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A Strategy to Achieve Efficient Dual-Mode Luminescence of Eu³⁺ in Lanthanides Doped Multifunctional NaGdF₄ Nanocrystals

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Trivalent lanthanide (Ln³⁺) ions doped luminescent nanocrystals (NCs) of various compositions, albeit most of their bulk counterparts have been well studied previously, have attracted reviving interest and come to the forefront in nanophotonics owing to their distinct electrical, optical and magnetic properties as well as their potential applications in diverse fields such as LEDs, lasers, biological labeling and imaging.^[1] Compared to conventional luminescent materials such as organic fluorescent dyes and quantum dots (QDs), these Ln³⁺ doped NCs show more superior features including narrow emission band widths (<10 nm),^[2] long luminescence lifetime (µs-ms range)^[2b,c] and low long-term toxicity.^[3] These features coupled with the higher resistance to photobleaching relative to that of organic fluorescent dyes make them highly suitable for use as alternatives to organic fluorescent dyes and QDs for various biological applications. In particular, inorganic fluorides have the advantages of high chemical stability and intrinsic low phonon energies (~350 cm⁻¹), and thereby are often employed as host materials for the doping of Ln³⁺ to achieve the desirable downconversion (DC) or upconversion (UC) luminescence of Ln³⁺.^[4] Because of well-established efficient UC luminescence, considerable efforts have been devoted to the synthesis and multicolor tuning of Ln³⁺-doped NaYF₄ UC NCs, where Yb³⁺ acting as the sensitizer with a large absorption cross-section at ~980 nm is usually codoped along with the most common UC activator ions (Er³⁺, Tm³⁺ and Ho³⁺) to produce strong red, green, and violet UC emissions.[5]

Hexagonal-phase NaGdF₄ (β -NaGdF₄), another excellent candidate as the host of UC materials, has been occasionally used to fabricate Ln³⁺-doped UC NCs in the past few years.^[6] In comparison with the NaYF₄ counterpart, NaGdF₄ can not only offer comparable UC luminescence, but also serve as an ideal UV sensitizer or intermediate to activate specific DC of Ln³⁺ ions such as Eu³⁺ and Tb³⁺, inducing intense red and green DC emissions in the visible region.^[6b,7] These optical features of NaGdF₄ thus enable the designing of multifunctional NaGdF₄ NCs with combined dual-mode (that is, UC and DC) detection. Li et al. recently reported dual-mode luminescence from colloidal spheres assembled from the binary mixture of LaF₃ and

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NaYF₄ NCs.^[8] However, to the best of our knowledge, there is no report on the functionalization of single NaGdF4 NC that combines both UC and DC modes from identical Ln³⁺ ions, though individual UC or DC luminescence can be readily realized in NaGdF₄:Ln³⁺ NCs. Furthermore, it should be noted that the vast majority of UC studies are limited to the Er3+, Tm3+ and/ or Ho³⁺ ions doped NCs at present, in view of their ladder-like energy levels that will facilitate the energy transfer (ET) from sensitizer to activator in UC processes.^[9] It is highly desirable that intense UC luminescence can be extended to other Ln3+ ions such as Eu³⁺, so that it may possess typical long-lived luminescence of Eu³⁺ as well as the advantage of near infrared (NIR) excitation (~980 nm). Nevertheless, due to large energy mismatch (~5000 or 7000 cm⁻¹) for the ET between the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of Yb³⁺ and the ${}^{7}F_{0} \rightarrow {}^{7}F_{6}$ (or ${}^{5}D_{0}$) transition of Eu³⁺,^[10] it is formidably difficult to achieve efficient UC emission of Eu³⁺ via conventional approaches by simply co-doping Yb³⁺ in NCs. Herein, we demonstrate a strategy to fabricate uniform β-NaGdF₄ NCs that are composed of the NaGdF₄:Yb,Tm core and the NaGdF4:Eu shell in order to achieve dual-mode (UC and DC) luminescence from identical Eu³⁺ ions (Figure 1a). Efficient UC luminescence of Eu³⁺ is observed in NaGdF₄ core/ shell NCs upon NIR excitation at 976 nm by taking advantage of Yb^{3+} and Tm^{3+} ions in the cores as double sensitizers and the merit of core/shell nanostructures. Meanwhile, intense red DC emission of Eu³⁺ can be obtained via the sensitization of Gd³⁺ when excited at 273 nm. The combination of intense UC and DC luminescence of Eu³⁺ coupled with the paramagnetic property of Gd³⁺ in NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs should offer one type of promising multifunctional nanomaterial, showing potentials to be used as a multiplexed luminescent biolabel and magnetic resonance imaging (MRI) contrast agent.

