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Monofunctionalized Gold Nanoparticles Stabilized by a Single Dendrimer Form Dumbbell Structures upon Homocoupling

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Supporting Information

ABSTRACT: The assembly of dumbbell structures as organic−inorganic hybrid materials is presented. Gold nanoparticles (NPs) with a mean diameter of 1.3 nm were synthesized in very good yields using a stabilizing dendrimer based on benzylic thioether subunits. The extended dendritic ligand covers the NP surface and contains a peripheral protected acetylene, providing coated and monofunctionalized NPs. These NPs themselves can be considered as large molecules, and thus, applying a wet-chemical deprotection/oxidative acetylene coupling protocol exclusively provides dimers of NPs interlinked by a diethynyl bridge. The concept not only enables access to novel organic/inorganic hybrid architectures but also promises new approaches in labeling technology.

Gold nanoparticles (Au NPs) are promising model compounds for nanoelectronic devices,[1,2] sensor applications[3] and catalysis.[4,5] Au NPs are also intensively used for labeling, as represented in numerous review articles addressing this topic.[6−9] In many cases, Au NPs are functionalized with DNA or peptides as recognition sites for labeling purposes. These protocols are limited to aqueous or polar organic conditions and are usually statistical reactions with low yields of monofunctionalized Au NPs. To date, monofunctionalization of Au NPs in apolar organic media has been achieved only by the use of a solid support as a protecting group[10,11] or by ligand polymerization on the NP surface.[12] In addition, single polymer strands were reported to stabilize one NP on average.[13] The strategy presented here involves the design of an organic ligand that (i) controls the particle formation by coating and passivating the NP surface and (ii) allows the introduction of a controlled number of functional groups at the NP periphery. Such NPs exposing a restricted number of functional groups can be considered as molecules with nanoscale dimensions and can be addressed by wet-chemical protocols. While di- and monofunctionalized NPs are promising building blocks of well-defined organic−inorganic hybrid architectures, the latter ones are in addition particularly appealing as potential labels.

It was recently shown that benzylic thioether oligomers have promising stabilizing features as multidentate ligands during the synthesis of Au NPs.[14] In the presence of larger thioether oligomers, NPs with narrow dispersity are obtained in excellent yields. Furthermore, these NPs are decorated with only two ligands, allowing the introduction of a controlled number of peripheral functional groups dictating their chemical behavior. Thus, these functionalized NPs can be considered as large artificial molecules; as a first example, Au NPs containing two peripheral ethynyl groups were interlinked to form oligomers by a wet-chemical oxidative acetylene coupling protocol.[15] By expanding the benzylic thioether motif to dendritic structures, we recently synthesized unfunctionalized dendrimers, and one second-generation representative was able to stabilize exactly one Au NP.[16] The observed 1/1 ligand/Au NP ratio might make available monofunctionalized NPs, which are much better suited both for labeling and as building blocks for discrete organic−inorganic hybrid architectures. The acetylene homocoupling of functionalized NPs is a new approach for covalent assembly of NP architectures in nonpolar organic media (the concept is illustrated in Figure 1). Other approaches for the direct assembly of NP dumbbells have been reported,[10−12,17−20] and recent review articles have presented the formation of various NP architectures and their interparticle forces.[21−24]

The thioether dendrimer design presented here is based on a structural motif that recently demonstrated its potential as a coating and surface-passivating ligand during the synthesis of Au NPs. Important design aspects are the dilution of the branching points and the steric surface protection using bulky *tert*-butyl groups in the "diluting" subunits. The reduced branching was chosen to favor enwrapping by the dendritic ligand rather than a scenario where the NPs grow inside a ball-shaped dendrimer.[25,26] Our dendritic ligands were further functionalized by introducing a central oligo(phenylene ethynylene) (OPE) rod comprising a central pyridine unit and a triisopropylsilyl (TIPS)-protected acetylene (Figure 1). The pyridine nitrogen not only provides an additional coordination site for the Au NP but was recently also shown to result in a perpendicular arrangement of the rod on the NP surface.[27,28] The masked acetylene is introduced as a peripheral functionality, providing an integer number of wet-chemically addressable functional groups in each obtained Au NP. The thioether dendrimers **G1** and **G2** were synthesized by S_N2 reactions of already reported compounds (Scheme 1). The

