Electronic supporting information

Experimental details

General

Gold spherical NPs with an average diameter of 13 nm were purchased from BB International (Cardiff, UK). The oligonucleotides with the sequences: (5' NH_2- A_{10} TAG GAA TAG TTA TCA(T_6) 3' and 5' NH_2 – A_{10} TGA TAA CTA TTC CTA(T_6) 3') were prepared according to standard on-support oligonucleotide synthesis. T6 phosphorothioate tail was prepared by using Beaucage reagent during oxidation steps and 5-amino group was introduced at the last step of DNA synthesis by using the corresponding phosphoramidite C6-amino linker from Eurogentec. All other chemicals used in the synthesis of conjugates wee purchased from Sigma-Aldrich.

Conjugation of 3'-T6-phosphorothioate-modified oligo-nucleotides to metallic NPs

1.5 mL of gold nanospheres or gold-nanorings brought to a concentration of 8 nM were mixed with 5 µL of oligonucleotides (100 µM) and incubated for 24h at room temperature, in the dark and under gentle shaking. The concentration of NaCl was gradually brought to 0.3 M over three days and left to incubate for a final 24h. A Shimadzu UV-1601 UV - Visible Spectrophotometer was used to measure particle absorption. A Jeol 2100 Transmission Electron Microscope (TEM) was used to image all metal NPs. The CD spectra were recorded on a JASCO J-810 spectropolarimeter, typically using a scan rate of 200 nm/min and five accumulations per scan. Hydrodynamic radii and zeta potential of NPs were measured on a Malvern Zetasizer Nano Series V5.10.

Synthesis of gold nanorings

Silver seeds were produced by the addition of 5 mL of $AgNO_3$ (0.5 mM) at a rate of 2 mL/min to a solution containing 5 mL TSC (2.5 mM), 250 µL PSSS (500 mg/L) and 300 µL $NaBH_4$ (10 mM). 350 µL of these seeds were diluted in 5 mL of Millipore water to which were added 75 µL of ascorbic acid (10 mM) and 3 mL of $AgNO_3$ (0.5 mM) at a rate of 4 mL/min. 2.5 mL of TSC (25 mM) were added, followed by

150 µL of ascorbic acid (10 mM) and 390 of $HAuCl_4$ (0.5 mM) at 2 mL/min. The excess ascorbic acid was washed out by centrifuging the sample for 30 min at 10 000 rpm, removing the supernatant and resuspending the particles in the same volume of Millipore water.

Sonication experiments

Conjugates of gold nanoparticles or nanorings and oligonucleotides were agitated for 30 seconds in an ultrasonic bath. Effects on aggregation and CD response were assessed by absorption and CD spectroscopy.

Heating experiments

CD scans of conjugates were recorded as a function of the temperature which was gradually increased from 20 to 50 degree Celsius using a Peltier PTC-423 temperature controller.

Characterisation

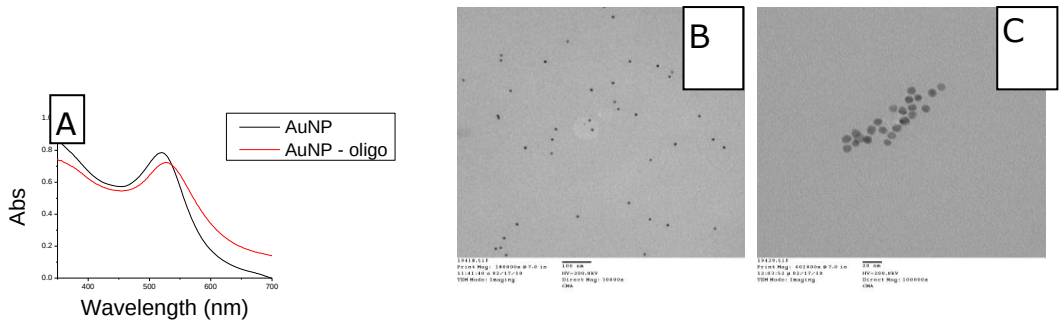

Figure S1: (A) Absorption spectra of bare and oligonucleotide-conjugated spherical gold NPs. TEM images of (B) bare and (C) oligonucleotide-conjugated spherical gold NPs.

