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Supporting Information

808 nm Excited Energy Migration Upconversion Nanoparticles Driven by Nd^{3+}-Trinity System with Color-Tunability and Superior Luminescent Properties

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1. Experimental Section

1.1 Reagents

Oleic acid (OA, 90 %, tech), 1-octandence (1-ODE, 90 %, tech), sodium hydroxide (NaOH), ammonium fluoride (NH_4F) and lanthanide acetate ($Ln(CH_3CO_2)_3$•xH_2O, Ln = Gd (Gadolinium), Yb (Ytterbium) Nd (Neodymium), Tm (Thulium), Eu (Europium), Tb (Terbium)),dissolved in deionized water to form the solution with concentration of 0.16 M. All materials were purchased from Sigma-Aldrich and used without purifications.

1.2 Synthesis of the EMU core UCNPs:

Synthesis of the $NaGdF_4$:$Yb_{49\%}$, $Tm_{1\ \%}$ UCNPs: 8 mL OA and **0.8 mmol $Ln(CH_3CO_2)_3$•xH_2O DI water solution (Ln= Gd,Yb,Tm)** were placed in a 100 ml three-neck flask, and degassed by nitrogen for 15 min. The mixture was heated to 150 ℃and the temperature was kept for 0.5 h to remove water. 12 mL 1-ODE was then added and the mixture was kept at 150 ℃ for 0.5 h to form a uniform solution. Cooling down the solution to 50 ℃, 5 mL methanol that contained 80 mg NaOH and 240 mg NH_4F was added drop wise. And then kept for 0.5 h at 50 ℃ with stirring. The solution was then heated to 120 ℃ to remove water and methanol, and keeping under vacuum for 10 min preventing bumping at high temperature, and subsequently heated to 290 ℃ and kept for 1.5 h under nitrogen protection. The product was precipitated by adding excess methanol and collected by configuring at 12,000 rpm for 10 min. The purification was repeated for 3 times. After that, the UCNPs were redispersed in cyclohexane for further synthesis and characterization.

Modified EMU cores, that are $NaGdF_4$:$Yb_{49\%}$, $Tm_{1\ \%}$@$NaGdF_4$:$Yb_{10\ \%}$, X(Eu/Tb)$_{15\ \%}$: 8 mL OA and **0.8 mmol $Ln(CH_3CO_2)_3$•xH_2O DI water solution (Ln= Gd,Yb,Eu/Tb)** were placed in a 50 ml three-neck flask, and degassed by nitrogen for 15 min. The mixture was heated to 150 ℃and the temperature was kept for 0.5 h to remove water. 12 mL 1-

ODE was then added and the mixture was kept at 150 ℃ for 0.5 h to form a uniform solution. Cooling down the solution to 50 ℃, **0.4 mmol $NaGdF_4:Yb_{49\%}$, $Tm_{1\%}$ UCNPs** that dispersed in cyclohexane was added in following with 5 mL methanol that contained 80 mg NaOH and 240 mg NH_4F was added drop wise. And then kept for 0.5 h at 50 ℃ with stirring. The solution was then heated to 120 ℃ to remove water and methanol, and keeping under vacuum for 10 min preventing bumping at high temperature, and subsequently heated to 290 ℃ and kept for 1.5 h under nitrogen protection. The product was precipitated by adding excess methanol and collected by configuring at 12,000 rpm for 10 min. The purification was repeated for 3 times. After that, the UCNPs were redispersed in cyclohexane for further synthesis and characterization.

1.3 Synthesis the core-multishell Nd^{3+}-Trinity EMU UCNPs:

Coating of the transition layer ($NaGdF_4:Yb_{10\%}$ or $NaGdF_4:Yb_{10\%},Nd_{20\%}$): 4 mL OA and **0.4 mmol $Ln(CH_3CO_2)_3$•xH_2O DI water solution (Ln= Gd,Yb,Nd)** were placed in a 50 ml three-neck flask, and degassed by nitrogen for 15 min. The mixture was heated to 150 ℃and the temperature was kept for 0.5 h to remove water. 6 mL 1-ODE was then added and the mixture was kept at 150 ℃ for 0.5 h to form a uniform solution. Cooling down the solution to 50 ℃, **0.8 mmol EMU cores UCNPs** that dispersed in cyclohexane was added in following with 5 mL methanol that contained 40 mg NaOH and 120 mg NH_4F was added drop wise. And then kept for 0.5 h at 50 ℃ with stirring. The solution was then heated to 120 ℃ to remove water and methanol, and keeping under vacuum for 10 min preventing bumping at high temperature, and subsequently heated to 290 ℃ and kept for 1.5 h under nitrogen protection. The product was precipitated by adding excess methanol and collected by configuring at 12,000 rpm for 10 min. The purification was repeated for 3 times. After that, the UCNPs were redispersed in cyclohexane for further synthesis and characterization.

Coating of the harvest layer ($NaNdF_4:Yb_{20\%}$ or $NaGd_{100\%-x-y}F_4:Yb_x,Nd_y$): 4 mL OA and **0.4 mmol $Ln(CH_3CO_2)_3$•xH_2O DI water solution (Ln= Gd,Yb,Nd)** were placed in a 50 ml three-neck flask, and degassed by nitrogen for 15 min. The mixture was heated to 150 ℃and the temperature was kept for 0.5 h to remove water. 6 mL 1-ODE was then added and the mixture was kept at 150 ℃ for 0.5 h to form a uniform solution. Cooling down the solution to 50 ℃, **0.8 mmol EMU cores@transition layer UCNPs** that dispersed in cyclohexane was added in following with 5 mL methanol that contained 40 mg NaOH and 120 mg NH_4F was added drop wise. And then kept for 0.5 h at 50 ℃ with stirring. The solution was then heated to 120 ℃ to remove water and methanol, and keeping under vacuum for 10 min preventing bumping at high temperature, and subsequently heated to 290 ℃ and kept for 1.5 h under nitrogen protection. The product was precipitated by adding excess methanol and collected by configuring at 12,000 rpm for 10 min. The purification was repeated for 3 times. After that, the UCNPs were redispersed in cyclohexane for further synthesis and characterization

