Supplementary Information (SI) for Nanoscale Horizons.

Supplementary Information

Enhanced Upconversion and Photoconductive Nanocomposites of Lanthanide-Doped Nanoparticles Functionalized with Low-Vibrational-Energy Inorganic Ligands

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Materials and Methods

Chemicals

Tin (IV) chloride pentahydrate ($SnCl_4•5H_2O$, 98%), Tetrafluoroboric acid diethyl ether complex (HBF_4 diethyl ether complex), N,N-Dimethylformamide (DMF, 99.8%), sodium trifluoroacetate (NaTFA, 98%), ytterbium (III) chloride ($YbCl_3$, 99.9+%), erbium (III) chloride ($ErCl_3$, 99.9+%), gadolinium (III) chloride ($GdCl_3$, 99.9+%), thulium (III) chloride ($TmCl_3$, 99.9+%), yttrium (III) chloride (YCl_3, 99.9+%), ammonium fluoride (NH_4F, 99.9%), oleic acid (OAc, 90%), oleylamine (OAm, technical grade, 70%), and octadecene (ODE, technical grade, 90%) were purchased from Sigma Aldrich. Sodium oleate (>97.0%) was purchased from TCI Chemicals. N-Methylformamide (NMF, 99%) was purchased from Alfa Aesar. Sodium sulfide nonahydrate ($Na_2S•9H_2O$, 98+%) was purchased from Thermo Scientific.

Synthesis of lanthanide-doped $NaYF_4$ UCNPs

Lanthanide-doped $NaYF_4$ UCNP core synthesis. The syntheses of doped $NaYF_4$ nanoparticles were carried out according to a previously described procedure, with scaling up and modifications.[1] In a typical synthesis, to a dry 100 mL 3-neck round bottom flask was added rare earth salts (total of 2 mmol) such as YCl_3 and other lanthanide chloride dopant salts (e.g., $TmCl_3$, $YbCl_3$, $ErCl_3$), oleic acid (19 mmol, 10.74 g, 12 mL), and octadecene (22.09 g, 28 mL). The mixture was stirred and degassed under vacuum at 100 °C for at least 1 hr (a clear solution is obtained). After degassing, the flask was put under N_2, and to it was added sodium oleate (5 mmol, 1.522 g) and ammonium fluoride (8 mmol, 0.296 g). The mixture was then stirred and degassed under vacuum again at 100 °C for 45 min. During this time, two N_2 refill/degas cycles were carried out (at the 7th min mark and the 14th min mark). After this, the flask was put under N_2 and rapidly heated to 310 °C and held at this temperature for 30 mins. After this, the flask is quickly cooled down to <80 °C using a directed airflow.

The cooled reaction mixture was transferred into a 50 mL centrifuge tube and toluene (usually a few mL) was added to get a total volume of 45 mL. This volume was then split among two 50 mL tubes, and to each tube was added 20 mL of ethanol (reagent alcohol) as the non-solvent. The suspension was centrifuged (3000 × g, 4 min), the supernatant discarded, and the pellet in each tube dissolved in 5 mL of hexanes. The tubes were vortexed, sonicated for 5 min, and centrifuged (3000 × g, 2 min) without the addition of any non-solvent to pellet out any insoluble by-products. The supernatant of each tube was combined in a fresh tube, to which was added 10 mL of ethanol. The suspension was then centrifuged (3000 × g, 4 min), the supernatant discarded, and the pellet finally redissolved in 4 mL of hexanes to give a solid concentration of ~10 wt%.

This procedure yielded hexagonal-phase UCNPs from sizes between 6 nm and 15 nm. Small (6-nm) cubic-phase UCNPs were prepared by following the same procedure as above but using a mixture of oleylamine (8 g, 9.8 mL) and octadecene in place of neat octadecene.

