

Sensitive Water Probing through Nonlinear Photon Upconversion of Lanthanide-Doped Nanoparticles

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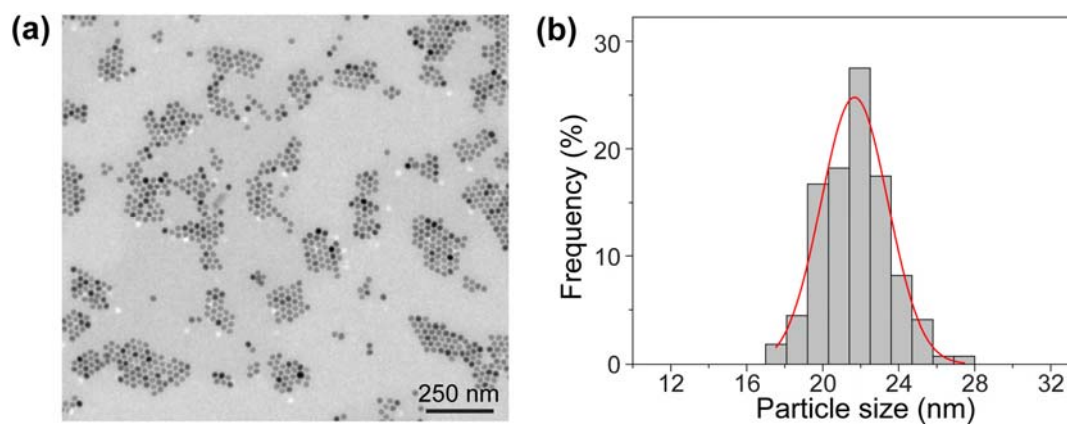


Figure S1. (a) TEM image and (b) corresponding size distribution of the oleic acid capped $\text{NaYF}_4:\text{Yb/Er}(18/2 \text{ mol } \%)$ nanoparticles.

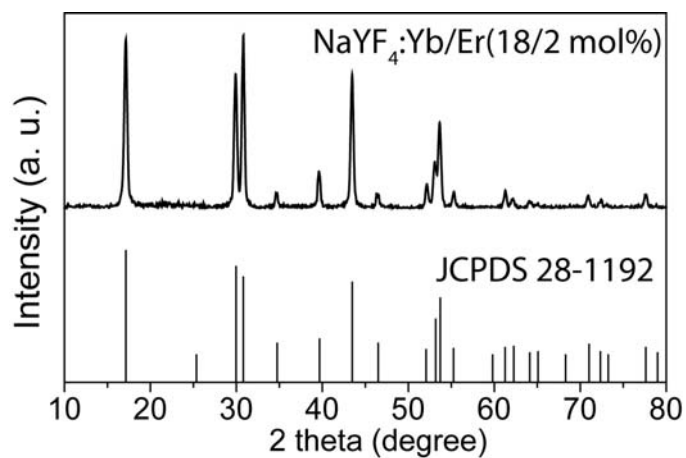


Figure S2. XRD pattern of the as-synthesized $\text{NaYF}_4:\text{Yb/Er}(18/2 \text{ mol } \%)$ nanoparticles. The diffraction pattern at the bottom is the literature reference for hexagonal NaYF_4 crystal (Joint Committee on Powder Diffraction Standards file number 28-1192).

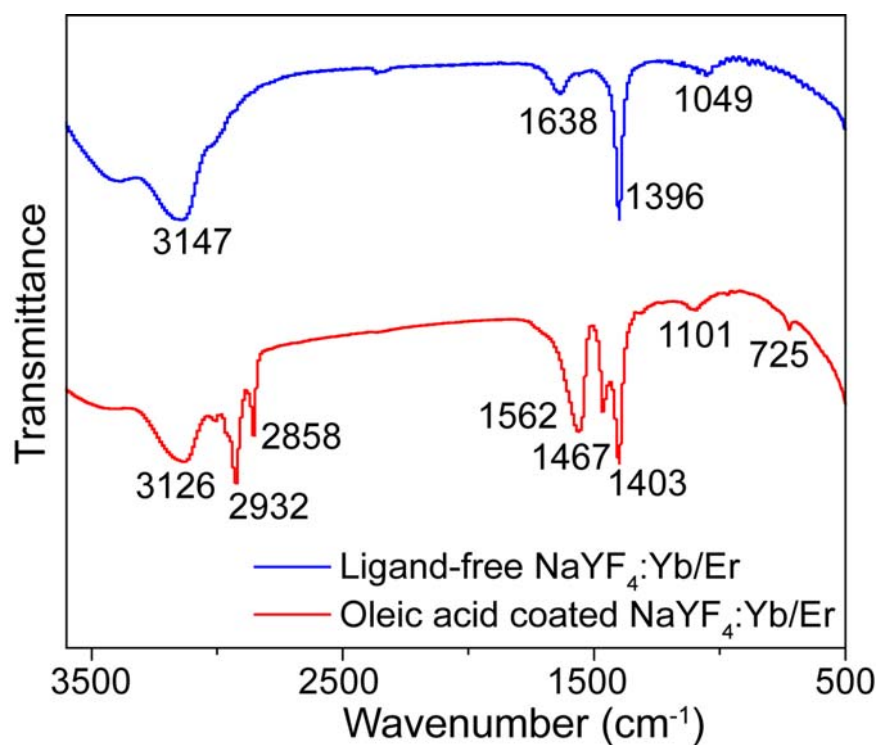


Figure S3. FTIR spectra of oleic acid coated NaYF₄:Yb/Er and corresponding ligand-free nanoparticles, respectively. The disappearance of the peaks at 2932, 2858, 1562, and 1467 cm⁻¹ indicates the successful removal of oleic acid.

