

## Supplementary Information

(Please note: this file replaces the previous version which omitted the "Materials & Methods" section)

# **Precision tuning of NaYF<sub>4</sub>:Yb,Er,Tm upconversion nanoparticles by droplet microfluidic screening**

**Shangkun Li,<sup>1</sup> Yingchao Meng,<sup>1</sup> Yujia Guo,<sup>1</sup> Tian Liu,<sup>2</sup> Stavros Stavrakis,<sup>1</sup>  
Philip D. Howes<sup>1,\*</sup> and Andrew J. deMello<sup>1,\*</sup>**

[1] Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, 8093 Zürich, Switzerland.

[2] Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir Prelog Weg 1, 8093 Zürich, Switzerland.

## **1 Materials & Methods**

### **1.1 Chemicals**

Yttrium acetate hydrate (99.9%), ytterbium acetate hydrate (99.9%), erbium acetate hydrate (99.9%), and thulium acetate tetrahydrate (99.9%) were obtained from ABCR. Cesium fluoride anhydrous (99.9%) was procured from Apollo Scientific Ltd. Sodium 2-ethylhexanoate (>98.0%) and 2-ethylhexanoic acid (>99.0%) were obtained from Tokyo Chemical Industry. Tetraethylene glycol dimethyl ether (TEGDME, 99%) was obtained from Acros Organics. Dioctylamine (98%) was procured from Aldrich-Fine Chemicals. Galden fluorinated fluid (HT 270) was obtained from Blaser Swissslube AG. All the chemicals were used as received and without further purification. Sylgard 184 polydimethylsiloxane (PDMS) base and curing agent were purchased from Dow Corning. GM 1070 SU-8 was purchased from Gersteltec.

## 1.2 Preparation of precursors

*Na<sup>+</sup> Precursor:* Sodium 2-ethylhexanoate (1.875 mmol) was loaded into a 20 mL Schlenk flask together with 5 mL of TEGDME, dried for 10 minutes at room temperature before being loaded into a 10 mL Hamilton glass syringe.

*RE<sup>3+</sup> Precursors:* Y<sup>3+</sup>, Yb<sup>3+</sup>, Er<sup>3+</sup> and Tm<sup>3+</sup> precursors were prepared separately in four different flasks by the same method. RE acetate hydrate (1.25 mmol) was loaded into a 20 mL Schlenk flask along with 3.5 mL of TEGDME, 0.7 mL of 2-ethylhexanoic acid and 0.8 mL dioctylamine. The cloudy mixture was heated to 100°C and maintained for 30 minutes until the solid dissolved. Subsequently, the clear solution was cooled to room temperature and dried for 10 minutes. Y<sup>3+</sup> and Yb<sup>3+</sup> precursors were loaded into 10 mL and 1 mL Hamilton glass syringes, respectively, while Er<sup>3+</sup> and Tm<sup>3+</sup> precursors were loaded into 0.1 mL glass syringes.

*F<sup>-</sup> Precursor:* Cesium fluoride (5 mmol) was loaded into a 20 mL Schlenk flask together with 2 mL of TEGDME and 3 mL 2-ethylhexanoic acid. The mixture was heated to 100°C and maintained for 30 minutes until the solid dissolved. Subsequently, the clear solution was cooled to room temperature and dried for 10 minutes before being loaded into a 10 mL Hamilton glass syringe.

## 1.3 Microfluidic synthesis of NaYF<sub>4</sub>:Yb,Er,Tm

Syringes loaded with precursors were mounted on precision neMESYS syringe pumps (Cetoni GmbH). Seven syringes were used in total, including four syringes filled with RE precursors with the same molar concentration, two syringes loaded with Na<sup>+</sup> and F<sup>-</sup> precursors, and another syringe used to inject the carrier Golden fluorinated fluid. The four RE<sup>3+</sup> precursors were initially mixed using a polyether ether ketone (PEEK) 7-port manifold (0.5 mm thru-hole, IDEX Health & Science). Then the RE<sup>3+</sup> precursors were mixed with Na<sup>+</sup> and F<sup>-</sup> precursors as well as oil and segmented into droplets (65 nL volume at a frequency of 7.6 s<sup>-1</sup>) at second PEEK 7-port manifold. Such a geometry allows for precise control of the ratios between RE<sup>3+</sup>, as well as the ratios of Na<sup>+</sup> to RE<sup>3+</sup> and RE<sup>3+</sup> to F<sup>-</sup>. Formed droplets subsequently travelled through a heating module, where the droplets are conveyed through PTFE tubing around a heated copper rod. The formed UCNPs were monitored *in situ* with an inline photoluminescence system (see below). The minimum time required per parameter to

collect inline photoluminescence data was 3 minutes. Scatter plots derived from the collected data, as presented herein, were fitted with a piecewise cubic hermite interpolating polynomial (PCHIP) as a visual guide only.

