

Supporting Information

In Vivo Selective Imaging of Metabolic Glycosylation with Tetrazine-Modified Upconverting Nanoprobe†

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Materials

$\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, PEI (branched 25 kDa), NH_4F , 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide hydrochloride (EDC), ethanol, acrylic acid, methanol and N, N-dimethylformamide (DMF) were purchased from Aladdin Reagent, Ltd. All chemicals used in this work were of analytical grade. Cell-counting kit-8 (CCK-8) was obtained from Dojindo Laboratories (Kumamoto, Japan). Fetal bovine serum (FBS), penicillin, streptomycin, and Dulbecco's modified Eagle's medium (DMEM) were obtained from GIBCO and used as received. The water used in this study was deionized to a specific resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ with a Milli-QSP reagent water system (Millipore).

Instruments

The ^1H NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. The absorption spectra were collected using a UV-vis spectrometer (Lambda 35, Perkin-Elmer, USA) and the upconversion luminescence emission spectra of upconversion nanoparticles were measured using a 600 mW cm^{-2} 980 nm diode CW laser (Changchun New Industries Optoelectronics Tech. Co., Ltd.) as the excitation source. The confocal fluorescence images of cell was collected on an Olympus fluoview FV10 microscope (Olympus Imaging America Inc., JAPAN).

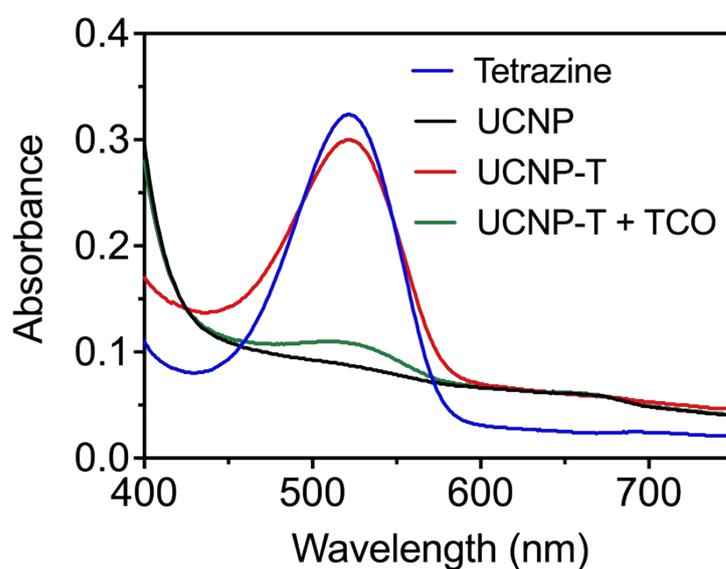


Fig. S1 The absorbance spectra of Tetrazine, UCNP, UCNP-T in the absence or presence of TCO.

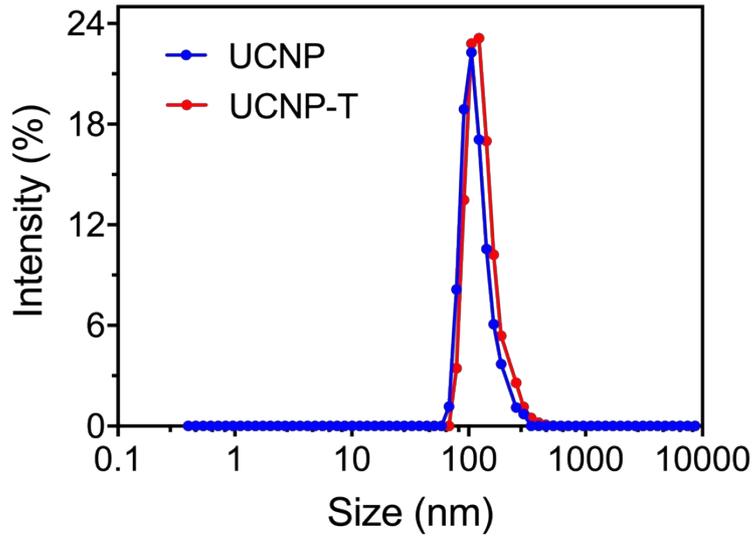


Fig. S2 The DLS results of UCNP and UCNP-T.

