Supporting Information for "On the interaction between gold and silver metal atoms and DNA/RNA nucleobases - A comprehensive computational study of ground state properties"

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I. CHOOSING THE XC FUNCTIONAL

The guanine was the chosen nucleobase used as benchmark system for the evaluation and choice of the exchange-correlation functional used in this work. We test the interaction with both noble metal atoms: gold and silver in the three charge states: neutral, cationic and anionic at two levels with three XC functionals: PZ (LDA), PBE (GGA) and RPBE (GGA). We perform structural optimization using the Basin Hopping algorithm and we extracted the values of the binding energies and electronic gaps. The results for the guanine gold and silver structures are summarized in the Figure 1. The obtained values of the binding energy and electronic gap at PBE level for the adenine, thymine, cytosine and uracil appear in the Figure 2.

The results in the neutral systems show that PZ-LDA overestimates the binding energy in comparison with the PBE and RPBE and predicts alternative binding sites to GGA exchange-correlation approaches. The PBE approximation in comparison with its correction RPBE give lower energy bindings but they predict the same binding sites and almost the same number of structures. In the cationic and anionic structures the results are similar but in this case the local approximation overestimates in minor value the binding energy and the results for the gradient corrected functionals the results are close each other. This results show that PBE is a the best method to describe the interaction in metal-DNA/RNA system taking in account the ratio between accuracy and computational cost.

In the electronic HOMO-LUMO gap, the results for different exchange-correlation functionals show that in most cases the obtained values are practically the same, with exceptions in the results for the local methodology in the cationic hybrid gold structures and the silver neutral systems.

II. STRUCTURES

In this section we summarize (in order of stability) the most stable structures (up to six) for the three charge states: neutral (0), cationic (+1) and anionic (-1) (from left to right) in both hybrid Au/AG-DNA/RNA systems. In the Figure 3 we present the gold-guanine systems. The result for equivalent silver-guanine system appears in the Figure 4. The final results for the gold-adenine and silver-adenine are depicted in the Figures 5 and 6 respectively. Gold-thymine and silver-thymine in the Figures 7 and 8, gold-cytosine and silver-cytosine in the Figures 9 and 10 and for the gold-uracil and silver-uracil the Figures 11 and 12.

The obtained hybrid metal Watson-Crick base pairs structures are depicted in the Figure 13 and Figure 14 for guanine-cytosine and adenine-thymine both with gold respectively. In the Figure 15 and Figure 16 for the silvered guanine-cytosine and adenine-thymine respectively. The obtained structures for both Au/Ag-guanosine monophosphate are showed in the Figure 17 and Figure 17 respectively.

In the respective legends the bond lengths and binding energies values are showed for each optimized structure.

The coordinates of all obtained structures in this review can be made available in a *xyz* data file upon request.

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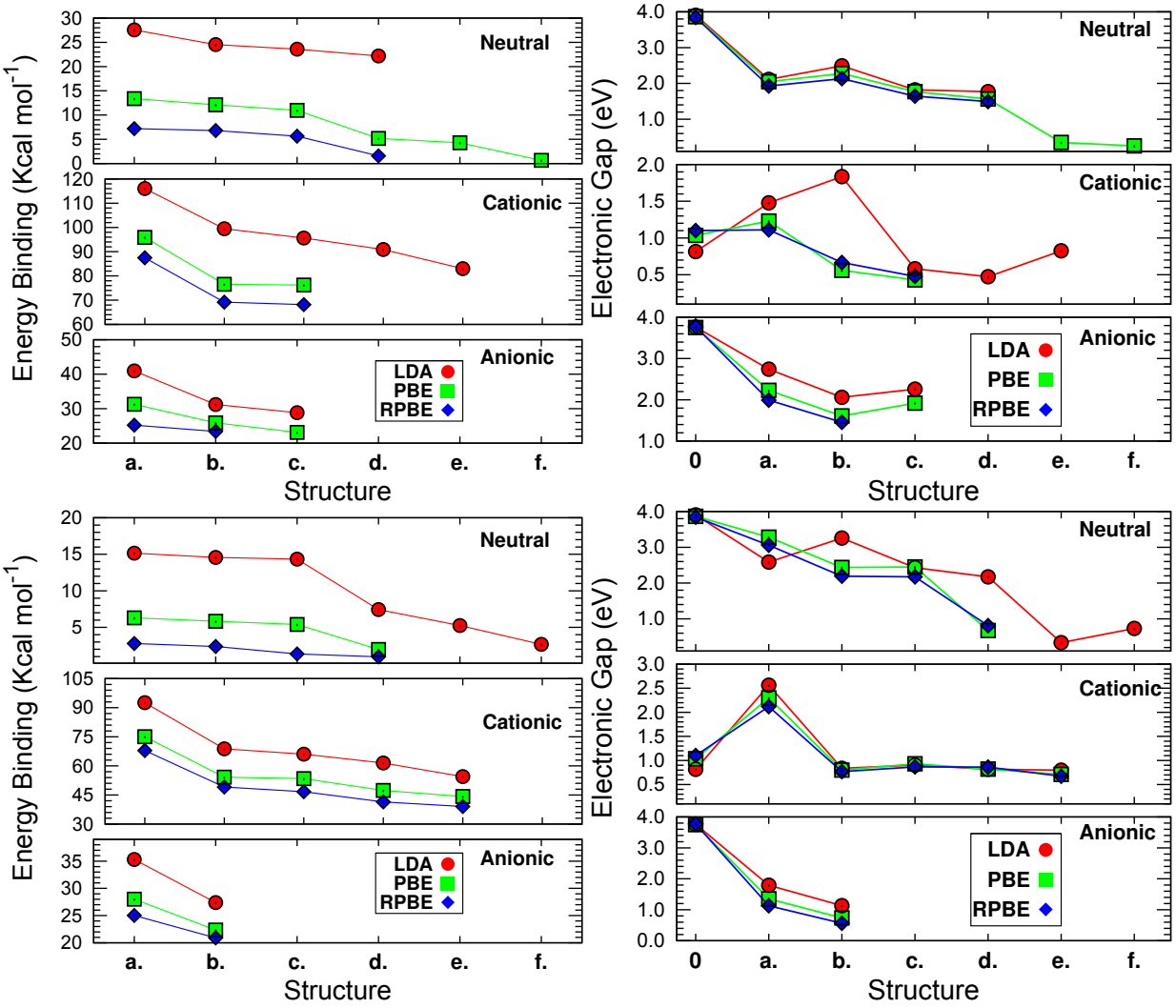

