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Hydrophobic Dendrimers as Templates for Au Nanoparticles

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We report the synthesis, characterization, and extraction of Au dendrimer-encapsulated nanoparticles (DENs) prepared in organic solvents. DENs composed of 31 and 55 Au atoms were prepared using organic solvents and poly(amidoamine) (PAMAM) dendrimer templates modified on their periphery with dodecyl groups. The spectral and microscopic properties of the resulting materials were identical to those prepared using water-soluble PAMAM dendrimers. It was possible to extract the organic-soluble DENs into water using the water-soluble thiols tiopronin and glutathione. The properties of the resulting monolayer-protected clusters were nearly identical to those of the precursor DENs. A mechanistic model for the extraction process is discussed. The synthetic methodology reported here provides a convenient method for preparing DENs of non noble metals such as Ni and Fe.

Introduction

Here we report the synthesis of nearly monodisperse Au nanoparticles encapsulated within hydrophobic dendrimers.[1,2] Extraction of these nanoparticles from the dendrimer interior using hydrophilic ligands results in equally monodisperse, water-soluble Au monolayer-protected clusters (MPCs).[3−5] The results reported here complement previous studies in which we showed that hydrophilic dendrimers could be used to template nanoparticles in water[1,2] and that subsequent extraction with hydrophobic ligands leads to MPCs soluble in low-dielectric-constant solvents such as toluene.[6−9] The distinction between these two approaches is important, because this new methodology lays the groundwork for forthcoming studies in which we will show that stable dendrimer-encapsulated nanoparticles (DENs) composed of easily oxidizable metals, such as Ni and Fe, can be prepared in organic solvents. The point of the present paper, however, is to evaluate the synthetic approach using Au nanoparticles, which have been extensively studied by us[6,10] and others.[3−5]

Dendrimer templates have been used to synthesize a variety of metallic (Cu, Au, Ag, Pd, and Pt), bimetallic (PdPt, AuAg, PdAu, PdRh, and PtAu), and semiconducting (CdS) DENs.[2] DENs are prepared by mixing solutions containing appropriate dendrimers and metal ions or complexes. In favorable cases, the ions are sequestered within the dendrimer through specific interactions with its interior functional groups. Subsequent reduction of the metal ions with BH_4^- or other reducing agents leads to zerovalent, encapsulated metal nanoparticles. The size of the resulting DENs depends on the metal-ion-to-dendrimer ratio present within the dendrimer prior to reduction. This means that the particle size after reduction is kinetically controlled and does not rely on the thermodynamics of nucleation and growth. This translates into populations of nanoparticles having narrow size distributions.

Normally DENs are prepared in water using dendrimers that have hydrophilic amine or hydroxyl end groups.[2] There is only one prior report of the synthesis of DENs using organic solvents.[11] In this case, Pd and Cu DENs were prepared. Attempts to synthesize Au nanoparticles in organic solvents using dendrimers have resulted in the formation of materials that are probably stabilized by multiple dendrimers.[12,13] We term such materials "dendrimer-stabilized nanoparticles", because they consist of a relatively large metal core (with a diameter often nearly as large as or even larger than the diameter of the stabilizing dendrimer) surrounded by multiple dendrimers.

We showed previously that Au DENs can be extracted from their host dendrimers and converted into highly monodisperse MPCs.[6,7,14] Extraction occurs when a biphasic solution, which contains DENs in the aqueous phase and alkanethiols in the organic phase, is shaken. The resulting microemulsion allows hydrophobic thiols to penetrate the dendrimer periphery, encounter the DEN,

