From solution to solid state: energy- and electron-transfer in complex materials

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Chapter 7

Oligothia dendrimers for the controlled formation of gold nanoparticles

Abstract

The synthesis, characterization, X-ray analysis of oligothia dendrimers and their use for the formation of gold nanoparticles is described. The role played by these dendrimers, in controlling the stability and size of the particles, is discussed. It is shown that the generation of the dendrimers as well as the position of the sulfur atoms in the dendritic structure (S₉G₁ and S₉G₁) lead to different formation and reactivity of the nanoparticles. UV/visible spectroscopy, ^{1}H-NMR spectrometry and high resolution TEM has been employed for the characterization of the nanoparticles. Furthermore, purification by soxhlet extraction has been performed.

7.1 Introduction

The pioneering work of Schmid et al.[1] and of Brust et al.[2-4] has introduced a fascinating route to prepare and use small well-defined clusters of gold atoms as normal chemical compounds to build new structures in the nano-world. Even though many synthetic ways have been provided to form and stabilize these nanoparticles[5-7] so far no general strategies have been developed. Only few scattered examples, to create and control the size and functionalization of the nano-clusters, using the binding and the interactions with organic molecules have been reported[8-16]. In order to achieve such goals, sulfur, nitrogen or phosphorous containing molecules with an appropriate structure for organization have been used.[17-19] As for metal ions, the possibility to use multi-binding ligands in order to increase the stability and extended branched molecules is an interesting approach to achieve some control, growth and functionalization of nanoparticles. Several groups have worked on this topic by employing amido-(or amino-) dendrimers where the coordinating nitrogens stabilize the gold clusters.[5, 20-22] Also dendrons with a free thiol group have been described.[23, 24] The use of oligo-branched molecules has the advantage to protect the gold nanoparticle as well as to introduce solubilizing groups and different functionalities. The interest in the use of dendrimers for the stabilization and size control of nanoparticles can be easily understood by the intrinsic properties of these complex structures such as their branched nature that allows the positioning of coordinating atoms in desired places, their nanosize dimension controllable with the different generation, their multiple possible functionalization leading to new chemical and physical properties.[25-33] It has recently been shown that depending upon the dendrimer generation, the stabilized nanoparticles can have different sizes, dispersity[21] and properties.[34] The branches of the dendrimers are important as well because they might create a site isolation effect. In fact, for different dendrimers, the free space available between the branches (that can be used to incorporate nanoparticles) varies following the dendrimer’s shape and generation. It has been shown that nanoparticles could be encapsulated in a cavity where they will be isolated from other nanoparticles.[21] Furthermore, dendrimers offer possibilities to act as a scaffold for the attachment of numerous functional groups to gold nanoparticles. Such functionalization may broaden the application of gold nano-structures in the fields of biomedicine,[35-38] catalysis[21, 39-41] or electronics.[42, 43]

To our knowledge, only few reports on the use of dendrimers containing sulfur as a suitable core, have been published.[44, 45] However, the use of disulfide as a core leads to the decomposition of the S-S bond into thiolates in presence of a metal, resulting in the equivalent
of thiol dendrons. The presence of organyl sulfide (thioether) functions implemented inside the dendritic structure, would result in a new approach to control the growth, the size and functionalization of nanoclusters.

Here, we report on the preparation and on the use of oligothia dendrimers for the controlled formation of gold clusters. Comparison is made with two reference compounds that contain the same number of sulfur atoms, but are not dendritic structures. Synthesis, structure, particle formation, purification, characterization and relative stability of different ligand stabilized gold nanoparticles are described.

7.2 Results and discussion

One of the major challenges in the nanoclusters field is the possibility to control the size, the stability and the monodispersity of metal and semiconductive nanoparticles. In order to be able to reach a general strategy for the formation and selective functionalization of the nanoparticle, it is important to determine the effect of the chemical structure of the ligands that promote the formation or that are necessary for their stabilization. To rationalize several parameters such as the nature of the sulfur atom that will interact with the Au atoms, number of anchoring groups per molecule of ligand, size of the stabilizing ligand, we have synthesized, investigated and compared several sulfur containing molecules. All the investigated compounds and their abbreviations are depicted in Figure 1.

