Dipicolinate Sensitization of Europium Luminescence in Dispersible 5% Eu:LaF₃ Nanoparticles

Ann M. Cross,[†] P. Stanley May,[†] Frank C. J. M. van Veggel,[‡] and Mary T. Berry^{*,†}

Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069 and Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 3 V6

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An earlier synthetic procedure was adapted to produce water-dispersible, citrate-stabilized LaF₃ nanoparticles of 3-4 nm diameter, which exhibit a high degree of crystallinity (tysonite structure). The samples, as isolated from synthesis, consist of nanoparticles with a monolayer coverage of citrate capping ligands (with no excess, unbound citrate) and ammonium ions which balance charge. In aqueous dispersions, dipicolinate (DPA) displaces citrate on the surface of 5%Eu-doped LaF₃ nanoparticles and strongly sensitizes Eu³⁺(⁵D₀) emission. At low concentrations, the DPA does not adversely affect the dispersibility or the structural integrity of the nanoparticles and binds to the particle surface, selectively sensitizing Eu³⁺ surface and near-surface sites. The DPA, therefore, serves both as a sensitizer of Eu³⁺ luminescence and as a selective probe of the surface. The dipicolinate strongly sensitizes Eu³⁺(⁵D₀) emission, increasing the 614 nm emission intensity by a factor of 100 with less than 1% citrate replacement. Addition of an LaF₃ shell (thickness ≈ 4 Å) over the 5%Eu:LaF₃ core (3–4 nm) results in dispersible nanoparticles which exhibit 4-fold reduction in dipicolinate sensitization. The DPA probe gives strong evidence that a true core—shell structure is formed and that DPA sensitization can penetrate to near-surface sites to which the DPA is not directly bound.

Introduction

Trivalent lanthanide ions (Ln^{3+}) remain one of the most important classes of activators for luminescent materials for both technological applications and fundamental research.¹ The technological applications of Ln^{3+} -based phosphors include lasers, luminescent displays, optical data transmission, and lightemitting diodes.^{1–5} The much publicized effort to rid the globe of the inefficient incandescent light bulb is made possible by an efficient alternative provided in the form of the compact Ln^{3+} activated fluorescent lamp. The lanthanides also play important roles as luminescent probes and stains in biomedical research.^{4,6,7}

The broad applicability of Ln³⁺ phosphors is rooted in the unique nature of the fundamental photophysics governing the $4f \rightarrow 4f$ transitions responsible for Ln³⁺ emission.⁸ The valence 4f electrons are spatially encapsulated within the filled 5s and 5p orbitals and, therefore, interact only weakly with the chemical environment. For example, the effect of the crystal field on the 4f energy-level structure of the lanthanide ion is generally much smaller than that of the major free-ion interactions, such as electron-electron repulsion and spin-orbit coupling. The freeion energy-level structure of Ln3+ is, therefore, largely preserved in any chemical matrix, and the crystal field can be treated theoretically as a small perturbation on the free-ion state.9 Another major consequence of the shielded nature of the 4f electrons is that the equilibrium bond distance between the lanthanide ion and the coordinating species is essentially independent of the Ln^{3+} energy level within the 4f configuration. As a result, the optical spectra of lanthanide ions are dominated by sharp-line structure, corresponding to pure electronic (i.e., zero-phonon) transitions.

Perhaps most importantly, the weak interaction of the 4f electrons with the chemical environment results in relatively inefficient vibrational quenching of lanthanide emission.^{10,11} As a result, Ln^{3+} phosphors can exhibit efficient room-temperature emission from the UV to the mid-IR. Several lanthanide ions (Eu³⁺, Tb³⁺, and Gd³⁺) are luminescent in virtually any chemical environment. Also, a number of Ln^{3+} ions commonly exhibit two or more luminescent states, even at room temperature; this property has been exploited to produce unique optical processes, such as quantum cutting^{1,12} (producing two long-wavelength photons from one short-wavelength photon from two long-wavelength photons).

The principal disadvantage to lanthanide ions as phosphors is the low molar absorptivity values associated with $4f \rightarrow 4f$ transitions, which leads to inefficient optical excitation. A welldeveloped strategy to overcome this shortcoming is to use ligands bonded to the Ln³⁺ ion as sensitizers of $4f \rightarrow 4f$ emission.^{4,6,7,15–17} Briefly, the excitation wavelength used is in resonance with a strong ligand absorbance. The excited ligand then efficiently transfers its energy to the lanthanide ion. The net result of this so-called "antennae effect" is to increase the effective molar extinction coefficient of the phosphor complex by several orders of magnitude.

This ligand sensitization is thought to be a short-range effect occurring via (i) an electron exchange mechanism and, therefore, effective only when the ligand is directly coordinated to the Ln^{3+} ion or (ii) a dipole–dipole mechanism where the energy-transfer efficiency, η , falls off with distance, R, as in

$$\eta = 1/(1 + (R/R_0)^{\circ}) \tag{1}$$

[‡] University of Victoria.

where R_0 is a constant, characteristic of a particular lanthanide– ligand pair, falling typically in the range of 5–20 Å.¹⁸ Ligands

^{*} To whom correspondence should be addressed. E-mail: mary.berry@ usd.edu.

[†] University of South Dakota.

are used not only as sensitizers but also to shield the Ln^{3+} ions from high-energy oscillators, such as -OH groups, in the chemical matrix (e.g., the solvent).^{7,19} Such shielding is absolutely essential for the observation of NIR emission from lanthanide complexes in common solvents.⁷ Even so, only modest NIR quantum efficiencies have been achieved using this strategy, due to the fact that the protecting ligands themselves have relatively high-energy vibrational modes that quench NIR emission.

