

Upconversion Multicolor Fine-Tuning: Visible to Near-Infrared Emission from Lanthanide-Doped NaYF₄ Nanoparticles

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The ability to manipulate color output of nanomaterials is important for their applications as light emitting displays, lasers, and optoelectronic devices to multiplexed biological labeling. Various approaches, based upon tailoring surface plasmon resonance,¹ controlling emission wavelengths,² and utilizing multicolor-encoded microbeads,³ have been used to tune the color output. Most of these approaches involve excitation in the ultraviolet or blue spectral region, thus posing limitations in bioimaging studies due to autofluorescence, photobleaching, and photodamage to biological specimens. In contrast, near-infrared (NIR) multiphoton microscopy that has been used to excite organic dyes and quantum dots for fluorescence imaging offers high penetration depth and high spatial and temporal resolution.⁴ However, these systems typically require complex experimental setup, high excitation densities (10^6 – 10^9 W cm⁻²), and expensive pulsed lasers due to the involvement of a nonstationary quantum mechanical state.⁵

Alternatively, photon upconversion can be used for the generation of visible emission by NIR excitation of lanthanide (Ln³⁺)-doped nanoparticles (NPs).⁶ Owing to the ladder-like arranged energy levels of Ln³⁺ ions, high efficiency of the photon upconversion can be obtained by lamp excitation or continuous wave lasers with moderate excitation densities (1 – 10^3 W cm⁻²). Although multicolor upconversion emission has been reported by using different host/activator combinations,^{6b,d,j} there is no established approach to *fine-tuning* upconversion emission for a much broader range of color output by single-wavelength excitation. Here, we present a general approach, based on tuning relative emission intensity of Ln³⁺-doped NaYF₄ NPs, to color modulation from visible to NIR emission.

The synthesis of Ln³⁺-doped NaYF₄ NPs was developed via a modified literature procedure (Supporting Information).⁶ⁱ Polyethylenimine (PEI) molecules were used to stabilize Ln³⁺ ions and subsequently control the growth of NPs upon addition of fluoride ions. More importantly, the PEI-coated NPs provide a platform for direct surface functionalization of biomolecules by bioconjugate chemistry (vide infra). The NPs were dispersible in various solvents including water, ethanol, dimethylformamide, dimethylsulphoxide, and ethylene glycol (Figure S1, Supporting Information). Unlike metallic particle (or dye) solutions, the Ln³⁺-doped particle solutions are largely transparent (>90%) to visible light as evidenced by the optical transmission spectrum shown in Figure 1a. Transmission electron microscopy (TEM) shows spherical morphology of the NaYF₄:Yb/Er (18/2 mol %) particles with an average diameter of 20 nm (Figure 1b). High-resolution TEM (inset, Figure 1b) shows lattice fringes with an observed *d*-spacing of 0.31 nm, which is in good agreement with the lattice spacing in the (111) planes of cubic NaYF₄ (0.316 nm, JCPDS file number 77-2042). Compositional analysis

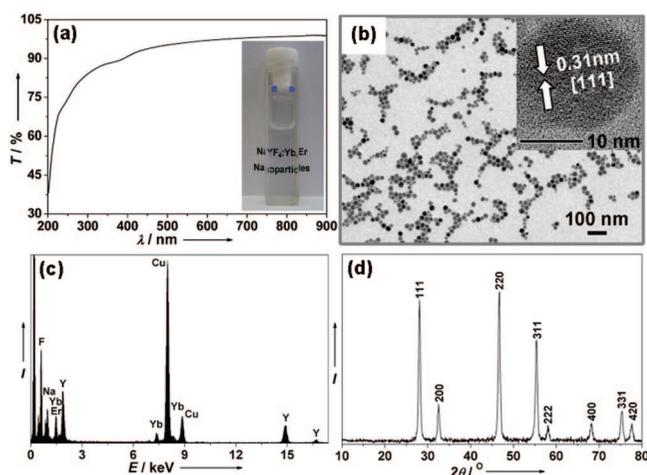


Figure 1. (a) A typical transmission spectrum of the NaYF₄:Yb/Er (18/2 mol %) particles in ethanol solutions (inset: a photograph showing transparency of the particle solution). (b) TEM image of the particles (inset: HRTEM showing the lattice fringes). (c) EDX and (d) XRD patterns of the particles. Note that the strong signals for Cu in (c) come from the copper TEM grid.

of an individual particle by energy-dispersive X-ray spectroscopy (EDX) reveals the presence of the doped elemental Yb and Er (Figure 1c). X-ray powder diffraction (XRD) patterns of the NPs exhibit peak positions and intensities that can be well indexed in accord with cubic NaYF₄ crystals, suggesting high crystallinity of the product (Figure 1d). The NPs that comprise varied dopants or dopant concentrations exhibit essentially the same crystal phase (Figure S2, Supporting Information).

