One pot synthesis and systematic study of photophysical, magnetic properties and thermal sensing of α and β-phases $NaLnF_4$ and β-phase core@shell nanoparticles

*Emille M. Rodrigues[1], Diogo A.Gálico[1], Maykon A. Lemes[2], Jefferson Bettini[3], Erico Teixeira Neto[3], Italo O. Mazali[1], Muralee Murugesu[2], Fernando A. Sigoli[1]**

[1]Laboratory of Functional Materials – Institute of Chemistry - University of Campinas – UNICAMP, Campinas, Sao Paulo, Brazil, P.O. Box 6154, 13083-970

[2]Department of Chemistry and Biomolecular Sciences - University of Ottawa, 10 Marie Curie, Ottawa, Ontario, KIN 6N5, Canada

[3]Brazilian Nanotechnology National Laboratory – LNNano, Campinas, Sao Paulo, Brazil, 13083-970

KEYWORDS: upconversion, nanothermometry, magnetic properties, lanthanide fluoride.

Supporting Information

Synthesis of $[Ln(CF_3COO)_3]$ and CF_3COONa precursors

The trifluoracetate precursors of all lanthanides $[Ln(CF_3COO)_3]$, except the $[Pr(CF_3COO)_3]$ were obtained by the reaction between 5 mL of CF_3COOH (Aldrich, 99%) in 5 mL of distilled water with 300 mg of the lanthanide oxides (Gd_2O_3, Yb_2O_3, Er_2O_3, Tm_2O_3, Ho_2O_3, all from Aldrich, 99.99%). The mixture was kept in a 50 mL round bottom flask under magnetic stirring at 90 °C overnight, resulting in a transparent solution. After this time, the solvent was evaporated to obtain the solid $[Ln(CF_3COO)_3]$ precursors. A similar approach was used for the synthesis of CF_3COONa but using NaOH (Alkimia, PA) as the sodium source. 100 mg of NaOH was dissolved in a beaker containing 10 mL of water, and the CF_3COOH was added to completely neutralize the basic solution. After that, the solvent was evaporated to obtain the solid CF_3COONa precursor.

In the case of $[Pr(CF_3COO)_3]$, first 200 mg of Pr_6O_{11} (Aldrich, 99.9%, composed by a mixing between Pr_2O_3 and PrO_2) were treated with stoichiometric amounts of HCl (Aldrich, 37%) and H_2O_2 (Synth, 29 %) in order to reduce all Pr^{4+} to Pr^{3+}. The mixture was kept in a beaker under magnetic stirring at room temperature until it became transparent. After that, the solvent was evaporated and the solid $PrCl_3$ was obtained, and treated with 5 mL of CF_3COOH acid and 5 mL of distilled water following the same procedure as previously described for the Ln_2O_3.

In order to obtain the molecular weight of $[Ln(CF_3COO)_3]$, a complexometric titration was performed using EDTA 0.01 mol L^{-1}. Briefly, 30 mg of each $[Ln(CF_3COO)_3]$ sample was dissolved in 20 mL of acetate/acetic acid buffer (pH = 5.9) and 3 mg of xylenol orange (in KBr 5 wt%) indicator were used to check the turning point of the titration (purple to yellow). The obtained molecular weight was used for further calculation of the Ln^{3+} amount used in the UCNP synthesis.

In the following Table S1 are given the experimetal conditions used for the syntesis of all the nanoparticles synthesis reported on this work.

Table S1: Temperature/time and shell addition steps conditions used during the synthesis of the Ln-UCNP.

	Temperature patamar/time		**Shell addition steps**	**Temperature/time of each shell addition step**
	1st	**2nd**		
$NaGdF_4$ based compositions				
α-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$	310°C/15’	-	-	-
β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$	310°C/15’	330°C/15’	-	-
β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$*	310°C/15’	330°C/10’	-	-
β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@1$NaYF_4$	310°C/15’	330°C/10’	1	260°C/30’
β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@3$NaYF_4$	310°C/15’	330°C/10’	3	260°C/30’
β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@3$NaYF_4$:Yb	310°C/15’	330°C/10’	3	260°C/30’
$NaYbF_4$ based compositions				
α-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$	310°C/15’	-	-	-
β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$	310°C/15’	330°C/15’	-	-
β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@1$NaYF_4$	310°C/15’	330°C/15’	1	260°C/30’
β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@3$NaYF_4$	310°C/15’	330°C/15’	3	260°C/30’
B-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@3$NaYF_4$:Yb	310°C/15’	330°C/15’	3	260°C/30’

* This was the core β-$NaGdF_4$:Pr:Er:Yb sample used in all luminescent and magnetic characterizations within this manuscript.