A very promising approach for obtaining highly luminescent lanthanide-activated 'solutions' is to use solvent-dispersible lanthanide-doped nanoparticles of inorganic insulators. Two of the most intensely investigated nanocrystalline hosts for this purpose are LaF3²⁰⁻²⁶ and NaYF4.²⁷⁻³⁷ Here, the majority of Ln³⁺ ions are shielded within the crystal lattice of the nanoparticle host. The luminescent nanoparticles are made solvent dispersible by capping ligands bonded to the surface of the nanoparticles. The nanocrystal approach has three major advantages over traditional lanthanide chelates. First, emission from lanthanide-doped insulators is intrinsically more efficient compared to that from lanthanide chelates. Second, the dispersibility of the nanoparticles can be customized to the desired solvent through the choice of capping ligand. Third, the nanoparticles can be functionalized for specific chemical interactions (for biological probes, for example) without significant disturbance of the intrinsic optical properties of the nanoparticles.

As a cautionary note, Dong et al.³⁸ have shown that citratestabilized GdF₃ nanoparticles in aqueous dispersion are unstable to cation exchange with La^{3+} or Eu^{3+} and that NdF₃ nanoparticles are unstable to cation exchange with excess La^{3+} . Specifically, the exchange,

$$GdF_3(np) + excess La^{3+}(aq) \rightarrow LaF_3(np) + Gd^{3+}(aq)$$

was found to go to completion in less than 1 min at room temperature. The analogous exchange of Eu^{3+} for Gd^{3+} resulted in incomplete replacement and resultant nanoparticles which incorporated both cations, $Eu:GdF_3$. In general, exchange was found to be reversible, e.g., LaF_3 nanoparticles in aqueous medium were unstable in the presence of excess Gd^{3+} , although the reverse process did not proceed to the same extent. They also showed that dispersions of cubic-NaYbF₄ nanoparticles were unstable in the presence of excess La^{3+} , with the cubic starting material being converted entirely to trigonal Yb:LaF₃. This work calls into question the capacity for creating true core—shell structures with distinct cation content in the different layers as well as the stability of the nanoparticles against cation extraction by strongly binding sensitizing ligands.

However, Zhang et al. recently demonstrated that the antennae effect can be exploited to sensitize emission from Ln^{3+} -doped nanoparticles.³⁹ In that study, the tropolonate (Trop⁻) capping ligand of Yb³⁺- and Nd³⁺-doped NaYF₄ nanoparticles (hexagonal phase) was shown to sensitize NIR luminescence from the Ln³⁺ ions. Moreover, the luminescence quantum efficiency for the sensitized nanoparticle emission was shown to be significantly higher than that for the [Ln(Trop⁻)₄]⁻ complex, clearly illustrating an important advantage of dispersible nanoparticles over lanthanide chelates. Kokuoz et al.⁴⁰ also demonstrated that 3-(4-formylphenyl)benzoate could sensitize Eu³⁺ luminescence in Eu:LaF₃ nanoparticles.

In the present study, it is demonstrated that the antenna effect can be used not only to sensitize Ln^{3+} emission but also as a

spectroscopic tool for selective analysis of the Ln³⁺ surface sites of lanthanide-doped nanoparticles. In order to truly understand the luminescence properties of nanoparticles, the ability to differentiate the spectroscopic properties of the surface sites vs the interior sites is essential. Previously, differences in the luminescence properties of the interior vs surface Ln³⁺ sites have been investigated through site-selective spectroscopy^{41,42} and inferred from the observation of multiexponential decay curves^{24,43} and from the effect of different capping ligands on the luminescent properties of the nanoparticles.²⁴ Here, the Eu³⁺ surface sites of citrate-stabilized 5%Eu:LaF3 nanoparticles in aqueous dispersions are investigated using the dipicolinate (DPA) ligand as a sensitizing probe. DPA is shown to displace the citrate capping ligands and strongly and selectively sensitize luminescence from $Eu^{3+}({}^{5}D_{0})$ sites at or near the surface. The luminescence properties of these Eu³⁺ "surface" sites are compared to the overall spectroscopic properties of the 5%Eu: LaF₃ nanoparticles. As shown in this study, the antenna effect also proves useful in assessing the efficacy of the putative core-shell structure for shielding core Ln³⁺ from surface influences.

Experimental Section

Preparation of Citrate-Stabilized 5% Eu:LaF₃ Nanoparticles. In this work we adapt an earlier LaF₃ synthesis published by Sudarsan et al.²⁴ An aqueous solution of 2.00 g (10.4 mmol) of citric acid in 35 mL of nanopure H₂O was partially neutralized with ~ 1.5 mL of concentrated NH₄OH to a pH of 5.5. The solution was heated to 75 °C in a water bath while stirring. A solution of 0.55 g (1.3 mmol) of $La(NO_3)_3 \cdot 6H_2O$ and 0.027 g (0.061 mmol) of Eu(NO₃)₃·6H₂O in 2 mL of methanol was added dropwise to the citrate solution. Then, a solution of 0.18 g (4.3 mmol) of NaF in 2 mL of H₂O was added dropwise to the reaction medium. Addition of NaF resulted in some initial clouding, which quickly cleared. The reaction mixture was stirred continually for 2 h at 75 °C and then allowed to cool to room temperature. The resulting nanoparticles were precipitated by adding 50 mL of 95% ethanol and separated from the suspension by centrifugation. The precipitate was washed thoroughly with 95% ethanol and dried under vacuum overnight. This synthesis, in contrast to that in ref 24, uses excess NaF as opposed to excess La(NO₃)₃. Both methods produce nanoparticles in similar yields with similar size and crystallinity. However, the use of excess fluoride results in more complete reaction of the lanthanide and results in a higher doping percentage of europium. DiMaio et al.44 made a similar recommendation in their synthesis of complex multishell doped LaF₃ nanoparticles.

