Supporting Infomation

Kinetics of Aggregation and Growth Processes of PEG-Stabilised Mono- and Multivalent Gold Nanoparticles in Highly Concentrated Halide Solutions

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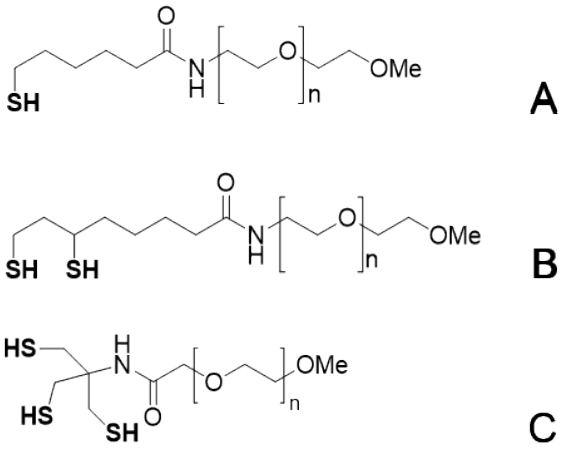

Figure S1. Structures of the mono-, di-, and trivalent thiol PEG ligands

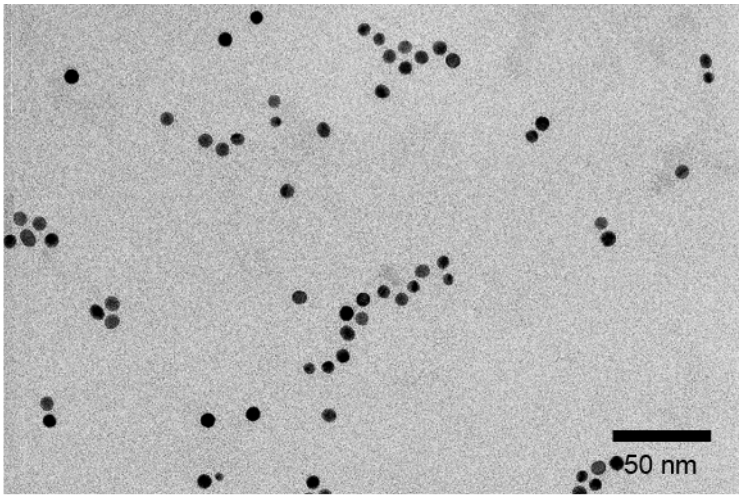

Figure S2. TEM image of gold nanoparticles which are in situ functionalized with the monovalent thiol PEG ligand

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Table S1 Results of the fit of the time dependent decrease of the intensity at the extinction maximum of monothiol PEG-stabilised gold nanoparticles in an aqueous solution of NaBr at different temperatures, according to Equation (2). The data for the 4.5 M solution at 25°C are fitted by Equation (3).

Temperature [°C]	Concentration [M]	R_∞ [arb. units]	A_1 [arb. units]	k_1 [min]	A_2 [arb. units]	k_2 [min]	Correlation coefficient
15	2	0.979±0.001	0.022±0.002	0.18±0.05	-	-	0.94
25	2	0.843±0.037	0.163±0.034	0.009±0.003	-	-	0.98
35	2	0.817±0.008	0.200±0.008	0.018±0.001	-	-	0.9997
45	2	0.663±0.008	0.362±0.006	0.019±0.001	-	-	0.998
25	3	0.720±0.043	0.278±0.041	0.0074±0.0016	-	-	0.994
25	4.5	-	0.081±0.005	0.096±0.011	0.923±0.004	0.0011±0.0001	0.995

[a] Only the values for the first 45 min were fitted since sampling for TEM after 45 min (see Table S2) slightly influenced the kinetics

Table S2 Results of the fit of changes of the spectral broadening factor R of monothiol PEG-stabilised gold nanoparticles in an aqueous solution of NaI at different temperatures, according to Equation (12).

Batch	Temperature [°C]	Concentration [M]	R∞ [arb. units]	A_1 [arb. units]	A_2 [arb. units]	k_1 [10^{-2}min^{-1}]	k_2 [min^{-1}]	k_3 [min^{-1}]	Correlation coefficient
I	15	2	0.46±0.31	0.83±0.02	0.79±0.29	0.049±0.006	0.07±0.002	0.002±0.001	0.9997
I	25	2	0±3.74	0.81±0.03	1.24±3.71	0.026±0.006	0.14±0.01	0.001±0.004	0.9993
I	35	2	1.02±0.01	0.99±0.07	0.39±0.06	0.64±0.24	0.50±0.05	0.049±0.008	0.998
I	45	2	0.96±0.02	1.08±0.21	0.53±0.20	0.48±0.56	0.55±0.15	0.056±0.019	0.9889
II	25	1	R(t) is not changing with time, no fit possible.						
II	25	1.25	0.11±2.89	0.63±0.01	0.93±2.90	0.020±0.0003	0.08±0.0003	0.0006±0.002	0.99998
II	25	2	1.01±0.07	1.08±0.09	0.52±0.06	0.10±0.05	0.23±0.02	0.015±0.006	0.995
II	25	3	1.09±0.002	0.91±0.01	0.30±0.01	3.03±0.11	0.44±0.01	0.038±0.002	0.9998

