Supporting Information

T. Pellegrino[1,2,3,#], R. A. Sperling[1,#], A. P. Alivisatos[2], W. J. Parak[1,2,*]

[1] Center for Nanoscience, Ludwig Maximilians Universität München, München, Germany
[2] Department of Chemistry, University of California and Lawrence Berkeley National Lab, Berkeley, California, USA
[3] National Nanotechnology Lab of INFM, Lecce, Italy
[#] both authors contributed equally to this work

[*]to whom correspondence should be addressed
Dr. Wolfgang J. Parak; email: Wolfgang.Parak@physik.uni-muechen.de

I) Gel Electrophoresis of Gold-DNA Nano-Conjugates - Data Recording

I.1) Phosphine stabilized Au nanoparticles

To 500 ml citrate-stabilized gold nanoparticles (5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 150, 200 nm diameter; #15702 - # 15709, British Biocell (BBC), United Kingdom) 150 mg of bis(p-sulfonatophenyl)phenylphosphine dehydrate, dipotassium salt (#15-0463, Strem Chemicals, Newbutyport, MA, USA) were added and the mixture was stirred for 2 days. The samples were then concentrated using centrifuge filters (Centriplus, 100000 MWCO, Millipore, USA) to around 2 ml. The concentrated particles were diluted with phosphine solution (3 mg of bis(p-sulfonatophenyl)phenylphosphine dehydrate, dipotassium salt per 10 ml Millipore water) to around 15 ml and reconcentrated to 2 ml using centrifuge filters. The dilution and reconcentration step were repeated three times. The final solutions contained Au particles dissolved in 3 mg /10 ml phosphine solution. The concentration of the samples was determined by their absorption at the plasmon peak. The used molecular extinction coefficients are enlisted in Table SI-1: The extinction coefficients had been derived in the following way: The absorption spectra of the as-delivered particle solutions were recorded (1 cm pathlength) and the absorption at the plasmon peak A was extracted. Now the extinction coefficient ε was calculated as $\varepsilon = A \cdot c^{-1} \cdot cm^{-1}$, whereby c [M] was the particle concentration as provided in the data sheet of the vendor of the particles. The same procedure was applied for different batches of particles and the resulting mean values were used as extinction coefficients.

particle diameter [nm]	wavelength of absorption peak [nm]	molecular extinction coefficient [$M^{-1}cm^{-1}$]
5	517	1.0×10^7
10	518	8.5×10^7
15	520	3.8×10^8
20	524	8.7×10^8
30	525	2.9×10^9
40	525	6.8×10^9
50	530	1.0×10^{10}

***Table SI-1**: Molecular extinction coefficients at the absorption peak and wavelength of the plasmon absorption peak in dependence of the nominal particle diameter d.*

Typical concentrations for the concentrated phosphine-stabilized Au particles were 10 - 40 μM, 1-5 μM, and 0.1 - 0.5 μM for 5nm, 10 nm, and 20 nm Au nanoparticles, respectively.

The citrate shell was exchanged for a phosphine shell because phosphine-stabilized particles turned out to be more stable in aqueous solution than citrate stabilized ones. In particular higher particle concentrations without agglomeration of the Au particles could be achieved with the phosphine coating. We speculate that this should be due to a higher binding-affinity of the phosphine compared to the citrate to the Au surface. We have to

mention that in contrast to citric acid shells phosphine shells have a small fluorescence, which can be undesirable for fluorescence measurements (personal information Eric Dulkeith). The phosphine shell could not be completely replaced by competitive binding (e.g. by adding DNA molecules with -SH modification). Always some fluorescence of the phosphine adsorbed to the particles remained (personal information Eric Dulkeith).

I.2) Attachment of DNA to phosphine-stabilized Au nanoparticles

Single stranded DNA (with and without thiol modification) was added (as received from the supplier) to phosphine-stabilized nanoparticles. The reactions were performed in 50 mM NaCl, 25 mM phosphate buffer (pH = 7.3), and in 25 mM NaCl, 12 mM phosphate buffer (pH = 7.3) for 5nm, 10 nm, and for 20 nm Au particles, respectively. The absolute Au particle concentrations in the reactions were 0.4 - 4 μM, 0.05 - 1 μM, and 0.005 - 0.01 μM for 5 nm, 10 nm, and 20 nm Au particles, respectively. The typical volume for one reaction mixture was 10-20 μl. Series with different amounts of added DNA were prepared. The maximum amount of added DNA molecules per Au nanoparticle was 15000, 30000, and 60000 for 5 nm, 10 nm, and 20 nm particles, respectively. For each series reaction mixtures with a different amount of added DNA molecules were used. The sequences of the used DNA molecules are enlisted in Table SI-2.

As an example a series of 10 nm Au particles with maximum 10700 DNA molecules added per nanoparticle was prepared in the following way. 30 vials were filled with 5 μl of 0.41 μM Au solution. To each vial 5 μl DNA mix was added. The DNA mix comprised DNA dissolved in 100 mM NaCl and 50 mM phosphate buffer of pH 7.3. To the first vial a DNA mix with a DNA concentration of 4800 μM was added, to the second one a DNA mix with a DNA concentration of 4800 μM / 2 = 2400 μM, to the third one a DNA mix with a DNA concentration of 2400 μM / 2 = 1200 μM, etc. In this way all vials had the same concentration of Au particles, the same buffer conditions, the same volume, but a different DNA/Au ratio. In this case the DNA/Au ratio in the first, second, third,....vial was ca. 12000, 5800, 2900, ..., respectively. This means a series has been generated in which the DNA/Au ratio is reduced by a factor of two from vial to vial.

DNA-sequence	sequence of bases from 5' to 3' end
8a	5'-GGT TAT CA-3'
8b	5'-TTC GAT CA-3'
12	5'-TGC TGT TCC CAT-3'
16	5'-CTA AAT GGG AAC AGC A-3'
21	5'-GCT TGA CTC GTA GTG AAA AAA-3'
24	5'-CCA TCC CAA TCG ACA CCG GGG TCC-3'
30	5'-CGC CTT GTT GTT AGC CAT AAA GTG ATA ACC-3'
35	5'-TGC TGT TCC CAT CTG ATA CGG AGT TGC TTA GGG GT-3'
36a	5'-AAA AAA CGC CTT GTT GTT AGC CAT AAA GTG ATA ACC-3'
36b	5'-CCA GAT CCC GGA CCC CGG TGT CGA TTG GGA TGG CTA-3'
43a	5'-CCA GAT CCC GGA CCC CGG TGT CGA TTG GGA TGG CTA TTC GCC G-3'
43b	5'-GCA GTA ACG CTA TGT GAC CGA GAA GGA TTC GCA TTT GTA GTC T-3'
54	5'-TGC TGT TCC CAT CTG ATA CGG AGT TGC TTA GGG GTG TCC AGG TTT CGT GCG GGC-3'
65	5'-TGC TGT TCC CAT CTG ATA CGG AGT TGC TTA GGG GTG TCC AGG TTT CGT GCG GGC TCA AGA CTA CA-3'
85	5'-TGC TGT TCC CAT CTG ATA CGG AGT TGC TTA GGG GTG TCC AGG TTT CGT GCG GGC TCA AGA CTA CAA ATG CGA ATC CTT CTC GGT C-3'
100a	5'-GCA GTA ACG CTA TGT GAC CGA GAA GGA TTC GCA TTT GTA GTC TTG AGC CCG CAC GAA ACC TGG ACA CCC CTA AGC AAC TCC GTA TCA GAT GGG AAC AGC A-3'
100b	5'-TGC TGT TCC CAT CTG ATA CGG AGT TGC TTA GGG GTG TCC AGG TTT CGT GCG GGC TCA AGA CTA CAA ATG CGA ATC CTT CTC GGT CAC ATA GCG TTA CTG C-3'
120	5'-AAG TGT CGA TTG GGA TGG CTA TTC GCC GCC TTT CAG CAG TAA CGC TAT GTG ACC GAG AAG GAT TCG CAT TTG TAG TCT TGA GCC CGC ACG AAA CCT GGA CAC CCC TAA GCA ACT CCG TAT-3'
135	5'-AAG TGT CGA TTG GGA TGG CTA TTC GCC GCC TTT CAG CAG TAA CGC TAT GTG ACC GAG AAG GAT TCG CAT TTG TAG TCT TGA GCC CGC ACG AAA CCT GGA CAC CCC TAA GCA ACT CCG TAT CAG ATG GGA ACA GCA-3'

Table SI-2*: DNA sequences. The name of the sequence corresponds to the number of bases of the single stranded DNA. The sequence of the bases is listed from the 5' to the 3' end. In some case two different oligonucleotides with the same number of bases but with different sequences were used. This is indicated by "a" or "b" in the name of the sequence.*

The reaction mixtures were incubated for one hour to 6 days at room temperature. The actually chosen conditions depended from the expected result. For the experiments in which a saturation of the Au nanoparticles with DNA was desired the reaction time was

chosen long and the DNA/Au ratio as high as possible. For the experiments in which discrete bands during gel electrophoresis were expected, the reaction time was only about 1 hour (because this yielded sharper bands due to reduced nonspecific adsorption) and only as much DNA was added as was needed to observe the bands.

We want to point out the following observations. The binding efficiency of thiol-modified DNA (as received from the supplier) to the Au nanoparticles is relatively low. This might be in part due to the protection of the -SH group of the DNA by the supplier. Sometimes around 10000 DNA molecules had to be added until the Au surface was saturated with DNA. However, much less than 10000 DNA molecules can stick to the surface of the Au particles. This means that a significant fraction of the added DNA remained unbound in solution. This might be explained by the fact that the Au nanoparticles were dissolved in phosphine-containing solution (3 mg /10 ml). This means that the thiolated DNA and the phosphine molecules had to compete to be adsorbed to the Au surface. Due to its importance we have to point it out again: the number of added DNA molecules per Au particle is not equal to the number of DNA molecules that are actually bound per Au particle. The reaction also seemed to be quite slow. Only after approximately one day the solutions had reached equilibrium and the number of actually attached DNA molecules per Au particle did not increase further. Again this could be explained with a competition of thiolated DNA and phosphine molecules for the adsorption to the Au particles.

I.3) Gel electrophoresis experiments

For 0.5%, 1%, 2%, 3%, 4%, 5%, and 6% gels 0.5g, 1g, 2g, 3g, 4g, 5g, and 6 g of agarose powder (Gibco BRL, # 15510-027) were added to 100 ml of 0.5 x TBE buffer (Tris-Borate-EDTA Buffer, #T3913, Sigma-Aldrich), respectively. The solution was heated to around 90° C until it became homogeneous and transparent and was then cast in a gel tray (Sub-Cell GT Agarose Gel Electrophoresis System, Biorad, USA).

For gel electrophoresis experiments glycerol was added to the samples to a final glycerol content of about 10%. Around 10 µl of glycerol-modified sample was loaded in each well of the gel. Gels were run 1 hour at 100 V in 0.5 x TBE buffer (corresponds to 44.5 mM TBE, pH around 8.3 - 8.5). For very slow running samples the running time was doubled and the mobilities were afterwards divided by a factor of 2 to have normalized conditions. Together with the samples, on each gel, we have always run two reference samples: the plain phosphine-coated gold (without DNA added) and free single and double stranded DNA of different lengths.

Although the distance between the two electrodes in the gel-electrophoresis set-up is bigger than the length of the tray we consider that due to the law of a voltage divider the applied voltage drops only along the tray, since there the resistance is higher due to the thinner layer of electrolyte. The length of the tray is 10.1 cm and 100 V were applied. This corresponds to an electric field of 100V / 10.1 cm = 9.9 V/cm. This is in contrast to our own previous studies, where we wrongfully assume an electric field of 7.1 V/cm [1-3].

To visualize the Au particles on the gel after gel electrophoresis digital pictures were taken by using an Eagle Eye II digital camera (Biorad, USA). At the chosen gold concentration the gold bands appeared violet under illumination with visible light and could be seen by eye. We have adjusted the photos in such a way that the length of the gel (10.1 cm) corresponded always to 500 pixels.

I.4) Electrophoretic mobility of Au particles

We determined the migration of each band as the distance (in pixel) of the band after gel electrophoresis to the position where the particles had been loaded. Two examples are shown in Figure SI-1 and Figure SI-5. By using the calibration factor 500 pixels per 10.1 cm the migration of each band could be converted to centimeters.

In order to obtain the absolute mobilities m [$cm^2/(Vs)$] of the particles the values obtained for the migration l [cm] had to be modified in the following. The velocity of the particles is defined as the absolute migration on the gel (in cm) divided by the time the gel has been run. This time was 60 minutes = 3600 s (or the results have been converted to this normalized running time). The mobility of the particles finally is defined as the velocity per applied electric field. As described above the applied electric field was 9.9 V / cm.

The absolute mobilities were determined for 10 nm Au particles on 0.5, 1, 2, 3, 4, 5, and 6% agarose gels. For each gel percentage at least 30 different gels were run. The results are enlisted in Table SI-3. As described above, the absolute electrophoretic mobilities $m_{x,y}$ [$cm^2V^{-1}s^{-1}$] were derived by the measured migration $l_{x,y}$ [cm] of the particles during electrophoresis using the following equation:

$$m_{x,y}\ [cm^2V^{-1}s^{-1}] = (l_{x,y}\ [cm]\ /3600\ s)\ /\ 9.9\ Vcm^{-1} \qquad \text{Formula SI-1}$$

x refers to the diameter of the Au particle and y to the gel percentage.

0.5% gel	1% gel	2% gel	3% gel
$m_{10nm,0.5\%}$ [$cm^2/(Vs)$]	$m_{10nm,1\%}$ [$cm^2/(Vs)$]	$m_{10nm,2\%}$ [$cm^2/(Vs)$]	$m_{10nm,3\%}$ [$cm^2/(Vs)$]
$(1.57 \pm 0.08)\times 10^{-3}$	$(1.43 \pm 0.14)\times 10^{-3}$	$(1.07 \pm 0.12)\times 10^{-3}$	$(0.77 \pm 0.17)\times 10^{-3}$

4% gel	5% gel	6% gel
$m_{10nm,4\%}$ [$cm^2/(Vs)$]	$m_{10nm,5\%}$ [$cm^2/(Vs)$]	$m_{10nm,6\%}$ [$cm^2/(Vs)$]
$(0.51 \pm 0.13)\times 10^{-3}$	$(0.31 \pm 0.07)\times 10^{-3}$	$(0.16 \pm 0.04)\times 10^{-3}$

***Table SI-3**: Absolute mobility m of d(Au) = 10 nm Au particles for agarose gels of different percentage. For all further experiments the relative mobilities relate to these absolute mobilities. $m_{10nm,y\%}$ is the absolute electrophoretic mobility of 10 nm Au particles in an agarose gel of y% (y = 0.5, 1, 2, 3, 4, 5, 6). Each value corresponds to the mean value of 30 - 300 experiments.*

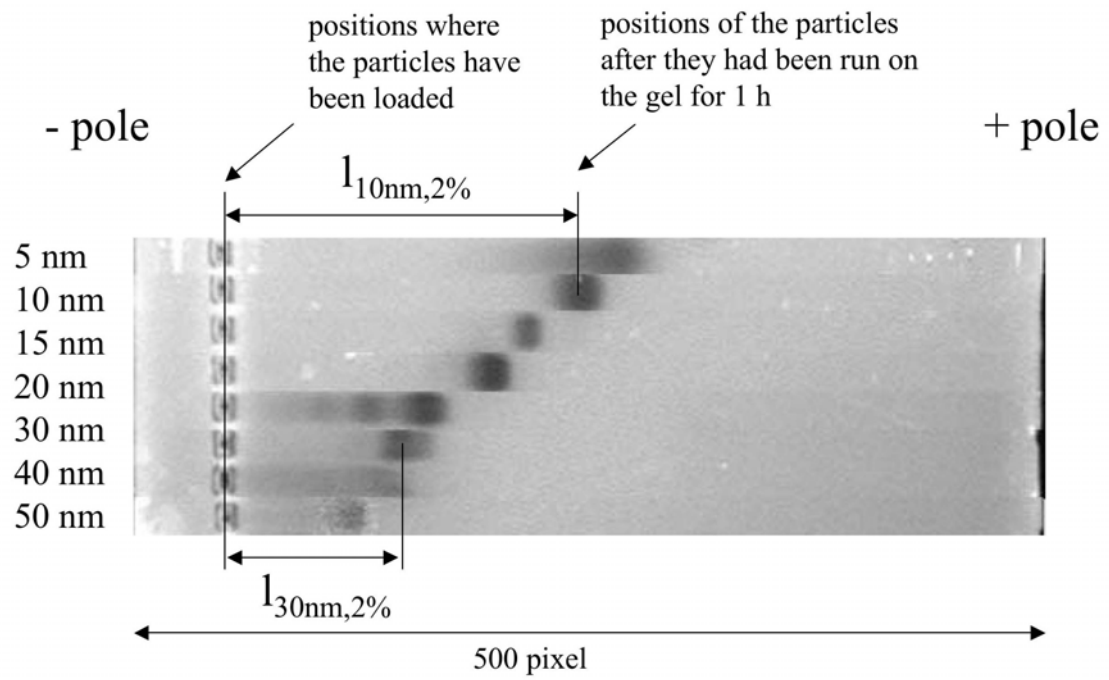

Figure SI-1*: 2% agarose gel on which phosphine stabilized Au nanoparticles of different size (diameter d of the Au core = 5, 10, 15, 20, 30, 40, 50 nm) have been run for 1 hour at 100 V (this corresponds to an electric field of 9.9 V/cm). During the gel electrophoresis the negatively charged particles migrated from the positions where they have been loaded to the gel towards the positive electrode. The length of the gel of 10.1 cm corresponds to 500 pixels on the photo. The migration l of the particles is the distance they have moved towards the positive electrode during gel electrophoresis.* $l_{x,y}$ *describes the migration of particles of x nm diameter (x = 5, 10, 15, 20, ...) in a y % agarose gel (y = 0.5, 1, 2, 3, 4, 5, 6). The migration in pixel can be directly extracted from the gel and converted to an absolute value in cm. In the example shown here the values are:* $l_{10nm,2\%}$ *= 195 pixel / (500 pixel / 10.1 cm) = 3.93 cm and* $l_{30nm,2\%}$ *= 110 pixel / (500 pixel / 10.1 cm) = 2.22 cm.*

The error for measuring relative quantities instead of absolute one is always lower. In the case of gel-electrophoresis for example small deviations in the gel percentage, in the TBE-buffer concentration, in the exact positions of the electrodes in the gel electrophoresis chamber, and in the height of the TBE-buffer above the gel tray in the gel electrophoresis chamber can affect the values for the absolute electrophoretic mobilities. In order to reduce this error we measured relative instead of absolute mobilities. On every gel a reference sample with know absolute mobility was run. The mobilities of the other samples on the same gel were then related to this mobility. Since all samples of one series were run on the same gel deviations in the absolute mobilities due to experimental uncertainties are cancelled out by considering only the relative mobilities. In order to measure the mobility of Au nanoparticles of different sizes gels with nanoparticles of different diameter were run as shown in Figure SI-1. Typically only the relative mobilities were determined. They are identical to the relative migration:

$$m / m_{reference} = l / l_{reference} \qquad \text{Formula SI-2}$$

For example, the relative mobility of the 30 nm Au particles shown in Figure SI-1 relative to the 10 nm Au particles on a 2% agarose gel is $m_{30nm,2\%} / m_{10nm,2\%} = l_{30nm,2\%} / l_{10nm,2\%} = 2.22$ cm / 3.93 cm = 0.56. By using the table of the absolute mobilities (Table SI-3) the relative mobilities can be converted to absolute ones: $m_{30nm,2\%} = (m_{30nm,2\%} / m_{10nm,2\%}) \times m_{10nm,2\%} = 0.56 \times 1.07 \times 10^{-3}$ $cm^2V^{-1}s^{-1} = 0.60 \times 10^{-3}$ $cm^2V^{-1}s^{-1}$. We want to stress this idea again. First, the absolute mobilities for reference particles were recorded (see Table SI-3). This was done for many gels (30-300) for each gel percentage. Therefore the obtained values are highly significant (as mean values from 30 - 300 experiments). In all the following experiments on each gel also reference particles were run. The mobilities were then always referred to the mobilities of the reference particles. Therefore much fewer gels (3-10) had been run, since only relative data were extracted from each gel.

In Table SI-4 / Figure SI-2 the obtained relative electrophoretic mobilities for phosphine-stabilized nanoparticles are shown. Each value corresponds to the mean value of 3-10 different measurements.

Certainly the high percentage gels (in particular the 6% gels) are highly viscous and may not be homogeneous and thus might affect the experimentally obtained electrophoretic mobilities. For this reason the data derived from the higher percentage gels where not used for the results shown in the main paper and also not for the Ferguson analysis[1] (see Chapter II.4).

[1] The data of the higher percentage gels cannot be used for the Ferguson plots also for other reasons (see II.4).

