein organic chromophore (tropolonate) ligands were bound to the surface of  $\text{NaYF}_4$  NCs doped with  $\text{Nd}^{3+}$  or  $\text{Yb}^{3+}$  ions that display more efficient near-infrared emission than  $\text{KLn}[(\text{tropolonate})]$  chelate.<sup>10a</sup> In this approach, the NC host protects the dopant ions from external quenchers, and the surface ligands sensitize the dopants. Further, Ballato and co-workers showed that when 3,4-(formylphenyl)benzoic acid is used as a capping ligand to  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  nanoparticles, both ligand and sensitized  $\text{Eu}^{3+}$  emissions are observed and the balance between the two can be tuned by the excitation energy.<sup>10b</sup> In a few recent reports, this strategy of surface sensitization of lanthanide-doped NCs by organic capping ligands was used to obtain ultraviolet (UV) wavelength excitable enhanced  $\text{Eu}^{3+}$  luminescence as compared to direct excitation.<sup>11,12</sup> The UV excitation of these NCs restricts their use in bio-imaging and energy-efficient  $\text{Eu}^{3+}$ -based optoelectronic devices.<sup>13</sup> Further, prolonged exposure to the UV light can potentially make them photochemically unstable.<sup>14</sup> Recent synthetic efforts have produced many novel visible light excitable luminescent europium complexes.<sup>13,15</sup> However, it is important to develop  $\text{Eu}^{3+}$ -doped NCs containing surfaces capped organic ligands which are capable of providing visible light sensitization to the dopant ions inside the NC matrix.  $\text{LaF}_3$  is an ideal host for luminescent  $\text{Ln}^{3+}$  ions due to its size compatibility with the  $\text{La}^{3+}$  ion.<sup>16</sup> The fluoride lattices allow high coordination number for the dopant  $\text{Ln}^{3+}$  ions and high ionicity of the  $\text{Ln}^{3+}$  to fluorine bond which leads to a wide bandgap and low vibrational energies ( $<350 \text{ cm}^{-1}$ ).<sup>17</sup> The very low vibrational energy of the host is advantageous because it protects the dopant ions from sources of non-radiative deactivation. In contrast however, the wide bandgap of the host is disadvantageous since it does not sensitize the dopant  $\text{Ln}^{3+}$  ions.

In this work, we report the facile synthesis of ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs that contain 9-oxidophenalenone (the anion of 9-hydroxyphenalenone) ligands attached to the surface. 9-Oxidophenalenone was selected as a surface capping ligand since it has previously been reported to be a visible light sensitizer for  $\text{Eu}^{3+}$  when it is coordinated with the ion.<sup>18</sup> However, 9-oxidophenalenone is a highly fluorescent ligand and displays strong blue emission (see ESIT). When it is attached to the surface of ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs, a partial energy transfer occurs from higher energy excited states of the ligands to the  ${}^5\text{D}_0$  emitting states of doped  $\text{Eu}^{3+}$  sites in the  $\text{LaF}_3$  host. Due to this, the blue emission component of the capping ligands is not fully quenched and still dominates over the sensitized



**Fig. 1** A schematic representation of the 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs. The 9-oxidophenalenone capping ligand upon visible light excitation partially transfers energy to the doped  $\text{Eu}^{3+}$  sites on the surface of the NC and the resulting sensitized red emission can only be observed with time delay due to its long lifetime. The rest of the excitation energy is leaked in the form of short-lived steady-state blue fluorescence by the ligand itself.  $\text{Eu}^{3+} \rightarrow \text{Eu}^{3+}$  energy migration is also probably happening from doped sites on the surface to the interior  $\text{Eu}^{3+}$  sites in the NCs.

emission from  $\text{Eu}^{3+}$  sites. Further, only sensitized red emission from  $\text{Eu}^{3+}$  sites of the NCs is observed when the emission is collected with a time delay due to the very short lifetime of the ligand fluorescence and the long lifetime of the  $\text{Eu}^{3+}$  emission. This results in a color tunable nanomaterial that displays steady-state blue ligand dominating emission and time-delayed red europium emission, sensitized using visible light (Fig. 1). Such color tunable materials are of considerable interest and can be used in optoelectronic devices to define or modify environments, moods and brands.<sup>10b,19</sup> The PL properties of the NCs are compared with similar 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs capped by citrate ligands (non-sensitizing ligands for  $\text{Eu}^{3+}$  dopants), to demonstrate the effect of visible light sensitization of  $\text{Eu}^{3+}$  dopants by surface-capping 9-oxidophenalenone ligands as compared to direct UV excitation. Moreover, we report time-resolved emission spectroscopy of the NCs to demonstrate that 9-oxidophenalenone capping ligands act as probes and reveal three different coordination environments around doped  $\text{Eu}^{3+}$  sites on the surface and in the interior of the  $\text{LaF}_3$  host. We propose a possible  $\text{Eu}^{3+} \rightarrow \text{Eu}^{3+}$  energy migration from the sensitized  $\text{Eu}^{3+}$  sites on the surface to the  $\text{Eu}^{3+}$  sites in the interior of the NC host.

## Experimental section

### Materials

All the chemicals and solvents used in this study were used as received.  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 99.0\%$ ),  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.9%),

NaF (99.99%), NaOH ( $\geq$ 97.0%), citric acid, 2-methoxynaphthalene, cinnamoyl chloride and 1,2-dichloroethane were purchased from Sigma-Aldrich. Electronic grade methanol was purchased from Spectrochem while all other solvents were purchased from Sigma-Aldrich. The 9-hydroxyphenalenone ligand was synthesized by a published procedure,<sup>20</sup> and fully characterized before use (see ESI†).