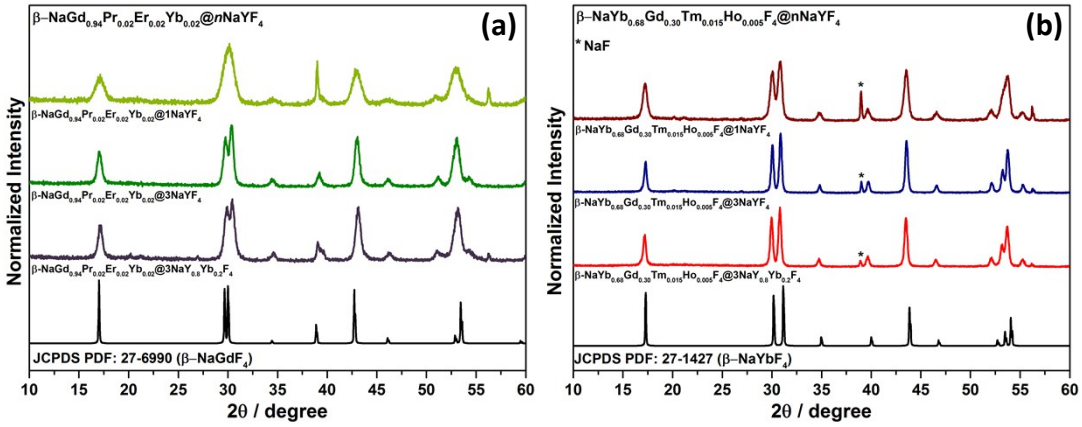

Figure S1. XRD patterns of the core@shell Ln-UCNP: (a) β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@*n*$NaYF_4$ (b) β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@*n*$NaYF_4$.

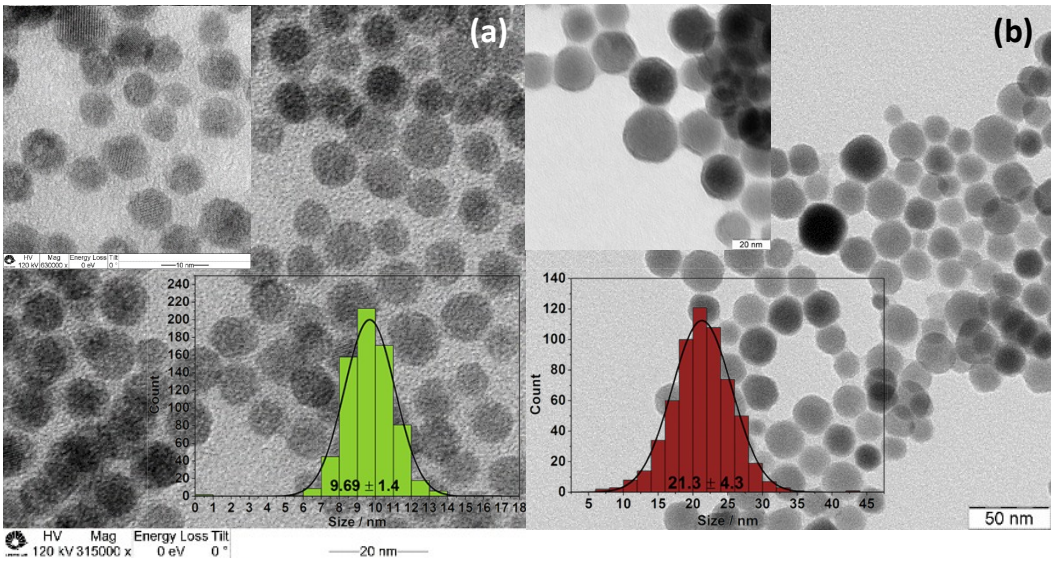

Figure S2. TEM images of the core@shell UCNP β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@1$NaYF_4$ (a) and β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@1$NaYF_4$ (b). The inset shows the size distribution histogram of both samples.

