

Supporting Information

Tuning Luminescence of Lanthanide-doped Upconversion Nanoparticles through Simultaneous Binary Cation Exchange

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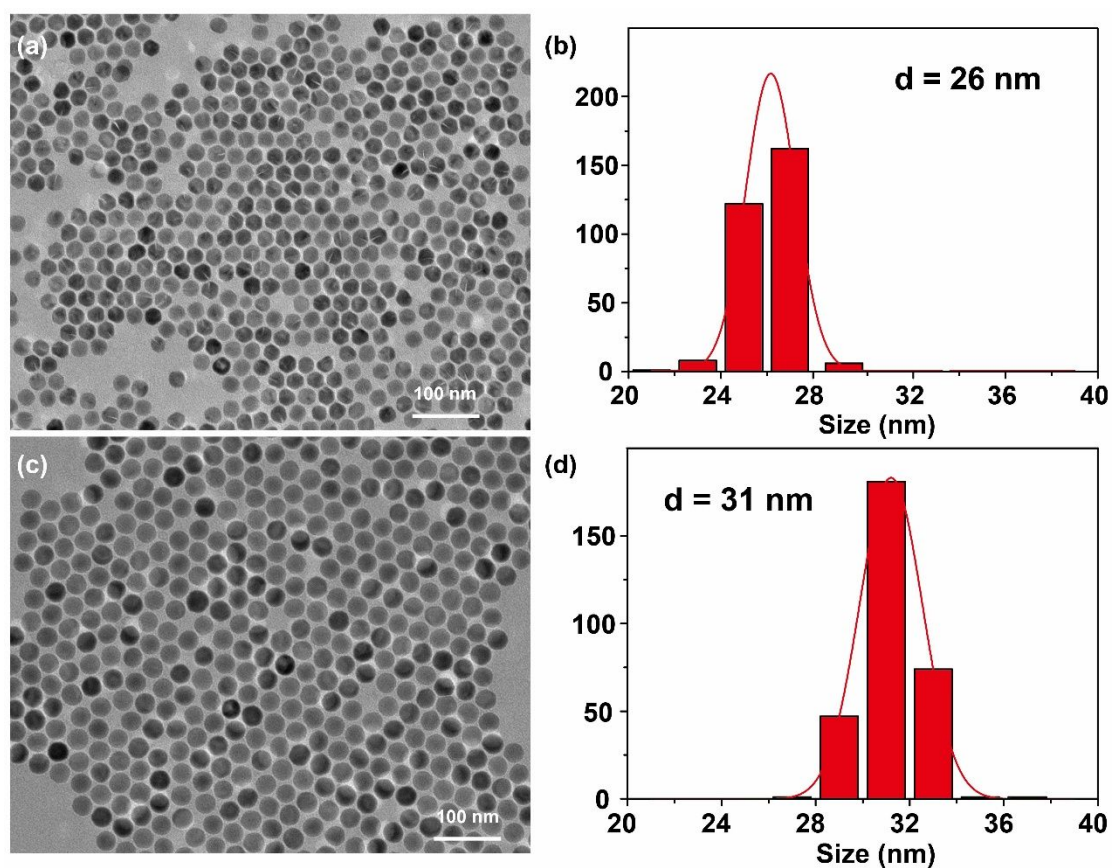


Figure S1. (a and c) TEM images of NaYF₄:Yb/Er (18/2 mol%) and core@shell NaYF₄:Yb/Er (18/2 mol %)@NaYF₄ NPs. (b and d) The particle size distributions of the corresponding NaYF₄:Yb/Er (18/2 mol%) and core@shell NaYF₄:Yb/Er (18/2 mol %)@NaYF₄ NPs.

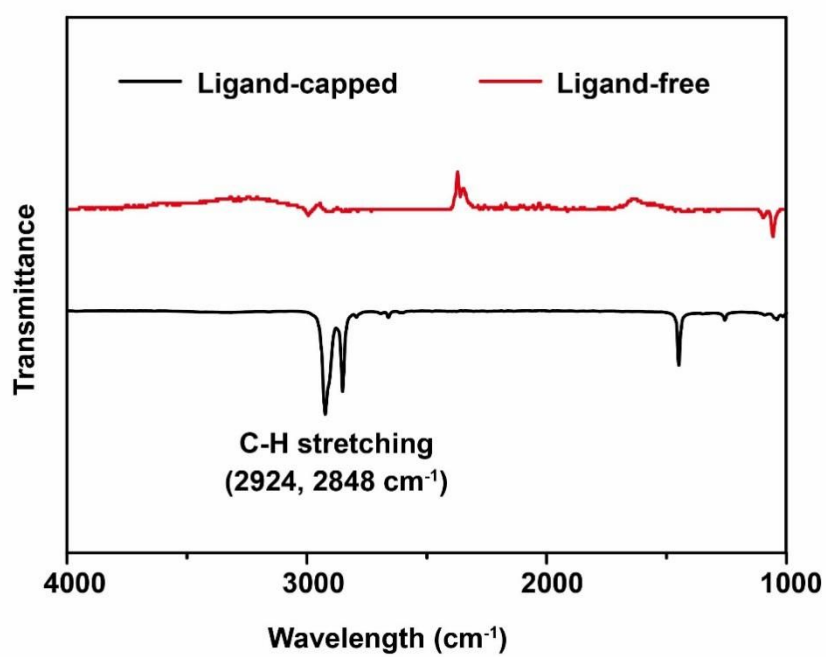


Figure S2. FT-IR spectrum comparison of the oleate-capped NaYF₄:Yb/Er (18/2 mol %>@NaYF₄ nanoparticles before and after removing the surface ligands.