The syntheses of β -NaGdF₄:Yb,Tm core and β -NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs were adapted from the procedure reported for β -NaYF₄/NaYF₄ core/shell NCs.^[11] The β -NaGdF₄:Yb,Tm core NCs were grown first and then served as the seed crystals for the shell growth in the presence of oleic acid and 1-octadecene, resulting in the formation of β -NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs. The oleic acid was chosen as the capping ligand to control the particle growth and to prevent the NCs from aggregation. As expected, the oleic acidcapped NCs are rendered hydrophobic and dispersible readily in a variety of nonpolar solvents such as cyclohexane, forming a clear colloidal solution (Figure 1b-e). The hydrophobic nature of these NCs will provide a platform for surface functionalization to endow these oleic acid-capped NCs with aqueous solubility prior to their biological applications, by using surface modification strategies such as ligand oxidation and ligand exchange.^[12]

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Figure 1. a) Schematic illustration of the general strategy to achieve the dual-mode luminescence of Eu^{3+} in NaGdF₄ NCs. b) A photograph shows the transparency of NaGdF₄:Yb,Tm/ NaGdF₄:Eu core/shell NCs in cyclohexane solution. c) UC luminescence photograph of NaGdF₄:Yb (18 mol%),Tm (1 mol%) core only NCs in cyclohexane solution upon excitation at 976 nm. d) DC and e) UC luminescence photographs of NaGdF₄:Yb (18 mol%),Tm (1 mol%)/ NaGdF₄:Eu (10 mol%) core/shell NCs in cyclohexane solution when excited at 273 and 976 nm, respectively. f,g) TEM images of monodisperse NaGdF₄:Yb (18 mol%),Tm (1 mol%) core and (h,i) NaGdF₄:Yb (18 mol%),Tm (1 mol%)/NaGdF₄:Eu (10 mol%) core/shell NCs at different magnifications. ET, NIR, UV, UC, and DC denote the energy transfer, near infrared, ultraviolet, upconversion, and downconversion, respectively.

Figure 1f–i show transmission electron microscopy (TEM) images of the resulting NCs before and after the shell growth. From the TEM image in Figure 1f, it can be seen that the β -NaGdF₄:Yb,Tm cores are monodisperse and uniform NCs with an average diameter of 15 ± 0.7 nm. The high-resolution TEM (HRTEM) image (Figure 1g) shows lattice fringes with an observed d-spacing of 0.52 nm, which is in good agreement

peaks centered at ~591, 615 and 696 nm can be easily assigned to the de-excitation from 5D_0 to its lower states of 7F_1 , 7F_2 and 7F_4 of Eu $^{3+}$ (Figure 2a, right), respectively.^[15]

Figure 2b shows the UC emission spectra for both the core only and core/shell NCs. Upon NIR excitation at 976 nm (power density of ~6 W/cm²), the NaGdF₄ core only NCs co-doped with Yb/Tm (18/1 mol%) exhibit characteristic

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with the lattice spacing in the (100) planes of

hexagonal-phase NaGdF₄, indicative of high

crystallinity of the core NCs. Similarly, the β -NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs

are also uniform and monodisperse with the diameter of 25 ± 0.9 nm (Figure 1h–i). The size increase of the core/shell NCs along with

highly uniform morphology, similar to that

observed in NaYF₄/NaGdF₄ core/shell^[13] and

NaGdF₄ active core/active shell^[14] NCs, suggests that the NaGdF₄:Eu shell was grown on the surface of NaGdF₄:Yb,Tm core NCs. Lattice fringes corresponding to the (100) planes

of hexagonal-phase NaGdF4 can be observed

in HRTEM image (Figure 1i) and show the highly crystalline nature of the core/shell NCs. The highly crystalline core and core/ shell NCs can be further confirmed by the

X-ray powder diffraction (XRD) analysis. All the

XRD peaks for both core and core/shell NCs

(Figure S1 in the Supporting Information) can be well indexed in accordance with the standard pattern of hexagonal-phase NaGdF₄ (JCPDS. No. 27-0699), indicating the formation of pure β -NaGdF₄ NCs. Compositional analyses by energy dispersive X-ray spectroscopy (EDS) reveal the presence of the doped elements of Yb, Tm for core NCs and Yb, Tm

and Eu for core/shell NCs (Figure S2).

