

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229461802>

Oligothia Dendrimers for the Formation of Gold Nanoparticles

ARTICLE *in* ADVANCED FUNCTIONAL MATERIALS · DECEMBER 2004

Impact Factor: 11.81 · DOI: 10.1002/adfm.200400101

CITATIONS

26

READS

14

9 AUTHORS, INCLUDING:



Anthony D'Aléo

CINaM - Centre Interdisciplinaire de Nanosc...

53 PUBLICATIONS 792 CITATIONS

SEE PROFILE



René M Williams

University of Amsterdam

86 PUBLICATIONS 2,768 CITATIONS

SEE PROFILE

Oligothia Dendrimers for the Formation of Gold Nanoparticles**

By Anthony D'Aléo, René M. Williams, Friederike Osswald, Prasad Edamana, Uwe Hahn, Jeroen van Heyst, Frans D. Tichelaar, Fritz Vögtle, and Luisa De Cola*

The synthesis and characterization 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 (S_6G1 and S_9G1), influence the formation and reactivity of the nanoparticles. UV-visible spectroscopy, 1H nuclear magnetic resonance spectroscopy and high-resolution transmission electron microscopy have been employed for the characterization of the nanoparticles. Furthermore, purification by Soxhlet extraction has been performed.

1. Introduction

The pioneering work of Schmid et al.^[1] and of Brust et al.^[2–4] has introduced a fascinating route to the preparation and use of small, well-defined clusters of gold atoms as if they are traditional chemical reagents to build new structures in the nanoworld. Even though many synthetic methods have been developed to form and stabilize these nanoparticles,^[5–7] so far no general strategies have been reported. Only a few scattered examples of creating and controlling the size and functionalization of the nanoclusters using binding and other interactions with organic molecules have been reported.^[8–16] In order to reach 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 of using multiple-binding ligands in order to increase the stability and create 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-containing 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 of protecting the gold nanoparticle, as well as introducing 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. These include their branched nature, which allows the positioning of coordinating atoms in desired places; their nanometer-sized dimensions, controllable by the number of generations; and their multiple possible functionalizations, leading to new chemical and physical properties.^[25–33] It has recently been shown that, depending upon the dendrimer generation, stabilized nanoparticles can have different sizes, dispersities,^[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 (which can be used to incorporate nanoparticles) varies, depending upon the shape and generation of the dendrimer. It has been shown that nanoparticles can be encapsulated in a cavity where they are isolated from other nanoparticles.^[21] Furthermore, dendrimers offer possibilities of acting as scaffolds for the attachment of numerous functional groups to gold nanoparticles. Such functionalization may broaden the application of gold nanostructures in the fields of biomedicine,^[35–38] catalysis,^[21,39–41] and electronics.^[42,43]

To our knowledge, few of the sulfur-containing dendrimers^[44–46] reported so far have been used for stabilizing nanoparticles.^[47,48] However, the use of disulfide as a core leads to the decomposition of the S–S bond into thiolates in the presence of a metal, resulting in the equivalent of thiol dendrons.^[48] The presence of organyl sulfide (thioether) functions^[49,50] implemented inside the dendritic structure would result in a new approach to control the growth, 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.

[*] Prof. L. De Cola, A. D'Aléo, Dr. R. M. Williams
Universiteit van Amsterdam, HIMS
Nieuwe Achtergracht 166, NL-1018 WV Amsterdam (The Netherlands)
E-mail: ldc@science.uva.nl

Dr. F. Osswald, Dr. P. Edamana, Dr. U. Hahn,
J. van Heyst, Prof. F. Vögtle
Kekulé-Institut für Organische Chemie und Biochemie
Universität Bonn
Gerhard-Domagk-Str. 1, D-53121 Bonn (Germany)
Dr. F. D. Tichelaar
Laboratorium voor Materiaalkunde
National Centre for High-Resolution Electron Microscopy
Technische Universiteit Delft, TNW, TMK
Rotterdamseweg 137, NL-2628 AL Delft (The Netherlands)

[**] We wish to thank the EU project SUSANA (HPRN-CT-2002-00185) for funding, Dr. E. A. Plummer for help in writing the manuscript, Dr. M. Nieger for crystal structure determinations.

2. Results and Discussion

One of the major challenges in the nanoclusters field is the possibility of controlling the size, the stability, and the monodispersity of metal and semiconducting nanoparticles. In order to be able to devise a general strategy for the formation and selective functionalization of nanoparticles, it is important to determine the effect of the chemical structure of the ligands that promote their 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, the number of anchoring groups per molecule of ligand, and the 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.

Three of the ligands are dendritic structures: two of the same family, S_6G0 and S_6G1 , containing the sulfur atoms only in the core; and S_9G1 , in which the sulfur atoms are also in the branches. The two reference systems, SH_6 and MS_6 , contain the same number of sulfur atoms (six) arranged in a non-branched structure, and have also been investigated and compared with the dendritic species. All these molecules have been synthesized, characterized, and employed as templates for the formation of gold nanoparticles.

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^[51–53] (see Experimental section). The cores of S_6G0 and S_6G1 are 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 induces a bent geometry, which is important since direct connection to the benzene ring would result in a flat core that would not be ideal for nanoparticle stabilization. The methylene group is also indispensable for providing the possibility of accommodating the rigid, bulky branches of the dendrimer, and for conferring a different electron density to the sulfur atom as compared to e.g. unit.

S_6G0 was prepared by adding benzyl bromide to SH_6 using Na^0 as a base (Fig. 2). This dendrimer, present in solution in different conformations, has an estimated distance of 2.2 nm between the extremities of two opposite phenyl groups in the extended-flat representation, which decreases to 1.5 nm in the conformation where the six sulfur atoms are on the same side of the benzene ring. This distance is 2.0 nm in the conformation where three sulfur atoms (atoms 1,3,5) are above the ben-

