

Stimuli-responsive organization of block copolymers on DNA nanotubes

Supporting information

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Table of contents

| | |
|---|-----|
| I. General | S1 |
| II. Instrumentation | S2 |
| III. Oligonucleotide synthesis | S3 |
| IV. Rolling circle amplification (RCA) | S5 |
| V. RCA-nanotube assembly | S7 |
| VI. PEG-DNA conjugate syntheses | S9 |
| VII. PEG-DNA conjugates nanotube incorporation | S14 |
| VIII. Light scattering experiments of graft-PEG aggregation | S17 |
| IX. Other polymer-DNA conjugates | S18 |
| X. Additional AFM images | S23 |
| XI. References | S28 |

I. General

3-hydroxypicolinic acid, acetic acid, ammonium citrate, acetic acid, boric acid, cyanogen bromide (5M in acetonitrile), EDTA, formamide, urea, 4-morpholineethanesulfonic acid (MES), magnesium chloride, StainsAll[®], and tris(hydroxymethyl)-aminomethane (Tris) were purchased from Aldrich. Nucleoside (dA, T, dC, dG) derivatized 1000 Å and 2000Å LCAA-CPG supports with loading densities between 25-40 μmol/g, 5-ethylthiotetrazole and reagents used for automated DNA synthesis, Sephadex G-25 (super fine, DNA grade) 3'-alkyne-modifier and 5'-amino-modifier C6 were purchased from Glenn Research. 1000Å Phosphate-CPG was purchased from ChemGenes. Exonuclease VII (ExoVII, source: recombinant) was used as purchased from BioLynx Incorporated. 40% acrylamide/bis-acrylamide 19:1 solution and agarose were purchased from BioShop. A RepliPHI[™] Phi29 reagent set was purchased from Epicentre Biotechnologies for rolling circle amplification. Grade SPI-1 highly ordered pyrolytic graphite (HOPG) was purchased from SPI Supplies INC. and Ruby Red mica sheets (1 x 3") were purchased from B & M MICA CO., while etched silicon cantilevers (OMCL-AC160TS) were purchased from Olympus for AFM imaging. 1 x TBE buffer is composed of 90 mM Tris, 90 mM boric acid and 11 mM EDTA with a pH ~8.3. 1 x TA_{Mg} buffer is composed of 40 mM Tris and 7.6 mM MgCl₂·6H₂O. The pH was adjusted to 8.0 using glacial acetic acid. 1 x MES_{Mg} buffer is composed of 250 mM MES, 20 mM MgCl₂, with pH 7.6.

II. Instrumentation

Standard automated oligonucleotide solid-phase synthesis was performed on a BioAutomation MerMade MM6 DNA synthesizer. UV-Vis measurements were performed with a BioTek Synergy HT microplate reader. Gel electrophoresis experiments were carried out on an acrylamide 20 x 20 cm vertical Hoefer 600 electrophoresis unit. Thermal anneal cycles and enzymatic digestions were conducted using a Flexigene Techne 96 well thermocycler. AFM was performed with a MultiMode[™] SPM connected to a Nanoscope[™] IIIa controller, from the Digital Instruments Veeco Metrology Group. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectrophotometer. Dynamic light scattering (DLS) measurements were performed on a Brookhaven Instruments Corporation system equipped with a

BI-200SM goniometer, a BI-9000AT digital correlator and a Compass 315-150 CW laser light source from Coherent Inc. operating at 532 nm (150 mW).

Oligonucleotide synthesis

The sequences used in this manuscript were chosen to minimize unintended secondary interactions, and are summarized below. Careful consideration was also given to the predicted melting temperatures of each domain; for example, the triangle edges have a higher thermal denaturation temperature (T_m) than the RCA binding region, which in turn has a higher T_m than the linking strand sticky ends. This was done to allow for selective anneals that could target specific interactions. DNA nanotubes were created from RCA strands with a repeating sequence of either 72 or 61 base pairs. RCA nanotubes with a 72 base pair repeat were used for hybridization with PEG-DNA conjugates, while RCA nanotubes with a 61 base pair repeat were used for all other conjugates. Changing the repeat had no observable effect on nanotube assembly.

| Name | DNA Sequence (5'-3') |
|---------------------------------|--|
| RCA template (72bp) | CCATAGCTTTTAAGCCAGTTTCTCAGCAGCGAAAAAAGGC GGCGTTAAATAGACGCGGCCATCGGTGACGTG-phosphate |
| RCA template (61bp) | CCATAGCTTCTCAGCAGCGAAAAAAGGCGGCGTTAAATA GACGCGGCCATCGGTGACGTG-phosphate |
| RCA template_T | AAAGCTATGGCACGTCACCG |
| Primer | TATTTAACGCCGCCTTTT |
| Triangle | TATTGGTTTG-V-TGACCAATAACACAAATCGG-V-TCAGTAATC TCTTGAAGGTA-V-GGAAACGACA-phosphate |
| Triangle_T | CAAACCAATATGTCGTTTCC |
| CS1 | CTCAGCAGCGAAAATACCTTCAAGAGATTACTGAGTCTTGGAG TCGGATTGAGC |
| CS2 | TCGGCAGACTCTACTTGGTGCAAACCAATATGTCGTTTCCGGCG GCGTTAAATA |
| CS3 | CGGTGCATTT AGTCGTGTCG CCGATTTGTGTTATTGGTCA CGCGAATCAT GCGTACTCGT |
| RS1 | ACTCCAAGACTTCGACACGACT |

| | |
|-----------------------|--|
| RS2 | ATGATTCGCG TT CACCAAGTAG |
| BB (72bp) | GACGCGGCCATCGGTGACGTGCCATAGCTTTTAAGCCAGTTT |
| LS1 (72bp) | AGTCTGCCGAGCTACCAGGTGAATTTCAAACGCAATTACGAC GAGTACGC |
| LS2 (72bp) | AAATGCACCGGCTACCAGGTGAATTTCAAACGCAATTACGGC TCAATCCG |
| DS(61bp) | CGTAATTGCGTTTGAAATTCACCTGGTAGC |
| BB (61bp) | GACGCGGCCATCGGTGACGTGCCATAGCTTT |
| LS1 (61bp) | AGTCTGCCGAGCTACCAGGTGAATTTCAAACGAGTACGC |
| LS2 (61bp) | AAATGCACCGGCTACCAGGTGAATTTCAAGCTCAATCCG |
| DS(61bp) | TTGAAATTCACCTGGTAGC |

Table S1: Oligonucleotides prepared via solid-phase synthesis for RCA and nanotube assembly.

DNA synthesis was performed on a 1 μ mole scale, and deprotection carried out in concentrated ammonium hydroxide (55°C, 16 hours). When required, 5'-amino-modifier C6 (NH₂) phosphoramidite was site-specifically incorporated into each sequence and coupled onto the growing oligonucleotide chain as an artificial base with a prolonged coupling time of 5 minutes. Additionally, a triaryl vertex **V** (**Figure S 1**) was site-specifically incorporated into the **triangle** strand with prolonged coupling and deprotection times of 10 minutes. The ligation of the **triangle** strand was carried out according to a previously reported method.¹ The extinction coefficient of the vertex insertion was measured via UV-vis titration, giving a value of 3.5×10^4 L/(mol • cm). Crude products were purified on 12-19% polyacrylamide/8M urea polyacrylamide gels (PAGE; up to 20 OD₂₆₀ of crude DNA per gel) at constant current of 30 mA for 1-2 hours, using 1 x TBE running buffer. Following electrophoresis, the gels were wrapped in plastic, placed on a fluorescent TLC plate and illuminated with a UV lamp (254 nm). The bands were quickly excised, and the gel pieces were crushed and incubated in 10 mL of deionized, sterile water at 55°C for 16 hours. Samples were then dried to 1.5 mL, desalted using size exclusion chromatography (Sephadex G-25), and quantified (OD₂₆₀) via UV-

vis spectroscopy using the extinction coefficient ϵ_{260} as calculated with Integrated DNA Technologies Inc.'s OligoAnalyzer.

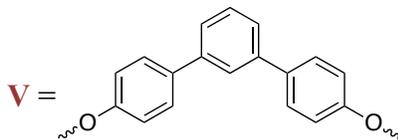


Figure S 1: Chemical structure of triaryl vertex

III. Rolling circle amplification (RCA)

Circular RCA template ligation

Cyclization was achieved via chemical ligation, using the following procedure. Linear **RCA template** strand was grown on phosphate-CPG, yielding a 3' phosphate to facilitate ligation. Next, 3.5 nmoles of **RCA template** and **RCA template_T** were separately evaporated to dryness and re-suspended in 250 μL of MES buffer. They were combined and incubated for 30 minutes at room temperature. 500 μL of cyanogen bromide was added, and the mixture was placed on a rotary shaker on ice for 30 minutes. 40 equivalents of LiClO_4 in acetone (2% w/v) were added, the solution incubated on dry ice for 30 minutes, and then centrifuged at 4°C to precipitate the DNA. This pellet was re-suspended in minimal deionized, sterile water, and desalted using Sephadex G-25 size exclusion column chromatography. Denaturing PAGE purification was then used to isolate the cyclic product (**RCA template**), which had a reduced mobility relative to the linear analogue. Selective enzymatic degradation confirmed the cyclic nature of the resulting products. ExoVII is selective for the digestion of single-stranded open DNA over that of cyclic DNA. 14 pmoles of DNA in 5 μL of 1 x TBE were subjected to 2 units of ExoVII at 15°C for 2 hours. As shown in **Figure S 2**, the successfully ligated products remain intact while linear analogues are degraded upon nuclease treatment.

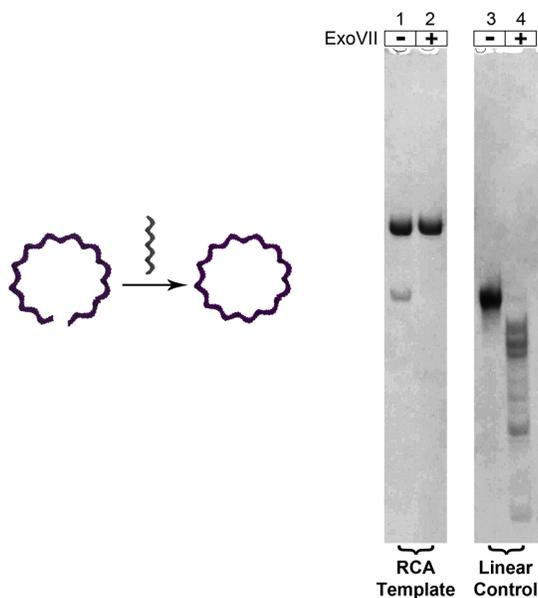


Figure S 2: Scheme of ligation of **RCA template** (left) and denaturing gels of ExoVII degradation for RCA template and linear control (right).

