Supplementary Information

CTAB-induced Morphological Transition of DNA Micro-Assembly from Filled Spheres to Hollow Capsules

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Experimental Section

General. Reagents were obtained from commercial source and used without further purification. All type of synthetic ODNs (purified by HPLC), including 6-caboxy-fluorescein (FAM)-labeled ODN, were purchased from Espec Co., Ltd. as lyophilized powders. YOYO-1 iodide was purchased from Molecular Probe Co., Ltd. as 1 mM dimethyl sulfoxide solution. Deionized water of high resistivity (> 18 MΩcm) purified with a Millipore Purification System (Milli-Q water) was used as a solvent in this study. The concentration of ODN was determined by UV absorbance at 260 nm. UV-vis spectra were recorded in a 1 mm quartz cell with a JASCO V-570 spectrophotometer.

Typical Procedure for Construction of Nucleospheres and their complexes with CTAB. Equimolar aqueous solutions of ODN **1**, **2**, and **3** were mixed at room temperature ($[ODN]_{total}$ = 20 μM, [NaCl] = 0.5 M). After heating the mixture at 70 ºC for 5 min, it was cooled spontaneously to 10 ºC and then aged at this temperature for 12h. Aqueous solution of CTAB was added to the solution of nucleospheres, and then the suspension was voltexed for 30s.

Conforcal Laser Scanning Microscopy (CLSM). CLSM was conducted on an LSM 510 instruct (Carl Zeiss) equipped with an LP 505 filter (cut off < 505 nm). An aliquot (typically 30 μL) of aqueous nucleospheres was placed on a glass dish. The sample was stained by YOYO-1 iodide (1 μM) for 6 h, when necessary. The dish was subjected to CLSM observations with excitation at 488 nm (Ar^+ laser) through an LP505 filter.

Synchrotron Small Angle X-ray Scattering (SAXS). SAXS was measured at 40B2

beam line of SPring-8 Japan. The sample to detector distance was 1652 mm and an imaging plate detector was used to measure the SAXS intensities at 10 ºC. The incident beam wavelength was tuned at 0.10 nm. The scattering intensity was accumulated for 1200 s the range of q = 0.12-3.0 nm^{-1} with a Rigaku R-AXIS IV^{++} system, where q is the magnitude of the scattering vector defined by eq 1:

$$q = \frac{4\pi}{\lambda} \sin(\theta/2) \qquad (1)$$

where θ is the scattering angle and λ is the wavelength. The experimental data were corrected for background scattering (aqueous solutions of 0.5 M NaCl and 1 mM CTAB) and then radially averaged.

Effect of Addition of Surfactants on the Morphology of Nucleospheres.

Figure S1 shows CLSM images of nucleospheres ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl) in the presence of cationic surfactants. CTAB and $2C_{12}N^{+}2C_1$ Br^{-} induced the structural transition to the hollow nucleospheres at the concentration of 0.5 mM and more. In contrast, DTAB required more high concentration (5 mM) for the transition, and OTAB hardly induced the transition even at 50 mM.

Figure S2 shows effect of anionic (SDS) and nonionic (triethyleneglycol mono-*n*-dodecyl ether) surfactants on the morphology of nucleospheres ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl). The addition of these surfactants minimally affected the size and morphology of nucleo-cages even at 50 mM.

Effect of Addition of Condensing Agents on the Morphology of Nucleospheres.

Figure S3 shows effect of condensing agents on the morphology of nucleospheres ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl). Addition of polyethyleneglycol (Mw=18~25kDa, 50 mg/mL), spermine (1mM), hexaamine cobalt (III) complex (1mM), and protamine from salmon ([Arg] = 0.9 mM), afforded only shrunken structures (1~3 μm) of nucleospheres, but did not induce the transition to hollow structures.

CLSM images of DNA three-way junction without sticky ends in the presence of CTAB. As shown in Figure S4, CLSM image of DNA three-way junction without sticky ends (**4**+**5**+**6**) in the presence of 1 mM CTAB gave rod-like structures with the length over several μm.

