Electronic Supplementary Material (ESI) for Analytical Methods


# Supplementary Information for the following manuscript

# Newly synthesized glycol chitosan-*graft*-carboxymethyl *β*-cyclodextrin as potential pH-sensitive anticancer drug carrier

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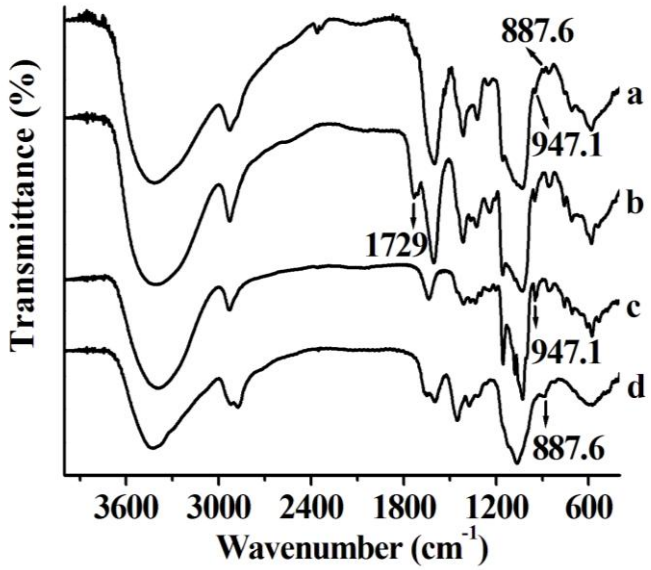


**Fig. S1** FT-IR spectra of (a) GCH-*g*-CM *β*-CD, (b) CM *β*-CD, (c) *β*-CD, and (d) GCH. The samples were prepared as pellets using spectroscopic grade KBr. In the spectrum of *β*-CD (curve c), the characteristic peak at 947.1 $cm^{-1}$ represents *α*-pyranyl vibration of *β*-CD. Comparison with curve c, there is a strong peak at 1729 $cm^{-1}$ in the spectrum of CM *β*-CD (curve b), which is ascribed to the stretching vibration of carbonyl group, indicating the carboxymethylation of *β*-CD was succeeded. The characteristic peak at 887.6 $cm^{-1}$ represents *β*-pyranyl vibration of GCH (curve d). In the spectrum of GCH-*g*-CM *β*-CD (curve a), there are both characteristic peaks of *β*-CD (947.1 $cm^{-1}$) and GCH (887.6 $cm^{-1}$) and the peak at 1729 $cm^{-1}$ belonging to the stretching vibration of carbonyl group almost disappeared after reacting with the amino of GCH, so all the results indicate CM *β*-CD has been grafted onto GCH.

