Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

What controls the unusual melting profiles of small AuNPs/DNA complexes

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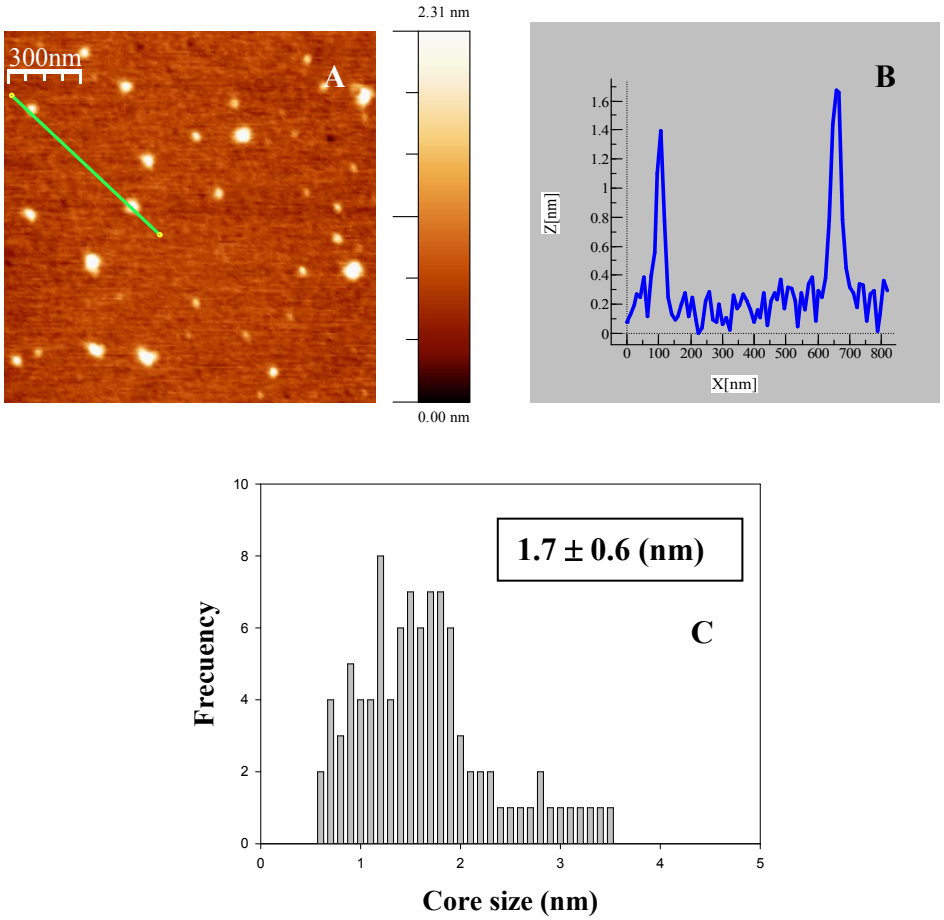

Figure S1. AFM characterization of tiopronin gold nanoparticles in water solution. (A) AFM image; (B) cross sectional analysis along the selected lines for image A, and (C) histogram of size distribution of AuNPs.

