

Supporting Information

Certain vendors and commercial instruments are identified to adequately specify the experimental procedure. In no case does such identification imply endorsement by the National Institute of Standards and Technology or the Naval Research Laboratory.

Materials. We used standard, unmodified (dA)₅, (dC)₅, (dG)₅, (dT)₅, (dA)₂₅, (dT)₂₅ oligonucleotides and 5'-thiol-modified (dT)₂₅ [3'-(dT)₂₅-(CH₂)₆-SH-5'] purchased from Integrated DNA Technologies and Research Genetics (purity analysed by mass spectroscopy). NaCl-TE buffer solution was prepared from 1 M NaCl (Sigma-Aldrich) and 1 × TE (10 mM Tris-HCl, 1 mM EDTA; ResGen), and adjusted to pH 7 by adding HCl. 1 μM DNA solution for immobilization experiments was typically prepared by mixing 10 μl of 200 μM DNA with 2 ml of NaCl-TE buffer.

DNA Immobilization. Polycrystalline gold films on single-crystal Si(001) wafers were used as substrates. Prior to depositing the films, the wafers were cleaned using a “piranha solution” consisting of 70% H₂SO₄ and 30% H₂O₂ (30% H₂O₂ in H₂O). (Note that Piranha solution must be handled with care: it is extremely oxidizing, reacts violently with organics, and should only be stored in loosely tightened containers to avoid pressure buildup.) After cleaning, a Cr adhesion layer (20 nm) was deposited by vapor deposition, followed by 200 nm of Au. Each substrate was again cleaned with piranha solution and rinsed thoroughly with deionized water (18.3 MΩ) immediately prior to immobilizing the ssDNA.

2 ml of 1 μM ssDNA solutions of individual oligonucleotides (confirmed by UV absorption measurements) or the specified mixtures were immobilized per ≈2 cm² substrate for 20 h. Before analysis, each sample was rinsed thoroughly with deionized water and blown dry under flowing nitrogen.

DNA Hybridization. For oligo(dT)-oligo(dA) hybridization, 10:1(=T:A) mixture was prepared. 25 ml of 200 mM (dT)₂₅ and 2.5 μl of 200 μM (dA)₂₅ were mixed in 5 ml of NaCl-TE buffer, heated to 80 °C for 2 min, allowed to slowly cool to room temperature, and then stored for 24 h prior to use.

FTIR Measurements. FTIR absorption spectra were measured with a Digilab FTS7000 series spectrometer with a PIKE Technologies wire grid infrared polarizer (*p* polarized) and a VeeMax variable angle specular reflectance accessory (reflectance angle 75°). Spectra (2000–900 cm⁻¹) were collected from 2050 scans at 2 cm⁻¹ resolution using a cryogenic mercury cadmium telluride detector.