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Formation of gold colloids using thioether derivatives as stabilizing ligands

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Thioethers were used as adsorbates for preparing gold nanoparticles. Different thioether derivatives having from 1 to 4 thioether functionalities were synthesized. Colloids were prepared in a two-phase system, and characterized by ^{1}H NMR and transmission electron microscopy (TEM). The stability of colloids protected by thioethers increases with the number of ligands per molecule. Monothioethers need longer chain lengths or costabilization by $(oct)_4NBr$ in order to give stable, redispersible gold colloids. Gold colloids stabilized by the bis(thioether) **5** could not be redispersed after precipitation. Colloids stabilized by the tris(thioether) **6** were only formed at elevated temperature (60 °C) indicating the need of chain reorientation for attaining stable colloids. Tris(thioether) **7** gave stable colloids at room temperature, which could be redispersed even after precipitation. Tetrakis(thioether) **8** gave the smallest particle size and narrowest size distribution.

Introduction

Functionalized metal colloids have generated ample opportunities in chemistry, materials science, and nanotechnology, owing to their optical, magnetic, catalytic, and electronic properties. Recently, initiated by reports by Brust *et al.*[1–3] and others,[4,5] the investigation of self-assembled monolayer-protected gold nanoclusters (MPCs) has become an active area of interdisciplinary research. Compared to other metal clusters, monolayer-protected gold colloids offer exceptional properties such as easy preparation, solubility in various solvents, air stability, and isolation as a solid. Furthermore, these substances can be analyzed by solution-based techniques, such as NMR, IR, and UV/Vis spectroscopy, and are suited for further functionalization and exchange reactions.[6]

The structure and the dynamic behavior of the alkyl chains of the thiol adsorbate have been studied extensively by using solid state NMR,[7] IR spectroscopy,[8] and X-ray photoelectron spectroscopy (XPS).[9] It was found that alkanethiols on MPCs bind in the same way as in the case of thiolate formation on flat gold surfaces. (Functionalized) alkanethiols[2,3,10–13] or dialkyl disulfides[14] have been used almost exclusively as ligands to cap the gold nanoclusters. To our knowledge, no work has been reported for using thioethers as ligands for colloid preparation. Only recently Sorensen *et al.* reported a gold colloid formation using a reverse micelle method which gave soluble gold colloids upon treatment with a thioether derivative.[15]

Self-assembled monolayers on flat gold have been subject to extensive study owing to their prospects for the development of sensors, interfaces, and nanoconstruction. In our group, interest has focused on adsorbate molecules with multiple attachment points, such as resorcin[4]arene,[16] calix[4]arene,[17] carceplexes,[18] and β-cyclodextrins,[19] in order to create well-ordered, functional monolayers on gold. All these adsorbates are anchored to gold *via* thioether moieties. Thioethers give a less strong Au–S interaction than thiols, but the combination of multiple thioether–gold interactions can lead to very stable and well-ordered monolayers.[16–19]

The motivation of this study is to address the possibility and scope of using thioethers as passivating ligands for direct gold colloid preparation and the stability of those gold colloids (here we refer to the colloid stability as kinetic stability, *i.e.* the ability against irreversible aggregation, which is reflected in the way of preparation, handling, and possible storage time) in comparison to thiolate gold colloids. We have varied chain lengths of thioether ligands and the number of thioether–gold interactions per adsorbate in order to study their cooperativity in providing colloid stability.

^{1}H NMR was used to address the binding of the ligands to Au. Transmission electron microscopy (TEM) was used to determine the size distribution of the nanoparticles. UV/Vis spectroscopy was used to characterize the surface plasmon band of the gold colloids.