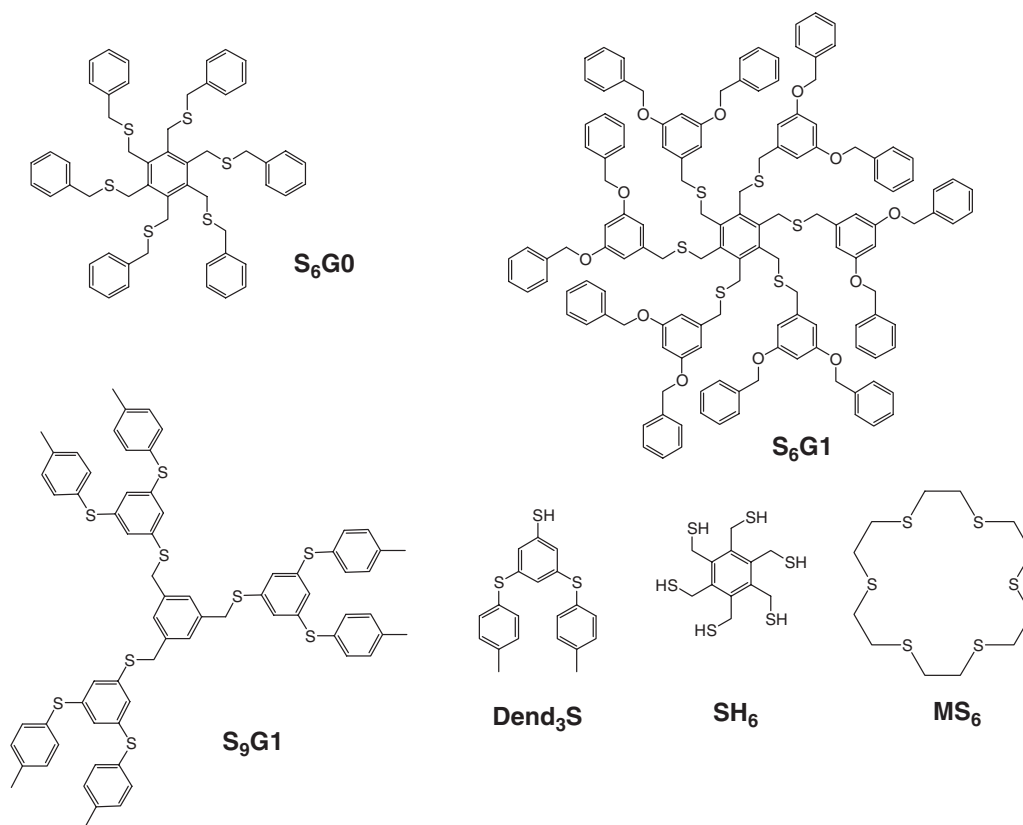


Figure 1. Structures and abbreviations of the investigated compounds.

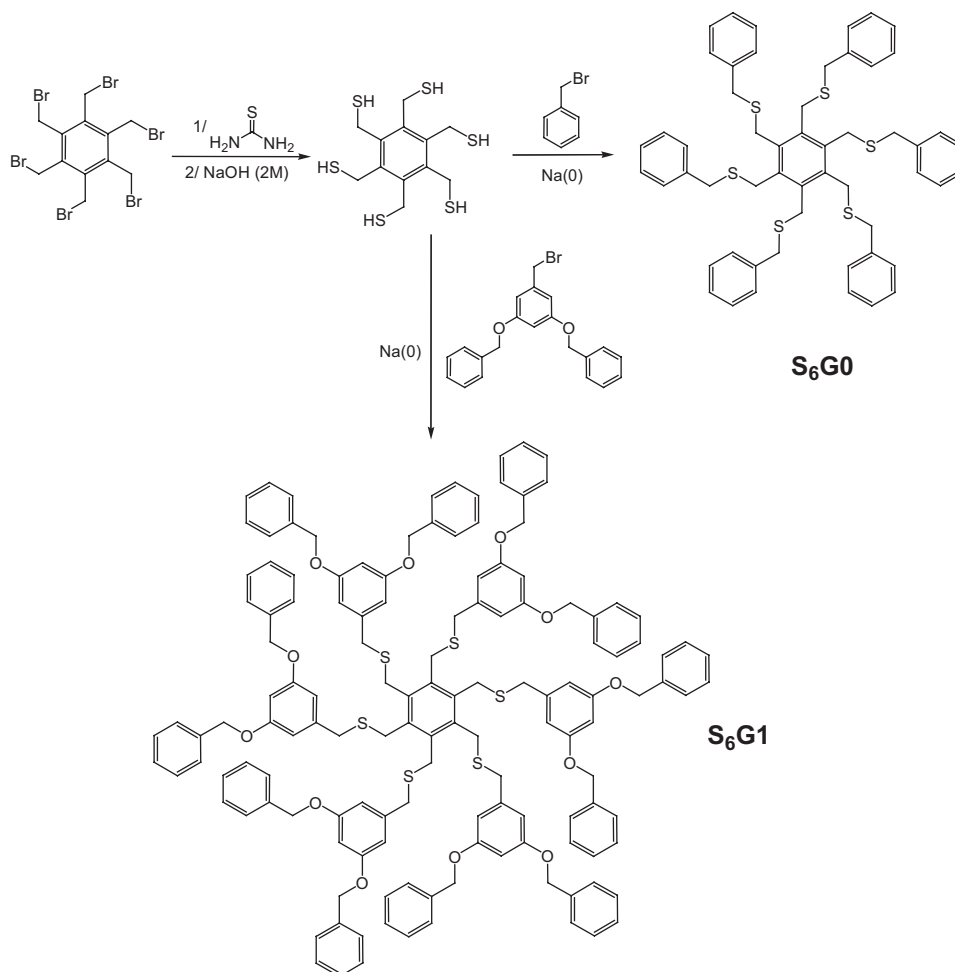


Figure 2. Synthetic scheme for the preparation of S_6G0 and S_6G1 .

zyl plane and the three others (atoms 2,4,6) are below the plane. This conformation has been confirmed in the solid state by X-ray analysis^[52,53] (Fig. 3).

The coupling of SH_6 with G1 Fréchet-type dendrons was performed under the same conditions as for S_6G0 , and gave S_6G1 (Fig. 2). The average distance between the extremes of opposite phenyl groups in the extended conformation of S_6G1 is 2.8 nm, while in the bent structure the distance is roughly 2.1 nm. The synthesis of S_9G1 was carried out analogously to S_6Gn ($Gn = G0$ and $G1$), using a different dendron^[54] and a tri-substituted benzene ring (Fig. 4; see Experimental section). S_9G1 is composed of only three dendritic branches, but each branch contains three sulfur atoms. This dendrimer is less crowded than S_6G1 , and, while in S_6G1 every sulfur atom is connected to two sp^3 carbons, every sulfur atom in S_9G1 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

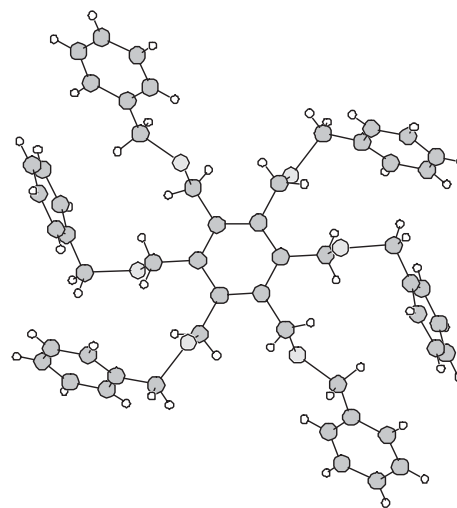


Figure 3. X-ray crystal structure of S_6G0 .

expect enhanced stability of benzylic sulfur derivatives compared to aromatic thiols or thioethers or aliphatic thioethers. We have, in fact, noticed that commercially available hexa-