	0.5% gel	1% gel	2% gel	3% gel
d(Au)	$m/m_{10nm,0.5\%}$	$m/m_{10nm,1\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,3\%}$
5 nm	1.05 ± 0.1	1.07 ± 0.03	1.11 ± 0.02	1.21 ± 0.06
10 nm	1.00 ± 0.00	1.00 ± 0.00	1.00 ± 0.00	1.00 ± 0.00
15 nm	0.93 ± 0.03	0.91 ± 0.03	0.84 ± 0.03	0.71 ± 0.04
20 nm	0.92 ± 0.01	0.87 ± 0.02	0.75 ± 0.03	0.56 ± 0.06
30 nm	0.87 ± 0.04	0.77 ± 0.03	0.57 ± 0.02	0.32 ± 0.10
40 nm	0.87 ± 0.02	0.68 ± 0.06	0.51 ± 0.03	0.21 ± 0.05
50 nm	0.80 ± 0.02	0.62 ± 0.04	0.30 ± 0.09	0.09 ± 0.04
60 nm	0.76 ± 0.06	0.57 ± 0.05	0.24 ± 0.04	0.04 ± 0.02
80 nm	0.69 ± 0.05	0.44 ± 0.04	0.10 ± 0.04	0.03 ± 0.02
100 nm	0.62 ± 0.07	0.27 ± 0.08	0.04 ± 0.02	0.02 ± 0.02
150 nm	0.15 ± 0.04	0.07 ± 0.06	0.04 ± 0.02	0.02 ± 0.02
200 nm	0.03 ± 0.03	0.02 ± 0.02	0.02 ± 0.02	0.00 ± 0.00

	4% gel	5% gel	6% gel
d(Au)	$m / m_{10nm,4\%}$	$m/m_{10nm,5\%}$	$m / m_{10nm,6\%}$
5 nm	1.45 ± 0.13	1.73 ± 0.20	2.04 ± 0.40
10 nm	1.00 ± 0.00	1.00 ± 0.00	1.00 ± 0.00
15 nm	0.48 ± 0.12	0.31 ± 0.10	0.24 ± 0.07
20 nm	0.39 ± 0.13	0.21 ± 0.15	0.10 ± 0.06
30 nm	0.08 ± 0.02	0.04 ± 0.03	0.03 ± 0.03
40 nm	0.05 ± 0.01	0.03 ± 0.03	0.02 ± 0.02
50 nm	0.03 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
60 nm	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
80 nm	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
100 nm	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
150 nm	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
200 nm	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

***Table SI-4**: Relative electrophoretic mobility $m / m_{10nm,y\%}$ of Au nanoparticles of different hard core diameters d(Au) in agarose gels of different percentage (y = 0.5, 1, 2, 3, 4, 5, 6%) related to the mobility of 10 nm Au particles. The absolute diameters $m_{10nn,y\%}$ are enlisted in Table SI-3. The data are graphically displayed in Figure SI-2.*

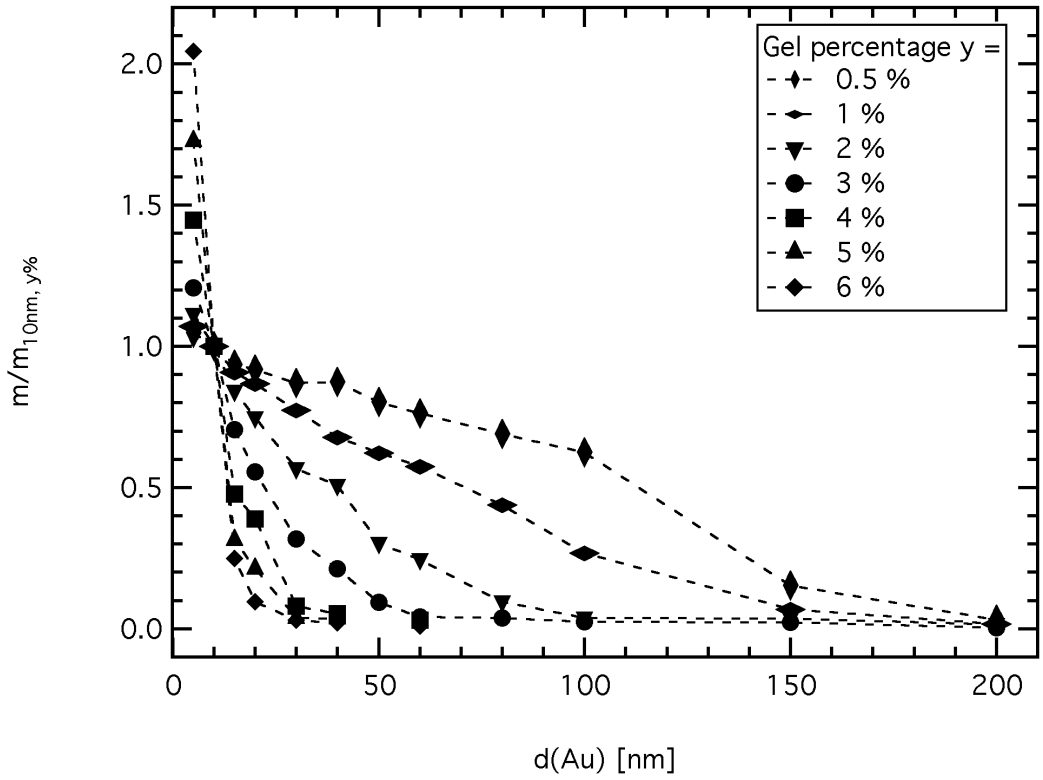

***Figure SI-2**: Relative electrophoretic mobility m / $m_{10nm,y\%}$ of Au nanoparticles of different hard core diameter d(Au) in agarose gels of different percentage (y = 0.5, 1, 2, 3, 4, 5, 6%). The data correspond to Table SI-4.*

I.5) Electrophoretic mobility of DNA

In Table SI-5 / Figure SI-3 and Table SI-6 / Figure SI-4 the electrophoretic mobilities of single stranded and double stranded DNA molecules (referring to the mobility of 10 nm Au particles) are shown, respectively.

	0.5% gel	1% gel	2% gel	3% gel	4% gel
DNA-sequence	$m / m_{10nm,0.5\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,3\%}$	$m / m_{10nm,4\%}$
Cy3-**8a**	1.12 ± 0.04	1.24 ± 0.05	1.47 ± 0.09	2.03 ± 0.22	2.84 ± 0.27
Cy3-**12**	1.15 ± 0.03	1.28 ± 0.04	1.53 ± 0.10	2.06 ± 0.21	2.84 ± 0.27
Cy3-**16**	1.19 ± 0.03	1.28 ± 0.04	1.53 ± 0.08	2.00 ± 0.20	2.68 ± 0.27
Cy3-**21**	1.18 ± 0.04	1.30 ± 0.05	1.53 ± 0.08	1.92 ± 0.19	2.54 ± 0.24
Cy3-**24**	-	1.30 ± 0.04	1.50 ± 0.07	1.88 ± 0.19	-
Cy3-**30**	1.16 ± 0.03	1.25 ± 0.06	1.42 ± 0.08	1.76 ± 0.18	2.33 ± 0.23
Cy3-**36a**	1.13 ± 0.03	1.21 ± 0.04	1.37 ± 0.06	1.66 ± 0.17	2.18 ± 0.21
Cy3-**36b**	1.19 ± 0.03	1.27 ± 0.04	1.46 ± 0.07	1.80 ± 0.18	2.37 ± 0.23
Cy3-**43a**	1.18 ± 0.03	1.25 ± 0.04	1.41 ± 0.07	1.71 ± 0.17	2.23 ± 0.21
Cy3-**43b**	1.14 ± 0.03	1.21 ± 0.04	1.34 ± 0.06	1.62 ± 0.16	2.11 ± 0.20
Cy3-**54**	1.12 ± 0.03	1.17 ± 0.05	1.29 ± 0.06	1.51 ± 0.15	1.91 ± 0.18
Cy3-**65**	1.11 ± 0.03	1.15 ± 0.04	1.23 ± 0.06	1.42 ± 0.14	1.77 ± 0.17
Cy3-**85**	1.08 ± 0.03	1.12 ± 0.04	1.16 ± 0.06	1.30 ± 0.14	1.56 ± 0.15
Cy3-**100a**	1.07 ± 0.03	1.10 ± 0.04	1.13 ± 0.06	1.26 ± 0.14	1.48 ± 0.15

	5% gel	6% gel
DNA-sequence	$m / m_{10nm,5\%}$	$m / m_{10nm,6\%}$
Cy3-**8a**	4.79 ± 0.92	7.73 ± 1.73
Cy3-**12**	4.49 ± 0.88	7.14 ± 1.58
Cy3-**16**	4.34 ± 0.83	6.68 ± 1.48
Cy3-**21**	4.02 ± 0.77	5.99 ± 1.33
Cy3-**24**	-	-
Cy3-**30**	3.60 ± 0.70	5.29 ± 1.17
Cy3-**36a**	3.27 ± 0.62	4.81 ± 1.06
Cy3-**36b**	3.65 ± 0.72	5.21 ± 1.15
Cy3-**43a**	3.29 ± 0.63	4.74 ± 1.05
Cy3-**43b**	3.19 ± 0.63	4.57 ± 1.01
Cy3-**54**	2.72 ± 0.52	3.92 ± 0.89
Cy3-**65**	2.42 ± 0.48	3.53 ± 0.81
Cy3-**85**	2.00 ± 0.39	2.80 ± 0.67
Cy3-**100a**	1.84 ± 0.37	2.56 ± 0.66

***Table SI-5**: Electrophoretic mobility m of single stranded DNA molecules on agarose gels of different percentage y (y = 0.5, 1, 2, 3, 4, 5, 6%). The DNA sequences are listed in Table SI-2. DNA molecules with a Cy3-fluorophore attached to their 5' end were used. The number of bases per DNA strand is indicated by the number in the name of the sequence. The mobility of the DNA molecules is always given relative to the mobility $m_{10nm,y\%}$ of phosphine-coated Au nanoparticles of 10 nm diameter on the same gel. The mobilities of the reference Au particles $m_{10nm,y\%}$ are given in Table SI-3. The data of this table are graphically displayed in Figure SI-3.*

	0.5% gel	1% gel	2% gel	3% gel
length of DNA [base pairs]	$m / m_{10nm,0.5\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,3\%}$
100	1.16 ± 0.05	1.18 ± 0.04	1.16 ± 0.07	1.21 ± 0.14
200	-	1.11 ± 0.05	1.01 ± 0.08	0.94 ± 0.12
300	-	1.04 ± 0.06	0.89 ± 0.08	0.77 ± 0.11
400	-	0.98 ± 0.06	0.80 ± 0.08	0.65 ± 0.10
500	-	0.93 ± 0.06	0.72 ± 0.08	0.57 ± 0.09
600	-	0.89 ± 0.06	0.66 ± 0.08	0.51 ± 0.09
700	-	0.85 ± 0.06	0.61 ± 0.08	0.46 ± 0.09
800	-	0.81 ± 0.06	0.58 ± 0.07	0.43 ± 0.09
900	-	0.78 ± 0.06	0.54 ± 0.07	0.38 ± 0.09
1000	1.00 ± 0.06	0.72 ± 0.12	0.50 ± 0.07	0.33 ± 0.07

	4% gel	5% gel	6% gel
length of DNA [base pairs]	$m / m_{10nm,4\%}$	$m / m_{10nm,5\%}$	$m / m_{10nm,6\%}$
100	1.27 ± 0.13	1.30 ± 0.28	1.54 ± 0.41
200	0.86 ± 0.10	0.74 ± 0.17	0.88 ± 0.26
300	0.66 ± 0.08	0.54 ± 0.12	0.65 ± 0.20
400	0.52 ± 0.07	0.42 ± 0.09	0.63 ± 0.15
500	0.44 ± 0.06	0.35 ± 0.08	0.55 ± 0.12
600	0.38 ± 0.05	0.31 ± 0.06	-
700	0.35 ± 0.04	-	-
800	0.34 ± 0.04	-	-
900	-	-	-
1000	0.24 ± 0.06	0.22 ± 0.05	-

***Table SI-6**: Electrophoretic mobility m of double stranded DNA molecules on agarose gels of different percentage y (y = 0.5, 1, 2, 3, 4, 5, 6%). Double stranded DNA of different length was used (a so called DNA-ladder). The double stranded DNA molecules were modified with a fluorescein label for visualization (1 kb DNA ladder, #15615, Gibco, USA). The mobility of the DNA molecules is always given relative to the mobility $m_{10nm,y\%}$ of phosphine-coated Au nanoparticles of 10 nm diameter on the same gel. The mobilities of the reference Au particles $m_{10nm,y\%}$ are given in Table SI-3. The data of this table are displayed in Figure SI-4.*

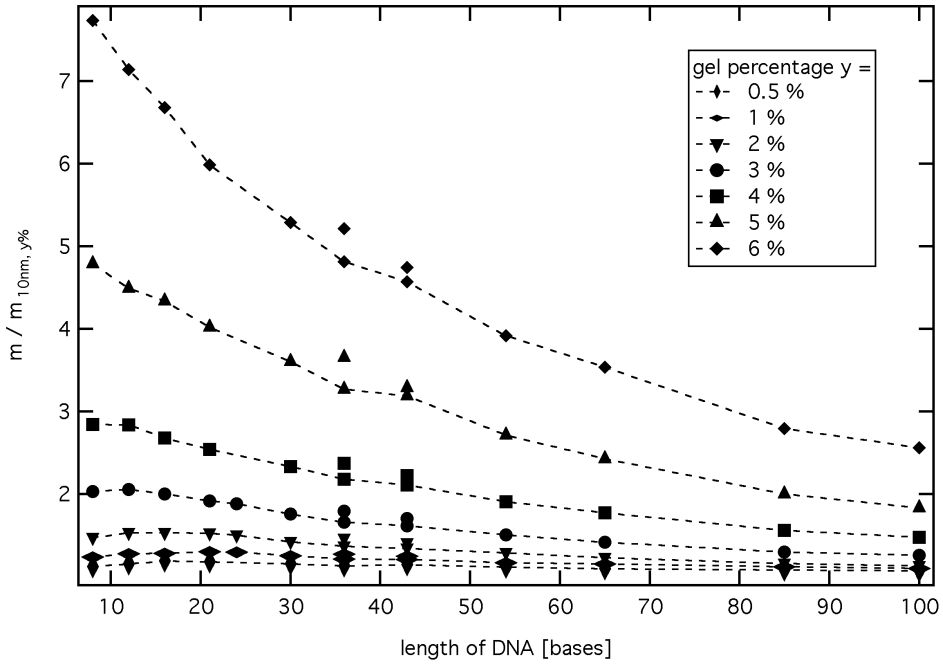

***Figure SI-3**: Electrophoretic mobility m of single stranded DNA molecules on agarose gels of different percentage y (y = 0.5, 1, 2, 3, 4, 5, 6%) in dependence of the length of the DNA. The mobility of the DNA molecules is given relative to the mobility $m_{10nm,y\%}$ of phosphine-coated Au nanoparticles of 10 nm diameter on the same gel. This graph corresponds to the data of Table SI-5.*

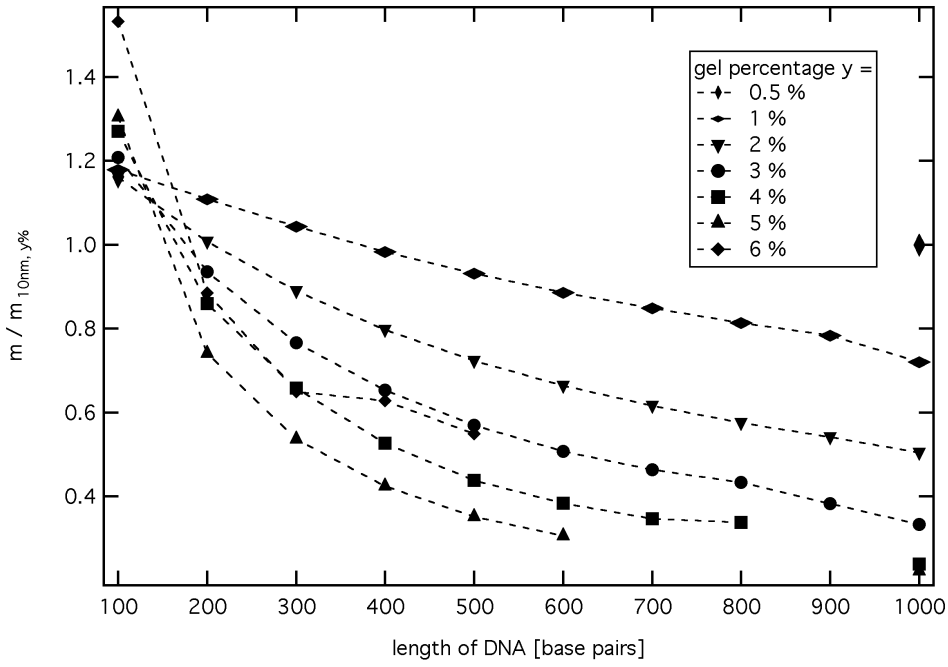

***Figure SI-4**: Electrophoretic mobility m of double stranded DNA molecules on agarose gels of different percentage y (y = 0.5, 1, 2, 3, 4, 5, 6%) in dependence of the length of the DNA. The mobility of the DNA molecules is always relative to the mobility $m_{10nm,y\%}$ of phosphine-coated Au nanoparticles of 10 nm diameter on the same gel. This graph corresponds to the data of Table SI-6.*

I.6) Electrophoretic mobility of Au-DNA conjugates: Extracted Parameters

Au-DNA conjugates with different DNA/Au ratios were prepared as shown in I.2 and run on gels of different percentage as shown in I.3. An example is shown in Figure SI-5. When DNA is attached to Au particles the Au-DNA conjugate becomes bigger than the plain Au particle. This has been discussed in detail in our previous manuscripts [1, 3]. In this way we explain the retardation on the gel of the Au-DNA conjugates on the gel compared to the plain Au-particles as sorting by size. We believe that the addition of DNA to the particles does not significantly change the surface charge density of the particles. This might be explained by the fact that the oligonucleotides are closely packed on the Au surface and that at the used salt concentrations all the charges in the inside of the DNA shell are screened with counter ions. When the particle surface is saturated with DNA, then also a saturation of the retardation of the mobility can be seen (Figure SI-5). From each gel the mobility m of the saturated particles is extracted. This is described in I.7. When only few DNA molecules are added per Au particle discrete bands in the gel can be seen. These bands are referred to Au particles with exactly one, two, three, etc... DNA molecules bound per particle manuscripts [1, 3]. From each gel also the mobility m of these bands is extracted, as will be described in I.8. For each different DNA sequence Au-DNA conjugates with variable DNA/Au ratio have been made and run on a gel. From each gel the following data can be extracted: the saturation mobility and in the case of long-enough DNA the mobility of the conjugates with exactly one, two, etc... DNA strands attached per each particle.

For all the data shown in I.7 and I.8 the mobility of the conjugates m was always referred to the mobility of the plain, unconjugated Au nanoparticles $m_{x,y}$ (with the same Au x size and gel percentage y). For each DNA sequence, particle size, and gel percentage at least 3 different gels were run. The data shown correspond to the mean values and their standard deviations.

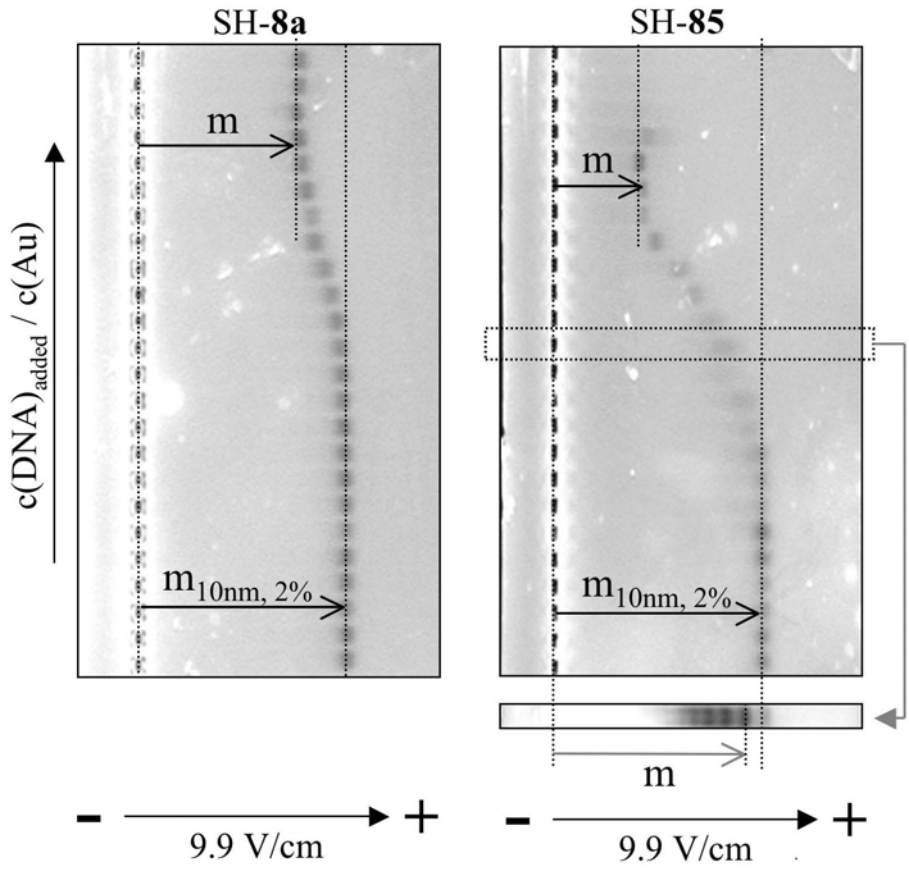

Figure SI-5*: Thiolated single stranded DNA with a length of 8 and 85 bases (sequences SH-8a and SH-85) has been added in different concentrations to 10 nm Au particles. For the two gels the DNA/Au ratio had been varied in 24 steps between 10000, 5000, 2500,....., whereby the absolute concentration of the Au particles was 0.05 μM. After mixing the Au-DNA conjugates were incubated 7 days. For the two upper diagrams very high DNA/Au ratios were used. Therefore we used as low absolute Au concentrations as possible in order to keep the absolute amount of required DNA minimum. After incubation the 24 samples were run on a 2% agarose gel 1 hour at 100 V, whereby the sample were loaded on the gel so that the sample with the highest DNA/Au ratio was on the upper lane of the gel. For very low DNA/Au ratios (lanes on the bottom part of the gel) basically no DNA is attached per Au particle and the "conjugates" run with the same mobility $m_{10nm,2\%}$ as plain, unconjugated Au particles. When more DNA is added per particle the size of the conjugates gets bigger and the particles are retarded on the gel. At one point the surface of the particles is saturated with DNA and the mobility does not decrease further upon addition of more free DNA (see the lanes on the top of the gel). Under this condition the mobility m of the conjugates remains constant. We refer to this mobility as saturation mobility. It is the mobility of particles saturated with DNA. When only as much DNA has been added to the particles that the bands just start being retarded, the bands also appear broader. In this regime the particles with one, two, and three DNA molecules per particle appear. In order to visualize these conjugates better, different incubation conditions have to be used. Higher Au concentrations (1 μM) and only one hour of incubation before running the conjugates on the gel were used. This reduced nonspecific adhesion of DNA to the particles and the bands remained sharper. An example is shown in the bottom part of the figure. The arrow indicates here the mobility m of Au particles, which have exactly one strand of DNA attached per particle.*

I.7) Electrophoretic mobility of Au-DNA conjugates: Au particles saturated with DNA

Au-DNA conjugates were prepared for different DNA sequences, Au particle diameters with variable DNA/Au ratios and run on gels of different agarose percentage as described in I.6. From each gel the mobility of the particles saturated with DNA was determined and related to the mobility of the plain Au particles. The saturation mobilities (i.e. the mobilities of Au particles whose surface is saturated with DNA) were determined and are shown in Tables SI-7.1 - SI-7.4 and in Figures SI-6.1 - SI-6.4.