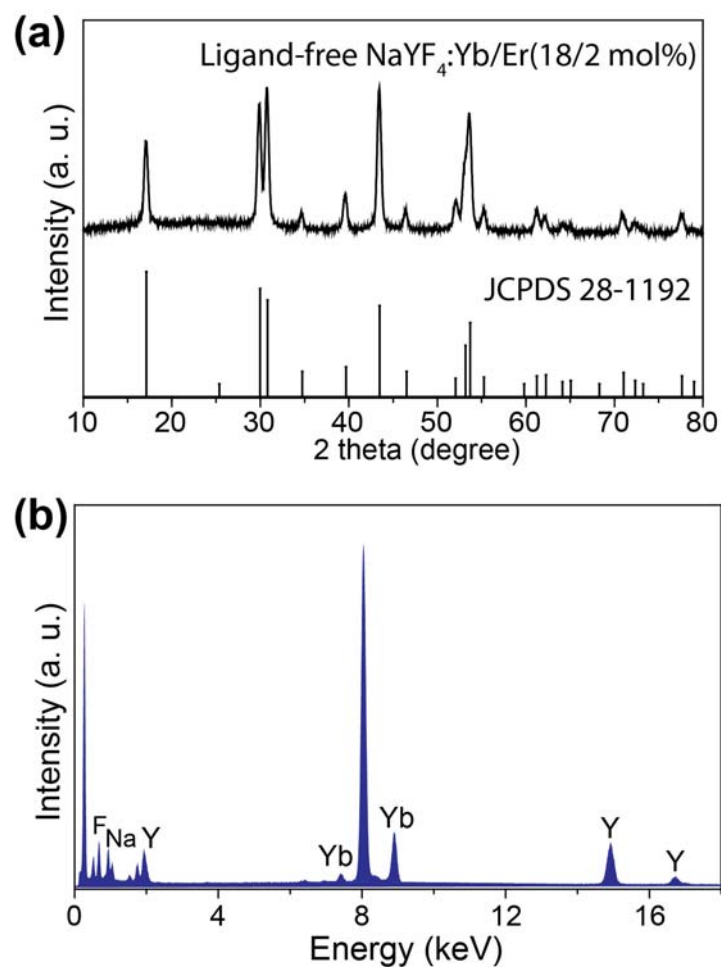


Figure S4. (a) XRD pattern of ligand-free $\text{NaYF}_4\text{:Yb/Er(18/2 mol \%)}$ nanoparticles. The diffraction pattern at the bottom is the literature reference for hexagonal NaYF_4 crystal (Joint Committee on Powder Diffraction Standards file number 28-1192). (b) The energy dispersive X-ray spectrum of the ligand-free $\text{NaYF}_4\text{:Yb/Er(18/2 mol \%)}$ nanoparticles, indicating the existence of Na^+ , F^- , Y^{3+} , and Yb^{3+} .

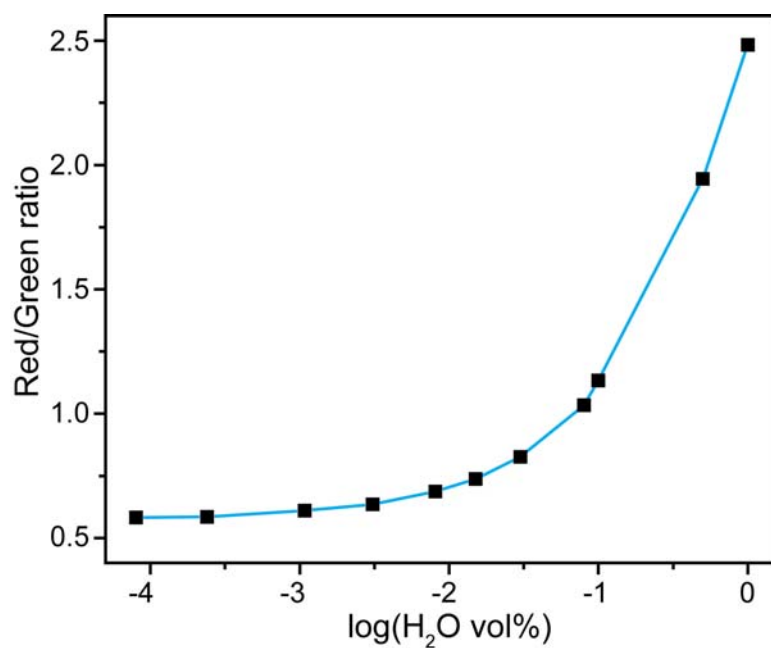


Figure S5. Integrated ratio of red-to-green emission of ligand-free NaYF₄:Yb/Er nanoparticles as a function of H₂O concentration (0.008-100 vol %). The concentration of ligand-free nanoparticles was 0.1 mg/mL. Note that the integrated intensity of red and green emission are from the ²H_{11/2} (⁴S_{3/2}) to ⁴I_{15/2} and ⁴F_{9/2} to ⁴I_{15/2} transitions, respectively.