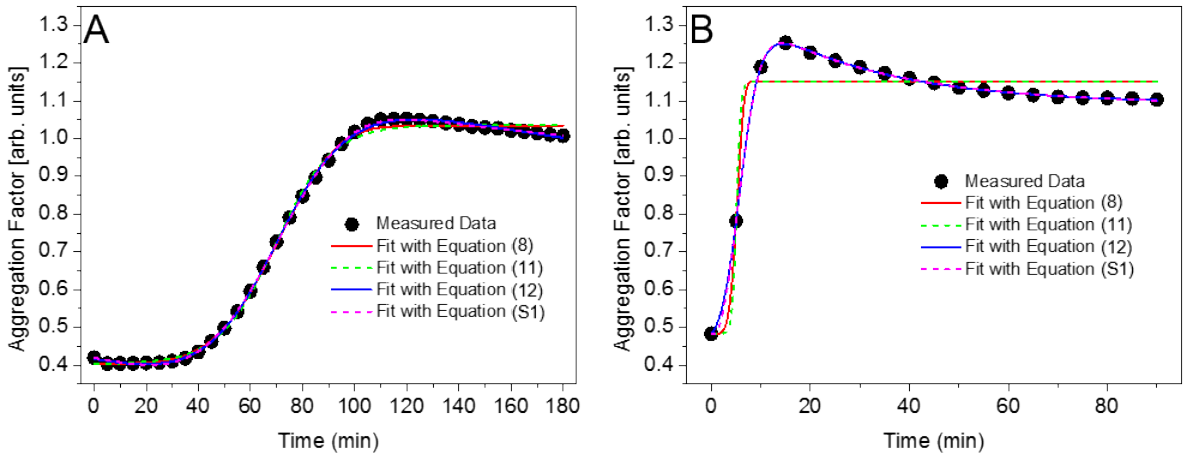

Figure S3. Time-dependent changes of the spectral broadening factor R of monothiol PEG-stabilized gold nanoparticles in (a) a 2 M aqueous solution of NaI at 15°C and (b) a 3 M aqueous solution of NaI at 15°C. Both data sets are fitted with the Equations (8), (11), and (12) as well Equation (S1). Whereas the data in Figure (a) can be also reasonably fitted with the Equations (8) and (11), this is not possible for the data in Figure (b). The Equations (12) and (S1) can be used for successfully fitting both data sets.

$$R(t) = R_0 + A_{g,1}\left[1 - exp\left(-k_{g,1}t\right)^n\right] + A_4 e x p\left(-k_4 t\right) \qquad \text{(S1)}$$

Equation (S1): This equation corresponds to Equation (8) with an additional exponential decay term. Here, R(t) is the time-dependent spectral broadening factor, R_0 is R(t) for t =0, $k_{g,1}$ is the rate constant for sigmoidal process, and n is the Avrami exponent of this process (see Equation 8). Parameter k_4 is the rate constant of the additional exponential decay process. $A_{g,1}$ and A_4 are the amplitudes of the sigmoidal and the exponential process.

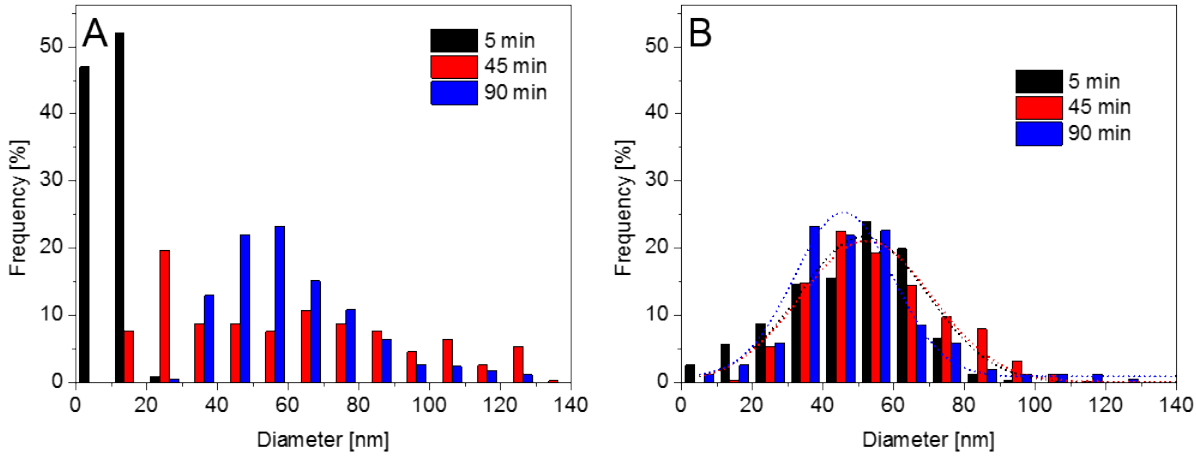

Figure S4: Statistical distribution of the particle diameter of monothiol PEG-stabilized gold nanoparticles in a 2 M aqueous solution of NaI at (a) 35°C and (b) 45°C. In Figure (b) Gaussian distributions were plotted for a better comparison. In Figure (a) the distributions after 5 min and 45 min could not be well described by a Gaussian distribution.