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Exploring novel lanthanide activated upconversion nanoparticles with distinctive spectral fingerprints and emission lifetimes has always been a great concern for extended optical applications. Here, we report the study on photon upconversion emissions in Yb<sup>3+</sup>–Tb<sup>3+</sup> and Yb<sup>3+</sup>–Eu<sup>3+</sup> activated nanoparticles with near-infrared excitation. In these nanoparticles, high content of Yb<sup>3+</sup> is required for the simultaneous excitation of two Yb<sup>3+</sup> ions, yielding a Yb<sup>3+</sup> dimer with higher excited energy to upconvert photons onto Tb<sup>3+</sup> and Eu<sup>3+</sup>. The optimum doping concentration of Yb<sup>3+</sup> ions for Yb<sup>3+</sup>–Tb<sup>3+</sup> and Yb<sup>3+</sup>–Eu<sup>3+</sup> pairs was determined to be 80% and 60%, respectively, which are much higher than that of Yb<sup>3+</sup> Er<sup>3+</sup>/Tm<sup>3+</sup> pairs. Notably, the upconversion emission lifetime of as-prepared nanoparticles is prolonged to 2.3 ms (Tb<sup>3+</sup>) and 4.0 ms (Eu<sup>3+</sup>), respectively. By epitaxial growth of Nd<sup>3+</sup> doped shell layer, upconversion emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> has intensified by 25 times. In the meanwhile, an extra excitation band at shorter near-infrared region from Nd<sup>3+</sup> at 808 nm was achieved. Moreover, emissions of Tm<sup>3+</sup> were employed to compensate those of Tb<sup>3+</sup> and Eu<sup>3+</sup> for multicolor emissions. These results highlight the upconversion emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> for potential multicolor imaging and multiplexed detection applications.

### Introduction

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Lanthanide activated upconversion nanoparticles (UCNPs) have been extensively studied as optical probes and light transducers for bioimaging,1-3 theranostic,4-7 sensing and detection,<sup>8,9</sup> photovoltaic devices<sup>10,11</sup> and photoactivation reactions,12,13 due to their excellence in converting nearinfrared (NIR) light into visible and ultraviolet (UV) ones.14-17 Overwhelmingly substantial attention has been paid to Yb3+-Er<sup>3+</sup>/Tm<sup>3+</sup>/Ho<sup>3+</sup> activated UCNPs for their high emission efficiency.<sup>18,19</sup> Yet these emissions are fixed in wavelength, and emission lifetimes are limited to microseconds, thus many extended applications such as multicolor imaging and multiplexed detection are greatly hindered by limited choices of sensitizer-activator.<sup>20–22</sup> Therefore, it is desirable to explore novel UCNPs with distinctive spectral fingerprints and emission lifetimes. However, matched energy level between Yb3+ and activators, as a prerequisite for efficient upconversion emission, makes the exploration of novel UCNPs a daunting challenge.

Tb<sup>3+</sup> and Eu<sup>3+</sup>, typical luminescent centers for green and red emissions respectively, exhibit distinctive spectral profiles and much longer luminescent lifetimes compared with those of Er<sup>3+</sup>/Tm<sup>3+</sup>/Ho<sup>3+</sup>. And Tb<sup>3+</sup> and Eu<sup>3+</sup> activated complexes and down-shifting nanoparticles are usually employed as probes for bioassays and time-gated detections.<sup>23-25</sup> However, considering the unmatched energy diagram, it is difficult to sequentially pump NIR photons onto Tb<sup>3+</sup> and Eu<sup>3+</sup> as upconverted in Yb3+-Er3+/Tm3+/Ho3+ pairs. Recently, a series of Tm<sup>3+</sup>, Gd<sup>3+</sup>, and Tb<sup>3+</sup>/Eu<sup>3+</sup> co-activated UCNPs were developed to produce typical emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> under 980 nm excitation.<sup>26</sup> In these UCNPs, Tb<sup>3+</sup> and Eu<sup>3+</sup> were activated with sequential energy transfer from Tm<sup>3+</sup> and Gd<sup>3+</sup> in separated layers. The upconverting process is relatively complicated, in the meanwhile, spectral fingerprints from both Tm<sup>3+</sup> and  $Tb^{3+}/Eu^{3+}$  were always simultaneously displayed in spectra.