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$m / m_{5nm,1\%}$	$m / m_{10nm,1\%}$	$m / m_{15nm,1\%}$	$m / m_{20nm,1\%}$
SH-**8a**	0.86 ± 0.01	0.87 ± 0.02	-	0.86 ± 0.02
Cy3-**8a**-SH	-	0.87 ± 0.03	-	-
Cy5-**8a**-SH	-	0.89 ± 0.02	-	-
8a	0.97 ± 0.01	0.98 ± 0.03	-	0.97 ± 0.02
SH-**12**	0.79 ± 0.01	0.82 ± 0.02	-	0.82 ± 0.01
12	-	0.94 ± 0.01	-	-
SH-**16**	0.77 ± 0.02	0.77 ± 0.03	-	0.75 ± 0.01
SH-**21**	0.71 ± 0.03	0.72 ± 0.03	-	-
21	0.91 ± 0.06	0.94 ± 0.02	-	0.80 ± 0.10
SH-**30**	0.67 ± 0.01	0.69 ± 0.04	-	0.66 ± 0.02
30	0.92 ± 0.01	0.96 ± 0.01	-	-
SH-**35**	0.68 ± 0.02	0.69 ± 0.04	-	-
SH-**36a**	0.64 ± 0.13	0.70 ± 0.03	-	-
36a	0.87 ± 0.04	0.84 ± 0.06	-	0.75 ± 0.16
SH-**36b**	-	0.71 ± 0.02	-	-
SH-**43a**	0.74 ± 0.05	0.76 ± 0.02	0.74 ± 0.06	0.71 ± 0.01
Cy5-**43a**-SH	0.73 ± 0.02	0.74 ± 0.02	-	-
SH-**43b**	0.64 ± 0.02	0.60 ± 0.02	-	-
SH-**50**	0.59 ± 0.02	0.60 ± 0.02	-	-
SH-**54**	0.58 ± 0.01	0.57 ± 0.06	-	0.63 ± 0.07
SH-**65**	-	0.57 ± 0.03	-	-
SH-**85**	-	0.59 ± 0.07	-	-
SH-**100a**	0.46 ± 0.01	0.52 ± 0.09	-	-
100a	0.80 ± 0.11	0.82 ± 0.02	-	0.78 ± 0.08
SH-**120**	-	0.64 ± 0.11	-	-
SH-**135**	-	0.40 ± 0.10	-	-

Table SI-7.1*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used.* ***30*** *refers to DNA of 30 bases length. SH-****35*** *refers to DNA of 35 bases length that was modified with a -SH group at the 5' end. Cy5-****43a****-SH refers to DNA of 43 bases length that was modified with a Cy5 dye at the 5' end and a -SH group at the 3' end. DNA without -SH groups could only adsorb nonspecifically to the surface of Au nanoparticles, whereas DNA with -SH modification was bound to Au-particles via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels in 0.5×TBE buffer. The mobility of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-6.1.*

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$m / m_{5nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{15nm,2\%}$	$m / m_{20nm,2\%}$
SH-**8a**	0.84 ± 0.02	0.81 ± 0.03	-	0.80 ± 0.02
8a-SH	-	0.83 ± 0.02	-	-
Cy3-**8a**-SH	-	0.83 ± 0.02	-	-
Cy5-**8a**-SH	0.80 ± 0.02	0.80 ± 0.03	-	-
Tamra-**8a**-SH	-	0.79 ± 0.02	-	-
8a	0.98 ± 0.01	0.97 ± 0.04	-	0.96 ± 0.03
8b-SH	-	0.84 ± 0.01	-	-
SH-**12**	0.74 ± 0.04	0.72 ± 0.04	-	0.75 ± 0.02
12	-	0.96 ± 0.02	-	-
SH-**16**	0.66 ± 0.04	0.67 ± 0.04	-	0.66 ± 0.01
SH-**21**	0.60 ± 0.04	0.59 ± 0.06	-	-
21	0.88 ± 0.08	0.92 ± 0.02	-	0.79 ± 0.11
SH-**30**	0.53 ± 0.06	0.52 ± 0.04	-	0.47 ± 0.05
30	0.89 ± 0.01	0.95 ± 0.02	-	-
SH-**35**	0.48 ± 0.03	0.54 ± 0.09	-	-
SH-**36a**	0.55 ± 0.04	0.51 ± 0.09	-	-
36a	0.86 ± 0.06	0.79 ± 0.07	-	0.77 ± 0.16
SH-**36b**	-	0.54 ± 0.03	-	-
SH-**43a**	0.57 ± 0.04	0.55 ± 0.02	0.56 ± 0.05	0.53 ± 0.06
Cy5-**43a**-SH	0.55 ± 0.03	0.57 ± 0.03	-	-
SH-**43b**	0.44 ± 0.02	0.44 ± 0.04	-	-
SH-**50**	0.39 ± 0.02	0.34 ± 0.04	-	-
SH-**54**	0.34 ± 0.05	0.35 ± 0.04	-	0.39 ± 0.07
SH-**65**	-	0.32 ± 0.07	-	-
SH-**85**	-	0.31 ± 0.07	-	-
SH-**100a**	0.20 ± 0.01	0.21 ± 0.10	-	-
100a	0.67 ± 0.19	0.68 ± 0.05	-	0.90 ± 0.11
SH-**120**	-	0.34 ± 0.11	-	-
SH-**135**	-	0.07 ± 0.06	-	-

Table SI-7.2*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used.* ***30*** *refers to DNA of 30 bases length. SH-****35*** *refers to DNA of 35 bases length that was modified with a -SH group at the 5' end. Cy5-****43a****-SH refers to DNA of 43 bases length that was modified with a Cy5 dye at the 5' end and a -SH group at the 3' end. DNA without -SH groups could only adsorb nonspecifically to the surface of Au nanoparticles, whereas DNA with -SH modification was bound to Au-particles via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-6.2.*

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$m / m_{5nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{15nm,3\%}$	$m / m_{20nm,3\%}$
SH-**8a**	0.79 ± 0.01	0.75 ± 0.04	-	0.70 ± 0.07
8a-SH	-	-	-	-
Cy3-**8a**-SH	-	0.72 ± 0.03	-	-
Cy5-**8a**-SH	-	0.74 ± 0.07	-	-
Tamra-**8a**-SH	-	-	-	-
8a	0.96 ± 0.01	0.94 ± 0.06	-	0.94 ± 0.05
8b-SH	-	-	-	-
SH-**12**	0.61 ± 0.01	0.59 ± 0.09	-	0.62 ± 0.02
12	-	0.91 ± 0.02	-	-
SH-**16**	0.63 ± 0.15	0.52 ± 0.06	-	-
SH-**21**	0.44 ± 0.01	0.43 ± 0.08	-	-
21	0.88 ± 0.06	0.87 ± 0.02	-	0.76 ± 0.08
SH-**30**	0.33 ± 0.05	0.31 ± 0.09	-	0.26 ± 0.04
30	0.85 ± 0.01	0.92 ± 0.04	-	-
SH-**35**	0.28 ± 0.05	0.35 ± 0.02	-	-
SH-**36a**	0.35 ± 0.11	0.36 ± 0.02	-	-
36a	0.80 ± 0.07	0.76 ± 0.06	-	0.69 ± 0.23
SH-**36b**	-	0.32 ± 0.02	-	-
SH-**43a**	0.40 ± 0.11	0.34 ± 0.07	0.40 ± 0.04	0.33 ± 0.04
Cy5-**43a**-SH	0.38 ± 0.04	0.37 ± 0.05	-	-
SH-**43b**	0.24 ± 0.04	0.23 ± 0.06	-	-
SH-**50**	0.19 ± 0.02	0.15 ± 0.02	-	-
SH-**54**	0.17 ± 0.03	0.19 ± 0.05	-	0.19 ± 0.11
SH-**65**	-	0.11 ± 0.02	-	-
SH-**85**	-	0.09 ± 0.04	-	-
SH-**100a**	0.06 ± 0.01	0.07 ± 0.05	-	-
100a	0.60 ± 0.08	0.64 ± 0.08	-	0.85 ± 0.11
SH-**120**	-	0.04 ± 0.04	-	-
SH-**135**	-	0.02 ± 0.02	-	-

Table SI-7.3*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used.* ***30*** *refers to DNA of 30 bases length. SH-****35*** *refers to DNA of 35 bases length that was modified with a -SH group at the 5' end. Cy5-****43a****-SH refers to DNA of 43 bases length that was modified with a Cy5 dye at the 5' end and a -SH group at the 3' end. DNA without -SH groups could only adsorb nonspecifically to the surface of Au nanoparticles, whereas DNA with -SH modification was bound to Au-particles via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-6.3.*

	0.5% gel	1% gel	2% gel	3% gel
DNA-sequence	$m / m_{10nm,0.5\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,3\%}$
SH-**30**	0.77 ± 0.01	0.69 ± 0.04	0.52 ± 0.04	0.31 ± 0.09
SH-**36a**	0.81 ± 0.04	0.70 ± 0.03	0.51 ± 0.09	0.36 ± 0.02
SH-**43a**	0.81 ± 0.02	0.76 ± 0.02	0.55 ± 0.02	0.34 ± 0.07
SH-**50**	0.66 ± 0.02	0.60 ± 0.02	0.34 ± 0.04	0.15 ± 0.02
SH-**100a**	-	0.52 ± 0.09	0.21 ± 0.10	0.07 ± 0.05

	4% gel	5% gel	6% gel
DNA-sequence	$m / m_{10nm,4\%}$	$m / m_{10nm,5\%}$	$m / m_{10nm,6\%}$
SH-**30**	0.13 ± 0.03	0.03 ± 0.03	0.03 ± 0.03
SH-**36a**	-	-	-
SH-**43a**	0.16 ± 0.03	0.06 ± 0.02	0.03 ± 0.03
SH-**50**	0.03 ± 0.04	0.00 ± 0.00	0.00 ± 0.00
SH-**100a**	0.03 ± 0.02	0.01 ± 0.01	0.02 ± 0.02

***Table SI-7.4**: Au particles of 10 nm diameter have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with thiol modification was used. SH-**43a** refers to DNA of 43 bases length that was modified with a -SH group at the 5' end. The DNA with -SH modification was bound to Au-particles via the formation of thiol-gold bonds. The Au-DNA conjugates were run on gels of different agarose percentage (0.5%, 1%, 2%, 3%, 4%, 5%, 6% w/v). The mobility of the Au-DNA conjugates (with the maximum number of attached DNA) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-6.4. Part of the data is the same as displayed in Table SI-6.1, Table SI-6.2, and Table SI-6.3.*

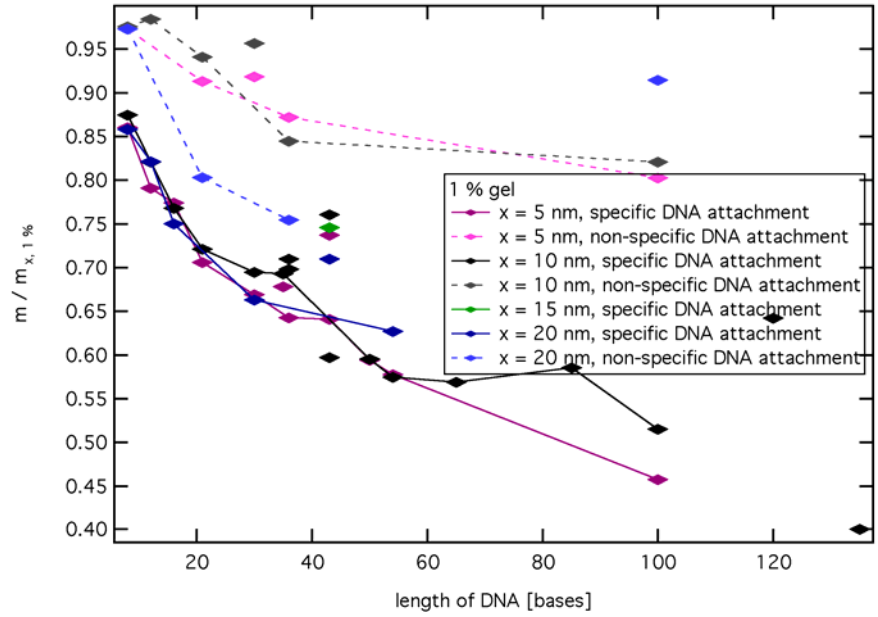

Figure SI-6.1*: Single-stranded DNA has been attached to Au nanoparticles of different diameter (x = 5, 10, 15, 20 nm) either nonspecifically or via the formation of specific thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. The mobility of the Au-DNA conjugates that were saturated with DNA relative to the mobility of the plain Au particles* $m/m_{x,\,1\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-7.1.*

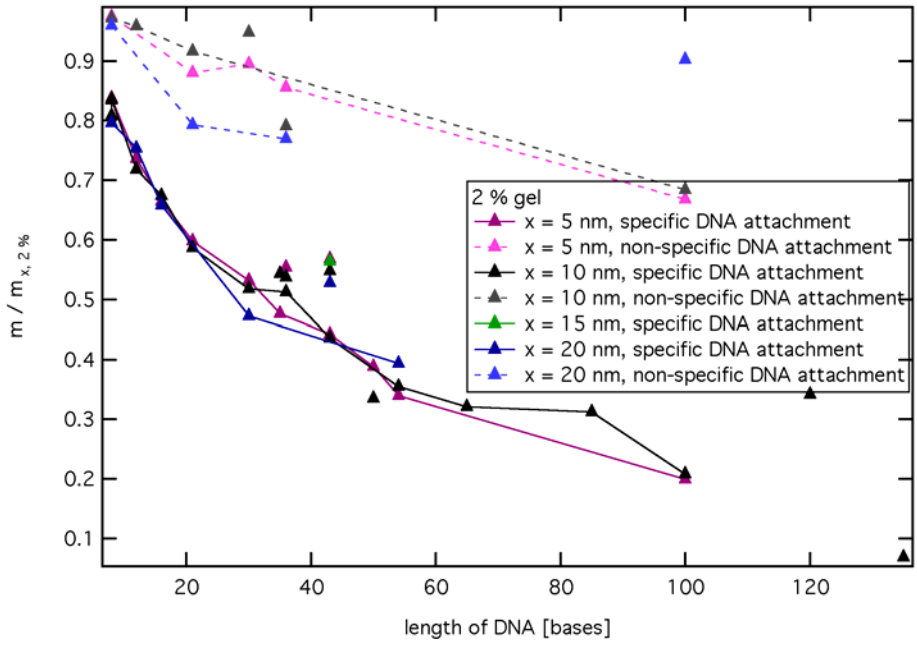

Figure SI-6.2*: Single-stranded DNA has been attached to Au nanoparticles of different diameter (x = 5, 10, 15, 20 nm) either nonspecifically or via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the Au-DNA conjugates that were saturated with DNA relative to the mobility of the plain Au particles* $m/m_{x,\,2\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-7.2.*

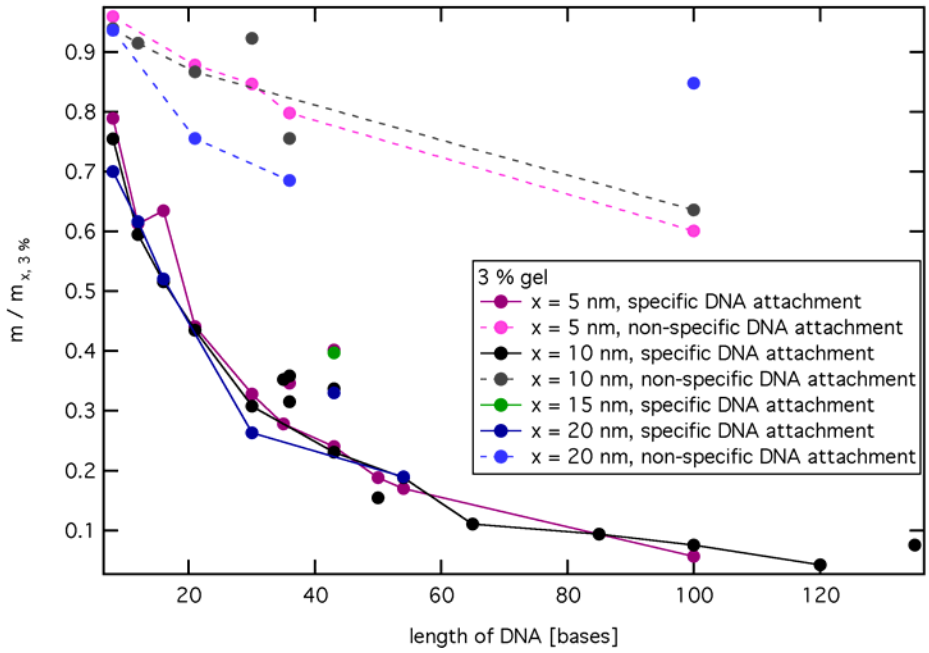

Figure SI-6.3*: Single-stranded DNA has been attached to Au nanoparticles of different diameter (x = 5, 10, 15, 20 nm) either nonspecifically or via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the Au-DNA conjugates that were saturated with DNA relative to the mobility of the plain Au particles* $m/m_{x,\ 3\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-7.3.*

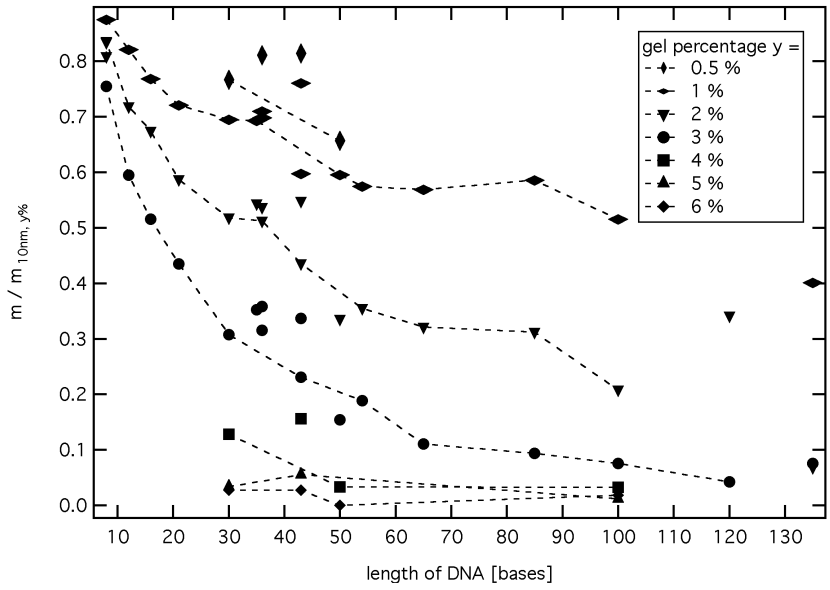

Figure SI-6.4*: Single-stranded DNA has been attached to Au nanoparticles of 10 nm diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on agarose gels of different percentage (y = 0.5%, 1%, 2%, 3%, 4%, 5%, 6%). The mobility of the Au-DNA conjugates that were saturated with DNA relative to the mobility of the plain Au particles* $m/m_{10\ nm,\ y}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-7.4.*

I.8) Electrophoretic mobility of Au-DNA conjugates: Au particles with a few strands of DNA

Au-DNA conjugates have been synthesized for different DNA sequences, Au particle diameters and have been run on gels of different agarose percentage. For long enough DNA sequences (≥ 43 bases) discrete bands on the gel could be observed, as shown in I.6. These bands are attributed to Au-DNA conjugates with an exactly known number of DNA molecules (1, 2, ...) per particle. The mobilities of these conjugates were related to the mobility of the plain Au particles. The results for 10 nm Au particles for different DNA sequences and different gel percentages are shown in Tables SI-8.1 - SI-8.3 and Figures SI-7.1 - SI-7.3. The results for DNA of 100 bases length are shown for different Au particles sizes and gel percentages in Tables SI-9.1 - SI-9.4 and Figures SI-8.1 - SI-8.4.

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$
1	0.98 ± 0.02	0.97 ± 0.01	0.98 ± 0.01	0.97 ± 0.01
2	0.95 ± 0.02	0.94 ± 0.02	0.95 ± 0.01	0.94 ± 0.01
3	0.93 ± 0.02	0.92 ± 0.02	0.92 ± 0.01	0.91 ± 0.01
4	0.90 ± 0.02	0.89 ± 0.02	0.89 ± 0.01	0.87 ± 0.01
5	0.87 ± 0.02	0.87 ± 0.02	0.87 ± 0.01	0.85 ± 0.01
6	0.86 ± 0.03	-	0.85 ± 0.01	0.83 ± 0.02
7	-	-	0.83 ± 0.01	-

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$	$m / m_{10nm,1\%}$
1	0.96 ± 0.01	0.97 ± 0.01	0.95 ± 0.01	0.95 ± 0.03
2	0.93 ± 0.01	0.93 ± 0.01	0.90 ± 0.02	-
3	0.89 ± 0.02	0.89 ± 0.01	0.86 ± 0.03	-
4	0.85 ± 0.02	0.86 ± 0.02	0.82 ± 0.03	-
5	0.82 ± 0.02	0.83 ± 0.02	0.77 ± 0.05	-
6	0.79 ± 0.03	0.80 ± 0.02	0.72 ± 0.07	-
7	0.77 ± 0.03	0.78 ± 0.02	0.69 ± 0.08	-

Table SI-8.1*: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. SH-**85** refers to DNA of 85 bases length that was modified with a -SH group at the 5' end. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 1% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-7.1.*

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$
1	0.95 ± 0.01	0.94 ± 0.01	0.94 ± 0.00	0.93 ± 0.1
2	0.90 ± 0.01	0.88 ± 0.01	0.88 ± 0.00	0.86 ± 0.02
3	0.86 ± 0.02	0.83 ± 0.02	0.83 ± 0.01	0.80 ± 0.03
4	0.80 ± 0.03	0.78 ± 0.02	0.78 ± 0.01	0.74 ± 0.03
5	0.77 ± 0.03	0.74 ± 0.03	0.73 ± 0.01	0.69 ± 0.03
6	0.73 ± 0.03	0.71 ± 0.04	0.71 ± 0.01	0.65 ± 0.03
7	0.70 ± 0.04	0.68 ± 0.04	0.67 ± 0.02	0.61 ± 0.03
8	-	-	0.65 ± 0.03	-
9	-	-	0.63 ± 0.03	-

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,2\%}$
1	0.91 ± 0.02	0.90 ± 0.01	0.91 ± 0.01	0.87 ± 0.01
2	0.83 ± 0.03	0.81 ± 0.03	0.78 ± 0.02	0.76 ± 0.02
3	0.76 ± 0.04	0.73 ± 0.03	0.70 ± 0.04	0.67 ± 0.02
4	0.70 ± 0.04	0.66 ± 0.04	0.63 ± 0.04	-
5	0.63 ± 0.04	0.62 ± 0.03	0.57 ± 0.04	-
6	0.58 ± 0.04	0.56 ± 0.03	0.52 ± 0.04	-
7	0.54 ± 0.04	0.53 ± 0.03	0.51 ± 0.04	-
8	-	0.49 ± 0.03	0.49 ± 0.04	-
9	-	0.47 ± 0.04	-	-

Table SI-8.2*: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. SH-**85** refers to DNA of 85 bases length that was modified with a -SH group at the 5' end. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-7.2.*

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$
1	0.91 ± 0.01	0.91 ± 0.01	0.90 ± 0.01	0.87 ± 0.01
2	0.82 ± 0.01	0.81 ± 0.01	0.81 ± 0.02	0.76 ± 0.03
3	0.75 ± 0.01	0.73 ± 0.01	0.73 ± 0.03	0.65 ± 0.03
4	0.69 ± 0.02	0.67 ± 0.02	0.67 ± 0.03	0.58 ± 0.03
5	0.64 ± 0.02	0.60 ± 0.01	0.60 ± 0.03	0.51 ± 0.03
6	0.58 ± 0.03	0.56 ± 0.01	0.55 ± 0.03	0.46 ± 0.04
7	0.55 ± 0.03	0.52 ± 0.02	0.50 ± 0.03	0.41 ± 0.04
8	-	0.49 ± 0.02	0.48 ± 0.03	0.38 ± 0.04
9	-	0.46 ± 0.03	0.44 ± 0.03	0.35 ± 0.04

