Supplementary Material

Nd^{3+} sensitized core-shell-shell nanocomposites loaded with IR806 dyes for photothermal therapy and up-conversion luminescence imaging by single wavelength NIR light irradiation

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Method S1. Geometric TEM morphological and ICP data analysis of core, core-shell and core-shell-shell UCNPs.

From the TEM images we were able to estimate the volumes of the core and shells in the UCNPs according to a literature publised method with some modifications.[66] Assuming the UCNPs are all cylindrical with the respective diameters and height, D_{core}=17.6 nm, H_{core}=23.5 nm ; $D_{core\text{-}shell1}$=20.6 nm, $H_{core\text{-}shell1}$=32.3 nm; $D_{core\text{-}shell1\text{-}shell2}$=25 nm, $H_{core\text{-}shell1\text{-}shell2}$=41 nm for the core, core-shell and core-shell-shell UCNPs, the volumes (V) could be easily calculated using the equation, $V=4/3\ pi\ (D/2)^2\ H$ to be $V_{core} = 4/3\ pi\ (D_{core}/2)^2\ H_{core}$= 5.71E+3 nm^3, $V_{core\text{-}shell} = 4/3\ pi\ (D_{core\text{-}shell}/2)^2\ H_{core\text{-}shell}$ = 10.76E+3 nm^3 and $V_{core\text{-}shell\text{-}shell} = 4/3\ pi\ (D_{core\text{-}shell\text{-}shell}/2)^2\ H_{core\text{-}shell\text{-}shell}$ = 20.12E+3 nm^3. The volume ratio of $V_{core} : V_{core\text{-}shell} : V_{core\text{-}shell\text{-}shell}$ is then normalized to be 1.00 : 1.88 : 3.52.

If V_{shell1} is defined as the volume of the inner shell, it can be calculated using the volume ratio data, i.e. by $V_{core\text{-}shell} - V_{core} = 1.88 – 1.00 = 0.88\ V_{core}$, and similarly, the volume of the outer shell $V_{shell2} = V_{core\text{-}shell\text{-}shell} - V_{core\text{-}shell} = 3.52 – 1.88 = 1.64\ V_{core}$. Thus, the normalized volume ratio of $V_{core} : V_{shell1} : V_{shell2}$ is 1.00 : 0.88 : 1.64.

Additionally, assuming the volume ratio is similar to the mole ratio, and taking the core-shell UCNPs as an example, the apparent formula from TEM image analysis is actually $[NaYF_4$:Yb(20%), $Er(2\%)]_1$@$[NaYF_4$: $Yb(20\%)]_{0.88}$. In 1 mmol core-shell UCNPs, the Y^{3+} content is 0.78 (in core) +0.88*0.8 (in shell) = 1.484 mmol, the Yb^{3+} content is 0.2 (in core) +0.88*0.2 (in shell) = 0.376 mol, and the Er^{3+} content is 0.15 (in core) + 0.00 (in shell) mol. The respective mole% of Y^{3+} is therefore

1.484 /(1.484+ 0.376 + 0.15) = 78.9%, and similarly, Yb^{3+} mole% = 32.5%, Er^{3+} mole% = 1.7%. On the other hand, the mass of Lu^{3+} is 88.91 mg/mol* 1.484 = 131.94 mg. Similarly, the respective masses for the Yb^{3+} and Er^{3+} are 65.07 mg and 3.35 mg. The Y^{3+} wt% is therefore 131.94/(131.94+65.07+3.35) or 65.9 %, and similarly, Yb^{3+} wt% = 32.5 %, Er^{3+} wt% = 1.7 %.

For the ICP data, taking the core-shell-shell UCNPs as an example, the Y^{3+}, Yb^{3+}, Er^{3+} and Nd^{3+} contents are 8.48, 4.87, 0.13 and 1.17 ppm, respectively. The wt% for Lu^{3+} is therefore 8.48/(8.48+4.87+ 0.13+1.17) = 57.9%; similarly, the wt% for Yb^{3+}, Er^{3+} and Nd^{3+} are 33.2%, 0.9% and 8.0%, respectively. The mole% for Y^{3+} is (8.48/88.91)/[(8.48/88.91)+(4.87/173.05)+(0.13/167.26)+(1.17/144.24)] = 72.0%; similarly, the mole% for Yb^{3+}, Er^{3+} and Nd^{3+} are 21.3%, 0.6% and 6.1%, respectively.

