Supporting information

Core-Shell-Shell $NaYbF_4$:Tm@CaF_2@$NaDyF_4$ Nanocomposites for Upconversion/T_2-weighted MRI/ Computed Tomography Lymphatic Imaging

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Synthesis of $NaDyF_4$:Yb,Tm nanoparticles capped with oleic acid (OA-$NaDyF_4$:Yb,Tm). 0.327 mmol $Yb(TFA)_3$, 3 μmol $Tm(TFA)_3$, 0.67 mmol $Dy(TFA)_3$ and 1 mmol NaTFA were added to a 100 mL flask containing 2.84 g oleic acid (OA), 2.67 g oleylamine (OM) and 5.04 g 1-octadecene (ODE). The resulting mixture was heated to 110 ^oC with magnetic stirring to form a transparent solution. The flask was sealed and degassed for 30 min with N_2 gas. The solution was slowly heated to 300 ^oC and maintained for 30 min under the nitrogen environment. Then, the solution was cooled down to room temperature. The $NaDyF_4$:Yb,Tm nanoparticles were collected by centrifugation at 15000 rpm for 10 min and washed several times with ethanol/cyclohexane, after that dispersed in cyclohexane.

Synthesis of core-shell $NaYbF_4$:Tm@$NaDyF_4$ nanoparticles capped with oleic acid (OA-$NaYbF_4$:Tm@$NaDyF_4$). The core-shell $NaYbF_4$:Tm@$NaDyF_4$ nanoparticles were synthesized similarly to that of $NaYbF_4$:Tm@CaF_2. 5 mL as-prepared solution of $NaYbF_4$:Tm nanoparticles dispersed in cyclohexane, and 0.5 mmol $Dy(TFA)_3$ and 0.5 mmol NaTFA were add in a 100 mL flask containing 2.84 g oleic acid (OA), 2.68 g oleylamine (OM) and 5.04 g 1-octadecene (ODE). The mixture was then heated to 110 ^oC for 30 min to remove the cyclohexane. After the cyclohexane was evaporated, the flask was sealed and degassed for 30 min. Subsequently, the reaction was slowly heated to 300 ^oC under the nitrogen environment and kept at it for 8 min, then cooling down to room temperature. The $NaYbF_4$:Tm@CaF_2 nanoparticles were collected by centrifugation at 15000 rpm and washed several times with ethanol/cyclohexane, then dispersed in cyclohexane.

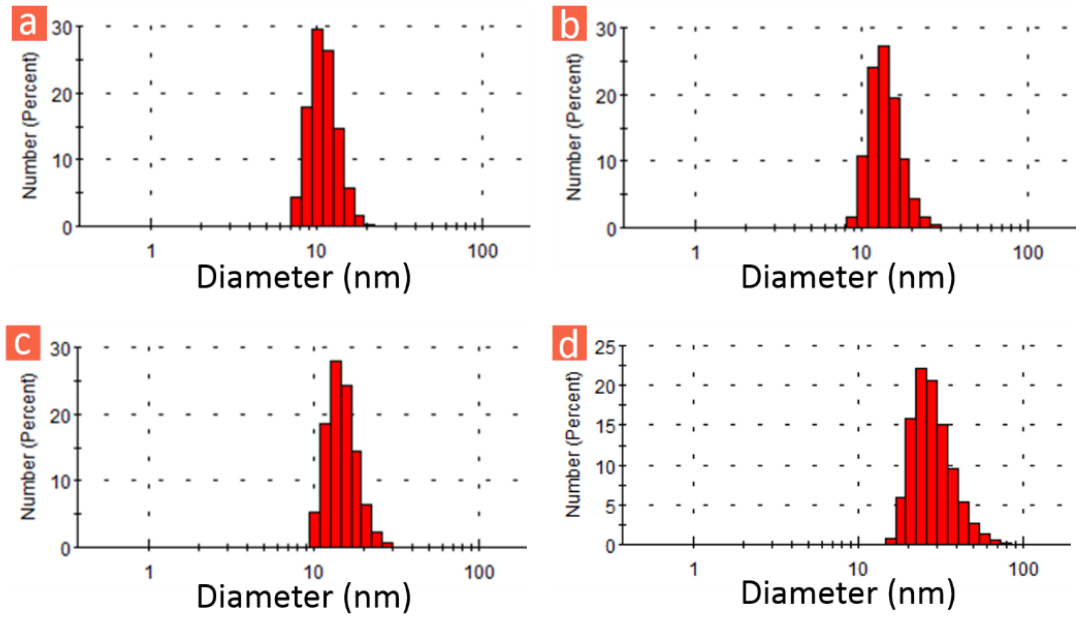

Figure S1. DLS data of these nanoparticles OA-$NaYbF_4$:Tm (a), OA-$NaYbF_4$:Tm@CaF_2 (b), OA-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ and Cit-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ (d).