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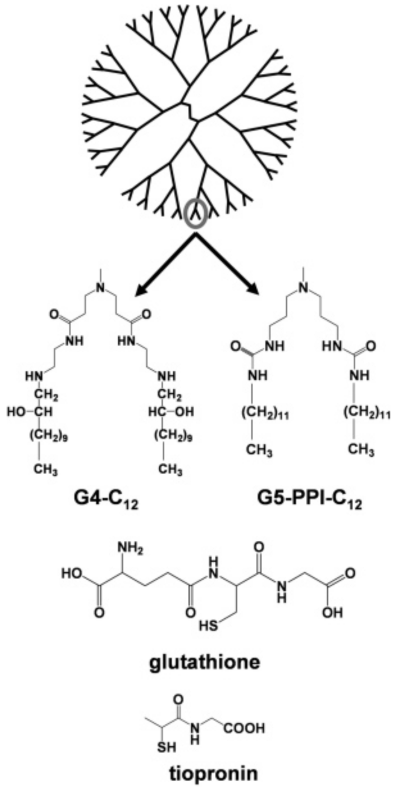
Scheme 1



and assemble on its surface. Once the nanoparticle is passivated and rendered hydrophobic by the presence of the alkanethiol, it is extracted from the dendrimer into the organic phase when the microemulsion settles. The dendrimer templating/extraction method for preparing MPCs is quite different from the usual synthetic approach used to prepare these materials.[3] That is, MPCs are typically prepared by direct reduction of a metal salt in the presence of stabilizing ligands. The size of MPCs prepared in this way is controlled through the surface-ligand-to-metal-precursor ratio and is also highly dependent on the identity of the ligand.[3] Although a high degree of monodispersity can be obtained after purification of MPCs synthesized by this route, the crude product is usually rather polydisperse.[15,16]

In this paper we describe the dendrimer-templated synthesis of nearly monodisperse Au_{31} and Au_{55} nanoparticles prepared in organic solvents and their subsequent extraction into water using the ligands tiopronin and glutathione. An amine-terminated, fourth-generation PAMAM dendrimer modified on its periphery with dodecyl groups (denoted G4-C_{12}) was employed for this synthesis (Scheme 1). Using a single-phase synthesis in toluene, we prepared Au DENs having diameters of <1.3 nm and standard deviations ranging from 0.3 to 0.4 nm. The particles were characterized before and after extraction using UV–vis spectroscopy, transmission electron microscopy (TEM), and near-IR fluorescence spectroscopy. The results indicate that the extraction process leads to the formation of nearly monodisperse Au_{31} and Au_{55} MPCs regardless of the thiolate extractant. These MPCs are stable in aqueous solutions and are not fluorescent.

Experimental Section

Chemicals. Amine-terminated, fourth-generation PAMAM dendrimers substituted on the periphery with dodecyl functional groups (G4-C_{12}) were purchased from the Aldrich Chemical Co. (Milwaukee, WI) as a 10.0 wt % solution in methanol. The manufacturer indicates that 50% of the 128 H atoms on the surface of the dendrimer are substituted by dodecyl groups. Prior to use, the methanol was removed under vacuum at 25 °C and a 200 μM stock solution of G4-C_{12} was prepared in toluene. Fifth-generation poly(propylenimine) dendrimers modified on their periphery with dodecyl groups (G5-PPI-C_{12}) were prepared as previously described,[17] and then a 200 μM stock solution was prepared in toluene. Note that the G4-PAMAM dendrimer and the G5-PPI dendrimer both have 64 total functional groups on their periphery. $HAuCl_4$ and $NaBH_4$ were purchased from Aldrich and used as received. Organic solvents were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. The phenol contained 12 wt % water. Milli-Q water (18 MΩ·cm; Millipore, Bedford, MA) was used throughout. Cellulose dialysis tubing (12000 molecular weight cutoff) was purchased from Sigma Diagnostics, Inc. (St. Louis, MO).

Characterization. UV–vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and cuvettes having a path length of 1.00 cm. The spectrum of either toluene or water was used as the background depending on the solution being analyzed. TEM images were obtained using a JEOL-2010 TEM operating at 200 kV and having a resolution of 0.19 nm. Samples were prepared by dropwise addition of the sample onto a carbon-coated Cu grid (EM Sciences, Gibbstown, NJ). Fluorescence analysis was performed using a Photon Technology International fluorometer (LPS-220B, MD-5020, PMT-814). MPC solutions were purified by dialysis to remove excess thiol prior to analysis.