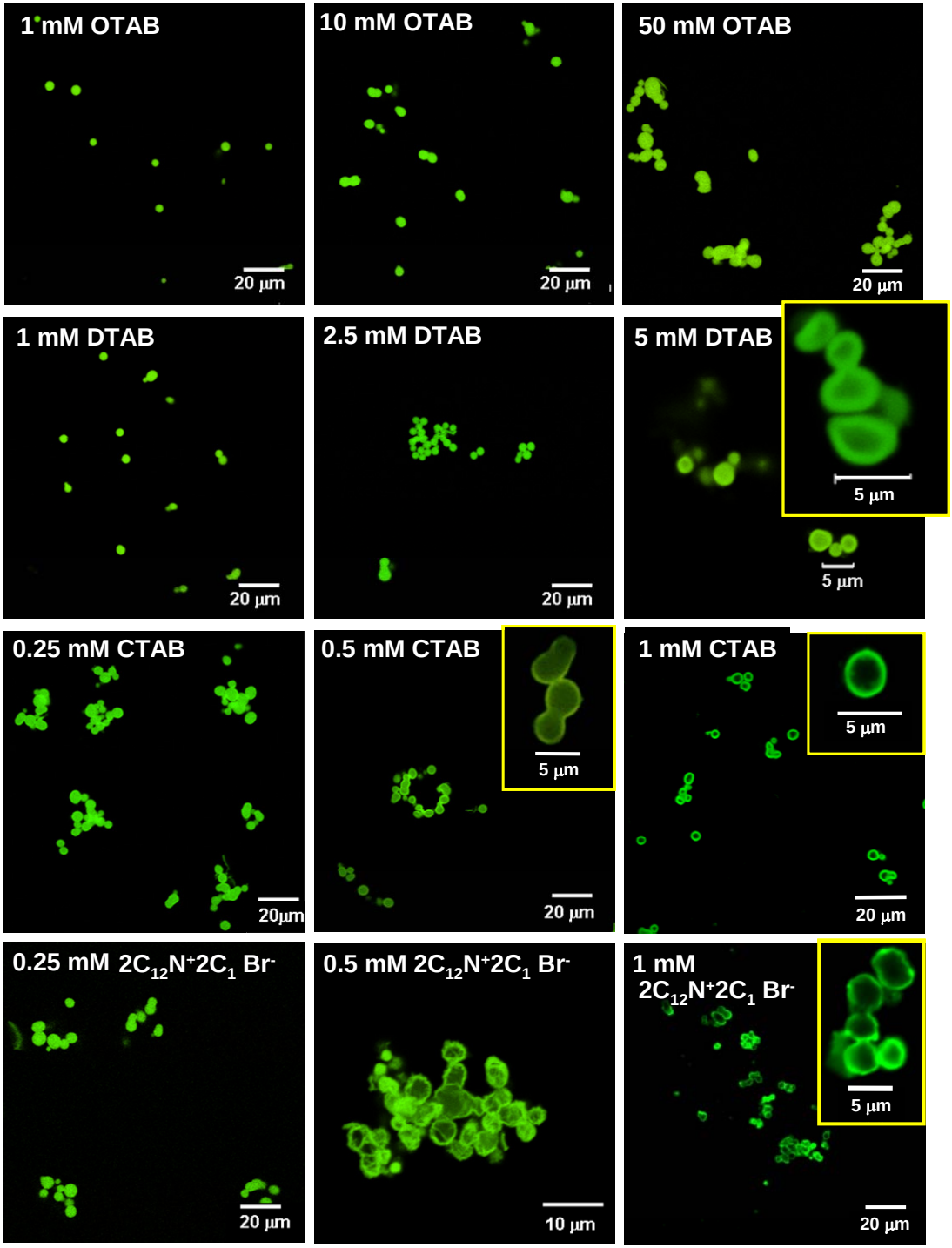

Fig. S1 CLSM images of Nucleospheres ($[ODN]_{total}$ = 20 µM, 0.5 M NaCl) in the presence of cationic surfactants at the various concentration: 1, 10, 50 mM octyltrimethylammonium bromide (OTAB); 1, 2.5, 5 mM dodecyltrimethylammonium bromide (DTAB); 0.25, 0.5, 1 mM cetyltrimethylammonium bromide (CTAB); 0.25, 0.5, 1 mM didodecyldimethylammonium bromide ($2C_{12}N^{+}2C_1\ Br^{-}$).