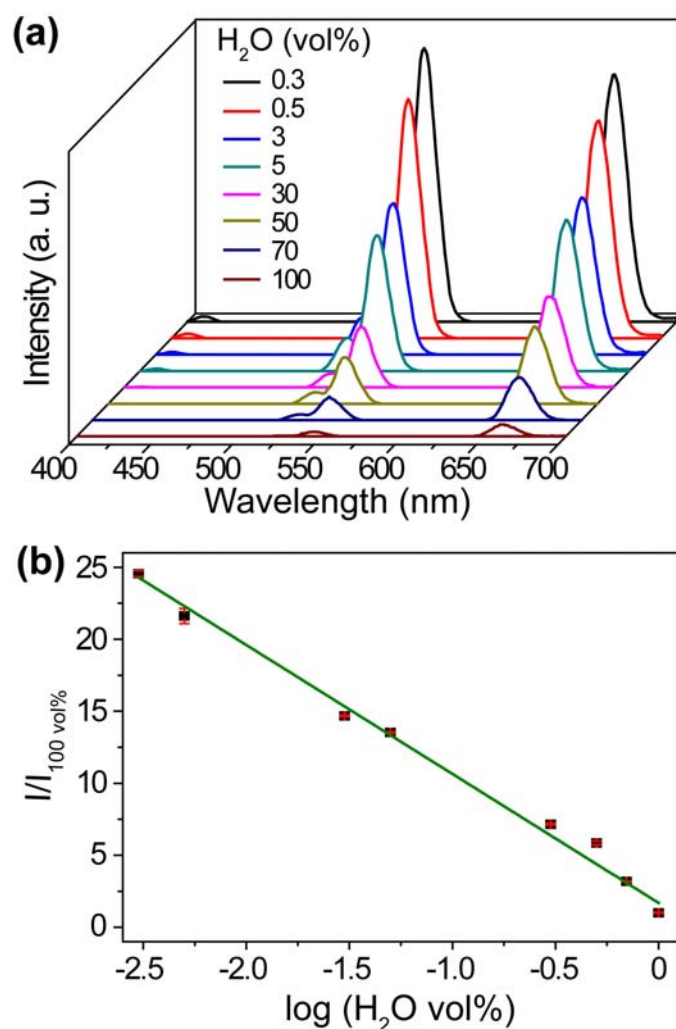


Figure S6. (a) Upconversion emission changes of the redispersed ligand-free NaYF₄:Yb/Er nanoparticles as a function of H₂O concentration (0.3-100 vol %) in DMF. (b) Corresponding relative emission intensity dependence on H₂O concentration. Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. Data are presented as the average from three measurements.

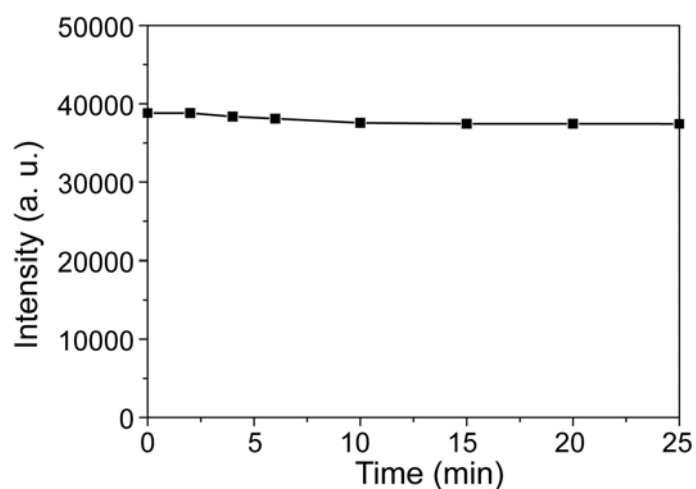


Figure S7. The photoluminescence of ligand-free NaYF₄:Yb/Er nanoparticles in DMF solution containing 10 vol % of water under continuous excitation (980 nm laser) for 25 min.

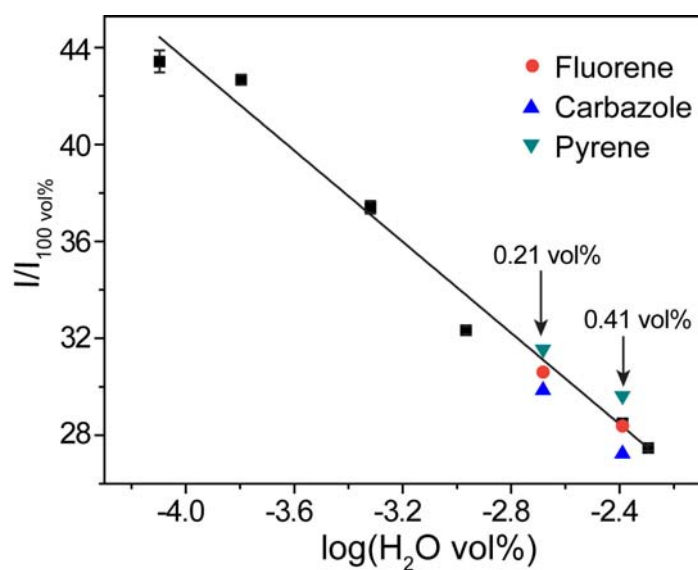


Figure S8. The photoluminescence response of ligand-free NaYF₄:Yb/Er upconversion nanoparticles to DMF solution containing organic dye disruptors (Fluorene: 12 μ M, Carbazole: 24 μ M, Pyrene: 10 μ M). Upconversion emission response to DMF containing both H₂O (0.21 and 0.408 vol %) and organic dyes is almost in line with the calibration curve, indicating small influence of the organic dyes on water probing.

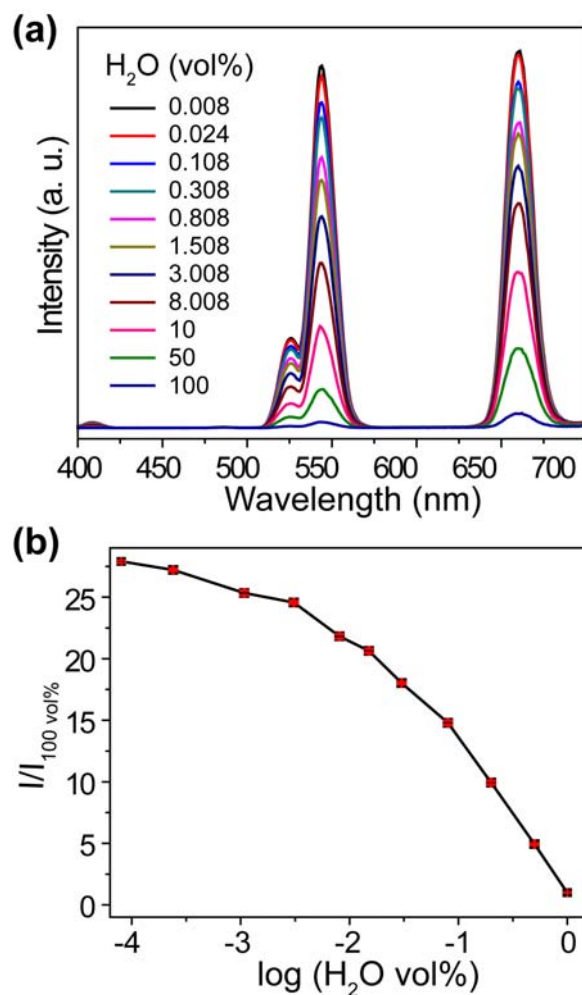


Figure S9. (a) Upconversion emission changes of ligand-free NaYF₄:Yb/Er nanoparticles as a function of H₂O concentration (0.008-100 vol %) in DMSO. (b) Corresponding relative emission intensity dependence on H₂O concentration. Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. The line serves as a guide to the eye and data are presented as the average from three measurements.