FIG. S1. ***Top-left:*** Binding energies for the guanine-Au geometries in the three charge state obtained with three different XC functionals: LDA (red-circles), PBE (green-squares) and RPBE (blue-diamonds) in each binding site. In the *top*: neutral, *center*: cationic and *bottom*: anionic. ***Top-right:*** Electronic gaps for the guanine-Au geometries with different Exchange-Correlation levels: LDA (red-circles), PBE (green-squares) and RPBE (blue-diamonds) in each binding site. *Top*: Neutral, *center*: cationic and *bottom*: anionic. The values at atomic level: 0 are the electronic gaps without the gold atom. ***Bottom-left:*** Binding energies for the guanine-Ag geometries in the three charge state obtained with three different XC functionals: LDA (red-circles), PBE (green-squares) and RPBE (blue-diamonds) in each binding site. In the *top*: neutral, *center*: cationic and *bottom*: anionic. ***Bottom-right:*** Electronic gaps for the guanine-Ag geometries with different Exchange-Correlation levels: LDA (red-circles), PBE (green-squares) and RPBE (blue-diamonds) in each binding site. *Top*: Neutral, *center*: cationic and *bottom*: anionic. The values at atomic level: 0 are the electronic gaps without the gold atom.

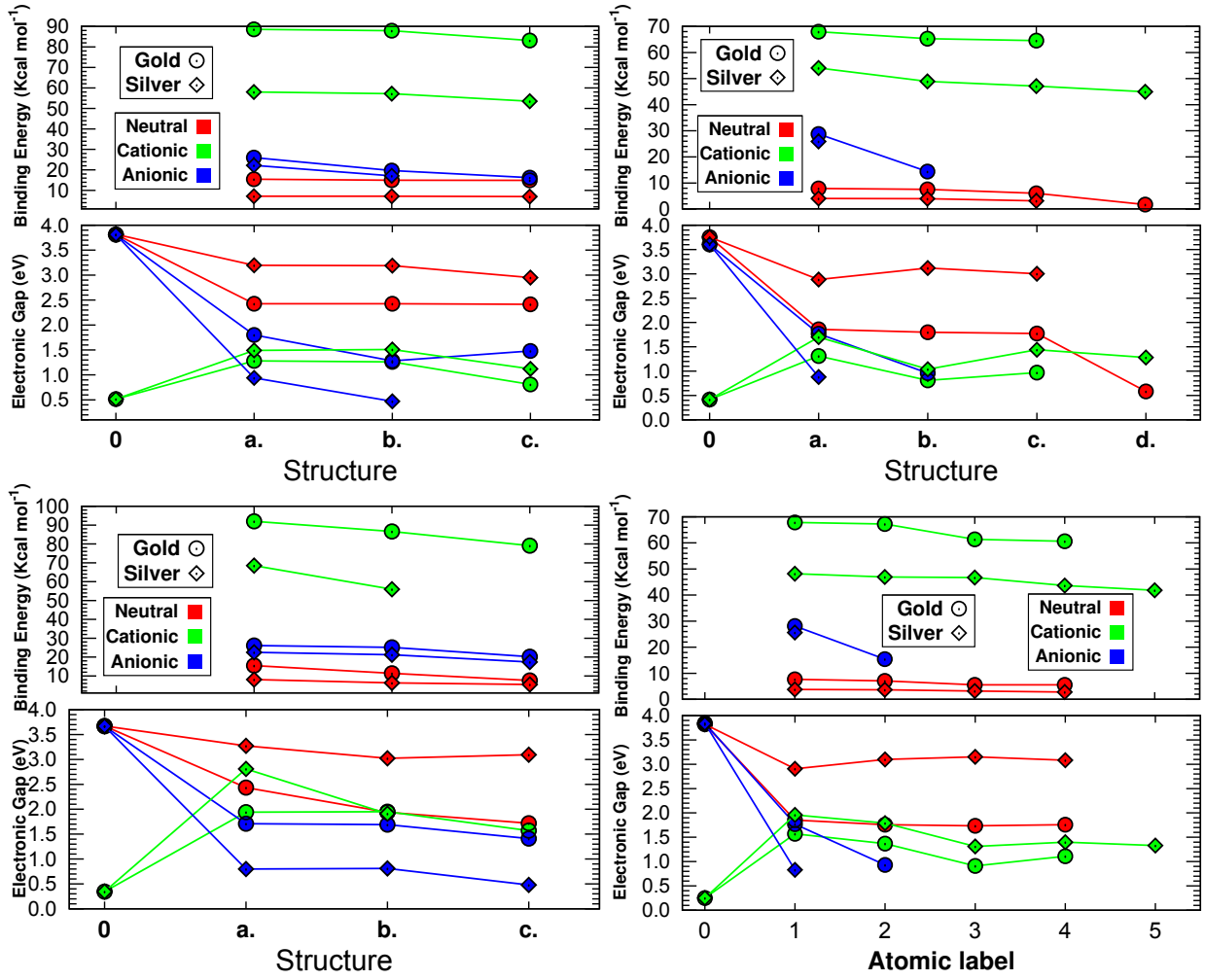

FIG. S2. ***top-left:*** Binding energies and *bottom*: electronic gap for the adenine-Au(circles)/Ag(diamonds) geometries in the three charge states: Neutral (red), Cationic (green) and Anionic (blue) in each binding site for the gold (Circle) and Silver (Diamond). ***Top-right:*** Binding energies and *bottom*: electronic gap for the thymine-Au(circles)/Ag(diamonds) geometries in the three charge states: Neutral (red), Cationic (green) and Anionic (blue) in each binding site for the gold (Circle) and Silver (Diamond). ***Bottom-left:*** Binding energies and *bottom*: electronic gap for the cytosine-Au(circles)/Ag(diamonds) geometries in the three charge states: Neutral (red), Cationic (green) and Anionic (blue) in each binding site for the gold (Circle) and Silver (Diamond). ***Bottom-right:*** Binding energies and *bottom*: electronic gap for the uracil-Au(circles)/Ag(diamonds) geometries in the three charge states: Neutral (red), Cationic (green) and Anionic (blue) in each binding site for the gold (Circle) and Silver (Diamond).

