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Control of Green and Red Upconversion in NaYF₄:Yb³⁺,Er³⁺ Nanoparticles by Excitation Modulation

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Abstract

Control of the two strongest upconversion emission lines in NaYF₄:Yb³⁺, Er³⁺ nanoparticles is demonstrated by varying the excitation repetition rate. This technique may enable new multiplexed sensing modalities based on multicolor luminescent nanoparticles, currently contemplated for biomedical imaging and diagnostics.

Upconverting lanthanide nanoparticles are quickly developing as viable contrast agents for biomedical sensing applications due to their near infrared (NIR) absorption, anti-Stokes shifted and well-defined emission bands, long luminescence lifetime, and extreme photostability.^{1–3} Among upconverting nanoparticles, those composed of NaYF₄ doped with Yb³⁺,Er³⁺ or Yb³⁺,Tm³⁺, first synthesized by Heer et al in 2004, are well known for having exceptional upconversion efficiency.⁴ Excitation of these nanoparticles commonly utilizes the ²F_{7/2}→²F_{5/2} transition of trivalent ytterbium at 980 nm in order to sensitize a co-doped lanthanide ion. This NIR excitation allows for a greater depth of penetration than can be obtained with shorter wavelengths of light in tissue, while the resulting anti-Stokes shifted emission minimizes endogenous fluorescence interference and can occur at many different wavelengths based on selection of an appropriate co-doped ion. The exceptional photostability of these nanoparticles is such that photobleaching effects are virtually nonexistent.⁵ A number of improved preparative methods have been described since, and compatibility of coated or uncoated particles with water has been demonstrated.^{6–8}

Significant effort has been put into modification of preparative techniques to control relative intensities of Er³⁺ emission bands, yielding NaYF₄:Yb³⁺,Er³⁺ nanoparticles of desired colors in a broad spectral range.^{9–11} In a different approach, color selection has been demonstrated in hybrid systems by selective quenching of individual emission bands by absorbers placed proximate to NaYF₄:Yb³⁺,Er³⁺ nanoparticles.^{12,13} The presence of multiple emission bands in these nanoparticles enabled their application as ratiometric pH and temperature sensors by taking advantage of surface group vibrational modes in the former and the Boltzmann distribution of energetically close states in the latter.^{7,14,15}

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[†]Electronic Supplementary Information (ESI) available: X-ray diffraction data, power density dependence plots, luminescence decays for select NaYF₄:Er³⁺,Yb³⁺ transitions, sizing information, and constants associated with rate equations. See DOI: 10.1039/b000000x/

Of particular interest for biomedical assays are well resolved Er^{3+} emission lines in green, red and, to a lesser extent, in blue. The lack of spectral overlap and, perhaps fortuitous, match with the spectral separation of the Bayer filter mosaic widely used in color imaging, suggest opportunities in various multiplexed sensing and imaging modalities. To examine these opportunities we investigated the spectral properties of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ particles suspended in organic solvent under pulsed illumination. In this communication we report experimental control of the intensity ratio between red and green emission lines in $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles through control of the excitation timing.

$\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles were synthesized via a high temperature method similar to one previously demonstrated by Boyer et al.⁸ Briefly described, lanthanide precursors were prepared by dissolving lanthanide oxides at a molar ratio of 2% Er^{3+} , 20% Yb^{3+} , and 78% Y^{3+} in 50% aqueous trifluoroacetic acid at 80 °C. Ln-TFA precursors were then added to a solution of 1-octadecene and oleic acid and heated to 100 °C for 30 minutes. The resulting solution was heated to 300 °C for 1.5 hours under Ar. Following synthesis, the sample was precipitated with acetone, separated from solution via centrifugation, and washed twice with ethanol before being vacuum dried and dispersed in chloroform for analysis. A second set of nanoparticles was also synthesized with 20% Yb^{3+} and 80% Y^{3+} in order to measure the decay constant for the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition in Yb^{3+} .

