ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

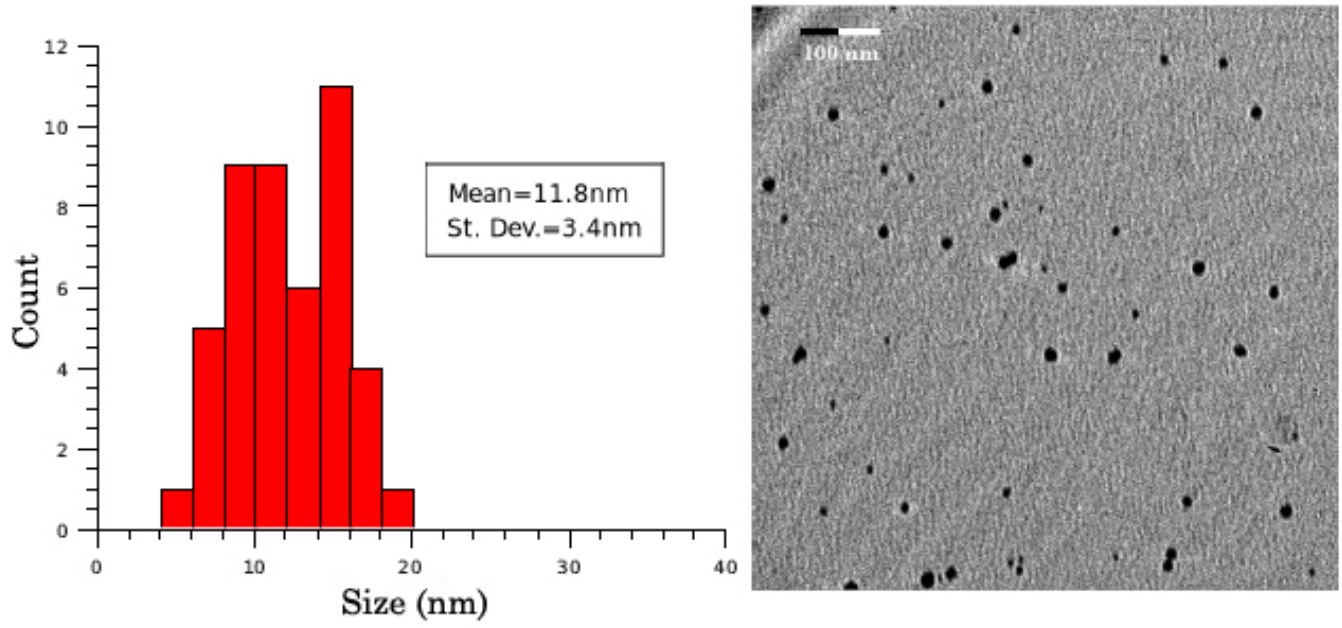

Figure 1S. Histogram of size distribution and TEM image of gold cores of AO-TEG-Au NPs.

