

# Extraction of Au Nanoparticles Having Narrow Size **Distributions from within Dendrimer Templates**

Joaquin C. Garcia-Martinez and Richard M. Crooks\*

Contribution from the Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

Received June 10, 2004; E-mail: crooks@tamu.edu

Abstract: Here, we show that Au nanoparticles having diameters of less than 2.2 nm can be extracted from within the interior of PAMAM dendrimers using n-alkanethiol extractants. Extraction proceeds quickly, regardless of the size of the nanoparticle, the dendrimer generation, or the peripheral functionalization of the dendrimer. The extraction rate is fastest for the lowest generation dendrimers, the smallest nanoparticles, and the shortest chain-length n-alkanethiols. Other important results of this study include the following. First, within the accuracy of absorbance spectroscopy, the extraction yield is quantitative. Second, NMR and FT-IR spectroscopy indicate that after extraction the dendrimer remains in the aqueous phase and can be used to template additional metal particles. Third, the size and optical characteristics of the extracted nanoparticles are the same as the precursor dendrimer-encapsulated nanoparticles (DENs). Fourth, a 100fold excess of *n*-alkanethiol molecules is required to prevent aggregation of DENs during extraction.

## Introduction

We recently presented preliminary findings that demonstrated the feasibility of extracting 1.7 nm diameter Pd nanoparticles from within fourth-generation poly(amidoamine) (PAMAM) dendrimers using *n*-hexanethiol as a stabilizer/extractant.<sup>1</sup> The synthesis of extracted nanoparticles follows the three-step process shown in Scheme 1. First, metal ions are complexed within the dendrimer in fixed stoichiometries. Second, the encapsulated metal ions are chemically reduced using BH<sub>4</sub><sup>-.2-8</sup> This results in dendrimer-encapsulated nanoparticles (DENs) having a narrow size distribution.<sup>3-10</sup> Third, a toluene solution containing an n-alkanethiol is added to the aqueous DEN solution. When the two-phase system is shaken, *n*-alkanethiols presumably self-assemble onto the surface of the encapsulated metal nanoparticles, extract them from the dendrimers, and transport them to the toluene phase. The dendrimers remain in the aqueous phase. This process occurs without significant change to the physical or chemical properties of the DENs. Here, we expand upon our preliminary findings<sup>1</sup> by demonstrating the generality of the approach and, more significantly, reporting quantitative information about the effect of nanoparticle size, dendrimer generation, and the length of the *n*-alkanethiol

- (1) Garcia-Martinez, J. C.; Scott, R. W. J.; Crooks, R. M. J. Am. Chem. Soc. **2003**, *125*, 11190–11191.
- (2) Zhao, M.; Sun, L.; Crooks, R. M. J. Am. Chem. Soc. 1998, 120, 4877-4878. Crooks, R. M.; Lemon, B. I.; Sun, L.; Yeung, L. K.; Zhao, M. Top. Curr.
- (3)*Chem.* 2001, 212, 81–135. Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. Acc. Chem. *Res.* 2001, 34, 181–190. (4)
- (5) Zhao, M.; Crooks, R. M. Angew. Chem., Int. Ed. 1999, 38, 364-366.
- Kim, Y.; Crooks, R. M. C. R. Chinie 2003, 6, 1049–1059.
   Balogh, L.; Tomalia, D. A. J. Am. Chem. Soc. 1998, 120, 7355–7356.
- (8) Tomalia, D. A.; Majoros, I. J. Macromol. Sci., Polym. Rev. 2003, C43, 411 - 477
- (9) Zhao, M.; Crooks, R. M. Adv. Mater. 1999, 11, 217-220.
- (10) Kim, Y.-G.; Oh, S.-K.; Crooks, R. M. Chem. Mater. 2004, 16, 167–172.

#### Scheme 1



hydrocarbon chain on the extraction process. These data make it possible to begin to understand how DENs are retained within and extracted from dendrimers.

Au DENs have been synthesized by a number of research groups.<sup>11–18</sup> In contrast to other metals.<sup>2,5,9,19–21</sup> DENs prepared

- (11) Esumi, K.; Kameo, A.; Suzuki, A.; Toriogoe, K. Colloids Surf., A 2001, *189*, 155–161. (12) Esumi, K.; Hosoya, T.; Suzuki, A.; Torigoe, K. *Langmuir* **2000**, *16*, 2978–
- 2980.
- (13) Esumi, K.; Torigoe, K. Prog. Colloid Polym. Sci. 2001, 117, 80-87.
- (14) Esumi, K.; Hosoya, T.; Suzuki, A.; Torigoe, K. J. Colloid Interface Sci. 2000, 229, 303–306.
   (15) Gröhn, F.; Kim, G.; Bauer, B. J.; Amis, E. J. Macromolecules 2001, 34,
- 2179 2185.(16) Esumi, K.; Satoh, K.; Torigoe, K. Langmuir 2001, 17, 6860-6864.
- Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L.; Amis, E. J. *Macromolecules* **2000**, *33*, 6042–6050. (17)
- (18) West, R.; Wang, Y.; Goodson, T. J. Phys. Chem. B 2003, 107, 3419-3426
- (19) Chechik, V.; Crooks, R. M. J. Am. Chem. Soc. 2000, 122, 1243-1244.

using Au complex ions often have polydisperse size distributions.<sup>11-18</sup> This is likely a consequence of the poorly defined chemistry responsible for encapsulation of Au complexes within dendrimers. Specifically, many metal ions and complex metal ions, such as Cu<sup>2+</sup>, PdCl<sub>4</sub><sup>2-</sup>, and PtCl<sub>4</sub><sup>2-</sup>, interact with dendrimers in fixed stoichiometries, 2,5,9,19,20,22 but there is apparently no such relationship between AuCl<sub>4</sub><sup>-</sup> and the dendrimer.<sup>14,17,23</sup> However, we recently reported the synthesis of Au DENs in the 1-2 nm size range that have more narrow size distributions.<sup>10</sup> This improvement is probably a consequence of the dendrimer structure (partial quaternization of the periphery, which likely reduces agglomeration)<sup>20,24</sup> and the use of magic numbers of Au ions, which results in particular particle sizes and shapes that are energetically favorable.<sup>25–28</sup>

