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Supporting Information

Direct cation exchange of surface ligand capped upconversion nanocrystals to produce strong luminescence

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1-Materials

Gadolinium chloride hexahydrate ($GdCl_3 \cdot 6H_2O$, 99.99%), thulium chloride hexahydrate ($TmCl_3 \cdot 6H_2O$, 99.9%), ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, 99.998%), ammonium fluoride (NH_4F, 99.99%), sodium hydroxide (NaOH, 98%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), terbium chloride hexahydrate ($TbCl_3 \cdot 6H_2O$, 99.99%), europium chloride hexahydrate ($EuCl_3 \cdot 6H_2O$, 99.99%) were purchased from Sigma-Aldrich. Toluene (99.5%), Ethanol (100%), Methanol (100%), N,N-dimethylformamide (DMF, 99.5%), dimethylsulfoxide (DMSO, 99.5%) were purchased from Chem-Supply (Australia). All reagents were used as received without further purification.

2-Synthesis of Materials

Synthesis of $NaGdF_4$: Yb^{3+}/Tm^{3+} (49%/1%) UCNCs: The core-only $NaGdF_4$: Yb^{3+}/Tm^{3+} (49%/1%) nanoparticles were prepared according to the previous[1]. Typically, methanol solution of 0.5 mmol $GdCl_3$, 0.49 mmol $YbCl_3$, 0.01 mmol $TmCl_3$ were mixed with 10 ml OA and 15 ml ODE in a 50 mL flask. The mixture was heated at 150℃ under stirring for 30 min until solution became clear. After cooling down to 50℃, a methanol solution containing NH_4F (3.3 mmol) and NaOH (2.5 mmol) was added with vigorous stirring for more than 1 hour. Then, the mixed solution was heated up to 90 ˚C to evaporate methanol and to 150 ˚C to evaporate all the residual water. Finally, the solution was heated to 290 ℃ and then kept for 1.5 h under a flow of argon. After reaction and cooling down to room temperature, the synthesized nanocrystals were washed with cyclohexane/ethanol for several times and dispersed in toluene (or cyclohexane) for use. By adjusting the mole ratio of NH_4F and NaOH, different size of UCNPs can be synthesized.

Synthesis of $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaGdF_4$ core-shell UCNCs: For the synthesis core-shell structure UCNCs, a modified hot-injection method was used for growing shells onto the core UCNCs[2]. 0.2 mmol $NaGdF_4$:Yb^{3+}/Tm^{3+} nanocrystals were dispersed in cyclohexane and mixed with OA (8mL) and ODE (12mL) in a 50mL three-neck flask. The mixture was degassed under Ar flow and kept at 100 ˚C for 30 min to completely remove cyclohexane. Then heated up to 150 ˚C and kept at this temperature for 30 min to remove the any possible water. The mixture solution was quickly heated to 290˚C and a certain amount of pure $NaGdF_4$ source solution was injected to the core nanocrystals mixture solution using syringe. The injection rate is 0.05 ml / 2 min. After the reaction, the precipitate was washed with cyclohexane/ethanol for several times and dispersed in toluene for use.

For synthesizing pure $NaGdF_4$ shell precursor, typically, methanol solution of 1 mmol $GdCl_3$ was mixed with 10 ml OA and 15 ml ODE in a 50 mL flask. The mixture was heated at 150℃

under stirring for 30 min until solution became clear. After cooling down to 50℃, a methanol solution containing NH_4F (3.3 mmol) and NaOH (2.5 mmol) was added with vigorous stirring for more than 1 hour. Then, the mixed solution was heated up to 90 ˚C to evaporate methanol and to 150 ˚C to evaporate all the residual water. After reaction and cooling down to room temperature, pure $NaGdF_4$ precursor was obtained.

