Electronic Supplementary Material for

Nanosupramolecular Assembly of Amphiphilic Guest Mediated by Cucurbituril for Doxorubicin Delivery

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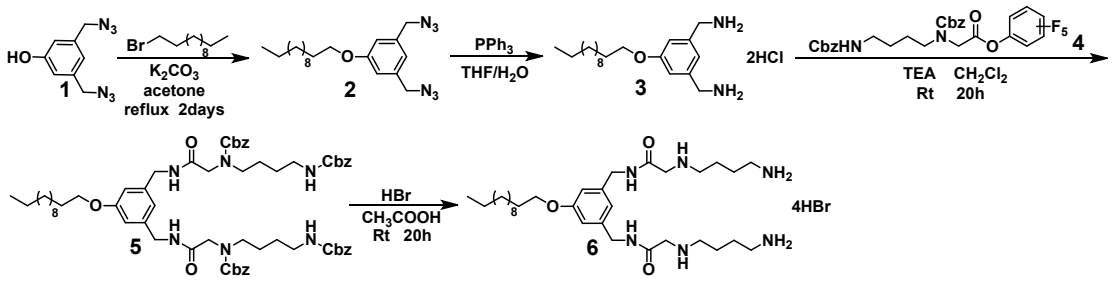

1-Bromododecane (255.2 mg, 0.74 equiv), compound **1**[1] (284.2 mg, 1.39 mmol), and potassium carbonate (527.0 mg, 3.0 equiv) were added into acetone. Then the mixture was heated at reflux for 2 days. Adding water into the reaction mixture, and the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over magnesium sulfate. Removing the solvent and purification by column chromatography on silica (ethyl acetate/hexane = 1:8) yielded compound **2** (153 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 3H), 4.32 (s, 4H), 3.97 (t, J = 8.0 Hz, 2H), 1.90–1.70 (m, 2H), 1.51–1.16 (m, 18H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 136.4, 118.7, 113.0, 67.2, 53.5, 30.9, 28.6, 28.3, 25.0, 21.7, 13.1. HRMS (MALDI): m/z: 395.2535 $[M + Na]^+$.

Triphenylphosphine (416.7 mg, 4.0 equiv) and compound **2** (150.0 mg, 0.40 mmol) were added into 50 mL THF, and the resulting solution was stirred at room temperature for 12 h. After removal of the solvent, the residue was redissolved in ethyl acetate. Addition of HCl (125 mL, 3.0 equiv) to the solution produced a white precipitate, which was collected by centrifuging to yield compound **3** (149.0 mg, 94%). ^{1}H NMR (400 MHz, D_2O) δ 7.05 (s, 3H), 4.13 (s, 4H), 4.06 (s, 2H), 1.73 (s, 2H), 1.40 (s, 2H), 1.22 (s, 18H), 0.81 (t, J = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 159.3, 135.1, 121.3, 115.9, 68.6,

42.7, 31.9, 29.8, 29.7, 29.6, 29.4, 29.1, 25.9, 22.6, 13.9. HRMS (MALDI): *m*/*z*: 321.2907 $[M - HCl - Cl]^+$.

Compound **4**[2] (422.0 mg, 2.5 equiv) was added to a solution of **3** (92.9 mg, 0.29 mmol) and triethylamine (164.0 mL, 4.0 equiv) in dichloromethane, and the resulting solution was stirred at room temperature for 20 h. Removing the solvent and purification by column chromatography on silica (ethyl acetate/hexane = 4:1) yielded compound **5** (258.3 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 20H), 6.65 (s, 3H), 5.11 (s, 4H), 5.06 (s, 4H), 4.31 (m, 4H), 3.90 (m, 6H), 3.33 (s, 4H), 3.10 (s, 4H), 1.71 (m, 2H), 1.53 (m, 4H), 1.40 (m, 4H), 1.25 (m, 18H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 159.7, 156.9, 156.6, 139.9, 136.6, 136.2, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 118.5, 112.5, 68.0, 67.7, 66.6, 51.5, 50.8, 48.4, 45.5, 43.2, 40.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.9, 26.1, 25.4, 25.0, 22.7, 14.2, 8.4. HRMS (MALDI): *m*/*z*: 1135.6098 $[M + Na]^+$.