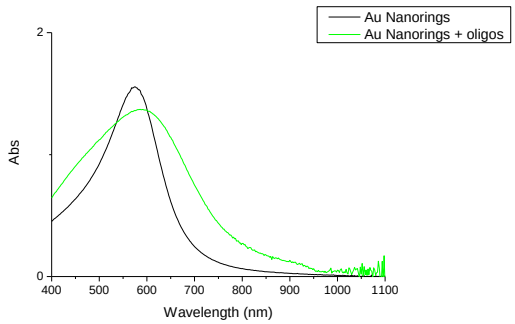

Figure S2*:* Absorption spectra of initial (black) and oligonucleotide-conjugated (green) gold nanorings.

DLS and Zeta-potential measurements

Further characterisation of the conjugated particles involved zeta potential measurements. The results are presented in Table S1. Both the initial citrate-stabilised gold nanoparticles and the free oligonucleotides bore a strong negative charge, as expected. The conjugates however had a lower absolute value of zeta potential. This can be explained by the fact that citrate molecules are much smaller than our 31-mer oligonucleotides. Therefore it is likely that each oligonucleotide that binds to the particle surface replaces several citrate molecules thus reducing the effective surface charge of the particle.

Table S1: Zeta potential measurements

Sample	Zeta potential (mV)	Std deviation
AuNP	-29	2.15
oligonucleotide	-30	2.88
AuNP-oligonucleotide conjugate	-18	3.05

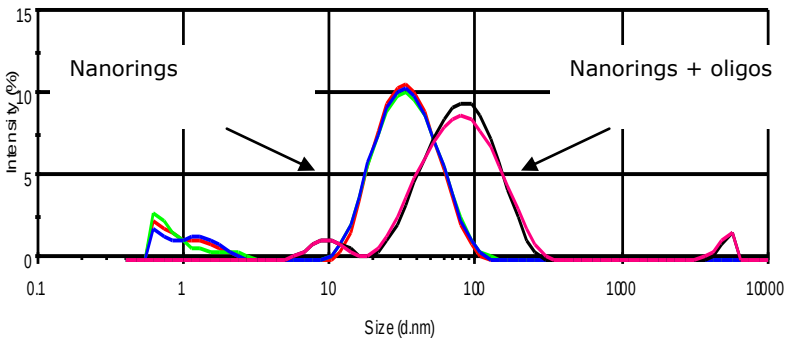

Figure S3: DLS measurement of bare and oligonucleotide-conjugated gold nanorings

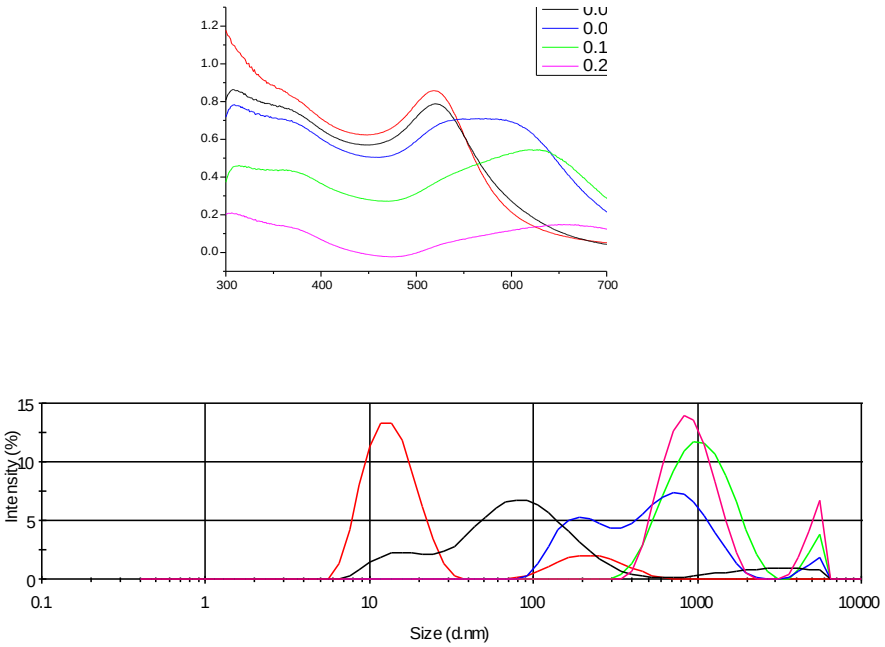

Figure S4: Monitoring of the size of aggregates induced by increasing concentrations of NaCl, by UV-Vis absorption spectroscopy (top) and DLS (bottom).