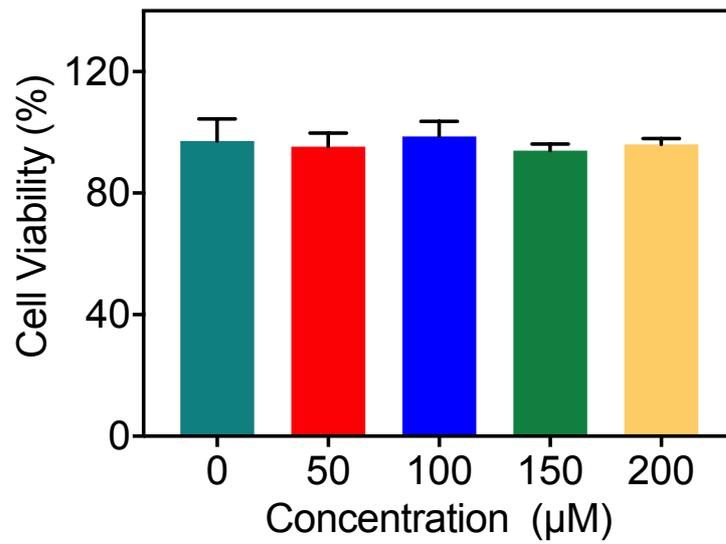


Fig. S3 In vitro cell viability of EMT6 cells incubated with different concentration UCNP-T.

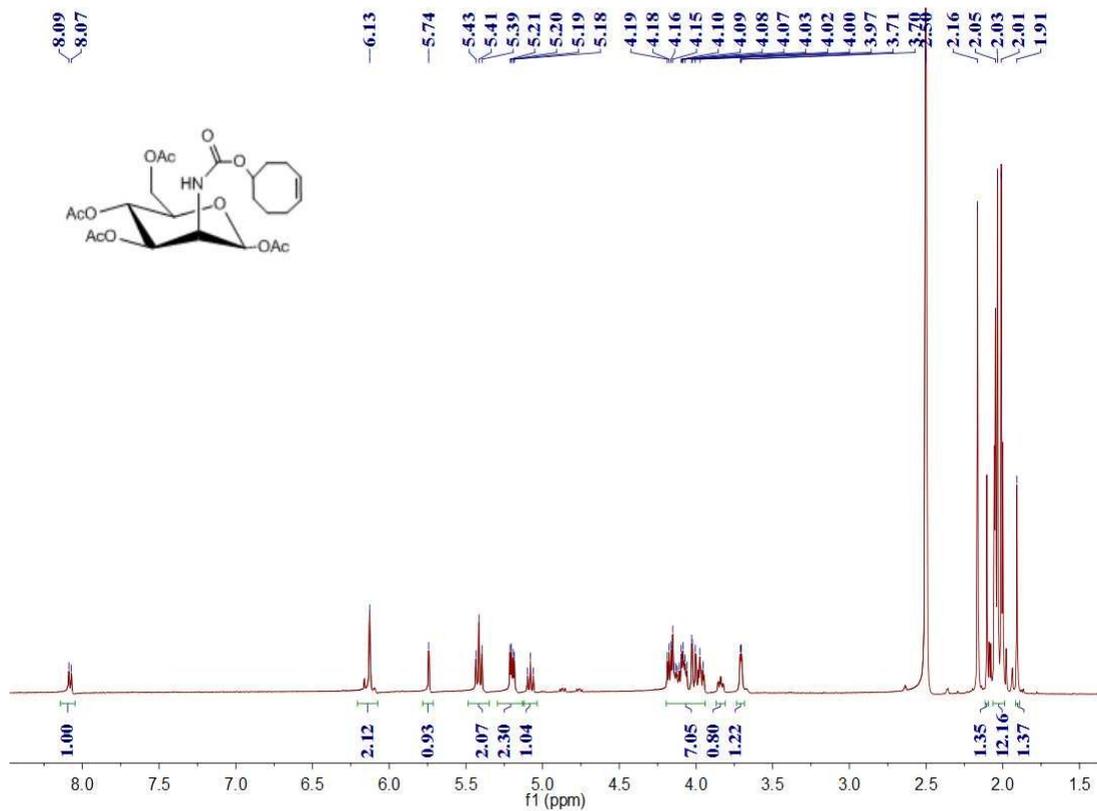


Fig. S4 ¹H NMR (400 MHz, d₆-DMSO) spectrum of Ac₄ManNTCO.

