Supporting Information for

Superparamagnetic and Upconversion Emitting Fe_3O_4/$NaYF_4$:Yb,Er Hetero-Nanoparticles via a Crosslinker Anchoring Strategy

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Experimental Section

Chemicals: 1,10-decanedicarboxylic acid (DDA, Alfa Aesar), 11-mercaptoundecanoic acid (MUA, Alfa Aesar), Oleic acid (OA; 90%, Alpha), Oleylamine (OAm; >80%, Acros), 1-octadecene (ODE, Acros), CF_3COONa (>97%, Acros), iron(III) acetylacetonate ($Fe(acac)_3$, Acros), Ln_2O_3 (Ln = Y, Yb, Er), ethanol (AR), hexane (AR) and cyclohexane (AR) were used as received. $Ln(CF_3COO)_3$ were prepared with the literature method (Roberts, J. E. *J. Am. Chem. Soc.* **1961**, *83*, 1087).

Synthesis of 100 nm β-$NaYF_4$:Yb,Er NPs: As a typical synthesis procedure for 1 mmol β-$NaYF_4$:Yb,Er, 1.9 mmol CF_3COONa, 0.78 mmol $Y(CF_3COO)_3$, 0.20 mmol $Yb(CF_3COO)_3$ and 0.02 mmol $Er(CF_3COO)_3$ was added into a three-necked flask with 20 mmol OA and 20 mmol ODE, followed by vacuum degassing at 120 °C for 30 min to remove water and oxygen. Then the solution was heated to 330 °C at a rate of 20 $K \cdot min^{-1}$ under nitrogen protection. After maintained at 330 °C for 30 min, the reaction was cooled down to room temperature. The β-$NaYF_4$:Yb,Er NPs were centrifugally separated within an excess amount of ethanol, and the white powder was collected for the second round synthesis.

Synthesis of 200 nm β-$NaYF_4$:Yb,Er NPs: The synthetic procedure was the same as that used for the 100 nm β-$NaYF_4$:Yb,Er NPs, except that the quantity of CF_3COONa was increased to 2.1 mmol.

Synthesis of Fe_3O_4/β-$NaYF_4$:Yb,Er hetero-NPs with DDA: In the DDA-assisted synthesis route, the β-$NaYF_4$:Yb,Er NPs with 200 nm diameters were utilized. Typically, 0.5 mmol $Fe(acac)_3$, 0.5 mmol DDA, and the as-synthesized β-$NaYF_4$:Yb,Er NPs powder (with 1 mmol of Ln) were dissolved in 4 mmol OA, 5 mmol OAm and 20 mmol ODE in a three-necked flask, followed by vacuum degassing at 120 °C for 30 min. Then the solution was heated at a rate of 20 $K \cdot min^{-1}$ and maintained at 265 °C for 40 min under nitrogen atmosphere. After that, the reaction was cooled down and 50 mL of cyclohexane/ethanol mixture (1:1 in volume) was poured into the flask. The product was centrifugally precipitated and washed in cyclohexane/ethanol mixture for 3 times to remove excess DDA. The as-prepared Fe_3O_4/β-$NaYF_4$:Yb,Er hetero-NPs could be easily dispersed in nonpolar organic solvents, such as cyclohexane and chloroform.

Synthesis of Fe_3O_4/β-$NaYF_4$:Yb,Er hetero-NPs with MUA: The MUA-assisted synthesis followed the same procedure as that for DDA system, except β-$NaYF_4$:Yb,Er NPs in 100 nm diameters and 1 mmol MUA was used instead. The solvent compositions were also changed a

little, with 3 mmol OA, 5 mmol OAm and 20 mmol ODE.

Surface Modification of Fe_3O_4/β-$NaYF_4$:Yb,Er hetero-NPs: The product obtained from DDA-assisted route were utilized in this experiment. Typically, 10 mg of hetero-NPs were dissolved in 50 mL *n*-hexane, and cooled down to −78 °C in a dry ice/acetone bath with vigorous stirring. Then the solution was bubbled up by an ozone flow (1.2 $L \cdot h^{-1}$) for 5 min. It will be a signal for the reaction accomplishment by the solution color variation from brown to blue-gray. To get rid of the excessive ozone, the solution was further bubbled by oxygen flow until the blue color was faded. Then the solution was added with 50 mL ethanol, 0.5 mL CH_3COOH and 0.5 mL 30% H_2O_2, and stirred at room temperature for 24 h. The hydrophilic hetero-NPs was purified by centrifuging, and re-dispersed in water.