Coating of the activation layer ($NaGdF_4$): 4 mL OA and **0.4 mmol $Ln(CH_3CO_2)_3$•xH_2O DI water solution (Ln= Gd)** were placed in a 50 ml three-neck flask, and degassed by nitrogen for 15 min. The mixture was heated to 150 ℃ and the temperature was kept for 0.5 h to remove water. 6 mL 1-ODE was then added and the mixture was kept at 150 ℃ for 0.5 h to form a uniform solution. Cooling down the solution to 50 ℃, **0.8 mmol EMU cores@transition layer@harvest layer UCNPs** that dispersed in cyclohexane was added in following with 5 mL methanol that contained 40 mg NaOH and 120 mg NH_4F was added drop wise. And then kept for 0.5 h at 50 ℃ with stirring. The solution was then heated to 120 ℃ to remove water and methanol, and keeping under vacuum for 10 min preventing bumping at high temperature, and subsequently heated to 290 ℃ and kept for 1.5 h under nitrogen protection. The product was precipitated by adding excess methanol and collected by configuring at 12,000 rpm for 10 min. The purification was repeated for 3 times. After that, the UCNPs were redispersed in cyclohexane for further synthesis and characterization

2. Characterization

2.1 Morphological, structural and elemental analysis

Transmission electron microscopy (TEM), high resolution (HR)-TEM, selected area electron diffraction (SAED) and Energy dispersive X-ray (EDX) Spectroscopy (JEOL operating at 200 kV) were used to characterize the UCNPs. Samples were dispersed in cyclohexane and dropped on the amorphous carbon-coated copper grids.

2.2 Emission Spectra

All the emission spectra were measured by Edinburgh FLS920 spectrometers conjugated with 808/980 nm laser (CW, tunable, 0–2 W, Changchun New Industries Optoelectronics Technology Co., Ltd.). A condenser lens was used to focus the laser beam. Measurement conditions, including power density, sample concentration, instrument settings (especially the emission band width) as well as the optical path of the lasers to the spectrometer are strictly controlled to realize the comparability among the UCL intensity of the obtained UCNPs in the investigation and characterization of the Nd^{3+}-Trinity EMU system UCNPs.

2.3 Lifetime/decay curves measurement

All the decay curves were measured by Edinburgh FLS 920 conjugated with DG-535 Digital Delay/Pulse Generator and 808/980 nm laser (modulation mode, Changchun New Industries Optoelectronics Technology Co., Ltd.).

3. Investigation of the quenching factors in the Nd^{3+}-Trinity EMU system

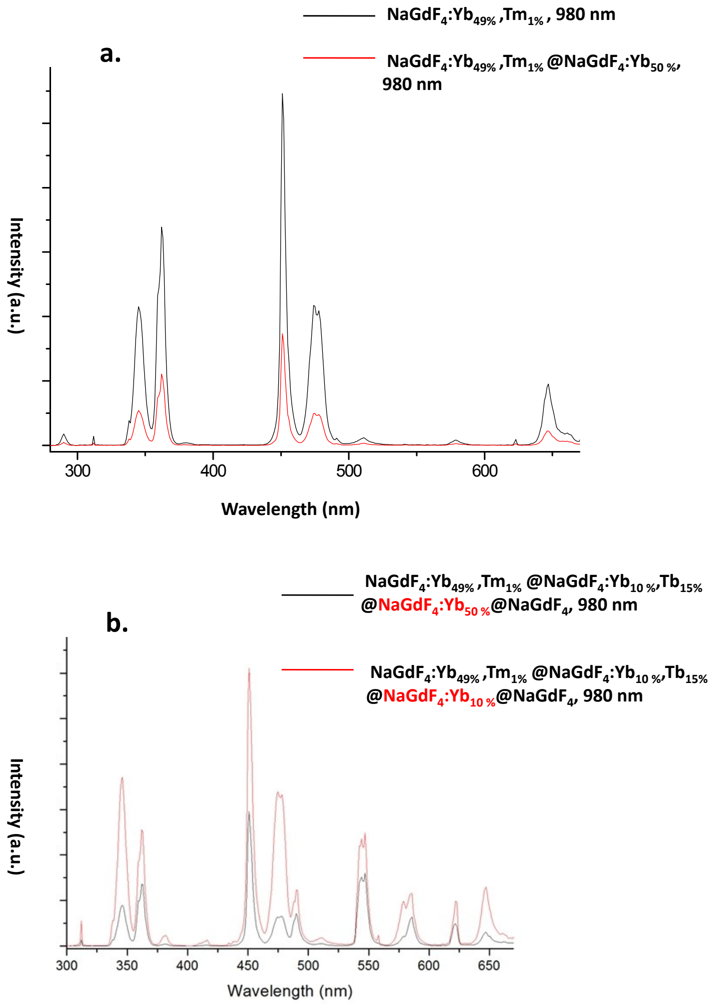


Figure S1. Investigation on Yb^{3+} energy back-transfer. (a). Emission spectra of NaGdF$_4$:Yb$_{49\%}$, Tm$_{1\%}$ and NaGdF$_4$:Yb$_{49\%}$, Tm$_{1\%}$@NaGdF$_4$:**Yb$_{50\%}$(high Yb^{3+} dopants)** under excitation of 980 nm laser, which illustrates the detriments of Yb^{3+} energy back-transfer on the Tm^{3+} accumulation. (b). Emission spectra of NaGdF$_4$:Yb$_{49\%}$, Tm$_{1\%}$@ NaGdF$_4$:Yb$_{10\%}$,Tb$_{15\%}$@NaGdF$_4$:**Yb$_{50\%}$(high Yb^{3+} dopants)**@NaGdF$_4$ and NaGdF$_4$: Yb$_{49\%}$,Tm$_{1\%}$@NaGdF$_4$:Yb$_{10\%}$,Tb$_{15\%}$ @NaGdF$_4$:**Yb$_{10\%}$**@NaGdF$_4$ under excitation of 980 nm laser, which illustrates the detriments of Yb^{3+} energy back-transfer on the activators (Eu^{3+}/Tb^{3+}) in the EMU system. (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

