

## **Pr<sup>3+</sup>-doped Nanoscintillators with Concentration- Quenching-Free Property**

Lin Zhang, Yantao Li, Huiru Ye, Lei Zhao, Qingwei Song, Weidong Du, Yue Zhou,  
Xukai Chen, Wei Wei\*

MOE & Guangdong Provincial Key Laboratory of Laser Life Science, Guangzhou Key Laboratory of Spectral  
Analysis and Functional Probes, College of Biophotonics, South China Normal University, Guangzhou, 510631,  
China

\* Corresponding author: [weiwei@senu.edu.cn](mailto:weiwei@senu.edu.cn).

# Experimental Details

## Materials

Praseodymium(III) acetate hydrate ( $\text{PrAc}_3 \cdot x\text{H}_2\text{O}$ , 99.9%), gadolinium(III) acetate hydrate ( $\text{GdAc}_3 \cdot x\text{H}_2\text{O}$ , 99.9%), europium(III) acetate hydrate ( $\text{EuAc}_3 \cdot x\text{H}_2\text{O}$ , 99.9%), terbium(III) acetate hydrate ( $\text{TbAc}_3 \cdot x\text{H}_2\text{O}$ , 99.9%), ytterbium(III) acetate hydrate ( $\text{YbAc}_3 \cdot x\text{H}_2\text{O}$ , 99.9%), yttrium(III) oxide ( $\text{Y}_2\text{O}_3$ , 99.9%), terbium(III) oxide ( $\text{Tb}_4\text{O}_7$ , 99.9%), sodium hydroxide ( $\text{NaOH}$ ,  $\geq 98\%$ ), ammonium fluoride ( $\text{NH}_4\text{F}$ ,  $\geq 99.9\%$ ), 1-octadecene (ODE,  $>90\%$ ), cyclohexane (99.5%), methanol (99.5%) were purchased from Macklin (Shanghai, China). Oleic acid (OA, 90%) was purchased from Sigma-Aldrich. All the reagents were used without further purification.

## Characterization

Transmission Electron Microscopy (TEM) images were obtained using a JEOL JEM-1400 PLUS operating at 120 kV. X-ray powder diffraction (XRD) patterns were conducted on a BRUKER D8 ADVANCE diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ) from  $10^\circ$  to  $70^\circ$  at a step of  $0.02^\circ/\text{s}$ . The emission spectra were recorded with a Horiba FluoroMax Plus Spectrofluorometer, in conjunction with X-ray laser (50 KV, 200  $\mu\text{A}$ ) and 980 nm (CNI MDL-III-980, China) continuous-wave lasers.

## Synthesis of $\text{NaYF}_4:\text{Pr}$ nanoscintillators with different $\text{Pr}^{3+}$ doping concentrations.

The scintillator  $\text{NaYF}_4:\text{Pr}$  were synthesized by using a co-precipitation method. Firstly, the mixture of oleic acid (7.5 mL) and 1-octadecene (15 mL), and 1 mmol of  $\text{REAc}_3$  ( $\text{RE} = \text{Y}, \text{Pr}$ ) with designed concentrations were contemporaneously added into a 100-mL three-necked flask under vigorous stirring (the ratio of RE varied according to the experiment requirements). The resulting mixture was heated at  $160^\circ\text{C}$  for 1 hour with nitrogen protection, and then cooled down to room temperature. After that a methanol solution (10 mL) containing  $\text{NaOH}$  (0.1 g) and  $\text{NH}_4\text{F}$  (0.148 g) was then added into the flask. The temperature was first elevated to  $80^\circ\text{C}$ , during which methanol can be removed from the mixture. After the methanol was evaporated completely, the mixture was increased to  $120^\circ\text{C}$  to remove the water and oxygen. This reaction was then heated to  $300^\circ\text{C}$  for 1 hour. All the above reactions were in nitrogen atmosphere. After that, the temperature was cooled down to room temperature. The as-prepared nanoparticles were collected by centrifugation at 7500 rpm for 5 min, and then dispersed in cyclohexane (5 mL).

