Controllable DNA condensation through cucurbit[6]uril in 2D pseudopolyrotaxanes

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Experiment Section

6-[(6-Aminohexyl)amino]-6-deoxy-β-CD chloride was synthesized using our method.[1]

Preparation of Pseudopolyrotaxane 1 (PPR-0).

In a solution of 6-[(6-Aminohexyl)amino]-6-deoxy-β-CD chloride (800 mg in 5 mL water), PPG 4000 diamine was added at room temperature. The mixture was put in a ultrasonic bath for 2 h and then stirred for another 24 h. Then, the result solution was washed by ethylacetate (10 mL × 3) to remove the unreacted PPG4000 diamine and dried under reduce pressure. Crude product was purified by Sephadex G-25 to afford a white solid with the yield 17%. Calculated by NMR spectrum, about 25 CDs were threaded on. ^{1}H NMR (400 MHz, D_2O, ppm): 4.87 (d, 25 × 7H), 3.79-3.25 (m, 25 × 42H + 68 × 3H), 2.87 (t, 25 × 2H), 2.78 (t, 25 × 2H), 1.47 (m, 25 × 4H), 1.21 (m, 25 × 4H), 0.947 (d, 68 × 3H); FTIR (KBr): ν = 3342, 2929, 1735, 1558, 1474, 1420, 1374, 1324, 2594, 2536, 1190, 1147, 1029, 964, 923, 816, 800, 758, 673, 630, 445 cm^{-1}; elemental analysis calcd for $(C_{48}H_{86}Cl_2N_2O_{34})_{25}$ $(C_{204}H_{408}O_{68}N_2H_4)$ $(H_2O)_{80}$: C 44.29 %, H 7.20 %, N 1.91 %; found: C 44.23 %, H 7.28 %, N 1.87 %.

General procedure for preparation of PPR-(20, 40, 70, 100).

Pseudopolyrotaxane **1** was dissolved in a minimum of water. Then, some mount of CB[6]s (0, 20, 40, 70, 100% calculated reference to each CD unit) was added with stirring until all CB[6]s were dissolved. The solution was dried under reduce pressure. The crude product was washed with little ethylacetate and water and dried under

vacuum and stored in desiccator.

PPR-20: ^{1}H NMR (400 MHz, D_2O, ppm): 5.56 (tert, 25 ×0.2× 12 H), 5.38 (s, 25 ×0.2× 12H), 4.88 (d, 25 × 7H), 4.13 (tert, 25 ×0.2× 12 H), 3.77-3.31 (m, 25 × 42H + 64 × 3H), 2.86-2.75 (m, 25 ×4H), 1.48 (m, 25 × 0.8 × 4H), 1.20 (s, 25 × 0.8 × 4H), 0.96 (d, 68 × 3H), 0.45 (s, 25 × 0.2 × 4H), 0.31 (s, 25 × 0.2 × 4H). Yielding 91%.

PPR-40: ^{1}H NMR (400 MHz, D_2O, ppm): 5.56 (tert, 25 ×0.4× 12 H), 5.38 (s, 25 ×0.4× 12H), 4.88 (d, 25 × 7H), 4.12 (tert, 25 ×0.4× 12 H), 3.75-3.31 (m, 25 × 42H + 64 × 3H), 2.86-2.75 (m, 25 ×4H), 1.48 (m, 25 × 0.6 × 4H), 1.20 (s, 25 × 0.6 × 4H), 0.96 (d, 68 × 3H), 0.45 (s, 25 × 0.4 × 4H), 0.30 (s, 25 × 0.4 × 4H). Yielding 95%.

PPR-70: ^{1}H NMR (400 MHz, D_2O, ppm): 5.55 (tert, 25 ×0.7× 12 H), 5.38 (s, 25 ×0.7× 12H), 4.87 (d, 25 × 7H), 4.13 (tert, 25 ×0.7× 12 H), 3.77-3.32 (m, 25 × 42H + 64 × 3H), 2.86-2.75 (m, 25 ×4H), 1.48 (m, 25 × 0.3 × 4H), 1.20 (s, 25 × 0.3 × 4H), 0.96 (d, 68 × 3H), 0.46 (s, 25 × 0.7 × 4H), 0.31 (s, 25 × 0.7 × 4H). Yielding 93%.

PPR-100: ^{1}H NMR (400 MHz, D_2O, ppm): 5.55 (tert, 25× 12 H), 5.38 (s, 25× 12H), 4.87 (d, 25 × 7H), 4.13 (tert, 25× 12 H), 3.77-3.32 (m, 25 × 42H + 64 × 3H), 2.85-2.74 (m, 25 ×4H), 0.96 (d, 68 × 3H), 0.46 (s, 25 × 4H), 0.31 (s, 25 × 4H). Yielding 90%.

