

Multidentate thioether ligands coating gold nanoparticles†

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The design and synthesis of oligomeric ligands based on benzylic thioethers is presented together with their ability to enwrap and stabilize gold nanoparticles with diameters below 2 nm, which become—with increasing length of the oligomer—more monodisperse and stable.

Although gold colloids have been used for centuries as colourants,¹ the controlled synthesis of monodisperse gold nanoparticles remains a challenge. Well-defined gold nanoparticles, such as thiolate protected Au₂₅ clusters, have been obtained only after separation from other cluster sizes² or by choosing the reaction conditions carefully. However, the formed nanoparticles depend strongly on slight variations of the reaction conditions.³ Recently, even the solid state structure of a thiolmonolayer protected gold nanoparticle has been obtained after purification of the sample by numerous recrystallization steps.⁴ The control over size, shape and surface chemistry of nanoparticles would allow their integration in devices as stable building blocks providing size dependent physical properties. While wet chemistry has already been applied successfully to organize surface functionalized Au particles in one, two and three dimensions,⁵ their integration in electronic devices remains a challenge. In particular single electron memory devices oblige one to control the size and the assembly of particles, as only particles with diameters below 2 nm provide the required coulomb blockade properties.⁶

Here, investigations geared towards controlling the size and surface chemistry of Au particles by tailor-made multidentate ligands are presented. A large multidentate structure might favour well defined particle sizes by enwrapping the whole particle by an integer number of ligands. Furthermore, the concept enables to control the number and topology of functional groups on the particle surface, subjecting the particle itself to wet chemistry as synthetic building block.

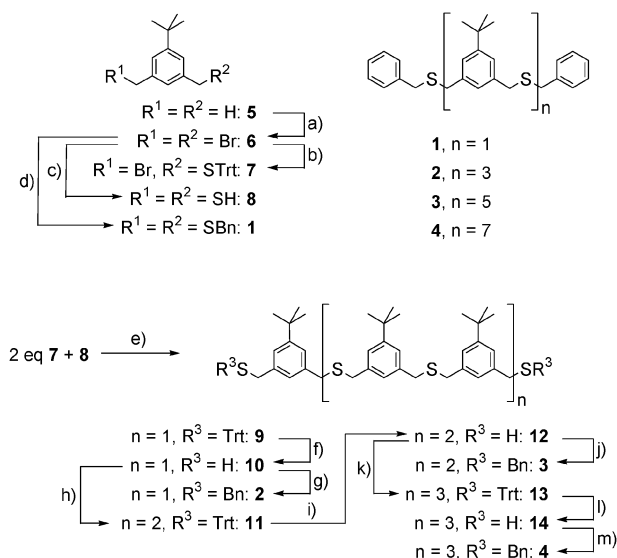
Gold particles have already been stabilized by rather weak interactions with thioether moieties, whereas increased stabi-

lity and monodispersity has been reported for multidentate ligands comprising more than one thioether unit.^{7–10} Investigated thioether ligands vary from flexible long chain dialkylsulfides⁷ to rather rigid dendritic structures containing thioethers either at the core structure⁹ or peripherally.¹⁰ However, the comparability of these studies is further limited by various additional functional groups like ethers or acetals, which may influence their ability to stabilize the nanoparticles.

Here, the synthesis and characterization of thioether oligomers **1–4** as a series of di- to octadentate linear ligands is reported. Their ability to stabilize nanoparticles and correlations between ligand structure and properties of the formed nanoparticles are investigated.

The ligands **1–4** (Scheme 1) are designed to bind to the gold nanoparticle surface *via* flexible benzylic sulfides. The *tert*-butyl groups *meta* to the benzylic thioethers are used to enhance the stability of the resulting gold nanoparticles by steric repulsion as well as to enhance the solubility and thus the processability of the large ligands and the coated nanoparticles in common organic solvents.

The monomeric ligand **1** was synthesized by the reaction of 5-*tert*-butyl-1,3-bis(bromomethyl)benzene¹¹ (**6**) with benzyl



Scheme 1 Molecular structures and synthesis of the ligands **1–4**.† (a) NBS, AIBN, CHOOCH₃, *hν*, 3 h, 70%; (b) TrtSH, K₂CO₃, THF, reflux, 12 h, 51%; (c) thiourea, DMSO, 12 h, NaOH, 64%; (d) BnSH, NaH, THF, rt, 1 h, 95%; (e) NaH, THF, rt, 1 h, 96%; (f) Et₃SiH, TFA, DCM, rt, 15 min, 99%; (g) BnCl, NaH, THF, rt, 1 h, 98%; (h) **7**, NaH, THF, rt, 1 h, 96%; (i) Et₃SiH, TFA, DCM, rt, 15 min, 99%; (j) BnCl, NaH, THF, rt, 1 h, 99%; (k) **7**, NaH, THF, rt, 1 h, 91%; (l) Et₃SiH, TFA, DCM, rt, 15 min, 99%; (m) BnCl, NaH, THF, rt, 1 h, 86%. Bn = benzyl, Trt = trityl.

