

## 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 NaYF<sub>4</sub>:Yb,Tm and NaYF<sub>4</sub>:Yb,Tm@NaGdF<sub>4</sub> nanocrystals (NaYF<sub>4</sub>:Yb,Tm@NaGdF<sub>4</sub> named as UCNPs)**

In details, YCl<sub>3</sub> (1.56 mmol, 78%), YbCl<sub>3</sub> (0.4 mmol, 20%), and TmCl<sub>3</sub> (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 NH<sub>4</sub>F (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 NaYF<sub>4</sub>:Yb,Tm was redispersed in 20 mL cyclohexane.

For the synthesis of NaYF<sub>4</sub>:Yb,Tm@NaGdF<sub>4</sub> nanocrystals, the process was similar with above method. 800 μmol GdCl<sub>3</sub> 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 NaYF<sub>4</sub>: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 NH<sub>4</sub>F (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 SiO<sub>2</sub> coated UCNPs nanocomposite spheres (denoted as UCNPs@mSiO<sub>2</sub>)**

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

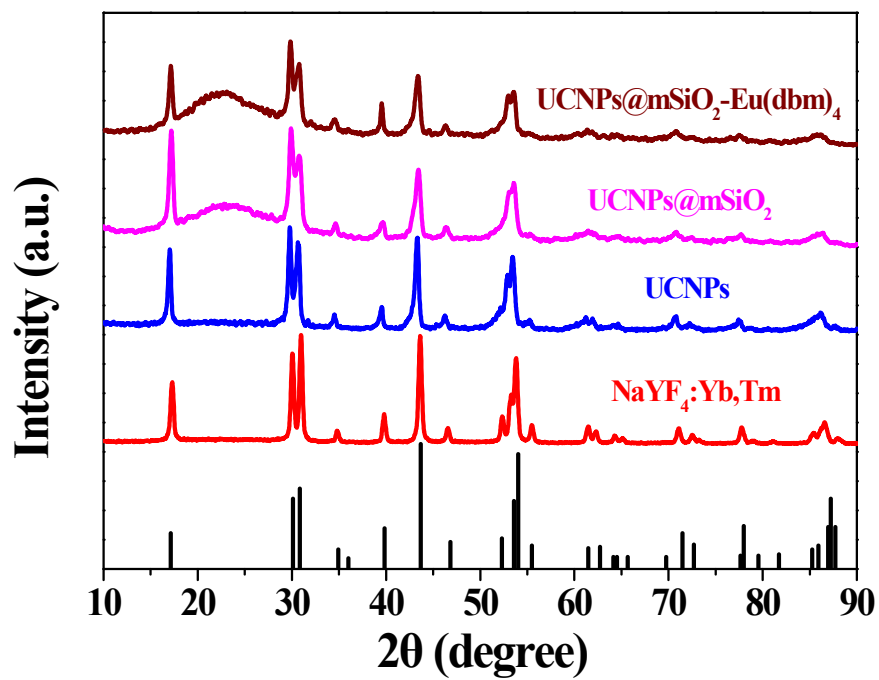
solvent at room temperature, resulting in a transparent UCNPs/CTAB water solution (0.5 mg/mL). The excess amount of CTAB must be removed via decreasing the temperature to 0 °C and centrifuging. Then, 20 mL water, 3 mL ethanol and 150  $\mu$ L NaOH solution (2 M) were added in above 10 mL UCNPs/CTAB water solution, and then heated to 70°C. When the temperature was stable, 200  $\mu$ L 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  $\text{NH}_4\text{NO}_3$  was mixed with the as-synthesized UCNPs@mSiO<sub>2</sub> (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 $\beta$ -Diketonate-Functionalized Alkoxy-Silane (dbm-Si)**

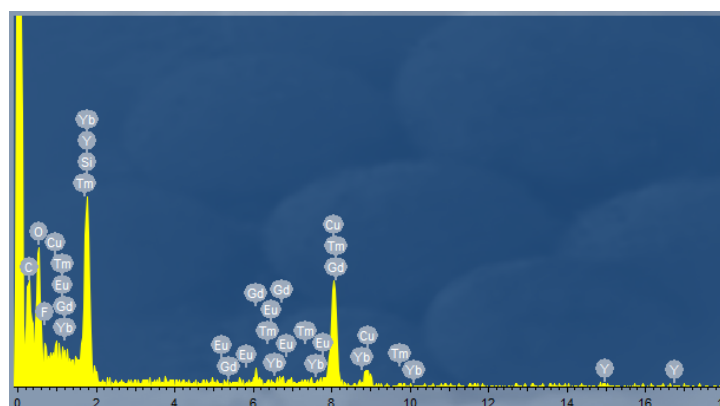
The dibenzoylmethane was dissolved in 40 mL dehydrate THF, and NaH was added (dibenzoylmethane/NaH = 1:2, molar ratio) with stirring. After 2 h, TEPIC was added the refluxing solution with a molar ratio of 1:1. The mixture was refluxed at 70 °C for 12 h under an argon atmosphere. Then, the solvent was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

