

Supporting Information

Water-triggered optical response in Tb³⁺-doped CaSnF₆ crystal for high-security anti-counterfeiting application

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Experimental

Materials and synthesis of $\text{CaSnF}_6:\text{Tb}^{3+}$: CaCl_2 (99.9%), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (99.995%), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), and NaOH (97%) were purchased from Aladdin, and HF acid (40 wt%) was purchased from Sinopharm Chemical. All the chemicals were used as received without further purification. The $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ was prepared via the fluorination of $\text{CaSn}(\text{OH})_6:\text{Tb}^{3+}$ precursor. First, the $\text{CaSn}(\text{OH})_6:\text{Tb}^{3+}$ precursor was synthesized by the coprecipitation method using 2.25 mmol CaCl_2 , 2.5 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 0.25 mmol $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ and excess sodium hydroxide (10 M, 3 mL). Then, $\text{CaSn}(\text{OH})_6:\text{Tb}^{3+}$ was collected by centrifugation and added to 34 mL anhydrous ethanol with an appropriate amount of HF acid incorporated during the stirring process. Finally, the mixture solution was put into a 50 mL Teflon-lined autoclave and heated in a furnace at 120°C for 12 h. The $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ was successfully collected after cooling, centrifugation, drying, and grinding. Additionally, the CaSnF_6 samples with different doping concentrations of Tb^{3+} could be synthesized using the same method but changing the CaCl_2 and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ amount. The samples were stored in a desiccator for subsequent testing.

Preparation of intermediate phase between CaSnF_6 and CaF_2 phase: The synthesized CaSnF_6 and DI water were mixed in a centrifuge tube at a certain mass ratio. Then, the mixture was subjected to ultrasonic oscillation to achieve complete and uniform dispersion. To quench the state of the samples at various reaction times, the samples were promptly immersed in liquid nitrogen for 30 s until complete freezing occurred. Then, the hygroscopic mixture was subjected to freeze-drying in a vacuum freeze-dryer (LGJ-S20, Beijing Sihuan Qihang Technology Co., LTD.) to remove water. Finally, samples with different reaction times were obtained. Additionally, the aforementioned method can also be utilized to obtain intermediate-phase samples with varying sample/water ratios. The procedure is illustrated in Figure S1.

Fabrication of the specific logo patterns: The fabrication of these patterned templates is based on computer numerical control (CNC) machining technology. Firstly, a graphic

template with 1 mm depth was fabricated by standard CNC machine tools (Annoytools, CNC3018Pro Max) on the acrylonitrile butadiene styrene (ABS) plastic substrates. Then, the $\text{CaSnF}_6:\text{Tb}^{3+}$, $\text{CaF}_2:\text{Tb}^{3+}$, and SiO_2 ethanol solutions were separately injected into the graphic templates and dried in a drying oven at 70°C for 1 h. The above graphics were placed in a humidity chamber at 95% humidity for about 30 min and then transferred to a drying oven for drying. A humidity chamber and a drying oven were used for water content control.

Characterization: The crystal structure and phase composition of the fluoride materials were measured by a powder X-ray diffractometer (DMAX-2500PC, Rigaku) with $\text{Cu K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a scanning speed of $10^\circ/\text{min}$. The micro/ nano-structure was analyzed using a field-emission high-temperature scanning electron microscope (SEM, JSM-7800F, JEOL) and a high-resolution transmission electron microscope (HR-TEM, JEM-2100, JEOL). The excitation and emission spectra were all tested by the Edinburgh FLS1000 fluorescence spectrometer. PL photographs under 365 nm UV light were taken by a digital camera (Canon, EOS 800D with EF-S 18-55 mm) in a manual mode (exposure time: 1 s, aperture: f/4, and sensitivity: ISO 200).

