

Electronic Supplementary Material

Dye-Sensitized Upconversion Nanoprobes with a pH-Modulated Reversible Sensitizing Switch

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Materials

$\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, $\text{Yb}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, $\text{Er}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, $\text{Nd}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, oleic acid and DSPE-PEG2000 were purchased from Sigma Aldrich. 1-octadecene, NH_4F , NaOH , methanol and Dimethyl sulfoxide (DMSO) were from Aladdin Reagent, Ltd. All the chemicals used in this study are analytical grade. Fetal bovine Serum (FBS), penicillin, streptomycin, and Roswell Park Memorial Institute (RPMI-1640) were procured from GIBCO and used as directed.

Instruments

The UV-Vis spectrum was collected by the Lambda 35 spectrophotometer (Perkin-Elmer). Using $0.5\text{W}\cdot\text{cm}^{-2}$ 808 nm diode continuous wave laser (Changchun New Industries Optoelectronics Tech Co., Ltd.) as the excitation source, the upconversion luminescence spectra of the upconversion nanoparticles were measured. Fourier Transform infrared (FT-IR) spectroscopy was performed on the FTS 6000 spectrometer (Bio-Rad Inc., USA) using KBr particles (Nicolet, USA). Transmission electron microscope (TEM) images were taken at 200 kV using JEM-2100HR (JEOL, Japan). The hydrodynamic dimensions of nanoparticles were measured at 25°C using ZEN3690 zetasizer (Malvern Instruments, Zetasizer Nano-ZS). Confocal laser scanning microscope (CLSM) images were obtained on Olympus FV3000 microscope (Olympus Imaging America Inc., JAPAN) equipped with an 808nm laser source. In vitro cytotoxicity assays were performed on a Spark microboard Reader (TECAN, Switzerland). In vivo UCL images were recorded using the in vivo imaging system of IVScope 8500 (Shanghai Qinxiang Scientific Instruments Co., LTD.) equipped with 808 nm laser source.

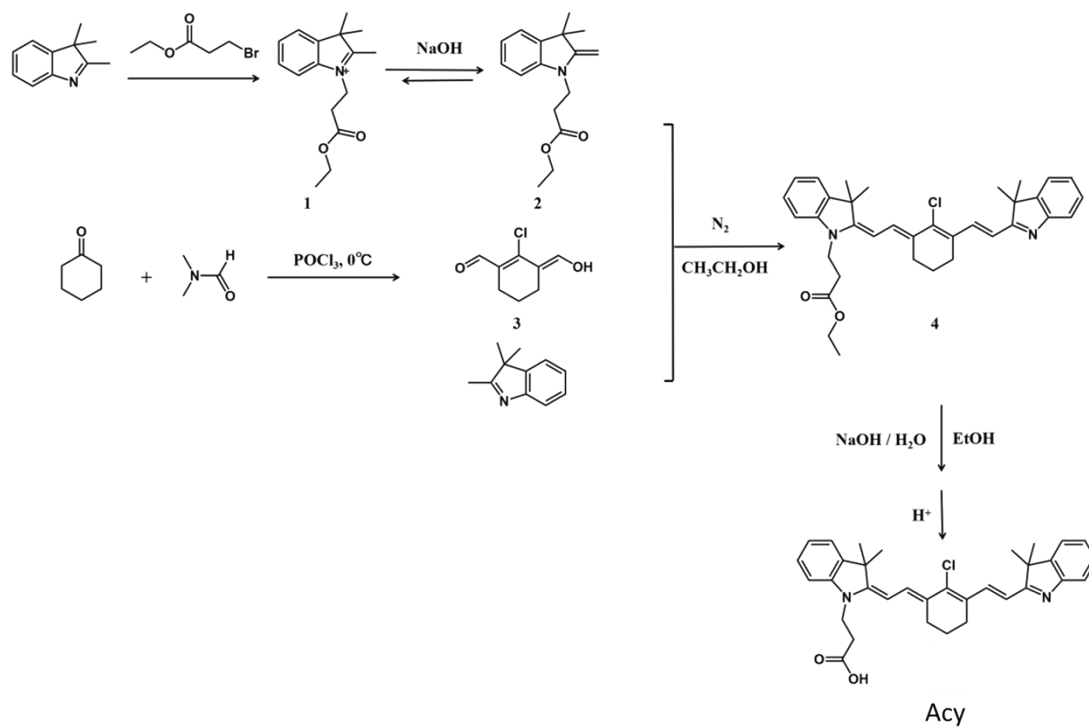


Fig. S1. Synthetic scheme for the dye Acy.

