

Supporting Information

Simultaneous Ultraviolet-C and Near-Infrared Enhancement in Heterogeneous Lanthanide Nanocrystals

Yachong Liu,^{‡a} Mingzhu Zhou,^{‡a} Meng-Tao Zhou,^a Han-Lin Wei,^a Yan Su,^b and Qianqian Su^{a*}

^aInstitute of Nanochemistry and Nanobiology, Shanghai University, Shanghai 200444, China.

^bGenome Institute of Singapore, Agency of Science Technology and Research, 138672, Singapore.

*Corresponding authors: Q. Su, Email: chmsqq@shu.edu.cn.

Experimental Section

Materials: Y(CH₃CO₂)₃·xH₂O (99.9%), Nd(CH₃CO₂)₃·xH₂O (99.9%), Gd(CH₃CO₂)₃·xH₂O (99.9%), Yb(CH₃CO₂)₃·xH₂O (99.9%), Tm(CH₃CO₂)₃·xH₂O (99.9%), Er(CH₃CO₂)₃·xH₂O (99.9%), NaOH (>98%), NH₄F (>98%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), Nitrosonium tetrafluoroborate (NOBF₄) were all purchased from Sigma-Aldrich. Indocyanine green (ICG) were obtained from Aladdin. N-N dimethylformamide (DMF) (AR), Trichloromethane (AR), hydrochloric acid (AR), cyclohexane (AR) and Ethanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. DSPE-COOH-PEG (PEG) was purchased from Peng Shuo Biology. All chemicals were used as received without further purification.

Physical Measurements: Transmission electron microscopy (TEM) measurements were performed using a HT7700 field emission transmission electron microscope operated at an acceleration voltage of 120 kV. High-resolution TEM and the energy-dispersive X-ray (EDX) measurements were conducted on a FEI Talos F200S transmission electron microscope operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) results were recorded on a Rigaku D/MAX-2200 equipped with a rotating anode and a Cu K α radiation source ($\lambda = 0.15418$ nm). Luminescence spectra and lifetime measurements were recorded with a FS5 (Edinburgh), in conjunction with 793 nm (MDL-III-793), 808 nm (MDL-III-808) and 980 nm (MDL-III-980) at room temperature. Quantum yields were recorded at room temperature with an FLS1000 equipping with integrating sphere (Edinburgh). Elemental mapping images and Energy dispersive X-ray mapping analysis were performed with an FEI Themis Z (200 kV) transmission electron microscope. UV-vis absorption spectra were performed using a PerkinElmer Lambda 750 ultraviolet-visible-near infrared spectrometer. FTIR spectra were recorded using a PerkinElmer Spectrum Two. Unless otherwise specified, all spectra were recorded under identical

experimental conditions. Key experiments were repeated 3 times and other experiments were repeated twice.

Synthesis of NaGdF₄:49%Yb,1%Tm core nanocrystals: Yb/Tm co-doped NaGdF₄ nanocrystals were prepared according to a modified literature procedure^[1]. Gd(CH₃CO₂)₃ (0.134 g, 0.4 mmol), Yb(CH₃CO₂)₃ (0.138 g, 0.392 mmol) and Tm(CH₃CO₂)₃ (0.002 g, 0.008 mmol) in a aqueous stock solution (4 mL) were added into a 50 mL three-neck round-bottom flask charged with OA (10 mL) and ODE (10 mL) at room temperature. The mixture was heated to 150 °C and maintained at this temperature for 1.5 h. After cooling to room temperature, sodium oleate (6.4 mmol) was added to the solution and stirred evenly. The temperature was raised to 100 °C for 1 h under vacuum conditions. Subsequently, NH₄F (3.2 mmol) was added to the solution under nitrogen protection, and the solution was slowly heated to 160 °C and kept at this temperature for 1 h. After 10 min at this temperature, the solvent is removed *in vacuo*. The reaction mixture was then heated to 320 °C at a constant rate under a nitrogen atmosphere and kept for 30 min before cooling to room temperature. The as-prepared nanocrystals were collected by centrifugation at 8000 rpm for 5 min, and washed with ethanol and cyclohexane several times. The core nanocrystals were dispersed in 4 mL cyclohexane prior to being used for shell coating.

Synthesis of NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb core-shell nanocrystals: The synthesis of core-shell nanocrystals was developed via a similar literature procedure^[2]. The pre-obtained NaGdF₄:49%Yb,1%Tm core nanocrystals were served as seeds for shell coating. Rare earth acetate Y(CH₃CO₂)₃ (0.0851 g, 0.32 mmol), Yb(CH₃CO₂)₃ (0.0282 g, 0.08 mmol) was added to a 50 mL three-neck round-bottom flask, and then 4 mL oleic acid and 6 mL octadecene was added to the solution and heated to 150 °C for 1.5 h. After cooling to 50 °C, a methanol solution (4.4 mL) containing NH₄F (0.05 g, 1.36 mmol) and NaOH (0.04 g, 1 mmol) was added quickly and stirred for 30 min. Then, the resulting mixture was then heated to 80 °C for 30 min to remove methanol prior to being an injection. Meanwhile, NaGdF₄:Yb/Tm core nanocrystals dispersed in cyclohexane (4 mL) was added into a 50 mL three-neck flask containing 4 mL oleic acid and 6 mL octadecene, stirred at 80 °C for 30 min to remove cyclohexane. The mixture was then heated at 100 °C for 30 min *in vacuo*. Subsequently, the temperature was heated to 310 °C, and the shell precursor was injected at a constant rate within 20 min before cooling to room temperature. The resulting nanocrystals were collected by adding ethanol and washed with ethanol and cyclohexane before being dispersed in 4 mL cyclohexane.

Synthesis of NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNF₄:10%Yb and NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNF₄:10%Yb@NaYF₄ (GYNY) core-multishell nanocrystals: The

synthesis of the above mentioned and other core-multishell nanocrystals including NaGdF₄:49%Yb,1%Tm@NaGdF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄ (GGNY), NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄:20%Yb,2%Er@NaYF₄ (GNYN_{20%Yb,2%Er}Y), NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄:30%Gd (GYN@Y30Gd), NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄@NaYF₄ (GYNYY), NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄@NaYF₄@NaYF₄ (GYNYYY) was identical to that for core-shell nanocrystals except for the use of a shell stock solution with different lanthanide dopants.