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mercaptan and sodium hydride as base, in high yield. The bifunctional compound **7**, comprising one trityl protected thiol and a bromide leaving group, turned out to be an ideal building block for the assembly of the higher oligomers **2–4**. Monofunctionalisation of **6** was achieved in good yields by using the sterically demanding tritylthiol as the sulfur source, which also allows chromatographic separation of the desired product from the starting material and the disubstituted compound. Reaction of the dithiol **8**¹² with the monomer **7** and sodium hydride as base yielded the trityl protected trimer **9**, which was deprotected in the presence of trifluoroacetic acid and triethylsilane to the dithiol **10**. Benzyl protection of the terminal thiols was achieved by the reaction with benzyl chloride to give the trimeric ligand **2**. The pentameric ligand **3** and the heptameric ligand **4** were synthesized from **10**, using similar elongation/deprotection/end capping sequences that were used to assemble the trimer **2**. All precursors and oligomeric ligands **1–4** have been fully characterized by ¹H- and ¹³C-NMR spectra, MALDI-ToF mass spectrometry and elemental analysis.

Gold nanoparticles have been formed in the presence of the oligomeric thioether ligands **1–4** to investigate the ability of these ligands to stabilize nanoparticles and to prevent them from coagulation. The preparation of the nanoparticles was carried out in a two-phase water/dichloromethane system, closely following the procedure developed by Brust *et al.*¹³ for the synthesis of alkanethiol protected gold nanoparticles.† The gold(III) precursor tetrachloroauric acid was transferred to the organic phase by tetra-*n*-octylammonium bromide (TOAB). To keep the ratio between the gold(III) precursor and thioether moieties comparable, the amount of added ligand was normalized to its number of thioethers. Hence, equimolar amounts of sulfide units and the gold(III) precursor were used. The reduction of gold(III) in the presence of the thioether ligands was then carried out by adding an aqueous sodium borohydride solution to the two-phase system.

In the case of the monomer ligand **1**, a black precipitate was formed immediately after addition of the reducing agent to the two-phase reaction system, suggesting rather limited stabilization features of this ligand system. However, the reddish brown colour of the liquid phase points at the formation of Au particles. Nevertheless, if the larger oligomers **2**, **3** or **4** were present instead of **1**, no precipitate was formed during the reaction. The intense dark coloured organic phases indicated the formation of gold nanoparticles in all three cases. The UV-vis absorption spectra† of the dispersions are very similar to previously reported spectra of alkanethiol capped gold nanoparticles. The absence of a strong plasmon resonance band at around 520 nm in the cases of the longer oligomers **2**, **3** or **4** points towards gold nanoparticles with a diameter smaller than 2 nm.¹⁴ On the other hand, the presence of such an absorption band indicates the presence of larger nanoparticles stabilized by the monomer **1** remaining in the liquid phase.

The stability of the formed nanoparticles increased strongly with the length of the stabilizing oligomer. The bidentate monomer **1** stabilized nanoparticles coagulate fast, as was evidenced by further precipitation of bulk gold and a colour change to red of the remaining dispersed nanoparticles after a few hours. The colour change is attributed to the formation of

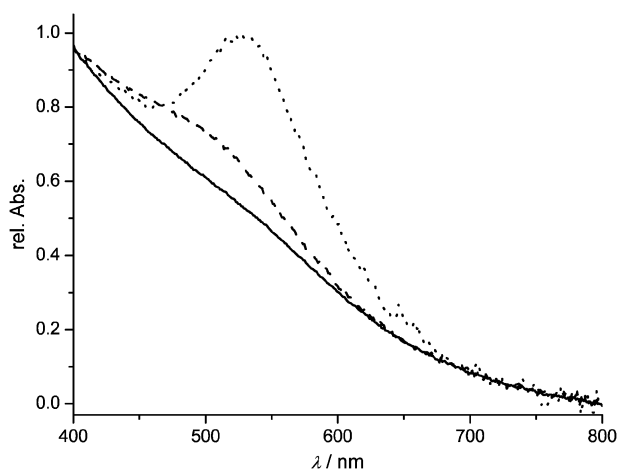


Fig. 1 UV-Vis absorption spectra of gold nanoparticles stabilized by monomer **1** (directly after synthesis: dashed line; after 24 h in dispersion: dotted line) and heptamer **4** (after 1 month in dispersion: straight line) in dichloromethane.

larger particles, as was further corroborated by the increasing surface plasmon resonance after 24 h in dispersion (dashed and dotted lines in Fig. 1). However, the dispersions of the nanoparticles stabilized by the pentameric and heptameric thioether oligomers **3** and **4** remained unchanged even after several weeks, as displayed in Fig. 1 for heptamer stabilized clusters. The UV-vis spectra obtained directly after the syntheses of the nanoparticles in the presence of **3** and **4**† were similar to the one shown in Fig. 1 of the heptameric ligand **4** after one month in dispersion. In contrast to that, particles stabilized by the trimeric ligand **2** slowly coagulate when stored in dispersion. This manifests in the formation of a fine gold layer on the glass surface of the storage vessel after a few days.