3-Cation exchange in organic solvent (OSCE): To obtain the optimal emission intensity, we prepared a series of UCNCs by OSCE with different amounts of activators (Tb^{3+} and Eu^{3+}). In a typical experiment, a stock toluene solution (666 uL) of the 0.05mmol as-prepared UCNCs ($NaGdF_4$:Yb/Tm or $NaGdF_4$:Yb/Tm@$NaGdF_4$) was mixed with an ethanol solution (333 ul) of $LnCl_3$ (Ln = Tb^{3+}, Eu^{3+}). The resulting mixture was shaken thoroughly under room temperature for 10 min. Subsequently, the products were collected by centrifugation, washed with toluene/ethanol (2:1) several times, and re-dispersed in toluene. When use methanol, DMF, DMSO for dissolving $LnCl_3$, corresponding mole ratio of toluene and organic solution should be optimised. Corresponding samples by WACE were prepared according to the previous reports[3].

4-Characterization

TEM Characterization: The morphology of the synthesize nanocrystals was characterized using transmission electron microscopy (TEM) imaging (Philips CM10 TEM) with an operating voltage of 100 kV. The samples were prepared by placing a drop of a dilute suspension of nanocrystals onto the formvar-coated copper grids (300 meshes) and allowing it to dry in a desiccator at room temperature.

XRD Characterization: The X-ray diffraction (XRD) patterns were recorded on a D8 Advance (Bruker Corporation, Germany) X-ray powder diffractometer using Cu-Kα1 radiation (40 kV, 25 mA, $\lambda = 0.15418$ nm) in the 2θ range from 5° to 100°. Scan steps are 0.02°and scan

4s for each step. Rietveld refinement was performed by using TOPAS 4.2 program. The XRD samples were prepared by several drops of nanocrystal dispersions in toluene cast on a glass wafer.

High-resolution transmission electron microscopy (HRTEM) imaging and Electron energy loss spectroscopy (EELS): Element mapping images were collected with an aberration-corrected analytical transmission electron microscopy (TEM, JEOL ARM-200F) equipped with a Centurio SSD energy-dispersive X-ray spectroscopy (EDS) detector set at 77 K. The TEM was operated at 80 kV. The line profiles were processed with the LOWESS smoothing algorithm as implemented in OriginPro.

Photoluminescence spectra by spectrofluorometer: The upconversion luminescence spectra were obtained using of a Fluorolog-Tau3 spectrofluorometer (JobinYvon-Horiba) equipped with an external 980 nm CW diode laser with a pump power density of $5*10^5$W/cm^2. The upconversion nanocrystals were dispersed in the toluene and were prepared to the concentration of 1 mg/ml by the subtractive weighting method for the entire specimen. Corresponding samples by WACE also were prepared to the concentration of 1 mg/ml. The dispersion was transferred to quartz cuvettes with 10 mm path length and three measurements were conducted for each sample.

Photoluminescence characterization for single UCNPs:

We used a modified laser scanning confocal microscope for the intensity measurement of single UCNP. The monodispersed single UCNPs samples were prepared first. The excitation source is a 976 nm single mode polarized laser (power density of 30MW cm^{-2}) which is focused onto the sample through a 100x objective lens (NA 1.4). The emission from sample is collected by same objective lens then refocused into an optical fiber which has a core size matching with system Airy disk. A Single Photon Counting Avalanche Diode (SPAD) detector is connected to the collection optical fiber to detect the emission intensity. The scanning is achieved by moving the 3D piezo stage.