RCA process

10 pmol of cyclic **RCA template** was combined with 50 pmol of **primer**, and brought to a volume of 30 μL with a final composition of 0.2 $\mu\text{g}/\mu\text{L}$ bovine serum albumin, 1 x Phi29 reaction buffer (provided with enzyme), and 0.25 mM deoxynucleotide triphosphates. This mixture was heated to 95°C and cooled to room temperature over 30 minutes to maximize binding of primer. 100 units of Phi29 polymerase enzyme were added, and the reaction incubated for 16 hours at 30°C. DNA was then ethanol precipitated, resuspended in autoclaved water, and quantified by UV-vis. The resulting RCA product (**RCA**) was characterized by denaturing agarose gel electrophoresis, and stained with SYBR® Safe, as shown in **Figure S 3**.

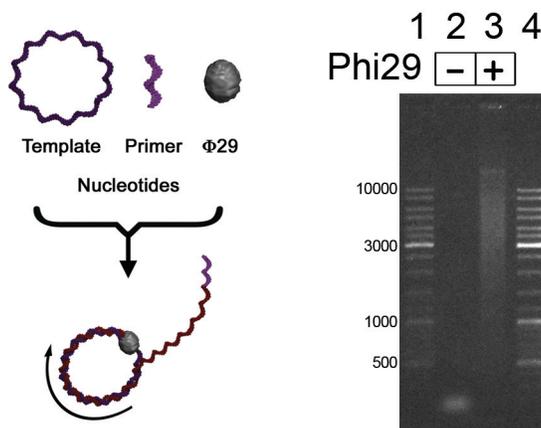


Figure S 3: Scheme for RCA process (left) and its characterization by agarose gel electrophoresis (right). Lanes 1 and 4: DNA ladder, lane 2: cyclic **RCA template_T**, lane 3: product of RCA process (note that **RCA template_T** is no longer visible, as it is present in much lower amounts than the RCA products).

RCA strand has a distribution of lengths that ranges from about 1400 to 15000 bases, corresponding to 0.5 to 5.1 μm . Since longer DNA strands will stain more intensely than shorter ones, the average strand length is not necessarily the midpoint of the band. To determine this, a weighted average was taken from the gel in **Figure S 3**. The DNA ladder (lanes 1 and 4) was used to gate sections of the product band in lane 3, and assign them an approximate length. The density of the band for a given length was determined with ImageJ, which was divided by the given length to yield a relative weight. The resulting weighted average was $0.85 \pm 1.51 \mu\text{m}$ (2500 bases).

IV. RCA-nanotube assembly

RCA-nanotube rung assembly

Triangular rung was generated by the equimolar combination of strands **triangle**, **CS1-3**, and **RS1-2**, with a final concentration of 2.0 μM in 1 x TAMg . This mixture was annealed from 95°C to 4°C over 3.5 hours to maximize clean product formation. Double-stranded linkers were prepared in the same manner with appropriate strands, to a final concentration of 30 μM . Native PAGE (8%, 1 x TBE running buffer, stained with StainsAll®) confirmed the clean hybridization of each product, as shown in **Figure 1** (main text) and **Figure S 4** (below).

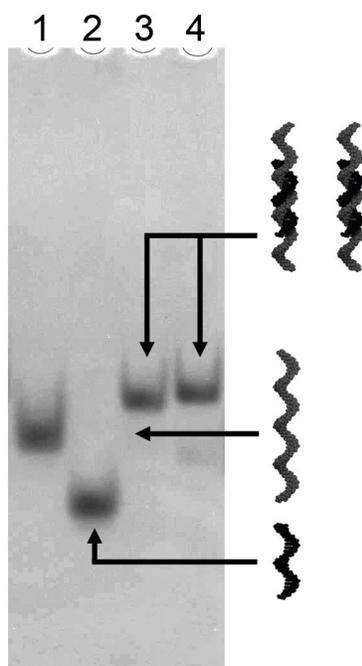


Figure S 4: Hybridization of linking strands. Lane 1: strand **LS1**, lane 2: strand **DS**, lane 3: double-stranded linker **3**, lane 4: double-stranded linker **4**.

Construction of RCA-nanotubes

Due to the distribution of strand lengths associated with RCA process, molar quantification was not possible. Instead, overall material (estimated by absorbance) in the mixture was used to determine the amount required for a given experiment. The determination for the exact amounts of RCA strand used is described elsewhere.ⁱⁱ In order to assemble RCA-nanotubes, the desired amount of RCA strand was combined with **BB** strand and sufficient $10 \times \text{TA}_{\text{Mg}}$ buffer to achieve a final composition of $1 \times \text{TA}_{\text{Mg}}$. Triangular rung was added, and the mixture was annealed from 56°C to 20°C over one hour to maximize efficient binding. Double-stranded linkers were then added, and the mixture was annealed from 44°C to 20°C over 45 minutes. The final DNA concentration was $130\text{-}270 \mu\text{g}/\text{mL}$ (corresponding to roughly $1.5 \mu\text{M}$ of each non-repeating strand), depending on the concentration of the polymer-DNA conjugate solution used.

Atomic force microscopy

AFM was performed in air on a HOPG surface. Typically 1.5 μL of the assembled nanotube solution was deposited on freshly cleaved HOPG and allowed to dry under ambient conditions (15-60 minutes). Imaging was then performed using tapping mode at a scan rate of 1.2 Hz using etched silicon cantilevers (resonance frequency ~ 300 kHz, spring constant ~ 42 N/m, tip radius < 10 nm) and medium tip oscillation damping (20-30%). Large, bundled fibers were observed, as seen in for the previous DNA nanotube design, with an apparent height of roughly 1 nm.ⁱⁱⁱ Typical micrographs of DNA nanotubes bundled and not bundled are shown in Figure 1 (main text).

V. PEG-DNA conjugates syntheses

Linear PEG-DNA conjugates synthesis

DNA synthesis was performed on a 0.5 μmole scale, starting from the 3'-alkyne modified 1000 Å LCAA-CPG solid-support. PEG₂₀₀₀-N₃ was coupled with 3'-alkyne DNA via the click chemistry reaction, by modifying a previously reported protocol (Figure S 5).^{iv} The procedure described below is for 50 μL -scale reactions.

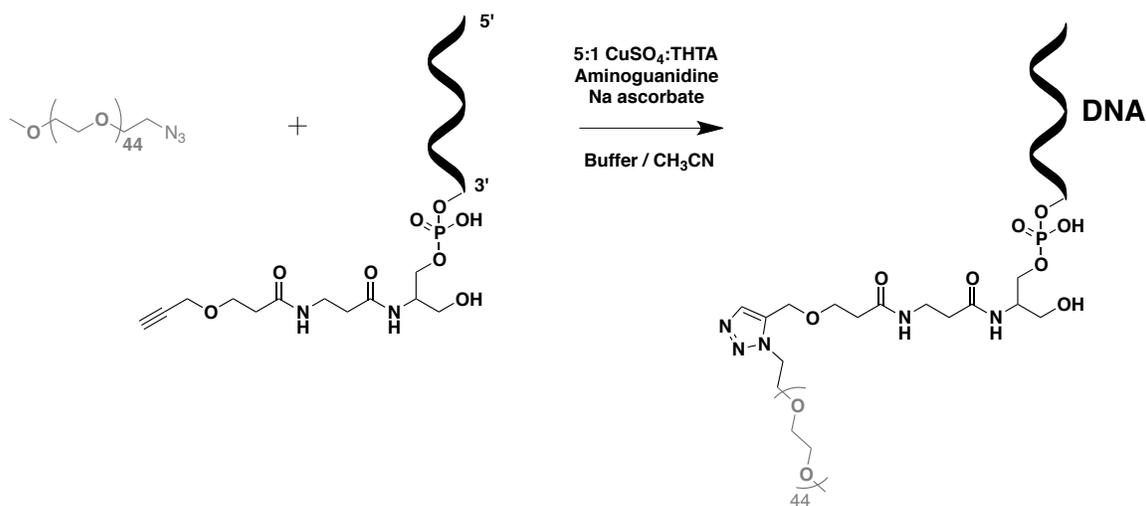


Figure S 5: Reaction scheme of click chemistry reaction between 3'-alkyne DNA and PEG-N₃

1. 25 μL of 100 μM 3'-alkyne DNA in deionized water
2. 15 μL of acetonitrile
3. 3 μL of 20 mM PEG₂₀₀₀-N₃ in deionized water

- 1.5 μL of 20 mM 5:1 CuSO_4 : THPTA (tris(hydroxypropyltriazolyl)methylamine in deionized water
- 3 μL of 20 mM aminoguanidine in deionized water
- 2.5 μL of 100 mM sodium ascorbate in phosphate buffer
- The reaction mixture was mixed well, and placed on a rotary shaker at room temperature for 48 hours.

The yield of the reaction was moderate, as characterized by a denaturing gel (15%, 1 x TBE running buffer, stained with StainsAll®) of the crude material (**Figure S 6a**). The product was purified from the reaction mixture through ethanol precipitation and denaturing gel electrophoresis (**Figure S 6b**). Native PAGE (7%, 1 x TAMg running buffer, stained with StainsAll®) confirmed the clean hybridization of the linear-PEG conjugate with LS2, as shown in **Figure S 6c**.

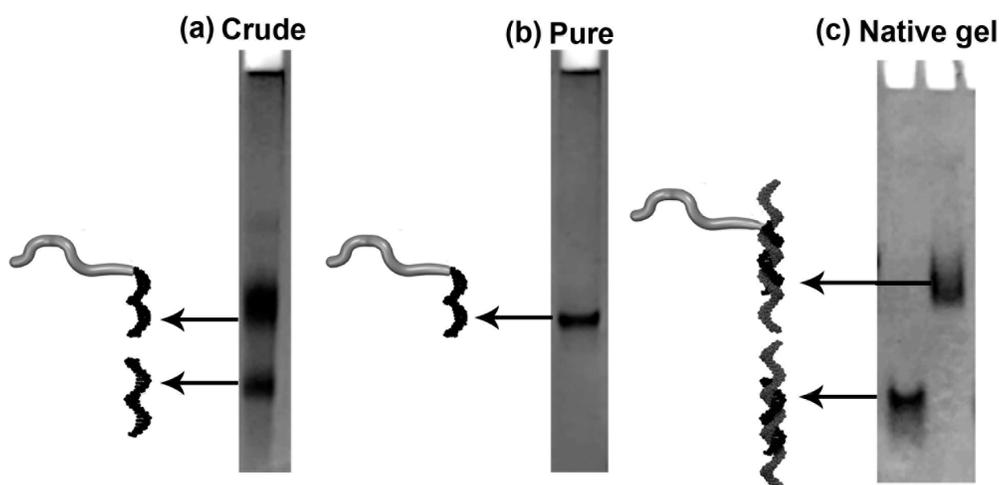


Figure S 6: (a) 15% denaturing gel of crude reaction mixture, (b) 15% denaturing gel of purified linear-PEG DNA conjugate, and (c) 7% native gel of double stranded linking strand (Lane 1) and double-stranded linear PEG-DNA linking strand (Lane 2).

