Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

An Efficient Synthetic Strategy for Ligand-Free Upconversion Nanoparticles

Chunning Sun,*[,a] Jan Ron Justin Simke [b] and Michael Gradzielski*[,a]

[a] Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany

[b] Zentraleinrichtung Elektronenmikroskopie (ZELMI), Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

*Corresponding authors:

E-mail: sunchunning@gmail.com (C. Sun); michael.gradzielski@tu-berlin.de (M. Gradzielski)

Experimental Procedures

Materials

Yttrium(III) acetate tetrahydrate (99.9%), ytterbium(III) acetate hydrate (99.9%), erbium(III) acetate hydrate (99.9%), Lanthanum(III) acetate hydrate (99.9%) were purchased from Alfa Aesar, oleic acid (OA, 90%), 1-octadecene (ODE, 90%), sodium acetate (CH_3COONa, 99%), cesium acetate (CH_3COOCs, 99.9%), ammonium fluoride (NH_4F, ≥98%), sodium hydroxide (NaOH, ≥98%), methanol (MeOH, 99.8%), ethanol (≥99.8%), c yclohexane (99.5%), chloroform (≥99%), toluene (99.9%), N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, ≥99.5%), acetonitrile (ACN, 99.8%), N-methyl-2-pyrrolidone (NMP, 99.5%), formamide (FAM, ≥99%), formic acid (FA, ≥98%), acetic acid (AcOH, >99.5%), DL-lactic acid (LA, ~90%), boric acid (H_3BO_3, ≥99.5%), phosphoric acid (H_3PO_4, ≥99%), polyethylenimine (PEI, branched, Mw ~25,000), poly(acrylic acid) solution (PAA, 50 wt. % in H_2O, Mw ~5,000), polyvinylpyrrolidone (PVP, Mw ~10,000), Eriochrome Black T (EBT, indicator grade) were purchased from Sigma-Aldrich. Britton Robinson buffer (BRB) solution (100 mM, pH 3) was prepared by mixing with 100 mM H_3BO_3, 100 mM H_3PO_4, and 100 mM AcOH, and then titrated to pH 3 with 5 M NaOH. Nitrate salts (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Mn^{2+}, and Cr^{3+}) were used for all sensing experiments. All the commercial chemicals were used as received. Milli-Q water (18.2 MΩ·cm at 25 °C) was used in all experiments.

Instruments

Fourier transform infrared (FT-IR) spectra were acquired on a Thermo Scientific Nicolet iS5 FT-IR spectrometer using the KBr method. The spectra were recorded in transmission mode with the wavenumber range from 4000-500 cm^{-1}. Proton nuclear magnetic resonance (^1H NMR) spectra were collected by using a Bruker Advance II 500 MHz NMR spectrometer. UV-Vis absorption spectra were obtained by using a CARY 50 spectrophotometer. Transmission electron microscopy (TEM) images were obtained by FEI Tecnai G2 20 S-TWIN with a LaB_6 cathode operating at 200 kV. Powder X-ray diffraction (XRD) spectra were obtained by using Philips X'Pert MPD Pro X-ray diffractometer at a scanning rate of 4°/min in the 2θ range from 10° to 90° with Cu Kα radiation (λ = 0.15406 nm). ζ-potential measurements were carried out with an Anton Paar Litesizer™ 500. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/DSC1 Star System analyzer under N_2 atmosphere flow at a ramp rate of 10 °C/min. Upconversion luminescence (UCL) emission spectra were collected at room temperature with a fibre-coupled spectrometer (Ocean HDX, Ocean Optics) equipped with an external 980 nm CW laser (Roithner Lasertechnik GmbH) with tunable power from 0 to 5 W.

Preparation

Synthesis of OA-UCNPs[1]

Typically, 3.12 mL $Y(CH_3COO)_3$ (0.2 M), 0.8 mL $Yb(CH_3COO)_3$ (0.2 M) and 0.8 mL $Er(CH_3COO)_3$ (0.02 M) were added to a three-neck flask containing 6 mL OA and 14 mL ODE at room temperature. The mixed solution was heated to 110 °C for 30 min to remove the water, followed by heating to 160 °C for 40 min to form lanthanide-oleate

complexes and then cooled down to 50 °C. A methanol solution (10 mL) containing NH_4F (3.2 mmol) and NaOH (2.0 mmol) was added afterwards and stirred at 50 °C for 30 min. After evaporating the methanol, the solution was heated to 305 °C at a ramp rate of 10 °C/min and maintained at this temperature for 45 min under N_2 atmosphere. After cooling down to room temperature, OA-UCNPs were precipitated out by adding excess ethanol, collected by centrifugation at 6000 r.p.m for 5 min, repeatedly washed with ethanol, and finally redispersed in cyclohexane, chloroform, or toluene.