### Synthesis of 9-oxidophenalenone-capped ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs

In a typical experimental procedure, 9-oxidophenalenone-capped ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs were prepared as follows. The capping ligand 9-hydroxyphenalenone (0.196 g, 1.0 mmol) was dissolved in 150 mL methanol and neutralized with equivalent amount of NaOH at 70 °C under stirring. The pH of the solution was kept just below 7. NaF (0.1 g, 2.38 mmol) dissolved in 20 mL 1 : 1 methanol–water mixture was added dropwise to the above solution under stirring while maintaining at 70 °C. After 15 minutes, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.32 g, 0.74 mmol) and Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (17 mg, 0.04 mmol) dissolved in 10 mL methanol were also added dropwise to the above solution. The reaction mixture was refluxed with constant stirring at 70 °C for 6 hours and then allowed to cool. The dark yellow precipitates were recovered by centrifugation. The precipitates were further washed with excess Milli-Q water and then with methanol to remove any unreacted metal salt and dried in a vacuum oven. The product was finally washed several times with excess dichloromethane until no dark yellow color appeared in the solvent due to unbound capping ligand.

### Synthesis of citrate-capped 5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs

The citrate-capped 5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> nanoparticles were synthesized according to the procedure reported in the literature.<sup>11b</sup> The capping ligand citric acid (2.0 g, 10.4 mmol) was dissolved in 35 mL of Milli-Q water and partially neutralized with  $\sim$ 2 mL of 30% NH<sub>4</sub>OH, until the pH reached 5.8. The solution was heated in a water bath under stirring to a temperature of 75 °C. La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.55 g, 1.3 mmol) and Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.027 g, 0.061 mmol) dissolved in 2 mL of methanol were added dropwise to the above solution under stirring while maintaining at 75 °C. This was followed by the addition of NaF (0.18 g, 4.3 mmol) dissolved in 2 mL Milli-Q water to the above reaction mixture under stirring at 75 °C, which results in initial clouding but clears in a few seconds. The resulting clear reaction mixture was stirred continuously for 3 h at 75 °C and allowed to cool to room temperature. The addition of 50 mL absolute ethanol resulted in the precipitation of the NCs which were recovered from the suspension by centrifugation. The white precipitates were washed thoroughly with excess absolute ethanol and dried in a vacuum oven.

### Sample characterization

Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy of the NCs were performed with a Philips CM200 microscope with operating voltages of 20–200 kV

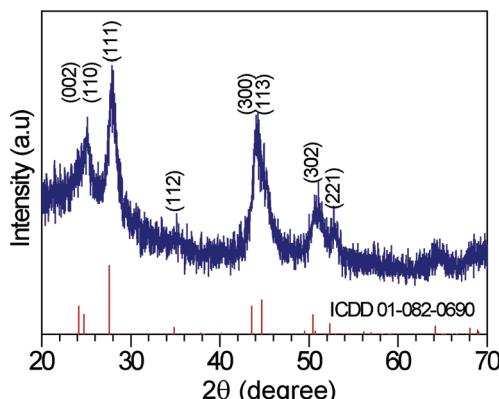
and a resolution of 2.4 Å. Each sample was prepared by drop-casting NCs dispersed in tetrahydrofuran (THF) onto a carbon-coated copper grid and the solvent was immediately dried using an IR lamp. X-ray diffraction (XRD) patterns of the NCs were recorded using a Philips PW3040/60 powder diffractometer with Cu Kα (0.15406 nm) radiation. The average size (diameter) of the NCs was calculated from the broadening of the diffraction peaks by using the Debye–Scherrer formula,  $D = k\lambda/\beta \cos \theta$ , where  $D$  is the average size of the particles,  $k$  is the Scherrer constant (0.89),  $\lambda$  is the wavelength of the X-ray source (0.15406 nm),  $\beta$  is the full width of the peak at half maximum in radians and  $\theta$  is the position of the maximum of the diffraction peak. UV-visible absorption spectra were recorded at room temperature with a JASCO V 530 spectrophotometer, using standard quartz cuvettes of 1 cm pathlength. Steady-state emission and excitation spectra were recorded at room temperature with a Varian Cary Eclipse spectrofluorimeter, using standard quartz fluorescence cuvettes of 1 × 1 cm pathlength. Time-delayed excitation and emission spectra of the NCs were recorded in phosphorescence mode with the Varian Cary Eclipse spectrofluorimeter. These spectra were acquired with a delay time of 0.1 ms and a gate time of 5 ms; the emission and excitation slits were set to 10 nm. The samples of dried (solid) NCs for emission and excitation measurements were prepared from NC powder, deposited between two quartz plates, which were then placed in front of the excitation path of the spectrofluorimeter, such that the emission was collected at an angle of approximately 45 degrees. The Commission International de l'Eclairage (CIE) color coordinates were calculated in MATLAB by following the international CIE standards.<sup>21</sup> The lifetimes of ligand fluorescence were obtained from a picosecond pulsed diode laser-based time-correlated single photon counting (TCSPC) instrument (IBH, United Kingdom) with  $\lambda_{ex} = 406$  nm. The time-resolved (Eu<sup>3+</sup>) emission spectra were collected from dried (solid) NC samples by exciting the ligand absorption band at 457 nm, with various time delays varying between 0.1 and 5.0 ms and a fixed 5.0 ms gate time, using a Varian Cary Eclipse spectrofluorimeter. The decay curve was obtained by plotting delay times vs. intensity of the  $^5D_0 \rightarrow ^7F_2$  emission transition, which was best fit to a tri-exponential function to obtain ( $\tau_1$ ,  $\tau_2$  and  $\tau_3$ ) and the relative amplitudes ( $A_1$ ,  $A_2$  and  $A_3$ ). The average lifetime ( $\tau_{avg}$ ) was obtained by using the formula:

$$\tau_{avg} = (\tau_1 \times A_1 + \tau_2 \times A_2 + \tau_3 \times A_3)/(A_1 + A_2 + A_3)$$

