

Supplementary Information

Synthesis of cationic β -cyclodextrin functionalized silver nanoparticles and their drug-loading applications

Ke Yang,^{a,b} Laichun Luo,^a Junfeng Liu,^{*a,b} Meilin Li,^{a,b} Tanfang Xu,^{a,b} Junfeng Zan^a

a College of Pharmacy, Hubei University of Chinese Medicine; Hubei University of Chinese Medicine, Wuhan 430065, P. R. China

b Key Laboratory of Traditional Chinese Medicine Resource and Compound Prescription, Ministry of Education, Hubei University of Chinese Medicine, Wuhan 430065, P. R. China

e-mail: *liujf456@hotmail.com or 1105787683@qq.com, mobile: +86-15629118698.

1. Synthesis of Diaminopropane- β -cyclodextrin (DAP- β -CD):

Two-step synthesis of DAP- β -CD^{1,2}: Briefly, 50.0 g of β -CD was dissolved in 500 mL of a 0.4 M NaOH solution (0~5 °C), then 35.0 g of TsCl was added in batches within 5 min and stirred for another 30 min below 5 °C, after removing the unreacted TsCl by filtration, the filtrate was neutralized to pH 8 with 3 M HCl and stirred for 1 h. The resultant precipitates were filtered off, washed three times with water, and finally dried under vacuum at 40 °C. 4.0 g of Ts- β -CD was dissolved in 20 mL of 1,3-propanediamine and stirred at 80°C for 4 h. Then poured into 250 mL of EtOH. The precipitates were collected by filtration and were washed by EtOH thoroughly. The solid was dried under vacuum at 40 °C to obtain the DAP- β -CD. (yield: 94%). ¹H-NMR (600 MHz, D₂O): δ (ppm)5.09-5.04 (m,7H), δ 3.98-3.82 (m, 26H), δ 3.67-3.55 (m, 14H), δ 3.46-3.41 (t, 1H), δ 3.11-3.03 (m, 1H), δ 2.87-2.60 (m, 7H), δ 1.73-1.62 (m, 2H); ¹³C-NMR (151 MHz, D₂O): δ (ppm)101.84, 83.65, 81.12, 73.10, 72.04, 71.83, 60.26, 49.44, 46.43, 37.86, 30.25. FT-IR: (KBr, cm⁻¹): ν 3377, 2929, 1639, 1570, 1156, 1080, 1032, 945, 580. ESI-MS (*m/z*): 1190.44 (Calcd.) and 1191.45 (Found) for [M + H]⁺

2. Synthesis of cationic- β -cyclodextrin (C- β -CD):

C- β -CD was synthesized as follows: 0.6 g of EPTAC was dissolved in 10 mL of DMSO, subsequently, 4.5 g of DAP- β -CD was dissolved in 10 mL of DMSO solution and added to the above EPTAC solution, and then reacted at 80 °C for 4 h. Then poured into 250 mL of EtOH. The precipitates were collected by filtration and were washed by EtOH thoroughly. The solid was dried under vacuum at 40 °C to obtain the C- β -CD. (yield: 82%). ¹H-NMR (600 MHz, D₂O): δ (ppm)5.10-5.01 (m,7H), δ 4.09-3.73 (m, 26H), δ 3.67-3.55 (m, 14H), δ 3.47-3.35 (m, 2H), δ 3.31-3.13 (s, 5H), δ 3.09-3.03 (d, 2H) δ 2.89-2.55 (m, 8H), δ 1.83-1.60 (m, 2H); ¹³C NMR (151 MHz, D₂O) δ 102.94, 83.65, 81.87, 73.07, 72.04, 71.82, 69.12, 64.68, 60.29, 54.15, 52.29, 49.39, 46.97, 46.32, 38.19. FT-IR: (KBr, cm⁻¹): ν 3377, 2928, 1639, 1570, 1155, 1080, 1032, 945, 580. ESI-MS (*m/z*): 1341.52 (Calcd.) and 1306.55 (Found) for [M - Cl]⁺