## Synthesis of $\text{NaGdF}_4:\text{Yb}40\%,\text{Pr}1\%$ UCNPs and $\text{NaYF}_4:\text{Eu}$ nanoscintillators with different $\text{Eu}^{3+}$ doping concentrations.

The synthetic procedure for  $\text{NaGdF}_4:\text{Yb}40\%,\text{Pr}1\%$  and  $\text{NaYF}_4:\text{Eu}$  were identical to the synthesis of  $\text{NaYF}_4:\text{Pr}$ , except for the use of different lanthanides and ratios.

## Synthesis of $\text{NaYF}_4:\text{Tb}$ nanoscintillators with different $\text{Tb}^{3+}$ doping concentrations.

The scintillator  $\text{NaYF}_4:\text{Tb}$  were synthesized by using a thermal decomposition method. Firstly, a gross of 1 mmol

Y<sub>2</sub>O<sub>3</sub> and Tb<sub>4</sub>O<sub>7</sub> with designed concentrations, CF<sub>3</sub>COOH (5 mL), and deionized water (5 mL) were together added into a 100-mL three-necked flask. Then, the mixture was heated at 100 °C under vigorous stirring. After the residual water and acid were evaporated to dryness, the solid cooled down to room temperature. Next, CF<sub>3</sub>COONa (0.136 g), OA (10 mL) and ODE (10 mL) were added into the flask. The system was heated to 120 °C in order to remove the water in the mixture and kept for 15 min under nitrogen environment and then risen to 300 °C and kept for 1 hour. After that, the temperature was cooled down to room temperature. The as-prepared nanoparticles were collected by centrifugation at 7500 rpm for 5 min, and then dispersed in cyclohexane (5 mL).

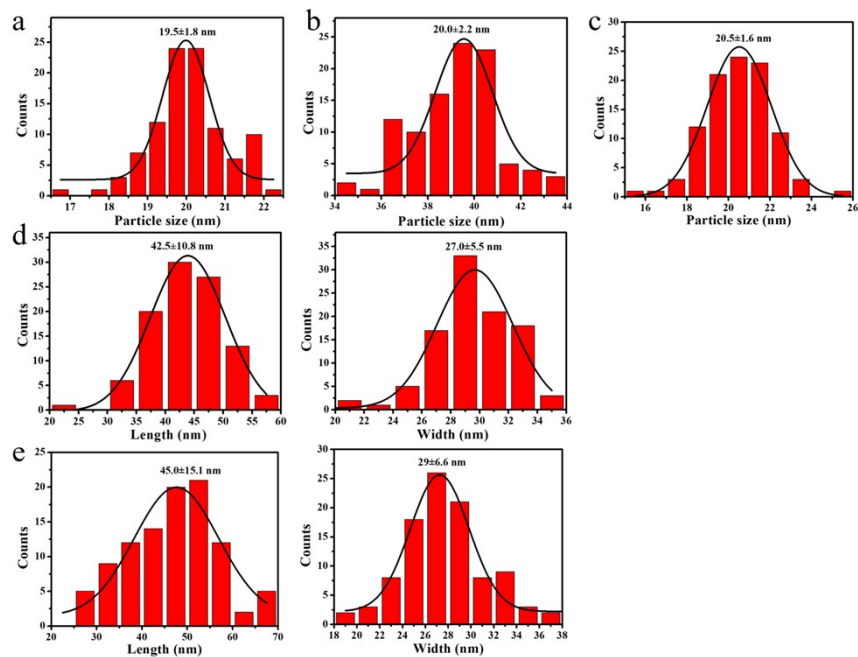
### **Synthesis of NaLnF<sub>4</sub>@NaYF<sub>4</sub> (Ln=Pr, Eu, Tb) and NaGdF<sub>4</sub>:Yb40%,Pr1%@NaPrF<sub>4</sub> core@shell NPs**