In addition to the dendrimer templating approach, there are many other methods for preparing Au nanoparticles in the <4 nm size range.<sup>29</sup> One of the most well-known and effective involves reduction of Au complex ions in the presence of alkanethiols or other ligands that strongly complex to the growing metal nanoparticles.<sup>28,30–34</sup> The fundamental properties of these materials, which are known as monolayer-protected clusters (MPCs), have been widely studied, 35-39 and their possible use for applications to molecular recognition,<sup>40,41</sup> electronic devices, 38,42,43 and catalysis 44-47 have also been examined. MPCs have many desirable attributes: they can be repeatedly isolated from and redissolved in common organic solvents without irreversible aggregation or decomposition,<sup>39</sup>

- (20) Scott, R. W. J.; Ye, H.; Henriquez, R. R.; Crooks, R. M. Chem. Mater. 2003, 15, 3873-3878.
- (21) Niu, Y.; Yeung, L. K.; Crooks, R. M. J. Am. Chem. Soc. 2001, 123, 6840-6846.
- (22) Zhao, M.; Crooks, R. M. Adv. Mater. 1999, 11, 217-220.
- (23) Garcia, M. E.; Baker, L. A.; Crooks, R. M. Anal. Chem. 1999, 71, 256-258.
- (24) Oh, S.-K.; Kim, Y.-G.; Ye, H.; Crooks, R. M. Langmuir 2003, 19, 10420-10425.
- (25) Cleveland, C. L.; Landman, U. J. Chem. Phys. 1991, 94, 7376-7396.
- (26) Cleveland, C. L.; Landman, U.; Schaaff, T. G.; Shafigullin, M. N.; Marat, N.; Stephen, P. W.; Whetten, R. L. *Phys. Rev. Lett.* **1997**, *79*, 1873–1876. (27) Brack, M. *Sci. Am.* **1997**, *277*, 50–55. (28) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar,
- I.; Alvarez, M. M.; Wilkinson, A. Acc. Chem. Res. 1999, 32, 397-406.
- (29) Daniel, M.-C.; Astruc, D. Chem. Rev. 2004, 104, 293-346. (30) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. Chem.

- Soc., Chem. Commun. 1994, 801–802.
  (31) Schreiber, F. Prog. Surf. Sci. 2000, 65, 151–256.
  (32) Pradeep, T.; Sandhyarani, N. Pure Appl. Chem. 2002, 74, 1593–1607. (33) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Acc. Chem. Res. 2000,
- 33, 27-36.
- (34) Brust, M.; Kiely, C. J. Colloids Surf., A 2002, 202, 175-186.
- (35) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephen, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. Adv. Mater. 1996, 8, 428-433.
- (36) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. Science
- 1998, 280, 2098–2101.
  (37) Templeton, A. C.; Hostetler, M. J.; Kraft, C. T.; Murray, R. W. J. Am. Chem. Soc. 1998, 120, 1906–1911.
- (38) Gittins, D. I.; Bethell, D.; Schiffrin, D. J.; Nichols, R. J. *Nature* **2000**, 408, 67 - 68
- (39) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-Z.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. Langmuir 1998, 14, 17-30.
- (40) Lazarides, A. A.; Schatz, G. C. J. Phys. Chem. B 2000, 104, 460-467.
- (41) Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. J. Am. Chem. Soc. 1998, 120, 1959–1964.
   (42) Hiroshi, S.; Yamamoto, Y.; Yakabe, H.; Tokonami, S.; Nagaoka, T. Chem.
- Commun. 2003, 1038–1039. (43) Schmid, G.; Liu, Y.-P.; Schumann, M.; Raschke, T.; Radehaus, C. Nano
- Lett. 2001, 1, 405-407.
- (44) Li, H.; Luk, Y.-Y.; Mrksich, M. Langmuir 1999, 15, 4957-4959.
- (45) Pietron, J. J.; Murray, R. W. J. Phys. Chem. B 1999, 103, 4440–4446.
  (46) Bartz, M.; Küther, J.; Seshadri, R.; Tremel, W. Angew. Chem., Int. Ed. **1998**, *37*, 2466–2468.
- Pasquato, L.; Rancan, F.; Scrimin, P.; Mancin, F.; Frigeri, C. Chem. Commun. 2000, 2253-2254. (47)

their surface can be functionalized with a vast range of modifiers,37,48,49 and they can be linked to polymers, biomolecules, and monolithic surfaces.<sup>28,32-34</sup> A significant drawback of the synthetic approach used to prepare MPCs is that it results in polydisperse size distributions of nanoparticles.<sup>28,33,35,39,50-55</sup> This is a consequence of the thermodynamics that govern the nucleation and growth of these materials. Note, however, that purification of the raw materials by repeated fractional crystallization,35,56 extraction and annealing,57,58 or chromatography<sup>56,59</sup> can lead to large quantities of MPCs having narrow size distributions.

Here, we present a detailed study of the parameters that control the conversion of DENs to MPCs. The fundamental question to be answered is how such large nanoparticles escape the confinement of the dendrimer interior. To begin addressing this issue, we have examined the effect of the size of the nanoparticle, the concentration and length of the *n*-alkanethiol extractant, the generation of the dendrimer, and the composition of its periphery on the extraction process. Specifically, we focused on Au nanoparticles containing (on average) 55, 147, 561, and 1022 Au atoms (Au<sub>55</sub>, Au<sub>147</sub>, Au<sub>561</sub>, and Au<sub>1022</sub>, respectively) contained within generation 4, 6, and 8 hydroxylterminated PAMAM dendrimers (G4-OH, G6-OH, and G8-OH, respectively) and within an eighth-generation, amine-terminated PAMAM dendrimer (G8-NH<sub>2</sub>). The properties of the nanoparticles before and after extraction were analyzed by UV-vis spectroscopy and high-resolution transmission electron microscopy (HRTEM). The results show that metal nanoparticle extraction does not affect the distribution of particle sizes or their optical properties and that the dendrimer remains exclusively within the aqueous phase after extraction. Consequently, the dendrimer can be recycled and used as a template to synthesize additional metal particles.

