Electronic Supplementary Information

Luminescence of Nanocrystalline BaFCl Codoped With $Eu^{2+/3+}$ and Tb^{3+}

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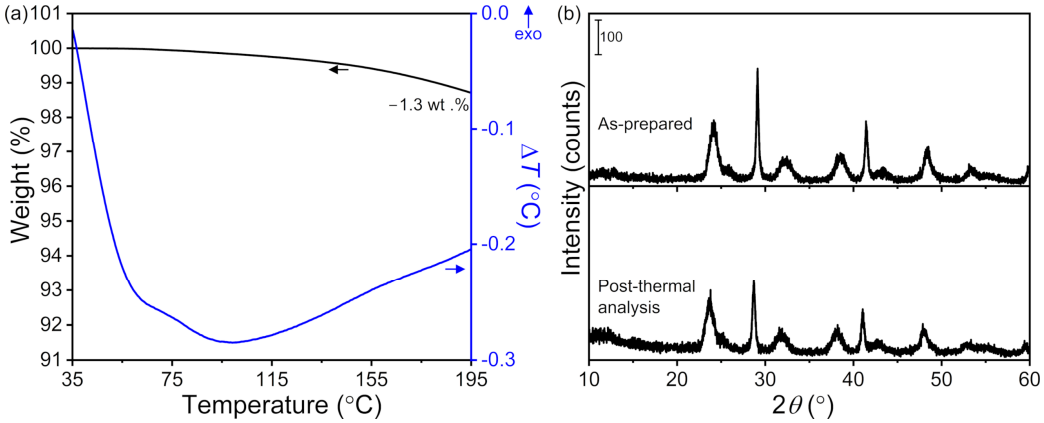

Figure S1. (a) Thermogravimetric (TGA) and differential thermal analysis (DTA) of BaFCl:Eu,Tb nanocrystals. Total weight loss is indicated. (b) PXRD patterns of BaFCl:Eu,Tb before and after thermal analysis. Thermal analysis was conducted under flowing nitrogen (100 mL min^{-1}) using an SDT2960 TGA–DTA analyzer (TA Instruments). ≈10 mg of sample were placed in an alumina crucible, held at 35 °C for 10 min, ramped to 200 °C at a rate of 10 °C min^{-1}, and kept at that temperature for 5 min. PXRD patterns were collected in the 10–60° 2θ range using a step size and time of 0.02° and 0.5 s, respectively.

Table S1. Refined Structural Parameters of BaFCl:Eu,Tb Nanocrystals

a (Å)	4.3857(3)
c (Å)	7.2505(15)
V (Å^3)	139.46(4)
zBa	0.2087(3)
zCl	0.6328(8)
$U_{Ba}{}^a$	0.39(9)
$U_F{}^a$	1.2(3)
$U_{Cl}{}^a$	0.77(19)
Ba–F (Å)	2.6644(10)
Ba–Cl (Å)	3.307(3) (×4), 3.075(7) (×1)

[a] Given as 100 × U.

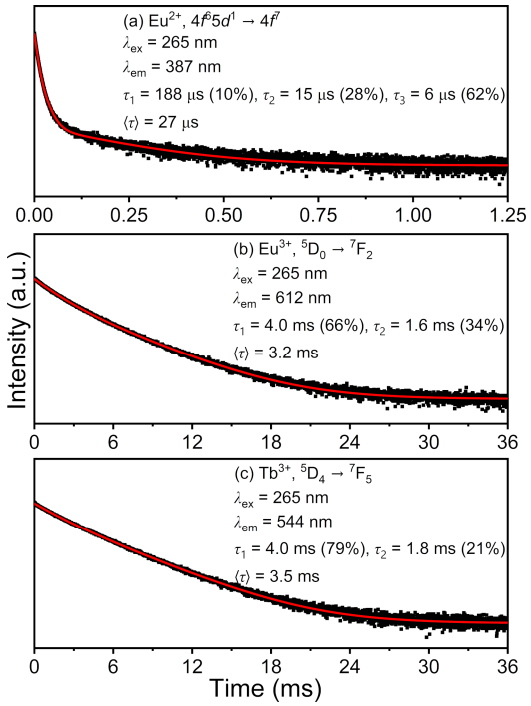

Figure S2. Multiexponential fits of room-temperature luminescence decays of Eu^{2+} (a), Eu^{3+} (b), and Tb^{3+} (c) in BaFCl:Eu,Tb nanocrystals. Fits are depicted as solid red lines. Plots are shown in logarithmic scale. The longest component obtained in the decay of Eu^{2+} (188 μs, 10% fractional contribution) likely arises from a slow decaying background associated with chemical species other than Eu^{2+} (e.g., host emission).

