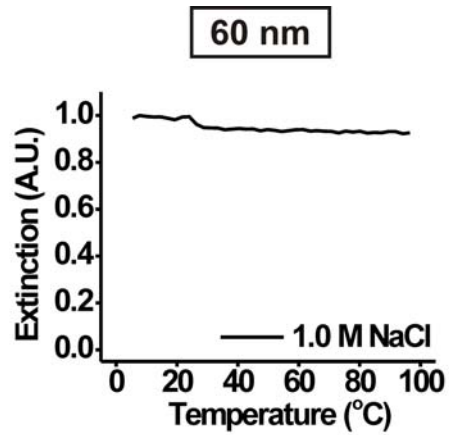


Supporting Information

Curvature-Induced Base Pair “Slipping” Effects in DNA-Nanoparticle Hybridization

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Figure S1



Control: A = B = 3' SH TTT TTT TTT TTT TTT TTT TTT TTT 5'

**Figure S1.** Temperature profile (monitored at 260 nm) for 60 nm DNA-Au NPs functionalized with a poly-T DNA sequence in 1.0 M NaCl.

**Table S1.** Thermodynamic values for Reaction 1 (Scheme 1A).

| Name           | $T_m$<br>(°C) | FWHM<br>(°C) | $\Delta H_{tot}$<br>(kcal/mol) | $\Delta S$ (4°C)<br>(cal/mol) | $\Delta S$ (25°C)<br>(cal/mol) | $\Delta G$ (4°C)<br>(kcal/mol) | $\Delta G$ (25°C)<br>(kcal/mol) | $K_{eq}$<br>(4°C)       | $K_{eq}$<br>(25°C)      |
|----------------|---------------|--------------|--------------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------------|-------------------------|-------------------------|
| TCG-           | 14.8<br>± 0.9 | 3.2<br>± 0.4 | -166.3<br>± 8.4                | -538.0<br>± 0.03              | -622.5<br>± 0.03               | -6.3<br>± 0.5                  | 5.9<br>± 0.5                    | 8.6<br>$\times 10^4$    | 5.0<br>$\times 10^{-5}$ |
| TGC-           | 19.9<br>± 0.4 | 5.1<br>± 0.4 | -121.4<br>± 13.3               | -400.1<br>± 0.05              | -461.8<br>± 0.05               | -6.6<br>± 0.7                  | 2.1<br>± 0.2                    | 1.5<br>$\times 10^5$    | 2.7<br>$\times 10^{-2}$ |
| TCGC-          | 22.0<br>± 0.7 | 5.1<br>± 0.3 | -118.6<br>± 13.5               | -393.8<br>± 0.05              | -454.1<br>± 0.05               | -7.2<br>± 0.9                  | 1.2<br>± 0.1                    | 5.0<br>$\times 10^5$    | 1.3<br>$\times 10^{-1}$ |
| TGCG-          | 39.5<br>± 0.6 | 3.4<br>± 0.3 | -179.3<br>± 12.3               | -629.3<br>± 0.04              | -720.5<br>± 0.04               | -20.4<br>± 1.4                 | -8.3<br>± 0.6                   | 1.1<br>$\times 10^{16}$ | 1.2<br>$\times 10^6$    |
| TCGC-<br>-GCGT | 50.7<br>± 0.4 | 2.5<br>± 0.7 | -320.7<br>± 118.6              | -1161.2<br>± 0.4              | -1324.2<br>± 0.4               | -46.7<br>± 17.1                | -25.4<br>± 9.4                  | 3.1<br>$\times 10^{36}$ | 4.7<br>$\times 10^{18}$ |

The error values on the numbers in **Table S1** are determined based upon the differences in  $T_m$ s for the 5-6 experiments run for each sequence. Note that the values for  $\Delta G$  and  $K_{eq}$  (both at 4 and 25 °C) are consistent with the trends shown by the melting temperatures, which directly correlate with the strength of binding in the aggregate structure. Although a clear trend is seen in these values,  $\Delta H_{tot}$  and  $\Delta S$  (the components comprising the Gibbs free energy) do not exhibit a clear trend. For example, we see that the TGC- system has a higher melting temperature than the TCG- system. Accordingly, the TGC- system has a larger binding constant and a more favorable (more negative) value of  $\Delta G$  at both of the temperatures that were investigated. However, for example, we also see that in comparing the TGC- system to the TCG- system that  $\Delta H_{tot}$  is smaller in magnitude (less negative, less favorable) and  $\Delta S$  is smaller in magnitude (less negative, more favorable). These discrepancies arise (binding in the TGC- system is not both more enthalpically and more entropically favored) because the simple model presented in the work of Jin *et al* does not take into account the sharpness of the melting curves or the possibility of kinetic structure formation.<sup>S1</sup> Finally, note the thermodynamic values,  $\Delta H_{tot}$  and  $\Delta S$ , are

consistent with the hybridization process being enthalpically driven and the dehybridization process being entropically driven.

(S1) Jin, R. C.; Wu, G. S.; Li, Z.; Mirkin, C. A.; Schatz, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 1643-1654.