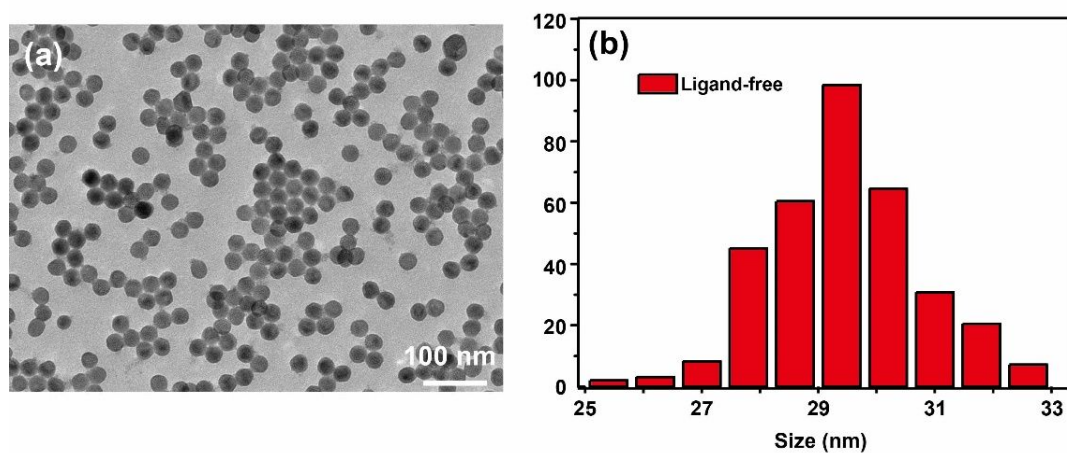


Figure S3. (a) TEM images of core@shell NaYF₄:Yb/Er (18/2 mol %)/NaYF₄ NPs after removing surface ligand. (b) The particle-size distribution of the as-prepared ligand-free core@shell NaYF₄:Yb/Er (18/2 mol %)/NaYF₄ NPs. Note that the average size was estimated to be 29 nm.

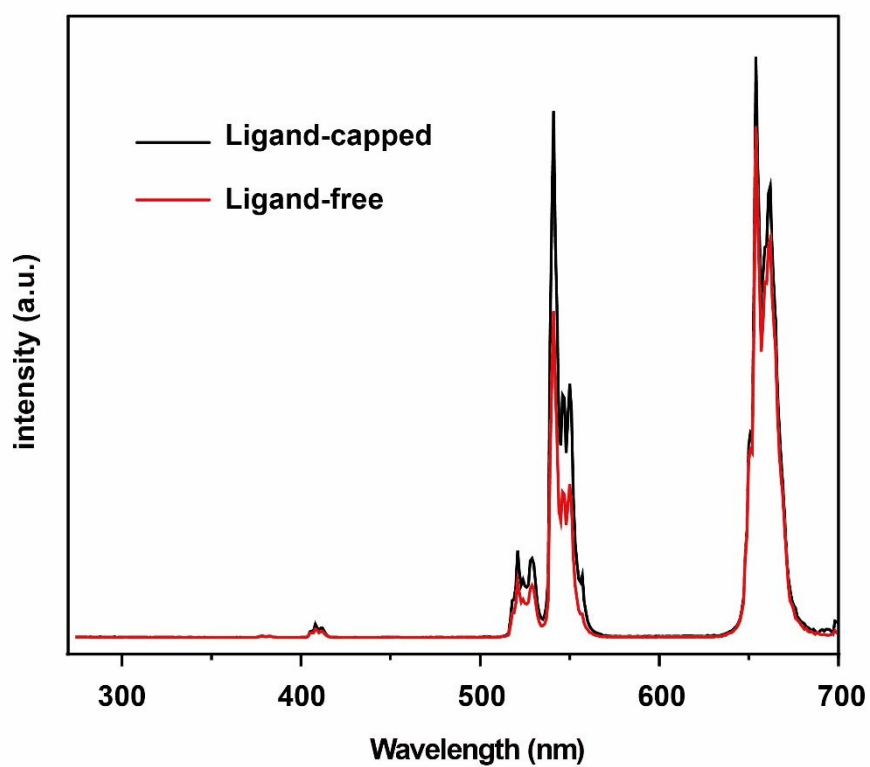


Figure S4. Upconversion spectrum comparison of core@shell $\text{NaYF}_4\text{:Yb/Er}$ (18/2 mol %) @NaYF_4 nanoparticles before and after removing the surface ligand.

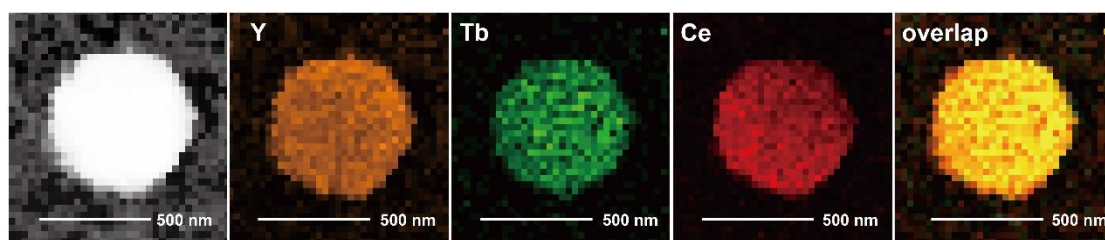


Figure S5. The TEM and elemental mapping images of Tb³⁺-doped CeF₃ microparticles.

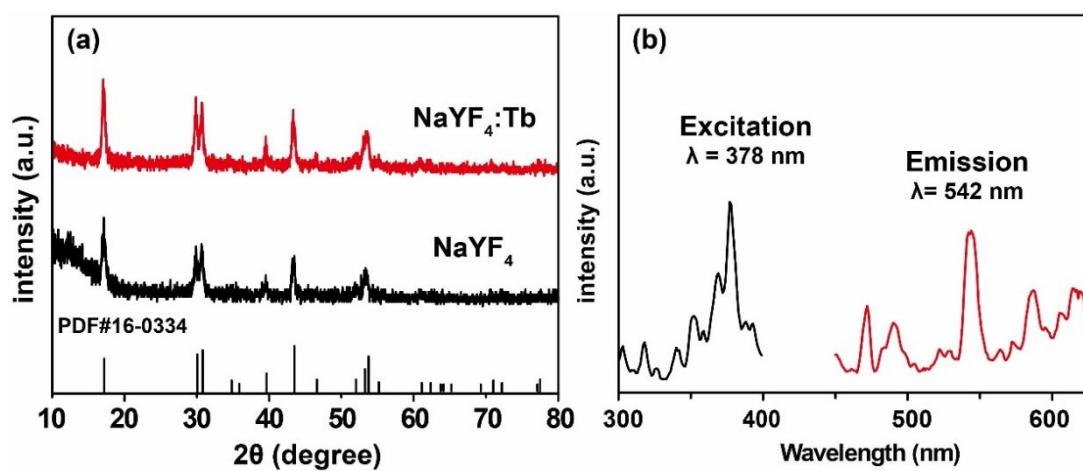


Figure S6. XRD patterns of NaYF_4 and Tb^{3+} -exchanged NaYF_4 NPs. Excitation and emission profiles of an aqueous dispersion of as-prepared $\text{NaYF}_4:\text{Tb}$ NPs.