![Figure 1. Schematic formulas of the investigated compounds](image-url)
Three of the ligands are dendritic structures, two of the same family, $S_6G0$, $S_6G1$, containing the sulfur atoms only in the core, and $S_6G1$ in which the sulfurs are also in the branches. The two reference systems, $SH_6$ and $MS_6$, containing the same number of sulfur atoms (six) arranged in a non-branched type structure have also been investigated and compared with the denritic species. All these molecules have been synthesized, characterized, and employed as templates for the formation of gold nanoparticles.

7.2.1 Synthesis of the ligands and nanoparticle formation

The synthesis of the oligothia core ($SH_6$), of the dendrimers was performed as described before\textsuperscript{[48-50]} (see also experimental part). The core for $S_6G0$, and $S_6G1$ is composed of a central benzene ring which is functionalized with six methylenethiol groups. The sulfur atoms are not in the same plane as the central benzene ring but are alternately above and below the plane of the ring. The presence of a methylene spacer between the benzene rings and the sulfur atoms is inducing a bent geometry since direct connection to the benzene ring would result in a flat core which could not be ideal to stabilize nanoparticles. The methylene group is also indispensable in order to have the possibility to introduce the rigid bulky branches of the dendrimer and confer a different acidity to the sulfur atom than an aromatic unit.

![Synthetic scheme for the preparation of $S_6G0$ and $S_6G1$.](image-url)
Oligothia dendrimers for the controlled formation of gold nanoparticles

$\text{S}_6\text{G}0$ was prepared by adding benzylbromide to $\text{SH}_6$ using sodium(0) as a base (Figure 2). This dendrimer, present in solution in different conformations, has in the extended flat representation, from the extremities of two opposite phenyl, an estimated distance of 2.2 nm, and an average size of about 1.5 nm in the conformation where the six sulfur atoms are on the same side of the benzene ring. The distance is 3.0 nm in the conformation where three sulfur atoms (atoms 1, 3, 5) are on top of the benzyl plane and the three others (atoms 2, 4, 6) are below the plane. This conformation has been proven in solid state by X-ray analysis\textsuperscript{49, 50} (see Figure 3).

![Figure 3. Crystal structure of $\text{S}_6\text{G}0$](image)

The coupling of $\text{SH}_6$ with Fréchet-type-dendrons $\text{G}1$ was performed under the same conditions as for $\text{S}_6\text{G}0$ and gave $\text{S}_6\text{G}1$ (see Figure 4).

The average size for the extended conformation of $\text{S}_6\text{G}1$ being 2.8 nm while in the bent structure the size is roughly 2.1 nm. The synthesis of $\text{S}_9\text{G}1$ was carried out analogously to $\text{S}_6\text{G}n$ ($\text{G}n = \text{G}0$ and $\text{G}1$), using a different dendron and a tris substituted benzene ring (see Figure 3 and experimental part). $\text{S}_9\text{G}1$ is composed of only three dendritic branches but each contains three sulfur atoms. This dendrimer is less crowded than $\text{S}_6\text{G}1$ and, while in $\text{S}_6\text{G}1$, every sulfur atom is connected to two sp$^3$ carbons, every sulfur atom in $\text{S}_9\text{G}1$ is connected to one sp$^3$ carbon (benzylic fragment) and one sp$^2$ carbon (phenyl carbon). Such a difference in the chemical structure is relevant since it is known that thiol groups connected to a benzylic carbon are more acidic, than those connected to phenyl systems. Therefore, the strength of the binding of the sulfur group to gold is related to the nature of the substituent on the sulfur. In the case of gold nanoparticle formation, one should expect a different stability related to the
chemical nature of the sulfur containing structure, being more stable with benzylic sulfur derivatives. We have in fact noticed that the commercially available hexakis(thiobenzyl)benzene does not stabilize the formation of nanoparticles.

All the nanoparticles were prepared following Brust’s synthesis\textsuperscript{[21]}. They were precipitated three times in ethanol in order to purify them before the measurements. Furthermore, using the method reported recently by Schiffrin et al.\textsuperscript{[15]}, the nanoparticles were purified using a soxhlet extraction to eliminate all organic impurities. We have compared the purity of the particles before and after soxhlet extraction (vide infra). The general preparation of the clusters involves the use of one equivalent of gold (hydrogen tetrachloroaurate) for one equivalent of sulfur atoms (for more details see experimental part).