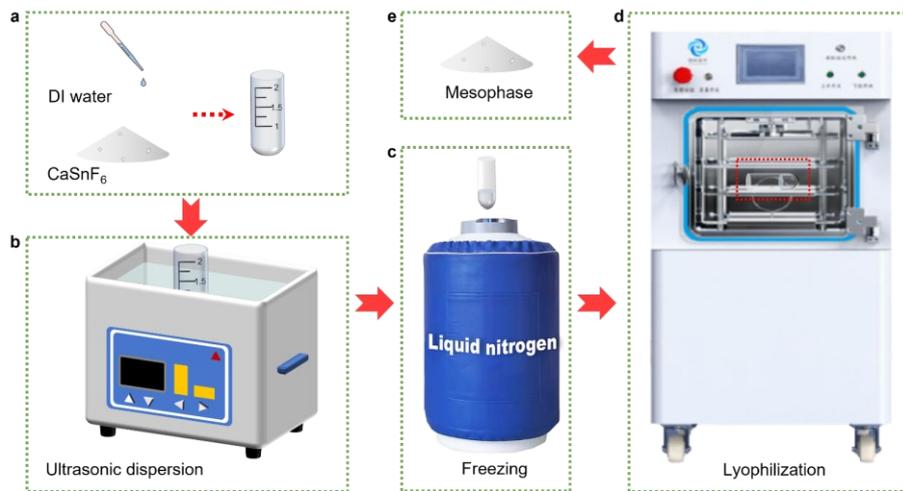


Figure S1. Schematic of the preparation of mesophase.

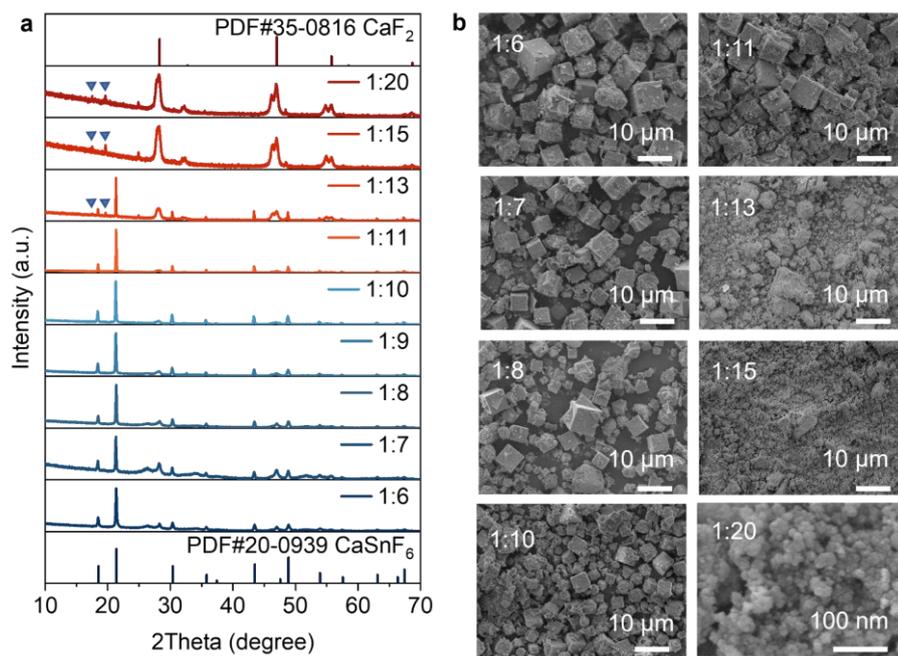


Figure S2. a) XRD patterns and b) SEM images of CaSnF₆:10%Tb³⁺ with varying Ca-F ratios.

