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Synthesis, Characterization, and Structure-Selective Extraction of 1−3-nm Diameter AuAg Dendrimer-Encapsulated Bimetallic Nanoparticles

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Abstract: The synthesis and characterization of 1−3-nm diameter, structurally well-defined, bimetallic AuAg dendrimer-encapsulated nanoparticles (DENs) are reported. Three different bimetallic structures were examined: AuAg alloys synthesized by cocomplexation and subsequent reduction of dendrimer-encapsulated Au^{3+} and Ag^+ and core/shell [Au](Ag) and [AuAg alloy](Ag) structures (for structured materials, brackets indicate the core metal and parentheses indicate the shell metal) synthesized by a sequential loading method. Depending on the shell metal and its oxidation state, the AuAg nanoparticles can be extracted from the dendrimer into an organic phase using different surfactants. This provides a means for analyzing the composition of the shell. UV−vis, TEM, and single-particle X-ray energy dispersive spectroscopy (EDS) were used to characterize the bimetallic DENs before and after extraction and show that the extraction step does not alter the size or composition of the bimetallic nanoparticles.

Introduction

Here we report the synthesis and characterization of 1−3-nm diameter bimetallic AuAg dendrimer-encapsulated nanoparticles (DENs)[1−3] having both alloy and core/shell structures. We further show that, depending on the surface metal and its oxidation state, these nanoparticles can be extracted from the dendrimer into an organic phase using appropriate ligands.[4,5] Specifically, three structurally unique bimetallic materials were synthesized and characterized (Scheme 1): AuAg alloys, core/shell [Au](Ag), and core/shell [AuAg alloy](Ag) structures (for structured materials, brackets indicate the core metal and parentheses indicate the shell metal).[6,7] All three types of bimetallic DENs can be extracted from their dendrimer hosts using *n*-alkanethiol ligands present in a reducing environment. In contrast, only those DENs having an oxidized Ag surface

Scheme 1
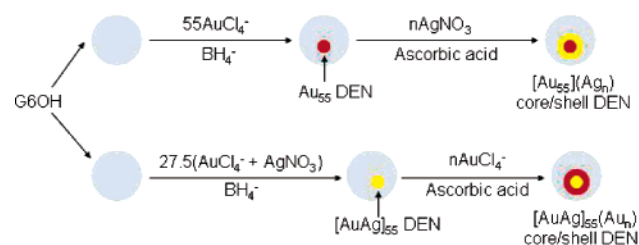
can be extracted using *n*-alkanoic acids.[5] Thus, this selective extraction strategy provides an important new tool for chemical analysis of the structure of bimetallic nanoparticles in the 1−3-nm diameter size range. In addition to selective extraction, UV−vis spectroscopy, high-resolution transmission electron microscopy (TEM), and single-particle X-ray energy dispersive spectroscopy (EDS) were used to characterize the bimetallic DENs before and after extraction. The results indicate that extraction does not alter the size or composition of these materials but may slightly change the structure of the core/shell materials.

Since our first report that Cu^{2+} could be sequestered within poly(amidoamine) (PAMAM) dendrimers and subsequently reduced to zerovalent nanoparticles,[1,2,8] we and others have demonstrated the use of dendrimer templates for the synthesis of a variety of metallic DENs, including Au,[9,10] Ag,[11,12] Pd,[13−20]

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and Pt.[20,21] Bimetallic PdPt DENs can also be prepared by cocomplexation of the two corresponding metal complexes by interior amines of hydroxyl-terminated PAMAM dendrimers, followed by reduction.[6] The size and composition of the resulting DENs were found to depend on the metal-complex-to-dendrimer ratio and the relative percentages of each metal complex, respectively. Similar results have been reported by Chung and Rhee for PdPt and PdRh bimetallic DENs.[22,23] More recently, we demonstrated that core/shell PdAu bimetallic DENs can be prepared using a sequential-loading approach.[7] This technique involves selective reduction of the shell metal onto a core or seed of the first metal. By choosing a weak reducing agent for the second step, the reduction can be efficiently catalyzed by the seed of the first metal. This approach ensures that the shell metal only deposits onto the pre-existing cores.[24,25] Regardless of how they are prepared, both PdPt and PdAu DENs possess enhanced catalytic efficiency for the hydrogenation of allyl alcohol compared to physical mixtures of analogous monometallic DENs.[6,7]

While the dendrimer templating method has obvious advantages for the synthesis of highly monodisperse bimetallic nanoparticles, physical characterization of such small entities remains a challenge. We have addressed this issue by developing a new selective extraction method that provides information about the chemical identity of the nanoparticle shell. This method, which will be discussed in detail later, builds on our earlier finding that size-monodisperse Pd[4] and Au[26] nanoparticles can be extracted intact from dendrimer templates using *n*-

alkanethiol ligands as extractants. The model we proposed to explain extraction involves insertion of the thiol group into the dendrimer, partial functionalization of the Au DEN surface with *n*-alkanethiols, extraction of the DEN as a monolayer-protected cluster (MPC),[27] and then additional passivation of the MPC surface with *n*-alkanethiol ligands.[4] Additional studies have shown that it is possible to selectively extract monometallic Au and Ag DENs from a mixture using *n*-alkanethiol and *n*-alkanoic acid ligands that are selective for each of the two metals.[5] These studies were based on earlier findings that such ligands would selectively self-assemble onto planar metal surfaces patterned with different materials.[28]

AuAg bimetallic nanoparticles having different structures and Au/Ag ratios are one of the most widely studied bimetallic systems in the literature.[29-45] These materials display interesting optical properties that are dependent not only on the percentage elemental composition of the component elements but also on their geometrical arrangement, specifically, whether the nanoparticle is composed of a random alloy or has a core/shell structure.[30] AuAg alloy nanoparticles are usually synthesized by the simultaneous reduction of both salts in solution,[34,37,41,46,47] while core/shell [Au](Ag) or [Ag](Au) nanoparticles have been synthesized by controlled deposition of the shell metal onto a seed of the core metal.[30,32,33,35,38,39] Only a few of these studies

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report AuAg bimetallic nanoparticles having diameters less than 5 nm,[38,42–44,48] and of those that do only one[38] describes the synthesis of core/shell structures.