In this work, we describe the photon upconversion in a category of  $Yb^{3+}-Tb^{3+}$  and  $Yb^{3+}-Eu^{3+}$  activated nanoparticles, which are sensitized by straightforward energy transfer from  $Yb^{3+}$  dimers (Fig. 1a) under NIR excitation. In these nanoparticles, high content of  $Yb^{3+}$  is required to facilitate the simultaneous excitation of two adjacent  $Yb^{3+}$  ions, resulting in an  $Yb^{3+}$  dimer with higher virtual excited state to match that of  $Tb^{3+}$  and  $Eu^{3+}$ . Investigations on emissions from  $Tb^{3+}/Eu^{3+}$  with  $Yb^{3+}$  dimer sensitization have covered bulk materials, especially glasses and polymers,<sup>27-29</sup> and also nanoscale materials.<sup>30-37</sup> Nonetheless, due to the low efficiency and prominent quenching from surface defects and ligands,<sup>38-41</sup> photon upconverison in  $Yb^{3+}$ - $Tb^{3+}$  and  $Yb^{3+}$ - $Eu^{3+}$  activated

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**Fig. 1** (a) Simplified energy transfer diagram for  $Yb^{3+}-Tb^{3+}$  and  $Yb^{3+}-Eu^{3+}$  activated nanoparticles with NIR excitation. Only partial energy levels of Nd<sup>3+</sup> and A<sup>3+</sup> (A = Tb, Eu) are shown for clarity. (b, c) Typical TEM images of core and core/shell nanoparticles, respectively. (d) HRTEM image of the core/shell nanoparticle. (e) Linear EDX scanning of a single core/shell nanoparticle and corresponding elemental ratio analysis. (f) Absorption spectra of core (blue line) and core/shell (red line) nanoparticles.

UCNPs is very low-efficient. To address this issue, we have systematically studied the photon upconversion processes in Yb<sup>3+</sup>–Tb<sup>3+</sup> and Yb<sup>3+</sup>– Eu<sup>3+</sup> pairs, including the composition and architecture correlated emissions. The doping concentration of Yb<sup>3+</sup> and Tb<sup>3+</sup>/Eu<sup>3+</sup>, which is crucial for energy transfer efficiency, has been precisely optimized. Moreover, core/shell architecture was introduced to separate Tb<sup>3+</sup> and Eu<sup>3+</sup> from surface quenchers, facilitating the intensification of upconversion emissions. Aiming at enriching the excitation features, Nd<sup>3+</sup> is introduced to expand the NIR excitation band to shorter wavelength at 808 nm.<sup>42–45</sup> On this basis, emissions of Tm<sup>3+</sup> were used to compensate those of Tb<sup>3+</sup> and Eu<sup>3+</sup> for releasing multicolor upconversion emissions. These results suggest that  $Tb^{3+}$  and  $Eu^{3+}$  activated UCNPs should be promising candidates for applications as multicolor bioimaging and multiplexed applications.

### **Experimental Section**

#### Materials

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Rare earth oxides (RE = Gd, Yb, Tb, Eu, Nd, Y; China Rare Earth Online Co., Ltd.), Oleic Acid (OA; >90 %, Sigma-Aldrich), Oleylamine (OM; >80%, Acros), 1-octadecene (ODE; >90%, Acros), trifluoroacetic acid (99%, Acros), trifluoroacetic acid sodium salt (99%, Acros), ethanol (AR), and cyclohexane (AR) were used as received without further purification. BALB/c nude mice were bought from Vital River Co. Ltd., Beijing.