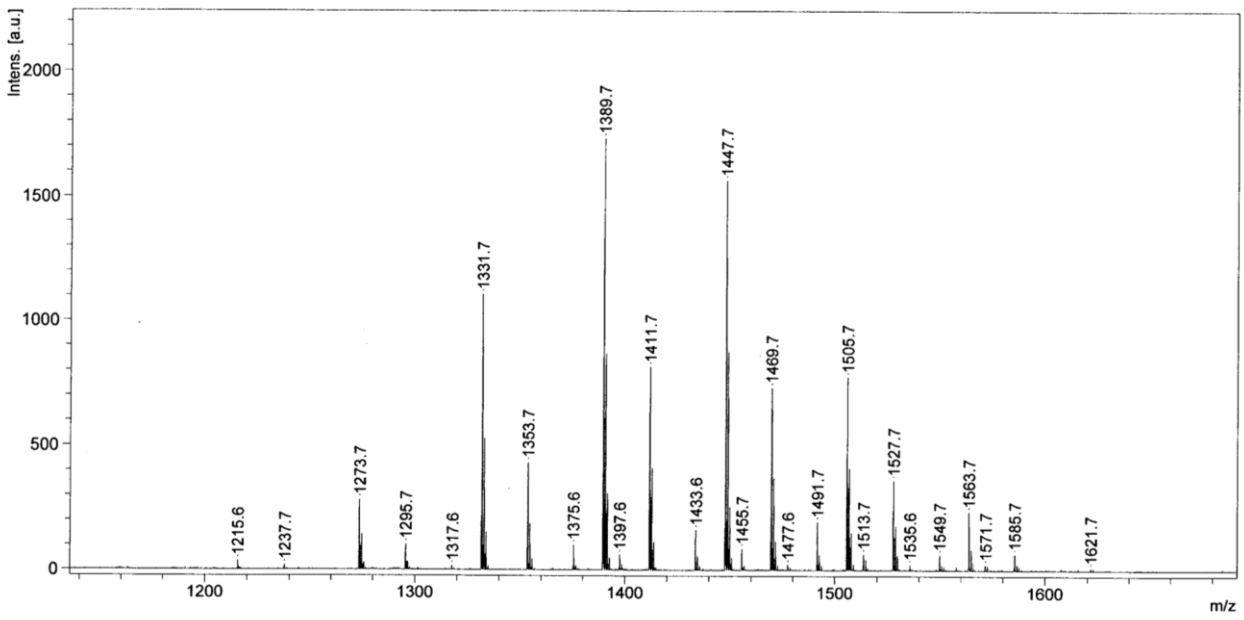


**Fig. S2** MALDI-TOF MS spectra of CM $\beta$-CDs. By analyzing the mass to charge ratios (m/z), 1215.6 m/z presents $[\beta\text{-CDNa-CH}_2\text{COOH}]^+$, 1273.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_2]^+$, 1331.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_3]^+$, 1389.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_4]^+$, 1447.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_5]^+$, 1505.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_6]^+$, and 1563.7 m/z presents $[\beta\text{-CDNa-(CH}_2\text{COOH)}_7]^+$.

