Supporting Information

NIR/Blue light emission optimization of $NaY_{1-(x+y)}Yb_xF_4:Tm_y$ upconversion nanoparticles via Yb^{3+}/Tm^{3+} dopant balancing

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Experimental Section

Materials

Rare-earth chlorides ($LnCl_3 \cdot 6H_2O$, where Ln = Y, Yb, Tm; 99.9% trace metals basis), oleic acid (OA), 1-octadecene, sodium hydroxide (NaOH) and ammonium fluoride (NH_4F), were all purchased from Sigma-Aldrich and used as received.

Table S1: Elemental composition of $NaY_{1-(x+y)}$ Yb_xF_4: Tm_y doped with Yb and Tm obtained from ICP-MS analysis

Sample	Designed Compositions (mole fraction)			Measured Compositions (mole fraction)		
	Y^{3+}	Yb^{3+}	Tm^{3+}	Y^{3+}	Yb^{3+}	Tm^{3+}
UC1	0.1317	0.8511	0.0172	0.1642	0.8193	0.0165
UC2	0.1451	0.8511	0.0038	0.1450	0.8503	0.0047
UC3	0.7539	0.2289	0.0172	0.7320	0.2509	0.0171
UC4	0.7673	0.2289	0.0038	0.7449	0.2516	0.0036
UC5	0.4590	0.5400	0.0010	0.3823	0.6167	0.0010
UC6	0.4400	0.5400	0.0200	0.4160	0.5664	0.0177
UC7	0.0095	0.9800	0.0105	0.0078	0.9827	0.0096
UC8	0.8895	0.1000	0.0105	0.8623	0.1269	0.0108
UC9	0.4495	0.5400	0.0105	0.3360	0.6553	0.0089
UC10	0.4495	0.5400	0.0105	0.4436	0.5467	0.0096
UC11	0.4495	0.5400	0.0105	0.4450	0.5452	0.0098
UC12	0.4495	0.5400	0.0105	0.4480	0.5426	0.0095

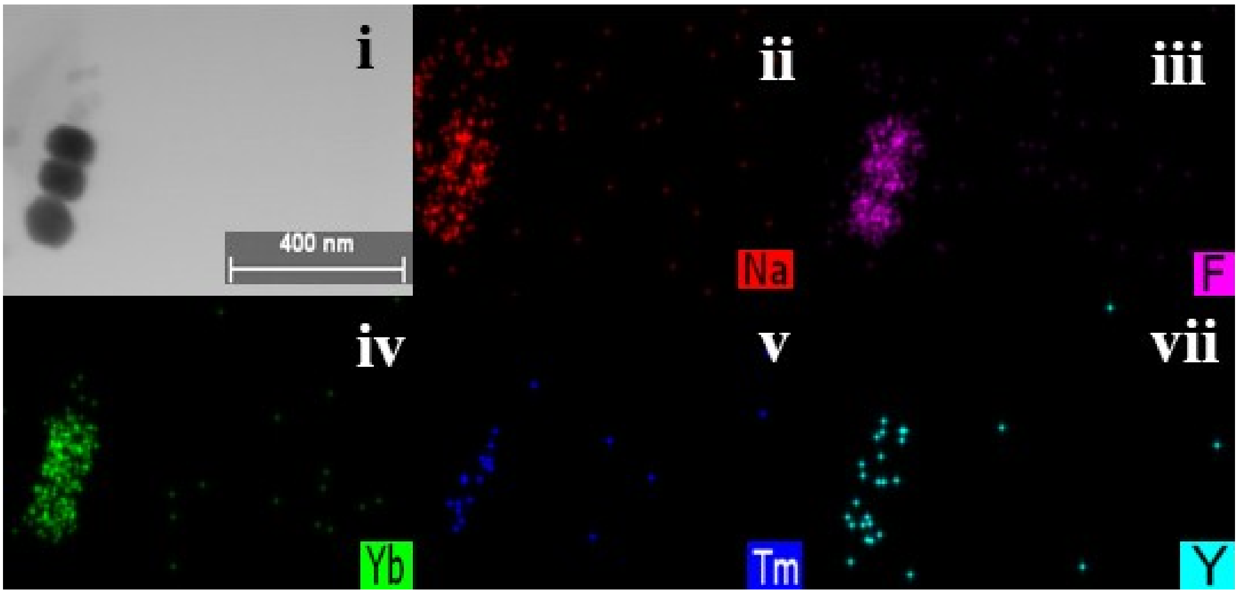

Figure S1. (i) TEM image, (ii-vii) EDX elemental mapping images of $NaY_{1-(x+y)}Yb_xF_4:Tm_y$ UCNPs where the mole fractions of the Yb^{3+} sensitizer and Tm^{3+} activator are x=0.98 and y=0.0105, respectively (sample UC7). Scale bar shows the length of 400 nm.