These four core@shell NPs were separately synthesized by employing the initial NaPrF<sub>4</sub>, NaEuF<sub>4</sub>, NaTbF<sub>4</sub> and NaGdF<sub>4</sub>:Yb40%,Pr1% core as seeds. Briefly, a gross of 0.5 mmol Y<sub>2</sub>O<sub>3</sub>, CF<sub>3</sub>COOH (5 mL), and deionized water (5 mL) were together added into a 100-mL three-necked flask. Then, the mixture was heated at 100 °C under vigorous stirring. After the residual water and acid were evaporated to dryness, the solid cooled down to room temperature. Next, CF<sub>3</sub>COONa (0.068 g), OA (10 mL), ODE (10 mL), and the NaPrF<sub>4</sub> core seeds (0.5 mmol) were added into the flask. The system was heated to 80 °C in order to remove the cyclohexane from the mixture under N<sub>2</sub> atmosphere. Then the temperature was increased to 120 °C to remove the water in the mixture and kept for 20 min and then risen to 300 °C and kept for 30 min under nitrogen environment. After cooling down to room temperature, the as-synthesized NaPrF<sub>4</sub>@NaYF<sub>4</sub> core@shell NPs were obtained by centrifugation at 7500 rpm for 5min. Finally, they were dispersed in cyclohexane (10 mL). The synthetic procedure for NaEuF<sub>4</sub>@NaYF<sub>4</sub>, NaTbF<sub>4</sub>@NaYF<sub>4</sub> and NaGdF<sub>4</sub>:Yb40%,Pr1%@NaPrF<sub>4</sub> were identical to the synthesis of NaYF<sub>4</sub>:Pr, except for the use of different lanthanides.

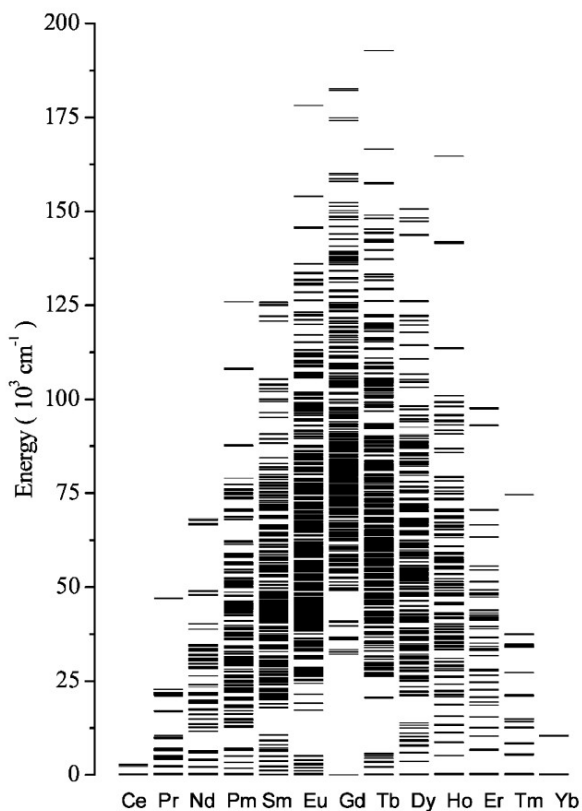
### **Preparation of PDMS film with NaGdF<sub>4</sub>:Yb40%,Pr1%@NaPrF<sub>4</sub> NPs**

1 mmol NaGdF<sub>4</sub>:Yb40%,Pr1%@NaPrF<sub>4</sub> NPs were redispersed in 5 mL methanol by sonication. Then 0.55 g PDMS (prepolymer and crosslinker in a 10:1 weight ratio) was mixed with the above solution and sonicated for 5 min to ensure a uniform distribution of NPs. Then, the mixture was heated to 70 °C under vigorous stirring in order to remove the methanol. After cooling down to room temperature, the NPs-containing solution was coated on the transparent PDMS film in the shape of "SCNU", and the obtained film was solidified at 60 °C for 4 h.

## **Supplementary Figures**



**Fig. S1.** Corresponding size distributions of the samples in (a) Fig. 1a, (b) Fig. 1b, (c) Fig. 1c, (d) Fig. 1d, (e) Fig. 1e.



**Fig. S2.** Complete  $4f^n$  energy level diagram for the trivalent lanthanides calculated using parameters reported by Carnall<sup>1</sup>.

