Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Near-infrared light-triggered drug release from UV-responsive diblock copolymer-coated upconversion nanoparticles with high monodispersity

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1. Synthetic route

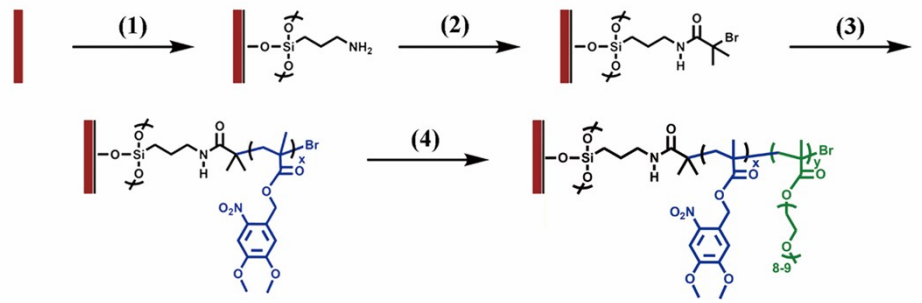

Figure S1. Surface modification of UCNP through a bottom-up strategy: (1) silica layer coating, (2) immobilization of ATRP initiators, (3) growth of hydrophobic block that is a UV-responsive polymer (PNB), and (4) growth of hydrophilic block (POEG). The UCNP and thin silica layers are depicted as red and black rods, respectively.

2. TEM images

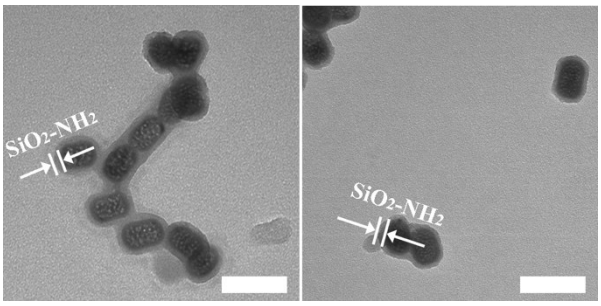

Figure S2. TEM images for UCNP-NH_2. Scale bar is 60 nm.

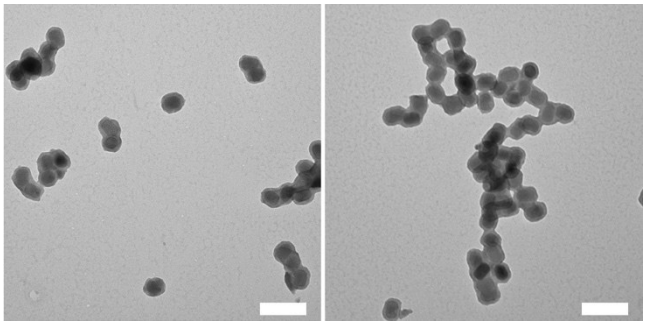

Figure S3. TEM image of UCNP-Br. Scale bar is100 nm.

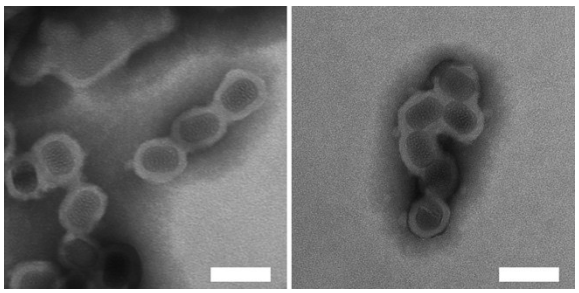

Figure S4. TEM images of UCNP@PNB. Scale bar is 60 nm.

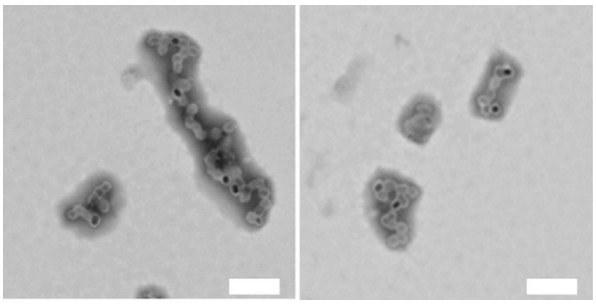

Figure S5. TEM images of UCNP@PNB-*b*-POEG. Scale bar is 200 nm.