### Instrumentation

Low resolution transmission electron microscopy (TEM) measurements were performed with a JEOL JEM-2100 TEM operated at 200 kV. High resolution transmission electron

microscopy (HRTEM) measurements, energy, energ spectroscopy mapping (EDX-Mapping), and a sector scanning measurements were carried out with a JEOL JEM-2100F TEM operated at 200 kV. NIR absorption spectra were recorded on a SHIMADZU UV-3100 spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2° at a scanning rate of 2° min–1, using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). ICP-AES characterization was performed with a Leeman Profile SPEC. Upconversion emission spectra were measured on a Hitachi F-4500 fluorescent spectrometer with the PMT voltage of 700 V. Lasers used as excitation sources for 980 nm and 808 nm are high-power multimode pump lasers (Hi-tech Optoelectronic Co. Ltd., with a maximum power 5.0 W for both lasers). The upconversion emission lifetime was measured on a customized UV to mid-infrared steady-state and phosphorescence lifetime spectrometer (FSP920-C, Edinburgh Instrument) equipped with a tunable mid-band OPO pulse laser as excitation source (410 -2400 nm, 10 Hz, pulse width ≤ 5 ns, Vibrant 355II, OPOTEK). Digital photographs were taken with a NIKON D3000 camera.

Synthesis of hexagonal NaGdF4:Yb,A@NaGdF4:Nd,Yb nanoparticles (A = Tb, Eu)

In a typical experiment, the hexagonal phased core/shell nanoparticles were derived from three steps, cubic phased core, hexagonal phased core, and hexagonal phased core/shell nanoparticles, respectively.

Synthesis of cubic phased core nanoparticles. A given amount of RE(CF<sub>3</sub>COO)<sub>3</sub> (RE = Gd, Yb, A, 1 mmol) and CF<sub>3</sub>COONa (1 mmol) were added to a mixture of OA, OM and ODE (40 mmol, molar ratio 1:1:2) in a three-necked flask (100 mL) at room temperature. Then the slurry was heated to 110 °C to remove water and oxygen with vigorous magnetic stirring under vacuum. The solution was heated to 310 °C and kept for 15 min under N<sub>2</sub> atmosphere. After cooling to room temperature, the cubic phased nanoparticles were precipitated by adding excess amount of ethanol into the solution, and then collected by centrifugation. The final product was dispersed in 10 mL of cyclohexane.

Synthesis of hexagonal phased core nanoparticles. The 5 mL asprepared cubic phased NaGdF<sub>4</sub>:Yb,A colloidal solution was redispersed in a 40 mmol OA, ODE mixture (molar ratio 1:1), and an extra RE(CF<sub>3</sub>COO)<sub>3</sub> (RE = Gd, Yb, A, 0.5 mmol) and CF<sub>3</sub>COONa (0.5 mmol) were added. Then the slurry was heated to 110 °C to remove cyclohexane, water and oxygen with vigorous magnetic stirring under vacuum, and formed a clear solution. The solution was heated to 310 °C and kept for 30 min under N<sub>2</sub> atmosphere. Upon cooling to room temperature, the hexagonal phased NaGdF<sub>4</sub>:Yb,A nanoparticles were collected by centrifugation after adding excess amount of ethanol. Finally, the product was dispersed in 10 mL of cyclohexane.

Synthesis of hexagonal phased core/shell nanoparticles. The 5 mL as-prepared hexagonal phased NaGdF<sub>4</sub>:Yb,A colloidal solutions were redispersed in a 40 mmol OA, ODE mixture (molar ratio 1:1), and an extra RE(CF<sub>3</sub>COO)<sub>3</sub> (RE = Gd, Nd, Yb, 1 mmol) and CF<sub>3</sub>COONa (1 mmol) were added. Then the slurry

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was heated to 110 °C to remove cyclohexane, water and oxygen with vigorous magnetic stirring under vacuum, and formed a clear solution. The solution was heated to 310 °C and kept for 30 min under N<sub>2</sub> atmosphere. Upon cooling to room temperature, the hexagonal phased NaGdF<sub>4</sub>:Yb,A@NaGdF<sub>4</sub>:Nd,Yb nanoparticles were collected by centrifugation after adding excess amount of ethanol. Finally, the product was dispersed in 5 mL of cyclohexane.