Experimental

Chemicals

All chemicals were used as received, unless otherwise stated. $HAuCl_4 \cdot xH_2O$ (99.99%) was purchased from Acros Organics, tetraoctylammonium bromide from Fluka. 5-Norbornene-2-*exo*-3-*exo*-dimethanol† (DMN), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), HOBT (1-hydroxybenzotriazole), and 4-(dimethylamino)-pyridine (DMAP) were purchased from Aldrich. Water was purified by Millipore membrane units. Solvents for colloid preparation were of reagent grade. Solvents used for organic synthesis were purified according to standard laboratory methods.[20] Thioether **1** was synthesized according to a literature procedure.[21] Thioethers **2**, **3** and **4** were synthesized in an analogous way. The synthesis of **8** has been published elsewhere.[17] Di-*tert*-butyl 4-nitro-4-[2-(*tert*-butoxycarbonyl)-ethyl]heptanedioate and Behera's amine were synthesized following literature procedures.[22] The synthesis of 11-bromoundecyl decyl sulfide has been published elsewhere.[23]

†The IUPAC name for 5-norbornene-2-*exo*-3-*exo*-dimethanol is 2,3-bis(hydroxymethyl)bicyclo[2.2.1]hept-5-ene

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Norbornene bis(thioether) 5

Thioether **1** (1.1 g, 2.62 mmol), DMN (0.2 g, 1.29 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.63 g, 5.16 mmol) were suspended in CH_2Cl_2 (20 mL). The mixture was cooled down to 0 °C, after which EDC (0.54 g, 2.84 mmol) was added. The reaction mixture was allowed to warm to room temperature, and kept at room temperature for 2 h. Another 20 mL of CH_2Cl_2 was added, and the solution was washed with 1 M HCl (2 ×), water (2 ×), brine, and dried over $MgSO_4$. Removal of the solvent under reduced pressure, and flash column chromatography (CH_2Cl_2–hexane: 1 : 1) gave pure **1** 0.58 g (48%) as a white solid. Mp 79 °C. ^{1}H NMR ($CDCl_3$) δ: 6.09–6.12 (m, 2H), 4.13–4.19 (m, 2H), 3.91–3.98 (m, 2H), 2.65–2.67 (m, 2H), 2.40–2.45 (t, 8H, J = 7.3 Hz), 2.22–2.28 (t, 4H, J = 7.3 Hz), 1.76–1.79 (m, 2H), 1.43–1.58 (m, 14H), 1.19–1.32 (m, 60H), 0.79–0.83 (t, 6H, J = 0.66 Hz). ^{13}C NMR ($CDCl_3$) δ: 173.20, 136.86, 64.69, 44.22, 42.08, 39.23, 33.87, 33.12, 31.67, 31.34, 29.20, 29.10, 28.72, 28.43, 24.43, 24.44, 22.16, 13.58. MS (FAB-MS): *m*/*z*, 913.8 ($[M+Na]^+$; calcd. for $C_{55}H_{102}O_4S_2$: 890.7).

11-Aminoundecyl decyl sulfide

To a solution of 11-bromoundecyl decyl sulfide (3.08 g, 7.56 mmol) in dimethylformamide (DMF) (150 mL) was added potassium phthalimide (2.83 g, 15.3 mmol) and a catalytic amount of potassium iodide at room temperature. The solution was refluxed overnight. Subsequently, hexane and water were added. The organic layer was concentrated *in vacuo*. Crystallization from EtOH yielded 11-phthalimidoundecyl decyl sulfide as a white solid (3.28 g, 7.50 mmol, 92%). ^{1}H NMR ($CDCl_3$) δ: 8.00–7.60 (m, 4H), 3.70 (t, 2H, J = 7.1 Hz), 2.52 (t, 2H, J = 6.8 Hz), 1.90–1.10 (m, 34H), 0.90 (t, 3H, J = 6.9 Hz). MS (FAB-MS) *m*/*z*: 474.3 ($[M+H]^+$; calcd. for $C_{29}H_{47}NO_2S$: 473.4). To a solution of 11-phthalimidoundecyl decyl sulfide (7.57 g, 16.0 mmol) in ethanol (600 mL) was added hydrazine (7.75 mL, 160 mmol). The solution was refluxed for 5 h. Subsequently, ethanol was evaporated; the residue was dissolved into dichloromethane and washed with water. Removal of the solvent and crystallization from EtOH yielded 11-aminoundecyl decyl sulfide as a white solid (4.92 g, 14.3 mmol, 90%). ^{1}H NMR ($CDCl_3$) δ: 2.93 (t, 2H, J = 7.5 Hz), 2.50 (t, 4H, J = 7.4 Hz), 1.80–1.65 (m, 2H), 1.58 (m, 4H), 1.50–1.20 (m, 28H), 0.89 (t, 3H, J = 6.6 Hz).