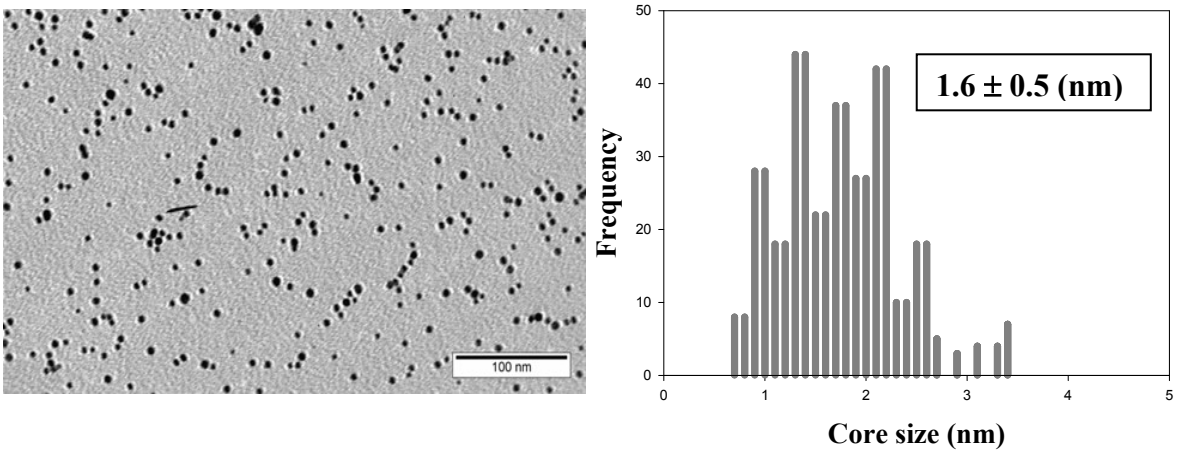

Figure S2. TEM image and histogram of core-size distribution of tiopronin-gold nanoparticles in water solution

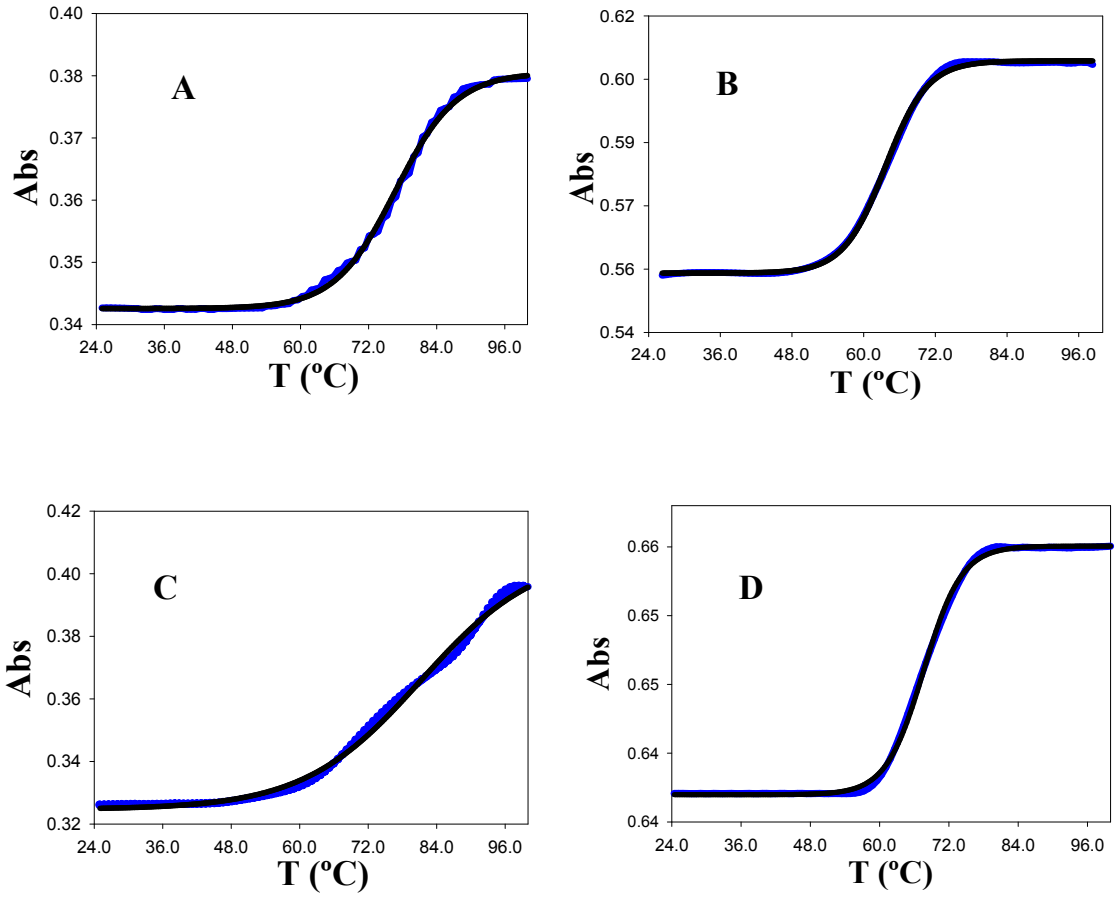

Figure S3. Examples of melting data fit to a two-state transition according to Boltzmann sigmoid analysis, experimental data obtained from Figure 1. The black lines represent the data fit to equation (2) from the text. (A) C_{DNA} = 50 μM, C_{AuNPs} = 0 M, in water; (B) C_{DNA} = 50 μM, R = 0.080, in water; (C) C_{DNA} = 50 μM, C_{AuNPs} = 0 M, C_{NaCl} = 0.015 M; (D) C_{DNA} = 50 μM, R = 0.007, C_{NaCl} = 0.015 M.