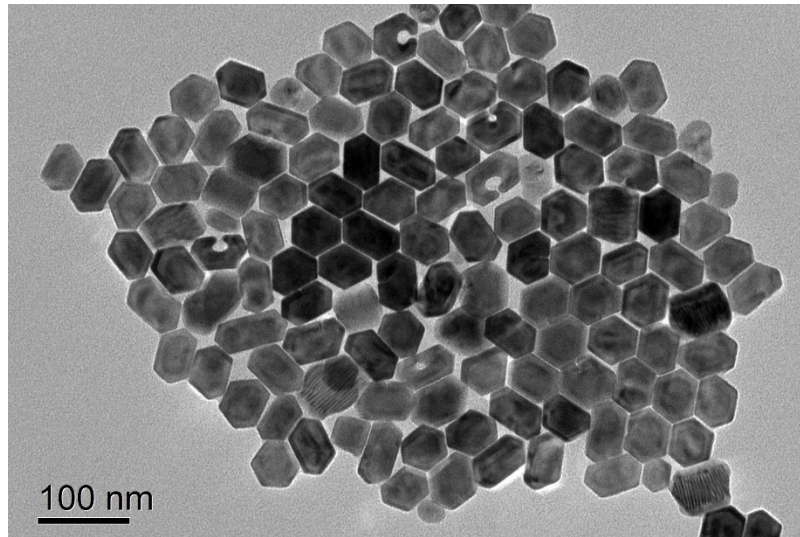


Fig. S3. TEM image of NaPrF<sub>4</sub>@NaYF<sub>4</sub>.