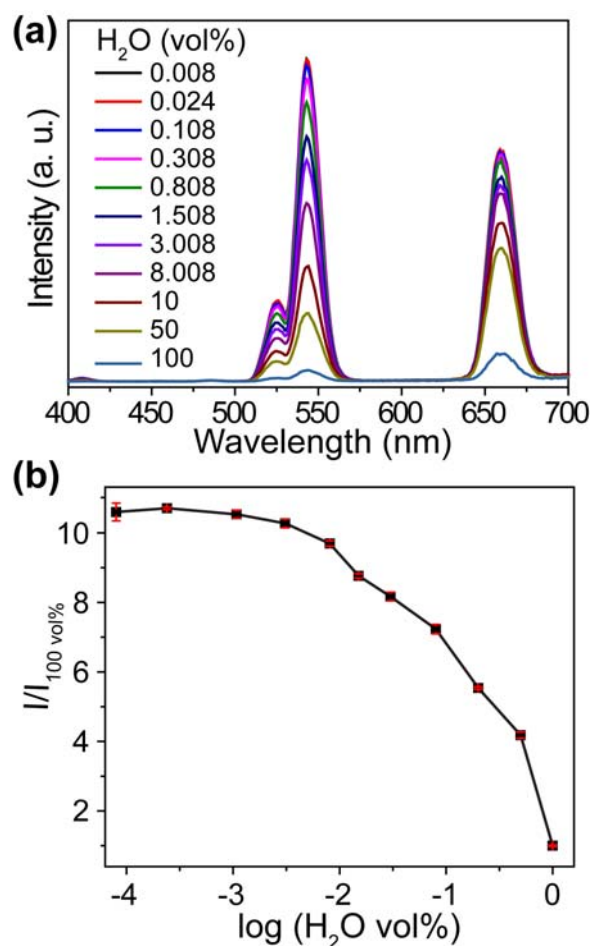


Figure S10. (a) Upconversion emission changes of ligand-free NaYF₄:Yb/Er nanoparticles as a function of H₂O concentration (0.008-100 vol %) in ethanol. (b) Corresponding relative emission intensity dependence on H₂O concentration. Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. The line serves as a guide to the eye and data are presented as the average from three measurements.