$NaYF_4$ UCNP shell growth. Epitaxial $NaYF_4$ inert shells were grown in a nitrogen-filled glovebox with a laboratory automation robot Workstation for Automated Nanocrystal Discovery and Analysis (WANDA) using a successive ion layer adsorption and reaction (SILAR) approach. A 0.10 M yttrium oleate [Y(OA)] solution was prepared by adding anhydrous YCl_3 (1 mmol, 195 mg) into a mixture of oleic acid (4 mL) and ODE (6 mL) in a 50 mL three-neck flask. This mixture was then heated up to 110 °C under vacuum for 1 h, forming a homogenous clear solution. In a separate flask, sodium trifluoroacetate (2 mmol, 272 mg) was added into a mixture of oleic acid (4 mL) and ODE (6 mL) and heated up to 50 °C under vacuum until the solution became clear, giving a 0.20 M Na-TFA-OA precursor solution. Both precursor solutions were cooled down and then brought into the glovebox for further shell growth.

To grow a ~4.5 nm inert $NaYF_4$ shells UCNPs, oleate-capped UCNPs in hexanes were pipetted in a 40 mL vial and dried under vacuum at room temperature. The vial was transferred into the glovebox, and degassed ODE (6 mL) and OA (4 mL) were added. The reaction vial and the precursor vials were loaded onto the robot deck and the automated shell growth procedure was executed. In this procedure, the reaction vial was placed under continuous magnetic stirring and the temperature was increased to 280 °C. Once the temperature stabilized, 10 SILAR cycles were carried out, with each cycle consisting of a Y(OA) injection followed by a Na-TFA-OA injection. Each injection was spaced apart by 20 min and heating was maintained at 280 °C throughout the whole duration until 20 min after the last injection. Then the reaction was rapidly cooled under a N_2 flow. The UNCPs were then washed with a similar washing procedure used for the cores, as described above.

TEM or STEM images of the UCNPs used in this study are shown in **Figure S6**.

Characterization techniques

Raman spectra were acquired using a Horiba Jobin Yvon LabRAM ARAMIS confocal microscope with a 532 nm laser. Zeta-potential and dynamic light scattering (DLS) measurements were done with a Malvern Zetasizer Nano-ZS. CW laser (Laser Quantum). Powder X-ray diffraction (XRD) patterns were acquired with a Bruker AXS D8 Discover GADDS X-ray diffractometer, using Co Kα radiation. Transmission electron microscopy (TEM) images were acquired using a FEI Themis 60−300 STEM/TEM (Thermo Fisher Scientific, US) operated at 300 kV at the National Center for Electron Microscopy. Scanning (transmission) electron microcopy was performed with a Zeiss Gemini Ultra-55 analytical SEM. Lower-resolution scanning electron microcopy and EDS was performed with a Phenom Pro tabletop SEM. Upconversion emission spectra and lifetimes were obtained with an Edinburgh Instruments FLS980 spectrometer equipped with a 980 nm continuous-wave laser diode (CNI), a double emission monochromator, and a single-photon counting photomultiplier (Hamamatsu R928). Intensity-weighted lifetimes, $\tau_{ave},$ were calculated by the equation

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \, \tau_i}$$

Here, A_i and τ_i are amplitudes and lifetimes, respectively, of individual decay components from multi-exponential fitting of time-resolved luminescence decay curves.

Raman DFT calculations

Calculations were performed with the ORCA quantum chemistry program package. Geometric optimization was performed using the def2-TZVPP basis set with the r2SCAN-3c functional for coarse optimization and then with the PBE0 functional for finer optimization. The Raman modes were then determined using a numerical calculation of the polarizabilities.

Upconversion enhancement measurement

Two identical solutions (~2 mL) of ligand-stripped UCNPs were prepared at the same time and at the same concentration. To one of the solutions, a small volume (<0.1 mL) of $Sn_2S_6^{4-}$

ligand solution was added. The solutions were allowed to equilibrate overnight and their UCL then measured under identical conditions.