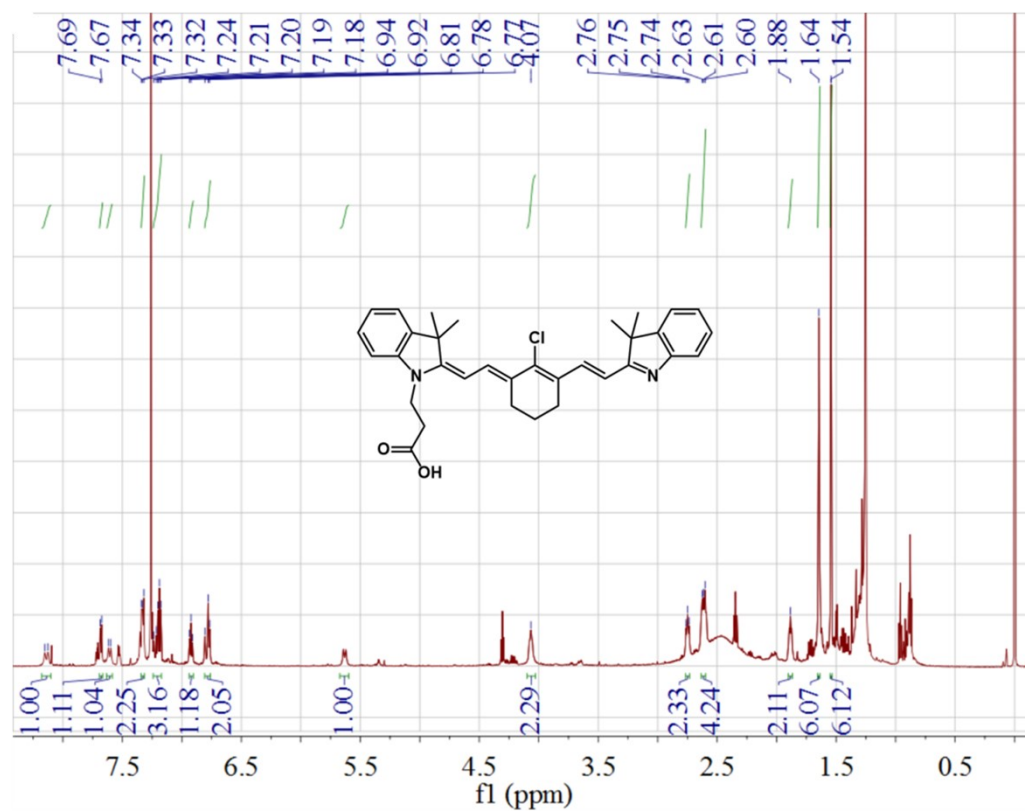


Fig. S2. ¹H NMR spectrum of Acy.

