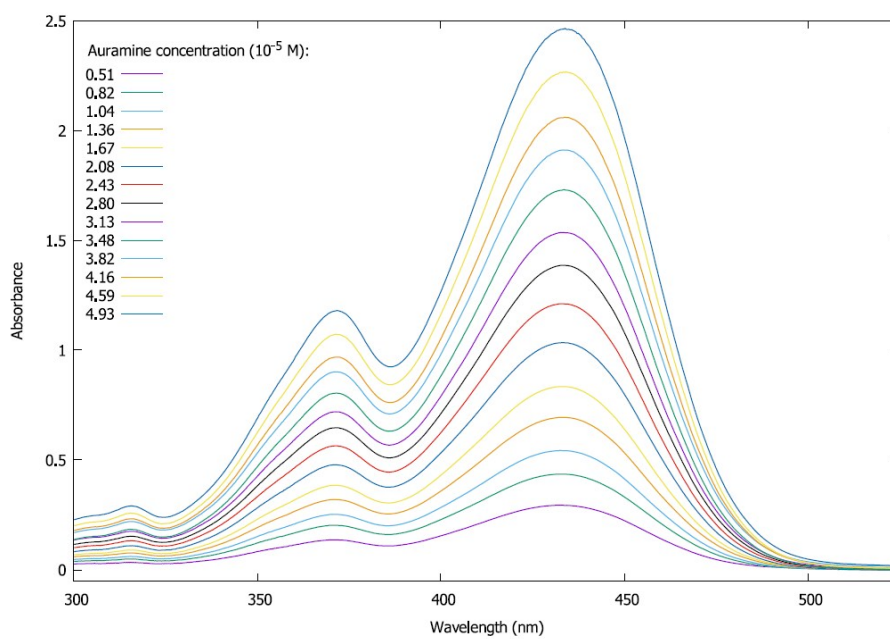
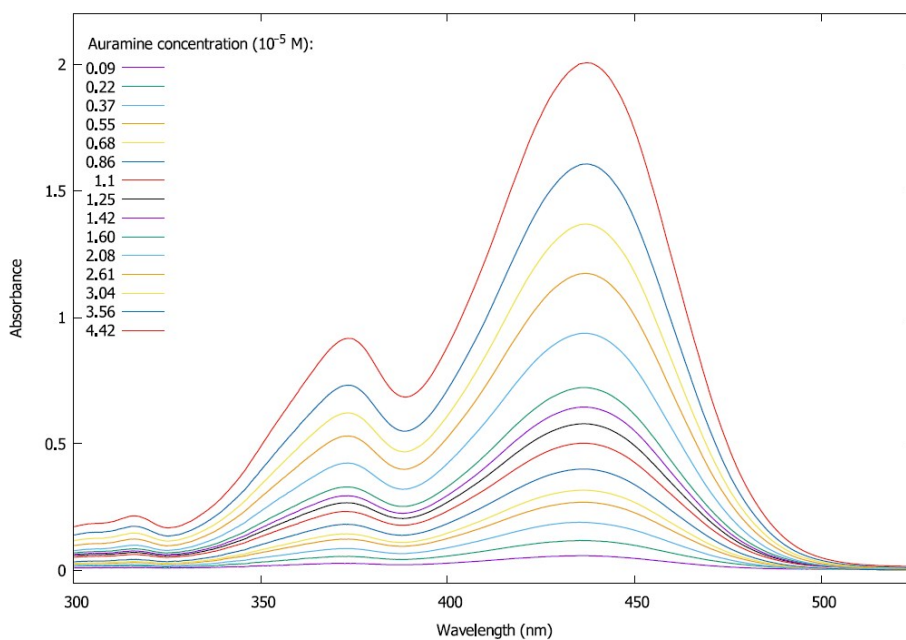


SUPPORTING INFORMATION



(A)



(B)

Figure S1. Absorption spectra of AuO at different dye concentrations, [NaCac] = 0.01 M, pH = 7.0, T = 25.0°C; (A) [NaCl] = 0.1 M, (B) [NaCl] = 3 M.