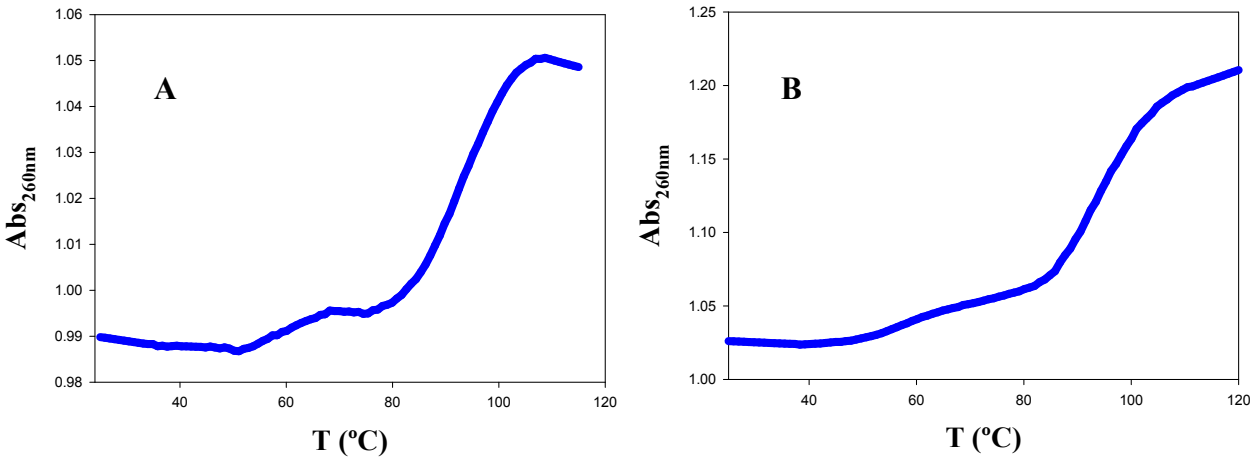

Figure S4. Melting profile of gold nanoparticles at $C_{AuNPs} = 8\times10^{-6}$ M in the absence of the biopolymer as control experiments: (A) in water and (B) in C_{NaCl} = 0.015 M solution.

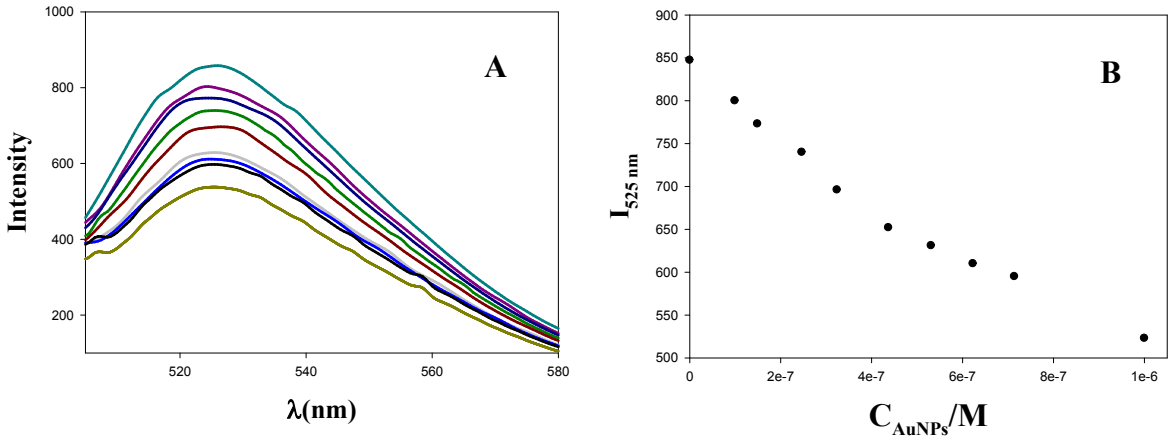

Figure S5. (A) Emission spectra of the SYBR Green I/DNA complex in the presence of different AuNPs concentrations (λ_{exc} = 484 nm; λ_{em} = 525 nm). Curves correspond to 0 (•), 9.93×10^{-8} (•), 1.49×10^{-7} (•), 2.47×10^{-7} (•), 3.24×10^{-7} (•), 4.37×10^{-7} (•), 6.23×10^{-7} (•), 7.14×10^{-7} M (•) and 1.00×10^{-6} (•) of AuNPs. C_{DNA}= 2.5×10^{-7} M; C_{SG} = 1.0×10^{-6} M. (B) Variation of the relative SYBR Green I/ds-DNA fluorescence intensity with C_{AuNPs} at 525 nm for Figure S5-A.

