Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

In-situ “grafting from” for the synthesis of polymer brushes on upconversion nanoparticles via NIR-mediated RAFT polymerization

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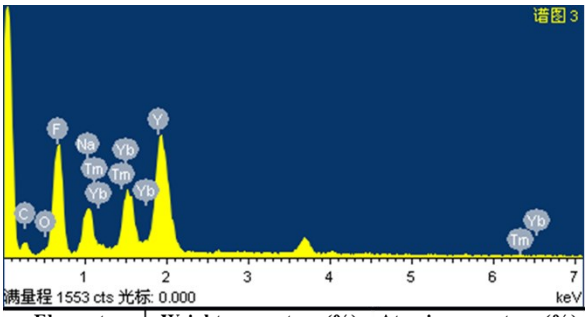


Elements	Weight percentage (%)	Atomic percentage (%)
C K	14.80	30.40
O K	2.47	3.81
F K	39.24	50.96
Na K	5.95	6.38
Y L	22.86	6.34
Tm L	0.62	0.09
Yb L	14.06	2.00
Total amount	100.00	

Figure S1. EDS spectrum of upconversion nanoparticles with OA molecular capped.

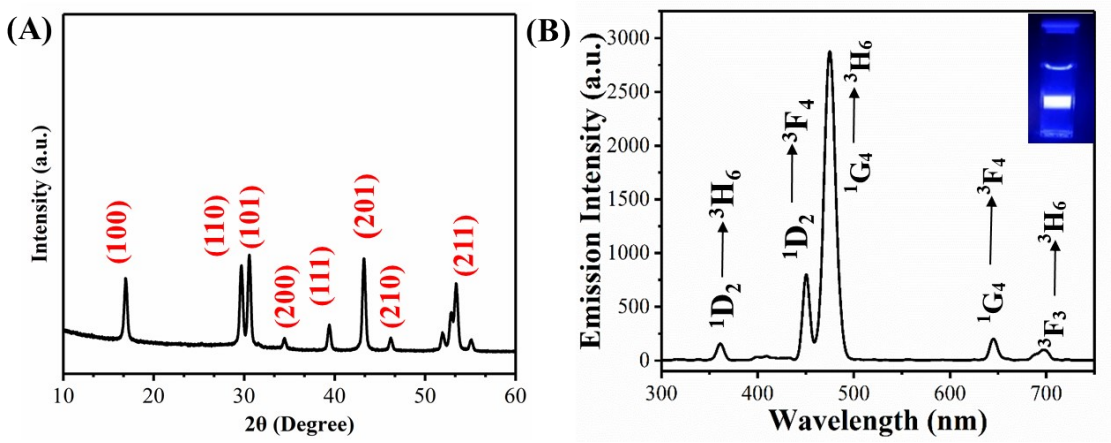


Figure S2. (A) Wide-angle XRD pattern of synthesized UCNP@OA; (B) Upconversion luminescence (UCL) spectrum of UCNP@OA (excited with 980 nm laser).

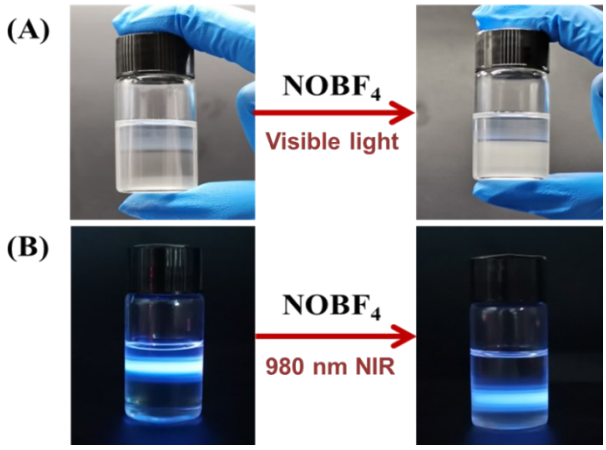


Figure S3. Digital photographs of upconversion nanoparticles dispersions (A) and upconversion luminescence (B) of $NaYF_4$:Yb/Tm nanoparticles before and after $NOBF_4$ modification, respectively. (The upper layer is cyclohexane and the bottom layer is DMF)

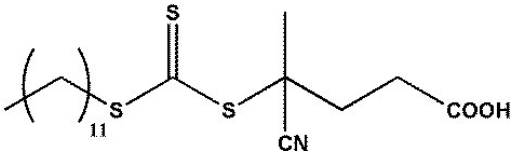


Figure S4. Chemical Structure of CDTPA as RAFT agent used in this study.