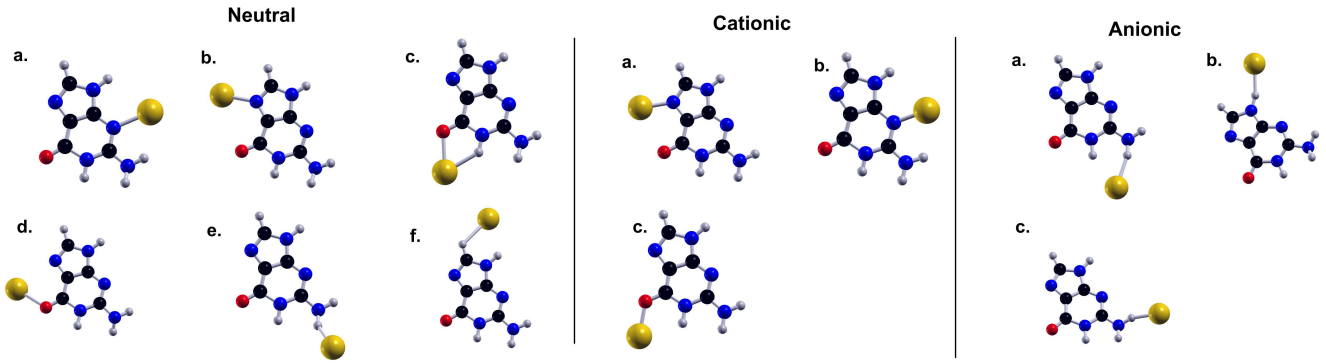

FIG. S3. In order of stability (binding energy - bond length), optimized guanine-Au geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 13.38 Kcal/mol - 2.264 Å, **(b)** 12.11 Kcal/mol - 2.246 Å, **(c)** 10.98 Kcal/mol - 2.371 Å (Au-O6) - 2.295 Å (Au-H1), **(d)** 5.17 Kcal/mol - 2.490 Å, **(e)** 4.29 Kcal/mol - 2.244 Å and **(f)** 0.65 Kcal/mol - 2.561 Å (C8-H) - 2.730 Å (N9-H). ***Center-Cationic***: **(a)** 95.92 Kcal/mol - 2.041 Å, **(b)** 76.53 Kcal/mol - 2.043 Å and **(c)** 76.25 Kcal/mol - 2.051 Å . ***Right-Anionic***: **(a)** 31.28 Kcal/mol - 2.198 Å, **(b)** 25.90 Kcal/mol - 2.136 Å and **(c)** 23.12 Kcal/mol - 2.200 Å .

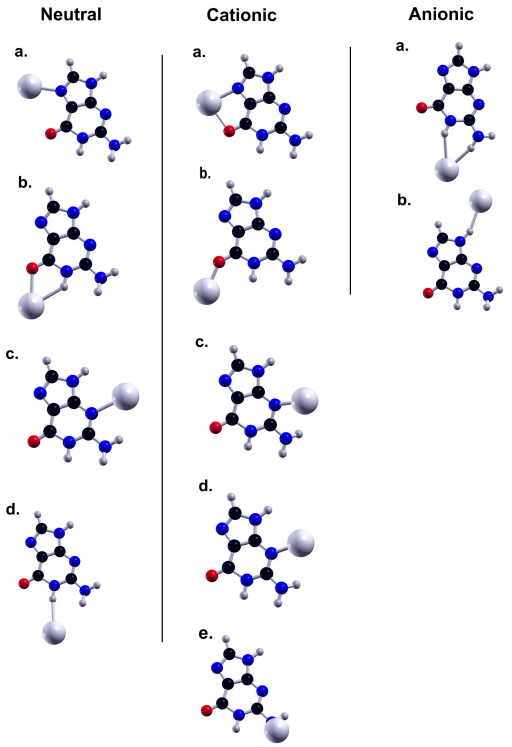

FIG. S4. In order of stability (binding energy - bond length), optimized guanine-Ag geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 6.30 Kcal/mol - 2.448 Å, **(b)** 5.83 Kcal/mol - 2.501 Å (Ag-O), 2.529 Å (Ag-H), **(c)** 5.40 Kcal/mol - 2.447 Å and **(d)** 1.98 Kcal/mol - 2.641 Å. ***Center-Cationic***: **(a)** 75.07 Kcal/mol - 2.432 Å (Ag-O) - 2.261 Å (Ag-N), **(b)** 54.19 Kcal/mol - 2.131 Å, **(c)** 53.40 Kcal/mol - 2.190 Å, **(d)** 47.31 Kcal/mol - 2.161 Å and **(e)** 44.19 Kcal/mol - 2.261 Å. ***Right-Anionic***: **(a)** 28.02 Kcal/mol - 2.770 Å (Ag-H1) - 2.368 Å (Ag-H2) and **(b)** 22.35 Kcal/mol - 2.418 Å.

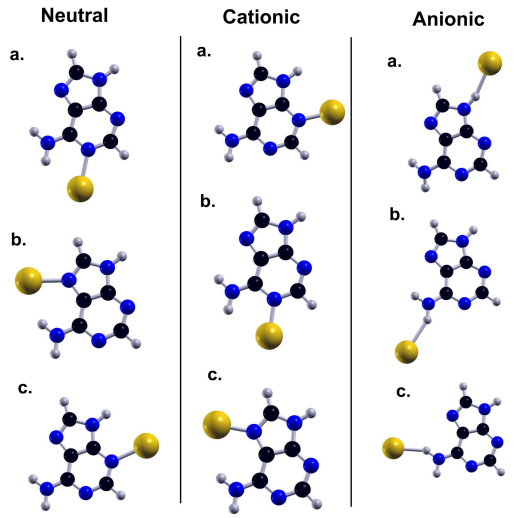

FIG. S5. In order of stability (binding energy - bond length), optimized adenine-Au geometries in the three charge state at PBE level: ***Left-Neutral***: **(a)** 15.45 Kcal/mol - 2.266 Å, **(b)** 14.99 Kcal/mol - 2.238 Å and **(c)** 14.92 Kcal/mol - 2.243 Å. ***Center-Cationic***: **(a)** 88.55 Kcal/mol - 2.031 Å, **(b)** 87.93 Kcal/mol - 2.041 Å and **(c)** 83.11 Kcal/mol - 2.023 Å . ***Right-Anionic***: **(a)** 26.03 Kcal/mol - 2.157 Å, **(b)** 19.67 Kcal/mol - 2.324 Å and **(c)** 16.21 Kcal/mol - 2.309 Å.

