SUPPORTING INFORMATION

A Thermodynamic Investigation into the Binding Properties of DNA Functionalized Gold Nanoparticle Probes and Molecular Fluorophore Probes

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In all melting experiments, the particle probes and target were allowed to incubate at room temperature for over 24 hours to insure that equilibrium was reached. Melting experiments were carried out on a Jobin Yvon Fluorolog FL3-22 at one-degree increments with a five-minute equilibration time at each temperature. For all systems, at least four separate experiments were performed for each concentration. The average melting temperatures with the standard deviation are shown in Table S1-S5.

Table S1 Melting data for 15mer molecular quencher/fluorophore.

Total Conc. (nM)	Melting Temp (°C)
2	38.27 $\pm$ 0.25
4	39.58 $\pm$ 0.43
10	41.48 $\pm$ 0.18
12	41.64 $\pm$ 0.15
14	42.06 $\pm$ 0.38
16	42.30 $\pm$ 0.41
18	42.60 $\pm$ 0.24
20	42.75 $\pm$ 0.17
22	42.80 $\pm$ 0.27
26	43.45 $\pm$ 0.10

Table S2 Melting data for A₁₀-15mer nanoparticle probe/fluorophore.

Total Conc. (nM)	Melting Temp (°C)
1	42.36 $\pm$ 0.88
2	43.72 $\pm$ 0.82
6	45.92 $\pm$ 0.40
8	46.26 $\pm$ 0.27
10	46.76 $\pm$ 0.38
12	46.72 $\pm$ 0.16
14	47.04 $\pm$ 0.05
16	47.12 $\pm$ 0.27
18	47.48 $\pm$ 0.19
20	47.58 $\pm$ 0.08
22	47.86 $\pm$ 0.29

Table S3 Melting data for A₂₀-15mer nanoparticle probe/fluorophore.

Total Conc. (nM)	Melting Temp (°C)
1	41.80 $\pm$ 0.21
6	45.45 $\pm$ 0.13
8	45.98 $\pm$ 0.10
10	46.50 $\pm$ 0.12
12	46.88 $\pm$ 0.05
14	47.00 $\pm$ 0.08
16	47.35 $\pm$ 0.17
18	47.43 $\pm$ 0.15
20	47.73 $\pm$ 0.13
22	47.93 $\pm$ 0.15

Table S4 Melting data for 21mer molecular quencher/fluorophore.

Total Conc. (nM)	Melting Temp (°C)
4	52.38 $\pm$ 0.21
6	52.65 $\pm$ 0.17
8	52.98 $\pm$ 0.10
10	53.63 $\pm$ 0.15
12	53.78 $\pm$ 0.36
14	54.20 $\pm$ 0.85
16	54.15 $\pm$ 0.13
18	54.50 $\pm$ 0.14
20	54.48 $\pm$ 0.17
22	54.60 $\pm$ 0.12

Table S5 Melting data for A₁₀-21mer nanoparticle probe/fluorophore.

Total Conc. (nM)	Melting Temp (°C)
1	53.35 $\pm$ 0.13
2	54.20 $\pm$ 0.18
4	55.45 $\pm$ 0.06
6	55.98 $\pm$ 0.15
8	56.43 $\pm$ 0.05
10	56.68 $\pm$ 0.13
12	57.03 $\pm$ 0.10
14	57.33 $\pm$ 0.14
16	57.43 $\pm$ 0.17
18	57.75 $\pm$ 0.10
20	57.88 $\pm$ 0.15
22	58.18 $\pm$ 0.26

Determination of DNA Thermodynamics

Melting data was graphed according to the equation:

$$\frac{1}{T_m} = \frac{R}{\Delta H^\circ} \ln C_T + \frac{\Delta S^\circ - R \ln 4}{\Delta H^\circ}$$

The enthalpy and entropy were determined from the slope and y-intercept respectively.

Effects of Fluorophore/Quencher Modification on Duplex Stability

To determine the effects of fluorophore and quencher modifications on our system, we performed melting experiments on duplexes **2/4**, **2/6**, and unmodified duplex of the same sequence. Each sample had a total DNA concentration of 2 μ M and the melting transition was monitored by UV-Vis spectroscopy. The unmodified duplex melted at 45.8°C, **2/6** melted at 48.2°C, and **2/4** melted at 50.6°C. Both the fluorophore and the quencher provided additional stabilization to the duplex of ~2.5°C each. Despite the stabilization due to the fluorophore or quencher, both the nanoparticle and molecular fluorophore probes are stabilized by the same amount so the relative binding strengths are unaffected.

100 nm Silica Particles

100 nm COOH modified silica particles were purchased from Kisker Inc. Particles were modified with 5'amine-modified DNA with the same as **1** using N-(3-dimethylamino)-N'-ethylcarbodiimide (EDAC) as the cross linker. Briefly, 1 mL (25 mg/1 mL) of silica particles was washed with 1mL 0.1 M NaOH twice using centrifugation to remove particles from solution. The particles were then washed three times with 1 mL NANOPure water. Next, 17.5 nmol of 5'amine-modified DNA (700 pmol/1 mg silica particles) in 25 mM MES pH 6 was added to the silica particles and allowed to mix for 30 minutes. Next 93 μ L of EDAC dissolved in cold 25 mM MES pH 6 (10 mg/1 mL) was added to the silica particles and the final volume was brought to 333 μ L. The silica particles were kept at 4°C with gentle mixing overnight. The concentration of DNA/silica particle was determined by measuring the amount of DNA in solution before and after cross linking using UV-Vis spectroscopy. Silica particles were found to have about 200 strands of DNA/particle.