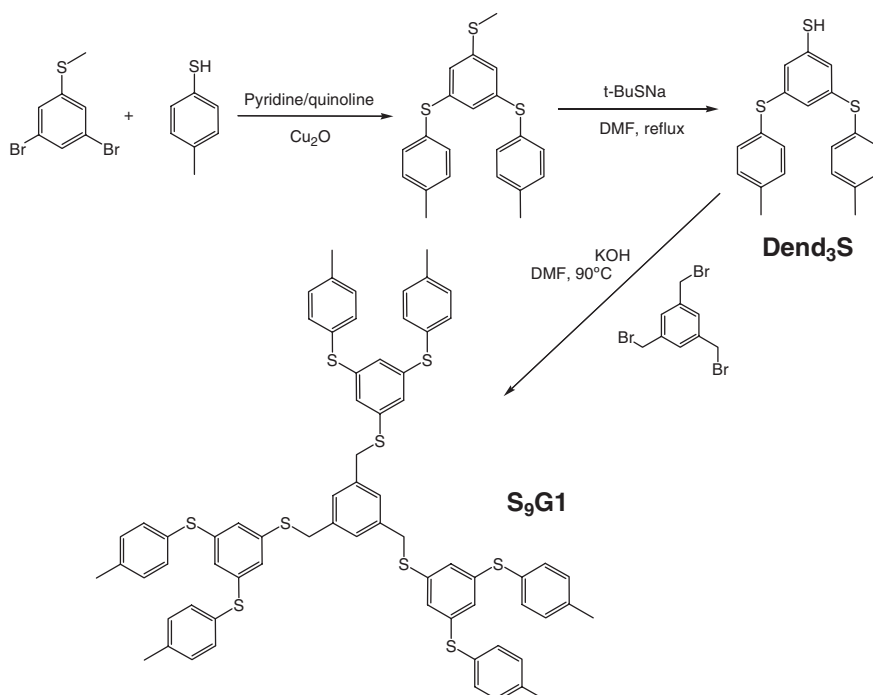


Figure 4. Synthetic scheme for the preparation of Dend₃S and S₉G1.

kis(thiobenzyl)benzene does not stabilize the formation of nanoparticles.

All the nanoparticles were prepared following Brust's synthesis.^[2] They were precipitated three times in ethanol in order to purify them before the measurements. Furthermore, using the method reported recently by Schiffrin and co-workers,^[55] the nanoparticles were purified using Soxhlet extraction to eliminate all organic impurities. We have compared the purity of the particles before and after Soxhlet extraction (see below). The general preparation of the clusters involves the use of one equivalent of gold (hydrogen tetrachloroaurate) per one equivalent of sulfur atoms (see Experimental).

The gold stabilized nanoparticles, Au/S₆G_n and Au/S₆G1, have been characterized by UV-visible (UV-vis) spectroscopy, ¹H nuclear magnetic resonance (NMR) spectroscopy, and high-resolution transmission electron microscopy (HR-TEM) before and after Soxhlet extraction.

2.2. UV-vis Absorption Spectroscopy

UV-vis absorption spectra have been recorded for all the compounds in toluene at room temperature. The spectra of Au/S₆G0 and Au/S₆G1 (Fig. 5) were compared with the bare nanoparticles (nanoparticles stabilized by tetraoctylammonium bromide,^[56] Au/TOAB) and with particles obtained in the same conditions with dodecanethiol (Au/C₁₂SH).

Before Soxhlet extraction, the absorption spectra show a clear band at 520 nm (the intensity and position of which is indicative of the size of the particles), attributed to the surface plasmon resonance of the gold.^[57,58] It can be seen that for the

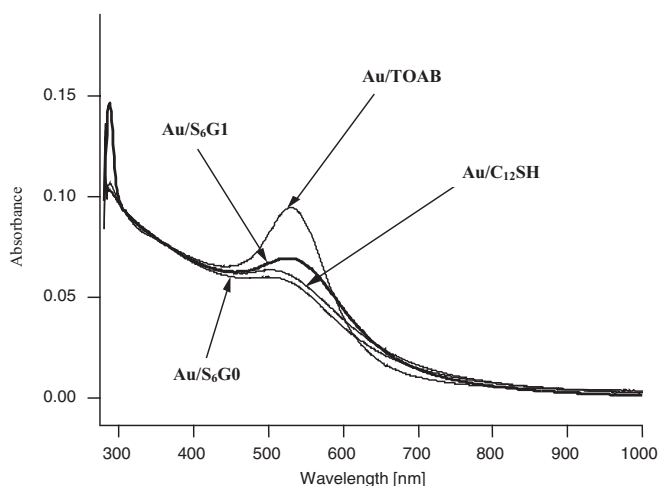


Figure 5. UV-vis absorption spectra in toluene of Au/S₆G0, Au/S₆G1, Au/C₁₂SH, and Au/TOAB.

non-stabilized particles, Au/TOAB, this band has a high intensity, while for the Au/S₆G0 and Au/S₆G1 particles, the intensity depends on the dendrimer used but it is much lower than for the bare nanoparticles.

Such important results suggest that the size of the gold clusters is dependent on the generation of the dendrimers. In particular, S₆G0 leads to particles (Au/S₆G0) smaller than those obtained with dodecanethiol (Au/C₁₂SH). The particles obtained using S₆G1 as template (Au/S₆G1) are, on the other hand, larger than Au/S₆G0, but smaller than the non-stabilized ones (Au/TOAB). For S₆G1, it is also possible to detect an ab-

sorption at about 300 nm characteristic of the π - π^* transition of the methoxybenzene moieties 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/S₆G0 adduct is much less stable than Au/S₆G1 under the same experimental conditions. The use of the S₆G1 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 the insolubility of the nanoparticles in the extraction solvent. This proves that TOAB is indispensable for the stabilization and isolation of Au/S₆G1 (see the discussion of the NMR results).

Similar spectroscopic behavior is observed for the other dendritic structure, S₉G1. The nanoparticles formed by reaction with S₉G1 (Au/S₉G1) exhibit the absorption spectrum shown in Figure 6, where a comparison with the analogous Au/S₆G1 is made. The absorption at 520 nm is weaker than that of Au/S₆G1, suggesting that the average size of the Au/S₉G1 nanopar-

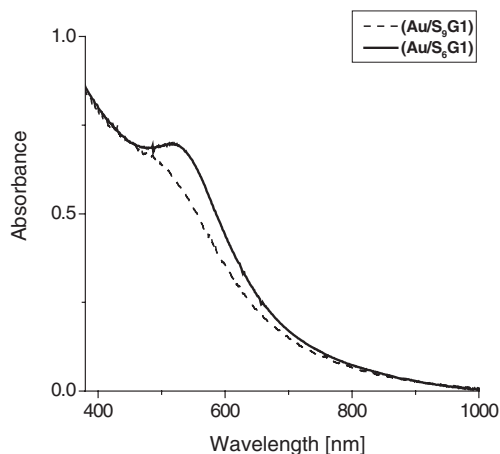


Figure 6. Comparison of the absorption spectra of Au/S₆G1 and Au/S₉G1.

ticles is smaller than that of the Au/S₆G1 nanoparticles. It is interesting to note that, after Soxhlet extraction, the absorption of the S₉G1 is identical to the samples that were not Soxhlet extracted.