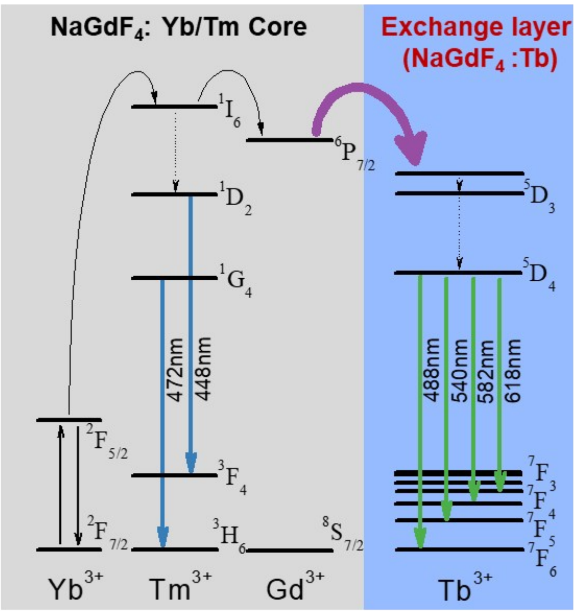

Figure S1 Level diagram and proposed energy transfer mechanism from the $NaGdF_4$: Tm^{3+}/Yb^{3+} core to cation-exchanged Tb^{3+} layer.

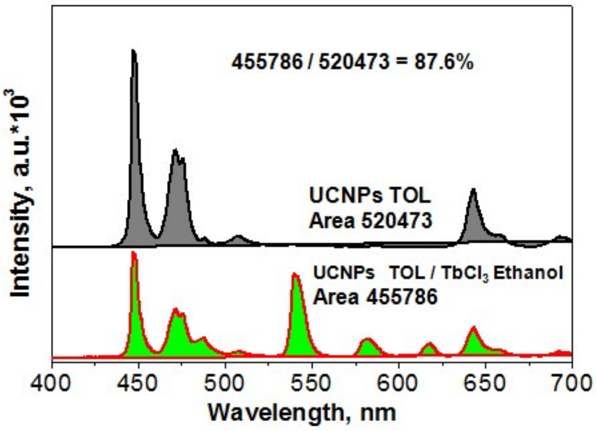

Figure S2 Upconversion emission intensity areas of initial core-only UCNPs template and UCNCs after OSCE: the integrated UC emission intensities area of $NaGdF_4$: $Tm^{3+}/Yb^{3+}/Tb^{3+}$ (UCNPs TOL / $TbCl_3$ Ethanol) is about 87.6% of initial $NaGdF_4$: Tm^{3+}/Yb^{3+} UCNCs template(UCNPs TOL) (455786 / 520473 = 87.6%).

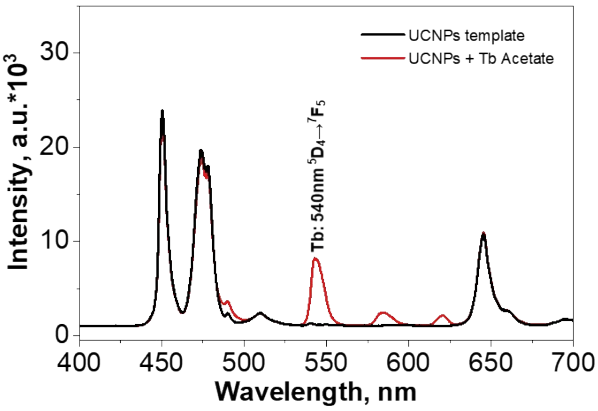

Figure S3 $Tb(CH_3COO)_3$ (Tb Acetate) instead of $TbCl_3$ for OSCE in $NaGdF_4$: Tm^{3+}/Yb^{3+} UCNCs: Tb emissions proved $Tb(CH_3COO)_3$ also can be used for cation exchanging.