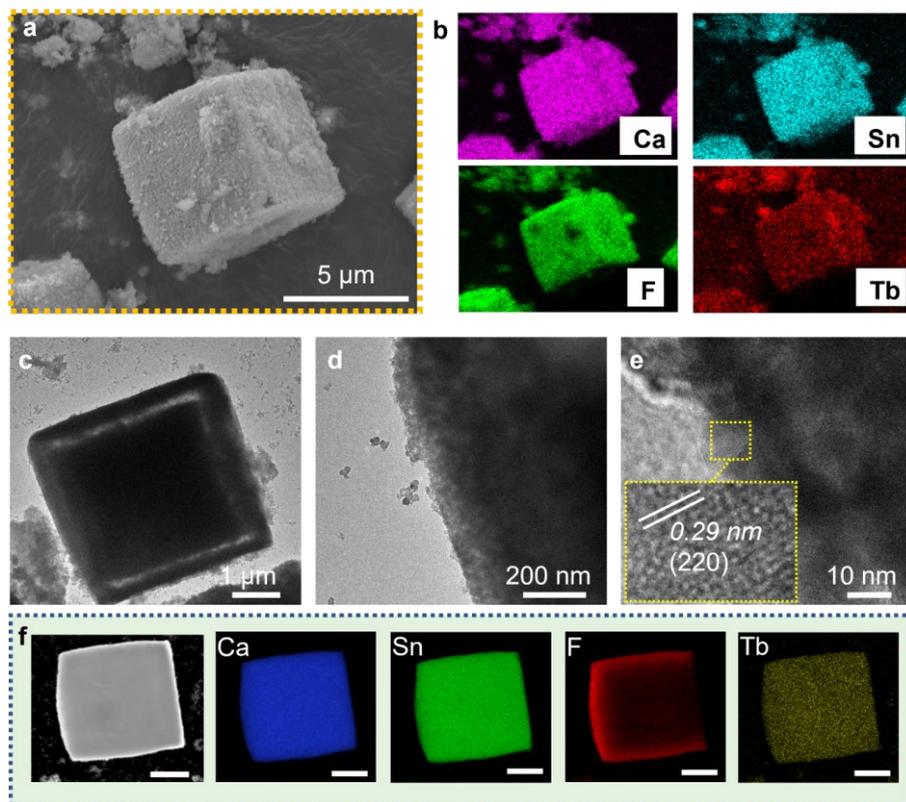


Figure S3. a) SEM image, b) SEM mapping, c) TEM image, d, e) HRTEM images of $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ when the Ca-F ratio is at 1:9. f) TEM-mapping images of $\text{CaSnF}_6:10\%\text{Tb}^{3+}$. Scale bar: 1 μm .

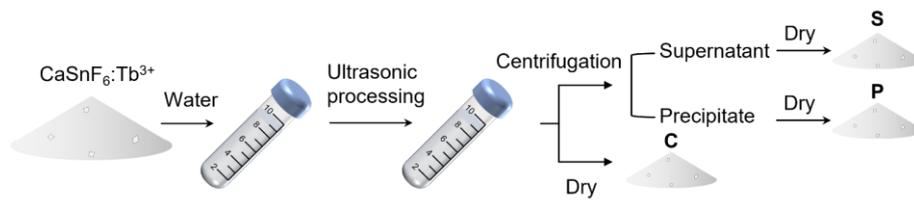


Figure S4. Schematic of the preparation of sample S, P, and C.

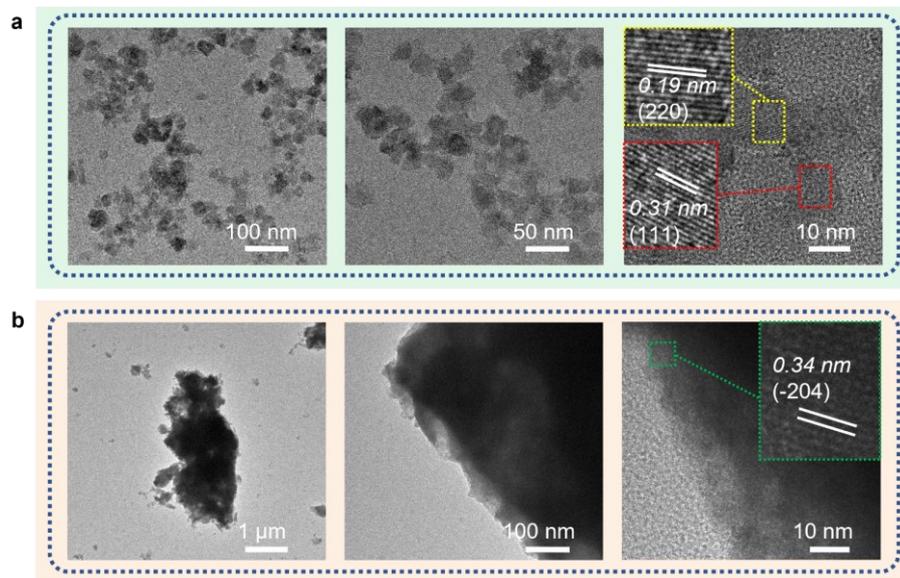


Figure S5. TEM mapping images of a) sample P ($\text{CaF}_2:\text{Tb}^{3+}$), and b) sample S (supernatant fluid).