Preparation of ICG-coated GYNY nanocrystals: First, GYNY nanocrystals modified with OA ligand were replaced with NOBF₄ ligand. In a typical experiment, 100 μL of GYNY nanocrystals dispersed in 4 mL cyclohexane solution were taken out, and then added with cyclohexane and ethanol at a ratio of 2 to 3 (8000 rpm, 5 min), centrifugal drying, weighing, and determined the concentration. Then, 5 mL of NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄ core-multishell nanocrystals dispersed in cyclohexane at 10 mg/mL was added to 5 mL of 0.1 M NOBF₄ dispersed in dimethylformamide (DMF) at 20 mL centrifuge tube. Shake gently in a shaker for 10 min. When the centrifuge tube is removed from the shaker, there is a distinct stratification with the cyclohexane solution on the top and the DMF solution on the bottom. Rare earth core-shell nanocrystals were extracted from cyclohexane phase to dimethylformamide (DMF) phase. The top layer of cyclohexane was poured out, and the lower layer of dimethylformamide (DMF) was removed from the centrifuge tube, and then a large amount of toluene and cyclohexane were added at 1:1, 12000 rpm, 15 min. The resulting precipitation was redispersed in dimethylformamide (DMF). The mass concentration was determined after centrifugal drying. The rare earth nanocrystals (5 mg/mL) were added to the brown bottle, and the ICG solution dispersed in DMF was added. After stirring for 2 h, the rare earth luminescent nanocrystals connected with ICG (UCNP@ICG) were obtained.

Preparation of PEG-linked indocyanine green (ICG) sensitized core-shell nanocrystals: The prepared NaGdF₄:49%Yb,1%Tm@NaYF₄:20%Yb@NaNdF₄:10%Yb@NaYF₄ rare earth core-shell nanocrystals were dispersed in 4 mL cyclohexane, 100 μL solution was taken out, cyclohexane and ethanol were added in a ratio of 2 to 3 (8000 rpm, 5 min), centrifugal drying, weighing, and determined the concentration. Add 200 μL (5 mg/mL) of the solution to a 50 mL round bottom flask and dry with nitrogen. DSPE-COOH-PEG (PEG) and indocyanine green (ICG) were dissolved in trichloromethane solution, in which indocyanine green (ICG) trichloromethane solution should be stored away from light at the concentration of 0.1 mg/mL. DSPE-COOH-PEG (PEG) and indocyanine green (ICG) in chloroform solution were added to the solid in the round bottom

flask, ultrasonic for 10 min. Attention should be paid to avoid light during the experiment. After the ultrasound, the chloroform solution in the round-bottom flask was removed (40 °C, 50 rpm) by a rotary evaporation instrument, and the solid was obtained in the round-bottom flask was added with 1 mL deionized water for ultrasonic dissolution. Finally, the solution in the round-bottom flask was taken out and centrifuged at 12000 rpm for 15 min. The solution was washed again and then dispersed in 1 mL deionized water.

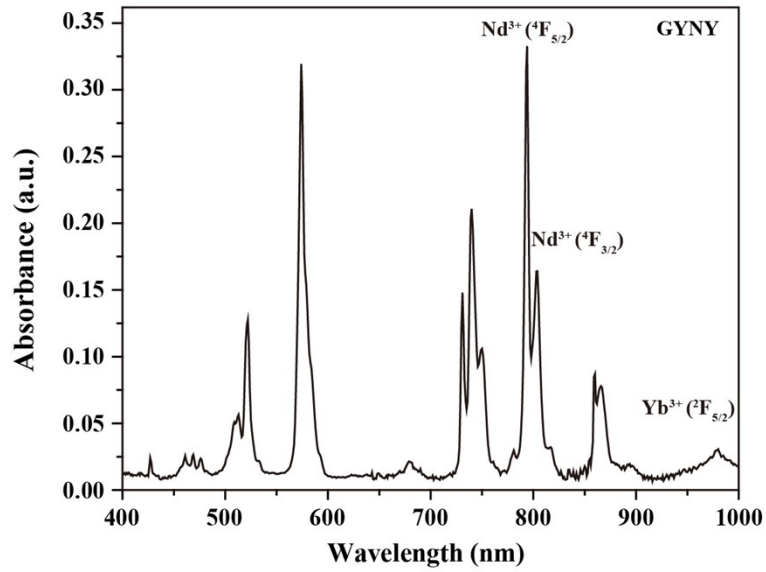


Figure S1. Absorption spectra of GYNY nanocrystals.

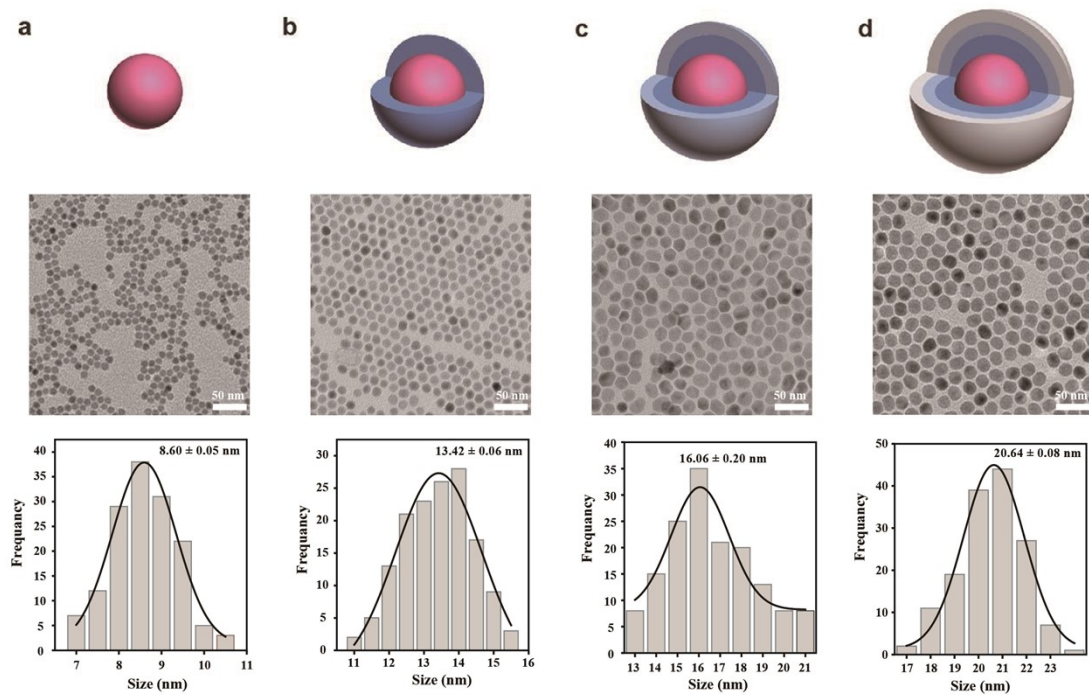


Figure S2. Schematic illustration, TEM images and size distributions of core (a), core-shell (b), core-shell-shell (c), and core-multishell (d) of the as-synthesized $\text{NaGdF}_4:49\%\text{Yb},1\%\text{Tm}@ \text{NaYF}_4:20\%\text{Yb}@ \text{NaNdF}_4:10\%\text{Yb}@ \text{NaYF}_4$ (GYNY) nanocrystal. The size distribution is fitted by a Gaussian curve (black full line).