Ferrocene tris(thioether) 6

Ferrocenecarboxylic acid (0.15 g, 0.65 mmol) and oxalyl chloride (1.6 g, 12.6 mmol) were refluxed in 20 mL CH_2Cl_2 for 5 h. The solvent was evaporated and the residue was dissolved in 20 mL CH_2Cl_2. After addition of triethylamine (1 mL) and Behera's amine (0.27 g, 0.65 mmol) the solution was stirred overnight. The organic layer was washed with a 10% aqueous $NaHCO_3$ solution (2 ×), 1 M HCl (2 ×), brine, and dried over $MgSO_4$. After removal of the solvent, the product was purified by column chromatography (first CH_2Cl_2, then EtOAc) to obtain the ferrocene tris-*tert*-butyl ester as an orange powder in 83% yield. This compound was prepared before by Kaifer *et al.*[24] Spectroscopic data of this compound closely resembled those reported here. ^{1}H NMR ($CDCl_3$) δ: 6.25 (s, 1H), 4.67–4.66 (m, 2H), 4.31–4.30 (m, 2H), 4.20 (s, 5H), 2.33–2.03 (m, 12H), 1.42 (s, 27H). MS (FAB-MS): *m*/*z*, 650.2 ($[M+Na]^+$; calcd. for $C_{33}H_{49}NO_7Fe$: 627.3). A solution of the ester was stirred overnight in formic acid at room temperature. After concentration, toluene was added and evaporated three times to remove any residual formic acid. The obtained ferrocene triacid was used without further purification and characterization. At 0 °C, EDC (450 mg, 2.35 mmol) was added to a solution of the ferrocene triacid (138 mg, 0.300 mmol), 11-aminoundecyl decyl sulfide (420 mg, 1.22 mmol), and DMAP (750 mg, 6.14 mmol) in 30 mL CH_2Cl_2. The solution was stirred for 1 h at 0 °C and for 5 d at ambient temperature. 100 mL CH_2Cl_2 was added and the organic layer was washed with 1 M HCl (3 ×), brine, and dried over $MgSO_4$, after which the solvent was evaporated. The crude product was purified by column chromatography (ethyl acetate–hexane: 1 : 4), to obtain **2** in 44% yield as a yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.51 (s, 1H), 5.90 (t, 3H, J = 5.4 Hz), 4.80–4.78 (m, 2H), 4.32–4.31 (m, 2H), 4.16 (s, 5H), 3.24–3.18 (m, 6H,), 2.48 (t, 12H, J = 7.8 Hz), 2.31–2.09 (m, 12H), 1.60–1.25 (m, 102H), 0.87 (t, 3H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 173.19, 170.80, 70.39, 69.52, 68.33, 58.10, 39.72, 32.16, 31.84, 31.27, 29.69, 29.27, 29.22, 28.92, 26.93, 22.62, 14.07. MS (FAB-MS) *m*/*z*: 1436.0 ($[M+H]^+$; calcd. for $C_{84}H_{154}N_4O_4S_3Fe$: 1435.0).