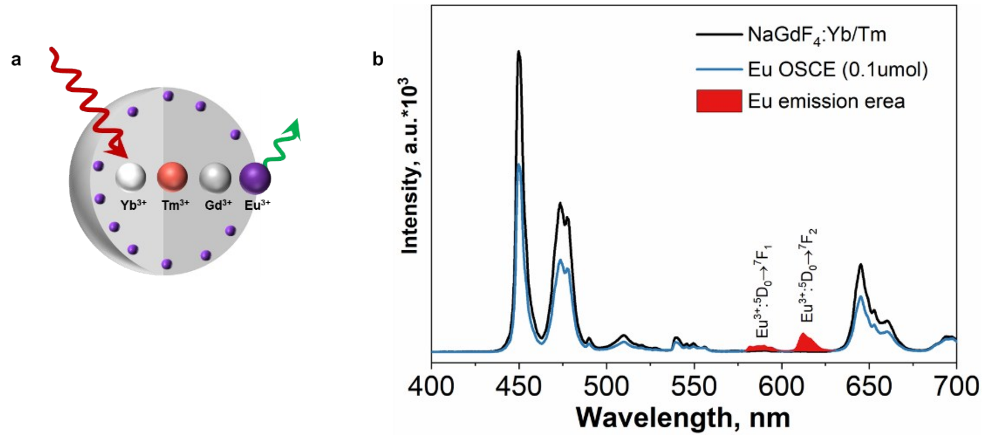

Figure S4 Eu^{3+} ions for OSCE in core-only $NaGdF_4$: Tm^{3+}/Yb^{3+} UCNCs: the emission peaks of 589 ($^5D_0 \rightarrow ^7F_1$) and 611 nm ($^5D_0 \rightarrow ^7F_2$) belongs to Eu^{3+} ions.

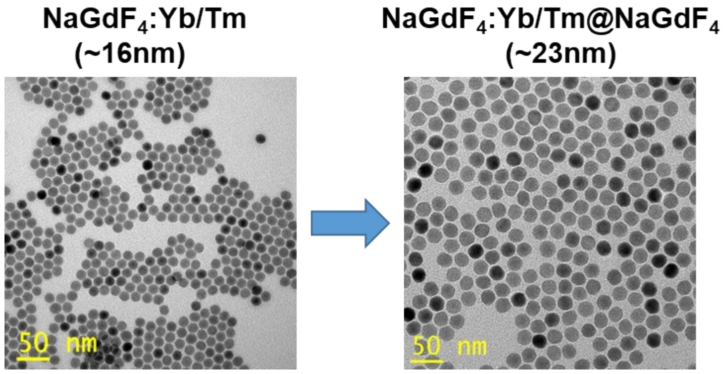

Figure S5 TEM images of core-shell UCNCs for cation exchange: firstly the core-only $NaGdF_4$:Yb/Tm nanocrystals about 16 nm in size was prepared, and then $NaGdF_4$:Yb/Tm@$NaGdF_4$ core-shell structure about 23 nm was prepared by hot-injection.

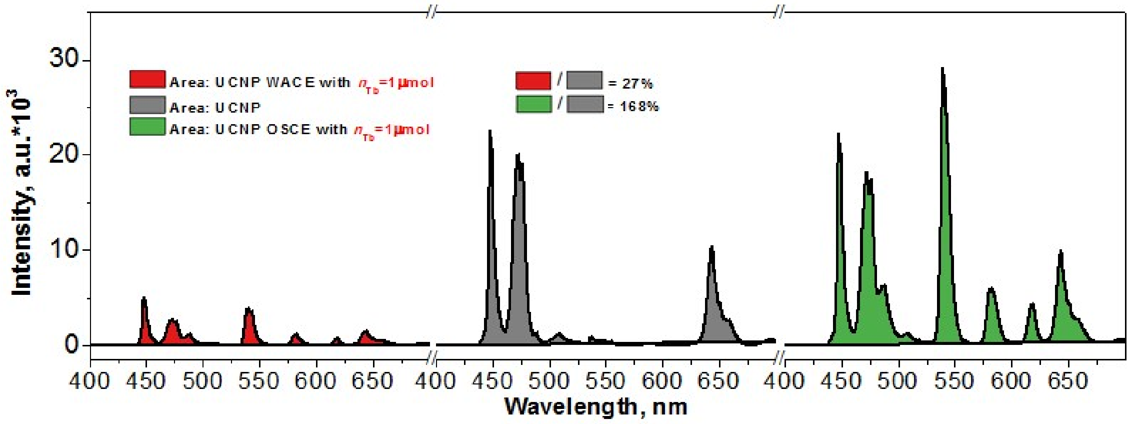

Figure S6 Upconversion emission intensity areas of core-shell UCNPs by WACE, initial core-shell UCNPs template, and core-shell UCNCs by OSCE (1 umol Tb content): the intensity of UCNCs shows 1.68-fold enhancement after OSCE, while the intensity decreases to 27% of the initial template after WACE.