Method S2. Calculation of the photothermal conversion efficiency (η) for UCNC-FAs.

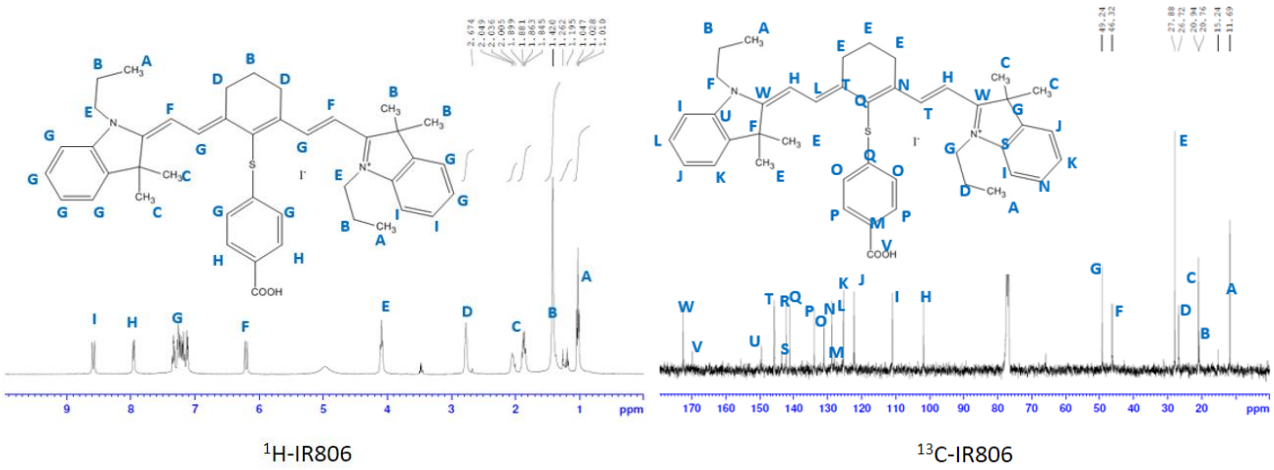
The photothermal conversion efficiency was calculated using eq. S1, where h is the heat transfer coefficient, S is the surface area of the container, the maximum steady temperature (T_{max}) of the solution of the FA-UCNCs was 45.4 ℃, the environmental temperature (T_{Surr}) was 29.3 ℃, Q_{dis} was the heat dissipated from the light absorbed by the solvent and quartz cuvette (i.e. 51.3 mW), I was the power of the 793 nm laser (i.e. 2 W/cm^2), and A_{793} was the absorbance of the UCNC-FAs at 793 nm (i.e. 0.650). The hS value could be obtained to be 45 mW/℃ from eq. S2, where τ_s was the time constant and was determined to be 280.0 s, and m_D is 3 g and C_d is 4.2 J/g·℃. Thus, substituting the values of these parameters into Eq. S1, the photothermal conversion efficiency (η) of the UCNC-FAs could be calculated to be 46%.

$$\eta = \frac{\mathrm{hS}(T_{\max}-T_{surr})-Q_{\mathrm{dis}}}{\mathrm{I}(1-10^{-\mathrm{A793}})} \quad \text{(Eq. S1)}$$

$$\mathrm{hS} = \frac{m_D C_{\mathrm{d}}}{\tau_s} \quad \text{(Eq. S2)}$$

Figures.

(A) (B)



^{1}H-IR806 ^{13}C-IR806

(C)