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 lower energies (700 nm) suggests that neither clustering of particles, nor the presence of two nanoparticles trapped by one dendrimer molecule, is possible.^[59] In order to gain insight into the role of multiple sulfur-binding sites within the same molecule, two other molecules containing six sulfur atoms (SH₆ and MS₆, Fig. 1) have been prepared and investigated. SH₆ forms nanoparticles, but also larger aggregates, observed in the UV-vis 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, while the typical band of the gold

cluster around 520 nm remains. Purification by Soxhlet extraction was not possible due to the extremely high solubility of the nanoparticles. It is interesting to note that, even though the SH₆ is the bare core of the S₆G1 dendrimer and has the same number of sulfur atoms in the same geometric configuration, it behaves very differently because of the lack of branching. In the case of MS₆, no nanoparticle formation was observed. The weak binding of the cyclic aliphatic thioethers does not provide enough stabilization of the gold nanoclusters.

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

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 effect of the presence of TOAB. Comparison between the free dendritic structures and the Au/S_nG_n nanoparticles 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 positions of the thiol groups^[60,61]), and it is indicative of the proximity and interactions of these protons with the nanoparticles. In all the dendritic gold nanoparticle structures, the signals of the protons in close proximity to the Au surface broaden, and in some cases split up into more signals. In particular, formation of nanoparticles incorporating the dendrimer S₆G1 causes all the signals to broaden as a result of the global interactions of each group with the Au surface (Fig. 7). The aromatic region cannot be explored in detail because of the solvent employed, deuterated toluene. Integration of the spectrum reveals the presence of an average of 23 molecules of TOAB per dendrimer. It is interesting to note that, despite the stability of the Au/S₆G1 nanoparticles in toluene, in dichloromethane the particles are only stable for less than an 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.

In the case of S₉G1, we can observe that all the ¹H NMR signals in deuterated dichloromethane are broadened, except for 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, Fig. 8). Comparison with the free S₉G1 clearly indicates that these groups are farther from the nanoparticle than all the other protons. This can be interpreted with the assumption that the dendrimers are acting like an octopus, where the arms of the dendrimers are the tentacles which trap the nanoparticles. Therefore, the groups close to the core which are bent to trap the nanoparticles are not in contact with the gold atoms. Also, in this case some residual stabilizing agent is present, but only three molecules of TOAB per S₉G1 moiety was found.

The ¹H NMR of Au/S₆G1 in deuterated toluene (not shown) reveals that the initial singlet (CH₂SH) in chloroform splits into a quartet. This suggests that more than one arm is in close

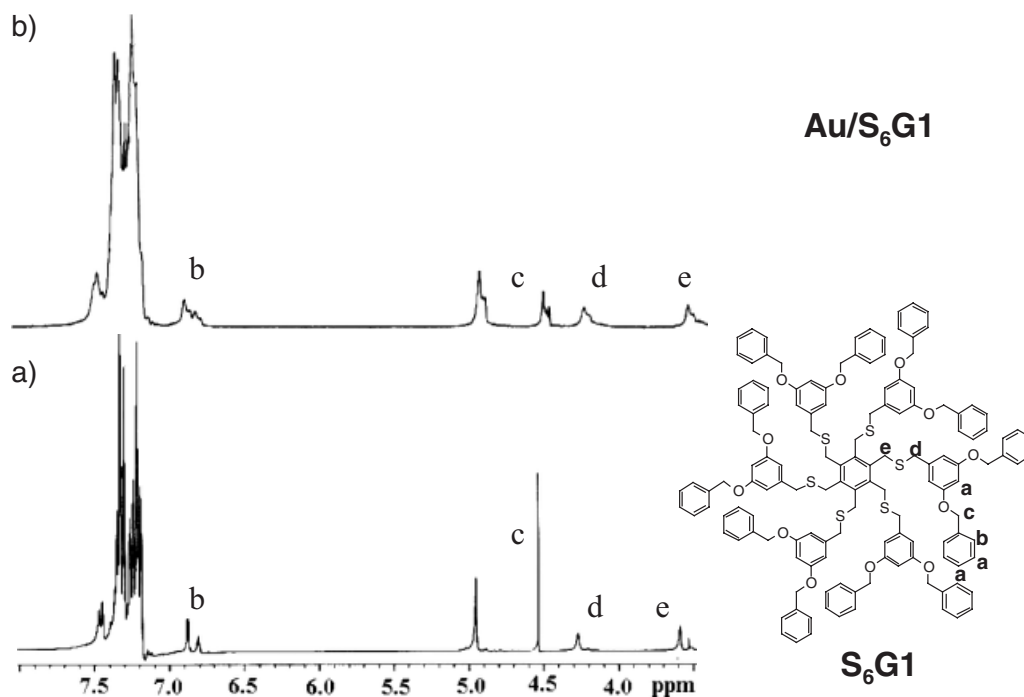


Figure 7. ^1H NMR spectra of a) $\text{S}_6\text{G1}$ and b) $\text{Au/S}_6\text{G1}$ in deuterated toluene.

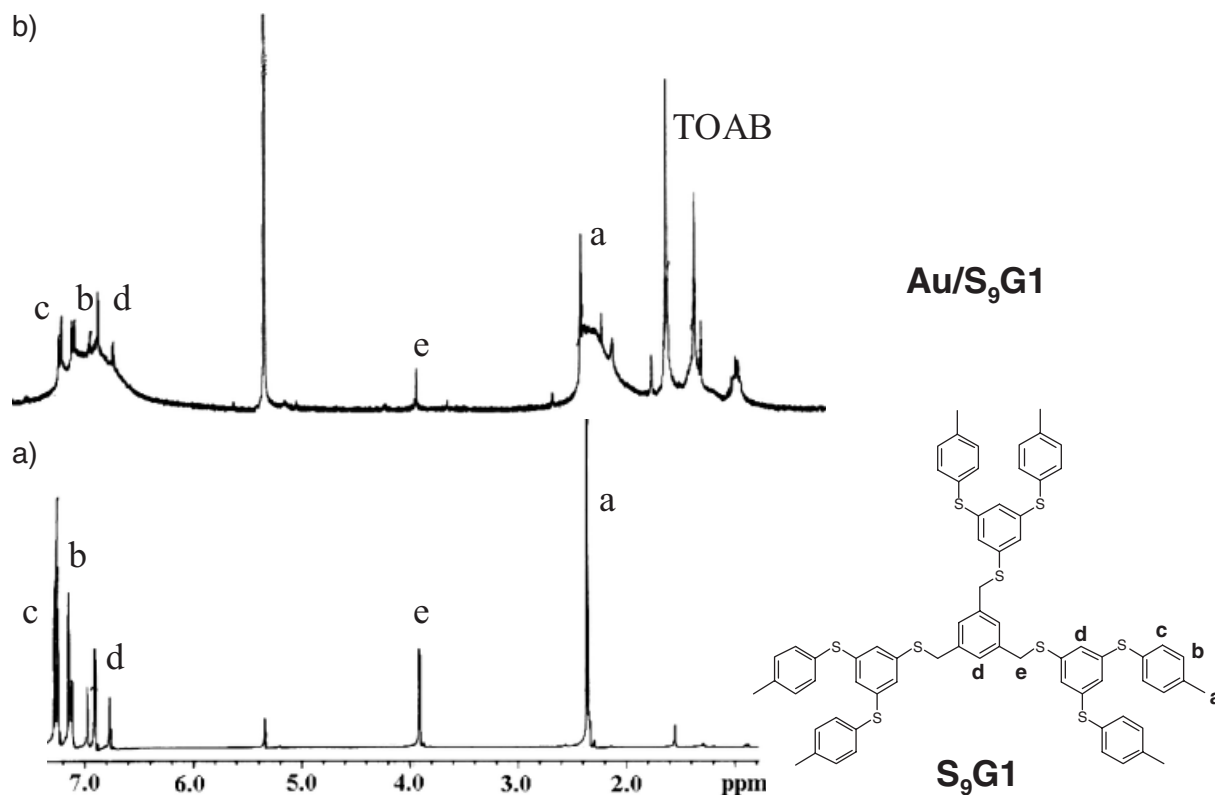


Figure 8. ^1H NMR spectra of a) $\text{S}_9\text{G1}$ and b) $\text{Au/S}_9\text{G1}$ in deuterated dichloromethane.