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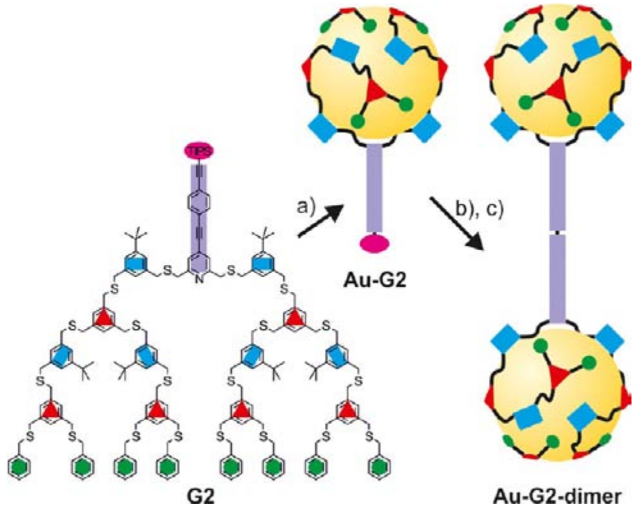
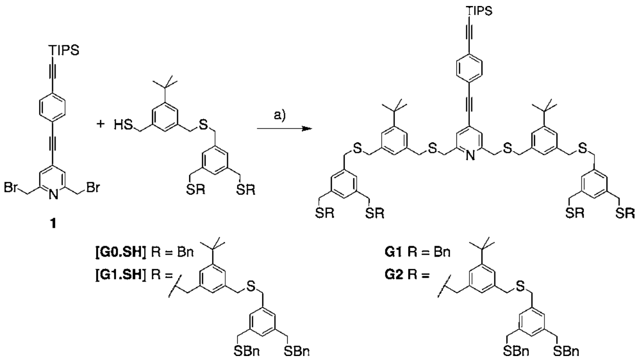


Figure 1. General concept of forming ligand-stabilized Au NPs and NP dimers. (a) NP synthesis: $HAuCl_4$, TOAB, $NaBH_4$, H_2O/CH_2Cl_2. (b) Deprotection: TBAF, CH_2Cl_2. (c) Oxidative coupling: CuCl, TMEDA, O_2 (ambient air). For a space-filling representation, see Figure S4.

thiol dendrons[16] [**G0.SH**] and [**G1.SH**] have substituted the benzylic bromines of the OPE rod **1**.[27] The monofunctionalized ligands were obtained in good to excellent yields.

Scheme 1. Synthesis of Monofunctionalized Thioether Dendrimers G1 and G2 as Stabilizing Ligands for Au NPs[a]



[a](a) NaH, THF, rt; 85−95%.