All spectra and emission intensity measurements were made using a QE65000 back-thinned CCD array spectrometer (Ocean Optics, Dunedin, Florida, USA). Luminescence lifetime measurements were made by single photon counting avalanche photodiode (PerkinElmer, Vaudreuil, Québec, Canada) and multichannel scaler (Picoquant, Berlin, Germany). Excitation was provided by a tunable optical parametric oscillator (OPO) pumped by a Nd:YAG laser Q-switched at 20 Hz with a 3 ns pulse width or by a 980 nm laser diode. Nanoparticles in suspension were sized by quasi elastic light scattering using a ZS-90 Zetasizer (Malvern, Worcestershire, United Kingdom) and powder X-ray diffraction (XRD) was performed to determine crystal structure of the particles obtained.

Nanoparticles we synthesized had an average diameter of ~14 nm and XRD confirmed an α - NaYF_4 crystal structure (Fig. S1, Supplemental Materials), similar to previous work by Boyer et al.⁸ As can be seen in Figure 1, emission peaks were observed at 525, 546, 668, 800, and 847 nm when the sample was excited by a 980 nm laser diode pulsed at 6 kHz with 10 μs pulse width. These can be attributed to transitions from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, and $^4\text{I}_{9/2}$ to $^4\text{I}_{15/2}$ for the first four peaks respectively and from $^4\text{S}_{3/2}$ to $^4\text{I}_{13/2}$ for the peak at 847 nm (Fig. 2). A peak was also present at 417 nm, but was of much lower intensity when compared to other transitions.

Linear regression of $\ln(\text{emission intensity})$ vs. $\ln(\text{excitation power})$ resulted in slopes of approximately 1.91 and 1.90 for the two green transitions and 1.90 for the red transition. Over the range of power densities used for these experiments, less than 8 W/cm^2 average power density, the ratio between various emission peaks was observed to be fairly constant (Fig. S2, Supplemental Materials). However, we observed that the ratio of green to red emission (GRR) can be tuned by varying excitation frequency or pulse width.

Figure 3 demonstrates the principal finding of this communication, the change of GRR with changing excitation pulse width and frequency. As excitation frequency is increased from 0.01 kHz to 100 kHz, the GRR decreases from ~1.4 to 0.28. The emission ratio was calculated by dividing the integrated emission from the 546 and 525 nm peaks by the integrated emission from the 668 nm peak. The three data sets exhibit asymptotic-like behavior at high and low frequency. In addition to frequency dependent effects, it can also be seen from Figure 3 that the GRR decreases as pulse width increases for mid and low-

range frequency values. This dependence diminishes with increasing pulse width, becoming nearly nonexistent for pulses longer than ~400 μ s (data not shown).

This phenomenon can be explained by the complex population process of the excited states leading to 668 nm emission. Population of the $^4F_{9/2}$ excited state may occur through several different pathways. Three of these are illustrated in Figure 2. Nonradiative decay from $^4S_{3/2}$ or $^2H_{11/2}$ may directly populate $^4F_{9/2}$ and result in red emission. If this was the only route to red emission, the GRR would not be expected to vary with changing excitation frequency, since all three transitions involved, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$, would result from the same initial population route, $^4I_{15/2} \rightarrow ^4I_{11/2} \rightarrow ^4F_{7/2}$. Instead, the ability to tune the GRR in these nanoparticles can be attributed to the long lived $^4I_{13/2}$ state (Table 2). Nonradiative decay from $^4I_{11/2}$ or radiative decay from $^4S_{3/2}$ both populate $^4I_{13/2}$, which can then be excited to $^4F_{9/2}$ by energy transfer from a nearby ytterbium ion. It follows that the population of $^4F_{9/2}$, and hence the intensity of red emission, depends on population of $^4I_{13/2}$ at the time of energy transfer from Yb^{3+} to Er^{3+} .