To demonstrate the feasibility of our

strategy, DC and UC photoluminescence (PL) studies were carried out on the core and core/ shell NCs, respectively. **Figure 2a** shows the PL excitation and DC emission spectra of Eu³⁺ in the shell of NaGdF₄:Yb(18%), Tm(1%)/ NaGdF₄:Eu(10%) core/shell NCs (hereafter referred to as the core/shell NCs). The PL excitation spectrum of Eu³⁺ (Figure 2a, left) is dominated by the sharp excitation lines centered at ~273 nm that correspond to the typ-

ical ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$ transitions of Gd³⁺, whereas the emission spectrum displays the fingerprint of

Eu³⁺ ions when indirectly excited at 273 nm

(Figure 2a, right), suggesting that the Eu³⁺

emission can be achieved via an ET process

from the host to emitters. In this process,

trivalent Gd³⁺ ions act as a light-harvesting

antenna (i.e. sensitizer) to absorb UV excita-

tion light and subsequently transfer energy

to the neighboring Eu^{3+} ions, resulting in the

overall red emission of Eu^{3+} as presented in the PL photo in Figure 1d. The DC emission





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Figure 2. a) PL excitation ($\lambda_{em} = 615$ nm) and DC emission ($\lambda_{exc} = 273$ nm) spectra for Eu³⁺ in NaGdF₄:Yb (18 mol%),Tm (1 mol%)/NaGdF₄:Eu (10 mol%) core/shell NCs, and b) UC emissions of NaGdF4:Yb (18 mol%),Tm (1 mol%) core and NaGdF₄:Yb (18 mol%),Tm (1 mol%)/ NaGdF₄:Eu (10 mol%) core/shell NCs ($\lambda_{exc} = 976$ nm).

sharp emission peaks, which can be attributed to the ${}^3P_0{\rightarrow}{}^3F_4$ (345 nm), ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ (361 nm), ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ (450 nm), ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ (476 nm), ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ (646 nm), and ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ (801 nm) transitions of Tm³⁺ (Figure 2b),^[1e,16] respectively, yielding an intense blue

color output that is visible to the naked eye (Figure 1c). The integrated blue UC intensity of Tm³⁺ for the NaGdF₄ core only NCs is ca. 1.7-fold higher than that of β -NaYF₄:Yb/Tm (18/1 mol%) NCs (a highly efficient blue UC emitter) synthesized using the same method (Figure S3), giving rise to a roughly estimated UC efficiency of 0.3-2.6% based on previous measurements for the blue UC efficiency of NaYF₄:Yb/Tm (which is within the order of magnitude of 0.2-1.5%).^[17] In stark contrast, the UC emission spectrum for the core/ shell NCs differs markedly from that of the original core NCs after coating an extra shell of NaGdF₄:Eu(10%) (Figure 2b). Although no significant enhancement in the UC emission of Tm³⁺ is observed, as opposed to that in NaYF₄:Yb,Tm/NaYF₄ core/shell NCs,^[11,18] a set of new UC emission peaks in addition to those of Tm³⁺ appear in Figure 2b following excitation at 976 nm. These unusual UC emissions emerging in the visible are originated from Eu³⁺ in the shells instead of Tm³⁺ in the cores, which can be unambiguously assigned to the ${}^{5}D_{2} \rightarrow {}^{7}F_{3}$ (510 nm), ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ (536 nm), ${}^{5}D_{1} \rightarrow {}^{7}F_{2}$ (556 nm), ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ (584 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (591 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (615 nm), and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (696 nm) transitions of Eu³⁺.^[10,15] The combination of intense UC emissions of Eu³⁺ and Tm³⁺ in the core/shell NCs can extend the overall UC color output to pink (Figure 1e). The UC efficiency for the red emissions of