The Au NP-stabilizing features of thioether dendrimers **G1** and **G2** were investigated using techniques that have been successfully applied in earlier studies.[15,16,27] The formation of functionalized Au NPs was performed in a H_2O/CH_2Cl_2 solvent mixture following a protocol developed by Brust et al.[29] The dendritic ligands **G1** and **G2** dissolved in CH_2Cl_2 were added to an aqueous solution of tetrachloroauric acid and the phase-transfer agent tetraoctylammonium bromide (TOAB) in CH_2Cl_2. Au NPs **Au-G1** and **Au-G2** were obtained after the addition of sodium borohydride in water. After aqueous workup and removal of TOAB with a precipitation/centrifugation protocol, the excess ligand was removed by gel-permeation chromatography (GPC). See the Supporting Information (SI) for a more detailed protocol. The purified NPs were obtained in yields exceeding 80% and were initially analyzed by UV/vis spectroscopy. The UV/vis spectra obtained (Figure S1 in the SI) showed the presence of Au NPs without a strong plasmon band of gold at 520 nm, indicating that the NPs had diameters below 2 nm.[30,31] The presence of the delocalized OPE structure in the periphery of the NPs was manifested by a broad peak at ~300 nm. Single drops of the solutions used for UV/vis spectroscopy were transferred to carbon-coated copper grids (CCCGs) for transmission electron microscopy (TEM) investigations. The micrographs (Figure 2 and Figures S5 and S6) showed small Au NPs with a narrow size distribution. An automatic investigation method using ImageJ[32] was applied to measure the size (diameter) of the NPs formed (see the SI for the analysis protocol). More than 5000 NPs from more than 10 dense TEM images were analyzed. Similar size distributions were obtained for **Au-G1** and **Au-G2**, with mean diameters of 1.3 ± 0.4 nm (Figure 2 inset). These diameters are similar to those recently measured for Au NPs stabilized by the parent unfunctionalized dendrimers.[16] For **Au-G2**, small-angle X-ray scattering (SAXS) was employed as a second tool to determine the NP size. The measured 2D scattering signal was integrated to obtain an intensity plot (Figure S2) that suggested form factors of spheres. The plot was fitted with a model for polydisperse, spherical NPs, and a mean NP diameter of 1.3 nm with a standard deviation of 0.5 nm was obtained, corroborating the values obtained by TEM. To analyze the coating ligand/Au NP ratio, thermogravimetric analysis (TGA) of **Au-G1** and **Au-G2** was performed. To remove the organic shell in the TGA experiments, the dry NPs were heated to 950 °C. The weight loss curves were similar for the two samples (Figure S3). The amounts of weight loss were 21% in the case of **Au-G1** and 26% for **Au-G2**. These values were used to calculate the average number of gold atoms stabilized per dendrimer (see the SI for details). We found that on average one **G1** dendrimer stabilizes 30 Au atoms, while **G2** coats 50 atoms. The dimensions of the **Au-G1** and **Au-G2** NPs determined by TEM and SAXS suggest an average number of ~55 gold atoms per NP. In analogy to the parent ligand structure,[16,28] a single **G2** dendrimer or a pair of **G1** dendrimers are required to stabilize one Au NP.

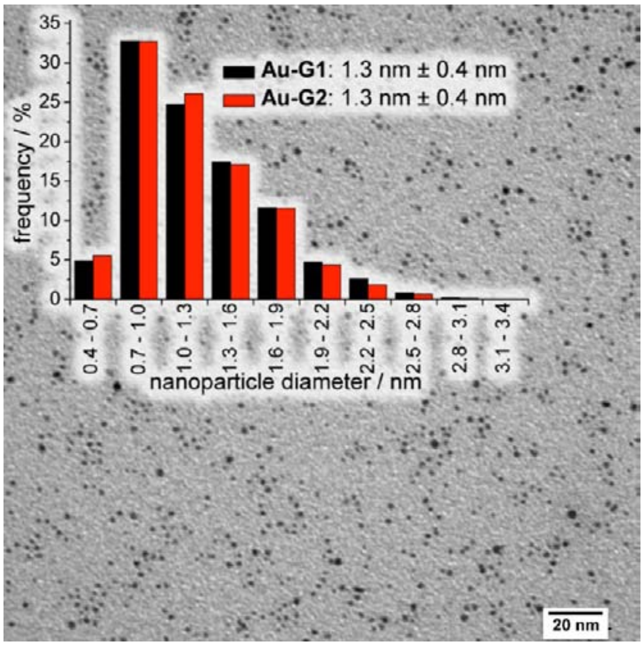


Figure 2. Representative dense TEM image of **Au-G1** NPs. Inset: size distributions for **Au-G1** (black) and **Au-G2** (red) NPs.

