

Synthesis, Characterization, and Surface Immobilization of Platinum and Palladium Nanoparticles Encapsulated within Amine-Terminated Poly(amidoamine) Dendrimers

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Platinum and palladium dendrimer-encapsulated nanoparticles (DENs) were prepared within commercially available, fourth-generation, amine-terminated, poly(amidoamine) dendrimers (G4-NH₂). The synthesis is carried out by selectively encapsulating metal complexes within the dendrimer and then reducing the resulting composite. Intradendrimer complexation requires control over the solution pH to prevent attachment of the metal complexes to primary amine groups on the dendrimer periphery. That is, the surface primary amines of the dendrimer must be selectively protonated in the presence of the interior tertiary amines. The metal-ion encapsulation and reduction processes were characterized by UV-vis spectroscopy. Forty-atom Pt and Pd DENs were examined by high-resolution transmission electron microscopy, which showed that the mean particle sizes were 1.4 and 1.5 nm, respectively, and that both were nearly monodisperse (standard deviation = 0.3 nm). The free amine groups on the dendrimer surface were used to link Pd DENs to monolithic Au surfaces via an intermediate self-assembled monolayer adhesion layer.

Introduction

This paper reports the preparation of Pt and Pd nanoparticles encapsulated within fourth-generation, amine-terminated, poly(amidoamine) (PAMAM) dendrimers (G4-NH₂). These new results are significant because the dendrimers used as templates for the nanoparticle synthesis are commercially available and because they have surface groups that provide a reactive handle for linking nanoparticles to surfaces and other polymers. We illustrate this point here by covalently attaching dendrimer-encapsulated nanoparticles (DENs) to a reactive self-assembled monolayer (SAM).¹ It should be possible to use this same basic strategy for linking DENs to a wide variety of substrates for heterogeneous catalysis, linking DEN-based biomarkers to proteins and DNA,² and creating new types of functional substrates that require highly monodisperse metal nanoparticles.

We and others previously reported the preparation and characterization of dendrimer-encapsulated Cu,³ Pt,^{4–7} Pd,^{4,7–16} Au,^{17–20} CdS,²¹ and bimetallic^{22,23} nanoparticles.^{24,25} These materials are prepared by extracting metal ions into the interior of dendrimers and then chemically reducing the metal ions to yield encapsulated nanoparticles. Although there are a few exceptions,^{6,7,11–16} Pt and Pd DENs are normally prepared using PAMAM dendrimers terminated with hydroxyl groups.^{3–5,8–10,22,23,26}

There are two reasons for this. Foremost, hydroxyl groups are noncomplexing toward most metal ions. This is important, because metal ions cross-link dendrimers terminated with good metal ligands, and this leads to precipitation. Second, both hydroxyl-terminated dendrimers and most metal ions and metal-ion complexes are water soluble.

We previously showed that monolayers of Pt DENs terminated with hydroxyl functional groups could be physisorbed to Au surfaces and used for the electrocatalytic reduction of O₂.⁵ However, because of the low reactivity of the peripheral hydroxyl groups, it was not possible to covalently link the dendrimer to the electrode surface,

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and consequently the stability of the dendrimer monolayer was poor under electrochemical conditions. In contrast, we knew from previous studies that amine-terminated dendrimers (without encapsulated nanoparticles) could be covalently attached to electrode surfaces to yield stable monolayers.^{27,28} We reasoned that if DENs could be prepared within amine-terminated dendrimers, then the peripheral primary amines would form stable covalent bonds.

We previously described two approaches for preparing DENs in amine-terminated dendrimers. In one case, the dendrimer surface was partially quaternized.⁷ This strategy takes advantage of the large number of functional groups on the dendrimer surface, in that different fractions of the surface can be functionalized to perform specific tasks. Specifically, the unquaternized fraction of the periphery was shown to be reactive, while a positive charge on the quaternized fraction prevented agglomeration of DENs. While this approach is effective, it requires chemical modification of the dendrimer periphery. In the second case, we observed that the peripheral amines of PAMAM dendrimers could be selectively protonated by judicious control of solution pH and that this provided a means for encapsulation of Pd nanoparticles.^{11,12} The new results provided here expand upon these preliminary findings. Specifically, we now describe optimal conditions for preparing both Pd and Pt DENs in amine-terminated dendrimers, fully characterize the resulting metal nanoparticles, and show that this family of DENs forms stable, high-density monolayers on surfaces.

