

Supplemental Information

S1. Experimental Section

S1.1 Synthesis

S1.1.1 Materials

La(NO₃)₃·6H₂O (99.999%), Yb(NO₃)₃·5H₂O (99.999%), and Tm(NO₃)₃·5H₂O (99.9%), Ba(NO₃)₂ (99.95%), NH₄F (>99.99%), and sodium trifluoroacetate (≥99.0%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification. Oleic acid (>97%), water (Optima grade), NH₄OH (Certified ACS Plus), and trifluoroacetic acid (≥99.5%) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Ethanol (200 proof, anhydrous, USP) was purchased from KOPTEC (King of Prussia, PA, USA). Rare earth trifluoroacetates were prepared as per Hara *et al.* [1] using rare earth oxides purchased from Alfa Aesar (Ward Hill, MA, USA) of no less than 99.997% purity. Barium trifluoroacetate was prepared in the same fashion using BaCO₃ (99.997%; Alfa Aesar).

Teflon autoclave sleeves (120 mL) were soaked overnight in a base bath of 2-propanol and potassium hydroxide, rinsed with distilled water, subjected to aqua regia (3:1 HCl:HNO₃) for 30 min, rinsed again with distilled water, then treated again under base bath for an additional 20 min. The sleeves were subsequently rinsed thoroughly with distilled water and ethanol and left to dry in air prior to use.

S1.1.2 LaF₃ Synthesis

LaF₃ containing no sodium dopant was generated in similar fashion to the Na-doped LaF₃ synthesis [2] with substitution of NaOH for NH₄OH (2.36 mL, 0.035 mol, 14.8 N soln.) and KF for NH₄F (111.11 mg, 3 mmol). All other reagent concentrations and reaction and purification conditions remained the same.

S1.1.3 BaLaF₅ Synthesis

Following a modified thermal decomposition approach of Vetrone *et al.* [3], to a clean, oven dried, 100 mL, 2-neck roundbottom flask with magnetic stir bar, thermocouple, and affixed reflux condenser was added 5.08 mg Tm(TFA)₃ (0.010 mmol), 204.83 mg Yb(TFA)₃ (0.40 mmol), 759.92 mg La(TFA)₃ (1.59 mmol), 726.70 mg Ba(TFA)₂ (2.00 mmol), 20 mL 1-Octadecene (90%, Sigma-Aldrich, St. Louis, MO, USA), and 20 mL Oleic acid. The apparatus was evacuated (<15 mtorr) and stirred at 125 °C for 45 min to remove residual water then sparged with argon for 20 min. The reaction apparatus was then transferred to a molten eutectic salt bath and the reaction heated over a 7 min ramp to an internal temperature of 315 °C and held at temperature for 1 h under argon. The reaction was then cooled to RT, poured into an equivalent volume of absolute ethanol, sonicated, and centrifuged at 21k rcf (~14k RPM) for 20 min. The resulting pellet was resuspended and centrifuged in similar fashion with 50:50 *n*-hexane:ethanol, followed by a wash of 50:50; water:ethanol, and a final wash of absolute ethanol. The purified nanocrystals were then dried in air overnight.

S2. Results and Discussion

Figure S1. Transmission Electron Microscopy (TEM) images of 0.5%Tm, 20%Yb codoped UCNCs in host lattices (a) (Na)LaF₃ [80 kx, 100 nm scale bar]; (b) (Na)LaF₃ [700 kx, 10 nm scale bar]; (c) Ba(Na)LaF₅ [80 kx, 100 nm scale bar]; (d) Ba(Na)LaF₅ [700 kx, 10 nm scale bar]; (e) (Na)LaF₃ core@shell [80 kx, 100 nm scale bar]; (f) (Na)LaF₃ core@shell [700 kx, 10 nm scale bar]; (g) Ba(Na)LaF₅ core@shell [200 kx, 50 nm scale bar]; (h) Ba(Na)LaF₅ core@shell [700 kx, 10 nm scale bar].