Preparation of Au DENs. A 50.0 μL portion of the 200 μM G4-C_{12} stock solution was diluted in toluene to a concentration of 2.00 μM. The dendrimer/metal-ion complexes G4-$C_{12}(Au^{3+})_{31}$ and G4-$C_{12}(Au^{3+})_{55}$ were prepared by adding 31 or 55 mol equiv, respectively, of a freshly prepared 38.0 mM $HAuCl_4$ solution in methanol to the dendrimer solution. Note that we represent all forms of Au ions present within the dendrimer as Au^{3+} prior to reduction. The final volume of these solutions was 5.00 mL. After the solutions were stirred for 10 min, 25.0 μL of a 100 mM $NaBH_4$ solution in methanol was added to complete the synthesis of the Au DENs (G4-$C_{12}(Au_{31})$ and G4-$C_{12}(Au_{55})$, respectively). The reduction was allowed to proceed for at least 5 min before the solutions were analyzed. Identical reaction conditions were used for synthesizing DENs within the G5-PPI-C_{12} dendrimer template.

Extraction of Au Nanoparticles. The extraction was carried out by placing 5.00 mL of an aqueous thiol solution containing 5 vol % HCl into a 30 mL vial. Acidic solutions were used to ensure protonation of the aqueous thiol. The concentrations of the thiol solutions were 0.619 mM for G4-$C_{12}(Au_{31})$ and 1.09 mM for G4-$C_{12}(Au_{55})$. Next, 5.00 mL of a freshly prepared 2.00 μM DEN solution in toluene was placed atop the aqueous layer. The vial was shaken vigorously for 5 min and then allowed to settle (about 10 min). After settling, the aqueous phase was removed and dialyzed for 24 h to ensure complete removal of excess thiol.

Results and Discussion

Synthesis and Characterization of Au DENs. We previously showed that Cu and Pd DENs could be prepared in organic solvents using PPI dendrimers having dodecyl-substituted surfaces.[11] For Au, however, the use of PPI templates resulted in polydisperse DENs. We thought this might be a consequence of the low-dielectric-constant interior of the PPI dendrimers;[18] therefore, PAMAM dendrimers, which have a less dense and more polar interior, were used for the studies reported here. To ensure

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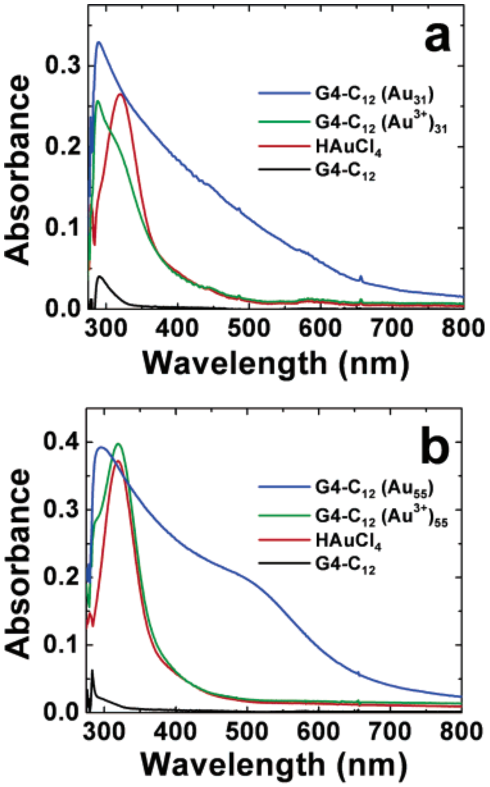

Figure 1. UV−vis spectra of (a) G4-$C_{12}(Au^{3+})_{31}$ and (b) G4-$C_{12}(Au^{3+})_{55}$ before and after reduction. Spectra of the dendrimer only and $HAuCl_4$ only ([$HAuCl_4$] = 62.0 μM for (a) and 110 μM for (b)) are also shown. The dendrimer concentration was 2.00 μM in all cases.

solubility in organic solvents, the surfaces of the PAMAM dendrimers were rendered hydrophobic by covalent addition of dodecyl functional groups (G4-C_{12}).

