Supporting Information

Selective recognition and sensing for adenosine triphosphate by label free electrochemistry based on its inclusion with per-6-ammonium-β-cyclodextrin

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Synthesis and Characterization of the *p*ABCD

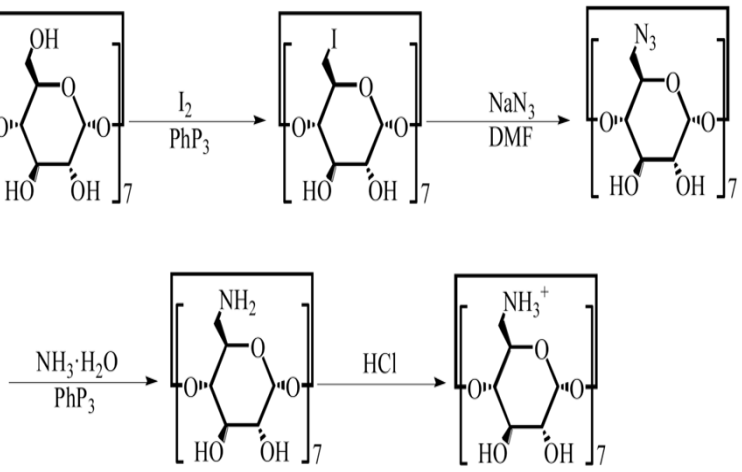
Synthesis of per-6-iodo-β-cyclodextrin (2) Ph_3P (22 g, 84 mmol) was dissolved in DMF with stirring (50 mL), followed by adding I_2 (22.5 g, 88 mmol) dropwisely in 30 min. β-cyclodextrin **(1)** (5.7 g, 5 mmol) was then added to this dark brown solution, and the reaction mixture was heated to 65 ºC and maintained under N_2 atmosphere for 18 h. The solution was concentrated under vaccum to remove DMF. The left oilly liquid was poured into 35 mL sodium methoxide solution (3 mol/L) under N_2 atmosphere and kept stirring at 0 for 1 h. Then 400mL MeOH was added to precipitate the product. After that the precipitate was filtered and washed with MeOH, acetone and water. The crude product was extracted with MeOH by Soxhlet for 22 h and dried for 6 h under vacuum at 65 ºC. White powder was obtained (6.799 g). m.p: 235-236 ºC; ^{1}HNMR (DMSO-d_6): 3.29-3.43 (m, 21H, H_2, H_4, H_{6a}), 3.59 (m, 14H, H_3, H_5), 3.81 (d, 7H, J = 9.0 Hz, H_{6b}), 4.99 (s, 7H, J = 3 Hz, H_1), 5.94 (s, 7H, OH_3), 6.04 (d, 7H, OH_2); ^{13}CNMR (DMSO-d_6): 38.89-40.15 (C_6), 70.97 (C_2), 71.93 (C_3), 72.19 (C_5), 85.97 (C_4), 102.14 (C_1); IR (cm^{-1}): 3290 (O–H); 2910 (C–H)

Synthesis of per-6-azido-β-cyclodextrin (3) Per-6-iodo-β-cyclodextrin **(2)** (2.995 g, 1.573 mmol) and NaN_3 (1.25 g, 19.25 mmol) were dissolved in 50 mL DMF and

heated at 60 ºC for 19 h under N_2 atmosphere. The almost clear solution was then concentrated under vacuum (approximately 5 mL). Next, a large of H_2O was added, giving a white precipitate at once. In order to remove remained NaN_3, the solid product was washed with ethanol until the disappearance of blood red in the filtrate by means of the reaction with $FeCl_3$.The product dried for 6 h under vacuum at 75 ºC to yield a white powder (1.498 g). m.p: 220-222 ℃. ^{1}HNMR（DMSO-d_6): 3.38-3.32 (m, 21H, H_2 H_4, H_{6a}）, 3.58 （m, 14H, H_3, H_5）, 3.78 (m, 7H, H_{6b}), 4.91 (s, 7H, J = 3 Hz, H_1) , 5.76 (s, 7H, OH_3), 5.90 (d, 7H, OH_2); ^{13}CNMR (D_2O): 51.4 (C_6), 70.55 (C_2), 72.22 (C_3), 72.82 (C_5), 83.42 (C_4), 102.27 (C_1); IR (cm^{-1}): 3380 (O–H), 2920 (C–H), 2108 (N_3); EA ($C_{42}H_{63}N_{21}O_{28}$): C (38.5), H (4.81), N (22.4) Found: C (38.5), H (5.05), N (21.9)