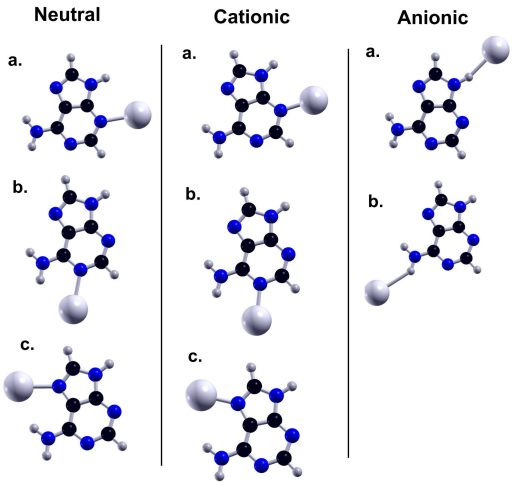

FIG. S6. In order of stability (binding energy - bond length), optimized adenine-Ag geometries in the three charge state at PBE level: ***Left-Neutral***: **(a)** 7.15 Kcal/mol - 2.404 Å, **(b)** 7.14 Kcal/mol - 2.430 Å and **(c)** 6.99 Kcal/mol - 2.401 Å. ***Center-Cationic***: **(a)** 57.90 Kcal/mol - 2.152 Å , **(b)** 57.18 Kcal/mol - 2.161 Å and **(c)** 53.49 Kcal/mol - 2.145 Å. ***Right-Anionic***: **(a)** 22.24 Kcal/mol - 2.417 Å and **(b)** 17.10 Kcal/mol - 2.740 Å.

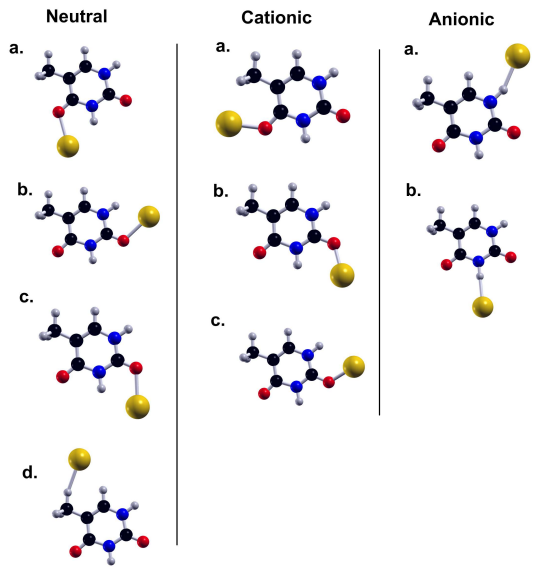

FIG. S7. In order of stability (binding energy - bond length), optimized thymine-Au geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 7.91 Kcal/mol - 2.390 Å, **(b)** 7.56 Kcal/mol - 2.415 Å, **(c)** 6.06 Kcal/mol - 2.412 Å and **(d)** 1.73 Kcal/mol - 2.359 Å. ***Center-Cationic***: **(a)** 67.97 Kcal/mol - 2.077 Å, **(b)** 65.31 Kcal/mol - 2.064 Å and **(c)** 64.54 Kcal/mol - 2.067 Å. ***Right-Anionic***: **(a)** 28.75 Kcal/mol - 2.172 Å and **(b)** 14.37 Kcal/mol - 2.167 Å.

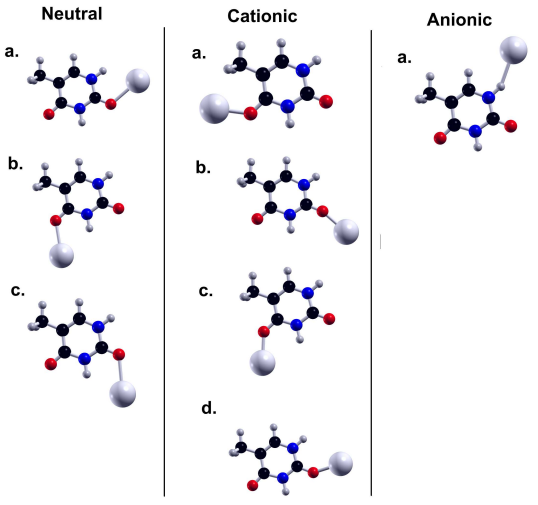

FIG. S8. In order of stability (binding energy - bond length), optimized thymine-Au geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 4.08 Kcal/mol - 2.588 Å, **(b)** 3.99 Kcal/mol - 2.551 Å and **(c)** 3.18 Kcal/mol - 2.639 Å. ***Center-Cationic***: **(a)** 54.05 Kcal/mol - 2.186 Å, **(b)** 48.92 Kcal/mol - 2.193 Å, **(c)** 47.14 Kcal/mol - 2.146 Å and **(d)** 44.96 Kcal/mol - 2.157 Å. ***Right-Anionic***: **(a)** 25.94 Kcal/mol - 2.439 Å.

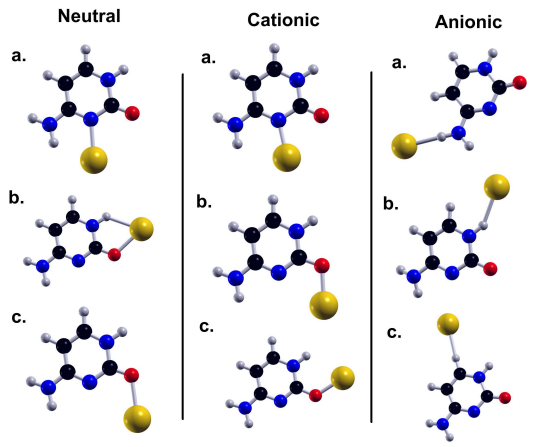

FIG. S9. In order of stability (binding energy - bond length), optimized cytosine-Au geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 15.47 Kcal/mol - 2.261 Å, **(b)** 11.37 Kcal/mol - 2.341 Å and **(c)** 7.61 Kcal/mol - 2.405 Å. ***Center-Cationic***: **(a)** 91.97 Kcal/mol - 2.051 Å, **(b)** 86.62 Kcal/mol - 2.092 Å and **(c)** 79.11 Kcal/mol - 2.039 Å. ***Right-Anionic***: **(a)** 26.13 Kcal/mol - 2.219 Å, **(b)** 25.18 Kcal/mol - 2.321 Å and **(c)** 20.20 Kcal/mol - 2.351 Å.