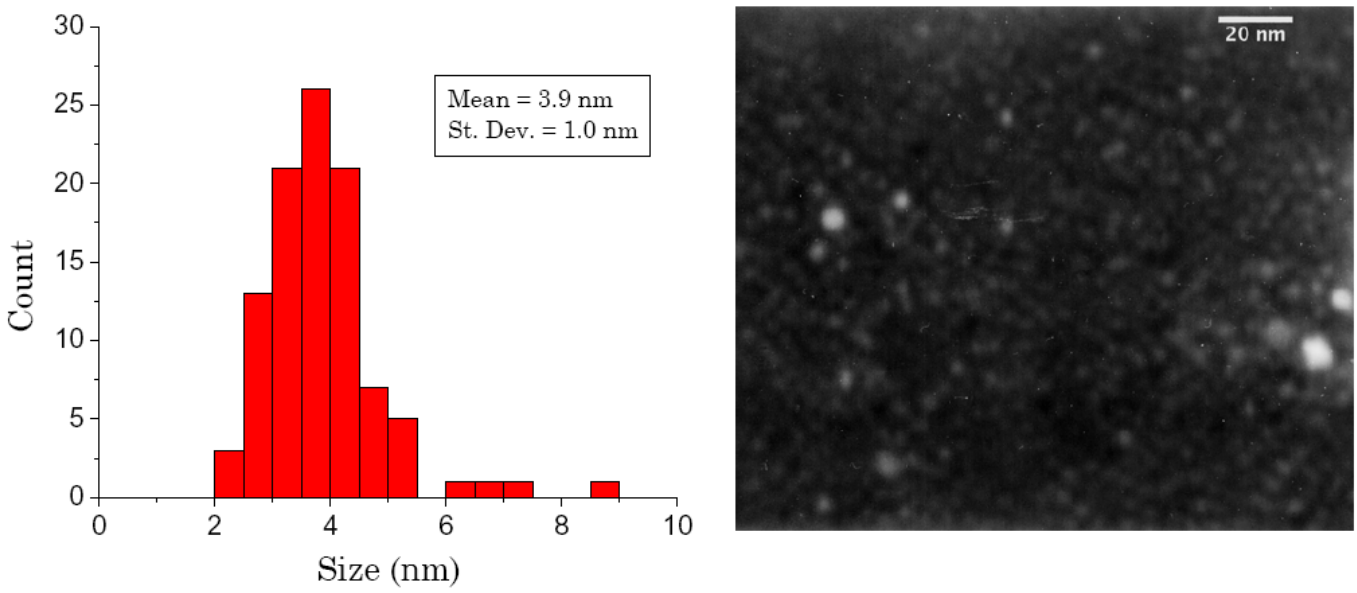

Figure 2S. Histogram of size distribution and TEM image of gold cores of AO-PEG-Au NPs.

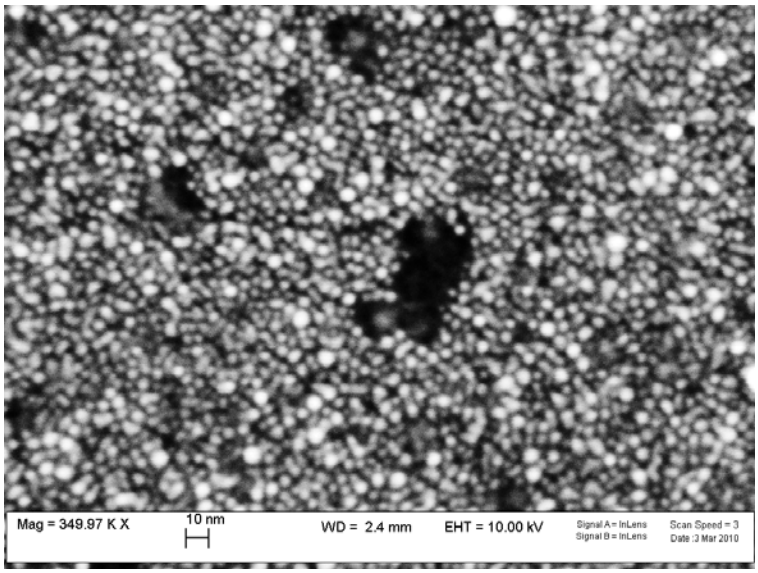

Figure 3S. SEM image of gold cores of AO-PEG-Au NPs.