### **4. Synthesis of $\text{Ln}(\text{dbm})_3(\text{H}_2\text{O})_2$ Complexes (Ln=Eu, Sm, Er, Nd, Yb)**

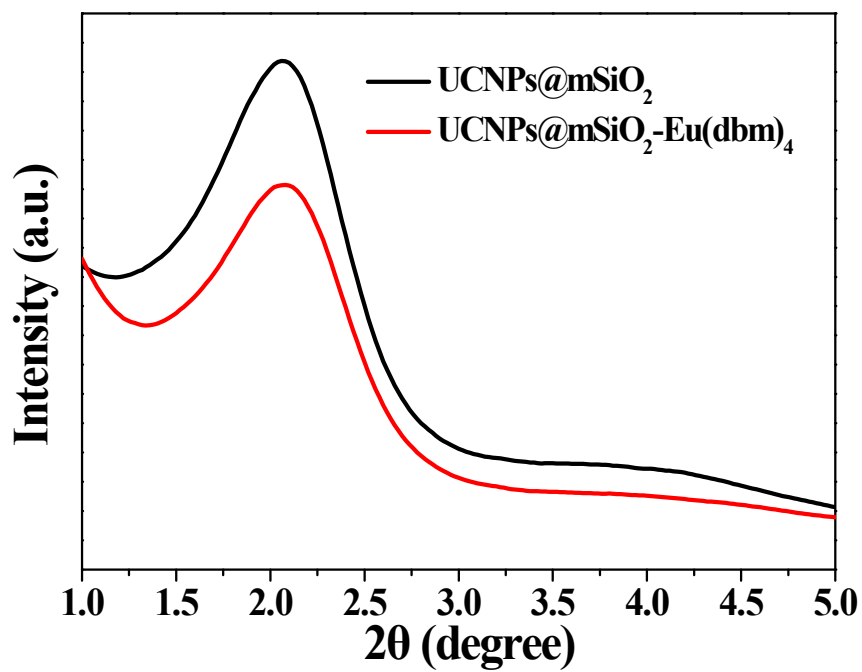
A certain amount of Hdbm was dissolved in ethanol, and the pH value was adjusted to approximately 7 with an appropriate amount of sodium hydroxide solution (1 M). The  $\text{LnCl}_3$  ethanol solution was added into this mixture under stirring ( $\text{LnCl}_3$ :dbm = 1:3, molar ratio). Then an appropriate 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<sub>4</sub>:Yb,Tm, UCNPs, UCNPs@mSiO<sub>2</sub>, UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub>, and the standard card of β-NaYF<sub>4</sub> (JCPDS: 16-0334).



**Fig. S2.** energy dispersive X-ray (EDX) spectrum of UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub>.



**Fig. S3.** The low-angle XRD patterns of UCNPs@mSiO<sub>2</sub>, and UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub>.