As a proof-of-concept experiment, a binary dopant system (Yb³⁺/Er³⁺) was chosen for upconversion multicolor fine-tuning. Upon excitation at 980 nm, the NaYF₄ nanoparticles co-doped with Yb/Er (18/2 mol %) exhibit characteristic sharp emission peaks, which can be attributed to ²H_{9/2}→⁴I_{15/2}, ²H_{11/2}, ⁴S_{3/2}→⁴I_{15/2}, and ⁴F_{9/2}→⁴I_{15/2} transitions of Er³⁺ (Figure 2a). These peaks correspond to respective blue, green, and red emissions that result in an overall yellow color output (Figure 2k). We reasoned that introduction of an elevated amount of Yb³⁺ dopants in the NaYF₄ host lattice would decrease Yb···Er interatomic distance and thus facilitate back-energy-transfer from Er³⁺ to Yb³⁺ (Figure S3, Supporting Information). The energy transfer should subsequently suppress the population in excited levels of ²H_{9/2}, ²H_{11/2}, and ⁴S_{3/2}, resulting in the decrease of blue (²H_{9/2}→⁴I_{15/2}) and green (²H_{11/2}, ⁴S_{3/2}→⁴I_{15/2}) light emissions. As anticipated, upon doping with increased concentrations of Yb³⁺ (25–60%), one can precisely manipulate the relative

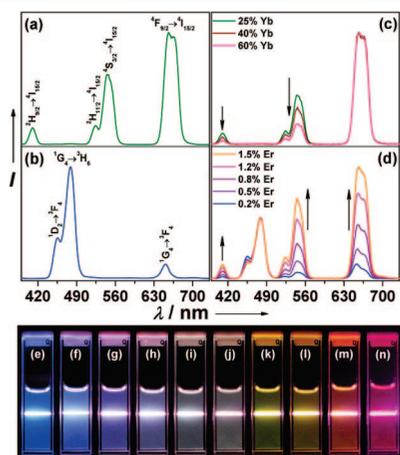


Figure 2. Room temperature upconversion emission spectra of (a) NaYF₄:Yb/Er (18/2 mol %), (b) NaYF₄:Yb/Tm (20/0.2 mol %), (c) NaYF₄:Yb/Er (25–60/2 mol %), and (d) NaYF₄:Yb/Tm/Er (20/0.2/0.2–1.5 mol %) particles in ethanol solutions (10 mM). The spectra in (c) and (d) were normalized to Er³⁺ 650 nm and Tm³⁺ 480 nm emissions, respectively. Compiled luminescent photos showing corresponding colloidal solutions of (e) NaYF₄:Yb/Tm (20/0.2 mol %), (f–j) NaYF₄:Yb/Tm/Er (20/0.2/0.2–1.5 mol %), and (k–n) NaYF₄:Yb/Er (18–60/2 mol %). The samples were excited at 980 nm with a 600 mW diode laser. The photographs were taken with exposure times of 3.2 s for e–l and 10 s for m and n.

emission intensities of the three constituent colors, thus resulting in tunable color output of the NPs from yellow to red (Figure 2l–n).

In a further set of experiments, we demonstrated that upconversion multicolor fine-tuning in the visible spectral region can be alternatively achieved via a three-component dopant system (NaYF₄:Yb/Er/Tm) in a dual emission process. Prior to doping of Er³⁺, the co-doped NaYF₄:Yb/Tm system exhibits a blue color emission (Figure 2e), resulting from ¹D₂→³F₄, ¹G₄→³H₆, and ¹G₄→³F₄ transitions of Tm³⁺ (Figure 2b). By adding a second emitter (Er³⁺) with different concentrations to the system, the relative intensity ratio of the dual emissions can be precisely controlled. For example, subtle variations in the Er³⁺ concentration (0.2–1.5%) lead to prominent changes in the green (²H_{11/2}, ⁴S_{3/2}→⁴I_{15/2}) and red (⁴F_{9/2}→⁴I_{15/2}) spectral region, accompanied by a slight change in the blue emission (²H_{9/2}→⁴I_{15/2}) (Figure 2d). Consequently, the adjustable balance of emission intensities allows the tri-doped (Yb³⁺/Er³⁺/Tm³⁺) particle system to display tunable color output from blue to white as shown in Figure 2f–j.

To expand the emission fine-tuning in the NIR spectral region, we utilized NaYF₄:Yb/Tm (20/0.2%) NPs that exhibit a weak emission maximum at around 800 nm (³H₄→³H₆) upon excitation at 980 nm. By increasing the Tm³⁺ concentration up to 2%, the intensity of NIR emission was considerably enhanced (Figure 3). The phenomenon is primarily attributed to enhanced population of ³H₄ level generated by the energy resonant between ¹G₄→³H₄ and ³F₂←³F₄.^{6a} Cross-relaxation becomes significant as the Tm···Tm distance decreases because of the increased Tm content in the host lattice. Thus, we can precisely manipulate the relative intensity of the blue to NIR emissions by varying the dopant concentration of Tm³⁺.