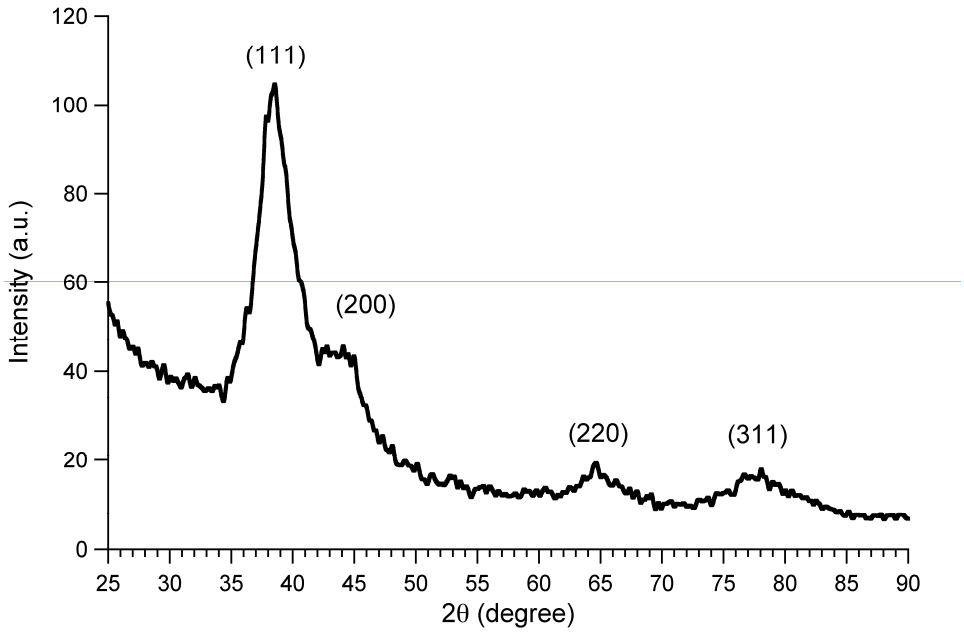

Figure 4S. XRD spectrum of AO-PEG-Au NPs.

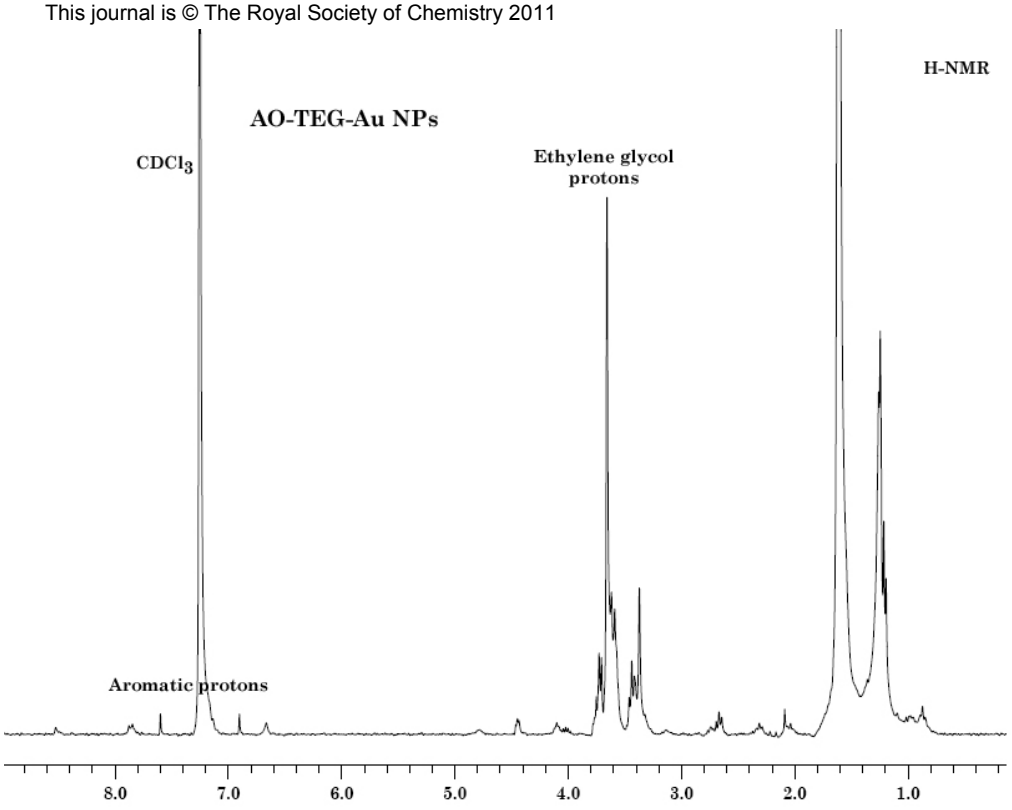

Figure 5S. ^{1}H-NMR spectrum of AO-TEG-Au NPs in $CDCl_3$.