Synthesis of per-6-amino-β-cyclodextrin (4) The per-6-azido-β-cyclodextrin **(3)** (2.022 g, 1.539 mmol) was suspended in DMF (40 mL), and Ph_3P (6.5 g, 24.73 mmol) was added. The reaction mixture was stirred for 1 h under N_2 atmosphere at room temperature. Concentrated aqueous ammonia (12 mL, approximately 28%) was added to the mixture and kept under stirring for 18 h. The resulting suspension was concentrated under vaccum to about 7 mL. The product was then precipitated by addition of EtOH (100 mL). The precipitate was washed with EtOH，acetone and water. Then dried for 6 h under vacuum at 65 ºC to yield a white powder (1.112 g). m.p: 208-210 ℃; ESI-MS (*m/z*): $[M]^+$ = 1128.5614; ^{1}HNMR (D_2O): 3.18 (dd, 7H, H_{6a}), 3.36 (m, 7H, H_4), 3.52 (m, 7H, H_2), 3.66 (d, 7H, H_5), 3.98 (m, 7H, H_3), 4.09 (s, 7H, H_{6b}), 5.12 (s, 7H, J = 3 Hz; H_1); ^{13}CNMR (D_2O): 57.99 (C_6), 71.70 (C_2), 72.36 (C_3), 74.8 (C_5), 82.3 (C_4), 101.24 (C_1)

Synthesis of per-6-ammonium-β-cyclodextrin (5) Per-6-amino-β-cyclodextrin **(4)** (1.112 g, 0.98 mmol) was suspended in a small volume of water followed by addition of 0.01 mol/L HCl down to pH = 6, At this pH, a clear solution formed which gave a yellow glass when evaporated under reduced pressure and dried for 6 h under vacuum at 65 ºC to yield a yellow glass (1.312 g).



