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Exploiting the Directionality of DNA: Controlled Shrinkage of Engineered Oligonucleotide Capsules

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Materials. Poly(ethyleneimine) (PEI, M_w = 25 000 g mol^{-1}), sodium chloride (NaCl), sodium citrate, hydrofluoric acid (HF), ammonium fluoride, and 3-aminopropyltrimethoxysilane (APS) were obtained from Sigma-Aldrich. Unlabeled oligonucleotides (Scheme 2) were custom synthesized by Geneworks (Adelaide, South Australia). The oligonucleotide poly$A_{15}G_{15}$ (AAAAAAAAAAAAAAAGGGGGGGGGG-GGGGG) was modified with the fluorescent label 5' carboxytetramethylrhodamine (TAMRA) (SigmaGenosys). High purity water with a resistivity greater than 18 MΩ cm was obtained from an inline Millipore RiOs / Origin system (MilliQ water). QCM electrodes (Q-Sense AB, Västra, Frölunda, Sweden), and quartz microscope slides were cleaned with Piranha solution (70/30 v/v% sulfuric acid:hydrogen peroxide). *Caution! Piranha solution is highly corrosive. Extreme care should be taken when handling Piranha solution and only small quantities should be prepared*. 500 mL of buffer containing 500 mM NaCl and 50 mM citrate (SSC buffer) was prepared with 4.8 g of citric acid and 14.6 g of NaCl. The pH of the buffer solution was measured with a Mettler-Toledo MP220 pH meter and adjusted to pH 6.5 using 1 M sodium hydroxide. Approximately 6 μm diameter silica particles were purchased from MicroParticles GmbH (Germany).

Methods. *Quartz Crystal Microgravimetry.* QCM measurements were performed using a Q-Sense D300 device with a flow cell (Q-Sense AB, Västra, Frölunda, Sweden). The temperature was kept constant at 23.4 ºC during the experiments. A gold-coated 5 MHz AT-cut crystal was excited at its third overtone at ~15 MHz and the change in the resonance frequency was recorded. The resulting frequencies were divided by 3 to be comparable to the results at the base frequency of 5 MHz. All frequency values quoted are for the third overtone. The other overtones measured (fifth and seventh overtones) followed the same trend. After initially depositing a layer of PEI (1 mg mL^{-1} for 5 min), DNA (500 μL of 4 μM in SSC buffer) was adsorbed/hybridized to the film for 20 min. After each adsorption step, the film was washed with 2 mL of SSC buffer.

Hollow DNA Capsules. To impart a positive charge on the silica particles, the spheres were coated with amine groups as follows. 100 μL of a 1 wt% solution of particles was suspended in 1 mL of ethanol and 50 μL of 25 wt% ammonia solution. 200 μL of APS was then added to the suspension and the particles were allowed to react for 4 h. The particles were washed twice with ethanol and three times with Milli-Q water. The DNA multilayers were deposited on the particles by suspending 10 μL of the particles in 50 μL of a 10 μM DNA solution (in SSC buffer), and allowing the oligomers to hybridize to the surface for 20 min. After hybridization, the particles were washed three times in SSC buffer before the addition of the next layer. To form hollow capsules, the silica core was dissolved by mixing 1 μL of the particle suspension with 1 μL of ammonium fluoride (8 M) buffered HF (2 M) at pH 5 and the capsules were visualized *in situ*. (*Caution! HF is highly toxic and great care must be taken when handling)*. Dissolution of the silica core occurred within 1 min. The particles were imaged on an Olympus IX71 fluorescence microscope.