3. TGA analysis

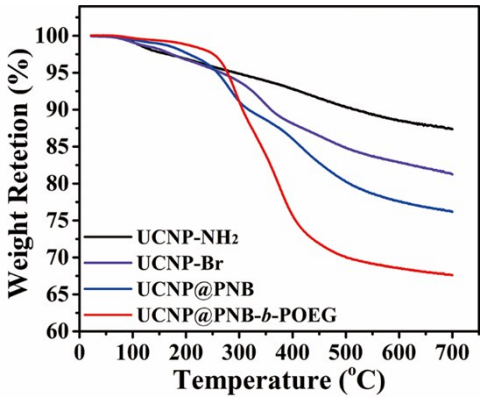

Figure S6. TGA analysis of UCNP-NH_2, UCNP-Br, UCNP@PNB and UCNP@PNB-*b*-POEG.

4. SEC

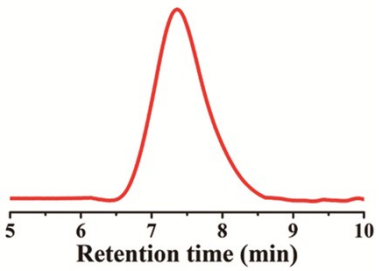

Figure S7. SEC curve of PNB-*b*-POEG cleaved by HF etching of UCNP-*b*-POEG.

5. Calculations

Table S1. Basic information of nanoparticles.

Mass of NPs at room temperature: **1. assuming the residual mass of all NPs is 10 mg at 700 °C.** **2. equation to calculate the mass of NPs at room temperature: mass = (10 mg) / (the wt.% of NPs at 700 °C).**		
mass of UCNP-NH_2 at room temperature (mg)	= 10/0.874	= 11.44
mass of UCNP-Br at room temperature (mg)	= 10/0.813	= 12.30
mass of UCNP@PNB-*b*-POEG at room temperature (mg)	= 10/0.676	= 14.79
Mole weight of organic species in NPs (MWO, g/mol)		
MWO in UCNP-NH_2 (g/mol)	$-(CH_2)_3-NH_2$	= 58
MWO in UCNP-Br (g/mol)	$-(CH_2)_3-NH-C=O-C(CH_3)_2-Br$	= 207
MWO in UCNP@PNB-*b*-POEG	–PNB-*b*-POEG	= 1.09×10^4
UCNP and UCNP-Br: **1. the shape of the UCNP is approximated to be a cylinder and the density of $NaYF_4$:Yb,Tm@$NaYF_4$ is taken to be the same as for $NaYF_4$.** **2. the shape of the UCNP-Br is approximated to be a cylinder and the thickness of silica-Br layer is 6 nm.** **3. assuming the density of silica is 2.1 g/m^3 [a] and the density of silica-Br is taken to be the same as for silica.**		
density of UCNP (g/cm^3) [b]		= 4.31
length of UCNP (nm)		= 34.7
width of UCNP (nm)		= 22.1
volume of one UCNP (nm^3) using $v = \pi r^2 h$	$= 3.14 \times (22.1/2)^2 \times 34.7$	$= 1.33 \times 10^4$
mass of one UCNP (mg)	$= 4.31 \times 10^{-18} \times 1.33 \times 10^4$	$= 5.73 \times 10^{-14}$
surface area of one UCNP (nm^2) using $s = 2\pi r^2 + 2\pi rh$	$= 2 \times 3.14 \times (22.1/2)^2 + 2 \times 3.14 \times (22.1/2) \times 34.7$	$= 3.20 \times 10^3$
length of UCNP-Br (nm)		= 47
width of UCNP-Br (nm)		= 34
volume of one UCNP-Br (nm^3) using $v = \pi r^2 h$	$= 3.14 \times (34/2)^2 \times 47$	$= 4.26 \times 10^4$
surface area of one UCNP-Br (nm^2) using $s = 2\pi r^2 + 2\pi rh$	$= 2 \times 3.14 \times (34/2)^2 + 2 \times 3.14 \times (34/2) \times 47$	$= 6.8 \times 10^3$
volume of silica-Br (nm^3)	$= 4.26 \times 10^4 - 1.33 \times 10^4$	$= 2.93 \times 10^4$