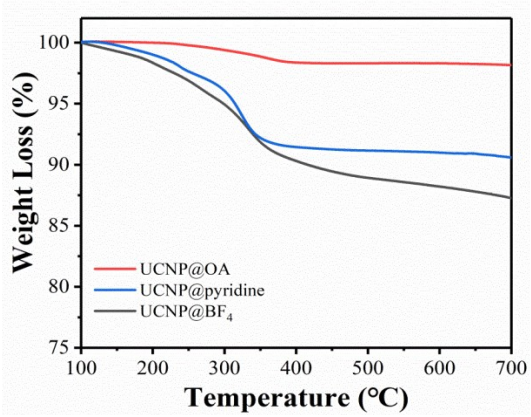


Figure S5. TGA analysis of UCNP@ligand after ligand exchange with CDTPA. The same amounts (10 mg) of UCNP@OA, UCNP@pyridine, UCNP@BF_4 were added to the 2 mL DMF solution of CDTPA (0.05 mmol/mL), and centrifuged to collect the powders after stirring for 3 h, separately.

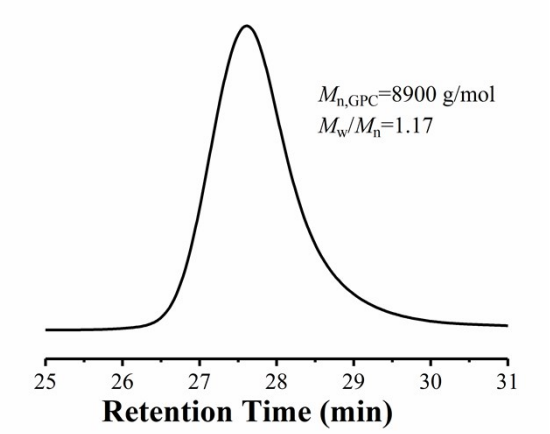


Figure S6. SEC characterization of purified free PMMA corresponding to the same sample of ^{1}H NMR characterization.

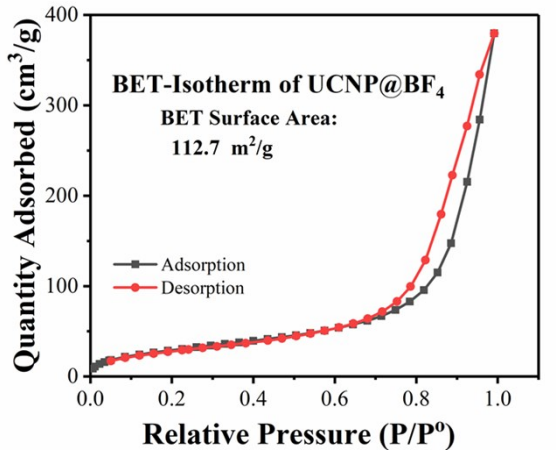
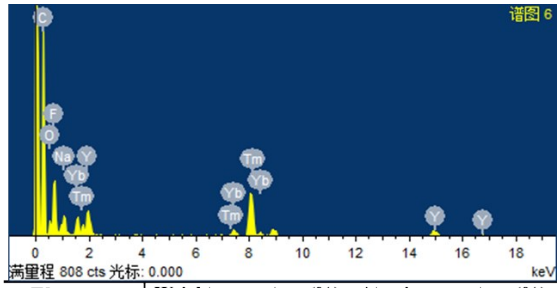


Figure S7. Nitrogen adsorption–desorption isotherms of UCNP@BF_4^- sample.



Elements	Weight percentage (%)	Atomic percentage (%)
C K	55.20	81.24
O K	2.51	2.77
F K	11.30	10.52
Na K	2.20	1.69
Y K	8.33	1.66
Tm L	11.04	1.16
Yb L	9.40	0.96
Total amount	100.00	

Figure S8. EDS spectrum of upconversion nanoparticles with PMMA capped.