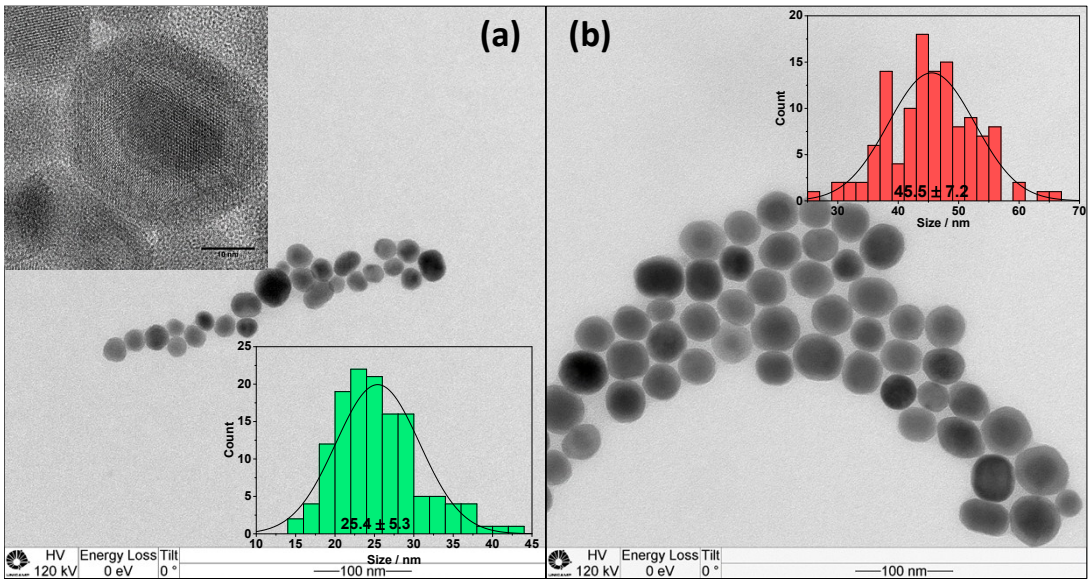

Figure S3. TEM images of the core@shell UCNP β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@$3NaY_{0.8}Yb_{0.2}F_4$. (a) and β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@$3NaY_{0.8}Yb_{0.2}F_4$ (b). The inset shows the size distribution histogram of both samples. On the upper left of (a) it is shown the HRTEM image of another nanoparticle from this sample.