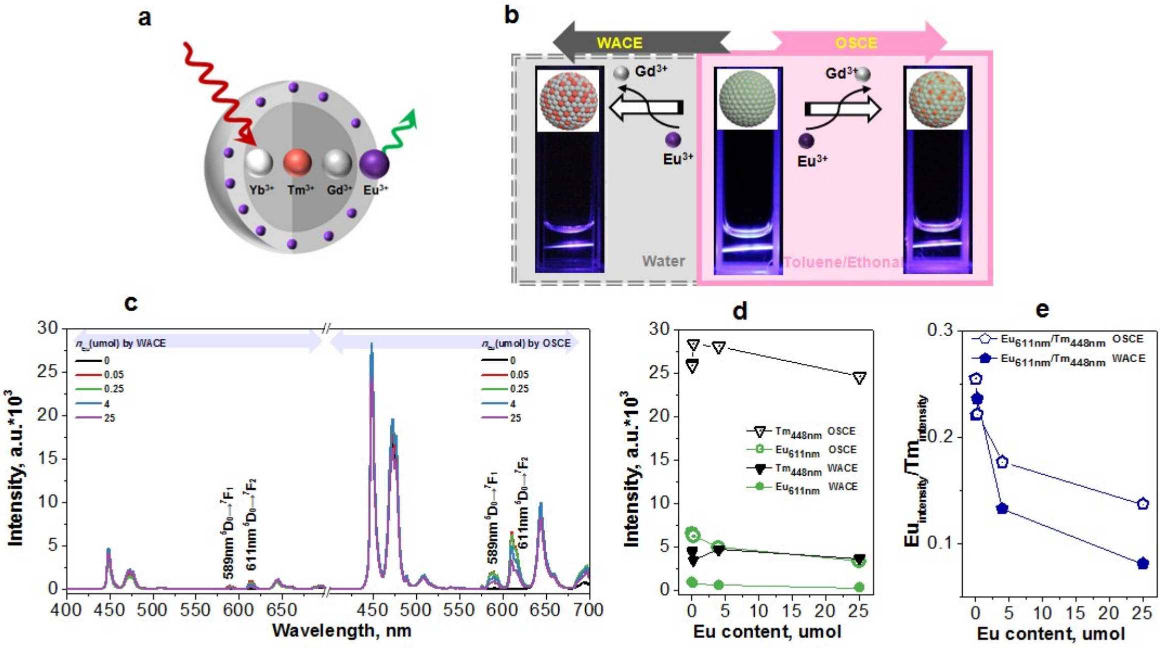

Figure S7 Eu^{3+} ions work as the exchange ions: **a)** Nanostructure of core-shell $NaGdF_4:Yb^{3+},Tm^{3+}@NaGdF_4$ UCNCs for cation exchange by Eu^{3+} ions ; **b)** Luminescent photos of UCNCs by WACE, initial UCNCs template, UCNCs by OSCE under the irradiation of a 980 nm laser; **c)** Upconversion emission spectra after cation exchanging through WACE and OSCE respectively (5 different kinds of Eu^{3+} content) , all samples are 1mg/mL; **d)** Intensities of Tm^{3+} and Eu^{3+} emissions as a function of Eu^{3+} content; **e)** Intensity ratio of Eu^{3+}/Tm^{3+} emissions as a function of Eu^{3+} content. All spectra were recorded under 980 nm excitation with power density of $5*10^5$ W cm^{-2}.