ROMP (NHS₁)(PEG₂₀₀₀) synthesis

Unless otherwise stated, all reagents and solvents were purchased from Sigma-Aldrich Chemicals and used without further purification. Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen at room temperature. Monomers **S1** and **S2** were prepared according to literature procedures.^v Column chromatography was carried out using Silica 60A (particle size 35-70 μm , Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F₂₅₄, Merck,

Germany) and observed under UV light. Petrol refers to the fraction of petroleum ether boiling between 40 °C - 60 °C. IPA refers to isopropyl alcohol. Gel permeation chromatography (GPC) was performed in DMF at 30 °C on a Viscogel G-MBLMW-3078 column equipped with a Waters 410 refractive index detector that was calibrated with polyethylene glycol standards. ^1H and ^{13}C spectra were recorded on a Variant Oxford 400 instrument. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad. **Figure S 7** (below) is a synthetic scheme for the polymerization.

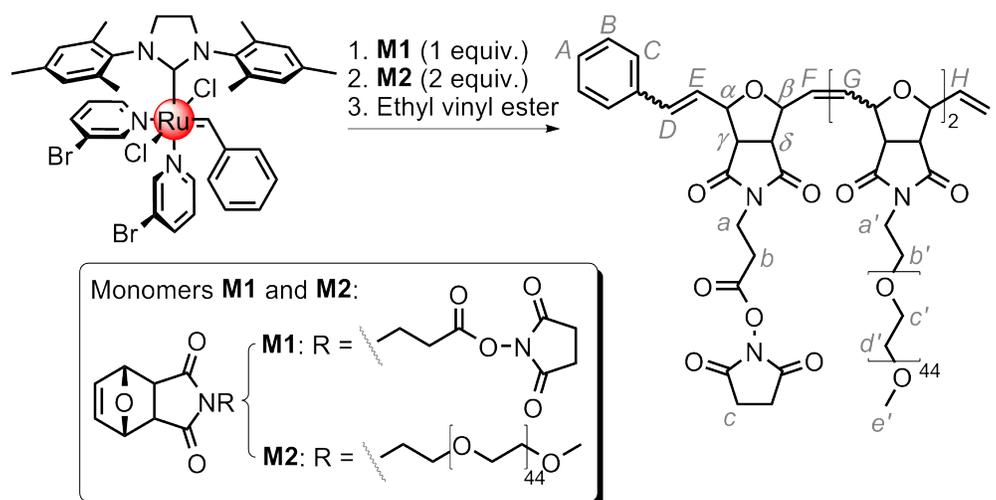


Figure S 7: Reaction scheme for the polymerization of graft-PEG polymer

A dry Schlenk tube was charged with Grubbs' catalyst 3rd generation (100.0 mg, 0.112 mmol, 1 equiv.) under an argon atmosphere. Dry CH_2Cl_2 (5 mL) was added and the mixture was stirred at room temperature for 5 minutes. A solution of NHS-monomer (**M1**, 39.3 mg, 0.112 mmol, 1 equiv.) in dry CH_2Cl_2 (5 mL) was added and the mixture was stirred for 30 minutes. A solution of PEG-monomer (**M2**, 487.9 mg, 0.224 mmol, 2 equiv.) in dry CH_2Cl_2 (5 mL) was then added and the reaction mixture was stirred for another 30 minutes before ethyl vinyl ether (1 mL, excess) was added to quench the polymerisation. The polymer was precipitated by addition of petroleum ether. The resulting brown oil was re-dissolved in MeOH, precipitated with Et_2O and filtered. This

operation was repeated until the filtrate was colourless. The residue was dried on air to afford the pure polymer **A** as a light beige solid. The final product was characterized by ^1H NMR (peak assignment is below) and GPC (**Figure S 8**).

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ = 7.42 (d, J = 6.5 Hz, 2H, H_B), 7.32 (t, J = 7.0 Hz, 2H, H_C), 7.26 (q, J = 6.8 Hz, 1H, H_A), 6.74 (d, J = 15.7 Hz, 1H, H_D), 6.33 (dd, J = 6.1, 15.7 Hz, 1H, H_E), 5.90-6.15 (m, 6H, H_F , H_G and H_H), 5.77 (bd, J = 5.9 Hz, 1H, H_I), 5.42 (d, J = 17.2 Hz, 1H, H_I'), 4.65-5.10 (m, 2H, H_α and H_β), 4.30-4.65 (m, 4H, $\text{H}_{\alpha'}$ and $\text{H}_{\beta'}$), 3.75 (t, J = 3.8 Hz, 4H, $\text{H}_{\alpha'}$), 3.45-3.53 (m, 354H, H_a , $\text{H}_{\text{c}'}$ and $\text{H}_{\text{d}'}$), 3.32 (s, 6H, $\text{H}_{\text{e}'}$), 2.79 (bs, 4H, H_c), 2.65 (bt, J = 6.0 Hz, 2H, H_b), 1.93-2.10 (m, 2H, H_γ and H_δ), 1.65-1.84 (m, 4H, $\text{H}_{\gamma'}$ and $\text{H}_{\delta'}$). GPC (DMF, 1 mL/min): M_p = 4650, PDI = 1.10.

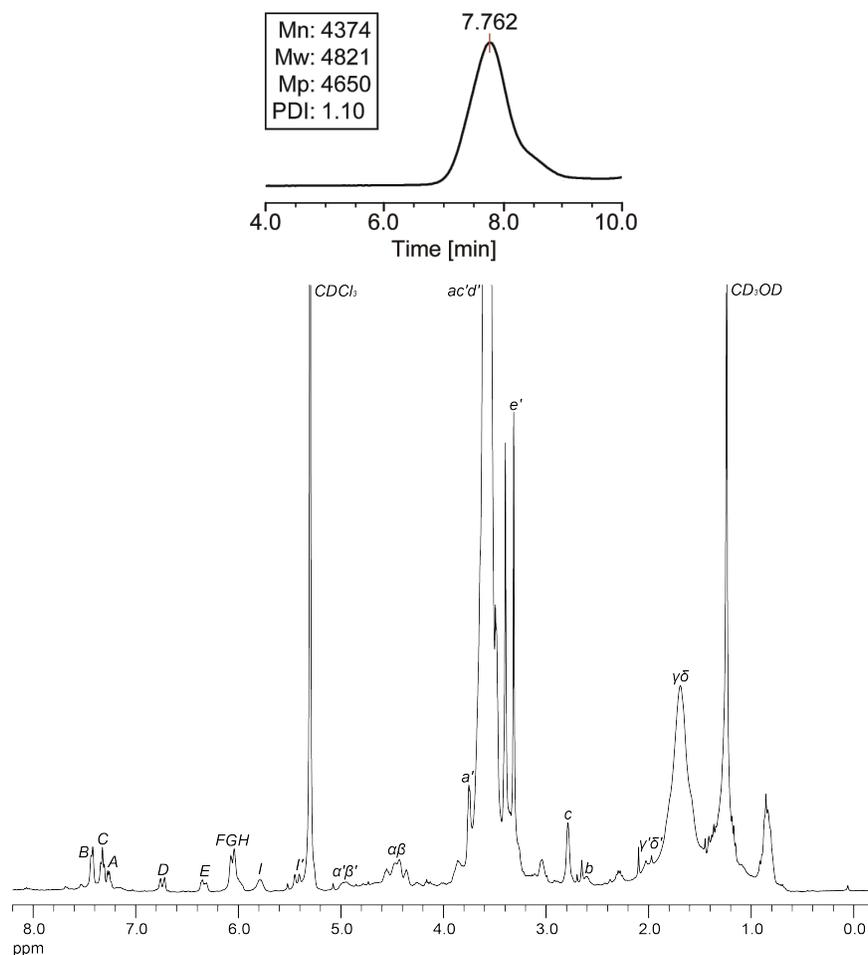


Figure S 8: GPC trace and ^1H NMR of purified graft-PEG polymer.

Graft PEG-DNA conjugates synthesis

NH₂-DNA synthesis was performed on a 0.5 μmole scale, starting from universal 1000 Å LCAA-CPG solid-support. The procedure described below is for 50 μL-scale reactions. The coupling efficiency was monitored after trityl removal. The (NHS₁)(PEG₂₀₀₀) polymer was incorporated onto the DNA strand on-column via NHS-coupling reaction (**Figure S 9**). All sequences were fully deprotected in concentrated ammonium hydroxide (55 °C, 16 hours).

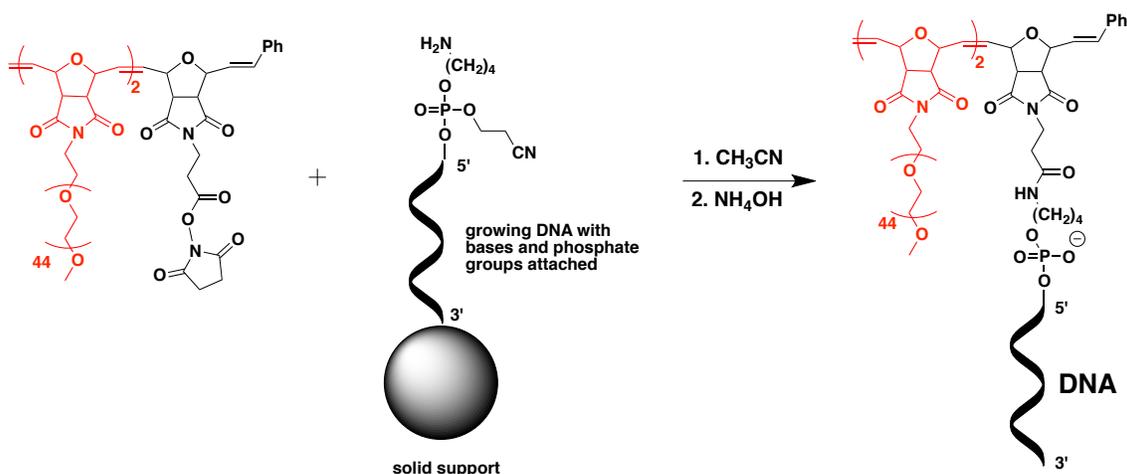


Figure S 9: Reaction scheme for graft-PEG DNA synthesis.