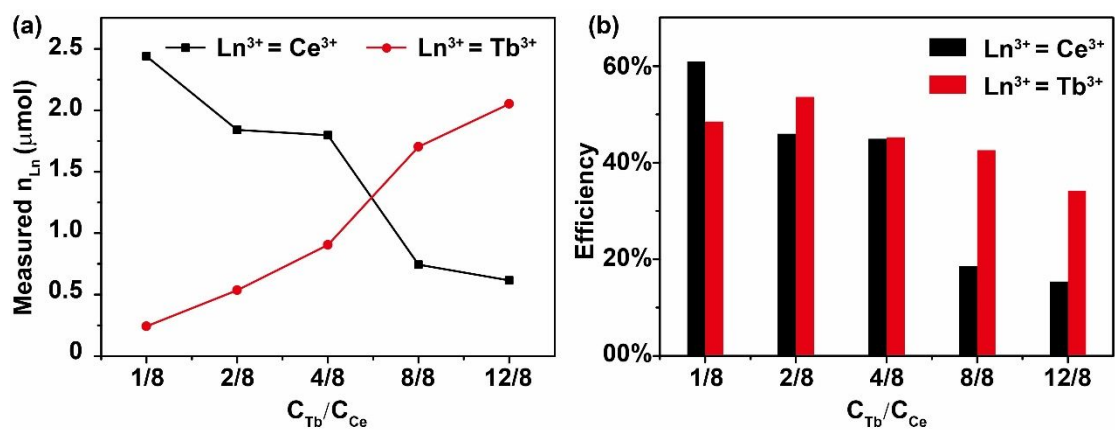


Figure S7. (a) The contents of Ce^{3+} and Tb^{3+} ions in the cation-exchanged core@shell $\text{NaYF}_4\text{:Yb/Er}$ (18/2 mol%)@ NaYF_4 NPs as a function of $C_{\text{Tb}^{3+}}/C_{\text{Ce}^{3+}}$ in the reaction mixture. (b) The utilization efficiencies of incoming Ce^{3+} and Tb^{3+} ions as a function of $C_{\text{Tb}^{3+}}/C_{\text{Ce}^{3+}}$ in the reaction mixture.

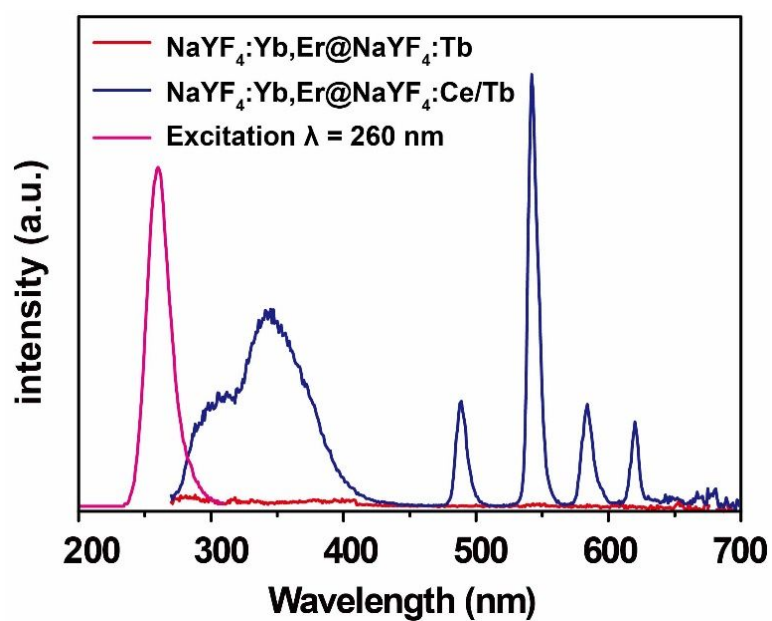


Figure S8. Excitation spectra (purple curve), and down-conversion emission spectra of NaYF₄:Yb/Er (18/2 mol %)@NaYF₄:Ce/Tb (blue curve), and NaYF₄:Yb/Er (18/2 mol%)@NaYF₄:Tb (red curve) under 254 nm excitation respectively.

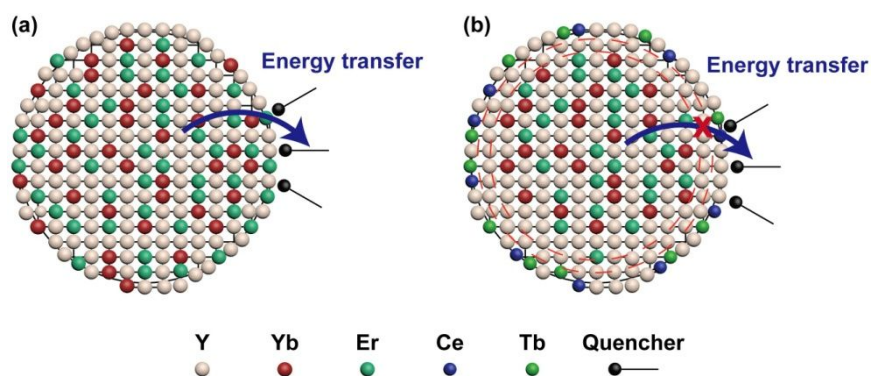


Figure S9. Schematic of the role of a thin layer of NaYF₄ lattices in protecting upconversion excitation energy from surface quenchers. The integrity of the surface NaYF₄ layer of the cation-exchanged NPs shows high dependence on the Tb³⁺-to-Ce³⁺ molar ratio in the reaction solution.