Magnetic Patterning and UC Luminescent Readout: The home-made ferreous mask had a periodic spacing of 200 μm. It could regulate the intensity distribution of a parallel magnetic field. A drop of water solution contained hetero-NPs (1 $mg \cdot mL^{-1}$) was transferred onto a coverslip with a soakage area of 1 cm^2. Then the ferreous mask at the backside will magnetically trap the hetero-NPs onto the coverslip according to its shape. After the evaporation of water, the coverslip was imaged on a Nikon fluorescent microscope with 980 nm laser excitation. By the way, the cyclohexane solution will be evaporated too fast for the patterned trapping of NPs, so the aqueous solution was preferred.

Control Experiments for the Second synthesis Step: The preparation was conducted with the similar procedure as that for hetero-NPs, except for the different reagents as indicated in the table. (TEM images of the products were displayed in Fig. 2)

No.	$NaYF_4$:Yb,Er	$Fe(acac)_3$	Crosslinker	OA	OAm	ODE
a	1 mmol	0.5 mmol	/	5 mmol	5 mmol	20 mmol
b	/	0.5 mmol	/	5 mmol	5 mmol	20 mmol
c	/	0.5 mmol	0.5 mmol DDA	4 mmol	5 mmol	20 mmol
d	/	0.5 mmol	1 mmol MUA	3 mmol	5 mmol	20 mmol

Instrumentation. Samples for transmission electron microscopy (TEM) analysis were made from drying a drop of nanocrystal dispersion in cyclohexane or water on carbon-coated copper grids. TEM and HRTEM data were acquired on Hitachi H-9000 NAR TEM under a working voltage of 300 kV. The same copper grids were also utilized for the imaging on an *Olympus* laser scanning confocal microscope equipped with 980 nm laser. Powder X-ray diffraction (XRD) patterns of the dried powders were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2 ° at a scanning rate of $2° \cdot min^{-1}$, using Cu-Ka radiation (l = 1.5406 Å). Inductively Coupled Plasma (ICP-AES, Plasma-Spec, Leeman Labs. Inc.) measurement was used to determine Y and Fe contents in the hetero-NPs. Room temperature UC luminescent spectra were measured on a Hitachi F-4500 spectrophotometer equipped with an external 980 nm laser diode. The magnetic measurements were performed on a Quantum Design Superconducting Quantum Interference Device magnetometer (SQUID). Hysteresis loops were measured in a magnetic field varied from +50 to −50 kOe at 300 K. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were measured under an applied field of 50 Oe between 2 and 300 K.

Data Section

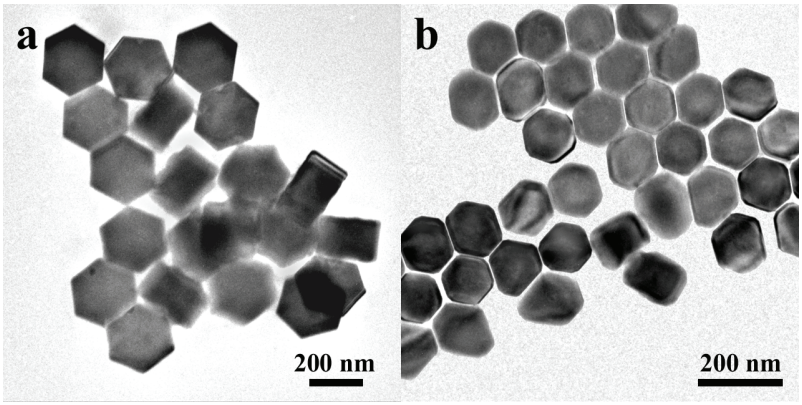

Figure S1. TEM images of the β-$NaYF_4$:Yb,Er NPs with diameters of ca. 200 nm (a) and ca. 100 nm (b).

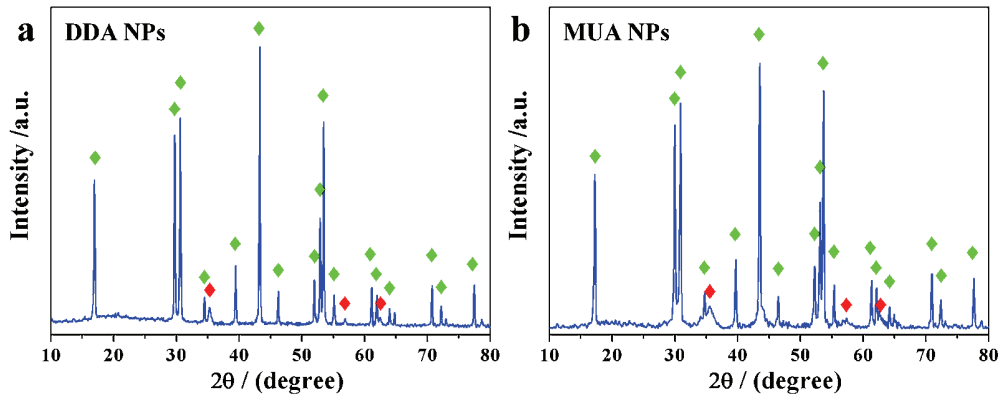

Figure S2. XRD patterns of the Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs synthesized with DDA (a) and MUA (b). The diffraction peaks of Fe_3O_4 and β-$NaYF_4$:Yb,Er are labeled with red and green symbols, respectively.