#### **1.4 Sample collection and purification for microfluidics**

When sample collection was required, the reactor was run with fixed reaction parameters for 60 minutes and the crude reaction solution collected. The reaction solution was then separated from the carrier fluid, and the final product obtained after centrifugation at 8000 rpm and two washes in ethanol.

#### **1.5 Device fabrication and operation**

A solid-state device was made within a PDMS chip, fabricated using standard soft lithographic methods. Briefly, patterns were designed using AutoCAD 2018 (Autodesk) and printed onto a high-resolution film photomask (Micro Lithography Services Ltd). This photomask was then used to fabricate master structures on an SU-8-coated silicon wafer. Subsequently, a 10:1 wt/wt mixture of PDMS base to curing agent were poured over the master and cured overnight at 70°C. The cured PDMS structure was peeled off the master, and inlet and outlet ports punched using a hole-puncher (Technical Innovations). The structured PDMS substrate was then bonded to a 24×75 mm glass slide (ThermoScientific) after treatment in a Zepto air plasma chamber (Diener Electronic) for 60 seconds. Finally, the assembled device was placed on a hot plate at 120°C for at least 2 hours to ensure complete bonding. All channels were 55 μm in height. To prepare the device, NaYF<sub>4</sub>:Yb,Er,Tm (20% Yb) UCNPs dispersed in ethanol were injected into separated letter patterns ('E', 'T', and 'H') with R5 at 0%, 70% and 100%, respectively. After heating the device for 20 minutes at 120°C, the ethanol was completely removed, leaving a solid layer of UCNPs. The device was illuminated using a 980 nm laser at 4 W/cm<sup>2</sup> power density, to excite the UCNPs. Emitted light was collected by a 4× 0.1 NA objective lens (AmScope), passed through a FESH0750↓ filter (Thorlabs) and finally imaged using a Mi 9 smartphone (Xiaomi).

#### **1.6 Characterization**

Transmission electron microscopy (TEM) was performed on a HT7700 Hitachi TEM at an accelerating voltage of 100 kV. XRD measurements were performed on a PANalytical

Empyrean diffractometer equipped with a Cu K $\alpha$  X-ray tube (45 kV, 40 mA). Inline PL was accomplished using a 980 nm laser source (Changchun New Industries Optoelectronics Technology) with a 10 W/cm<sup>2</sup> power density. The emission signal was filtered by an FESH0750 $\downarrow$  filter (Thorlabs) to remove the laser light. Finally, the PL emission originating from NaYF<sub>4</sub>:Yb,Er,Tm UCNPs was collected by an optical fiber (placed in a 90° orientation with respect to the excitation beam) and detected by a fiber-coupled Ocean FX spectrometer (Ocean Optics). The laser power densities were measured with a PM100D compact power and energy meter console (Thorlabs).

## 2 COMSOL simulation

COMSOL Multiphysics 5.4 was used for the CFD simulation. The physics used in the simulation are heat transfer in solids and fluids mode and creeping flow mode. Due to the complexity of the simulation, only the continuous flow was considered in the modes programed by COMSOL Multiphysics 5.4. The equations, which used in heat transfer in solids and fluids mode and creeping flow mode, are showed in equations 1 to 5.