# **Experimental Section**

Chemicals and Materials. G4-OH, G6-OH, G8-OH, and G8-NH2 PAMAM dendrimers having an ethylenediamine core were obtained as 10-25% aqueous solutions from Dendritech, Inc. (Midland, MI). All n-alkanethiols, triphenylmethanethiol, deuterated benzene, NaBH4, and HAuCl<sub>4</sub> were used as received from the Aldrich Chemical Co. (Milwaukee, WI). HPLC grade ethanol, toluene, and hexane were purchased from EMD Chemicals Inc., and 18 MQ-cm Milli-Q water (Millipore, Bedford, MA) was used to prepare aqueous solutions. Cellulose dialysis sacks having a molecular weight cutoff of 12 000 were purchased from Sigma Diagnostics, Inc. (St. Louis, MO).

- (48) Templeton, A. C.; Cliffel, D. E.; Murray, R. W. J. Am. Chem. Soc. 1999, 121, 7081-7089.
- (49) Wang, G.; Zhang, J.; Murray, R. W. Anal. Chem. 2002, 74, 4320–4327.
  (50) Chen, S.; Murray, R. W. Langmuir 1999, 15, 682–689.
  (51) Shon, Y.-S.; Dawson, G. B.; Porter, M.; Murray, R. W. Langmuir 2002, 18. 3880-3885.
- (52) Cliffel, D. E.; Zamborini, F. P.; Gross, S. M.; Murray, R. W. Langmuir 2000, 16, 9699-9702.
- (53) Chen, S.; Templeton, A. C.; Murray, R. W. Langmuir 2000, 16, 3543-3548
- (54) Kohlmann, O.; Steinmetz, W. E.; Mao, X.-A.; Wuelfing, W. P.; Templeton, A. C.; Murray, R. W.; Johnson, C. S., Jr. J. Phys. Chem. B 2001, 105, 8801–8809.
- (55) Templeton, A. C.; Chen, S.; Gross, S. M.; Murray, R. W. Langmuir 1999, 15. Ĝ6–76
- (56) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutiérrez-Wing, C.; Ascensio, J.; Jose-Yacamán, M. J. J. Phys. Chem. B 1997, 101, 7885–7891.
- (57) Quinn, B. M.; Liljeroth, P.; Ruiz, V.; Laaksonen, T.; Kontturi, K. J. Am. Chem. Soc. 2003, 125, 6644-6645.
- (58) Hicks, J. F.; Miles, D. T.; Murray, R. W. J. Am. Chem. Soc. 2002, 124, 13322 - 13328.
- (59) Jimenez, V.; Leopold, M. C.; Mazzitelli, C.; Jorgenson, J. W.; Murray, R. W. Anal. Chem. 2002, 75, 199–206.

**Preparation of Au DENs.** A literature method was used to prepare Au DENs,<sup>10</sup> but small deviations from this procedure were necessary in some cases. These are identified in the appropriate locations in the Results and Discussion section. Nevertheless, a short summary of the basic procedure follows, with specific reference to G4-OH containing a 55-atom Au nanoparticle (G4-OH(Au<sub>55</sub>)). A 10 mL aqueous solution containing 2.0  $\mu$ M G4-OH and 110  $\mu$ M HAuCl<sub>4</sub> was vigorously stirred for 2 min, and then a 5-fold molar excess of NaBH<sub>4</sub> (150 mM in 0.3 M NaOH) was quickly added to this stirred solution. The reduction of the intradendrimer Au complex to zerovalent Au can be easily followed as the color changes from yellow to brown. No purification of Au DENs was necessary.

Extraction of Au Nanoparticles from the Interior of PAMAM Dendrimers. Extraction experiments were carried out in 30 mL vials containing 10 mL of an aqueous Au DEN solution (2.0  $\mu$ M based on the dendrimer concentration). A 150-fold molar excess of NaBH<sub>4</sub> powder was directly added to the aqueous Au DEN solution. After the NaBH<sub>4</sub> was completely dissolved, 10 mL of a 20 mM n-dodecanethiol (HSC12) solution in toluene were added, and the vial was shaken for 5 min. The resulting microemulsion was allowed to settle for 5 min, after which phase separation was complete. The toluene layer containing the MPC product was purified by first concentrating the solution to 1 mL on a rotary evaporator and then adding 15 mL of ethanol to precipitate the MPCs. Centrifugation resulted in separation of the MPCs from excess free n-alkanethiol and others impurities. The MPCs were washed and centrifuged twice with ethanol to ensure complete purification. The extracted DENs had a sufficiently narrow size distribution immediately following the synthesis that no additional purification was necessary for the experiments described in this paper.

**Dendrimer Recycling.** Following extraction of the DENs into the organic phase, the original dendrimeric templates used for nanoparticle synthesis could be recycled by dialyzing the aqueous phase. This was accomplished as follows. The aqueous phase was placed in a cellulose dialysis sack and stirred in a deionized water bath for 24 h, after which the water bath was replaced with fresh deionized water, followed by stirring for an additional 24 h. The final concentration of the dendrimer in the aqueous phase was determined by extrapolating Beer–Lambert plots (UV–vis) prepared using dendrimer-containing reference solutions. The recovered dendrimers were then used to prepare Pd MPCs following the three-step sequence shown in Scheme 1 (See Supporting Information).

Effect of *n*-Alkanethiol Concentration on the Extraction of DENs. A 20 mL G4-OH(Au<sub>55</sub>) solution was prepared as previously described, and then four aliquots of this solution were extracted with the following concentrations of HSC<sub>12</sub> in toluene: 110  $\mu$ M, 330  $\mu$ M, 550  $\mu$ M, and 1100  $\mu$ M ([HSC<sub>12</sub>]/[Au<sup>0</sup>] = 1, 3, 5, and 10). Following extraction, UV– vis spectra and HRTEM micrographs of the toluene phase were collected without purification of the extracted product.

Effect of the *n*-Alkanethiol Chain Length on DEN Extraction. Four different sizes of Au nanoparticles were prepared within G8-OH dendrimers using the experimental procedure described earlier: G8-OH(Au<sub>55</sub>), G8-OH(Au<sub>147</sub>), G8-OH(Au<sub>561</sub>), and G8-OH(Au<sub>1022</sub>). Three aliquots were taken from each solution, and each was extracted with a different *n*-alkanethiol: *n*-hexanethiol (HSC<sub>6</sub>), *n*-dodecanethiol (HSC<sub>12</sub>), and *n*-hexadecanethiol (HSC<sub>16</sub>). To ensure homogeneous water—toluene emulsions, and thereby maintain reproducible extraction conditions, a vortexer was used to mix the aqueous and organic phases. To measure the DEN extraction kinetics, the two-phase system was vortexed for 5 s and allowed to settle for a few seconds, and then a UV—vis absorbance spectrum of the organic phase was obtained. Plots of  $\lambda$  (at 510 nm) vs time provided an estimate of the extraction kinetics as a function of the length of the *n*-alkanethiol chain.