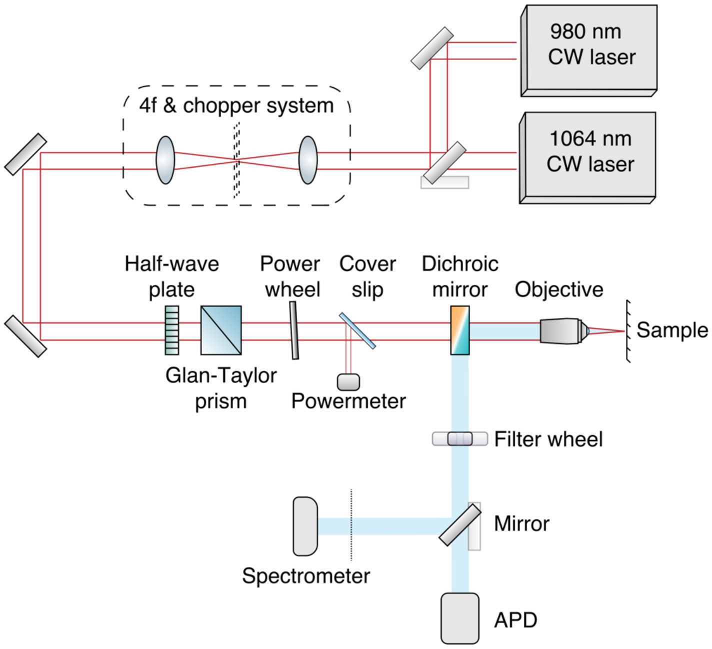
Photoconductivity measurements

Interdigitated indium tin oxide (ITO) substrates with variable channel lengths were purchased from Ossila. For the photoconductivity measurements, the channel widths and lengths were 30 mm and 150 μm respectively. The 980 nm laser power density was estimated to be about 300 mW/cm^2, while the 395 nm LED power density was estimated to be about 60 mW/cm^2.

Laser scanning microscopy setup

Films of UCNPs on Si were patterned and characterized in ambient conditions (room temperature, air exposure) using a custom-built confocal inverted microscope (**Scheme S1**). The sample was excited by a 980-nm continuous-wave laser (QFBGLD-980-750, Qphotonics) or a 1064-nm continuous-wave laser source (Opus 1064 3000, Laser Quantum) coupled through a 950 nm short-pass dichroic mirror and a long working distance air objective (60x 0.7NA, Nikon). The emission was collected by the same objective, spectrally filtered using an 850 nm short-pass filter and detected either by (1) a single-photon avalanche photodiode (PDM series, Micro Photon Devices), for 2D mapping or (2) an EMCCD camera (Andor iXon Ultra 897) equipped spectrometer (Acton Research Corp., SpectraPro-300i), for spectroscopy.

For power dependence measurements and lithography, a continuously variable, reflective neutral density filter wheel (Thorlabs) was inserted in the laser beam path for coarse power selection, and fine power steps were obtained by motorized rotation of a half-wave plate coupled with a Glan-Taylor prism (Thorlabs), power selection was synchronized and automated with the collection system. Powers were simultaneously recorded by a Thorlabs power meter from a glass cover slip which reflected ~10% of the incoming flux. Average excitation power densities were calculated using measured laser powers (at the objective) and the 1/e^2 area based on the employed excitation wavelength and NA of the microscope objective. To selectively measure the 800-nm emission from Tm^{3+}, a band-pass emission filter (FF01-809/81, Semrock) was used instead of the short-pass filter.



Scheme S1. Principle arrangement of the custom-built confocal laser scanning microscope, equipped with 980 nm and 1064 nm CW lasers; automatized coarse and fine power adjustment by power wheel and half-wave plate + Glan-Taylor prism, respectively; and spectrometer or APD laser photoluminescence detection.

Estimation of the Sn2S64- ligand coverage for 14-nm UCNPs

For a 14.4-nm hexagonal-phase UCNP,

UCNP volume = 1563 nm^3

Volume of one hexagonal-phase $(\mathrm{NaYF}_4)_{1.5}$ unit cell = 0.109 nm^3

Number of $(\mathrm{NaYF}_4)_{1.5}$ unit cells in one UCNP = 1563/0.109 = 14,339

Number of F atoms in one UCNP = 14,339 $\times$ 4 $\times$ 1.5 = 86,037

From EDS analysis (**Figure S7**),

Atomic ratio of Sn:F = 0.52/49.37 = 0.0105

Hence,

Number of Sn atoms per UCNP = 86,037 $\times$ 0.0105 = 903

And since each $\mathrm{Sn}_2\mathrm{S}_6^{4-}$ ligand has 2 Sn atoms,

Number of $\mathrm{Sn}_2\mathrm{S}_6^{4-}$ ligands per UCNP = 903/2 = 452

Since the UCNP surface area is $\pi \times (14.4\ \mathrm{nm})^2 = 651\ \mathrm{nm}^2$,