$$\rho c_p u \cdot \nabla T + \nabla \cdot q = Q \quad (1)$$

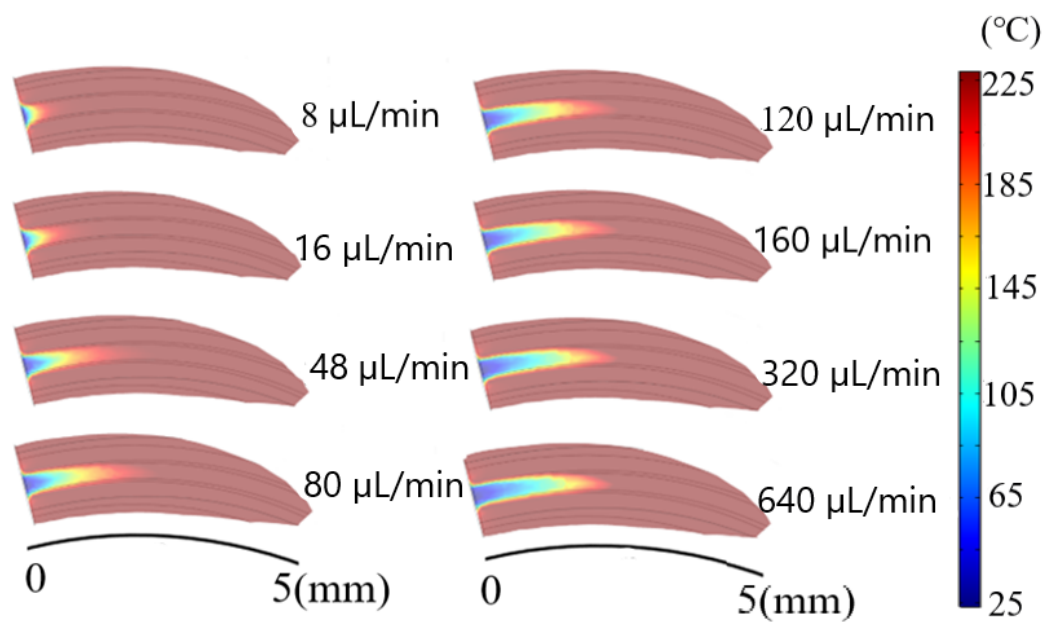
$$q = -k \nabla T \quad (2)$$

$$0 = \nabla \cdot [-pI + k] + F \quad (3)$$

$$\nabla \cdot (\rho u) = 0 \quad (4)$$

$$k = \mu (\nabla u + (\nabla u)^T) - 2/3 \mu (\nabla \cdot u) I \quad (5)$$

Here,  $u$  is the velocity vector,  $\rho$  is the solution density,  $c_p$  is the heat capacity at constant pressure,  $q$  is the thermal flux,  $k$  is the heat conductivity,  $p$  is the pressure,  $F$  is mass force distribution density,  $\mu$  is the dynamic viscosity. First, we built a 3D geometric model, then added the corresponding materials to the model. The physics field was then set to the initial temperature, boundary conditions, and fluid velocity. In **Figure S1**, the heating speed of the reactor with different flow rate was simulated. In general, the heating distance is reduced with the decreasing of flow rate.



**Figure S1.** Temperature distribution of the flow at the beginning of the heater changes with the different flow rate.

### 3 Conversion to CIE

To convert spectra to a representation of a color, a calculation based on the CIE colour matching functions (**Figure S2**),  $\bar{x}(\lambda)$ ,  $\bar{y}(\lambda)$  and  $\bar{z}(\lambda)$  was used. These model the chromatic response of a "standard observer" by mapping a spectrum,  $P(\lambda)$ , to a set of tristimulus values, X, Y and Z, analogous to the actual response of the three types of cone cell in the human eye.