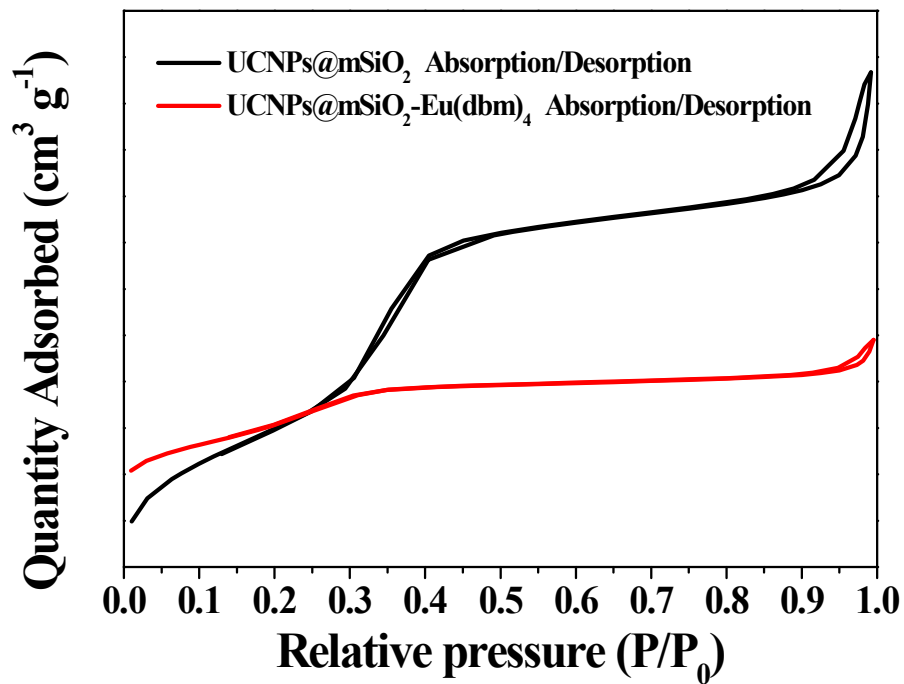


Fig. S4. N<sub>2</sub> adsorption-desorption isotherms of UCNP@mSiO<sub>2</sub> and UCNP@