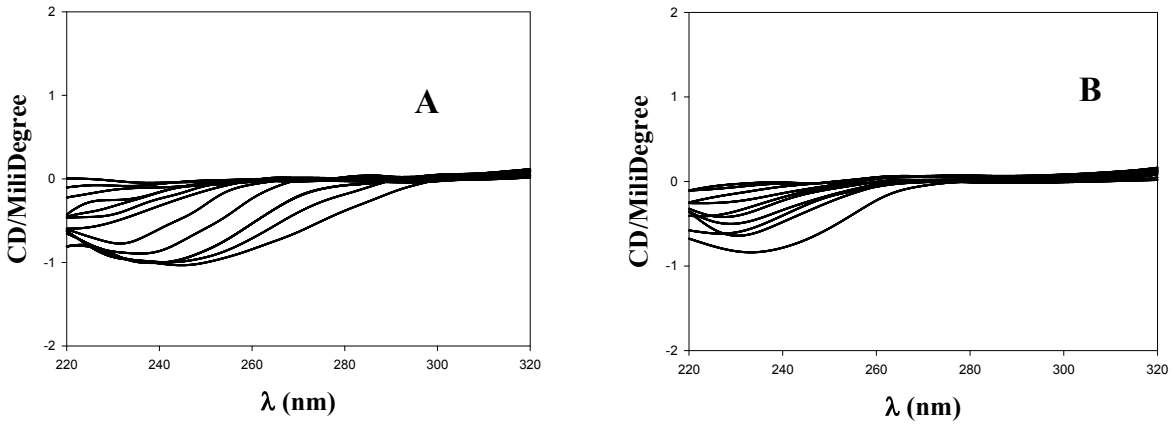

Figure S6. CD spectra of small AuNPs at different C_{AuNPs} concentrations. (A) in water, C_{AuNPs} for the spectra from a to l is 0.05, 0.15, 0.24, 0.29, 0.48, 0.58, 0.70, 1.00, 1.50, 2.00, 3.00 and 4.00 μM; (B) in salt, C_{NaCl} = 0.015 M, C_{AuNPs} for the spectra from a to k is 0.05, 0.15, 0.29, 0.48, 0.58, 0.70, 1.00, 1.50, 2.00, 3.00 and 4.00 μM.

