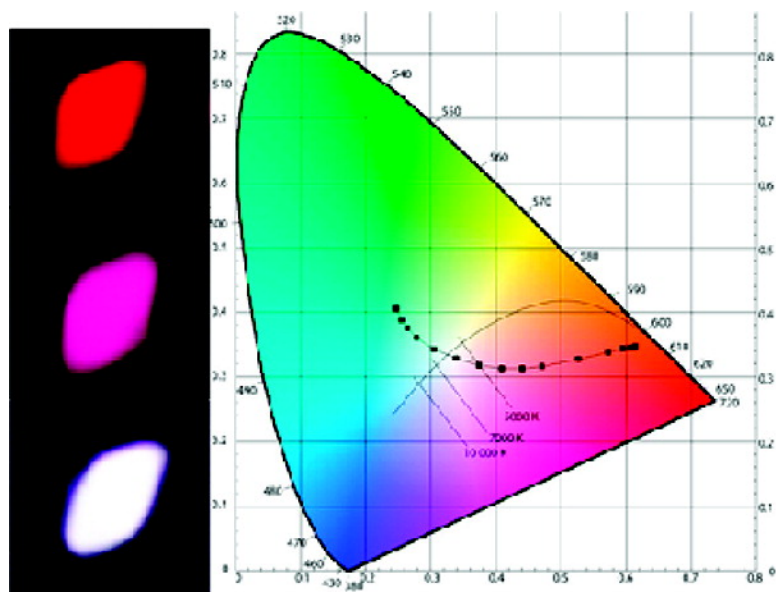


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Considerable interest exists for optical materials that exhibit tunability in their emission spectra. Such “color kinetic” materials can be used to define or modify environments, moods, and brands. Methods of controlling an emissive material’s color temperature include thermochromism, photochromism, and mechanochromism.¹

Inorganic nanoparticles, which typically are more thermally and mechanically robust than organic analogues, can permit tailoring of a dopant’s emission characteristics through compositional changes.^{2,3} Color tuning within a specific inorganic composition is a rare phenomenon^{4–6} especially in rare earth (RE) doped materials. Although transitions exist that could yield narrow line width (~20 nm) emissions across a wide range of wavelengths, one can not simply create an additive spectral output by codoping multiple REs into a host material. This is because energy transfer typically quenches one or more of the emission pathways thereby restricting the transitions that define the output spectrum. Recently, we reported multiple emissions by tailoring the energy transfer between different dopants by controllably sequestering them into either the core or successive shells of a microstructured nanoparticle.⁷ Using these multiply but selectively doped core/shell particles, separate red, green, and blue emissions were obtained, respectively, using Eu³⁺, Tb³⁺, and Tm³⁺ doped into different shells to yield different color temperature white light emissions.⁸

In this work we focus on multiple emissions from lanthanide ions doped into low vibrational energy nanoparticles that experience energy transfer from an organic ligand under selected excitation conditions. Although surface functionalized rare earth doped nanoparticles are not themselves new, this work engineers the particles and the ligand chemistry in order to achieve a desired tunability in color temperature with excitation wavelength. More specifically, we report here Eu³⁺ doped LaF₃ particles with a benzoic acid ligand that exhibit color tunability from the red to greenish-blue as a function of excitation wavelengths ranging from 250 to 400 nm.

Lanthanide doped LaF₃ nanoparticles were prepared as described previously.⁹ Briefly, nanoparticles with an organic shell was prepared as follows: 0.9 mmol of 3,4-(formylphenyl) benzoic acid and 3 mmol of NH₄F were dissolved in deionized water at 70 °C. The pH of the solution was adjusted to 7 by the addition of NH₄OH and followed by the addition of 1.3 mmol of Ln(NO₃)₃ solution. Reaction was completed after 2 h, and particles were recovered by centrifuge. Particles then were washed with water/EtOH and dried under vacuum.

Thermal gravity analysis showed that a 10 wt % organic component was presented as a sensitization ligand. A low crystallinity LaF₃ structure was confirmed by XRD, and the particle size was determined to be 5–10 nm by TEM analysis.

The absorption spectrum for the Eu/LaF₃ nanoparticles with the 3–4 formylphenyl benzoic acid ligand in THF is shown in Figure 1. A broad absorption feature can be observed extending to wavelengths above 325 nm. The peak at 280 nm coincides with

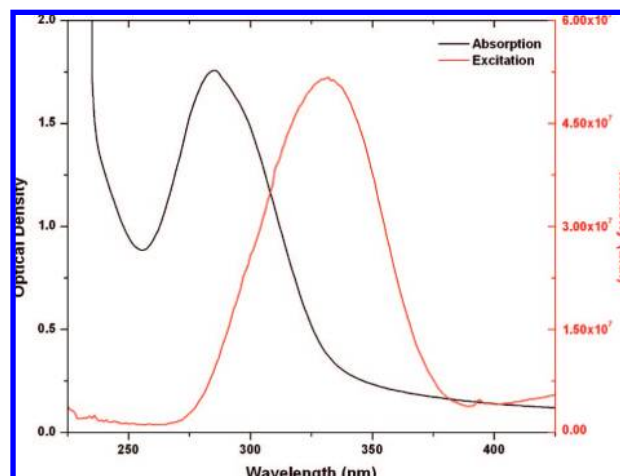


Figure 1. Absorption and excitation (614 nm) spectra.