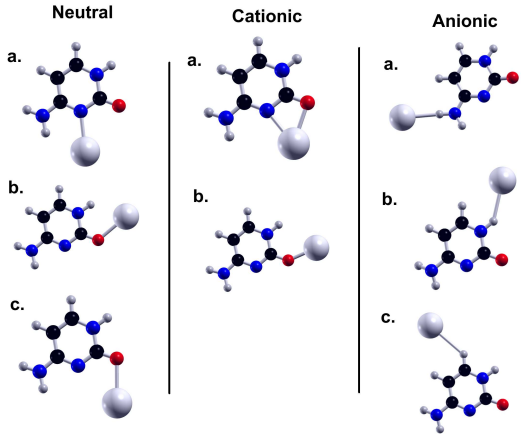

FIG. S10. In order of stability (binding energy - bond length), optimized cytosine-Ag geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 8.12 Kcal/mol - 2.414 Å, **(b)** 6.32 Kcal/mol - 2.466 Å and **(c)** 5.47 Kcal/mol - 2.606 Å. ***Center-Cationic***: **(a)** 68.50 Kcal/mol - 2.373 Å (Ag-O) - 2.365 Å (Ag-N) and **(b)** 55.95 Kcal/mol - 2.117 Å. ***Right-Anionic***: **(a)** 22.53 Kcal/mol - 2.463 Å, **(b)** 21.26 Kcal/mol - 2.615 Å and **(c)** 17.38 Kcal/mol - 2.946 Å.

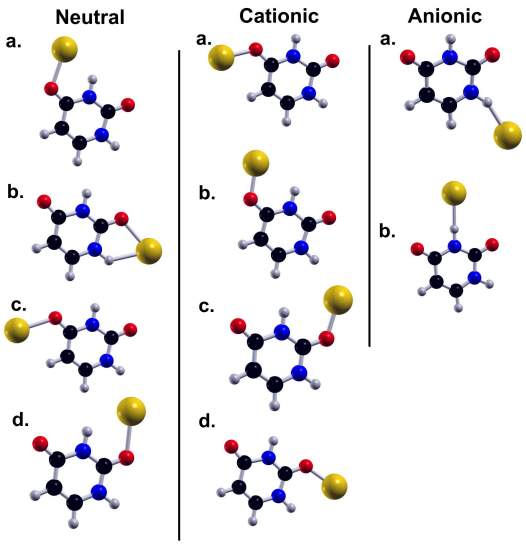

FIG. S11. In order of stability (binding energy - bond length), optimized uracil-Au geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 7.70 Kcal/mol - 2.398 Å, **(b)** 7.10 Kcal/mol - 2.453 Å, **(c)** 5.60 Kcal/mol - 2.413 Å and **(d)** 5.56 Kcal/mol - 2.430 Å. ***Center-Cationic***: **(a)** 67.85 Kcal/mol - 2.069 Å, **(b)** 67.25 Kcal/mol - 2.060 Å, **(c)** 61.34 Kcal/mol - 2.066 Å and **(d)** 60.62 Kcal/mol - 2.071 Å. ***Right-Anionic***: **(a)** 28.13 Kcal/mol - 2.175 Å and **(b)** 15.45 Kcal/mol - 2.171 Å.

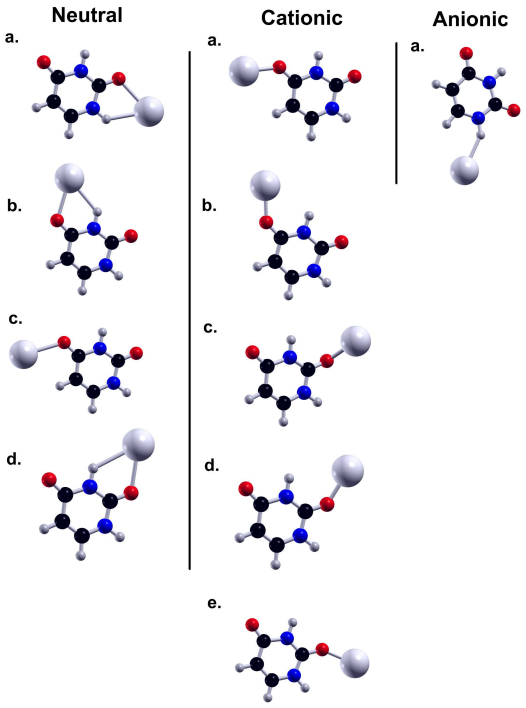

FIG. S12. In order of stability (binding energy - bond length), optimized uracil-Ag geometries in the three charge state at PBE level. ***Left-Neutral***: **(a)** 3.80 Kcal/mol - 2.655 Å (Ag-O2)-2.584 Å (Ag-NH1), **(b)** 3.69 Kcal/mol - 2.627 Å, **(c)** 3.20 Kcal/mol - 2.628 Å and **(d)** 2.81 Kcal/mol - 2.656 Å. ***Center-Cationic***: **(a)** 48.16 Kcal/mol - 2.156 Å, **(b)** 46.92 Kcal/mol - 2.152 Å, **(c)** 46.70 Kcal/mol - 2.152 Å, **(d)** 43.63 Kcal/mol - 2.161 Å and **(e)** 41.85 Kcal/mol - 2.158 Å. ***Right-Anionic***: **(a)** 25.62 Kcal/mol - 2.439 Å.