 Eu^{3+} can be roughly estimated to be in the range of 0.6–4.6% by utilizing the blue UC emissions of Tm³⁺ as an internal standard for the core/shell NCs. Moreover, it is found that the observed UC emissions of Eu³⁺ increase with increasing Eu³⁺ concentration (1, 5 and 10 mol%). By contrast, when the concentration of Tm^{3+} doped in the core increases from 0.3 to 1 mol%, the UC emissions of Eu³⁺ increase first, reaching the maximum at 0.5 mol%, and then remain nearly unaltered in the concentration range from 0.5 to 1 mol% (Figure S4). To the best of our knowledge, such efficient UC luminescence of Eu³⁺ has not been reported in monodisperse Eu³⁺-doped NaGdF₄ NCs previously.

Different from Tm³⁺ (or Er³⁺) in Yb³⁺ ions co-doped UC NCs, Eu³⁺ can not be directly sensitized via the ET between Yb³⁺ and Eu³⁺, since there exists large energy mismatch between the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of Yb³⁺ and the ${}^{7}F_{0} \rightarrow {}^{7}F_{6}$ (or ${}^{5}D_{0,1}$) transition of Eu³⁺. This can be verified from the absence of the UC luminescence of Eu³⁺ in NaGdF₄:Yb,Eu NCs or NaGdF₄:Yb/ NaGdF₄:Eu core/shell NCs under identical experimental conditions (not shown). Interestingly, after the introduction of Tm³⁺ into the NaGdF4:Yb core, intense UC emissions of Eu3+ that are comparable to that of Tm³⁺ can be detected, which indicates that Tm^{3+} is an essential dopant ion that serves as a bridge to transfer energy from Yb³⁺ to activators as established in previous reports.^[19] To shed more light on the effect of Tm³⁺ on the UC emissions of Eu³⁺, we measured the UC luminescence of Yb³⁺/Tm³⁺/Eu³⁺ (18/1/10,5,1 mol%) triply-doped NaGdF₄ NCs (Figure 3a). With increasing Eu³⁺ dopant concentrations up to



Figure 3. a) The comparison of UC emissions of Yb/Tm/Eu (18/1/10,5,1 mol%) triply-doped and the core/shell NCs upon excitation at 976 nm. b) In-In plots of the UC emission intensity versus NIR excitation power for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ and the ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$, ${}^{3}H_{6}$ transitions of Tm³⁺. c) UC luminescence decays of the ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition of Tm³⁺ for (1,2) Yb/Tm/Eu (18/1/ 10,1 mol%) triply-doped NaGdF₄, (3) NaGdF₄:Yb (18 mol%),Tm (1 mol%) core and (4) the core/ shell NCs ($\lambda_{exc} = 976$ nm). d) DC luminescence decays of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ for (1,2) Yb/Tm/Eu (18/1/10,1 mol%) triply-doped NaGdF4 and (3) the core/shell NCs when excited at 273 nm. All the luminescence decay curves are fitted by using a single exponential function.

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Energy (10³ cm⁻¹)

a 40

30

20

10

0

7/2

Gd



Figure 4. a) Proposed energy transfer processes responsible for the intense DC and UC luminescence of Eu^{3+} in the core/shell NCs. b) Time evolution of UC emission spectra for the core/shell NCs when excited at 976 nm and c) their corresponding CIE chromaticity coordinates.

Yb

0.0

0.0

0.2

0.4

0.6

0.8

Tm³⁺

10 mol%, the UC intensity of the ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ peak of Tm³⁺ at 450 nm decreases fastest compared to that in the core/shell NCs. This phenomenon implies that the ET (denoted as ET2) process occurs primarily from the ${}^{1}D_{2}$ state of Tm³⁺ to the ${}^{5}L_{I}$ state of Eu³⁺ due to their well-matched energy levels (Figure 4a), as will be further confirmed by the number of pump photons (n) responsible for the UC emissions of Eu³⁺ and Tm³⁺. Figure 3b shows the typical pump power dependence of UC luminescence of ⁵D₀ (Eu³⁺) and ¹D₂ (Tm³⁺) under the excitation at 976 nm. The resulting values of pump photon number are 3.38, 3.25, and 3.08 for UC emission peaks at 615.5 (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ of Eu³⁺), 475 (${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ of Tm³⁺), and 362 nm (${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ of Tm³⁺), respectively, suggesting that these transitions are all fourphoton UC processes and thereby verifying the existence of ET between ${}^{1}D_{2}$ (Tm³⁺) and ${}^{5}L_{I}$ (Eu³⁺). The deviation from the theoretically predicted photon number $(n = 4)^{[16]}$ for the populations of ${}^{1}D_{2}$ (Tm³⁺) and ${}^{5}D_{0}$ (Eu³⁺) is most probably due to the UC saturation^[1e] caused by the middle-to-high pump power regime we employed.