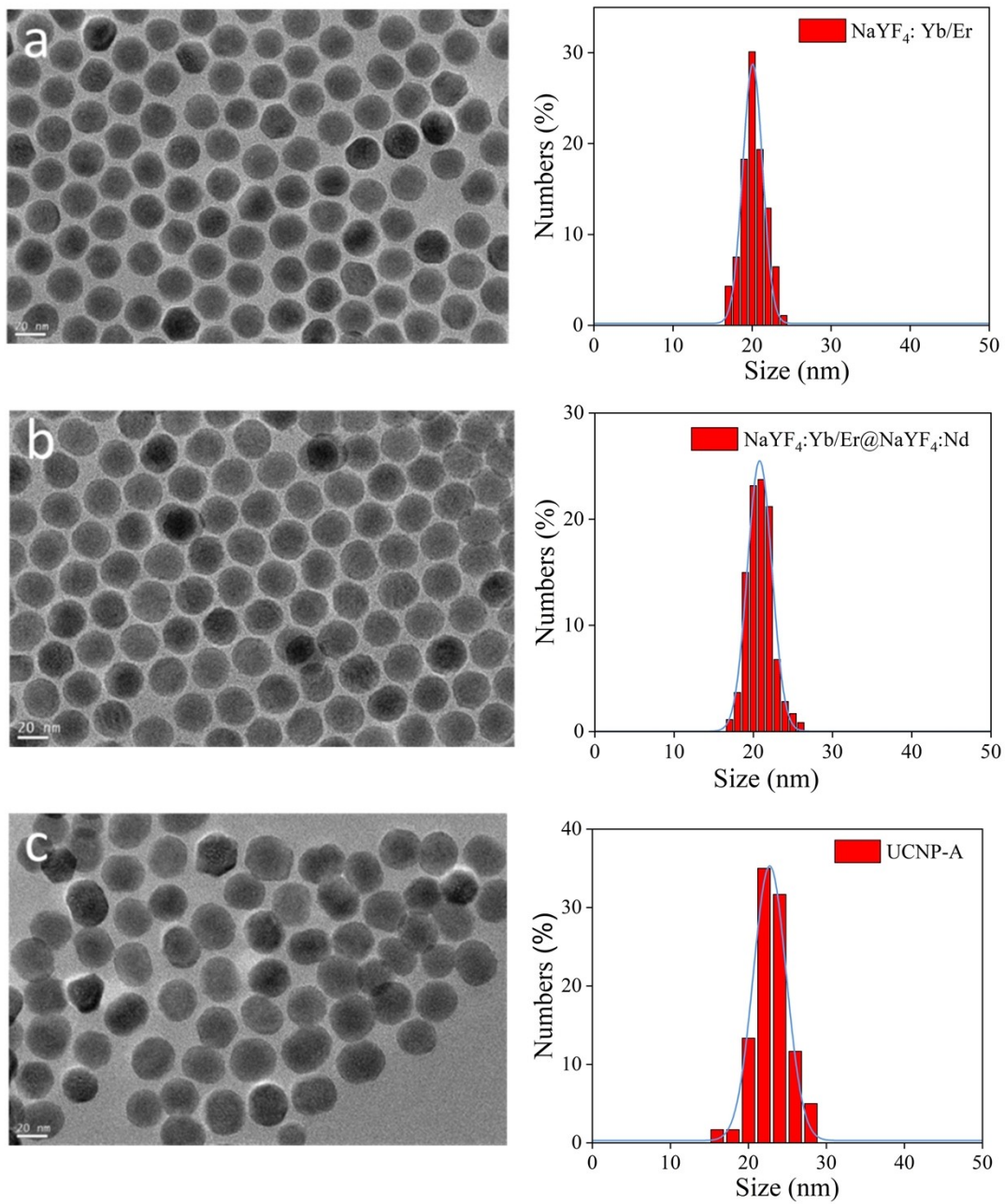


Fig. S3. TEM images and particle size histograms of (a) $\text{NaYF}_4:\text{Yb/Er}$, (b) $\text{NaYF}_4:\text{Yb/Er}@ \text{NaYF}_4:\text{Nd}$ and (c) UCNP-A.

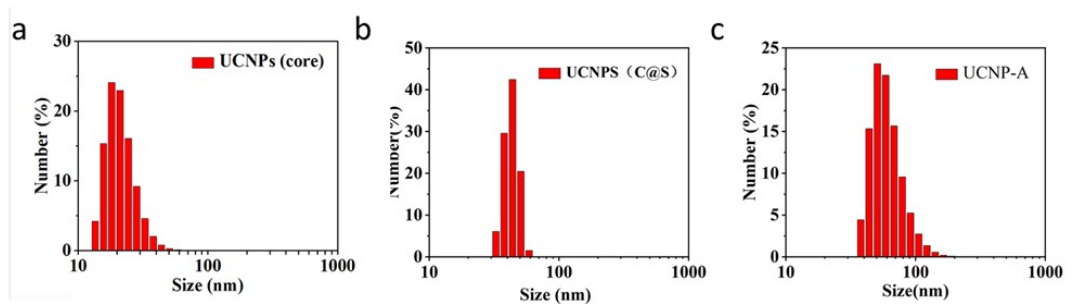


Fig. S4. The DLS result of (a) NaYF₄: Yb/Er, (b) NaYF₄:Yb/Er@NaYF₄:Nd and (c) UCNP-A.