**Spectroscopic Characterization.** UV-vis absorbance spectra were obtained at  $23 \pm 2$  °C using quartz cells and a Hewlett-Packard model 8453 UV-vis spectrometer system (Hewlett-Packard, Wilmington, DE). UV-vis spectra of Au DENs at the following concentrations were

collected using deionized water as the reference: 2.0  $\mu$ M for G4-OH-(Au<sub>55</sub>), G6-OH(Au<sub>55</sub>), G8-OH(Au<sub>55</sub>), G8-NH<sub>2</sub>(Au<sub>55</sub>), G4-OH(Au<sub>147</sub>), G6-OH(Au<sub>147</sub>), G8-OH(Au<sub>147</sub>), and G8-NH<sub>2</sub>(Au<sub>147</sub>); 0.50  $\mu$ M for G8-OH(Au<sub>561</sub>), G8-NH<sub>2</sub>(Au<sub>561</sub>), G8-OH(Au<sub>1022</sub>), and G8-NH<sub>2</sub>(Au<sub>1022</sub>). UV-vis spectra of Au MPCs were obtained immediately after extraction and without purification using toluene as a reference.

Infrared absorbance spectra were acquired using a Nicolet Nexus 670 FT-IR spectrometer. The IR samples were prepared by precipitation of MPCs with ethanol. The resulting black powder was then dissolved in 500  $\mu$ L of hexane, and this solution was drop-cast onto KBr plates until a homogeneous film formed (at least five drops).

<sup>1</sup>H NMR spectra were recorded using a 300 MHz Unity p300 spectrometer. Solutions of Au MPCs analyzed by NMR were prepared using  $d_6$ -benzene in a standard 5 mm NMR tube. The Au concentrations were as follows: 2.6 mg(Au)/mL for MPC-12(Au<sub>55</sub>); 7.0 mg(Au)/mL for MPC-12(Au<sub>147</sub>); 5.0 mg(Au)/mL for MPC-12(Au<sub>561</sub>); 9.0 mg(Au)/mL for MPC-12(Au<sub>1022</sub>). Here, the notation MPC-X(Au<sub>m</sub>) refers to an extracted MPC containing *m* Au atoms stabilized with *n*-hexanethiol (X = 6), *n*-dodecanethiol (X = 12), or *n*-hexadecanethiol (X = 16). The Au concentrations assume that all Au transfers to the toluene phase during extraction.

**Microscopy.** HRTEM was performed using a JEOL 2010 transmission electron microscope (JEOL USA Inc., Peabody, MA). Samples were prepared by placing one drop of a DEN-containing solution on a holey-carbon-coated Cu grid (EM science, Gibbstown, NJ) and allowing the solvent to evaporate in air.

### **Results and Discussion**

Spectroscopic Analysis of DENs before and after Extraction. Au DENs were synthesized using the first two steps of the process shown in Scheme 1. First, AuCl<sub>4</sub><sup>-</sup> was sequestered within the dendrimer, and second the resulting composite was chemically reduced. Specifically, either 55 or 147 equiv of HAuCl<sub>4</sub> per dendrimer were mixed with 2.0  $\mu$ M dendrimer solutions, or 561 or 1022 equiv of HAuCl<sub>4</sub> per dendrimer were mixed with 0.50  $\mu$ M dendrimer solutions. Prior to reduction with BH<sub>4</sub><sup>-</sup>, the resulting pale yellow solutions were vigorously stirred for 2 min in the case of Gn-OH dendrimers and for 1 h in case of G8-NH2 dendrimers. The AuCl4<sup>-</sup>-containing Gn-OH dendrimers were reduced relatively quickly to avoid premature reduction of the Au complex by the hydroxyl groups on the dendrimer periphery, which results in formation of large, polydisperse Au particles that are not encapsulated within a single dendrimer but rather stabilized by multiple dendrimers bound to the nanoparticle surface.<sup>12,18,23</sup> Such premature reduction is not observed for amine-terminated dendrimers. After mixing the dendrimer and HAuCl<sub>4</sub> solutions, a 5-fold molar excess of NaBH<sub>4</sub> in 0.3 M NaOH was quickly stirred into the resulting mixture to reduce Au<sup>3+</sup> to zerovalent Au. This resulted in the solution turning from yellow to brown, which is characteristic of Au nanoparticles.<sup>10,60</sup>

Au DENs are extracted from within the dendrimer by first adding a large excess of NaBH<sub>4</sub> to the aqueous solution and then introducing a toluene solution containing an appropriate *n*-alkanethiol (step 3 of Scheme 1). The role of NaBH<sub>4</sub> will be discussed later. After shaking for 5 min, the aqueous phase turned from brown to colorless and the toluene phase turned from colorless to brown, indicating extraction of the nanoparticles from the dendrimer and transport of the resulting MPCs into the toluene phase (Supporting Information, Figure S1). Note

<sup>(60)</sup> Esumi, K.; Suzuki, A.; Aihara, N.; Usui, K.; Torigoe, K. Langmuir 1998, 14, 3157–3159.



**Figure 1.** UV-vis absorbance spectra demonstrating extraction of (a) Au<sub>55</sub> and (b) Au<sub>147</sub> nanoparticles from 2.0  $\mu$ M G8-OH solutions and of (c) Au<sub>561</sub> and (d) Au<sub>1022</sub> nanoparticles from 0.50  $\mu$ M G8-OH solutions. The solid line corresponds to the aqueous phase before extraction, and the dashed line was obtained from the organic phase after extraction with a toluene solution containing 20 mM *n*-dodecanethiol.

that Esumi and co-workers have previously reported that n-alkanethiol and disulfide ligands adsorb onto the surface of Au DENs,<sup>16,61</sup> but in those cases the nanoparticles did not extract. This is a likely a consequence of our finding that both a thiol and a sufficiently high ionic strength are required for extraction of DENs.<sup>62</sup> Here, we rely on an excess of NaBH<sub>4</sub> to serve this need, but identical results were obtained when NaCl, Mg(NO<sub>3</sub>)<sub>2</sub>, or Na<sub>2</sub>SO<sub>4</sub> were used to increase the ionic strength of the extraction solution.