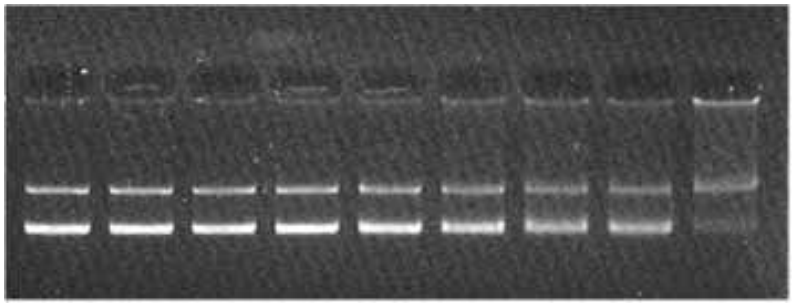

Fig. S1 DNA condensation induced by 6-[(6-Aminohexyl)amino]-6-deoxy-β-CD chloride. The molar ratios between complex and DNA nucleotide from lane 1 to lane 9 are 0, 38.75, 77.50, 154.93, 232.75, 309.82, 387.30, 464.75 and 800.0 separately

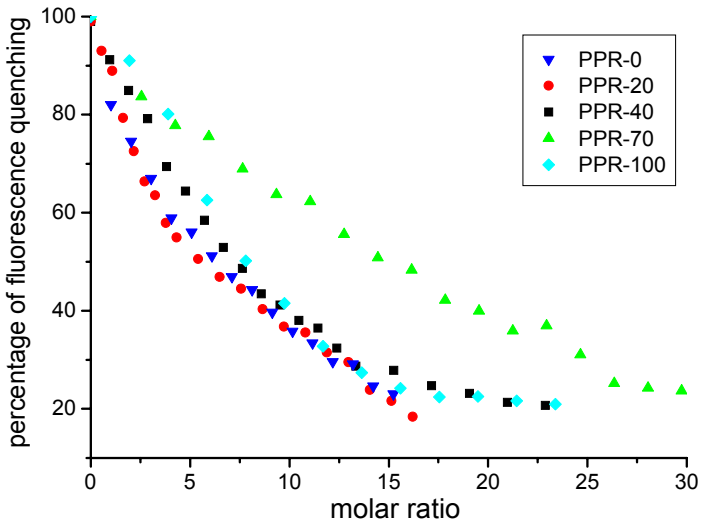

Fig. S2 Ethidium bromide displacement assay of PPR(0-100) in TE buffer. Excitation wavelength: 260 nm and data were recorded using the emission intensity at 611 nm.

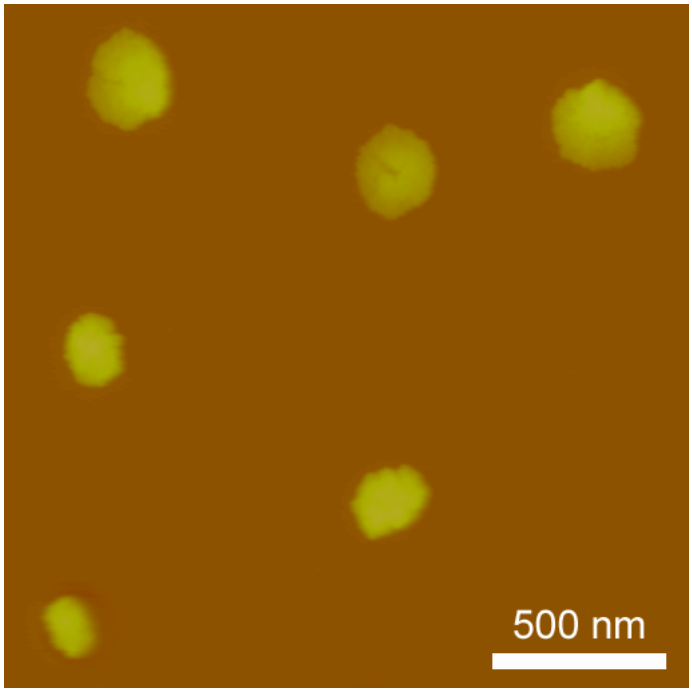

Figure S3. AFM height images of a plasmid DNA's condensates induced by 2D PPR-100 on mica in tapping mode in the air.

[1] Y. Liu, C.-F. Ke, H.-Y. Zhang, W.-J. Wu, S. Jun, *J. Org. Chem.*, 2007, **72**, 280-283.