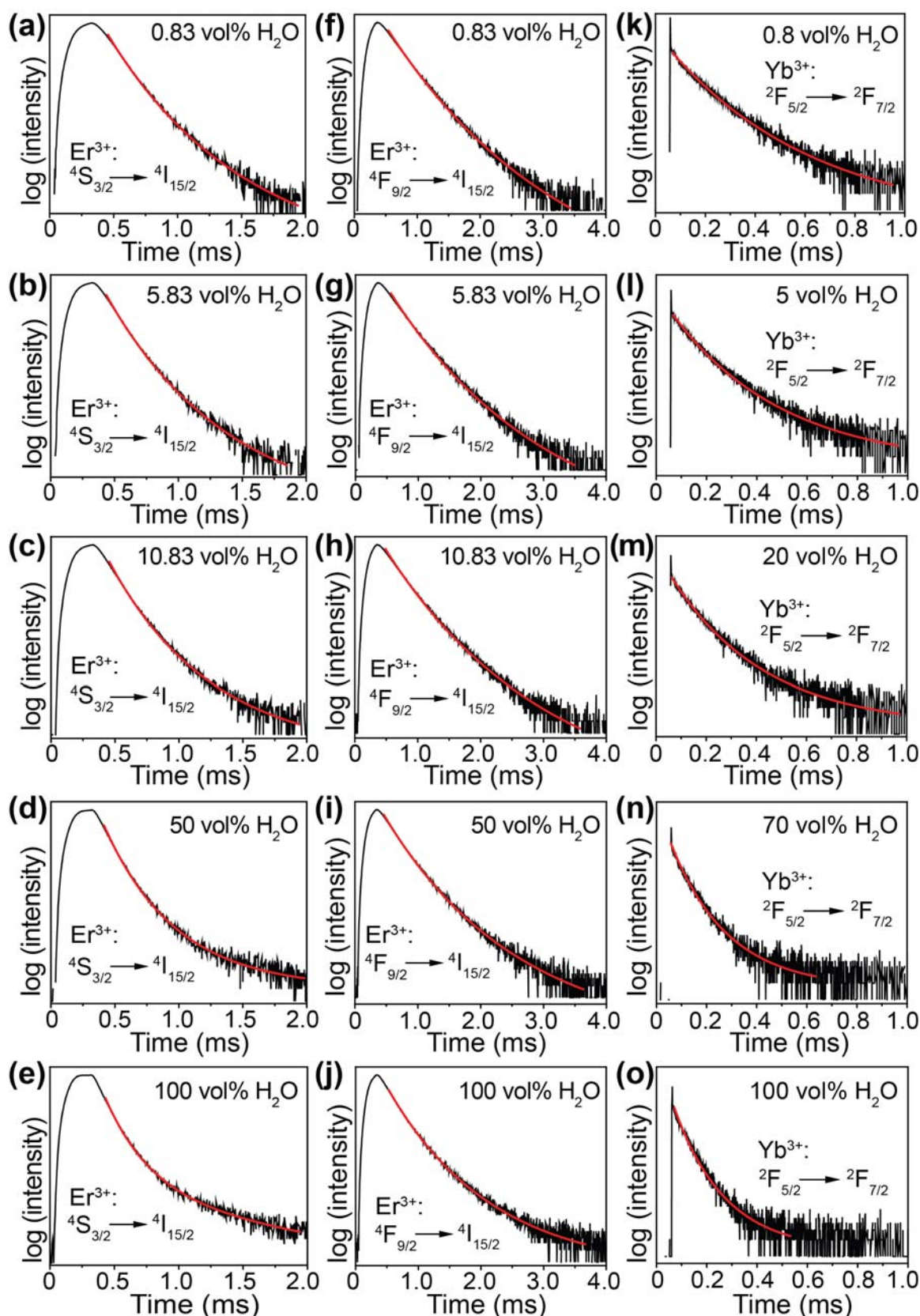


Figure S11. Upconversion luminescence decay curves of ligand-free NaYF₄:Yb/Er nanoparticles dispersed in DMF containing varied water content. (a-j) Decay curves of Er³⁺ measured at (a-e) 540 and (f-j) 654 nm (excitation: 980 nm), respectively. The water

concentration was 0.83, 5.83, 10.83, 50 and 100 vol %, respectively. (k-o) Decay curves of Yb^{3+} measured at 985 nm (excitation: 975 nm). The water concentration was 0.8, 5, 20, 70 and 100 vol %, respectively. Note that the red curve in each profile is the fitting curve.

Table S1. Decay time of Er^{3+} emission transitions in ligand-free $\text{NaYF}_4:\text{Yb}/\text{Er}$ nanoparticles^a

Water content (vol%)	Lifetime of green emission (μs)	Lifetime of red emission (μs)
0.83	τ_1 : 96 (97.6%), τ_2 : 270 (2.4%)	τ_1 : 200 (97.7%), τ_2 : 960 (2.3%)
5.83	τ_1 : 84 (97.1%), τ_2 : 160 (10.9%)	τ_1 : 190 (94.5%), τ_2 : 480 (5.5%)
10.83	τ_1 : 77 (80.3%), τ_2 : 140 (19.7%)	τ_1 : 190 (93.3%), τ_2 : 420 (6.7%)
50	τ_1 : 69 (85.2%), τ_2 : 150 (14.8%)	τ_1 : 170 (83.3%), τ_2 : 320 (16.7%)
100	τ_1 : 64 (84.4%), τ_2 : 150 (15.6%)	τ_1 : 140 (76.3%), τ_2 : 280 (23.7%)

^aThe decay curves were analyzed and fitted by XPFit fitting software.

Table S2. Decay time of Yb^{3+} emission in ligand-free $\text{NaYF}_4:\text{Yb}/\text{Er}$ nanoparticles^a

Water content (vol%)	Lifetime of Yb^{3+} (μs)
0.8	89
5	82
20	74
70	56
100	50

^aThe decay curves were analyzed and fitted by XPFit fitting software.

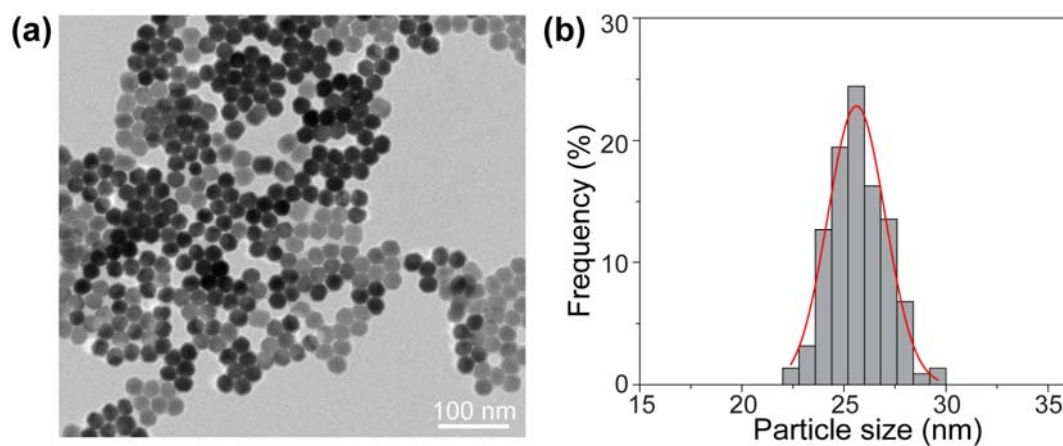


Figure S12. (a) TEM image and (b) corresponding size distribution of the ligand-free $\text{NaYF}_4:\text{Yb/Er}(18/2 \text{ mol } \%)\text{@NaYF}_4$ core-shell nanoparticles.

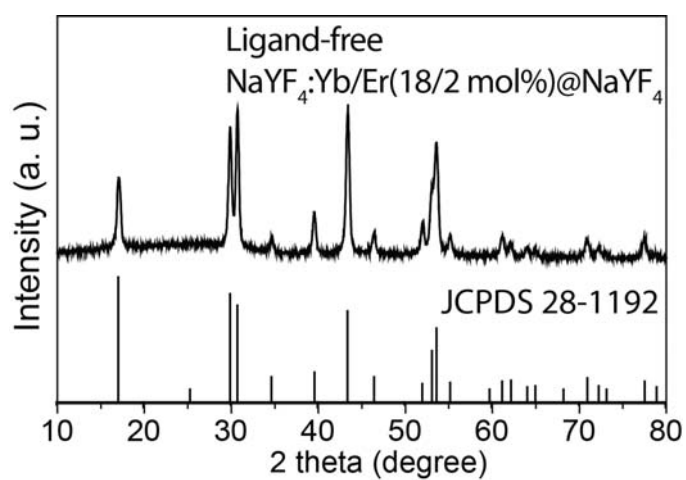


Figure S13. XRD pattern of ligand-free $\text{NaYF}_4:\text{Yb/Er}(18/2 \text{ mol } \%)\text{@NaYF}_4$ core-shell nanoparticles. The diffraction pattern at the bottom is the literature reference for hexagonal NaYF_4 crystal (Joint Committee on Powder Diffraction Standards file number 28-1192).