Most of the characterization discussed below is of samples obtained using citrate, NH_4OH , $Ln(NO_3)_3$, and NaF, as detailed above. However, in order to identify the source of nitrogen observed in the elemental analysis of the nanoparticles, an analogous synthesis substituting lanthanide chlorides for the nitrates was performed. Also, a separate synthesis was conducted substituting NaOH for NH_4OH to neutralize the citric acid.

Preparation of Citrate-Stabilized 5% Eu:LaF₃ Core–LaF₃ Shell Nanoparticles. An aqueous solution of 2.00 g (10.4 mmol) of citric acid in 35 mL of nanopure H₂O was neutralized with ~1.5 mL of NH₄OH until the pH reached 5.5. The resulting solution was heated to 75 °C in a water bath while stirring. A solution of 0.55 g (1.3 mmol) of La(NO₃)₃·6H₂O and 0.027 g (0.061 mmol) of Eu(NO₃)₃·6H₂O in 2 mL of methanol was added dropwise to the citrate solution. In contrast to the synthesis for the simple core, a solution of 0.35 g (8.3 mmol or 6.3 equiv) of NaF in 2 mL of H_2O was added dropwise to the reaction medium. The reaction was allowed to continue for 2 h at 75 °C. Then a solution of 0.57 g (1.3 mmol) of La(NO₃)₃·6H₂O in 2 mL of methanol was added dropwise. The reaction was allowed to continue for another 2 h at 75 °C and then allowed to cool to room temperature. The core—shell nanoparticles were precipitated by adding 50 mL of 95% ethanol and separated by centrifugation. The precipitate was washed with 95% ethanol and dried under vacuum overnight.

For the core—shell synthesis, all of the fluoride, for both the core and the shell, is already present in the first (core preparation) step. This strategy is expected to yield a purer shell, reducing the possibility of free europium in solution at the commencement of shell formation and potentially suppressing the cation exchange described in ref 38.

Preparation of 5%Eu:LaF₃ Core-LaF₃ Double-Thickness-Shell Nanoparticles. An aqueous solution of 2.00 g (10.4 mmol) of citric acid in 35 mL of nanopure H₂O was neutralized with ~ 1.5 mL of NH₄OH until the pH reached 5.5. The resulting solution was heated to 75 °C in a water bath while stirring. A solution of 0.55 g (1.3 mmol) of La(NO₃)₃·6H₂O and 0.027 g (0.061 mmol) of Eu(NO₃)₃·6H₂O in 2 mL of methanol was added dropwise to the citrate solution. Excess fluoride in a solution of 0.52 g (12.4 mmol or 9.3 equiv) of NaF in 2 mL of H₂O was added dropwise to the reaction medium. The reaction was allowed to continue for 2 h at 75 °C. Then a solution of 1.16 g (2.67 mmol) of La(NO₃)₃·6H₂O in 2 mL of methanol was added dropwise. The reaction was allowed to continue for another 2 h at 75 °C and then allowed to cool to room temperature. The core-double-thickness-shell nanoparticles were precipitated by adding 50 mL of 95% ethanol and separated by centrifugation. The precipitate was washed with 95% ethanol and dried under vacuum overnight.

Preparation of Citrate-Stabilized 10% Eu:LaF₃ Core– LaF₃ Shell Nanoparticles and 5% Eu:LaF₃ Core–5% Eu LaF₃ Shell. In order to further test the efficacy of the core–shell synthetic strategy described above, nanoparticles of similar size with similar total europium content were needed. Citratestabilized 10% Eu:LaF₃ core–LaF₃ shell nanoparticles and 5% Eu:LaF₃ core–5% Eu:LaF₃ shell nanoparticles were prepared as described previously for the 5% Eu:LaF₃ core–LaF₃ shell except that the europium/lanthanum proportions were adjusted.

Powder X-ray Diffraction Studies. Powder X-ray diffraction studies (XRD) were performed on a Scintag Pad V diffractometer. The instrument is fitted with a copper X-ray tube with K α 1 wavelength at 1.54 Å. The powder XRD patterns were collected in continuous scan mode with a scan rate of 1.00 deg/min with a 2 θ range 20–70°. The samples were prepared by sifting through granule sifts to remove any large particles prior to analysis. Identification of the samples was made by comparing the sample XRD pattern to the International Centre for Diffraction Data (ICDD) powder diffraction file for LaF₃ (82-0690).

Atomic Force Microscopy Studies. Atomic force microscopy (AFM) studies were acquired using a Nano-R₂ Atomic Force Microscope from Pacific Nanotechnology in noncontact mode. The sample was prepared by dispersing ~ 30 mg of nanoparticles in 4 mL of nanopure water and sonicating the solution for 15–20 min. Then, 1 drop of this solution was diluted with 4 mL of nanopure water and sonicated for an additional 30 min to ensure the dispersion of the nanoparticles. Finally, 1 drop of the diluted solution was dropped on a mica sheet (5 × 5 mm²) and dried under vacuum prior to mounting on the holder for analysis. **Transmission Electron Microscopy.** Transmission electron microscopy (TEM) studies of the 5%Eu:LaF₃ nanoparticles were made with a TF20 S-Twin from FEI (200 kV) by FEI technicians in Hillsboro, OR. Fifteen images were recorded from different regions on the same sample spread.

