

Amphiphilic Copolymer Coated Upconversion Nanoparticles for Near-Infrared Light-Triggered Dual Anticancer Treatment

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Supplementary Information

*Mn*²⁺ ion-doped *NaY(Mn)F₄:Yb/Er* nanocrystals (UCNPs) were prepared according to literature with some modification. In brief, 1.2 mL of 0.5 M *MnCl₂*, 2 mL of 0.5 M *Y(NO₃)₃*, 1.8 mL of 0.2 M *Yb(NO₃)₃*, and 0.2 mL of 0.2 M *Er(NO₃)₃* were added to a mixture of NaOH (0.6 g), deionized water (3.0 mL), oleic acid (10 mL) and ethanol (20 mL) under stirring. 4 mL of deionized water containing 8 mmol of NaF was then dropwisely added into the mixture. After vigorous stirring for 15 min at room temperature, the colloidal solution was transferred into a 60 mL Teflon-lined autoclave,

which was sealed and heated at 200 °C for 8 h. The system was then allowed to cool naturally to roomtemperature. The final product was collected by centrifugation; and then washed with ethanol and deionized water several times to remove any possible remnants. The obtained UCNPs could be re-dispersed in various non-polar organic solvents.

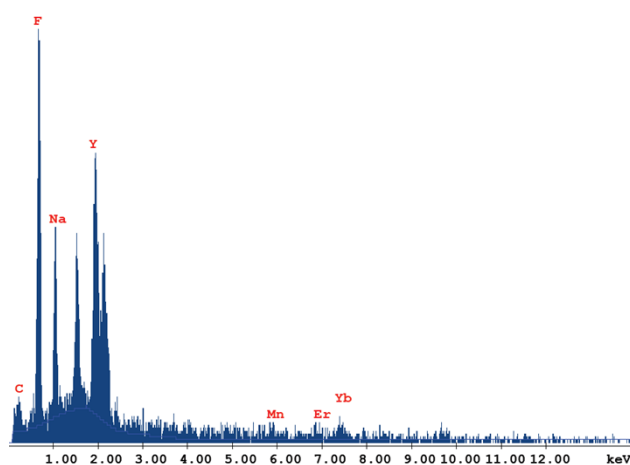


Figure S1 EDS spectrum of UCNPs.

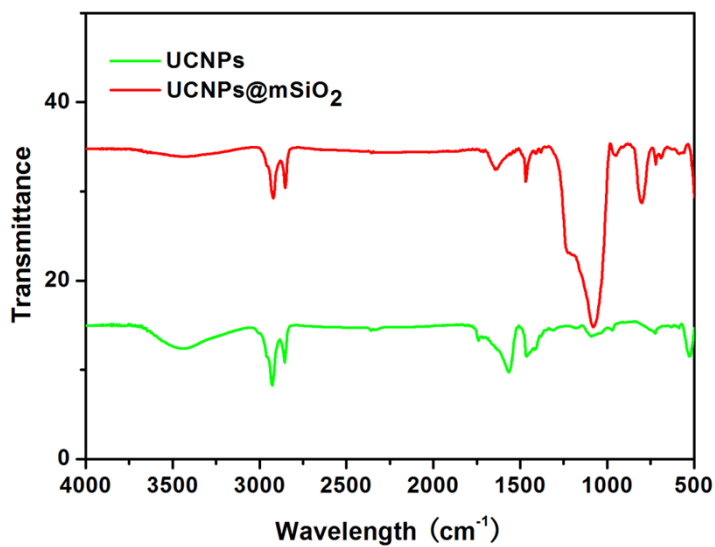


Figure S2 FT-IR spectra of UCNPs and UCNPs@SiO₂.