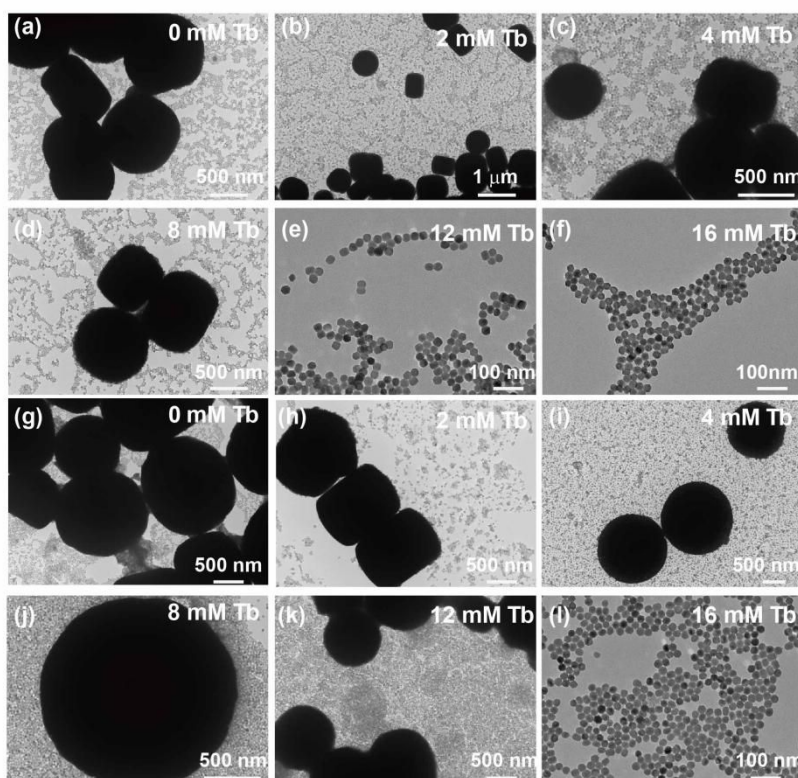


Figure S10. (a-f) TEM images of ligand-free NaYF₄:Yb/Er (18/2 mol %)/NaYF₄ NPs after being reacted with a combination of Ce³⁺ (16 mM) and Tb³⁺ (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (g-l) TEM images of ligand-free NaYF₄:Yb/Er (18/2 mol %)/NaYF₄ NPs after being reacted with a combination of Ce³⁺ (32 mM) and Tb³⁺ (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h.

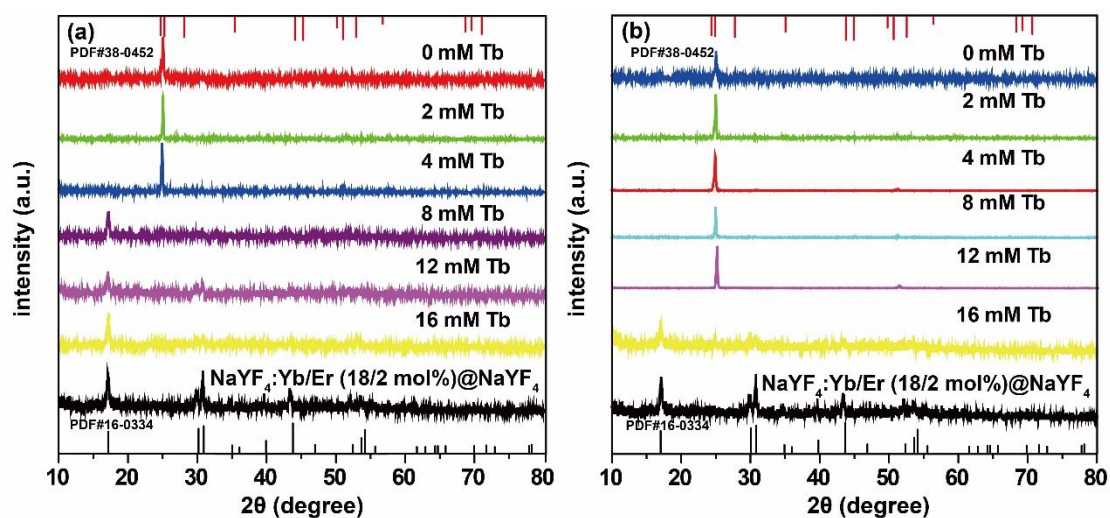


Figure S11 (a) XRD patterns of ligand-free $\text{NaYF}_4:\text{Yb/Er}$ (18/2 mol %)@ NaYF_4 NPs before and after being reacted with a combination of Ce^{3+} (16 mM) and Tb^{3+} (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (b) XRD patterns of ligand-free $\text{NaYF}_4:\text{Yb/Er}$ (18/2 mol %)@ NaYF_4 NPs before and after being reacted with a combination of Ce^{3+} (32 mM) and Tb^{3+} (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h.