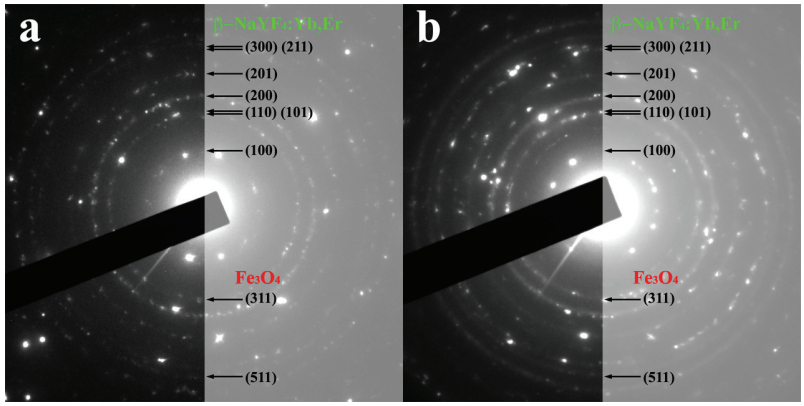

Figure S3. Selected area electron diffraction (SAED) analysis of the Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs synthesized with DDA (a) and MUA (b).

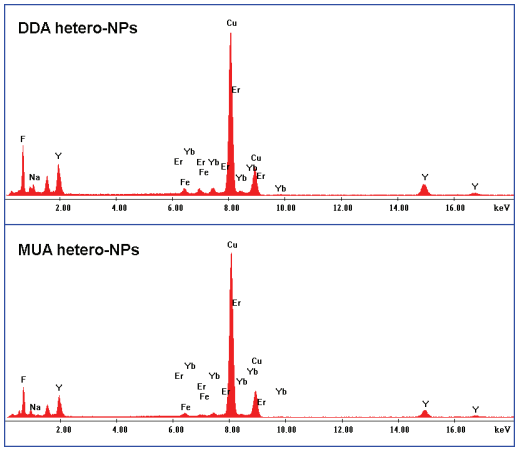

Figure S4. EDAX spectra of Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs synthesized with DDA (up) and MUA (down).

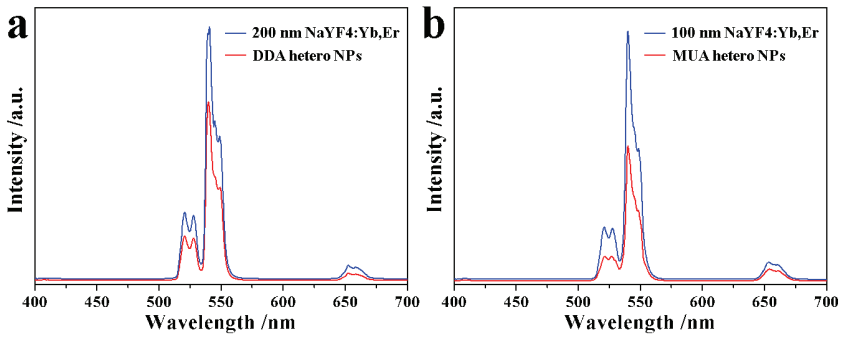

Figure S5. UC luminescent spectra of Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs and their UC NPs counterparts: (a) DDA-assisted route; (b) MUA-assisted route. The Ln concentration was fixed as 0.01 mmol in 10 mL cyclohexane for the sake of comparing the luminescent intensity.

