**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} \text{ M}, pH = 7.0, I = 0.01 \text{ M (NaCac)}; (B) C_{AO} = 3.4\times10^{-7} – 2.9\times10^{-6} \text{ M}, pH = 7.0, I = 0.1 \text{ 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_{\text{experimental}} = A + A_{\text{LS}} with A_{\text{LS}} = k\lambda^{-n}) and after correction (b); C_{AO} = 2.9\times10^{-6} \text{ M}, pH = 7.0, I = 0.01 \text{ 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 ($C_{AO} = 1.6 \times 10^{-5} - 2.1 \times 10^{-4}$ M) and (B) plot of the ratio of absorbance maxima vs. AHLB concentration ($C_{AO} = 1.6 \times 10^{-5} - 5.5 \times 10^{-5}$ M); pH = 7.0, T = 25 °C.

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

Figure 11S. (A) Fluorescence spectra for the AHLB/DNA system, pH = 7.0, T = 25 °C; $C_{AO} = 1.9 \times 10^{-7}$ M, (a) $C_{DNA} = 0$ M, (b) $C_{DNA} = 1.5 \times 10^{-4}$ M. (B) Corresponding binding isotherm, $\lambda_{ex} = 480$ nm, $\lambda_{em} = 520$ 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, \( C_{AO} = 2.0 \times 10^{-7} \) M; \( C_{DNA} = 0 \) (a, blue) – \( 2.2 \times 10^{-7} \) (b, green) – \( 5.7 \times 10^{-6} \) (c, red) M; \( I = 0.1 \) M (NaCl), pH = 7.0, T= 25 °C. (C) Relevant binding isotherm at 507 nm.

**Figure 13S.** (A) Fluorescence spectra collected for the AO-PEG-Au NPs/DNA system. \( C_{AO} = 2.0 \times 10^{-7} \) M; \( C_{DNA} = 0 – 4.4 \times 10^{-5} \) M; \( I = 0.1 \) M (NaCl), pH = 7.0, T= 25 °C. (B) Relevant binding isotherm at \( \lambda_{ex} = 480 \) nm and \( \lambda_{em} = 520 \) nm, the continuous line is data fit to eqn (9).
DERIVATION OF EQUATION (9)

Taking into account the following system:

\[ 2 \text{M} \rightleftharpoons \text{D} \quad (1S) \]
\[ \text{M} + \text{S} \rightleftharpoons \text{MS} \quad (2S) \]
\[ \text{D} + \text{S} \rightleftharpoons \text{DS} \quad (3S) \]

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

\[ K_D = \frac{[\text{D}]}{[\text{M}]} \quad (4S) \]
\[ K_{\text{mon}} = \frac{[\text{MS}]}{[\text{M}] \times [\text{S}]} \quad (5S) \]
\[ K_{\text{dim}} = \frac{[\text{DS}]}{[\text{D}] \times [\text{S}]} \quad (6S) \]

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

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

The mass conservation law for the nanoparticle is

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

Thus

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

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

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

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

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

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

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

$$C_{DNA} = [S] + [MS] + [DS] = [S] + K_{mon}[M][S] + K_{D}K_{dim}[M]^{2}[S]$$

that gives:

$$[S] = \frac{C_{DNA}}{1 + K_{mon}[M] + K_{D}K_{dim}[M]^{2}}$$

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 $\Delta\varepsilon K_{D}K_{dim}[M][S]$ terms can be neglected, rearranged, turns to eqn (15S)

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

where $\Delta A = A - \varepsilon_{M}C_{AO}$ is the change of absorbance during titration, $\varepsilon_{M} = \varepsilon_{o}C_{AO}$ where $\varepsilon_{o}$ 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.