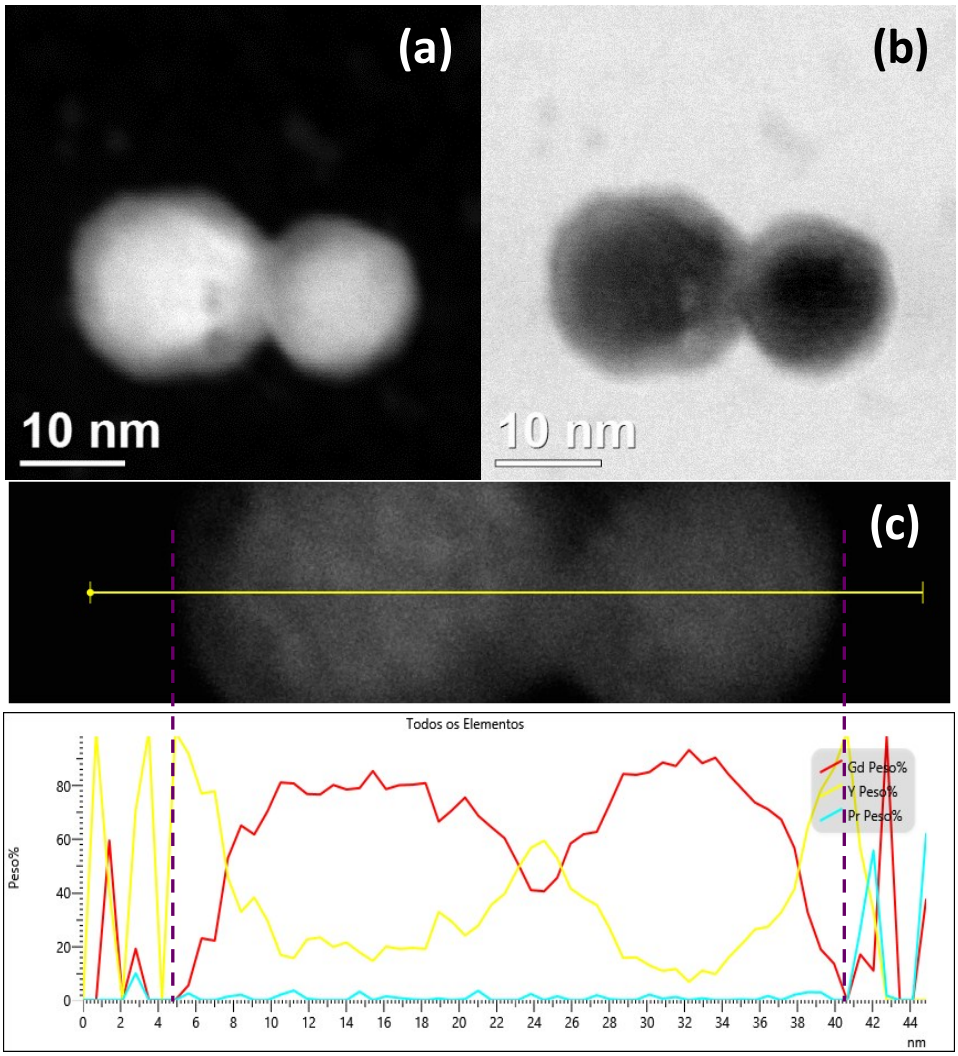

Figure S4. Bright Field (a) and Dark Field image (b) of the β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@$3NaYF_4$. Line Scan mapping of Gadolinium (Gd^{3+}), Yttrium (Y^{3+}) and Praseodimium (Pr^{3+}) elements (c) of the UCNP showing the core@shell structure.