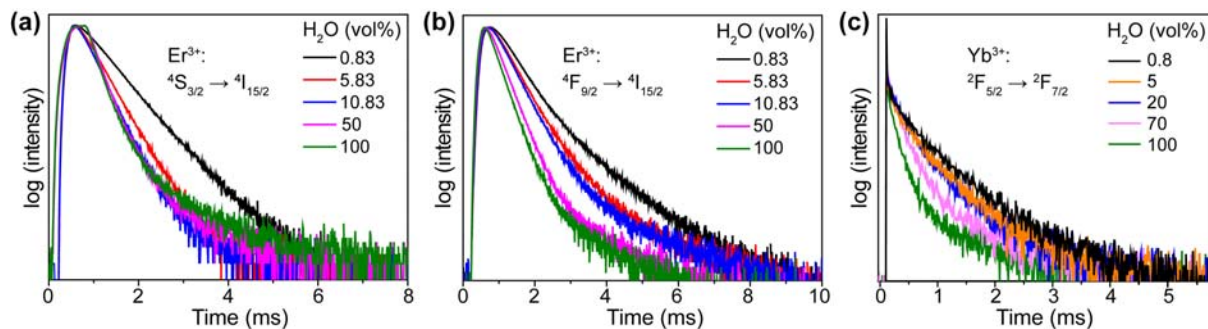


Figure S14. Upconversion luminescence decay curves of ligand-free NaYF₄:Yb/Er@NaYF₄ core-shell nanoparticles dispersed in DMF containing varied water contents. (a, b) Decay curves of Er³⁺ measured at 540 nm and 654 nm (excitation: 980 nm), respectively. The water concentration was 0.83, 5.83, 10.83, 50 and 100 vol %, respectively. (c) Decay curves of Yb³⁺ measured at 985 nm (excitation: 975 nm). The water concentration was 0.8, 5, 20, 70 and 100 vol %, respectively.

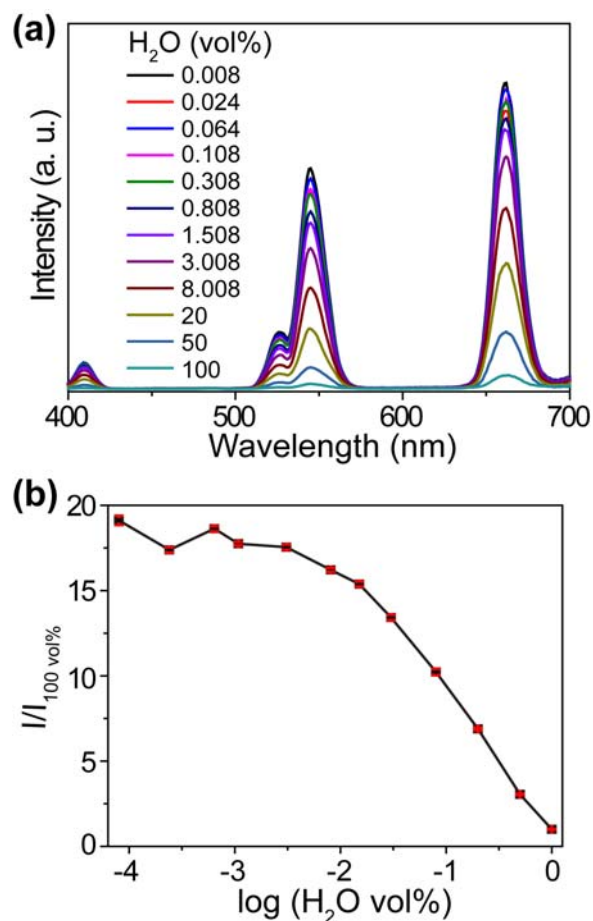


Figure S15. (a) Upconversion emission changes of ligand-free NaYF₄:Yb/Er@NaYF₄ core-shell nanoparticles as a function of H₂O concentration (0.008-100 vol %) in DMF. (b) Corresponding emission intensity dependence on H₂O concentration. Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. The line serves as a guide to the eye and data are presented as the average from three measurements.

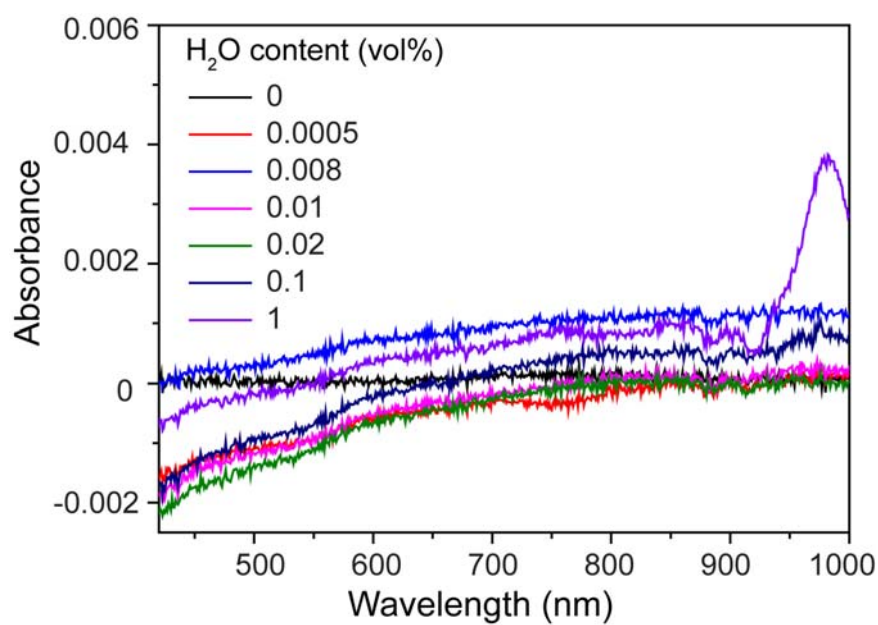


Figure S16. Absorption spectra of DMF containing varied water content (0-1 vol %).