contact to the gold, as expected for the case of different CH_2SH groups complexing the same nanoparticle. This NMR spectrum also reveals that the proton resonance of the SH is significantly broadened (from 5.1 to 5.9 ppm). This broadening is indicative of a strong interaction between the thiol group and the gold. For this small molecule, an average of 117 ammonium bromide moieties corresponding to TOAB per SH_6 molecule were found. These nanoparticles were re-dissolvable in all organic solvents (e.g., ethanol, acetone, dichloromethane, toluene).

2.4. High-Resolution Transmission Electron Microscopy

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 gold/ligand nanoparticle isolated.

The HR-TEM measurements show that two populations of the $\text{Au/S}_6\text{G1}$ particles are present, one of about 1.8 ± 0.6 nm in diameter, and the other about 3.1 ± 0.2 nm (Fig. 9). The measurements also suggest that, for the two populations, the dispersity is not the same, and indicate that the larger particles possess the higher stability and are more favorably formed. As already mentioned, the edge-to-edge size of this dendrimer is 2.1 nm, and therefore it is reasonable to think that, in the case

of the 3.1 nm particles, two (or more) dendritic structures can template the formation of one gold 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.

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 (Fig. 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 above). From the NMR data, it is also clear that 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 (number of sulfur atoms) per gold atom, confirming that the chemical structure of the template determines the size and stability of the nanoparticles.

The gold nanocluster obtained with the dendrimer $\text{S}_6\text{G0}$, reveals, after two precipitations, a size of 2.8 ± 1.1 nm and a higher polydispersity than $\text{Au/S}_6\text{G1}$. Furthermore, the nanoparticles obtained with the smallest dendrimer are less stable, decomposing after two days in solution. If the synthesis of the nanoparticles is performed using two equivalents of gold per equivalent of sulfur, similar sizes and distributions are found, suggesting that the precipitated nanoparticles have the same

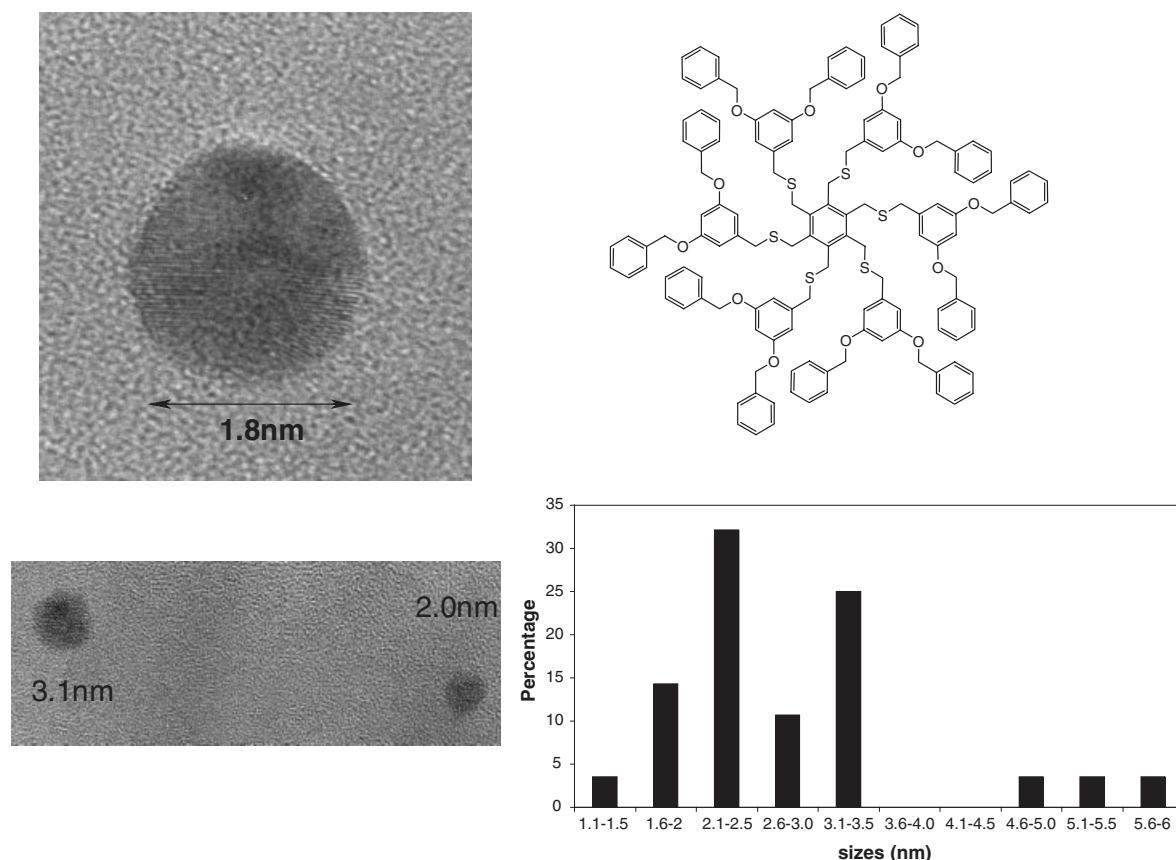


Figure 9. HR-TEM images of the $\text{Au/S}_6\text{G1}$ particles, their size distribution, and the structure of the dendrimer used to form the nanoparticles.

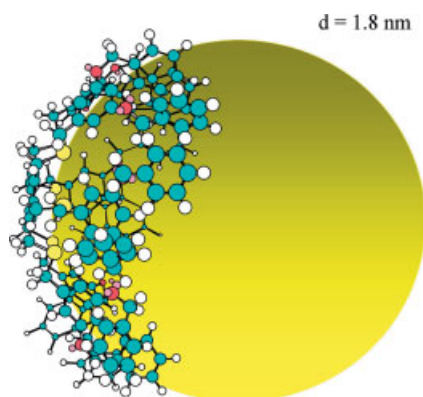


Figure 10. Schematic representation of dendrimer S_6G1 on the nanoparticle. The molecule and the particle are drawn to the same scale.

characteristics independent of the amount of gold employed. These nanoparticle sizes (for Au/S_6G1 and Au/S_6G0) are in perfect agreement with the UV-vis absorption spectra (Fig. 5): the 2.8 nm-diameter nanoparticles (S_6G0) are smaller than the 3.2 nm-diameter nanoparticles (S_6G1). We can clearly state that it is not only the number of sulfur atoms that plays a major role in stabilizing the nanoparticles. In fact, while SH_6 possesses the same number of S atoms as the S_6Gn dendrimers, very few stable SH_6 particles could be isolated, but with an average size of 3.0 ± 1.2 nm.