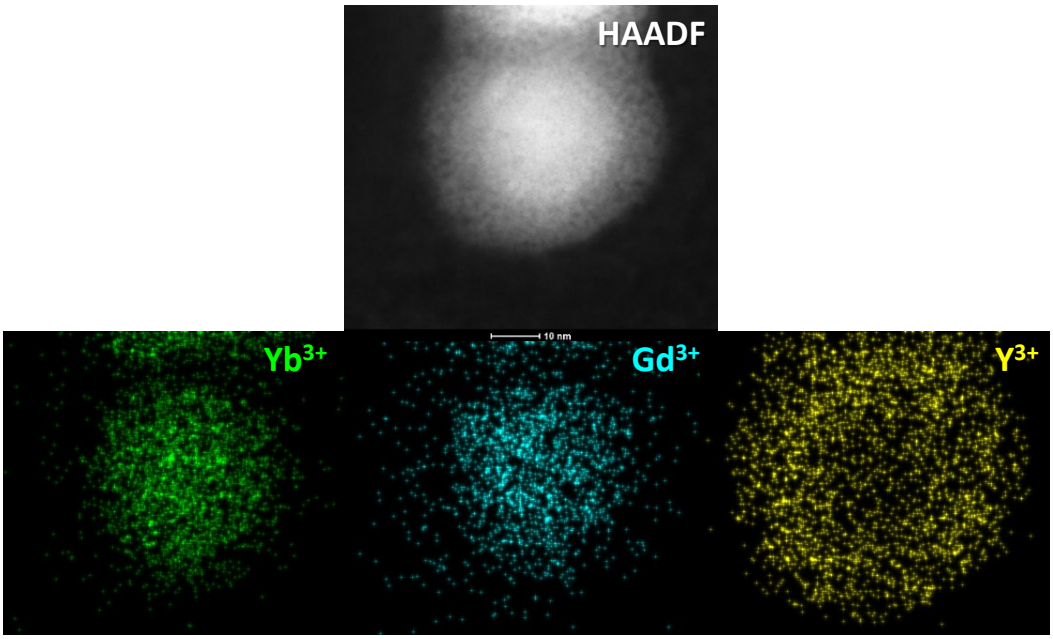

Figure S5. EDS mapping showing the elements composition of β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@$3NaYF_4$ sample. At the top: HAADF image, at the bottom from left to right Yb^{3+}, Gd^{3+} and Y^{3+} mapping.

The following Table S2 gives all the mean size values and the corresponding TEM figures of all the nanoparticles samples discussed in this work.

Table S2: Samples composition, temperature of synthesis, size and location of the corresponding TEM images/size distribution of all the NP discussed within this work.

Composition: $NaGdF_4$:Pr:Er:Yb		*Corresponding TEM Figure*	*Composition: $NaYbF_4$:Gd:Tm:Ho*		*Corresponding TEM Figure*
Core α (310 °C/15')	*11.1 ± 1.2*	*2a, manuscript*	*Core α (310°C/15')*	*11.5 ± 2.4*	*3a, manuscript*
Core β (330 °C/10')	*10.4 ± 1.7*	*2c, manuscript*	*Core β (330 °C/15')*	*11.5 ± 2.8*	*3b, manuscript*
Core@1shell (330 °C/10')	*9.7 ± 1.4*	*S2a from SI*	*Core@1 shell (330 °C/15')*	*21.3 ± 4.3*	*S2b from SI*
Core@3shell undoped (330 °C/10')	*13.6 ± 1.9*	*4a manuscript*	*Core@3 shell undoped (330 °C/15')*	*56.2 ± 9.5*	*4b manuscript*
Core@3shell Yb-doped (330 °C/10')	*25.4 ± 5.3*	*S3a from SI*	*Core@3shell Yb-doped (330 °C/15')*	*45.5 ± 7.2*	*S3b from SI*
Core β (330°C/15')*	*40.2 ± 7.9*	*2b, manuscript*	-	-	

**This was the core β-$NaGdF_4$:Pr:Er:Yb sample used in all luminescent and magnetic characterizations within this manuscript.*