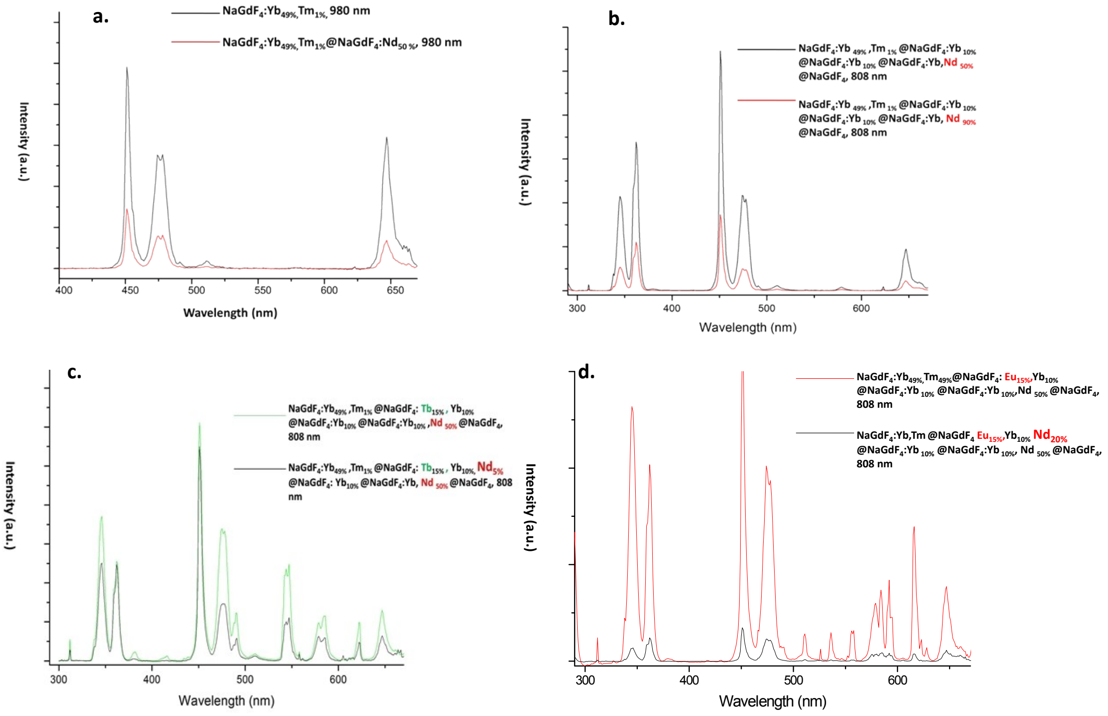


Figure S2. Investigations on the effect of Nd^{3+} energy back-transfer: (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

On the accumulators (Tm^{3+}) that revealed by emission spectra of (a) $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$ and $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$@**$NaGdF_4$:$Nd_{50\%}$ (high Nd^{3+} dopants)** under excitation of 980 nm laser; (b). $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$@**$NaGdF_4$:$Yb_{10\%}$(transition layer) @$NaGdF_4$: $Nd_{50\%}$(high Nd^{3+} dopants)** @$NaGdF_4$ and $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$ @**$NaGdF_4$:$Yb_{10\%}$ (transition layer) @$NaGdF_4$:$Nd_{90\%}$ (comparatively high Nd^{3+} dopants)** @$NaGdF_4$;

On the activators of Tb^{3+}: (c). $NaGdF_4$:$Yb_{49\%}$, $Tm_{1\%}$ @$NaGdF_4$:**$Tb_{15\%}$,** $Yb_{10\%}$@**$NaGdF_4$:$Yb_{10\%}$(transition layer)**@$NaGdF_4$:$Yb_{10\%}$,**$Nd_{50\%}$ (harvest layer)** @$NaGdF_4$ and $NaGdF_4$:$Yb_{49\%}$, $Tm_{1\%}$ @$NaGdF_4$:**$Tb_{15\%}$,** $Yb_{10\%}$@ $NaGdF_4$:$Yb_{10\%}$@ $NaGdF_4$:$Yb_{10\%}$, **$Nd_{90\%}$ (comparatively high Nd^{3+} dopants)** @$NaGdF_4$;

On the activators of Eu^{3+}: (d). $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$ @$NaGdF_4$: **$Eu_{15\%}$**,$Yb_{10\%}$ @$NaGdF_4$:$Yb_{10\%}$@$NaGdF_4$:$Nd_{50\%}$@$NaGdF_4$ and $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$@ $NaGdF_4$:**$Eu_{15\%}$,** $Yb_{10\%}$, **$Nd_{20\%}$ (Nd^{3+} co-dopants with activators)** @$NaGdF_4$:$Yb_{10\%}$ @$NaGdF_4$: $Yb_{10\%}$, $Nd_{50\%}$ @$NaGdF_4$.