Experimental Section

Chemicals. G4-NH₂ was purchased as a 10–25% methanol solution (Dendritech, Inc., Midland, MI). Prior to use, methanol was removed under vacuum. K₂PtCl₄, K₂PdCl₄ (Strem Chemicals, Inc.), and NaBH₄ (The Aldrich Chemical Co.) were used without further purification. 11-Mercaptoundecanoic acid (MUA), ethyl chloroformate, 4-methylmorpholine, dichloromethane (99.8%, anhydrous), and *N,N*-dimethylformamide (99.8%, anhydrous) were purchased from Aldrich and used for surface modification without further purification. Milli-Q deionized water (18 MΩ·cm, Millipore, Bedford, MA) was used to prepare aqueous solutions.

Characterization. Absorption spectra were obtained using a Hewlett-Packard HP8453 UV–vis spectrometer. The optical path length was 0.1 or 1.0 cm, and deionized water or aqueous dendrimer solutions were used as references. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL-2010 TEM with a point-to-point resolution of 0.19 nm. Samples were prepared by placing a drop of solution on a holey-carbon-coated grid and allowing the solvent to evaporate in air. Fourier transform infrared external reflection spectroscopy (FTIR-ERS) was carried out using an FTS-6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossing, NY) and a liquid-N₂-cooled, narrow-band mercury cadmium telluride detector. The spectra were taken at 4 cm⁻¹ resolution using p-polarized light at an 84° angle of incidence with respect to the substrate normal.

Preparation of Pt and Pd DENs. Dry G4-NH₂ was dissolved in sufficient deionized water (pH adjusted with HCl to ~5 for Pt DENs and ~3 for Pd DENs) to yield 2.5–50 μM dendrimer solutions, and then 30 or 40 mol equiv of an aqueous 0.1 M K₂PtCl₄ or 0.1 M K₂PdCl₄ solution was added. Zerovalent Pt and Pd DENs were synthesized by slow addition of a 20-fold excess of 0.1–0.5 M NaBH₄ dissolved in deionized water. Following addition of NaBH₄, the solution pH was adjusted to 8 by addition of aqueous HCl, and then the DEN solution was dialyzed with a cellulose dialysis sack having a molecular weight cutoff of 12 000 (Sigma Diagnostics, Inc., St. Louis, MO) to remove impurities.⁸

Surface Immobilization of DENs. MUA monolayers were prepared by immersing ozone-cleansed Au substrates into a 1 mM ethanolic solution of MUA for 24 h. The MUA substrates were then washed with ethanol, dried under flowing N₂ gas, and transferred to vials containing ethyl chloroformate and 4-methylmorpholine dissolved in DMF or CH₂Cl₂ for 1 h. This resulted in the formation of activated anhydride surfaces.^{27–31} Next, the substrates were removed from solution, rinsed with DMF or CH₂Cl₂, and dried under flowing N₂ gas. The activated substrates were dipped into 10 mL of a Pd DEN solution (0.05 mM G4-NH₂ dendrimer) containing 0.1 mL of 4-methylmorpholine. As a control experiment to ensure covalent attachment to the surface, Pd DEN-modified substrates were prepared using the same procedure, but in this case, ethyl chloroformate was omitted. This prevents formation of a covalent bond.