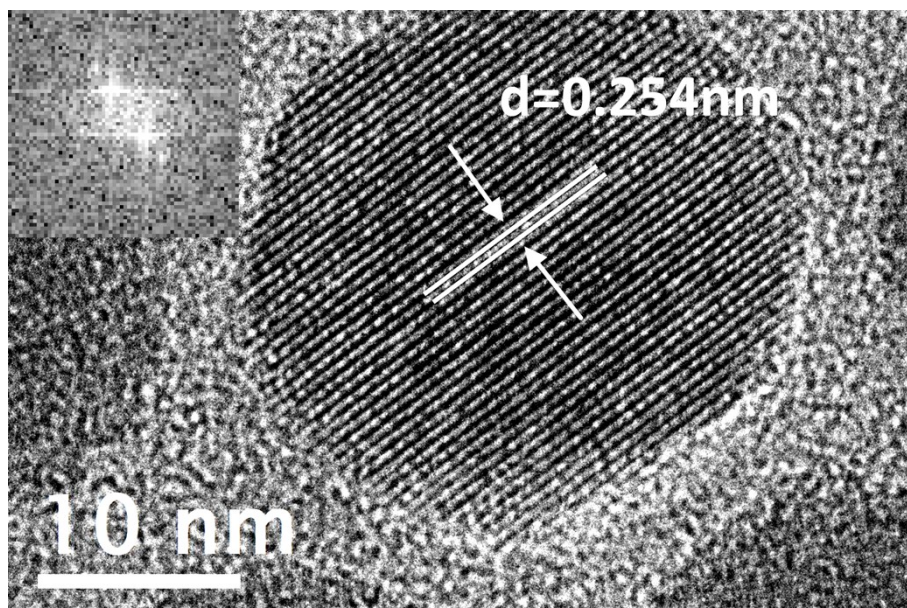


Fig. S5. HR-TEM micrograph of the UCNP-A. (Inset: IFFT image).

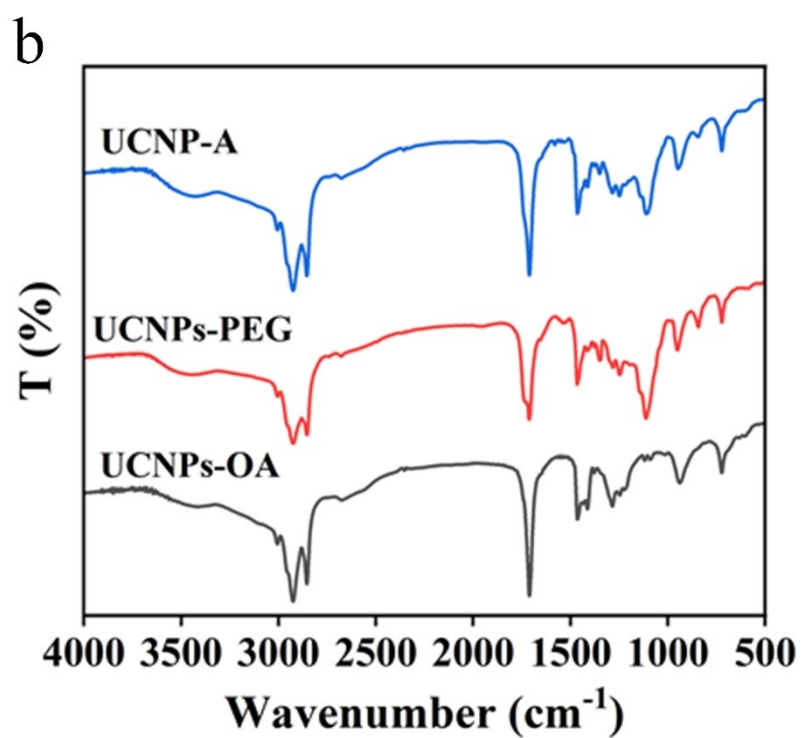
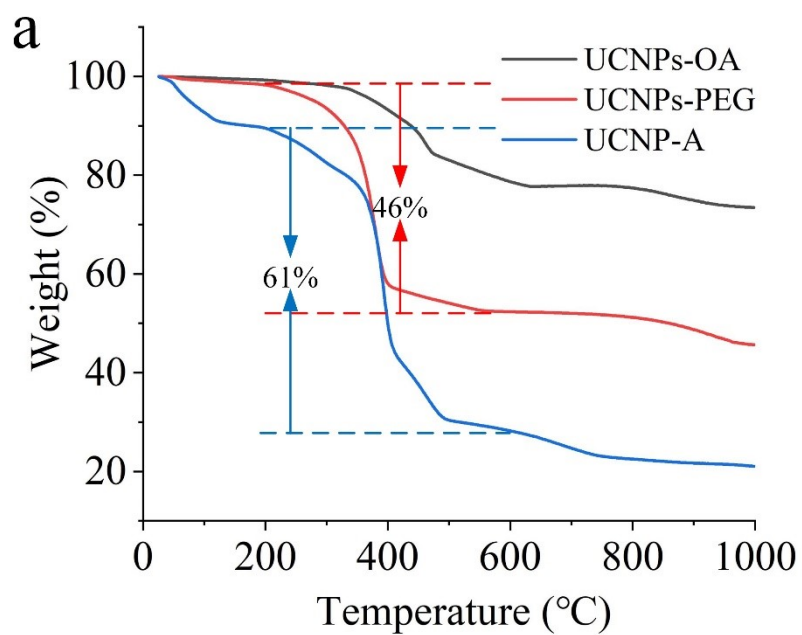