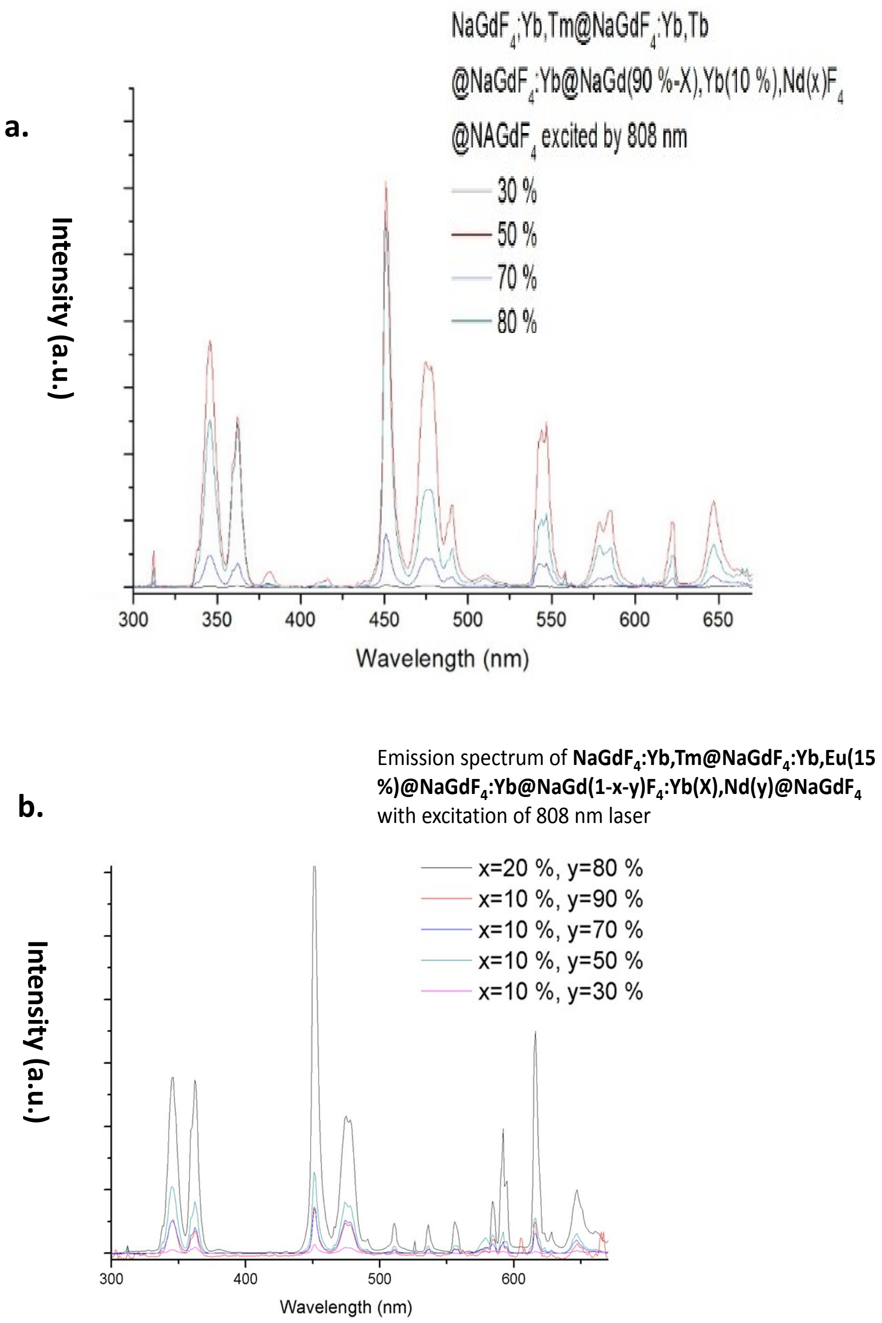


Figure S3. Optimization of the harvest layer in the Nd^{3+}-Trinity EMU system with activator of Tb^{3+} ions (a) and Eu^{3+} ions (b). (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

4. Luminescent properties of the Nd^{3+} -trinity EMU system

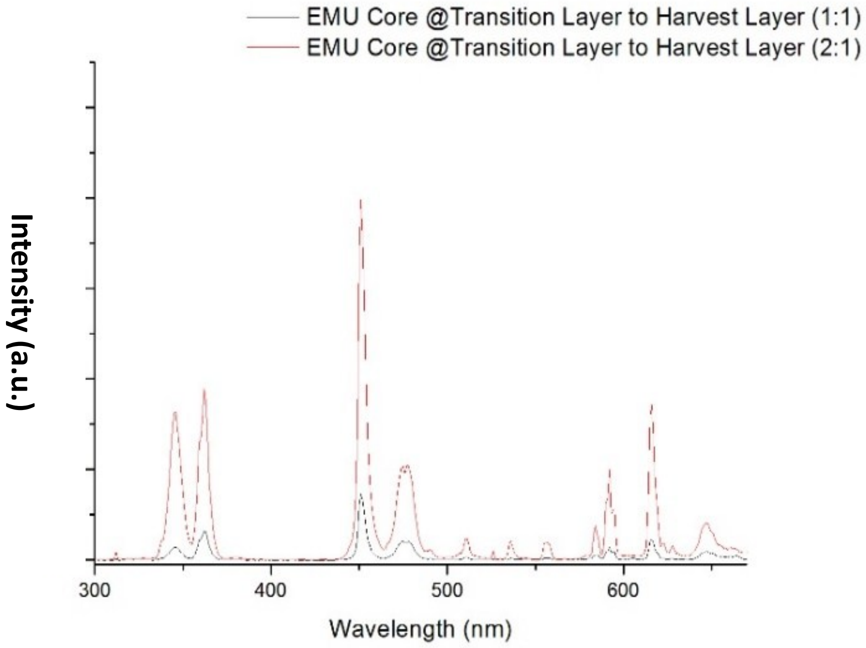


Figure S4. The optimization of the Nd^{3+}-Trinity EMU system on the precursors of the core-shell ratio. (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