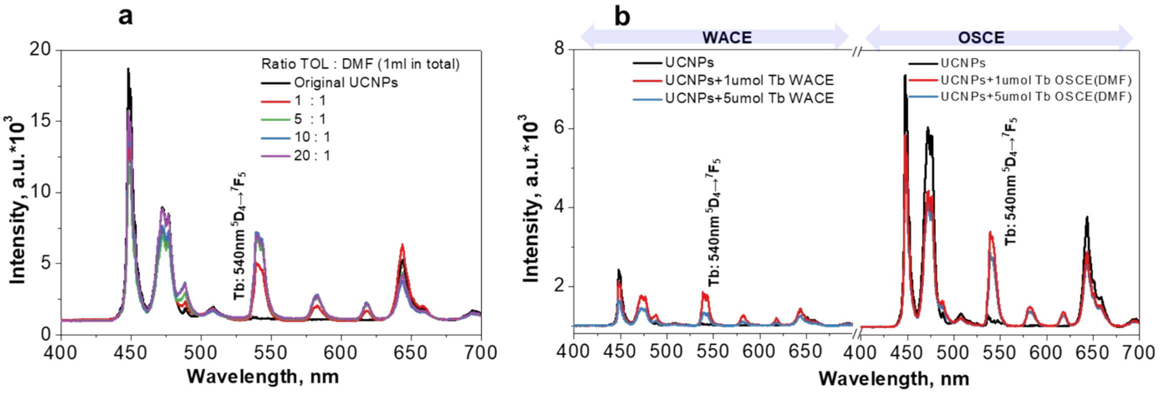

Figure S8 OSCE by using DMF as solvent to dissolving $TbCl_3$: a) the optimum ration of Toluene : DMF is decided as 10 :1; b) the integrated UC luminescent intensities of all samples by OSCE (DMF as solvent) are much stronger than the corresponding ones by WACE (2 different kinds of Tb concentration).

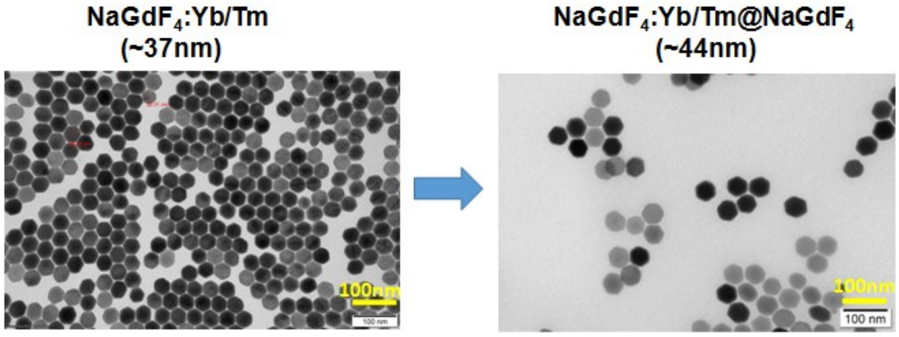

Figure S9 TEM images of core-shell UCNCs for single particles test: firstly the core-only $NaGdF_4$:Yb/Tm nanocrystals about 37 nm in size was prepared, and then $NaGdF_4$:Yb/Tm@$NaGdF_4$ core-shell structure about 44 nm was prepared by hot-injection.

Reference

(1) Wang, F.; Deng, R.; Liu, X. Preparation of core-shell $NaGdF_4$ nanoparticles doped with luminescent lanthanide ions to be used as upconversion-based probes. *Nat Protoc* **2014,** *9* (7), 1634-44.
(2) Liu, D.; Xu, X.; Du, Y.; Qin, X.; Zhang, Y.; Ma, C.; Wen, S.; Ren, W.; Goldys, E. M.; Piper, J. A.; Dou, S.; Liu, X.; Jin, D. Three-dimensional controlled growth of monodisperse sub-50 nm heterogeneous nanocrystals. *Nat Commun* **2016,** *7*, 10254.
(3) Han, S.; Qin, X.; An, Z.; Zhu, Y.; Liang, L.; Han, Y.; Huang, W.; Liu, X. Multicolour synthesis in lanthanide-doped nanocrystals through cation exchange in water. *Nat Commun* **2016,** *7*, 13059.