$$X = \int P(\lambda)\bar{x}(\lambda)d\lambda,$$

$$Y = \int P(\lambda)\bar{y}(\lambda)d\lambda,$$

$$Z = \int P(\lambda)\bar{z}(\lambda)d\lambda,$$

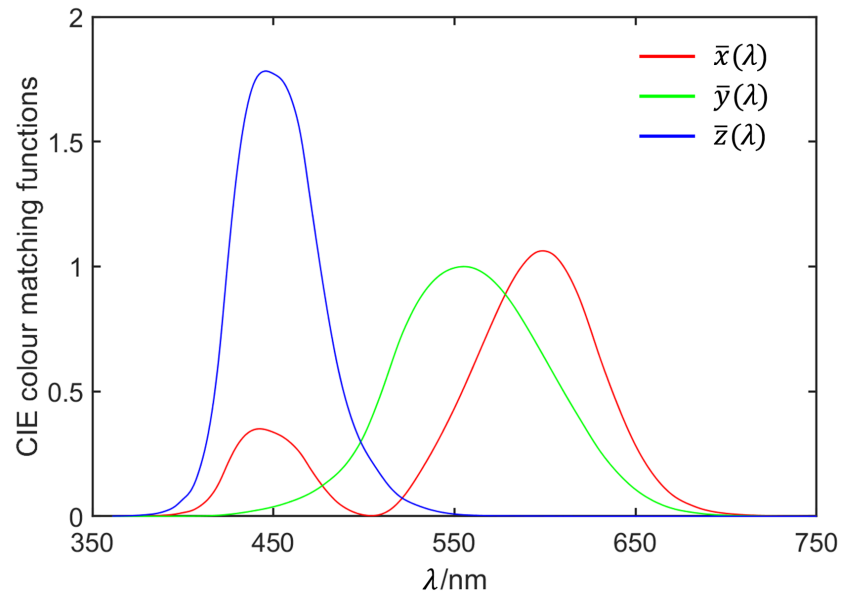
Then, X, Y and Z can be normalized by dividing by their sum as following:

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z}, \quad z = \frac{Z}{X+Y+Z} = 1 - x - y$$

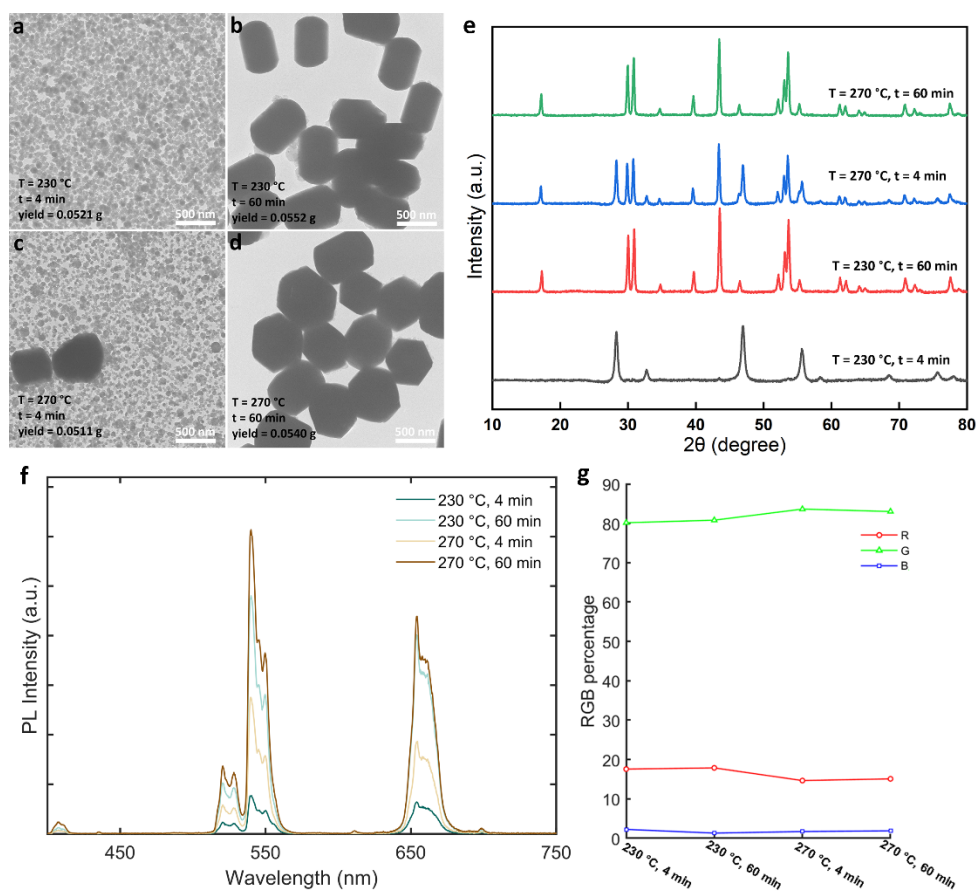
Finally, x and y are used to describe the color of the light in CIE standard chromaticity diagram.