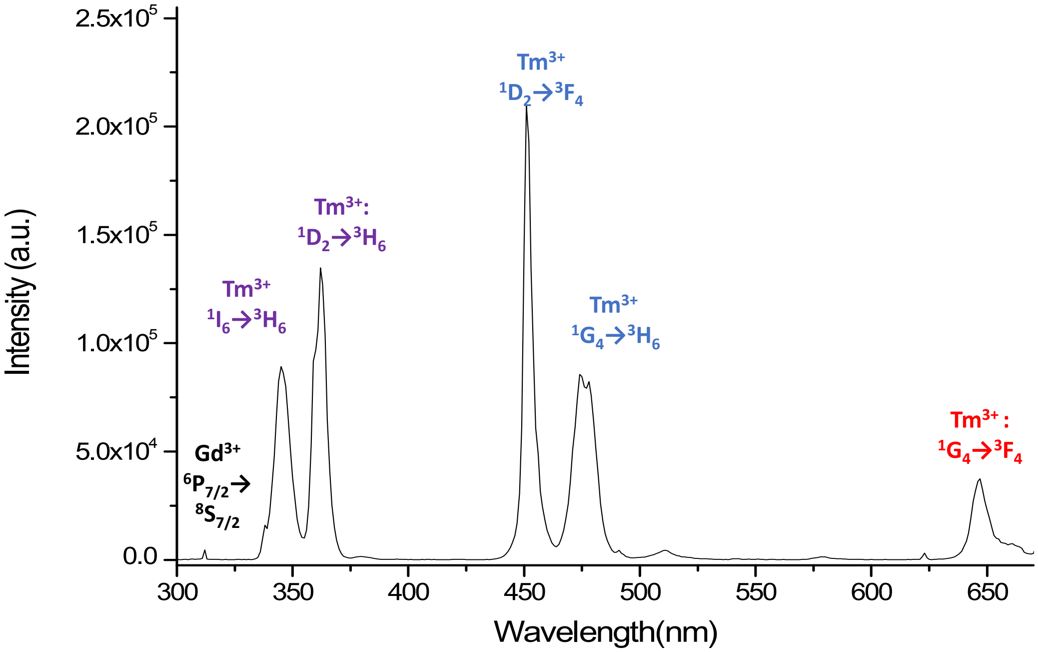


Figure S5. Emission spectrum of the Nd^{3+}-Trinity EMU system without activator that is $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$@$NaGdF_4$:$Yb_{10\%}$@$NaGdF_4$:$Yb_{10\%}$@$NaGdF_4$:$Nd_{50\%}$,$Yb_{10\%}$@$NaGdF_4$. (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

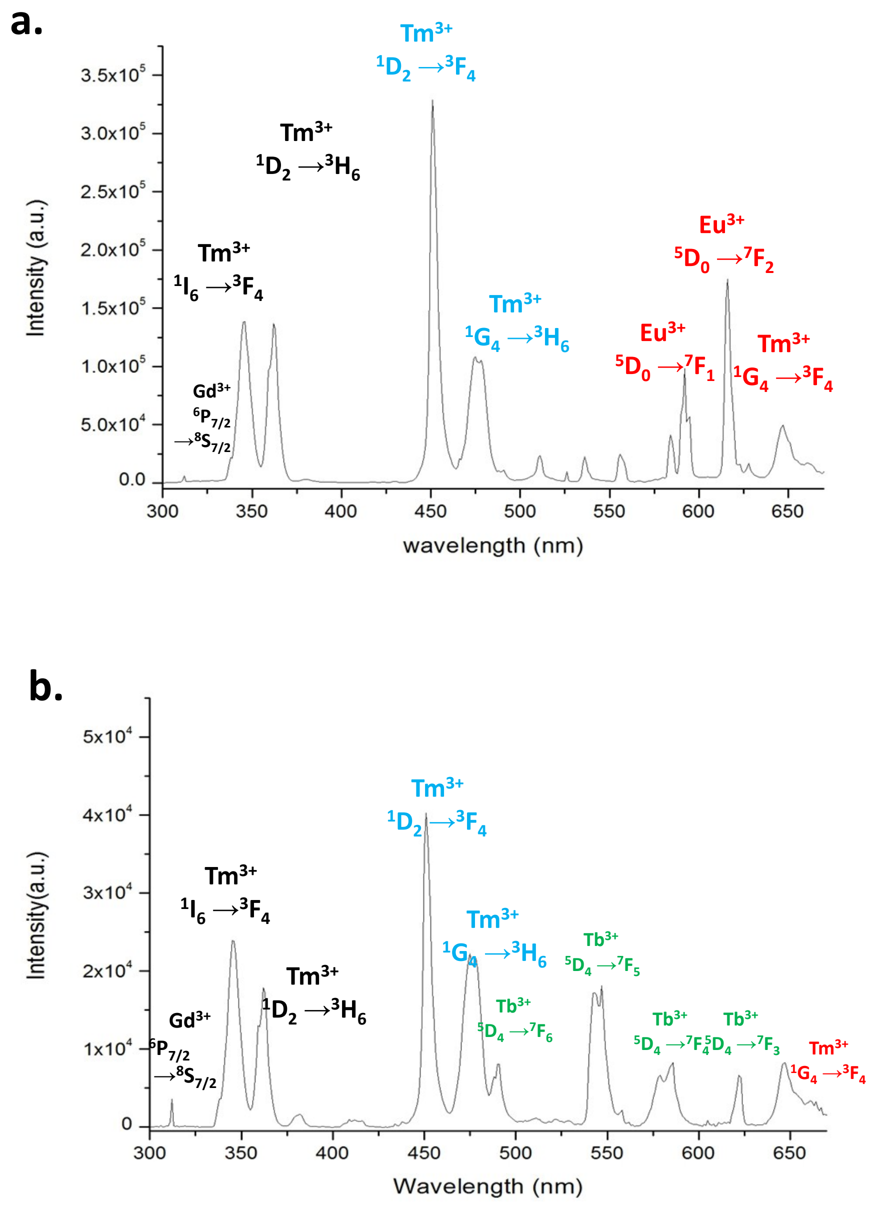


Figure S6. The emission spectra of the Nd^{3+}-Trinity EMU system (type II). (Measurement conditions: power density: 80 mW/ 1 mm^2 for 808/ 980 nm diode laser; emission bandwidth: 2 nm, concentration: 1.0 wt %.)