More importantly, as compared in Figure 3a, the integrated intensity of UC emissions of Eu^{3+} in the core/shell NCs is about one order of magnitude higher than that in Yb³⁺/Tm³⁺/ Eu^{3+} triply-doped NaGdF₄ NCs. This remarkable enhancement in UC emissions of Eu^{3+} clearly demonstrates the overwhelming advantage of our strategy by employing the core/shell structures against the triply-doping method in core only nanoparticles. Coating an inert or active shell on the core NCs has already been proved to be an effective way to improve the UC efficiency of Ln^{3+} ions situated at the core.^[14,18] Nevertheless, enhancement of UC emissions of Ln^{3+} ions in the shell has not ever been reported so far. It is well known that, the dopant concentration that determines the distance between the two

neighboring activator ions, has a great impact on the UC efficiency in Ln3+ ions doped NCs.[9] High doping concentrations of Tm³⁺ and Eu³⁺ ions within the core NCs may facilitate the desired ET2 process aforementioned, however it also leads to deleterious cross-relaxations between the adjacent dopant ions, resulting in the quenching of excitation energy and thereby weak UC emissions. As revealed in Yb/Tm/Eu triply-doped NaGdF4 NCs in Figure 3a, the higher doping concentration of Eu³⁺ produces the weaker UC emissions of Tm³⁺ and Eu³⁺. Similar quenching phenomenon is also observed with increasing Tm³⁺ concentration (from 0.5 to 1 mol%) when the Eu³⁺ concentration is fixed at 10 mol% (Figure S5). It is worthy of mentioning that these unwanted cross-relaxations between dopant ions will significantly decrease the lifetimes of Tm³⁺ and Eu³⁺. As shown in Figure 3c (1–3), the UC lifetime of the ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition of Tm³⁺ is reduced from 0.8 to 0.48 and 0.31 ms after doping 1 and 10 mol% Eu³⁺ ions into the NaGdF₄:Yb(18%),Tm(1%) core NCs. Most likely, the cross-relaxation process occurs in such a manner of ${}^{3}H_{4} \rightarrow {}^{3}H_{5}$ (Tm³⁺) : ${}^{7}F_{0} \rightarrow {}^{7}F_{5}$ (Eu³⁺) (denoted as CR6 in Figure 4a).^[20] By this way, the excitation energy absorbed by Tm³⁺ ions can be transferred to $^7F_{\rm I}$ of the nearest Eu³⁺ and then dissipates nonradiatively as heat. As a result, much weaker UC emissions of Eu3+ and Tm3+ are detected in Yb/Tm/Eu triply-doped samples (Figure 3a). In contrast, a much longer UC lifetime of ${}^{3}H_{4}$ of Tm³⁺ (1.35 ms) is observed in the core/ shell NCs (Figure 3c (4)), which shows unambiguously that the growth of NaGdF₄:Eu shell around the NaGdF₄:Yb,Tm cores is a feasible way to suppress those deleterious cross-relaxations between Tm³⁺ and Eu³⁺ ions. Consequently, much stronger UC emissions of Eu³⁺ in the core/shell NCs can be achieved than in Yb/Tm/Eu triply-doped NaGdF4 NCs. Likewise, due to the inhibition of cross-relaxations between Eu³⁺ and Tm³⁺ such as



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 ${}^{5}D_{0}\rightarrow{}^{7}F_{J}$ (Eu³⁺) : ${}^{3}H_{6}\rightarrow{}^{3}F_{2,3}$, ${}^{3}H_{4}$ (Tm³⁺), we observed an increase in the DC lifetime of ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ for Eu³⁺ in the core/shell NCs (5.7 ms) relative to that in Yb/Tm/Eu (18/1/10,1 mol%) triplydoped core NCs (3.4 and 4.5 ms, Figure 3d).