Au DENs were prepared in toluene by stoichiometric addition of $HAuCl_4$ to a vigorously stirred 2.00 μM solution of G4-C_{12}. This resulted in a pale yellow solution and no evidence of precipitation. Note, however, that solutions stirred for <10 min resulted in polydisperse metal nanoparticles after reduction, presumably because the metal ions were not fully encapsulated within the dendrimer. Although the driving force for encapsulation of the Au complex in the dendrimer is uncertain, we hypothesize that it results from a combination of preferential solubility of the complex in the dendrimer interior and specific interactions between functional groups within the dendrimer and the complex.[19] Reduction with $NaBH_4$ produced a pale brown solution characteristic of Au DENs.[6,10]

UV−vis spectra obtained after each step of the synthesis of G4-$C_{12}(Au_{31})$ and G4-$C_{12}(Au_{55})$ are provided in parts a and b, respectively, of Figure 1. The band at 280 nm in the spectrum of the G4-$C_{12}(Au^{3+})_{31}$ complex (Figure 1a) has been reported to arise from formation of a complex between the amide groups of the dendrimer and Au^{3+}.[12] This band is absent in the spectra of both the dendrimer and the gold precursor (Figure 1a and Supporting Information, Figure S1). After reduction there is a monotonic increase in absorbance toward lower wavelengths, which is characteristic of nanoparticle formation.[6,14] This spectrum also lacks a plasmon band, which is typical for Au particles having diameters of less than 2.0 nm.[6,10]

Figure 1b shows that the UV−vis spectra for G4-$C_{12}(Au^{3+})_{55}$ and G4-$C_{12}(Au_{55})$ are similar to those of G4-$C_{12}(Au^{3+})_{31}$ and G4-$C_{12}(Au_{31})$, except that a weak plasmon band is evident for the larger DENs. Normally, a plasmon band would not be expected for a Au_{55} nanoparticle, but the presence of BH_4^- results in charging of the particle and thus enhances the plasmon band.[9] The spectra for both particle sizes are consistent with results previously obtained for DENs of this size in water.[6,8−10]

In addition to toluene, we examined the effect of several other solvents on the synthesis of Au DENs encapsulated within hydrophobic dendrimers (Supporting Information, Figure S2). For example, solvents having hydroxyl functional groups, such as liquefied phenol and methanol, prematurely reduced the gold complex. This result is consistent with previous reports.[6,10,20] Syntheses carried out in acetonitrile produced a dark red precipitate immediately after addition of BH_4^-. This finding is attributable to the formation of a gold/nitrile complex, which prevents encapsulation of Au ions within the dendrimer.[21,22] The remaining solvents, CH_2Cl_2, $CHCl_3$, THF, and DMF, yielded nanoparticles having optical properties similar to those obtained in toluene. We used toluene for the remainder of the experiments as it yielded the most consistent and optimal results.

Figure 2 shows TEM images and particle-size distributions for G4-$C_{12}(Au_{31})$ and G4-$C_{12}(Au_{55})$ prepared in toluene. Analysis of more than 100 particles indicated average diameters of 0.9 ± 0.3 and 1.2 ± 0.4 nm for Au_{31} and Au_{55} DENs, respectively. These values are comparable to calculated values of 1.0 and 1.2 nm.[10]

We compared the properties of DENs prepared within the just-discussed alkyl-functionalized PAMAM dendrimers to those synthesized using the analogous poly(propylenimine) dendrimers (G5-PPI-C_{12}). PPI and PAMAM dendrimers are similar in many ways, but the PPI dendrimers lack interior amide groups and consequently have much less polar interiors than the corresponding PAMAM dendrimers.[18] We attempted to prepare DENs within G5-PPI-C_{12} using the same procedure described earlier for the PAMAM dendrimers. However, a dark precipitate formed upon addition of BH_4^-. When the precipitate was removed by centrifugation, a pale red solution remained. The UV−vis spectrum of this solution revealed a strong plasmon absorption at ~520 nm regardless of the Au^{3+}:G5-PPI-C_{12} ratio (Supporting Information, Figure S3). Taken together, these observations suggest formation of large Au particles.