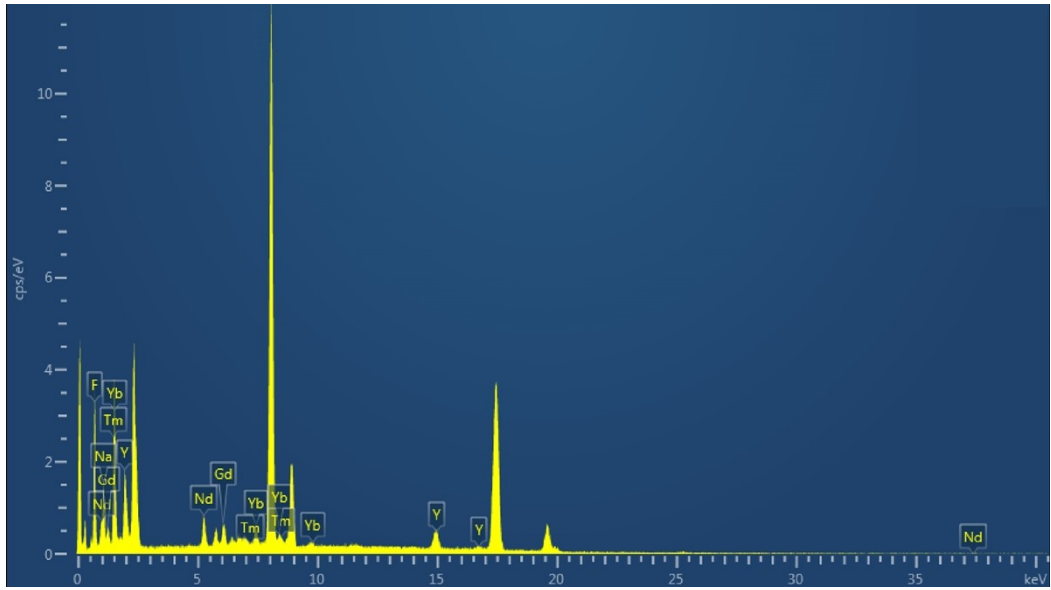


Figure S3. Energy dispersive X-ray (EDX) spectrum of GYNY nanocrystals.

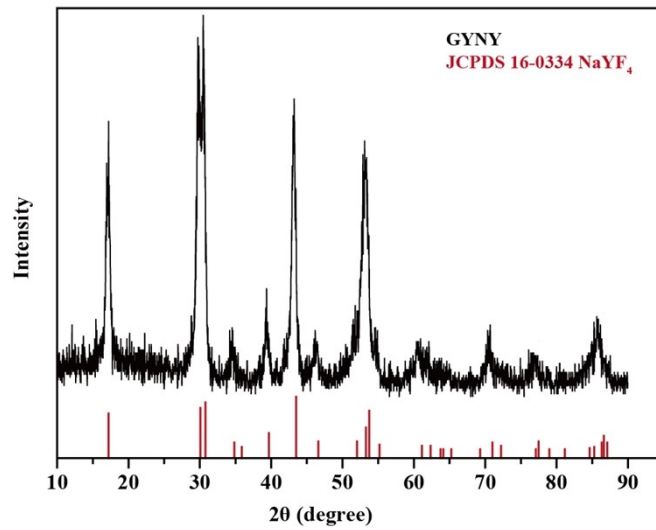


Figure S4. XRD pattern of GYNY nanocrystals.

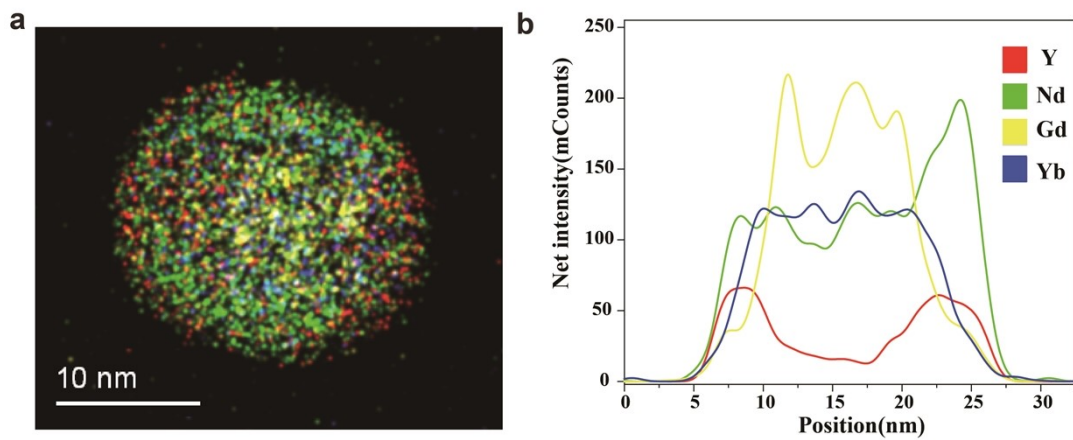


Figure S5. (a) Elemental mapping of a single GYNY nanoparticle. (b) Energy dispersive X-ray mapping analysis of the core-multishell nanoparticle.