Figure 1 shows UV-vis absorption spectra of aqueous-phase G8-OH(Au<sub>m</sub>) (where m = 55, 147, 561, or 1022 and represents the average number of Au atoms contained within each dendrimer) prior to extraction (solid lines) and the corresponding toluene-phase, n-dodecanethiol-stabilized MPCs (MPC-12(Au<sub>m</sub>)) after extraction (dashed lines). Prior to DEN extraction, all of the aqueous solutions display an increasing absorbance toward higher energy, which results from interband electronic transitions of the encapsulated zerovalent metal nanoparticles.<sup>5</sup> The small peak at 290 nm, which is superimposed on the rising background, is more difficult to assign. Although there is controversy in the literature regarding the origin of this band,<sup>60,63</sup> it is reproducibly observed during Au DEN syntheses<sup>10,60</sup> and does not seem to affect nanoparticle properties. The only other aspect of Figure 1 that merits comment is the appearance of a plasmon band for the two largest DENs. Plasmon bands arising from Au nanoparticles larger than  $\sim 2$  nm are typically observed in the range of 500-550 nm.<sup>64,65</sup> This band is clearly present in

(64) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Marat, N.; Vezmar, I.; Whetten, R. L. J. Phys. Chem. B 1997, 101, 3706–3712.

the spectra of G8-OH(Au<sub>561</sub>) and G8-OH(Au<sub>1022</sub>), but the broad width and small absorbance suggest that the particles are very small. $^{66-68}$ 

The UV-vis spectra of the MPCs in the toluene phase after nanoparticle extraction are very similar to those of the aqueousphase DENs in both form and intensity (these spectra are cut off below 285 nm due to toluene absorption). The slight spectral variations probably result from differences in nanoparticle concentration and solvent properties; the latter are known to affect the plasmon absorption.<sup>67,68</sup>

Au DENs templated within G8-NH<sub>2</sub> dendrimers are very similar to those prepared in G8-OH dendrimers (Supporting Information, Figure S2). One minor difference is that very low intensity plasmon bands are apparent for G8-NH<sub>2</sub>(Au<sub>55</sub>) and G8-NH<sub>2</sub>(Au<sub>147</sub>) DENs (recall that the plasmon band was absent for the corresponding G8-OH DENs), and the plasmon bands for G8-NH<sub>2</sub>(Au<sub>51</sub>) and G8-NH<sub>2</sub>(Au<sub>1022</sub>) DENs are somewhat more intense than those for the corresponding *Gn*-OH DENs. These results might suggest that there is some nucleation of Au on the periphery of amine-terminated dendrimers, resulting in formation of some larger particles. Regardless of these small differences, however, the main point is that Au DENs can be extracted from either hydroxyl- or amine-terminated dendrimers, and the spectra of the resulting MPCs are essentially identical to those of the DEN precursors.

Both before and after extraction, absorption spectra of Au<sub>55</sub> nanoparticles are nearly independent of dendrimer generation. For example, parts a and b of Figure 2 show the similarity of UV-vis absorption spectra obtained for solutions of G*n*-OH-(Au<sub>55</sub>), n = 4, 6, and 8, before extraction and the corresponding MPC-12(Au<sub>55</sub>) nanoparticles after extraction. Likewise, parts c

<sup>(61)</sup> Satoh, K.; Yoshimura, T.; Esumi, K. J. Colloid Interface Sci. 2002, 255, 312–322.

<sup>(62)</sup> A salt-free, dialyzed aqueous solution of G4-OH(Au<sub>55</sub>) was mixed with the same volume of 20 mM *n*-dodecanethiol in toluene. After both phases were vigorously shaken for 10 min, the brown color remained in the aqueous phase indicating that no particle transfer occurred. Likewise, when an aqueous solution of G4-OH(Au<sub>55</sub>) containing an excess of NaBH<sub>4</sub> was mixed with the same volume of toluene in the absence of thiol, no extraction was observed. No Au precipitation was observed in either experiment.

<sup>(63)</sup> Lee, W. I.; Bae, Y.; Bard, A. J. J. Am. Chem. Soc. 2004, 126, 8358-8359.

<sup>(65)</sup> Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. Chem.-Eur. J. 2002, 8, 28–35.

<sup>(66)</sup> Mulvaney, P. Langmuir 1996, 12, 788-800.

<sup>(67)</sup> Underwood, S.; Mulvaney, P. *Langmuir* 1994, *10*, 3427–3430.
(68) Templeton, A. C.; Pietron, J. J.; Murray, R. W.; Mulvaney, P. J. Phys. Chem. B 2000, *104*, 564–570.



*Figure 2.* UV-vis absorbance spectra of (a)  $Au_{155}$  and (c)  $Au_{147}$  DENs within G4-OH (black line), G6-OH (red line), and G8-OH (blue line) and the corresponding MPCs (parts b and d, respectively) after extraction with *n*-dodecanethiol. The spectra were collected using deionized water and a 20 mM *n*-dodecanethiol solution in toluene as references, respectively.

and d of Figure 2 indicate that the UV–vis spectra of solutions containing  $Au_{147}$  nanoparticles prepared using *Gn*-OH dendrimers are also approximately the same before and after extraction. Note, however, that in the case of G4-OH(Au\_{147}) a plasmon band is present at ~510 nm both before and after extraction. This band probably signals that the interior of these low-generation dendrimers is insufficiently large to contain all 147  $AuCl_4^-$  complex ions, and therefore a significant number of larger Au particles form outside of the dendrimers. As we have previously shown, these larger nanoparticles are stabilized by adsorption of multiple dendrimers onto their surface.<sup>23</sup> It is interesting to note that the plasmon band associated with G4-OH(Au\_{147}) is preserved upon nanoparticle extraction (Figure 2d).