Nitrotris(thioether) 7

Di-*tert*-butyl 4-nitro-4-[2-(*tert*-butoxycarbonyl)ethyl]heptanedioate (3.04 g, 6.82 mmol) was hydrolyzed by stirring in 10 mL of 96% formic acid overnight at room temperature. The solvent was removed *in vacuo* to give quantitatively the Behera's nitro triacid as a white solid, which was used without further purification. ^{1}H NMR (THF-d_8): 2.26 (s, 12H). To a solution of 11-aminoundecyl decyl sulfide (105 mg, 0.305 mmol), EDC (64 mg, 0.334 mmol), DMAP (83 mg, 0.679 mmol), and HOBT (45 mg, 0.333 mmol) in dry THF (50 mL) was mixed Behera's nitro triacid (19 mg, 0.069 mmol). The suspension was stirred at room temperature for 3 d. The reaction mixture was concentrated and dissolved in dichloromethane, washed with 0.1 M HCl and water. The organic layer was dried over Na_2SO_4 and gave thioether **4** as a white solid after removal of the solvent (87 mg, 0.069 mmol, 100%). ^{1}H NMR ($CDCl_3$) δ: 5.82 (br s, 3H), 3.30–3.15 (m, 6H), 2.50 (t, 12H, J = 7.5 Hz), 2.40–2.20 (m, 12H), 1.70–1.20 (m, 34H), 0.88 (t, 9H, J = 6.8 Hz). ^{13}C NMR $CDCl_3$) δ: 171.01, 93.57, 39.76, 32.22, 31.88, 30.90, 30.76, 29.75, 29.51, 29.26, 28.96, 26.93, 22.66, 14.08. MS (FAB-MS) *m*/*z*: 1254.2 ($[M+H]^+$; calcd. for $C_{73}H_{144}N_4O_5S_3$: 1253.0).

Preparation of the gold colloids

To compare the thioethers' ability for gold colloid formation, all colloids were synthesized using the same molar ratio of starting reagents, *i.e.* $Au : S : (n\text{-oct})_4NBr : NaBH_4 = 1 : 3 : 2 : 12$, closely following the method developed by Brust *et al.*[2] All reactions were carried out at room temperature, except when stated otherwise. A typical synthesis procedure is as follows: to a 0.1 M (0.8 mL) solution of tetraoctylammonium bromide in toluene (for **7**, CH_2Cl_2 was used as a solvent), 0.03 M (1.3 mL) aqueous tetrachloroauric acid solution was added. The aqueous phase became colorless quickly while the organic phase turned orange–brown due to the transfer of $AuCl_4^-$ into toluene. The mixture was stirred vigorously for 20 min to ensure complete transfer. Hereafter 0.04 M thioether in toluene (**1**, **2**, **3**, **4**, **5**, **6**, **8**) or in dichloromethane solution (**7**) was added. After 5 minutes, 0.1 M (4.8 mL) freshly prepared aqueous $NaBH_4$ was added quickly to the mixture. The colloids were formed instantaneously as witnessed by the color change of the solution from orange to red, and finally to black–brown. After 15 h, the organic layer was collected, washed with water, and dried over Na_2SO_4. The solvent was concentrated to a minimum amount under reduced pressure. Then the colloids were suspended in mixture of ethanol–toluene (1 : 1) solution at –20 °C for 4 hours. The precipitated colloids were collected by centrifugation as dark-brown solids and dried under vacuum. ^{1}H NMR was performed to check if there was still tetraoctylammonium bromide present. For **6**, preparation was also carried out at 60 °C.

TEM

Transmission electron microscopy (TEM) images were collected on a Philips CM 30 Twin STEM, fitted with Kevex delta plus X-ray dispersive electron spectroscopy (EDX) and Gatan model 666 PEELs, operating at 300 kV. Samples were prepared by drop-casting a drop of gold colloid dichloromethane solution onto a 200 mesh copper grid, and leaving to dry for 10 min.

NMR

NMR spectra were recorded at 25 °C using a Varian Inova 300 spectrometer. ^{1}H NMR chemical shifts (300 MHz) are given relative to residual $CHCl_3$ (7.25 ppm) as an internal standard. ^{13}C NMR chemical shifts (75 MHz) are given relative to $CDCl_3$ (77.0 ppm).