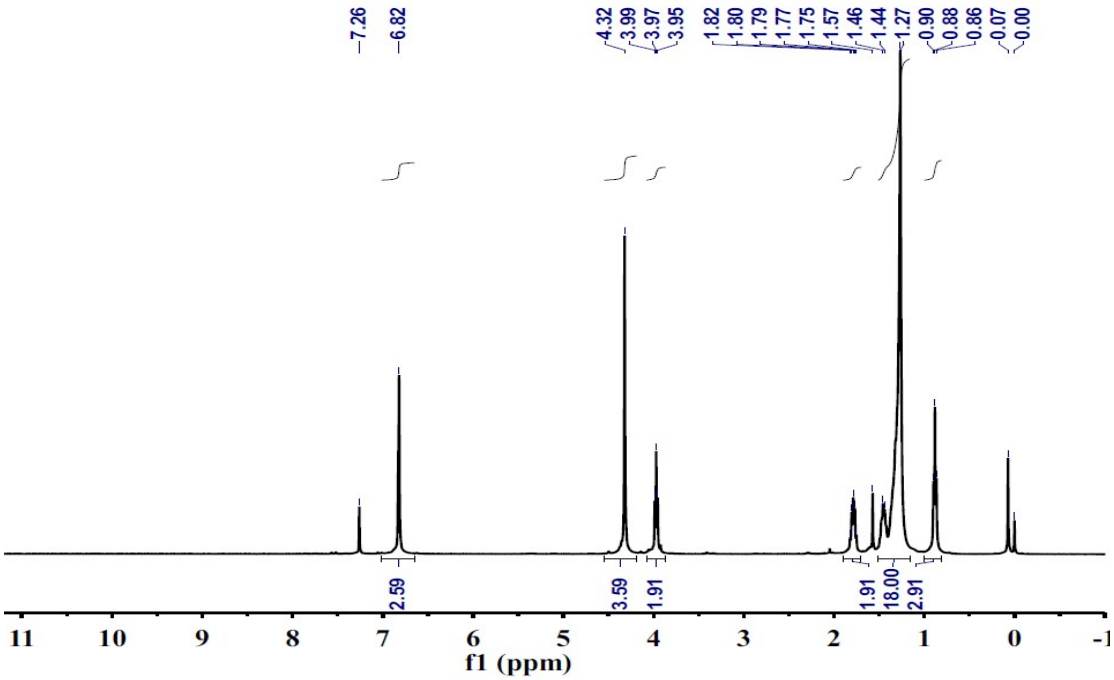

Figure S1. ^{1}H NMR (400 MHz) spectrum of compound **2** in $CDCl_3$ at 25 °C.

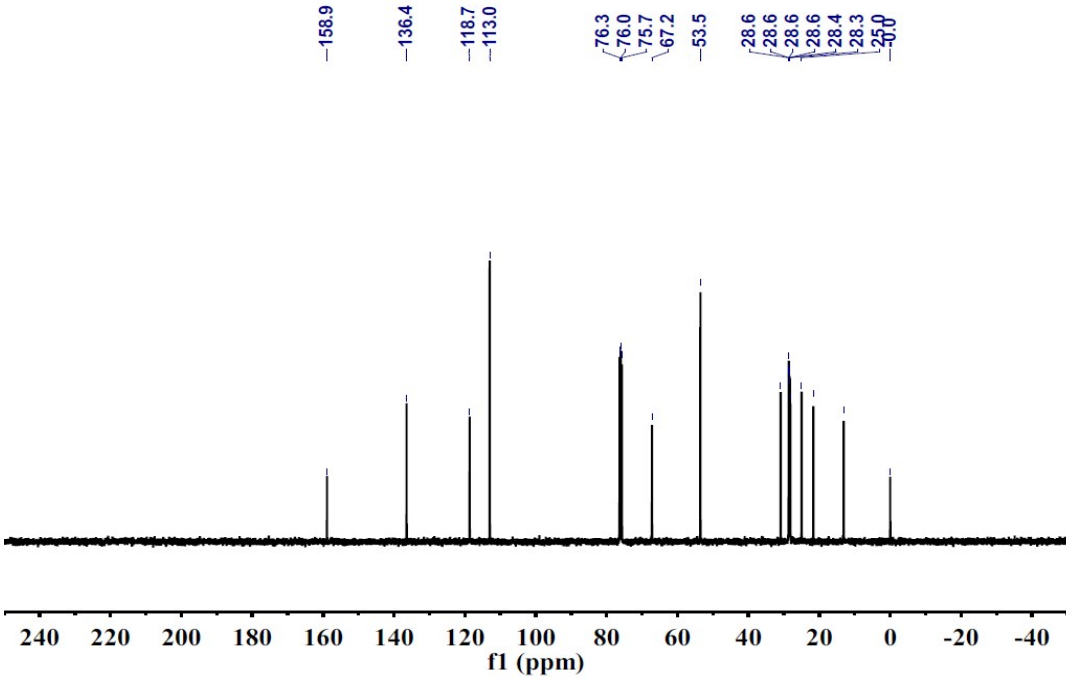

Figure S2. ^{13}C NMR (100 MHz) spectrum of compound **2** in $CDCl_3$ at 25 °C.