Figure 3 shows that it is possible to recycle dendrimer templates after nanoparticle extraction. The black line in Figure 3a is the UV-vis spectrum of G8-OH(Au<sub>1022</sub>) prior to extraction, and the red line is the spectrum of the corresponding MPC in the toluene phase. These spectra are essentially identical to those shown in Figure 1d (except note that the wavelength axis is extended to 190 nm). After extraction, the aqueous phase was dialyzed for 48 h to remove toluene, unreacted BH4-, and reduction byproducts. The resulting absorbance spectrum (Figure 3a, blue line) did not reveal the characteristic interband absorption signature of Au DENs; only the peak corresponding to the G8-OH dendrimer is present at 200 nm indicating that extraction is quantitative. This result was found for all extractions discussed in this study. FT-IR spectroscopy of both the toluene and aqueous phases after extraction indicated that the dendrimer resides only in the aqueous phase (Supporting Information, Figure S3). Together with the previously discussed UV-vis results, these FT-IR spectra conclusively prove extraction of the nanoparticles from the dendrimer. Note that we have previously shown that it is also possible to simultaneously extract the encapsulated nanoparticles along with their host



**Figure 3.** UV-vis absorbance spectra demonstrating that dendrimer templates can be recycled. (a) Synthesis and extraction of Au<sub>1022</sub> DENs. Black line: the aqueous phase containing G8-OH(Au<sub>1022</sub>) before extraction. Red line: the toluene phase containing MPC-12(Au<sub>1022</sub>) after extraction. Blue line: the aqueous phase after extraction and subsequent dialysis. (b) Synthesis of Pd<sub>1022</sub> nanoparticles using the recycled dendrimer from part a. Black line: the aqueous phase containing MPC-12(Pd<sub>1022</sub>) before extraction. Blue line: the toluene phase containing MPC-12(Pd<sub>1022</sub>) after extraction. Blue line: the aqueous phase after the second extraction and subsequent dialysis. The concentration of Pd atoms was 327  $\mu$ M.

dendrimer from an aqueous phase into an organic or fluorous phase using suitable surfactants.<sup>19,69</sup>

**Table 1.** Size Distributions (in nm) for DENs before and after (MPCs) Extraction<sup>a</sup>

nanoparticle		G4-OH	G6-OH	G8-OH	G8-NH <sub>2</sub>
Au <sub>55</sub> (1.2) Au <sub>147</sub> (1.6) Au <sub>561</sub> (2.6)	DEN MPC DEN MPC DEN	$\begin{array}{c} 1.2 \pm 0.3 \\ 1.2 \pm 0.3 \\ 3.8 \pm 0.5 \\ 3.8 \pm 0.5 \end{array}$	$\begin{array}{c} 1.3 \pm 0.3 \\ 1.2 \pm 0.4 \\ 1.5 \pm 0.4 \\ 1.5 \pm 0.4 \end{array}$	$\begin{array}{c} 1.2 \pm 0.2 \\ 1.3 \pm 0.4 \\ 1.5 \pm 0.3 \\ 1.5 \pm 0.3 \\ 1.9 \pm 0.5 \end{array}$	$1.8 \pm 0.4$
Au <sub>1022</sub> (3.2)	MPC DEN MPC			$1.9 \pm 0.4$ $2.1 \pm 0.7$ $2.2 \pm 0.5$	$1.7 \pm 0.3$ $2.2 \pm 0.4$ $2.4 \pm 0.4$

 $^a$  The size distribution corresponds to one standard deviation from the mean. The number in parentheses is the calculated diameter of the nanoparticles.  $^{10,70}$ 

Because the nanoparticle-free dendrimers are retained within the aqueous phase, it is possible to recycle them and thus prepare additional DENs and MPCs. This principle is demonstrated in Figure 3. Here, the dendrimer solution corresponding to the blue line in Figure 3a was used to prepare Pd DENs. Specifically, 1022 equiv of K<sub>2</sub>PdCl<sub>4</sub> and a 5-fold molar excess of NaBH<sub>4</sub> were sequentially added to the recycled dendrimer solution. Figure 3b shows that the resulting UV-vis spectrum (black line) is characteristic of G8-OH(Pd1022) DENs.1,5,19,21 Next, this G8- $OH(Pd_{1022})$  solution was treated with a 20 mM toluene solution of HSC<sub>12</sub> to extract the Pd DENs. The resulting UV-vis spectrum of the organic phase (red line) reproduces the spectrum of the aqueous phase prior to extraction, indicating that the G8-OH(Pd<sub>1022</sub>) DENs are quantitatively converted into MPC-12-(Pd<sub>1022</sub>) without loss of size or structural fidelity. Additional characterization of MPC-12(Pd<sub>1022</sub>) by HRTEM confirmed this assertion (Supporting Information, Figures S4). After extraction, the aqueous phase was dialyzed, and the resulting UV-vis spectrum (blue line) revealed only the dendrimer absorbance band at 200 nm. This aqueous phase was then divided in four aliquots and diluted by factors of 5, 8, 10, and 15, and the concentration of the dendrimer in each solution was determined from a Beer-Lambert calibration plot (Supporting Information, Figure S5). The results indicate that, after using the same aqueous solution to template two different types of nanoparticles,  $Au_{1022}$  and  $Pd_{1022}$ , more than 80% of the original dendrimer was recovered. The loss is attributable to the multistep recycling process and particularly the two dialysis steps.

HRTEM micrographs were obtained to evaluate average particle sizes and size distributions for Au nanoparticles before and after extraction from the dendrimer templates. This information is summarized in Table 1. The average diameters were obtained by measuring the size of 150 randomly selected particles. Note that there is probably a bias in these measurements toward larger particles, because it was not possible to accurately measure the size of particles < 1 nm in diameter; however, this bias should be consistent for all the data shown in Table 1. In all cases, the size of the Au nanoparticles is, within experimental error, identical before and after extraction. Moreover, the average size of the Au<sub>55</sub> nanoparticles within G4-OH, G6-OH, and G8-OH dendrimers and the Au147 nanoparticles within G6-OH and G8-OH dendrimer measured by HRTEM is very close to the calculated value (Table 1).<sup>70</sup> As indicated earlier, the G4-OH(Au147) nanoparticles are probably

a mixture of DENs and larger nanoparticles stabilized by adsorption of multiple dendrimers, which leads to a larger average particle diameter and a broader size distribution.<sup>23</sup> This is likely a consequence of the small G4-OH dendrimer template being overloaded with a stoichiometric excess of AuCl<sub>4</sub>-. Additionally, the diameters of the Au<sub>561</sub> and Au<sub>1022</sub> DENs prepared using G8-OH and G8-NH2 dendrimers are smaller than the calculated values (Table 1).70 This is an unanticipated, but easily reproduced, result for which we are unable to offer a conclusive explanation at the present time. However, there is precedent for formation of multiple nanoparticles within highgeneration dendrimers, and therefore it is possible that a similar situation exists here.<sup>17</sup> The important point is that together with the just-discussed spectroscopy results, the data in Table 1 conclusively prove that individual nanoparticles are extracted from the dendrimer without significant loss of metal or aggregation.