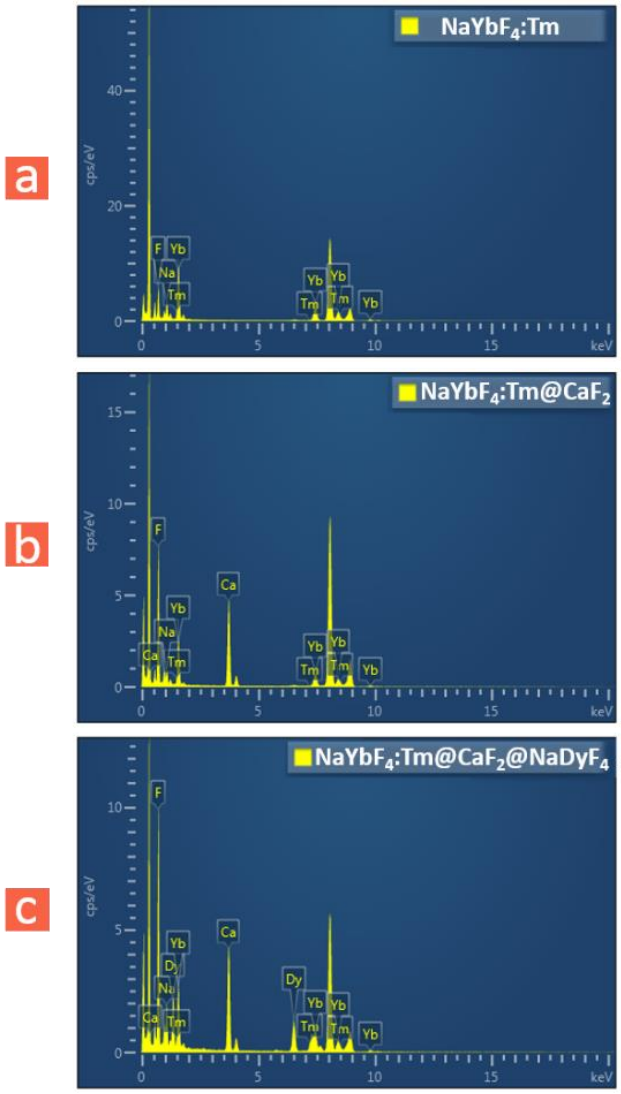

Figure S2. EDXA pattern of these nanoparticles OA-$NaYbF_4$:Tm (a), OA-$NaYbF_4$:Tm@CaF_2 (b), and OA-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ (c).

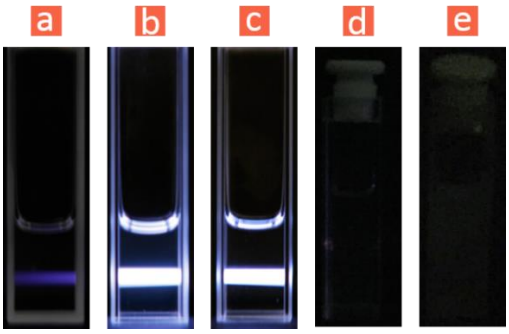

Figure S3. Photograph of the nanoparticles OA-$NaYbF_4$:Tm (a) , OA-$NaYbF_4$:Tm@CaF_2, (b) OA-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ (c), OA-$NaDyF_4$:Yb,Tm (d), OA-$NaYbF_4$:Tm@$NaDyF_4$:Tm (e) in cyclohexane solution under excitation with a 980 nm laser. The Tm^{3+} concentration of all samples was fixed at 1 mg/mL.

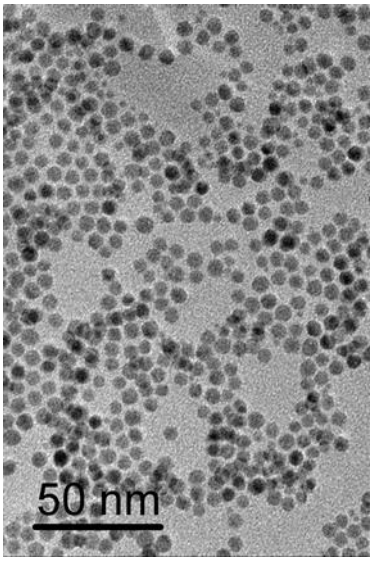

Figure S4. TEM image of the OA-$NaDyF_4$:Yb,Tm nanoparticles.