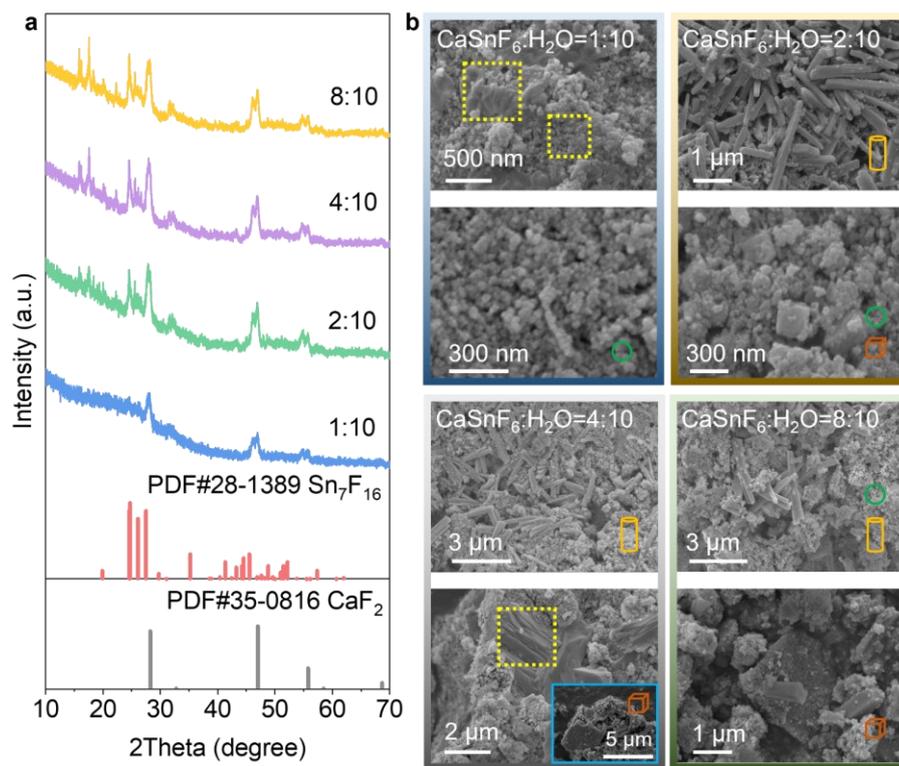


Figure S6. a) XRD patterns and b) SEM images of the $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ treated with varying water content.

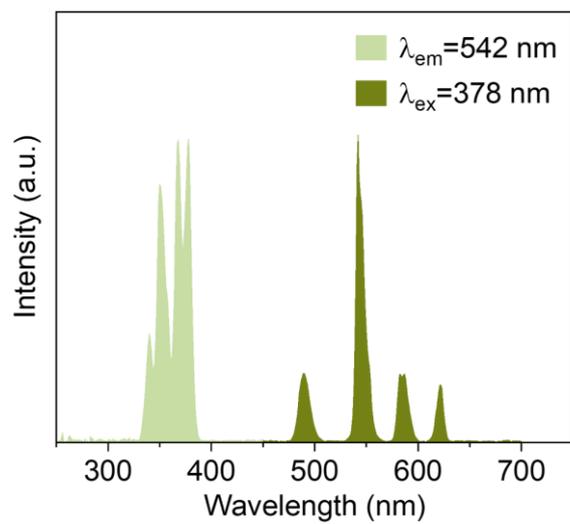


Figure S7. PLE and PL spectra of CaSnF₆:10%Tb³⁺.

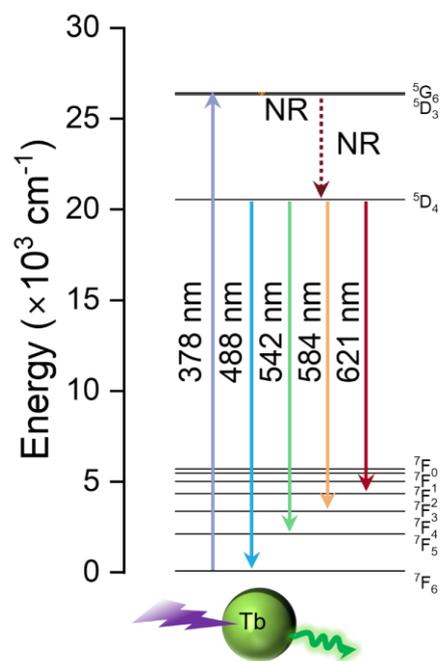


Figure S8. Simplified energy level diagram of Tb³⁺ ions in the fluoride host lattices.