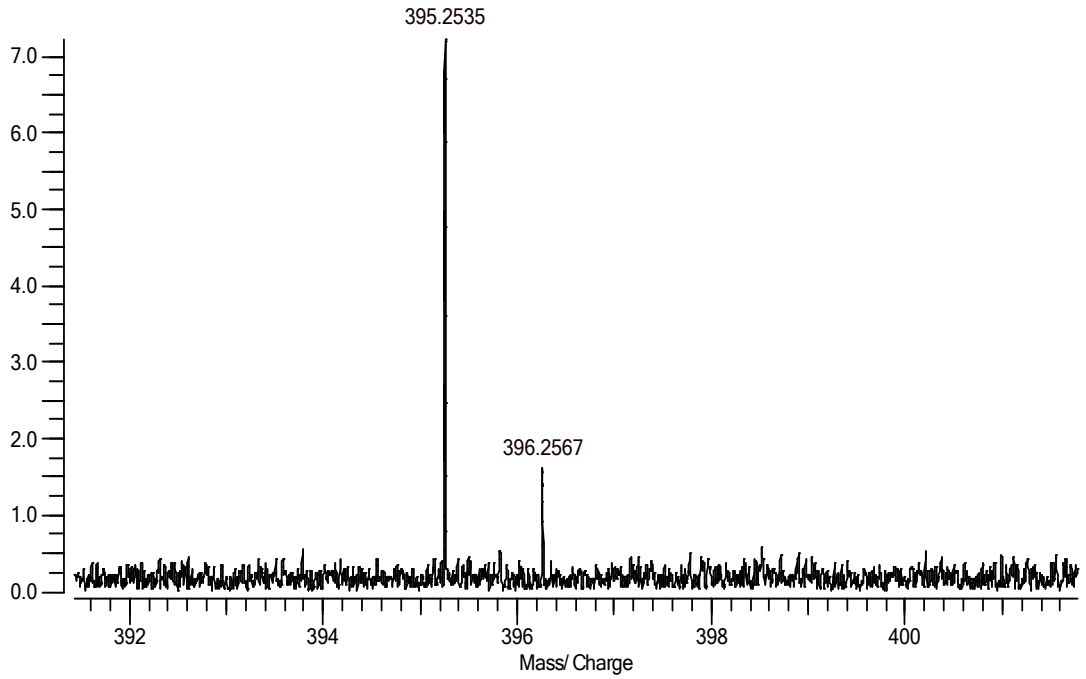

Figure S3. HRMS of compound **2**.

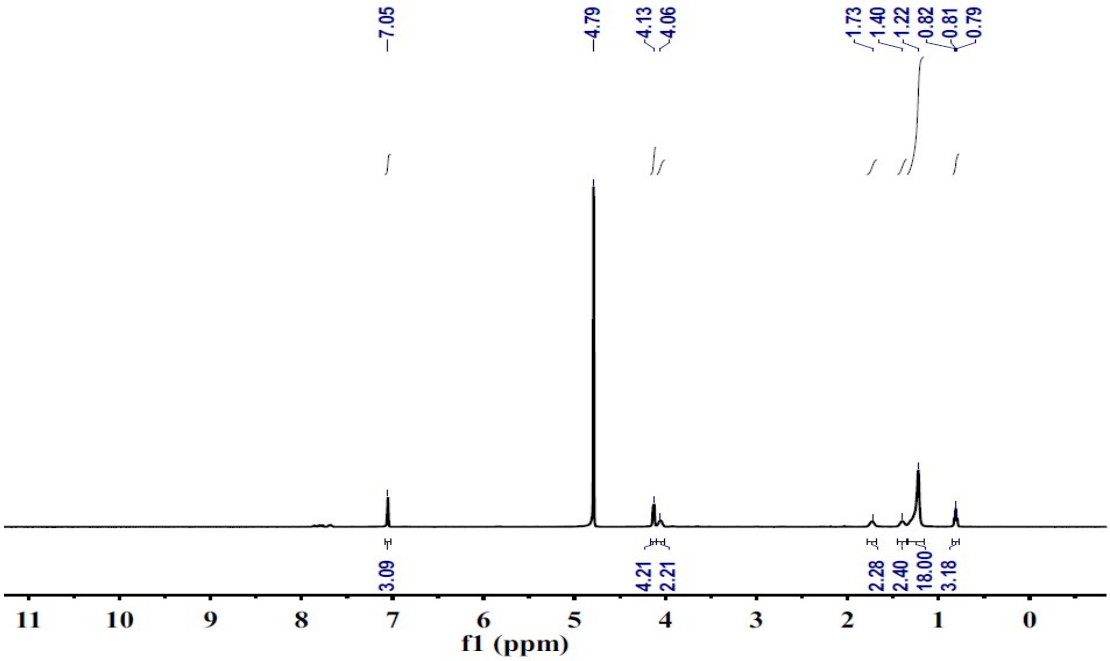

Figure S4. ^{1}H NMR (400 MHz) spectrum of compound **3** in D_2O at 25 °C.