Table S1. Peak area ratio of the 808 nm excited Nd^{3+}-trinity EMU system with activator of Tb^{3+} compares with the 980 nm excited EMU system with activator of Tb^{3+}.

Emission Band	**Tm^{3+} Ultraviolet**	**Tm^{3+} (blue)**	**Tb^{3+} (483,547,586,622**	**Tm^{3+} (red)**	**Visible Emission**

	(348, 362 nm)	(450, 478 nm)	nm)	647 nm	
Ratio of 808 nm sensitized EMU-Tb compares with 980 nm sensitized EMU-Tb	2.96	2.94	1.85	4.75	2.58

Table S2. Peak area ratio of the 808 nm excited Nd^{3+}-trinity EMU system with activator of Eu^{3+} compares with the 980 nm excited EMU system with activator of Eu^{3+}.

Emission Band	**Tm^{3+} ultraviolet (348, 362 nm)**	**Tm^{3+} (blue) (450,475 nm)**	**Eu^{3+} (584, 592,616 nm)**	**Tm^{3+} (red) 647 nm**	**Visible Emission**
Ratio of 808 nm sensitized EMU-Tb compares with 980 nm sensitized EMU-Tb	0.83	0.71	0.85	0.84	0.73

Table S3. Lifetime of the Nd^{3+}-Trinity EMU-Tb^{3+} system with excitation of 808 nm and 980 nm laser compares with EMU system with excitation of 980 nm laser. The unit for the lifetimes is μs.

Emission wavelength (nm)	**290**	**312**	**345**	**362**	**450**	**475**	**495**	**550**	**647**
Nd^{3+}-EMU-*Tb* (808)	365	470	358	449	707	873	1532	4227	1028
Nd^{3+}-EMU-*Tb* (980)	321	394	348	417	891	840	1166	4054	1154
EMU-*Tb* (980)	247	597	240	308	315	514	2975.	3685	524

Table S4. Lifetime of the Nd^{3+}-Trinity EMU-Eu^{3+} system with excitation of 808 nm and 980 nm laser compares with EMU system with excitation of 980 nm laser. The unit for the lifetimes is μs.

Emission wavelength (nm)	**290**	**312**	**345**	**362**	**450**	**475**	**592**	**616**	**647**
Nd^{3+}-EMU-*Eu* (808)	206	338	193	238	216	517.	4538	4535	497
Nd^{3+}-EMU-*Eu* (980)	199	292	230	247	282	508	4284	4339	381
EMU-*Eu* (980)	410	597	425	463	572	806	3922	3920	663

5. Investigations on the mechanism

Supporting Note I:

“Nd^{3+}→Yb^{3+} photons-assisted energy transfer”: by generation of the “k” photons by Yb^{3+} ions and “n-k” photons by Nd^{3+} ions, on one hand, makes the overlapped Nd^{3+} $^4F_{3/2}$ emission and Yb^{3+} $^2F_{5/2}$ absorption to the equal virtual intermediate level, thus makes the Nd^{3+} $^4F_{3/2}$+ Yb^{3+} $^2F_{7/2}$ →Yb^{3+} $^2F_{5/2}$+ Nd^{3+} $^4I_{9/2}$ in high efficiency; on the other hand, realized Nd^{3+} $^4F_{3/2}$+ Yb^{3+} $^2F_{7/2}$ →Yb^{3+} $^2F_{5/2}$+ Nd^{3+} $^4I_{11/2}$ [1, 2], as shown in **Figure S7.**

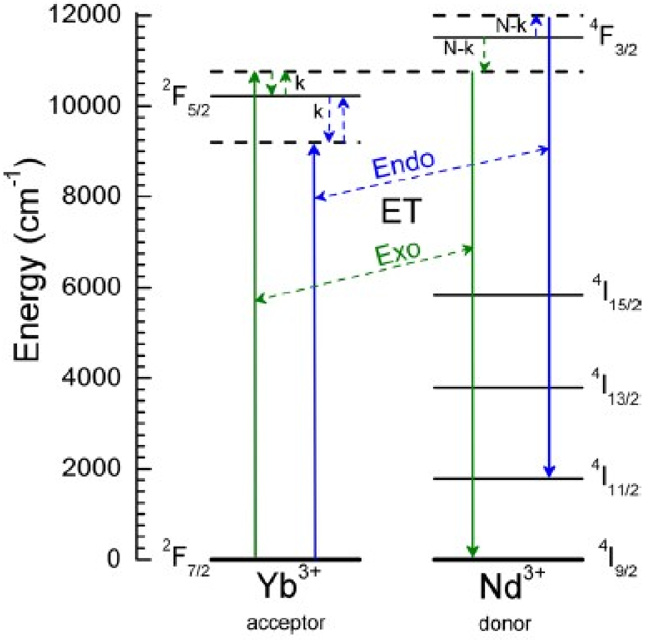


Figure S7. Photon-assisted Nd^{3+}→Yb^{3+} energy transfer [1, 2].