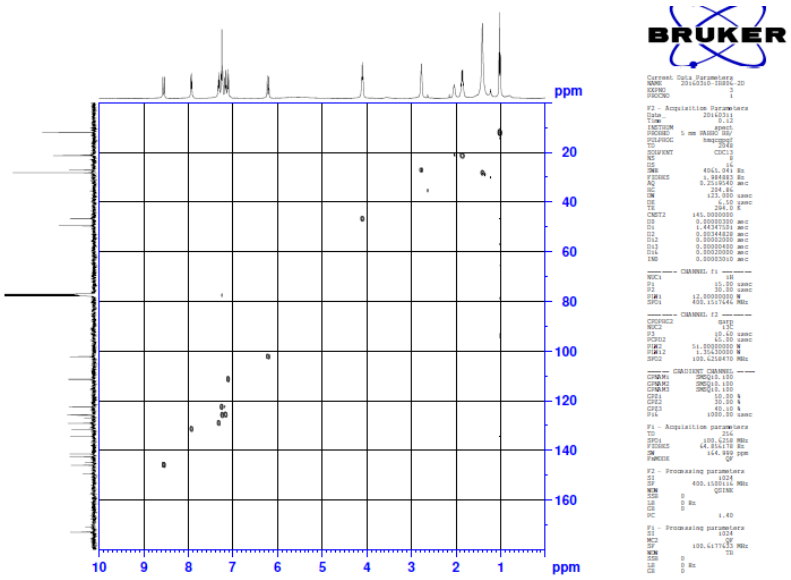


Figure S1. (A) ^{1}H NMR (400MHz, D_2O) spectrum of IR806, (B) ^{13}C NMR (400MHz, D_2O) spectrum of IR806 and (C) 2D-NMR (x: ^{1}H ; y: ^{13}C) of IR806.

(A) (B)

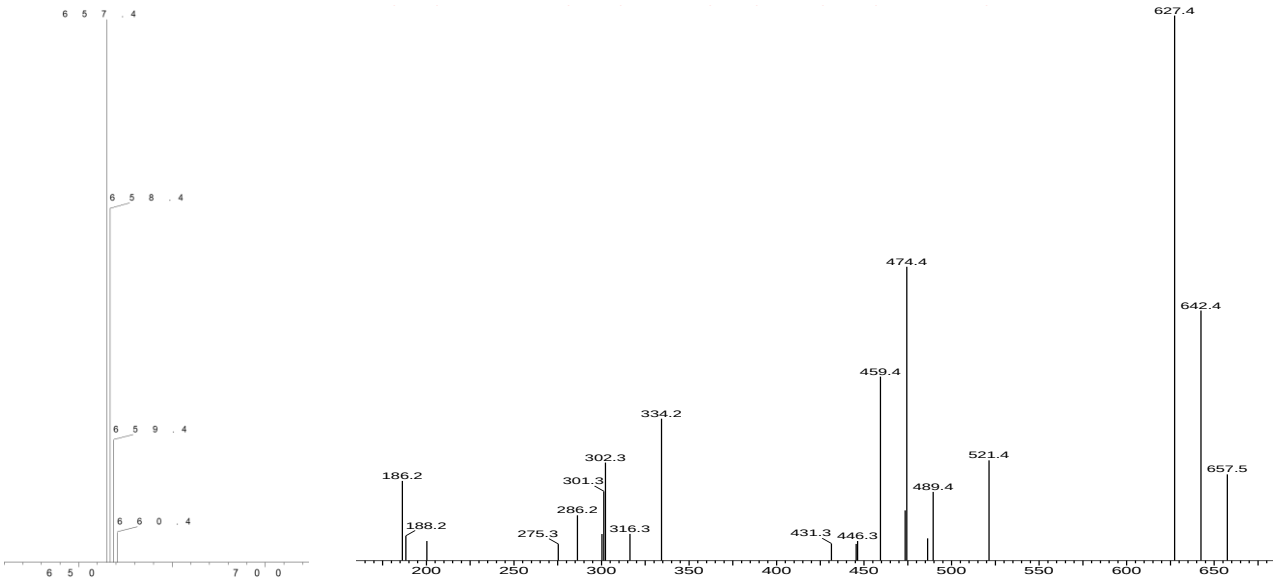


Figure S2. (A) The ESI+ mass spectrum of IR806. $[M]^+$ calc. for $C_{43}H_{49}N_2O_2S^+$, 657.35(100.0%), 658.35(48.0%), 659.36(11.3%) , found 657.4, 658.4, and 659.4. (B) MS-MS spectra of IR806.

(A) (B) (C)