The low extreme of the GRR shown in Figure 3 is obtained by maximizing the population of $^4F_{9/2}$, while limiting excitation of Er^{3+} ions to $^4F_{7/2}$. This is accomplished by repeating excitation of the sample when the population of $^4I_{13/2}$ has peaked from the previous excitation pulse. To determine when this occurs, luminescence lifetimes were collected for red and green emission following 980 nm excitation (Table 1), as well as following direct excitation at 546, and 630 nm (Table 2). The decays observed following direct excitation of excited states were fit fairly well with a single exponential term; however, some nonexponential behaviour was observed. This may be due to some population of Er^{3+} ions being more easily quenched than others. For example, ions located near the surface of the nanoparticles may be influenced more readily by vibrational modes of oleic acid, the solvent, or surface defects.

A brief treatment of the rate equations involved in upconversion luminescence of $NaYF_4:Yb^{3+},Er^{3+}$ nanoparticles illustrates how specific transitions are involved in the generation of green and red light. This treatment builds upon lanthanide luminescence analysis presented elsewhere.^{17,18} First, we assume that back energy transfer and excited state absorption (ESA) effects are negligible. Weak transitions and those that occur rapidly, such as $^4F_{7/2} \rightarrow ^4S_{3/2}$, are neglected, and transitions that would populate $^4F_{7/2}$ are instead listed as population routes for $^4S_{3/2}$. In addition, energy migration between Yb^{3+} ions is ignored here. With these simplifying assumptions, the rate equations may be described as follows:

$$\frac{dN_{s^*}}{dt} = F(t)\sigma_{s^*}N_{s^0} - (k_{02}N_0 + k_{13}N_1 + k_{24}N_2 + \frac{1}{\tau_s})N_{s^*} \quad (1)$$

$$\frac{dN_4}{dt} = k_{24}N_2N_{s^*} - W_{43}N_4 - \frac{N_4}{\tau_4} \quad (2)$$

$$\frac{dN_3}{dt} = k_{13}N_1N_{s^*} + W_{43}N_4 - \frac{N_3}{\tau_3} \quad (3)$$

$$\frac{dN_2}{dt} = F(t)\sigma_{02}N_0 + k_{02}N_0N_{s^*} - k_{24}N_2N_{s^*} - W_{21}N_2 - \frac{N_2}{\tau_2} \quad (4)$$

$$\frac{dN_1}{dt} = -k_{13}N_1N_{S^*} + W_{21}N_2 - \frac{N_1}{\tau_1} \quad (5)$$

where N_i represents the population of state i , as illustrated in Figure 2, k_{ij} (σ_{ij} , W_{ij} , τ_{ij}) represents the coefficient for energy transfer from Yb^{3+} to Er^{3+} (absorption cross-section, nonradiative decay, radiative decay) resulting in the transition from state i to state j , and $F(t)$ is the excitation photon flux. From here, we examine the extreme case for which the system relaxes completely to ground between excitation pulses, and the ground state populations, N_{S^0} and N_0 , are large and constant relative to other populations in the system. We examine the system following a narrow excitation pulse at $t = 0$ such that the excitation term may be replaced with an initial population in states S^* and N_2 . In equation 1, terms $k_{13}N_1$ and $k_{24}N_2$ are neglected as they are likely small compared to $k_{02}N_0$. Similarly, the $k_{13}N_0$ term is neglected in equation 5. With these assumptions, we obtain the following solutions for the first two excited state populations:

$$N_{S^*} = N_{S^*}^0 e^{-W_S t} \quad (6)$$

$$N_2 = C_{21}e^{-W_2 t} + C_{22}e^{-W_S t} \quad (7)$$

where W_i is the sum of decay rates for state i and W_S is the sum of decay rates for the sensitizer, Yb^{3+} , and C_{ik} are constants.