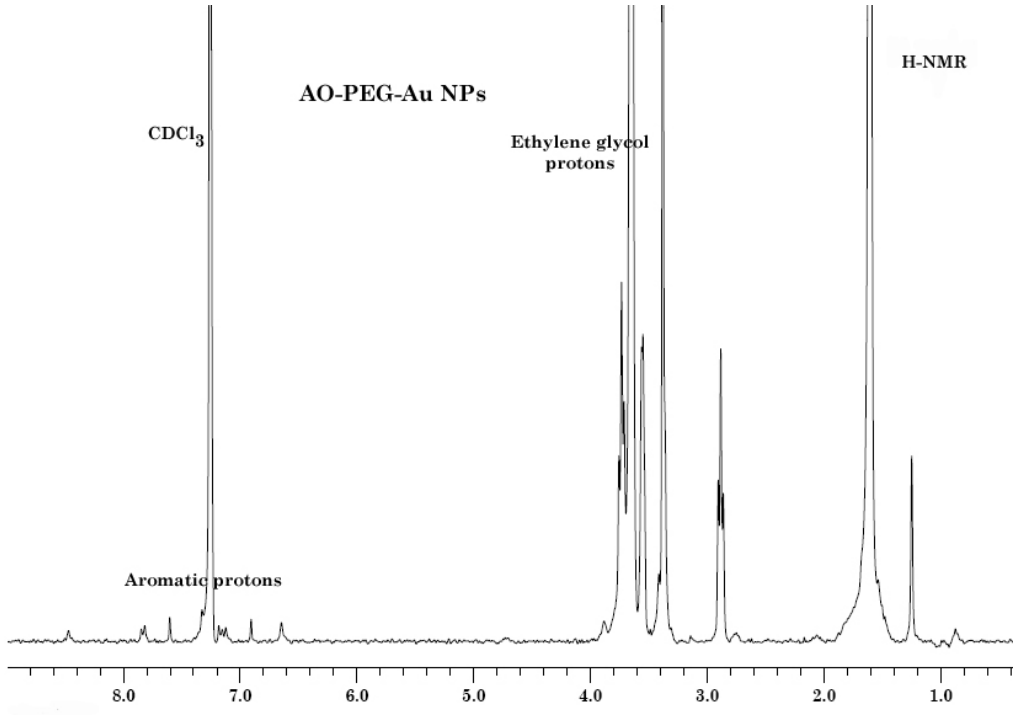

Figure 6S. ^{1}H-NMR spectrum of AO-PEG-Au NPs in $CDCl_3$.

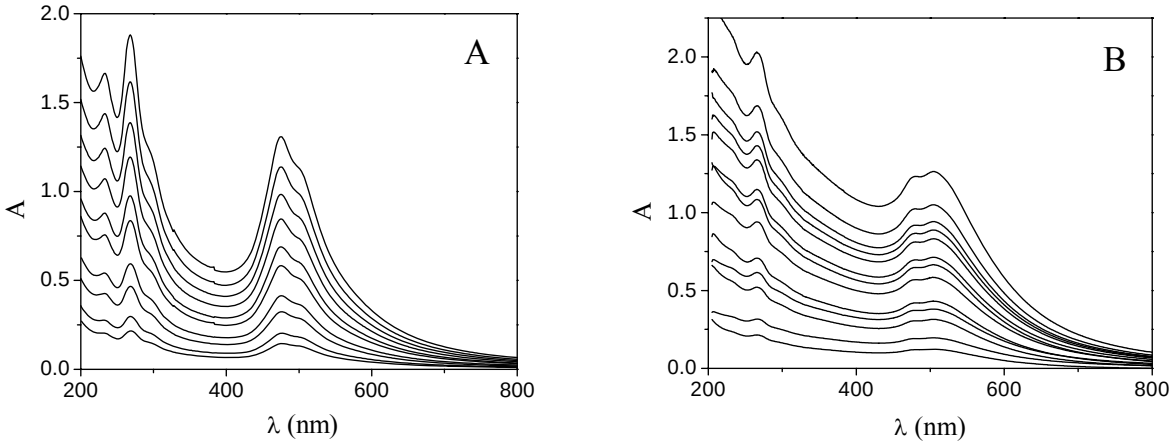

Figure 7S. Absorbance spectra of AO-TEG-Au NPs (A) and of AO-PEG-Au NPs (B) at various NPs concentrations, T = 25°C. (A) $C_{AO} = 3.6\times10^{-7} – 2.9\times10^{-6}$ M, pH = 7.0, I = 0.01 M (NaCac); (B) $C_{AO} = 3.4\times10^{-7} – 2.9\times10^{-6}$ M, pH = 7.0, I = 0.1 M (NaCl).