TEM analysis of the Au particles prepared using G5-PPI-C_{12} confirmed the presence of a polydisperse distribution of particles having average diameters >5 nm (Supporting Information, Figure S4). Because this value is larger than the size of the dendrimer (~4.0 nm, not including the alkyl groups on the surface),[23] we conclude that these Au particles are not encapsulated within individual dendrimers.

Extraction and Characterization of Au MPCs. We previously reported that DENs can be extracted from water-soluble dendrimers using alkanethiols present in an organic phase.[6−10] Here we show that DENs confined within toluene-soluble G4-C_{12} dendrimers can be released

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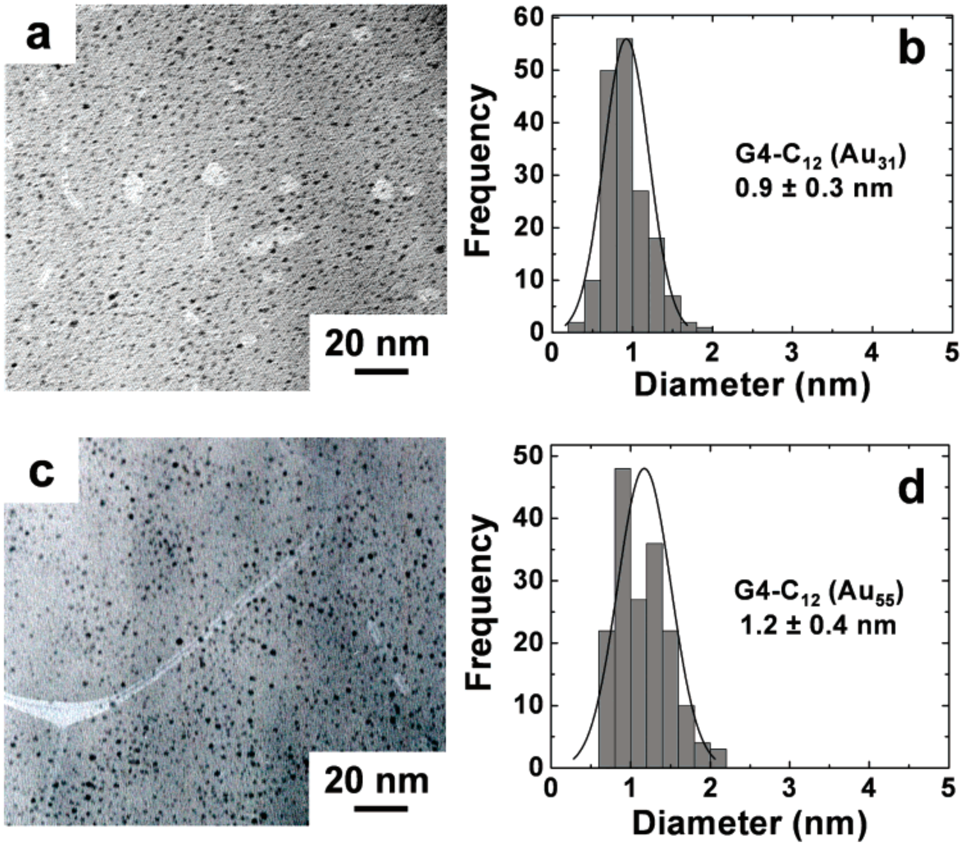

Figure 2. TEM micrographs and particle-size distributions for G4-C$_{12}$(Au$_{31}$) (a and b, respectively) and G4-C$_{12}$(Au$_{55}$) (c and d, respectively) prepared in toluene.

from the dendrimer and extracted using water-soluble ligands and that the properties of the resulting MPCs[3] are not affected by the extraction process. The extraction is carried out as follows. First, G4-C$_{12}$(Au$_{31}$) and G4-C$_{12}$(Au$_{55}$) were prepared in toluene as discussed previously. Second, the dendrimer-containing toluene solution was placed above an aqueous solution containing either tiopronin or glutathione (Scheme 1). Third, the solution was shaken to form a microemulsion, which was subsequently allowed to settle. This process results in transfer of the Au nanoparticles from the organic phase to the aqueous phase.