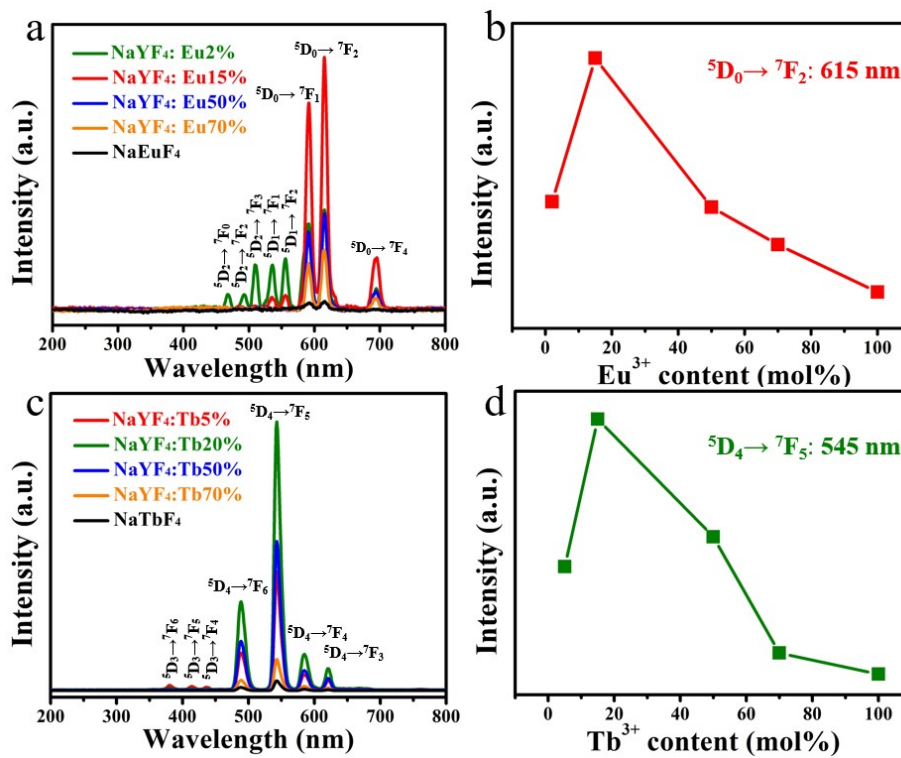
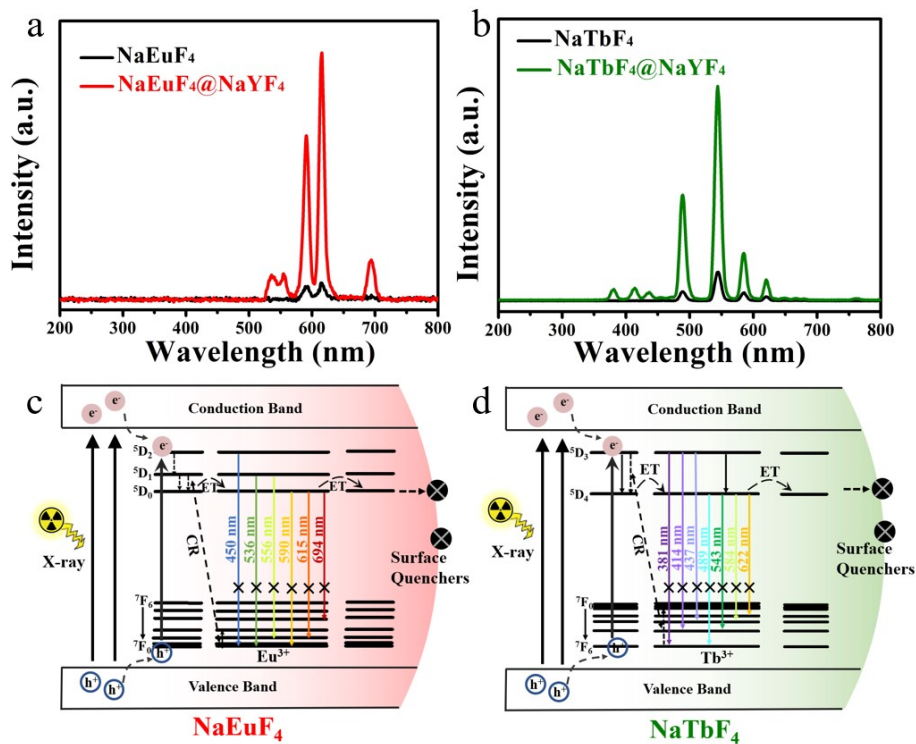
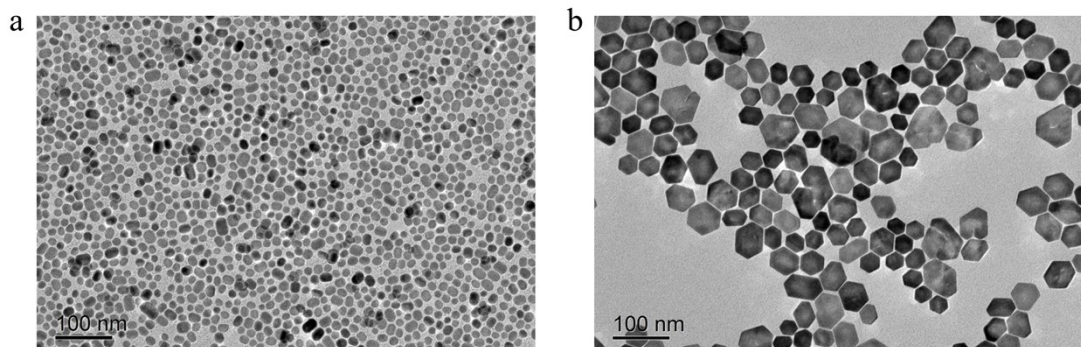


Fig. S4. Radioluminescent properties of NaYF<sub>4</sub>:Ln with Eu<sup>3+</sup> and Tb<sup>3+</sup> as the activators. a, c, Radioluminescence spectra of NaYF<sub>4</sub>:Ln (Ln= Eu, Tb) nanoscentillators with different Ln contents. b, d, Their corresponding characteristic peak intensity trend graph.



**Fig. S5.** Radioluminescence intensity change by the surface-passivated core-shell structure. a, b, Radioluminescence spectra of  $\text{NaLnF}_4$  and  $\text{NaLnF}_4@NaYF_4$  ( $\text{Ln} = \text{Eu}, \text{Tb}$ ) nanoscintillators monitored in the range of 200-800 nm. c, d, Their corresponding energy transfer mechanisms at high doping concentration levels.