![Synthetic scheme for the preparation of $\text{Dend}_3S$ and $S_6G1$.](image)

The gold stabilized nanoparticles, $\text{Au/S}_6\text{Gn}$ and $\text{Au/S}_6\text{G1}$, have been characterized by UV/visible spectroscopy, $^1\text{H}$-NMR spectrometry and high resolution transmission electron microscopy (HR-TEM) before and after soxhlet extraction.

7.2.2 UV/visible absorption spectroscopy

UV/visible absorption spectra have been recorded for all the compounds in toluene at room temperature. The spectra of $\text{Au/S}_6\text{G0}$ and $\text{Au/S}_6\text{G1}$ (see Figure 5) were compared with the bare nanoparticles (nanoparticles stabilized by tetraoctylammonium bromide\textsuperscript{[52]})
Oligothia dendrimers for the controlled formation of gold nanoparticles

Au/TOAB) and with particles obtained in the same conditions with dodecanethiol (Au/C_{12}SH).

![Absorption spectra](image.png)

**Figure 5.** Absorption spectra in toluene of Au/S\textsubscript{6}G\textsubscript{0}, Au/S\textsubscript{6}G\textsubscript{1}, Au/C\textsubscript{12}SH and Au/TOAB.

Before soxhlet extraction, the absorption spectra show a clear band at 520 nm (which intensity and position is indicative of the size of the particles) attributed to the surface plasmon resonance of the gold.\cite{53, 54} It can be seen that for the non-stabilized particles, Au/TOAB, this band has a high intensity, while for the Au/S\textsubscript{6}G\textsubscript{0} and Au/S\textsubscript{6}G\textsubscript{1}, the intensity depends on the dendrimer used and it is much lower than for the bare nanoparticles.

![Absorption spectra](image.png)

**Figure 6.** Comparison of the absorption spectra of Au/S\textsubscript{6}G\textsubscript{1} and Au/S\textsubscript{6}G\textsubscript{1}
Such important result suggests that the size of the gold clusters is dependant on the generation of the dendrimers. In particular, $S_6G0$ leads to particles ($Au/S_6G0$) smaller than those obtained with dodecanethiol ($Au/C_{12}SH$). The particles obtained using $S_6G1$ as template ($Au/S_6G1$) are on the other hand larger than $Au/S_6G0$ but smaller than the non-stabilized ones ($Au/TOAB$). For $S_6G1$, it is also possible to detect an absorption at about 300 nm characteristic of the $\pi-\pi^*$ transition of the methoxybenzenes moities of the dendritic structure. The two dendrimers have an influence not only on the size of the particles but also on their stability. In fact, the $Au/S_6G0$ adduct is much less stable than $Au/S_6G1$ in the same experimental conditions. The use of the $S_6G1$ dendrimer leads to clusters that can be stable for months in solution. Interestingly, the attempt to wash the nanoparticles by soxhlet extraction was not successful despite that the nanoparticles are not soluble in the extracting solvent. This proves that TOAB is indispensible to the stabilization and isolation of $Au/S_6G1$ (see also NMR section).

A similar spectroscopic behaviour is observed for the other dendritic structure $S_9G1$. The nanoparticles formed by reaction with $S_9G1$ ($Au/S_9G1$) have an absorption spectrum shown in Figure 6 where a comparison with the analogous $Au/S_6G1$ is made. The absorption at 520 nm is weaker than that of $Au/S_6G1$ suggesting that the average size of such nanoparticles is smaller than the $Au/S_6G1$. It is interesting to notice that after soxhlet extraction the absorption of the $S_9G1$ is identical to that without soxhlet purification.