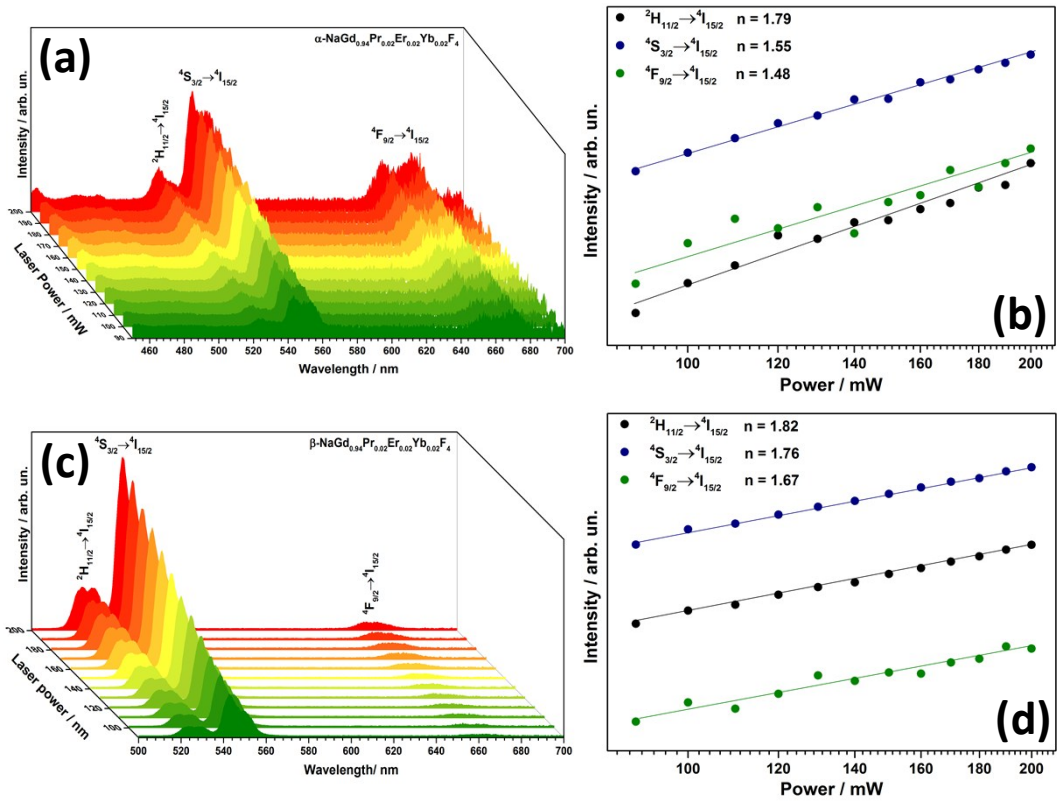

Figure S6. Upconversion emission spectra as a function of different 980 nm laser power (a) and (c) and log-log plots of the upconversion luminescence intensity versus 980 nm laser power (b) and (d) of the nanoparticle samples. α-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$ (a,b) and β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$ (c,d).

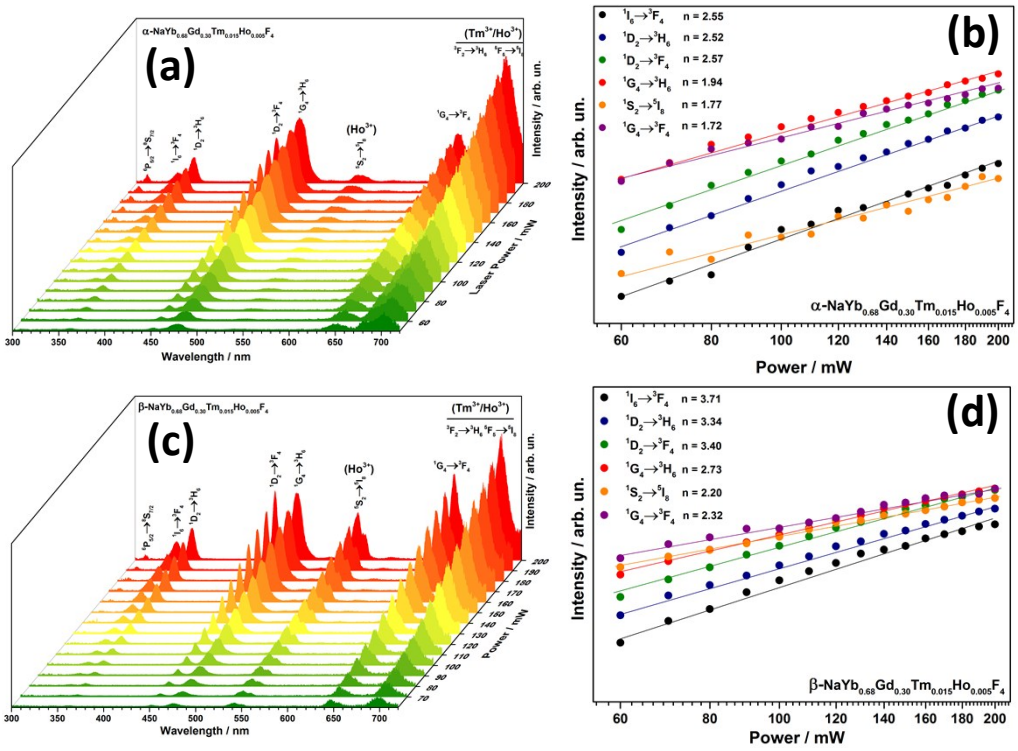

Figure S7. Upconversion emission spectra as a function of different 980 nm laser power (a) and (c) and log-log plots of the upconversion luminescence intensity versus 980 nm laser power (b) and (d) of the nanoparticle samples. α-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$ (a,b) and β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$ (c,d).