Fig S6. (a) TGA of UCNPs-OA, UCNPs-PEG, and UCNP-A. (b) FT-IR transmission spectrum of UCNPs-OA, UCNPs-PEG and UCNP-A.

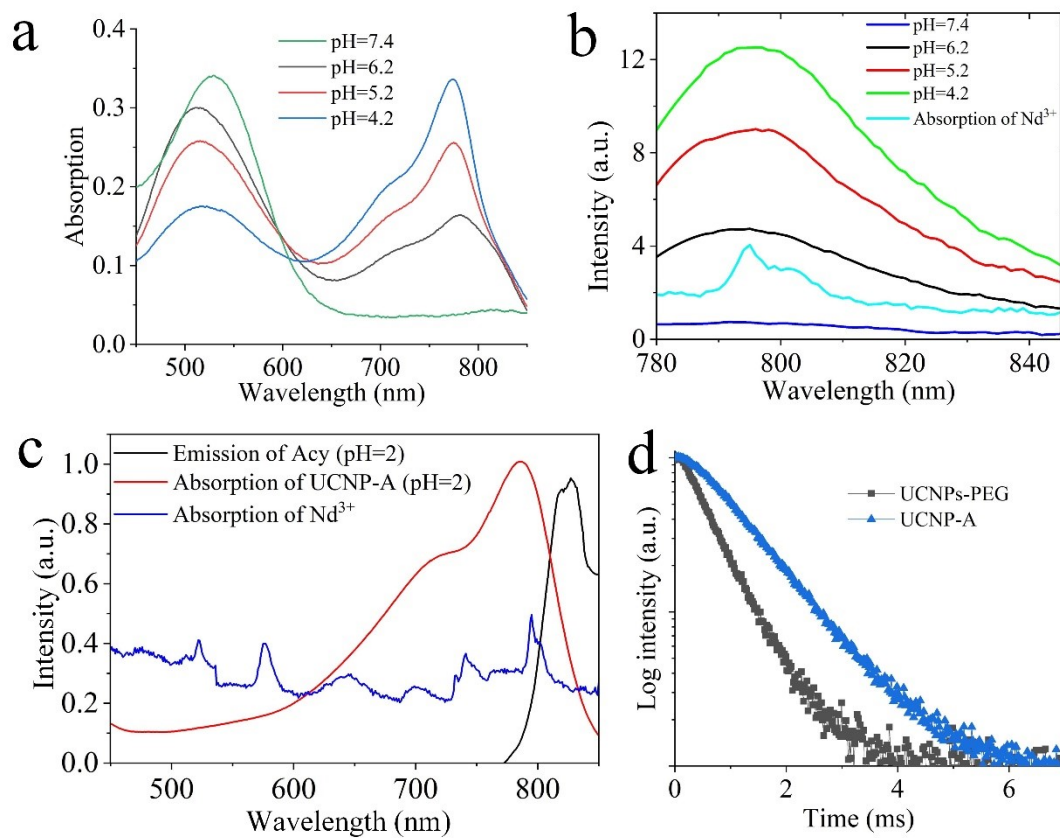


Fig. S7 (a) Absorption spectra of the dye Acy in PBS at different pH. (b) Fluorescence emission spectrum of dye Acy in PBS at different pH and absorption spectrum of Nd^{3+} . (c) The absorption spectrum of UCNP-A and fluorescence emission spectrum of the dye Acy in PBS (pH=2), and absorption spectrum of Nd^{3+} . (d) Luminescence decay curves of 540 nm emission of UCNPs-PEG and UCNP-A in PBS (pH=2) excited by 808 nm laser.