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{10nm,3\%}$
1	0.83 ± 0.04	0.82 ± 0.03	0.82 ± 0.02	0.77 ± 0.01
2	0.68 ± 0.06	0.67 ± 0.05	0.61 ± 0.03	0.60 ± 0.03
3	0.56 ± 0.07	0.55 ± 0.06	0.49 ± 0.04	0.47 ± 0.04
4	0.47 ± 0.07	0.46 ± 0.06	0.39 ± 0.05	-
5	0.39 ± 0.07	0.39 ± 0.06	0.32 ± 0.05	-
6	0.34 ± 0.07	0.32 ± 0.06	0.28 ± 0.05	-
7	0.30 ± 0.07	0.27 ± 0.06	0.23 ± 0.06	-
8	-	0.24 ± 0.06	-	-
9	-	0.23 ± 0.06	-	-

***Table SI-8.3**: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. SH-**85** refers to DNA of 85 bases length that was modified with a -SH group at the 5' end. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-7.3.*

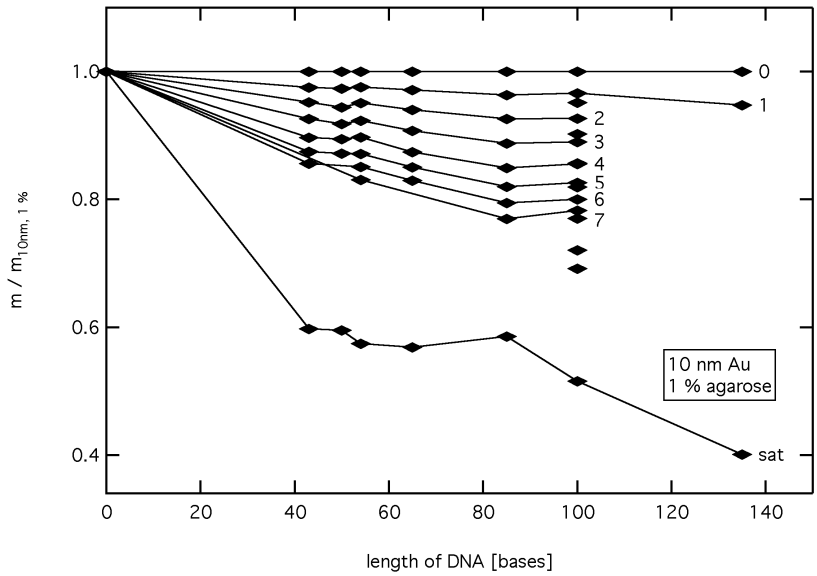

Figure SI-7.1*: Single-stranded DNA has been attached to Au nanoparticles of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain 10 nm Au particles* $m/m_{10nm,1\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-8.1. In addition the mobilities of Au nanoparticles saturated with DNA ("sat") are displayed (taken from Table SI-7.1).*

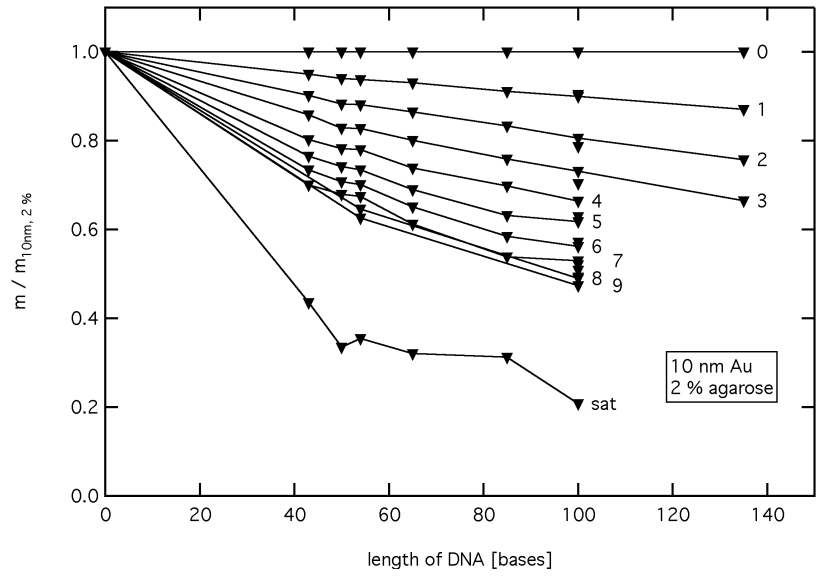

Figure SI-7.2*: Single-stranded DNA has been attached to Au nanoparticles of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles* $m/m_{10nm,2\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-8.2. In addition the mobilities of Au nanoparticles saturated with DNA ("sat") are displayed (taken from Table SI-7.2).*

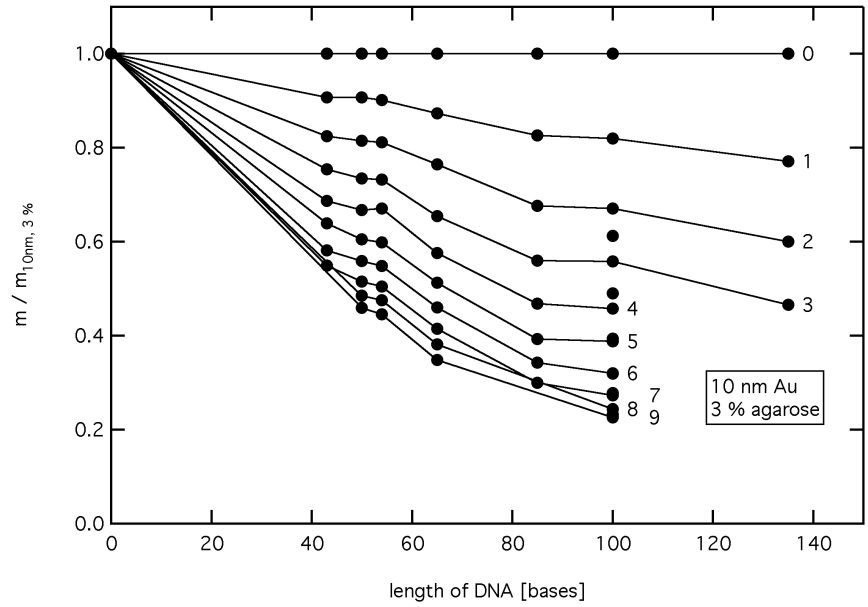

Figure SI-7.3*: Single-stranded DNA has been attached to Au nanoparticles of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles* $m/m_{10nm,3\%}$ *is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-8.3. In addition the mobilities of Au nanoparticles saturated with DNA ("sat") are displayed (taken from Table SI-7.3).*

	5 nm Au	10 nm Au
number of DNAs per particle	$m / m_{5nm,1\%}$	$m / m_{10nm,1\%}$
0	1.0	1.0
1	0.92 ± 0.03	0.97 ± 0.01
2	0.86 ± 0.05	0.93 ± 0.01
3	0.82 ± 0.04	0.89 ± 0.01
4	0.78 ± 0.06	0.86 ± 0.02
5	0.73 ± 0.06	0.83 ± 0.02
6	0.71 ± 0.05	0.80 ± 0.02
7	0.69 ± 0.05	0.78 ± 0.02

Table SI-9.1*: Au particles of 5 nm and 10 nm have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 1% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-8.1.*

	5 nm Au	10 nm Au	20 nm Au
number of DNAs per particle	$m / m_{5nm,2\%}$	$m / m_{10nm,2\%}$	$m / m_{20nm,2\%}$
0	1.0	1.0	1.0
1	0.85 ± 0.3	0.90 ± 0.01	0.87 ± 0.03
2	0.74 ± 0.5	0.81 ± 0.03	-
3	0.65 ± 0.07	0.73 ± 0.03	-
4	0.59 ± 0.08	0.66 ± 0.04	-
5	0.53 ± 0.09	0.62 ± 0.03	-
6	0.50 ± 0.9	0.56 ± 0.03	-
7	0.46 ± 0.9	0.53 ± 0.03	-
8	-	0.49 ± 0.03	-
9	-	0.47 ± 0.04	-

Table SI-9.2*: Au particles of 5 nm, 10 nm, and 20 nm have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-8.2.*

	5 nm Au	10 nm Au	20 nm Au
number of DNAs per particle	$m / m_{5nm,3\%}$	$m / m_{10nm,3\%}$	$m / m_{20nm,3\%}$
0	1.0	1.0	1.0
1	0.76 ± 0.04	0.82 ± 0.03	0.83 ± 0.04
2	0.60 ± 0.03	0.67 ± 0.05	0.71 ± 0.05
3	0.48 ± 0.03	0.55 ± 0.06	0.60 ± 0.07
4	0.40 ± 0.03	0.46 ± 0.06	0.51 ± 0.08
5	0.34 ± 0.03	0.39 ± 0.06	0.47 ± 0.07
6	0.30 ± 0.02	0.32 ± 0.06	0.41 ± 0.08
7	0.26 ± 0.02	0.27 ± 0.06	0.37 ± 0.08
8	-	0.24 ± 0.06	-
9	-	0.23 ± 0.06	-

Table SI-9.3*: Au particles of 5 nm, 10 nm, and 20 nm have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-8.3.*

	1% gel	2% gel	3% gel
number of DNAs per particle	$m / m_{10nm,1\%}$	$m / m_{10nm,2\%}$	$m / m_{10nm,3\%}$
0	1.0	1.0	1.0
1	0.97 ± 0.01	0.90 ± 0.01	0.82 ± 0.03
2	0.93 ± 0.01	0.81 ± 0.03	0.67 ± 0.05
3	0.89 ± 0.01	0.73 ± 0.03	0.55 ± 0.06
4	0.86 ± 0.02	0.66 ± 0.04	0.46 ± 0.06
5	0.83 ± 0.02	0.62 ± 0.03	0.39 ± 0.06
6	0.80 ± 0.02	0.56 ± 0.03	0.32 ± 0.06
7	0.78 ± 0.02	0.53 ± 0.03	0.27 ± 0.06
8	-	0.49 ± 0.03	0.24 ± 0.06
9	-	0.47 ± 0.04	0.23 ± 0.06

	4% gel	5% gel	6% gel
number of DNAs per particle	$m / m_{10nm,4\%}$	$m / m_{10nm,5\%}$	$m / m_{10nm,6\%}$
0	1.0	1.0	1.0
1	0.73 ± 0.01	0.58 ± 0.04	0.53 ± 0.03
2	0.53 ± 0.01	0.32 ± 0.04	0.27 ± 0.03
3	0.38 ± 0.02	0.18 ± 0.03	0.17 ± 0.03
4	0.28 ± 0.02	0.10 ± 0.03	-
5	0.21 ± 0.02	0.03 ± 0.03	-
6	0.16 ± 0.02	-	-
7	0.14 ± 0.03	-	-
8	-	-	-
9	-	-	-

Table SI-9.4*: Au particles of 10 nm have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on agarose gels with 1% - 6%. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles, see Figure SI-5. The data are graphically displayed in Figure SI-8.4.*

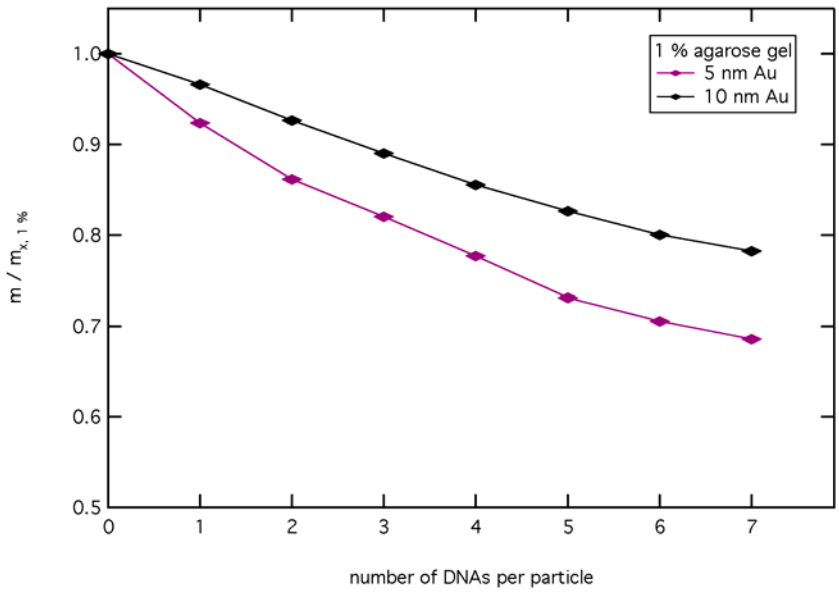

Figure SI-8.1*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm and 10 nm diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles $m/m_{x,1\%}$ is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-9.1.*

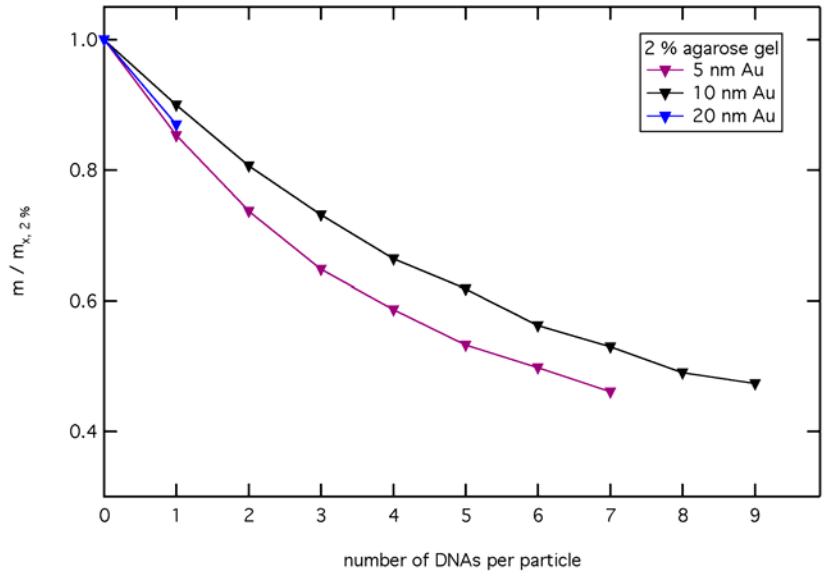

Figure SI-8.2*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm, 10 nm, and 20 nm diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles $m/m_{x,2\%}$ is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-9.2.*

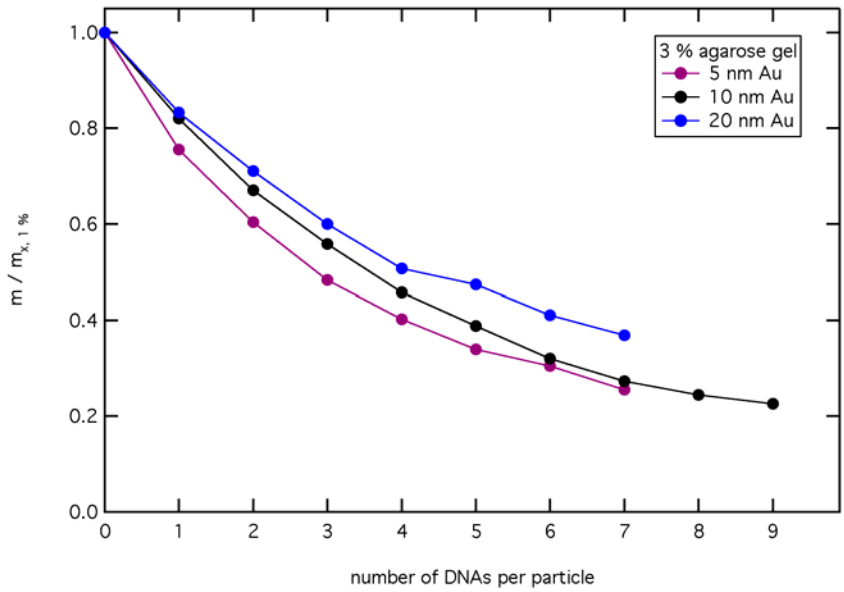

Figure SI-8.3*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm, 10 nm, and 20 nm diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles $m/m_{x,3\%}$ is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-9.3.*

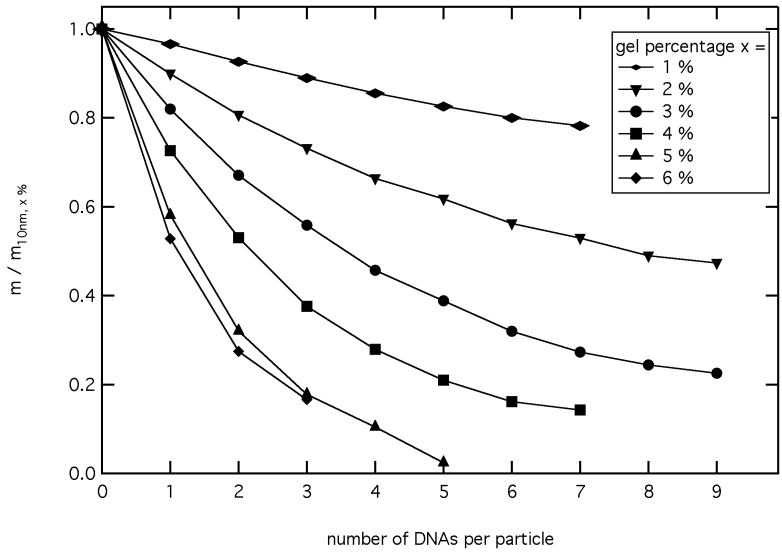

Figure SI-8.4*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 10 nm diameter of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on gels of different agarose percentage (y= 1% - 6%). Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles $m/m_{10nm,y\%}$ is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-9.4.*

I.9) Some comments about the mobilities of Au-DNA conjugates

As already reported in previously published work [3] the mobility of the nanoparticles decreases the more and the longer DNA has been attached specifically via thiol-gold bonds. The results for Au particles of different diameter and different agarose concentrations are qualitatively the same. Consequently the degree of retardation for attachment of the same number of DNA molecules of the same length to nanoparticles of different diameter is highest for the smallest nanoparticles, since here the relative increase in the effective diameter is the highest. This is of particular importance for the extraction of discrete bands with an exactly known number of DNA molecules attached per nanoparticle [1]. In the case of 10 nm diameter Au particles the binding of one single single-stranded DNA molecule of 43 bases yields a sufficient increase in the effective diameter so that this conjugates migrates on a band that is retarded enough on a 2% agarose gel that it can be clearly resolved from the band of plain Au nanoparticles. The increase in size upon attachment of one single DNA molecule with fewer bases is not big enough to yield a band that is well resolved from the band of plain Au particles. For 20 nm particles longer DNA molecules have to be attached in order to resolve discrete bands, whereas for 5 nm diameter particles discrete bands should be observable also for DNA with fewer bases. This number is important for the calculation of the minimum distance reachable for DNA-mediated assemblies of Au nanoparticles. Upon hybridization between Au-DNA conjugates of complementary DNA sequences the DNA between the Au particles is double stranded and thus relatively stiff (persistence length 50 nm [4]). By using the contour length of double stranded DNA (0.34 nm per base pair [4, 5]; under neglecting the thiol-anchor and spacer molecules between the DNA and the thiol group) 43 bases correspond to around 15 nm (in case more sophisticated structures in which part of the linker DNA would be single stranded and thus could be bent). Thus, the minimum distance between the surfaces of two DNA-mediated Au particles in an Au dimer is 15 nm. This is due to the fact that for the isolation of Au nanoparticles with exactly one strand of DNA the length of the DNA has to be at least 43 bases in order to be resolved on an agarose gel. In previous work a Au to Au distance of 29 nm in dimers of 10 nm Au nanoparticles could be directly observed with transmission electron microscopy (TEM) using 50 base pair DNA[2].

II) Gel Electrophoresis of Gold-DNA Nano-Conjugates - Data Evaluation

II.1) Effective diameter of Au-DNA conjugates

In I) the mobilities of Au-DNA conjugates are investigated in dependence of the diameter of the Au particles, of the length of the DNA, of the number of DNA molecules attached per particle, and of the gel percentage. However, the mobility is not an illustrative quantity. Therefore we intended to convert the mobilities in effective diameters of the Au-DNA conjugates. The more DNA is attached per Au particle, the bigger conjugate will be and the slower its mobility is. For the conversion we have applied two different methods, which are described in II.2 and II.3.

II.2) Calibration curve for the size dependent of the electrophoretic mobility

The idea of this approach is to make a calibration curve that relates mobility to size. For this purpose phosphine-coated Au particles of different size have been run on gels with different percentage and their mobilities have been obtained, see Tables SI-3 and SI-4 and Figure SI-2. For all the following we assume that the mobility in our experiments predominantly only depends on size and not on charge. Tables SI-3 and SI-4 and Figure SI-2 relate to the diameter d(Au) of the Au cores. However, since the Au cores are coated with a monolayer of phosphine-molecules, we have to consider an effective diameter $d_{eff}(Au)$ of the Au particles that takes into account the thickness of the phosphine shell that is adsorbed to the surface of the inorganic Au core:

$$d_{eff}(Au) = d_{core} + d_{surfactant} = d(Au) + 1\ nm \quad \text{(Formula SI-3)}$$

We have roughly estimated the thickness of the phospine layer as 0.5 nm, which leads to an increase in 2 • 0.5 nm = 1 nm in the effective thickness of the Au particles. The mobility of the Au particles in dependence of the effective diameter of the Au particles is shown in Figure SI-9.