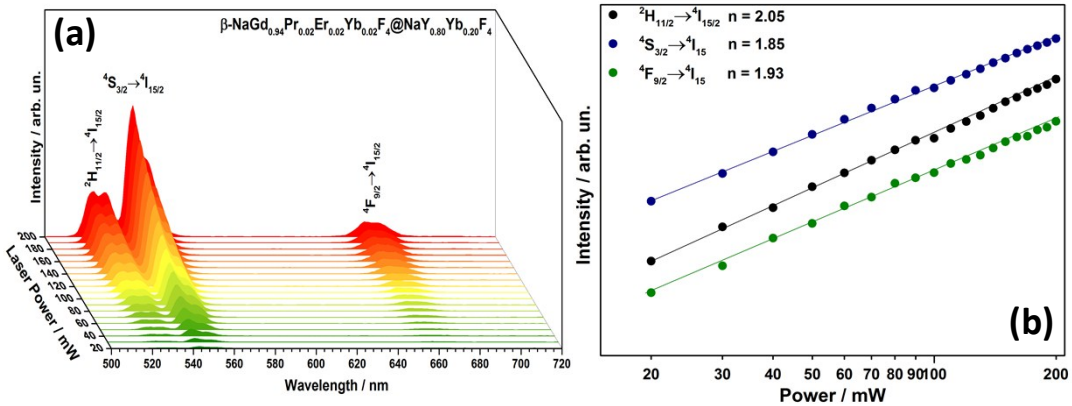

Figure S8. Upconversion emission spectra as a function of different 980 nm laser power (a) and log-log plots of the upconversion luminescence intensity versus 980 nm laser power (b) of the β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@$3NaY_{0.8}Yb_{0.2}F_4$ sample.

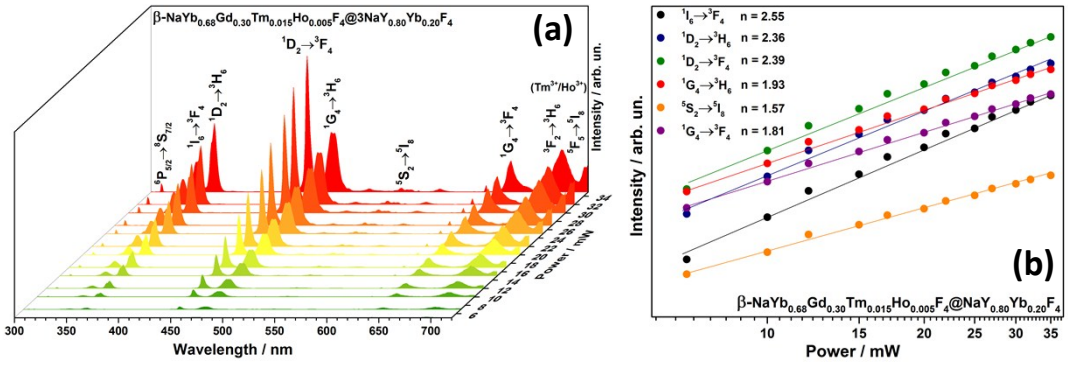

Figure S9. Upconversion emission spectra as a function of different 980 nm laser power (a) and log-log plots of the upconversion luminescence intensity versus 980 nm laser power (b) of the β-$NaYb_{0.68}Gd_{0.30}Tm_{0.015}Ho_{0.005}F_4$@$3NaY_{0.8}Yb_{0.2}F_4$ sample.