The gold nanoparticles obtained employing the S_9G1 dendrimer are shown in Figure 11. 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 favor of the particles 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 ten 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 $Dend_3S$ (dendron used for the synthesis of S_9G1 , Fig. 3) was 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 ± 0.3 nm, and they have a high degree of monodispersity. Interestingly, changing the ratio between dendrons and gold to 0.33 equivalents of gold per sulfur atom led to the formation of smaller particles of average size 1.8 ± 0.3 nm. Furthermore, the stability of $Au/Dend_3S$ is comparable to that of alkane thiol-stabilized nanoparticles.

Finally, to prove the integrity of the dendritic structures after formation of the gold nanoparticles, a comparison with the clusters obtained using benzylthiol and 3,5-bis(benzyloxy)ben-

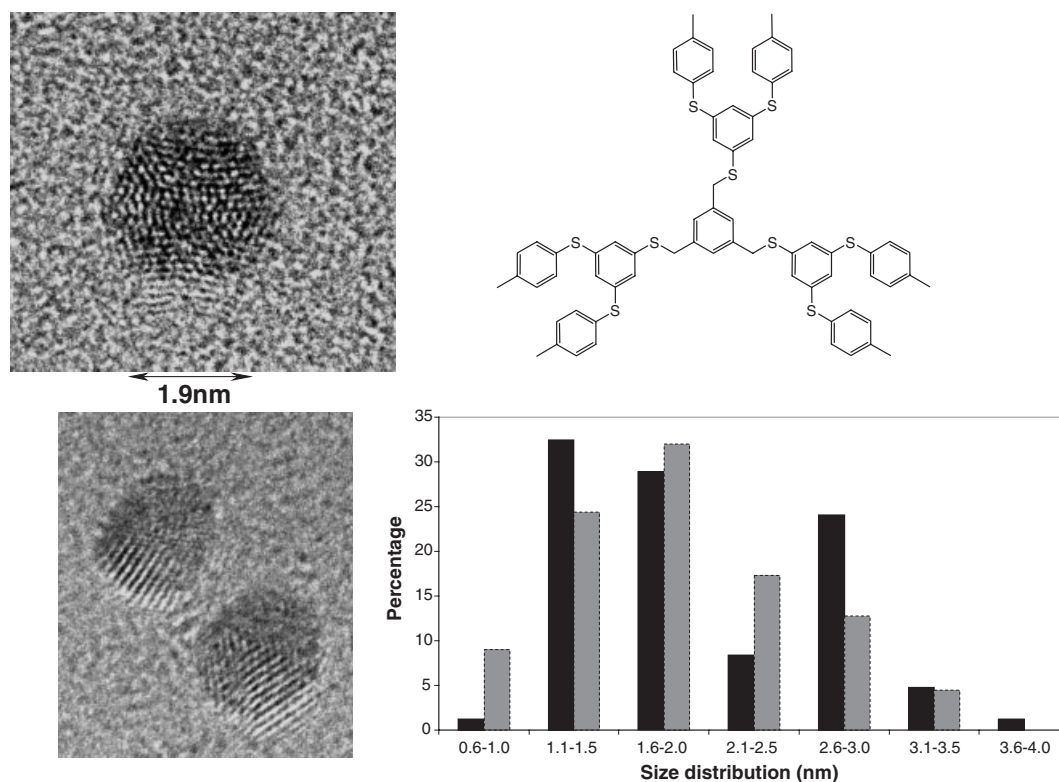


Figure 11. HR-TEM images of the Au/S_9G1 particles, their size distribution (black: before Soxhlet extraction; gray: after Soxhlet extraction), and the structure of the dendrimer used to form the nanoparticle.

zylthiol dendrons of S_6G0 and S_6G1 , respectively,^[24,62] was made. The average sizes for these stabilized nanoparticles were about 3.1 nm (3 S atoms per Au atom)^[62] and 2.4–3.0 nm,^[24] respectively. Besides the different sizes and stabilities of the particles, we can certainly exclude that bond breaking occurs (producing the same Au/dendrons described above) in the dendrimers, since no shift in the 1H NMR for the Au/dendrimer nanoparticles was observed (see above).

The surprisingly high degree of stabilization induced by the thioether moiety of the dendrimers is in strong disagreement with the comparatively poor stabilization of the non-dendritic thioether 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 binding sites, resulting in kinetic stabilization. Furthermore, contribution to the stability could come from the electron-rich phenyl groups lying on the surface of the nanoparticles, that provide a strong electron-accepting capacity.

3. Conclusions

We have described the synthesis and characterization of dendritic sulfur-containing structures and their use as templates for the formation of gold nanoparticles. A comparison was made with simpler molecules in order 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. 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 binding sites, consisting of six or nine sulfur atoms arranged in a desired fashion, is not the only determining factor in favoring the formation of the gold nanoparticles. The branches and the nature of the groups connected with the sulfur in fact play a crucial role in the stability and solubility of the metal clusters. The kind of stabilization involved can be compared to that obtained with alkanethiols, with the advantage that the thickness of the shell around the particle is much smaller.

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

4. Experimental

General: All chemicals were purchased from Acros or Aldrich and were used as received. All solvents purchased and used were analytical grade, except for solvents used for UV-visible (UV-vis) spectroscopy, which were spectroscopic grade. 3,5-Bis(benzyloxy)benzyl bromide was synthesized according to literature [63,64]. Absorption spectra were recorded on a Hewlett–Packard 8453 diode array spectrophotometer. 1H nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini-300 spectrometer (for the nanoparticles synthesis) or a Bruker AM 400 spectrometer (for the dendrimer syntheses).

Chemical shifts (δ) are reported in ppm, using the deuterated solvent as internal standard. High-resolution transmission electron microscopy (HR-TEM) and cross-sectional TEM electron microscopy was performed using a HR-TEM Philips CM30T and a CM30UT-FEG, respectively, both operating at 300 kV. A drop of dilute solution containing a suspension of particles was placed on a copper grid with a carbon foil, and solvent was evaporated at room temperature and atmospheric pressure.