Table S2. Scheme of CCRD with the results of responses on independent factors

Run/Samples	Compositions of dopant ions (mole fraction)		Responses/observed values (CPS)		
	Yb^{3+}	Tm^{3+}	UCL $_{475\ nm}$ [a]	UCL $_{800nm}$ [b]	Total UC emission [c]
UC1	0.8511	0.0172	2.051129×10^5	5.56029040×10^8	5.62293195×10^8
UC2	0.8511	0.0038	4.024866×10^4	4.051487675×10^7	4.0914163×10^7
UC3	0.2289	0.0172	2.622874×10^4	1.314106459×10^8	1.41754875×10^8
UC4	0.2289	0.0038	8.804392×10^4	1.240787462×10^8	1.35621972×10^8
UC5	0.5400	0.0010	1.519943×10^4	1.601579923×10^7	1.8129107×10^7
UC6	0.5400	0.0200	1.338236×10^4	8.364038445×10^7	8.4703533×10^7
UC7	0.9800	0.0105	2.203131×10^5	4.527912046×10^8	4.57292948×10^8
UC8	0.1000	0.0105	8.784378×10^4	1.495043665×10^8	1.55239543×10^8
UC9	0.5400	0.0105	1.528179×10^4	4.155060498×10^7	4.2355694×10^7
UC10	0.5400	0.0105	1.252329×10^4	2.54286443×10^7	2.5776982×10^7
UC11	0.5400	0.0105	1.11975×10^4	2.486714003×10^7	2.5119235×10^7
UC12	0.5400	0.0105	1.029185×10^4	2.452103414×10^7	2.4795265×10^7

Integrated emissions were calculated using MATLAB R2017a software as follow: [a] Integrated counts of blue emission (three-photon UC 475 nm) $UCL_{475\ nm}$ were taken into account between 465 nm and 485 nm; [b] the integrated counts of (two-photon UC 800 nm) UCL_{800nm} were taken into account between 750 nm to 850 nm; [c] Total integration of all UCL peaks.

Table S3. values of the intercept coefficient (β_0), linear coefficients (β_i), squared coefficients (β_{ii}), and $interaction\ coefficients\ (\beta_{ij})$ when a second-order polynomial (equ.1) was used to correlate the integrated emission intensities at 800 nm (UCL_{800nm}) and 475 nm ($UCL_{475\ nm}$) to the Yb^{3+} sensitizers (x) and Tm^{3+} activators (y) concentrations.

Emission	β_0	β_x	β_y	β_{xx}	β_{yy}	β_{xy}
$UCL_{475\ nm}$	3.01069×10^5	-9.63518222×10^3	-1.38960×10^5	7.469878×10^1	5.35101177×10^3	2.71147593×10^3
UCL_{800nm}	5.72143×10^8	-1.95124×10^7	-3.05067×10^8	1.50215×10^5	4.37634×10^7	6.07874×10^6

Consequently, two second-order polynomial equations represent $UCL_{475\ nm}$ and UCL_{800nm} respectively as a function of the parameters of formulations:

$$\mathbf{UCL_{475nm}} = (3.01069\times10^5) - ((-9.63518222\times10^3)\times Yb) - ((1.38960\times10^5)\times Tm) + ((7.469878\times10^1)\times Yb^2) + ((5.35101177\times10^3)\times Tm^2) + ((2.71147593\times10^3)\times Yb\times Tm) \quad \textbf{(S.1)}$$

$$\mathbf{UCL_{800nm}} = (5.72143\times10^8) - ((1.95124\times10^7)\times Yb) - ((3.05067\times10^8)\times Tm) + ((1.50215\times10^5)\times Yb^2) + ((4.37634\times10^7)\times Tm^2) + ((6.07874\times10^6)\times Yb\times Tm) \quad \textbf{(S.2)}$$

Table S4. The ANOVA table for CCRD of UC 800 nm

Source	$UCL_{800\ nm}$ (R^2 =0.9232)				
	Sum of Squares	Mean Squares	F-value	P-value	
Model	3.224607874×10^{17}	6.448×10^{16}	14.43	0.0027	**significant**
A-Yb	7.411×10^{16}	7.411×10^{16}	16.59	0.0066	
B-Tm	4.781×10^{16}	4.781×10^{16}	10.70	0.0170	
AB	6.456×10^{16}	6.456×10^{16}	14.45	0.0089	
A^2	1.353×10^{17}	1.353×10^{17}	30.29	0.0015	
B^2	2.496×10^{15}	2.496×10^{15}	0.56	0.4830	

Table S5. The ANOVA table for CCRD of UC 475 nm.