Synthesis of OA-csUCNPs[2]

Typically, $Y(CH_3COO)_3$ (3.2 mL, 0.2 M) and $Yb(CH_3COO)_3$ (0.8 mL, 0.2 M) were added to a three-neck flask containing 6 mL OA and 14 mL ODE at room temperature. The mixed solution was heated to 110 °C for 30 min to remove the water, followed by heating to 160 °C for 40 min to form lanthanide-oleate complexes and then cooled down to room temperature. The as-synthesized OA-UCNPs core nanoparticles dispersed in cyclohexane were added to the flask. The solution was heated to 110 °C to remove the cyclohexane and then subsequently cooled down to room temperature. A methanol solution (10 mL) containing NH_4F (3.2 mmol) and NaOH (2.0 mmol) was added afterwards and stirred at 50 °C for 30 min. After heating to 110 °C to evaporate the methanol, the solution was heated to 305 °C at a ramp rate of 10 °C/min and maintained at that temperature for 45 min under N_2 atmosphere. After cooling down to room temperature naturally, the resultant was precipitated out with the addition of excess ethanol, collected by centrifugation at 6000 r.p.m for 5 min, washed with ethanol several times, and finally redispersed in cyclohexane.

Synthesis of oleate-capped $NaLaF_4$ nanorods[3]

Typically, $La(CH_3COO)_3$ (4 mL, 0.2 M), CH3COONa (4 mL, 0.2 M), and CH3COOCs (6 mL, 0.4 M) were added to a three-neck flask containing 6 mL OA and 14 mL ODE at room temperature. The mixed solution was heated to 110 °C for 30 min to remove the water, followed by heating to 170 °C for 30 min to form metal-oleate complexes and then cooled down to 45 °C. A methanol solution (10 mL) containing NH_4F (4.8 mmol) was added afterwards and stirred at 45 °C for 120 min. After evaporating the methanol, the solution was heated to 310 °C at a ramp rate of 10 °C/min and maintained at this temperature for 60 min under N_2 atmosphere. After cooling down to room temperature, oleate-capped $NaLaF_4$ nanorods were precipitated out by adding excess ethanol, collected by centrifugation at 6000 r.p.m for 5 min, repeatedly washed with ethanol, and finally redispersed in cyclohexane.

Preparation of ligand-free UCNPs

Ligand removal in single solvent systems

FA (5 mmol) was added to 2 mL cyclohexane, chloroform, or toluene solution containing OA-UCNPs (10 mg/mL) directly, the mixture was then shaken for 10 s (3000 r.p.m) on a vortex mixer, ligand-free UCNPs were precipitated out. The resultant nanoparticles were obtained by centrifugation at 6000 r.p.m for 20 min, washed

one time with ethanol and three times with water, and finally redispersed in water. Samples treated with FA were labelled as FA-Cy, FA-Chl, and FA-Tol.

AcOH can also be used as the stripping agent, the procedure was similar to that of OA-UCNPs treated by FA, except that 10 mmol of AcOH was added. A homogeneous solution was finally obtained, ligand-free UCNPs were collected by centrifugation at 15000 r.p.m for 20 min, washed one time with ethanol and three times with water, and finally redispersed in water. Samples treated with AcOH were labelled as AA-Cy, AA-Chl, and AA-Tol.

LA can be applied as the stripping agent as well, the procedure was similar to that of OA-UCNPs treated by FA, except for the use of chloroform as the dispersant. Ligand-free UCNPs were transferred to the LA layer and collected by centrifugation at 15000 r.p.m for 20 min, washed one time with ethanol and three times with water, and finally redispersed in water. Samples treated with LA were labelled as LA-Cy and LA-Tol.

Ligand removal in biphasic solvent systems

FA (5 mmol) was initially dissolved in 2 mL polar solvents (ACN, DMF, DMSO, FAM, MeOH, or NMP), 2 mL cyclohexane solution containing OA-UCNPs (10 mg/mL) was added gently afterwards to form a biphasic solvent system. After shaking for 10 s (3000 r.p.m) by simple vortexing, UCNPs were transferred from the upper cyclohexane layer to the bottom polar solvent. Ligand-free UCNPs were obtained by centrifugation at 15000 r.p.m for 20 min, washed one time with ethanol and three times with water, and finally redispersed in water. Ligand-free nanoparticles prepared under FA treatment with different polar solvents were labelled as FA-Cy/ACN, FA-Cy/DMF, FA-Cy/DMSO, FA-Cy/FAM, FA-Cy/MeOH, and FA-Cy/NMP. AcOH (10 mmol) can also be used as the stripping agent, except for the use of ACN, DMSO, or FAM as the polar solvent. Oleate-free UCNPs prepared under AcOH treatment with different polar solvents were labelled as AA-Cy/DMF, AA-Cy/MeOH, and AA-Cy/NMP.

Surface functionalization of ligand-free UCNPs

Ligand-free UCNPs capped by other water-soluble capping molecules were prepared according to the previous work with some modifications.[4] Typically, 50 mg capping molecules (PVP, PAA, or PEI) were first dissolved in 5 mL H_2O, and the solution was adjusted to pH 8 with 50 mM NaOH (except for PEI). 5 mL bare UCNPs solution (5 mg/mL) were then added, followed by overnight stirring. The products were obtained via centrifugation at 15000 r.p.m for 20 min, washed three times with water, and finally redispersed in water with a concentration of 1 mg/mL.