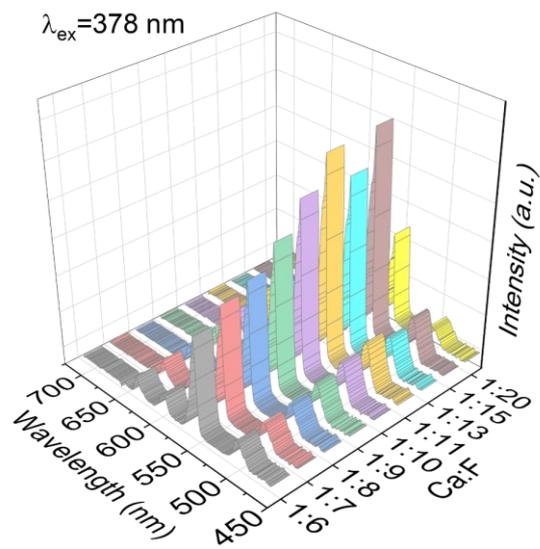


Figure S9. PL spectra of $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ with varying Ca-F ratio.

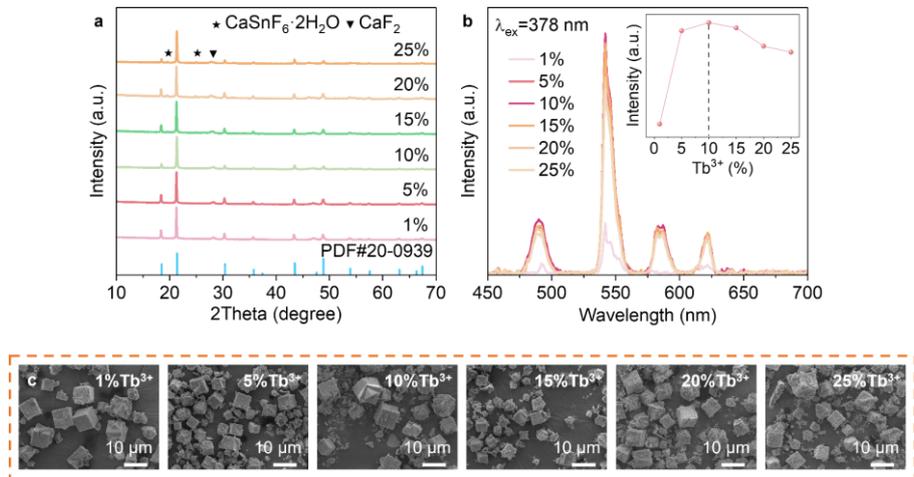


Figure S10. a) XRD patterns, b) PL emission spectra, and c) SEM images of CaSnF_6 : $x\%\text{Tb}^{3+}$ ($x = 1, 5, 10, 20, 25$).

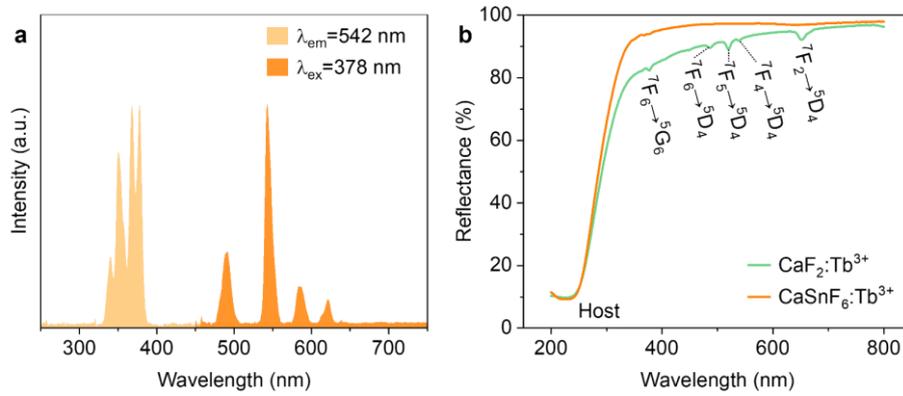


Figure S11. a) PLE and PL spectra of $\text{CaF}_2:\text{Tb}^{3+}$. b) The reflectance spectrum of $\text{CaSnF}_6:\text{Tb}^{3+}$ and $\text{CaF}_2:\text{Tb}^{3+}$.