Further conversion of X, Y, Z to RGB values for output by a display device requires transformation by the appropriate chromaticity matrix.

$$\begin{pmatrix} R \\ G \\ B \end{pmatrix} = \begin{pmatrix} 0.41847 & -0.15866 & -0.082835 \\ -0.091169 & 0.25243 & 0.015708 \\ 0.00092090 & -0.0025498 & 0.17860 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$



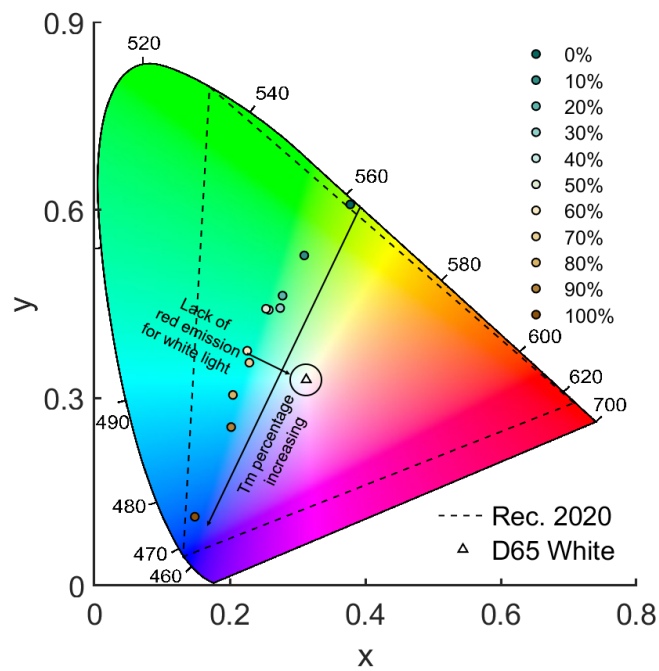
**Figure S2.** The CIE XYZ standard observer color matching functions.



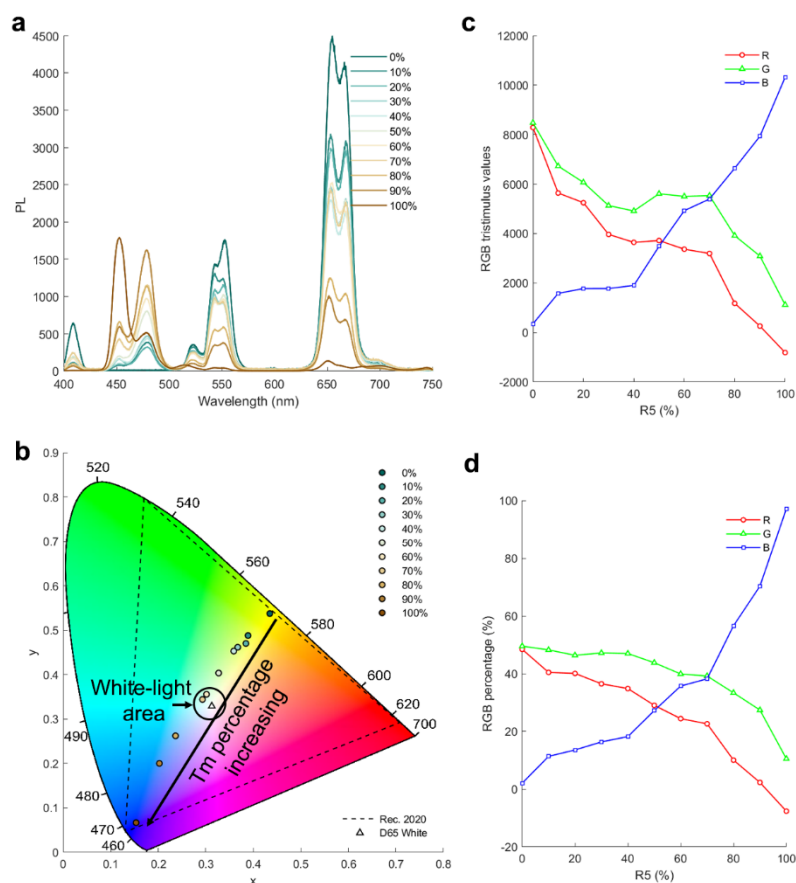
**Figure S3.** a-d) TEM images of nanocrystals from four different reactions. e) XRD of nanocrystals from four conditions. f) Spectra of NaYF<sub>4</sub>:Yb,Er UCNPs. g) The RGB percentage of UCNPs for four conditions.