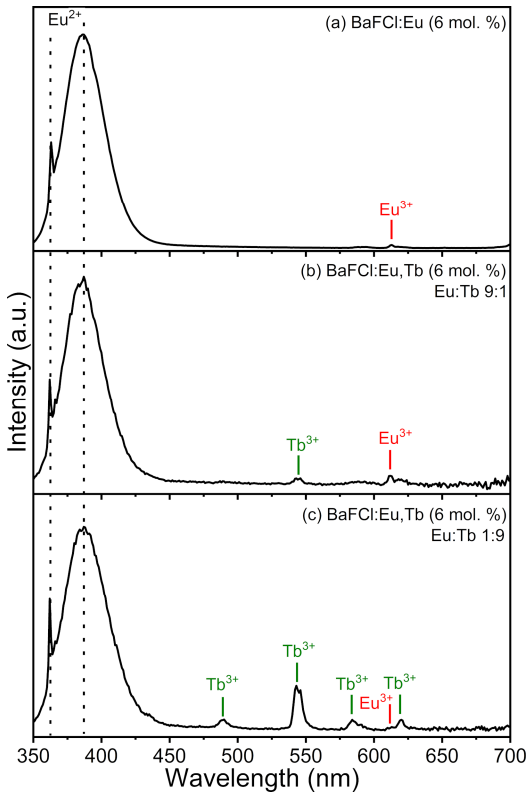

Figure S3. Room-temperature emission spectrum of (a) singly-doped BaFCl:Eu nanocrystals, and (b,c) BaFCl:Eu,Tb nanocrystals codoped with different Eu:Tb ratios (6 mol. % total rare-earth concentration). Eu^{2+} emission bands are indicated with dotted lines. Spectra were collected under 275 nm excitation.

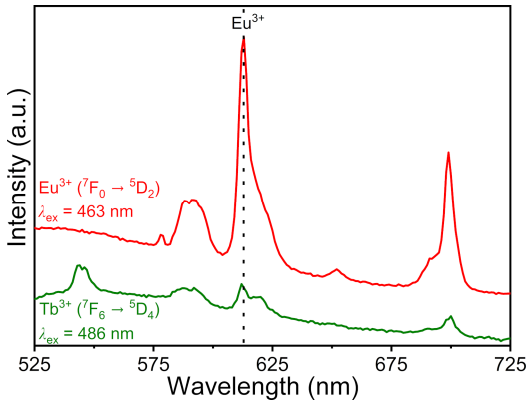

Figure S4. Room-temperature emission spectra of BaFCl:Eu,Tb nanocrystals collected upon direct excitation of Eu^{3+} (red curve) and Tb^{3+} (green curve). Eu^{3+} emission at 612 nm is observed in both cases.

Table S2. Peak Intensities for Calculation of Peak-Intensity-Weighted Eu^{2+} Centroid[a,b]

Temperature (K)	$I_{f\rightarrow f}^{\widetilde{\nu_1}}$	$I_{fd\rightarrow f}^{\widetilde{\nu_2}}$
80	2.92334	0.4407
130	2.18397	0.72453
180	1.14993	0.84889
230	0.72655	1
280	0.46059	0.84923
330	0.40594	0.84923
380	0.34539	0.74659
430	0.31579	0.67706

[a] Normalized with respect to $I_{fd\rightarrow f}^{\widetilde{\nu_2}}$ (230 K).
[b] $\widetilde{\nu_1}$ = 27548 cm^{-1} (363 nm) and $\widetilde{\nu_2}$ = 25774 cm^{-1} (388 nm).

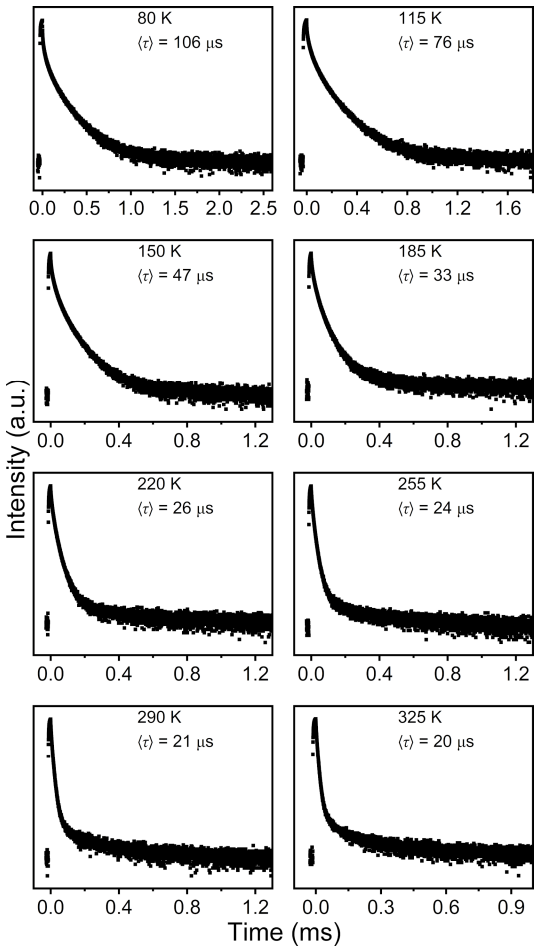

Figure S5. Variable-temperature luminescence decays of Eu^{2+} in BaFCl:Eu,Tb nanocrystals. Decays were excited at 265 nm and monitored at 387 nm. Intensity-weighted average lifetimes ($\langle\tau\rangle$) are given. Decays are plotted in logarithmic scale.