# Preparation of hydrophilic polyacrylic acid (PAA) modified nanoparticles

A ligand exchange strategy was employed to transfer the hydrophobic nanoparticles to aqueous phase.<sup>48</sup> Typically, 1 mL colloidal solutions containing as-prepared nanoparticles were dispersed in a mixture of cyclohexane and N,N-Dimethylformamide (DMF) (10 mL, volume ratio 1:1), then 50 mg NOBF<sub>4</sub> was added. The slurry was stirred for 30 min at room temperature to leave the OA ligands in the cyclohexane phase while the naked nanoparticles transfer to the DMF phase. After that, the cyclohexane phase was removed and the nanoparticles were collected by centrifugation (18000 rpm, 15 min) after adding an excess amount of toluene. The naked nanoparticles were redispersed in 10 mL DMF containing 10 mg PAA (25% saponification). The mixture was stirred overnight to render PAA modification process. Finally, excess amount of acetone was added to the solution to precipitate PAA modified UCNPs. Hydrophilic UCNPs were collected by centrifugation (18000 rpm, 15 min). The resulting PAA modified UCNPs can be easily dispersed in aqueous phase.

### **Results and Discussion**

As a proof-of-concept experiment, hexagonal NaGdF<sub>4</sub> was chosen as the host matrix due to its low phonon energy.<sup>46</sup> Activators Tb<sup>3+</sup>/Eu<sup>3+</sup> together with sensitizers Yb<sup>3+</sup> were co-doped in inner core region to ensure efficient sensitization, while sensitizers Nd<sup>3+</sup> and Yb<sup>3+</sup> were embedded in the neighboring separated layer to absorb NIR light (Fig. 1a).

The UCNPs were synthesized with a modified thermolysis method.<sup>47,48</sup> Typical transmission electron microscopy (TEM) images of as-prepared nanoparticles reveal the uniformity in size and morphology. The mean particle size of NaGdF<sub>4</sub>:Yb,A (A = Tb, Eu) core and NaGdF<sub>4</sub>:Yb,A@NaGdF<sub>4</sub>:Nd,Yb (A = Tb, Eu) core/shell nanoparticles are 18.4  $\pm$  0.7 nm and 28.4  $\pm$  1.0 nm respectively, with a shell thickness of ~5 nm (Fig. 1b,c). High resolution TEM (HRTEM) image shows a single crystal nature with a lattice spacing of 0.52 nm, corresponding to the  $(10\overline{1}0)$ plane of hexagonal NaGdF<sub>4</sub> (Fig. 1d). XRD patterns depicted in Fig. S1 further confirm the hexagonal structure of as-prepared nanoparticles. Linear energy dispersive spectroscopy (EDX) scanning (Fig. 1e) and EDX-mapping (Fig. S2) illustrate the elemental distribution of as-prepared core/shell nanoparticles. It is evident that Tb<sup>3+</sup> ions are mainly distributed in core, while Nd<sup>3+</sup> ions are located in shell, which is well correlated to the expected core/shell structure. Moreover, apart from the NIR absorption band at 980 nm from Yb3+, extra NIR absorptions of Nd<sup>3+</sup> emerged with the epitaxial layer (Fig. 1f). This makes the



**Fig. 2** Upconversion emission spectra (a) and Logarithmic *I*–*P* curves (b) of NaGdF<sub>4</sub>:30%Yb,10%Tb@NaGdF<sub>4</sub>:50%Nd,10%Yb nanoparticles under 980 nm excitation. Inset image is the digital luminescence photograph. Marked with "\*", emissions at 525 nm, and 655 nm come from the ppm impurity of Er<sup>3+</sup> in Yb<sup>3+</sup> precursors, respectively. (c, d) Upconversion emissions of Tb<sup>3+</sup> as a function of the doping concentration of Tb<sup>3+</sup> (c) and Yb<sup>3+</sup> (d), respectively.

core/shell nanoparticles could be excited at these two prominent NIR absorption bands.