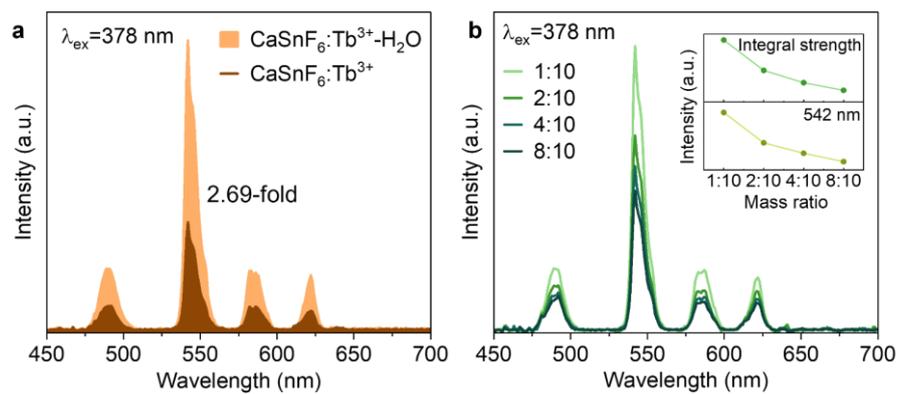


Figure S12. a) PL spectra of $\text{CaSnF}_6:10\text{Tb}^{3+}$ and $\text{CaSnF}_6:10\text{Tb}^{3+}-\text{H}_2\text{O}$. b) PL spectra of $\text{CaSnF}_6:10\text{Tb}^{3+}$ treated with different water content.

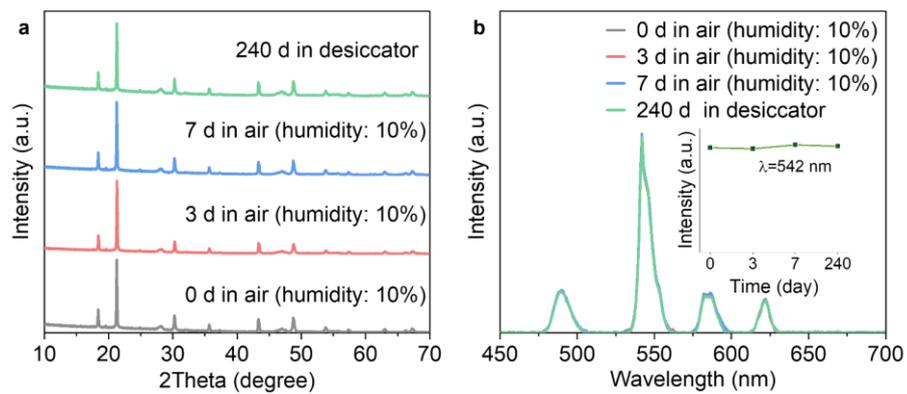


Figure S13 a) XRD patterns and b) PL emission spectra of CaSnF₆:10%Tb stored in air with 10% humidity for 0, 3, and 7 days, and in a desiccator for 240 days.