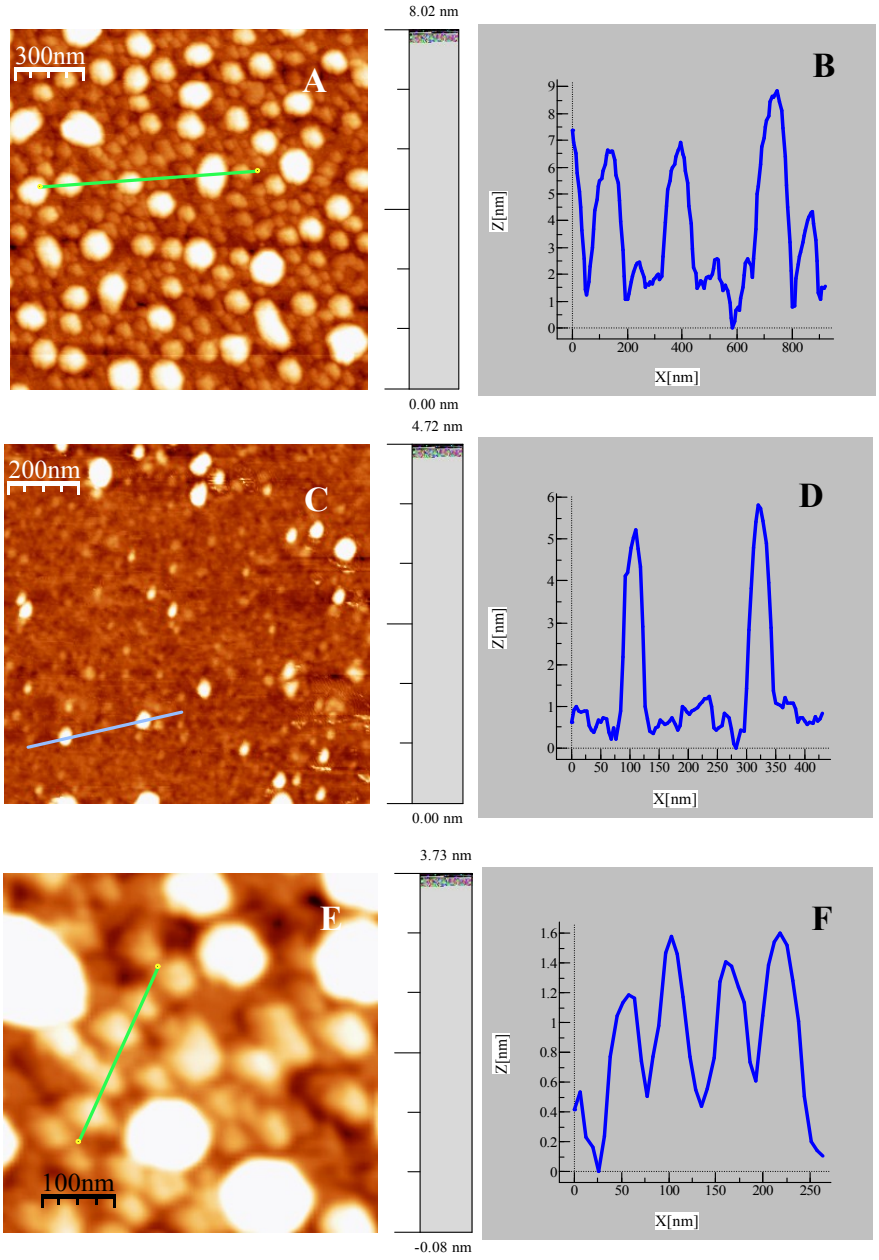

Figure S7. Analysis of AFM topographic images in Fig. 8 obtained at $C_{DNA} = 3.0\times10^{-7}$ M, $C_{AuNPs} = 2.0\times10^{-6}$ M and $C_{NaCl} = 0.015$ M, T = 25.0 ºC. (A) AuNPs/ss-DNA system showing the formation of aggregate compact structures; (C) AuNPs/ds-DNA system highlighting the formation of compact structures; (E) AuNPs/ss-DNA system showing multiple interconnections among the aggregates mediated by small AuNPs. Figures B, D, and F correspond to cross sectional analysis of the heights along the selected line for images A, C, and E, respectively.