Synthesis of csUCNPs/EBT nanoprobes

PEI-csUCNPs were prepared with the same procedure as mentioned above and redispersed in water with a concentration of 1 mg/mL, the EBT stock solution was prepared by dissolving EBT dye in water with a concentration of 2 mM. 0.5 mL of EBT solution was mixed with 0.5 mL of PEI-csUCNPs solution, and the mixed

solution was vortexed (3000 r.p.m) for 5 min. The precipitate was obtained by centrifugation at 9000 r.p.m for 20 min and repeatedly washed three times with water to remove excess EBT. Finally, the csUCNPs/EBT nanocomposites were redispersed in the BRB solution (100 mM, pH 3).

Procedures for ions sensing

Stock solutions of the cations (2 mM) were prepared in water. The sensing of csUCNPs/EBT nanocomposites to Cu^{2+} was performed by adding different amounts of Cu^{2+} stock solution to csUCNPs/EBT nanocomposites solution, the concentration of csUCNPs was kept at 0.5 mg/mL. Selectivity experiments were performed by adding appropriate amounts of other cations stock solution with a similar procedure. All UCL spectra were recorded under the excitation of a 980 nm laser with a power of 3 W.

Ligand Density Calculation

Ligand density (φ, molecules/nm^2) was calculated from the weight loss fraction of ligand by TGA.

$$\varphi = \frac{N_{OA}}{S} \tag{1}$$

Where N_{OA} is the number of OA, S is the total surface area of UCNPs.

$$N_{OA} = n_{OA} \cdot N_A \tag{2}$$

$$n_{OA} = \frac{m_{OA}}{M_{OA}} \tag{3}$$

Where n_{OA} is the amount of OA, m_{OA} is the weight of OA, which is determined by TGA, N_A is the Avogadro constant; N_A = 6.02×10^{23} mol^{-1}, M_{OA} is the molar mass of OA ions, M_{OA} = 281.45 g mol^{-1}.

$$S = N_{UC} \cdot S_{UC} \tag{4}$$

$$N_{UC} = \frac{m_t}{m_{UC}} \tag{5}$$

$$m_{UC} = \rho_{UC} \cdot V_{UC} \tag{6}$$

$$V_{UC} = \frac{4}{3}\pi r_{UC}^3 \tag{7}$$

$$S_{UC} = 4\pi r_{UC}^2 \tag{8}$$

Where N_{UC} is the number of UCNPs, S_{UC} is the surface area of single UCNP, m_t is the net weight of UCNPs, which is determined by TGA, m_{UC} is the weight of single UCNP, ρ_{UC} is the density of single UCNP, ρ_{UC} = 4.31×10^{-21} g nm^{-3}, V_{UC} is the volume of single UCNP, r_{UC} is the radius of UCNP. The prepared uniform UCNPs show a low aspect ratio (*ca.* 1.04), therefore, we approximate their shape as spheres for the ligand density calculation.

$$\varphi = \frac{\rho_{UC} r_{UC} m_{OA} N_A}{3(1 - m_{OA}) M_{OA}}$$

The ligand density is calculated to be 1.8 OA/nm^2.

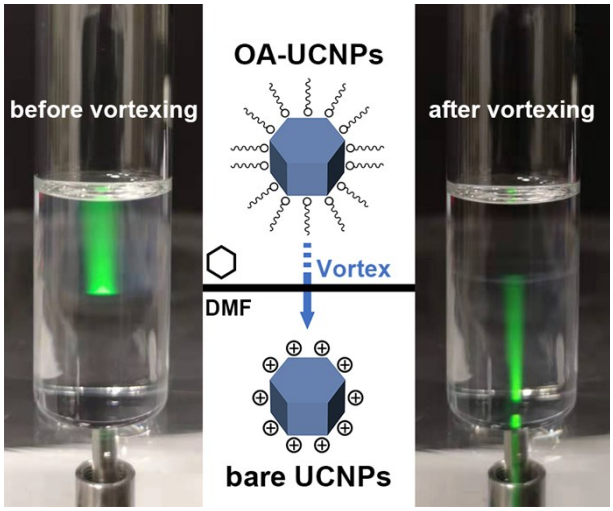

Fig. S1 Typical illustration of the ligand removal process in a biphasic solvent system by the vortexing method (DMF is used as the polar solvent and cyclohexane is used as the hydrophobic solvent). The luminescence light switches from the upper layer to the bottom layer along with the displacement of the UCNPs (activation by a 980 nm laser that illuminates from the bottom).