In order to inter- and extrapolate these data we fitted empirically with a mono-exponential function with 2 fit-parameters A_y and T_y to the size-dependent mobilities:

$$m/m_{10nm,y}\,(d_{eff}(Au)) = A_y * \exp(-\ (d_{eff}(Au) - 6\ nm) / T_y) \quad \text{(Formula SI-4)}$$

We have used an exponentially decaying fit function as it has turned out that our data can be interpolated well with a function of this type. Since the effective diameter of the smallest nanoparticles we used (5 nm Au core + 2 • 0.5 nm phosphine shell = 6 nm) was 6 nm we used a shifted exponential function with 6 nm shift in the exponent. For the fit we have taken into account only the data for Au particles from Table SI-4 with diameter $5 \leq d(Au) \leq 60$ nm. The fits are shown in Figure SI-9 and the resulting fit parameters are enlisted in Table SI-10. The variable y describes the gel percentage.

y	A_y	T_y
0.5%	1.017 ± 0.015	189 ± 19
1%	1.049 ± 0.012	85.0 ± 3.7
2%	1.120 ± 0.024	37.7 ± 1.9
3%	1.236 ± 0.025	18.8 ± 0.8
4%	1.476 ± 0.061	10.3 ± 0.9
5%	1.759 ± 0.079	7.16 ± 0.66
6%	2.073 ± 0.083	5.77 ± 0.49

***Table SI-10**: Obtained parameters for fitting the mobility data in dependence of the effective size for different gel percentages y.*

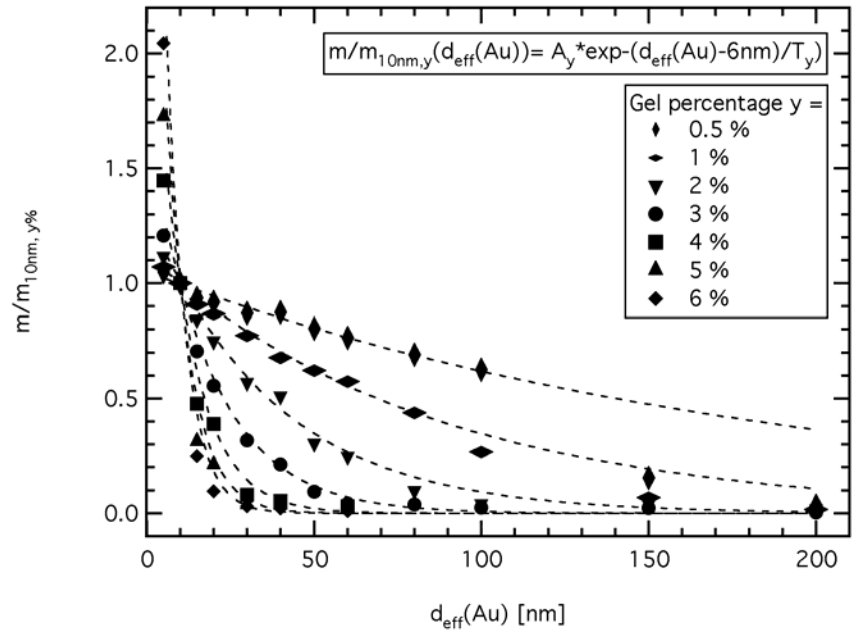

***Figure SI-9**: Mobility $m/m_{10nm,y}$ of phosphine-coated Au particles versus the effective Au diameter $d_{eff}(Au)$. The data correspond to Figure SI-2. The data are empirically fitted with a mono-exponential function (Formula SI-4).*

In this way we have an analytical function (the inverse exponential) which converts mobilities to effective sizes:

$d_{eff} = -T_y * \ln((m/m_{10nm,y}) /A_y) + 6$ nm (Formula SI-5)

With this function the effective diameters of all Au-DNA conjugates can be determined from their mobilities. So far the mobilities are the ones normalized to the mobility of plain 10 nm Au particles. When the mobilities have been normalized to the mobilities of particles with another diameter x, the conversion goes as follows:

$m / m_{10nm,y} = (m / m_{x,y}) * (m_{x,y} / m_{10nm,y})$ (Formula SI-6)

The $(m_{x,y} / m_{10nm,y})$ values can be taken from Table SI-4. For example:
$m_{5nm,1\%} / m_{10nm,1\%} = 1.07$

From Figure SI-9 it is obvious that for gels with different percentage only effective diameters within certain rages can be extracted, because data $m/m_{x,y} << 0.1$ are not very reliable. For low percentage gels the size range is biggest. For high percentage gels only small particles can be investigated, but the resolution is better. With gels of y% agarose the following particle size can be analyzed: 0.5%: 0-120 nm, 1%: 0-100 nm, 2%: 0-70 nm, 3%: 0-50 nm, 4%: 0-30 nm, 5%: 0-20 nm, 6%: 0-15 nm.

Since the fit function Formula SI-5 does not exactly go through the point $m_{10nm,y}(11$ nm) = 1 for Au particles with a core diameter of 10 nm (the fit function had been determined

in a way that it hits this point as close as possible), the mobility m = 1 is not converted into an effective diameter of exactly d_{eff} = 11 nm by the inverse fit function. In other words: $m_{10nm,y}(d_{eff}=11\ nm) = 1$ has been used as point to obtain the fit function $d_{eff} = d_{eff}(m)$ Formula SI-5. This function has been chosen to include this data point as close as possible. However, since this data point will not lie exactly on the function, the inverse function does not return exactly the effective diameter that has been the "input" for the fit: $d_{eff}(m_{10nm,y})$ will not be exactly 11 nm, but only close to it.

We have to point out that Formula SI-5 can in a strict way be only applied for objects that are in their nature as similar as possible to phosphine-coated Au particles and which are bigger than 5 nm. This is due to the fact that the fit functions have been obtained with data recorded on Au particles. Rigid objects certainly show different electrophoretic properties than soft ones. In this way Formula SI-5 cannot be used for example to convert the electrophoretic mobilities obtained with DNA molecules (see Chapter I.5) into effective diameters for two reasons: First the calibration function has been obtained for objects bigger than 5 nm and therefore the DNA particles are out of the range of extrapolation. Second the calibration curve has been obtained for rigid objects and can't be directly applied for soft objects.

The difference in electrophoretic behavior between soft and rigid objects can directly be seen in Figure SI-10. Whereas the logarithm of the mobilities obtained for different gel percentages scales linearly for soft objects such as DNA, there is different behavior for rigid objects as Au particles and objects with rigid core and soft shell as DNA-Au conjugates.

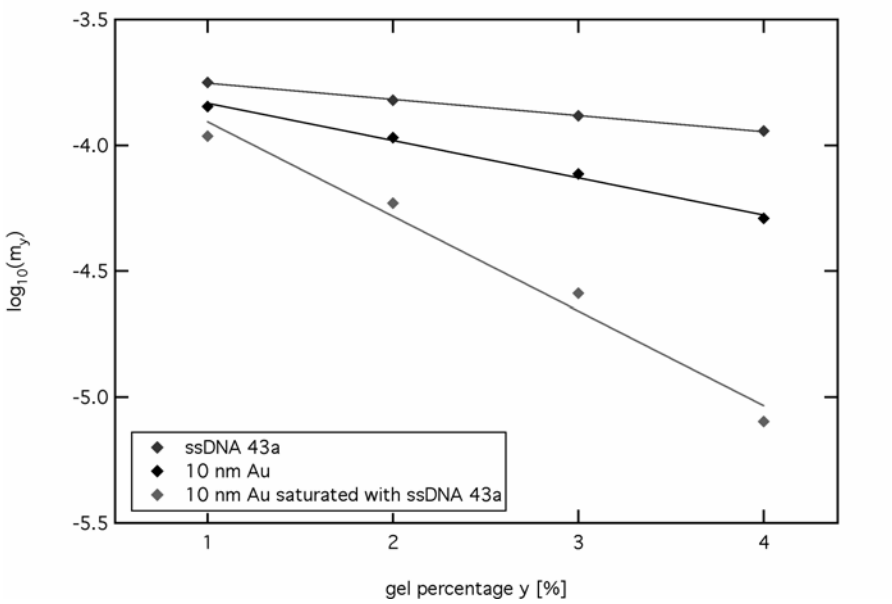

*Figure SI-10: Logarithm of the absolute electrophoretic mobilities of single stranded DNA (sequence Cy3-**43a**, data taken from Table SI-5), phosphine coated Au nanoparticles of nominal diameter of 10 nm (data taken from Table SI-4), and phosphine coated Au nanoparticles whose surface has been saturated with SH-**43a** DNA (data taken from Tables SI-7.1-SI-7.4). In order to convert the relative mobilities in absolute one the data of Table SI-3 were used.*

II.3) Effective diameter of Au-DNA conjugates derived by a calibration curve that relates mobilities to effective diameters

In the following tables and graphs all the mobility data shown in I) are converted into effective diameters.

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]
SH-**8a**	22.8	21.4	-	23.0
Cy3-**8a**-SH	-	-	-	-
Cy5-**8a**-SH	-	-	-	-
8a	12.4	12.1	-	12.4
SH-**12**	30.0	26.8	-	26.8
12	-	11.4	-	-
SH-**16**	31.8	32.5	-	34.5
SH-**21**	39.6	37.8	-	-
21	17.8	15.2	-	28.7
SH-**30**	44.2	41.0	-	45.0
30	17.3	13.8	-	-
SH-**35**	43.1	41.2	-	-
SH-**36a**	47.6	40.6	-	-
36a	21.7	24.4	-	34.0
SH-**36b**	-	39.2	-	-
SH-**43a**	35.9	33.3	35.0	39.1
Cy5-**43a**-SH	-	-	-	-
SH-**43b**	47.8	53.8	-	-
SH-**50**	54.2	54.1	-	-
SH-**54**	56.7	57.1	-	49.7
SH-**65**	-	58.0	-	-
SH-**85**	-	55.5	-	-
SH-**100a**	76.5	66.3	-	-
100a	28.7	26.8	-	17.7
SH-**120**	-	47.7	-	-
SH-**135**	-	87.7	-	-

Table SI-11.1*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm core diameter have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used. The Au-DNA conjugates were run on 1% agarose gels. The mobilities of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles. The mobility data (that are displayed in Table SI-7.1) were then converted to effective diameters d_{eff} with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-11.1.*

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]
SH-**8a**	17.0	18.3	-	18.9
8a-SH	-	17.1	-	-
Cy3-**8a**-SH	-	-	-	-
Cy5-**8a**-SH	-	-	-	-
Tamra-**8a**-SH	-	-	-	-
8a	11.2	11.4	-	11.8
8b-SH	-	17.0	-	-
SH-**12**	21.8	22.7	-	20.9
12	-	11.9	-	-
SH-**16**	25.7	25.1	-	26.0
SH-**21**	29.6	30.4	-	-
21	15.1	13.6	-	19.0
SH-**30**	34.1	35.1	-	38.5
30	14.5	12.3	-	-
SH-**35**	38.2	33.2	-	-
SH-**36a**	32.5	35.5	-	-
36a	16.1	19.1	-	20.1
SH-**36b**	-	33.7	-	-
SH-**43a**	31.6	32.9	31.9	34.3
Cy5-**43a**-SH	-	-	-	-
SH-**43b**	41.0	41.6	-	-
SH-**50**	45.9	51.5	-	-
SH-**54**	51.0	49.3	-	45.4
SH-**65**	-	53.1	-	-
SH-**85**	-	54.1	-	-
SH-**100a**	71.1	69.5	-	-
100a	25.5	24.6	-	14.1
SH-**120**	-	50.8	-	-
SH-**135**	-	111.2	-	-

Table SI-11.2*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm core diameter have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used. The Au-DNA conjugates were run on 2% agarose gels. The mobilities of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles. The mobility data (that are displayed in Table SI-7.2) were then converted to effective diameters d_{eff} with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-11.2.*

	5 nm Au	10 nm Au	15 nm Au	20 nm Au
DNA-sequence	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]
SH-**8a**	14.4	15.2	-	16.7
8a-SH	-	-	-	-
Cy3-**8a**-SH	-	-	-	-
Cy5-**8a**-SH	-	-	-	-
Tamra-**8a**-SH	-	-	-	-
8a	10.8	11.1	-	11.2
8b-SH	-	-	-	-
SH-**12**	19.1	19.7	-	19.1
12	-	11.6	-	-
SH-**16**	18.5	22.4	-	22.2 -
SH-**21**	25.3	25.6	-	-
21	12.4	12.7	-	15.2
SH-**30**	30.9	32.1	-	35.0
30	13.1	11.5	-	-
SH-**35**	34.0	29.5	-	-
SH-**36a**	29.9	29.2	-	-
36a	14.2	15.2	-	17.1
SH-**36b**	-	31.6	-	-
SH-**43a**	27.1	30.4	27.3	30.8
Cy5-**43a**-SH	-	-	-	-
SH-**43b**	36.7	37.5	-	-
SH-**50**	41.3	45.0	-	-
SH-**54**	43.2	41.3	-	41.1
SH-**65**	-	51.2	-	-
SH-**85**	-	54.4	-	-
SH-**100a**	63.8	58.5	-	-
100a	19.5	18.5	-	13.1
SH-**120**	-	69.3	-	-
SH-**135**	-	58.4	-	-

Table SI-11.3*: Au particles of 5 nm, 10 nm, 15 nm, and 20 nm core diameter have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with and without thiol modification was used. The Au-DNA conjugates were run on 3% agarose gels. The mobilities of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles. The mobility data (that are displayed in Table SI-7.3) were then converted to effective diameters d_{eff} with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-11.3.*

	0.5% gel	1% gel	2% gel	3% gel
DNA-sequence	$d_{eff,0.5\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,3\%}$ [nm]
SH-**30**	59.5	41.0	35.1	32.1
SH-**36a**	49.0	40.6	35.5	29.2
SH-**43a**	48.1	33.3	32.9	30.4
SH-**50**	88.8	54	51.5	45.0
SH-**100a**	-	66.3	69.5	58.5

	4% gel	5% gel	6% gel
DNA-sequence	$d_{eff,4\%}$ [nm]	$d_{eff,5\%}$ [nm]	$d_{eff,6\%}$ [nm]
SH-**30**	31.3	34.3	31.0
SH-**36a**	-	-	-
SH-**43a**	29.2	30.8	31.0
SH-**50**	45.2	-	61.4
SH-**100a**	45.4	41.8	33.3

***Table SI-11.4**: Au particles of 10 nm core diameter have been saturated with single stranded DNA until no more DNA could be attached. DNA with different sequences (see Table SI-2) with thiol modification was used. The Au-DNA conjugates were run on gels of different agarose percentage. The mobilities of the Au-DNA conjugates (with the maximum number of attached DNA) were measured relative to the mobility of the free Au nanoparticles. The mobility data (that are displayed in Table SI-7.4) were then converted to effective diameters d_{eff} with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-11.4.*

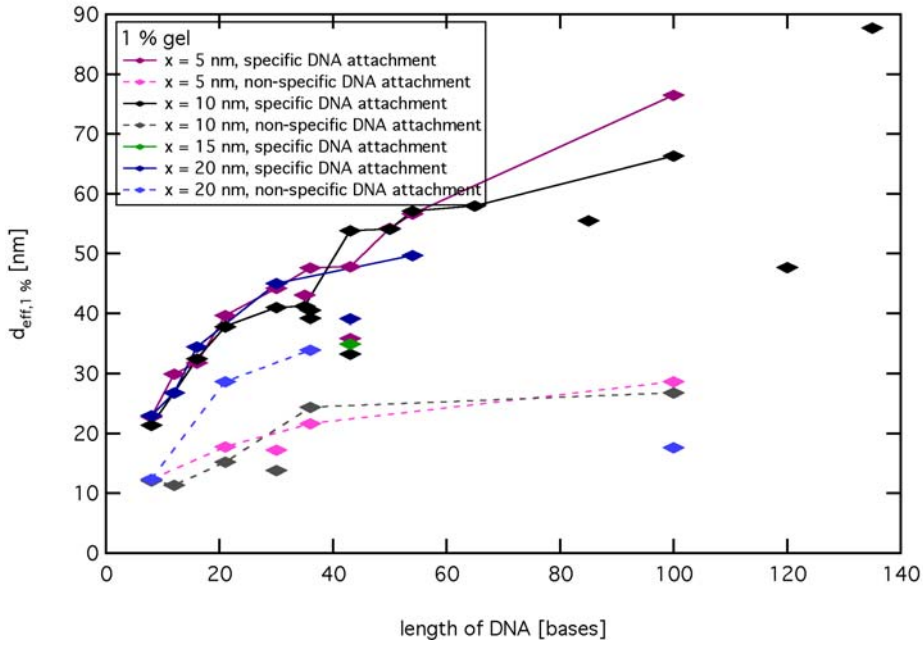

Figure SI-11.1*: Single-stranded DNA has been attached to Au nanoparticles of different core diameter d (x = 5, 10, 15, 20 nm) either nonspecifically or via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. The resulting effective diameter d_{eff} is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-11.1. The plain lines correspond to specific attachment via thiol-gold bonds, the dotted lines to nonspecific adsorption.*

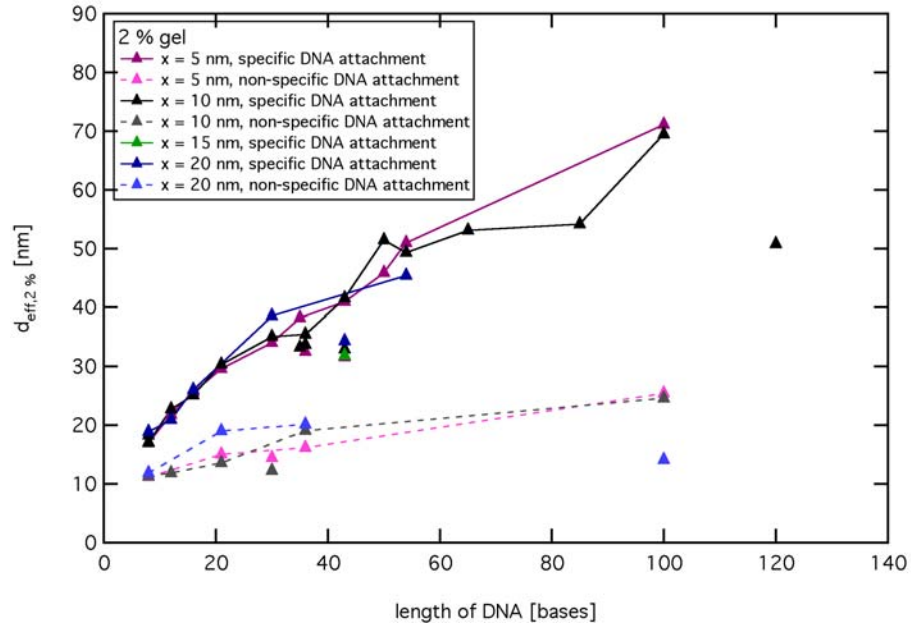

Figure SI-11.2*: Single-stranded DNA has been attached to Au nanoparticles of different core diameter (x = 5, 10, 15, 20 nm) either nonspecifically or via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. The resulting effective diameter is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-11.2.*

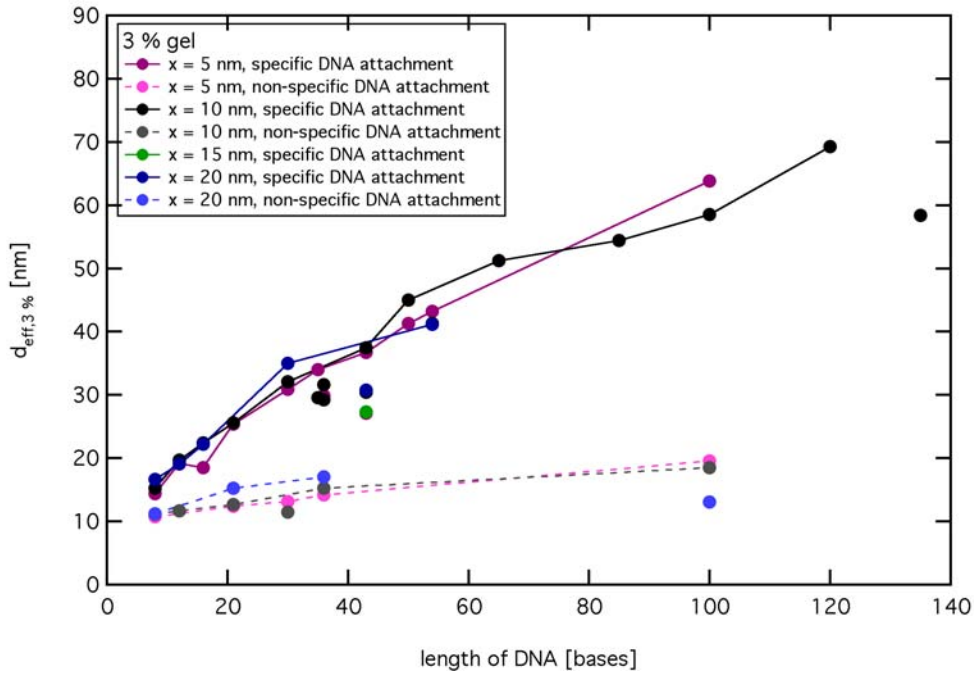

Figure SI-11.3: *Single-stranded DNA has been attached to Au nanoparticles of different core diameter (x = 5, 10, 15, 20nm) either nonspecifically or via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. The resulting effective diameter is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-11.3.*

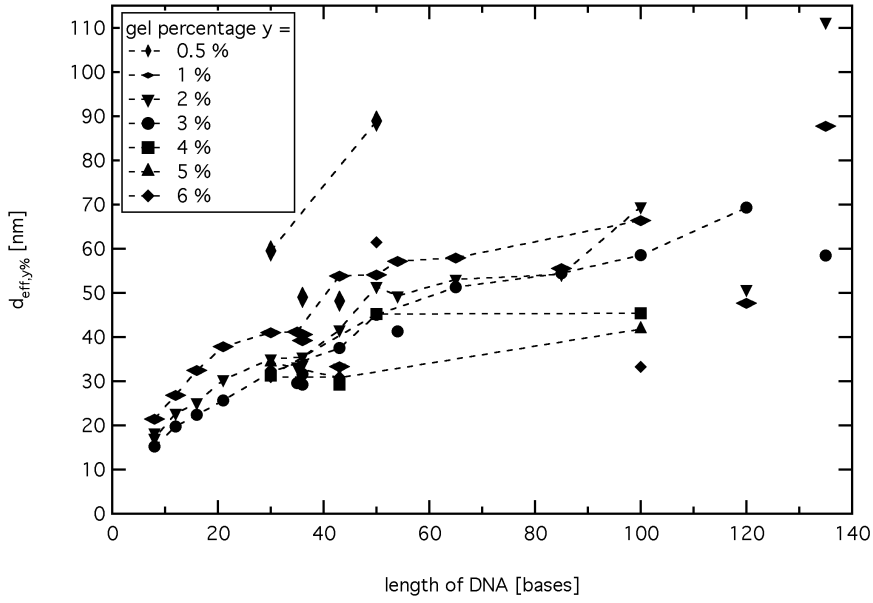

Figure SI-11.4: *Single-stranded DNA has been attached to Au nanoparticles of 10 nm core diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on gels of different agarose percentage (y = 0.5%, 1%, 2%, 3%, 4%, 5%, 6%). The effective diameters of the Au-DNA conjugates that were saturated with DNA are plotted versus the length of the DNA. The corresponding data are displayed in Table SI-11.4.*

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]
0	10.1	10.1	10.1	10.1
1	12.2	12.3	12.2	12.5
2	14.2	14.9	14.3	15.3
3	16.6	17.3	16.2	18.3
4	19.3	19.5	19.3	21.5
5	21.4	21.7	21.8	23.8
6	23.3	-	23.8	25.9
7	-	-	25.8	-

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]
0	10.1	10.1	10.1	10.1
1	13.2	13.0	14.2	14.6
2	16.6	16.5	18.8	-
3	20.2	19.9	23.2	-
4	23.9	23.3	27.0	-
5	26.9	26.3	32.2	-
6	29.6	29.0	37.9	-
7	32.3	30.9	41.3	-

***Table SI-12.1**: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 1% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (see Table SI-8.1). From these data the effective diameters d_{eff} of the conjugates were derived with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-12.1. It has to be noted, that as input for the Au-particles with no DNA attached the mobility m = 1 was used. By using Formula SI-5 this mobility was converted into an effective diameter $d_{eff,1\%}$ of 10.1 nm. This is not the initially assumed effective diameter of 11 nm (10 nm core + 2 • 0.5 nm phosphine shell)! The initially assumed effective diameter was used as input (one data point) to create the fit function. The inverse of the fit function does not necessarily need to return exactly the initial value.*

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]
0	10.3	10.3	10.3	10.3
1	12.2	12.6	12.7	13.0
2	14.1	15.0	15.0	15.8
3	16.0	17.3	17.4	18.6
4	18.5	19.5	19.6	21.7
5	20.3	21.5	21.9	24.2
6	21.9	23.3	23.6	26.4
7	23.7	24.8	25.1	28.8
8	-	-	26.7	-
9	-	-	27.9	-

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]
0	10.3	10.3	10.3	10.3
1	13.8	14.3	14.0	15.5
2	17.1	18.4	19.3	20.7
3	20.7	22.1	23.5	25.6
4	23.8	25.7	27.7	-
5	27.6	28.4	31.4	-
6	30.5	32.0	34.9	-
7	33.6	34.2	35.7	-
8	-	37.2	36.9	-
9	-	38.4	-	-

***Table SI-12.2**: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (see Table SI-8.2). From these data the effective diameters d_{eff} of the conjugates were derived with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-12.2.*

.