Surface coverage of $\mathrm{Sn}_2\mathrm{S}_6^{4-}$ ligand = 452 / 651 nm^2 = 0.7 ligands/nm^2

Supporting figures

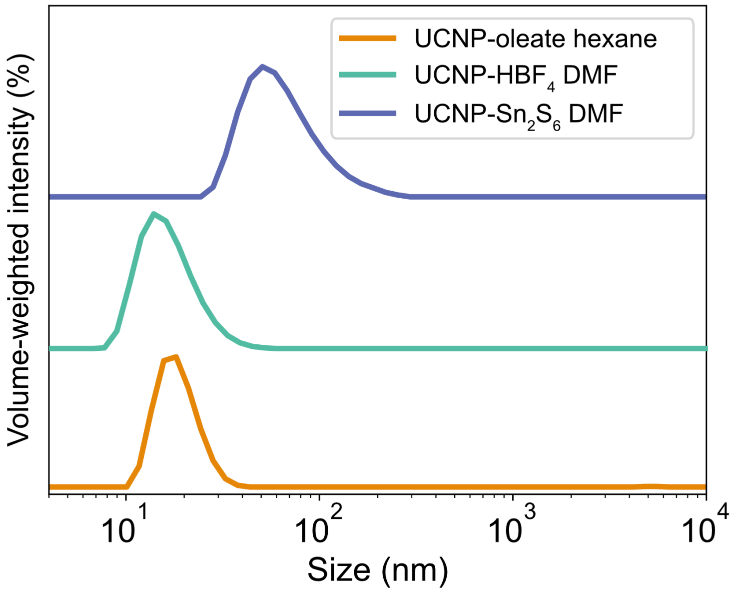


Figure S1. Dynamic light scattering spectra of 15-nm NaYF$_4$: 20% Yb^{3+}, 2% Er^{3+} UCNPs capped with oleate ligands, after HBF$_4$ ligand stripping, and after Sn$_2$S$_6$ ligand functionalization.