1. 1 μmol of (PEG₂₀₀₀)₂-NHS were dissolved in 100 μL acetonitrile.
2. Next, 500 nmol DNA-NH₂ attached to the solid support were added.
3. Reaction mixture was stirred at room temperature for 24 hours.

The yield of the reaction was moderate, as characterized by a denaturing gel (15%, 1 x TBE running buffer, stained with StainsAll®) of the crude material (**Figure S 10a**). The product was purified from the reaction mixture through ethanol precipitation and denaturing gel electrophoresis (**Figure S 10b**). Native PAGE (7%, 1 x TA_{Mg} running buffer, stained with StainsAll®, **Figure S 10d**) and circular dichroism confirmed the clean hybridization of the graft-PEG conjugate with LS2 (**Figure S 10d**). The presence of only one attached DNA strand within the polymer was ensured through native PAGE titration experiments (**Figure S 10e**) and MALDI-TOF experiment (**Figure S 11**).

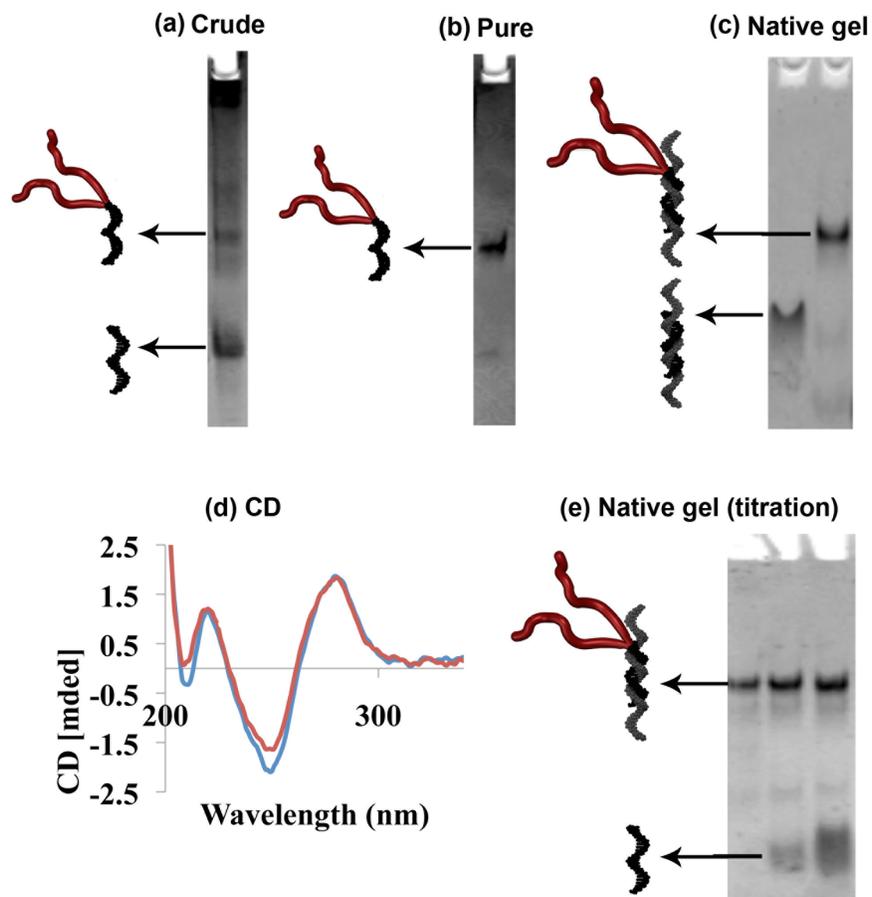


Figure S 10: (a) 15% denaturing gel of crude reaction mixture, (b) 15% denaturing gel of purified graft-PEG DNA conjugate, (c) 7% native gel of double stranded linking strand (Lane 1) and double-stranded graft PEG-DNA linking strand (Lane 2), (d) circular dichroism of double stranded linking strand (blue) and double-stranded graft PEG-DNA linking strand (red), and (e) 7% native gel of double stranded linking strand and double-stranded graft PEG-DNA linking strand in a 1:1 (Lane 1), 2:1 (Lane 2) and 5:1 (Lane 3) ratio.

| | Calculated MW |
|--|---------------|
| Graft (PEG ₂₀₀₀) ₁ -DNA | 11878.24 |
| Graft (PEG ₂₀₀₀) ₂ -DNA | 14072.33 |
| Graft (PEG ₂₀₀₀) ₃ -DNA | 16266.42 |

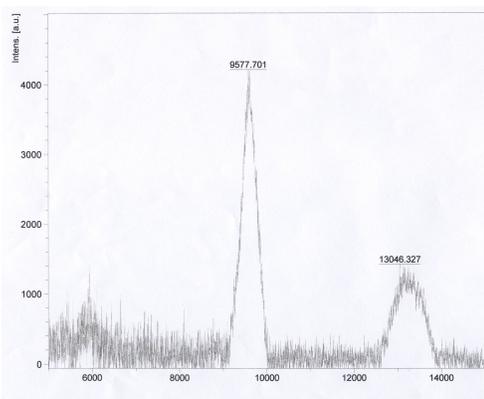


Figure S 11: Calculated molecular weight (MW) of possible graft-PEG DNA conjugates and MALDI-TOF of graft-(PEG₂₀₀₀)₂ DNA conjugate

VI. PEG-DNA conjugates nanotube incorporation

Construction of RCA-nanotubes

RCA-nanotubes, unfunctionalized double-stranded linker, and double-stranded linker functionalized with either linear- or graft-PEG were assembled in the same manner as previously described, to a final concentration of 30 μM . Native PAGE (7%, 1 x TA_{Mg} running buffer, stained with StainsAll®) confirmed the clean hybridization of each product, as shown in **Figure S 6c** and **10c** (above). RCA-nanotubes containing on one side either linear- or graft-PEG DNA ds linking strand were verified by PAGE (7%, 1 x TA_{Mg} running buffer, stained with StainsAll®), where no bands corresponding to PEG-DNA linking strands were observed (data not shown).

Atomic force microscopy

AFM samples were prepared and analyzed in the same manner as previously described. **Figure S 12** is a representative image of the linear-PEG DNA decorated RCA-nanotube, while **Figure 2b** (main text) is a representative image of the graft-PEG DNA decorated RCA-nanotube.

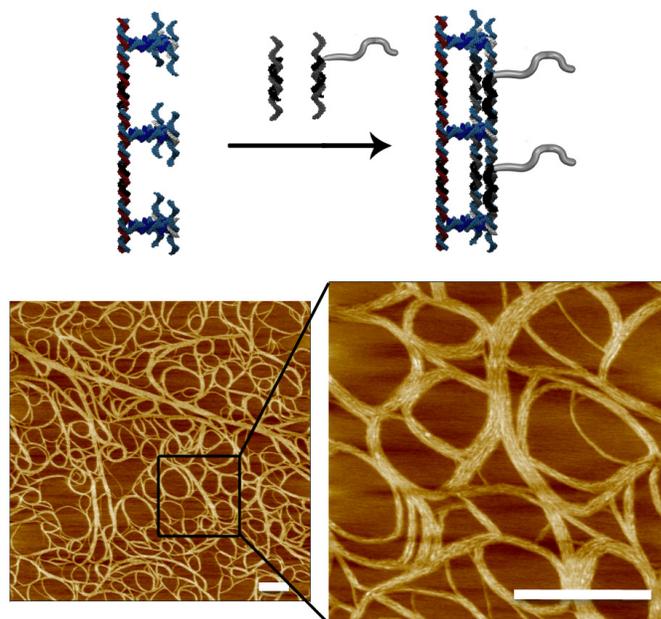


Figure S 12: Scheme of linear-PEG DNA conjugate hybridized to RCA-nanotube (top) and a representative AFM image (below, phase image, bar is 1 μm).

The distances between the centers of each dark aggregate on the AFM images of the DNA nanotubes decorated with graft-PEG DNA conjugates were measured using ImageJ. The data is summarized in **Figure S 13**, and shows no obvious relationship to the structure of the nanotubes (which have a repeat distance of ~ 21 nm).

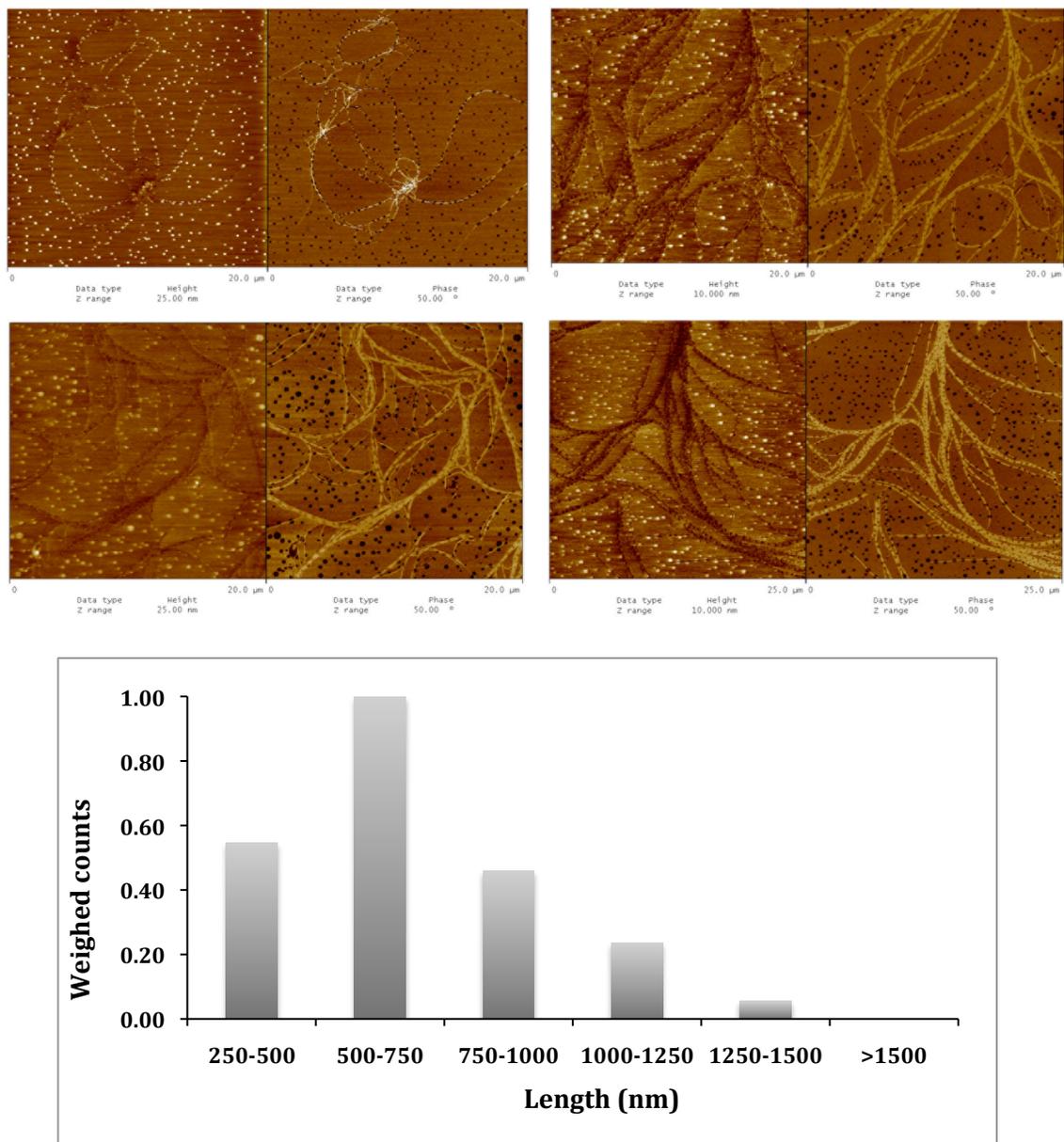


Figure S 13: Measured distances between the dark spots of graft-PEG DNA conjugates sitting (bottom) on a DNA nanotube on AFM micrographs (top).