The discrete number of coating ligands also results in an equally well-defined number of peripheral masked acetylene functions per Au NP, and thus, the extent of surface functionalization per NP must be reflected in the connectivity of the NP subunits in the hybrid architectures obtained upon exposing them to acetylene coupling chemistry. While chains of NPs would be expected for the bifunctional **Au-G1**, similar to another example of bifunctional NPs,[33] the monofunctionalized analogue **Au-G2** should form dimers exclusively. Samples of both Au NPs (**Au-G1** and **Au-G2**) were exposed to a Glaser−Hay[34] wet-chemical oxidative acetylene coupling protocol. In brief, tetrabutylammoniumfluoride (TBAF) was first added to liberate the masked acetylene, and then tetramethylethylenediamine (TMEDA) and CuCl were added under ambient atmosphere to provide molecular oxygen. After 20 min, precipitation was observed only for the reaction mixture containing **Au-G1**, while the one containing **Au-G2** remained as a dark solution. The precipitation of bifunctional Au NPs due to the formation of too-long oligomeric chains was previously found for comparable systems.[15,27] To keep the oligomers short and dissolved, a small sample of the reaction mixture containing **Au-G1** was worked up after 10 min. After further dilution to avoid accidental proximities of NPs that were not covalently bound, samples were deposited on CCCGs and investigated by TEM. The micrographs showed the presence of single NPs, dimers, and higher oligomeric assemblies of NPs. These oligomers were predominantly found as chains of NPs, and typical representatives of these **Au-G1** superstructures are displayed in Figure 3. A more comprehensive overview of the micrographs is displayed in Figures S7 and S8. The chainlike arrangement of the NPs in these micrographs not only corroborates the wet-chemical coupling chemistry as the origin of the interlinked NPs but also supports the picture of having two functional groups per **Au-G1** NP on opposite sides. Strong similarities between **G1** and linear thioether ligands that were investigated in earlier studies[14,15,27,35] are obvious. Dendrimer **G1** and the linear ligands have similar sizes and consist of eight thioether moieties. NPs stabilized by these two ligands have comparable sizes with two coating ligands per NP. When the ligands bear an acetylene, chains are formed upon oxidative acetylene coupling and precipitate if their lengths exceed a certain threshold value.[15,27]

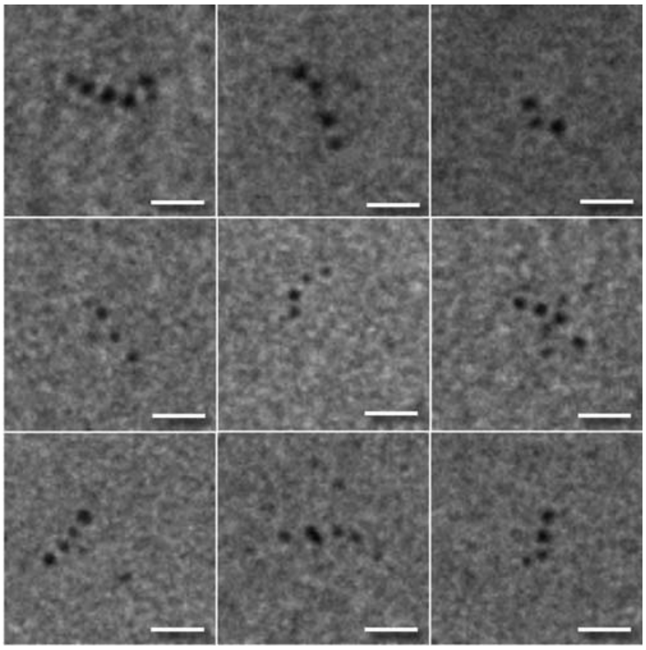


Figure 3. Representative TEM images of diluted solutions of **Au-G1** superstructures. The scale bars represent 10 nm.

In contrast to these bifunctional NPs, the monofunctionalized **Au-G2** NPs were expected to form dimers only, and indeed, even after prolonged reaction times or with excessive amounts of coupling chemicals, precipitation was not observed. The protected **Au-G2** NP monomers were first deprotected with a large excess of TBAF in CH_2Cl_2. After aqueous workup, the solution was concentrated to dryness using a stream of nitrogen. The homocoupling was then conducted in small amounts of CH_2Cl_2 in an open reaction vessel for 3 h using excesses of CuCl and TMEDA (see the SI for a detailed protocol). Samples of the reaction mixture containing the NP hybrid architectures were deposited as highly diluted solutions on CCCGs for TEM investigations. Thus, only a few NPs were present in each TEM image and showed sizes similar to the protected **Au-G2** monomers (Figure 4 and Figures S9 and S10). In these micrographs of diluted samples, the yield of NP dimers was analyzed. On 20 TEM images, ~400 NPs were counted, and almost half of them were dimers (47% yield); 46% of the NPs found were still present as monomers, and only 7% NPs existed in trimeric structures. The yield of dimers represents a 2−3-fold increase compared with the yield of superstructures formed with bifunctional NPs stabilized with linear thioether ligands (16−20%).[27] At first glance, the formation of trimeric structures from monofunctionalized NPs was surprising, and only a more detailed analysis of the interparticle spacing shed light on this unexpected observation.