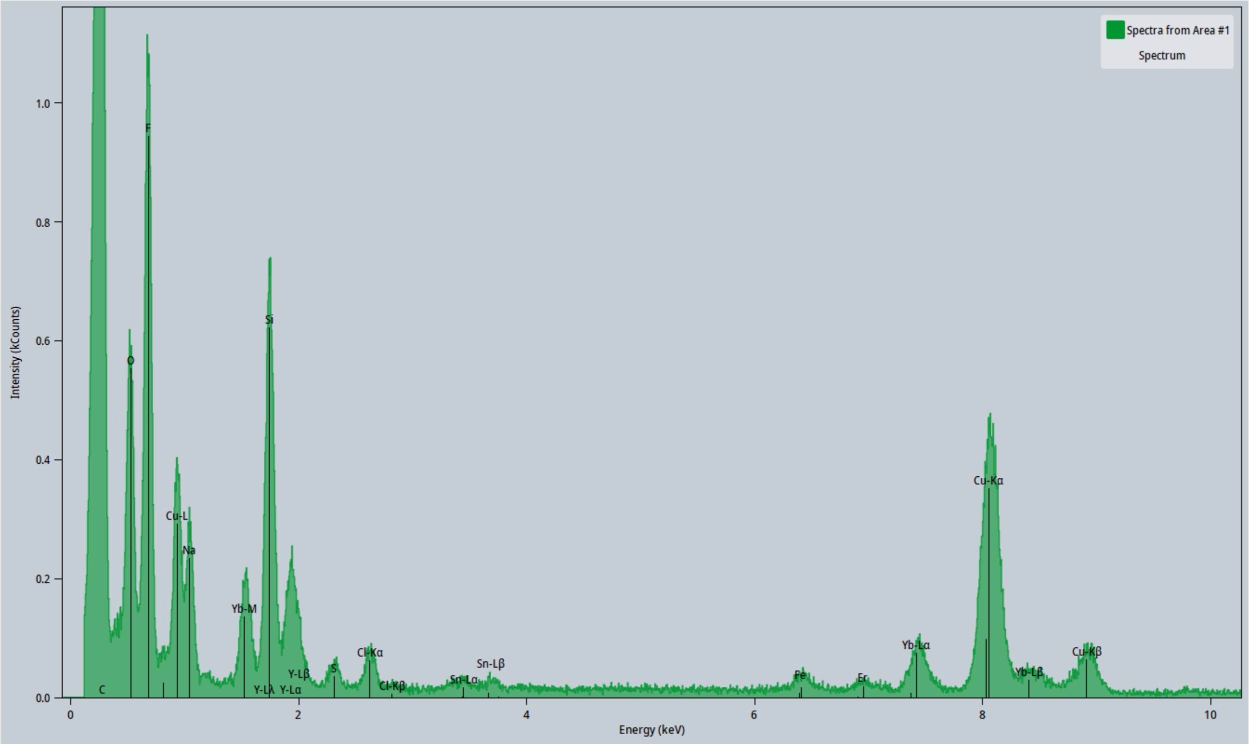


Figure S2. Nanoscale EDS spectrum of Sn_2S_6-capped 14-nm $NaYF_4$: 30% Yb^{3+}, 0.5% Tm^{3+} UCNPs.