## Results and discussion

### Synthesis and characterization

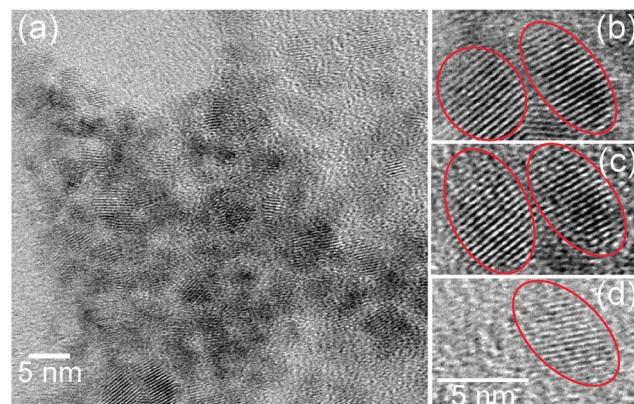
A facile solution-based method to prepare ~5% Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs containing surface-capping 9-oxidophenalenone ligands was optimized on the basis of an earlier report on the synthesis of Eu<sup>3+</sup>-doped LaF<sub>3</sub> NCs containing 3,4-(formyl-phenyl)benzoic acid capping ligands.<sup>10b</sup> The synthesis was carried out using methanol as solvent. However, due to the



**Fig. 2** Powder XRD diffractogram of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs shown along with the crystallographic pattern of pure  $\text{LaF}_3$  tysonite (ICDD code: 01-082-0690).

negligible solubility of  $\text{NaF}$  in methanol, it was dissolved in 1 : 1 methanol-water mixture. The dark yellow NCs precipitated without the aid of any precipitating agent. These NCs are not dispersible in common organic solvents like chloroform, hexane and dichloromethane, and are sparingly dispersible in highly polar solvents like DMSO and THF. The phase structure of 9-oxidophenalenone-capped NCs was investigated by XRD. Fig. 2 shows the powder XRD pattern of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs along with the International Centre for Diffraction Data (ICDD) powder diffraction file for  $\text{LaF}_3$  (01-082-0690). The positions of the diffraction peaks of the sample can be easily indexed to the pure tysonite structure of  $\text{LaF}_3$  with  $P\bar{3}c1$  space group which indicates that the prepared sample is single crystalline with no impurity phases. The diffraction peaks of the sample are significantly broad which further indicates the very small size of the NCs. The position and broadening of the diffraction peaks of the sample are comparable with those of the powder XRD patterns of ultrasmall  $\text{Ln}^{3+}$ -doped  $\text{LaF}_3$  NCs reported in the literature.<sup>11b,d,16b</sup> A Scherrer analysis of best fit data obtained by a Gaussian distribution of the diffraction peak of NCs at  $2\theta = 44.42^\circ$  gave an average value of particle size of  $D = 4.53 \pm 0.4$  nm. We note that there are very few reports of  $\text{Ln}^{3+}$ -doped  $\text{LaF}_3$  NCs with a size less than 10 nm, and this size regime is very advantageous for achieving real nanosize-based biological applications.<sup>11b,d,16b,22</sup> The powder XRD pattern of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs synthesized in this work is also easily indexed to pure  $\text{LaF}_3$  tysonite structure (see ESI†).

Fig. 3 shows high-resolution TEM (HR-TEM) images of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs. The HR-TEM measurements were carried out to study the size and morphology of the NCs. From the HR-TEM image (Fig. 3a) it can be seen that these NCs show some degree of agglomeration and a diffuse cloud around the primary particles. This could be due to poor dispersibility of the NCs in THF and large amounts of strongly capped 9-oxidophenalenone stabilizing and sensitizing ligands around the small sized particles.<sup>17a</sup> High-magnification TEM images (Fig. 3b-d) show that NCs are

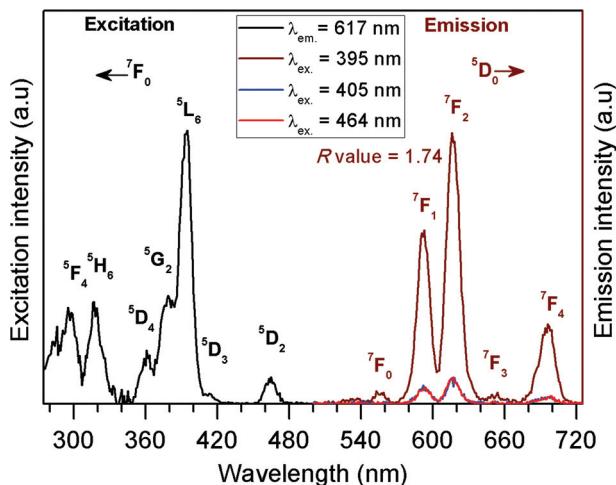


**Fig. 3** (a) High-resolution TEM image of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs taken from a randomly selected area of the sample. The higher magnification TEM images of representative individually discernible NCs are highlighted in (b), (c) and (d). Images (b) and (c) have the same scale bar as shown for (d).

slightly ellipsoid as opposed to spherical shape. The HR-TEM size measurements from 30 discernible NCs taken at random locations from a single sample preparation show that the NC size (diameter) varies from 2.6 nm (smallest NC) to 6.9 nm (largest NC) with an average size of  $4.43 \pm 1.2$  nm, strikingly in very good agreement with the estimated size obtained from the Scherrer analysis. On the contrary, the TEM images of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs synthesized in this work give an average size of  $30.7 \pm 12.7$  nm (see ESI†). These NCs also cluster into larger agglomerates similar to  $\text{Ln}^{3+}$ -doped  $\text{LaF}_3$  NCs reported in the literature.<sup>16b</sup> The HR-TEM images of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs display very high degree of crystallinity as is evident from the clear and well-grown lattice fringes, in agreement with the XRD pattern. The EDX analysis of the 9-oxidophenalenone-capped NCs shows 4.53% (atomic percentage) content of the doped  $\text{Eu}^{3+}$  ions which is very close to the initial 5% europium used in the reaction. The binding of organic 9-oxidophenalenone capping ligands to the surface of  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs was monitored through  $^1\text{H}$  NMR spectroscopy.<sup>23</sup> The  $^1\text{H}$  NMR resonances observed are easily assigned to the protons of the 9-oxidophenalenone ligands bound to the surface of the NCs, which are weak because of poor dispersibility in DMSO and slightly broadened as compared to very sharp resonances observed for the free ligand (see ESI†). The broadening of the resonances is attributed to the inhomogeneous distribution of the magnetic environment around the NC and decrease in the rotational freedom of the capping ligand.<sup>24</sup> Further, a sharp resonance observed due to OH protons in the  $^1\text{H}$  NMR spectrum of free 9-hydroxyphenalenone ligand is absent in the spectrum of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs.