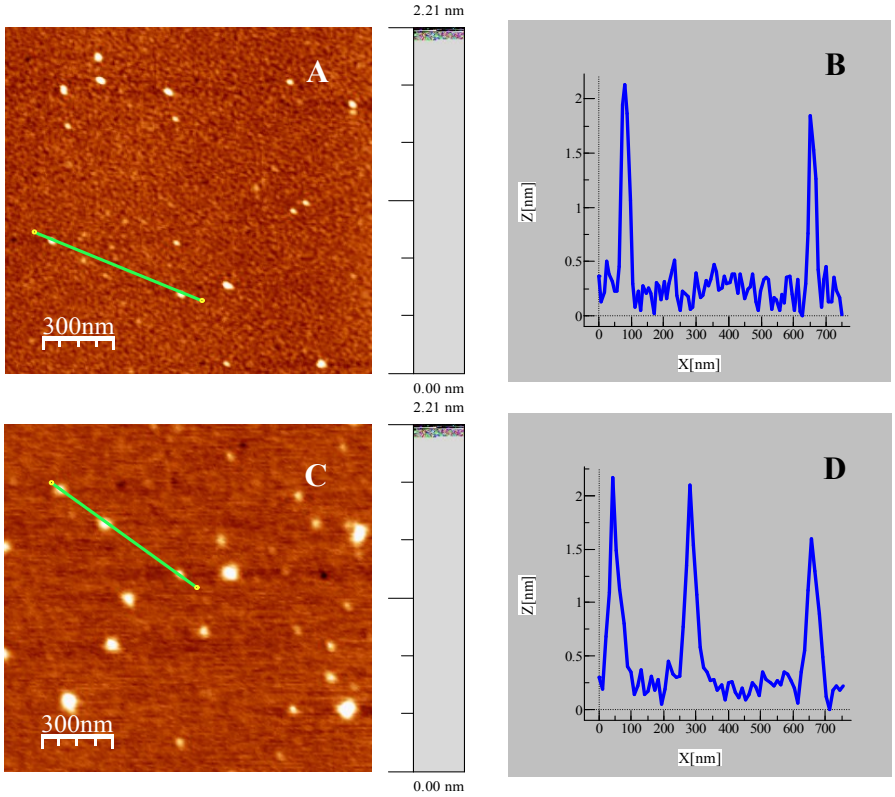

Figure S8. AFM topographic images of AuNPs at different NaCl concentration. (A) C_{AuNPs} =1×10^{-6} M; C_{NaCl} = 0.006 M; (C) C_{AuNPs} =1×10^{-6} M; C_{NaCl} = 0.015 M. Figures B and D correspond to cross sectional analysis along the selected lines for images A and C, respectively.

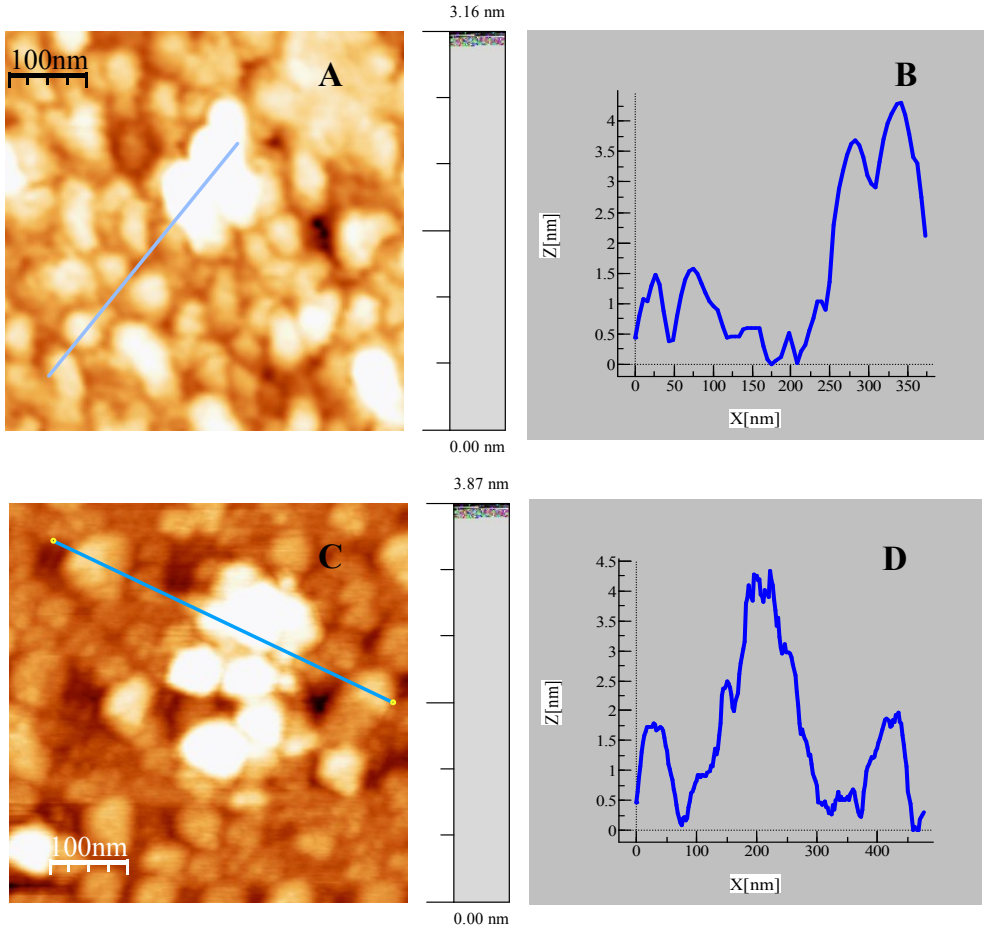

Fig S9. Analysis of AFM topographic images described in Fig. 9 showing multiple interconnection among the aggregates mediated by small AuNP. The images were obtained at $C_{DNA} = 3.0\times10^{-7}$ M, $C_{AuNPs} = 5.0\times10^{-8}$ M and $C_{NaCl} = 0.015$ M, T = 65.0 ºC. (A) AuNPs/ss-DNA; (C) AuNPs/ds-DNA. Figures B and D correspond to cross sectional analysis of the heights along the selected line for images A, and C, respectively.