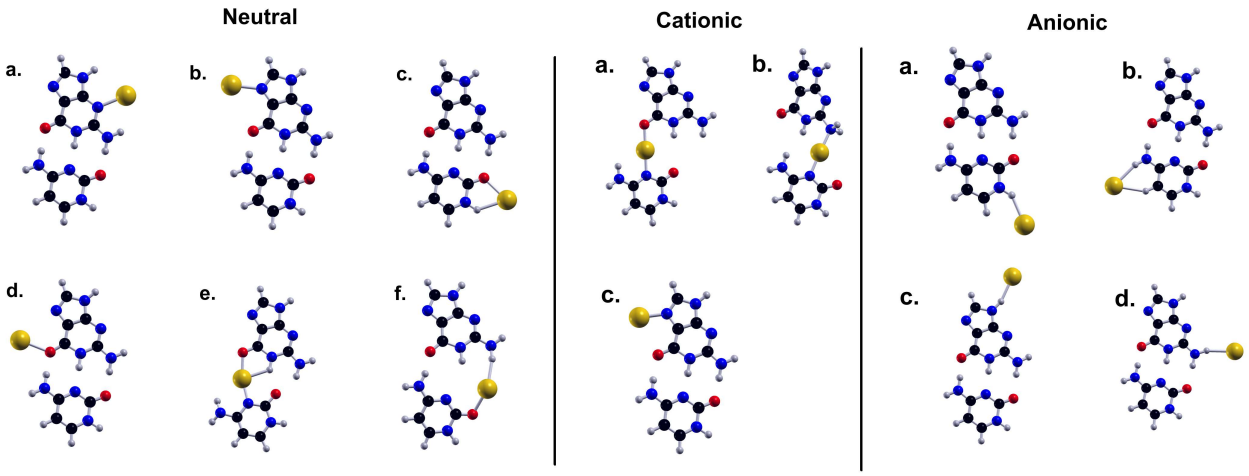

FIG. S13. In order of stability (binding energy - bond length), optimized **GC**+Au geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 41.25 Kcal/mol - 2.247 Å, **(b)** 39.42 Kcal/mol - 2.236 Å, **(c)** 34.26 Kcal/mol - 2.378 Å, **(d)** 32.05 Kcal/mol - 2.413 Å, **(e)** 29.39 Kcal/mol - 2.096 Å (Au-O6)-2.302 Å (Au-NH1)-2.026 Å (Au-N3) and **(f)** 27.48 Kcal/mol - 2.295 Å (Au-O2)-2.337 Å (Au-NH2). ***Center-Cationic***: **(a)** 151.77 Kcal/mol - 2.052 Å (Au-O6)-2.044 Å (Au-N3), **(b)** 138.33 Kcal/mol - 2.102 Å (Au-N2)-2.056 Å (Au-N3) and **(c)** 129.28 Kcal/mol - 2.034 Å. ***Right-Anionic***: **(a)** 55.44 Kcal/mol - 2.343 Å, **(b)** 51.86 Kcal/mol - 2.400 Å (Au-NH4)-2.708 Å (Au-CH5) , **(c)** 48.52 Kcal/mol - 2.271 Å and **(d)** 40.01 Kcal/mol - 2.428 Å.

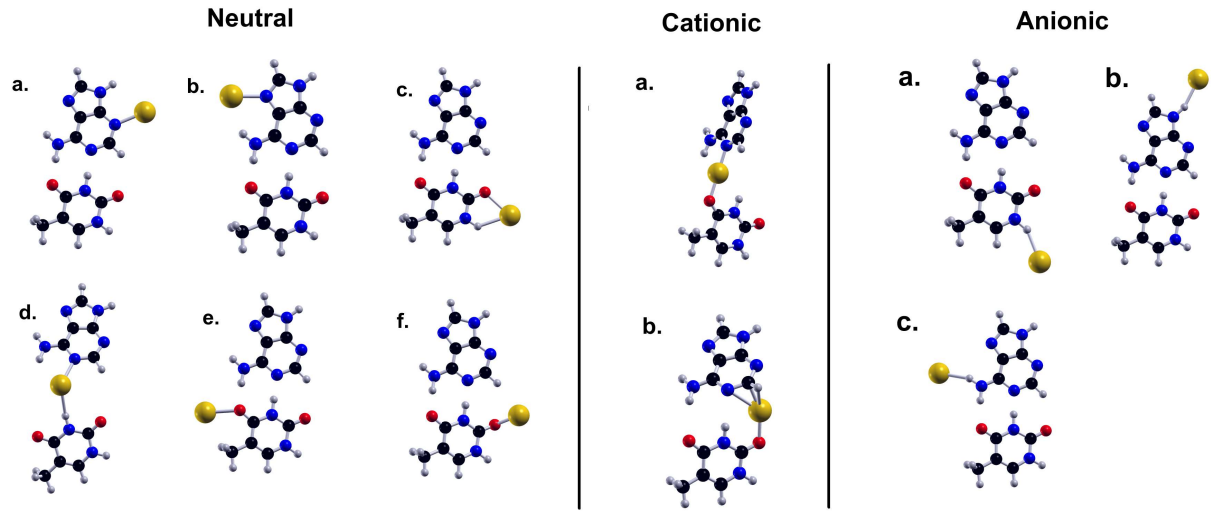

FIG. S14. In order of stability (binding energy - bond length), optimized **AT**+Au geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 28.47 Kcal/mol - 2.245 Å, **(b)** 28.07 Kcal/mol - 2.231 Å, **(c)** 22.07 Kcal/mol - 2.396 Å (Au-O2)-2.405 Å (Au-NH1), **(d)** 18.40 Kcal/mol - 2.253 Å (Au-N1)-2.479 Å (Au-NH3), **(e)** 17.99 Kcal/mol - 2.453 Å and **(f)** 17.62 Kcal/mol - 2.417 Å. ***Center-Cationic***: **(a)** 141.22 Kcal/mol - 2.041 Å (Au-N1)-2.063 Å (Au-O4) and **(b)** 106.29 Kcal/mol - 2.682 Å (Au-N1)-2.164 Å (Au-C2)-2.148 Å (Au-O2) . ***Right-Anionic***: **(a)** 42.58 Kcal/mol - 2.229 Å, **(b)** 41.01 Kcal/mol - 2.259 Å and **(c)** 26.96 Kcal/mol - 2.376 Å.