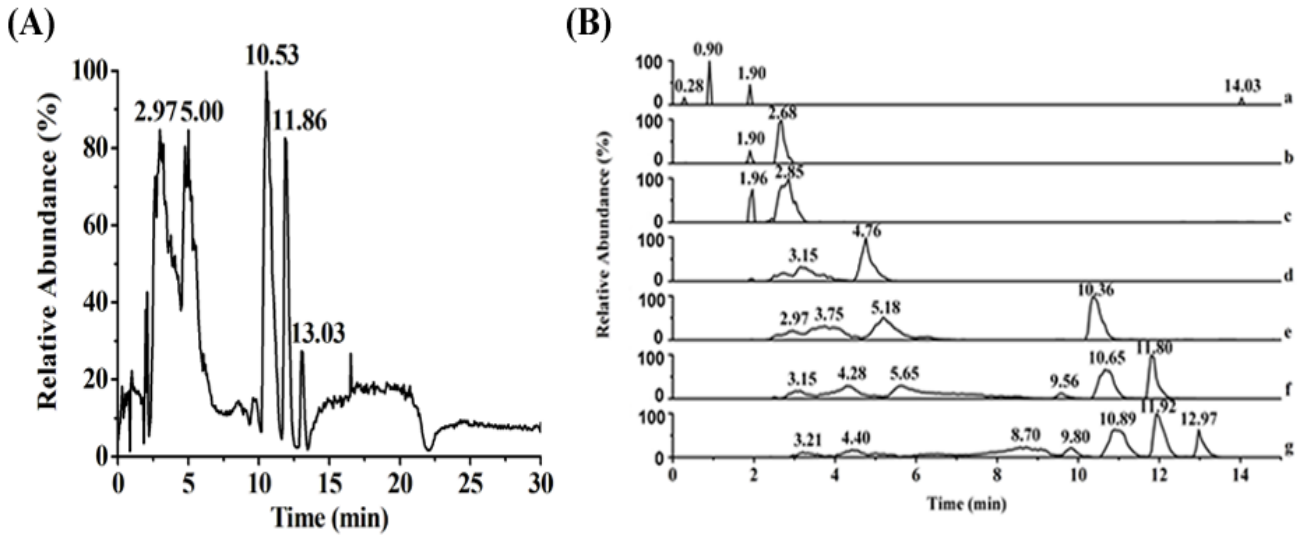


**Fig. S3** (A) Total ion current chromatogram of seven CM *β*-CD components. (B) The selected ion chromatograms of (a) *β*-CD-$CH_2COOH$, m/z: 1191.5–1192.5; (b) *β*-CD-$(CH_2COOH)_2$, m/z: 1249.5–1250.5; (c) *β*-CD-$(CH_2COOH)_3$, m/z: 1307.5–1308.5; (d) *β*-CD-$(CH_2COOH)_4$, m/z: 1365.5–1366.5; (e) *β*-CD-$(CH_2COOH)_5$, m/z: 1423.5–1424.5; (f) *β*-CD-$(CH_2COOH)_6$, m/z: 1481.5–1482.5; (g) *β*-CD-$(CH_2COOH)_7$, m/z: 1539.5–1540.5. Conditions: column: Agilent ZORBAX SB-$C_{18}$ (2.1×150 mm, 5 μm) using Agilent 1100 system; mobile phase: (A) $H_2O$, (B) Acetonitrile; gradient: 0–30 min, 10%–90% B; flow rate: 0.2 mL/min. The online identification was performed on electrospray ionization mass spectrometry (ESI-MS): Thermo Finnigan LCQ DECA XP MS. From figure A, it can be seen that there are five main components. From figure B, the peak area of every CM *β*-CD component and the total peak area can be obtained. The peak area of every CM *β*-CD component divided by the total peak area is equal to the relative content of every CM *β*-CD component. The calculated relative contents from *β*-CD-$(CH_2COOH)_3$ to *β*-CD-$(CH_2COOH)_7$ are 2.468%, 16.481%, 33.513%, 28.902%, and 18.266%, respectively.

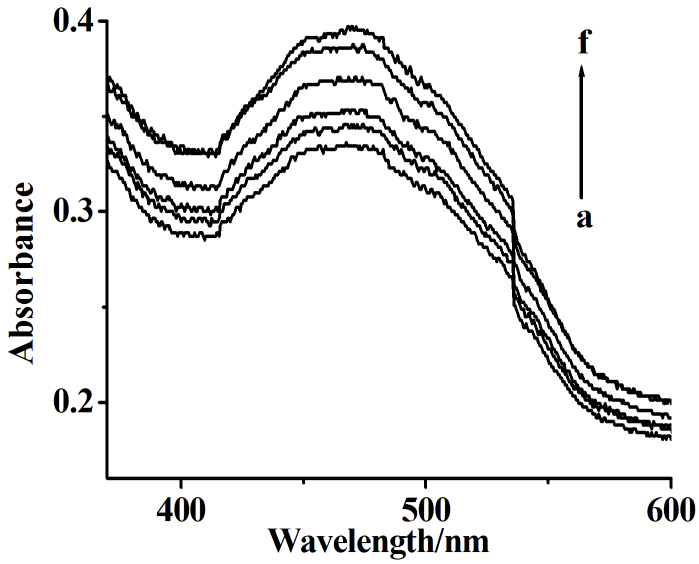


**Fig. S4** UV-vis absorption spectra of DXR-CM *β*-CD at different molar ratios, and the molar ratios between GCH-*g*-CM *β*-CD and DXR are (a) 0:1, (b) 0.25:1, (c) 0.5:1, (d) 2:1, (e) 1.5:1, and (f) 1:1. At the beginning [(a) 0:1, (b) 0.25:1, (c) 0.5:1], the absorbance increased upon addition of GCH-*g*-CM *β*-CD, indicating that CM *β*-CD has formed inclusion complex with DXR through host-guest interaction. Then, the absorbance approaches the maximum when the molar ratio between GCH-*g*-CM *β*-CD and DXR is 1:1 (curve f), but the absorbance decreased with continuing to add GCH-*g*-CM *β*-CD [curves (e) 1.5:1 and (d) 2:1]. These results indicate that 1:1 is the matching molar ratio, that is to say, one CM *β*-CD group grafted on GCH binds one molecule of DXR.