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub>.

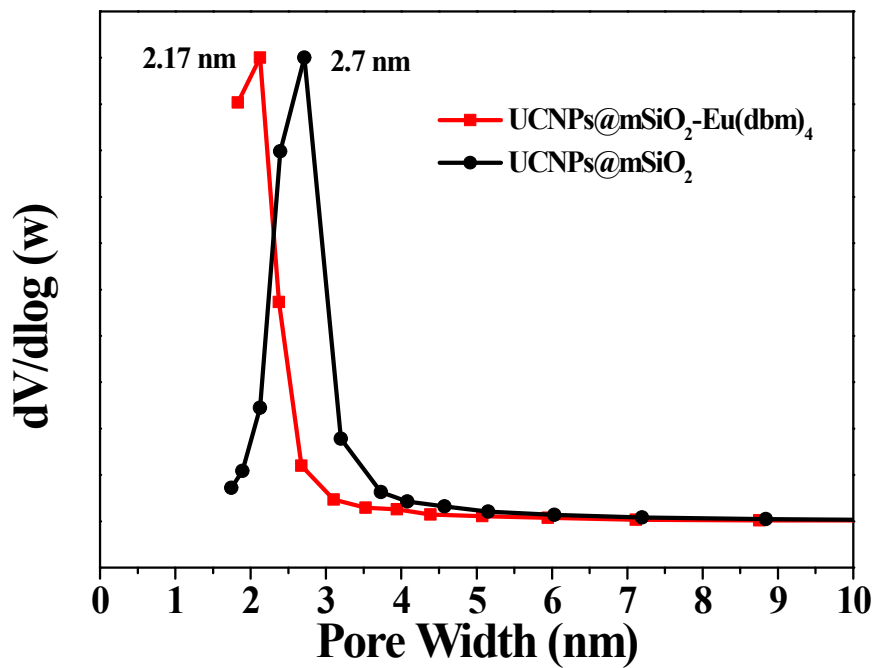
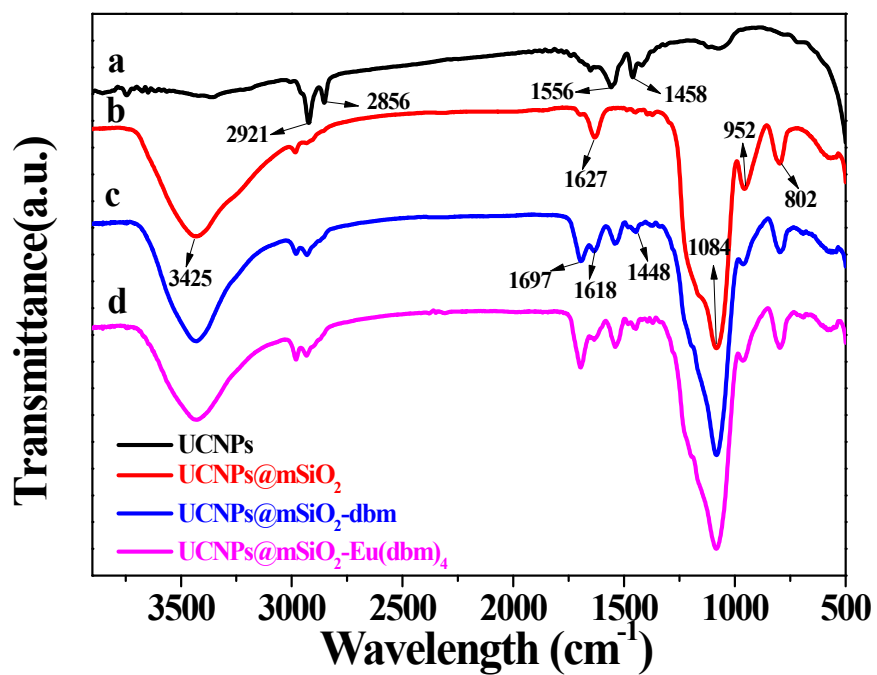
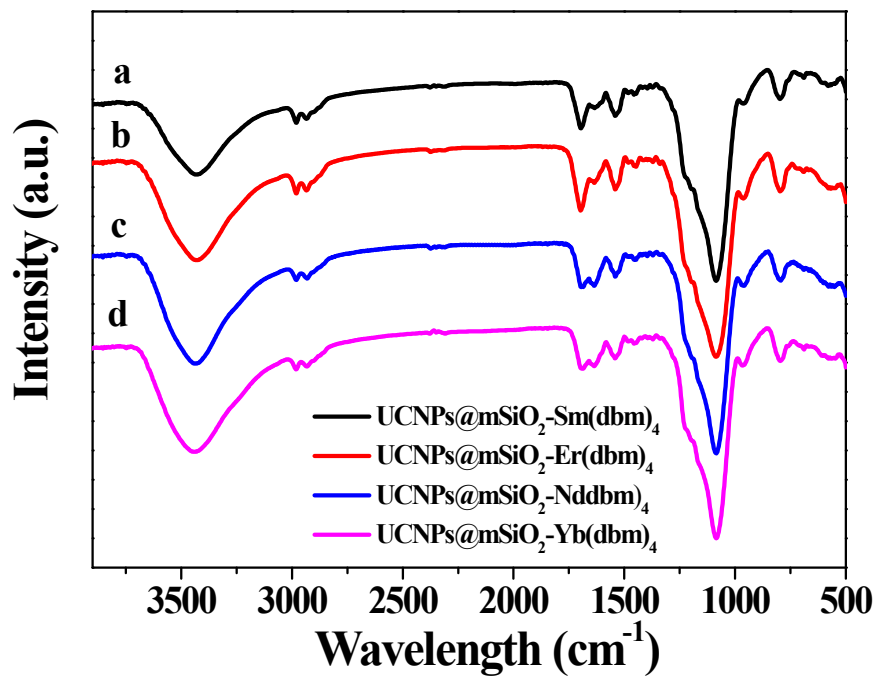