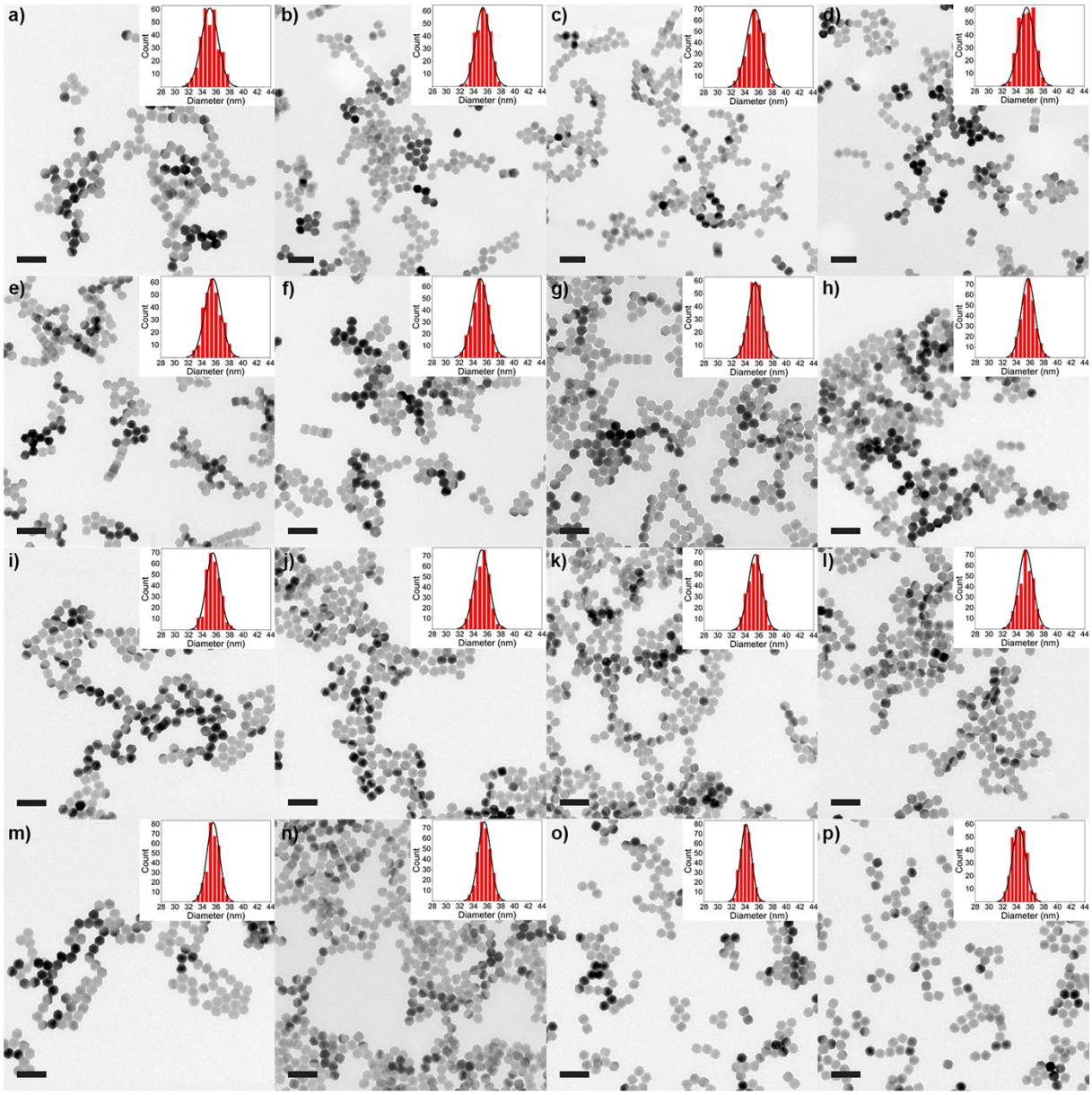

Fig. S2 TEM images of ligand-free UCNPs prepared in different systems. (a) FA-Cy/ACN, (b) FA-Cy/DMF, (c) FA-Cy/DMSO, (d) FA-Cy/FAM, (e) FA-Cy/MeOH, (f) FA-Cy/NMP, (g) FA-Chl, (h) FA-Tol, (i) AA-Cy/DMF, (j) AA-Cy/MeOH, (k) AA-Cy/NMP, (l) AA-Cy, (m) AA-Chl, (n) AA-Tol, (o) LA-Cy, (p) LA-Tol. Insets: corresponding size histograms. Scale bars: 100 nm. Average particle sizes: (a) 35.1 ± 1.2 nm, (b) 35.3 ± 1.1 nm, (c) 35.4 ± 1.3 nm, (d) 35.5 ± 1.2 nm, (e) 35.6 ± 1.2 nm, (f) 35.1 ± 1.2 nm, (g) 35.5 ± 1.0 nm, (h) 35.7 ± 0.9 nm, (i) 35.6 ± 1.0 nm, (j) 35.2 ± 1.1 nm, (k) 35.5 ± 1.0 nm, (l) 35.3 ± 1.0 nm, (m) 35.6 ± 0.9 nm, (n) 35.6 ± 1.0 nm, (o) 34.2 ± 0.8 nm, (p) 34.4 ± 1.0 nm. (FA: formic acid, AA: acetic acid, LA: lactic acid, Cy: cyclohexane, Chl: chloroform, Tol: toluene, ACN: acetonitrile, DMF: N,N-dimethylformamide, DMSO: dimethyl sulfoxide, FAM: formamide, MeOH: methanol, NMP: N-methyl-2-pyrrolidone).