	SH-**43b**	SH-**50**	SH-**54**	SH-**65**
number of DNAs per particle	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]
0	10.0	10.0	10.0	10.0
1	11.8	11.8	11.9	12.5
2	13.6	13.8	13.9	15.0
3	15.3	15.8	15.8	17.9
4	17.0	17.5	17.5	20.3
5	18.4	19.6	19.6	22.5
6	20.1	21.2	21.2	24.5
7	21.2	22.8	22.8	26.5
8	-	23.9	23.9	28.1
9	-	25.1	25.1	29.8

	SH-**85**	SH-**100a**	SH-**100b**	SH-**135**
number of DNAs per particle	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]
0	10.0	10.0	10.0	10.0
1	13.6	13.7	13.7	14.8
2	17.3	17.5	19.2	19.5
3	20.9	20.9	23.3	24.3
4	24.2	24.6	27.4	-
5	27.5	27.7	31.4	-
6	30.1	31.4	34.0	-
7	32.6	34.3	37.3	-
8		36.4	-	-
9	-	37.9	-	-

***Table SI-12.3**: Au particles of 10 nm have been incubated with single stranded DNA. DNA with different sequences (see Table SI-2) with thiol modification was used. The DNA/Au ratio and the length of the DNA were chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (see Table SI-8.3). From these data the effective diameters d_{eff} of the conjugates were derived with Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-12.3.*

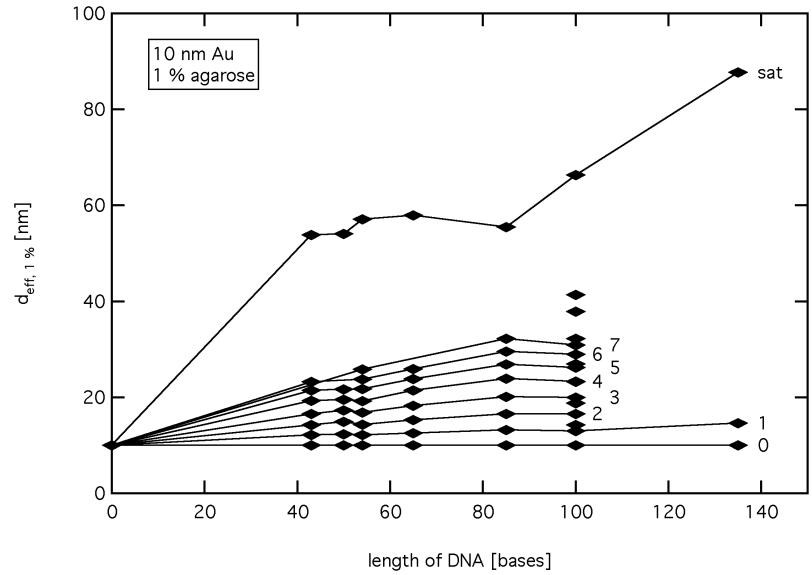

Figure SI-12.1*: Single-stranded DNA has been attached to Au nanoparticles (core diameter d = 10 nm) of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The effective diameter d_{eff} of the Au-DNA conjugates was determined with Formula SI-5 from mobility data and is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-12.1. In addition the effective diameters of Au nanoparticles saturated with DNA ("sat") are displayed (taken from Table SI-11.1).*

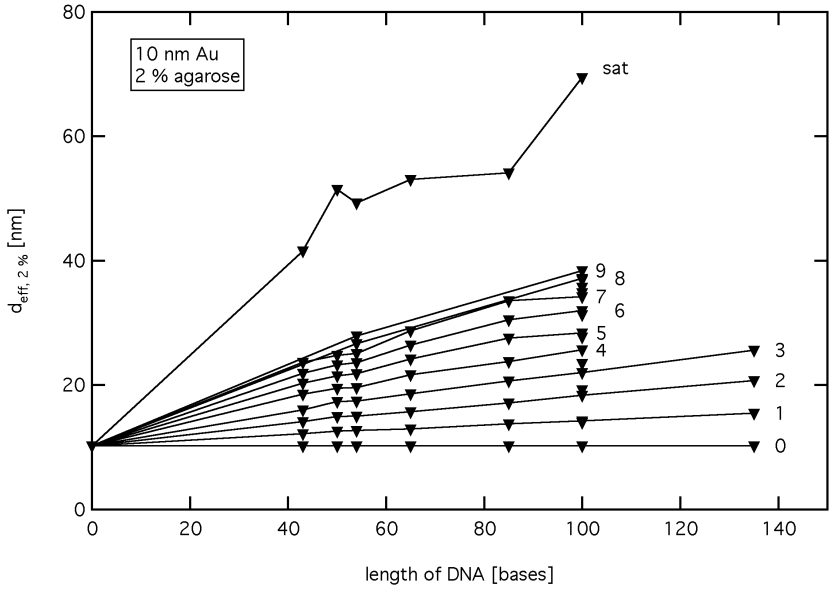

Figure SI-12.2*: Single-stranded DNA has been attached to Au nanoparticles of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The effective diameter of the Au-DNA conjugates was determined and is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-12.2. In addition the effective diameters of Au nanoparticles saturated with DNA ("sat") are displayed (taken from Table SI-11.2).*

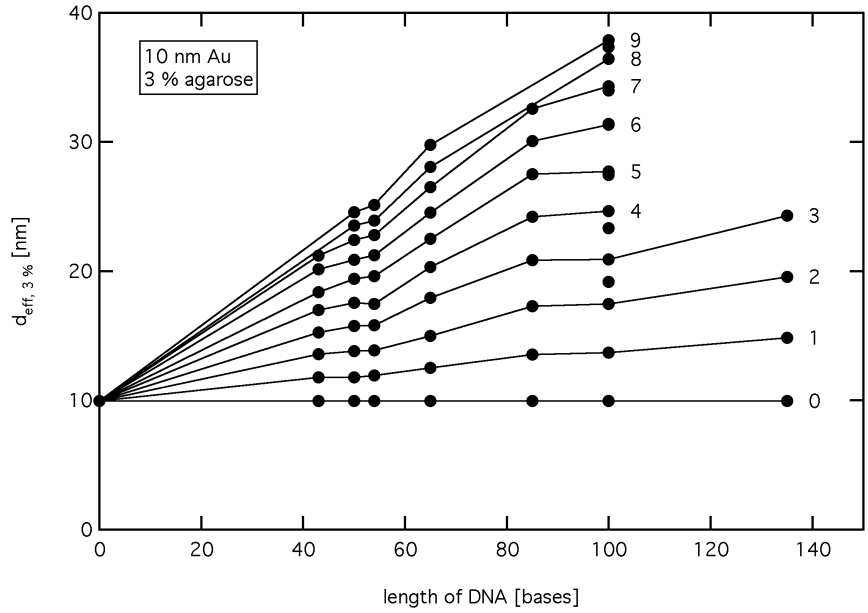

Figure SI-12.3*: Single-stranded DNA has been attached to Au nanoparticles of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The effective diameter of the Au-DNA conjugates was determined and is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-12.3.*

	5 nm Au	10 nm Au	20 nm Au
number of DNAs per particle	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,1\%}$ [nm]
0	4.3	10.1	18.2
1	11.0	13.0	-
2	16.9	16.5	-
3	21.1	19.9	-
4	25.7	23.3	-
5	30.9	26.3	-
6	33.9	29.0	-
7	36.3	30.9	-

Table SI-13.1*: Au particles of 5 nm, 10 nm, and 20 nm core diameter d have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 1% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (Table SI-9.1). From these data the effective diameters d_{eff} have been obtained using Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-13.1. The data shown here are the effective diameters d_{eff} returned from the fit function using the relative mobilities as input. It is important to note that for 5 nm and 10 nm Au core particles the resulting effective diameters from the fit function (m = 1) are not 6 nm and 11 nm, respectively. The fit function will not necessarily return the original data points, as they only had been used as data points to create the fit function, but the fit function can't "hit" all input-values perfectly.*

	5 nm Au	10 nm Au	20 nm Au
number of DNAs per particle	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,2\%}$ [nm]
0	6.2	10.3	16.8
1	12.2	14.2	22.1
2	17.7	18.4	-
3	22.6	22.1	-
4	26.3	25.7	-
5	30.0	28.4	-
6	32.5	32.0	-
7	35.4	34.2	-
8	-	37.2	-
9	-	38.4	-

Table SI-13.2*: Au particles of 5 nm, 10 nm and 20 nm core diameter have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 2% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (Table SI-9.2). From these data the effective diameters have been obtained using Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-13.2.*

	5 nm Au	10 nm Au	20 nm Au
number of DNAs per particle	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]	$d_{eff,3\%}$ [nm]
0	6.4	10.0	16.6
1	11.7	13.7	19.9
2	15.9	17.5	22.9
3	20.1	20.9	26.1
4	23.5	24.6	29.2
5	26.7	27.7	30.5
6	28.7	31.4	33.2
7	32.0	34.3	35.2
8	-	36.4	-
9	-	37.9	-

Table SI-13.3*: Au particles of 5 nm, 10 nm and 20 nm core diameter have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on 3% agarose gels. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (Table SI-9.3). From these data the effective diameters have been obtained using Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-13.3.*

	1% gel	2% gel	3% gel
number of DNAs per particle	$d_{eff,1\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,3\%}$ [nm]
0	10.1	10.3	10.0
1	13.0	14.2	13.7
2	16.5	18.4	17.5
3	19.9	22.1	20.9
4	23.3	25.7	24.6
5	26.3	28.4	27.7
6	29.0	32.0	31.4
7	30.9	34.2	34.3
8	-	37.2	36.4
9	-	38.4	37.9

	4% gel	5% gel	6% gel
number of DNAs per particle	$d_{eff,4\%}$ [nm]	$d_{eff,5\%}$ [nm]	$d_{eff,6\%}$ [nm]
0	10.0	10.0	10.2
1	13.3	13.9	13.9
2	16.6	18.2	17.7
3	20.1	22.4	20.6
4	23.2	26.2	-
5	26.2	36.7	-
6	28.9	-	-
7	30.2	-	-
8	-	-	-
9	-	-	-

Table SI-13.4*: Au particles of 10 nm core diameter have been incubated with single stranded DNA (sequence SH-**100a**, see Table SI-2) with thiol modification. The DNA/Au ratio was chosen in a way that single bands could be observed with gel electrophoresis. The Au-DNA conjugates were run on agarose gels with different percentages. The mobility of the discrete Au-DNA conjugates (e.g. the mobility of the individual bands that correspond to Au particles with exactly 1, 2, ... DNA molecules bound per particle) was measured relative to the mobility of the free Au nanoparticles (Table SI-9.4). From these data the effective diameters have been obtained using Formulas SI-5 and SI-6. The data are graphically displayed in Figure SI-13.4.*

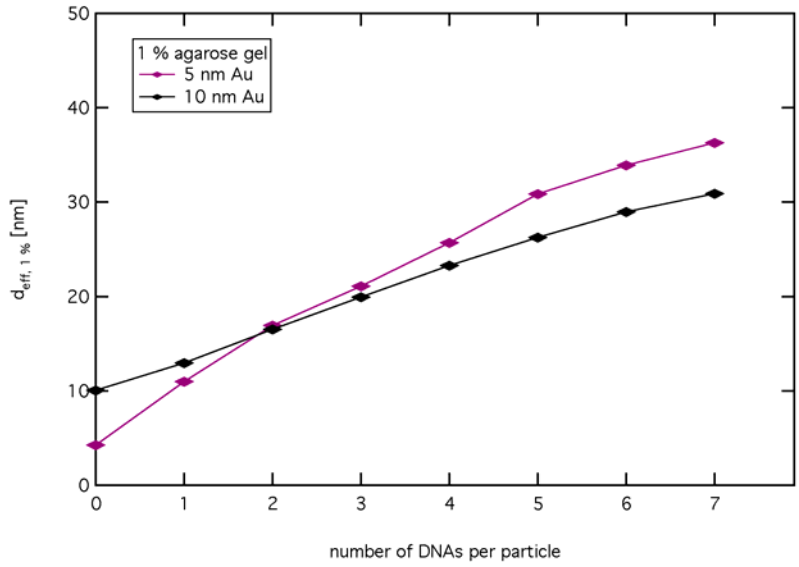

Figure SI-13.1*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm and 10 nm core diameter d via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 1% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles was evaluated from the gels. Using a calibration curve the mobilities were converted to effective diameters d_{eff}. In the diagram the effective diameter of Au-DNA conjugates with a discrete number of attached DNA molecules per particle is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-13.1.*

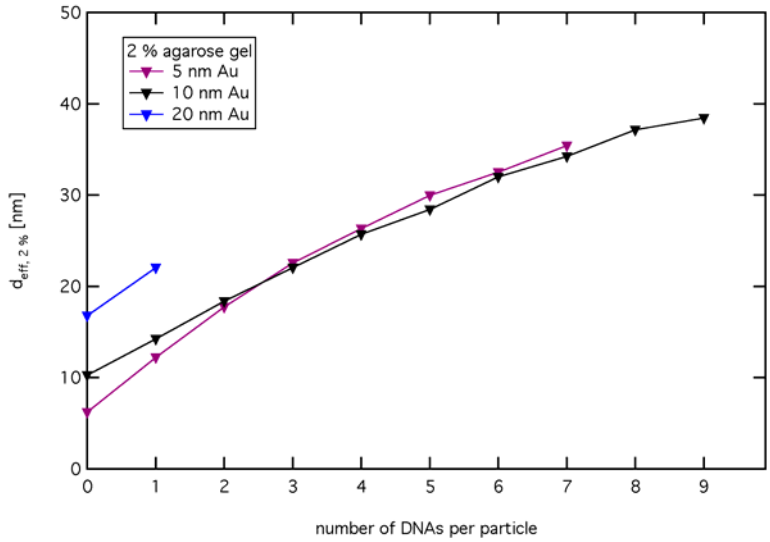

Figure SI-13.2*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm, 10 nm and 20 nm core diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 2% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles was evaluated from the gels. Using a calibration curve the mobilities were converted to effective diameters. In the diagram the effective diameter of Au-DNA conjugates with a discrete number of attached DNA molecules per particle is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-13.2.*

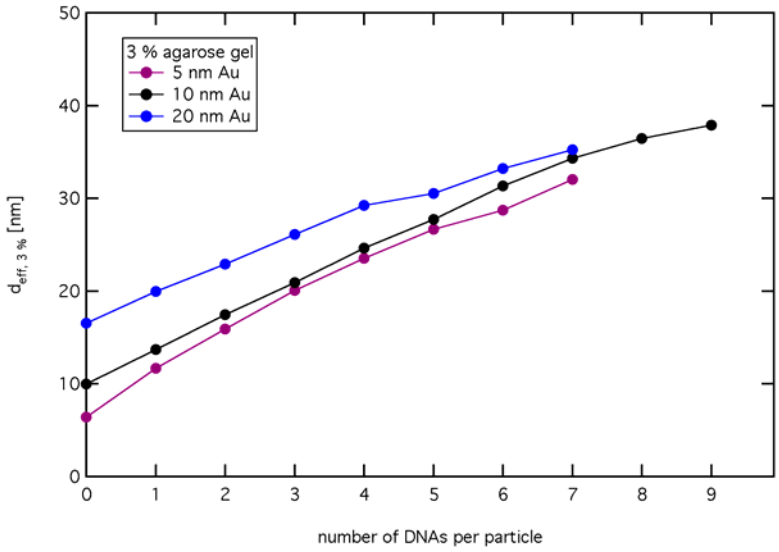

Figure SI-13.3*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 5 nm, 10 nm and 20 nm core diameter via the formation of thiol-gold bonds. The Au-DNA conjugates were run on 3% agarose gels. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles was evaluated from the gels. Using a calibration curve the mobilities were converted to effective diameters. In the diagram the effective diameter of Au-DNA conjugates with a discrete number of attached DNA molecules per particle is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-13.3.*

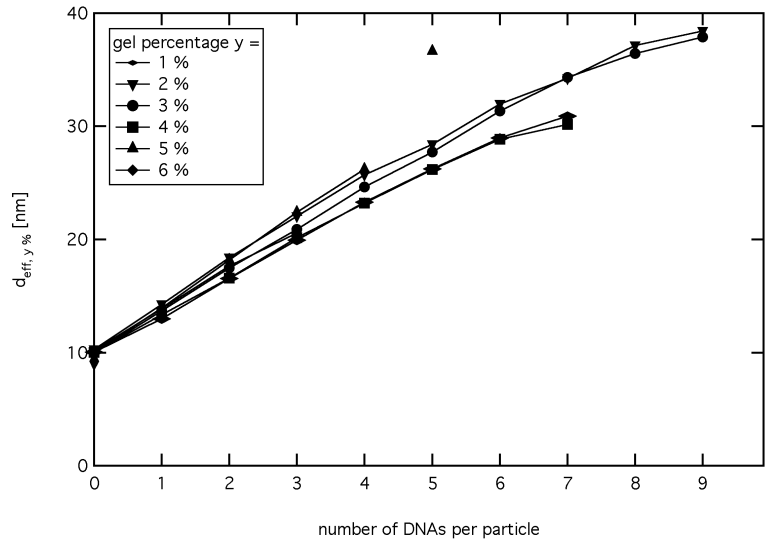

Figure SI-13.4*: Single-stranded DNA (with sequence SH-**100a**, see Table SI-2) has been attached to Au nanoparticles of 10 nm core diameter of via the formation of thiol-gold bonds. The Au-DNA conjugates were run on agarose gels of different percentages. Discrete bands corresponding to Au-DNA conjugates with exactly 1, 2, ... DNA molecules bound per Au particle were observed. The mobility of the bands of these Au-DNA conjugates relative to the mobility of the plain Au particles was evaluated from the gels. Using a calibration curve the mobilities were converted to effective diameters. In the diagram the effective diameter of Au-DNA conjugates with a discrete number of attached DNA molecules per particle is plotted versus the length of the DNA. The corresponding data are displayed in Table SI-13.4.*

II.4) Ferguson analysis

We also intended to obtain absolute numbers for the effective diameters of the conjugates by applying Ferguson analysis [6]. For the Ferguson analysis, absolute mobilities m_y obtained for the same sample run on gels of different percentage y are required. In Tables SI-4 to SI-9 the relative mobilities of many different Au-DNA conjugates are listed. By using the absolute mobilities of plain Au nanoparticles (Table SI-3) the relative mobilities were converted to absolute ones.

In a Ferguson plot the decadic logarithm of the absolute mobility m_y (at a certain gel percentage) is plotted versus the gel percentage y. The plot results in linear curves for DNA. However, for Au nanoparticles deviations from the linear behavior can be seen [2, 6], see Figure SI-14.

Within the linear range the Ferguson plot can be fitted with a linear function {Park, 2004 #9830:

$$\log(m_y) = \log(m_0) - K_r\, y \qquad \text{Formula SI-7}$$

The absolute mobility m_0 corresponds to a gel at percentage y = 0%. K_r is the so called retardation coefficient which is related to the characteristics of the gel and to the effective diameters d_{eff} of the sample by the following equation:

$$K_r^{1/2} = a\left((\pi l)^{1/2} d_{eff}/2 + (\pi l)^{1/2} r \right) = \alpha \bullet d_{eff}/2 + \beta \qquad \text{Formula SI-8}$$

Here a is a constant, and l and r define the length and the radius of the gel fiber. As abbreviations $\alpha = a(\pi l)^{1/2}$ and $\beta = a\,(\pi l)^{1/2} r$ are used.

Ferguson plots have been made for plain Au particles of different size (see Figure SI-14, relative mobility data see Table SI-4), and the retardation coefficient K_r has been obtained for each particle size, see Table SI-14. As particle size we use the effective size d_{eff} of the Au particles that includes their phosphine shell (see Formula SI-3). In this way a calibration curve in which $K_r^{1/2}$ is plotted versus d_{eff} is obtained. According to Formula SI-8 this is a linear curve. This calibration curve correlates mobilities to effective diameters. For any Au-DNA conjugate that has been run on several gels with different percentage a Ferguson plot $m_y(y)$ can be obtained from which the retardation coefficient K_r can be derived. From the calibration curve $K_r^{1/2}(d_{eff})$ finally the effective diameter of the Au-DNA conjugate d_{eff} can be obtained.

An example and the resulting effective diameters for the Au-DNA conjugates in our study are shown in the following.