Results and Discussion

Preparation of Pt DENs. Pt DENs were prepared by stirring aqueous pH 5 solutions containing G4-NH₂ and K₂PtCl₄ for 76 h and then reducing the encapsulated Pt metal complex with BH₄⁻. The lengthy stirring time is required, because reaction between the interior amines of G4-NH₂ and Pt²⁺ (unless indicated otherwise, Pt²⁺ and Pd²⁺ are used to represent all possible complex ions of the two metals)³² is slow.^{4,5} Because the exterior amines (pK_a = 9.2) are more basic than the interior amines (pK_a = 6.3),³³ metal ions selectively coordinate to the interior amines at pH 5. Slow addition of a 0.5 M aqueous NaBH₄ solution to the dendrimer/Pt²⁺ complex results in formation of a dark-brown, zerovalent Pt DEN solution. The solution pH increased to 8–9 after addition of NaBH₄ because of proton reduction. We have found that at pH > 8 these types of DENs aggregate after a few hours, and therefore the solution pH was adjusted back to 8 with HCl after reduction. We believe that aggregate formation at a high pH may be a consequence of DEN cross-linking facilitated by unreduced or reoxidized metal ions, because after purification by dialysis for 24 h, Pt DEN solutions do not precipitate at pHs as high as 10. Recent results from our group have shown that removal of complexing ligands from solution leads to much slower oxidation rates of Pd DENs.⁸

Figure 1 shows UV–vis absorbance spectra of pH 5 solutions of amine-terminated, fourth-generation, PAMAM dendrimers containing, on average, 30 Pt²⁺ ions (G4-NH₂(Pt²⁺)₃₀) obtained over a 76 h period as well as shortly (15 min) after reduction with NaBH₄. The peak at 216 nm, which corresponds to a ligand-to-metal charge-transfer (LMCT) band of PtCl₄²⁻, decreases and shifts slightly to 220 nm.^{34,35} Simultaneously, the peak at 260 nm, which arises from coordination of the Pt complex to interior dendrimeric amines,^{4,5} grows in intensity throughout the 3-day observation period. This suggests that a slow ligand-exchange reaction occurs between PtCl₄²⁻ and the interior amine groups of the dendrimer.³⁶ The isosbestic point at 236 nm indicates that PtCl₄²⁻ is exclusively converted to a single species, which we identify as amine-coordinated PtCl₃⁻. We previously reported that Pt

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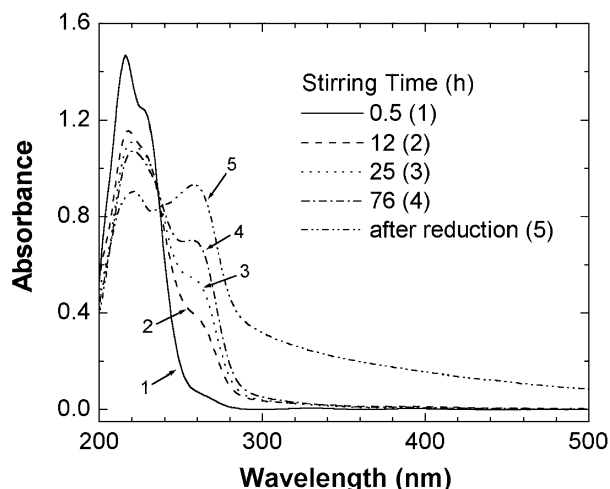


Figure 1. Time-resolved UV-vis absorbance spectra of $G4-NH_2(Pt^{2+})_{30}$ solutions (pH 5) over a 76 h period and 15 min after reduction with $NaBH_4$ to yield $G4-NH_2(Pt_{30})$ (the solution pH increased to 8 after addition of $NaBH_4$). The final concentration of $G4-NH_2$ was $50 \mu M$. The optical path length was 0.1 cm .

complexation with hydroxyl-terminated PAMAM dendrimers was complete within 45 h.⁵ However, the solution was slightly basic in that case (because of the basicity of the PAMAM dendrimers); apparently, the reaction takes longer at a lower pH because of proton competition for the interior amine sites.