The goal of this study is the template synthesis of alloy and core/shell AuAg bimetallic nanoparticles and characterization of their structure and properties using UV–vis spectroscopy, TEM, and a new chemical approach based on selective extraction. AuAg nanoparticles with alloy structures are synthesized by the cocomplexation method in which both metals are loaded into the dendrimer and simultaneously reduced with NaBH₄. The sequential loading method was used to synthesize core/shell materials having either Ag or Au shells. In all cases the resulting bimetallic nanoparticles are <3 nm in diameter. A key aspect of this work involves the selective extraction of the nanoparticles from within their dendrimer hosts based on the chemical composition of the shell layer. We believe that such chemical approaches to structural analysis will become increasingly important for characterizing nanoparticles having diameters in the interesting size range of 1–3 nm.

Experimental Section

Materials. Sixth- and eighth-generation hydroxyl-terminated PAM-AM dendrimers (G6-OH and G8-OH, respectively) having ethylene-diamine cores were obtained as 10–25% methanol solutions from Dendritech Inc. (Midland, MI). HAuCl₄, AgNO₃, ascorbic acid, *n*-undecanoic acid, *n*-dodecanethiol, hexane, and NaBH₄ (The Aldrich Chemical Co., Milwaukee, WI) were used without further purification. 18 MΩ·cm Milli-Q deionized water (Millipore, Bedford, MA) was used to prepare aqueous solutions.

Preparation of Bimetallic AuAg DENs. G6-OH(Au₅₅) DEN seeds were prepared by adding 2.0 mL of a 0.010 mM G6-OH solution to 6.9 mL of water followed by the addition of 550 μL of 2.0 mM HAuCl₄.[10] This results in an average stoichiometric loading of 55 Au ions per dendrimer. After stirring for less than 2 min, 550 μL of a 10 mM NaBH₄ solution in 0.3 M NaOH[9] were added followed by stirring overnight. It is important to minimize the stirring time before addition of the NaBH₄, because it has been shown that peripheral hydroxyl groups have sufficient reducing power to convert AuCl₄⁻ to zerovalent Au.[10,49,50] Before addition of the shell metal the seed solution was neutralized by addition of 550 μL of 0.3 M HCl.

The following method was used to prepare G6-OH(Au₂₇.₅Ag₂₇.₅) alloy DENs by the cocomplexation route. A 2.0 mL aliquot of a 0.010 mM aqueous solution of G6-OH was added to 197.0 mL of water, followed by the addition of 275 μL of both 2.0 mM AgNO₃ and 2.0 mM HAuCl₄. After stirring for no more than 2 min, 550 μL of a 10 mM NaBH₄ solution in 0.3 M NaOH[9] were added with vigorous stirring. After stirring for several hours, the solution was reduced in volume to 10.0 mL on a rotary evaporator and dialyzed against deionized water overnight.

Bimetallic AuAg DENs prepared by sequential loading of metal ions began with either G6-OH(Au₅₅) or G6-OH(Au₂₇.₅Ag₂₇.₅) DENs. The nomenclature G6-OH[A$_m$](B$_n$), where A is the core metal and B is the shell metal, is used for the sequentially prepared bimetallic DENs. G6-

OH[Au₅₅](Ag$_n$) (*n* = 95, 254, 450) DENs were synthesized by adding 10*n* μL of 2.0 mM AgNO₃ to 10.0 mL of G6-OH(Au₅₅) in the presence of a 2-fold molar excess of ascorbic acid. The solution was diluted with water prior to addition of AgNO₃ to maintain the total metal concentration at 110 μM. G6-OH[Au₂₇.₅Ag₂₇.₅](Au$_n$) (*n* = 95, 254, 506) DENs were prepared in a similar manner starting with G6-OH(Au₂₇.₅-Ag₂₇.₅) alloy seeds. Specifically, 10*n* μL of 2.0 mM HAuCl₄ were added to an aqueous solution containing the G6-OH[Au₂₇.₅Ag₂₇.₅] seeds and a molar equivalent of ascorbic acid (based on the amount of Au³⁺ added).[7]

G8-OH(Au₂₈₀Ag₂₈₀) DENs prepared by the cocomplexation route were synthesized by addition of 178 μL of a 0.010 mM aqueous solution of G8-OH to 199 mL of water. 250 μL of both 2.0 mM AgNO₃ and 2.0 mM HAuCl₄ were subsequently added, the solution was stirred for 1 min, and 500 μL of a 10 mM NaBH₄ solution in 0.3 M NaOH[9] was added with vigorous stirring. The resulting faintly colored solution was stirred for several hours after which time the volume was reduced to 10.0 mL on a rotary evaporator.

Extraction of Bimetallic AuAg DENs. Extraction of Au₅₅, (Au₂₇.₅-Ag₂₇.₅), [Au₅₅](Ag$_n$), and [Au₂₇.₅Ag₂₇.₅](Au$_n$) DENs from within their dendrimer templates using *n*-alkanethiol ligands was carried out in the presence of excess NaBH₄.[4] A 5.0 mL aliquot of a 20.0 mM solution of *n*-dodecanethiol in hexane was added to 5.0 mL of an aqueous 110 μM DEN solution, and the biphasic mixture was shaken vigorously for 2 min. Extraction of (Au₂₇.₅Ag₂₇.₅) and [Au₅₅](Ag$_n$) nanoparticles (in the absence of reducing agent) using an *n*-alkanoic acid was carried out as follows: 5.0 mL of a 250 mM solution of *n*-undecanoic acid in hexane was added to 5.0 mL of an aqueous 110 μM DEN solution (pH = 8.0) followed by vortexing for 30 s. After extraction of the DENs as thiolated-MPCs (MPC-RSH[A$_m$](B$_n$)), the organic phase was isolated and excess ligand was removed by dissolution in ethanol.[51] Removal of excess *n*-dodecanethiol is necessary to prevent burning of the samples when they are examined by electron microscopy. Specifically, the organic phase was concentrated to 0.50 mL on a rotary evaporator, and then 10.0 mL of EtOH was added to the concentrate. This results in precipitation of the MPCs, which are insoluble in ethanol. The solution was subsequently centrifuged (12 000 rpm for 10 min), and then the precipitate was isolated and resuspended in hexane. Excess *n*-dodecanethiol that might have been present in the organic phase remains in the supernatant due to its solubility in EtOH. Excess *n*-undecanoic acid was not removed from the corresponding MPC-R′COOH[Au₅₅](Ag$_n$) composites as it did not interfere with the electron microscopy.

Characterization. Absorption spectra were recorded using a Hewlett-Packard HP 8453 UV–vis spectrometer. The optical path length was 1.0 cm, and as appropriate either water, hexane, and 20.0 mM *n*-dodecanethiol in hexane or 250 mM *n*-undecanoic acid in hexane was used as the reference.