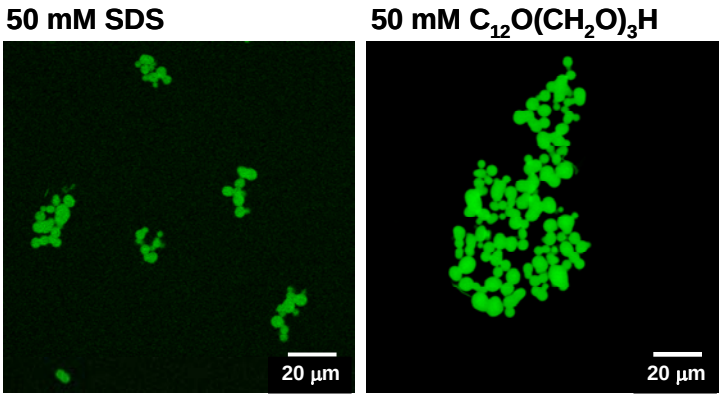

Fig. S2 CLSM images of Nucleospheres ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl) in the presence of anionic and nonionic surfactants: 50 mM sodium dodecylsulfate (SDS) and 50 mM triethyleneglycol mono-*n*-dodecyl ether. The samples were post-stained with 1 μM YOYO-1.

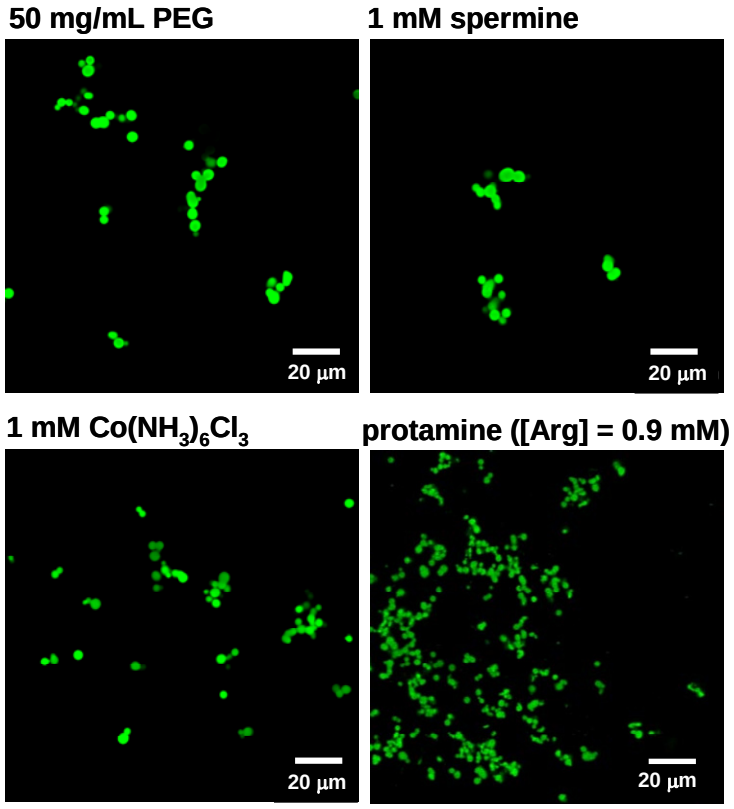

Fig. S3 CLSM images of Nucleospheres ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl) in the presence of condensing agents: 50 mg/mL polyethylene glycol (PEG20000, Mw=18~25kDa), 1 mM spermine, hexaamine cobalt (III) complex, and 43 μM protamine from salmon ([Arg] = 0.9 mM). The samples were post-stained with 1 μM YOYO-1.

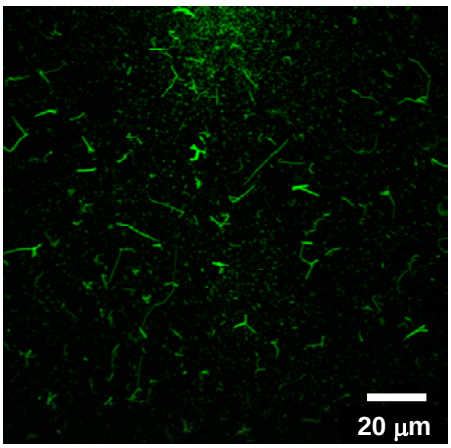

Fig. S4 CLSM image of equimolar mixture of **4+5+6** ($[ODN]_{total}$ = 20 μM, 0.5 M NaCl) in the presence of 1 mM CTAB. The samples were post-stained with 1 μM YOYO-1.