Fig. S5. The pore size distribution of UCNPs@mSiO<sub>2</sub> and UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub>.

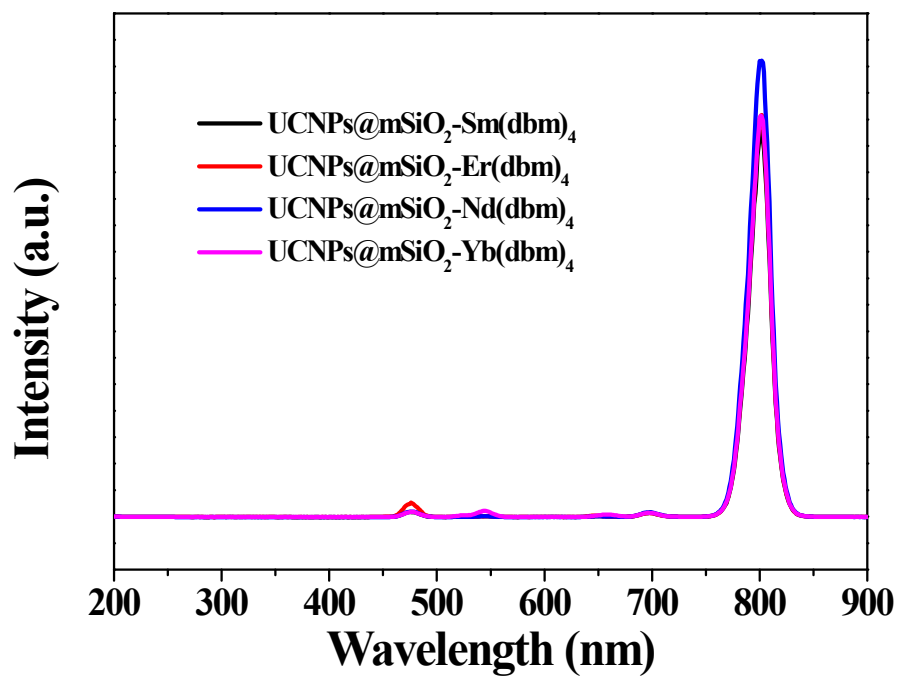




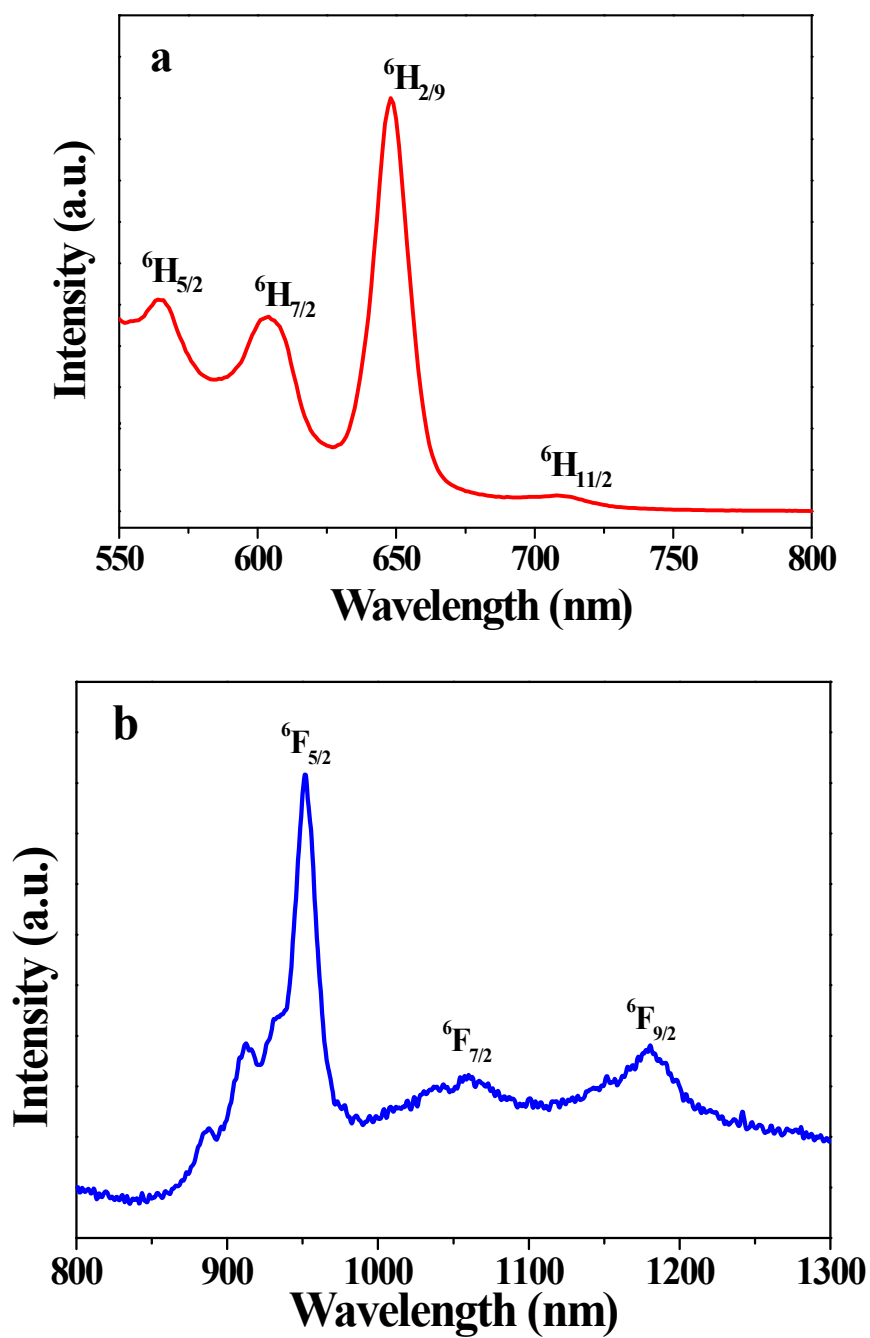
**Fig. S6.** FT-IR spectra of the UCNPs (a); UCNPs@mSiO<sub>2</sub> (b); UCNPs@mSiO<sub>2</sub>-dbm (c); UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub> (d).