Tiopronin and glutathione were chosen for the extraction for three reasons. First, neither is soluble in toluene.[24] Second, both possess an exposed thiol group that can adsorb to the nanoparticle surface.[25,26] Third, glutathione is substantially larger than tiopronin, which makes it possible to judge the effect of ligand size on the extraction process. For the extraction of water-soluble DENs into an organic phase using alkanethiols as the extracting ligand, we previously hypothesized that extraction occurs when the ligands penetrate the dendrimer and encounter the encapsulated nanoparticle surface.[6−9,14] This renders the nanoparticle soluble in the organic phase and also weakens its interactions with functional groups within the dendrimer; this in turn results in extraction to the organic phase. A similar (but not identical) process is probably responsible for extraction into the aqueous phase, but we will have more to say on this point later.

Parts a and b of Figure 3 show how the UV−vis spectra change during the extraction of Au$_{31}$ and Au$_{55}$, respectively, with tiopronin. Prior to extraction (solid lines) the characteristic absorbance of the nanoparticles is observed only in the organic phase. After extraction, transfer of the nanoparticles to the aqueous layer is observed both visually and by UV−vis analysis of the postextraction aqueous layer (dashed lines). The shapes of the pre- and postextraction spectra are nearly identical, but the intensities are lower following extraction. Such behavior has been observed previously and has been attributed to the pH sensitivity of the stabilizing ligands.[27] Spectroscopic analysis of the organic layer (dotted lines) indicates quantitative transfer of the nanoparticles from the organic layer to the aqueous layer. Importantly, the empty dendrimers precipitate at the interface of the two phases following extraction. We believe this is a consequence of the amphiphilic character of the G4-C$_{12}$ dendrimers (vide infra). This behavior is different from that observed for the reverse extraction from water into the organic phase: in that case, the dendrimers remained soluble in the aqueous phase.

Figure 4 shows TEM micrographs and histograms for MPCs obtained via tiopronin extraction. The average diameters for the MPCs derived from G4-C$_{12}$(Au$_{31}$) and G4-C$_{12}$(Au$_{55}$) are 1.1 ± 0.3 and 1.3 ± 0.4 nm, respectively. These values can be compared to those of the corresponding DENs: 0.9 ± 0.3 and 1.2 ± 0.4 nm. The small change in particle size before and after extraction, along with the UV−vis data presented earlier, indicates that the extraction process results in little change to the structure of the metal cores. Au$_{31}$ and Au$_{55}$ DENs extracted with glu-

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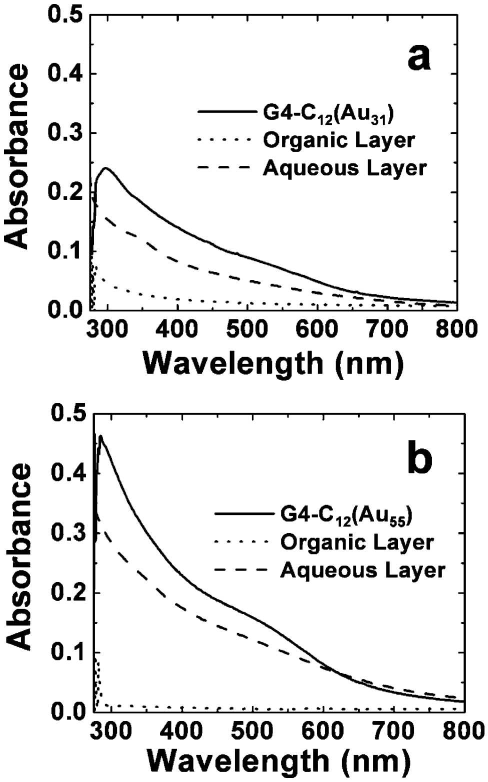