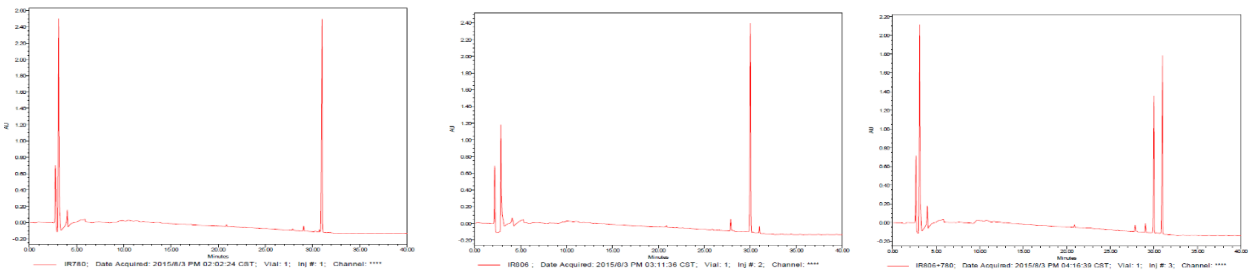


Figure S3. HPLC chromatograms of : (A) IR780, retention time = 31.0 min. (B) IR806, retention time = 30.0 min. and (C) mixture of IR806 and IR780. HPLC equipment: Waters 1525 pump with Waters 2489 UV/visible detector (220 nm); analytical column (C18 inertsil ODS-3, 5μm 4.6×250mm). Condition: mobile phase (solvent A, 0.1% TFA in water; solvent B, acetonitrile); gradient (5~30 min 95%~40% solvent A); flow rate: 1 mL/min.

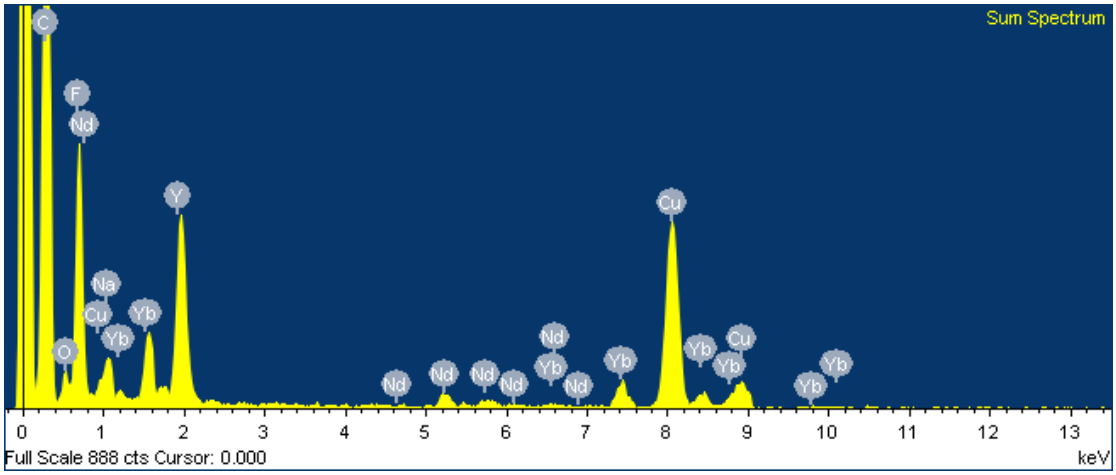


Figure S4. The EDS data of the core-shell-shell UCNPs. The Er^{3+} ions were confined in the inner region, thus could not be detected at outer region.

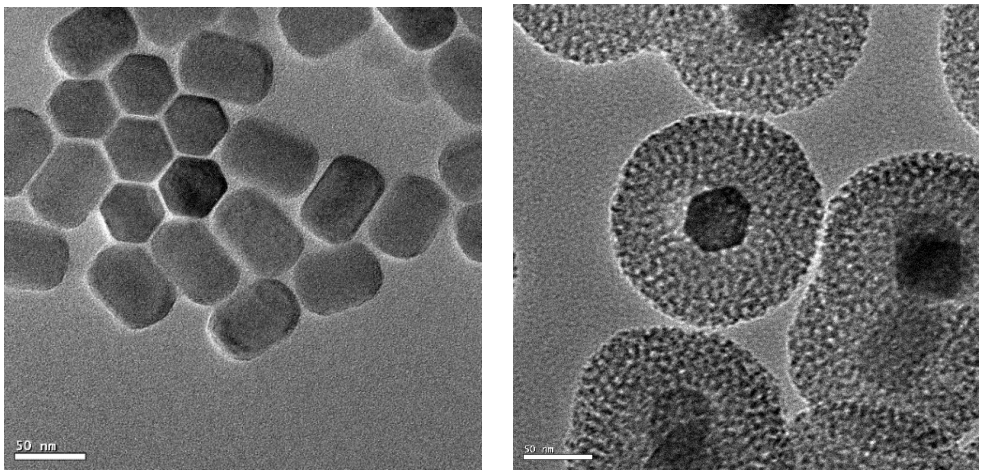


Figure S5. The high-resolution transmission electron microscopy (HR-TEM) images of the core-shell-shell UCNPs (left) and UCNP@mSiO_2 (right).