Elemental Analysis (CHN). Elemental analysis of the dried nanoparticles and of the citric acid reagent was performed using a CE-440 Elemental Analyzer from Exeter Analytical, Inc. For each analysis, an average sample mass of 6–7 mg was placed in a tin capsule and crimped before combustion. The percent carbon, hydrogen, and nitrogen present for each material was determined from an average of 3–5 samples.

Luminescence Measurements. Luminescence measurements were made using a FluoroMax spectrofluorometer from SPEX Industries, Inc. The excitation and emission scans were obtained with integration times of 0.5 s per wavelength increment of 0.5 nm. For the excitation scans, an excitation resolution of 2 nm and an emission resolution of 4 nm were used. For emission scans, an emission resolution of 2 nm and an excitation resolution of 4 nm were used. For emission resolution of 4 nm were used and emission resolution of a nm and an excitation resolution of a nm were used. All excitation and emission spectra presented herein have been corrected for instrument response to give relative photon flux per wavelength interval.

The asymmetry ratio, R, for europium luminescence was calculated by dividing the integrated peak intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition by that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition. For the figures contained herein, the intensities of different emission spectra are scaled to normalize the magnetic-dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition intensity in order to assist visual comparison of the asymmetry ratios, R.

Results and Discussion

Nanoparticle Size and Crystallinity. The core 5%Eu:LaF₃ nanoparticles were analyzed for size using atomic force microscopy, yielding an average diameter $D = 2.8 \pm 0.2$ nm. A Scherrer analysis of the powder X-ray diffraction from the 111 plane gave $D = 3.2 \pm 0.2$ nm, and analysis of the TEM image gave $D = 3.5 \pm 0.2$ nm, where the uncertainties given are twice the standard deviation of the mean. Sample standard deviations are larger. For example, the TEM measurement, which gave an average size of 3.5 nm, had a sample standard deviation of 0.8 nm. The TEM size measurement comes from 59 discernible particles in 15 separate micrographs taken at random locations within a single sample preparation. The TEM images show particles usually consisting of a single-crystalline domain with lattice spacing typical of the LaF3 tysonite structure (ICDD card 82-0690) as illustrated in Figure 1. Occasionally twinning and some dislocation, as illustrated in the image for the 111 plane, is also observed.

Elemental Analysis. The results of the elemental (CHN) analysis of the dried 5%Eu:LaF₃ nanoparticles is given in Table 1. These results are consistent with a mass content of 32% citrate and 68% LnF₃. Also in Table 1, the elemental analysis results are compared to the mass percentages that would be expected for monolayer coverage of citrate on the nanoparticles. The theoretical elemental composition was calculated assuming a 0.215 nm² footprint for citrate molecules on the surface of spherical nanoparticles with a 3.2 nm diameter, which implies 150 citrate ligands per particle. Given the simplicity of the model used to calculate the theoretical elemental composition for a monolayer of coverage, the agreement with experimental observation is quite good. The elemental analysis strongly indicates that the synthesis and workup procedures used here produce very clean samples of nanoparticles, free from excess capping agent or other impurities.



Figure 1. (a) High-resolution TEM images of 5%Eu:LaF₃ core nanoparticles. (b) Powder XRD of 5%Eu:LaF₃ core nanoparticles (core np) and 5%Eu:LaF₃ core-LaF₃ shell nanoparticles (core-shell np).

TABLE 1: Elemental Analysis of Dried 5% Eu:LaF3Nanoparticles (np) Compared to Theoretical ResultEstimated for a Monolayer Coverage of Citrate CappingLigands on 3.20 nm Diameter Spherical Particles^a

CHN	dried	theoretical	theoretical
elemental	nanoparticles	np + citrate	np + citrate +
analysis	(np)	(d = 3.2 nm)	NH ₄ ⁺
%carbon	12.0	12.0	12.0
%hydrogen	1.5	1.3	1.6
%nitrogen	1.2	0.0	1.0
%other	85.3	86.6	85.4
%citrate	32	32	32

 a The last column gives the content for monolayer citrate coverage on a 3.14 nm diameter spherical particle if the precipitate also contains 1.3% $\rm NH_4^+$ by weight.

The 1.2% nitrogen content reported in Table 1 has been confirmed for many different samples and far exceeds the baseline reading of $\sim 0.2\%$ typically obtained for compounds containing no nitrogen. There are two likely sources of nitrogen in the product: nitrate from the lanthanide salts used in the synthesis or ammonium ion from the citrate neutralization. Replacing the lanthanide nitrates with lanthanide chlorides in the synthesis does not reduce the nitrogen content. However, replacing NH₄OH with NaOH yields LaF₃ nanoparticles with less than 0.2% nitrogen content, typical of the baseline. Thus, a likely explanation for the nitrogen content is that NH_4^+ precipitates with the nanoparticles to provide charge balance. If so, the observed mass % of nitrogen would correspond to approximately 60 NH_4^+ ions per nanoparticle. This, in turn, suggests that the net charge on each citrate-stabilized nanoparticle (absent the NH_4^+) is 60⁻.