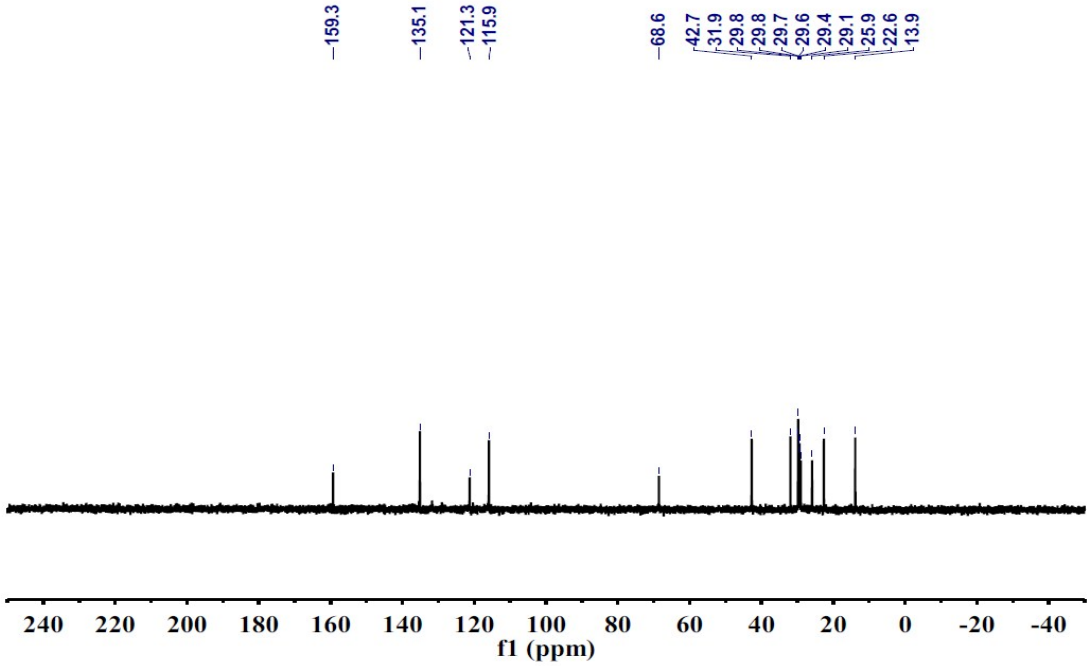

Figure S5. ^{13}C NMR (100 MHz) spectrum of compound **3** in D_2O at 25 °C.