UV/Vis

UV/Vis spectra were measured on a HP4852 spectrophotometer. The spectra were corrected for the background absorbance of the solvent (CH_2Cl_2).

FAB-MS

Mass spectra were recorded with a Finnigan MAT 90 spectrometer using NBA–NPOE as a matrix.

Results and discussion

A series of thioether derivatives (**1**–**8**) with one to four thioether functionalities has been synthesized to investigate their properties in stabilizing gold colloids as shown in Fig. 1.

We used these thioether derivatives as stabilizing agents in a two-phase system closely following the methodology developed by Brust *et al.*[2] The initial Au : S : $(n\text{-oct})_4NBr$ ratio was 1 : 3 : 2. The reduction of Au(III) was carried out with a fast addition of the reducing reagent ($NaBH_4$), which gives a narrower size distribution of colloids since nucleated cores grow at a constant S : $AuCl_4^-$ ratio.[25] After reduction of Au(III) to Au(0), a black precipitate was observed directly after preparation when the monothioether **1** or tris(thioether) **6** was used as the protecting ligand, and these solids could not be redispersed in any solvent. Monothioethers **2**, **3**, and **4** and polythioethers **5**, **7**, and **8** gave dark-brown solutions after preparation.

The reason that monothioether **1** can not form stable gold colloids may lie in the fact that the carboxylic acid functional group is not solvated well in toluene. The colloids may be soluble in some more polar solvents, however, we did not investigate this further.

Thioether **6** does not give stable gold colloids at room temperature. This probably stems from the relatively bulky head group. It is assumed that at higher temperatures the sulfide–gold interaction is reversible, and reorganization of a ligand on flat gold to an energetically more favorable structure with all alkyl chains oriented parallel takes place.[16] In this respect, the reduction reaction in the presence of **6** was tried also at 60 °C, and soluble gold colloids were obtained.

TEM was used to determine the size distribution of the colloids. The TEM images of gold colloids capped by **2**–**5**, **6** (prepared at 60 °C), **7** and **8** are shown in Fig. 2. The histograms of the particle size distributions are shown in Fig. 3. The crystal facets of the particles could be seen on some of the images indicating the crystalline nature of the gold particles. Thioethers **2**–**7** gave almost the same particle size within the experimental error: 2.7 nm (corresponding to approximately 800 gold atoms per core[26]) (Table 1). This particle size is larger than that of thiolated gold colloids prepared at the same initial gold : sulfur ratio, approximately 1.5 nm.[5] We attribute this to the weaker gold–thioether interaction, and the larger surface area per sulfur atom that is needed for monolayer formation. Overall, it seems that the particle size is controlled by the initial gold : sulfide ratio, instead of the number of ligands per adsorbate. This is in agreement with reported results which conclude that simply