The TEM micrographs shown in panels a–d show that small ‘popcorn-like’ NCs are obtained at 4 minute reaction times, which is consistent with the results presented in our manuscript. However, at 60 minutes, the NCs grew much larger (ca. 500 nm), and the XRD results showed that the 4 min/230°C reaction yields cubic ( $\alpha$ -) phase NCs, and the 4 min/270°C reactions yields products of mixed  $\alpha$ - and pure hexagonal ( $\beta$ -) phase. Both 60 min reactions yielded NCs of pure  $\beta$  phase.

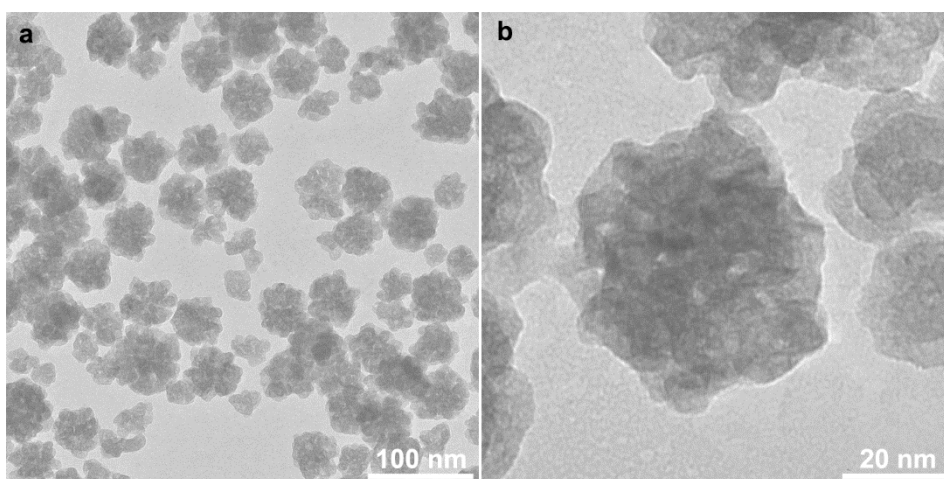




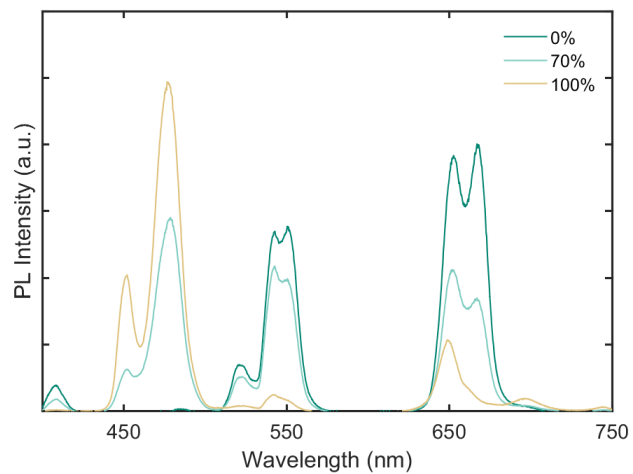
**Figure S4.** Plot of CIE1931 color coordinates of the NaYF<sub>4</sub>:Yb,Er,Tm UCNPs (20% Yb) with different values of  $R_5$ .



**Figure S5.** Color of NaYF<sub>4</sub>:Yb,Er,Tm (60% Yb) UCNP was tuned by changing the Tm doping degree ( $R_5$ ). a) Spectra of NaYF<sub>4</sub>:Yb,Er UCNP with Tm doping degree ( $R_5$ ) ranging from 0% to 100%. b) Plot of CIE1931 color coordinates of the NaYF<sub>4</sub>:Yb,Er,Tm UCNP with different value of  $R_5$ . c) The RGB tristimulus values of the NaYF<sub>4</sub>:Yb,Er with different values of  $R_5$ . d) The RGB percentage of UCNP with varying  $R_5$ .



**Figure S6.** TEM images of the NaYF<sub>4</sub>:Yb,Er,Tm UCNP under different magnification.



**Figure S7.** Spectra of NaYF<sub>4</sub>:Yb,Er UCNPs with Tm doping degree ( $R_5$ ) at 0%, 70%, and 100% for ETH logo anti-counterfeiting.