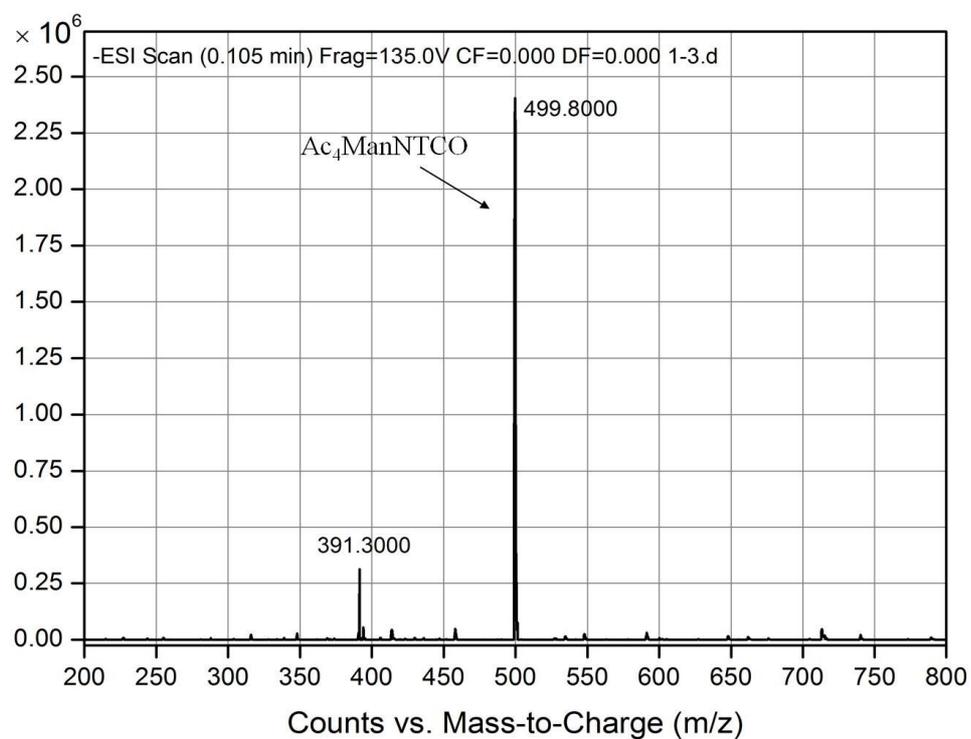


Fig. S5 ESI-MS spectrum of Ac₄ManNTCO.

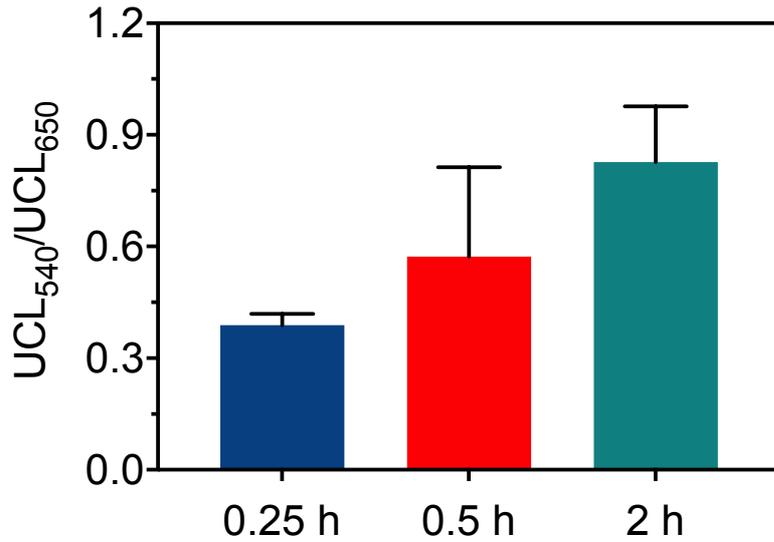


Fig. S6 The ratios of UCL₅₄₀/UCL₆₅₀ obtained from the Fig. 5.