For the equations above, the emission observed at 980 nm following a single 980 nm excitation pulse is made up of two decay components related to the luminescence lifetimes of states S^* and 2, which matches our experimental observation (Table 2). Using the solutions for these two states, we approximate the populations of the states that result in green and red emission:

$$N_4 = C_{41}e^{-W_4 t} + C_{42}e^{-(W_S + W_2)t} + C_{43}e^{-2W_S t} \quad (8)$$

$$N_3 = C_{31}e^{-W_3 t} + C_{32}e^{-(W_{10} + W_S)t} + C_{33}e^{-(W_2 + W_S)t} + C_{34}e^{-2W_S t} + C_{35}e^{-(W_4 + W_S)t} \quad (9)$$

While a complete assessment of C_{ik} constants is beyond the scope of this communication (see Supplemental Materials for a more detailed description), a general result that applies to many of the terms involved is that short lived states will determine the time constants associated with an exponential rise in the populations of N_3 and N_4 , while the longer time constants in the system will determine how these states decay over time. While we have made the fits in Table 1 using a single exponential rise and decay, the time constants we obtain experimentally do not correspond directly to any pair of time constants within this system. Instead, they represent a mixture of different transition rates which are well fit with a single time constant for the rise and decay each.

Because the lifetime of $^4\text{F}_{9/2}$ is shorter than other time constants involved in the generation of red emission, we argue that the decay profile is largely determined by decay of the states leading up to $^4\text{F}_{9/2}$ and the rise profile is determined by the population of those states as well as the decay of $^4\text{F}_{9/2}$. For this reason, we conclude that the peak of red emission occurs at approximately the same time as peak $^4\text{I}_{13/2}$ population, $\sim 123 \mu\text{s}$ after excitation (Fig. S3, Supplemental Materials). This minimum GRR is seen in Figure 3, at a pulse repetition frequency of 6 kHz, corresponding to a pulse repetition interval of $167 \mu\text{s}$. Exciting the

nanoparticles more often than once every 167 μs will favor red emission less as peak green emission occurs after $\sim 40 \mu\text{s}$ (Fig. S3, Supplemental Materials).

As the excitation frequency is decreased from 6 kHz, the population of $^4\text{I}_{13/2}$ upon arrival of the next pulse in the train decreases. This is expressed as an increase in the GRR until $^4\text{I}_{13/2}$ completely depopulates between pulses, at which point the GRR is determined entirely by the properties of a single pulse in the train and approaches an asymptotic maximum (Fig. 3). At these low frequencies, the GRR decreases with increasing pulse width, which can be attributed to continuing excitation of Yb^{3+} ions and subsequent energy transfer to Er^{3+} at later times in a single pulse, after some number of Er^{3+} ions have entered the $^4\text{I}_{13/2}$ excited state. This also explains the change in GRR with changing pulse width reported in prior work by Morgan and Mitchell.¹⁹

Asymptotic behaviour observed at low frequency is likely the result of two limiting activities. First, multiphonon decay from $^4\text{S}_{3/2}$ to $^4\text{F}_{9/2}$ will result in some level of red emission under any excitation profile that results in green emission. Second, because the excited state lifetime of Yb^{3+} is comparable to the rate constants for other processes within this system, $\sim 146 \mu\text{s}$ in $\text{NaYF}_4\cdot\text{Yb}^{3+}$ particles, energy transfer continues to occur after the laser excitation pulse has ended. This allows time for the $^4\text{I}_{13/2}$ state of erbium to populate such that $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$ may occur via energy transfer after the excitation pulse has ended, resulting in red emission. A complete analysis of the GRR as it relates to the excitation repetition rate and pulse width can be facilitated by an appropriate choice of $F(t)$ in equations 1 and 4 and subsequent evaluation of the ratio: $\int_0^\infty N_4 dt / \int_0^\infty N_3 dt$

It should be noted that the phenomena described herein are necessarily dependent on the medium in which the nanoparticles are suspended. We carried out these experiments in chloroform in order to examine the case where solvent quenching is negligible, as would be the case for particles rendered inaccessible to water by an appropriately chosen coating. However, in the presence of a solvent that quenches particle emission, such as water, we expect a change in the GRR's dependence on excitation frequency. If all states involved are affected equally by solvent quenching, then the expected change is a shift in the GRR curve presented in Figure 3 toward higher repetition rates. However, if solvent quenching affects each of the involved states differently, the change in GRR is likely to be less intuitive.