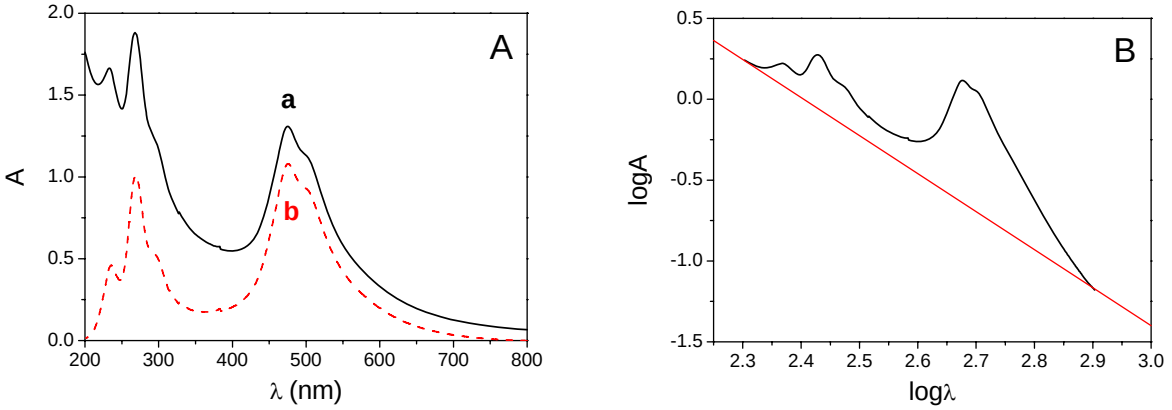

Figure 8S. Example of absorbance spectrum correction for the light scattering (LS) contribution (for further details see ref. 30). (A) Absorbance spectrum of AO-TEG-Au NPs before correction (a, $A_{experimental} = A + A_{LS}$ with $A_{LS} = k\lambda^{-n}$) and after correction (b); $C_{AO} = 2.9\times10^{-6}$ M, pH = 7.0, I = 0.01 M (NaCac), T = 25°C. (B) Double logarithmic plot of the absorbance spectrum: the linear extrapolation indicates the scattering contribution and enables log k and -n be evaluated respectively as intercept and slope of the straight line.

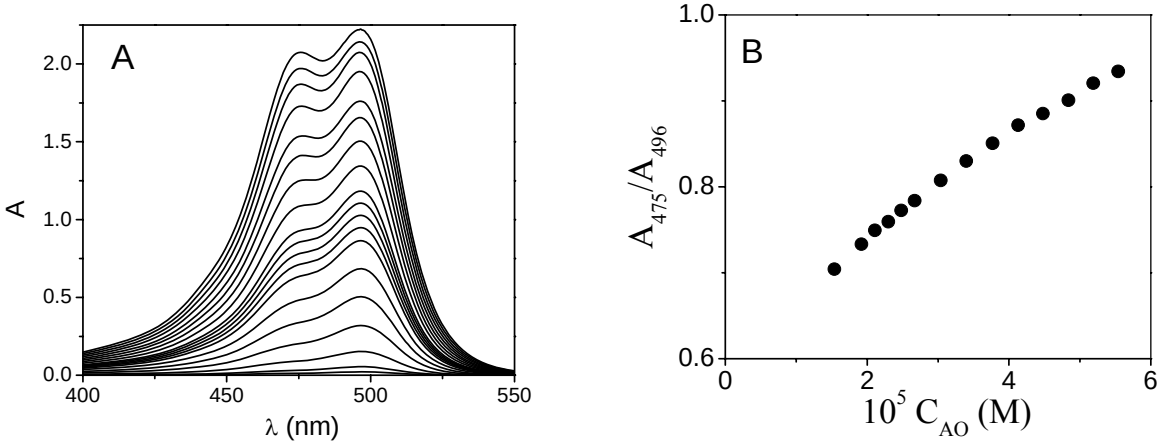

Figure 9S. (A) Absorbance spectra of AHLB at various concentrations (C_{AO} = 1.6×10^{-5} – 2.1×10^{-4} M) and (B) plot of the ratio of absorbance maxima *vs.* AHLB concentration (C_{AO} = 1.6×10^{-5} – 5.5×10^{-5} M); pH = 7.0, T = 25 ^{o}C.