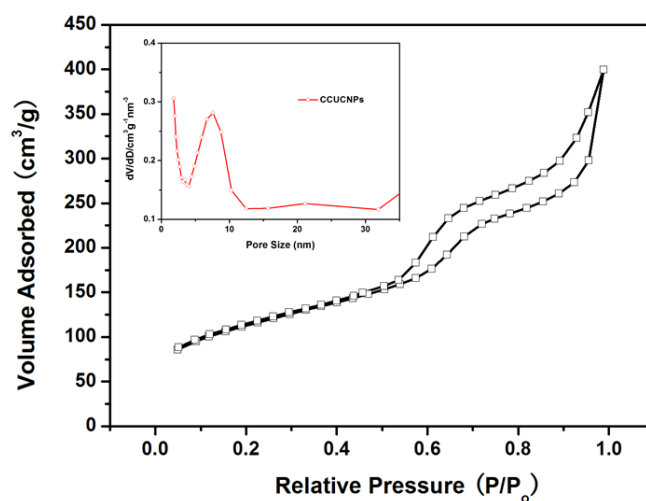


Figure S3 N₂ adsorption–desorption isotherm and the corresponding pore size distribution inset of CCUCNPs.

Synthesis of hydrophobic monomer 3-((10-(3-(methacryloyloxy)propoxy) anthracen-9-yl)oxy) propyl stearate (MAPS): 3-Chloro-1-propanol (10 g, 0.1mol) and sodium iodide (60 g, 0.4 mol) were added to dry acetone (100 mL) and stirred at 60 °C under N₂ for 24 h. The mixture was filtered and the solvent evaporated. Then, a 1:1 mixture of diethyl ether/hexane was added and stirred for 10 min and then filtered. The solution was washed with a dilute sodium thiosulfate solution followed by water and then brine. The organic layer was dried with MgSO₄, filtered and the solvent evaporated in vacuum giving a pale yellow liquid (12.4 g, 67%). ¹HNMR (400 MHz, CDCl₃), δ (ppm): 3.74 (t, 2H, CH₂OH), 3.29 (t, 2H, CH₂I), 2.09 (m, 2H, CH₂CH₂CH₂).

9, 10-Bis(3-hydroxypropyloxy) anthracene: Nitrogen-saturated water (150 mL) and CH₂Cl₂ (150 mL) was added to a mixture of 9,10-anthraquinone (2.57 g, 12.36 mmol), Na₂S₂O₄ (4.3 g, 24.7 mmol) and Adogen 464 (4.64 g, 10 mmol). The mixture was stirred for 5 min and then NaOH (4.94 g, 123.5 mmol) was added. Stirring was continued for 10 min and 3-Iodo-1-propanol was added dropwise. The mixture was

stirred overnight at 25 °C. Then the phase was separated and the water phase was washed with CH₂Cl₂. The combined organic phases were washed with water and dried over MgSO₄. The solution volume was reduced to 40 mL and the product was precipitated overnight at -20 °C. The solid was purified by column chromatography with a mixture of ethyl acetate/CH₂Cl₂ (1/4, v/v) Yield 1.13 g, 28%; (¹HNMR (400 MHz, DMSO-*d*₆), δ (ppm): 8.24 (dd, J=6.8, 3.2 Hz, 4H, anthracene), 7.52 (dd, J=6.8, 3.2 Hz, 4H, anthracene), 4.63 (t, J=5.2 Hz, 2H, CH(O)), 4.16 (t, J=6.5 Hz, 4H, OCH₂CH₂), 3.76 (m, CH₂CH₂OH, 4H), 2.1 (m, CH₂CH₂CH₂, 4H).