Samples of bimetallic DENs were prepared for TEM analysis by depositing a drop of the DEN solution on a carbon-coated Cu grid (400 mesh, Electron Microscopy Sciences, Fort Washington, PA), which had been pretreated by glow-discharge to render the carbon surface slightly hydrophilic and then allowing the solvent to evaporate in air. Samples of bimetallic MPCs were prepared as described above but without the pretreatment step, which was unnecessary because the MPCs are hydrophobic and adhere well to the untreated carbon surface. Single-particle EDS was used to confirm that the bimetallic nanoparticles consisted of two metals before and after extraction. EDS analysis was carried out at the SHaRE User Center in the Metals and Ceramics Division of Oak Ridge National Laboratory using a Philips CM200FEG 200 kV TEM equipped with an Oxford light-element EDS detector and an EMiSPEC Vision data acquisition system. The single-particle EDS data were collected using a tilt angle of 5°, an acceleration voltage

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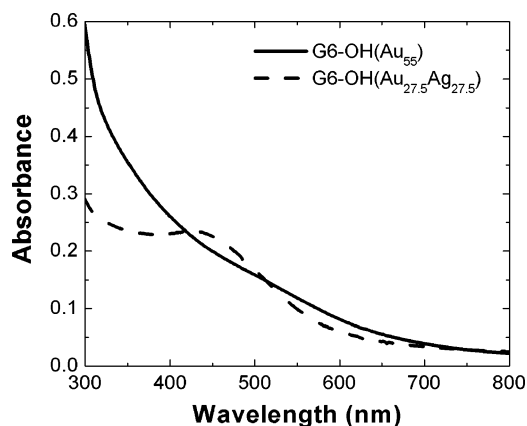
Figure 1. UV−vis spectra of G6-OH(Au$_{55}$) and G6-OH(Au$_{27.5}$Ag$_{27.5}$) DEN seeds. The total metal concentration in both cases was 0.11 mM.

of 200 kV, a collection time of 100 s, and a 1.5-nm diameter probe in the stopped-scan mode. To minimize localized contamination ("burning") under the high probe current required for the single-particle EDS, samples were cleaned by exposure to an Ar plasma for 5 min and an O$_2$ plasma for 10 min prior to analysis. Integrated intensities from the Ag L$\alpha_{1,2}$ and the Au L$\alpha_{1,2}$ lines were used for quantification, because they did not overlap other X-ray emission lines.

Results and Discussion

Synthesis of Au$_{55}$ and Au$_{27.5}$Ag$_{27.5}$ DEN Seeds. G6-OH dendrimers were used as templates for the synthesis of bimetallic AuAg DENs. Although we have previously shown that hydroxyl-terminated dendrimers can themselves reduce Au^{3+} to zerovalent Au, resulting in agglomeration of Au,[49,52] addition of the BH$_4^-$ reducing agent within several minutes of mixing the Au^{3+} and dendrimer solutions leads to nearly monodisperse DENs.[10,26] The synthesis of AuAg DEN alloys by cocomplexation requires that the concentrations of the metal complexes be controlled to avoid formation of AgCl, that is, to ensure that the K_{sp} of AgCl is not exceeded.[37] As a result, the total metal concentration used for preparation of the bimetallic cores was 5.5 μM for G6-OH(Au$_{27.5}$Ag$_{27.5}$), compared to 0.11 mM for G6-OH(Au$_{55}$). After synthesis, the concentration of the G6-OH-[Au$_{27.5}$Ag$_{27.5}$] DENs was increased to 0.11 mM by removing solvent by rotary evaporation. We chose to use magic number metal-to-dendrimer ratios for the nanoparticle cores, because these result in energetically favorable structures.[27,53,54] Further, we have recently shown that Au DENs synthesized using magic number ratios (55 and 140) are significantly more monodisperse in size than Au DENs prepared with non-magic number ratios.[10] The size (measured by TEM) of Au DENs containing magic numbers of atoms are very close to the values calculated by assuming that the materials are spherical in shape.[55]

Figure 1 shows UV−vis spectra of 0.11 mM aqueous solutions of G6-OH(Au$_{55}$) and G6-OH(Au$_{27.5}$Ag$_{27.5}$) DENs. Consistent with previously reported results, the spectrum of G6-

OH(Au$_{55}$) exhibits a monotonically increasing absorbance toward higher energies.[10] This spectrum is suggestive of Au nanoparticles that are less than 2 nm in diameter,[56−58] because larger Au particles give rise to a characteristic surface plasmon band at ∼520 nm (which is absent here). The UV−vis spectrum of the G6-OH[Au$_{27.5}$Ag$_{27.5}$] DENs in Figure 1 reveals a broad peak centered at ∼450 nm. However, the spectrum of Ag-only nanoparticles having a diameter of ∼3 nm consists of a single, narrow plasmon band that appears at 390 nm.[59,60] An early report of the absorption spectra of AuAg alloys,[29] which were synthesized by melting Au and Ag, showed that there is a linear dependence of λ_{max} on the composition of the nanoparticles. Subsequently this relationship was found to apply to AuAg alloys formed by coreduction.[37,41,47] What this means is that AuAg alloys exhibit a single peak in their absorption spectra, and the position shifts continuously from that of pure Au (∼520 nm) to that of pure Ag (∼390 nm) as the Ag/Au molar ratio in the nanoparticles increases.[29,37,41] Accordingly, λ_{max} for a AuAg alloy containing 50 at. % of each metal was found to occur in the range of 450 to 460 nm.[37,41] The position of λ_{max} in Figure 1 (∼450 nm) is within this range, and thus the optical spectroscopy results are consistent with the presence of AuAg bimetallic DENs containing equal percentages of Au and Ag.

Figure 2 shows representative TEM micrographs and particle-size distributions of G6-OH(Au$_{55}$) and G6-OH(Au$_{27.5}$Ag$_{27.5}$) DENs. The G6-OH(Au$_{55}$) DENs have a diameter of 1.4 ± 0.2 nm, while the G6-OH(Au$_{27.5}$Ag$_{27.5}$) DENs have an average size of 1.5 ± 0.6 nm. These values agree with previously reported results,[10,26] although both are slightly larger than the calculated value of 1.2 nm.[61] This discrepancy arises partly from the inherent resolution limit of the TEM, while the slightly larger discrepancy in the case of G6-OH(Au$_{27.5}$Ag$_{27.5}$) DENs may be a result of limited aggregation that occurs during the concentration step.