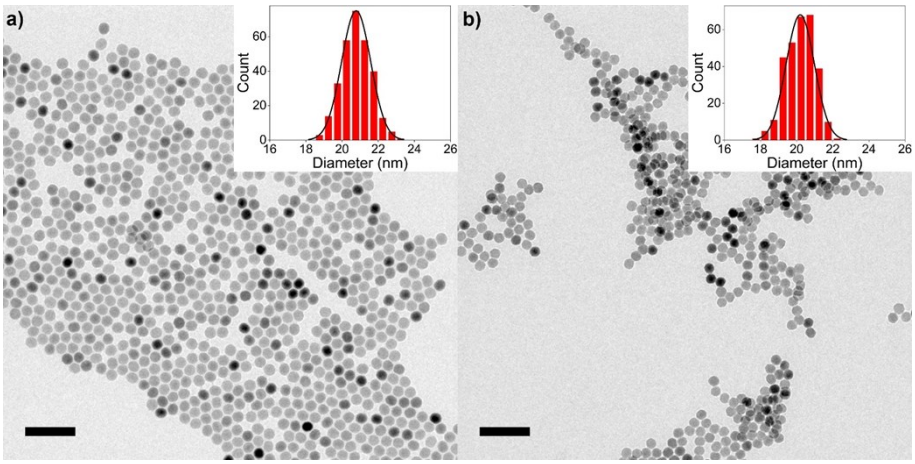

Fig. S3 TEM images of small-sized (a) OA-UCNPs and (b) ligand-free UCNPs prepared in the FA-Cy system. Insets: corresponding size histograms. Scale bars: 100 nm. Average particle sizes: (a) 20.8 ± 0.8 nm, (b) 20.2 ± 0.8 nm.

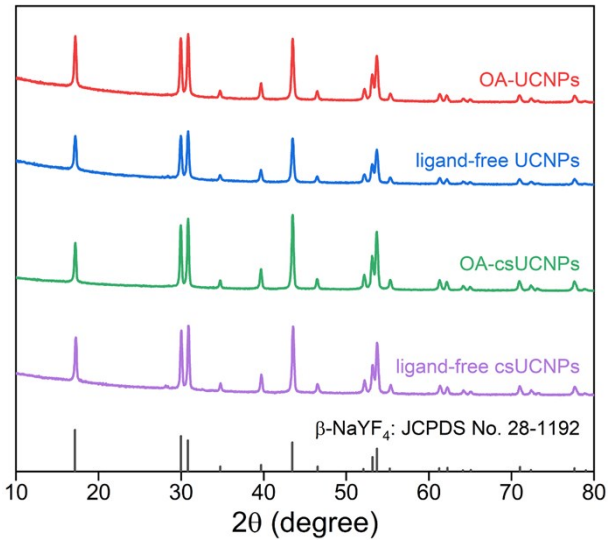

Fig. S4 XRD patterns of oleate-capped and ligand-free UCNPs, oleate-capped and ligand-free csUCNPs, and the standard data of hexagonal $NaYF_4$ (JCPDS No. 28-1192).

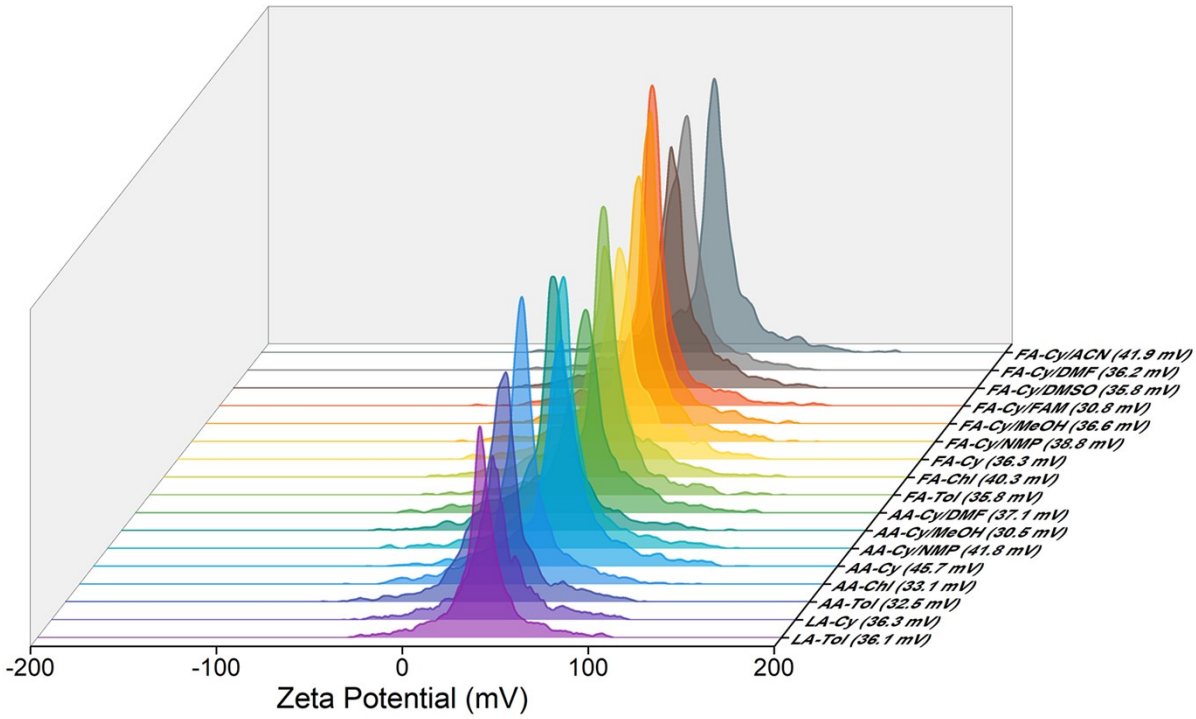

Fig. S5 ζ-potential of ligand-free UCNPs prepared under different conditions (measured at pH ~5.5).