Source	UCL $_{475\ nm}$ (R^2 =0.9704)				
	Sum of Squares	Mean Squares	F-value	P-value	
Model	6.121×10^{10}	1.224×10^{10}	39.29	0.0002	**significant**
A-Yb	1.267×10^{10}	1.267×10^{10}	40.67	0.0007	
B-Tm	1.262×10^{9}	1.262×10^{9}	4.05	0.0908	
AB	1.285×10^{10}	1.285×10^{10}	41.22	0.0007	
A^2	3.346×10^{10}	3.346×10^{10}	107.39	< 0.0001	
B^2	3.732×10^{7}	3.732×10^{7}	0.12	0.7411	

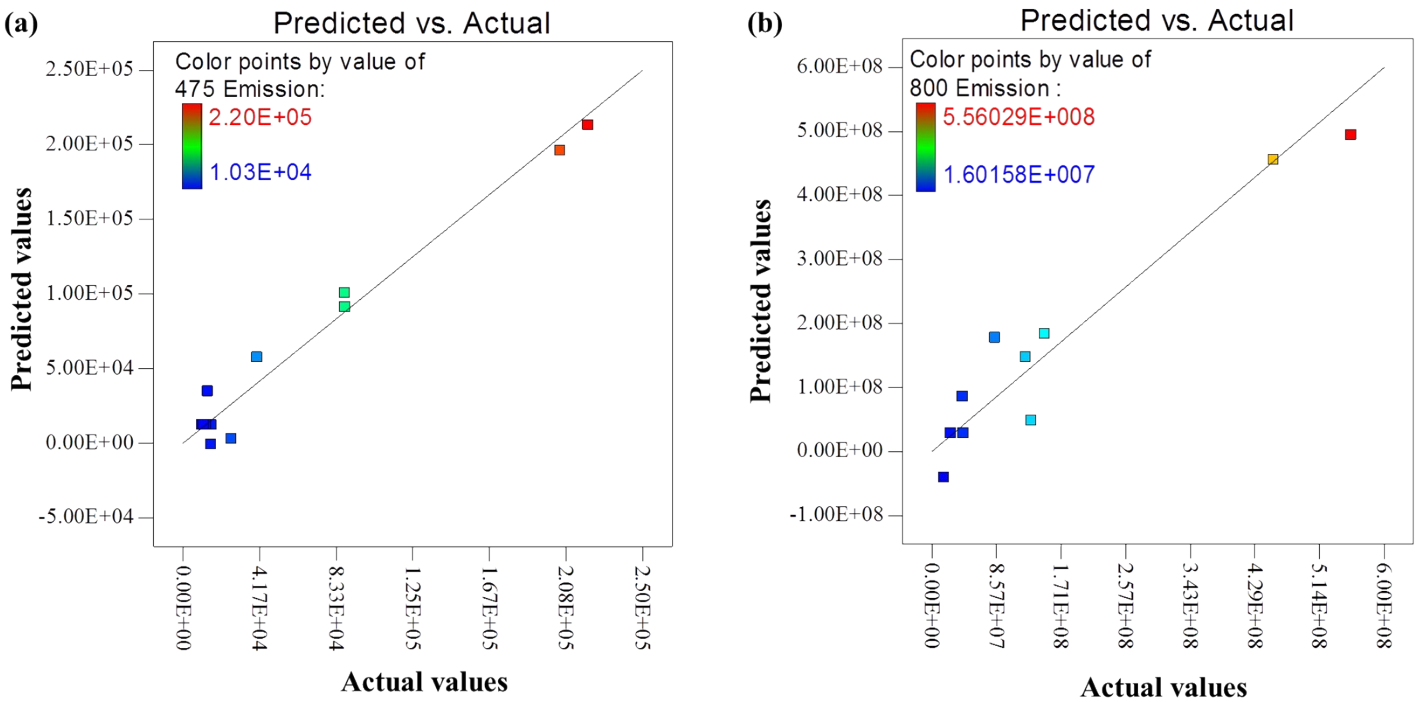

Figure S2. Predicted versus actual UCL emissions at (a) 475 nm and (b) 800 nm based on the chosen quadratic model.