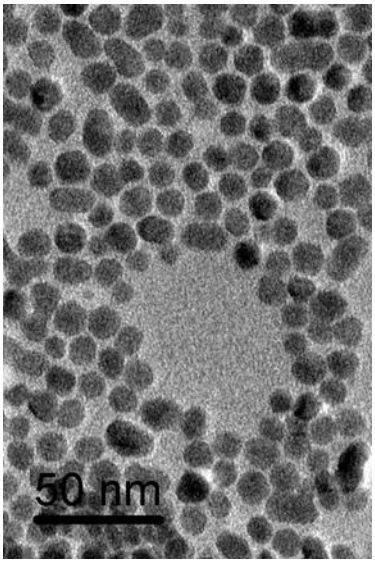

Figure S5. TEM image of the OA-$NaYbF_4$:Tm@$NaDyF_4$ nanoparticles.

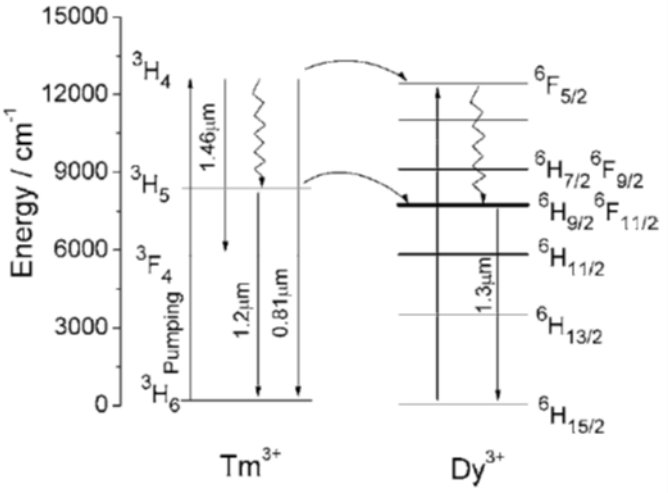

Figure S6. The energy level diagram of Tm^{3+} and Dy^{3+} showing their energy transfer process.

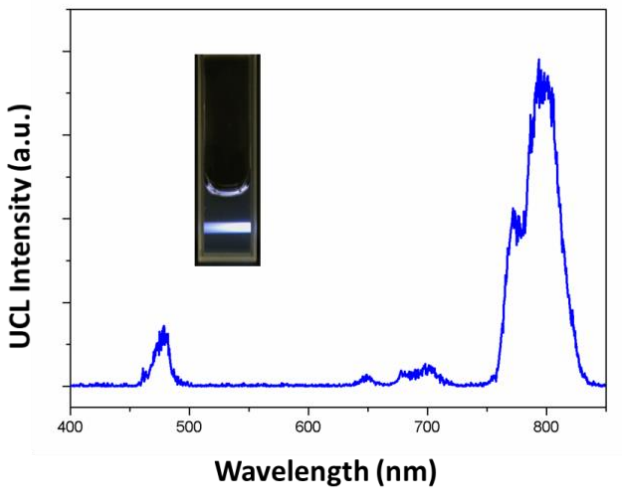

Figure S7. UCL emission spectrum of the nanoparticles Cit-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ dispersed in deionized water under excitation at 980 nm.

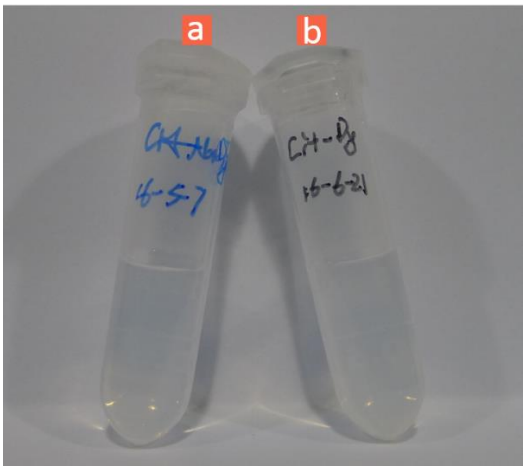

Figure S8. The photo showing the stability of Cit-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ (30 mg/mL) dispersed in water for more than one month.