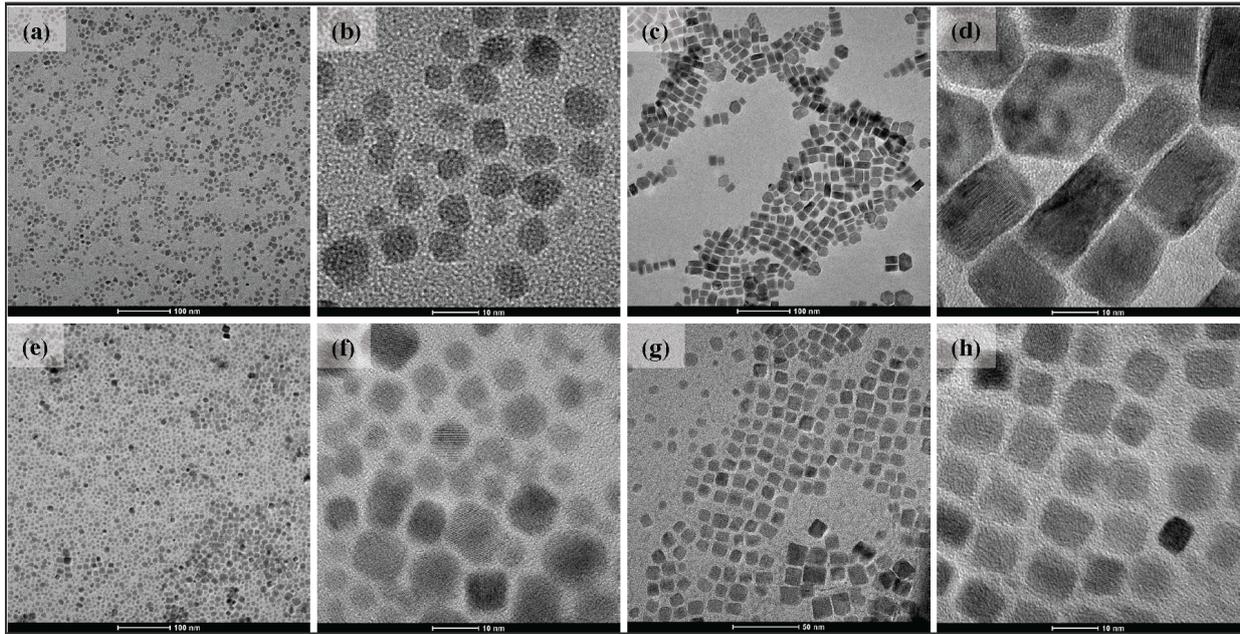


Figure S2. Transmission Electron Microscopy (TEM) images of 0.5%Tm, 20%Yb codoped UCNCs in host lattices (a) LaF₃ [80 kx, 100 nm scale bar], (b) LaF₃ [700 kx, 10 nm scale bar], (c) BaLaF₅ [80 kx, 100 nm scale bar], (d) BaLaF₅ [700 kx, 10 nm scale bar].

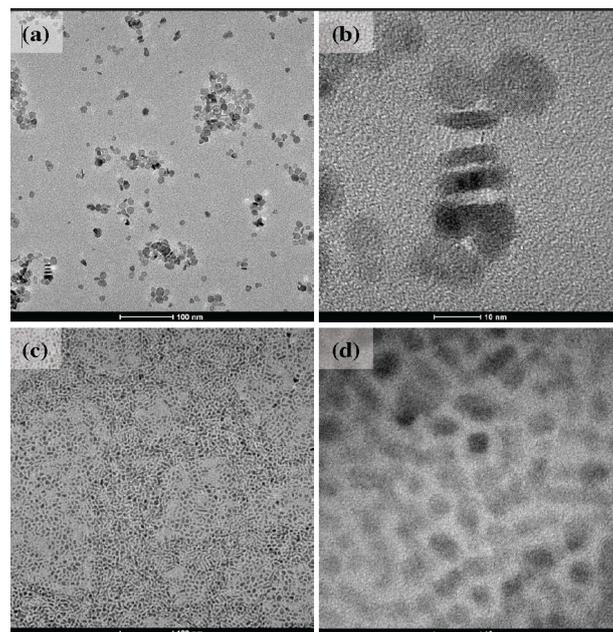


Table S1. X-Ray Powder Diffractions (XRD) 2θ ($^\circ$) values of (a1) LaF_3 [pale Green]; (a2) $(\text{Na})\text{LaF}_3$ core [pale Blue]; (a3) $(\text{Na})\text{LaF}_3@(\text{Na})\text{LaF}_3$ [pale Violet]; (b1) BaLaF_5 [Green]; (b2) $\text{Ba}(\text{Na})\text{LaF}_5$ core [Blue]; (b3) $\text{Ba}(\text{Na})\text{LaF}_5@(\text{Na})\text{LaF}_3$ [Violet]; associated Miller indices (hkl).