### Photoluminescence properties

**Photoluminescence by direct excitation.** We first present steady-state PL properties of citrate-capped 5%  $\text{Eu}^{3+}$ -doped

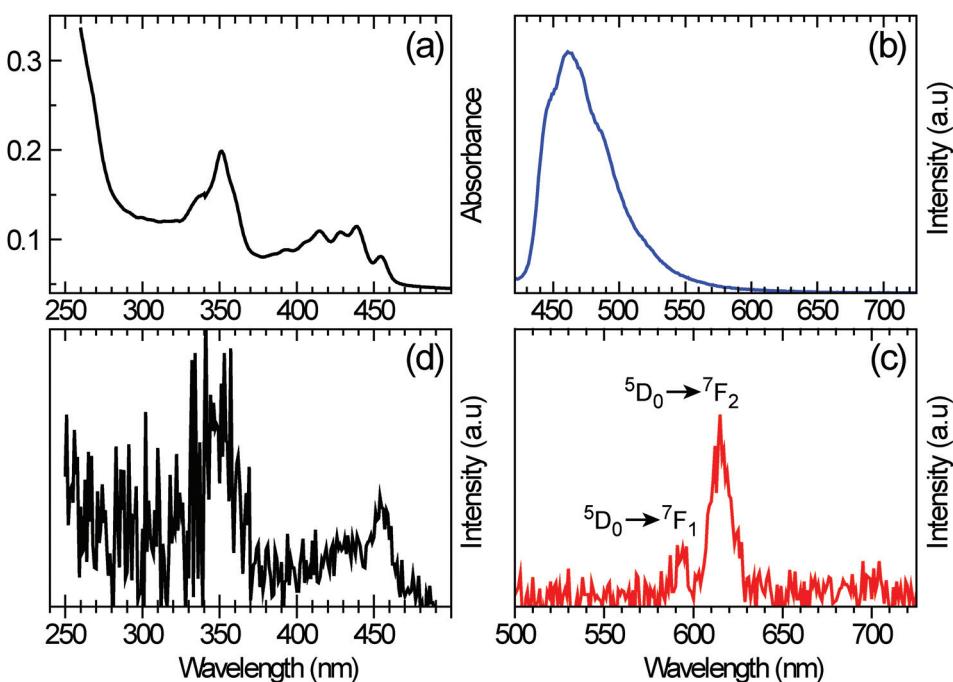


**Fig. 4** Excitation spectrum and emission spectra with different excitation wavelengths, of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs recorded from a sample dispersed in water, at room temperature. The excitation spectrum was recorded by monitoring the most intense emission peak of the NCs at 617 nm. The excitation and emission of the NCs originate from  ${}^7\text{F}_0$  and  ${}^5\text{D}_0$  ground and excited states of  $\text{Eu}^{3+}$  dopants, respectively.

$\text{LaF}_3$  NCs which were synthesized in this work and compare them with the 9-oxidophenalenone-capped NCs later. The PL properties of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs can only be investigated by directly exciting  $\text{Eu}^{3+}$  dopants since neither citrate capping ligands nor the  $\text{LaF}_3$  host is capable of providing sensitization to these dopant ions.<sup>11b,25</sup> Fig. 4 shows room temperature excitation spectrum and emission spectra acquired at different wavelengths, of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs dispersed in water. These NCs display typical  $\text{Eu}^{3+}$  emission transitions in the 500–725 nm range which are assigned to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  (555 nm);  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (592 nm);  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (617 nm);  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  (653 nm); and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (696 nm) transitions of  $\text{Eu}^{3+}$  ion. The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition which is electric dipole in nature is most intense followed by the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition which is magnetic dipole in nature. The excitation spectrum was obtained by monitoring the most intense  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (617 nm) emission line of the NCs, which displays various peaks in the 270–500 nm range, assigned to  ${}^5\text{F}_4 \leftarrow {}^7\text{F}_0$  (295 nm),  ${}^5\text{H}_6 \leftarrow {}^7\text{F}_0$  (317 nm),  ${}^5\text{D}_4 \leftarrow {}^7\text{F}_0$  (361 nm),  ${}^5\text{G}_2 \leftarrow {}^7\text{F}_0$  (379 nm),  ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$  (395 nm),  ${}^5\text{D}_3 \leftarrow {}^7\text{F}_0$  (413 nm) and  ${}^5\text{D}_2 \leftarrow {}^7\text{F}_0$  (464 nm) 4f–4f transitions of  $\text{Eu}^{3+}$ .<sup>26</sup> The appearance of only 4f–4f transitions of  $\text{Eu}^{3+}$  in the excitation spectrum proves that doped  $\text{Eu}^{3+}$  sites of the NCs are directly excited and there is no sensitization from the host. The emission obtained by exciting the lower energy  ${}^5\text{D}_2$  level (464 nm) of the  $\text{Eu}^{3+}$  ions is ~10 times weaker in intensity than the emission obtained by exciting the higher energy  ${}^5\text{L}_6$  level (395 nm). A similar less intense emission is also observed by exciting the tail (405 nm) of  ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$  transition. From the emission spectra of  $\text{Eu}^{3+}$ -based materials, the ratio of the integrated emission intensity of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition to the integrated emission intensity of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition is known as the asymmetric ratio,  $R$ .<sup>25,27</sup> The

geometrical environments (or symmetry) experienced by doped  $\text{Eu}^{3+}$  sites in nanostructures can be probed by evaluating the  $R$  values: higher  $R$  value is an indication of higher asymmetry around the  $\text{Eu}^{3+}$  site in a host lattice.<sup>11b,25,28</sup> This is due to the fact that the electric dipole  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is very sensitive to the local environment around the  $\text{Eu}^{3+}$  ion compared to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  magnetic dipole transition, which is not much affected by the local environment around the ion.<sup>29</sup> The value of  $R$  obtained from the emission spectra of citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs is 1.74, close to the  $R$  values reported in the literature for similar citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs.<sup>11b,25</sup> A slightly higher  $R$  value reported in this work can be related to the change in NC size.<sup>11b,25</sup>

