Supporting Information - Luminescence Dynamics and Enhancement of the UV and Visible Emissions of Tm$^{3+}$ in LiYF$_4$: Yb$^{3+}$, Tm$^{3+}$ Upconverting Nanoparticles

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Table S1

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<tr>
<th>Ion</th>
<th>Nominal Tm$^{3+}$ Concentration</th>
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<tr>
<td></td>
<td>0.1% Tm$^{3+}$</td>
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<tr>
<td>Y$^{3+}$</td>
<td>71.12 ± 3.55%</td>
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<tr>
<td>Tm$^{3+}$</td>
<td>0.08 ± 0.00%</td>
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<tr>
<td>Yb$^{3+}$</td>
<td>28.80 ± 1.44%</td>
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Table S1 Inductively coupled plasma – mass spectrometry (ICP-MS) measured ionic concentration of Y$^{3+}$, Tm$^{3+}$ and Yb$^{3+}$ in UCNP compositions studied.
**Fig. S1** Instrument response functions of the PMTs used in this work for 976 nm excitation with a 200 μs pulse width.

**Fig. S2** Powder X-ray diffraction (PXRD) patterns for different UCNP compositions studied, compared to the theoretical pattern for the tetragonal phase with space group $I4_1/a$.\textsuperscript{51}
Fig. S3 Particle size distributions for the compositions studied in this work, measured from 300 nanoparticles.
**Fig. S4** Energy level diagram depicting energy transfer upconversion between Yb$^{3+}$ and Tm$^{3+}$.

**Fig. S5** Emission spectra for LiYF$_4$: 25% Yb$^{3+}$, x% Tm$^{3+}$ after 976 nm excitation, normalized to the $^1$I$_6$ transitions.
**Fig. S6** Integrated emission intensities for each $^1I_6$ and $^1D_2$ transition, as well as the sum for each excited state.
Rise and Decay times were calculated using Equations S1 and S2, respectively.\textsuperscript{53,54}

\[
\tau_r = \frac{1}{I_{\text{max}}} \int_0^{I_{\text{max}}} f(t) \, dt
\] \hspace{1cm} \text{(S1)}

\[
\tau_d = \frac{1}{I_{\text{max}}} \int_{I_{\text{max}}}^{\infty} f(t) \, dt
\] \hspace{1cm} \text{(S2)}

\textbf{Fig. S7} Luminescence decay curves for LiYF\textsubscript{4}: 25\% Yb\textsuperscript{3+}, x\% Tm\textsuperscript{3+} UCNPs for the Yb\textsuperscript{3+} \textsuperscript{2}F\textsubscript{5/2} \rightarrow \textsuperscript{2}F\textsubscript{7/2} transition (1030 nm) after a pulse of 976 nm excitation. The instrument response curve is reported as a dashed gray line for reference.
Fig. S8 NIR emission spectrum for LiYF₄: 25% Yb³⁺, x% Tm³⁺ UCNPs after 976 nm excitation, normalized to the (A) \(^3\text{F}_4 \rightarrow ^3\text{H}_6\) and (B) \(^3\text{H}_4 \rightarrow ^3\text{F}_4\) emissions of Tm³⁺, indicated by the asterisks.
Fig. S9  \(^1\)H-NMR spectrum for \(-3\)-(4-phenylazophenoxy)propanol. Resulting shifts interpreted as followed: 1.90 ppm (m, 2H), 3.58 ppm (m, 1H), 4.15 ppm (m, 2H), 4.58 ppm (m, 1H), 7.12 (m, 2H), 7.57 (m, 3H), 7.85 ppm (m, 4H).\(^{55}\)

Fig. S10 Mass spectrometry results for trans-3-(4-phenylazophenoxy)propanol. Resulting peaks interpreted as followed: M+1 (257.137 m/z), M+Na (279.124 m/z).\(^{55}\)
References