[Au](Ag) and [AuAg](Au) Core/Shell DENs Prepared by Sequential Loading. The synthesis of core/shell DENs was carried out as depicted in Scheme 1. The metal seed was synthesized as described in the previous section, and then the shell metal was catalytically reduced onto the seed. The use of a weak reducing agent (ascorbic acid) ensured that nucleation of the shell metal was confined to the seed DENs. The synthesis of G6-OH[Au$_{55}$](Ag$_n$) (n = 95, 254, 450) core/shell DENs started from G6-OH(Au$_{55}$) seeds, while G6-OH[Au$_{27.5}$Ag$_{27.5}$]-(Au$_n$) (n = 95, 254, 506) core/shell bimetallic DENs were prepared using G6-OH(Au$_{27.5}$Ag$_{27.5}$) seeds. G6-OH(Au$_{27.5}$Ag$_{27.5}$) seeds were used instead of G6-OH(Ag$_{55}$), because near-monodisperse Ag DENs are difficult to reproducibly synthesize due to the weak interaction between Ag$^+$ and the interior amines

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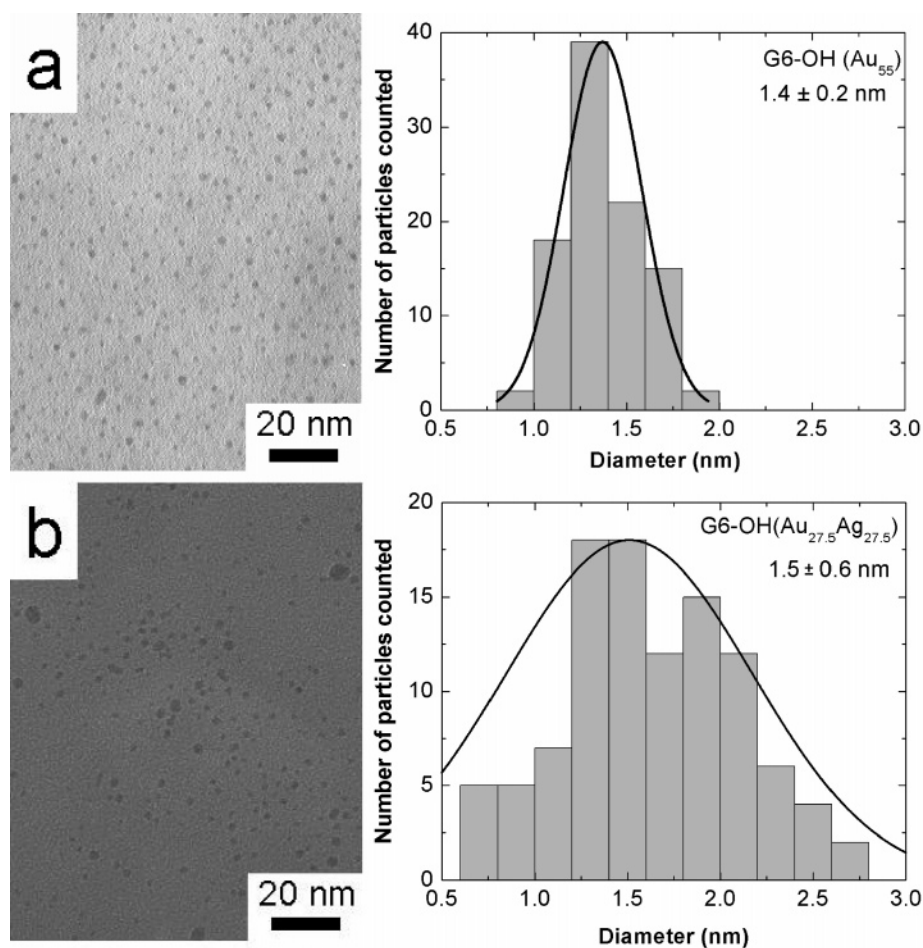
Figure 2. TEM micrographs and particle-size distributions of the (a) G6-OH(Au$_{55}$) and (b) G6-OH(Au$_{27.5}$Ag$_{27.5}$) DEN seeds.

of PAMAM dendrimers.[2,11,12] A clear increase in the size of the G6-OH[Au$_{55}$](Ag$_n$) nanoparticles is observed as the amount of Ag$^+$ added to the solution increases (see Supporting Information). Specifically, when n = 0, 95, 254, and 450, the particle sizes are 1.4 ± 0.2, 1.6 ± 0.3, 1.9 ± 0.3, and 2.4 ± 0.3 nm, respectively.

Figure 3a shows UV−vis absorbance spectra of G6-OH(Au$_{55}$) seeds and the series of G6-OH[Au$_{55}$](Ag$_n$) (n = 95, 254, 450) core/shell bimetallic DENs. Prior to deposition of Ag, the Au seed spectrum is featureless and monotonically increases toward higher energy. However, as Ag is deposited onto the Au seed, two plasmon bands appear. For example, in the spectrum of G6-OH[Au$_{55}$](Ag$_{95}$) there is a narrow plasmon band corresponding to the Ag shell at 410 nm and a broader plasmon band at 510 nm arising from the Au core. The presence of two peaks is consistent with theory. Specifically, Liz-Marzan and Philipse have calculated the absorption spectra of AuAg core/shell particles having diameters of 1.8−3.1 nm using Mie theory and shown that, at all molar ratios examined, characteristic features of both Au and Ag are present.[47] The contrast between the spectra of these materials (two peaks) and the alloys (a single peak, Figure 1) is a good indication that the G6-OH[Au$_{55}$](Ag$_{95}$) DENs have a core/shell structure. Moreover, as the Ag content of the DENs increases, the absorbance at 410 nm increases but the peak does not shift as would be expected in the case of alloys. For the largest core/shell structure, G6-OH[Au$_{55}$](Ag$_{450}$),

the absorption spectrum appears similar to that of pure Ag; that is, only a single peak is present.