Yb^{3+}→Yb^{3+} migration of the two kinks of photons: in the Yb^{3+}→Yb^{3+} transition by Yb^{3+} sublevels ~10250 cm^{-1} and ~785 cm^{-1}, emitting by Yb^{3+} $^2F_{5/2}$ (~10250 cm^{-1})→$^2F_{7/2}$ (785 cm^{-1}) transition that result in the 1056 nm emission, as shown in **Figure S8**. (the peak located in 1048 nm could be explained as in consequence of transitions between sublevels of Yb^{3+} sublevels :10327 cm^{-1} and 785 cm^{-1} [3], as shown in **Figure S8**, which is caused by crystal field splitting [4]).

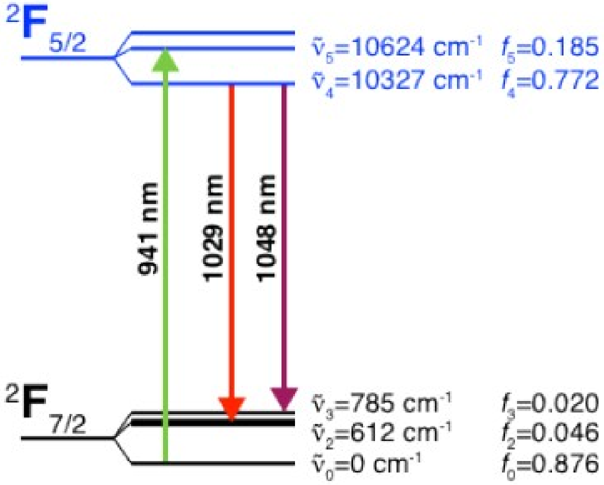


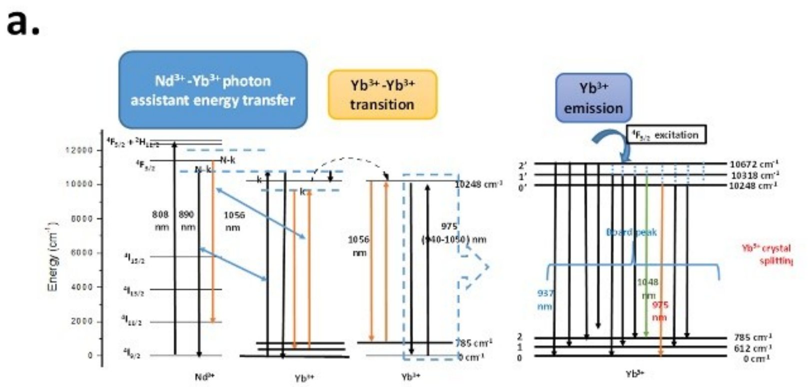
Figure S8. Yb^{3+} upper and ground energy level. [3]

Supporting Note II:

1056 nm participation in the EUT process of Er^{3+} under 808 nm excitation: (Explanation on **Figure 6** in the manuscript): The NIR emission spectra of the of Nd^{3+}-Trinity system is coated on the NaGdF$_4$:Yb$_{20\%}$ cores (NaGdF$_4$:Yb$_{20\%}$ @NdGdF$_4$:Yb$_{10\%}$ @NaNdF$_4$:Yb$_{20\%}$ @NaGdF$_4$, **Figure 6(a)**) and NaGdF$_4$:Yb$_{20\%}$, Er$_{2\%}$ (NaGdF$_4$:Yb$_{20\%}$, Er$_{2\%}$ @NdGdF$_4$:Yb$_{10\%}$ @NaNdF$_4$:Yb$_{20\%}$ @NaGdF$_4$, **Figure 6(b)**) cores, are measured to reveal the NIR photons participation in the ETU process.

In the NIR emission spectra of Nd^{3+}→Yb^{3+} energy transfer system with 808 nm excitation (**Figure 6(a)**), it presents a broad emission band (940-1050 nm) with peak maximum at 975 nm as observed, which could be interpreted as the Yb^{3+} emission with excitation of Nd^{3+} $^4F_{5/2}$ [5]; the peak located at 1048 nm could be explained as result in sublevels of Yb^{3+} (sublevels :10327 cm^{-1} and 785 cm^{-1} [3]), which is caused by crystal field splitting [4]; compared with Yb^{3+} emission [6], the peak around 1056 nm could be concluded as induced by Nd^{3+}-sensitization and transfer to Yb^{3+} by

Nd^{3+}→Yb^{3+} photons assisted energy transfer, and further transfers in the Yb^{3+} sub-levels, as shown in **Scheme 1 (a)**. Compares with the emission spectra of Nd^{3+}→Yb^{3+}, the emission spectra of Nd^{3+}→Yb^{3+}→Er^{3+}→Yb^{3+} shows discontinuous peak in 940-1050 nm and disappearance of the 1056 nm peak, which reveals that the photons participated in the ETU process of Er^{3+} that is initiated by Yb^{3+}→Er^{3+} energy transfer, could be generalized as two kinds of photons in Nd^{3+}→Yb^{3+} energy transfer and Yb^{3+}→Yb^{3+} transition: (i) 940-1050 nm photons (with maximum at 975 nm); (ii) 1056 nm photons. Moreover, the sharp discontinuous at 940-1050 nm could be explained as a result of the recurring cycles of energy transfer and energy back-transfer between Er^{3+} and Yb^{3+} under 808 nm excitation, which could be depicted as the association effect and dynamic process of energy transfer from Er^{3+} to Yb^{3+} and emitted by Yb^{3+} $^2F_{5/2}$, as shown in **Scheme 1 (b,c)**.



Scheme 1. Energy transfer of Nd^{3+}→Yb^{3+} (a) and Nd^{3+}→Yb^{3+}→ Er^{3+}→Yb^{3+} (b,c).