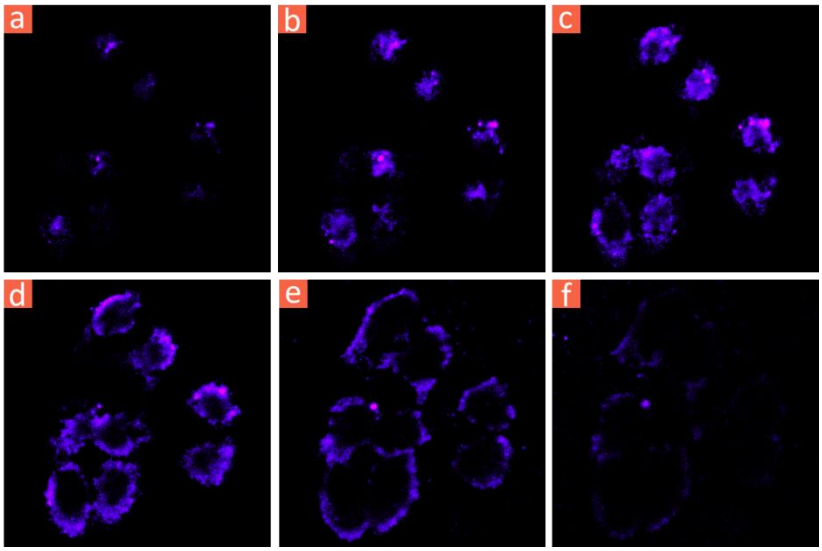

Figure S9. The overlap Z-scan confocal UCL image of the living HeLa cells incubated with 20 μg/mL Cit-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ for 90 min at 37 ^oC (λ_{ex} = 980 nm).

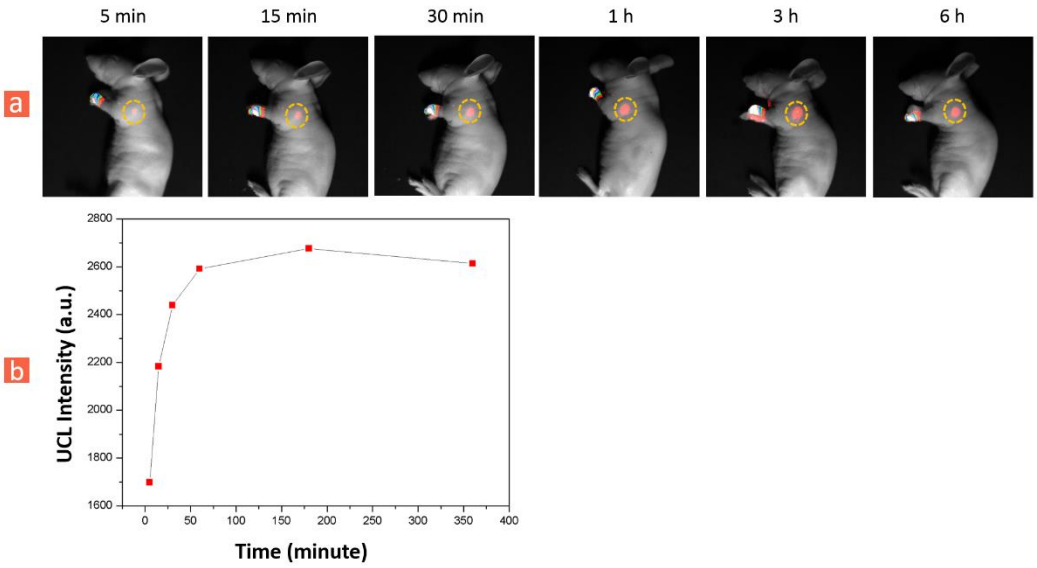

Figure S10. (a) *In vivo* lymphatic drainage of bright-field and UCL imaging overlay images after injection with 50 μL of Cit-$NaYbF_4$:Tm@CaF_2@$NaDyF_4$ nanocomposites (30 mg/mL) on the left forepaw. All images were acquired under the same instrumental conditions. (Power density: 50 mW cm^{-2}. λ_{ex} = 980 nm, λ_{UCL} = 800 $\pm$ 12 nm). (b) Average UCL intensity measured in region of interest (ROI) at 5, 15, 30, 60, 180 and 360 minutes.