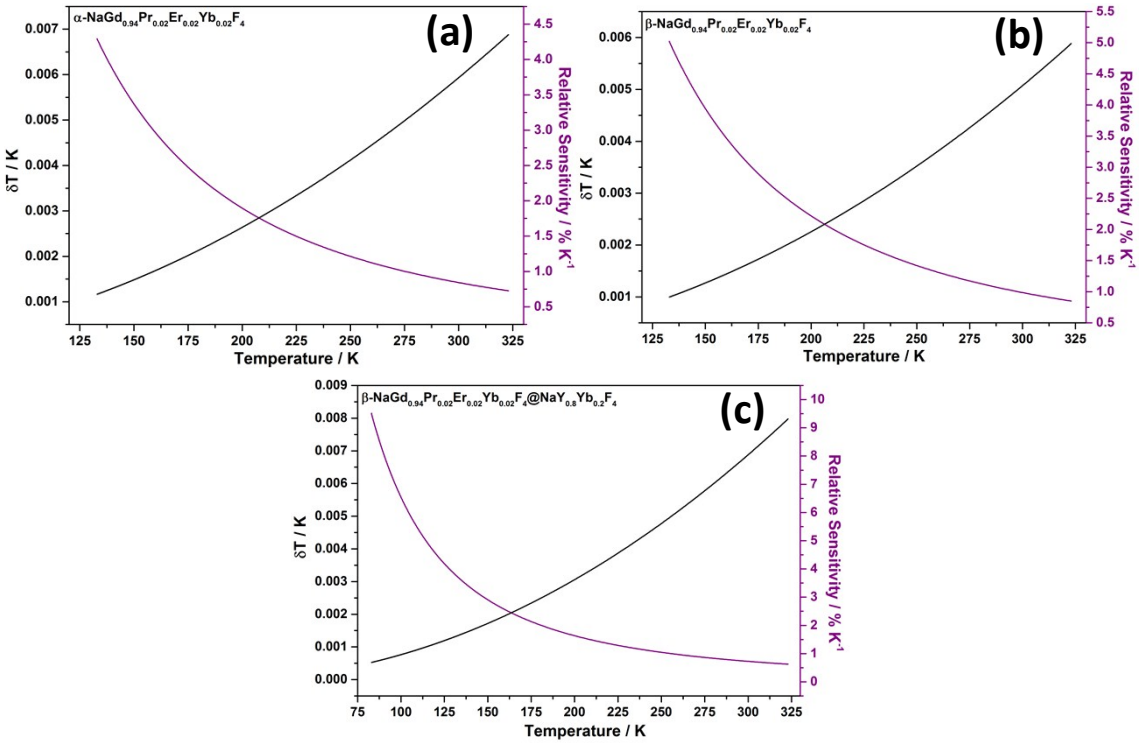

Figure S10. Comparison between the temperature uncertainty (black line) and relative sensitivity (purple line) for the samples (a) α-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$, (b) β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$ and (c) β-$NaGd_{0.94}Pr_{0.02}Er_{0.02}Yb_{0.02}F_4$@$3NaY_{0.8}Yb_{0.2}F_4$.

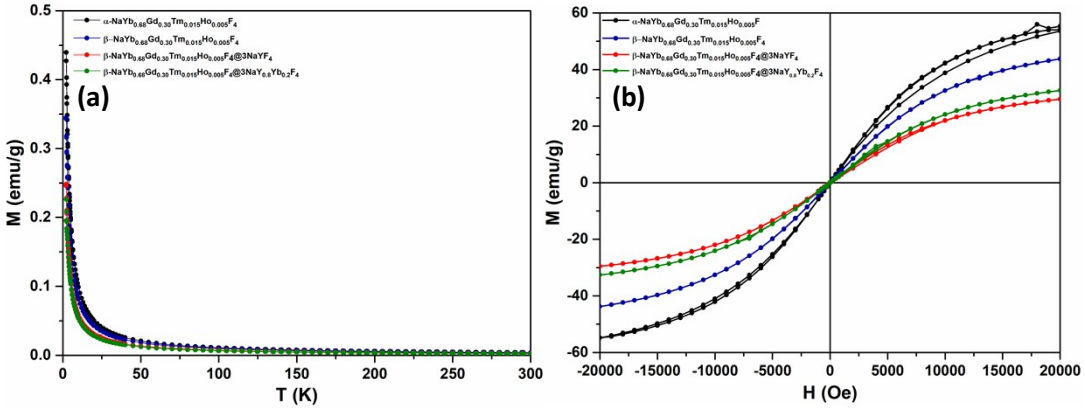

Figure S11. Zero-Field Cool/Field Cool (ZFC/FC) measurements performed from 2 to 300 K for the nanoparticles using an applied field of 100 Oe (a) and magnetization curves performed at 2 K (b). The inset in (b) shows a zoom into the magnetization curve at 2 K.