The ET processes responsible for the intense DC and UC luminescence of Eu³⁺ in the core/shell NCs are proposed and illustrated in Figure 4a. For intense DC luminescence, UV excitation photons (273 nm) are absorbed by NCs to populate the ⁶I_I states of Gd³⁺ followed by very fast nonradiative relaxation to $^{6}\dot{P}_{7/2}$, which subsequently transfers its energy via Gd^{3+} lattice to a neighboring Eu³⁺ ion. Then the excitation energy is released as red emissions of Eu³⁺ in the shells (Figure 1d). Regarding the UC mechanism of Eu³⁺ in the shells, pumping photons of the 976-nm laser are first absorbed by the sensitizers (Yb³⁺) located in the cores that successively transfer their energies to Tm³⁺ ions via the ET upconversion (ETU) process to populate the ³F₄, ³H₄, ¹G₄ states of Tm³⁺ in turn.^[16,19b] Considering the large energy mismatch (~3500 cm⁻¹) between the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of Yb^{3+} and the $^1G_4{\rightarrow}^1D_2$ transition of Tm^{3+}, the ${}^{1}D_{2}$ state of Tm³⁺ can not be directly populated via the above ETU process, which may be populated alternatively through the cross-relaxation of ${}^{3}F_{3} \rightarrow {}^{3}H_{6}: {}^{3}F_{3} \rightarrow {}^{1}D_{2}$ (denoted as CR4) between two adjacent Tm³⁺ ions.^[16,19b] After the population of $^{1}D_{2}$ of Tm³⁺ in the cores, the energy can be partly transferred to the ${}^{5}L_{I}$ (or ${}^{5}G_{I}$) states of Eu³⁺ in the boundary of the core and shell structures, followed by nonradiative relaxation to ${}^{5}D_{2}$, ${}^{5}D_{1}$, and ${}^{5}D_{0}$ states, and then UC emissions of Eu³⁺ take place. However, it should be noted that the undesired cross-relaxation (CR6) between Tm^{3+} and Eu^{3+} is in competition with the ET2 process from ¹D₂ (Tm³⁺) to ⁵L_I (Eu³⁺) for achieving UC emissions of Eu³⁺ (Figure 4a). In the case of Yb/Tm/Eu triply-doped NaGdF₄ NCs, the deleterious cross-relaxations between Tm³⁺ and Eu³⁺ are predominant because of high doping concentrations of activators that are closely spaced, thereby only weak UC emissions of Eu^{3+} and Tm^{3+} can be detected (Figure 3a). On the contrary, the ET from ${}^{1}D_{2}$ of Tm³⁺ to ${}^{5}L_{J}$ (or ${}^{5}G_{J}$) of Eu³⁺ is prominent after coating an extra shell of NaGdF₄:Eu around the NaGdF₄:Yb,Tm core due to the effective restraint of the cross-relaxations between Tm3+ and Eu3+ that are space separated, giving rise to intense UC emissions of Eu³⁺ in the core/ shell NCs.

Because of the coexistent UC emissions of Tm³⁺ and Eu³⁺, it is difficult to achieve pure red UC emissions of Eu³⁺ in the core/shell NCs using the conventional steady-state luminescence detection aforementioned (Figure 2b). However, timeresolved luminescence detection technique (TRLDT) will facilitate the separation of UC emissions of Eu³⁺ from that of Tm³⁺ in view of their different luminescence lifetimes (Figure S6). By setting an appropriate delay time and gate time in TRLDT, the long-lived UC emissions of Eu³⁺ can be easily distinguished from that of Tm³⁺ (Figure 4b). In short delay time (1~3 ms), the whole UC emission spectra is dominated by the shortlived blue emission of Tm³⁺ upon excitation at 976 nm, while the long-lived red emissions of Eu³⁺ are prominent when the delay time is longer than 3 ms, inducing a significant UC color change from blue to red as revealed by their corresponding CIE chromaticity coordinates (Figure 4c). This time-resolved UC color outputs coupled with the DC mode and the good paramagnetic capability of the host cations (Gd³⁺) in such core/shell NCs may have versatile applications in multiplexed biolabeling and imaging, offering remarkably higher detection sensitivity than the steady-state luminescent nano-biolabels.