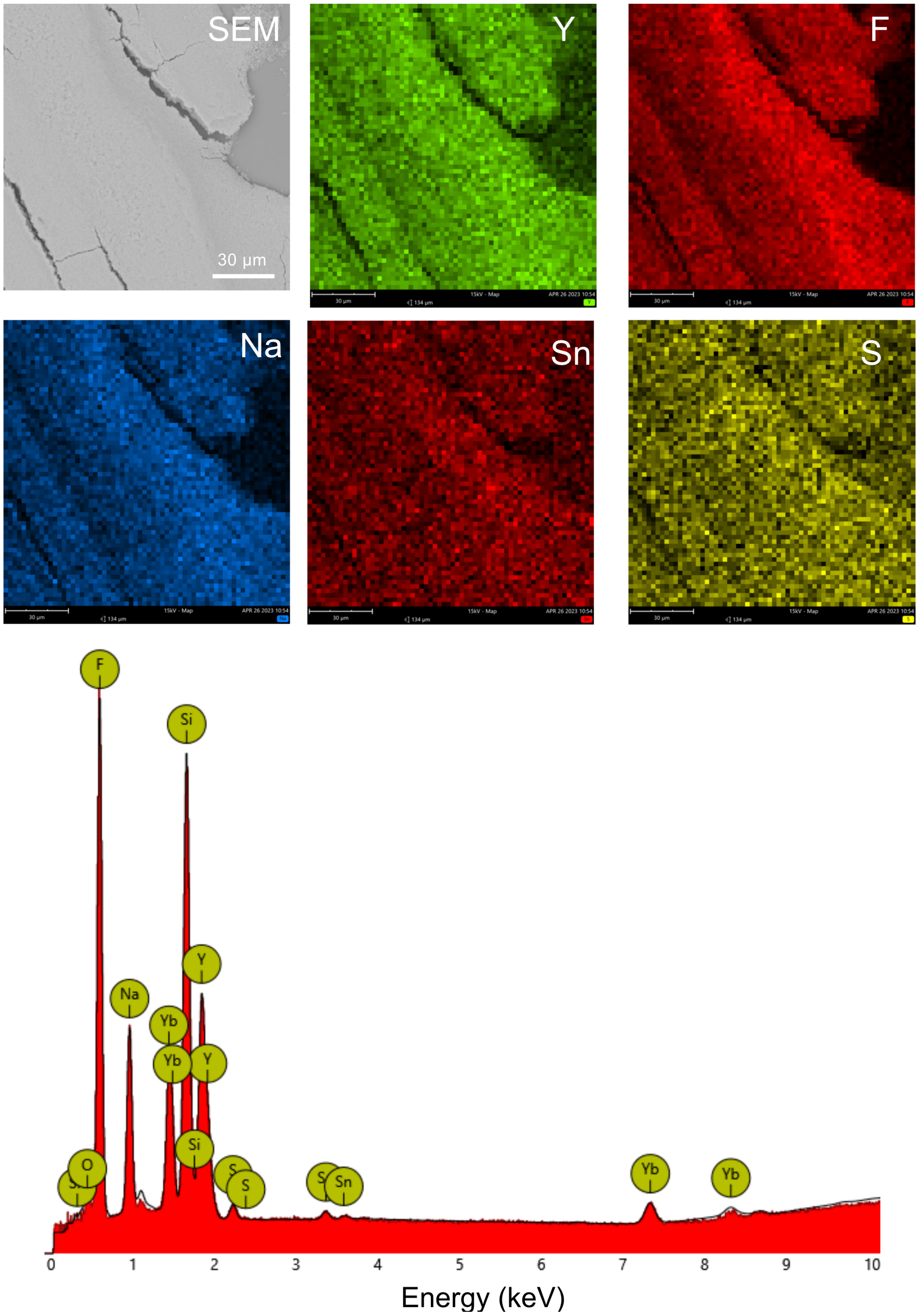


Figure S3. Microscale EDS mapping and spectrum of Sn_2S_6-capped 14-nm $NaYF_4$: 30% Yb^{3+}, 0.5% Tm^{3+} UCNPs.

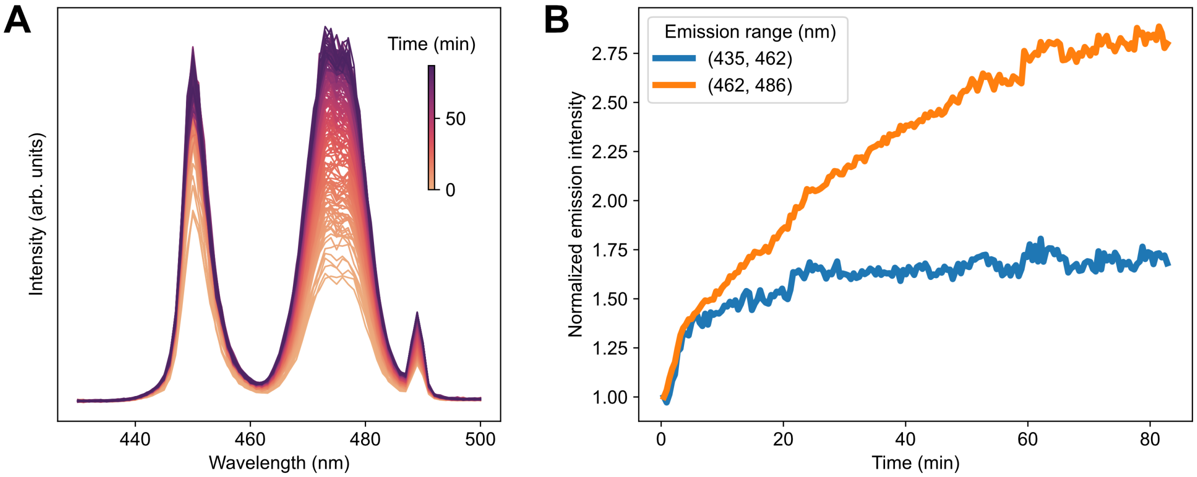


Figure S4. Kinetics of the UCL changes upon mixing BF_4-capped 8-nm $NaYF_4$: 20% Gd^{3+}, 49% Yb^{3+}, 1% Tm^{3+} UCNPs with 2 mM $Na_4Sn_2S_6$.