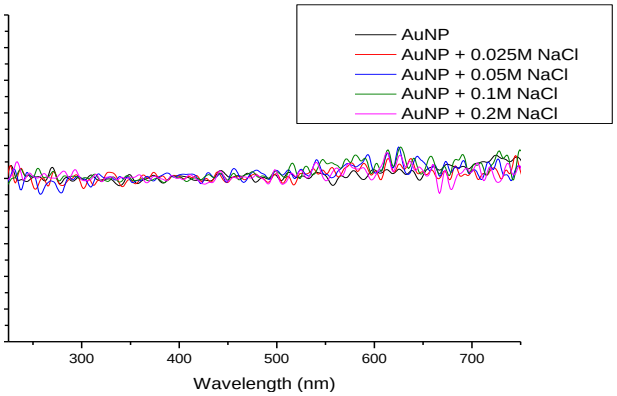

Figure S7: CD response of aggregated spherical gold NPs.

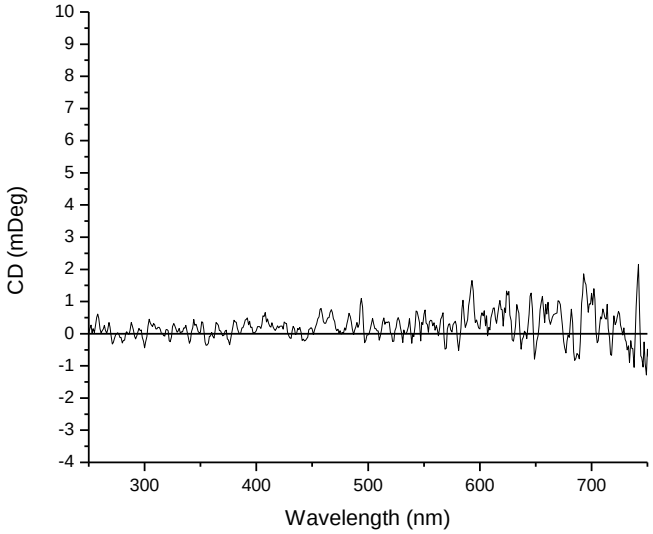

Figure S8: CD response of citrate

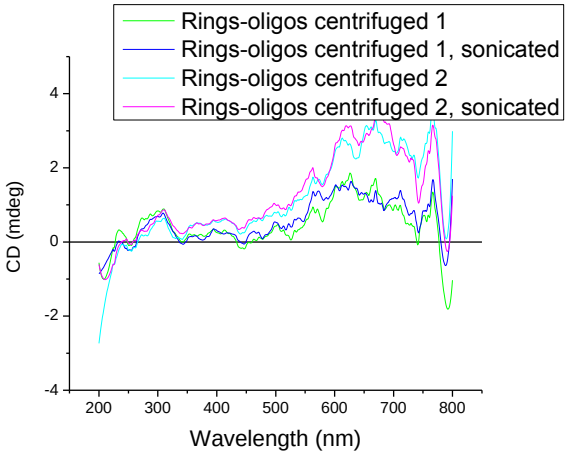

Figure S9: CD spectra of Au-NR conjugates after centrifiguation, sonication and second centrifugation and sonication.

***Conjugation of oligonucleotides to QDs**:*

The conjugation was first assessed by UV-Vis absorption spectroscopy as shown in Figure S8.