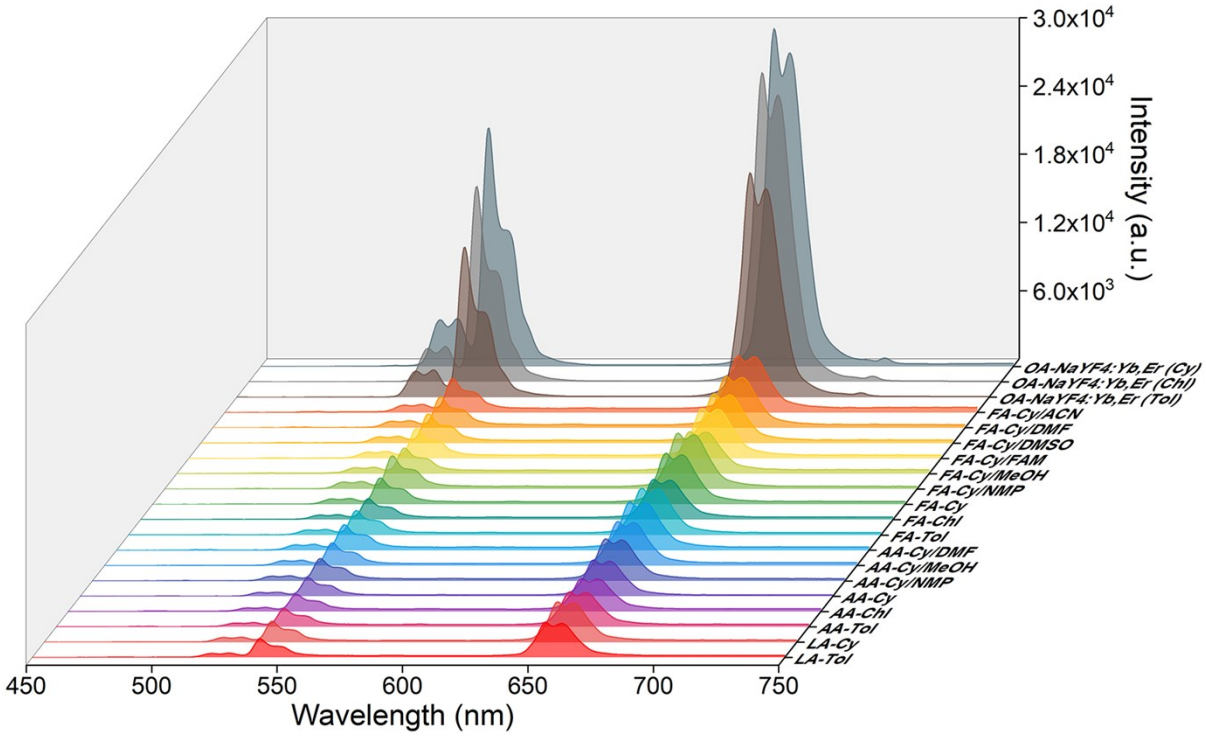

Fig. S6 UCL spectra of OA-UCNPs dissolved in different nonpolar solvents and ligand-free UCNPs prepared in different systems dissolved in water under excitation with a 3 W 980 nm CW laser (the concentration of UCNPs was fixed at 1 mg/mL).