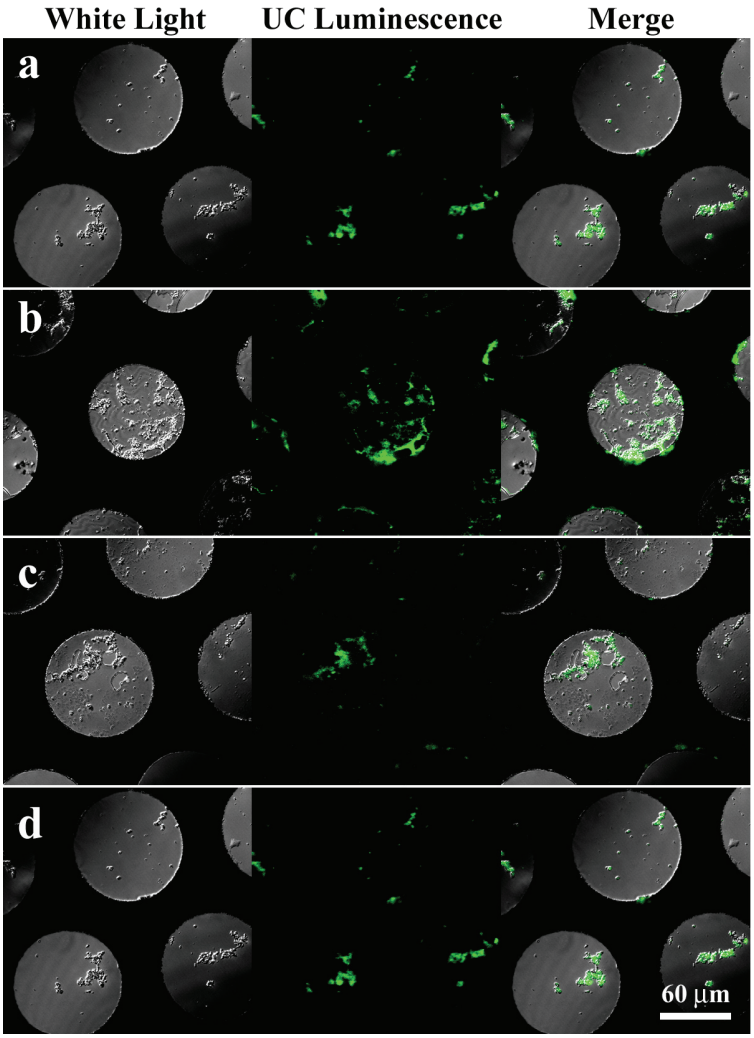

Figure S6. UC luminescent images of the TEM grids that loaded with 100 nm (a) and 200 nm (b) $NaYF_4$:Yb,Er NPs, and Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs synthesized with (c) MUA, (d) DDA.

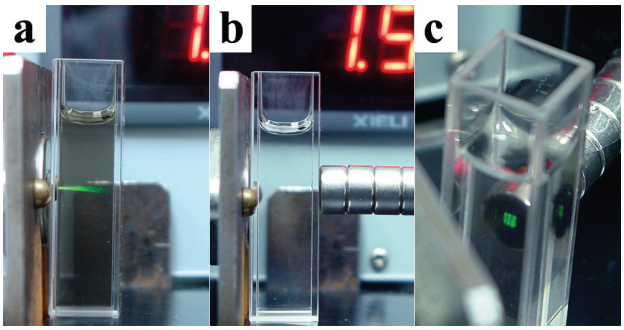

Figure S7. Magnetic tapping of MUA treated Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs from the cyclohexane solution: (a) the stock solution of hetero-NPs revealed green UC luminescent beam under 980 nm laser irradiation; (b) After magnetic tapping, the solution turned to be colorless and the luminescent beam was vanished; (c) From another direction, it can be observed that all hetero-NPs were tapped by the magnet, and still maintained UC luminescence with IR irradiating.

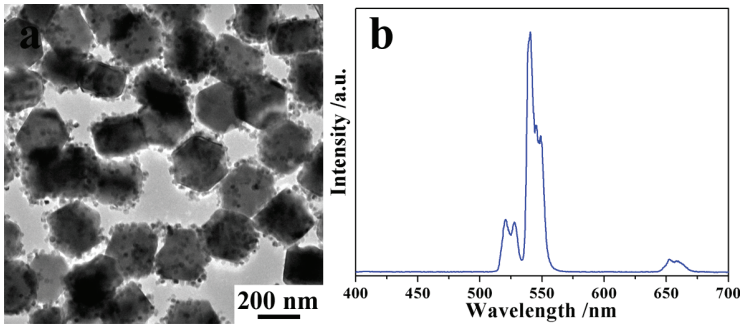

Figure S8. (a) TEM image of the ozonolysis treated Fe_3O_4/$NaYF_4$:Yb,Er hetero-NPs that dispersed in water. (b) UC luminescence spectrum of the aqueous solution of hetero-NPs.

Table S1. ICP-AES results for the Fe/Y ratio of hetero-NPs

	DDA hetero-NPs	MUA hetero-NPs
Fe/Y ratio	0.90	0.65