Finally, to demonstrate the potential application of NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs as luminescent biolabels, surface functionalization with hydrophilic ligands of these oleic-coated core/shell NCs was carried out by employing a general ligand exchange procedure.^[12b] The poly(acrylic acid) (PAA, Mw \approx 1800) is used to replace the original hydrophobic oleic acid on the surface of core/shell NCs. The replacement of PAA for oleic acid can be verified by the FT-IR spectra as well as the thermogravimetric analysis (TGA) for the core/shell NCs before and after ligand exchange (Figure S7). A strong IR band centered at 1733 cm⁻¹ was observed after the ligand exchange for the core/shell NCs, which is attributed to the C=O stretching mode of protonated carboxylate groups (-COOH) of PAA,^[21] indicating the replacement of PAA for oleic acid on the surfaces of core/shell NCs. This result has been further confirmed by the similar TGA curves observed for pure PAA and PAA modified core/shell NCs, which have the same decomposition temperature beginning at 200 °C (Figure S7). Moreover, the PAA modified core/shell NCs are found to possess good solubility and stability in water and physiological buffer solution, respectively. No noticeable precipitate was observed in the bottom of the core/shell NC water solution in a one-month observation. For the core/shell NCs in physiological buffer (pH = 7.2), no aggregate was observed in a ten-day observation. These PAA modified core/shell NCs were then characterized with dynamic light scattering (DLS) and ζ -potential measurements (Figure S8). The average hydrodynamic diameter for PAA modified core/shell NCs is determined to be ~44 nm with an estimated PAA thickness of ~10 nm, consistent with that of PAA coated NaYF4:Yb,Er(Tm)/ NaYF₄ core/shell NCs.^[18] The ζ-potential for PAA modified core/shell NCs is -50.7 mV, indicative of the negatively charged PAA on the surface of core/shell NCs.^[18] We have also examined the paramagnetic behavior of Gd^{3+} in the core/shell NC water solution. The specific relaxivity value (r_1) for the core/shell NCs after the ligand exchange is experimentally determined to be 1.21 mM⁻¹S⁻¹ (Figure S9). This value is comparable to that of the poly(ethylene glycol) (PEG) phospholipids encapsulated NaGdF₄:Yb,Er/NaGdF₄ NCs (1.40 and 1.05 $mM^{-1}S^{-1}$ for the 22 and 44 nm NCs, respectively).^[22] More importantly, UC emissions of Tm³⁺ and Eu³⁺ are found to remain nearly unchanged before and after ligand exchange (Figure S10). This is an important aspect for bioassays in that the UC luminescence of Ln³⁺ in core/shell NCs will not be quenched by high energy oscillators arising from the surface impurities, ligands, and solvents.

In summary, we have demonstrated a strategy to achieve dual-mode luminescence from identical Eu³⁺ ions in monodisperse hexagonal-phase NaGdF₄ NCs that consist of the NaGdF₄:Yb,Tm core and the NaGdF₄:Eu shell. Typical red DC luminescence of Eu³⁺ has been detected via the sensitization of Gd³⁺ ions ($\lambda_{exc} = 273$ nm). By using Yb³⁺ and Tm³⁺ embedded in the cores as double sensitizers, intense UC luminescence of Eu³⁺ in the shells can be achieved in NaGdF₄:Yb,Tm/NaGdF₄:Eu core/shell NCs upon excitation at 976 nm. The UC intensity of Eu³⁺ in core/shell NCs is found about one order of magnitude higher than the triply-doped core only counterparts, due to the



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inhibition of the deleterious cross-relaxations between Tm^{3+} and Eu^{3+} ions in core/shell NCs that are reasonably separated in space. By employing the core/shell technique, we have realized the dual-mode (UC and DC) luminescence of Eu^{3+} in single NaGdF₄ NC. Due to its excellent monodispersion, good solubility and stability in water solution, and high UC/DC efficiencies, the NaGdF₄ core/shell NCs may have versatile and promising applications as multiplexed luminescent nano-biolabels and MRI contrast agent. Currently, further efforts on the use of these nanocrystals in bioaffinity assays such as homogeneous fluorescence resonance energy transfer (FRET) are underway.

Experimental Section

Detailed experimental procedures are reported in the Supporting Information.

Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

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