We can therefore conclude that the size and the stability of the gold clusters are related to the dendrimer generation and indeed to the branched shape of the template molecules. The absence of any further absorption, at low energy (700 nm), suggests that no clustering of particles nor the presence of two nanoparticles trapped by one dendrimer molecule is possible. In order to gain insight into the role of multiple sulfur binding sites within the same molecule, two other molecules containing six sulfur atoms ($SH_6$ and $MS_6$) have been prepared and investigated. The $SH_6$ forms nanoparticles but also larger aggregates, observed in the UV/visible spectrum as a broad band extending up to 700 nm. After precipitation of the larger clusters, the soluble phase was isolated and re-dissolved in toluene. The absorption spectrum of the solution shows that the low energy band disappears and the typical band of the gold cluster around 520 nm remains. Purification with soxhlet techniques was not possible due to the extremely high solubility of the nanoparticles. It is interesting to notice that even though the $SH_6$ is the bare core of the $S_6G1$, having the same number of sulfur atoms in the same geometric configuration, it behaves very differently because of the lack of the branching effect.
In the case of MS₉, no nanoparticle formation was observed. As already mentioned the weak binding of the aromatic thiols does not provide enough stabilization of the gold nanoclusters.

Further evidences of the involvements of the branches and of the binding of dendrimers on gold came from ¹H-NMR measurements and HR-TEM.

7.2.3 ¹H-NMR analysis.

The ¹H-NMR spectra performed in deuterated toluene or dichloromethane provided some information on the interacting groups of the dendritic structures and on the presence of TOAB. Comparison between the free dendritic structures and the Au/S₉G₁ reveals a general broadening of the proton signals after formation of the nanoparticles in solution. This effect is well known for alkane thiols (especially for the protons in α, β and γ position of the thiol groups) and it is indicative of the proximity and interactions of these protons with the nanoparticles. In all the Au/dendritic structures, the signals of the protons in close proximity to the Au surface broadens and, in some cases, split up into more signals. In particular for the
dendrimer $S_9G1$ (see Figure 7), in deuterated toluene, upon formation of the nanoparticles, all the signals broaden as effect of a global interaction of each group with the Au surface. The aromatic region cannot be explored in detail because of the solvent employed. The integration of the spectrum reveals the presence in average of 23 molecules of TOAB per dendrimer. It is interesting to notice that despite the stability of the Au/$S_9G1$ in toluene, in dichloromethane the particles are stable only for less than one hour. Such behavior could be related to the presence of a large quantity of TOAB still present after the formation of the nanocluster or to the acidity of the dichloromethane.

![Figure 8. $^1$H-NMR of $S_9G1$ bottom, and Au/$S_9G1$ top, in deuterated dichloromethane.](image)

In the case of $S_9G1$, in deuterated dichloromethane, we can observe that all the $^1$H-NMR signals are broadened except the peak due to the protons of the methylene group between the central benzene ring and the sulfur atoms in the inner shell (peak e, figure 8). Comparison with the free $S_9G1$ clearly indicates that these groups are further from the nanoparticle than all the other protons. This can be interpreted with the assumption that the dendrimers are acting like an “octopus” (the arms of the dendrimers serving as tentacles) trapping the nanoparticles. Therefore the groups close to the core, being bent to “grab” the
nanoparticles, are not in contact with the gold atoms. Also in this case, some residual stabilizing agent is present but only three TOAB per S₀G₁ moiety have been found.

The $^1$H-NMR of Au/SH₆ in deuterated toluene shows that the initial singlet (CH₂SH) in chloroform splits into a quartet-like feature. This suggests that more than one arm is in close contact to the gold, as expected for different CH₂SH groups complexing the same nanoparticle. This NMR spectrum also reveals that the proton resonance of the SH is very broadened (from 5.1 to 5.9 ppm). This broadening is indicative of a strong interaction between the thiol group and the gold (type hydrogen bond). For this small molecule an average of 117 ammonium bromides (TOAB) were found per SH₆ molecule.

These nanoparticles were re-dissolvable in all organic solvents (ethanol, acetone, dichloromethane, toluene).

7.2.4 High Resolution Transmission Electron Microscopy, HR-TEM

HR-TEM measurements were performed on freshly made stabilized nanoparticles using the dendritic structures as templates. The diameters of more than one hundred nanoparticles were measured for each Au/Ligand isolated.