**Photoluminescence by sensitization and tuning of emission color.** Fig. 5a shows the absorption spectrum of a very dilute dispersion of 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs in THF. The spectrum displays two strong absorption bands, one in the UV region ( $\lambda_{\max}^{\text{ab}} = 351$  nm) and the other in the visible region ( $\lambda_{\max}^{\text{ab}} = 414, 428, 438$  and 457 nm) which are assigned to the  $\pi-\pi^*$  transitions of the ligand. These absorption bands compare well with the absorption bands observed for 9-hydroxyphenalenone ligand.<sup>20</sup> However, the visible absorption band of the 9-oxidophenalenone-capped NCs shows a bathochromic shift of ~15 nm as compared to the band observed for free ligand, which is an indication of a strong interaction between the capping ligands and the NC surface (see ESI†).<sup>15d</sup> The f-f absorption bands of the  $\text{Eu}^{3+}$  ion are not detected in the spectrum because they have very weak absorption coefficients as compared to that of the organic chromophore. The THF-dispersed NCs upon excitation of the visible absorption band display a strong emission in the range 420–600 nm with a maximum at 462 nm (Fig. 5b). We assign this emission to strong fluorescence from the capping ligands of the NCs since a similar fluorescence band can also be observed upon excitation of the 9-hydroxyphenalenone ligand (see ESI†). The lifetime of this fluorescence is very short ( $\tau < 1$  ns), almost identical to the lifetime observed for 9-hydroxyphenalenone fluorescence. Despite 9-oxidophenalenone being a known visible light sensitizer of the  $\text{Eu}^{3+}$  emission,<sup>18</sup> the characteristic emission from doped  $\text{Eu}^{3+}$  sites in the NCs could not be detected in the steady-state spectrum. This is due to the fact that  $\text{Eu}^{3+}$  dopant emission intensity is negligible as compared to the fluorescence intensity of the 9-oxidophenalenone ligands attached to the surface of the NCs. Strikingly, when the emission is collected with 0.1 ms time delay (Fig. 5c), the 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NC dispersions in THF, upon excitation at 457 nm, exhibit only characteristic sensitized  $\text{Eu}^{3+}$  emission transitions. The observation of sensitized  $\text{Eu}^{3+}$  emission after a time delay is possible due to its long lifetime which can be easily separated from the short-lived ligand emission by time resolution.<sup>6</sup> The sensitization of  $\text{Eu}^{3+}$  emission of the NCs dispersed in THF by 9-oxidophenalenone capping ligands is confirmed by the excitation spectrum (Fig. 5d), which was obtained by monitoring the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  line (at 615 nm) of the  $\text{Eu}^{3+}$  emission. This excitation spectrum is clearly different from that recorded for

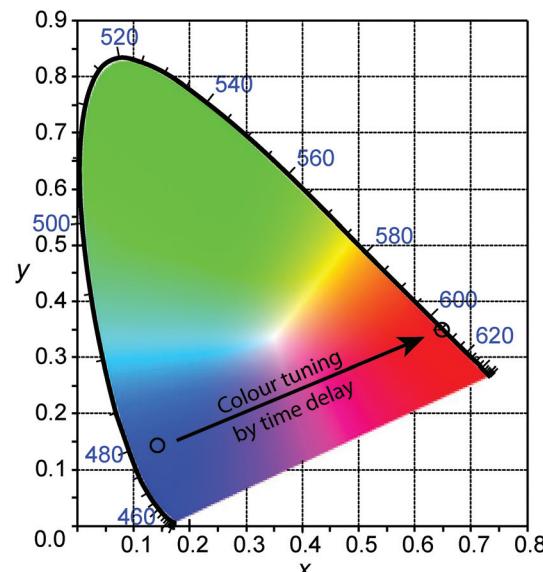


**Fig. 5** (a) Absorption and (b) emission spectra of 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs dispersed in THF; (c) emission and (d) excitation spectra of the same NC sample, recorded with a time delay of 0.1 ms (phosphorescence mode). The time-delayed excitation spectrum was recorded by monitoring the intense time-delayed emission spectrum peak of the NCs at 615 nm.

citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs dispersed in water (Fig. 4). Further, the excitation spectrum of 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs dispersed in THF clearly matches with the absorption spectrum (Fig. 5a) and no f-f transitions of  $\text{Eu}^{3+}$  are observed which demonstrates that energy transfer takes place from the capping ligands to the doped  $\text{Eu}^{3+}$  sites of the NCs.<sup>10–12</sup> The sensitized  $\text{Eu}^{3+}$  emission was also observed from a dried (solid) sample of 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs upon excitation at 457 nm, which clearly displays all the characteristic peaks assigned to  ${}^5D_0 \rightarrow {}^7F_j$  ( $j = 1\text{--}4$ ) transitions of  $\text{Eu}^{3+}$  (see ESI†).