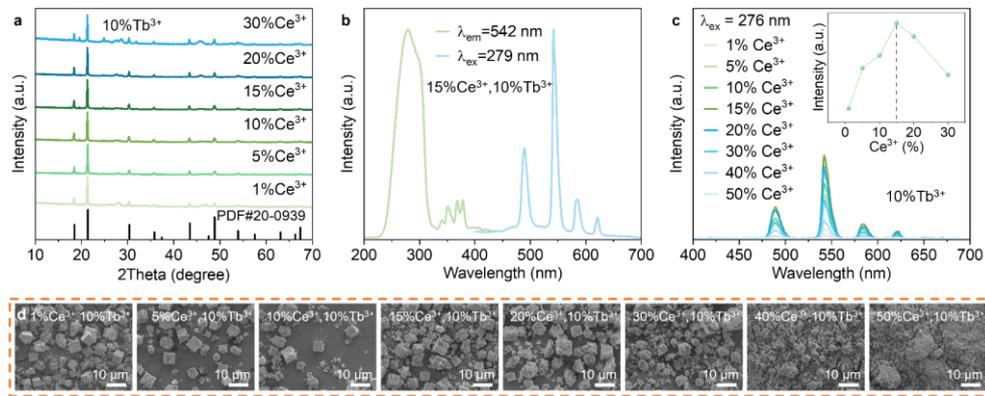


Figure S14. a) XRD patterns of $\text{CaSnF}_6:x\%\text{Ce}^{3+}, 10\%\text{Tb}^{3+}$ ($x = 1, 5, 10, 15, 20, 30$). b) PLE emission spectrum of $\text{CaSnF}_6:15\%\text{Ce}^{3+}, 10\%\text{Tb}^{3+}$. c) PL emission spectra and d) SEM images of $\text{CaSnF}_6:x\%\text{Ce}^{3+}, 10\%\text{Tb}^{3+}$ ($x = 1, 5, 10, 15, 20, 30$).

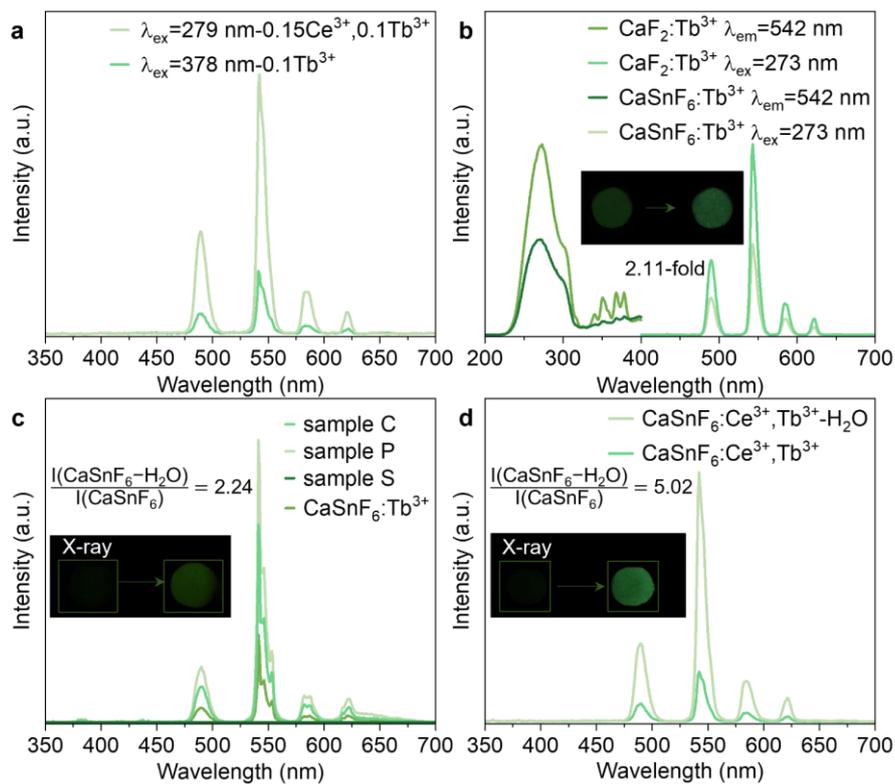


Figure S15. a) PL spectra of $\text{CaSnF}_6:10\%\text{Tb}^{3+}$ and $\text{CaSnF}_6:15\%\text{Ce}^{3+},10\%\text{Tb}^{3+}$. b) PLE spectra of $\text{CaSnF}_6:15\%\text{Ce}^{3+},10\%\text{Tb}^{3+}$, and the one treated with water. RL spectra of c) Tb^{3+} -doped CaF_2 , $\text{CaSnF}_6\text{-H}_2\text{O}$, CaSnF_6 and supernatant, and d) $\text{Ce}^{3+},\text{Tb}^{3+}$ co-doped $\text{CaSnF}_6\text{-H}_2\text{O}$, CaSnF_6 .