Upconversion emission from NaGdF<sub>4</sub>:Yb,Tb nanoparticles were firstly examined under 980 nm excitation. As depicted in Fig. 2a, typical emissions from Tb<sup>3+</sup>, which come from  ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 3 - 6) intra-configurational transitions, can be clearly observed. This suggests that the excitation energy has transferred from Yb3+ dimer to Tb3+. But for NaGdF4:Tb nanoparticles, as the control group without Yb3+ ions, did not exhibit any typical Tb<sup>3+</sup> emissions (Fig. S3) under 980 nm excitation. This indicates that sufficient amount of Yb3+ should be co-doped with Tb3+ for efficient sensitization. Moreover, upconversion emission of Tb3+ has intensified ~25 times after depositing a shell layer as NaGdF<sub>4</sub>:Yb,Tb@NaGdF<sub>4</sub>:Nd,Yb for the surface defects have been greatly minimized. In the meanwhile, emissions from  ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$  (J = 4 – 6) transitions of Tb<sup>3+</sup> with an energy higher than that of Yb<sup>3+</sup> dimer also emerged. The population of <sup>5</sup>D<sub>3</sub> state should come from the cross-relaxation of Yb<sup>3+</sup> ( ${}^{2}F_{5/2}$ ) + Tb<sup>3+</sup> ( ${}^{5}D_{4}$ )  $\rightarrow$  Yb<sup>3+</sup> ( ${}^{2}F_{7/2}$ ) + Tb<sup>3+</sup> (<sup>5</sup>D<sub>1</sub>) due to the similar energy gap between  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  of

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Yb<sup>3+</sup> (10400 cm<sup>-1</sup>) and  ${}^{5}D_{4} \rightarrow {}^{5}D_{1}$  of Tb<sup>3+</sup> (10113 cm<sup>-1</sup>), as well as a subsequent non-radiative relaxation from  ${}^{5}D_{1}$  to  ${}^{5}D_{3}$  (Scheme S1).

The number of photons involved in the emission is crucial to reveal the transition mechanism.<sup>49</sup> From the logarithmic excitation power dependent emission spectra (*I*–*P* curves, Fig. 2b), it can be found that the slopes of the linear fits were around 2 for all  ${}^5D_4 \rightarrow {}^7F_J$  (J = 6, 5, 4, 3) emissions. This suggests that two-photon upconverting process should be involved in the emissions of Tb<sup>3+</sup> under 980 nm excitation, which is well correlated to the proposed energy transfer via Yb<sup>3+</sup> dimer as shown in Fig. 1a. It is noteworthy that the slopes for these emissions should be similar because they are from the same excited state of  ${}^5D_4$ . Nonetheless, due to statistical erros from the integrated intensity of the transitions, especially the emission at 619 nm ( ${}^5D_4 \rightarrow {}^7F_3$ ), the slope may show a little deviation.

Subsequently, we studied the doping concentration of Tb<sup>3+</sup> and Yb<sup>3+</sup> dependent emissions, which significantly determines the energy transfer efficiency (Fig. S4–S7). According to the spectra in Fig. 2c, the optimum doping concentration of Tb<sup>3+</sup> is 10%. Compared with the Er<sup>3+</sup> (~2%) activated UCNPs,<sup>19</sup> this was largely elevated for Tb<sup>3+</sup>. The content of Yb<sup>3+</sup> ions, which directly affect the formation of Yb<sup>3+</sup> dimers, should be a crucial parameter. As shown in Fig. 2d,  ${}^5D_4 \rightarrow {}^7F_5$  emissions from Tb<sup>3+</sup> increased ~130 times as Yb<sup>3+</sup> increased from 10% to 80%, and further increment of Yb<sup>3+</sup> saturated the upconversion emissions. Therefore, 80% Yb<sup>3+</sup> should be adequate for sensitizing emissions of Tb<sup>3+</sup> via Yb<sup>3+</sup> dimer, which is much higher that in Yb<sup>3+</sup>–Er<sup>3+</sup> pairs.<sup>19</sup>