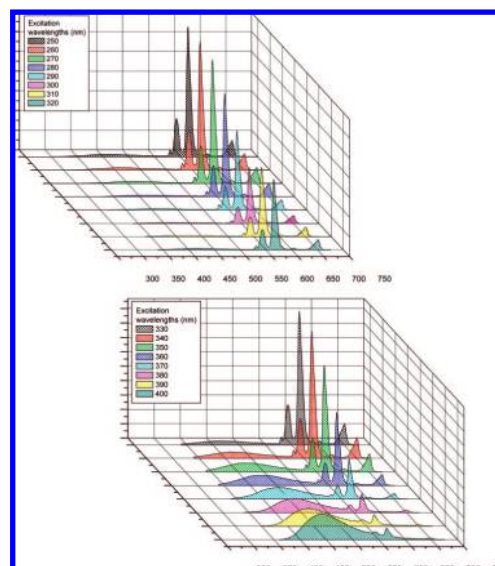


Figure 2. A waterfall representation of emission spectra (excitation 200–400 nm).

the $\Pi \rightarrow \Pi^*$ absorption of the ligand. Figure 1 also shows an excitation spectrum of the 614 nm Eu³⁺ emission from the nanoparticles. In this case, an intense peak is observed at 340 nm, which can be assigned to the excitation of the ligand followed by an energy transfer process to the Eu³⁺ ion. This is not a result of direct excitation of the Eu³⁺ ion, since the strength of organic ligand absorption is orders of magnitude stronger than direct excitation of the Eu³⁺ ion (i.e., $\lambda_{\text{exc.}} = 393\text{nm}$) and the line width is broader.

The emission spectrum of the nanoparticles is shown in Figure 2. Different emission spectra arise as a function of excitation

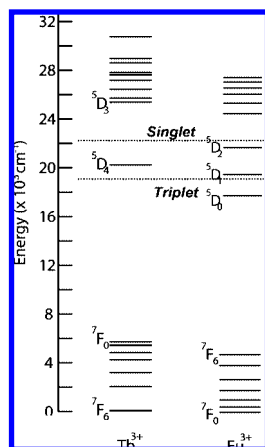


Figure 3. Position of the ligand singlet and triplet energy states and corresponding Eu^{3+} and Tb^{3+} energy states.

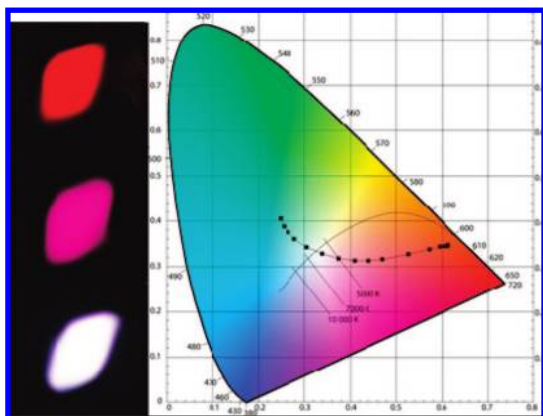


Figure 4. Spectra of Figure 2 plotted on a CIE diagram with excitation wavelength (right) and visual image of emission from nanoparticles at selected excitations (left), both showing tunability of chromaticity.

wavelength. It is generally accepted that the sensitization of RE^{3+} dopants by the ligand can occur through an electron exchange (Dexter) mechanism from the triplet state of the ligand to the lanthanide ion.¹⁰ Upon excitation of the electrons to the singlet excited state, a subsequent intersystem crossing populates the ligand triplet state. In the Dexter mechanism, the energy transfer rate is determined by the spectral overlap between the phosphorescence spectrum of the triplet state of the ligand and the absorption spectrum of RE^{3+} as well as the distance separating the donor (ligand) and acceptor (rare earth).

Excitations higher than 325 nm show a dramatic change in the photoluminescence spectra. At these wavelengths the ligand fluorescence increases while the Eu^{3+} emission decreases. Ultimately, the triplet state of the ligand is directly excited and results

in a Stokes shifted emission. Energy transfer to the rare earth can only occur as long as the higher vibrational levels of the triplet are populated. As a result these nanoparticles exhibit a tunable emission spectrum as a function of excitation wavelength via selective excitation of and partial emission from the ligand followed by energy transfer to the rare earth acceptor.

From the phosphorescence spectra at 77 K of the undoped LaF_3 particles and the free ligand excited at 350 nm, it is clear that the energy transfer occurs to the $\text{Eu}^{3+} \ ^5\text{D}_0$ state from the ligand. The singlet energy state at $22\ 200\ \text{cm}^{-1}$ (450 nm) and triplet energy state at $18\ 800\ \text{cm}^{-1}$ (532 nm) were determined. For comparison, a set of analogous particles but doped with Tb^{3+} were prepared in order to examine the energy transfer for a different dopant. From the emission spectra, none of the Tb^{3+} emissions were detected since the lowest triplet energy state of the ligand lies below the lowest emissive layer ($\ ^5\text{D}_4 \rightarrow 20\ 500\ \text{cm}^{-1}$) of Tb^{3+} . Thus it can be concluded that the lowest triplet energy state of the ligand lies above the $\ ^5\text{D}_0$ level and below the $\ ^5\text{D}_2$ level of the Eu^{3+} ion as is shown schematically in Figure 3.

The emission spectra resulting from each excitation wavelength was converted into the CIE 1931 color coordinate system and is shown in Figure 4. Due to the spectral dependence on energy transfer between ligand and lanthanide, the color of the sample can be tuned between red and greenish-blue with an excitation pump wavelength. In this case, the CIE coordinates can be made to cross the blackbody radiation curve at $x: 0.335$ and $y: 0.321$ which is accepted as white light.

In conclusion, color tunable Eu^{3+} -doped LaF_3 nanoparticles coated with a 3–4 formylphenyl benzoic acid ligand were synthesized. Through a balance between ligand and lanthanide emission, which are excitation energy dependent, a wide chromaticity tunability range was demonstrated.

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