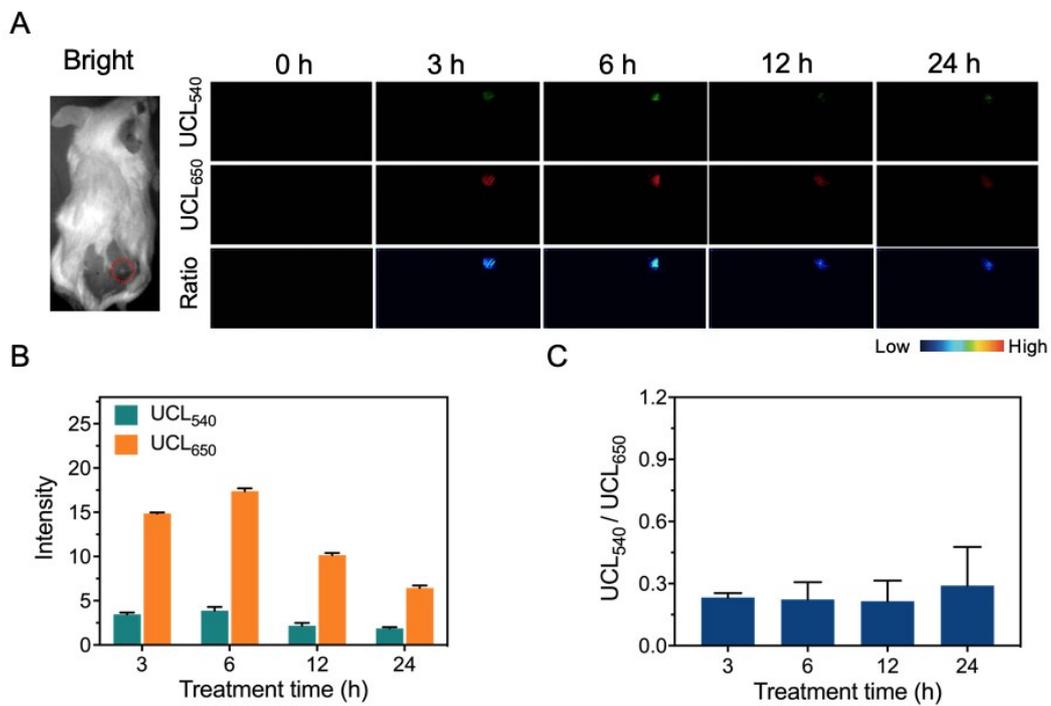


Fig. S7 In vivo UCL imaging of glycans status in tumor using UCNP-T. (A) Images of the tumor-bearing mice pretreated Ac₄ManNH₂ for 3 days by the intratumor injection and followed by i.v. injection of UCNP-T. The pseudo-colored bar represents the intensity of UCL₅₄₀, UCL₆₅₀ and UCL₅₄₀/UCL₆₅₀. (B) The intensity of the UCL emission UCL₅₄₀ and UCL₆₅₀ of (A). (C) Quantified ratios of UCL₅₄₀/UCL₆₅₀ intensity of (A).

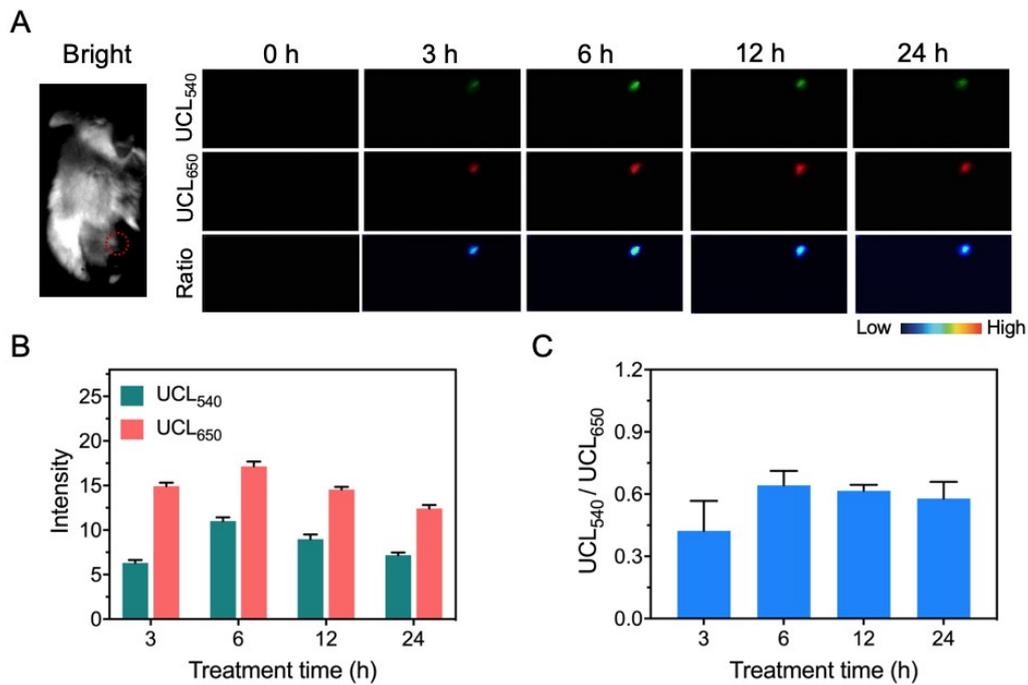


Fig. S8 In vivo UCL imaging of glycans status in tumor using UCNP-T. (A) Images of the tumor-bearing mice pretreated Ac₄ManNTCO (30 μ M) for 3 days by the intratumor injection and followed by i.v. injection of UCNP-T. The pseudo-colored bar represents the intensity of UCL₅₄₀, UCL₆₅₀ and UCL₅₄₀/UCL₆₅₀. (B) The intensity of the UCL emission UCL₅₄₀ and UCL₆₅₀ of (A). (C) Quantified ratios of UCL₅₄₀/UCL₆₅₀ intensity of (A).