Figure 9. HR-TEM pictures of the Au/S₀G₁ particles, their size distribution, and the schematic formula of the dendrimer used to form the nanoparticle.
The HR-TEM measurements show that the Au/S\textsubscript{6}G\textsubscript{1} particles are present in two sizes of about 1.8 ± 0.6 nm, and about 3.2 ± 0.2 nm (Figure 9). The measurements also suggest that for the two populations, the dispersity is not the same, indicating that the largest particles possess the highest stability and are the most favourably formed. As already mentioned, the size of this dendrimer is 2.1 nm and, therefore, it is reasonable to think that in the case of the 3.2 nm particles two (or more) dendritic structures can template the formation of one particle. For the smaller particles most probably only one dendrimer can interact with the gold assuming that all the branches are wrapped around the particle, and the rest of the particle is covered with TOAB (see Figure 10).

![Figure 10. Cartoon-type representation of S\textsubscript{6}G\textsubscript{1} on the nanoparticle. The size of the molecule and of the particle are on real scale.](image)

We realize that this is a very simplistic view and only one of the several possible conformations that the dendrimer can have in the formation of the gold nanoparticles (Figure 10). However, the NMR spectra also support such a bent conformation of the dendrimer on the gold since all the protons of the branches are broadened (see previous section). From the NMR data, it is also clear that tetraoctylammonium bromide (TOAB), needed for the formation of the nanoparticles, is still present after the precipitations and can therefore fill the surface of the gold nanoparticle that is not covered by the dendrimer.
The same results were obtained with different stoichiometries of dendrimer (sulfur atom) per gold atom confirming that the chemical structure of the template is determining the size and stability of the nanoparticles.

The gold nanocluster obtained with the dendrimer $S_6G0$, reveals, after two precipitations, a size of $2.8 \pm 1.1 \text{nm}$, with a higher polydispersity than $Au/S_6G1$. Furthermore, the nanoparticles obtained with the smallest dendrimer are less stable, decomposing after 2 days in solution. If the synthesis of the nanoparticles is performed using 2 equivalents of gold per sulfur, the same kind of size and distribution are found suggesting that independently on the amount of gold employed, the precipitated nanoparticles have the same characteristics.

These nanoparticle sizes (for $Au/S_6G1$ and $Au/S_6G0$) are in perfect agreement with the UV/Vis absorption spectra (see figure 5): the 2.8 nm diameter nanoparticles ($S_6G0$) being smaller than the 3.2 nm diameter nanoparticles ($S_6G1$). We can clearly state that it is not only the number of sulfurs that plays a major role in stabilising the nanoparticles. In fact for $SH_6$, possessing the same number of S atoms than the $S_6Gn$ dendrimers very few stable particles could be isolated with an average size of $3.0 \pm 1.2 \text{nm}$.

The gold nanoparticles obtained employing the $S_9G1$ dendrimer, are shown in Figure 11.

![Figure 11. HR-TEM pictures of the $Au/S_9G1$ particles, their size distribution, and the schematic formula of the dendrimer used to form the nanoparticle.](image)
They have a rather high polydispersity and a range of sizes between 1.2 and 3.1 nm with an average size of 1.9 nm. Soxhlet extraction improved the size distribution ratio in favour of the particle with an average size of 1.9 nm. The stability of these clusters is remarkable and no decomposition has been observed even after several months in solution. Also in this case, the ratio between the sulfur and gold atoms used for the formation of the particles was irrelevant and the same results were obtained even with 10 equivalents of gold per sulfur atom. This once again demonstrates that there is a specific stabilization of gold clusters by the dendrimers. In order to fully understand the dendritic effect, preparation of gold nanoparticles stabilized by the dendron $\text{Dend}_5\text{S}$ (dendron used for the synthesis of $\text{S}_6\text{G}1$, see figure 3) has been performed. The results show that it is indeed possible to synthesize and purify stable gold particles with this compound. The size of these clusters using a 1:1 stoichiometry is about $2.4 \pm 0.3$ nm and they have a quite good monodispersity. Interestingly changing the ratio between dendrons and gold, 0.33 equivalent of gold per sulfur atom, led to the formation of smaller particles, $1.8 \pm 0.3$ nm. Furthermore the stability of $\text{Au}/\text{Dend}_5\text{S}$ is comparable to the one of alkanethiol stabilizing nanoparticles.

