Electronic Supplementary Information for

Origin of strong red emission in Er\textsuperscript{3+}-based upconversion materials: Role of intermediate states and cross relaxation

\textit{Chiho Lee\textsuperscript{1,‡}, Heeyeon Park\textsuperscript{2,‡}, Woong Kim\textsuperscript{2,*}, and Sungnam Park\textsuperscript{1,3,*}}

\textsuperscript{1}Department of Chemistry and Research Institute for Natural Sciences, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

\textsuperscript{2}Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

\textsuperscript{3}Green School, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

*Authors to whom correspondence should be addressed.
Email addresses: woongkim@korea.ac.kr & spark8@korea.ac.kr
‡ These authors contributed equally to this work
Figure S1. XRD patterns of (a) NaErF$_4$, NaYF$_4$:Yb$^{3+}$,Er$^{3+}$ (Y$^{3+}$:Yb$^{3+}$:Er$^{3+}$=78:20:2), and (b) NaYF$_4$:x%Er$^{3+}$ (x=20~80) powders.
Figure S2. (a) Nanosecond time-resolved PL experimental setup. (b) Schematic illustration of an optical parametric oscillator (OPO) and nonlinear optical processes.
Figure S3. (a) PL spectra measured with NaErF$_4$ powders ($\lambda_{\text{exc}}$ = 489 and 978 nm). The excitation laser power is 20 mW. (b) The energy level diagram of Er$^{3+}$. The margent arrows indicate that the radiative relaxation from higher electronic states ($^2I_{11/2}$, $^2D_{7/2}$ and $^2D_{5/2}$ states) to $^2G_{9/2}$ and $^2G_{11/2}$ states. The non-radiative relaxations (nRR) are indicated by the black arrows.
Figure S4. (a) Power-dependent PL spectra measured with NaErF$_4$ powders ($\lambda_{\text{exc}}=520$ nm). A 532 nm Raman edge filter was used to block the Rayleigh scattering. The emission at ~520 nm is not shown. All PL spectra were normalized based on the peak at ~540 nm ($^4S_{3/2} \rightarrow ^4I_{15/2}$) for comparison. (b) Power-dependent emission peaks at ~380 and ~410 nm. (c) and (d) The log-log plot of the emission intensities ($I$) against excitation laser power ($P_{\text{exc}}$). Data points are experimental results and the line is the fit to Eq. (1). The slopes ($n$) are given.
**Figure S5.** (a) PL spectra and (b) time resolved PL signals measured with NaYF$_4$:Yb$^{3+}$:Er$^{3+}$($Y^{3+}$:Yb$^{3+}$:Er$^{3+}$=78:20:2) powders ($\lambda_{\text{exc}}$ = 355, 441, and 978 nm). PL spectra are normalized based on the peak at ~540 nm. The excitation laser power is set to 20 mW. (c) The energy level diagram and the possible transitions. The resonance energy transfers are indicated by the dashed arrows.

**Figure S5.** (a) PL spectra and (b) time resolved PL signals measured with NaYF$_4$:Yb$^{3+}$:Er$^{3+}$($Y^{3+}$:Yb$^{3+}$:Er$^{3+}$=78:20:2) powders ($\lambda_{\text{exc}}$ = 355, 441, and 978 nm). PL spectra are normalized based on the peak at ~540 nm. The excitation laser power is set to 20 mW. (c) The energy level diagram and the possible transitions. The resonance energy transfers are indicated by the dashed arrows.
**Figure S6.**

(a) PL spectra measured with NaErF$_4$ powders ($\lambda_{exc}$= 355 and 441 nm). PL spectra are normalized based on the peak at 655 nm for comparison. The sub-harmonic of 355 nm was deleted from the PL spectrum. The excitation laser power is set to 20 mW. (b) The energy level diagram of Er$^{3+}$. The peaks at ~810 and 978 nm result from the cross relaxation as indicated by the dashed arrows. The cross relaxation between neighboring Er$^{3+}$ ions are very efficient in NaErF$_4$ powders.
**Figure S7.**

![PL spectrum measured with NaErF₄ powder ($\lambda_{exc} = 1528$ nm). The electronic states are assigned to all the peaks.](image-url)

**Figure S7.** PL spectrum measured with NaErF₄ powder ($\lambda_{exc} = 1528$ nm). The electronic states are assigned to all the peaks.
### Table S1. Particle sizes of Er\(^{3+}\)-based upconversion materials

<table>
<thead>
<tr>
<th>UC material</th>
<th>Particle size (nm)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaErF(_4)</td>
<td>44.8</td>
</tr>
<tr>
<td>NaYF(_4);Er(^{3+}) (80%)</td>
<td>40.1</td>
</tr>
<tr>
<td>NaYF(_4);Er(^{3+}) (60%)</td>
<td>34.8</td>
</tr>
<tr>
<td>NaYF(_4);Er(^{3+}) (40%)</td>
<td>34.7</td>
</tr>
<tr>
<td>NaYF(_4);Er(^{3+}) (20%)</td>
<td>32.1</td>
</tr>
<tr>
<td>NaYF(_4);Yb(^{3+}), Er(^{3+}) (78% : 20% : 2%)</td>
<td>37.6</td>
</tr>
</tbody>
</table>

\(^a\) Particle sizes were estimated from the XRD data and the Scherrer equation.