[h k l]	LaF_3	$(\text{Na})\text{LaF}_3$ Core	$(\text{Na})\text{LaF}_3$ Core@Shell
[002] & [110]	24.95 $^\circ$	24.83 $^\circ$	24.29 $^\circ$
[111]	27.85 $^\circ$	27.49 $^\circ$	27.73 $^\circ$
[300]	44.15 $^\circ$	43.85 $^\circ$	43.83 $^\circ$
[113]	45.07 $^\circ$	44.55 $^\circ$	45.05 $^\circ$
[302]	51.09 $^\circ$	51.11 $^\circ$	50.81 $^\circ$
[221]	53.03 $^\circ$	52.83 $^\circ$	52.77 $^\circ$
[h k l]	BaLaF_5	$\text{Ba}(\text{Na})\text{LaF}_5$ Core	$\text{Ba}(\text{Na})\text{LaF}_5$ Core@Shell
[111]	25.05 $^\circ$	25.87 $^\circ$	25.97 $^\circ$
[200]	29.33 $^\circ$	29.91 $^\circ$	30.05 $^\circ$
[220]	42.69 $^\circ$	42.91 $^\circ$	43.01 $^\circ$
[311]	50.25 $^\circ$	50.71 $^\circ$	50.91 $^\circ$
[222]	NA	53.07 $^\circ$	53.37 $^\circ$

Figure S3. XPS region scans of $(\text{Na})\text{LaF}_3$ [Na 1s], $(\text{Na})\text{LaF}_3$ [La 3d], LaF_3 [La 3d], $\text{Ba}(\text{Na})\text{LaF}_5$ [Na 1s], $\text{Ba}(\text{Na})\text{LaF}_5$ [La 3d], and $\text{Ba}(\text{Na})\text{LaF}_5$ [Ba 3d].

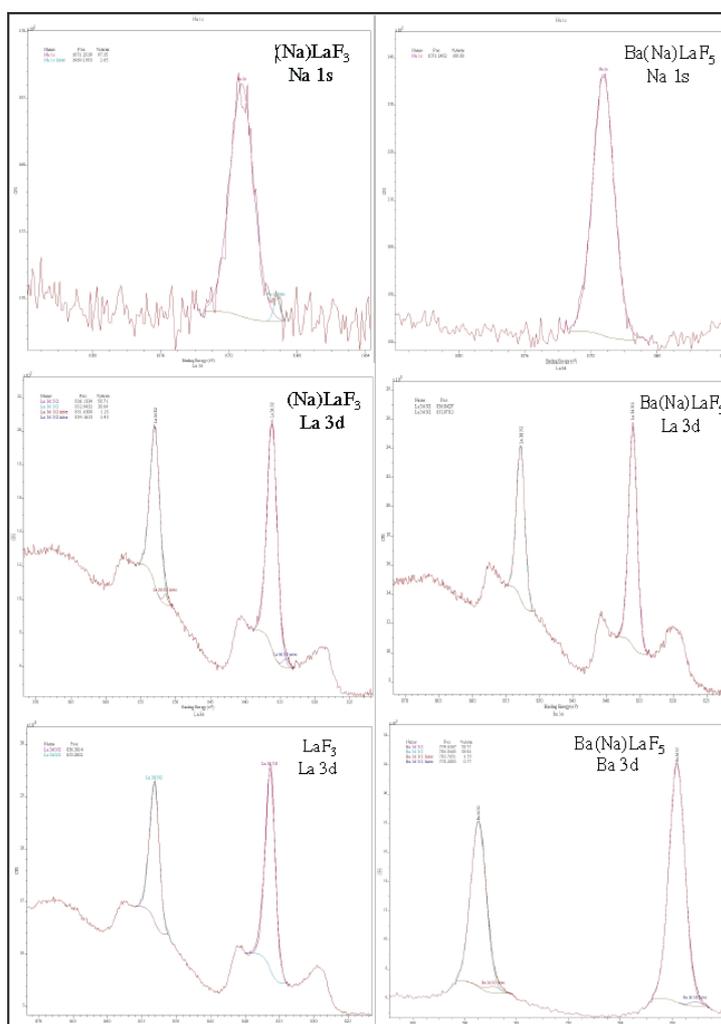


Figure S4. Emission intensity vs. 980 nm laser power density (W/cm^2), In-In IvP plot of 0.5%Tm, 20%Yb codoped (Na)LaF₃ UCNC in (a) UV/blue; (b) NIR; and (c) Vis regime and (d) ETU transition diagram of Yb³⁺-Tm³⁺. Experimental conditions: 1 mg/mL solutions in toluene at 23 °C; 980 nm CW laser excitation varying from 2.5 to 100 W/cm^2 .