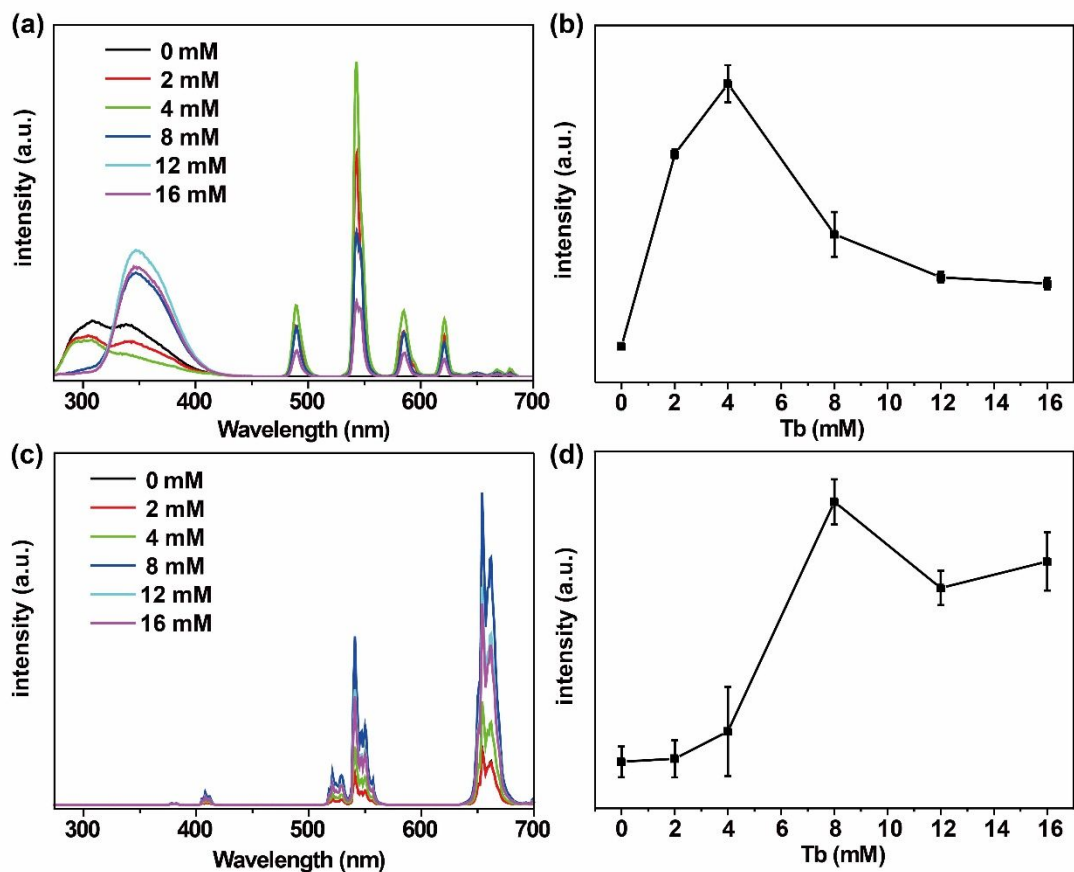


Figure S12. (a) Down-shifting emission profiles of ligand-free NaYF₄:Yb/Er (18/2 mol %>@NaYF₄ NPs before and after being reacted with a combination of Ce³⁺ (16 mM) and Tb³⁺ (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (b) The peak emission at 543 nm as a function of the concentration of Tb³⁺ ions. (c) Upconversion emission profiles of ligand-free NaYF₄:Yb/Er (18/2 mol %>@NaYF₄ NPs before and after being reacted with a combination of Ce³⁺ (16 mM) and Tb³⁺ (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (d) The peak emission at 654 nm as a function of the concentration of Tb³⁺ ions.

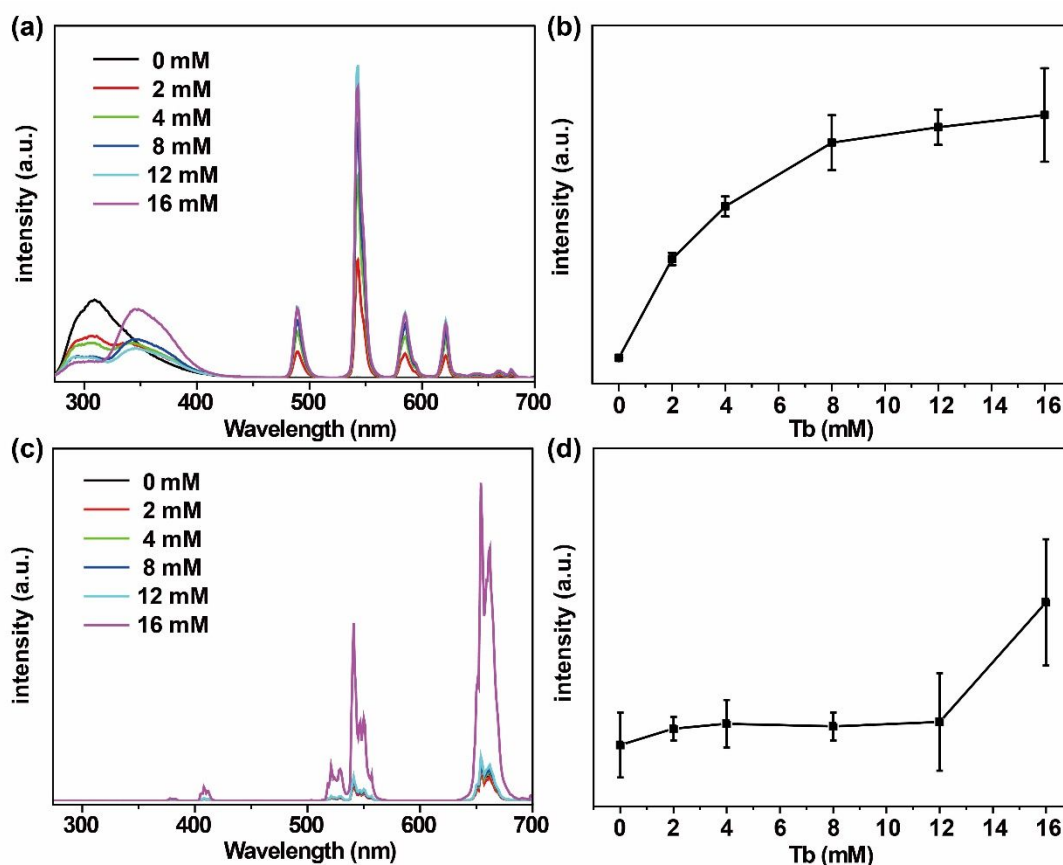


Figure S13. (a) Down-shifting emission profiles of ligand-free $NaYF_4:Yb/Er$ (18/2 mol %) $@NaYF_4$ NPs before and after being reacted with a combination of Ce^{3+} (32 mM) and Tb^{3+} (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (b) The peak emission at 543 nm of the resultant NPs as a function of the concentration of Tb^{3+} ions. (c) Upconversion emission profiles of ligand-free $NaYF_4:Yb/Er$ (18/2 mol %) $@NaYF_4$ NPs before and after being reacted with a combination of Ce^{3+} (32 mM) and Tb^{3+} (0, 2, 4, 8, 12, 16 mM) at 90 °C for 1 h. (d) The peak emission at 654 nm of the resultant NPs as a function of the concentration of Tb^{3+} ions.

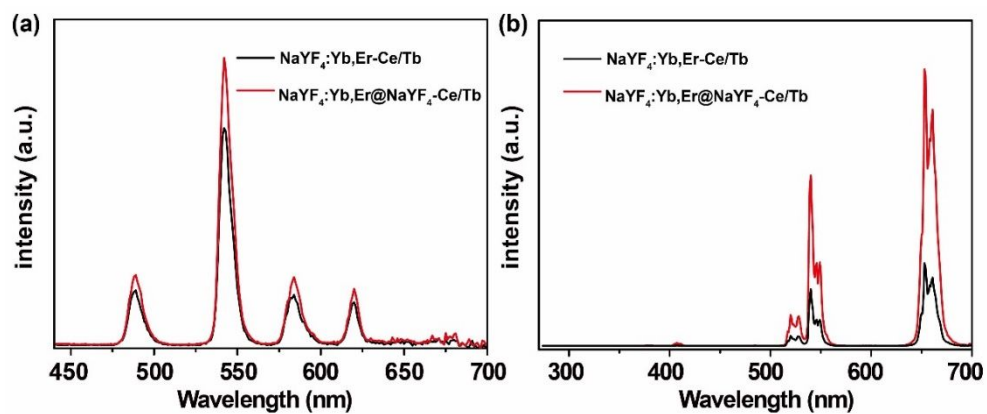


Figure S14. (a) Downshifting and (b) upconversion emission spectra of the resultant $\text{NaYF}_4\text{:Yb/Er/Ce/Tb}$ and $\text{NaYF}_4\text{:Yb/Er (18/2 mol\%)}@ \text{NaYF}_4\text{:Ce/Tb}$ NPs. Note that the downshifting and upconversion emissions were measured under excitation at 254 and 980 nm, respectively.