**Fig. S6.** TEM images of  $\text{NaEuF}_4$  (a) and  $\text{NaTbF}_4$  (b).

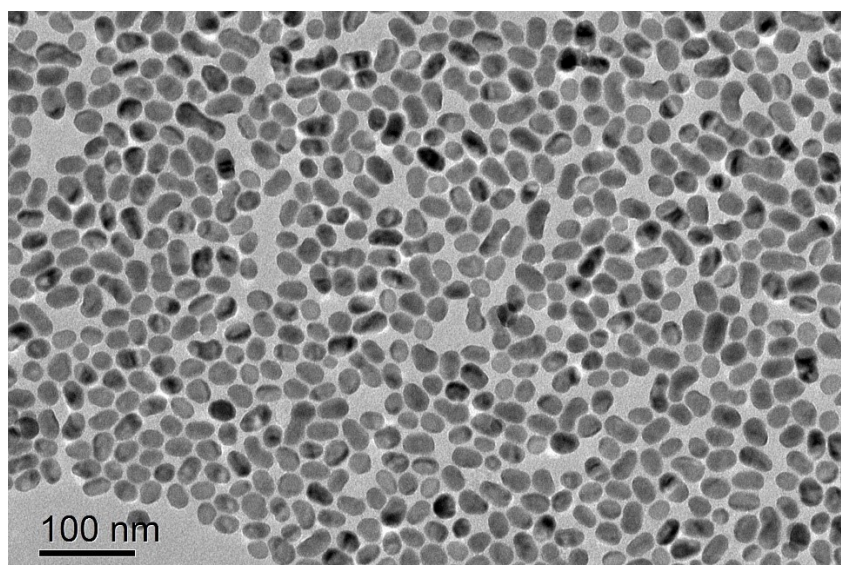


Fig. S7. TEM image of  $\text{NaGdF}_4:\text{Yb}40\%,\text{Pr}1\%@\text{NaPrF}_4$ .

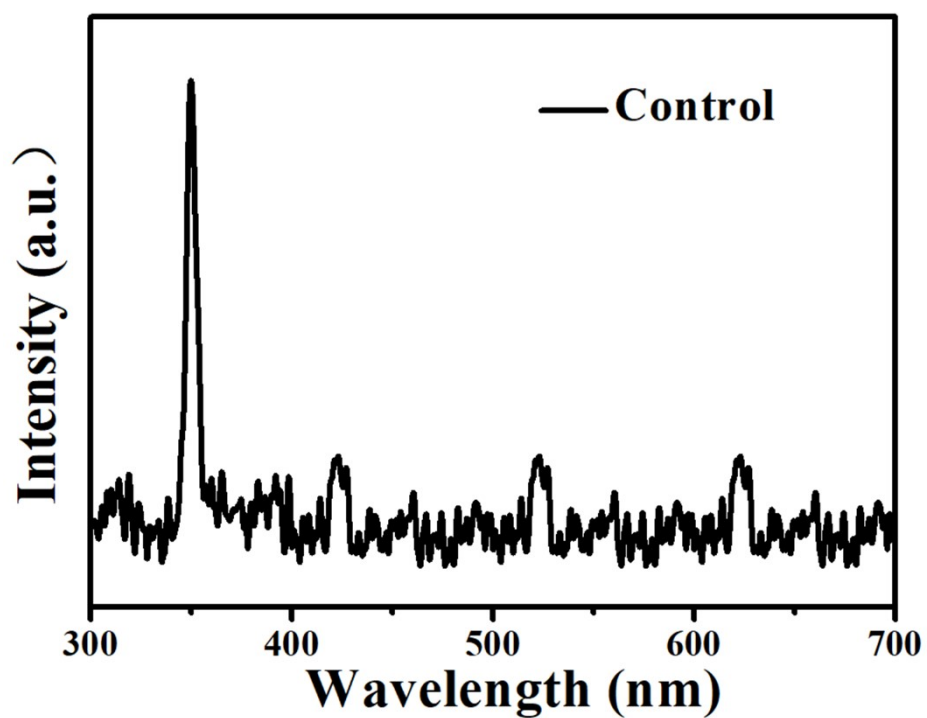


Fig. S8. The spectrum of the instrument with the absence of sample as control.

## References

1. Peijzel PS, Meijerink A, Wegh RT, Reid MF, Burdick GW. A complete energy level diagram for all trivalent lanthanide ions. *Journal of Solid State Chemistry*. 2005;178(2):448-453.