To investigate the direct surface biofunctionalization of the PEI-coated NPs, we covalently attached biotin to the surface of the NaYF₄:Yb/Er NPs (Supporting Information). The selective recognition of the particles to fluorescein isothiocyanate (FITC)-labeled avidin was confirmed by monitoring the FITC emission intensity. Upon incubation with the avidin, the emission

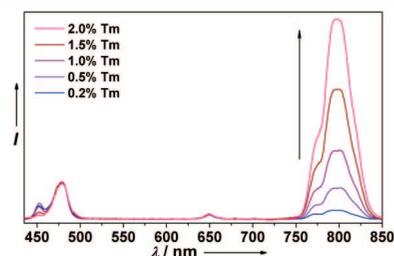


Figure 3. Room temperature upconversion emission spectra (normalized to Tm³⁺ 480 nm emission) of NaYF₄:Yb/Tm (20/0.2–2 mol %) particles in ethanol solutions (10 mM) under 980 nm excitation with a 600 mW diode laser.

spectrum of the particle solution exhibits a significant increase in FITC signal relative to the nonbiotinylated NPs (Figure S4, Supporting Information).

In conclusion, we have presented a general and versatile approach to fine-tuning the upconversion emission colors, based upon a single host source of NaYF₄ nanoparticles doped with Yb³⁺, Tm³⁺, and Er³⁺. By precise control of the emission intensity balance through control of different combinations of lanthanide dopants and dopant concentration, the luminescence emission can be deliberately tuned from visible to NIR under single-wavelength excitation. The approach can be readily applied to a broad range of host/activator combinations, and a significant increase of the emission intensities might also be expected when hexagonal NaYF₄ particles are used. These studies suggest a general route for the development of novel luminescent probes that are particularly useful in multiplexed labeling.

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Supporting Information Available: Experimental procedures, Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Shatz, G. C.; Zheng, J. *Science* **2001**, *294*, 1901. (b) Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316. (c) Schwartzberg, A. M.; Olson, T. Y.; Talley, C.; Zhang, J. Z. *J. Phys. Chem. B* **2006**, *110*, 19935. (d) Wiley, B. J.; Chen, Y.; McLellan, J. M.; Xiong, Y.; Li, Z.-Y.; Ginger, D. S.; Xia, Y. *Nano Lett.* **2007**, *7*, 1032. (e) Tao, A. R.; Sinsernsukakul, P.; Yang, P. *Nat. Nanotechnol.* **2007**, *2*, 435. (f) Kubo, S.; Diaz, A.; Tang, Y.; Mayer, T. S.; Khoo, I. C.; Mallouk, T. E. *Nano Lett.* **2007**, *7*, 3418.
- (a) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. (b) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (c) Medintz, I. L.; Uryeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater.* **2005**, *4*, 435. (d) Cao, Y. C.; Wang, J. *J. Am. Chem. Soc.* **2004**, *126*, 14336. (e) Pan, A.; Yang, H.; Liu, R.; Yu, R.; Zou, B.; Wang, Z. *J. Am. Chem. Soc.* **2005**, *127*, 15692.
- (a) Han, M.; Gao, X.; Su, J.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631. (b) Wang, L.; Tan, W. H. *Nano Lett.* **2006**, *6*, 84.
- (a) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73. (b) Larson, D. R.; Zipfel, W. R.; Williams, R. M.; Clark, S. W.; Bruchez, M. P.; Wise, F. W.; Webb, W. W. *Science* **2003**, *300*, 1434.
- König, K. *J. Microsc.* **2000**, *200*, 83.
- (a) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin, 1994. (b) Heer, S.; Lehmann, O.; Hasse, M.; Güdel, H.-U. *Angew. Chem., Int. Ed.* **2003**, *42*, 3179. (c) Auzel, F. *Chem. Rev.* **2004**, *104*, 139. (d) Heer, S.; Kömpe, K.; Güdel, H.-U.; Haase, M. *Adv. Mater.* **2004**, *16*, 2102. (e) Yi, G.; Lu, H.; Zhao, S.; Yue, G.; Yang, W.; Chen, D.; Guo, L. *Nano Lett.* **2004**, *4*, 2191. (f) Zeng, J.; Su, J.; Li, Z.; Yan, R.; Li, Y. *Adv. Mater.* **2005**, *17*, 2119. (g) Sivakumar, S.; van Veggel, F. C. J. M.; Raudsepp, M. *J. Am. Chem. Soc.* **2005**, *127*, 12464. (h) Boyer, J. C.; Vetrone, F.; Cuccia, L. A.; Capobianco, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 7444. (i) Wang, F.; Chatterjee, D. K.; Li, Z.; Zhang, Y.; Fan, X.; Wang, M. *Nanotechnology* **2006**, *17*, 5786. (j) Ehlert, O.; Thomann, R.; Darbandi, M.; Nann, T. *ACS Nano* **2008**, *2*, 120. (k) Chatterjee, D. K.; Rufaihah, A. J.; Zhang, Y. *Biomater.* **2008**, *29*, 937.

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