Scheme S1. The synthesis route for derivatives of β-cyclodextrin

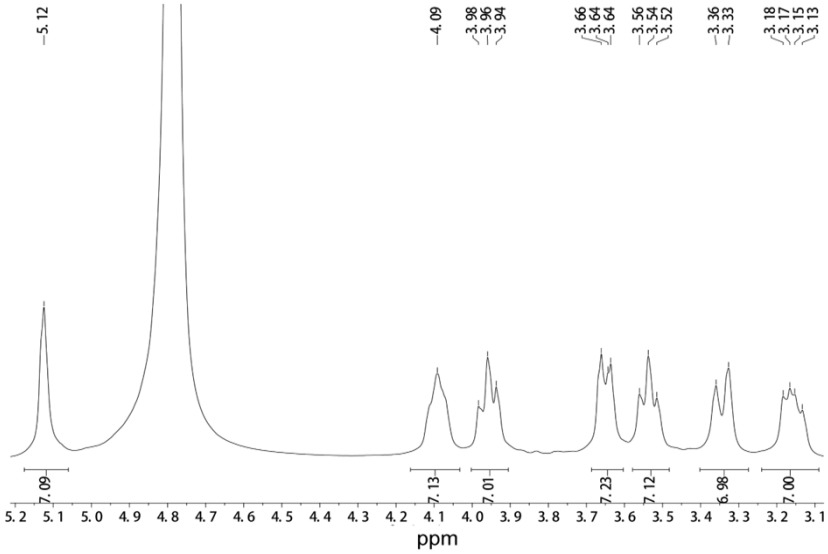


Fig.S1. The ^{1}HMNR spectrum of per-6-amino-β-cyclodextrin in D_2O

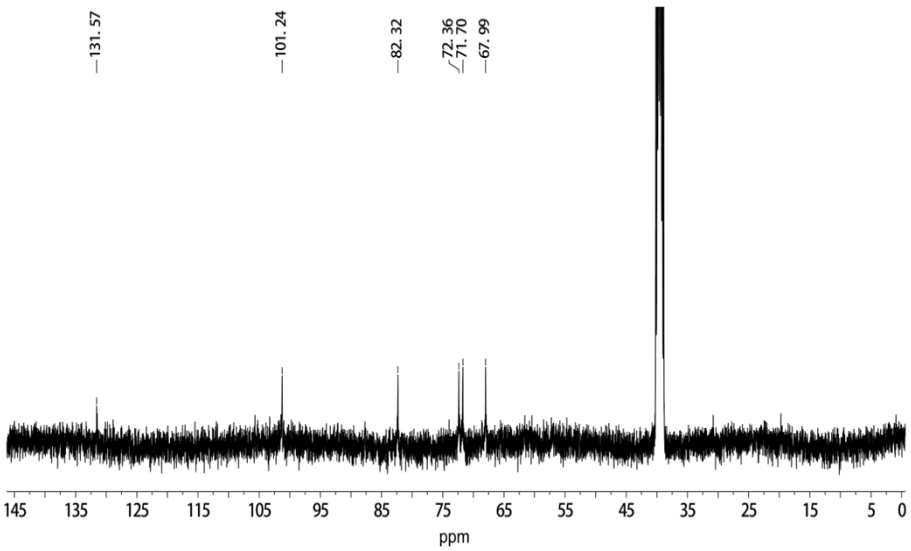


Fig.S2. The ^{13}CMNR spectrum of per-6-amino-β-cyclodextrin in D_2O

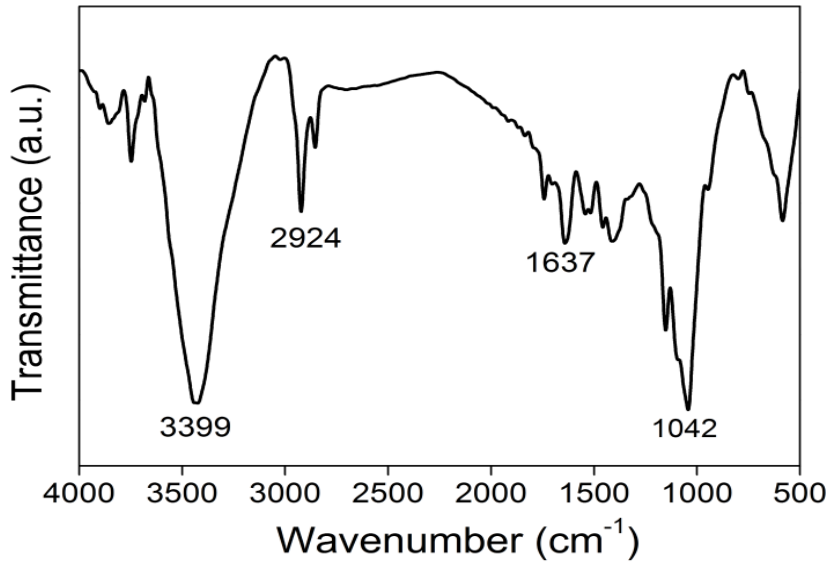


Fig.S3. The FT-IR spectrum of per-6-amino-β-cyclodextrin

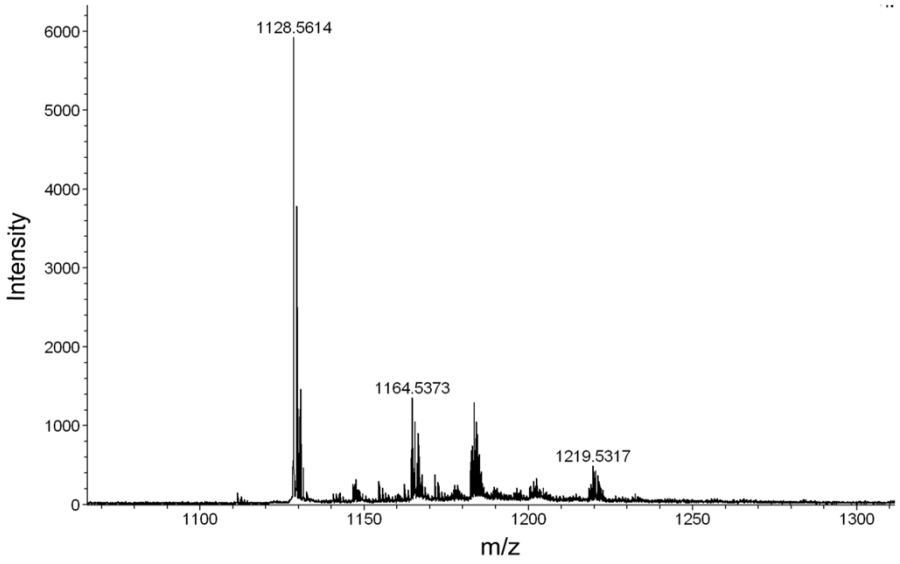


Fig.S4. The ESI-MS spectrum of per-6-amino-β-cyclodextrin.