Supporting Information

Quantification of Nucleobases/Gold Nanoparticles Interactions: Energetics of the Interactions through Apparent Binding Constants Determination.

J. M. Carnerero,[a] A. Sánchez-Coronilla,[a] E. I. Martín,[b] A. Jimenez-Ruiz [a] and R. Prado-Gotor [a]*

contribution from:

[a]Department of Physical Chemistry. Faculty of Chemistry. Universidad of Sevilla.

[b]Department of Chemical Engineering. Faculty of Chemistry. Universidad of Sevilla.

C/ Profesor García González s/n 41012 Sevilla. Spain.

* Author to whom correspondence should be addressed

e-mail: pradogotor@us.es

Tel 34-954 557177

Fax 34-954557174

Determination of the concentration of AuNPs

The mean number of Au atoms in a particle, n, can be calculated using Eq. 1:[1]

$$n = \frac{0.5\pi N_A d_m}{3V_m} \quad (1)$$

In the above equation, which assumes a spherical particle shape, N_A is the Avogadro's number, d_m is the diameter of the nanoparticle expressed in cm and V_m is the molar volume of bulk gold (10.215 cm^3).[1] Once the concentration of Au atoms in the nanoparticles solution is known from the reaction conditions, it is possible to calculate the average concentration of nanoparticles. From TEM measurements and considering that the reduction from gold (III) to gold atom was 100% complete, the AuNPs concentration was 3.0 $x10^{-9}$ M.

Interaction of nucleobases with gold nanoclusters

In order to test the effectivity of the system, adenine and thymine molecules were made to interact with multiple gold particles simultaneously. We have studied the interaction of the nitrogenous bases with two and three clusters of four gold atoms through different binding sites (Figure S3). The interaction of adenine was found to be through their basic nitrogen atoms (Figures S3a and S3b), while the interaction of thymine involved the oxygen atoms (Figure S3c). The results indicate that the interaction of adenine with two and three gold clusters is energetically favoured (ΔH_r = -117 and -163 kJ/mol, respectively) when compared to the interaction of thymine with two gold cluster (ΔH_r = -84 kJ/mol). Those results agree with those reported previously for adenine and thymine in their interactions with gold and gold clusters.[2–4]