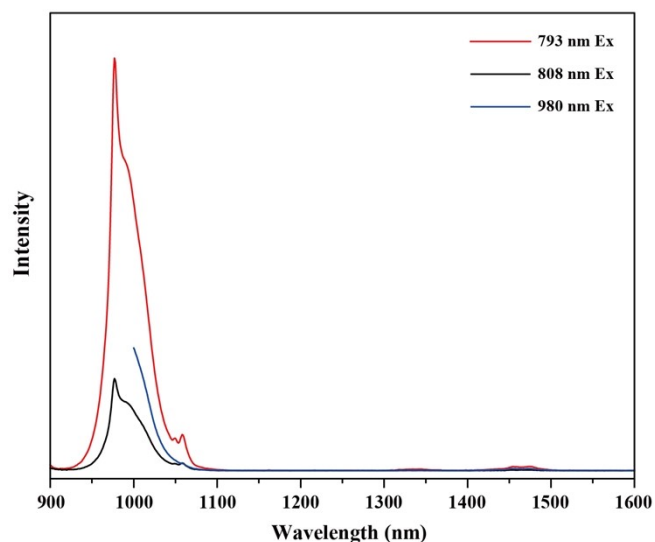


Figure S6. Downshifting luminescence spectra of GYNY nanocrystals in cyclohexane under 793, 808 and 980 nm excitation at a power density of 28.0 W cm^{-2} .

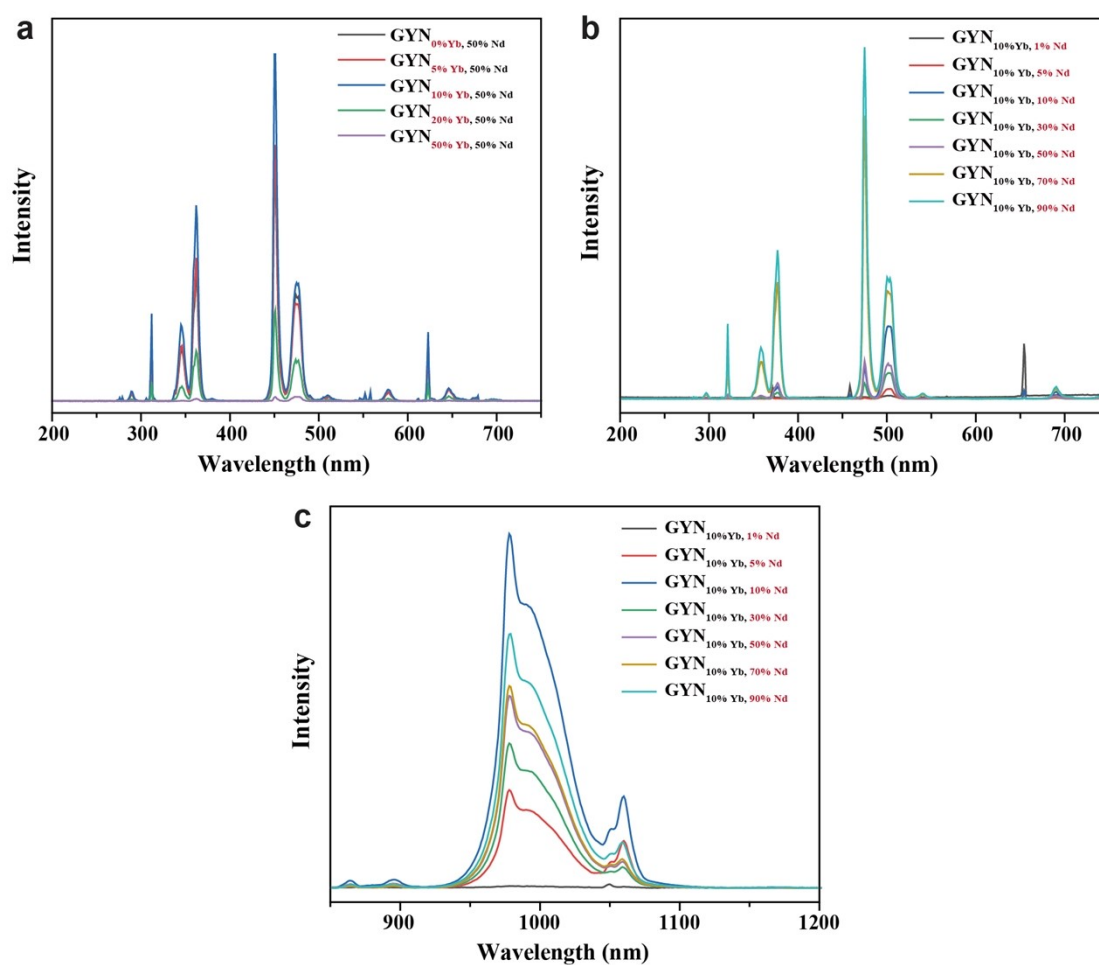


Figure S7. (a-b) Upconversion emission spectra for a series of core-multishell nanocrystals as a function of different Yb^{3+} and Nd^{3+} concentration. (c) Downshifting emission spectra of corresponding nanocrystals as a function of different Nd^{3+} concentration.

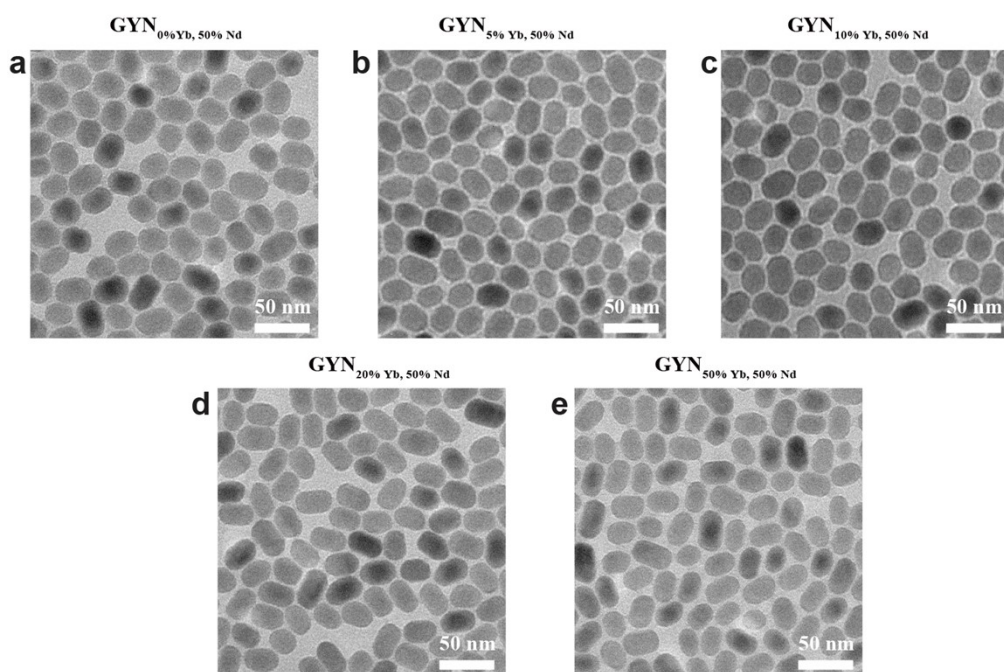


Figure S8. TEM images of a series of core-shell-shell nanocrystals as a function of different Yb^{3+} .