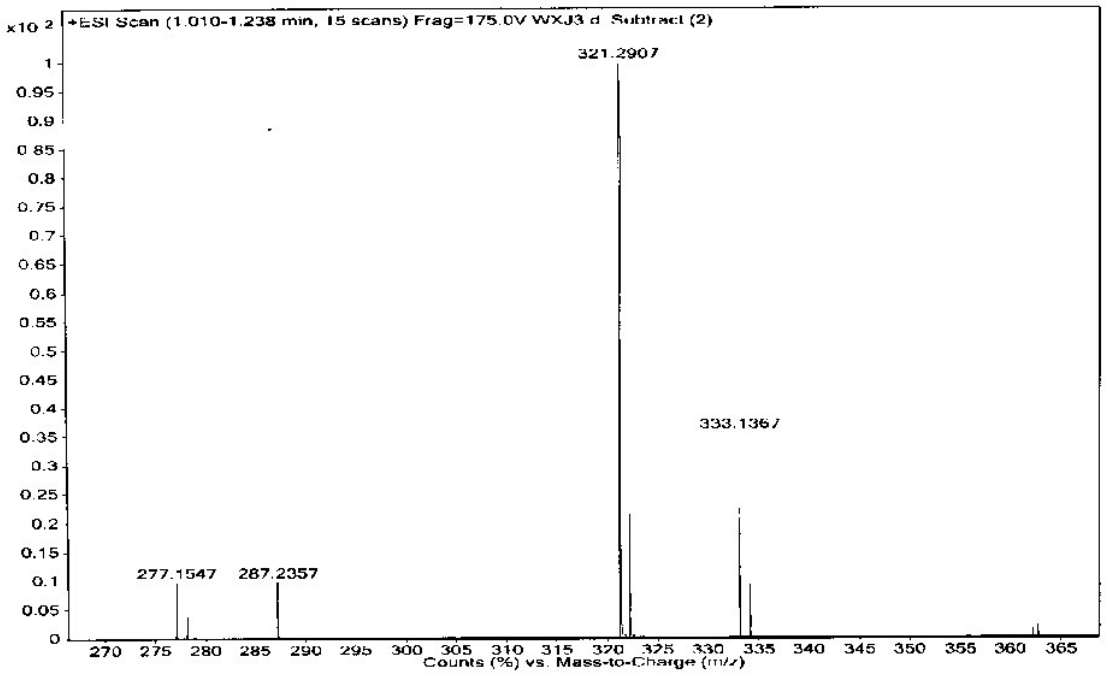

Figure S6. HRMS of compound **3.**

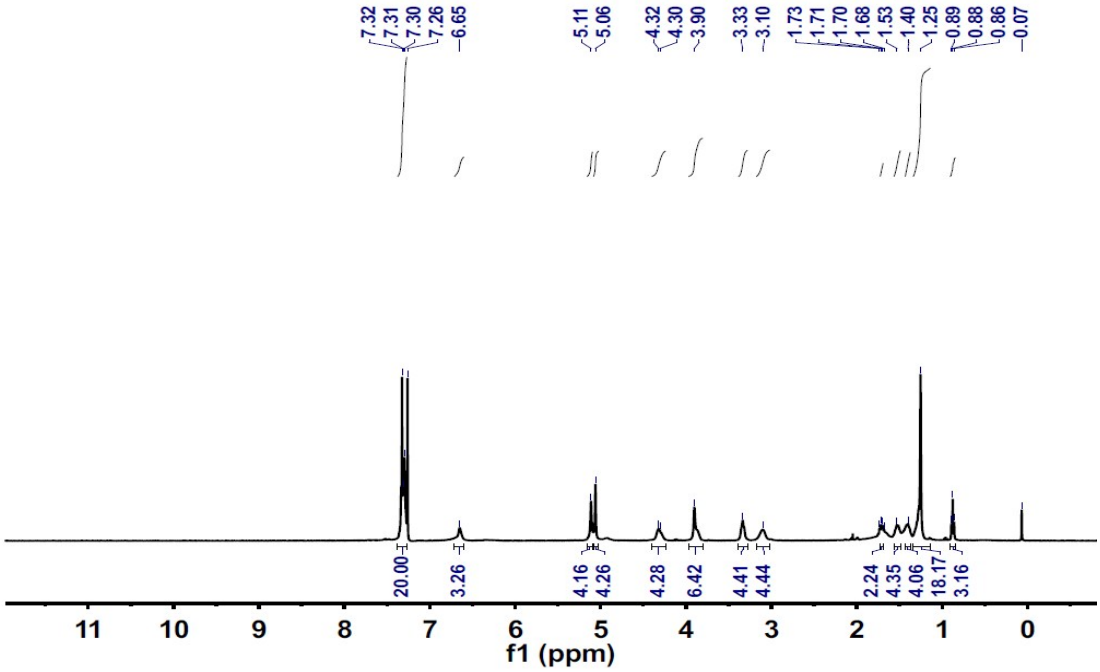

Figure S7. ^{1}H NMR (400 MHz) spectrum of compound **5** in $CDCl_3$ at 25 °C.

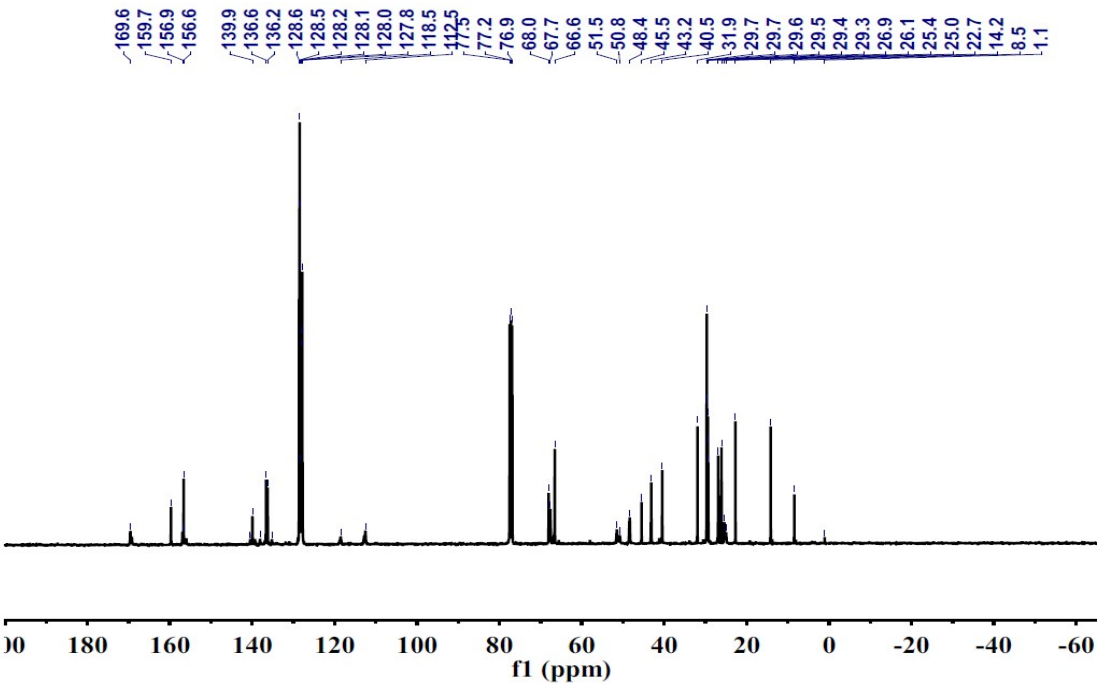

Figure S8. ^{13}C NMR (100 MHz) spectrum of compound **5** in $CDCl_3$ at 25 °C.