To the best of our knowledge no detailed UV−vis spectroscopy studies have previously been performed on AuAg core/shell particles having core diameters of <2 nm, and therefore it is not possible to directly compare the data in Figure 3a with literature reports. However, our results are entirely consistent with the description of UV−vis spectroscopic data for AuAg core/shell particles having Au cores in the range of 6−20 nm.[30,31,33] In these cases, the deposition of a small amount of Ag onto a Au core results in the appearance of the Ag plasmon band at 400 nm and a concomitant ∼10 nm blue shift of the Au plasmon band. Additional deposition of Ag onto the Au core leads to an increase in the intensity of the band at 400 nm, which continues to grow in intensity at the expense of the Au plasmon band until the latter eventually disappears.[30,31,33]

There is one interesting difference in the spectroscopy of core/shell particles having 1−2 nm Au cores that is not consistent with the larger materials. The spectra of Au nanoparticles >2 nm in diameter always exhibit a characteristic Au plasmon band at ∼ 520 nm. As mentioned earlier, 1−2 nm Au nanoparticles are too small for this band to develop. Note, however, that in Figure 3a an Au plasmon band at 510 nm, which was initially absent, emerges once Ag is deposited onto the Au core. We believe this is a consequence of two effects, both of which are attributable to the presence of the Ag shell: an increase in
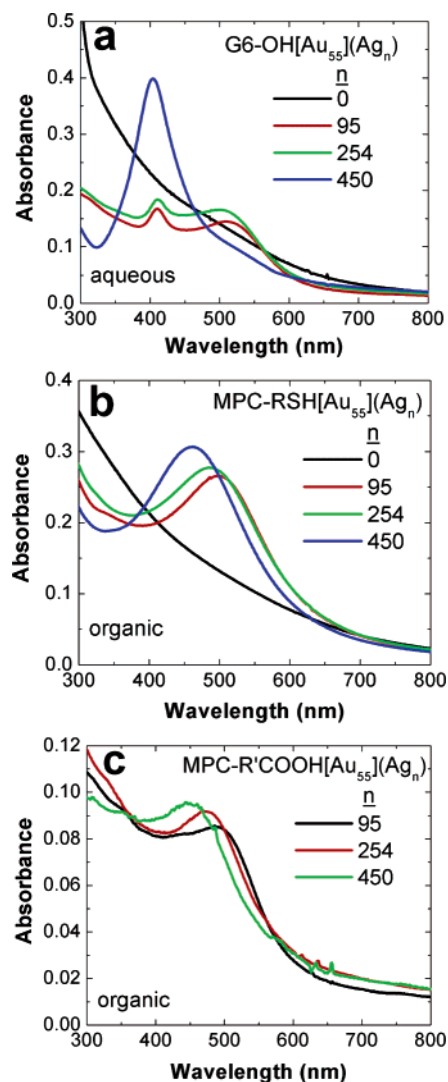
Figure 3. UV−vis absorbance spectra of G6-OH(Au$_{55}$) seeds and the G6-OH[Au$_{55}$](Ag$_n$) (n = 95, 254, 450) series of core/shell bimetallic nanoparticles (a) before extraction, (b) after extraction with *n*-dodecanethiol in hexane, and (c) after extraction with *n*-undecanoic acid in hexane. The dendrimer concentration was 2.0 μM for all the starting DEN solutions.

electron density on the Au core[7,62] and a diminution of the plasmon damping due to surface scattering of the conduction electrons.[57,63]

After obtaining the spectra shown in Figure 3a, the G6-OH-[Au$_{55}$](Ag$_n$) (n = 95, 254, 450) core/shell nanoparticles were extracted from within the dendrimers using *n*-dodecanethiol. As discussed earlier, this extraction experiment provides a means for characterizing the outermost shell of the nanoparticle. Figure 3b shows UV−vis absorbance spectra for [Au$_{55}$](Ag$_n$) core/shell nanoparticles extracted from G6-OH dendrimers in the presence of a reducing agent (MPC-RSH[Au$_{55}$](Ag$_n$), n = 95, 254, 450). The spectra of the core/shell MPCs exhibit a single peak that moves to higher energy as the Ag loading increases, and thus they are different than the corresponding DENs. There are two possible reasons for these differences. First, the environment of the metal surface of the MPCs is different than that of the

DENs, and it is known that changes in solvent and adsorbed ligands have a profound influence over the position of the plasmon band in Au and Ag nanoparticles.[62,64−66] Second, the core/shell DENs may lose some of their structure during extraction. Note, however, that neither the particle size nor the composition changes upon extraction (vide infra). Additionally, there is no evidence for metal nanoparticles in the aqueous phase after extraction. We conclude, therefore, that extraction proceeds just as it does for monometallic nanoparticles[4,26] but that there may be some scrambling of the nanoparticle structure in the case of the core/shell materials due to strong Au−thiol interactions. The likelihood of such rearrangements occurring is enhanced because Au and Ag are completely miscible at all compositions, have similar lattice parameters, and are known to translate from core/shell structures to alloys over time even at room temperature.[38]

The extraction of G6-OH[Au$_{55}$](Ag$_n$) (n = 95, 254, 450) DENs described in the previous paragraph was carried out in the presence of a reducing agent (see Experimental Section). This ensures that the Ag shell is fully reduced, which in turn permits self-assembly of *n*-alkanethiols onto the surface of the nanoparticles.[67,68] There have also been reports describing the formation of self-assembled monolayers (SAMs) of *n*-alkanoic acids onto Ag, Cu, and Al surfaces, providing there is a native oxide layer present.[69−73] Importantly, *n*-alkanoic acid SAMs do not form on oxide-free metals such as zerovalent Au. Indeed, we have previously shown that in the absence of a reducing agent *n*-alkanoic acids will selectively extract Ag nanoparticles (having a native oxide over-layer) from a mixture of monometallic Au DENs (no surface oxide) and Ag DENs.[5] We can use this finding to confirm the presence of a Ag shell on the Au-core/Ag-shell materials described earlier. That is, in the absence of a reducing agent *n*-alkanoic acids should only extract bimetallic nanoparticles having a Ag shell, which provides a very convenient analytical method for discriminating between DENs having different shell metals.