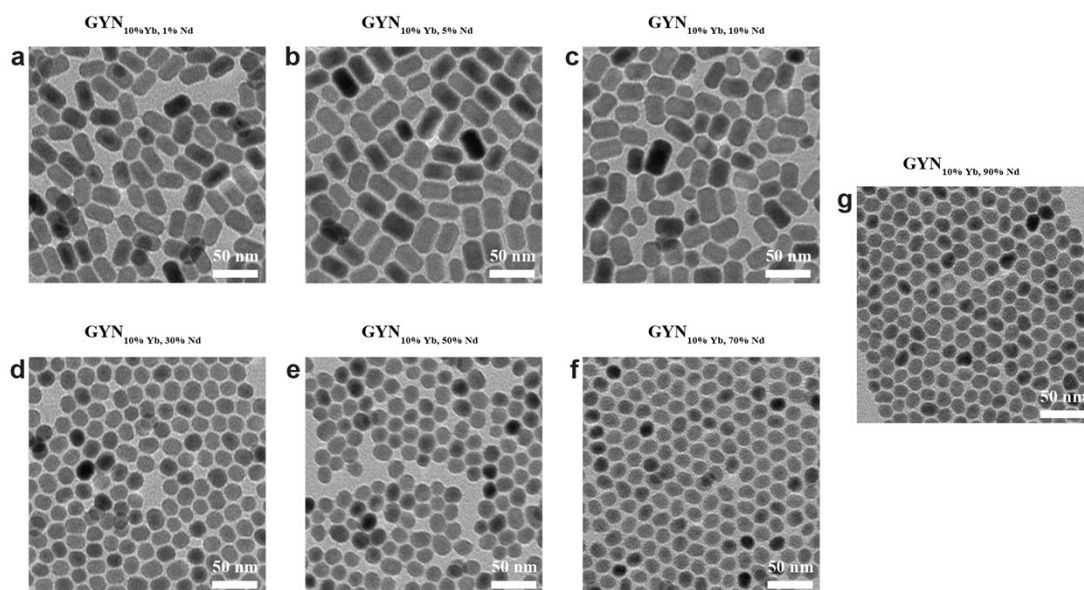


Figure S9. TEM images of a series of core-shell-shell nanocrystals as a function of different Nd^{3+} .

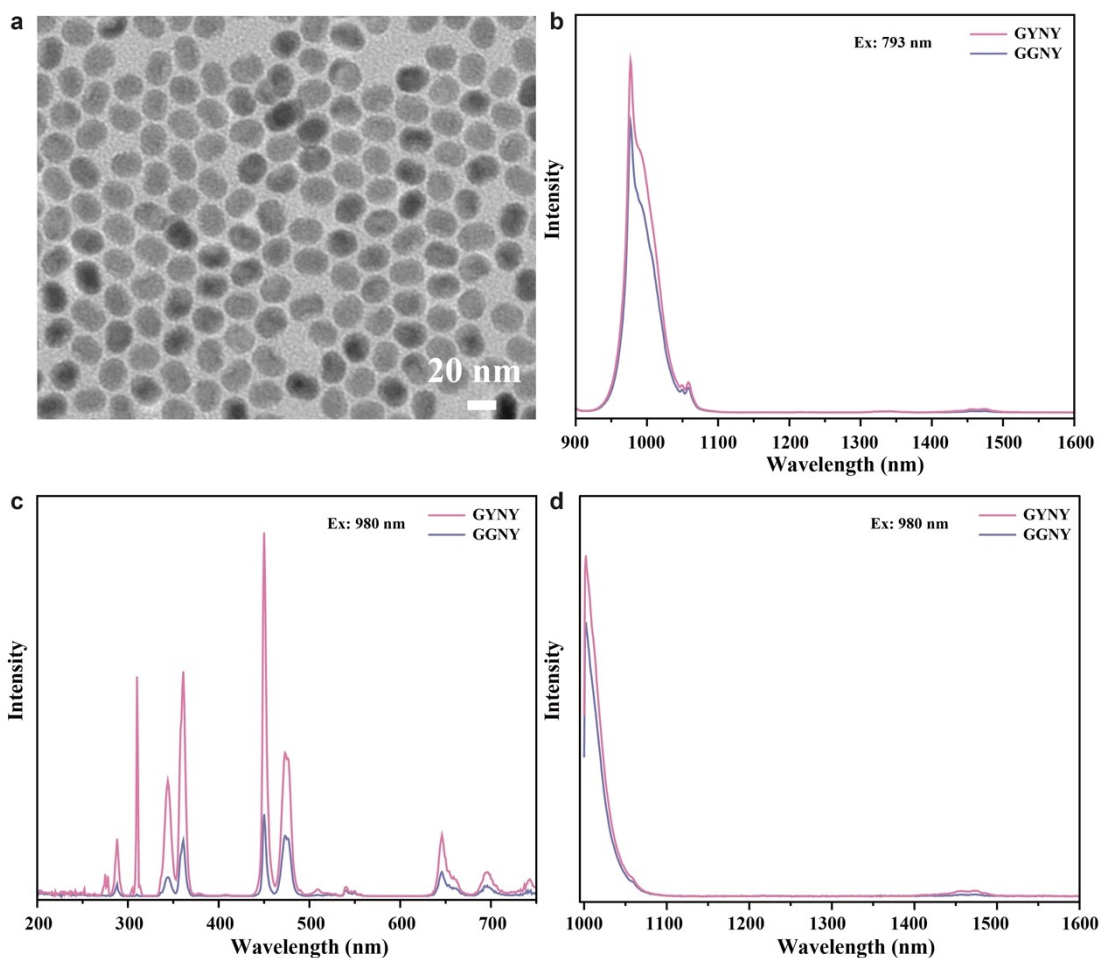


Figure S10. (a) TEM image of $\text{NaGdF}_4:49\%Yb,1\%Tm@NaGdF_4:20\%Yb@NaNdF_4:10\%Yb@NaYF_4$ (GGNY) nanocrystals. (b) Downshifting emission spectra of GYNY and GGNY nanocrystals under 793 nm excitation. (c-d) Upconversion and downshifting emission spectra of GYNY and GGNY nanocrystals under 980 nm excitation.