In summary, the results of elemental analysis are consistent with a monolayer coverage of approximately 150 citrate ligands on a 3.2 nm 5%Eu:LaF₃ particle. The particle samples, as isolated, contain essentially no excess capping agent. The nitrogen content of the precipitated particles suggests that the citrate-stabilized 5%Eu:LaF₃ nanocrystals bear an excess negative charge in solution, which would favorably impact dispersibility.



Figure 2. Excitation spectra of 5%Eu:LaF₃ nanoparticles dispersed in (a) 0.1 mM DPA and (b) H₂O, both monitoring 614 nm emission. The strong feature in (a) at 278 nm is interpreted as sensitization of Eu³⁺ emission by DPA ligands bound to the surface of the nanoparticles.

Excitation and Emission Spectra. Figure 2 shows a comparison of the luminescence excitation spectra of 5%Eu: LaF₃ nanoparticle dispersions (7.5 mg/mL) in water and in 0.1 mM DPA(aq) (pH = 5.5), obtained by monitoring the hypersensitive $\text{Eu}^{3+}: {}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 614 nm. Both spectra show essentially identical features for the Eu³⁺ 4f \rightarrow 4f transitions at wavelengths above 300 nm, the strongest of which corresponds to the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition at 395 nm. However, the dispersion in 0.1 mM DPA shows an additional strong feature at 278 nm, which matches DPA absorbance in both position and shape, clearly indicating efficient DPA sensitization of Eu³⁺ emission. The DPA sensitization of the europium emission corresponds to a 100-fold enhancement relative to the maximum emission intensity observed for $4f \rightarrow 4f$ excitation. As a control experiment, the excitation spectrum of 0.1 mM DPA, with no nanoparticles, was measured under identical experimental conditions. This spectrum indicates that there is no significant Eu contamination in the DPA solution or significant interfering emission from the DPA itself at 614 nm.

As discussed previously, elemental analysis implies that the nanoparticle samples are 32% citrate by mass, which would correspond to a citrate concentration of approximately 13 mM for the dispersions used to obtain the spectra in Figure 2. Thus, for the 0.1 mM DPA solution, fewer than 1% of the citrates on the surface of the nanoparticles could be replaced by DPA. If the DPA were to bind quantitatively to the nanoparticles, this would imply an average of one or two DPA ligands per nanoparticle.

A comparison of the emission spectra for the nanoparticles dispersed in 0.1 mM DPA with DPA excitation at 278 nm and $4f \rightarrow 4f$ excitation at 395 nm is shown in Figure 3a. The emission spectra for excitation at 278 and 395 nm are distinctly different from each other, particularly with regard to the asymmetry ratio, R (R is the ratio of the intensity of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission to that of the magnetic-dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ emission.).

A consistent interpretation of differences in the emission spectra seen in Figure 3a is that the emission spectrum resulting from DPA excitation at 278 nm is due to Eu^{3+} surface and near-surface sites which are closely associated with a DPA ligand, whereas the 4f \rightarrow 4f excitation at 395 nm generates emission, for the most part, nonselectively from all Eu^{3+} ions in the nanoparticle. This implies that Eu^{3+} surface sites have a higher asymmetry ratio, *R*, compared to Eu^{3+} ions within the core, which is consistent with the previous observations of Sudarsan et al.²⁴



Figure 3. (a) Emission spectra of 5% Eu:LaF₃ nanoparticles (np) dispersed in 0.1 mM DPA with 278 and 395 nm excitation. (b) Emission spectra with 395 nm excitation comparing np dispersed in water, np dispersed in 0.1 mM DPA, and bulk 5% Eu:LaF₃ precipitate. The spectra have been scaled to match the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity at 590 nm.

Emission from inner-particle Eu³⁺ following DPA excitation might also be observed if there were significant Eu³⁺ \rightarrow Eu³⁺ energy migration from surface sites to core sites. A comparison of the emission spectra ($\lambda_{ex} = 278$ nm) for 5%, 1%, 0.5%, and 0.25% Eu-doped LaF₃ nanoparticles dispersed in 0.1 M DPA (not shown) exhibited no discernible trend, toward increasing asymmetry ratio, despite the fact that the Eu³⁺ dilution decreases the probability of Eu³⁺ \rightarrow Eu³⁺ energy transfer, arguing against a contribution from energy migration away from the surface sites, even at 5% doping levels.

Figure 3b shows that, when using $4f \rightarrow 4f$ excitation at 395 nm, the emission spectra for 5%Eu:LaF₃ nanocrystals are identical in water and 0.1 mM DPA. This is not surprising, given that, at most, on average, only one or two DPAs are coordinated to a given nanoparticle. Figure 3b also shows the emission spectrum of microcrystalline 5%Eu:LaF₃ (s), obtained by direct combination of Ln(NO₃)₃(aq) and NaF(aq). The emission spectrum of this bulk precipitate exhibits a much lower asymmetry ratio (R = 0.95) compared to the nanocrystalline form (R = 1.6), reflecting the higher ratio of internal Eu³⁺ sites to surface sites in the bulk.