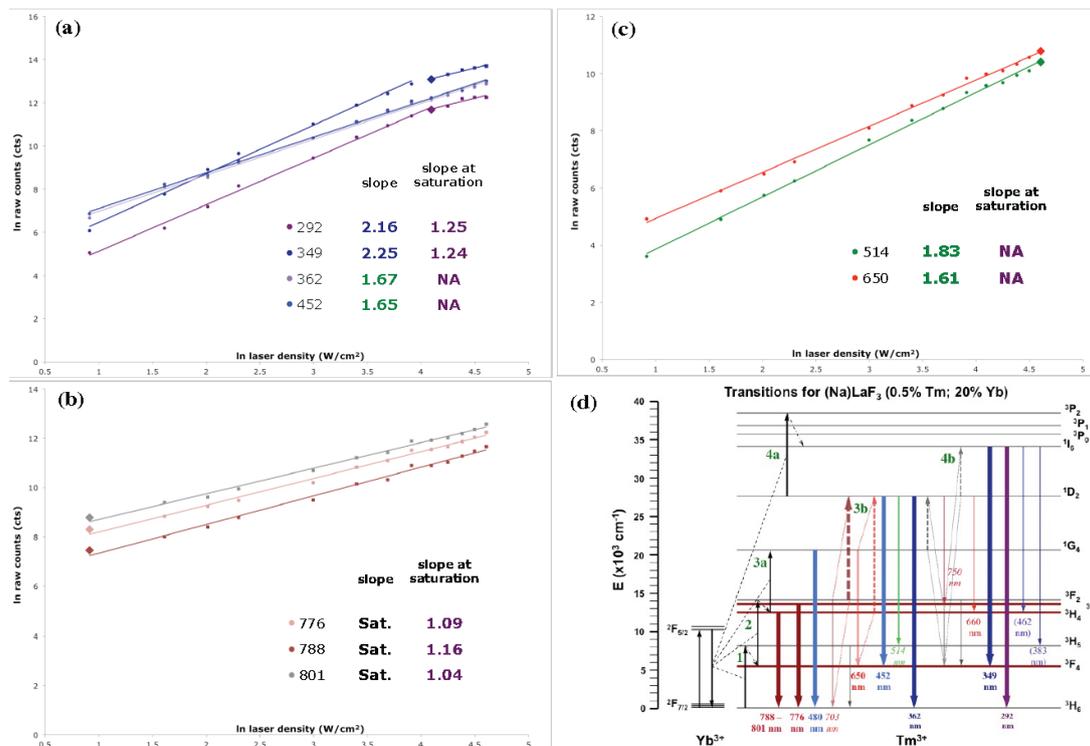


Figure S5. Emission intensity vs. 980 nm laser power density (W/cm^2), In-In IvP plot of 0.5%Tm, 20%Yb codoped (Na)LaF₃ core@shell in (a) UV/blue; (b) NIR; and (c) Vis regime and (d) ETU transition diagram of Yb³⁺-Tm³⁺. Experimental conditions: 1 mg/mL solutions in toluene at 23 °C; 980 nm CW laser excitation varying from 2.5 to 100 W/cm^2 .