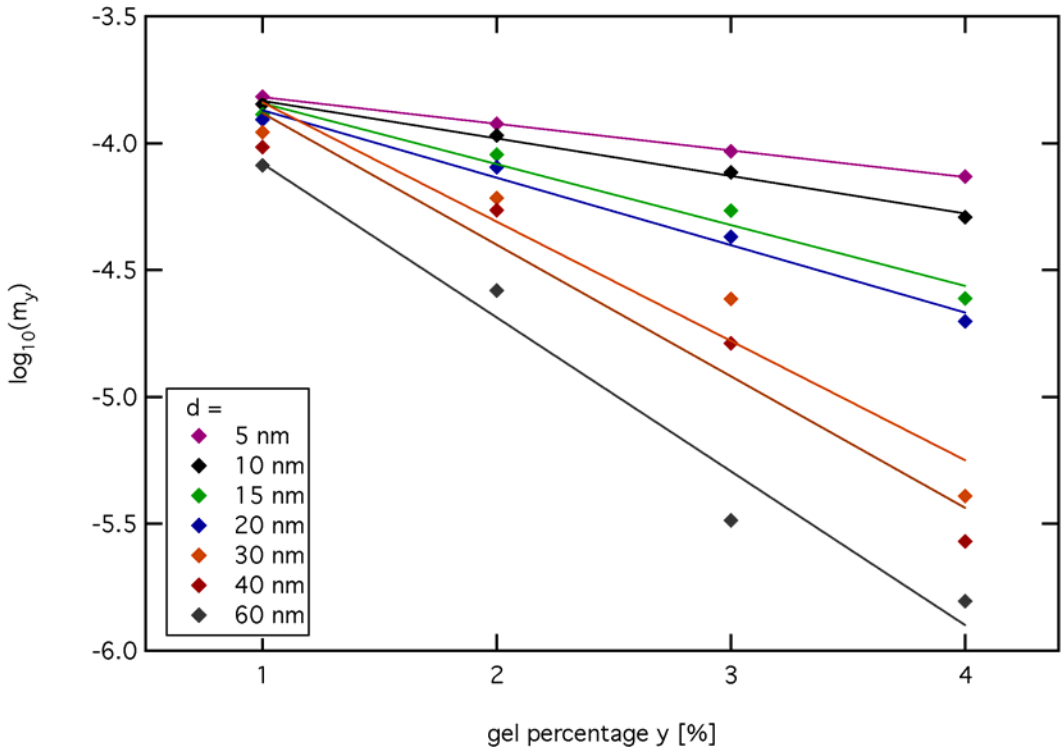

***Figure SI-14**: Ferguson plot of plain Au-nanoparticles of different core diameters d between 5 and 60 nm. The logarithm to the basis 10 of the absolute mobility of the gold particles log(m_y) versus the gel percentage y is reported. From each size of gold particles the data points of different gel percentages are fitted according to Formula SI-7 with a linear curve whose slope is called K_r. The obtained values of K_r for each gold particle size are reported in the Table SI-14.*

In Figure SI-14 the logarithm to the basis 10 log(m_y) of the mobility of gold particles with diameters d from 5 and 60 nm is plotted versus the gel percentages in the range between 1, 2, 3 and 4. The mobility values are taken from Table SI-4. For each particle size a linear fit was performed. According to Formula SI-7 the slope of the fit is called retardation coefficient K_r. The retardation coefficients that have been obtained are reported in Table SI-14. In Figure SI-15 these retardation coefficients are plotted versus the effective particle diameter d_{eff} of the gold particles.

d(Au) [nm]	d_{eff} (Au) [nm]	K_r	$d_{eff,cal}$ (Au) [nm] (d_{max} = 30 nm)	$d_{eff,cal}$ (Au) [nm] (d_{max} = 40 nm)
5	6.0	0.11	6.1	4.6
10	11.0	0.15	10	9.6
15	16.0	0.24	18	18
20	21.0	0.27	19	21
30	31.0	0.47	31	35
40	41.0	0.52	34	38
60	61.0	0.61	38	43

Table SI-14: *The retardation coefficients K_r have been obtained from Figure SI-14 for Au nanoparticles of different core diameter d. The effective diameter d_{eff} of the Au nanoparticles (including the phosphine shell) was calculated according to Formula SI-3. The square root of the retardation coefficient $K_r^{1/2}$ was plotted against the half of the effective diameter $d_{eff}/2$ and fitted with a linear curve $K_r^{1/2} = \alpha \bullet d_{eff}/2 + \beta$, see Figure SI-15 and Formula SI-8. The fit was performed for different data intervals. For the first fit only the data from d = 5 nm to d_{max} = 30 nm, for the second fit the one from d = 5 nm to d_{max} = 40 nm were taken into account. The obtained parameters are α = 0.0286, β = 0.237, and α = 0.0238, β = 0.270, respectively. In order to evaluate the quality of the fit the effective diameters $d_{eff,cal}$ were obtained from the K_r values and the fit-functions $d_{eff,cal}(K_r) = (K_r^{1/2} - 0.237) / 0.0286$ and $d_{eff,cal}(K_r) = (K_r^{1/2} - 0.270) / 0.0238$ (see Formula SI-9). The values can be compared with the original values for d_{eff}.*

According to Formula SI-8 the square root of the retardation coefficient $K_r^{1/2}$ scales linearly with the effective diameter d_{eff}, see Figure SI-15. By fitting the $K_r^{1/2}(d_{eff})$ data with a linear function ($K_r^{1/2}(d_{eff}) = \alpha\ d_{eff}/2 + \beta$, Formula SI-8) a calibration curve is obtained, that relates the measured mobilities (in terms of K_r) to an effective diameter d_{eff}. For this the Formula SI-8 is transformed to yield d_{eff}:

$$d_{eff}(K_r) = (K_r^{1/2} - \beta) / \alpha \qquad \text{Formula SI-9}$$

By using the fit parameters α and β the effective diameter d_{eff} can be derived with Formula SI-9 from the experimental data (the retardation coefficients K_r that have been obtained from the mobilities for different gel percentages). To decide in which the best linear fit can be performed, two ranges were examined. α and β were obtained by fitting the $K_r^{1/2}(d_{eff})$ data in the range of 5 nm ≤ d ≤ 30 nm, and 5 nm ≤ d ≤ 40 nm, respectively, see Figure SI-15. As results of the fit the parameters α = 0.0286, β = 0.237, and α = 0.0238, β = 0.270 were obtained, respectively. In order to evaluate the quality of the fit we used Formula SI-9 with these fit-parameters to obtain the effective diameters d_{eff} for Au nanoparticles from their measured K_r data. The K_r values are taken from the third column of Table SI-14 and the so obtained results for both sets of fit parameters are displayed in the forth and fifth column. By comparing the diameters obtained from the fit ($d_{eff,cal}$ (Au)) (forth and fifth column of Table SI-14) with the "real" values d_{eff} (second column of Table SI-14) we can judge the quality of the fits. It is obvious from the data that in the case of the first set of fit parameters (α = 0.0286, β = 0.237, derived in the fit range from 5 nm ≤ d ≤ 30 nm) the fit cannot be extrapolated to particles of sizes bigger than 30 nm. The second set of fit parameters α = 0.0238, β = 0.270, derived in the fit range from 5 nm ≤ d ≤ 40 nm) yields slightly better results for big particles, but worse

results for small particles. For this reason we decided to use in the following only the first set of fit parameters $\alpha = 0.0286$, $\beta = 0.237$. However, in this case on has to be aware that any effective diameters that are obtained from K_r data by using Formula SI-9 are only reliable if they are not bigger than approximately 30 nm. The size of bigger particles is underestimated.

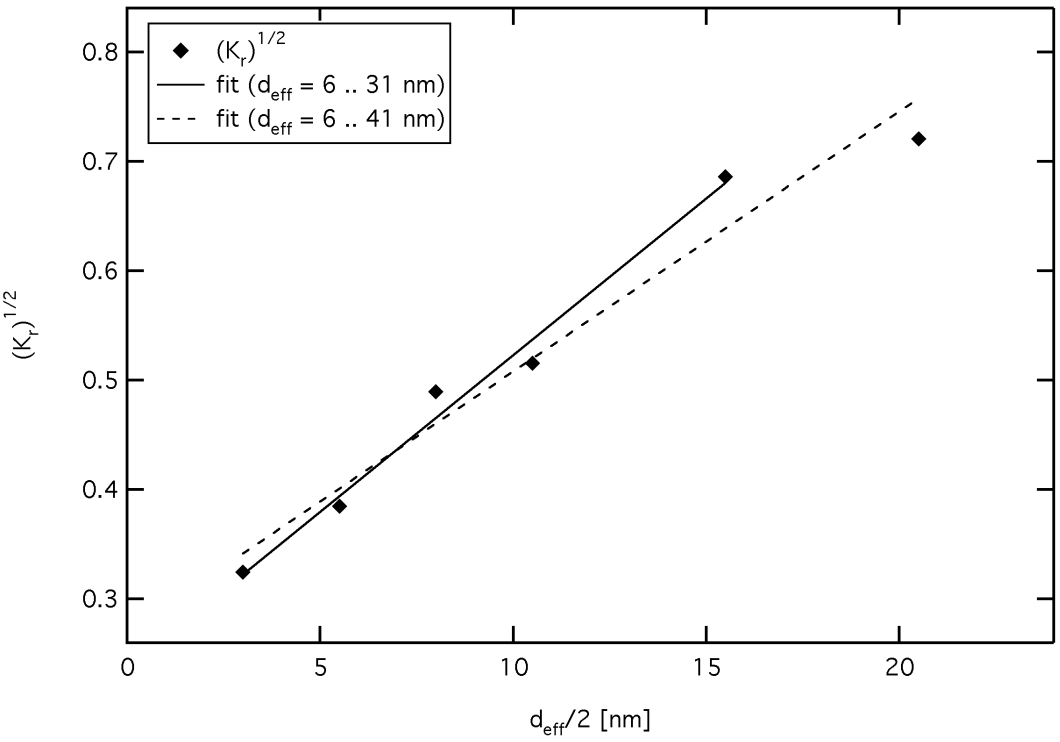

***Figure SI-15**: The square root of the K_r data that has been obtained from the mobilities of plain phosphine coated gold particles at different gel percentages is plotted versus the effective diameter of the gold particles (the diameter that is known from TEM images for the Au core + twice the estimated thickness of the phosphine shell). The data are taken from Table SI-14. The data are fitted with a linear function (Formula SI-8) in the range between d = 5-30 nm and d = 5-40 nm, respectively. The fits yielded the following parameters: $K_r^{1/2} = 0.0286\ d_{eff}/2 + 0.237$ and $K_r^{1/2} = 0.0238\ d_{eff}/2 + 0.270$. For all following calculations the first of the two fits was used, i.e. $\alpha = 0.0286$, $\beta = 0.237$.*

With the same procedure the effective diameters for a series of Au-DNA conjugates have been derived. We show the example of 10 nm Au particles that have been conjugated with thiolated DNA of 43 bases length (sequence SH-**43b**, see Table SI-2). The mobilities of Au particles with 0, 1, 2, 3, 4, 5, and 6 attached DNA molecules per particle and the one of Au particles saturated with DNA were measured for agarose gels with 1%, 2%, and 3% agarose content. For the individual DNA molecules attached per particle the mobility data $m / m_{10nm,y}$ are displayed in Table SI-8.1 (y = 1%), Table SI-8.2 (y = 2%), and Table SI-8.3 (y = 3%) in the second column. The $m / m_{10nm,y\%}$ data for the particles saturated with DNA are taken from the 3rd column ("10 nm Au") and line "SH-**43b**" are displayed in Table SI-7.1 (y = 1%), Table SI-7.2 (y = 2%), and Table SI-7.3 (y = 3%). The absolute mobilities are derived from the relative mobilities by using the values

$m_{10nm,y}$ from Table SI-3. The logarithm to the basis 10 of the mobilities of the DNA-conjugates is plotted versus the gel percentage in Figure SI-16. According to Formula SI-7 the curves for the different Au-DNA conjugates are fitted with a linear function. As fit parameter the retardation coefficient K_r and the intersection with the y=0 axis log(m_0) are obtained for each conjugate. The resulting K_r values are enlisted in Table SI-15. By using Formula SI-9 with the parameters α = 0.0286, β = 0.237 now effective diameters d_{eff} were obtained from the measured K_r data. The yielded d_{eff} values are displayed in Table SI-15 and are also compared with the estimated d_{eff} values that we have calculated in Chapter II.4 using Formula SI-5.

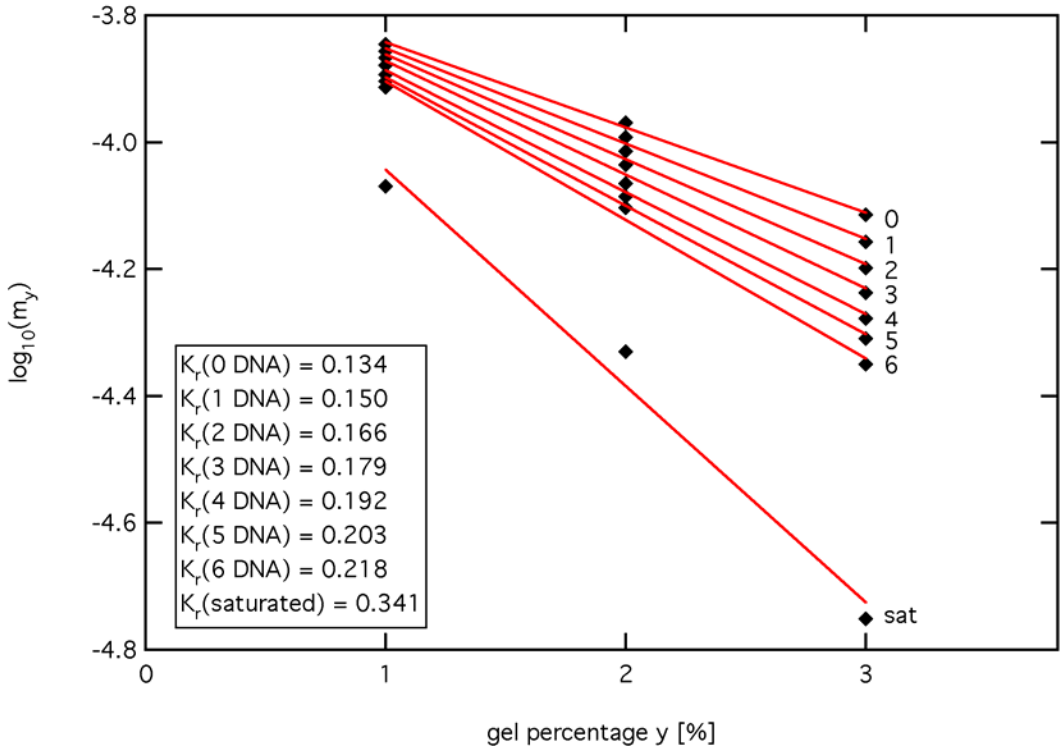

***Figure SI-16**: The logarithm to the basis 10 of the absolute mobility m_y recorded at gel percentages of y = 1, 2, 3% for Au-DNA conjugates of different type (plain gold particles, gold particles with one DNA molecule attached per particle, gold particles with two DNA molecules attached per particle, ..., and gold particles saturated with DNA) is plotted versus the gel percentage y. SH-**43b** DNA had been conjugated to 10 nm Au particles. The data were taken from Tables SI-3, SI-7.1, SI-7.2, SI-7.3, SI-8.1, SI-8.2, SI-8.3. The data points for each type of conjugate were fitted with a linear function (Formula SI-7), and the resulting fit parameters K_r and log(m_0) are displayed in Table SI-15.*

number of DNAs per Au particle	K_r	$\log(m_0)$	$d_{eff,F}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,3\%}$ [nm]
0	0.134	-3.708	9.09	10.1	10.3	10.0
1	0.150	-3.702	10.6	12.2	12.2	11.8
2	0.166	-3.695	11.9	14.2	14.1	13.6
3	0.179	-3.692	13.0	16.6	16.0	15.3
4	0.192	-3.694	14.1	19.3	18.5	17.0
5	0.203	-3.694	14.9	21.4	20.3	18.4
6	0.218	-3.686	16.1	23.3	21.9	20.1
7	-	-	-	-	23.7	21.2
sat	0.341	-3.702	24.3	53.8	41.6	37.5

***Table SI-15**: The K_r and $\log(m_0)$ values of Au-DNA conjugates were extracted from the $\log(m_y)$ versus y data shown in Figure SI-16 by applying Formula SI-7 (Ferguson analysis). The conjugates comprised plain 10 nm Au particles (with an originally estimated effective diameter d_{eff} = 11 nm), 10 nm Au particles with 1 DNA molecule (of sequence SH-**43b**) bound per particle, Au particles with 2 DNA molecules bound per particles, ..., and Au particles saturated with DNA. By using Formula SI-9 with the parameters α = 0.0286, β = 0.237 the K_r values were converted to effective diameters $d_{eff,F}$, which are enlisted in the fourth column of the table. In order to compare the effective diameters obtained with this Ferguson analysis ($d_{eff,F}$, 4th column) also the effective diameters that have been obtained by using the calibration curve Formula SI-5 are displayed for 1, 2, and 3% agarose gels. These data are taken from Tables SI-11.1, SI-12.1, Tables SI-11.2, SI-12.2, and Tables SI-11.3, SI-12.3 for the 1%, 2%, and 3% gels and are displayed in the 5th, 6th, and 7th column, respectively ($d_{eff,1\%}$, $d_{eff,2\%}$, $d_{eff,3\%}$). The effective diameters obtained with the different types of evaluation are plotted in Figure SI-17.*

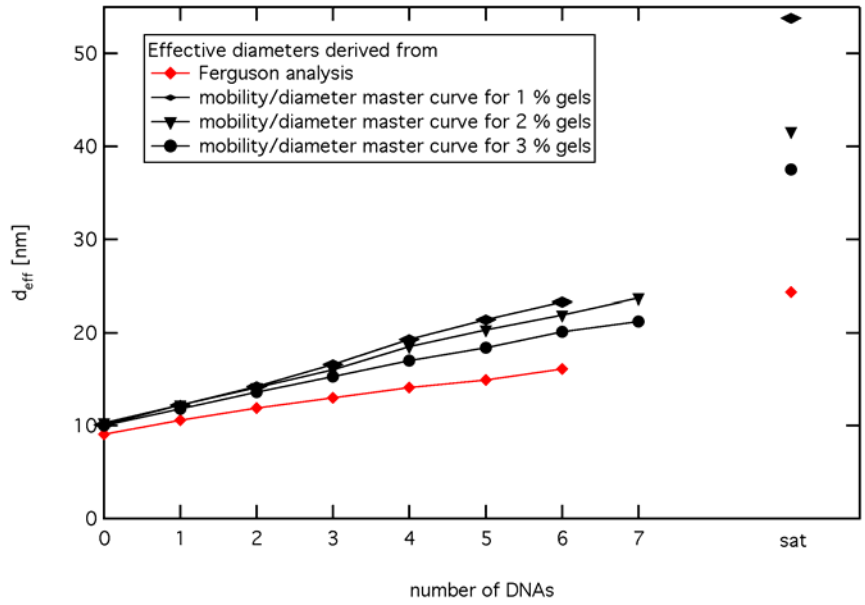

***Figure SI-17**: Effective diameters for Au-DNA conjugates with a different number of DNA molecules attached per Au particles (10 nm Au particles, with sequence SH-**43b**) have been obtained either by Ferguson analysis or by using a calibration curve that relates mobility to effective diameters for 1%, 2%, and 3% gels. The data originate from Table SI-15.*

From Figure SI-17 it is obvious, that by using different methods of evaluation significantly different values for the derived effective diameters are obtained. As already mentioned before, the Ferguson analysis reported here only yields reliable data for particles smaller than around 30 nm, because the range for the extrapolation was chosen this way. The size of all bigger particles is severely underestimated. Also the mobility-diameter master curves for 1, 2, and 3% gels yield significantly different effective diameters for the Au-DNA conjugates for big diameters. The effective diameters are smaller for gels of higher percentage. This direct comparison shows the limits of size determination with gel electrophoresis. It always has to be taken into account, that the data obtained with a certain gel percentage are only reliable for particles within a certain size range. In the following the Ferguson analysis is applied as described above for different Au-DNA conjugates and the retardation coefficients and yielded effective diameters are reported in Tables SI-16 and SI-17 and graphically displayed in Figures SI-18 to SI-19.

	SH-**43b**	SH-**43b**	SH-**50**	SH-**50**	SH-**54**	SH-**54**
number of DNAs per particle	K_r	$d_{eff,F}$ [nm]	K_r	$d_{eff,F}$ [nm]	K_r	$d_{eff.F}$ [nm]
0	0.134	9.1	0.134	9.1	0.134	9.1
1	0.150	10.5	0.151	10.6	0.152	10.7
2	0.166	11.9	0.167	12.0	0.169	12.2
3	0.179	13.0	0.184	13.4	0.185	13.5
4	0.192	14.1	0.197	14.5	0.204	15.0
5	0.203	14.9	0.216	16.0	0.216	16.0
6	0.218	16.1	-	-	0.230	17.0
7	-	-	-	-	0.243	17.9
saturation	0.341	24.3	0.427	29.2	0.376	26.4

	SH-**85**	SH-**85**	SH-**100a**	SH-**100a**	SH-**135**	SH-**135**
number of DNAs per particle	K_r	$d_{eff,F}$ [nm]	K_r	$d_{eff,F}$ [nm]	K_r	$d_{eff.F}$ [nm]
0	0.134	9.1	0.134	9.1	0.134	9.1
1	0.168	12.1	0.189	13.9	0.179	13.0
2	0.203	14.9	0.229	16.9	-	-
3	0.235	17.3	0.272	19.9	-	-
4	0.264	19.4	0.310	22.4	-	-
5	0.294	21.4	0.347	24.6	-	-
6	0.317	22.8	0.381	26.6	-	-
7	0.339	24.2	0.398	27.6	-	-
saturation	0.533	34.5	0.551	35.4	0.497	32.7

***Table SI-16**: Retardation coefficient K_r and effective diameter $d_{eff,F}$ of conjugates of 10 nm Au particles conjugated with discrete numbers of thiolated DNA molecules. The data for the K_r values have been derived by using the mobilities of Au-DNA conjugates from Tables SI-9.1, SI-9.2, and SI-9.3. The effective diameters $d_{eff,F}$ were obtained from the K_r values by using Formula SI-9 with the parameters $\alpha = 0.0286$, $\beta = 0.237$. Values are reported for conjugates with a discrete number of DNA strands per gold nanoparticle (from 0 to 7) and for particles saturated with DNA for thiol modified DNA molecules of different length (sequences see Table SI-2).*

DNA-sequence	K_r	$d_{eff,F}$ [nm]	$d_{eff,1\%}$ [nm]	$d_{eff,2\%}$ [nm]	$d_{eff,3\%}$ [nm]
SH-**8a**	0.166	12.0	21.4	18.3	15.2
8a	0.143	9.9	12.1	11.4	11.1
SH-**12**	0.204	15.1	26.8	22.7	19.7
12	0.150	10.6	11.4	11.9	11.6
SH-**16**	0.221	16.3	32.5	25.1	22.4
SH-**21**	0.244	18.0	37.8	30.4	25.6
21	0.152	10.7	15.2	13.6	12.7
SH-**30**	0.391	27.2	41.0	35.1	32.1
30	0.142	9.8	13.8	12.3	11.5
SH-**35**	0.281	20.5	41.2	33.2	29.5
SH-**36a**	0.279	20.4	40.6	35.5	29.2
36a	0.159	11.3	24.4	19.1	15.2
SH-**36b**	0.311	22.4	39.2	33.7	31.6
SH-**43a**	0.375	26.3	33.3	32.9	30.4
SH-**43b**	0.341	24.3	53.8	41.6	37.5
SH-**50**	0.427	29.2	54.1	51.5	45.0
SH-**54**	0.376	26.4	57.1	49.3	41.3
SH-**65**	0.490	32.4	58.0	53.1	51.2
SH-**85**	0.533	34.5	55.5	54.1	54.4
SH-**100a**	0.551	35.4	66.3	69.5	58.5
100a	0.190	13.9	26.8	24.6	18.5
SH-**120**	0.725	43.0	47.7	50.8	69.3
SH-**135**	0.497	32.7	87.7	111.2	58.4

Table SI-17: *Retardation coefficient K_r and effective diameter $d_{eff,F}$ for 10 nm Au particles that have been saturated with DNA of different sequences (see Table SI-2). The DNA was attached to the Au particles specifically via thiol groups and via nonspecific adsorption. The K_r values were derived according to the Ferguson analysis by using the mobility data of Au-DNA conjugates recorded at 1%, 2%, and 3% gels as displayed in Tables SI-7.1, SI-7.2, SI-7.3 (third column). The effective diameters $d_{eff,F}$ were obtained from the K_r values by using Formula SI-9 with the parameters α = 0.0286, β = 0.237. As comparison also the effective diameters obtained via a calibration curve for 1%, 2%, and 3% gels ($d_{eff,1\%}$, $d_{eff,2\%}$, $d_{eff,3\%}$) are displayed. These values are taken from Tables SI-11.1, SI-11.2, SI-11.3 (third column).*