Thus, for the nanoparticles dispersed in 0.1 mM DPA, we interpret the emission following 395 nm excitation as arising from a weighted average of surface- and interior-site emission and the emission resulting from 278 nm excitation as arising predominantly from DPA-bound surface sites. The weighting of the emission intensity from surface vs interior sites following 395 nm excitation is affected both by the relative number of surface to interior sites as well as by their relative luminescence quantum efficiencies. Surface-site emission in an aqueous environment is expected to be partially quenched both by water and by -OH oscillators in the coordinated citrate. Dipicolinate (the dianion) does not quench $Eu^{3+}({}^{5}D_{0})$ emission effectively.⁴⁵ The impact of water quenching can be seen by comparing the asymmetry ratio for the aqueous and dried citrate-stabilized nanoparticles with 395 nm excitation, given in Table 2. For the dried nanoparticles, the higher asymmetry ratio (R = 2.2 dried vs R = 1.6 aqueous) is consistent with a reduced quenching of the surface sites, which have a higher asymmetry ratio (R =2.8) compared to interior sites, where the latter are thought to be more similar to the microcrystalline bulk for which R = 0.95.

Effect of LaF₃ Shell on DPA Sensitization and Asymmetry **Ratio.** Our previous assertions regarding the binding of DPA to 5%Eu:LaF₃ nanoparticles and regarding the luminescence asymmetry ratio, *R*, of np surface sites relative to internal sites can be tested by comparing the luminescence properties of

TABLE 2: Asymmetry Ratios, R, for 5% Eu:LaF₃^{*a*}

	asymmetry ratio (R)		
5%Eu:LaF3	395 nm excitation	278 nm excitation	
citrate-stabilized nanoparticles (np), dried	2.2 ± 0.1		
np dispersed in water	1.6 ± 0.1		
np dispersed in 0.1 mM DPA	1.6 ± 0.1	2.8 ± 0.1	
bulk precipitate, dried	0.95 ± 0.01		

^{*a*} Stated errors represent twice the standard deviation of the mean (2σ) from multiple syntheses and measurements.

5%Eu:LaF₃ nanoparticles with and without an encapsulating LaF₃ shell. Citrate-stabilized, 5%Eu:LaF₃ core-LaF₃ shell nanoparticles, referred to hereafter as core-shell nanoparticles, were prepared as described in the Experimental Section. An equal amount of material was available for formation of the optically transparent shell as for the europium-containing core. In the simplest picture, for monodisperse 3.2 nm spherical core nanoparticles, an equal volume shell would be 0.4 nm thick, resulting in a 4.0 nm core-shell nanoparticle. There are several caveats to consider in invoking this simple picture: (1) the estimated shell thickness is less than the unit cell dimensions for LaF₃, 7.2 Å \times 7.2 Å \times 7.4 Å,⁴⁶ suggesting that a shell this thin may not be uniform in its coverage of the core; (2) some of the material added for the purpose of creating a shell might contribute to formation of new, pure LaF₃ nanoparticles, leaving an even thinner shell on the core nanoparticles; (3) as a third consideration, the propensity for cation exchange in doped-LaF₃ nanoparticles, as described by Dong et al.,³⁸ suggests the possibility of Eu³⁺ incorporation in the putative pure-LaF₃ shell. In fact, in light of the results from Dong et al., it becomes imperative to demonstrate whether or not we are in fact creating a core-shell structure or if, alternatively, there is equilibration of the Eu^{3+} dopant throughout both layers of the nanoparticle. Furthermore, as a fourth consideration, the possibility that DPA is extracting Eu³⁺ from the nanocrystals, and thus sensitizing aqueous Eu³⁺ as opposed to Eu³⁺ doped in the nanocrystals, must be considered.

A Scherrer analysis of the powder XRD (reflection from the 111 plane) of the core-shell nanoparticles suggests a diameter of 4.0 ± 0.1 nm (compared to 3.2 nm for the core np), in excellent agreement with the 4.0 nm diameter expected for the quantitative addition of the shell material to the core, although this result does not speak directly to the uniformity of the coverage.

Evidence for formation of a distinct core-shell structure and evidence for sensitization of Eu^{3+} in the nanoparticles, as



Figure 4. (a) Comparison of excitation spectra of 5%Eu:LaF₃ core nanoparticles (np) and 5%Eu:LaF₃-LaF₃ core-shell np in 0.1 mM DPA(aq) ($\lambda_{em} = 614$ nm). (b) Magnified view of the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ region of (a). The spectra have been scaled to match the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ intensity at 395 nm.



Figure 5. Comparison of the emission spectra of 5%Eu:LaF₃ core nanoparticles (core np) in 0.1 mM DPA(aq), 5%Eu:LaF₃ core–LaF₃ shell nanoparticles (core–shell np) in 0.1 mM DPA(aq), and microcrystalline 5%Eu:LaF₃(s) (bulk precipitate) using an excitation wavelength λ_{ex} = 395 nm. The spectra have been scaled to match the ⁵D₀ \rightarrow ⁷F₁ intensity at 590 nm.

opposed to sensitization of extracted cations, is provided in the spectroscopic data as discussed below. Figure 4 shows a comparison of the excitation spectra for the 5%Eu:LaF₃ core and 5%Eu:LaF₃ core-LaF₃ shell (core-shell) nanoparticles dispersed (7.5 mg/mL) in 0.1 mM DPA. The intensity for the core-shell spectrum is scaled upward to match the intensities of the ${}^7F_0 \rightarrow {}^5L_6$ transitions at 395 nm. The scaling factor accounts for the different net Eu^{3+} concentrations (2.5% vs 5%), changes in the relative intensity of the monitored ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, hypersensitive transition, and the difference in the quantum efficiencies of the core vs core-shell nanoparticles. Scaled in this fashion, it becomes evident that addition of a LaF₃ shell reduces the efficiency of the DPA sensitization by a factor of 4, consistent with the shell having dramatically reduced the number of Eu³⁺ surface sites available to DPA. Addition of a double-thickness LaF3 shell further reduces, but does not eliminate, the effect of DPA sensitization. The structure of the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition at 395 nm for the core-shell nanoparticles departs from that of the simple core nanoparticles and more closely resembles that of bulk LaF₃ doped with Eu³⁺.