Eu<sup>3+</sup>, which is widely used for commercial phosphors, has also been studied. As depicted in Fig. 3a, typical Eu<sup>3+</sup> emissions coming from  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  (J = 1, 2) transitions can be observed under 980 nm excitation. The population of <sup>5</sup>D<sub>0</sub> state of Eu<sup>3+</sup> is from the non-radiative relaxation of  ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$ , where  ${}^{5}D_{1}$  is activated by the energy transfer from Yb3+ dimer (Scheme S2).<sup>50</sup> Considering the  ${}^{5}D_{4}$  state of Tb<sup>3+</sup> is directly activated by energy transfer from Yb3+ dimer, upconversion emission of Yb<sup>3+</sup>-Eu<sup>3+</sup> pairs should be less efficient than that of Yb<sup>3+</sup>-Tb<sup>3+</sup> pairs. As shown in Fig. 3b, similar two-photon process sensitized from Yb<sup>3+</sup> dimers is responsible for the emissions of Eu<sup>3+</sup>. Investigation on the Eu<sup>3+</sup> concentration dependent emissions is shown in Fig.s 3c,d and Fig.s S8-S11. Similar to that of Tb<sup>3+</sup>, the optimum doping concentration of Eu<sup>3+</sup> is 10% (Fig. 3c), and 60% of Yb3+ content is desired to sensitize upconversion emissions of Eu<sup>3+</sup> (Fig. 3d).

Luminescent decay behaviors of Yb<sup>3+</sup>–Tb<sup>3+</sup>/Eu<sup>3+</sup> activated nanoparticles were subsequently studied. As shown in Fig. 4a, green emission lifetime of Tb<sup>3+</sup> at 542 nm is 2.26 ms under 980 nm excitation, and that of Eu<sup>3+</sup> collected at 614 nm reaches 4.08 ms at 980 nm excitation (Fig. 4b). It is much longer than that of Er<sup>3+</sup> doped UCNPs, which is in microseconds (Fig. S12). Next, the decay behaviors of Yb<sup>3+</sup>–Tb<sup>3+</sup> activated nanoparticles with varied doping concentration of Tb<sup>3+</sup> and Yb<sup>3+</sup> are employed for studying the composition dependent emission lifetimes, which can reflect the energy transfer efficiency. As shown in Fig. S13a, emission lifetime of Tb<sup>3+</sup> prolonged by 0.06



**Fig. 3** Upconversion emission spectra (a) and Logarithmic *I–P* curves (b) of NaGdF<sub>4</sub>:30%Yb,10%Eu@NaGdF<sub>4</sub>:50%Nd,10%Yb nanoparticles under 980 nm excitation. Inset image is the digital luminescence photograph. Marked with "\*", emissions at 525 nm, and 655 nm come from the ppm impurity of Er<sup>3+</sup> in Yb<sup>3+</sup> precursors. (b) Logarithmic *I–P* curves of Eu<sup>3+</sup> under 980 nm excitation. (c, d) Upconversion emissions of Eu<sup>3+</sup> as a function of the doping concentration of Eu<sup>3+</sup> (c) and Yb<sup>3+</sup> (d), respectively.



ms as the doping concentration of  $Tb^{3+}$  increased from 5% to 10%. This suggests that the energy transfer efficiency of  $Yb^{3+}$  dimer to  $Tb^{3+}$  should enhance little with elevating content of  $Tb^{3+}$ . In comparison, when the content of  $Yb^{3+}$  increased from

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20% to 80%, the emission lifetime of Tb<sup>3+</sup> prolonged noticeably by 1.76 ms (Fig. S13b), indicating that the content of Yb<sup>3+</sup> should be the crucial factor to affect the energy transfer from Yb<sup>3+</sup> dimer to Tb<sup>3+</sup> by affecting the amounts of Yb<sup>3+</sup> dimers.