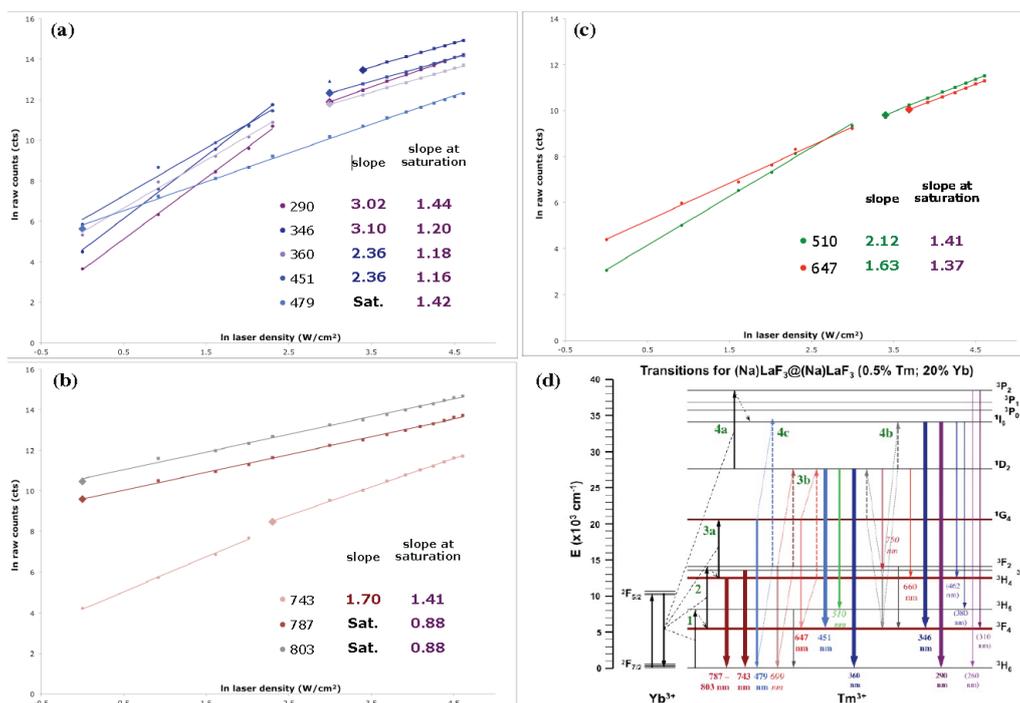


Figure S6. Emission intensity vs. 980 nm laser power density (W/cm^2), In-In IvP plot of 0.5%Tm, 20%Yb codoped Ba(Na)LaF₅ UCNC in (a) UV/blue; (b) NIR; and (c) Vis regime and (d) ETU transition diagram of Yb³⁺-Tm³⁺. Experimental conditions: 1 mg/mL solutions in toluene at 23 °C; 980 nm CW laser excitation varying from 2.5 to 100 W/cm^2 .