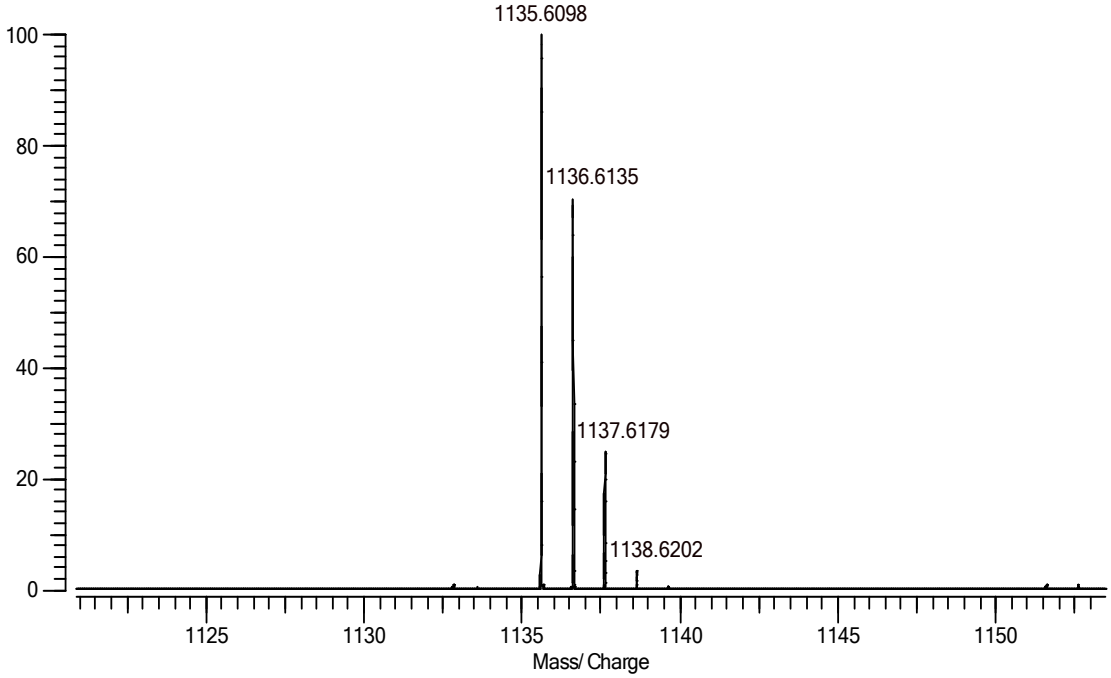

Figure S9. HRMS of compound **5.**

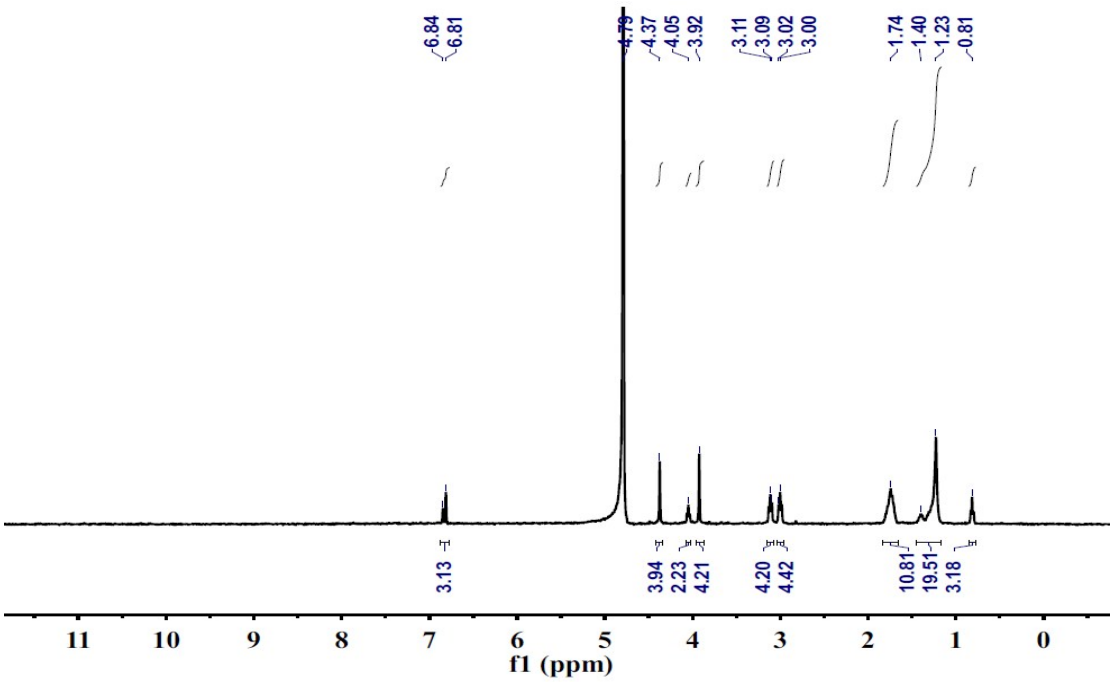

Figure S10. ^{1}H NMR (400 MHz) spectrum of compound **6** in D_2O at 25 °C.