Benefiting from Nd<sup>3+</sup> ions in the shell, as-prepared Tb<sup>3+</sup> and Eu<sup>3+</sup> activated nanoparticles are also expected to be excited with 808 nm NIR light.<sup>42</sup> As shown in Fig. 5a and Fig. S14, typical emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> were dominant, and the spectral profiles are almost the same to those under 980 nm excitation. Moreover, these emissions are also derived from two-photon absorption (Fig. 5b). It is postulated that Yb<sup>3+</sup> dimer is activated from two nearby Nd<sup>3+</sup> ions under 808 nm excitation. Upconversion emission lifetimes of Tb<sup>3+</sup> and Eu<sup>3+</sup> can also reach milliseconds of 2.69 ms and 3.96 ms under 808 nm excitation, respectively (Fig. S15), respectively, which are similar to those under 980 nm excitation.

The doping concentration of Nd<sup>3+</sup> and Yb<sup>3+</sup> in shell should be an important parameter to affect the energy transfer under 808 nm excitation.<sup>42</sup> Spectral results (Fig. S16a) showed that high content of  $Nd^{3+}$  was favorable for the emission of  $Tb^{3+}$ due to sufficient near-infrared absorption. The emission intensity of Tb<sup>3+</sup> increased about four times as the content of Nd<sup>3+</sup> increased from 10% to 50%, and green emission lifetime of Tb<sup>3+</sup> increased from 2.55 ms to 3.17 ms (Fig. S16b), which also suggests 50% Nd<sup>3+</sup> in shell are more suitable. The nearinfrared emission of Nd<sup>3+</sup> and Yb<sup>3+</sup> (Fig. S17a) also suggests that 50% Nd<sup>3+</sup> facilitates the energy transfer from Nd<sup>3+</sup> to Yb<sup>3+</sup>, which can be revealed from the prolonged emission lifetime of Yb<sup>3+</sup> (Fig. S17b). Yet when exciting Tb<sup>3+</sup> directly, possible Tb<sup>3+</sup>  $\rightarrow$  Nd<sup>3+</sup> back energy transfer may be significant with high Nd<sup>3+</sup> concentration as observed in pervious report.<sup>51</sup> High content of Yb<sup>3+</sup> in the shell led to a prominent decreased emission (Fig. S16c), for the over exposure of Yb<sup>3+</sup> to surface quenchers. Moderate amount of Yb<sup>3+</sup> in shell layer is necessary to mediate the energy from Nd<sup>3+</sup> (shell) to Yb<sup>3+</sup> (core). And the optimized composition for shell was determined as NaGdF<sub>4</sub>:50%Nd,10%Yb.

Intrigued by the success in NIR triggered emissions from  $Yb^{3+}-Tb^{3+}$  and  $Yb^{3+}-Eu^{3+}$  activated nanoparticles, their potential in yielding multicolor emissions was subsequently investigated.  $Tm^{3+}$  was introduced to compensate and



NaGdF<sub>4</sub>:30%Yb,10%Tb@NaGdF<sub>4</sub>:50%Nd,10%Yb (a) corresponding *I–P* curves (b) under 808 nm excitation. Inset is the luminescence photograph. Emissions of the ppm impurity of  $Er^{3+}$  in Yb<sup>3+</sup> precursors are marked with "\*".