Figure 5 compares the emission spectra, exciting at 395 nm, of the 5%Eu:LaF₃ core and 5%Eu:LaF₃ core–LaF₃ shell dispersions to that of solid, microcrystalline 5%Eu:LaF₃. The core–shell spectrum more closely resembles the microcrystalline sample (bulk precipitate in Figure 3), for which most of the europium resides in interior sites. This is consistent with Eu³⁺ residing in the core, protected by a LaF₃ shell, but size effects (vide infra) must be considered as well. The results shown in



Figure 6. Comparison of excitation spectra of 5%Eu:LaF₃ core nanoparticles (5% core np) and three different europium-doped core-shell nanoparticles in 0.1 mM DPA(aq) ($\lambda_{em} = 614$ nm). (b) Magnified view of the $^7F_0 \rightarrow ^5L_6$ region of a. The percentages refer to the Eu doping in the LaF₃ core and shell. The spectra have been scaled to match the $^7F_0 \rightarrow ^5L_6$ intensity at 395 nm.

Figure 5 also support the assertion that the asymmetry ratio for Eu^{3+} surface sites is significantly higher compared to interior sites.

In making comparisons between the core and core-shell spectra above, it is important to realize that the core and core-shell nanoparticles are of different sizes (3 vs 4 nm) and different net Eu³⁺ concentrations (5% vs 2.5%). Thus, a second set of experiments was performed using nanoparticles with a 10%Eu core and a pure LaF₃ shell compared to nanoparticles with a 5% Eu core and a 5% Eu shell: that is, 10%Eu:LaF₃ core-LaF₃ shell compared to 5%Eu:LaF₃ core-5%Eu:LaF₃ shell. We are thus comparing nanoparticles of the same size and same net 5% Eu³⁺ concentration.

Figure 6 shows a comparison of the excitation spectra. As previously, the concentrations are all at 7.5 mg/mL in 0.1 mM DPA(aq) and the spectra are scaled to match the intensities of the Eu³⁺:⁷F₀ \rightarrow ⁵L₆ transitions at 395 nm. The labels for the nanostructure types are abbreviated, where the percentages reflect the europium content in the LaF₃ core and shell, respectively. The DPA sensitization for the 10% core-0% shell is reduced by a factor of 4 as compared to the 5% core-5%shell, supporting the conclusion that the dopant cations are not entirely equilibrated throughout the nanoparticle and that a distinct core-shell structure has been achieved. The reason why the shell does not block the sensitization more effectively than the observed 75% diminution is potentially accounted for by a dipole-dipole sensitization mechanism as described in eq 1. For example, if the distance R in eq 1 is measured from the center of the DPA ring to the center of the lanthanide ion, such that R for an ion at the surface is ~ 5 Å, addition of a 4 Å shell will result in a drop in the efficiency η by a factor of 4, with R_0 falling in the physically reasonable range of 7-8 Å. The correct R_0 may be somewhat smaller because the calculation above does not take account of the presumably lower quantum efficiency of the true surface sites.

Figure 7 shows a comparison of the emission spectra from the various core and core—shell structures to that from microcrystalline 5%Eu:LaF₃ using excitation at 395 nm, thereby exciting all Eu³⁺ sites. Interestingly, all of the core—shell structures, including the structure with a 5%Eu:LaF₃ shell, show a significant reduction in the asymmetry ratio relative to the simple 5%EuLaF₃ core structure, suggesting that much of the reduction is due to the decrease in the surface-to-volume ratio associated with the larger nanoparticles. However, the spectra for the two structures with pure LaF₃ shells do show some



Figure 7. Comparison of the emission spectra of 5%Eu:LaF₃ core nanoparticles (5% core np) in 0.1 mM DPA(aq), three different europium-doped core-shell nanoparticles in 0.1 mM DPA(aq), and microcrystalline 5%Eu:LaF₃ (bulk precipitate) using an excitation wavelength λ_{ex} = 395 nm. The percentages refer to the Eu doping in the LaF₃ core and shell. The spectra have been scaled to match the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity at 590 nm.



Figure 8. Comparison of the emission spectra of 5% Eu:LaF₃ core nanoparticles (np) with several core–shell structures, all in 0.1 mM DPA(aq), using an excitation wavelength λ_{ex} = 278 nm. The percentages refer to the Eu doping in the LaF₃ core and LaF₃ shell. The emission patterns for the 5% core and 5% core–5% shell materials are nearly identical as are the emission patterns for the two materials with the 0% Eu shell. The spectra have been scaled to match the ⁵D₀ \rightarrow ⁷F₁ intensity at 590 nm.

further reduction in the asymmetry ratio and more closely approach the spectrum of the microcrystalline bulk.