9,10-Bis(3-hydroxypropyloxy) anthracene (0.4 g, 1.22 mmol) and pyridine (0.1 g, 1.22 mmol) were dissolved into dry CH₂Cl₂ (100 mL), then stearyl chloride (0.185 g, 0.61 mmol) was added dropwise to the solution under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 hours. The product was purified by column chromatography with a mixture of ethyl acetate/CH₂Cl₂ (1/20, v/v) and dried in a vacuum to get 3-((10-(3-hydroxypropoxy) anthracen-9-yl)oxy) propyl stearate. Yield: 0.25 g (0.42 mmol, 36%). Then the product (0.25 g, 0.42 mol) and triethylamine (0.101 g, 1 mmol) were dissolved into dry CH₂Cl₂ (50 mL), then Methacryloyl chloride (0.104 g, 1 mmol) was added dropwise to the solution under a nitrogen atmosphere. The mixture was stirred at room temperature for 12 hours. The product was purified by column chromatography with a mixture of ethyl acetate/CH₂Cl₂(1/20,v/v) and dried in a vacuum to get 3-((10-(3-(methacryloyloxy)propoxy) anthracen-9-yl)oxy) propyl stearate (MAPS). Yield: Yellow solid, 0.145 g (0.22 mmol), 52%. ¹HNMR (400 MHz, DMSO-*d*₆): 8.24 (d,

4H, anthracene), 7.48 (d, 4H, anthracene), 6.18 (s, 1H, CCH₂), 5.60 (s, 1H, CCH₂), 4.64 (t, J=6.0, 2H, CH₂OCO), 4.53 (t, J=6.4, 2H, CH₂OCO), 4.29 (m, 4H, CH₂CH₂O), 2.45-2.35 (m, 6H, CH₂CH₂OCO, COCH₂CH₂), 2.01 (s, 3H, CH₃), 1.69-1.65(m, 2H, CH₂CH₂CH₂), 1.29-1.25(m, 30H, CH₂), 0.88 (t, J=13.2, 3H, CH₂CH₃)