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differentiate the emissions for those of Tb<sup>3+</sup> and Eu<sup>3+</sup> of the incorporation way of Tm<sup>3+</sup> was respectively studied by 4601 doping and separation into shell. When Tb<sup>3+</sup> and Tm<sup>3+</sup> are co-doped in core, typical emissions of Tb<sup>3+</sup> and Tm<sup>3+</sup> can be simultaneously detected (Fig. S18,S19). In a similar way, multicolor emissions can also be noticed in Eu<sup>3+</sup> and Tm<sup>3+</sup> co-doped nanoparticles (Fig. S20,S21). By fine-tuning of the content of Tm<sup>3+</sup>, upconversion emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> can be enhanced ~3 times. This indicated that Tm<sup>3+</sup> could act as a bridge to activate Tb<sup>3+</sup> and Eu<sup>3+</sup>.<sup>52</sup>

When Tb<sup>3+</sup>/Eu<sup>3+</sup> and Tm<sup>3+</sup> were incorporated into separated regions as NaGdF<sub>4</sub>:Yb,A@NaGdF<sub>4</sub>:Yb,Tm@NaYF<sub>4</sub>:Nd,Yb (A = Tb, Eu), emissions of Tb<sup>3+</sup> and Eu<sup>3+</sup> can be activated by Yb<sup>3+</sup> dimers in core as well as Gd<sup>3+</sup> and Tm<sup>3+</sup> in shell. As shown in Fig. 6a and b, multicolor emissions from Tb<sup>3+</sup>/Eu<sup>3+</sup> and Tm<sup>3+</sup> can be released from these nanoparticles. Moreover, the content of Yb<sup>3+</sup> in core was found to be important for efficient multicolor emissions, ~4 times enhancement can be obtained with 20% Yb<sup>3+</sup> in core (Fig. S22–S25), which is relatively smaller than the optimum 80% and 60% Yb<sup>3+</sup> shown in Fig. 2d and 3d, respectively. This could be attributed to that Yb<sup>3+</sup> in the adjacent shell layer assisted the formation of Yb<sup>3+</sup> dimers.

With the distinctive upconversion emissions,  $Yb^{3+}-Tb^{3+}$  and  $Yb^{3+}-Eu^{3+}$  activated UCNPs should be promising candidates for multicolor bioimaging.<sup>53,54</sup> Here, a nude mouse was employed for detection. As-prepared hydrophobic multicolor UCNPs were functionalized with biocompatible polyacrylic acid (PAA) (Fig. S26).<sup>55,56</sup> For Tb<sup>3+</sup>/Tm<sup>3+</sup> co-activated nanoparticles, their upconversion emission signals can be simultaneously detected under 980 nm excitation (Fig. S27a). After adding a green filter, the emission from Tm<sup>3+</sup> could be blocked, and only green emission from Tb<sup>3+</sup> could be detected (Fig. S27b). For



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 $Eu^{3+}/Tm^{3+}$  co-activated nanoparticles, upconversion emission signal from these two centers can also be simultaneously detected (Fig. S27c). And the imaging signals from  $Eu^{3+}$  could be selected with a red filter (Fig. S27d). The above results imply the feasibility of multicolor imaging from selected lanthanide ions of such UCNPs. Moreover, multicolor *in vivo* imaging could also be performed with 808 nm excitation (Fig. S27e–h).

### Conclusions

In conclusion, we have described a novel series of  $Tb^{3+}$  and  $Eu^{3+}$  activated nanoparticles sensitized via  $Yb^{3+}$  dimers. The optimum doping concentration for  $Tb^{3+}/Eu^{3+}$  and  $Yb^{3+}$  is greatly elevated compared with that of  $Er^{3+}/Tm^{3+}/Ho^{3+}$  activated UCNPs. And the upconversion emission lifetimes is prolonged to several milliseconds, which could be beneficial to time-gated detections. Moreover, with Nd<sup>3+</sup> introduced in shell, these nanoparticles can also be triggered with 808 nm excitation, and the upconverting process is the same to that under 980 nm excitation. On this basis, emissions from  $Tm^{3+}$  are used to compensate with that of  $Tb^{3+}$  and  $Eu^{3+}$  for multicolor emissions and bioimaging. These achievements not only offer new insights into modulation of lanthanide related upconversion emissions, but also provide novel candidates for multicolor bioimaging applications.

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Photon upconversion emission in a series of  $Yb^{3+}-Tb^{3+}$  and  $Yb^{3+}-Eu^{3+}$  activated nanoparticles have been investigated in this work.