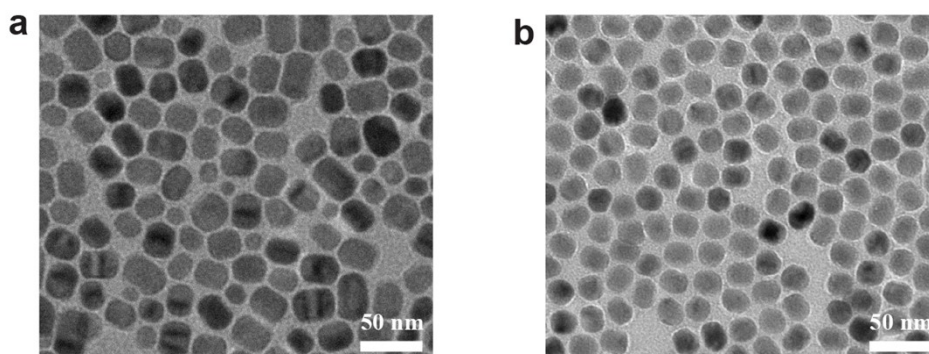


Figure S11. (a) TEM image of $\text{NaGdF}_4:49\%Y,1\%Tm@NaYF_4@NaNdF_4:10\%Y@NaYF_4$ (GYNY without Yb^{3+}). (b) TEM image of $\text{NaGdF}_4:49\%Yb,1\%Tm@NaYF_4:20\%Yb@NaNdF_4:10\%Yb@NaYF_4$ (GYNY with Yb^{3+}).

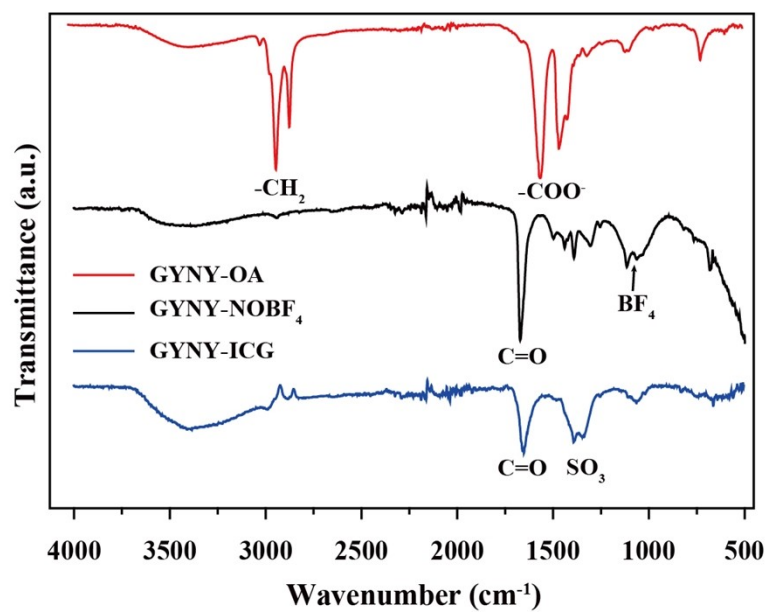


Figure S12. FTIR spectra of oleic acid (OA), NOBF₄ and ICG coated GYNY nanocrystals.

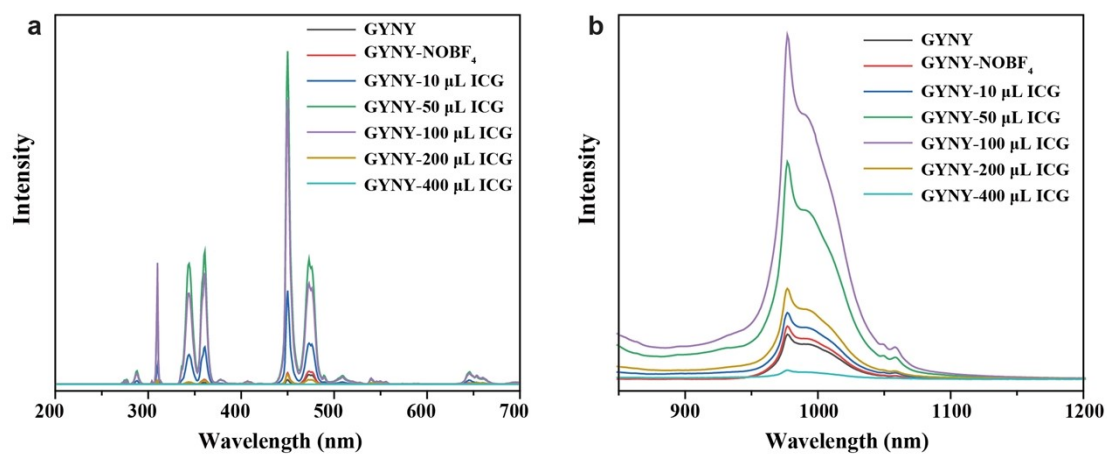


Figure S13. (a-b) Upconversion and downshifting emission spectra of GYNY nanocrystals as a function of ICG concentration in DMF solution.

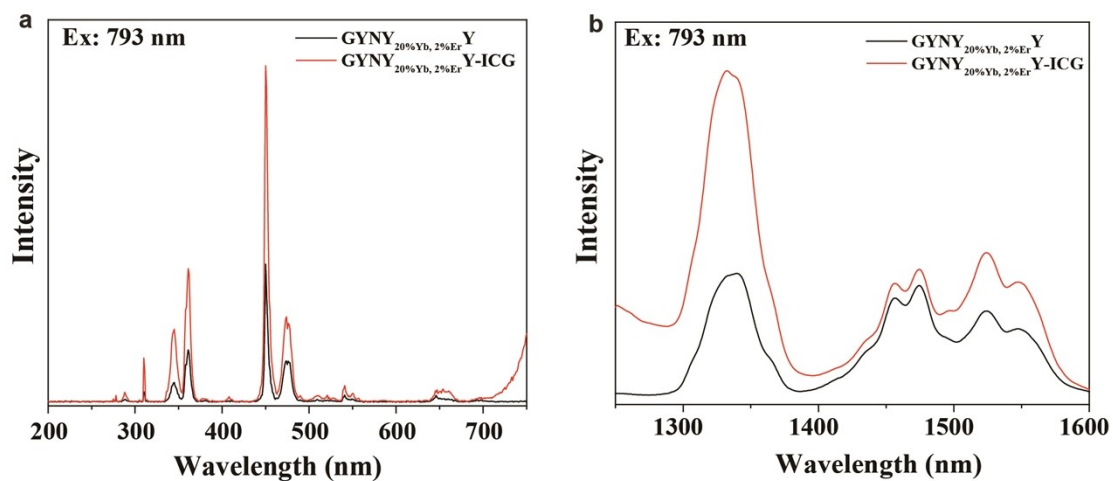


Figure S14. (a-b) Upconversion and downshifting emission of GYNY_{20%Yb, 2%Er}Y and ICG-coated GYNY_{20%Yb, 2%Er}Y nanocrystals. The concentrations of nanoparticles and ICG dye were 5 mg/mL and 2.5 $\mu\text{g/mL}$.