AFM image of a control experiment containing DNA nanotubes hybridized with graft-PEG DNA conjugate, followed by addition of a random DNA sequence. No

change is observed, confirming the sequence-selectivity of the write/erase experiment (**Figure S 14**).

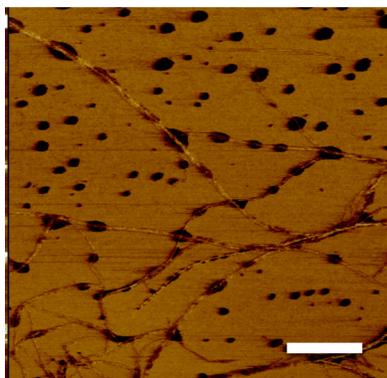


Figure S 14: AFM phase image on HOPG of graft-PEG DNA aggregates hybridized to RCA-nanotubes, followed by the addition of a non-complementary DNA strand (bar is 1 μm).

VII. Light scattering experiments of graft-PEG aggregation

Light scattering samples were prepared in the same manner and concentration as the solutions prepared for AFM experiments.

Graft-PEG DNA conjugate

Aggregates in water and buffer were observed, with an average R_H of 178 and 308 nm measured (**Figure S 15**).

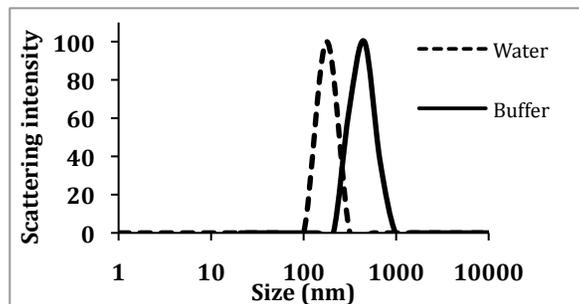


Figure S 15: Light scattering of graft-PEG DNA conjugates in water and in buffer.

Graft-PEG polymer

Light scattering experiment of a solution containing 1 mg/mL graft-PEG polymer had no aggregates, and therefore no scattering was measured. When deionized water or buffer was added to the polymer solution in acetonitrile (final concentration of 1 mg/mL),

aggregates with a measured R_H of 212 and 390 nm, respectively, were observed (**Figure S 16a**). When the polymer was directly dissolved in buffer, a R_H of 563 nm was measured (**Figure S 16b**).

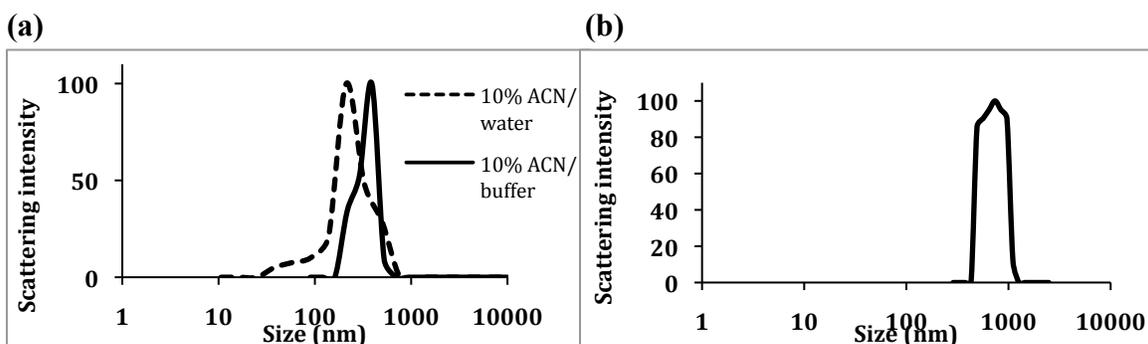


Figure S 16: Light scattering experiments of graft-PEG polymer in (a) 10% acetonitrile/water and 10% acetonitrile/ buffer, and (b) in 100% buffer.

VIII. Other polymer-DNA conjugates

Graft-PEG₆₆₀ DNA

The conjugate was synthesized in the same manner as previously described. The reaction scheme is summarized in **Figure S 17** below.

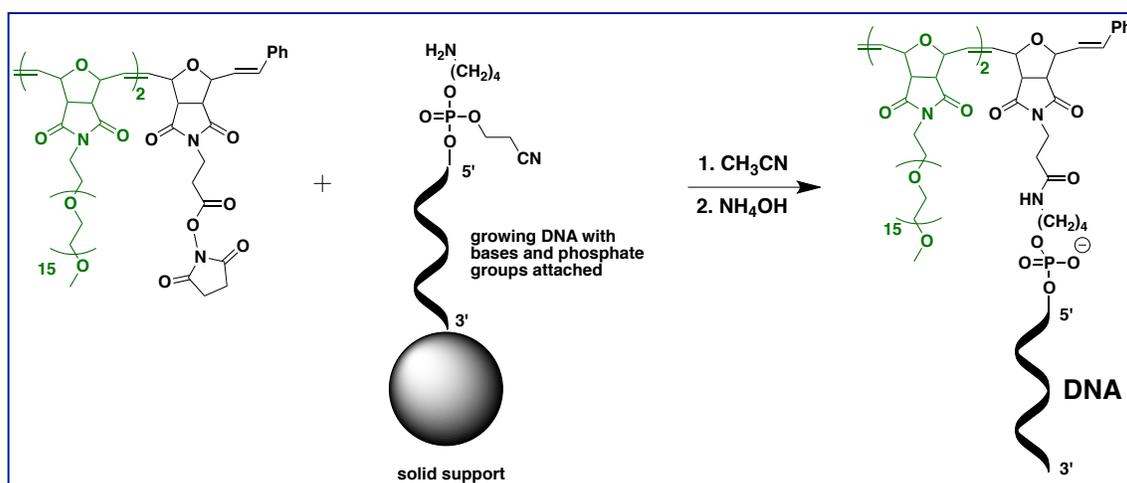


Figure S 17: Reaction scheme for graft-PEG₆₆₀ DNA synthesis

1. 1 μmol of (PEG₆₆₀)₂-NHS were dissolved in 100 μL acetonitrile.
2. Next, 500 nmol DNA-NH₂ attached to the solid support were added.
3. Reaction mixture was stirred at room temperature for 24 hours.

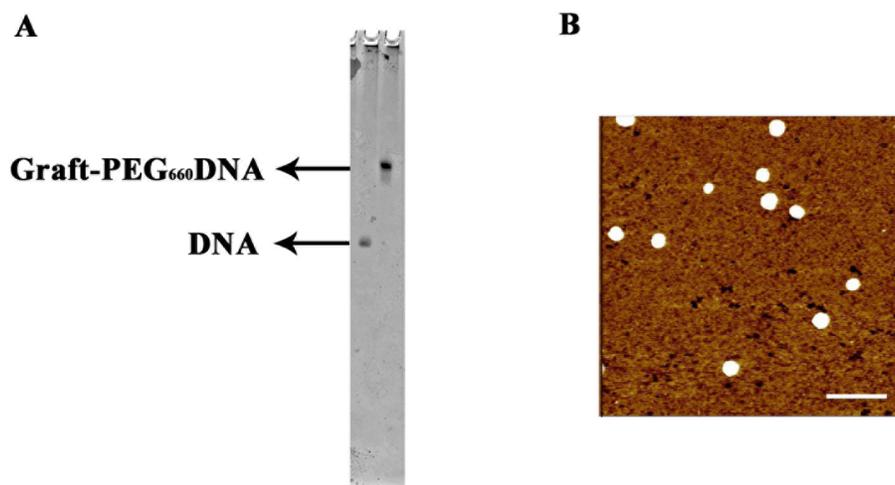


Figure S 18: (a) Denaturing PAGE of purified graft-PEG₆₆₀ DNA, and (b) AFM phase image of graft-PEG₆₆₀ DNA aggregates on HOPG (bar is 1 μm).

Phenyl-DNA

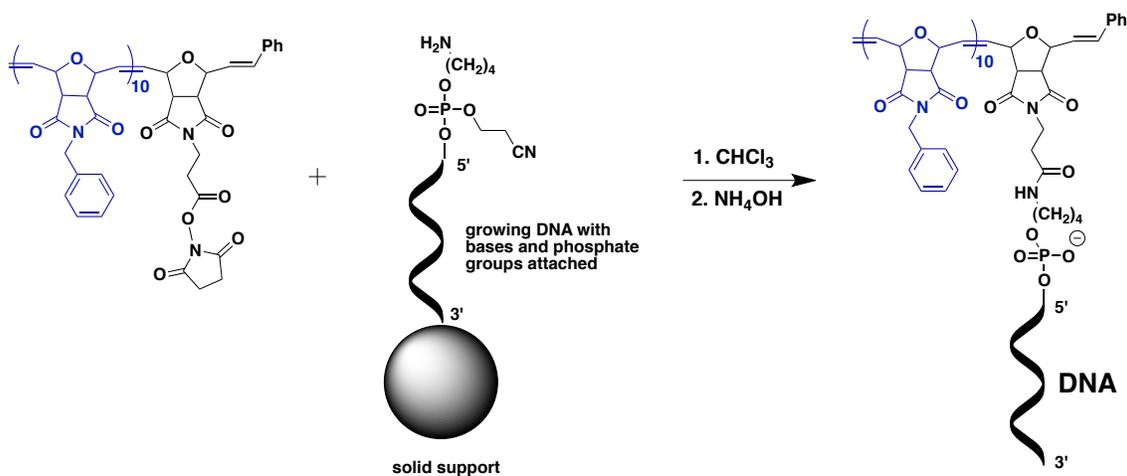


Figure S 19: Reaction scheme for phenyl-DNA synthesis

1. 5 μmol of Phenyl₁₀-NHS were dissolved in 100 μL chloroform.
2. Next, 500 nmol DNA-NH₂ attached to the solid support were added.
3. Reaction mixture was stirred at room temperature for 24 hours.