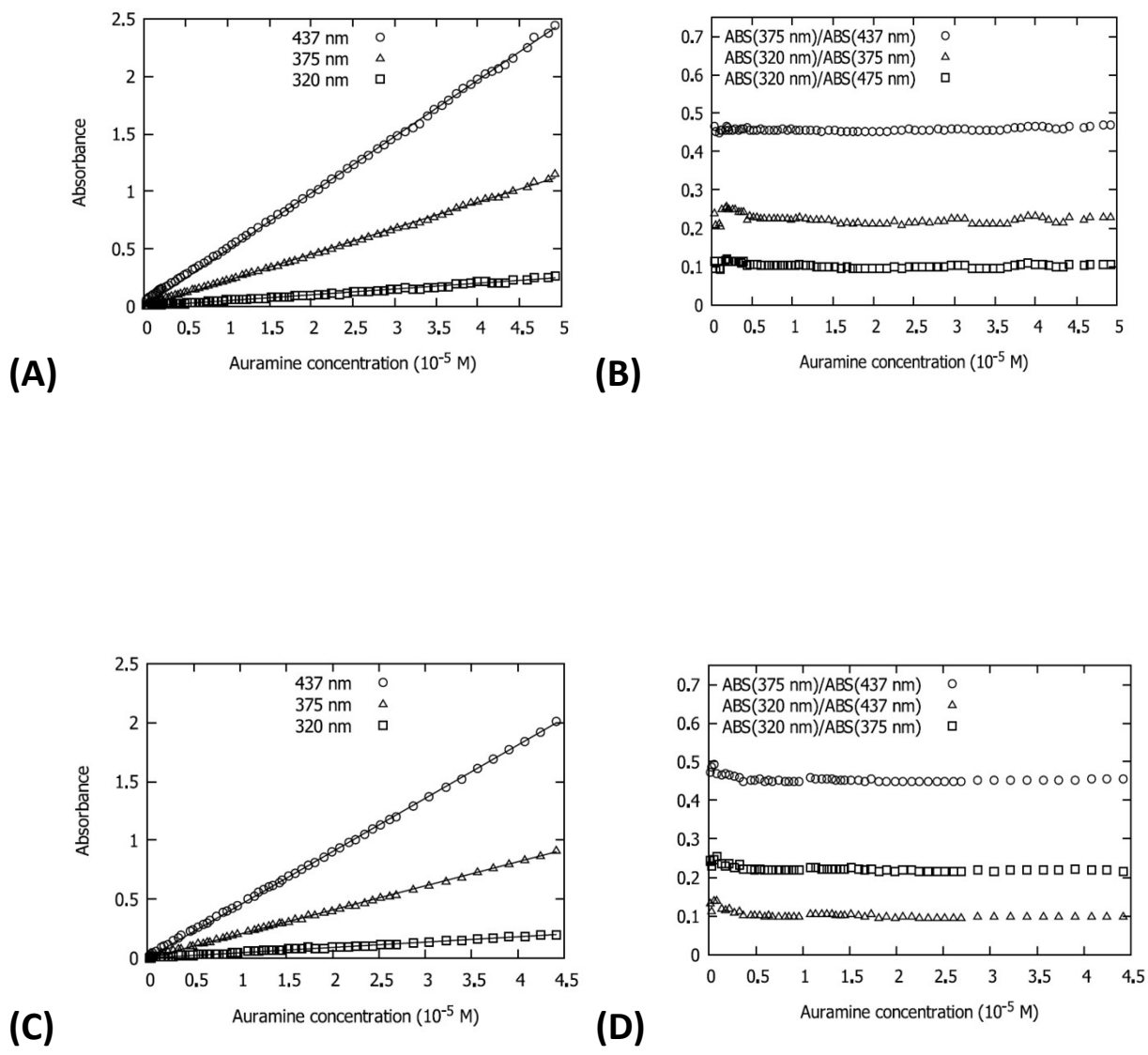


Figure S2. Concentration dependence of AuO absorption peaks intensities (A, C) and their ratio (B, D), [NaCac] = 0.01 M, pH = 7.0, T = 25.0°C; (A, B) [NaCl] = 0.1 M, (C, D) [NaCl] = 3 M.