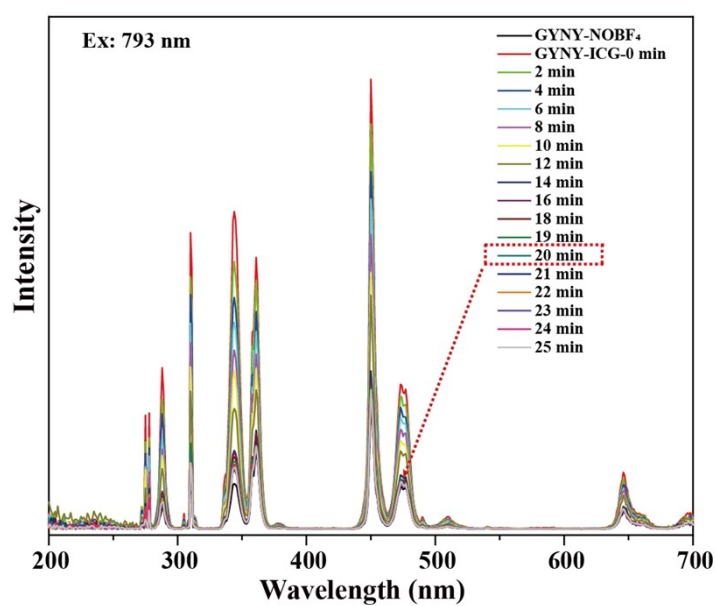


Figure S15. Characterization of photostability of GYNY@ICG under 793 nm excitation at a power density of 20 W cm^{-2} .

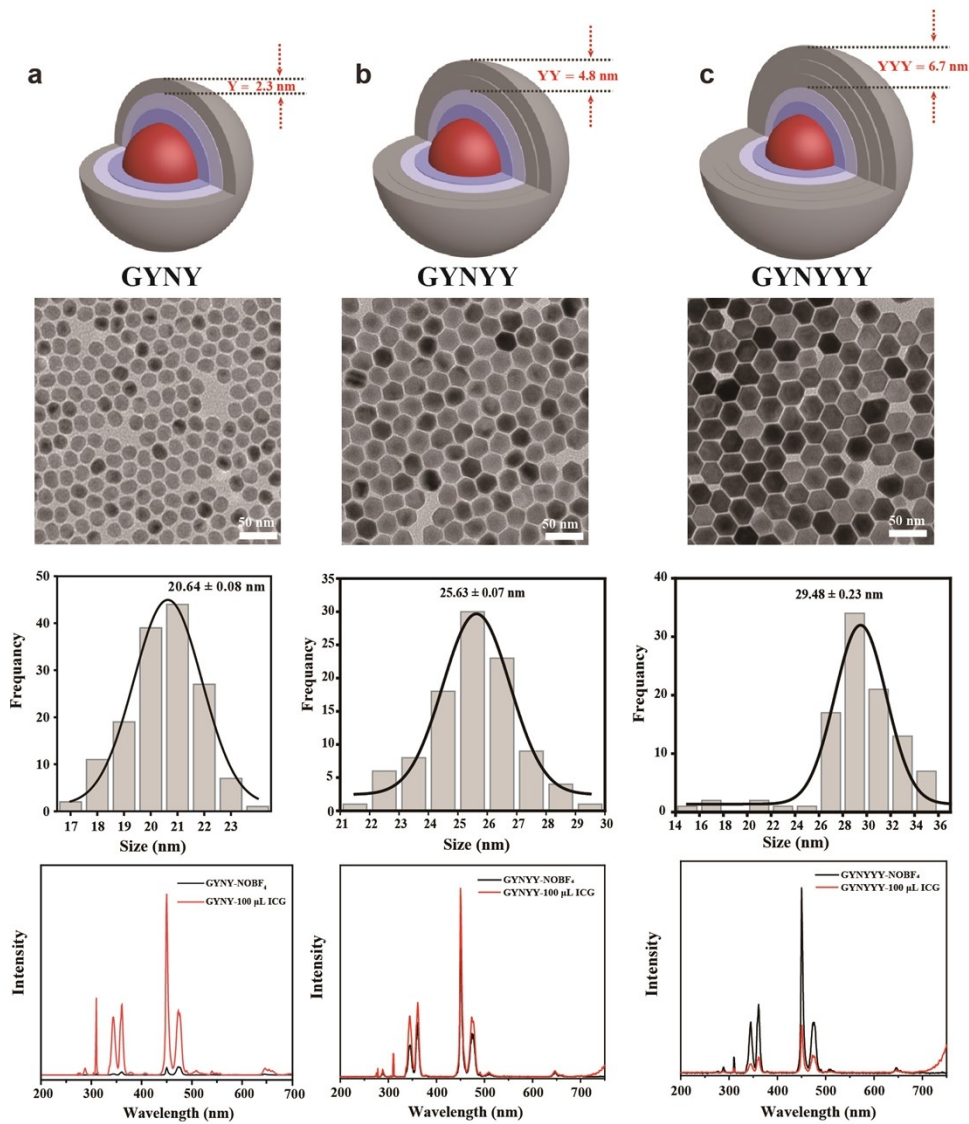


Figure S16. Schematic illustration, TEM images, size distributions, upconversion emission spectra of GYNY (a), GYNYN (b), GYNYNN (c) nanocrystals, and upconversion emission spectra of ICG-coated these nanocrystals. The size distribution is fitted by a Gaussian curve (black full line).