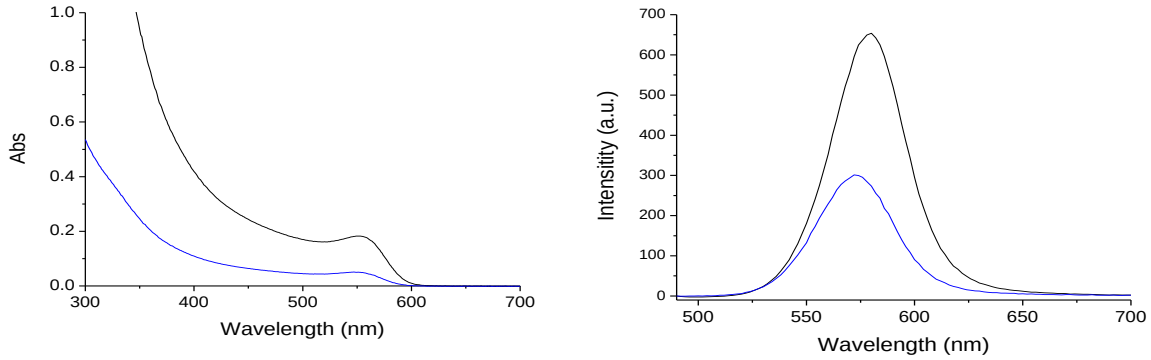

Figure S10: Absorption and PL spectra of TGA-capped CdTe QDs (black) and oligonucleotide-conjugated TGA-capped CdTe QDs (blue).

The absorption and PL spectra of oligonucleotide-conjugated QDs showed a blue shift and decrease in the luminescence intensity. This was attributed to partial degradation induced by EDC rather than an effect of the oligonucleotides. DLS measurements as shown in Figure S9 confirmed the presence of smaller partially etched particles as well as bigger ones compared to the initial QDs. The increase in the hydrodynamic radius suggested effective conjugation of the oligonucleotides.

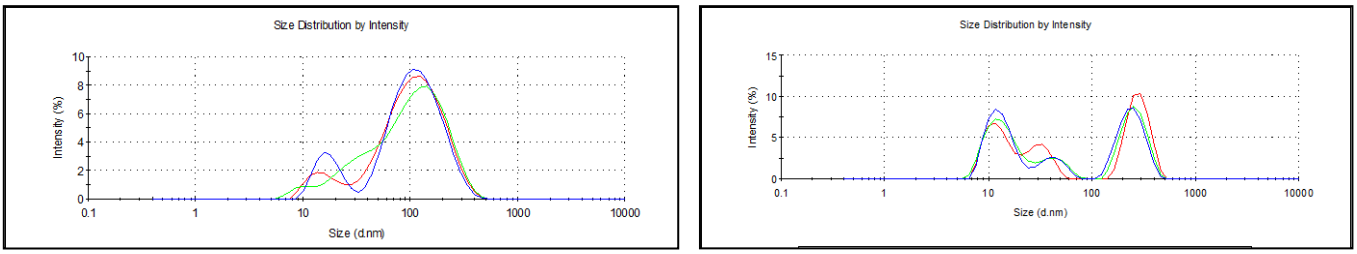

Figure S11: DLS measurements of bare (left) and oligonucleotide-conjugated (right) TGA-capped CdTe QDs.

Further characterisation of the conjugated QDs involved zeta potential measurements. The results are presented in Table S2. Both the initial TGA-capped CdTe QDs and the free oligonucleotides bore a strong negative charge, as expected. The conjugates however had a lower absolute value of zeta potential.

Table S2: Zeta potential measurements

Sample	Zeta potential (mV)	Std deviation
TGA-capped CdTe QD	-35	0.7
oligonucleotide	-30	2.8
QD-oligonucleotide conjugate	-22	1.5

Although the conjugation was mainly achieved through EDC coupling of the 5'end oligonucleotide amine group to the carboxylic acid group of TGA, the 3'end thiol groups may also bind to the surface of QDs *via* ligand exchange. As TGA is a very small molecule compared to an oligonucleotide, one of the latter could replace several TGA molecules. This mechanism would explain the decrease in surface charge.

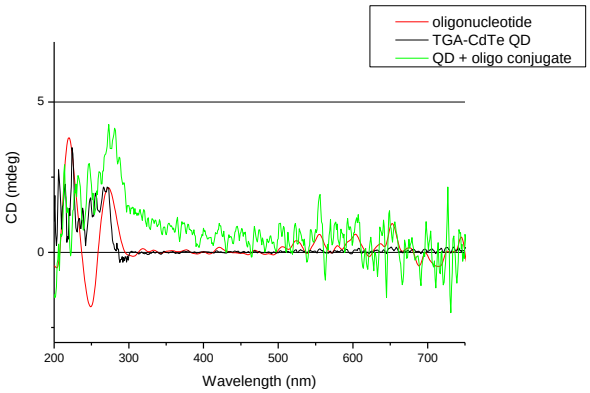

Figure S12: CD signal of TGA-capped CdTe QDs conjugated with oligonucleotides.