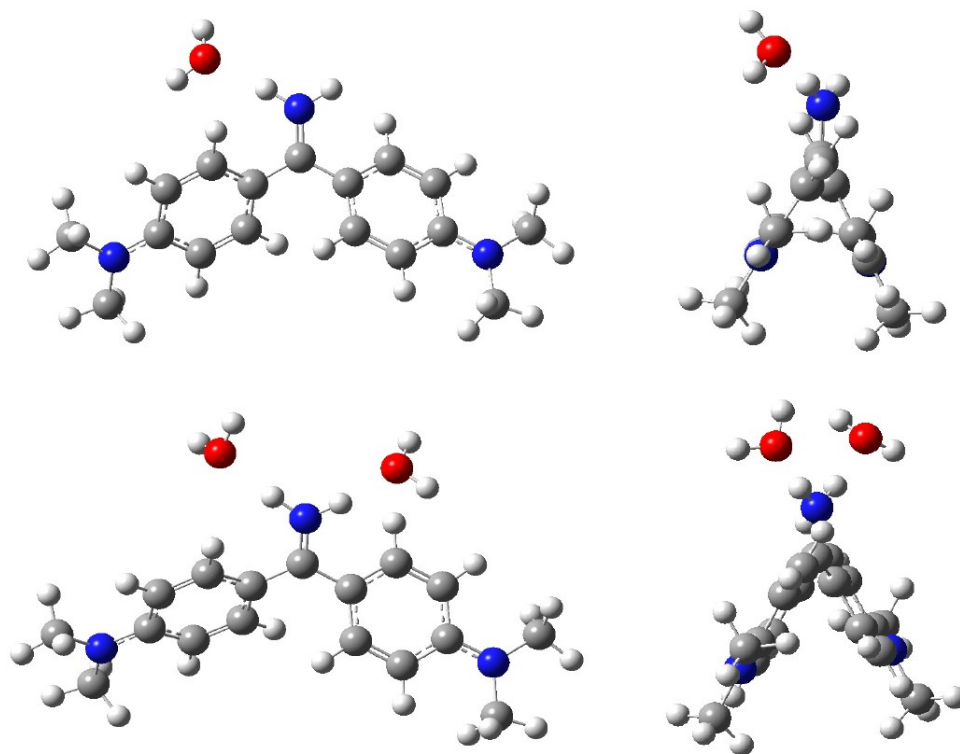


Figure S3. Geometry of the clusters of AuO with one and two hydrogen bonded waters optimized at the DFT/6-311+G(d,p) level: front view (left panels) and side view (right panels).

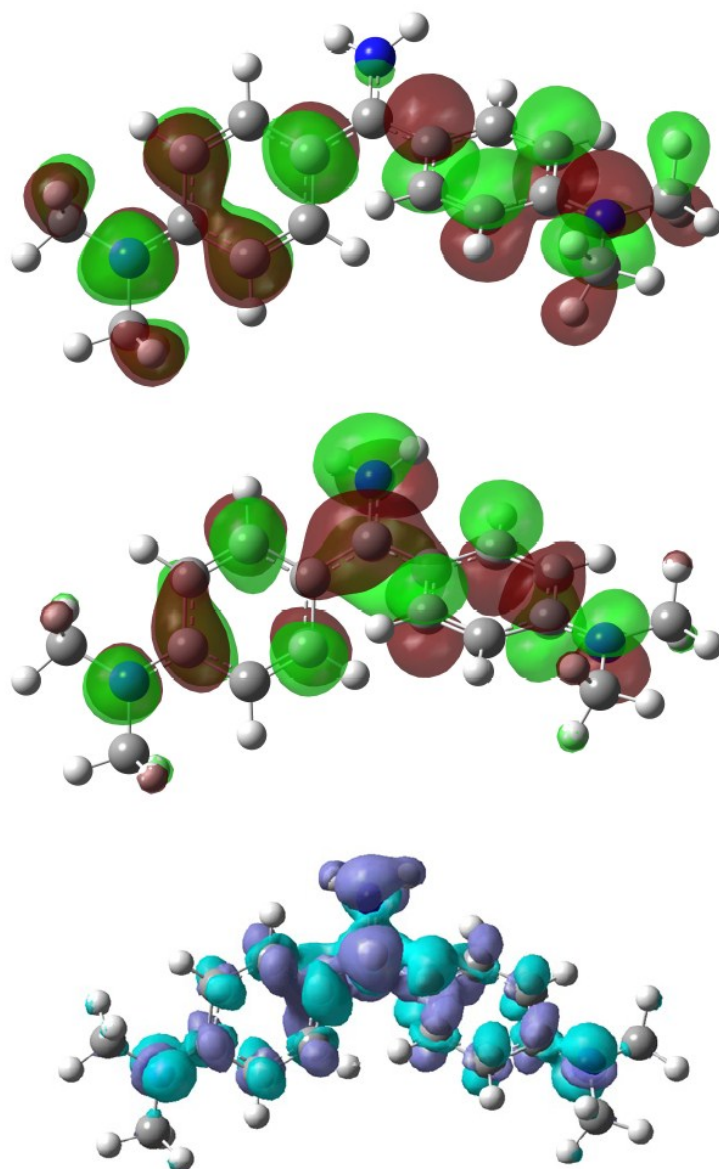


Figure S4. Molecular orbitals involved in the first electronic transition: HOMO (up) and LUMO (centre), with their phases. Lower panel: electron density difference between ground and first excited state. The regions coloured in light blue lost density in the transition while the ones coloured in dark blue gained density