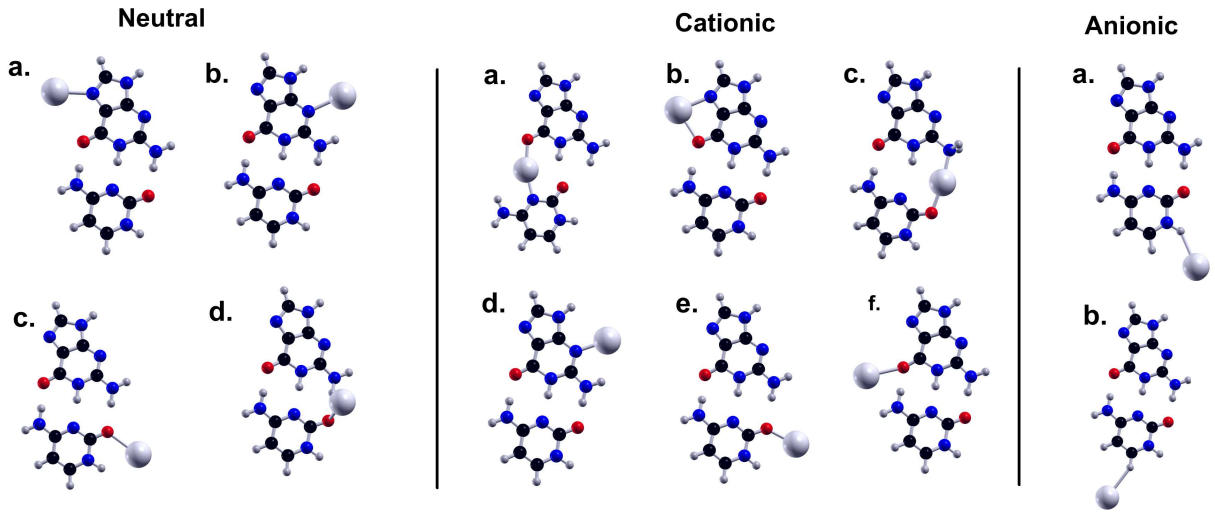

FIG. S15. In order of stability (binding energy - bond length), optimized **GC**+Ag geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 33.44 Kcal/mol - 2.405 Å, **(b)** 32.90 Kcal/mol - 2.407 Å, **(c)** 30.19 Kcal/mol - 2.554 Å and **(d)** 26.64 Kcal/mol - 2.716 Å. ***Center-Cationic***: **(a)** 111.05 Kcal/mol - 2.117 Å (Ag-O6) - 2.140 Å (Ag-N3), **(b)** 106.78 Kcal/mol - 2.240 Å (Ag-N7) - 2.427 Å (Ag-O6), **(c)** 100.34 Kcal/mol - 2.175 Å (Ag-N2) - 2.114 Å (Ag-O2), **(d)** 85.37 Kcal/mol - 2.139 Å, **(e)** 75.90 Kcal/mol - 2.194 Å and **(f)** 63.34 Kcal/mol - 2.575 Å. ***Right-Anionic***: **(a)** 53.39 Kcal/mol - 2.540 Å and **(b)** 49.95 Kcal/mol - 2.812 Å.

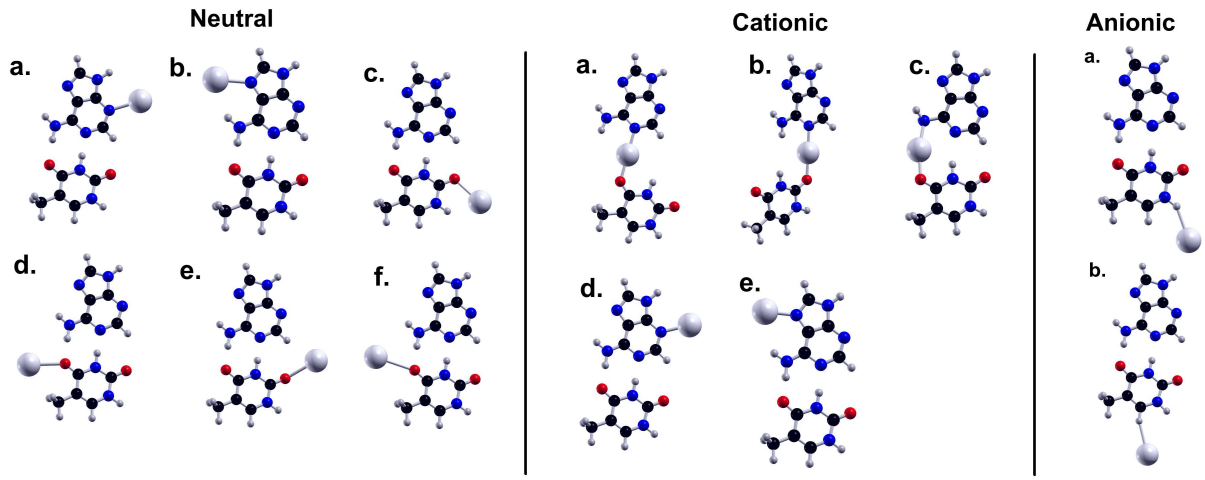

FIG. S16. In order of stability (binding energy - bond length), optimized **AT**+Ag geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 20.49 Kcal/mol - 2.418 Å, **(b)** 20.38 Kcal/mol - 2.403 Å, **(c)** 18.23 Kcal/mol - 2.574 Å (Ag-O2), 2.531 Å (Ag-NH1), **(d)** 15.99 Kcal/mol - 2.726 Å, **(e)** 15.23 Kcal/mol - 2.747 Å and **(f)** 14.90 Kcal/mol - 3.078 Å. ***Center-Cationic***: **(a)** 96.40 Kcal/mol - 2.119 Å (Ag-N1) - 2.117 Å (Ag-O4), **(b)** 94.42 Kcal/mol - 2.120 Å (Ag-N1) - 2.120 Å (Ag-O2), **(c)** 85.65 Kcal/mol - 2.189 Å (Ag-N6) - 2.142 Å (Ag-O), **(d)** 76.19 Kcal/mol - 2.150 Å and **(e)** 71.56 Kcal/mol - 2.140 Å. ***Right-Anionic***: **(a)** 40.08 Kcal/mol - 2.520 Å and **(b)** 36.56 Kcal/mol - 2.701 Å.