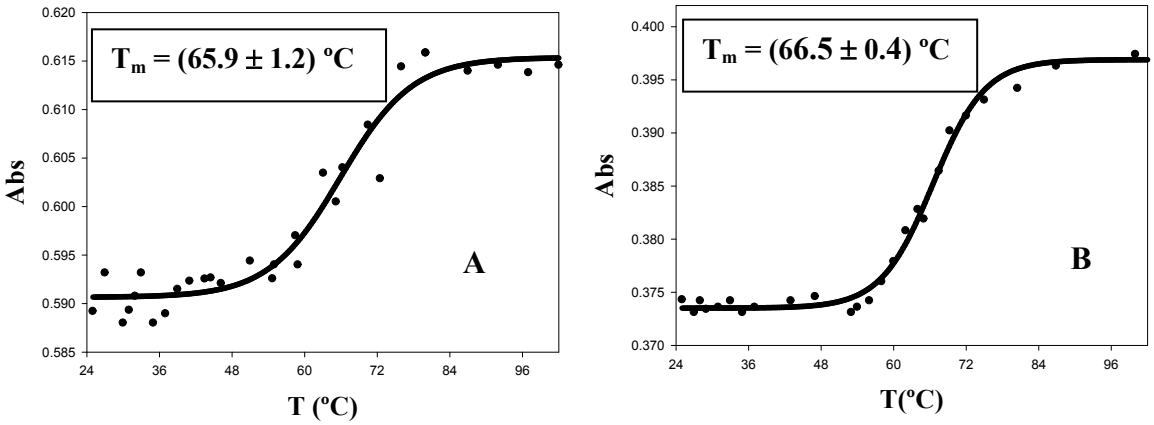

Figure S10. Absorbance versus temperature of the AuNPs/DNA nanocomplexes formed in at the low R ratio and heating the sample to 100 ºC of temperature. (A) in water, R = 0.080 and (B) in salt, C_{NaCl} = 0.015 M, R = 0.003 M. The black lines represent the data fit to equation (2) from the text. The experiments were done following the absorbance of the complexes at 260 nm after complex formation, and cooling the sample back down to room temperature.