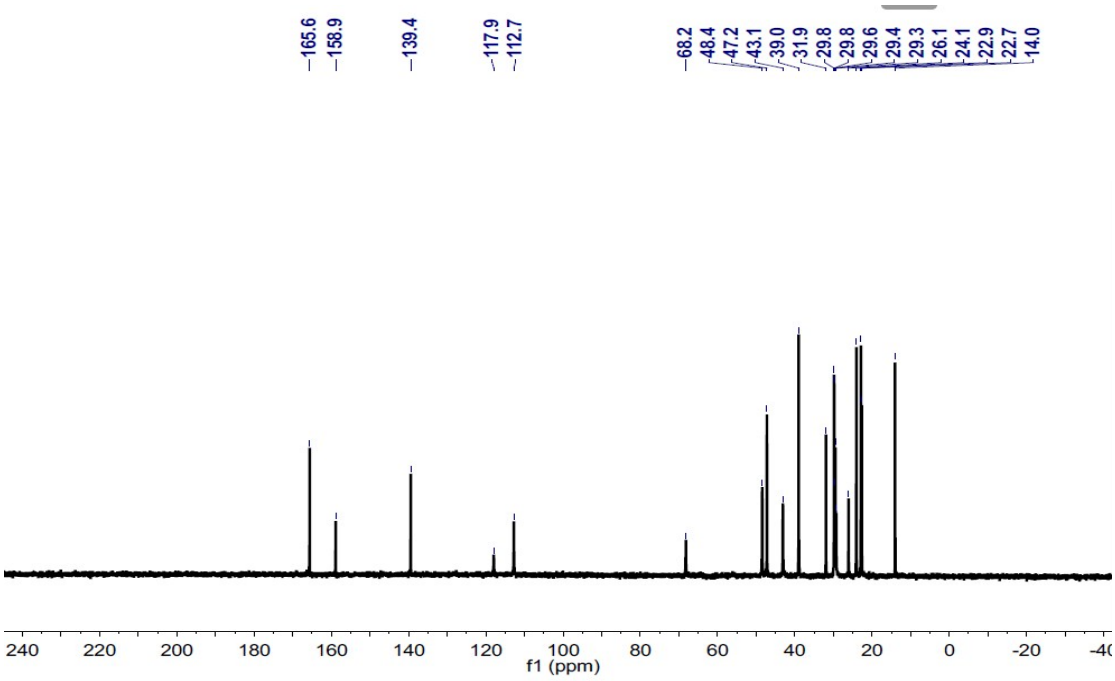

Figure S11. ^{13}C NMR (100 MHz) spectrum of compound **6** in D_2O at 25 °C.