NMR spectroscopy is informative about the structure of MPC monolayers, and it provides a means for determining the purity of solutions after nanoparticle extraction. This is possible because the <sup>1</sup>H NMR spectrum of the MPC *n*-alkanethiol shell is broadened compared to the corresponding free n-alkanethiols.<sup>39</sup> This has been attributed to multiple factors, including the high packing density of the monolayer and the distribution of chemical shifts caused by differences in Au binding sites (e.g., terraces, edges, and vertexes). Importantly, a correlation exists between the line width of the peaks arising from the distal methyl groups of the *n*-alkanethiols and the size of the Au nanoparticles.<sup>39</sup> Using these results to calibrate the line widths shown in the Supporting Information (Figure S6) for MPC-12-(Au<sub>*m*</sub>), we find that the results are consistent with particles < 3nm in diameter.<sup>39</sup> In addition, NMR does not reveal the presence of dendrimer impurities (Supporting Information, Figure S7) in the MPC solutions, indicating that within the detection limit of NMR only MPCs are present in the organic phase.

We carried out experiments to understand how the concentration and length of the *n*-alkanethiol ligand affects the extraction of the Au nanoparticles from within dendrimers. In the first set of experiments, G4-OH(Au<sub>55</sub>) was prepared and extracted using different concentrations of n-dodecanethiol. Specifically, four 5.0 mL aliquots of G4-OH(Au<sub>55</sub>) ([Au]= 110  $\mu$ M) were extracted using 5.0 mL of toluene containing HSC12 present at 110, 330, 550, and 1100  $\mu$ M. These solutions correspond to HSC<sub>12</sub>/Au mole ratios of 1, 3, 5, and 10, respectively, but note that only 76% of the Au atoms in a Au<sub>55</sub> cluster are on the surface so in all cases a stoichiometric excess of  $HSC_{12}$  is present in solution. UV-vis spectra of the toluene phases collected from all of these solutions after extraction (see Supporting Information, Figure S8) are essentially identical to that shown in Figure 1a (HSC<sub>12</sub>/Au mole ratio = 182), except for the case where the  $HSC_{12}/Au$  mole ratio = 1 where a plasmon band is observed near 500 nm. This suggests that a deficit of the *n*-alkanethiol ligand results in particle aggregation during extraction. This suspicion is confirmed by the HRTEM data shown in Figure 4. Parts a-d of Figure 4 are micrographs and particle-size distributions for  $HSC_{12}/Au$  mole ratios of 1, 3, 5, and 10, respectively. The results from these data are summarized in Figure 4e, which shows that both the average particle size and the particle-size distribution decrease as the HSC12/Au mole ratio increases from 1 to 10. We rationalize

<sup>(69)</sup> Chechik, V.; Zhao, M.; Crooks, R. M. J. Am. Chem. Soc. 1999, 121, 4910– 4911.

<sup>(70)</sup> Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. J. Phys. Chem. 1995, 99, 7036-7041.



**Figure 4.** HRTEM micrographs and particle-size distributions for MPC-12(Au<sub>55</sub>) extracted from G4-OH dendrimers using the following  $HSC_{12}/Au$  mole ratios: (a) 1, (b) 3, (c) 5, and (d) 10. The horizontal axis of the histograms is the same for each panel to facilitate comparison of the size distributions. (e) Average particle size (from HRTEM) vs the  $HSC_{12}/Au$ mole ratio. The vertical bars indicate the standard deviation of the particlesize distribution.

this finding in terms of the proposed extraction mechanism. That is, the nanoparticles undergo relatively slow extraction when low concentrations of *n*-alkanethiols are used, and the nascent MPCs are only partially passivated for some time following extraction. During this period, particle size increases via metal aggregation. It is possible to decrease the period of partial thiol passivation, and thus the likelihood of aggregation, by increasing the concentration of the *n*-alkanethiol. To avoid aggregation, and thus retain the desirable size distribution of DENs after extraction, we used a HSC<sub>12</sub>/Au mole ratio > 100 throughout this study (unless otherwise noted).

As mentioned earlier, we also examined the effect of the *n*-alkanethiol chain length on the size of the resulting MPCs and on the kinetics of nanoparticle extraction. For this part of the study we examined the extraction of  $Au_{1022}$  DENs from within G8-OH dendrimers using *n*-hexanethiol (HSC<sub>6</sub>), *n*-dodecanethiol (HSC<sub>12</sub>), and *n*-hexadecanethiol (HSC<sub>16</sub>). UV-vis spectra (Supporting Information, Figure S9), including the location of the plasmon band centered at 510 nm, of the three different MPC-*X*(Au<sub>1022</sub>) (X = 6, 12, and 16) extraction products are very similar to one another and to the spectrum of MPC-12(Au<sub>1022</sub>) shown in Figure 1d. This suggests that the sizes of the extracted Au particles are independent of the length of the stabilizing ligand.<sup>39</sup>

The DEN extraction rate was evaluated using UV-vis spectroscopy. Four aqueous solutions containing G8-OH(Au<sub>55</sub>), G8-OH(Au147), G8-OH(Au561), and G8-OH(Au1022) were prepared, and each was extracted with toluene solutions containing HSC<sub>6</sub>, HSC<sub>12</sub>, and HSC<sub>16</sub>. To minimize the likelihood of errors resulting from irreproducible mixing, this extraction was carried out using a vortexer. The extent of extraction was quantified every 5 s by measuring the UV-vis absorbance of the organic layer at 510 nm and comparing this to the absorbance upon completion of the extraction. Figure 5 shows the percentage of Au DENs extracted vs time for different combinations of the three n-alkanethiols and sizes of the Au DENs. The most obvious result of these experiments is that, regardless of conditions, all DENs are completely extracted from the dendrimers within 1 min. For example, Figure 5a shows that extraction of Au<sub>55</sub> from G8-OH is >70% complete within 5 s regardless of which *n*-alkanethiol is used for the extraction. Extraction of larger nanoparticles takes longer; for example, extraction of Au<sub>1022</sub> from G8-OH (Figure 5b) is about half as fast as that of Au<sub>55</sub>. The time resolution in Figure 5b is sufficient to reveal a significant dependence of the n-alkanethiol chain length on the extraction rate: exposure to HSC<sub>6</sub>, HSC<sub>12</sub>, and HSC<sub>16</sub> for 5 s leads to extraction of only 52%, 43%, and 33% of the Au DENs, respectively. This result is consistent with previous reports from our group, which have shown that larger molecules (longer *n*-alkanethiols in this case) have a more difficult time penetrating PAMAM dendrimers and encountering the surface of the encapsulated metal nanoparticles.<sup>21</sup> It follows that the largest nascent MPCs, which are formed by reaction with the longest *n*-alkanethiols, will have a more difficult time escaping from within the dendrimer interior.