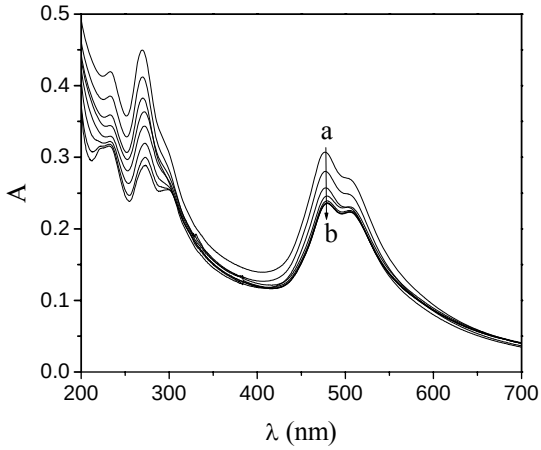

Figure 10S. Absorbance spectra of the AO-TEG-Au NPs/DNA system, C_{AO} = 1.2×10^{-6} M, pH = 7.0, T = 25 ^{o}C, (a) C_{DNA} = 0, (b) C_{DNA} = 6.8×10^{-5} M.

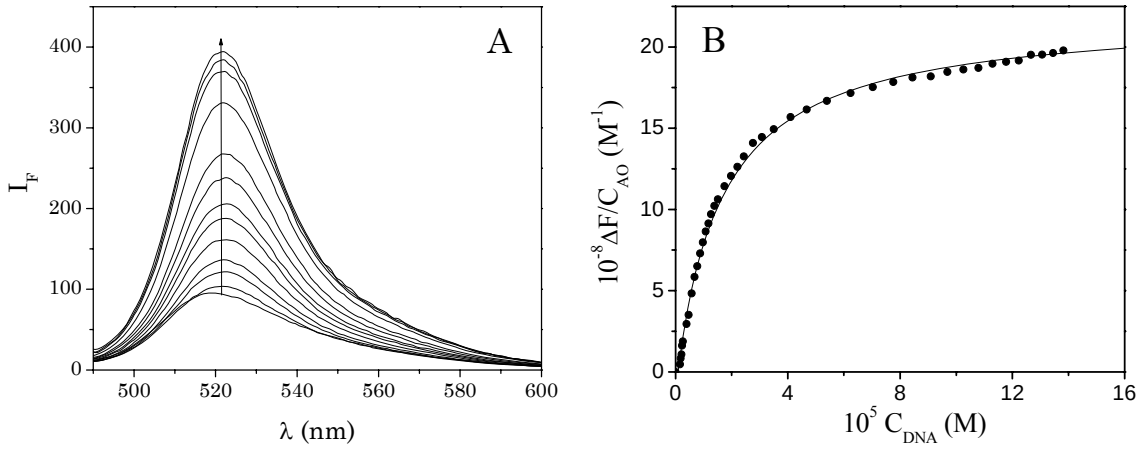

Figure 11S. (A) Fluorescence spectra for the AHLB/DNA system, pH = 7.0, T= 25 ^{o}C; C_{AO} = 1.9×10^{-7} M, (a) C_{DNA} = 0 M, (b) C_{DNA} = 1.5×10^{-4} M. (B) Corresponding binding isotherm, λ_{ex} = 480 nm, λ_{em} = 520 nm, the continuous line represents the trend calculated according to eqn (9).