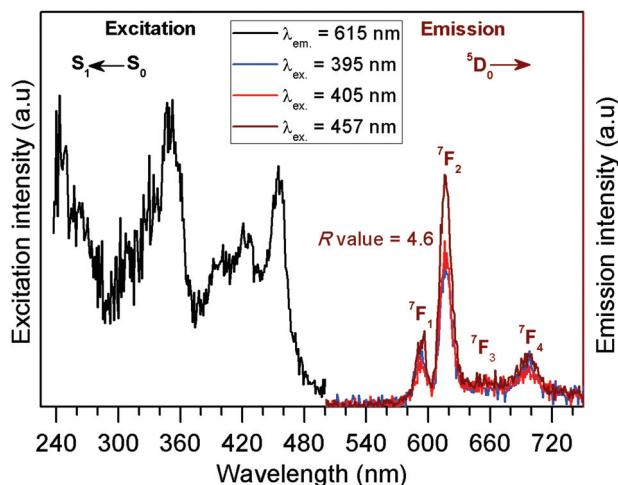
The PL spectra of the 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs resulting from the steady-state emission of the surface capping ligands and sensitized time-delayed emission from doped  $\text{Eu}^{3+}$  ions were converted into the CIE 1931 color coordinate system as shown in Fig. 6. The fluorescence from the surface capping ligands generates blue emission with CIE coordinates of  $x = 0.14$ ,  $y = 0.14$  while the time-delayed sensitized emission from the doped  $\text{Eu}^{3+}$  sites generates red emission with CIE coordinates of  $x = 0.65$ ,  $y = 0.34$ . Therefore, the 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs display novel emission color tunability from blue to red by a time-delay technique. Such behavior of tuning of emission color within a specific inorganic material including lanthanide-based materials has been rarely observed in the literature.<sup>10b,19,30</sup>

Further photophysical studies of the 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs were carried out on a dried (solid) sample since they are poorly dispersible even in strongly polar solvents resulting in weak time-delayed  $\text{Eu}^{3+}$



**Fig. 6** The two different emission spectra obtained from 9-oxidophenalenone-capped ~5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs (Fig. 4b and S9†), plotted on a CIE diagram showing blue to red color tuning by time delay.

emission. Fig. 7 shows the time-delayed excitation and emission spectra of the NCs obtained from a dried (solid) sample, which displays variation in the emission intensity upon change in the excitation wavelength. We find that the most intense emission is obtained upon excitation at the higher wavelength edge (457 nm) of the excitation band of these NCs that corresponds to the  $S_1 \leftarrow S_0$  transition of the 9-oxidophenalen-



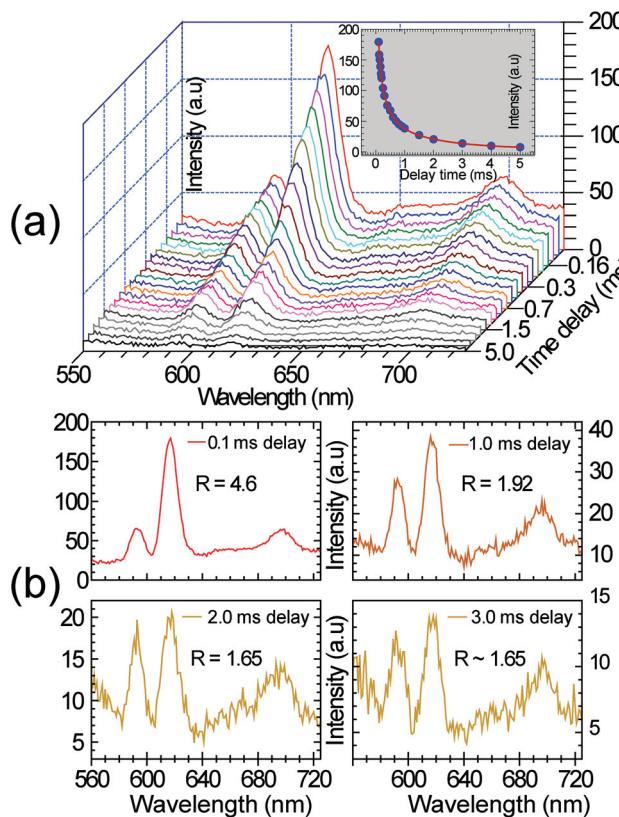
**Fig. 7** Time-delayed excitation spectrum and emission spectra with different excitation wavelengths, of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs recorded from a dried (solid) sample, at room temperature. The excitation spectrum was recorded by monitoring the most intense time-delayed emission spectrum peak of the NCs at 615 nm. The excitation spectrum originates from the ground singlet state ( $S_0$ ) of the capping ligands and emission spectra of the NCs originate from  ${}^5\text{D}_0$  excited states of  $\text{Eu}^{3+}$  dopants. The spectra were acquired with a fixed delay time of 0.1 ms and gate time of 5 ms.

enone capping ligand. This is contrary to the 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs capped by citrate ligands (non-sensitizing ligands) in which the most intense emission is obtained upon direct excitation of the  ${}^5\text{L}_6$  (395 nm) energy level of the  $\text{Eu}^{3+}$  ions. However, it is noteworthy that the emission obtained from 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs upon excitation at 395 nm is also due to the effect of sensitization by capping ligands. This is due to the fact that the higher wavelength absorption/excitation bands of these NCs encompass the absorption region of the  ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$  transition (395 nm) of  $\text{Eu}^{3+}$ . This is further verified by 405 nm excitation of these NCs which shows similar intensity to that of 395 nm excitation, contrary to the results obtained from the citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs (Fig. 4), and clearly demonstrates that the visible light sensitization of dopant  $\text{Eu}^{3+}$  sites is more effective as compared to the direct excitation of the energy levels. The excitation spectrum obtained from a dried (solid) sample of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs also confirms sensitization by capping ligands.

The time-delayed emission spectra of the 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs display a significantly higher  $R$  value of 4.6, as compared to the  $R$  value obtained from the citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs (1.74). A change in the  $R$  value is consistent with the observations reported in the literature that  $R$  values of the 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs depend on the nature of the stabilizing (capping) ligand.<sup>25</sup> We note that the capping ligands only affect the asymmetry of the  $\text{Eu}^{3+}$  sites on the surface of the NCs while asymmetry of the  $\text{Eu}^{3+}$  sites in the interior of the NCs remains unaffected by the nature of the capping ligand.<sup>11b,25</sup> The 9-oxidophenalenone surface capping ligands possibly sensitize only

surface or near-to-surface doped  $\text{Eu}^{3+}$  sites of the NCs since the rate of energy transfer in lanthanides is known to depend on the distance between the donor and the acceptor.<sup>31</sup> This implies that emission in these NCs occurs mostly from the surface doped  $\text{Eu}^{3+}$  sites which experience higher asymmetry due to coordination with the 9-oxidophenalenone ligands. The higher  $R$  value obtained from the surface sensitized NCs as compared to directly excited NCs in this work is consistent with similar results reported recently on surface sensitized  $\text{Eu}^{3+}$ -doped NCs.<sup>11b,e</sup> On the contrary, upon direct excitation, the emitting levels of all the  $\text{Eu}^{3+}$  sites (surface and interior) are populated in citrate-capped NCs, and smaller  $R$  value is thus an average value of more asymmetric surface and less asymmetric interior  $\text{Eu}^{3+}$  sites of the NCs.