Figure 8 shows the emission spectra acquired using 278 nm excitation, selectively exciting Eu³⁺ which are closely associated with DPA. The spectra have been scaled to give equal peak heights for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition. In this case, a striking difference is seen between the emission spectra of nanoparticles with a putatively undoped LaF₃ shell and those doped throughout the particle at the 5% Eu³⁺ level. For those nanoparticles with the 5% Eu³⁺ exterior, the emission spectrum exhibits a strong hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition with an asymmetry ratio Rof 2.8, the same as that reported above for the simple 5%Eu: LaF₃ core nanoparticles. For the two nanoparticles with the pure LaF₃ shell, the *R* value is only 1.7, with a relatively weak ${}^{5}D_{0}$ \rightarrow ⁷F₂ transition. This asymmetry ratio is lower than that observed for any of the aqueous $Eu(DPA)_n^{3-2n}$ complexes, supporting that the sensitization is indeed for Eu³⁺ imbedded in nanoparticles, as opposed to sensitization of free europium ions in solution. The R values we measure for the aqueous complexes are given in Table 3 as 2.2, 3.2, and 4.2 for the mono, bis, and tris complexes, respectively. The spectroscopic data in Figure 8, therefore, provide very strong evidence that a

TABLE 3: Asymmetry Ratios, *R*, for Selective (278 nm) and Nonselective (395 nm) Excitation of Eu³⁺ in DPA-Sensitized, Eu-Doped LaF₃ Nanoparticles and in a Comparison Group of Bulk Eu:LaF₃ and Aqueous Eu(DPA)_n³⁻²ⁿ

	asymmetry ratio (R)				
doped LaF ₃ nanoparticles in 0.1 mM DPA	395 nm excitation	278 nm excitation			
5%Eu:LaF3 core nanoparticles	1.6	2.8			
5% Eu core-5% Eu shell	1.3	2.8			
10% Eu core-0% Eu shell	1.2	1.7			
5% Eu core-0% Eu shell	1.1	1.7			
5% core-double-thickness 0% Eu shell	1.1	1.7			
comparison group					
bulk 5% Eu:LaF ₃ precipitate, dried (no DPA)	0.95				
$Eu(DPA)^+$ (aqueous)	2.2	2.2			
$Eu(DPA)_2^-$ (aqueous)	3.2	3.2			
$Eu(DPA)_3^{3-}$ (aqueous)	4.2	4.2			

significant level of integrity is maintained between the core and the shell and that DPA is sensitizing Eu³⁺ associated with the nanoparticles.

The R = 1.7 for 278 nm excitation of the species with the putative 0%Eu: LaF₃ shell has a further significance. This is much smaller than the $R = 2.8 \pm 0.1$ assigned to the nanoparticle surface-site sensitization and is more typical of what might be expected for more-interior or near-surface sites. This is consistent with the hypothesis that the residual sensitization that we observe in the core-shell structures is not due to Eu³⁺ contamination at the surface of the shell or to imperfect coverage of the core but rather to sensitization of Eu³⁺ ions to which the DPA is not directly coordinated: ions that do not lie directly on the surface of the nanoparticle. The potential for an efficient dipole-dipole mechanism for nonbonded-DPA sensitization of Eu³⁺ warrants further study.

At higher DPA concentrations and at higher DPA/Ln ratios we find that the nanoparticles are unstable. For example, with 1 mM DPA and a 5-to-1 DPA-to-lanthanide ratio, the emission spectrum and luminescent lifetime resemble aqueous $Eu(DPA)_3^{3-}$ and removal of solvent yields a luminescent microcrystalline (rather than nanocrystalline) product. This process will be examined in further detail in future work, but, for the purposes of this study, it was important to investigate the stability of the dispersions in dilute DPA.

The stability of the nanoparticle dispersions in 0.1 mM DPA was tested for the 10% core-0% shell nanoparticles and for the 5% core-5% shell. After 2 weeks at room temperature the dispersions developed some cloudiness that ultimately settled as a light precipitate on the bottom of the vial. The total intensity of the emission resulting from exciting the clear supernatant at 278 nm decreased by about 10% relative to the freshly prepared dispersions, presumably due to sample precipitation. However, the emission spectrum of the material which remains dispersed was identical to that of the freshly prepared dispersions. The 5% core-5% shell dispersion still exhibited R = 2.8, and the 10% core-0% shell dispersion still exhibited R = 1.7. The stability of the dispersions against precipitation is similar to that observed for aqueous dispersions in the absence of DPA. Thus, it would appear that the DPA sensitizes Eu³⁺ that is bound within the nanoparticles and that the europium does not significantly leach out from the nanoparticles in a 2-week time frame.

Conclusion

Highly crystalline citrate-stabilized 5%Eu:LaF₃ nanoparticles (3-4 nm) with an approximate monolayer coverage of ~150

citrate ligands were synthesized. The particles bear a net negative charge which is balanced upon precipitation by $\rm NH_4^+$ ions. Addition of dipicolinate (DPA) to aqueous dispersions of the particles strongly sensitizes $\rm Eu^{3+}(^5D_0)$ emission. This is interpreted as resulting from surface-citrate displacement by DPA, strong 278 nm absorbance by DPA, and subsequent DPA-to-europium energy transfer.

DPA-sensitized emission is largely characteristic of the surface sites and differs distinctly from the emission resulting from nonselective Eu^{3+} excitation at 395 nm. Application of a thin LaF₃ shell around the core nanoparticles decreases, but does not eliminate, DPA sensitization. The results support the hypothesis that a true core—shell structure is created, but also indicate that a weaker sensitization of nonsurface Eu^{3+} sites is possible.

This study demonstrates that there is great potential in exploiting the 'antennae effect' to sensitize lanthanide emission from lanthanide-activated inorganic nanocrystals. Not only can large increases in excitation efficiency be achieved, but ligand sensitization provides a sensitive probe of the nanoparticle surface sites and a measure of the extent to which interior ions can be isolated from surface interactions.

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