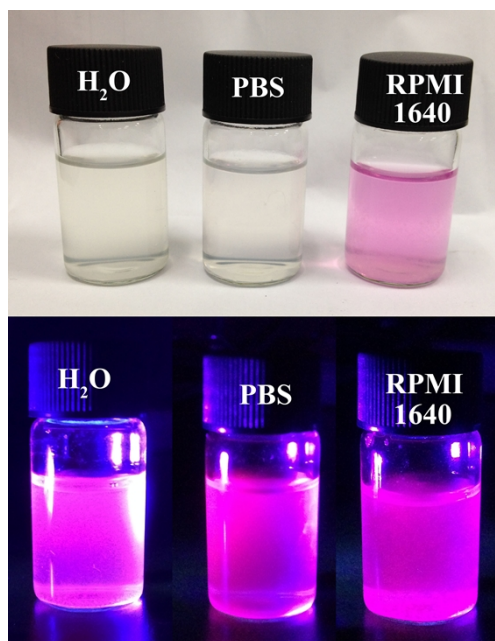
**Fig. S7.** FTIR spectra of the UCNP@mSiO<sub>2</sub>-Sm(dbm)<sub>4</sub> (a); UCNP@mSiO<sub>2</sub>-Er(dbm)<sub>4</sub> (b); UCNP@mSiO<sub>2</sub>-Nd(dbm)<sub>4</sub> (c); UCNP@mSiO<sub>2</sub>-Yb(dbm)<sub>4</sub> (d).



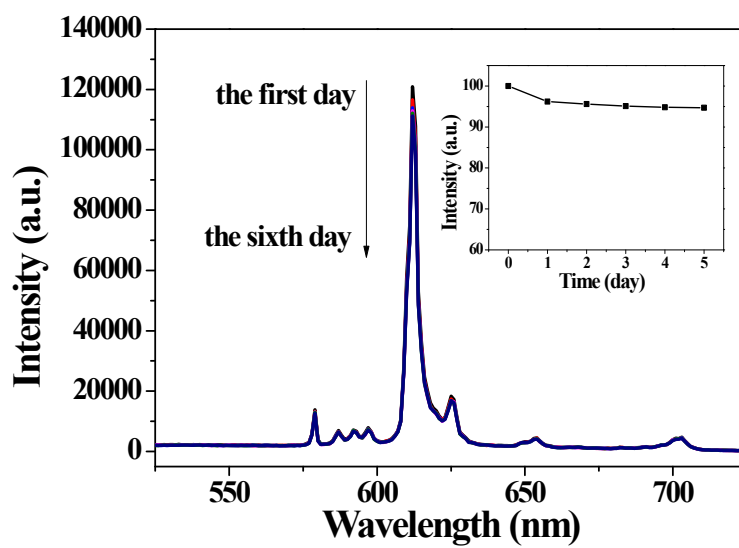
**Fig. S8.** Upconversion luminescence spectra of UCNP@mSiO<sub>2</sub>-Sm(dbm)<sub>4</sub>, UCNP@mSiO<sub>2</sub>-Er(dbm)<sub>4</sub>, UCNP@mSiO<sub>2</sub>-Nd(dbm)<sub>4</sub>, and UCNP@mSiO<sub>2</sub>-Yb(dbm)<sub>4</sub>.



**Fig. S9.** Visible emission ( $\lambda_{\text{ex}} = 401$  nm) spectrum (a) and NIR emission ( $\lambda_{\text{ex}} = 401$  nm) spectrum (b) of UCNPs@mSiO<sub>2</sub>-Sm(dbm)<sub>4</sub>. The visible and NIR emissions both come from the <sup>4</sup>G<sub>5/2</sub> excited state.



**Fig. S10.** Bright-field photos and phosphorescence photos of UCNPs@mSiO<sub>2</sub>-Eu(dbm)<sub>4</sub> 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<sub>2</sub>-Eu(dbm)<sub>4</sub> in water as a function of time (inset, time-dependent luminescence at 613 nm),  $\lambda_{\text{ex}} = 405$  nm.