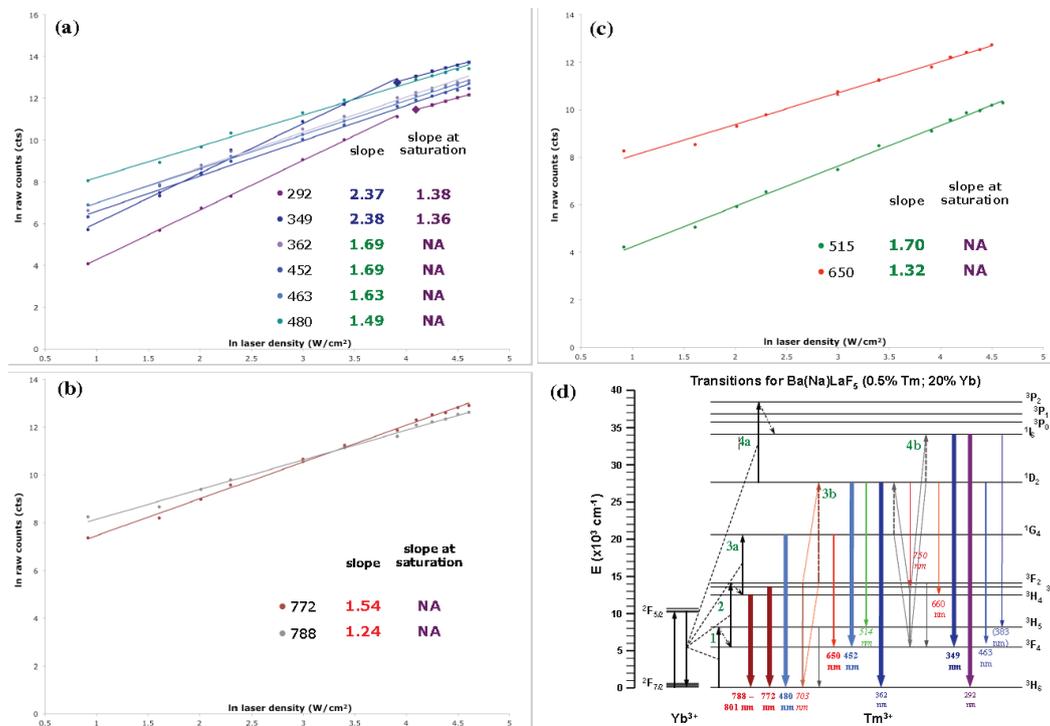
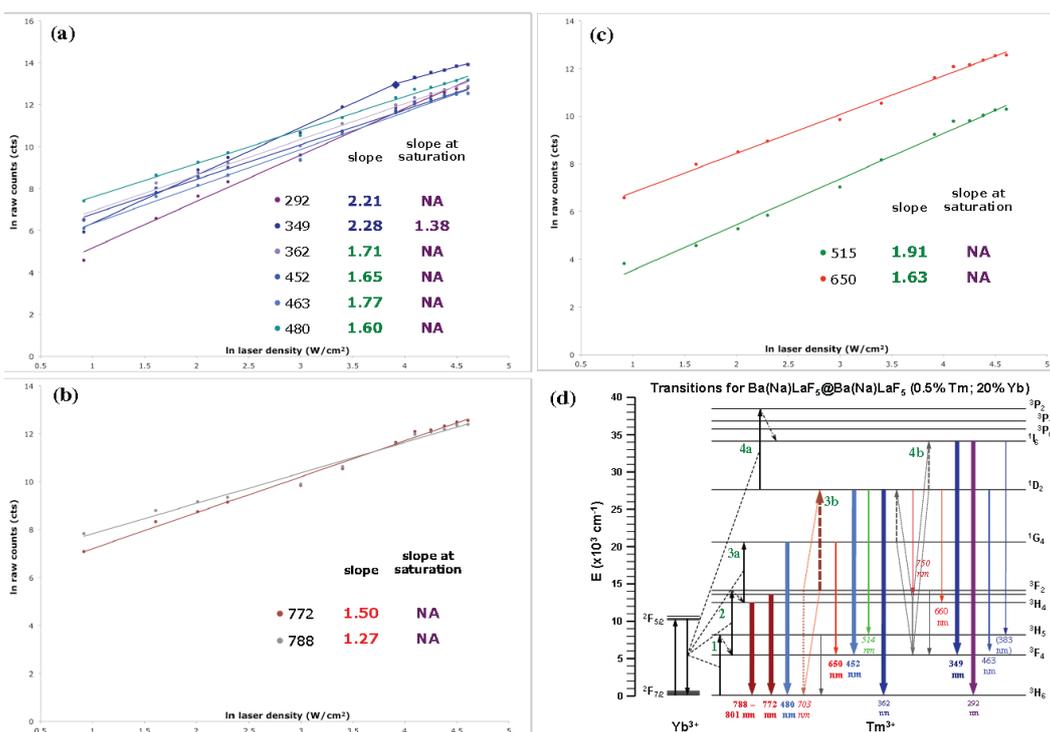


Figure S7. Emission intensity vs. 980 nm laser power density (W/cm^2), In-In IvP plot of 0.5% Tm, 20% Yb codoped Ba(Na)LaF₅ core@shell in (a) UV/blue; (b) NIR; and (c) Vis regime and (d) ETU transition diagram of Yb³⁺-Tm³⁺. Experimental conditions: 1 mg/mL solutions in toluene at 23 °C; 980 nm CW laser excitation varying from 2.5 to 100 W/cm^2 .



References

1. Hara, R.; Cady, G.H. Solubilities of salts in trifluoroacetic acid. *J. Am. Chem. Soc.* **1954**, *76*, 4285–4287.
2. Wang, Y.; Qin, W.P.; Di, W.-H.; Zhang, J.S.; Cao, C.-Y. Infrared-to-visible and infrared-to-violet upconversion fluorescence of rare earth doped LaF₃ nanocrystals. *Chin. Phys. B* **2008**, *17*, 3300–3305.
3. Vetrone, F.; Mahalingam, V.; Capobianco, J.A. Near-infrared-to-blue upconversion in colloidal BaYF₅:Tm³⁺, Yb³⁺ nanocrystals. *Chem. Mater.* **2009**, *21*, 1847–1851.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).