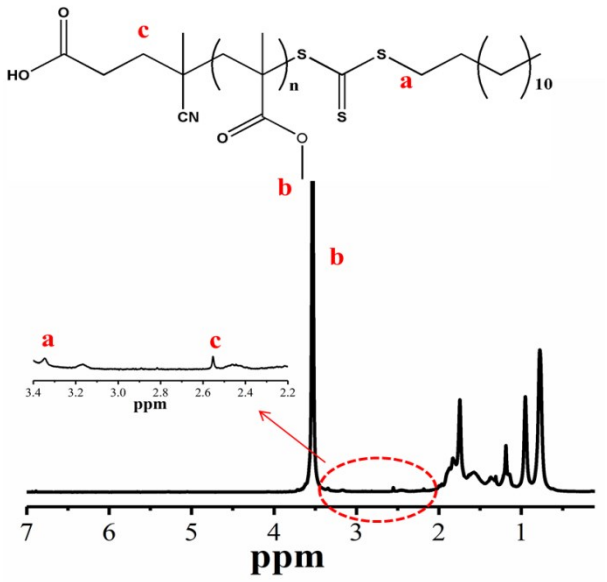


Figure S9. ^{1}H NMR spectra of UCNP grafted PMMA ended with RAFT agent synthesized by NIR-mediated RAFT polymerization.

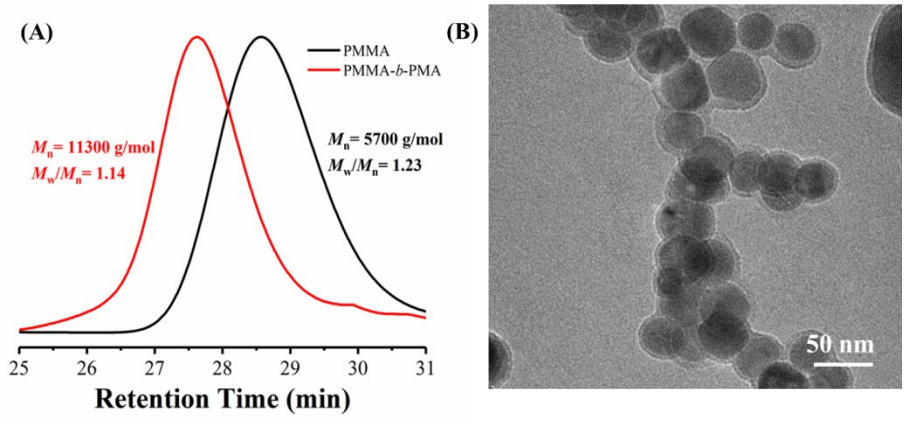


Figure S10. Molecular weight distributions of corresponding free polymers of UCNP@PMMA and UCNP@PMMA-*b*-PMA synthesized by grafting from the approach using NIR-mediated RAFT followed by chain extension with MA. (b) TEM image of the UCNP@PMMA-*b*-PMA after chain extension.

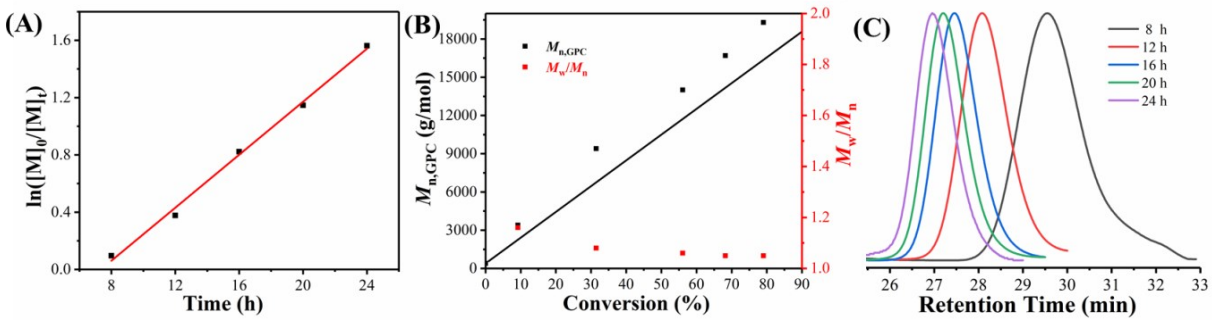


Figure S11. Kinetic analysis of the NIR-initiated RAFT polymerization of *t*BA under the conditions $[t\text{BA}]_0$:$[\text{CDTPA}]_0$=200:1 with 5 mg/mL UCNPs in 50% (v/v) DMSO at room temperature. (A) Plot of $\ln([\text{M}]_0/[\text{M}]_t)$ versus exposure time. (B) Evolution of number-average molecular weight and molecular weight distribution (M_w/M_n). (C) Molecular weight distributions at different time points.

