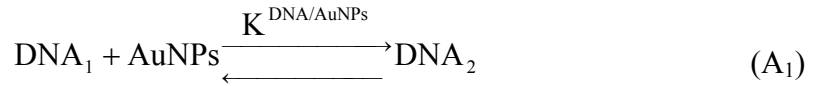


SUPPORTING INFORMATION.

The two state model for DNA conformational changes in the presence of two ligands: derivation of equation (10).

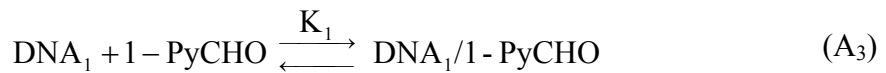
Assuming that gold colloid nanoparticles interact directly with DNA promoting a conformational change in the biomolecule, there are two kinds of DNA in the solution: free (DNA₁) and bound to the nanocluster (DNA₂). These forms of DNA present different affinity to interact with the fluorescent probe, pyrene-1carboxaldehyde. Thus, in the colloidal gold system, containing DNA and the 1-PyCHO probe, there are at least three equilibria implicated. One of them, the DNA/AuNPs equilibrium binding, appears as the DNA conformation changes from the state 1, where DNA is free in solution (DNA₁), to the state 2 in which DNA is stabilized on the nanoparticle surface (DNA₂):



$$K^{\text{DNA/AuNPs}} = \frac{[\text{DNA}_2]}{[\text{DNA}_1][\text{AuNPs}]} \quad (\text{A}_2)$$

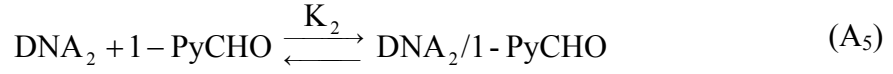
The remaining equilibria correspond to the binding of the probe with DNA in the two different DNA conformations that are present in the AuNPs/DNA system. One of them corresponds to the binding 1-PyCHO/DNA₁ where the biomolecule is free of AuNPs.

This binding is represented by equations A₃-A₄:



$$K_1 = \frac{[\text{DNA}_1/1 - \text{PyCHO}]}{[\text{DNA}_1][1 - \text{PyCHO}]} \quad (\text{A}_4)$$

On the other hand, the corresponding equilibrium for the binding of the probe to the DNA in state 2 (linked to gold nanoparticles) is given by equations A₅-A₆:



$$K_2 = \frac{[\text{DNA}_2/1 - \text{PyCHO}]}{[\text{DNA}_2][1 - \text{PyCHO}]} \quad (\text{A}_6)$$

In general, whatever property of interest of the system you consider, (P), the measured value quantity of interest, ($\langle P \rangle$), is the sum of the fractional contributions of each state:

$$\langle P \rangle = \sum X_i P_i \quad (\text{A}_7)$$

$$\langle P \rangle = P_1 X_1 + P_2 X_2 + P_3 X_3 \quad (\text{A}_8)$$

where $\langle P \rangle$ is the average value of a general property designed as “P” and X_i is the contribution of “P” to the state “i”. Regardless of the number of states, the set of numbers $\{X_i\}$ defines the distribution of states. In the present paper, the distribution corresponds to the fraction of 1-PyCHO that binds to DNA in state 1, DNA in the state 2, and the fraction of free 1-PyCHO. Considering that the fractional contribution of the free probe is meaningless compared to the 1-PyCHO bound (in our working conditions the intercalation process is almost complete), its fractional contribution can be neglected and the equation A₈ can be simplified. Taking into account the equilibria described previously, the fractional contribution to the state 1 and 2 is given by:

$$X_1 = \frac{[\text{DNA}_1]}{[\text{DNA}]} = \frac{K_1[\text{DNA}_1]}{1 + K_1[\text{DNA}_1] + K_2[\text{DNA}_2]} \quad (\text{A}_9)$$

$$X_2 = \frac{[\text{DNA}_2]}{[\text{DNA}]} = \frac{K_2[\text{DNA}_2]}{1 + K_1[\text{DNA}_1] + K_2[\text{DNA}_2]} \quad (\text{A}_{10})$$

$$X_1 + X_2 + X_3 (\approx 0) = 1 \quad (\text{A}_{11})$$

Combining the expressions A₉ and A₁₀ in the equation A₈ we have:

$$\langle P \rangle = \frac{P_1 K_1 [\text{DNA}_1] + P_2 K_2 [\text{DNA}_2]}{1 + K_1 [\text{DNA}_1] + K_2 [\text{DNA}_2]} \quad (\text{A}_{12})$$

Then, considering the equilibrium DNA/AuNPs described by the equations A₁-A₂, the DNA concentration in state 1 and 2 will be given by:

$$[\text{DNA}_1] = \frac{1}{1 + K^{\text{DNA/AuNPs}} [\text{AuNPs}]} [\text{DNA}] \quad (\text{A}_{13})$$

$$[\text{DNA}_2] = \frac{K^{\text{DNA/AuNPs}} [\text{AuNPs}]}{1 + K^{\text{DNA/AuNPs}} [\text{AuNPs}]} [\text{DNA}] \quad (\text{A}_{14})$$

The following expression is given introducing these DNA concentrations ([DNA₁] and [DNA₂]) into the equation (A₁₂) and reorganizing:

$$\langle P \rangle = \frac{P_1 + P_2 \frac{K_2}{K_1} K^{\text{DNA/AuNPs}} [\text{AuNPs}]}{1 + (1 + K_2) \frac{K^{\text{DNA/AuNPs}}}{K_1} [\text{AuNPs}]} \quad (\text{A}_{15})$$

This equation relates the changes of any property of the system with the changes in substrate concentrations ([AuNPs] in our case). Considering the corrected free energy of binding DNA/1-PyCHO, ΔG^{CORR} , as a property of interest we obtain the final expression (eq. (10) in the text):

$$\langle \Delta G^{\text{CORR}} \rangle = \frac{\Delta G_1^{\text{CORR}} + \Delta G_2^{\text{CORR}} \frac{K_2}{K_1} K^{\text{DNA/AuNPs}} [\text{AuNPs}]}{1 + (1 + K_2) \frac{K^{\text{DNA/AuNPs}}}{K_1} [\text{AuNPs}]} \quad (\text{A}_{16})$$