Supporting Information

Silver Nanoparticle-Oligonucleotide Conjugates Based on DNA with Triple Cyclic Disulfide Moieties

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Materials

Silver nanoparticles (31 nm in diameter)[1] were purchased from Ted Pella (Cat No. 15705-20SC). All of the chemicals required for oligonucleotide synthesis were purchased from Glen Research. All other chemicals were purchased from Sigma-Aldrich and used without any further purification.

Oligonucleotide Synthesis[2]

The oligonucleotides (**A**: 5′ (**DSP**)$_3$-A$_{10}$-ATT-ATC-ACT 3′; **B**: 5′ (**DSP**)$_3$-A$_{10}$-AGT-GAT-AAT 3′; **DSP**: cyclic disulfide-containing phosphate derivative, see Figure 2A of the main text) were prepared through solid-phase syntheses on 1 μmol scales using controlled pore glass beads (CPG) and standard phosphoramidite chemistry on an automated synthesizer (Milligene Expedite).

For the 5′ terminal modification of oligonucleotides with cyclic disulfide anchors, three disulfide-containing phosphoramidite units (**DTPA**; Glen Research, Cat. No. 10-1937-90, Figure 1S) were coupled in a series on the synthesizer with an extended coupling time (15 min) each. **DTPA** becomes **DSP** through the synthesis cycles. The synthesized oligonucleotides were cleaved from the CPG support by incubation in 1.5 mL of NH_4OH (30 % v/v) for 16 h at 56 ^oC. After the removal of ammonia under N_2 flow, the crude product was collected, filtered with 0.2

μm cellulose acetate (CA) syringe filter (Whatman), and purified by reverse-phase HPLC on a Hewlett-Packard Series 1100 system (10 × 250 mm Varian DYNAMAX C18 column). After HPLC purification, the protecting dimethoxytrityl (DMT) groups at 5′ termini of oligonucleotides were removed by incubating in 70 % glacial acetic acid aqueous solution for 30 min at room temperature followed by lyophilization to get dry product. The dry product was dissolved in water again, and the detached DMT was extracted from aqueous solution using ethyl acetate. The purified DNA was aliquoted, lyophilized and stored in a freezer (-20 ^{o}C).

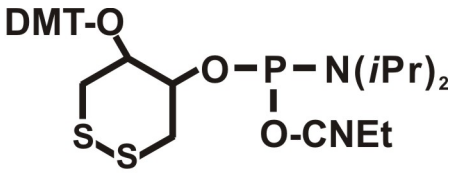

Figure 1S. Disulfide-containing phosphoramidite (**DTPA**).

TEM Analysis

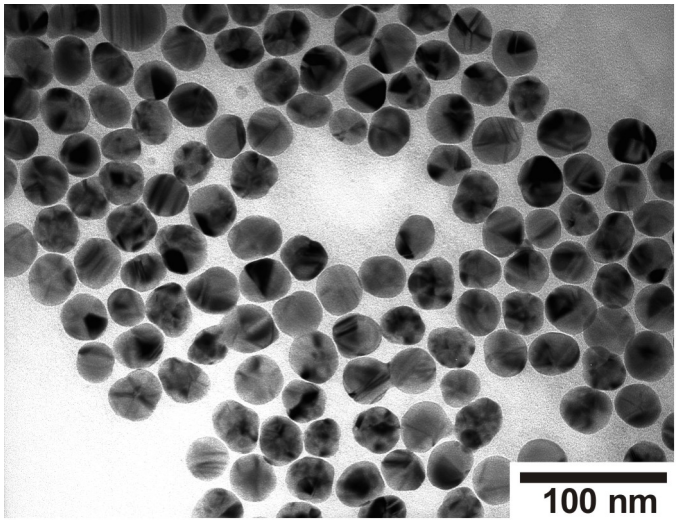

Figure 2S. A TEM image of oligonucleotide-functionalized silver nanoparticles.

Melting Transitions Obtained from Repeated Experiments

Melting transitions of hybridized DNA-Ag NPs were analyzed by monitoring the change in extinction at 410 nm at 0.5 ^{o}C interval at a rate of 1 ^{o}C / min. (Cary 5000 equipped with a Peltier temperature controller, Varian). The concentration of total DNA-Ag NPs is 1 nM, and the concentration of NaCl is 0.15 M.