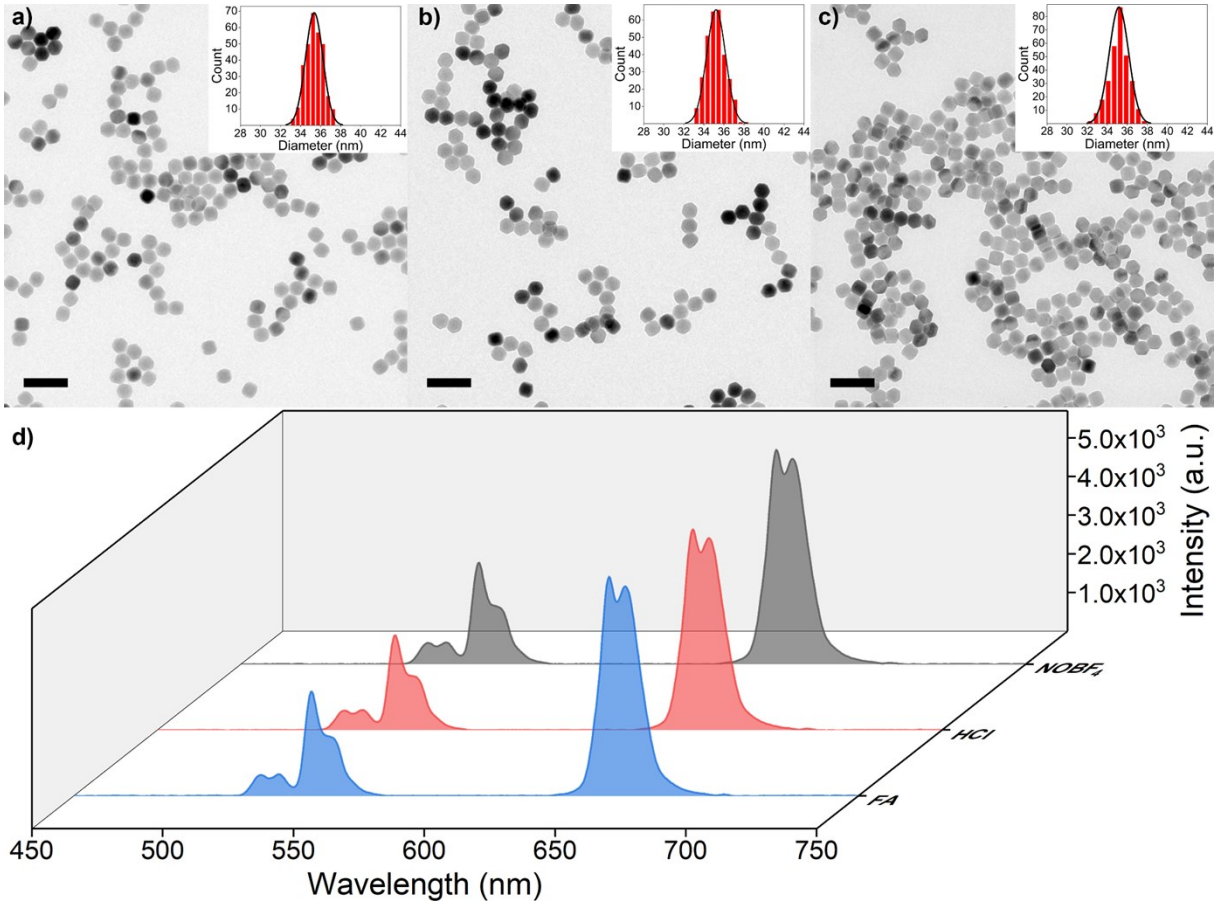

Fig. S7 TEM images of ligand-free UCNPs obtained by the treatment with (a) $NOBF_4$, (b) HCl, and (c) FA. Insets: corresponding size histograms. Scale bars: 100 nm. Average particle sizes: (a) 35.4 ± 0.8 nm, (b)35.2 ± 0.9 nm (c) 35.2 ± 1.0 nm. (d) UCL spectra of bare UCNPs after treatment by $NOBF_4$, HCl, and FA under the excitation with a 3 W 980 nm CW laser (the concentration of UCNPs in water was fixed at 1 mg/mL).

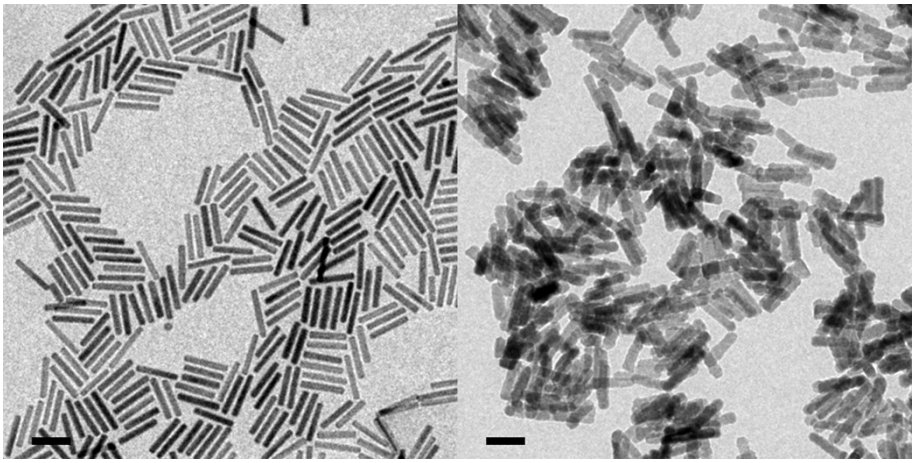

Fig. S8 TEM images of (a) oleate-capped $NaLaF_4$ nanorods and (b) acid-treated oleate-capped $NaLaF_4$ nanorods in the FA-NMP/Cy system. Scale bars: 50 nm.