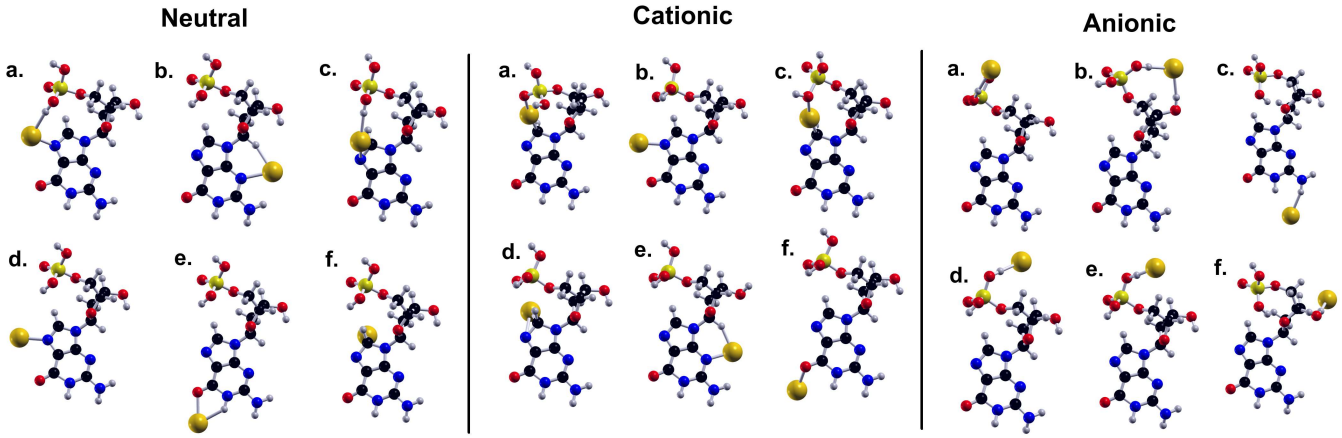

FIG. S17. In order of stability (binding energy - bond length), optimized **GMP**+Au geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 18.24 Kcal/mol - 2.241 Å (Au-N7)-2.236 Å (Au-H), **(b)** 13.23 Kcal/mol - 2.327 Å (Au-N3)-2.282 Å (Au-H), **(c)** 13.01 Kcal/mol - 2.763 Å (Au-N7)-2.257 Å (Au-C8)-2.200 Å (Au-H), **(d)** 11.51 Kcal/mol - 2.247 Å, **(e)** 10.82 Kcal/mol - 2.363 Å (Au-O6)-2.297 Å (Au-NH1) and **(f)** 8.89 Kcal/mol - 2.214 Å. ***Center-Cationic***: **(a)** 115.76 Kcal/mol - 2.074 Å (Au-C8)-2.148 Å (Au-O), **(b)** 104.32 Kcal/mol - 2.031 Å, **(c)** 100.87 Kcal/mol - 2.064 Å (Au-C8)-2.233 Å (Au-O)-3.206 Å (Au-P), **(d)** 90.32 Kcal/mol - 2.087 Å (Au-C8)-2.719 Å (Au-N7), **(e)** 84.58 Kcal/mol - 2.082 Å and **(f)** 82.05 Kcal/mol - 2.065 Å. ***Right-Anionic***: **(a)** 45.90 Kcal/mol - 2.137 Å (Au-OH)-2.115 Å (Au-OH), **(b)** 45.40 Kcal/mol - 2.046 Å (Au-OH)-2.294 Å (Au-OH), **(c)** 38.41 Kcal/mol - 2.233 Å (Au-NH2)-2.538 Å (Au-NH1), **(d)** 38.19 Kcal/mol - 1.970 Å, **(e)** 37.21 Kcal/mol - 1.969 Å and **(f)** 35.68 Kcal/mol - 2.116 Å.

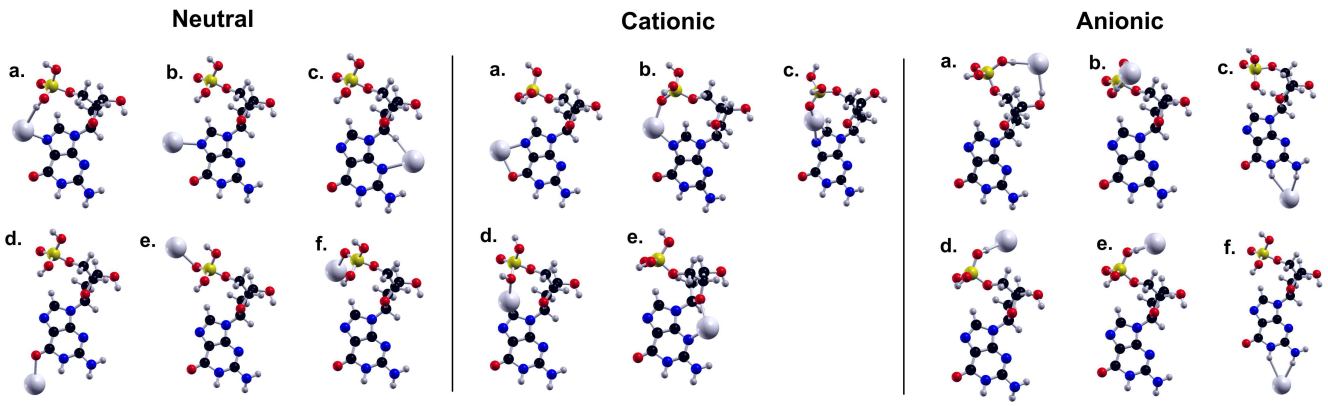

FIG. S18. In order of stability (binding energy - bond length), optimized **GMP**+Ag geometries at PBE level in the three charge states. ***Left-Neutral***: **(a)** 10.89 Kcal/mol - 2.377 Å (Au-N7)-2.438 Å (Au-H), **(b)** 6.18 Kcal/mol - 2.453 Å, **(c)** 5.58 Kcal/mol - 2.510 Å (Au-N3)-2.331 Å (Au-H), **(d)** 5.44 Kcal/mol - 2.526 Å, **(e)** 4.53 Kcal/mol - 2.577 Å (Au-O)-3.325 Å (Au-P) and **(f)** 3.86 Kcal/mol - 2.525 Å. ***Center-Cationic***: **(a)** 81.38 Kcal/mol - 2.249 Å (Au-N7)-2.445 Å (Au-O6), **(b)** 80.16 Kcal/mol - 2.195 Å (Au-N7)-2.869 Å (Au-C8)-2.339 Å (Au-O), **(c)** 78.50 Kcal/mol - 2.230 Å (Au-C8)-2.716 Å (Au-N7)-2.186 Å (Au-O)-3.242 Å (Au-P), **(d)** 64.67 Kcal/mol - 2.229 Å (Au-C8)-2.332 Å (Au-O)-3.161 Å (Au-P) and **(e)** 58.41 Kcal/mol - 2.227 Å (Au-N3)-2.358 Å (Au-O)-3.059 Å (Au-C). ***Right-Anionic***: **(a)** 40.78 Kcal/mol - 2.219 Å (Au-OH)-2.444 Å (Au-OH), **(b)** 39.52 Kcal/mol - 2.248 Å (Au-OH)-2.254 Å (Au-OH), **(c)** 34.78 Kcal/mol - 2.360 Å (Au-NH2)-2.705 Å (Au-NH1), **(d)** 34.26 Kcal/mol - 2.140 Å, **(e)** 32.97 Kcal/mol - 2.161 Å and **(f)** 30.88 Kcal/mol - 2.395 Å (Au-NH2)-2.847 Å (Au-NH1).