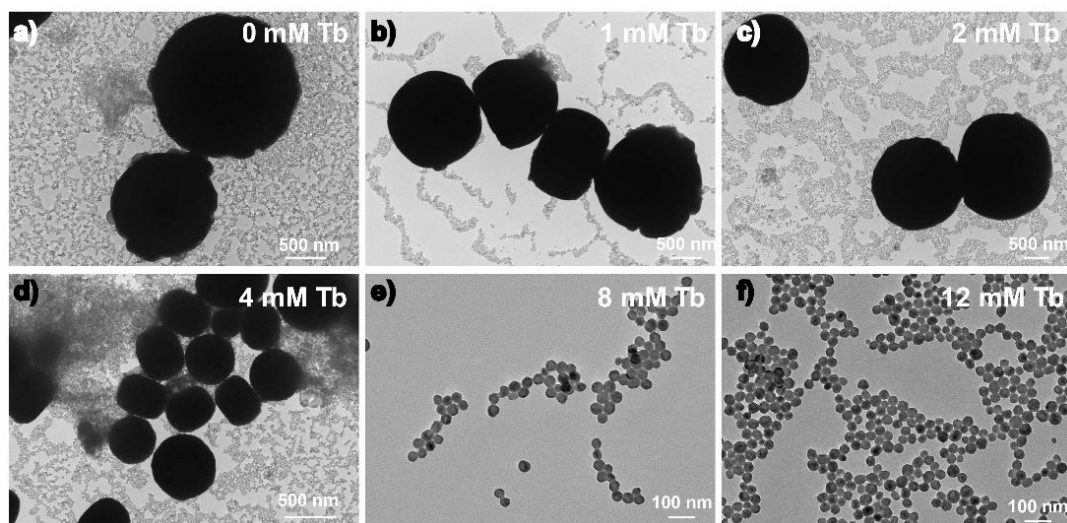


Figure S15. (a-f) TEM images of ligand-free NaYF₄:Yb/Er (18/2 mol %)/NaGdF₄ NPs after being reacted with a combination of Ce³⁺ (8 mM) and Tb³⁺ (0, 1, 2, 4, 8, 12 mM) at 90 °C for 1 h.

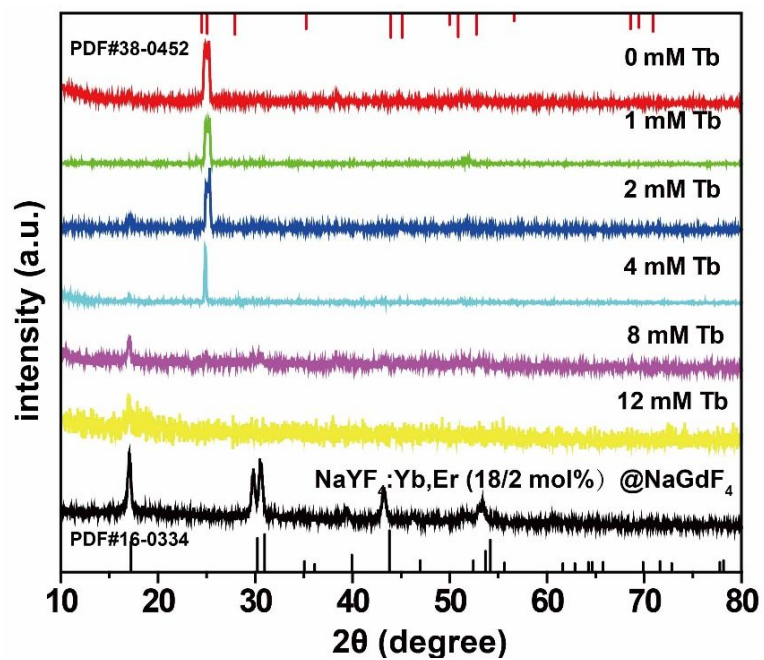


Figure S16. XRD patterns of NaYF₄:Yb/Er (18/2 mol %)@NaGdF₄ NPs before and after being reacted with a combination of Ce³⁺ (8 mM) and Tb³⁺ (0, 1, 2, 4, 8, 12 mM) at 90 °C for 1 h.