density of UCNP-Br (g/cm^3)	= (4.31 × 1.33 × 10^4 + 2.1 × 2.93 × 10^4) / (4.26 × 10^4)	= 2.79
mass of one UCNP-Br (mg)	= 2.79 × 10^{-18} × 4.26 × 10^4	= 1.19 × 10^{-13}
Number of NPs (10 mg NPs at 700 °C)	= (10) / (1.19 × 10^{-13})	= 8.41 × 10^{13}
Mole of NPs (10 mg NPs at 700 °C)	= (8.41 × 10^{13}) / (6.02 × 10^{23})	= 1.40 × 10^{-10}

[a] This value was obtained from *J. Eng. Thermophys-Rus.,* **2016***, 25,* 174.

[b] This value was obtained from *Nat. Commun.*, **2015**, *6*, 6938.

Table S2. Useful information from TGA analysis.

Mass loss at different temperature regions	**UCNP-NH_2 (mg)**	**UCNP-Br (mg)**	**UCNP@PNB-*b*-POEG (mg)**
T<80 °C	0.039	0.052	0.014
80 °C<T<150 °C	0.0217	0.175	0.081
250 °C<T<450 °C	0.492	1.11	3.80
Mass of organic species (mg)	= 0.492	= (1.11 - 0.492) = 0.618	= (3.80 - 1.11) = 2.69
Mole of organic species (mmol) [a]	= 8.5 × 10^{-3}	= 4.2 × 10^{-3}	= 2.5 × 10^{-4}
Number of organic species (N) [b]	= 5.12 × 10^{18}	= 2.47 × 10^{18}	= 1.51 × 10^{17}

[a] Mole of organic species = (mass of organic species) / (MWO), MWO is from **Table S1**.

[b] N = N_A × mole of organic species, N_A is Avogadro constant.

Based on the values from **Table S1** and **S2**, the grafting densities of initiator and polymer can be obtained by the equation below:

Grafting density = (number of organic species) / (surface area of one UCNP-Br × number of NPs)

Therefore, the initiator and polymer grafting densities are approximately 4.4 (or 0.34 mmol/g) and 0.26 chains/nm^2, respectively.

In addition, the initiation efficiency of initiators can be calculated by the following equation:

Initiation efficiency = (grafting density of polymer) / (grafting density of initiator)

Hence, the initiation efficiency is around 6%.

6. Upconversion emission spectra

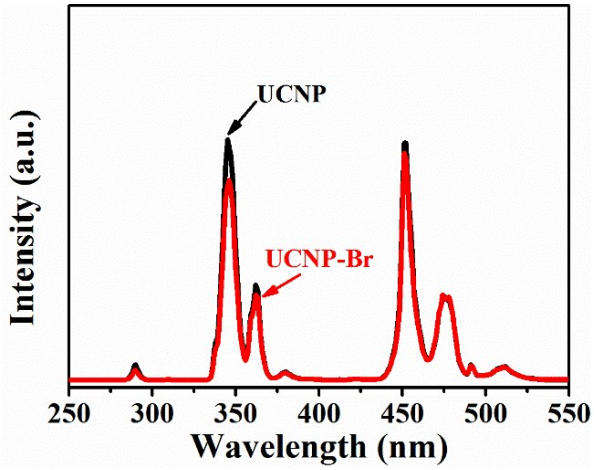

Figure S8. The emission spectra of the neat UCNP (black) in hexane and UCNP-Br (red) in DMF.