Nanoparticle Synthesis: Hydrogen tetrachloroaurate (n equivalents; where n is the number of sulfur atoms contained by one ligand) was dissolved in deionized water. When the stirred solution turned a light-yellow color, a solution of tetraoctylammonium bromide ($4n$ equivalents) in toluene was added. The solution was vigorously stirred until all the gold was transferred to the organic phase (the organic phase turned red, leaving the aqueous phase colorless), and then a solution of the sulfur-containing ligand ($1n$ 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 room temperature (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 for 18 h and the precipitate filtered over celite. In order to purify the precipitate, the solid was re-dissolved in toluene, and the above described procedure was repeated three 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 [51–53] (S_6H_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; 2 N), and refluxed for 3 h. The solution was brought to pH 4 with diluted aqueous HCl. The resulting precipitate was filtered and dried in vacuo, yielding 213 mg (77 %) of an amorphous solid. 1H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 12H, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 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(benzylsulfanylmethyl)benzene [51–53] (S_6G0): 1,2,3,4,5,6-Hexakis(mercaptomethyl)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 was stirred at RT for 15 min, and then a solution of benzyl bromide (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_2SO_4 , and the solvent removed in vacuo. Purification by column chromatography (SiO_2 , 2:1 cyclohexane/dichloromethane) yielded 30 mg (21 %) of a colorless solid; mp 142–143 °C; 1H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 12H, CH_2), 3.42 (s, 12H, CH_2) 7.14–7.36 (m, 30H, Ph–H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 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 [$M-PhCH_2S$]⁺ (19), 679.2 [$M-PhCH_2S-PhCH_2$]⁺ (6), 649.2 [$M-(PhCH_2S)_2$]⁺ (3), [$M-(PhCH_2S)_2-PhCH_2$]⁺ (14), 341.0 (42), 309.1 (16), 251.0 (80), 219 (100).

1,2,3,4,5,6-Hexakis[(3',5'-bis(benzyloxy)benzyl)sulfanylmethyl]benzene (S_6G1): 1,2,3,4,5,6-Hexakis(mercaptomethyl)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)benzyl bromide (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 h, and then water (20 mL) was added. The water phase was extracted five times with dichloromethane, the collected organic phase dried over Na_2SO_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. 1H NMR (400 MHz, $CDCl_3$): δ = 3.27 (s, 12H, CH_2), 3.56 (s, 12H, CH_2), 4.85 (s, 24H, CH_2O), 6.41 (s, 6H, Ar–H), 6.49 (s, 12H, Ar–H), 7.13–7.36 (m, 120H, Ph–H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.5, 37.9 (CH_2), 70.0 (CH_2O), 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-(methylsulfanyl)benzene [54]: A mixture of 3,5-dibromofluorobenzene (1.00 g, 3.90 mmol) and sodium methylthiolate (0.284 g, 4.05 mmol) in dry DMF (10 mL) under argon atmosphere was stirred for 5 days 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 Na_2SO_4 , and the solvent removed in vacuo. Purification by column chromatography (SiO_2 ; petroleum ether (40/60)) yielded 800 mg (70 %) of a colorless viscous liquid. ^1H NMR (400 MHz, CDCl_3): δ = 2.40 (s, 3H, CH_3), 7.21 (s, 2H, Ar-H), 7.33 (s, 1H, Ar-H); ^{13}C NMR (100.6 MHz, CDCl_3): δ = 15.5 (CH_3), 123.1, 127.3, 130.4, 143.0 (Ar-C); MS (EI): m/z (%) = 281 [M^+] (100), 249 (24).

1,3-Bis[(4'-methylphenyl)sulfanyl]-5-(methylsulfanyl)benzene [54]: 1,3-Dibromo-5-(methylsulfanyl)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 Al_2O_3 ; petroleum ether (40/60)) to give 1.20 g (81 %) of a colorless solid; mp 59 °C; ^1H NMR (400 MHz, CDCl_3): δ = 2.31 (s, 3H, SCH_3), 2.38 (s, 6H, Ar- CH_3), 6.72–7.23 (m, 11H, Ar-H); ^{13}C NMR (100.6 MHz, CDCl_3): δ = 15.5 (SCH_3), 21.8 (Ar- CH_3), 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)sulfanyl]benzenethiol (Dend₃S): 1,3-Bis[(4'-methylphenyl)sulfanyl]-5-(methylsulfanyl)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 to 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; 3 N) was rapidly added to adjust the mixture to pH 1. The mixture was transferred to an aqueous solution of HCl (85 mL; 3 N). The aqueous phase was extracted several times with dichloromethane. The collected organic phase was dried over Na_2SO_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. ^1H NMR (400 MHz, CDCl_3): δ = 2.38 (s, 6H, Ar- CH_3), 3.30 (s, 1H, SH), 6.72–7.23 (m, 11H, Ar-H); ^{13}C NMR (100.6 MHz, CDCl_3): δ = 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'-methylphenyl)sulfanyl]sulfanylmethyl]benzene (S₀G1): 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_2SO_4 , and the solvent removed in vacuo. Purification by column chromatography (SiO_2 ; 3:1 petroleum ether/dichloromethane) yielded 197 mg (38 %) of a colorless solid; mp 107.6 °C; ^1H NMR (400 MHz, CDCl_3): δ = 2.31 (s, 18H, Ar- CH_3), 3.78 (s, 6H, SCH_2), 6.72–7.23 (m, 36H, Ar-H); ^{13}C NMR (100.6 MHz, CDCl_3): δ = 21.1 (Ar- CH_3), 38.1 ($\text{S}-\text{CH}_2$), 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 [$\text{M}+\text{H}$] $^+$.

Received: March 9, 2004
Final version: June 24, 2004

- [1] G. Schmid, R. Pfeil, B. F. Boese, S. Meyer, G. Calis, J. W. A. van der Velde, *Chem. Ber.* **1981**, 114, 3634.
- [2] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- [3] M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, C. Kiely, *J. Chem. Soc., Chem. Commun.* **1995**, 1655.
- [4] M. Brust, D. Bethell, D. J. Schiffrin, C. J. Kiely, *Adv. Mater.* **1995**, 7, 795.