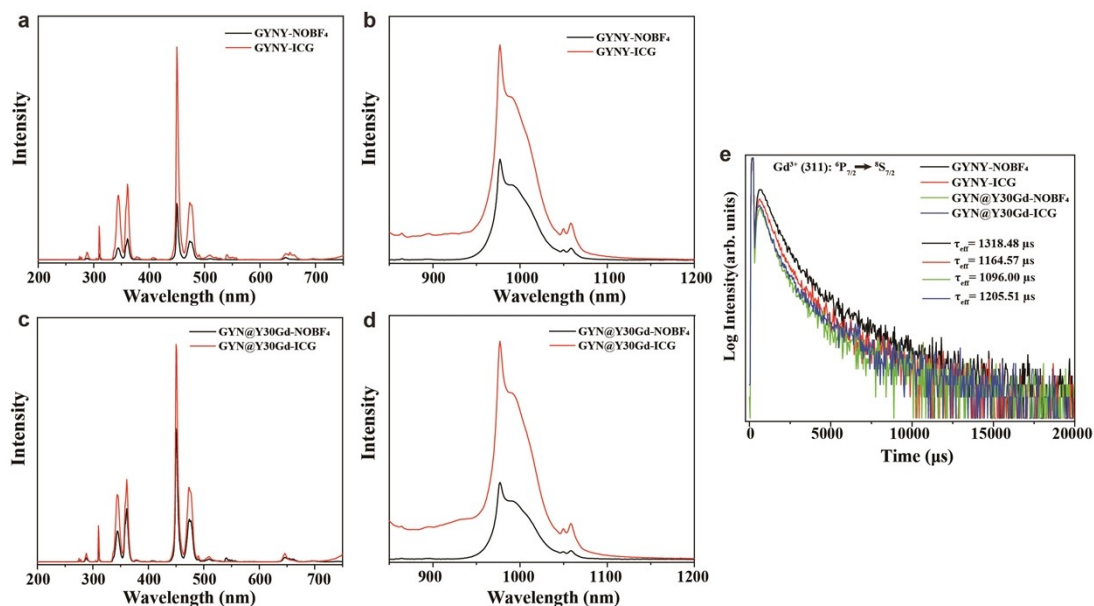


Figure S17. (a-b) Upconversion and downshifting emission spectra of GYNY nanocrystals before and after ICG dye coating. (c-d) Upconversion and downshifting emission spectra of GYN@Y30%Gd nanocrystals before and after ICG dye coating. (e) Comparison of the lifetimes of Gd³⁺ (311) in GYNY and GYN@Y30Gd nanoparticles before and after ICG coating under excitation of 793 nm. The nanocrystals with a concentration of 5 mg/mL were coated with ICG dye at 2.5 μg/mL.

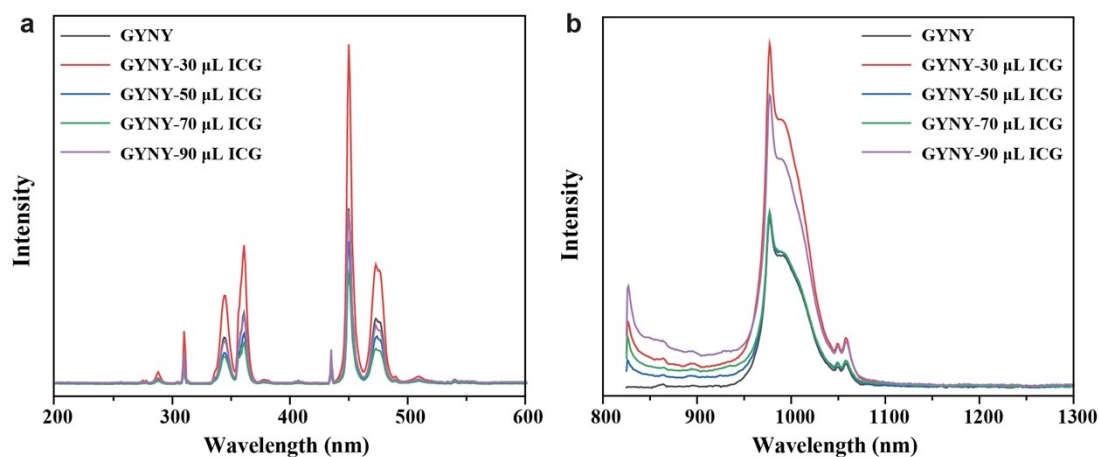


Figure S18. (a-b) Upconversion and downshifting emission spectra of GYNY nanocrystals as a function of ICG concentration in aqueous solution.

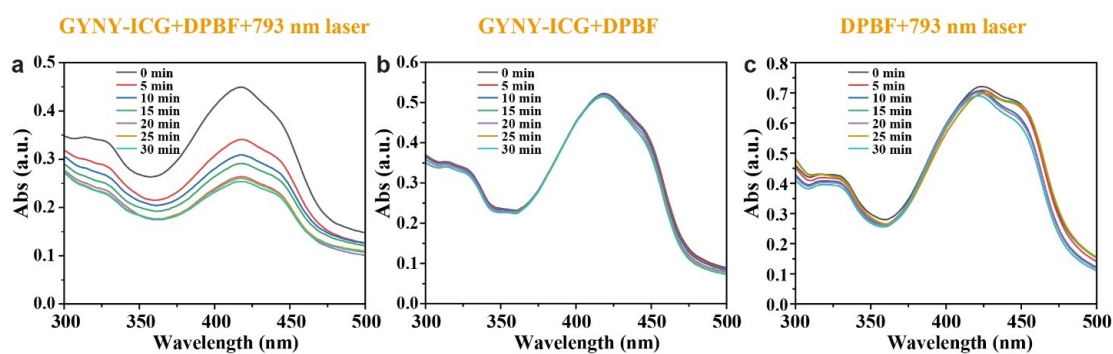


Figure S19. (a-c) Absorbance changes of DPBF treated with ICG-coated GYNY nanocrystals accompanied with 793 nm laser irradiation, ICG-coated GYNY, and 793 nm laser irradiation for different times.

References

- [1] R. Shi, X. Ling, X. Li, L. Zhang, M. Lu, X. Xie, L. Huang and W. Huang. *Nanoscale*, 2017, **9**, 13739-13746.
- [2] Q. Su, H. L. Wei, Y. Liu, C. Chen, M. Guan, S. Wang, Y. Su, H. Wang, Z. Chen and D. Jin, *Nat. Commun.*, 2021, **12**, 4367.