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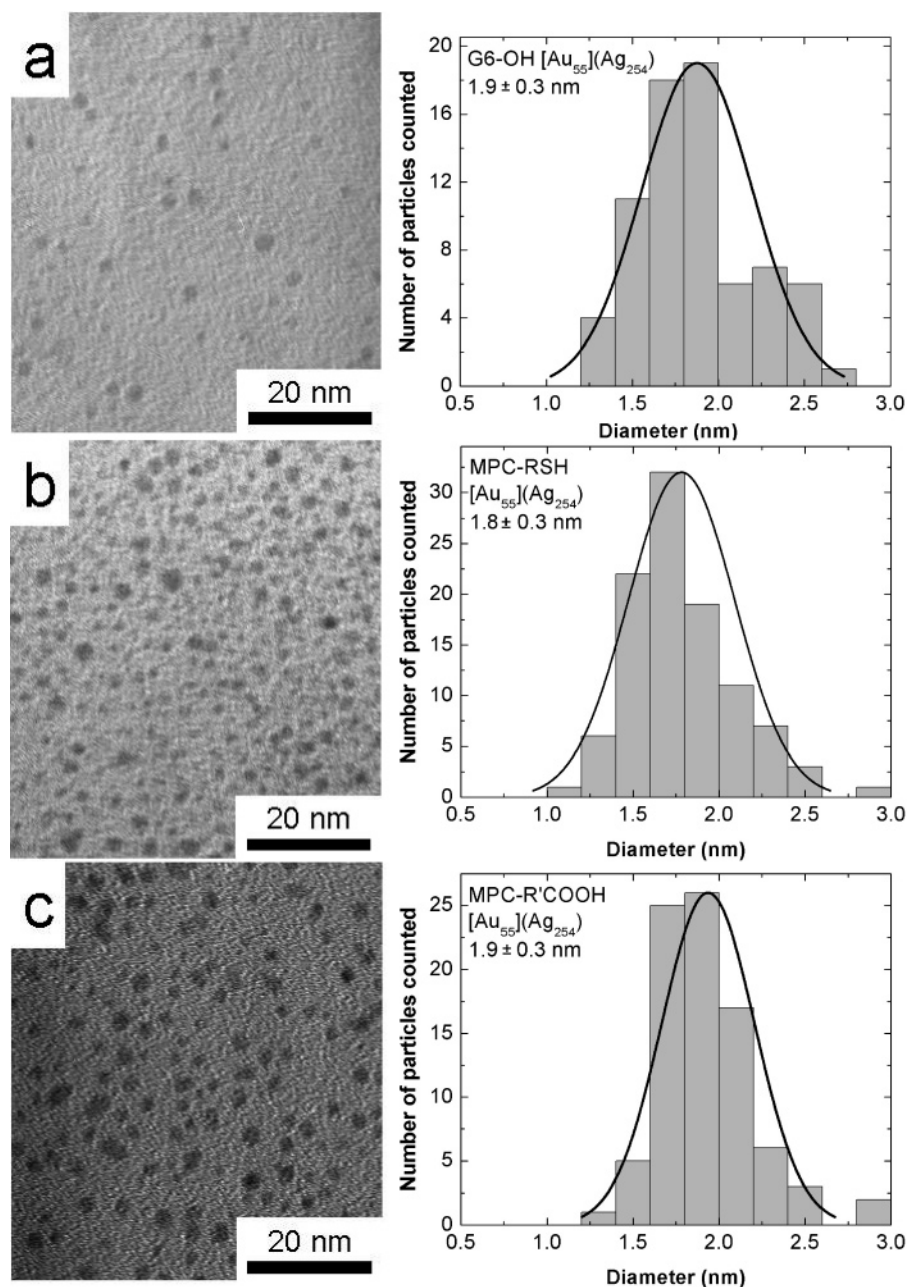
Figure 4. TEM micrographs and particle-size distributions for (a) G6-OH[Au$_{55}$](Ag$_{254}$) core/shell DENs, (b) [Au$_{55}$](Ag$_{254}$) core/shell MPCs after extraction with *n*-dodecanethiol in hexane, and (c) [Au$_{55}$](Ag$_{254}$) MPCs after extraction with *n*-undecanoic acid in hexane.

Figure 3c shows UV−vis absorption spectra for G6-OH[Au$_{55}$]-(Ag$_n$) (*n* = 95, 254, 450) bimetallic core/shell DENs after extraction with *n*-undecanoic acid. These extractions were carried out in the absence of a reducing agent to ensure the presence of an oxide layer on the nanoparticle surface. The spectra indicate that as the Ag content of the nanoparticles increases, the position of the corresponding plasmon band moves to higher energy and thus closer to the wavelength expected for a pure Ag nanoparticle. As for the extractions carried out in the reducing solvent, this trend may indicate that there is some scrambling of the nanoparticle structure. Differences in the way the *n*-alkanethiols and *n*-alkanoic acids interact with the nanoparticles,[71] the presence or absence of Ag oxide, and the presence or absence of the reducing agent are all likely to contribute to the differences in the spectra shown in Figure 3b and c.

Figure 4 shows TEM micrographs and particle-size distributions for the [Au$_{55}$](Ag$_{254}$) core/shell DENs before and after extraction. The average particle size of the G6-OH[Au$_{55}$](Ag$_{254}$) DENs is 1.9 ± 0.3 nm (Figure 4a). Following extraction with the *n*-alkanethiol in the presence of the reducing agent, the particle size is 1.8 ± 0.3 nm (Figure 4b). Figure 4c indicates a size of 1.9 ± 0.3 nm after extraction with *n*-undecanoic acid in the absence of the reducing agent. These results are a clear indication that the particles are not undergoing aggregation or size changes during extraction. Note, however, that the particle sizes in all cases are smaller than the calculated diameter of 2.3 nm for [Au$_{55}$](Ag$_{254}$) core−shell nanoparticles.[30,74] At present, we are unable to offer a satisfying explanation for this discrepancy.