Finally to prove the integrity of the dendritic structures also after formation of the gold nanoparticles, a comparison with the clusters obtained with benzylthiol and 3,5-bis(benzyloxy)benzylthiol, dendrons of $\text{S}_6\text{G}0$ and $\text{S}_6\text{G}1$ respectively,$^{[24, 58]}$ have been made. The average sizes for these stabilized nanoparticles are about 3.1 nm ($3\text{S}:1\text{Au})^{[58]}$ and 2.4 - 3.0 nm,$^{[24]}$ respectively. Besides the different size and stability of the particles, we can certainly exclude that bond breaking occurs (producing the same $\text{Au}/\text{dendrons}$ described above) in the dendrimers since no shift in the $^1\text{H}$-NMR for the ($\text{Au}/\text{dendrimers}$) nanoparticles has been observed (see previous section).

The surprising stabilization induced by the thioether of the dendrimers is in strong disagreement with the poor stabilization of the thioether vs. thiol for the formation of Au particles. We believe that the weaker interaction of the sulfur-ether atoms with the gold is partly compensated by the multiple-sites binding (kinetic stabilization). Furthermore contribution to the stability could come from the electron rich phenyl groups lying on the surface of the nanoparticles (strong electron acceptor).

7.3 Conclusions

We have described the syntheses and characterization of dendritic sulfur containing structures and their use as templates for the formation of gold nanoparticles. A comparison
with simpler molecules to understand the role played by the nature of the sulfur atoms, the
effect played by the branches of the dendritic architectures and the generation dependence on
the size and stabilization of the particles was made. The results show that the use of dendritic
structures is of particular interest since the size and stability of the gold clusters depend on the
generation of the dendrimers. The multiple sites binding, 6 or 9 sulfur atoms that are arranged
in a desired fashion, is not the only determining factor to favour the formation of the gold
nanoparticles. The branches and the nature of the groups connected with the sulfur play in fact
a crucial role for the stability and solubility of the metal clusters. The kind of stabilization
involved can be compared to that obtained with alkanethiol with the advantage that the
thickness of the shell around the particle is much lower.

The results obtained indicate that dendrimers can be used as a powerful tool to create
nano-objects with desired size, and therefore electronic properties, and their peripheral
functionalization could lead to a valuable approach to control the assembly of multiple
particles.

7.4 Experimental part

Nanoparticle synthesis: Tetrachloroaurate hydride (n equivalents; where n is the number of
sulfur atoms contained by one ligand) was dissolved in de-ionized water. When the stirred
solution became lightly yellow, a solution of tetraoctylammonium bromide (4n equivalents) in
toluene was added. The solution was vigorously stirred until all the gold was transferred in the
organic phase (the organic phase became red leaving the aqueous phase colorless) and then a
solution of the sulfur containing ligand (1/n equivalent) in toluene was added, followed by the
addition of a freshly prepared solution of sodium borohydride (12n equivalents) in water. The
mixture turned black and was stirred for 3 h at rt. The biphasic solution was separated, the
organic phase concentrated (to 3 ml), and a solid precipitated by adding ethanol (300 ml). The
mixture was cooled at 4°C during 18 h and the precipitate filtered over celite. In order to
purify the precipitate, the solid was redissolved in toluene and the above described procedure
was repeated 3 times. The solid was dried and cleaned employing a soxhlet extraction (using
acetone) for 15 h.

1,2,3,4,5,6-Hexakis(mercaptomethyl)benzene\(^{[46-48]}\) (SH\(_6\)):

A suspension of 1,2,3,4,5,6-hexakis(bromomethyl)benzene (500 mg, 0.78 mmol) and
thiourea (600 mg, 7.87 mmol) in dry ethanol (40 ml) was refluxed for 5 h. The arising
precipitate was filtered off and the solvent removed in vacuo. The residue was dissolved in aqueous NaOH (20 ml; 2N), and refluxed for 3 h. The solution was brought to pH 4 with diluted aqueous HCl. The arising precipitate was filtered and dried in vacuo, yielding 213 mg (77%) of an amorphous solid. $^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 3.58 (s, 12 H, CH$_2$); $^{13}$C-NMR (62.9 MHz, CDCl$_3$): $\delta$ (ppm) = 21.8 (CH$_2$), 137.3 (Ar-C); MS (EI): m/z (%) = 354 (15) [M-H]$^+$, 322 (2) [M-SH]$^+$, 320 (12) [M-H-SH]$^+$, 304 (15), 253 (80), 219 (100), 207 (95).