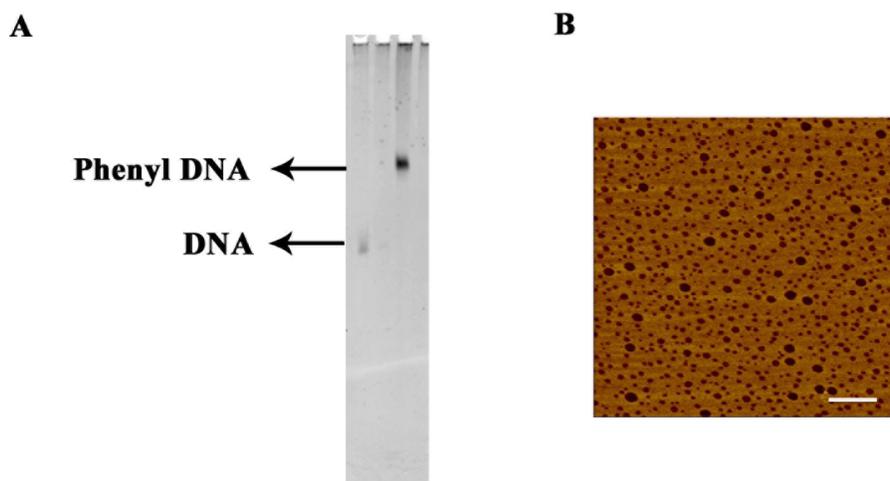


Figure S 20: (a) Denaturing PAGE of purified Phenyl-DNA, and (b) AFM phase image of Phenyl-DNA aggregates on HOPG (bar is 1 μm).

PS-DNA polymer

PS₁₃-monocarboxylic acid (PS₁₃-COOH) was synthesized by anionic polymerization, terminated with CO₂ to generate the carboxylic acid and the polymer was purified in the same manner as previously described.^{vi} PS₁₃-COOH was converted to its corresponding NHS ester by conversion to the acid chloride as an intermediate. A solution of 120 mg of PS₁₃-COOH (0.1 mmol) was prepared in 5 mL of benzene, and 1 mL of SOCl₂ (13.5 mmol) was then added. The mixture was kept under reflux for 3 hours and then evaporated to near dryness by distillation. The remaining film was reconstituted in 20 mL of fresh benzene and dried again under vacuum to ensure that most of the SOCl₂ had been removed. The acid chloride derivative was dissolved in 5 mL of chloroform, followed by 60 mg of NHS (0.5 mmol) and 200 μL of diisopropylethylamine (1.1 mmol). The reaction was allowed to proceed at room temperature under vigorous stirring overnight. The final product was isolated by precipitation into cold hexanes, and characterized by GPC (CHCl₃, 1 mL/min, M_n = 1529 and PDI = 1.17).

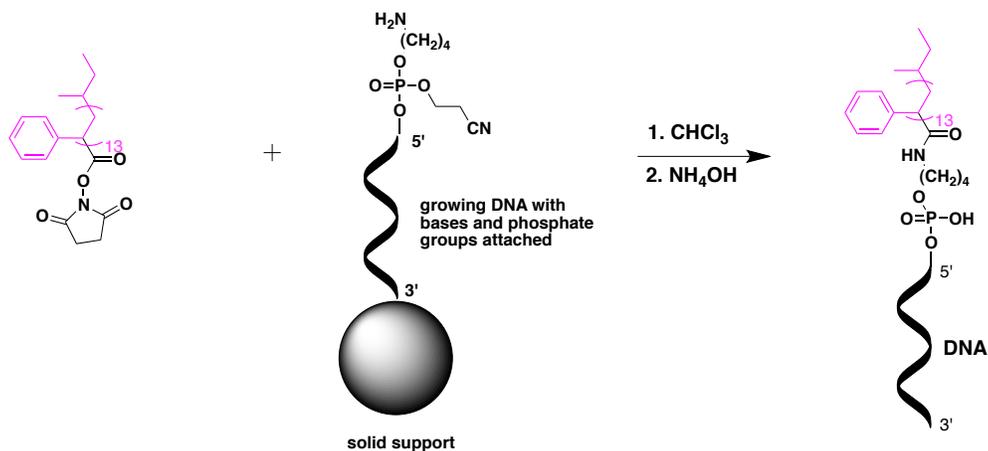


Figure S 21: Reaction scheme for PS-DNA synthesis

1. 5 μ moles of PS₁₃-NHS were dissolved in 950 μ L of acetonitrile and 50 μ L of chloroform.
2. Next, 500 nmoles DNA-NH₂ attached to the solid support were added.
3. Reaction mixture was stirred at room temperature for 24 hours.

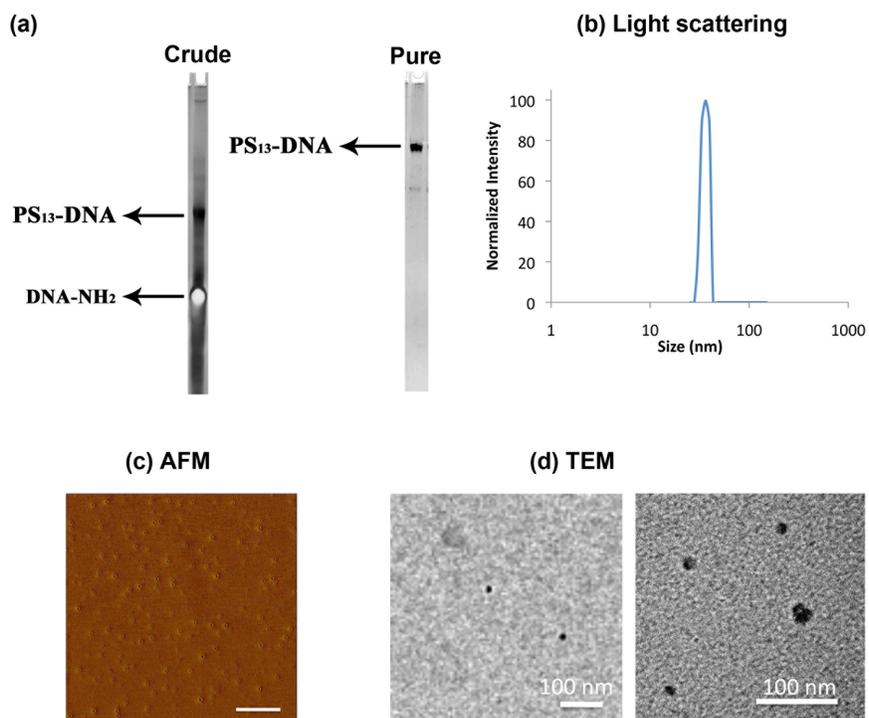
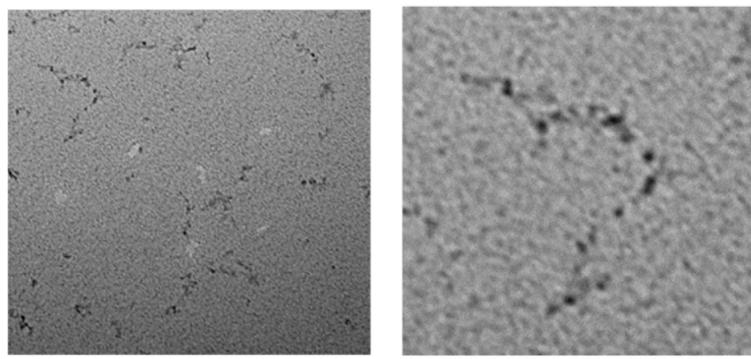


Figure S 22: (a) Denaturing PAGE of crude and purified PS-DNA, (b) light scattering experiment (c) AFM phase image on HOPG (bar is 1 μ m) and (d) TEM on carbon coated TEM grid of PS-DNA micelles.