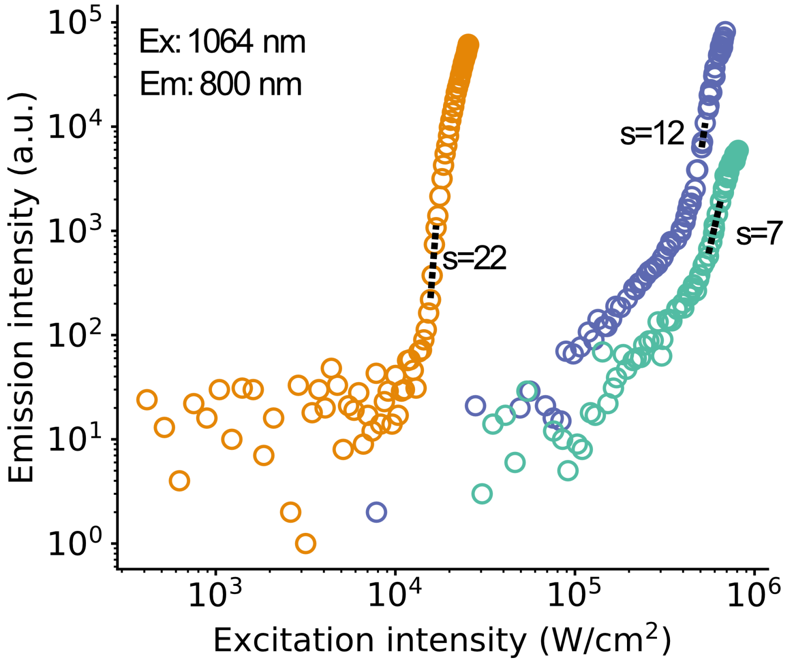
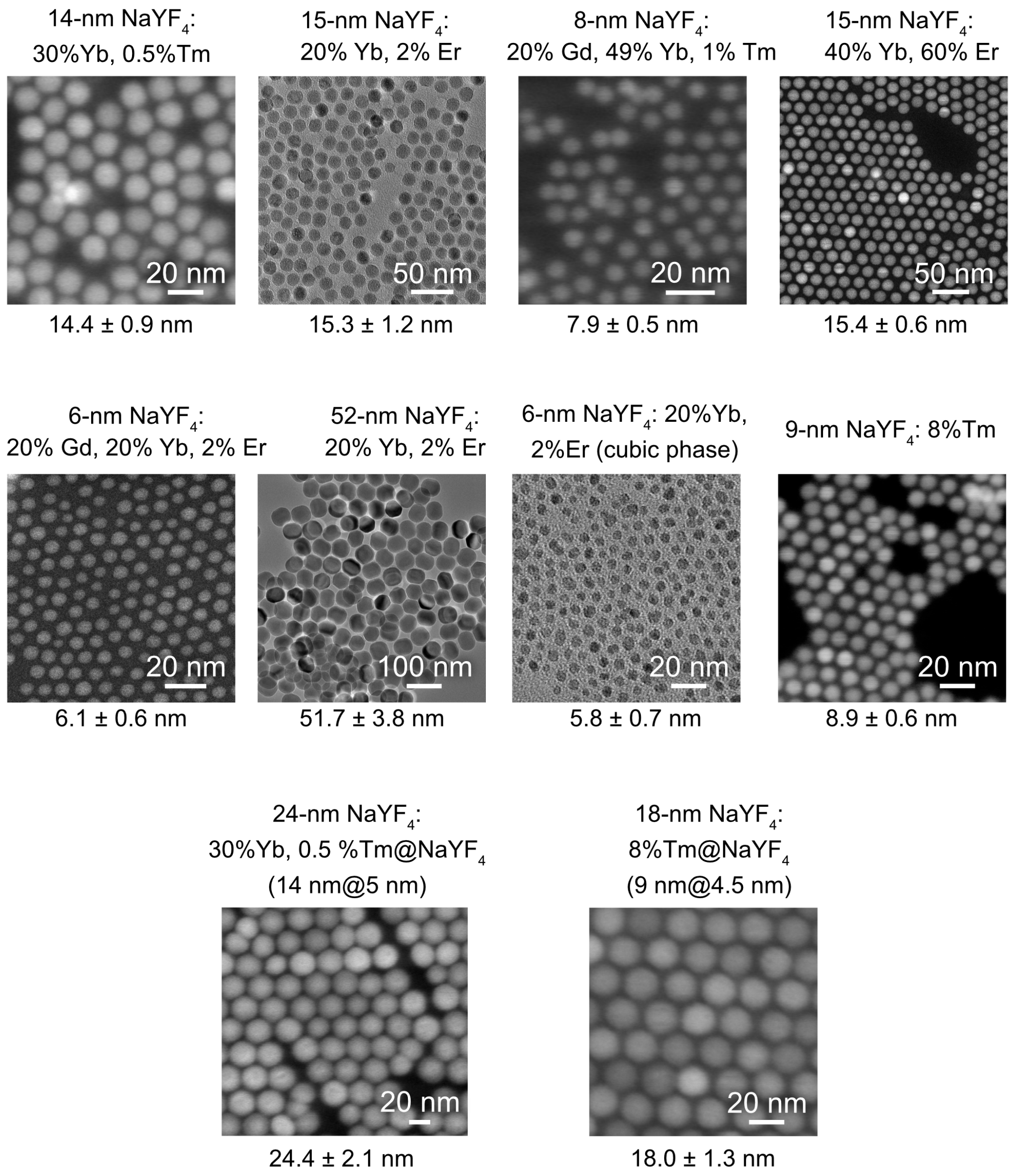