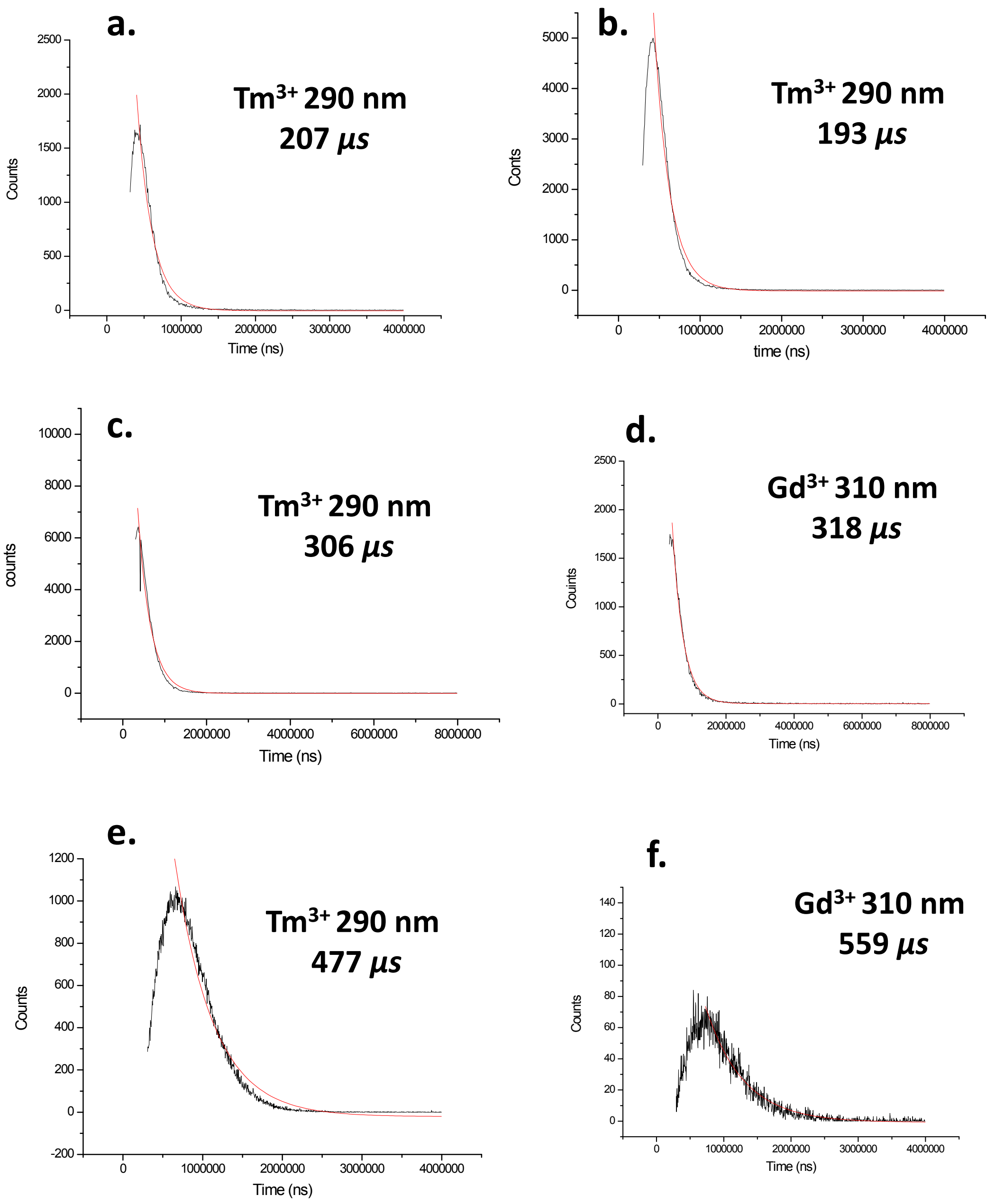


Figure S9. Decay curves of 290 nm emission of the **$NaYF_4$ (Y^{3+} host)**:$Yb_{49\%}$,$Tm_{1\%}$@ $NaGdF_4$:$Yb_{10\%}$, $Nd_{20\%}$@$NaGdF_4$ (a) and **$NaGdF_4$ (Gd^{3+} host)**: $Yb_{49\%}$,$Tm_{1\%}$ @$NaGdF_4$:$Yb_{10\%}$,$Nd_{20\%}$ @$NaGdF_4$ (b); Decay curves of 290 nm (c) and 310 nm (d) emission of $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$ @$NaGdF_4$:$Yb_{10\%}$,**$Eu_{15\%}$ (with activators)** @$NaGdF_4$:$Yb_{10\%}$ @$NaGdF_4$:$Nd_{50\%}$,$Yb_{10\%}$ @$NaGdF_4$; decay curves of 290 nm (e) and 310 nm (f) emission of $NaGdF_4$:$Yb_{49\%}$,$Tm_{1\%}$@$NaGdF_4$:$Yb_{10\%}$ **(without activators)** @$NaGdF_4$:$Yb_{10\%}$@$NaGdF_4$:$Nd_{50\%}$,$Yb_{10\%}$@ $NaGdF_4$.

References

1. F. Rivera-López, P. Babu, C. Basavapoornima, C. K. Jayasankar and V. Lavín, *Journal of Applied Physics*, 2011, **109**, 123514.
2. L. Marciniak, A. Bednarkiewicz, M. Stefanski, R. Tomala, D. Hreniak and W. Strek, *Physical Chemistry Chemical Physics*, 2015, **17**, 24315-24321.
3. C. João, J. Wemans and G. Figueira, *Applied Sciences*, 2013, **3**, 288.
4. O. L. Malta and L. D. Carlos, *Química Nova*, 2003, **26**, 889-895.
5. J. Azkargorta, I. Iparraguirre, R. Balda and J. Fernández, *Opt. Express*, 2008, **16**, 11894-11906.
6. V. Pukhkaya, P. Goldner, A. Ferrier and N. Ollier, *Opt. Express*, 2015, **23**, 3270-3281.