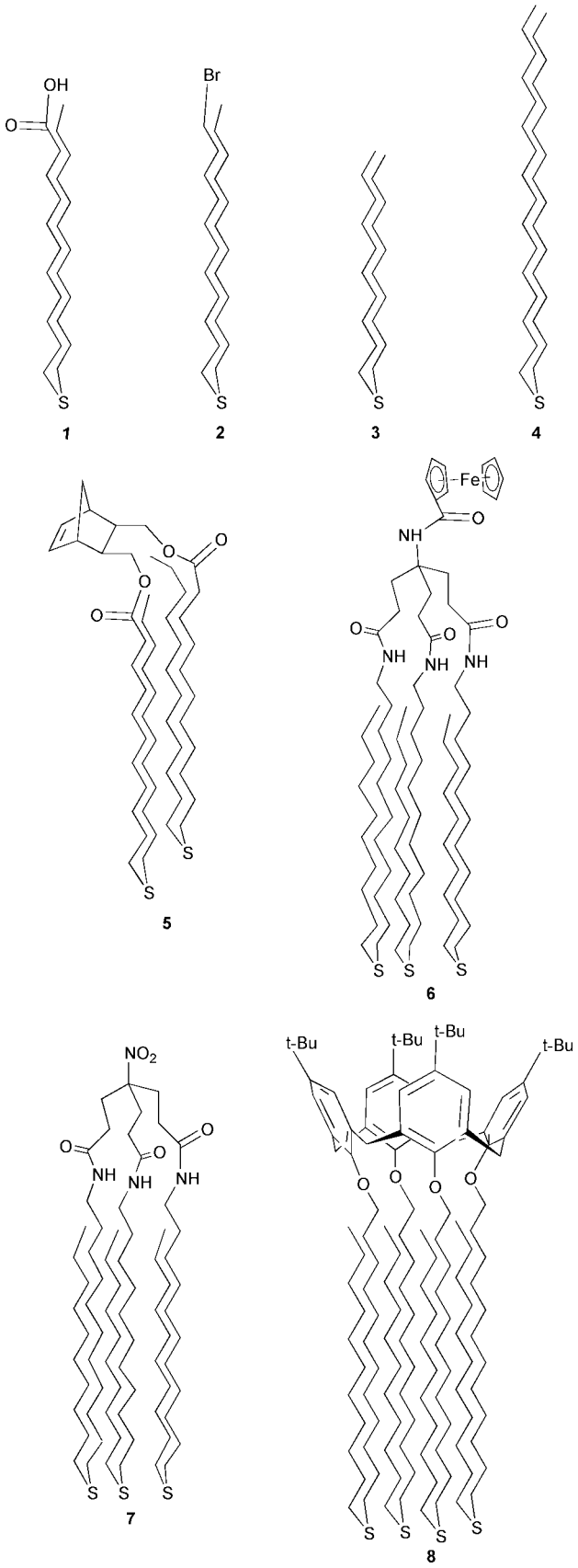

Fig. 1 Thioether derivatives used as ligands for preparation of gold colloids.