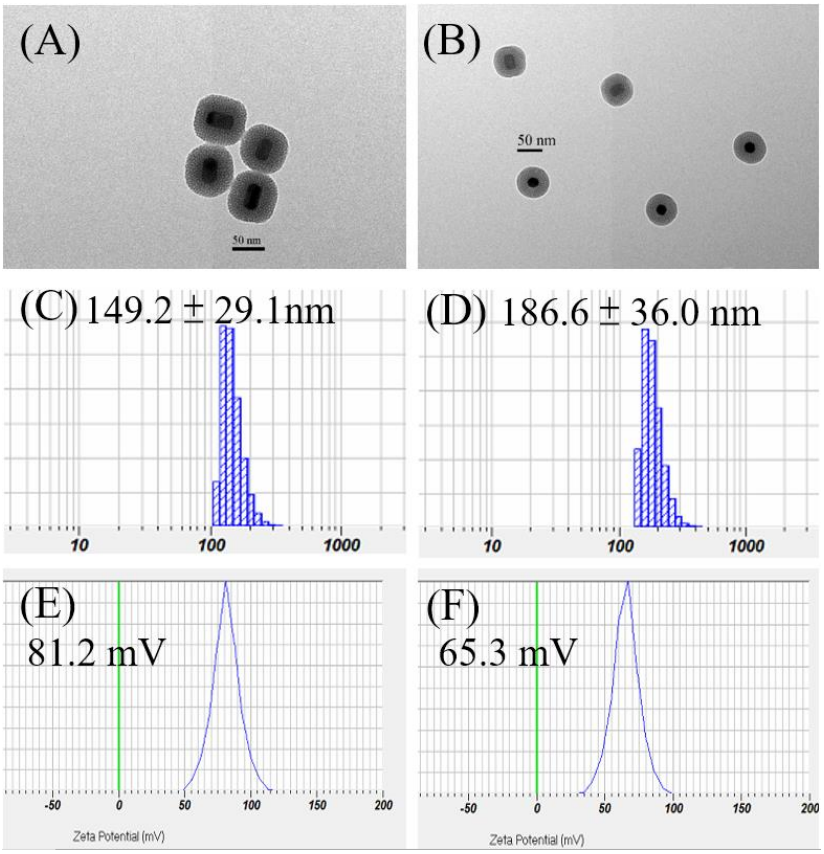


Figure S6. TEM images (A, B), DLS measurements (C, D) and Zeta Potenital measurements (E, F). (A)(C)(E): UCNPs@mSiO$_2$/IR806@ PAH; (B)(D)(F): and UCNPs@mSiO$_2$/IR806@PAH/PEG-FA.

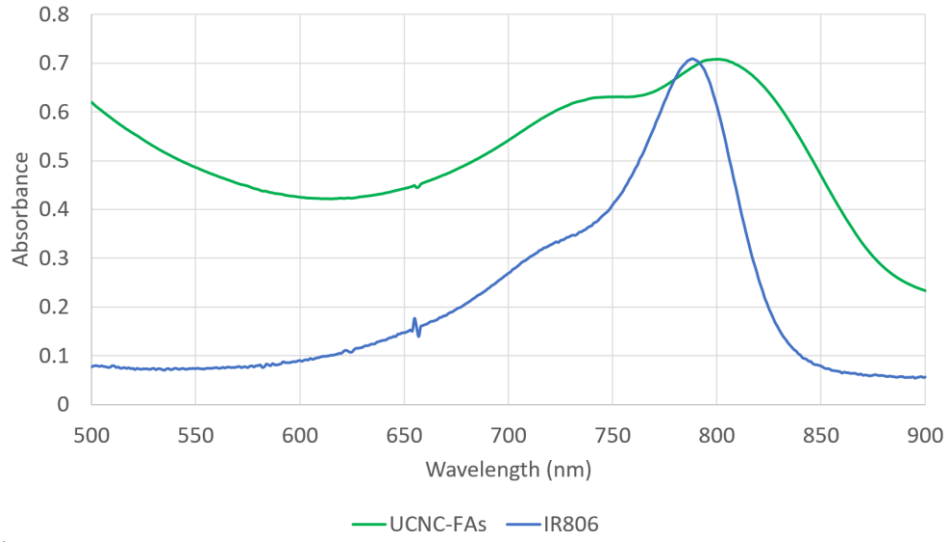


Figure S7. Absorption spectra of free type IR806 (green) and IR806 in UCNC-FAs (blue). [IR806] = 4.7 μM.