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(74) $D = D_{core}(1 + (V_{Ag}[Ag]/V_{Au}[Au]))^{1/3}$. D_{core} is the diameter of the experimentally measured Au$_{55}$ core, and V_{Ag}, V_{Au} and [Ag], [Au] are the molar volumes and concentrations of Ag and Au, respectively.
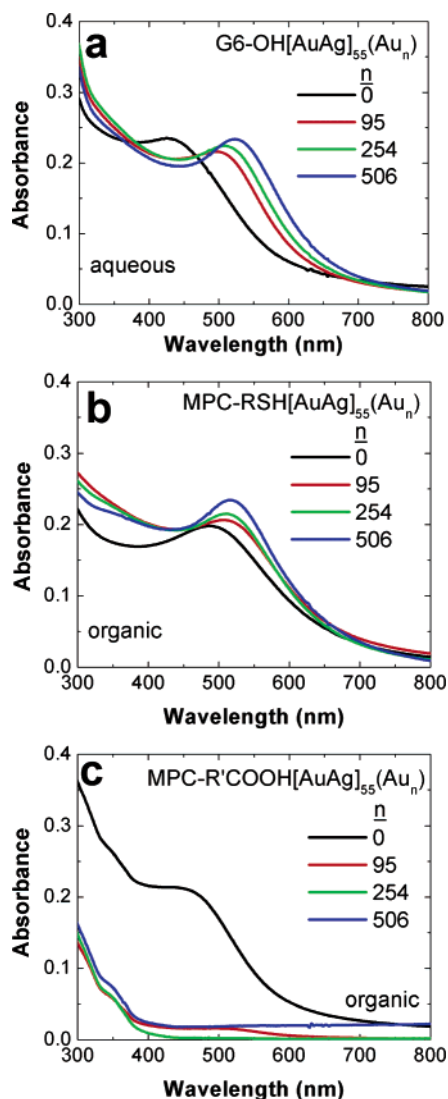
Figure 5. UV−vis absorption spectra of G6-OH(Au$_{27.5}$Ag$_{27.5}$) seeds and the G6-OH[Au$_{27.5}$Ag$_{27.5}$](Au$_n$) (n = 95, 254, 506) series of bimetallic core/shell DENs (a) before extraction, (b) after extraction with *n*-dodecanethiol in hexane, and (c) after attempted extraction with *n*-undecanoic acid in hexane. The dendrimer concentration was 2.0 μM for all the starting DEN solutions.

We have attempted to synthesize G6-OH(Au$_{55}$Ag$_{254}$) by the cocomplexation route to directly compare the extent of extraction for the core−shell and alloy particles. However, UV−vis and TEM analysis reveal a bimodal size distribution of nanoparticles (1.2 ± 0.3 nm and 3.9 ± 1.1 nm), which we believe correspond to pure Au$_{55}$ DENs and Ag dendrimer-*stabilized* (multiple dendrimers surrounding each nanoparticle) nanoparticles, respectively. While this result is clearly interesting because it suggests that there is an upper limit to the amount of Ag that may be present in a pure AuAg DEN alloy, it made it impossible to directly compare the products of core/shell and alloy extractions.

Figure 5a shows UV−vis absorption spectra for G6-OH-(Au$_{27.5}$Ag$_{27.5}$) seeds and the G6-OH[Au$_{27.5}$Ag$_{27.5}$](Au$_n$) (n = 95, 254, 506) series of bimetallic core/shell DENs. Recall that we used alloy cores in this case because highly monodisperse Ag-only cores are difficult to prepare.[11] When the first layer of Au is added to the alloy core (G6-OH[Au$_{27.5}$Ag$_{27.5}$](Au$_{95}$)) there is a red shift of the plasmon shoulder from 450 to 495 nm. This

is consistent with previous reports, which have shown that deposition of Au onto Ag seeds results in a red shift and damping of the Ag plasmon band.[30,32] The rapid damping of the Ag plasmon peak in these systems has been rationalized either by a broad absorption due to Au at wavelengths below 450 nm[30] or interfacial alloying.[32] The appearance of a single band is in contrast to the presence of both Ag and Au plasmon bands for Au-core/Ag-shell materials (vide supra). Further increases in the Au shell thickness result in continued shifts of the plasmon band to longer wavelengths and an increase in absorbance. Both of these observations are consistent with the development of more Au-like character and have been reported in the literature.[32,30] TEM images indicate that the average diameters of the G6-OH[Au$_{27.5}$Ag$_{27.5}$](Au$_n$) DENs increased from 1.5 ± 0.6 nm for n = 0 to 2.7 ± 0.4 nm for n = 506.

The [Au$_{27.5}$Ag$_{27.5}$](Au$_n$) core/shell bimetallic nanoparticles can be extracted from the dendrimer templates using a hexane solution of *n*-dodecanethiol in the presence of excess reducing agent.[75] UV−vis spectra of the extracted MPC-RSH[Au$_{27.5}$-Ag$_{27.5}$](Au$_n$) nanoparticles are shown in Figure 5b. The shift in the plasmon band of the core from 450 nm (before extraction) to 500 nm (after extraction) with *n*-dodecanethiol is likely due to changes in the dielectric constant of the solvents (water vs hexane), as well as the presence of the *n*-alkanethiol stabilizer. The UV−vis spectra of the core/shell particles after extraction are remarkably similar to those of the original DENs, strongly suggesting that the structure and composition of the bimetallic particles remain unaltered throughout the extraction process.

The UV−vis absorption spectra in Figure 5c show the effect of vortexing an aqueous [Au$_{27.5}$Ag$_{27.5}$](Au$_n$) core/shell DEN solution with a hexane solution containing 250 mM *n*-undeca-noic acid. The absence of a plasmon band arising from the organic phase indicates that extraction does not occur under these conditions. Importantly, this result confirms the absence of significant amounts of Ag in the Au shell. Note, however, that vortexing leads to visible precipitation of the nanoparticles at the water/hexane interface and that the color of the precipitate is pink. In contrast, control experiments indicated no precipitation when an aqueous G6-OH(Au$_{55}$) DEN solution was vortexed with a hexane/*n*-undecanoic acid organic phase. Thus, we can rule out the possibility that the interfacial precipitation arises from association of the *n*-alkanoic acids with the interior amines of the dendrimers.[76] The pink color of the precipitate is consistent with partial aggregation of nanoparticles, but at present the structure of these aggregates and the reason for their presence are unknown.

The extraction experiment provides a means for differentiating between the surface compositions of bimetallic DENs. This is important because there are few methods for characterizing core/shell nanoparticles in this size range, and this extraction method is by far the easiest and perhaps the most direct. Table 1 shows a summary of the extraction results for AuAg alloy DENs

(75) We have recently found that extraction of Au DENs does not depend on the presence of NaBH$_4$ but rather just a sufficient ionic strength that is independent of the identity of the ion present. In the studies reported here, therefore, the role of NaBH$_4$ is only to increase the ionic strength of the solution. However, extraction of both Ag-only and Ag-shell DENs does require the presence of NaBH$_4$, presumably due to the requirement that the native oxide layer must be absent for extraction by thiols. See ref 26 for additional information.