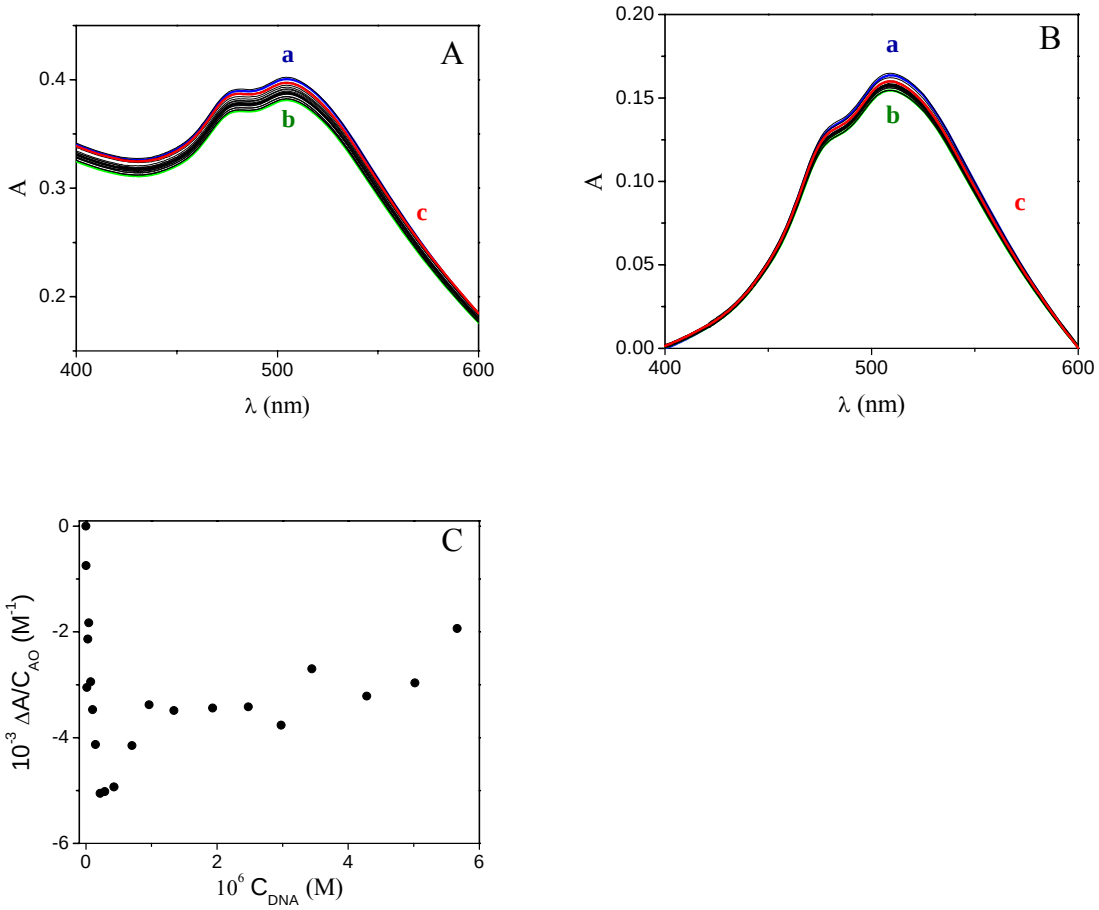

Figure 12S. Absorbance spectra collected for the AO-PEG-Au NPs/DNA system (A) without LS correction and (B) after LS correction, $C_{AO} = 2.0\times10^{-7}$ M; $C_{DNA} = 0$ (a, blue) – 2.2×10^{-7} (b, green) – 5.7×10^{-6} (c, red) M; I = 0.1 M (NaCl), pH = 7.0, T= 25 ^{o}C. (C) Relevant binding isotherm at 507 nm.

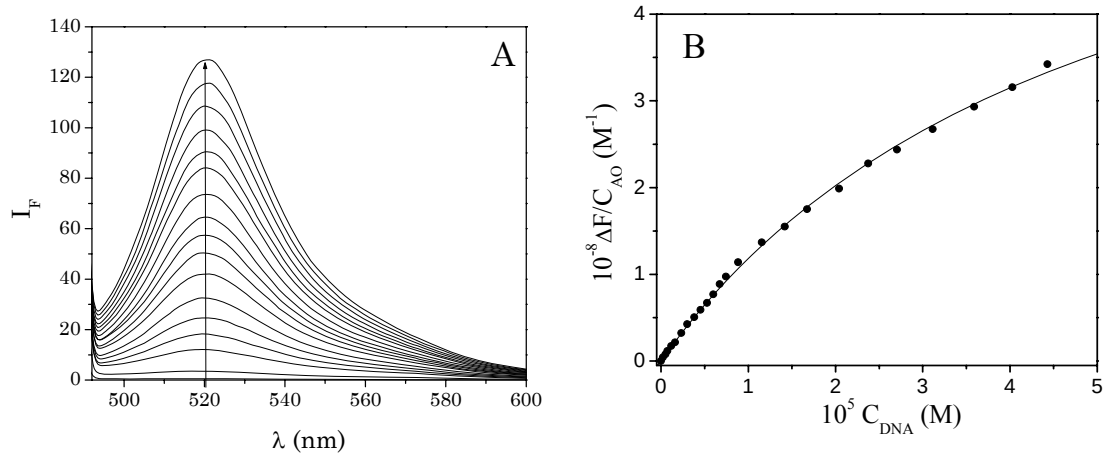

Figure 13S. (A) Fluorescence spectra collected for the AO-PEG-Au NPs/DNA system. $C_{AO} = 2.0\times10^{-7}$ M; $C_{DNA} = 0 – 4.4\times10^{-5}$ M; I = 0.1 M (NaCl), pH = 7.0, T= 25 ^{o}C. (B) Relevant binding isotherm at λ_{ex} = 480 nm and λ_{em} = 520 nm, the continuous line is data fit to eqn (9).