Figure S5. Power scan of avalanching $NaYF_4$: 8% Tm^{3+} UCNPs with oleate ligands (green) and Sn_2S_6 ligands (blue) after annealing at 350 °C in N_2 for 15 mins. Also shown is scan of the UCNPs after growing a 5-nm inert $NaYF_4$ shell (orange).



14-nm $NaYF_4$: 30%Yb, 0.5%Tm — 14.4 ± 0.9 nm

15-nm $NaYF_4$: 20% Yb, 2% Er — 15.3 ± 1.2 nm

8-nm $NaYF_4$: 20% Gd, 49% Yb, 1% Tm — 7.9 ± 0.5 nm

15-nm $NaYF_4$: 40% Yb, 60% Er — 15.4 ± 0.6 nm

6-nm $NaYF_4$: 20% Gd, 20% Yb, 2% Er — 6.1 ± 0.6 nm

52-nm $NaYF_4$: 20% Yb, 2% Er — 51.7 ± 3.8 nm

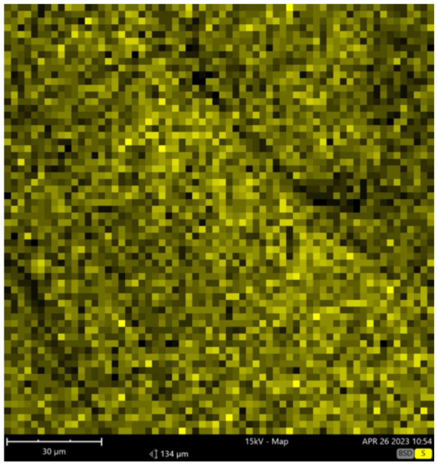
6-nm $NaYF_4$: 20%Yb, 2%Er (cubic phase) — 5.8 ± 0.7 nm

9-nm $NaYF_4$: 8%Tm — 8.9 ± 0.6 nm

24-nm $NaYF_4$: 30%Yb, 0.5 %Tm@$NaYF_4$ (14 nm@5 nm) — 24.4 ± 2.1 nm

18-nm $NaYF_4$: 8%Tm@$NaYF_4$ (9 nm@4.5 nm) — 18.0 ± 1.3 nm

Figure S6. TEM or STEM images of UCNPs used in this study along with their average sizes and standard deviations. All UCNPs were measured by X-ray diffraction to be in the hexagonal phase unless otherwise stated.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
9	F	Fluorine	49.37	22.56
14	Si	Silicon	20.51	13.86
39	Y	Yttrium	11.10	23.73
11	Na	Sodium	9.75	5.39
70	Yb	Ytterbium	7.75	32.26
16	S	Sulfur	0.87	0.67
50	Sn	Tin	0.52	1.48
8	O	Oxygen	0.14	0.05

Figure S7. SEM-EDS elemental analysis of $Sn_2S_6^{4-}$-capped 14-nm $NaYF_4$: 30% Yb^{3+}, 5% Tm^{3+} UCNPs.

References

(1) Ostrowski, A. D.; Chan, E. M.; Gargas, D. J.; Katz, E. M.; Han, G.; Schuck, P. J.; Milliron, D. J.; Cohen, B. E. Controlled Synthesis and Single-Particle Imaging of Bright, Sub-10 nm Lanthanide-Doped Upconverting Nanocrystals. *ACS Nano* **2012**, *6* (3), 2686-2692. DOI: 10.1021/nn3000737.