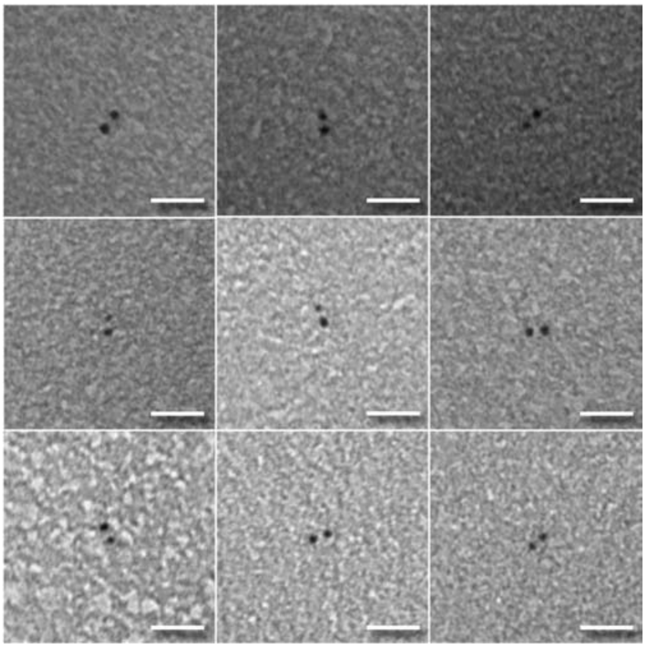


Figure 4. Representative TEM images of diluted solutions of **Au-G2** dimers. The scale bars represent 10 nm.

From the TEM images of the diluted samples, the distance between the NPs in the dimers was analyzed, and the interparticle distance distribution displayed in Figure 5 was obtained. A bimodal distribution was found, with one maximum matching the expected distance of the straight spacer at 2.5 nm. This distance results from a perpendicular arrangement of the rod on the gold surface[27] triggered by the coordination of the

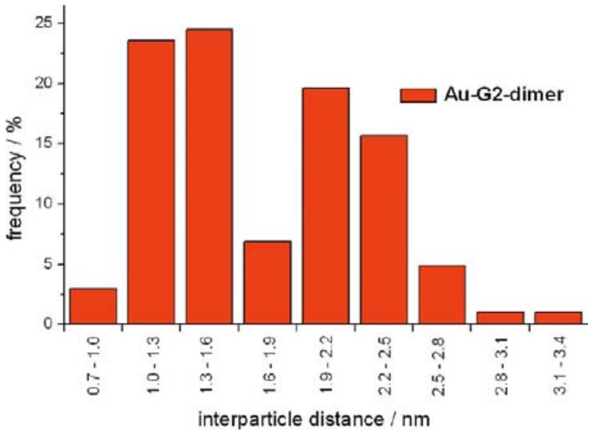


Figure 5. Interparticle distance distribution for **Au-G2** dimers measured from TEM images of very dilute solutions.

nitrogen lone pair of the central pyridine subunit.[28] An unexpected second maximum of the interparticle distance distribution at 1.3 nm was observed, probably indicating coordination of the free acetylene to the gold surface of a neighboring NP. A careful inspection of the interparticle distances in the trimeric structures supported this hypothesis, since in all of the trimeric structures at least one short distance was found. This result also provides a rationale for their formation, namely, the coordination of an acetylene-functionalized NP to the surface of an NP that was already engaged in a dimer structure.

In summary, the concept of controlling the size and surface functionalization of NPs with dentritic multidentate ligands has been demonstrated. The obtained mono- and difunctionalized NPs can be considered as nanoscale molecules that can be interlinked to form organic−inorganic hybrid architectures by wet-chemical reactions. Our current interest is geared toward increasing the size and stability of the functionalized NPs and exploring the potential of the approach for NP materials other than gold.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Descriptions of dendrimer synthesis, NP synthesis, NP coupling, and NP analysis by UV/vis, TGA, TEM, and SAXS as well as representative TEM images of NP monomers, dimers, and oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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