(a) TEM



(b) AFM

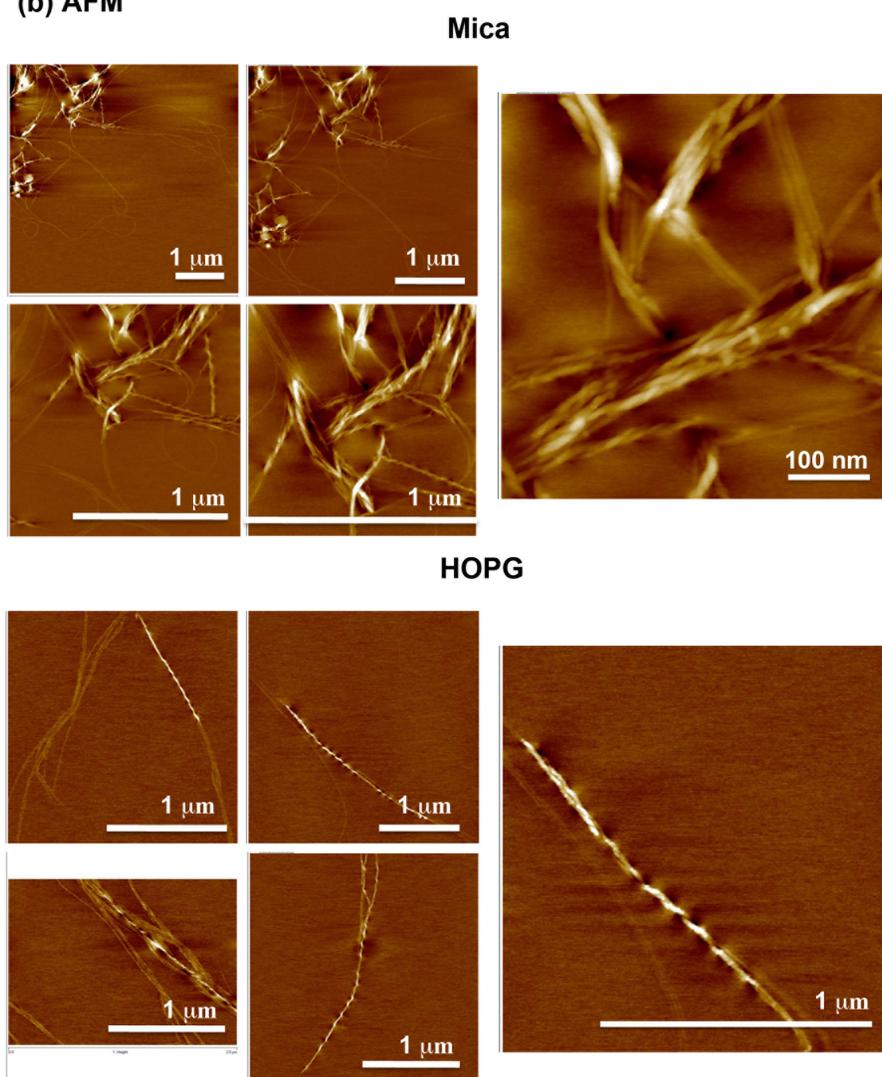
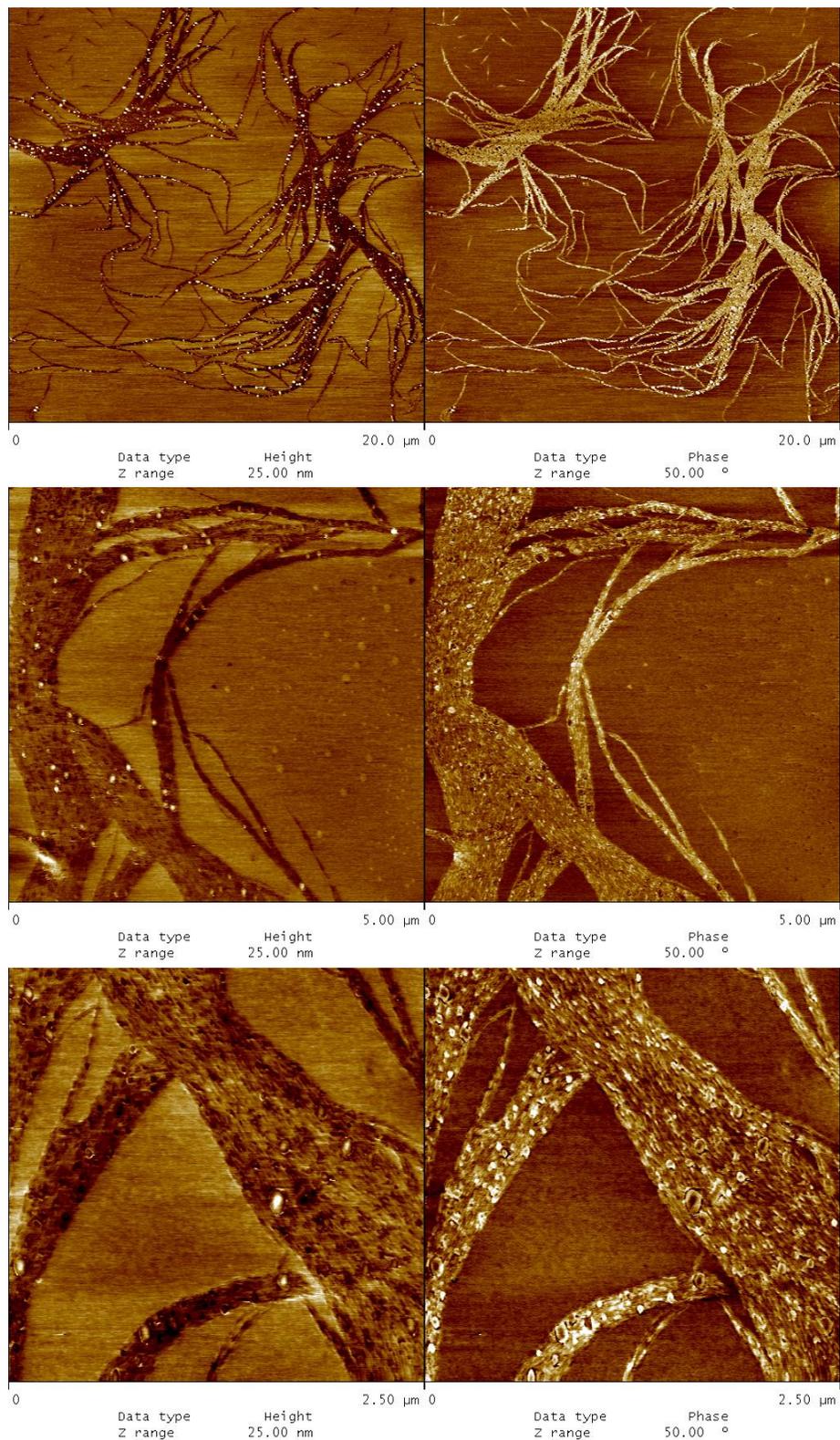


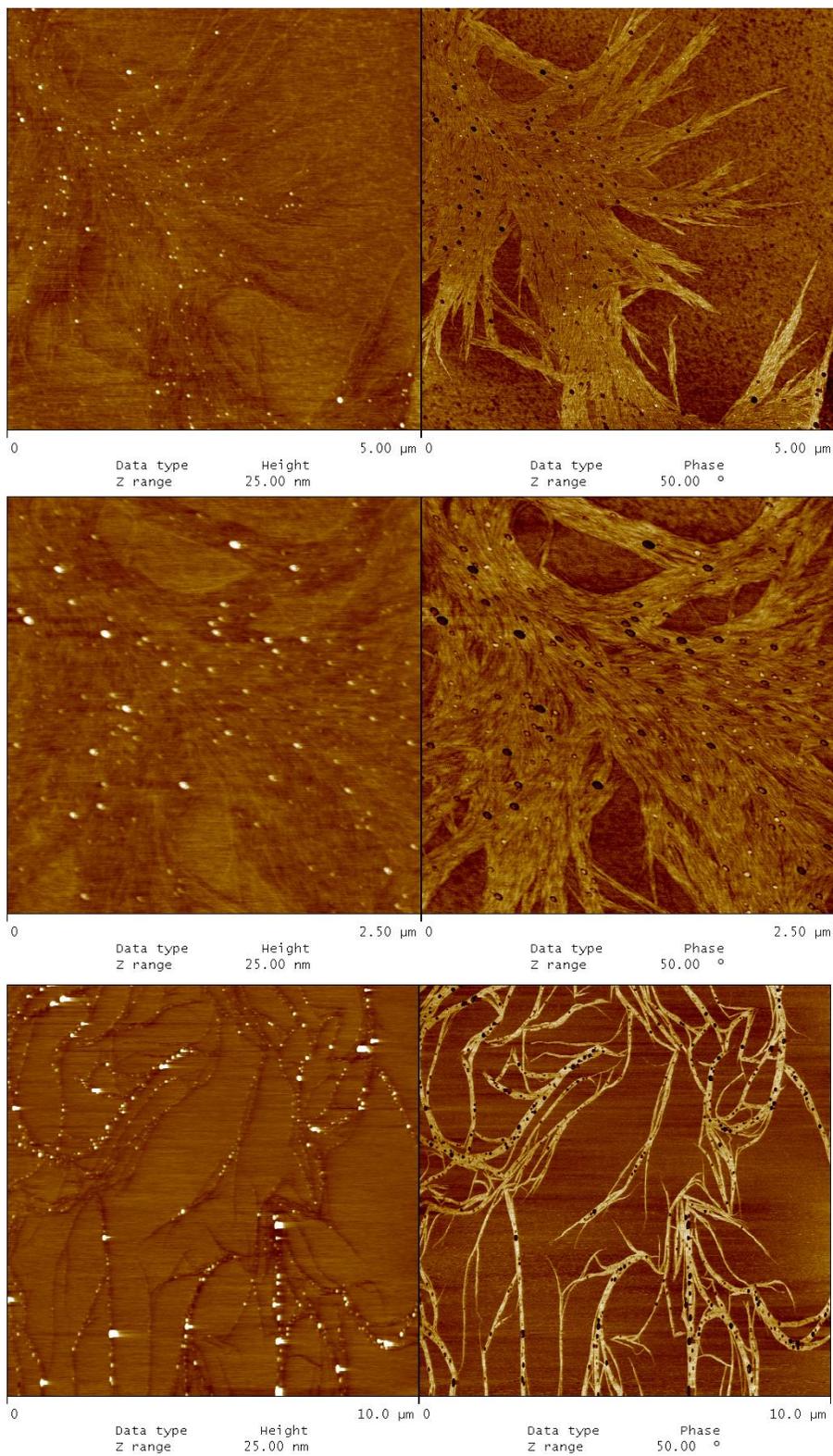
Figure S 23 PS-DNA micelles incorporation onto dilute RCA-nanotubes visualized by (a) TEM on carbon coated TEM grids (scale bar is 500nm) and (b) AFM on mica (top) and HOPG (bottom).