**Time-resolved emission spectroscopy.** The steady-state and time-delayed emission studies discussed in the previous sections suggest that only surface doped  $\text{Eu}^{3+}$  sites are sensitized by 9-oxidophenalenone capping ligands. However, there is a possibility that  $\text{Eu}^{3+}$  sites close to the surface are also sensitized by the capping ligands.<sup>11b</sup> The interior  $\text{Eu}^{3+}$  sites can also display emission if there is significant  $\text{Eu}^{3+} \rightarrow \text{Eu}^{3+}$  energy migration from the surface sensitized  $\text{Eu}^{3+}$  sites to the interior sites.<sup>11c,32</sup> The above possibilities can be investigated by time-resolved emission spectroscopy wherein  $\text{Eu}^{3+}$  emission spectra of the NCs are collected temporally over a period of several milliseconds by taking advantage of the long lifetime of europium emission.<sup>33</sup> Fig. 8a shows a plot of the emission spectra of a dried (solid) sample of 9-oxidophenalenone-capped  $\sim 5\%$   $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs recorded at different delay times when excited with 457 nm light. The spectra display a steady decay in the emission intensity upon increase in the delay time from 0.1 to 5.0 ms, beyond which no emission is observed. The emission intensity decay curve (inset of Fig. 8a) was obtained by monitoring the intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission line at 615 nm. The time-resolved emission intensity decay could be best fit to tri-exponential functions, the parameters of which are listed in Table 1. The average lifetime ( $\tau_{av.}$ ) of the  $\text{Eu}^{3+}$  emission obtained from tri-exponential function parameters of these NCs is 0.41 ms, which is much lower than  $\tau_{av.}$  (6.90 ms) reported for citrate-capped 5%  $\text{Eu}^{3+}$ -doped  $\text{LaF}_3$  NCs.<sup>25</sup> However, as compared to the lifetime of the  $\text{Eu}(9\text{-oxidophenalenone})_3$  chelate reported in the literature ( $\tau = 10 \mu\text{s}$  in THF solution, excited at 458 nm),<sup>18</sup> the lifetime of  $\text{Eu}^{3+}$  emission of these NCs is drastically increased. This is in agreement with the results obtained by Petoud and co-workers, wherein  $\text{Ln}^{3+}$ -doped  $\text{NaYF}_4$  NCs with surface capped tropolonate sensitizers are reported to display much longer lifetimes than  $\text{KLn}(\text{tropolonate})_4$  chelate.<sup>10a</sup> The enhanced lifetime of the  $\text{Eu}^{3+}$  emission of these NCs therefore demonstrates that the  $\text{LaF}_3$  host protects the  $\text{Eu}^{3+}$  ions from non-radiative deactivation *via* high-energy vibrations of the organic ligands as compared to  $\text{Eu}(9\text{-oxidophenalenone})_3$  chelate. The intrinsic quantum yield ( $\Phi_{\text{Eu}}$ ) of the  $\text{Eu}^{3+}$  emission of NCs was calculated from the ratio of the average lifetime of the  $\text{Eu}^{3+}$  emission ( $\tau_{av.}$ ) and radiative lifetime ( $\tau_{rad}$ ) of  $\text{Eu}^{3+}$  emission ( $\tau_{av.}/\tau_{rad}$ ).<sup>34,35</sup> The radiative lifetime ( $\tau_{rad}$ ) of  $\text{Eu}^{3+}$  emission of the NCs was



**Fig. 8** (a) The time-resolved emission spectra recorded from a dried (solid) sample of 9-oxidophenalenone-capped  $\sim 5\%$  Eu $^{3+}$ -doped LaF<sub>3</sub> NCs at room temperature with different delay times (0.1–5.0 ms) and gate time of 5 ms. [Inset: plot of the emission intensity decay of the  $^5D_0 \rightarrow ^7F_2$  transition with different delay times (circle) and tri-exponential fit (solid curve) of the decay curve.] (b) The representative time-resolved emission spectra with different *R* values.

obtained from the corrected emission spectrum, according to the method described by Verhoeven and co-workers.<sup>34</sup> The values of radiative lifetime and the intrinsic quantum yield of the Eu $^{3+}$  emission of the NCs are provided in Table 1. The radiative lifetime of the Eu $^{3+}$  emission of the NCs falls within the range (2.2–6.1 ms) obtained for the sensitized europium emission.<sup>34–37</sup>

Fig. 8b shows representative time-resolved emission spectra of 9-oxidophenalenone-capped NCs collected at 0.1, 1.0, 2.0 and 3.0 ms delay times. As mentioned earlier, the spectrum collected at 0.1 ms delay time displays an *R* value of 4.6. The various spectra obtained up to 0.9 ms delay times also display

similar asymmetric ratio with slight deviations. Interestingly, the spectrum collected at 1 ms delay time abruptly displays a smaller *R* value of 1.92. This suggests that the Eu $^{3+}$  emitting sites of the NCs that display this emission spectrum must have a less asymmetric environment than the average environment of all the Eu $^{3+}$  sites of NCs. Since most of the emission can be expected to arise from surface sensitized Eu $^{3+}$  sites, these Eu $^{3+}$  sites with less asymmetric environment are perhaps occupying host sites close to the surface of the NC. This is further corroborated by the lifetime component  $\tau_2$ , obtained from the tri-exponential fitting, which has the second largest contribution to the lifetime and decays more slowly than  $\tau_1$ , which has the largest contribution to the lifetime and decays faster (Table 1). A longer lifetime component of these Eu $^{3+}$  sites than the surface sensitized Eu $^{3+}$  sites indicates that these are more protected from the cross-relaxation and vibrational quenching of the 9-oxidophenalenone ligand.