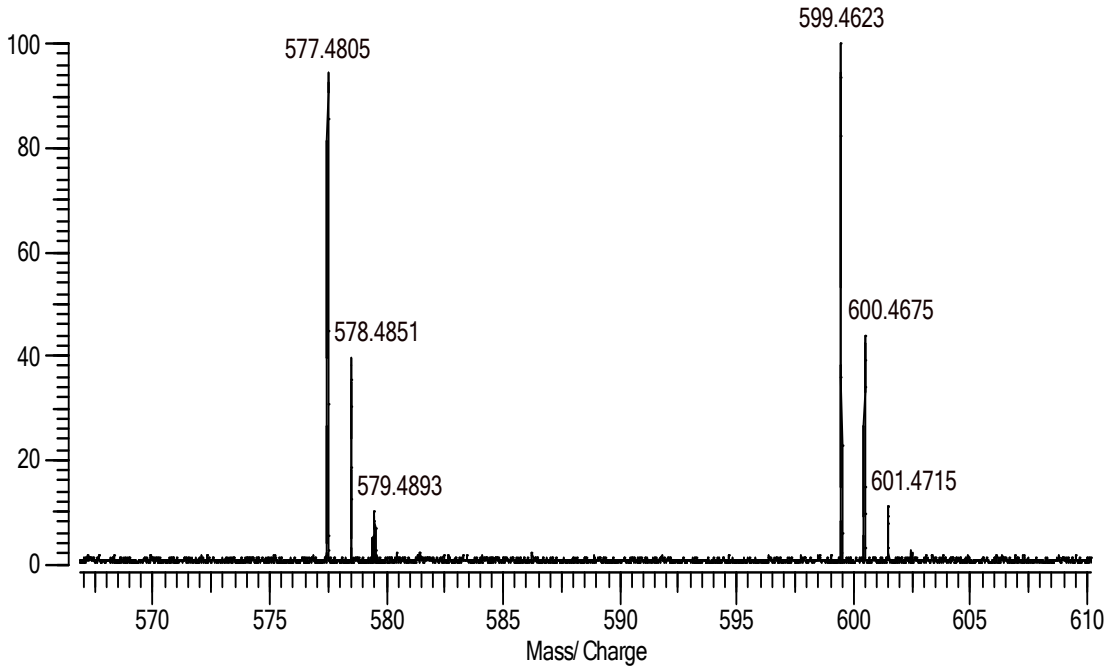

Figure S12. HRMS of compound **6.**

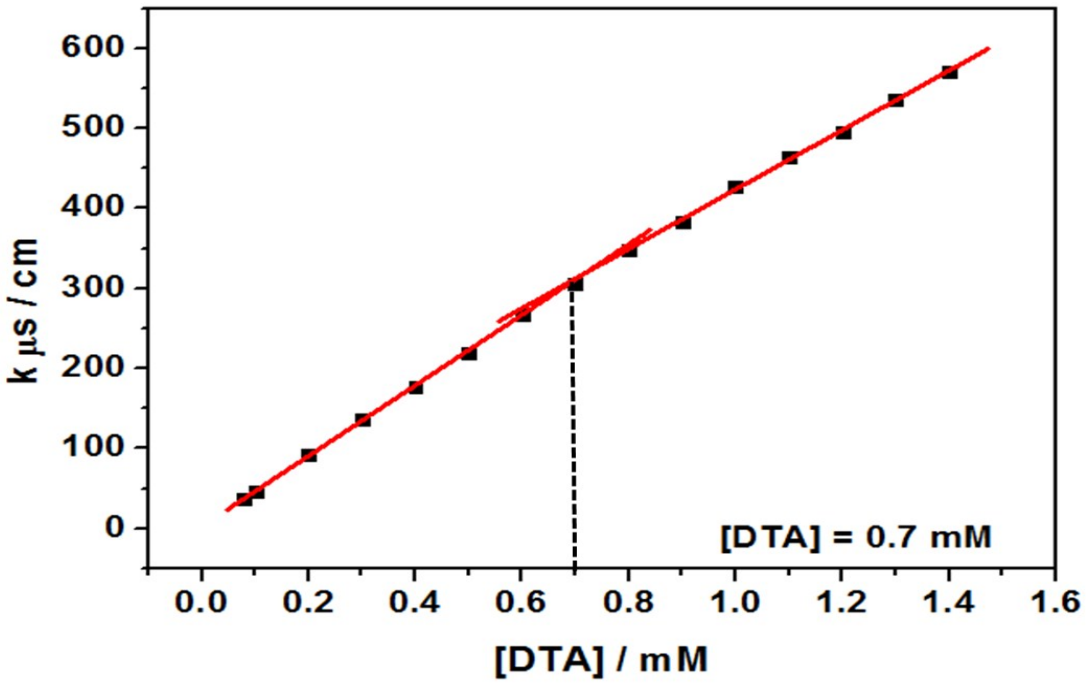

Figure S13. Dependence of electrical conductivity on the concentration of DTA in the presence of CB[6] ([CB[6]] = 2[DTA]) in water (25 °C, pH 7.0).

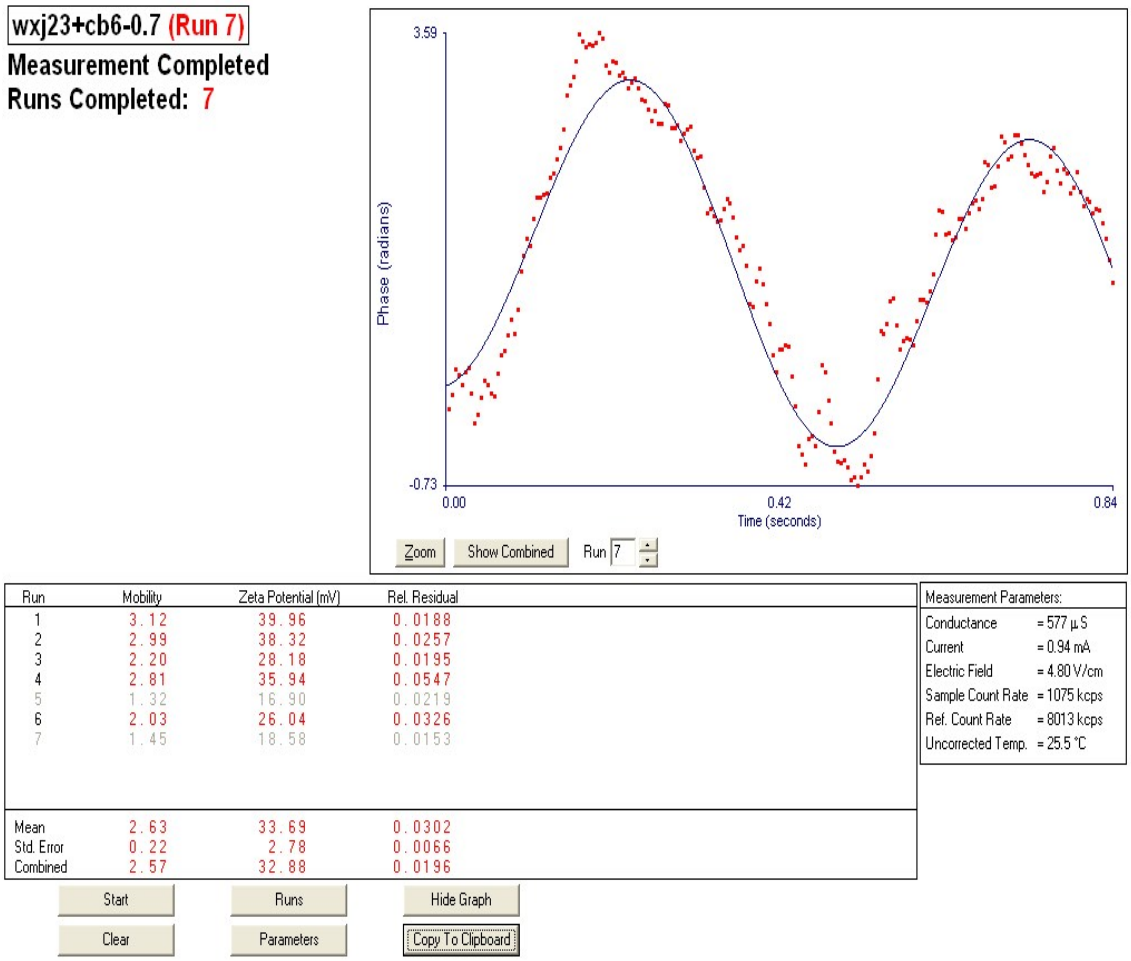

Figure S14. Zeta potential of NPs.

References

1 S.-Y. Kim, Y. H. Ko, J. W. Lee, S. Sakamoto, K. Yamaguchi, K. Kim, *Chem. Asian J.* 2007, **2**, 747–754.

2 J. W. Lee, Y. H. Ko, S-H Park, K. Yamaguchi, K. Kim, *Angew. Chem. Int. Ed.* 2001, **40**, 746–749.