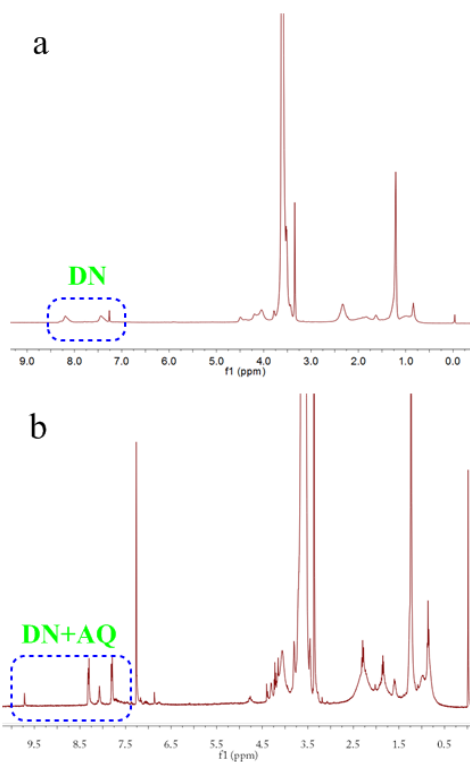


Figure S4 ¹H NMR spectrum of PM and photocleavage of PM

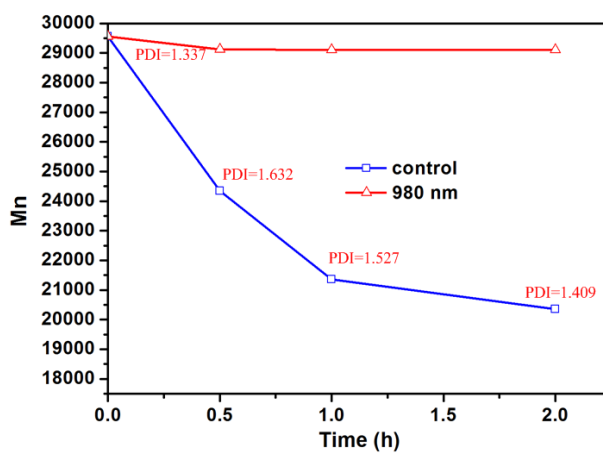


Figure S5 The decreased Mn of PM under ¹O₂

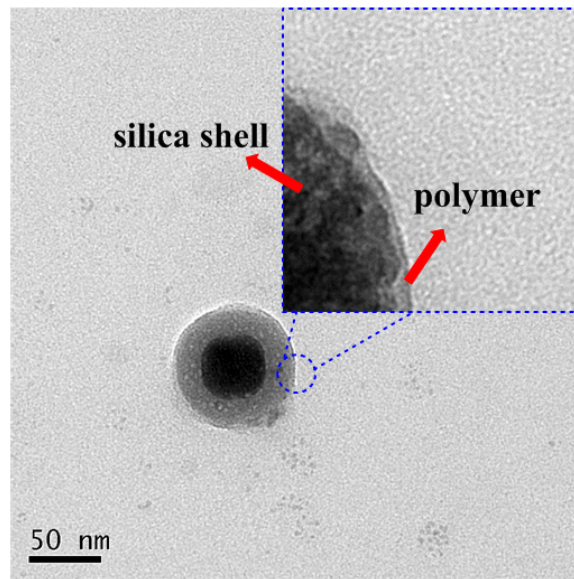


Figure S6 TEM of CCUCNPs@PM, inset:enlarged TEM images of CCUCNPs@PM

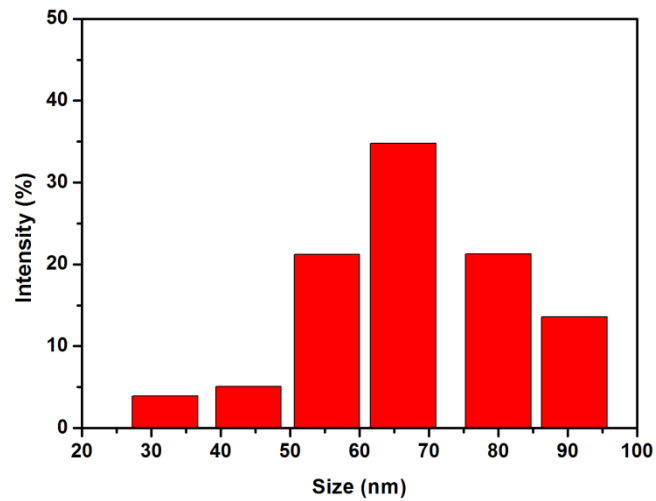


Figure S7 DLS of CCUCNPs@PM

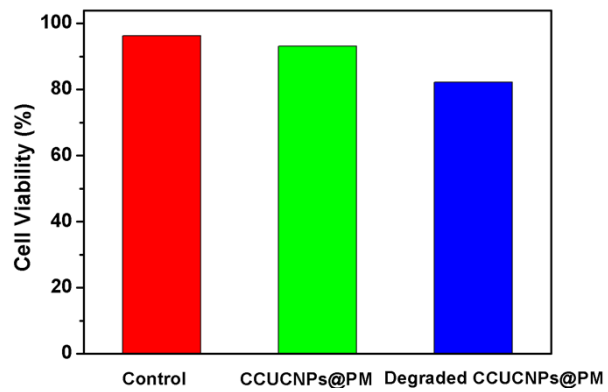


Figure S8 The toxicity of nanocomposite after degradation

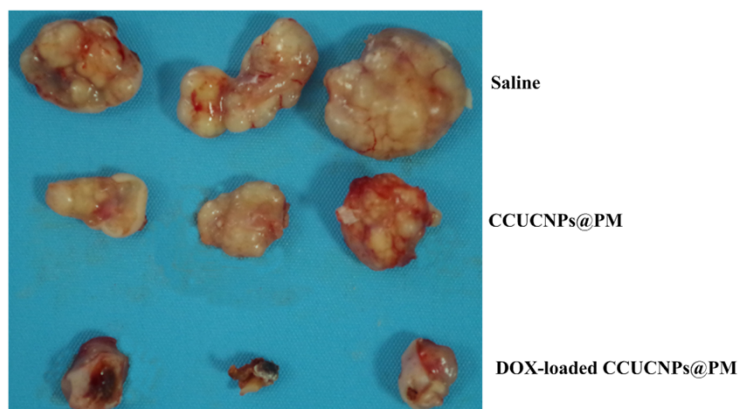


Figure S9 Photograph of the tumor tissue from sacrificed animal