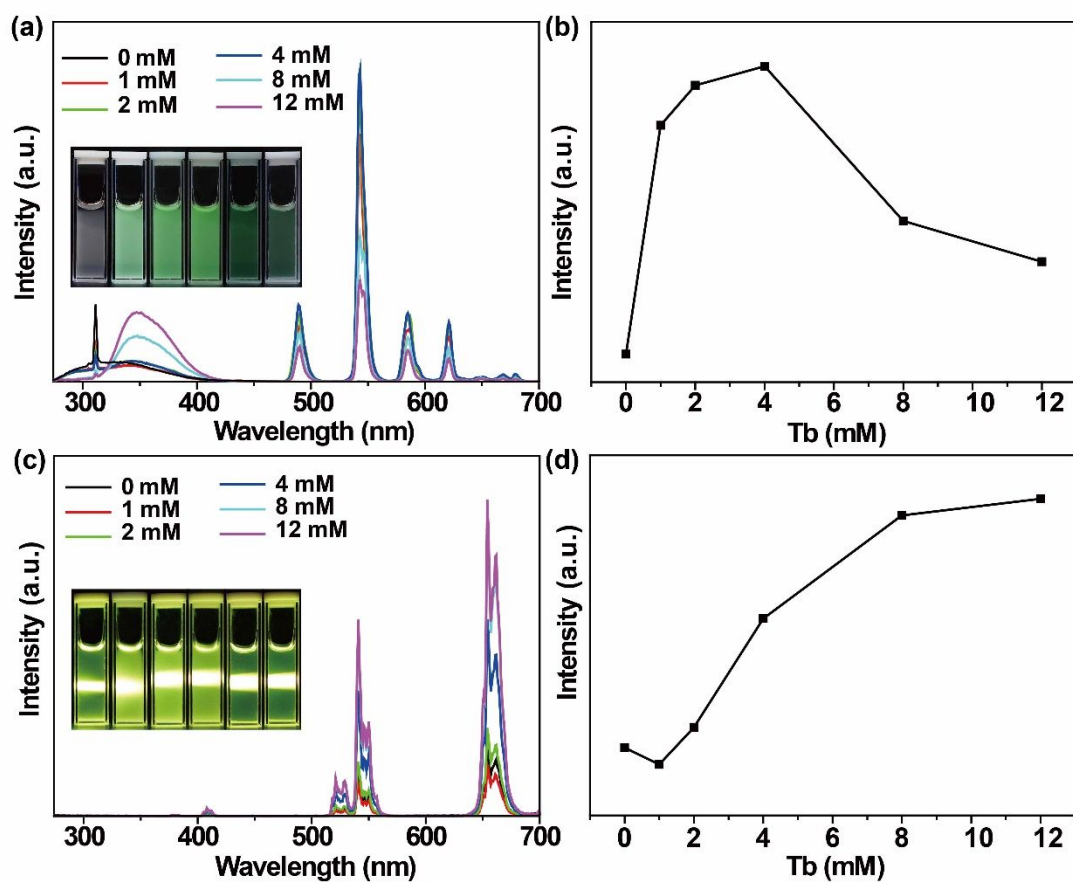


Figure S17. (a) Down-shifting emission profiles of ligand-free NaYF₄:Yb/Er (18/2 mol %)/NaGdF₄ NPs before and after being reacted with a combination of Ce³⁺ (8 mM) and Tb³⁺ (0, 1, 2, 4, 8, 12 mM) at 90 °C for 1 h. (b) The peak emission at 543 nm of the resultant NPs as a function of the concentration of Tb³⁺ ions. (c) Upconversion emission profiles of ligand-free NaYF₄:Yb/Er (18/2 mol %)/NaGdF₄ NPs before and after being reacted with a combination of Ce³⁺ (8 mM) and Tb³⁺ (0, 1, 2, 4, 8, 12 mM) at 90 °C for 1 h. (d) The peak emission at 654 nm of the resultant NPs as a function of the concentration of Tb³⁺ ions.

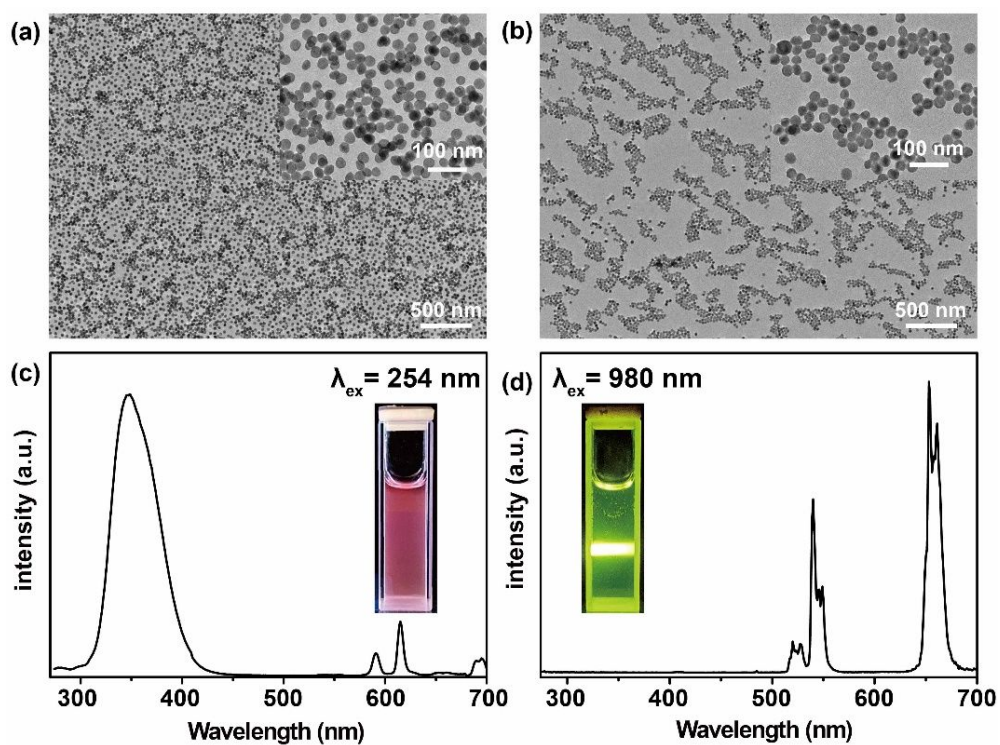


Figure S18. (a) TEM image of ligand-free core@shell $\text{NaYF}_4\text{:Yb/Er (18/2 mol\%)}@ \text{NaGdF}_4$ NPs. (b) TEM image of core@shell $\text{NaYF}_4\text{:Yb/Er (18/2 mol\%)}@ \text{NaGdF}_4\text{:Ce/Eu}$ NPs. (c and d) Downshifting and upconversion profiles for $\text{NaYF}_4\text{:Yb/Er (18/2 mol\%)}@ \text{NaGdF}_4\text{:Ce/Eu}$ NPs. Insets: photographs of the corresponding colloidal dispersions under UV (254 nm) and NIR (980 nm) excitation.

