Supporting Information

Multifunctional nanomesoporous materials with upconversion (in vivo) and downconversion (in vitro) luminescence imaging based on mesoporous capping UCNPs and linking lanthanide complexes

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1. Synthesis of NaYF₄:Yb,Tm and NaYF₄:Yb,Tm@NaGdF₄ nanocrystals (NaYF₄:Yb,Tm@NaGdF₄ named as UCNPs)

In details, YCl₃ (1.56 mmol, 78%), YbCl₃ (0.4 mmol, 20%), and TmCl₃ (0.04 mmol, 2%) in deionized water were added to a 100 mL flask and the solution heating to 110 °C to evaporate water until the solution became white powder. Then, 12 mL OA and 30 mL ODE were added in. The mixture was heated to 150 °C to form a homogeneous transparent solution, and then cooled to room temperature. 20 mL methanol solution containing NaOH (0.2 g, 1.6 mmol) and NH₄F (0.3 g, 8 mmol) was added into the flask and stirred for a while at 100 °C. After methanol was evaporated, the solution was heated to 300 °C and kept for 1 h under argon atmosphere and then cooled to room temperature. The obtained mixture was precipitated by the addition of acetone, separated by centrifugation, washed with cyclohexane. The sample NaYF₄:Yb,Tm was redispersed in 20 mL cyclohexane.

For the synthesis of NaYF₄:Yb,Tm@NaGdF₄ nanocrystals, the process was similar with above method. 800 μmol GdCl₃ water solution was added to a 100 mL flask, and then heated to 110 °C to evaporate the water. 12 mL oleic acid and 30 mL 1-octadecene were added in, when the solution became white powder. The mixture was heated to 150 °C to form a homogeneous transparent solution, and then cooled to room temperature. 5 mL pre-prepared NaYF₄:Yb,Tm was added to above mixture and kept for another 30 min before heated to 90 °C to remove cyclohexane. 1.25 mL methanol solution of NH₄F (0.039 g, 1.05 mmol) and NaOH (0.067 g, 1.68 mmol) was added and the solution was stirred at 100 °C for a while. After methanol was evaporated, the solution was heated to 300 °C and kept for 1 h under argon atmosphere and then cooled to room temperature. After centrifugation and washing, the final product was redispersed in 10 mL cyclohexane and denoted as UCNPs.

2. Synthesis of mesoporous SiO₂ coated UCNPs nanocomposite spheres (denoted as UCNPs@mSiO₂)

2 mL UCNPs cyclohexane solution (5 mg/mL) was mixed with 20 mL water and 0.1 g CTAB, the mixture was then stirred vigorously to evaporate the cyclohexane
solvent at room temperature, resulting in a transparent UCNPs/CTAB water solution (0.5 mg/mL). The excess amount of CTAB must be removed via decreasing the temperature to 0 °C and centrifuging. Then, 20 mL water, 3 mL ethanol and 150 μL NaOH solution (2 M) were added in above 10 mL UCNPs/CTAB water solution, and then heated to 70 °C. When the temperature was stable, 200 μL TEOS was added dropwise and the reaction mixture was stirred for 2 h. The product was washed 3 times with ethanol and dispersed in 10 mL of ethanol. The template CTAB was removed by a fast and efficient ion exchange method. 90 mL ethanol solution containing 0.6 g of NH₄NO₃ was mixed with the as-synthesized UCNPs@mSiO₂ (10 mL) and kept at 60 °C for 2 h under stirring. The final product was washed with ethanol and redispersed in 10 mL of ethanol.

3. Synthesis of β-Diketonate-Functionalized Alkoxy-Silane (dbm-Si)

The dibenzoylmethane was dissolved in 40 mL dehydrate THF, and NaH was added (dibenzoylmethane/NaH = 1:2, molar ratio) with stirring. After 2 h, TEPIC was added the refluxing solution with a molar ratio of 1:1. The mixture was refluxed at 70 °C for 12 h under an argon atmosphere. Then, the solvent was distilled off under reduced pressure, yielding the alkoxy silane modified dibenzoylmethane: a yellow solid, named as dbm-Si.

4. Synthesis of Ln(dbm)₃(H₂O)₂ Complexes (Ln=Eu, Sm, Er, Nd, Yb)

A certain amount of Hdbm was dissolved in ethanol, and the pH value was adjusted to approximately 7 with an appropriate amount of sodium hydroxide solution (1 M). The LnCl₃ ethanol solution was added into this mixture under stirring (LnCl₃:dbm = 1:3, molar ratio). Then an appropriate amount of water was added. The mixture was heated to 85 °C and refluxed for 6 h, then cooled to room temperature. The precipitates were collected by filtration, washed with water and ethanol, and dried at 50 °C.
Fig. S1. The XRD patterns of NaYF$_4$:Yb,Tm, UCNPs, UCNPs@mSiO$_2$, UCNPs@mSiO$_2$-Eu(dbm)$_4$, and the standard card of β-NaYF$_4$ (JCPDS: 16-0334).
Fig. S2. energy dispersive X-ray (EDX) spectrum of UCNPs@mSiO$_2$-Eu(dbm)$_4$. 
**Fig. S3.** The low-angle XRD patterns of UCNPs@mSiO$_2$ and UCNPs@mSiO$_2$-Eu(dbm)$_4$. 

![Graph showing XRD patterns](image-url)
**Fig. S4.** $N_2$ adsorption-desorption isotherms of UCNP@mSiO$_2$ and UCNP@mSiO$_2$-Eu(dbm)$_4$. 
Fig. S5. The pore size distribution of UCNPs@mSiO₂ and UCNPs@mSiO₂-Eu(dbm)₄.
**Fig. S6.** FT-IR spectra of the UCNPs (a); UCNPs@mSiO$_2$ (b); UCNPs@mSiO$_2$-dbm (c); UCNPs@mSiO$_2$-Eu(dbm)$_4$ (d).
Fig. S7. FTIR spectra of the UCNPs@mSiO$_2$-Sm(dbm)$_4$ (a); UCNPs@mSiO$_2$-Er(dbm)$_4$ (b); UCNPs@mSiO$_2$-Nd(dbm)$_4$ (c); UCNPs@mSiO$_2$-Yb(dbm)$_4$ (d).
Fig. S8. Upconversion luminescence spectra of UCNPs@mSiO$_2$-Sm(dbm)$_4$, UCNPs@mSiO$_2$-Er(dbm)$_4$, UCNPs@mSiO$_2$-Nd(dbm)$_4$, and UCNPs@mSiO$_2$-Yb(dbm)$_4$. 
Fig. S9. Visible emission ($\lambda_{ex} = 401$ nm) spectrum (a) and NIR emission ($\lambda_{ex} = 401$ nm) spectrum (b) of UCNPs@mSiO$_2$-Sm(dbm)$_4$. The visible and NIR emissions both come from the $^4G_{5/2}$ excited state.
**Fig. S10.** Bright-field photos and phosphorescence photos of UCNPs@mSiO$_2$-Eu(dbm)$_4$ under blue LED illumination (peak at 405 nm) in pure water, PBS and RPMI 1640 culture solution.
Fig. S11. The emission spectra of UCNPs@mSiO$_2$-Eu(dbm)$_4$ in water as a function of time (inset, time-dependent luminescence at 613 nm), $\lambda_{ex} = 405$ nm.