Remarkably, the emission spectra obtained for 2–5 ms delay times show a further decrease in the *R* value ( $\sim 1.65$ ) which indicates that these Eu $^{3+}$  sites experience a highly symmetric environment in these NCs as compared to other sites. These sites could be correlated with the lifetime component  $\tau_3$ , which has a very small contribution and decays much slower than the other components (Table 1). A very long lifetime component of these emission sites also suggests that they occupy interior sites in the LaF<sub>3</sub> host and are completely protected from the vibrational quenchers of the ligand. However, it is rather surprising to consider that the sensitized emission can be displayed from the interior sites of the  $\sim 5\%$  Eu $^{3+}$ -doped LaF<sub>3</sub> NCs since the sensitization process is limited to a very small distance between the donor and the acceptor. This can be rationalized as a result of higher molar concentration of the doped Eu $^{3+}$  ions ( $\sim 5\%$ ) in the NCs, the interior Eu $^{3+}$  sites possibly displaying emission due to significant Eu $^{3+} \rightarrow$  Eu $^{3+}$  energy migration from surface sensitized Eu $^{3+}$  sites of the NCs. A significantly lower intrinsic quantum yield of the Eu $^{3+}$  emission of the NCs also indicates that a very small fraction of the Eu $^{3+}$  sites relax radiatively once the  $^5D_0$  emitting levels of Eu $^{3+}$  sites are populated. The remaining Eu $^{3+}$  sites possibly transfer energy to the neighboring interior Eu $^{3+}$  sites of the NC.

## Conclusions

Very small and highly crystalline europium-doped LaF<sub>3</sub> NCs that contain surface-bound 9-oxidophenalenone ligands are

**Table 1** The tri-exponential function parameters along with average lifetime, radiative lifetime and intrinsic quantum yield calculated for 9-oxidophenalenone-capped  $\sim 5\%$  Eu $^{3+}$ -doped LaF<sub>3</sub> NCs

Lifetime components <sup>a</sup> (ms)	Relative amplitude ( <i>A</i> )	Chi square ( $\chi^2$ )	$I_{\text{total}}/I_{\text{MD},0}$	Radiative lifetime ( $\tau_{\text{rad}}$ ) (ms)	Average lifetime ( $\tau_{\text{av.}}$ ) (ms)	Intrinsic quantum yield ( $\Phi_{\text{Eu}}$ ) (%)
$\tau_1 = 0.08$ (52.66%)	$A_1 = 1.0$	0.999	7.156	3.08	0.41	13.25
$\tau_2 = 0.32$ (31.34%)	$A_2 = 0.59$					
$\tau_3 = 1.65$ (16.0%)	$A_3 = 0.30$					

<sup>a</sup>The percentages in parentheses are the contributions of the corresponding lifetime components of Eu $^{3+}$  dopant emission decay.

reported. The visible light excitation of the surface-bound ligands of the NCs generates a strong blue emission, which has a very short lifetime. A partial energy transfer also occurs from the surface-bound ligands to the doped europium sites on the surface and just below the surface of the NC host. This results in sensitization of red emission from the doped europium sites. The intensity of the sensitized red europium emission from the dopant Eu<sup>3+</sup> sites of these NCs is negligible as compared to the intensity of the blue emission of the capping ligands observed in the steady-state emission spectrum. Therefore, the sensitized red europium emission from these NCs can only be collected by a time-resolved method due to the long lifetime of the red europium emission. However, it is demonstrated that visible light excitation of the capping 9-oxido-phenalenone ligands at 457 nm (higher wavelength absorption/excitation maxima) generates more intense time-delayed sensitized europium emission as compared to the emission obtained by exciting at 395 nm, the wavelength used to generate intense emission from Eu<sup>3+</sup> dopant sites in citrate-capped NCs by direct excitation. This is in spite of the fact that surface-bound ligands transfer only partial energy to the doped europium sites and the capping ligand itself absorbs around 395 nm, indicating that surface sensitization of the dopants is more effective as compared to direct excitation of the dopant energy levels. The average lifetime of the 9-oxido-phenalenone-sensitized europium emission obtained from the NCs is much enhanced as compared to the lifetime reported for europium tris-chelate with 9-oxido-phenalenone. This demonstrates that the NC host protects the doped europium sites from non-radiative deactivation through high-energy vibrations of the 9-oxido-phenalenone ligand. The surface-bound 9-oxido-phenalenone ligands act as a probe to allow more understanding of the coordination environment of different europium sites in the NC host (*i.e.* surface europium sites *vs.* interior europium sites) by time-resolved emission spectroscopy. There are at least three different europium sites in the NC host, which are possibly surface sites, sites just below the surface as well as interior sites. We have shown that the surface europium sites of the NCs, which are directly bound to the capped ligands, experience a highly asymmetric environment as compared to other sites. On the other hand, the interior europium sites are more protected from the cross-relaxation and high-energy vibrations of the surface-bound ligands. The sensitized emission from interior europium sites of the NCs is rather surprising. We propose that a significant Eu<sup>3+</sup> → Eu<sup>3+</sup> energy migration occurs from surface sensitized europium sites of the NCs to interior europium sites, due to higher molar concentration of the doped europium ions. Therefore, this study demonstrates that visible light sensitizing organic ligands bound to the surface of the NCs help in achieving efficient luminescence from the doped europium ions, as well as acting as probes to help differentiate the luminescence characteristics of various europium sites on the surface and in the interior of the NCs. The visible light excitable and color tunable nanomaterial reported in this work can find potential applications in energy-efficient optoelectronic devices.

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