Figure 3. UV−vis spectra corresponding to the tiopronin extraction of (a) Au_{31} and (b) Au_{55} from within G4-C_{12} dendrimers. The solid lines correspond to 2.00 μM toluene solutions of the DENs prior to extraction. The dotted line corresponds to the spectrum of the organic layer after extraction, and the dashed line corresponds to the spectrum of the aqueous layer after extraction. Tiopronin concentrations of 0.619 and 1.09 mM were used for the extraction of Au_{31} and Au_{55}, respectively.

tathione had particle diameters of 0.9 ± 0.3 and 1.3 ± 0.5 nm, respectively, which are also close to the values of the DENs from which they are derived (Supporting Information, Figures S5 and S6). On the basis of these data, we conclude that the identity of the ligand has little effect on the extraction process.

When nanoparticle extraction is attempted in the absence of thiol, precipitation of a dark red solid is observed. This indicates release of Au nanoparticles from the dendrimer interior and subsequent agglomeration. This observation is consistent with the amphiphilic character of the structure of the dendrimers used in this study. That is, in the presence of a microemulsion we speculate that the dendrimers, which are composed of flexible branches,[28] undergo a major conformational change. Specifically, they expose their hydrophilic interiors to the aqueous phase and their hydrophobic surfaces to the organic phase. In essence, the dendrimers turn themselves inside out, and this results in loss of the encapsulated nanoparticle. In the presence of a 10-fold molar excess of thiol, the released nanoparticles are quickly passivated and thus they do not agglomerate. However, precipitation ensues in the absence of thiol.

To support this model of nanoparticle release, we carried out the following control experiment. A two-phase solution consisting of equal volumes of G4-C_{12} in toluene and aqueous 5.0 vol % HCl was prepared. When this solution was shaken, a microemulsion formed and a white precipitate immediately appeared. This behavior was observed whether thiol was initially present in the aqueous phase. After settling, the precipitate was found to reside exclusively at the two-phase interface. We attribute this result to the aforementioned flexibility of the dendrimer and its corresponding amphiphilic character.[29]

Fluorescence Analysis. Recent reports have suggested that aqueous dendrimer nanocomposite materials[30−34] and Au MPCs having diameters <2.0 nm[26,35−38] fluoresce. Although the basis of this fluorescence is not very well understood, it appears to be affected by the size and composition of the metal core, as well as the ligands adsorbed to the surface.[35,37,38] Two independent studies have shown that PAMAM dendrimers (or perhaps a decomposition product of the dendrimers) fluoresce in the blue,[39,40] and this may at least in part explain the reported luminescence of DENs. Because the dendrimer templating and extraction method leads to highly monodisperse materials of well-defined size and composition without the need for extensive purification, we thought that it might be possible to shed some light on the controversy surrounding the luminescence of Au nanoparticles in the <2.0 nm size range. To ensure the absence of impurities, free thiol was removed from the postextraction MPC solutions by dialysis prior to analysis by fluorescence spectroscopy. The interesting result of these studies is that no fluorescence was observed from the DENs (prior to extraction), the MPCs (after extraction), or the dendrimers only (before or after extraction) (Supporting Information, Figure S7). Although the apparent inconsistencies between our results and those cited above may be a consequence of differences in the methods and materials used to prepare the nanoparticles, the negative result reported here is somewhat surprising, and therefore, additional studies will be required to reconcile the various luminescence studies of DENs and dendrimers.[29−37]

Summary and Conclusions

We have shown that Au nanoparticles can be encapsulated within hydrophobic G4-PAMAM dendrimers dissolved in a variety of organic solvents. The resulting materials have properties that are essentially identical to those synthesized in water using hydrophilic dendrimers. This finding opens the door to the study of easily oxidizable metal DENs, such as Fe and Ni, that are unstable in the presence of water or air. Indeed, such studies are presently under way in our laboratory and will be reported shortly.