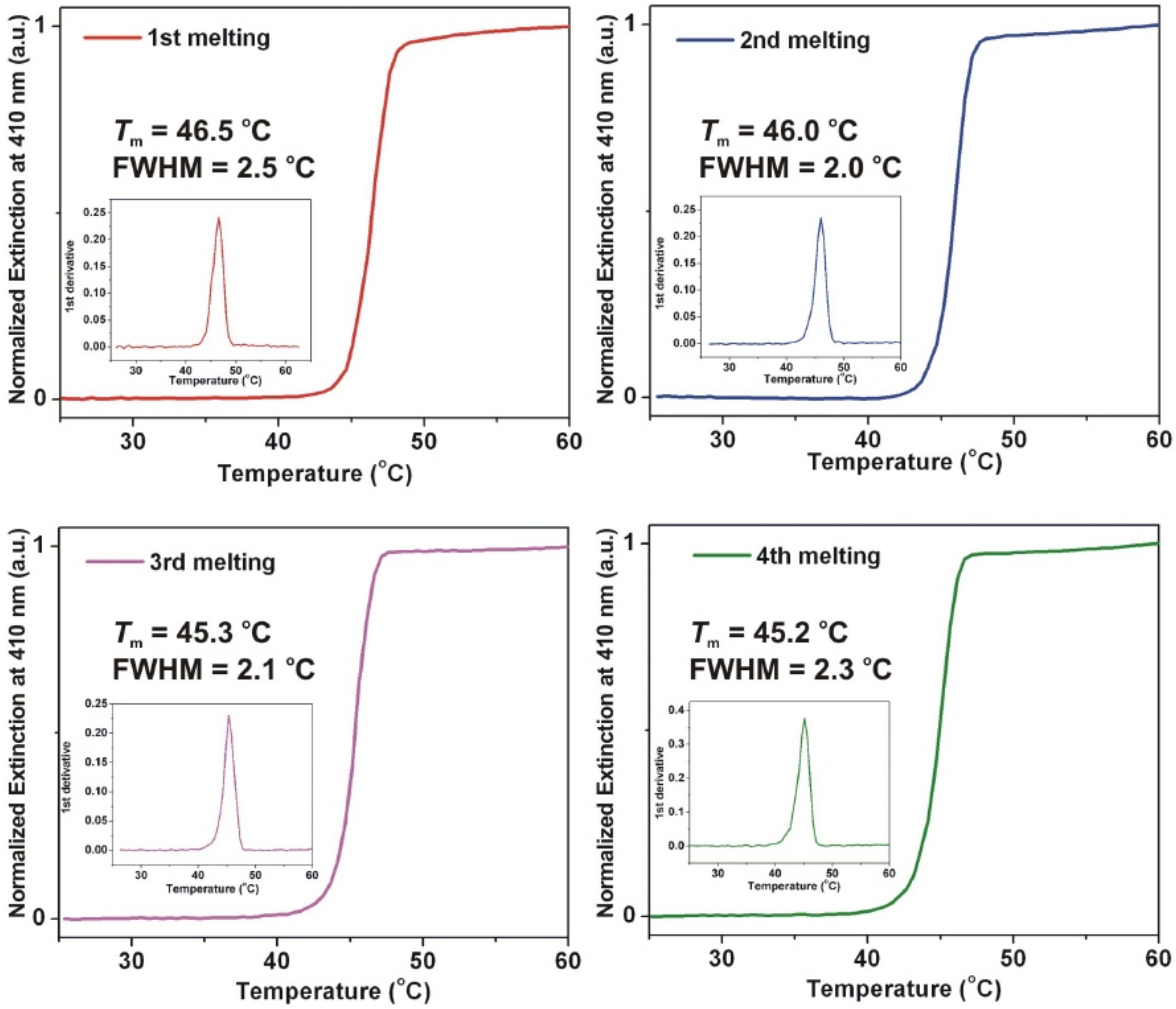

Figure 3S. Melting transitions repeatedly measured for the same DNA-Ag NP aggregates.

References

1) The diameter of the silver nanoparticle is known to be 20 nm from the manufacturer, but the actual diameter determined by TEM analysis is 31 nm on average.

2) Jin, R.; Wu, G.; Li, Z.; Mirkin, C. A.; Schatz, G. C. *J. Am. Chem. Soc.* **2003,** *125*, 1643-1654.