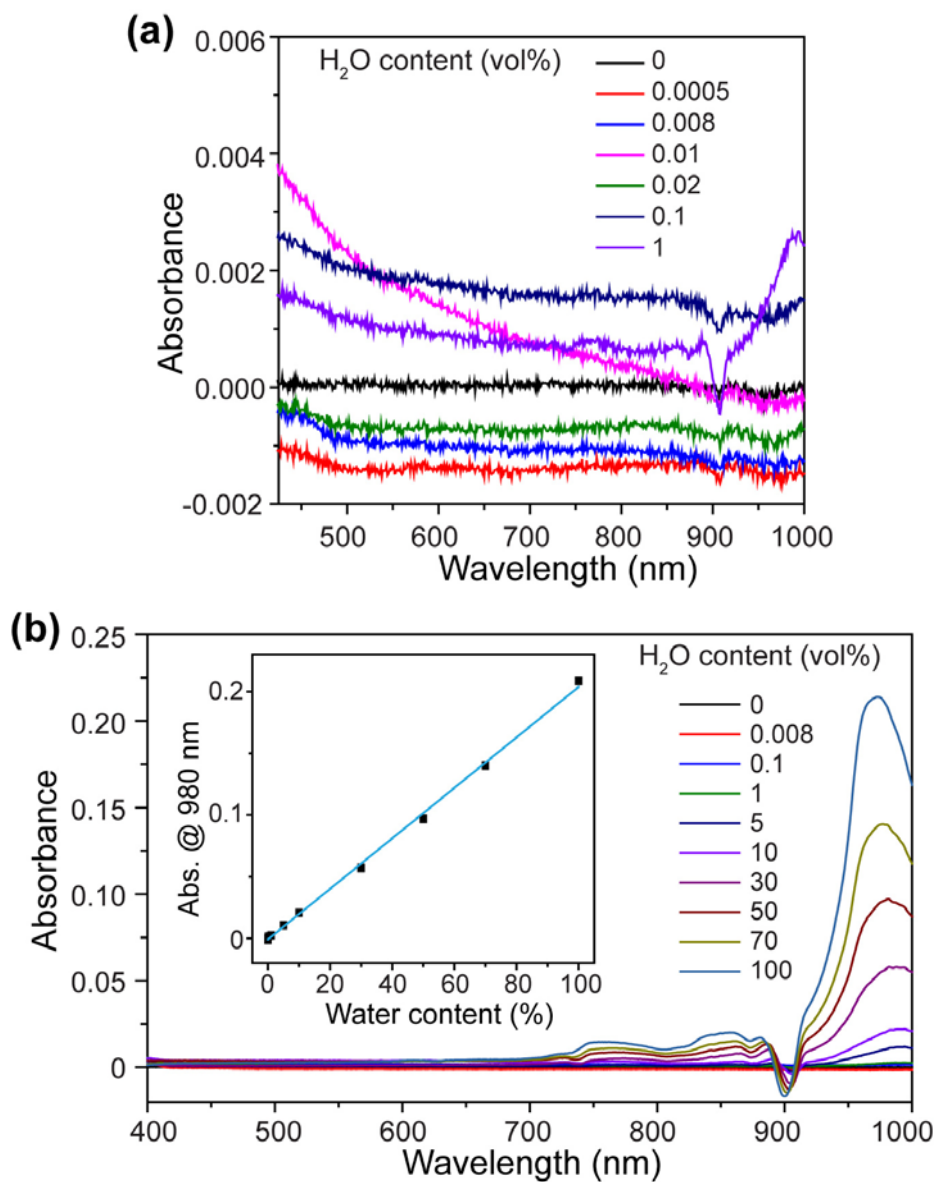


Figure S17. Absorption spectra of DMSO containing varied water content: (a) water content ranging from 0 to 1 vol %; (b) water content ranging from 0 to 100 vol %. The inset in (b) is corresponding absorbance at 980 nm as a function of water content.