DERIVATION OF EQUATION (9)

Taking into account the following system:

$$2\,M \leftrightarrows D \quad (1S)$$

$$M + S \leftrightarrows MS \quad (2S)$$

$$D + S \leftrightarrows DS \quad (3S)$$

where eqns (1S)-(3S) correspond to eqns (2), (5) and (6) of the text, respectively, and M is the nanoparticle monomer, D its dimer form, S a DNA site and MS and DS the monomer and dimer bound species respectively, the relevant equilibrium constants are defined as

$$K_D = \frac{[D]}{[M]^2} \quad (4S)$$

$$K_{mon} = \frac{[MS]}{[M]\times[S]} \quad (5S)$$

$$K_{dim} = \frac{[DS]}{[D]\times[S]} \quad (6S)$$

At a wavelength where the nanoparticle only do absorb light the following expression holds

$$A = \varepsilon_M[M] + \varepsilon_D[D] + \varepsilon_{MS}[MS] + \varepsilon_{DS}[DS] \quad (7S)$$

The mass conservation law for the nanoparticle is

$$C_{AO} = [M] + 2[D] + [MS] + 2[DS] \quad (8S)$$

Thus

$$[D] = \frac{C_{AO}}{2} - \frac{[M] + [MS] + 2[DS]}{2} \quad (9S)$$

Introducing [D] from eqn (9S) into eqn (7S), using eqns (4-6S) and rearranging we have

$$\frac{A}{C_{AO}} = \frac{\varepsilon_D}{2} + \frac{[M]}{C_{AO}} \times \left\{\Delta\varepsilon_1 + \Delta\varepsilon_2 K_{mon}[S] + \Delta\varepsilon_3 K_D K_{dim}[M][S]\right\} \quad (10S)$$

where $\Delta\varepsilon_1 = \varepsilon_M - (\varepsilon_D/2)$, $\Delta\varepsilon_2 = \varepsilon_{Ms} - (\varepsilon_D/2)$ and $\Delta\varepsilon_3 = \varepsilon_{DS} - \varepsilon_D$. Introducing eqns (4-6S) in eqn (8S) we have

$$C_{AO} = [M] \times \{1 + 2K_D[M] + K_{mon}[S] + 2K_D K_{dim}[M][S]\} \quad (11S)$$

Form eqn (11S) $[M]/C_{AO}$ is obtained and introduced in eqn (10S)

$$\frac{A}{C_{AO}} = \frac{\varepsilon_D}{2} + \frac{\Delta\varepsilon_1 + \Delta\varepsilon_2 K_{mon}[S] + \Delta\varepsilon_3 K_D K_{dim}[M][S]}{1 + 2K_D[M] + K_{mon}[S] + 2K_D K_{dim}[M][S]} \quad (12S)$$

Equation (12S) is eqn (9) of the text.

As concerns [M] evaluation, this is done by solving the second order relationship shown in eqn (11S). The free DNA concentration, [S], is obtained as following.

$$C_{DNA} = [S] + [MS] + [DS] = [S] + K_{mon}[M][S] + K_D K_{dim}[M]^2[S] \quad (13S)$$

that gives:

$$[S] = \frac{C_{DNA}}{1 + K_{mon}[M] + K_D K_{dim}[M]^2} \quad (14S)$$

Eqns (11S) and (14S) are used simultaneously until convergence is reached, first using attempts K_{mon} and K_{dim} values (while K_D is known), then using the results of data fit to eqn (12S).

Eqn (12S), under conditions where the three $2K_D[M]$, $2K_D K_{dim}[M][S]$ and $\Delta\varepsilon_3 K_D K_{dim}[M][S]$ terms can be neglected, rearranged, turns to eqn (15S)

$$\frac{\Delta A}{C_{AO}} = \frac{K\Delta\varepsilon[S]}{(1 + K[S])} \quad (15S)$$

where $\Delta A = A - \varepsilon_M C_{AO}$ is the change of absorbance during titration, $\varepsilon_M = A^o/C_{AO}$ where A^o denotes the absorbance of the nanoparticle solution in the absence of DNA, and $\Delta\varepsilon = \varepsilon_{MS} - \varepsilon_M$ is the amplitude of binding isotherm.