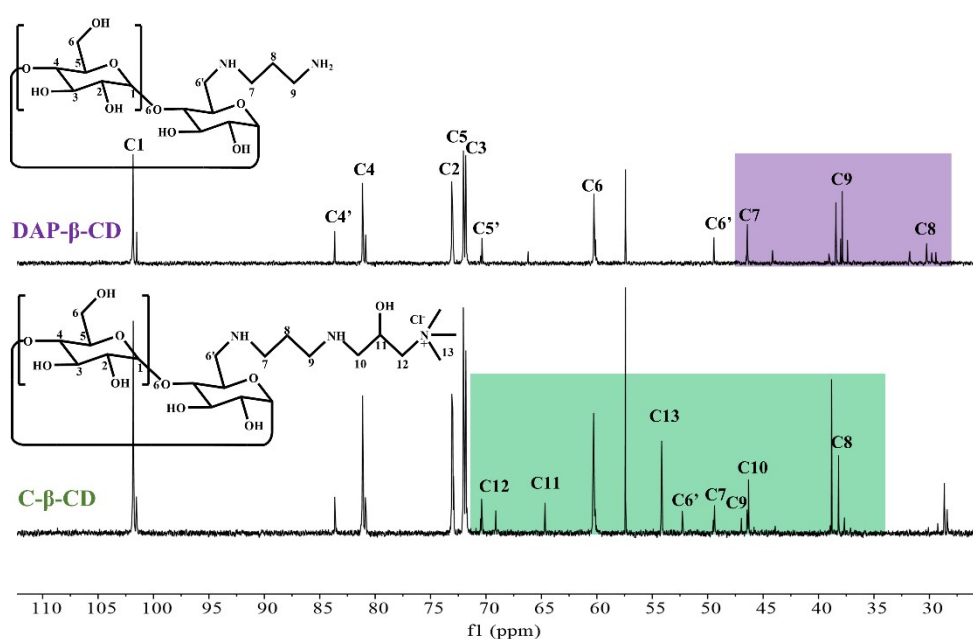


Figure S1 ¹³C-NMR spectrum of DAP- β -CD and C- β -CD.

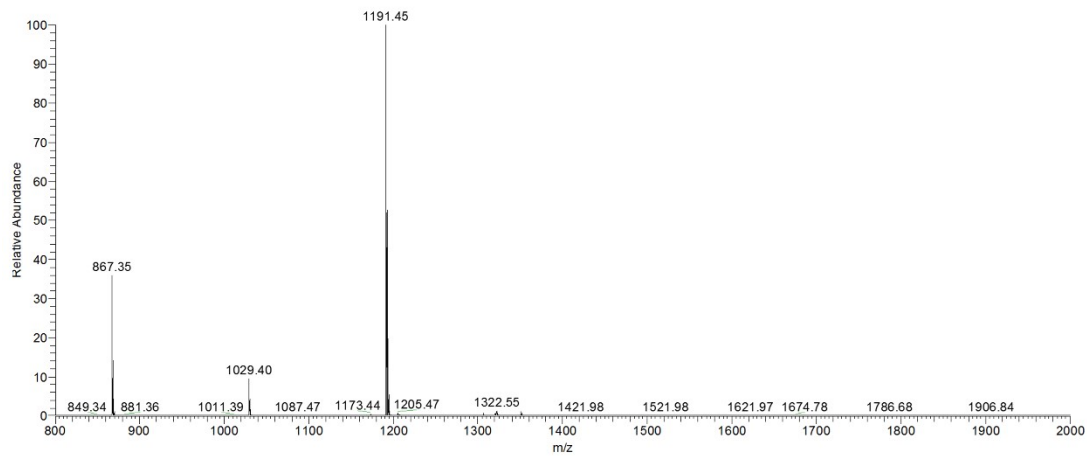


Figure S2 Mass spectrum of DAP-β-CD.

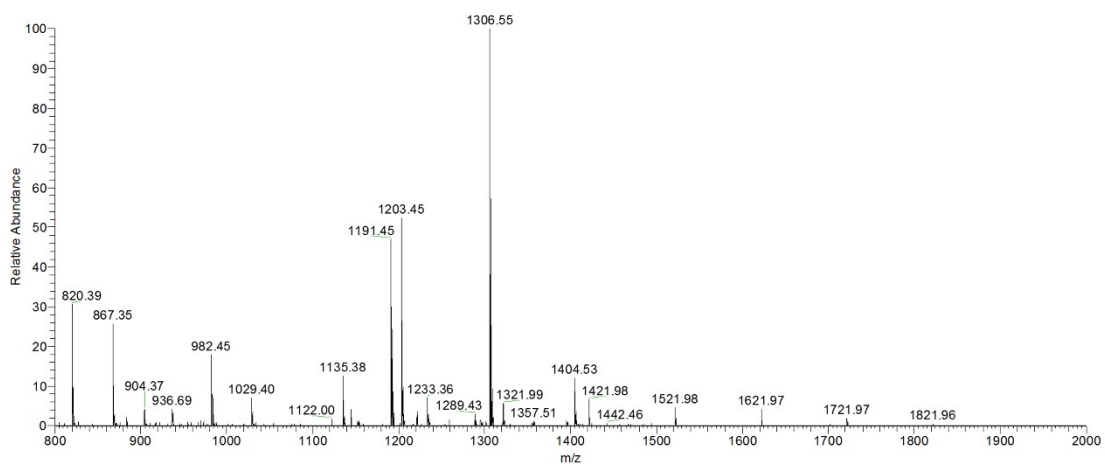


Figure S3 Mass spectrum of C-β-CD.

References:

1. J. Stadermann, H. Komber, M. Erber, F. Däbritz, H. Ritter and B. Voit, *Macromolecules*, 2011, 44, 3250–3259.
2. P. Jiao, H. Zhou, M. Otto, Q. Mu, L. Li, G. Su, Y. Zhang, E. R. Butch, S. E. Snyder, G. Jiang and B. Yan, *J. Am. Chem. Soc.*, 2011, 133, 13918–13921.