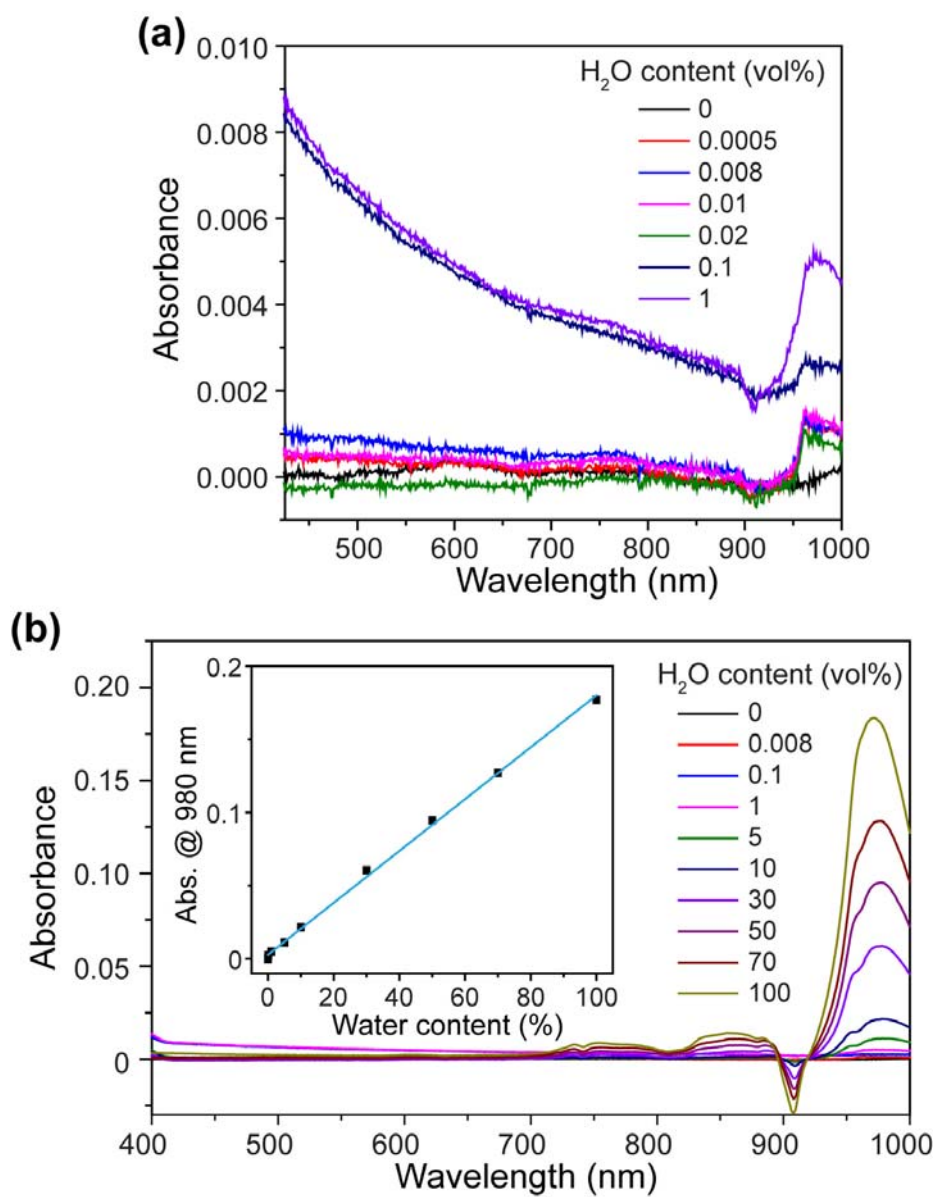


Figure S18. Absorption spectra of ethanol containing varied water content: (a) water content ranging from 0 to 1 vol %; (b) water content ranging from 0 to 100 vol %. The inset in (b) is corresponding absorbance at 980 nm as a function of water content.

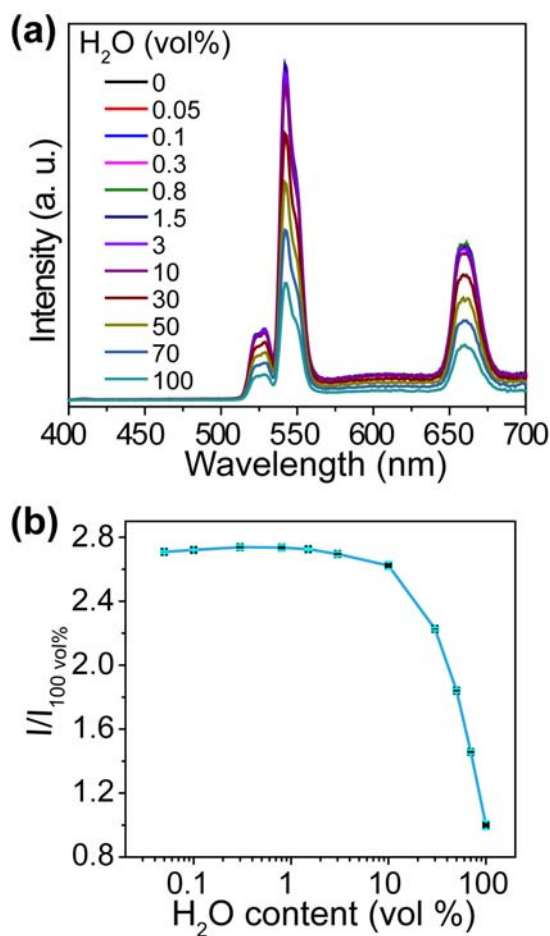


Figure S19. (a) Upconversion emission changes of NaYF₄:Yb/Er@NaYF₄ core-shell nanoparticles as a function of H₂O concentration (0-100 vol %) in DMSO utilizing noncontact method. (b) Corresponding emission intensity dependence on H₂O concentration (0.05-100 vol %). Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. The line serves as a guide to the eye and data are presented as the average from three measurements.

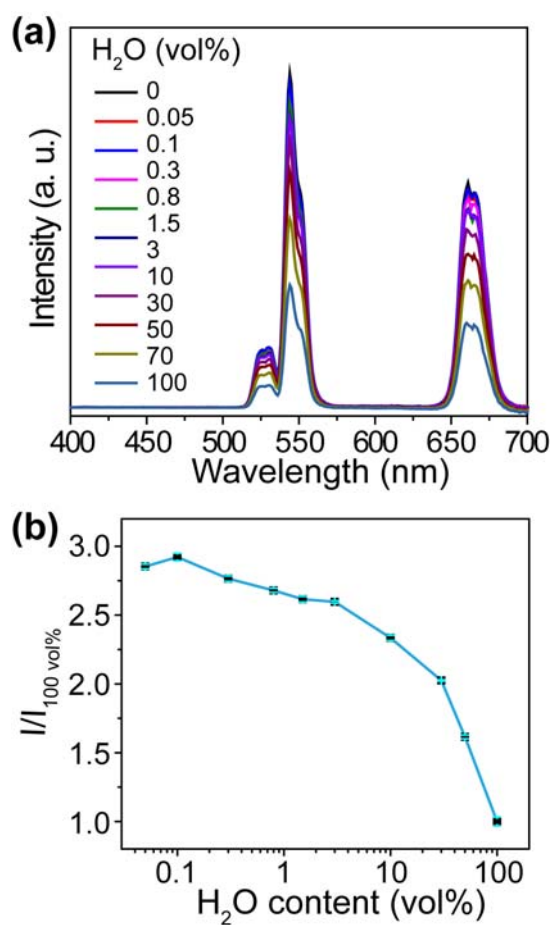


Figure S20. (a) Upconversion emission changes of NaYF₄:Yb/Er@NaYF₄ core-shell nanoparticles as a function of H₂O concentration (0-100 vol %) in ethanol utilizing noncontact method. (b) Corresponding emission intensity dependence on H₂O concentration (0.05-100 vol %). Note that the emission intensity was obtained by integrating the emission from 400 to 700 nm. The line serves as a guide to the eye and data are presented as the average from three measurements.