Another significant finding of this study is that nanoparticles contained within hydrophobic dendrimers can

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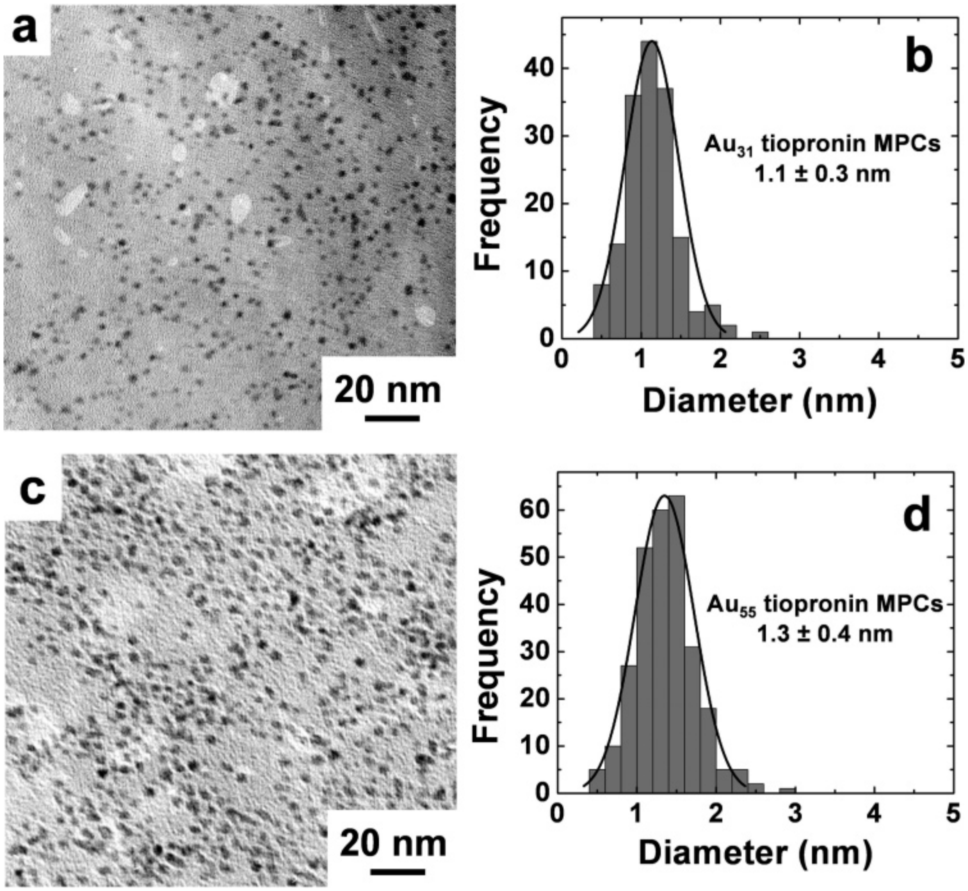

Figure 4. TEM micrographs and particle-size distributions for water-soluble tiopronin MPCs extracted from G4-C_{12}(Au_{31}) (a and b, respectively) and G4-C_{12}(Au_{55}) (c and d, respectively) DENs.

be extracted into water as MPCs. The data suggest that extraction relies on a major structural change in the amphiphilic G4-C_{12} dendrimer that is induced by the presence of the microemulsion. Specifically, we believe the dendrimers have the conformational freedom to essentially turn themselves inside out in the presence of a microemulsion, and this results in release of the encapsulated nanoparticle. In the presence of a large excess of a thiol ligand, the surfaces of the free nanoparticles are immediately passivated and thus stabilized, but in the absence of a thiol ligand, agglomeration ensues. This mechanism is different from the one we have reported for extraction of DENs from within water-soluble dendrimers. In that case, the first step of the extraction is adsorption of alkanethiols onto the surface of the encapsulated nanoparticle and the second step is extraction.

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Supporting Information Available: UV−vis analysis and solvent studies for the preparation of the Au DENs, UV−vis and TEM analysis of the materials produced using the G5-PPI-C_{12} template, analysis of the glutathione extraction by UV−vis and TEM, and fluorescence analysis of the materials studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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