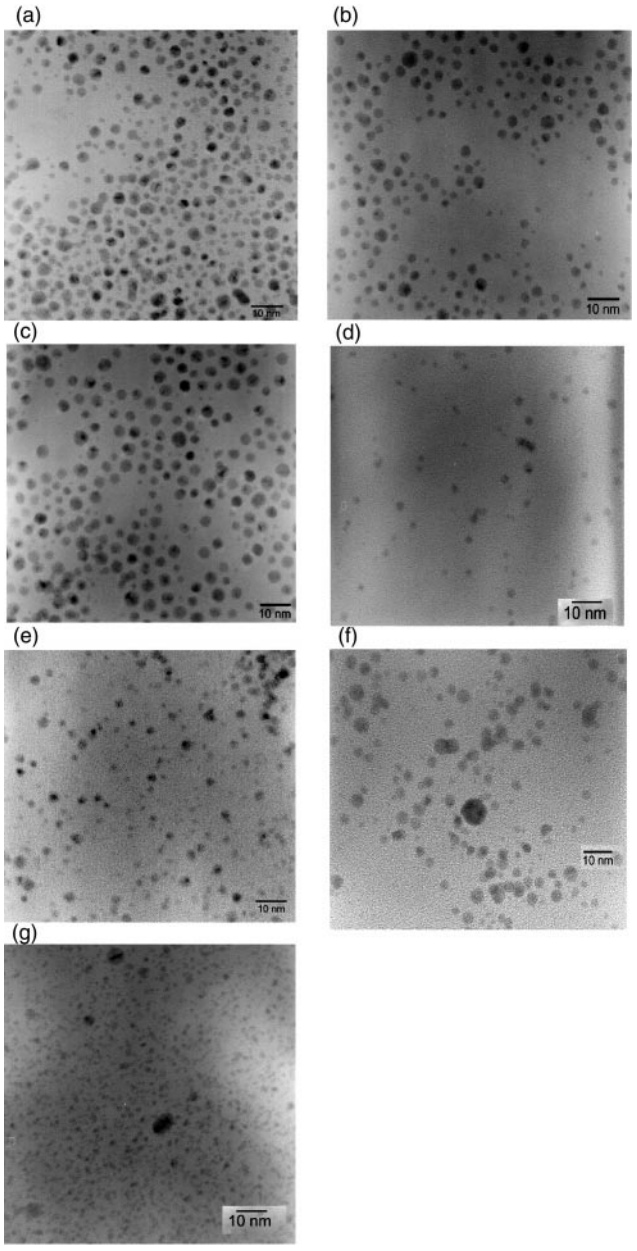

Fig. 2 Transmission electron micrographs of dropcast films of thioether-protected gold colloids. The protecting ligands are: **2** (a); **3** (b); **4** (c); **5** (d); **6** (prepared at 60 °C; e); **7** (f); **8** (g).

Table 1 Gold nanoparticle sizes and standard deviations

Thioether	Number of thioethers per molecule	Mean diameter/nm	Particle count
1	1	—[a]	—[a]
2	1	2.7±0.7	221
3	1	2.7±0.7	148
4	1	3.3±0.8[b]	139
5	2	2.4±0.5	134
6	3	2.7±0.6[c]	139
7	3	2.6±1.1	248
8	4	1.8±0.4	112

[a]No soluble colloids obtained. [b]Smaller particles were decanted during the precipitation process. [c]Colloids were prepared at 60 °C.

varying the initial gold : adsorbate ratio can sensitively control the particle size.[5] We expect that by changing the initial gold to thioether ratio, a broader size range of particles may be obtained in a controllable fashion. Gold colloids capped by **8** possess both a smaller average particle size and narrower size distribution. Maybe the orientation of the alkyl chains in **8** is more suitable for arranging in a densely packed fashion, and thus gave the smallest mean diameter (1.8 nm) and narrowest size distribution. This size corresponds to the presence of only 5–6 adsorbate molecules per particle.

To test the stability of the colloids, attempts were made to separate excess ligands from the colloidal mixtures. The freshly prepared gold colloids stabilized by **2**–**5**, **6** (prepared at 60 °C), **7**, and **8** were clear dark-brown solutions. The colloids were precipitated to remove excess free adsorbate (for details, see the Experimental Section). All ^{1}H NMR spectra of the obtained gold colloids after redissolution (if soluble) resemble those of the free ligands with slightly broadened peaks, indicating there is no splitting of the sulfur–carbon bond and/or the generation of thiolate. The visibility of the methylene resonance next to the sulfur is significantly different from the reported thiolate gold colloids, where this resonance is not detectable.[4,26]

For colloids stabilized by monothioethers **2** and **3**, the colloids remained soluble after one precipitation. There was still tetraoctylammonium bromide present after this precipitation step which stems from the preparation process. Repeated precipitation led to irreversible aggregation. The gold colloids stabilized by monothioether **4** remain soluble after two precipitations. ^{1}H NMR spectra of the obtained colloids showed that no tetraoctylammonium bromide remained. The colloids remain soluble for months if stored at −20 °C, however, bare gold formed on the glass wall of a test tube