This same sort of effect is observed when the length of thiol is kept constant and the particle size is varied. For example, Figure 5c indicates that nanoparticle extraction with HSC<sub>12</sub> is 80% complete within 5 s for the Au<sub>55</sub> DENs but only ~40% complete for the largest two DENs. The extraction rate of the two smallest DENs is not a strong function of the length of the *n*-alkanethiol (compare parts c and d of Figure 5), but there is a measurable difference for the two largest DENs.



*Figure 5.* Plots showing the percentage of Au DENs extracted as a function of time. Extraction of (a) Au<sub>55</sub> and (b) Au<sub>1022</sub> using ( $\blacksquare$ ) *n*-hexanethiol (HSC<sub>6</sub>), ( $\bigcirc$ ) *n*-dodecanethiol (HSC<sub>12</sub>), and ( $\blacktriangle$ ) *n*-hexadecanethiol (HSC<sub>16</sub>) from within G8-OH dendrimers. Extraction of ( $\square$ ) Au<sub>55</sub>, ( $\bigcirc$ ) Au<sub>147</sub>, ( $\triangledown$ ) Au<sub>561</sub>, and ( $\triangle$ ) Au<sub>1022</sub> DENs from within G8-OH dendrimers using (c) HSC<sub>12</sub> and (d) HSC<sub>16</sub> as the extractants.

In addition to the use of *n*-alkanethiols, we also attempted the extraction of G8-OH(Au<sub>m</sub>) (m = 55, 147, 561, and 1022) DENs using triphenylmethanethiol (Ph<sub>3</sub>CSH). In this case, the aqueous DEN phase remained colored and no extraction was observed regardless of the size of the DENs (see Supporting Information, Figures S10 and S11). We interpret this result in terms of the size and shape of the Ph<sub>3</sub>CSH. That is, this bulky ligand is unable to penetrate the sterically crowded periphery of the G8-OH dendrimer and thus unable to encounter the surface of the Au DENs. As mentioned earlier, we have previously observed this same type of size-dependent selective entry of small molecules into the dendrimer interior during the course of catalysis experiments.<sup>21</sup> We also attempted to extract Au<sub>55</sub> DENs from within the much less spatially crowded G4-OH dendrimers using Ph<sub>3</sub>CSH. In this case, the extraction was complete (the aqueous phase turned from brown to colorless), but a precipitate formed at the interface of the two phases.

# **Summary and Conclusions**

We have shown that Au nanoparticles having diameters of less than 2.2 nm can be rapidly extracted from within the interior of PAMAM dendrimers using *n*-alkanethiol extractants. Extraction proceeds quickly, regardless of the size of the DEN, the dendrimer generation, and the peripheral functionalization of the dendrimer. Importantly, however, ligands such as Ph<sub>3</sub>CSH, which are presumably too large to penetrate the dendrimer surface, are unable to extract DENs of any size from G8-OH dendrimers. The other key point is that the overall size of the nascent MPC and the dendrimer generation have an effect on the extraction rate: larger MPCs and higher generation dendrimers generally lead to significantly (factor of  $\sim$ 2) slower extractions. Other important results of this study include the following. First, within the accuracy of absorbance spectroscopy, the extraction yield is quantitative. Second, NMR and FT-IR

spectroscopy indicate that after extraction the dendrimer remains in the aqueous phase and can be used to template additional metal particles. Third, the size and optical characteristics of the extracted nanoparticles are the same as the precursor DENs. Fourth, a 100-fold excess of *n*-alkanethiol molecules is required to completely prevent aggregation of DENs during extraction.

These findings are consistent with an extraction model in which a substoichiometric number of n-alkanethiols penetrate the dendrimer periphery, encounter the DEN, and partially assemble on the surface. Extraction begins during this conversion of the DEN to a nascent MPC. If a large excess of the *n*-alkanethiol is present in solution, then additional self-assembly proceeds quickly and no metal aggregation is observed. Conversely, if only partially passivated MPCs encounter one another, which is a consequence of slow transport of sufficient *n*-alkanethiols to the surfaces of the nanoparticles, they aggregate and grow in size. Although this model is consistent with all of our findings, it is undoubtedly an oversimplification of the true situation. For example, it is difficult to understand how a relatively large object, such as a 2 nm diameter Au nanoparticle, can be extracted so readily from a dendrimer having a sterically crowded periphery. The implication is that PAMAM dendrimers are remarkably flexible and are able to readily adopt unusual structural configurations.<sup>71</sup> These results also imply the notvery-surprising conclusion that Au DENs are restrained by a combination of steric and chemical interactions. The latter are likely tertiary amine groups that interact with the Au surface. It is likely that the thiol groups of the extractants effectively compete with the dendrimeric amines for Au surface sites and that loss of these dendrimer/nanoparticle interactions, together with the change in contact angle of the Au surface upon *n*-alkanethiol self-assembly, leads to extraction. At present,

<sup>(71)</sup> Uppuluri, S.; Keinath, S. E.; Tomalia, D. A.; Dvornic, P. R. *Macromolecules* 1998, 31, 4498–4510.

however, this is just speculation, and additional experiments, involving other DENs and ligands having different functional groups, will be required to develop a full understanding of this important point.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant No. 0211068) for financial support of this work. J.C.G.-M. thanks the Ministerio de Educacion, Cultura y Deporte of Spain for postdoctoral fellowship support.

We thank Dr. Robert W. J. Scott, Dr. Julio Alvarez, and Orla M. Wilson for helpful discussions.

**Supporting Information Available:** Photographs demonstrating extraction; <sup>1</sup>H NMR, UV-vis, and FT-IR spectra, experimental procedure used for recycling, and HRTEM micrographs are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

JA046567N