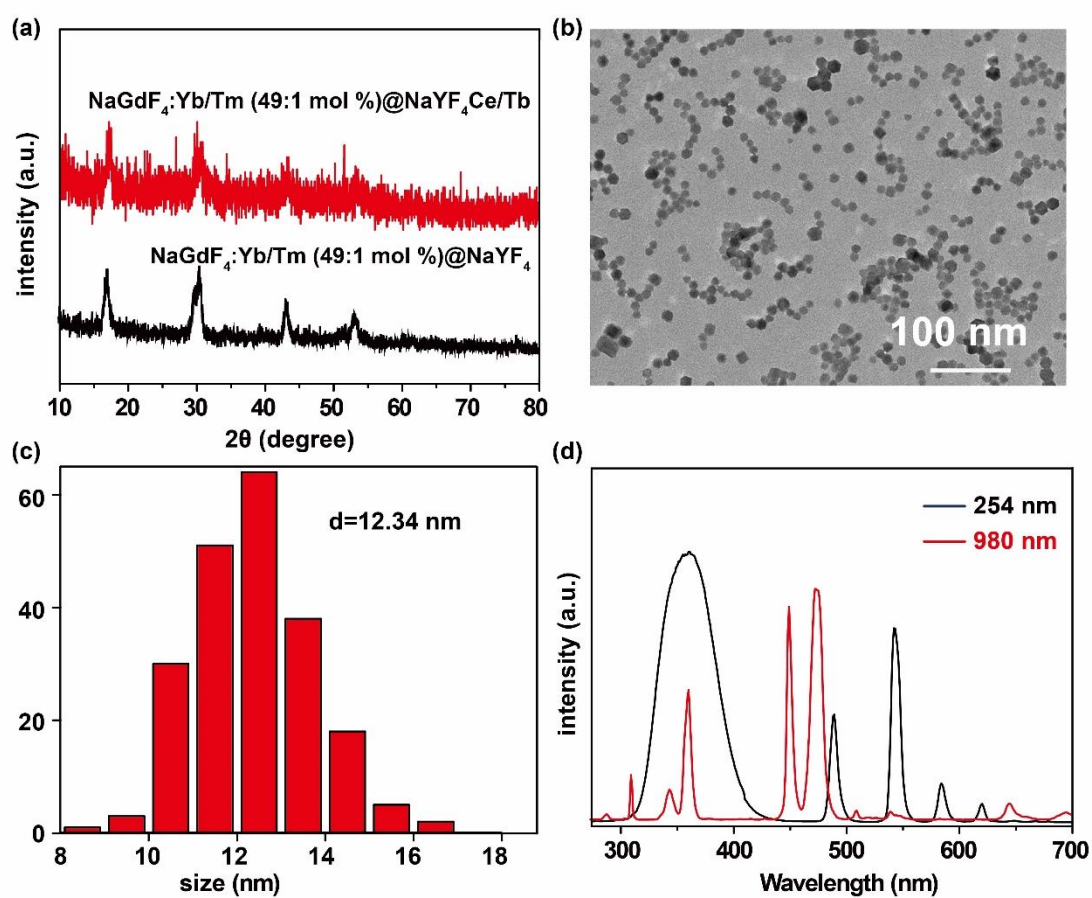


Figure S19. (a) XRD patterns of ligand-free $\text{NaGdF}_4:\text{Yb/Tm}$ (49/1 mol %) $@\text{NaYF}_4$ before and after being reacted with a mixture of Ce^{3+} (8 mM) and Tb^{3+} (12 mM) at 90 °C for 1 h. (b and c) TEM and size distribution of the cation-exchanged $\text{NaGdF}_4:\text{Yb/Tm}$ (49/1 mol %) $@\text{NaYF}_4:\text{Ce/Tb}$ NPs. (d) Upconversion and downshifting emission profiles of the cation-exchanged $\text{NaGdF}_4:\text{Yb/Tm}$ (49/1 mol %) $@\text{NaYF}_4:\text{Ce/Tb}$ NPs.

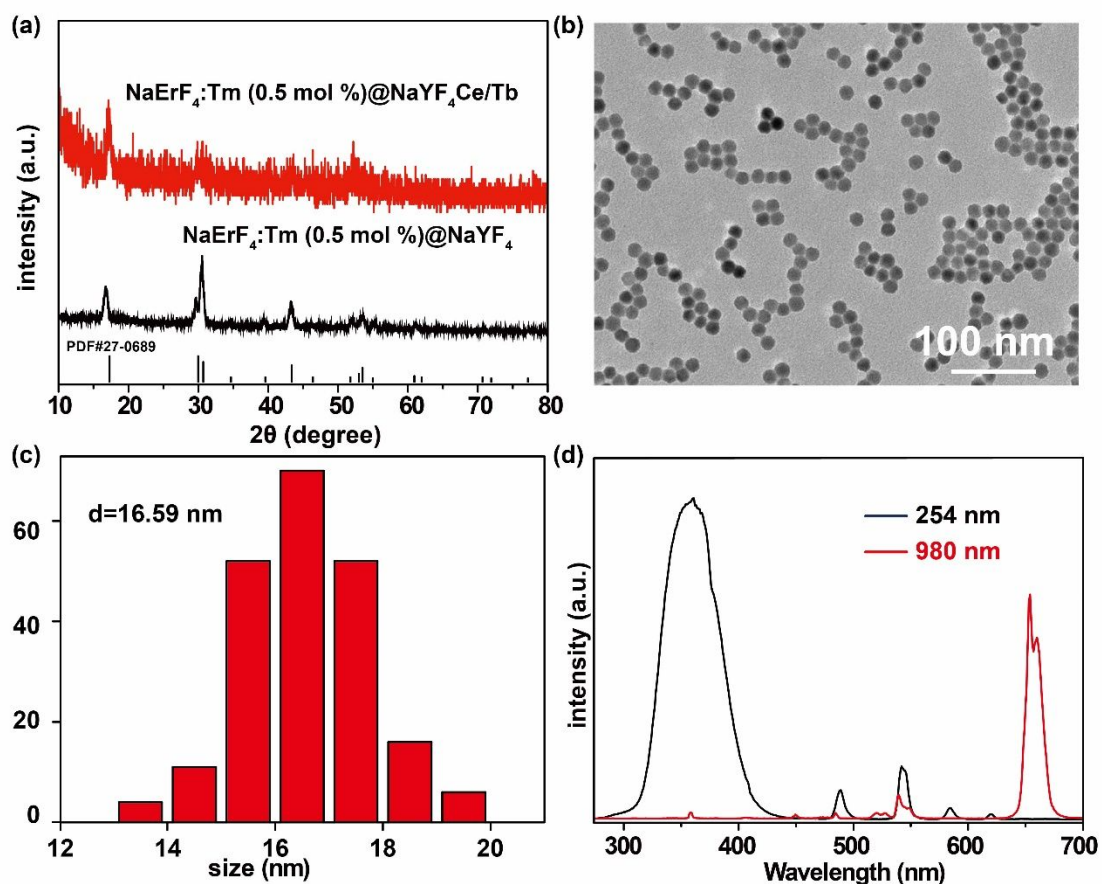


Figure S20. (a) XRD patterns of ligand-free NaErF₄: Tm (0.5 mol %)/NaYF₄ before and after being reacted with a mixture of Ce³⁺ (8 mM) and Tb³⁺ (8 mM) at 90 °C for 1 h. (b and c) TEM and size distribution of the cation-exchanged NaErF₄: Tm (0.5 mol %)/NaYF₄:Ce/Tb NPs. (d) Upconversion and downshifting emission profiles of the cation-exchanged NaErF₄: Tm (0.5 mol %)/NaYF₄:Ce/Tb NPs.