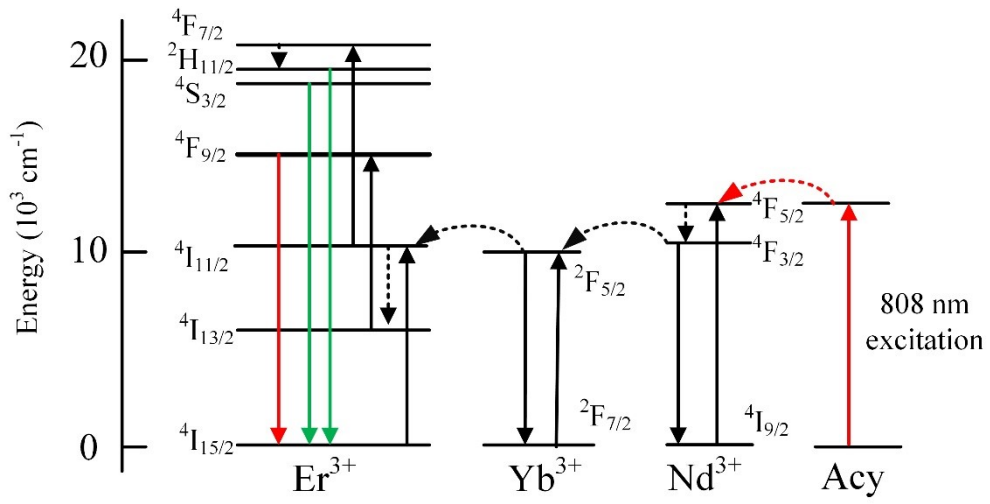


Fig. S8 The schematic diagram of the energy level transition mechanism of UCNP-A.

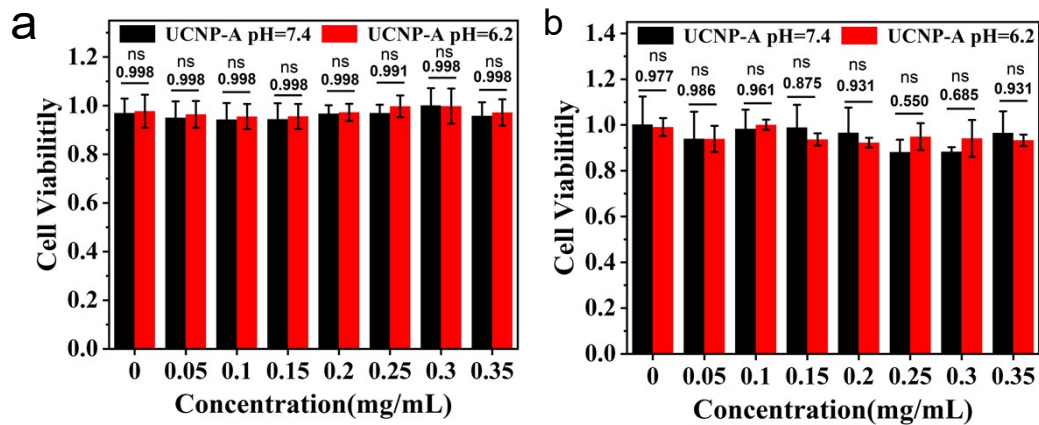


Fig. S9. In vitro cell viability of EMT-6 cells incubated with UCNP-A at different concentration for 24 h (a) in dark (b) under 808 nm laser irradiation, the number between groups represented p value. The differences between groups were analyzed using Two-tailed Student's t-test, ns no significance, * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.