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Table 1. Summary of Extraction Results for AuAg Alloys and [Au$_{55}$](Ag$_n$) and [Au$_{27.5}$Ag$_{27.5}$](Au$_n$) Core/Shell DENs

extractant/ DEN	RSH/BH$_4^-$ hexane	RCOOH hexane	RCOOH/BH$_4^-$ hexane
Au	yes	no	no
Au$_n$Ag$_{55-n}$	yes	yes^a	no
[Au$_{55}$](Ag$_n$)	yes	yes	no
[AuAg]$_{55}$(Au$_n$)	yes	no	no

^{a} No extraction for $n = 41$ or 55.

formed by the co-complexation method as well as [Au](Ag) and [AuAg alloy](Au) core/shell DENs formed by the sequential loading method (Scheme 1). All these DENs could be extracted with *n*-alkanethiols in the presence of NaBH$_4$, and conversely none of them could be extracted with *n*-undecanoic acid if NaBH$_4$ was present. We conclude that extraction with *n*-undecanoic acid requires an oxide layer on the surface of the nanoparticle. Core/shell structures having Ag shells, as well as Ag-only DENs, can be quantitatively extracted with *n*-dodecanethiol in the presence of a reducing agent and with *n*-undecanoic acid in the absence of a reducing agent. Au DENs and DENs having Au shells can be extracted with the *n*-alkanethiol in the presence of a reducing agent but do not under any circumstances undergo extraction with *n*-undecanoic acid.

Examination of the extraction of the G6-OH(Au$_n$Ag$_{55-n}$) (n = 14, 27.5, and 41) alloy nanoparticles indicates more than 25% of the atoms in each particle must be Ag for the nanoparticle to be quantitatively extracted from within the G6-OH dendrimer with *n*-alkanoic acids. That is, the (Au$_{41}$Ag$_{14}$) nanoparticles do not have sufficient Ag on their surface to undergo extraction and the particles remain in the aqueous phase, but the $n = 27.5$ and $n = 14$ alloy nanoparticles do extract. It has been reported that if two metals are coreduced and one of them is significantly more noble than the other, then the more noble metal is preferentially found at the core.[43] That is, the alloy structure in such cases may not form. If we consider the limiting case, where all of the Au in the G6-OH(Au$_{27.5}$Ag$_{27.5}$) DENs is in the core, then as much as 65% of the surface atoms could be Ag. Conversely, in the case of G6-OH(Au$_{41}$Ag$_{14}$) having a Au core, only 33% of the surface atoms could be Ag. While this is only a rough estimate based on 42 metal atoms being present in the outermost shell of a 55-atom cluster, it may provide a means for determining more precisely the composition of alloy surfaces. The point is that a selective interaction between nanoparticles and ligands has the potential to become a major tool for structural characterization.

We analyzed the elemental composition of individual particles before and after extraction to provide additional confidence in the selective extraction experiments. G8-OH(Au$_{280}$Ag$_{280}$) DENs prepared by the cocomplexation route were used for these measurements to maximize the signal-to-noise ratio of the EDS experiments. The average size of these particles determined by TEM was 2.3 ± 0.4 nm, which is comparable to the calculated value of 2.6 nm (see Supporting Information).[61] Single-particle EDS analysis conclusively demonstrated that these G8-OH-(Au$_{280}$Ag$_{280}$) DENs are bimetallic. Specifically, quantitative, standardless analysis of 10 particles resulted in an average Au composition of 63 ± 6% and an average Ag composition of 37 ± 6% (Supporting Information). Large-area EDS revealed a composition of 54% Au and 46% Ag for the same G8-OH-(Au$_{280}$Ag$_{280}$) sample. Given the low signal-to-noise ratio as-

sociated with elemental analysis of particles in this size range, we consider these values to be in general agreement with one another. Importantly, no monometallic particles were observed in the population of particles examined.

After extraction with *n*-undecanoic acid, the (Au$_{280}$Ag$_{280}$) MPCs were also examined by TEM and single-particle and large-area EDS. TEM images of the (Au$_{280}$Ag$_{280}$) nanoparticles after extraction provided an average particle size of 2.2 ± 0.5 nm, which was essentially identical to the average particle size of the original G6-OH(Au$_{280}$Ag$_{280}$) DENs. Quantitative, standardless analysis of 10 particles resulted in an average Au composition of 61 ± 12% and an average Ag composition of 39 ± 12% (Supporting Information). The postextraction large-area EDS revealed a composition of 61% Au and 39% Ag. This is definitive evidence that the composition of the bimetallic nanoparticles remains the same after extraction with *n*-undecanoic acid.

Summary and Conclusions

We have shown that the dendrimer templating approach can be used to prepare both alloy and core/shell AuAg dendrimer-encapsulated bimetallic nanoparticles having diameters of about 2 nm. Alloys are prepared by the cocomplexation route, which involves the simultaneous reduction of Au and Ag salts. Core/shell nanoparticles are prepared by sequential reduction of two different metals.

We have also introduced a new tool for characterizing the chemical composition and structure of nanoparticles in the ~2 nm size range. This is important because at present no chemical methods, other than those based on CO adsorption,[77] have been demonstrated effective for distinguishing between core/shell and alloy nanoparticles in this size range. The only instrumental method which has been shown to be useful to obtain such information is EXAFS, and for such small particles this method is challenging and the results are model-dependent.[38,78,79] Our results showed that, in the presence of NaBH$_4$, *n*-dodecanethiol will quantitatively extract all forms of AuAg nanoparticles into the organic phase. In the absence of the reducing agent, *n*-undecanoic acid will extract only Au-core/Ag-shell nanoparticles and AuAg alloy nanoparticles having significant Ag on their surface. TEM, single-particle EDS, and UV–vis studies indicate that the nanoparticles retain both their composition and size upon extraction from their dendrimer templates but that there might be some minor scrambling of the structure of the core/shell materials.

The selective extraction strategy has a number of interesting implications. First, it provides a means for characterizing AuAg bimetallic nanoparticles that depends entirely on both the structure and composition of the particles. Another important consequence of the selective extraction strategy lies in its potential use for the purification of ensembles containing bimetallic nanoparticles. For example, we envision that under

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certain conditions alloy nanoparticles could be separated from core/shell particles or from monometallic nanoparticles that may have formed during the reduction step. We are further exploring other metal and surfactant combinations to fully realize the power of this technique for purifying and characterizing the smallest of nanoparticles.

Supporting Information Available: TEM images and particle-size distributions for G6-OH[Au_{55}](Ag_n) ($n = 95$, 254, and 450) bimetallic DENs, photographs demonstrating extraction of [Au]-(Ag) and [AuAg alloy](Au) core/shell DENs with *n*-undecanoic acid, and TEM images of G8-OH($Au_{280}Ag_{280}$) DENs before and after extraction with *n*-undecanoic acid in hexane. This material is available free of charge via the Internet at http://pubs.acs.org.

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