In conclusion, we have shown that the ratio of green to red emission in upconverting $\text{NaYF}_4\cdot\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles is dependent on 980 nm excitation frequency and excitation pulse width. The ability to control the emission ratio through excitation frequency may have uses in biomedical sensing applications, specifically in super resolution microscopy and energy transfer techniques. For example, in the area of near-field optical microscopy with FRET probes,^{20,21} these excitation-controlled nanoparticles may enable mapping of multiple chromophores in functional assays by acting as switchable energy donors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

Left: Emission spectra for $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles normalized to peak green emission intensity. The spectrum shown by the dotted line was collected using a 980 nm diode laser pulsed at 6 kHz with a 10 μs pulse width. The spectrum shown by the solid line was collected with the same source pulsed at 20 Hz with a 10 μs pulse width. Right: Image of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles illuminated simultaneously by two 980 nm lasers at different frequencies and pulse widths. The top beam was pulsed at 166 kHz with a pulse width of 0.5 μs and the bottom beam was pulsed at 0.267 kHz with a pulse width of 200 μs .

Fig. 2.

Energy level diagram of energy transfer system between Yb^{3+} and Er^{3+} in $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. Grey arrows represent routes for nonradiative decay, dashed arrows represent excitation and decay by energy transfer from Yb^{3+} to Er^{3+} . The diagram was constructed based on prior work by Carnall et al.¹⁶ as well as experimental data.

Fig. 3. Change in ratio of green emission to red emission from NaYF₄:Yb³⁺,Er³⁺ nanoparticles with changing excitation pulse width and frequency. Excitation was by a pulsed 980 nm diode laser. Times listed in the legend refer to excitation pulse width. The inset shows the same data represented as the red to green ratio vs. time between pulses. This curve, well fit by a single exponential rise and decay with a decay time constant of 2.06 ms, is related to population of the ⁴I_{13/2} probed by subsequent excitation pulses.

Table 1

Time Constants Associated with Upconversion Resulting in Green and Red Emission

Color	Measured Transition	τ_r (μ s)	τ_d (μ s)
Green	$^4S_{3/2} \rightarrow ^4I_{15/2}$	11.35	231.7
Red	$^4F_{9/2} \rightarrow ^4I_{15/2}$	65.76	334.1

Excitation was by OPO/Nd:YAG laser tuned to 980 nm with 3 ns pulse width and 20 Hz pulse repetition rate. Time constants for rise and decay of luminescence were obtained by curve fitting data to two exponential terms representing the rise and decay of the involved states.

Table 2Luminescence Lifetimes of Transitions in NaYF₄:Er³⁺, Yb³⁺ Nanoparticles Following Direct Excitation

Transition	τ_1 (μ s)	A_1 (%)	τ_2 (μ s)	A_2 (%)
$^4F_{7/2} \rightarrow ^4I_{15/2}$	6.41	100	-	-
$^4S_{3/2} \rightarrow ^4I_{15/2}$	293.3	100	-	-
$^4F_{9/2} \rightarrow ^4I_{15/2}$	82.76	100	-	-
$^4I_{11/2}, ^2F_{5/2} \rightarrow ^4I_{15/2}, ^2F_{7/2}^a$	23.42	61	323.6	39
$^4I_{13/2} \rightarrow ^4I_{15/2}^b$	3200	100	-	-

Excitation was by 3 ns OPO/Nd:YAG laser tuned to match the energy gap between $^4I_{15/2}$ and the excited state of interest.

^a A two exponential fit was used. A_1 and A_2 are used here to describe the amplitude weights of the exponential decays.

^b Decay of this state was inferred from emission collected at 980 nm following excited state absorption with 1500 nm excitation (Fig. S4, Supplemental Materials).