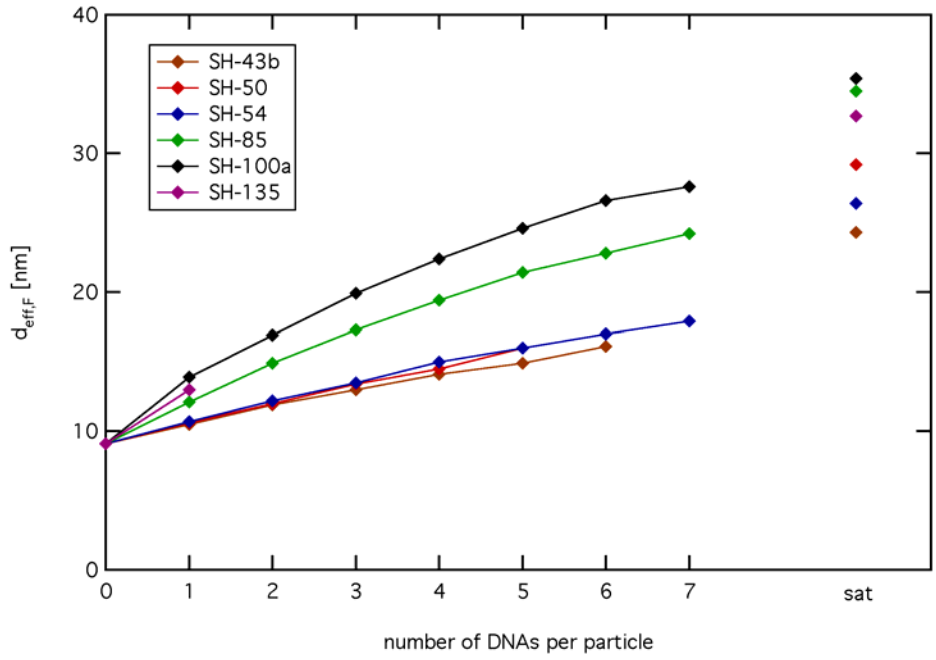

***Figure SI-18**: The effective diameters $d_{eff,F}$ of Au-DNA conjugates (10 nm Au particles, different DNA sequences) as obtained by Ferguson analysis are displayed for different numbers of DNA molecules bound per particle. The corresponding data are shown in Table SI-16.*

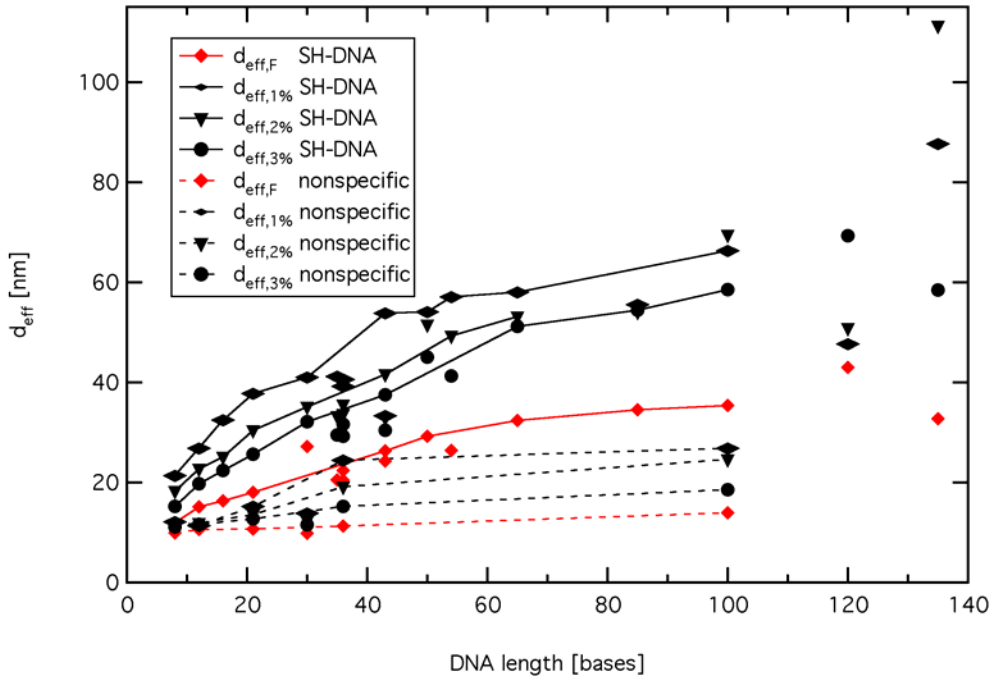

***Figure SI-19**: The effective diameters $d_{eff,F}$, $d_{eff,1\%}$, $d_{eff,2\%}$, and $d_{eff,3\%}$ of Au particles saturated with DNA (10 nm Au particles, different DNA sequences) as obtained by Ferguson analysis and diameter-mobility calibration curves for 1%, 2%, and 3% agarose gels are displayed. The corresponding data are shown in Table SI-17.*

III) Determination of the Maximum Number of Bound DNA Molecules per Nanoparticle

We have quantified the maximum number of DNA strands that can be attached per gold nanoparticle for particles with 5 nm and 10 nm diameter and single stranded DNA with 8 (sequence Cy5-**8a**-SH, see Table SI-2) and 43 bases (sequence Cy5-**43a**-SH, see Table SI-2). For this purpose single stranded DNA that was modified with a thiol group on one and a Cy5 dye on the other end has been attached via formation of thiol-Au bonds to the surface of Au particles. The DNA was added in different DNA to Au ratios and the conjugates were run on 2% agarose gels. The more DNA bound per Au nanoparticle the more the band of this conjugate was retarded on the gel {Parak, 2003 #8595}. At a certain amount of added DNA the retardation of the band of the conjugates did not increase further, which indicates that the Au surface is fully saturated with DNA [3], see Figure SI-20.

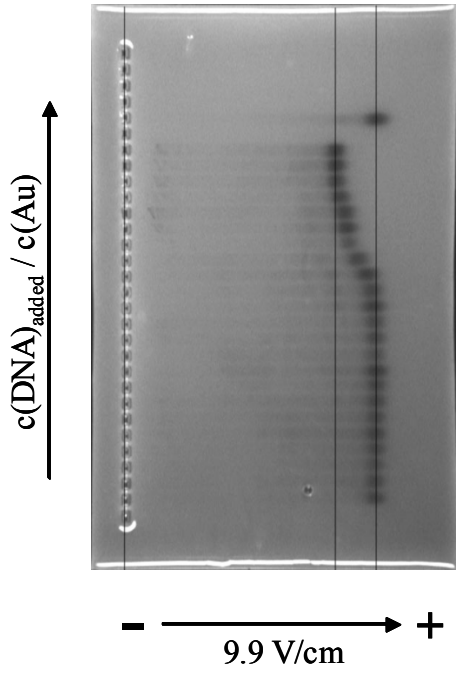

***Figure SI-20**: Cy5-**8a**-SH DNA has been added to 10 nm Au particles in different DNA/Au ratios: $c(DNA)_{added}$ / Au = 4200, 2100, 1050,..... .The absolute concentration of the Au particles was 0.21 μM. After several days of incubation the Au-DNA conjugates were run on a 2% agarose gel for 1 hour @ 100 V. The first lane from above corresponds to plain Au particles. The following lanes correspond to the Au-DNA conjugates with DNA/Au ratio of 4200, 2100, 1050,....For the highest DNA/Au ratios the retardation of the bands gets saturated, which indicates that the surface of the particles is fully loaded with DNA.*

For each band the relative mobility m / $m_{10nm,2\%}$ was determined as described in II). In total for each sample four gels were run in order to get a sufficient statistics. The bands of the Au-DNA conjugates were then extracted from the gel by cutting out the agarose piece that contained the band and immersing it in 0.5x TBE buffer solution. After two days the Au-DNA conjugates had diffused out of the gel in the buffer. The cutting and extraction procedure ensured that the Au-DNA conjugates were separated from any unbound DNA, that migrates much faster on the gel. Then UV/vis absorption spectra were recorded of all the extracted Au-DNA conjugates, see Figure SI-21. For each of the conjugates the DNA concentration was determined by the Cy5 absorption and the Au concentration was determined by the absorption at the plasmon peak and from both concentrations the number of attached DNA molecules per particles was derived.

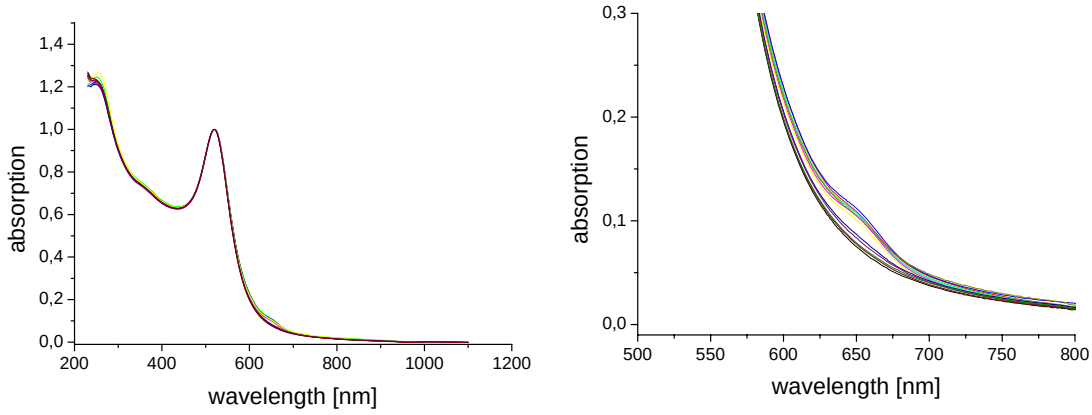

***Figure SI-21**: UV/vis spectra recorded for the Au-DNA conjugates that had been extracted from the gel shown in Figure SI-20. The intensities of all the absorption curves have been normalized to one at the plasmon peak of the Au particles (left image). The right image shows the wavelength range around 650 nm. This is the wavelength at which the Cy5 dye that is attached to the DNA absorbs. The more Cy5-labeled DNA is attached per Au particles, the more prominent the additional absorption peak at 650 nm becomes.*

The absorption spectra were then treated in the following way. First the background absorption at 1100 nm was subtracted. The spectra were then normalized, so that the absorption at the plasmon peak is equal to one. Then the absorption spectrum of plain Au particles was subtracted from all the other absorption spectra. This was done graphically to adjust for the shape of the curves. The residual spectrum corresponds to the absorption of the Cy5 dye that is attached to the DNA. We assume that each DNA molecule is labeled with exactly one Cy5 molecule. In this way we determined the Cy5 absorption for each Au-DNA conjugate. From the absorption values the concentrations were determined. We assumed the extinction coefficient of Cy5 to be ε(Cy5 at 650 nm) = 250 000 $M^{-1}cm^{-1}$. The extinction coefficients of the Au particles at their plasmon peaks are shown in Table SI-1. In this way the concentration of DNA was determined by the Cy5 absorption at 650 nm (after removing the Au signal) and the Au concentration was determined by the Au absorption at the plasmon peak. Cy5 was chosen as dye because of its large shift in absorption in relation to the plasmon peak of the Au (at the plasmon peak at around 520 nm there is almost no Cy5 absorption, the Cy5 absorbs around 650 nm). By dividing the DNA concentration by the Au concentration the actual DNA/Au ratio was finally derived.

Now the mobility of each band can be correlated with the DNA/Au ratio of the conjugates that formed the band. It has to be noted, that here the DNA/Au ratio describes the number of DNA molecules per particle that are actually bound per particle. Unbound DNA has been removed on the gel. The results are shown in Tables SI-18.1-SI-18.4 and Figure SI-22.

DNA/Au_{added}	4200	2100	1100	530	260	130	66	33	16	8.2	4.1	0
DNA/Au	46	44	50	44	40	35	41	16	12	3.3	4.6	0
$m/m_{10nm,2\%}$	0.84	0.84	0.84	0.85	0.88	0.88	0.89	0.93	0.97	0.98	1.0	1.0

Table SI-18.1*: 10 nm Au particles were incubated with Cy5-**8a**-SH DNA for several days at different DNA/Au ratios (see first line of the table). The conjugates were then run on a 2% agarose gel and their relative mobility corresponding to plain 10 nm Au particles was determined (last line of the table; an example of a gel is shown in Figure SI-20). The bands from the conjugates were extracted from the gel and UV/vis absorption spectra were recorded (examples are shown in Figure SI-21). From the Au and the Cy5 absorption the DNA/Au ratio of the conjugates extracted from each band was derived. This number (center line of the table) corresponds to the DNA molecules that have been actually bound to the Au particles. Most of the initially added DNA (as shown in the first lane of the table) did not bind to the Au. The data are graphically displayed in Figure SI-22.*

DNA/Au_{added}	4200	1000	520	260	130	65	16	8.1	4.1	2.0	0
DNA/Au	56	54	51	53	50	49	7.2	0.56	0.25	1.0	0
$m/m_{10nm,2\%}$	0.82	0.82	0.83	0.83	0.84	0.85	0.94	0.97	0.97	0.99	1.0

Table SI-18.2*: 10 nm Au particles were incubated with Cy5-**8a**-SH DNA for several days at different DNA/Au ratios (see first line of the table). The conjugates were then run on a 2% agarose gel and their relative mobility corresponding to plain 10 nm Au particles was determined (last line of the table; an example of a gel is shown in Figure SI-20). The bands from the conjugates were extracted from the gel and UV/vis absorption spectra were recorded (examples are shown in Figure SI-21). From the Au and the Cy5 absorption the DNA/Au ratio of the conjugates extracted from each band was derived. This number (second line of the table) corresponds to the DNA molecules that have been actually bound to the Au particles. Most of the initially added DNA (as shown in the first lane of the table) did not bind to the Au. The data are graphically displayed in Figure SI-22.*

DNA/Au_{added}	12000	5900	3000	1500	740	370	190	93	47	0
DNA/Au	40	44	34	43	39	32	41	37	29	0
$m/m_{10nm,2\%}$	0.56	0.56	0.59	0.58	0.60	0.62	0.62	0.62	0.66	1.0

Table SI-18.3*: 10 nm Au particles were incubated with Cy5-**43a**-SH DNA for several days at different DNA/Au ratios (see first line of the table). The conjugates were then run on a 2% agarose gel and their relative mobility corresponding to plain 10 nm Au particles was determined (last line of the table; an example of a gel is shown in Figure SI-20). The bands from the conjugates were extracted from the gel and UVVIS spectra were recorded (examples are shown in Figure SI-21). From the Au and the Cy5 absorption the DNA/Au ratio of the conjugates extracted from each band was derived. This number (middle line of the table) corresponds to the DNA molecules that have been actually bound to the Au particles. Most of the initially added DNA (as shown in the first lane of the table) did not bind to the Au. The data are graphically displayed in Figure SI-22.*

DNA/Au_{added}	1100	550	270	140	69	35	17	8.7	4.3	2.2	1.1	0
DNA/Au	13	12	12	12	11	9.9	9.2	5.3	1.3	0.67	0.02	0
$m/m_{5nm,2\%}$	0.82	0.85	0.85	0.86	0.87	0.87	0.87	0.90	0.94	0.97	0.98	1.0

***Table SI-18.4**: 5 nm Au particles were incubated with Cy5-**8a**-SH DNA for several days at different DNA/Au ratios (see first line of the table). The conjugates were then run on a 2% agarose gel and their relative mobility corresponding to plain 5 nm Au particles was determined (last line of the table; an example of a gel is shown in Figure SI-20). The bands from the conjugates were extracted from the gel and UVVIS spectra were recorded (examples are shown in Figure SI-21). From the Au and the Cy5 absorption the DNA/Au ratio of the conjugates extracted from each band was derived. This number (middle line of the table) corresponds to the DNA molecules that have been actually bound to the Au particles. Most of the initially added DNA (as shown in the first lane of the table) did not bind to the Au. The data are graphically displayed in Figure SI-22.*

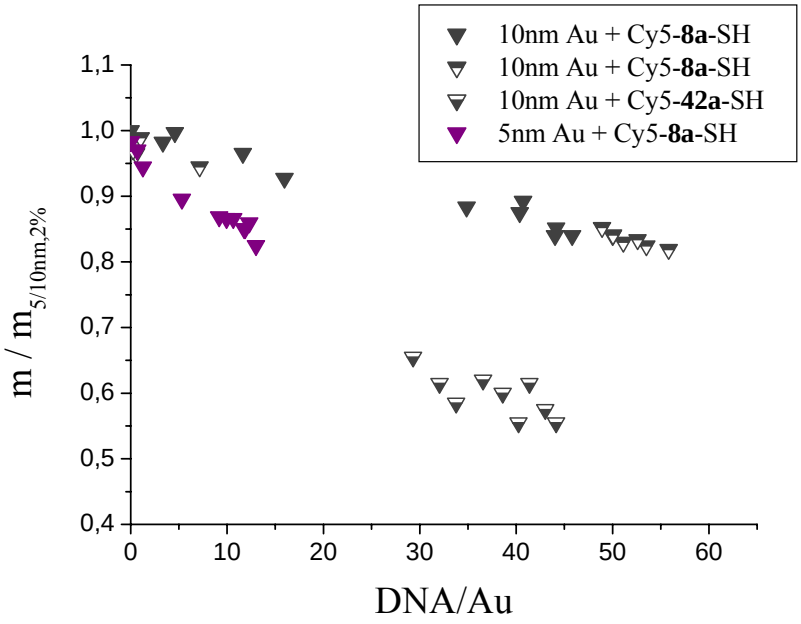

***Figure SI-22**: 5 and 10 nm Au particles were incubated with Cy5-**8a**-SH and Cy5-**43a**-SH DNA for several days at different DNA/Au ratios. The conjugates were then run on a 2% agarose gel and their relative mobility corresponding to plain Au particles was determined. The bands from the conjugates were extracted from the gel and UV/vis absorption spectra were recorded. From the Au and the Cy5 absorption the DNA/Au ratio of the conjugates extracted from each band was derived. The relative mobility of the conjugates $m/m_{10nm,2\%}$ (or $m/m_{5nm,2\%}$) is plotted against the number of DNA molecules that are actually bound per Au particle. The corresponding data are enlisted in Tables SI-18.1- SI-18.4.*

When the mobility of the bands does not further decrease upon the addition of more DNA we assume that the surface of the particles is saturated with DNA. From Tables SI-18.1- 18.4 and Figure SI-22 the maximum number of DNA molecules that can be bound per Au particle can be estimated: ca. 53 Cy5-**8a**-SH per 10 nm Au particle, ca. 43 Cy5-**43a**-SH per 10 nm Au particle, and ca. 13 Cy5-**8a**-SH per 5 nm Au particle. Particles with a nominal diameter d of 10 nm and 5 nm have a surface area of 314 nm^2 and 79 nm^2, respectively. In this way we can determine the surface density of the bound DNA molecules, i.e. the number of molecules bound per nm^2, see Table SI-19. Also the data from other studies are included in this table. 1 mol = $6.022 \cdot 10^{23}$ molecules.

diameter of the Au particle (without surface coating)	attached DNA sequence in number of bases	number of DNA molecules bound per particle	DNA density on Au particles [pmol/cm^2]	c(NaCl) [mM] during incubation	reference
10 nm	8	53	28	50	this study
10 nm	43	42	22	50	this study
5 nm	8	13	27	50	this study
7 nm	5	62	67	500	[7]
13 nm	12	115	36	100	[8]
13 nm	25	90	28	100	[8]
15.7 nm	12	157	34	100	[9]
15.7 nm	32	69	15	100	[9]

Table SI-19*: The surface of Au nanoparticles of different diameter has been saturated with single-stranded DNA molecules of different length. The maximum number of attached DNA molecules per particle has been determined. This number divided by the surface area of the Au nanoparticles determines the saturation DNA density on Au particles. The DNA density is displayed versus the length of the DNA molecules in Figure SI-23. The Au particles used in this study were phosphine-stabilized, the particles in the other studies citrate-stabilized.*

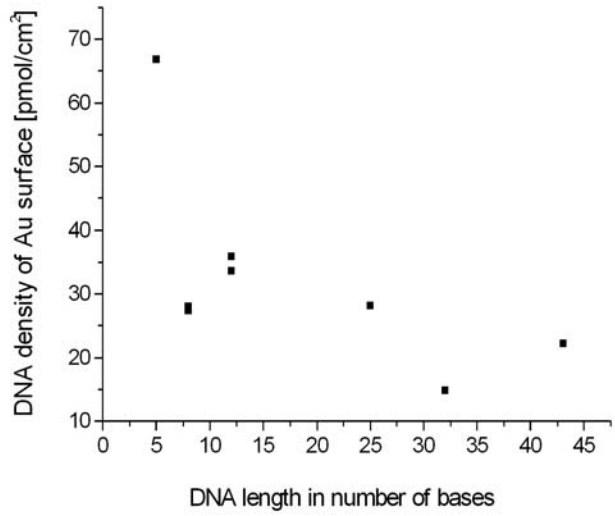

Figure SI-23*: The surface of Au nanoparticles of different diameter has been saturated with single-stranded DNA molecules of different length. The maximum number of attached DNA molecules per particle has been determined. This number divided by the surface area of the Au nanoparticles determines the saturation DNA density on Au particles. The DNA density is displayed versus the length of the DNA molecules. The corresponding data can be found in Table SI-19.*

IV) References

1. Zanchet, D., et al., *Electrophoretic isolation of discrete Au nanocrystal/DNA conjugates.* Nanoletters, 2001. **1**(1): p. 32-35.
2. Zanchet, D., et al., *Electrophoretic and Structural Studies of DNA-Directed Au Nanoparticle Groupings.* Journal of Physical Chemistry B, 2002. **106**(45): p. 11758-11763.
3. Parak, W.J., et al., *Conformation of oligonucleotides attached to gold nanocrystals probed by gel electrophoresis.* Nanoletters, 2003. **3**(1): p. 33-36.
4. Tinland, B., et al., *Persistence Length of Single-Stranded DNA.* Macromolecules, 1997. **30**(19): p. 5763-5765.
5. Rivetti, C., M. Guthold, and C. Bustamante, *Scanning Force Microscopy of DNA Deposited onto Mica: Equilibration versus Kinetic Trapping Studied by Statistical Polymer Chain Analysis.* Journal of Molecular Biology, 1996. **264**(5): p. 919-932.
6. Park, S., K.A. Brown, and K. Hamad-Schifferli, *Changes in Oligonucleotide Conformation on Nanoparticle Surfaces by Modification with Mercaptohexanol.* Nanoletters, 2004. **4**(10): p. 1925-1929.
7. Qin, W.J. and L.Y.L. Yung, *Efficient Manipulation of Nanoparticle-Bound DNA via Restriction Endonuclease.* Biomacromolecules, 2006. **7**(11): p. 3047-3051.
8. Sandström, P., M. Boncheva, and B. Åkerman, *Nonspecific and Thiol-Specific Binding of DNA to Gold Nanoparticles.* Langmuir, 2003. **19**(18): p. 7537-7543.
9. Demers, L.M., et al., *A Fluorescence-Based Method for Determining the Surface Coverage and Hybridization Efficiency of Thiol-Capped Oligonucleotides Bound to Gold Thin Films and Nanoparticles.* Analytical Chemistry, 2000. **72**(22): p. 5535-5541.