1,2,3,4,5,6-Hexakis(benzylsulfanyl)methyl)benzene$^{[46-48]}$ (S$_6$G0):

1,2,3,4,5,6-Hexakis(mercaptopethyl)benzene (60 mg, 0.17 mmol) was suspended in dry ethanol (20 ml) under argon atmosphere and sodium (50 mg, 2.17 mmol) was added. The suspension is stirred at rt for 15 min and then a solution of benzylbromide (0.12 ml, 1.00 mmol) in dry toluene (20 ml) was added dropwise over a period of 3 h. The suspension was stirred for another 15 h and then water (50 ml) was added. The water phase was extracted five times with dichloromethane, the collected organic phase dried over Na$_2$SO$_4$ and the solvent removed in vacuo. Purification by column chromatography (SiO$_2$; 2:1 cyclohexane/dichloromethane) yielded 30 mg (21%) of a colourless solid; mp 142-143 °C; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 3.26 (s, 12 H, CH$_2$), 3.42 (s, 12 H, CH$_2$); 7.14 - 7.36 (m, 30 H, Ph-H); $^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 30.3, 37.8 (CH$_2$), 127.1, 128.5, 129.4, 135.5, 138.9 (Ar-C); MS (FAB): m/z (%) = 893.3 [M-H]$^+$ (3), 803.3 [M-PhCH$_2$]$^+$ (12), 771.2 [M-PhCH$_2$S]$^+$ (19), 679.2 [M-PhCH$_2$S-PhCH$_2$]$^+$ (6), 649.2 [M-(PhCH$_2$S)$_2$]$^+$ (3), [M-(PhCH$_2$S)$_2$-PhCH$_2$]$^+$ (14), 341.0 (42), 309.1 (16), 251.0 (80), 219 (100).

1,2,3,4,5,6-Hexakis[3',5'-bis(benzyloxy)benzyl)sulfanyl)methyl]benzene (S$_6$G1):

1,2,3,4,5,6-Hexakis(mercaptopethyl)benzene (70 mg, 0.02 mmol) was suspended in dry ethanol (30 ml) under argon atmosphere and sodium (200 mg, 8.69 mmol) was added. The solution was stirred for 10 min at rt and then a solution of 3,5-bis(benzyloxy)benzylbromide (760 mg, 12 mmol) in dry toluene (30 ml) was added dropwise over a period of 4 h at rt. The reaction mixture was stirred for another 20 hours and then water (20 ml) was added. The water phase was extracted five times with dichloromethane, the collected organic phase dried over Na$_2$SO$_4$, and the solvent removed in vacuo. Purification by column chromatography (SiO$_2$; 2:1 cyclohexane/dichloromethane) yielded 160 mg (37%) of a colorless viscous liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 3.27 (s, 12 H, CH$_2$), 3.56 (s, 12 H, CH$_2$), 4.85 (s, 24 H, CH$_2$O), 6.41 (s, 6 H, Ar-H), 6.49 (s, 12 H, Ar-H); 13C-NMR
Oligothia dendrimers for the controlled formation of gold nanoparticles

(100.6 MHz, CDCl₃): δ (ppm) = 30.5, 37.9 (CH₂), 70.0 (CH₂O), 100.8, 108.0, 127.6, 127.9, 128.5, 135.7, 136.8, 141.2, 160.0 (Ar-C); MS (MALDI-TOF): m/z (%) = 2189.7 [M+Na]+ (12), 2207.9 [M+K]+ (8).

1,3-Dibromo-5-(methylsulfonyl)benzene:

A mixture of 3,5-dibromofluorobenzene (1.00 g, 3.90 mmol) and sodium methyliothiolate (0.284 g, 4.05 m mol) in dry DMF (10 ml) under argon atmosphere was stirred for 5 d at rt. The solvent was removed in vacuo and the residue suspended in water (50 ml). The aqueous phase was extracted several times with dichloromethane, dried over Na₂SO₄ and the solvent removed in vacuo. Purification by column chromatography (SiO₂; petroleum ether (40/60)) yielded 800 mg (70%) of a colourless viscous liquid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 2.40 (s, 3 H, CH₃), 7.21 (s, 2 H, Ar-H), 7.33 (s, 1 H, Ar-H); ¹³C-NMR (100.6 MHz, CDCl₃): δ (ppm) = 15.5 (CH₃), 123.1, 127.3, 130.4, 143.0 (Ar-C); MS (EI): m/z (%) = 281 [M+] (100), 249 (24).