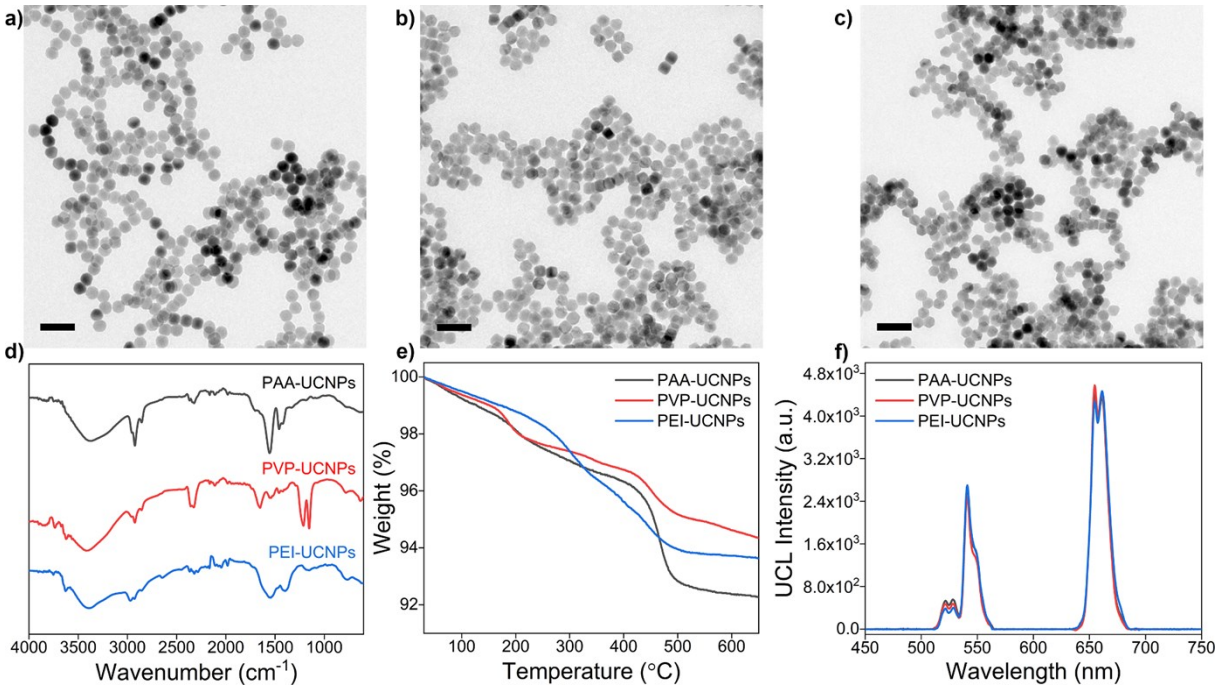

Fig. S9 TEM images of (a) PAA-UCNPs, (b) PVP-UCNPs, and (c) PEI-UCNPs. Scale bars: 100 nm. (d) FT-IR, (e) TGA, and (f) UCL of surface-modified ligand-free UCNPs under excitation with a 3 W 980 nm CW laser (the concentration of UCNPs in water was fixed at 1 mg/mL). ζ-potential of PAA-, PVP-, and PEI-UCNPs are determined to be -20.6 mV, 26.9 mV, and 30.6 mV, respectively (measured at pH 6).

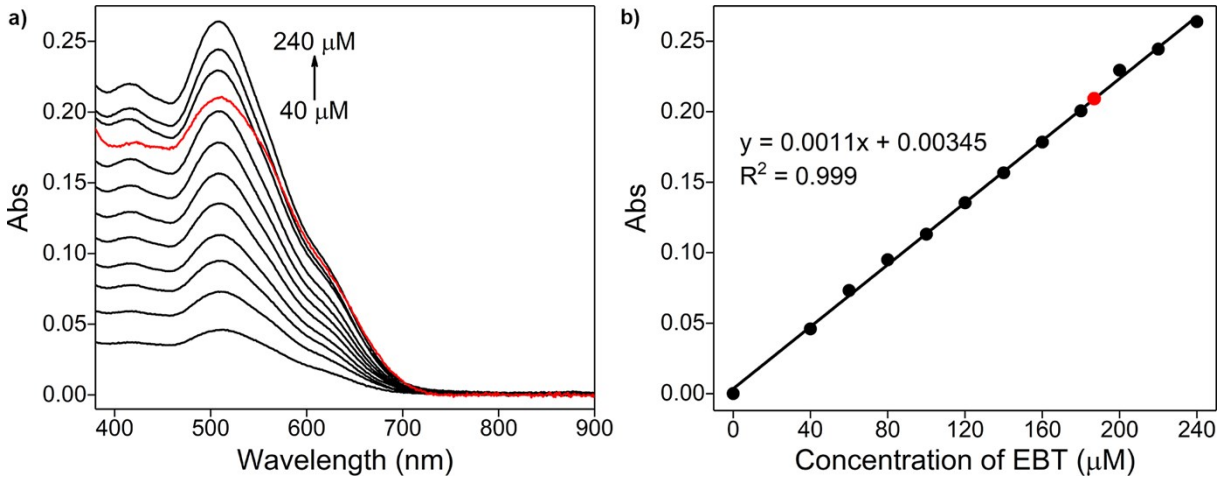

Fig. S10 (a) UV-vis absorption spectra of the EBT with different concentrations in BRB solution (100 mM, pH 3). The red curve represents the absorption data of csUCNPs/EBT nanoprobes (0.5 mg/mL csUCNPs). (b) The plot of absorbance intensities at 508 nm as a function of EBT concentration. The red dot represents the absorption intensity of csUCNPs/EBT at 508 nm.

References

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