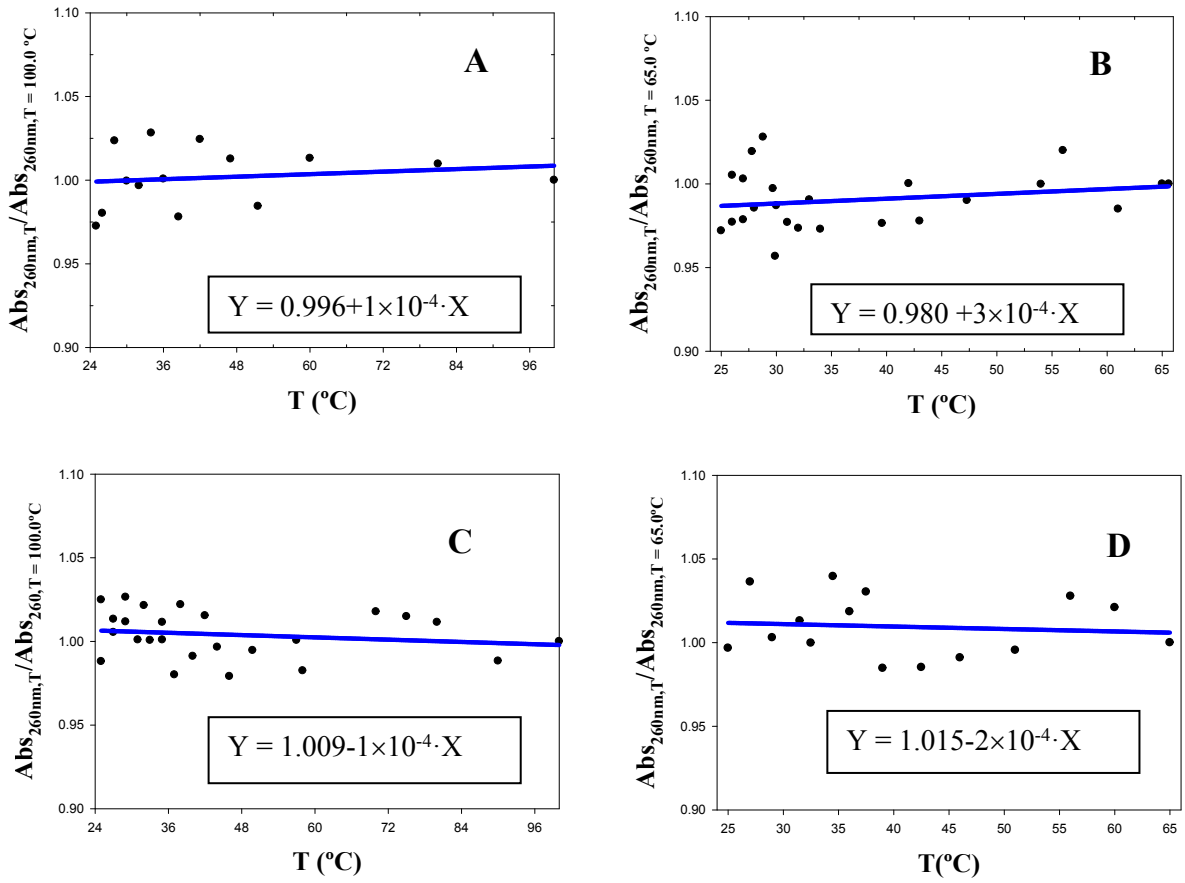

Figure S11. Absorbance relative versus temperature of the AuNPs/DNA nanocomplexes formed at the high R ratio and 100.0 ºC or 65.0 ºC of temperature. (A) in water, R = 0.16, T = 100.0 ºC; (B) in water, R = 0.16, T = 65.0 ºC; (C) C_{NaCl} = 0.015 M, R = 0.16, T = 100.0 ºC, and (D) C_{NaCl} = 0.015 M, R = 0.16, T = 65.0 ºC. The blue lines represent the data fit to linear regression. The experiments were done following the absorbance of the complexes at 260 nm after complex formation, and cooling the sample back down to room temperature (see section 2.2.5 for more details).

Table 1. Tm values of ds-DNA at different AuNPs and NaCl concentrations obtained from Boltzmann sigmoid analysis (see equation 2 from the text).

	C_{NaCl} = 0.000 /M			C_{NaCl} = 0.015/ M		
C_{AuNPs}/μM	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.000	76.8 ± 1.0 ºC	77.4 ± 0.8 ºC	76.6 ± 0.8 ºC	81.3 ± 0.4 ºC	79.4 ± 0.2 ºC	79.8 ± 1.1 ºC
0.150	75.8 ± 1.0 ºC	75.4 ± 0.8 ºC	75.7 ± 0.4 ºC	72.0 ± 1.0 ºC	71.1 ± 0.5 ºC	71.8 ± 0.4 ºC
0.350	75.6 ± 0.2 ºC	75.6 ± 0.8 ºC	75.2 ± 0.3 ºC	67.6 ± 0.5 ºC	68.0 ± 0.2 ºC	67.9 ± 0.4 ºC
0.500	74.6 ± 0.2 ºC	75.2 ± 0.2 ºC	75.0 ± 0.3 ºC	67.0 ± 0.2 ºC	67.2 ± 0.4 ºC	67.4 ± 0.4 ºC
1.000	71.9 ± 1.3 ºC	72.1 ± 0.3 ºC	70.7 ± 0.3 ºC	65.1 ± 1.2 ºC	64.8 ± 0.5 ºC	64.9 ± 0.6 ºC
4.000	63.6 ± 0.4 ºC	64.2 ± 0.4 ºC	64.5 ± 0.3 ºC	----------	----------	----------

Table S2. Tm mean values and standard deviations calculated from data in Table S1.

	C_{NaCl} = 0.000 /M	C_{NaCl} = 0.015/ M
C_{AuNPs}/μM	$Tm_{, Mean\ Value}$ /ºC	$Tm_{, Mean\ Value}$ /ºC
0.000	76.9 ± 0.3 ºC	80.2 ± 0.8 ºC
0.150	75.6 ± 0.2 ºC	71.4 ± 0.4 ºC
0.350	75.3 ± 0.2 ºC	67.8 ± 0.2 ºC
0.500	74.9 ± 0.3 ºC	67.2 ± 0.2 ºC
1.000	71.6 ± 0.6 ºC	64.9 ± 0.1 ºC
4.000	64.1 ± 0.4 ºC	----------