1,3-Bis[(4'-methylphenyl)sulfonyl]-5-(methylsulfonyl)benzene:

1,3-Dibromo-5-(methylsulfonyl)benzene (1.0 g, 4 mmol) was taken up in a mixture of pyridine (2 ml), quinoline (8 ml) and p-thiocresol (1.49 g, 12 mmol) and then copper(I) oxide (380 mg) was added. The reaction mixture was heated for 45 h at 160 °C under argon atmosphere. The reaction mixture was cooled to rt and the crude product purified by column chromatography (neutral Al₂O₃; petroleum ether (40/60)) to give 1.20 g (81 %) of a colourless solid; mp 59 °C; ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 2.31 (s, 3 H, SCH₂), 2.38 (s, 6 H, Ar-CH₂), 6.72-7.23 (m, 11 H, Ar-H); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 15.5 (SCH₂), 21.8 (Ar-CH₂), 123.1, 125.3, 129.6, 130.2, 133.1, 138.2, 139.4, 140.3 (Ar-C); MS (EI): m/z = 368 [M+] (100).

3,5-Bis[(4'-methylphenyl)sulfonyl]benzenethiol (Dend₃S):

1,3-Bis[(4'-methylphenyl)sulfonyl]-5-(methylsulfonyl)benzene (1.00 g, 2.7 mmol) was mixed with sodium tert.-butylthiolate (0.9 g, 8.1 mmol) under argon atmosphere. Dry DMF (10 ml) was added while stirring vigorously and the mixture heated at 160 °C. After 5 h the reaction mixture was cooled to 0 °C and stirred at this temperature for 30 min. An aqueous solution of HCl (15 ml; 3N) was rapidly added to the mixture until pH 1. The mixture was transferred to an aqueous solution of HCl (85 ml; 3N). The aqueous phase was extracted
several times with dichloromethane. The collected organic phase was dried over Na$_2$SO$_4$ and the solvent evaporated in vacuo. The crude product was purified by column chromatography (SiO$_2$; 95:5 petroleum ether (40/60)/ethyl acetate) to yield 620 mg (60 %) of a highly viscous liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 2.38 (s, 6 H, Ar-CH$_3$), 3.30 (s, 1 H, SH), 6.72-7.23 (m, 11 H, Ar-H); $^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 21.2 (Ar-CH$_3$), 125.5, 126.2, 129.3, 130.2, 132.6, 133.3, 138.4, 139.9 (Ar-C); MS (EI): m/z (%) = 354 [M$^+$] (100).

1,3,5-Tris[3',5'-bis[(4''-methylphenylsulfanyl)sulfanylmethyl]]benzene (S$_3$G1):

3,5-Bis[(4'-methylphenyl)sulfanyl]benzenethiol (622 mg, 1.8 mmol) was mixed with 1,3,5-tribromomethylbenzene (160 mg, 0.45 mmol) and KOH (283 mg, 5.0 mmol) in dry DMF (5 ml). The mixture was refluxed at 90 °C under argon atmosphere for 7 h. After cooling to rt, water was added and the resulting mixture extracted several times with dichloromethane. The collected organic phase was washed once with water, dried over Na$_2$SO$_4$ and the solvent removed in vacuo. Purification by column chromatography (SiO$_2$; 3:1 petroleum ether/dichloromethane) yielded 197 mg (38%) of a colourless solid; mp 107.6 °C; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 2.31 (s, 18 H, Ar-CH$_3$), 3.78 (s, 6 H, SCH$_2$), 6.72-7.23 (m, 36 H, Ar-H); $^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 21.1 (Ar-CH$_3$), 38.1 (SCH$_2$), 126.4, 128.3, 129.5, 130.1, 130.2, 133.1, 133.2, 137.4, 138.1, 138.2, 139.5, 139.6 (Ar-C); MS (MALDI-TOF): m/z = 1177.3 [M+H]$^+$.  

7.5 References

Oligothiur dendrimers for the controlled formation of gold nanoparticles


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