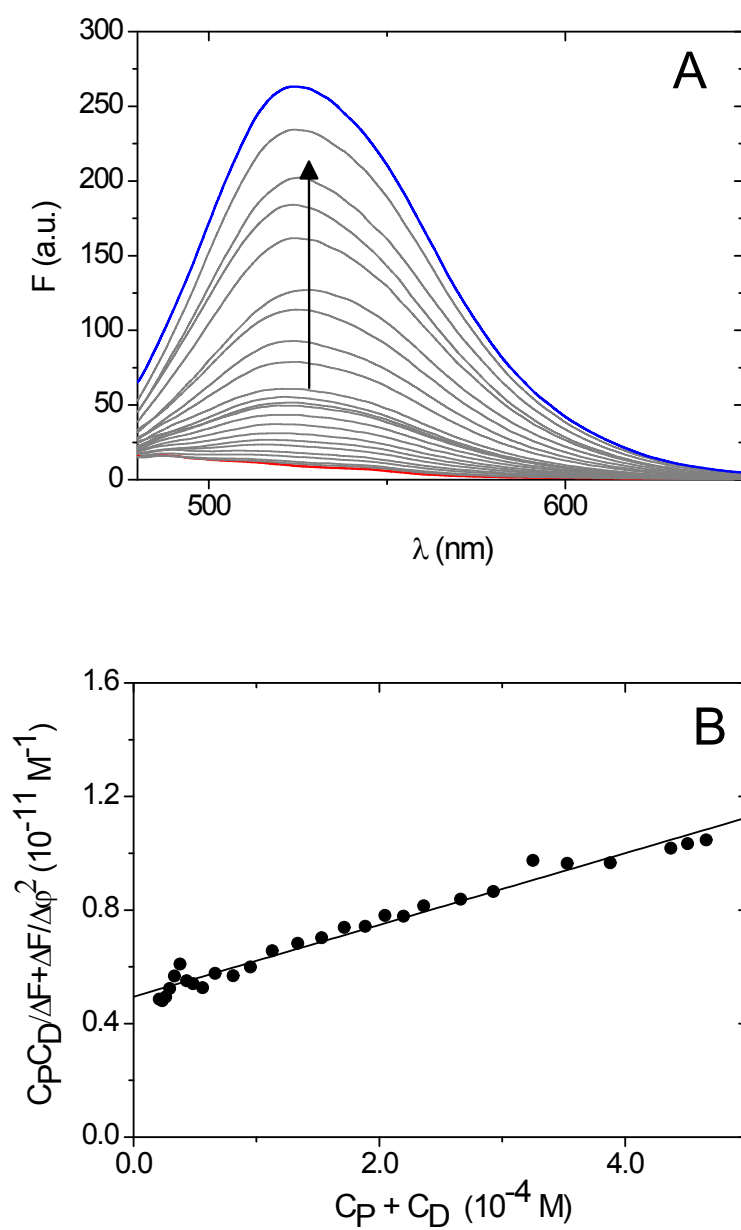


Figure S5. (A) Fluorescence spectra for the AuO/DNA system (arrow = trend upon DNA addition) and (B) relevant data analysis according to equation (1) at $\lambda_{em} = 526$ nm; $C_D = 1.24 \times 10^{-5}$ M, $[NaCl] = 0.1$ M, $[NaCac] = 0.01$ M, pH = 7.0, T = 15.9 °C.

Table S1. Effect of the DFT functional on excitation energies of AuO in four different environments.

Environment	B3LYP	PBE0	M06-2X	CAM-B3LYP
vacuo	2.93	3.01	3.21	3.26
water (PCM)	2.97	3.06	3.21	3.35
water (PCM + 1 explicit)	3.02	3.12	3.29	3.43
water (PCM + 2 explicit)	3.15	3.15	3.37	3.50

The table shows that the absolute value of the transition energy changes changing the functional but the shift from one environment to the other remains very similar in all functionals. On the basis of these homogeneous results for the excitation energies we finally decided to use M06-2X as suggested in comprehensive benchmark studies.