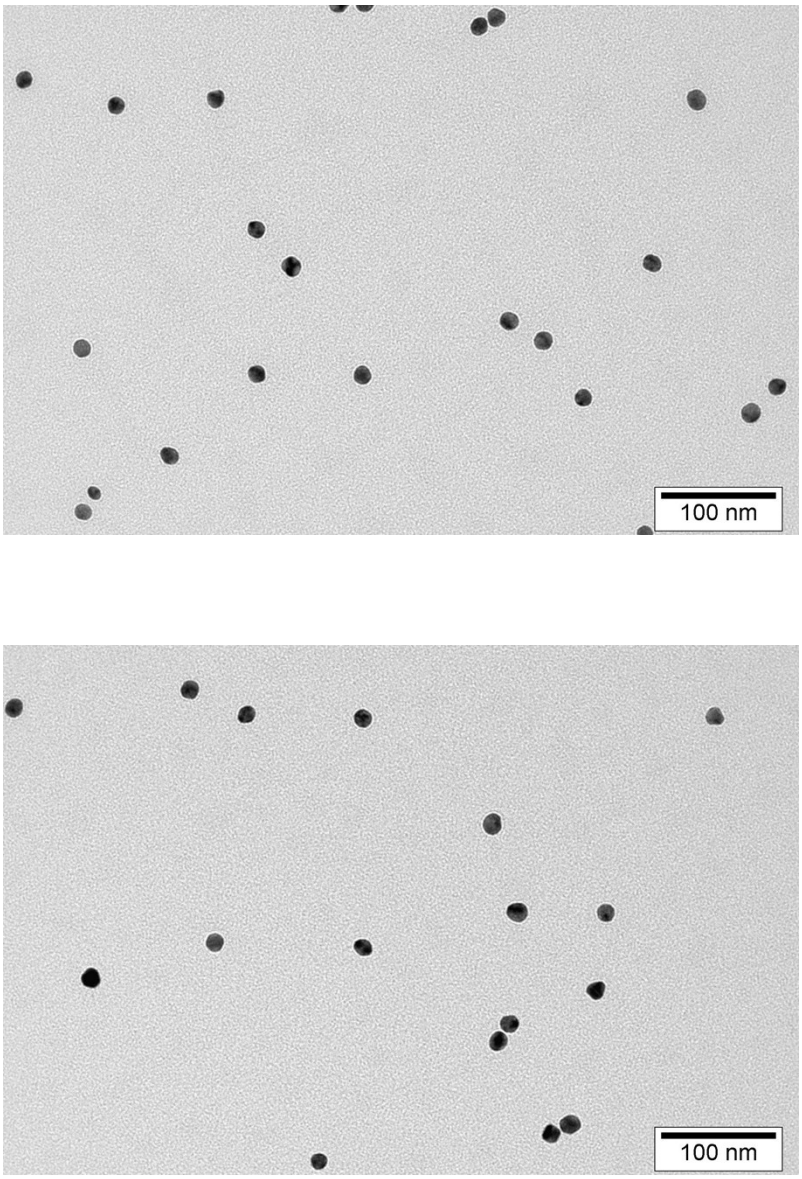

Figure S1. Examples of TEM images used for measuring AuNP average size. [AuNPs] = 3.0 x 10^{-10} M.

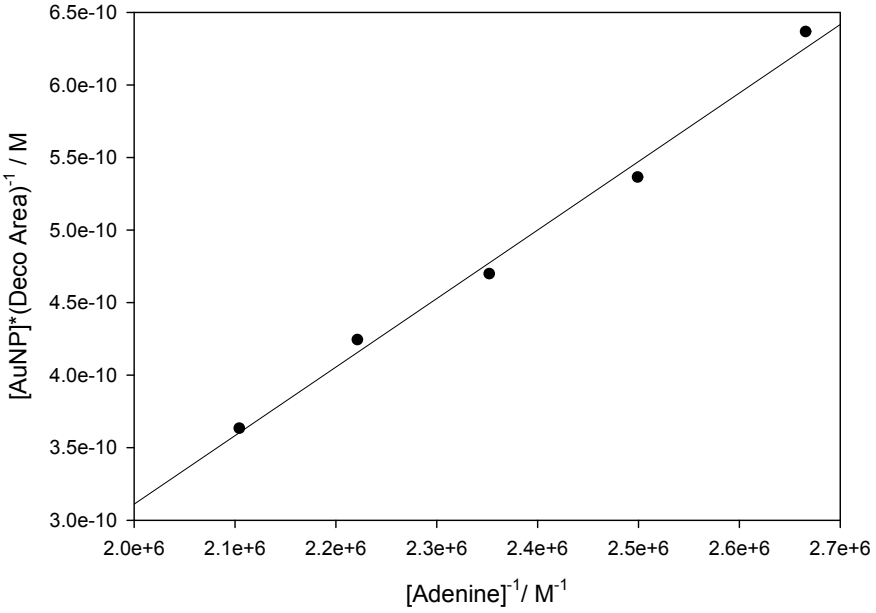

Figure S2. Benesi-Hildebrand plot for the decovoluted area proportion of aggregated AuNPs for [adenine] = 3.75 x 10^{-7} M to 4.75 x10^{-7} M.

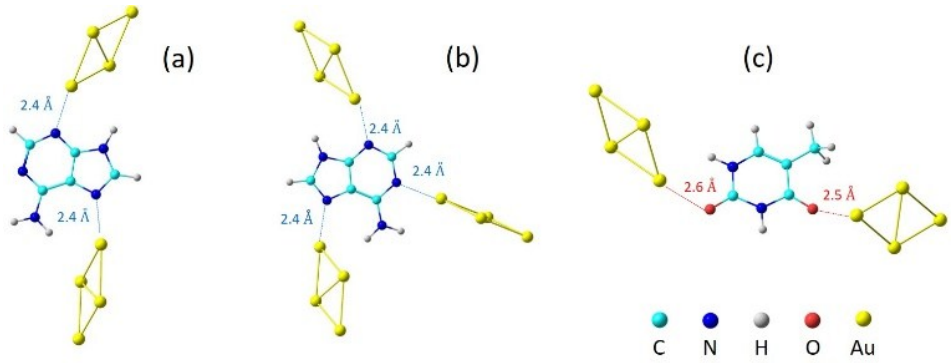

Figure S3. Optimized structures of adenine and thymine with 4-atom gold clusters.

References

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(3) De, H.; Paul, A.; Datta, A. Theoretical Study of Au4 Thymine, Au20 and Ag20 Uracil and Thymine Complexes for Surface Enhanced Raman Scattering. *Comput. Theor. Chem.* **2017**, *1111*, 1–13.

(4) Yao, G.; Zhai, Z.; Zhong, J.; Huang, Q. DFT and SERS Study of 15N Full-Labeled Adenine Adsorption on Silver and Gold Surfaces. *J. Phys. Chem. C* **2017**, *121*, 9869–9878.