- [5] R. M. Crooks, B. I. Lemon, L. Sun, L. K. Yeung, M. Q. Zhao, in *Dendrimers III: Design, Dimension, Function* (Ed: F. Vögtle), Topics in Current Chemistry, Vol. 212, Springer, Berlin **2001**, p. 81.
- [6] *Metal Nanoparticles: Synthesis, Characterization, and Applications* (Eds: D. L. Feldheim, C. A. J. Foss), Marcel Dekker, New York **2002**.
- [7] *Synthesis, Functionalization and Surface Treatment of Nanoparticles* (Ed: M.-I. Baraton), American Scientific, Los Angeles, CA **2003**.
- [8] M. Brust, C. J. Kiely, D. Bethell, D. J. Schiffrin, *J. Am. Chem. Soc.* **1998**, 120, 12367.
- [9] C. M. Niemeyer, *Angew. Chem. Int. Ed.* **2001**, 40, 4128.
- [10] C. J. Kiely, J. Fink, M. Brust, D. Bethell, D. J. Schiffrin, *Nature* **1998**, 396, 444.
- [11] R. Jordan, N. West, A. Ulman, Y. M. Chou, O. Nuyken, *Macromolecules* **2001**, 34, 1606.
- [12] J. P. Novak, L. C. Brousseau, F. W. Vance, R. C. Johnson, B. I. Lemon, J. T. Hupp, D. L. Feldheim, *J. Am. Chem. Soc.* **2000**, 122, 12029.
- [13] M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, 14, 17.
- [14] W. W. Weare, S. M. Reed, M. G. Warner, J. E. Hutchison, *J. Am. Chem. Soc.* **2000**, 122, 12890.
- [15] E. Bakkers, A. L. Roest, A. W. Marsman, L. W. Jenneskens, L. I. de Jong-van Steensel, J. J. Kelly, D. Vanmaekelbergh, *J. Phys. Chem. B* **2000**, 104, 7266.
- [16] E. Bakkers, A. W. Marsman, L. W. Jenneskens, D. Vanmaekelbergh, *Angew. Chem. Int. Ed.* **2000**, 39, 2297.
- [17] D. Fitzmaurice, S. N. Rao, J. A. Preece, J. F. Stoddart, S. Wenger, N. Zaccaroni, *Angew. Chem. Int. Ed.* **1999**, 38, 1147.
- [18] A. K. Boal, V. M. Rotello, *Langmuir* **2000**, 16, 9527.
- [19] G. Schmid, W. Meyer-Zaika, R. Pugin, T. Sawitowski, J. P. Majoral, A. M. Caminade, C. O. Turrin, *Chem. Eur. J.* **2000**, 6, 1693.
- [20] P. Braunstein, H. P. Kormann, W. Meyer-Zaika, R. Pugin, G. Schmid, *Chem. Eur. J.* **2000**, 6, 4637.
- [21] R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, 34, 181.
- [22] J. J. Michels, J. Huskens, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* **2002**, 102.
- [23] R. Y. Wang, J. Yang, Z. P. Zheng, M. D. Carducci, J. Jiao, S. Seraphin, *Angew. Chem. Int. Ed.* **2001**, 40, 549.
- [24] M. K. Kim, Y. M. Jeon, W. S. Jeon, H. J. Kim, S. G. Hong, C. G. Park, K. Kim, *Chem. Commun.* **2001**, 667.
- [25] M. Fischer, F. Vögtle, *Angew. Chem. Int. Ed.* **1999**, 38, 884.
- [26] F. Vögtle, S. Gesterman, R. Hesse, H. Schwierz, B. Windisch, *Prog. Polym. Sci.* **2000**, 25, 987.
- [27] S. Hecht, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **2001**, 40, 74.
- [28] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, Germany **2001**.
- [29] *Dendrimers IV: Metal Coordination, Self Assembly, Catalysis* (Eds: F. Vögtle, C. A. Schalley), Topics in Current Chemistry, Vol. 217, Springer, Berlin **2001**.
- [30] *Dendrimers V: Functional and Hyperbranched Building Blocks, Photophysical Properties, Applications in Materials and Life Sciences* (Eds: F. Vögtle, C. A. Schalley), Topics in Current Chemistry, Vol. 228, Springer, Berlin **2003**.
- [31] *Dendrimers and other Dendritic Polymers* (Eds: J. M. J. Fréchet, D. A. Tomalia), Wiley-VCH, Weinheim, Germany **2001**.
- [32] A. Dirksen, L. De Cola, *C. R. Chim.* **2003**, 6, 873.
- [33] D. K. Smith, *Tetrahedron* **2003**, 59, 3787.
- [34] M. E. Garcia, L. A. Baker, R. M. Crooks, *Anal. Chem.* **1999**, 71, 256.
- [35] M. R. J. Gibbs, *Curr. Opin. Solid State Mater. Sci.* **2003**, 7, 83.
- [36] W. J. Parak, D. Gerion, T. Pellegrino, D. Zanchet, C. Micheel, S. C. Williams, R. Boudreau, M. A. Le Gros, C. A. Larabell, A. P. Alivisatos, *Nanotechnology* **2003**, 14, R15.
- [37] S. J. Park, T. A. Taton, C. A. Mirkin, *Science* **2002**, 295, 1503.
- [38] R. C. Jin, G. S. Wu, Z. Li, C. A. Mirkin, G. C. Schatz, *J. Am. Chem. Soc.* **2003**, 125, 1643.

- [39] M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
- [40] M. Haruta, in *Science and Technology in Catalysis 2002: Proc. of the Fourth Tokyo Conf. on Advanced Catalytic Science and Technology* (Eds: M. Anpo, M. Onaka, H. Yamashita), Kodansha, Tokyo, Japan **2003**, p. 31.
- [41] B. L. V. Prasad, S. I. Stoeva, C. M. Sorensen, V. Zaikovski, K. J. Klambunde, *J. Am. Chem. Soc.* **2003**, *125*, 10488.
- [42] D. I. Gittins, D. Bethell, D. J. Schiffrin, R. J. Nichols, *Nature* **2000**, *408*, 67.
- [43] D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley, X. Y. Zhu, *J. Phys. Chem. B* **2003**, *107*, 6668.
- [44] M. Gingras, A. Pinchart, C. Dallaire, *Angew. Chem. Int. Ed.* **1998**, *37*, 3149.
- [45] M. Mayor, J. M. Lehn, K. M. Fromm, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2370.
- [46] M. Mayor, J. M. Lehn, *J. Am. Chem. Soc.* **1999**, *121*, 11231.
- [47] V. Chechik, R. M. Crooks, *Langmuir* **1999**, *15*, 6364.
- [48] K. R. Gopidas, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2003**, *125*, 6491.
- [49] X. M. Li, M. R. de Jong, K. Inoue, S. Shinkai, J. Huskens, D. N. Reinhoudt, *J. Mater. Chem.* **2001**, *11*, 1919.
- [50] E. J. Shelley, D. Ryan, S. R. Johnson, M. Couillard, D. Fitzmaurice, P. D. Nellist, Y. Chen, R. E. Palmer, J. A. Preece, *Langmuir* **2002**, *18*, 1791.
- [51] F. Vögtle, E. Weber (Merck Patent GmbH), *German Patent DE2556260*, **1977**.
- [52] A. D. U. Hardy, D. D. MacNicol, L. S. Swanson, D. R. Wilson, *Tetrahedron Lett.* **1978**, *19*, 3579.
- [53] A. D. U. Hardy, D. D. MacNicol, L. S. Swanson, D. R. Wilson, *J. Chem. Soc., Perkin Trans. 2* **1980**, 999.
- [54] A. Van Bierbeek, M. Gingras, *Tetrahedron Lett.* **1998**, *39*, 6283.
- [55] C. A. Waters, A. J. Mills, K. A. Johnson, D. J. Schiffrin, *Chem. Commun.* **2003**, 540.
- [56] J. Fink, C. J. Kiely, D. Bethell, D. J. Schiffrin, *Chem. Mater.* **1998**, *10*, 922.
- [57] C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York **1983**.
- [58] M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin, I. Vezmar, R. L. Whetten, *J. Phys. Chem. B* **1997**, *101*, 3706.
- [59] Y. Fang, *J. Chem. Phys.* **1998**, *108*, 4315.
- [60] R. H. Terrill, T. A. Postlethwaite, C. Chen, J. E. Hutchison, C. Poon, A. Tarzis, A. Chen, M. R. Clark, C. S. Johnson, E. T. Samulski, J. M. DeSimone, R. W. Murray, *Abstr. Pap. Am. Chem. Soc.* **1995**, *210*, 380.
- [61] O. Kohlmann, W. E. Steinmetz, X. A. Mao, W. P. Wuelfing, A. C. Templeton, R. W. Murray, C. S. Johnson, *J. Phys. Chem. B* **2001**, *105*, 8801.
- [62] S. W. Chen, R. W. Murray, *Langmuir* **1999**, *15*, 682.
- [63] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638.
- [64] C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.* **1990**, 1010.