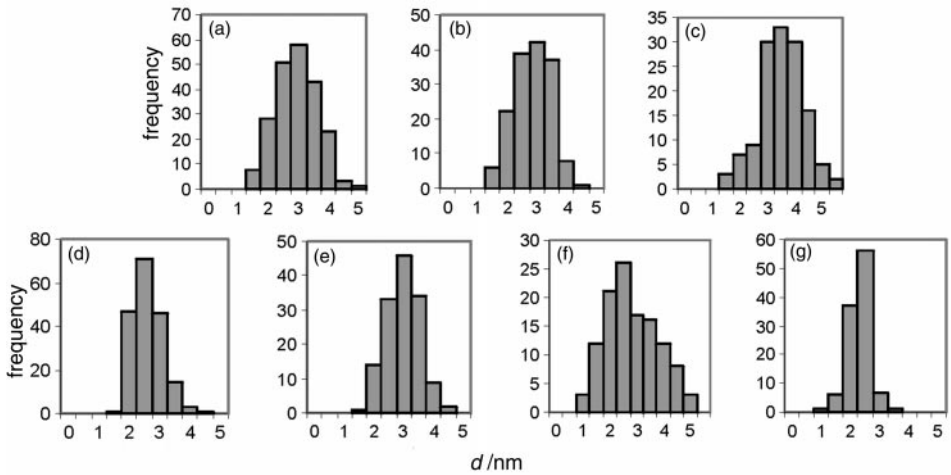

Fig. 3 Size histograms of gold colloids capped by thioether derivatives: **2** (a); **3** (b); **4** (c); **5** (d); **6** (prepared at 60 °C; e); **7** (f); **8** (g).

after a few days if stored at room temperature, again suggesting short-time stability of those colloids.

The fact that longer chain monothioether **4** gave more stable gold colloids compared to shorter ones probably stems from the stronger van der Waals interaction among longer chains and as a result a better ordered layer. For the shorter chain thioethers, it is plausible that tetraoctylammonium bromide also contributes to the stabilization of the colloids. Sorensen *et al.*[15] have claimed the use of inverse micelles for preparation of gold colloids protected by thioethers. Specifically, a micelle solution was formed by dissolving didodecyldimethylammonium bromide (DDAB) in toluene. Then gold chloride was dissolved in the prepared micelle solution to form a dark-orange solution. Gold colloids were obtained by the use of sodium borohydride as a reducing reagent. The colloids were then subjected to ligand modification, *e.g.* a thioether. After precipitation from ethanol, the colloids were still soluble in toluene. They claimed the resulting gold colloids to be passivated by the thioether. However, no information on the ligand shell was reported. Considering their colloid preparation methods, it is possible that these colloids are also stabilized by the ammonium salt, instead of solely by the thioether.

For bisthioether **5**, a black precipitate could be seen after 2–10 days in solution at room temperature after preparation. No soluble gold colloids were obtained after precipitation, indicating the low stability. Gel permeation chromatography (GPC) was used to remove the excess thioether and the ammonium salt, but after removing the solvent, the precipitated colloids could not be redispersed as well.

Compound **7** gave soluble gold colloids at room temperature. Dichloromethane was used as the organic phase since **7** does not dissolve in toluene. The colloids were precipitated from hexane. The obtained precipitates could be redissolved in dichloromethane, thus proving the stabilizing properties of **7**. Calix[4]arene derivative **8** gave soluble colloids, which also could be redispersed after precipitation from ethanol. The obtained colloids were kept in dichloromethane solution at room temperature to give a black precipitate only after 2 months.

UV/Vis spectra of gold colloids stabilized by thioether **2**–**5**, **6** (made at 60 °C), **7**, and **8** directly after their preparation showed broad UV absorption bands around 530 nm in agreement with literature data on thiol-stabilized gold colloids.[27]

Overall, gold colloids have been prepared with solely thioether as protecting ligands. The stability of the gold colloids appears to depend on several factors. For monothioethers, the longer the chain length, the more stable the obtained gold colloids. For multiple thioethers, a well-packing headgroup and matching between the head group and the thioether alkyl chains promote the stability of the colloids. The stability of gold colloids capped by multiple-thioether adsorbates is enhanced when they are prepared at higher temperatures at which adsorbate rearrangement can occur similar to the phenomena observed for molecules on flat gold.

Conclusions

This is the first direct formation of thioether-stabilized gold colloids. The obtained gold colloids were characterized by TEM and ^{1}H NMR. It was found that solely thioether ligands could stabilize gold colloids. The stability of the colloids was also addressed. The rather weak interaction between gold and thioether leads to a short time stability of those obtained colloids compared to that of reported thiolated colloids. Calix[4]arene tetrathioether derivative capped colloids were just as stable as thiolated gold colloids. We expect that widening the scope of the possible adsorbates for gold colloids from thiols to other organic compounds such as the thioethers presented here allows a more diverse functionalization of these nanoparticles which we view essential for nanotechnology.

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