Electronic Supplementary Information

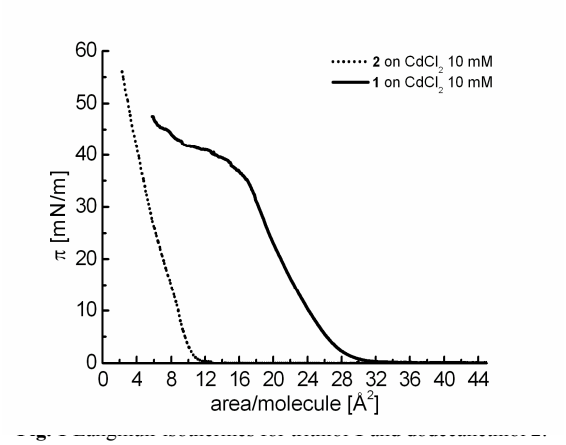
"Reliable stabilization and functionalization of nanoparticles through tridentate thiolate ligands"

1. Langmuir-trough experiments with **1** and **2**

A NIMA 710 trough with Wilhelmy-plate sensor was used for monolayer experiments.

The substances were dissolved in chloroform and then dropped on an aqueous subphases containing $CdCl_2$ (10 mM). The compression was started 10 minutes after application. Compression speed was 15 cm^2/min.

The area per molecules of **1** and **2** is estimated from extrapolating the Langmuir isotherms towards zero pressure.



The mean area per molecule amounts to 25-27 $Å^2$ for compound **1** compared to 8-9 $Å^2$ for compound **2**.

2. Ligand exchange of TOAB against **1** or **2**

10 mL of a gold colloid in toluene (after J. Fink, C. J. Kiely, D. Bethell, D. J. Schiffrin, *Chem. Mater.* **1998**, *10*, 922-926.) were diluted with 10 mL toluene. After that 0.2 mL of **1** or **2** are added. The solution is refluxed for 1 h. The thiolate stabilized particles are isolated by precipitation with CH_3CN, washed with EtOH and then dissolved in toluene.

3. Preparation of AuNP´s stabilized by **2**

In a 500 mL round bottom flask 450 mg $HAuCl_4 \cdot 3\ H_2O$ (1.32 mmol) are dissolved in 225 mL diethylether. 1.34 g **2** (6.65 mmol) are added. The reaction mixture is cooled to 0°C. Under stirring 15 mL of a 1M $LiBEt_3H$-solution in hexane (15 mmol) are added. After temperating to r.t. and addition of a further amount of **2** (500 mg, 2.49 mmol) the solution is stirred for another 30 min. After removing volatile components and addition of 2 mL dichlormethane a deep red solution is obtained. The thiolate content of the solution is determined by NMR. For that purpose $SiMe_4$ (TMS) is added to an NMR-sample of **2**@AuNP´ in $CDCl_3$. The concentration of particle bound thiolate can be calculated from the integrals of the signals at 0 ppm (TMS, 12H) and 0.86 ppm (methyl, 3H) taking into account the molar quantity of TMS and the utilized volume of **2**@AuNP´.

TEM <D> = (3.4 ± 0.4) nm; ^{1}H-NMR c(**2**@AuNP´) = 0.112 mmol/mL; UV-Vis λ_{max} = 532 nm

4. Lignd exchange leading to AuNP´s stabilized by **1**

1 mL (0.112 mmol **2**@uNP´) of the solution from 3. in dichloromethane in a round bottom flask are mixed with 5 mL of a 14 mM solution of **1** in hexane. After 30 min stirring at r.t. 20 mL ethanol are added. The particles are separated by centrifugation and dissolved in 2 mL chloroform. This procedure is repeated twice. The supernatants are collected; volatile components are removed *in vacuo*. The remaining oil is characterized by NMR-spectroscopy. **2** as free thiol replaced from the particle can be identified by a quartett at 2.47 ppm. The particles **1**@AuNP´ are dissolved in dichloromethane.

^{1}H-NMR c(**1**@AuNP´) = 0.0034 mmol/mL = 0.0102 mmol/mL thiolate-groups

UV-Vis λ_{max} = 532 nm

5. Sedimentation experiments with thiolate stabilized AuNPs

Solutions of thiolate stabilized gold nanoparticles (**1**@AuNP´; **2**@AuNP´) and 11-mercaptoundecanoic acid (MUNDA; 0.1 M) in dichloromethane are mixed in a quartz-cuvette according to the molar ratios given below and diluted with pure dichloromethane giving a total volume of 3 mL. The starting concentration of gold particles is chosen to result in an absorption of about 1. The measurement is started immediately after mixing of the solutions. The absorption is recorded at 535 nm in 60 s intervals. The monochromator slit is adjusted for a spectral resolution of 4 nm. The measurement is finished after 10 h. The resulting curves are fitted with the described mathematical models.

	addition *AuNP´*	addition *MUNDA*	molar ratio *L@Au:MUNDA*	Absorption *start/end*	k [min^{-1}]
2@AuNP´	10 µL (1.1 µmol)	22 µL (2.2 µmol)	1:2	1.35/1.10	0.013
	10 µL (1.1 µmol)	11 µL (1.1 µmol)	1:1	0.90/0.75	0.0082
	10 µL (1.1 µmol)	5.6 µL (0.056 µmol)	2:1	1.20/1.00	0.0073
1@AuNP´	1.9 mL (6.5 µmol)	11 µL (1.1 µmol)	6:1	1.14/1.15	-
	1.9 mL (6.5 µmol)	56 µL (5.6 µmol)	1.2:1	1.31/1.36	-
	0.5 mL (1.7 µmol)	51 µL (5.1 µmol)	1:3*	0.35/0.36	-

* 1:1 thiolate functions

6. General procedure for the photochemical addition of thiols to **3**@AuNP´

In a closed quartz-tube 2 mL of a solution containing about 20 mg/mL **3**@AuNP´ are mixed with an excess of the respective thiol and diluted with 8 mL dichloromethane. The solution is irradiated with a high pressure Hg-lamp for 1 h at r.t..