Fast, single-step and surfactant-free oligonucleotide modification of gold nanoparticles using DNA with a positively charged tail.

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Materials

40nm and 80nm diameter citrate coated gold nanoparticles were purchased from Nanocomposix, San Diego, USA. Additional 40nm gold nanoparticles were purchased from BBI, Cardiff, UK.

DNA sequences were purchased from IBA lifesciences, Göttingen, Germany.
ZNA modified DNA sequences were purchased from Metabion, Martinsried, Germany.

DNA sequence details:

<table>
<thead>
<tr>
<th>Sequence</th>
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<tbody>
<tr>
<td>HS-cap</td>
<td>5’ HS-AAA AAG GTG GAT AAC GTC TT 3’</td>
</tr>
<tr>
<td>ZNA-cap</td>
<td>5’ ZNA4-TTT TTG GTG GAT AAC GTC TT 3’</td>
</tr>
<tr>
<td>Tag-ZNA</td>
<td>5’ ACG CCT TCT TGT TGG TTT TT-ZNA4-3’</td>
</tr>
<tr>
<td>ZNA-PolyT</td>
<td>5’ ZNA4-TTT TTT TTT TTT TTT TT TTT TT 3’</td>
</tr>
<tr>
<td>Targ1</td>
<td>5’ CCA ACA AGA AGG CGT AAG ACG TTA TCC ACC 3’</td>
</tr>
<tr>
<td>NST</td>
<td>5’ TGG AAG TTA GAT TGG GAT CAT AGC GTC AT 3’</td>
</tr>
</tbody>
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Where ZNA4 means 4 insertions of spermine-phosphoramidite which after deprotection gives the following structure: )

Methods:

Nanoparticle modification:
The procedure for modification involved adding 1 mL of gold nanoparticles (at the stock concentration of the commercial product) to a 1.5 mL Eppendorf tube, followed by addition of 1 µL of 100 µM DNA (or ZNA-modified DNA) to the solution, with short vortex mixing. The solution was incubated for 5 minutes at room temperature on the bench. Subsequently, a 500 µL aliquot of the solution was transferred to a second Eppendorf, where 200 µL of 1 M NaCl solution was added drop by drop on the vortex. For purification, 700 µL of MilliQ water were
added and the tube was centrifuged at 6000g for 10 minutes. After the removal of the supernatant, and resuspension in 10 mM HEPES buffer, pH=7.4, the tube was centrifuged again under the same conditions.

Kinetics of peak absorbance change

Absorbance scans in the range of 500-550 nm, at a step size of 0.2 nm were performed on a Shimadzu 2401 PC UV-VIS spectrophotometer. The output was saved into an excel sheet. For determination of the peak position, a MATLAB script which reads the excel sheet and finds the peak by fitting the data to a Lorentzian function using the ‘lorentzfit’ function was used. The ‘lorentzfit’ function, created by Jered Wells, is freely available on MATLAB central.

DLS measurements

As can be seen in Fig. S1, for all samples, even after salt addition, there is no peak at high hydrodynamic sizes suggesting that the sample does not exhibit aggregation.

![DLS measurements](image)

Fig. S1: DLS measurements of 40nm gold nanoparticles before (red line), after 5 minute incubation with ZNA-cap (green line) and after the addition of salt to ~0.3 M final NaCl concentration (blue line).

Modification of 80nm gold nanoparticles

80 nm gold nanoparticles were modified under the same conditions as 40 nm particles. As can be seen in Fig. S2, the only difference in absorbance before modification and after modification (with salt addition) is the expected slight shift of the peak position towards the red.
Fig. S2: UV-VIS absorption of the gold nanoparticle before modification (blue diamonds), and after modification with ZNA-cap and the addition of salt (red squares).