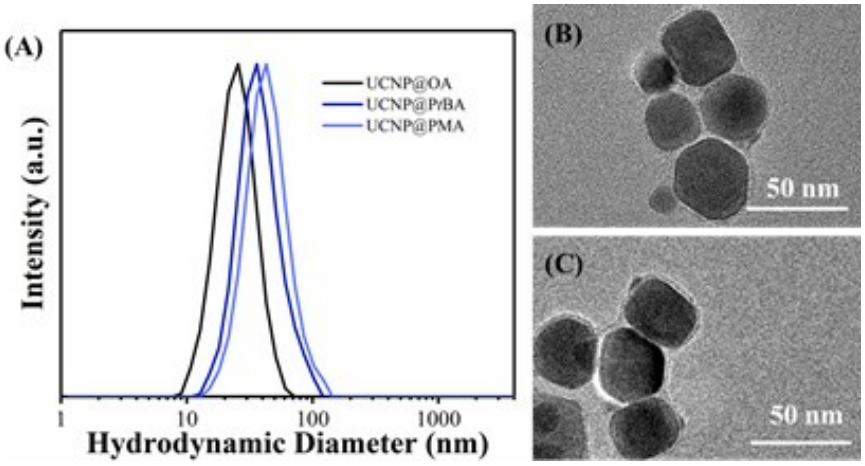


Figure S12. (A) DLS analysis of different nanoparticles of as-synthesized UCNP@OA, and PMA and P*t*BA coated particles. (B, C) TEM images of UCNP@P*t*BA and UCNP@PMA, respectively.

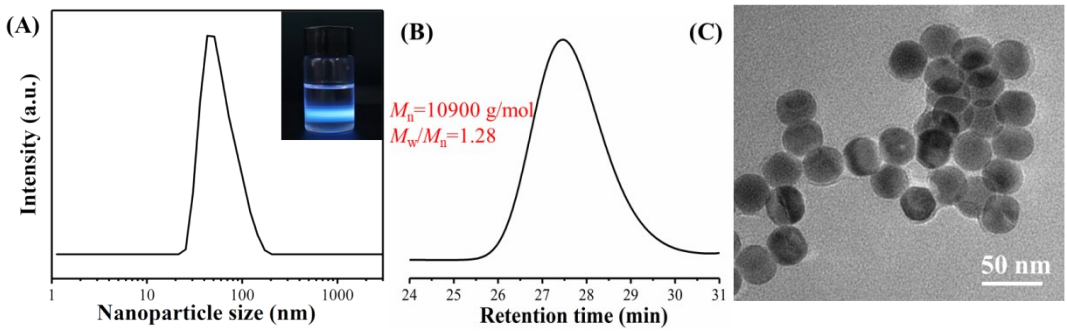


Figure S13. (A) DLS analysis, SEC characterization (B) and TEM image (C) of as-synthesized UCNP@PAA nanoparticles.

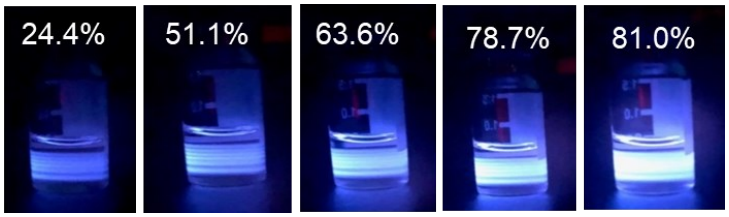


Figure S14. Digital photographs of upconversion nanoparticles during the polymerization process at different monomer conversions. (Reaction conditions: $[MMA]_0$:$[CDTPA]_0$=200:1 with 5 mg/mL UCNPs in 50% v/v DMSO at room temperature under total 980 nm laser irradiation).