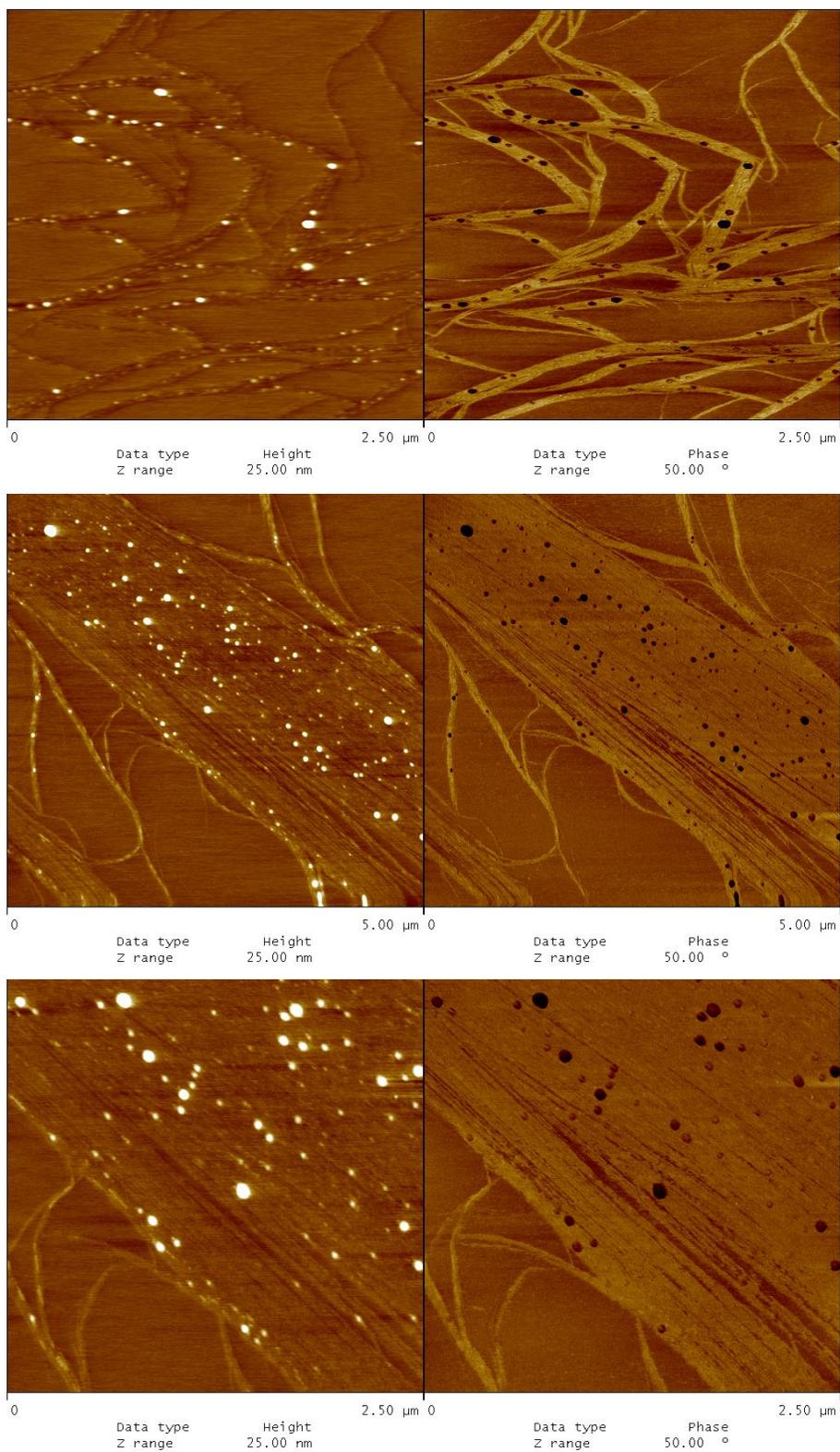
IX. Additional AFM images

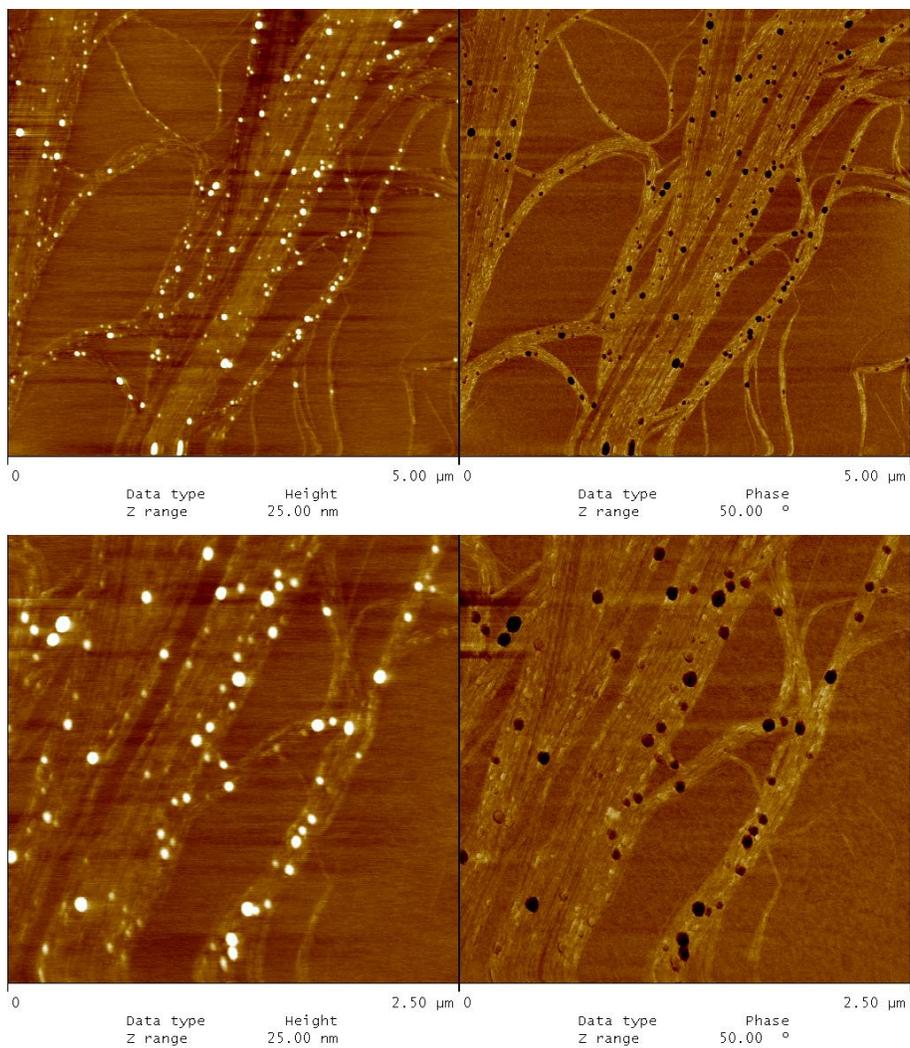
DNA nanotubes decorated with graft-PEG₆₆₀ DNA



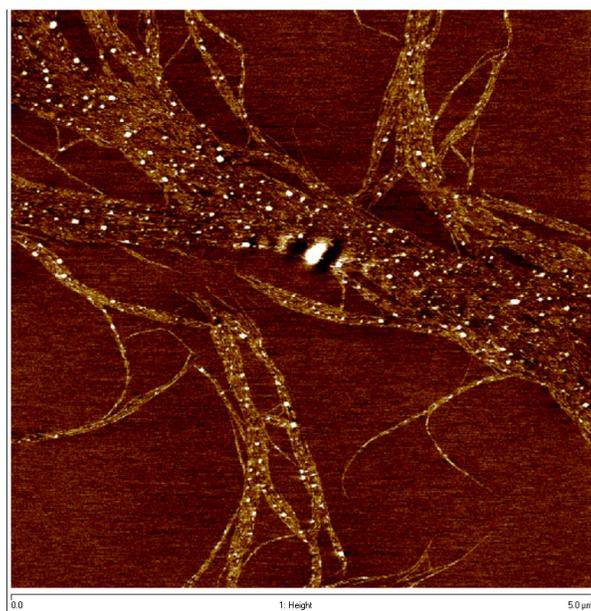
DNA nanotubes decorated with phenyl-DNA

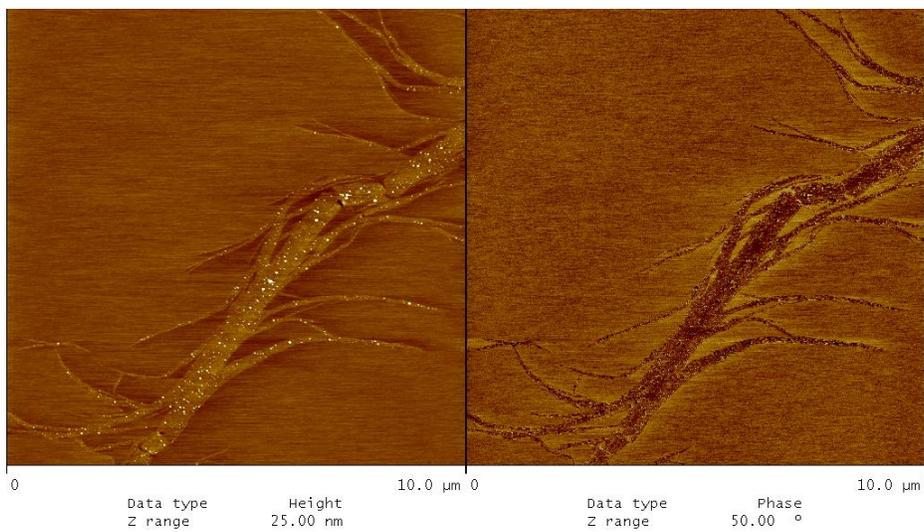
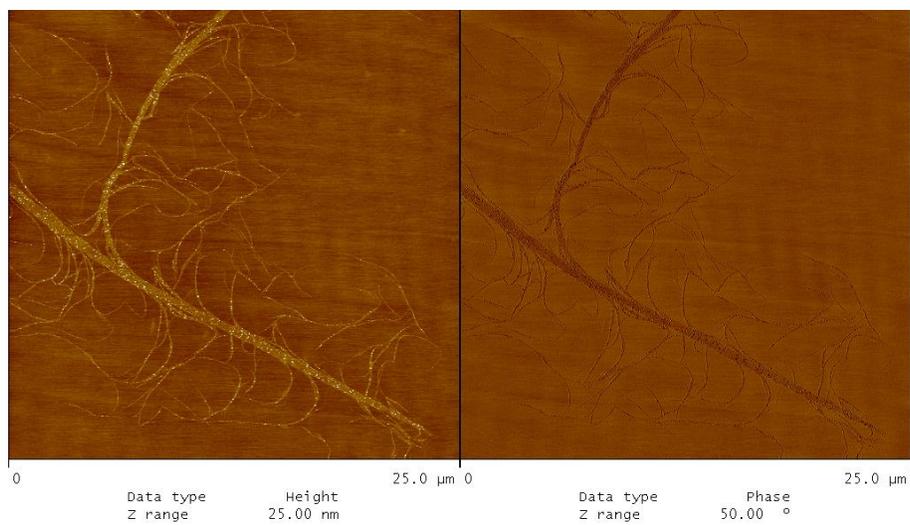
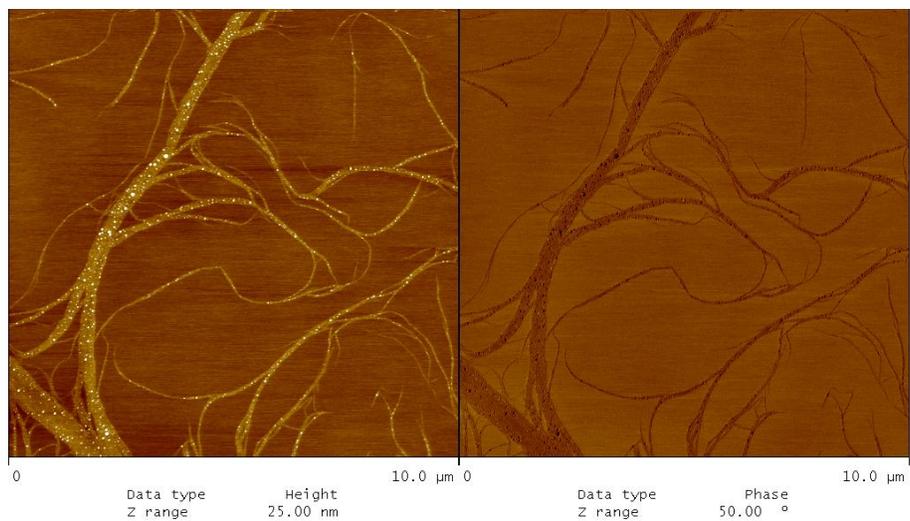






DNA nanotubes decorated with PS-DNA in concentrated nanotube solutions





X. References

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