Purification of the thioether stabilized nanoparticles was achieved by precipitation from a dichloromethane dispersion with ethanol. The precipitated particles were separated from the liquid phase by centrifugation. After three cycles of this procedure, the phase-transfer agent TOAB was no longer observed in the ¹H-NMR† spectrum of the nanoparticles. Even after these purification steps, a considerable yield of around 80% was determined by elemental analysis for the particles stabilized by ligand **4**. However, the method was only applicable in the case of particles stabilized with penta- or heptameric ligands **3** or **4**. If shorter oligomers were used to stabilize the particles, the obtained precipitates were no longer redispersible in dichloromethane or other organic solvents such as toluene or THF. The purified nanoparticles were obtained as waxy solids and are stable for months in the solid phase and in their dispersed form in dichloromethane. Also, the UV-vis spectra of the purified nanoparticles† resemble the spectrum shown in Fig. 1 even after one month at ambient conditions. Obviously, the coagulation to particles with diameters larger than 2 nm is strongly suppressed, demonstrating the considerable stabilization of these particles by the oligomeric thioether ligands **3** or **4**. These results further suggest that at least 5–6 thioether units are required for an efficient stabilization of each Au particle formed.

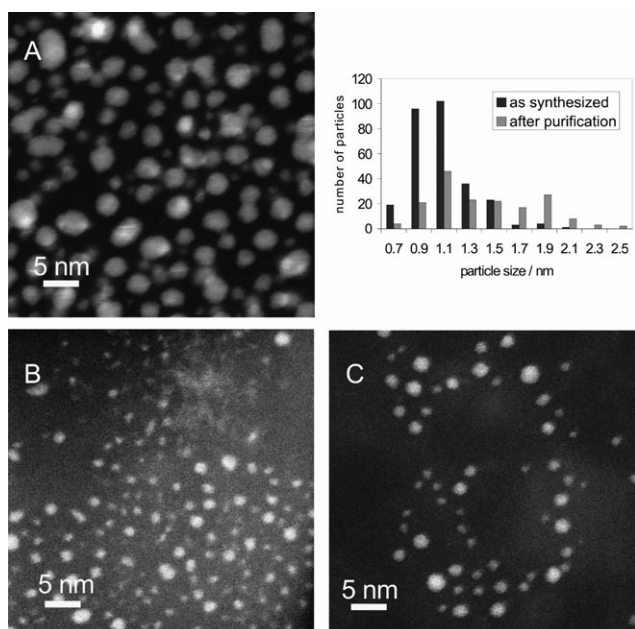


Fig. 2 Representative HRSTEM micrographs of gold nanoparticles stabilized by pentamer **3** (A) and heptamer **4** before (B) and after purification (C). The histogram illustrates the different particle size distributions in B and C.

The control of the particle sizes and particle size distributions was accomplished by High Resolution Scanning Transmission Electron Microscopy (HRSTEM).[‡] Particles stabilized by the pentameric ligand **3** show a large size distribution with diameters ranging from 1 to 5 nm. A much narrower size distribution is found in the case of the nanoparticles stabilized by the heptamer **4**. The histogram in Fig. 2 shows that the main yield of the particle stabilization reaction is about 1 nm large particles, though the distribution reveals a tail towards larger sizes up to 2.1 nm. Interestingly, after removal of the phase transfer agent by precipitation of the nanoparticles, a different size distribution is found. In addition to the parent accumulation with diameters around 1 nm a second one with a maximum at about 1.9 nm was observed. The results suggest a partial destabilization of the particles upon removing the TOAB resulting in some coalescence of small (1 nm) particles. Probably, these larger particles are stabilized by several ligands **4**. However, the defined size distribution of particles, as well as elemental analysis of the particles[†] are in agreement with the working hypothesis of an integer low number of ligands enwrapping the particles.

In summary, the synthesis of linear oligomeric multidentate thioether ligands **1–4** and their ability to stabilize gold nanoparticles was reported. A considerable increase in the stability and monodispersity of the formed Au particles with the increasing length of the oligomeric ligands has been observed, pointing at the potential of these systems in view of controlled nanoparticle formation and functionalization. Encouraged by

these results, we are currently working on dendritic ligands based on comparable structural motifs.

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Notes and references

[‡] HRSTEM was performed on a FEI Tecnai F20 operating at 200 kV and a FEI Titan S operating at 300 kV. For TEM studies, particles were brought on a conventional amorphous carbon TEM grid by carefully putting a drop of the dichloromethane suspension on a grid and letting it dry in air. Statistical analysis of the particle size distributions were carried out by averaging the results of evaluations from a large number of STEM micrographs (as ones shown in Fig. 2) taken from different areas of the same TEM specimen. The strong atomic number contrast employed in a STEM mode reveals the precise size of the gold core.

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