The amount of CDTPA and polymers grafted onto the surface of the upconversion nanoparticles was calculated using the weight loss (*loss-wt*) based on the residual weight at 650°C, as determined by TGA (**Figure 6**) and the surface area of UCNPs. The grafting density (*GD*) was estimated according to the following equation:

$$Grafting\ Density\left(\frac{chain}{nm^2}\right) = \frac{(loss-wt/M_{n,CDTPA}) \times N_a}{m_{UCNPs} \times S_{UCNPs}} \quad (S1)$$

$$Grafting\ Density\left(\frac{chain}{nm^2}\right) = \frac{(loss-wt/M_{n,polymer}) \times N_a}{m_{UCNPs} \times S_{UCNPs}} \quad (S2)$$

Where $M_{n,CDTPA}$, $M_{n,polymer}$ corresponds to the molcular weight of CDTPA and polymer grafted, respectively. N_a is Avogadro constant and m_{UCNPs} is the molar mass

of polymer grafted UCNPs used for the TGA analysis (e.g. mass of modified nanoparticles = initial mass before TGA analysis – loss of weight). The weight loss was calculated through the difference between the weights at 100°C temperature and at 650°C. S_{UCNPs} is the specific surface area of UCNPs. For example, for UCNP@CDTPA and UCNP@PMMA-14 h:

$$Grafting\ Density\ of\ CDTPA\left(\frac{chain}{nm^2}\right) = \frac{(0.116/403.67\ g/mol) \times 6.02 \times 10^{23}}{(1 - 0.116) \times 112.7\ m^2/g} = 1.736\ (\frac{chain}{nm^2}) \quad (S3)$$

$$Grafting\ Density\ of\ PMMA\left(\frac{chain}{nm^2}\right) = \frac{(0.295/13900\ g/mol) \times 6.02 \times 10^{23}}{(1 - 0.295) \times 112.7\ m^2/g} = 0.161\ (\frac{chain}{nm^2}) \quad (S4)$$

Table S1. Results of polymers synthesized by the "grafting from" approach using NIR-initiated RAFT polymerization with [MMA]:[CDTPA] = [200]: [1] in DMSO solvent at room temperature

Entry	Time (h)	$M_{n,GPC}$ [a] (g/mol)	M_w/M_n [a]	Shell Tickness [b] (nm)	Grafting Density [c] (chains/nm^2)
1	6	7500	1.21	~ 3.4	0.094
2	10	10800	1.29	~ 5.8	0.131
3	14	13900	1.22	~ 8.5	0.162
4	18	15500	1.14	~ 11.9	0.201

[a] Number-average molecular weight $M_{n,GPC}$ and dispersity (M_w/M_n) of corresponding free PMMA (unbound) after different polymerization time determined by GPC using polystyrene calibration. The reaction were performed at room temperature under 980

nm NIR laser 6 W/cm^2) in DMSO. [b] The thickness of the core-shell structure was measured by TEM. [c] The grafting density of the polymer on the UCNPs was calculated by TGA analysis.

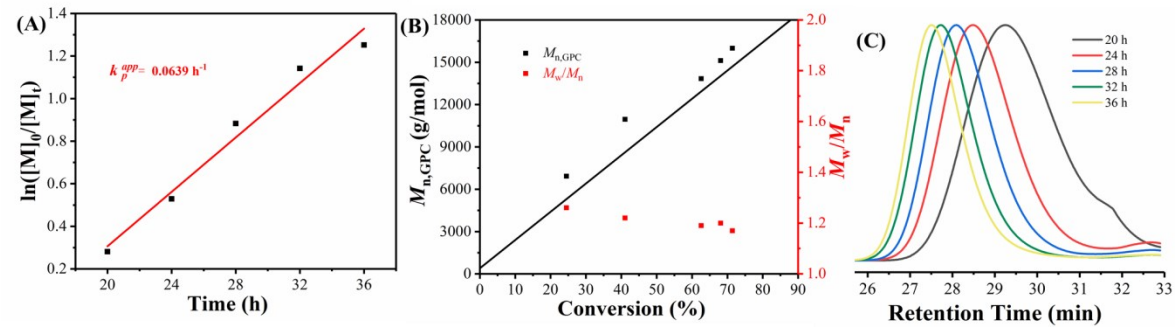


Figure S15. Kinetic analysis of the NIR-initiated RAFT polymerization of MMA when the polymerization vessel was shielded by chicken skin with a thickness of 1.2 mm under the conditions $[MMA]_0$:$[CDTPA]_0$=200:1 with 5 mg/mL UCNPs in 50% (v/v) DMSO at room temperature. (A) Plot of $\ln([M]_0/[M]_t)$ versus exposure time. (B) Evolution of number-average molecular weight and molecular weight distribution (M_w/M_n). (C) Molecular weight distributions at different time points.

Compared with nonscreened reaction ($k_p^{app} = 0.0849\ h^{-1}$), the apparent growth rate constant have a slight decrease ($k_p^{app} = 0.0639\ h^{-1}$).