Control experiments confirm that Pt salts coordinate with interior, rather than exterior, amines. For example, when a solution of K_2PtCl_4 is added to a dendrimer solution without pH control (slightly basic conditions), the solution precipitates after several hours. This is a consequence of interdendrimer cross-linking of the peripheral amines by the metal complex. Similarly, a Pt precipitate is observed when a solution of $G4-NH_2$ and K_2PtCl_4 are reduced at pH 5 prior to complete complexation of Pt with the interior dendrimer amines, that is, if less than 3 days is allotted for the complexation reaction.

Chemical reduction of an aqueous solution of $G4-NH_2-(Pt^{2+})_{30}$ with excess $NaBH_4$ yields Pt DENs, $G4-NH_2(Pt_{30})$. Figure 1 shows the UV-vis spectrum of the $G4-NH_2(Pt_{30})$ solution 15 min after reduction. The broad, featureless absorption at wavelengths $>300 \text{ nm}$ is consistent with the formation of colloidal Pt.^{4,5,24,37} There are also two peaks (220 and 260 nm) present at low wavelengths. Experimental observations and theoretical calculations have shown that the peak at 220 nm arises from absorbance of Pt nanoparticles in aqueous solution.^{38,39} The peak at 260 nm is more difficult to assign, but it has been previously observed.^{4,7} This peak may originate from unreduced Pt^{2+} that is still strongly bound to the tertiary amine groups of the dendrimers.⁴⁰

Preparation of Pd DENs. The method used to prepare Pd DENs is very similar to that used for Pt DENs. Solutions of $G4-NH_2$ and K_2PdCl_4 are mixed together, stirred for 30 min at pH 3, and then reduced with BH_4^- . The kinetics of Pd^{2+} ion coordination with the interior amines are much faster than those for Pt^{2+} , and therefore it was possible to use shorter reaction times and a lower pH. Figure 2a shows UV-vis spectra of an aqueous solution containing $2.5 \mu M G4-NH_2(Pd^{2+})_{30}$ before (at pH

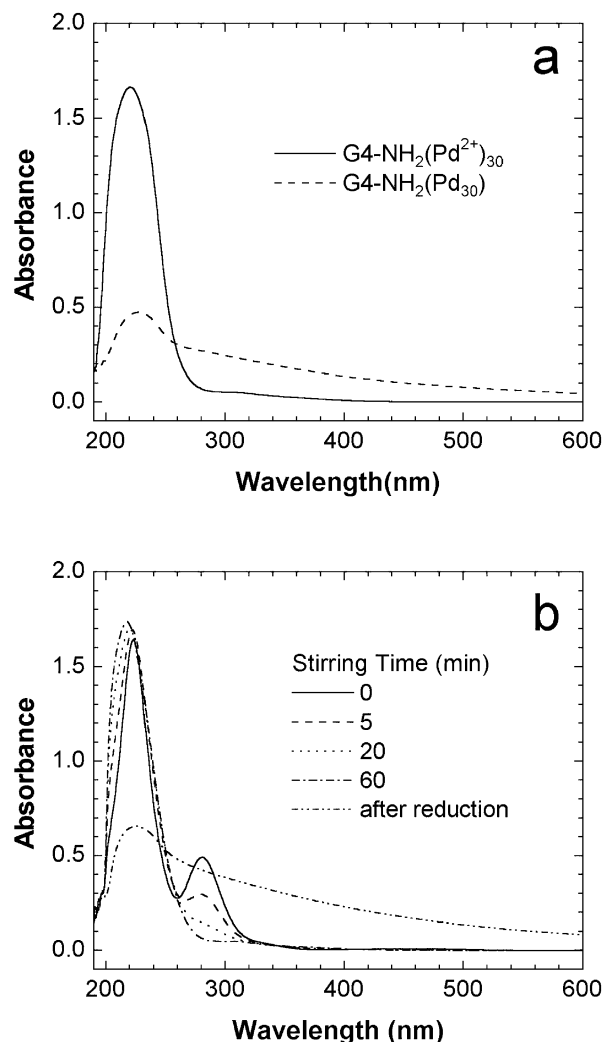


Figure 2. (a) UV-vis spectra of $2.5 \mu M$ solutions of $G4-NH_2-(Pd^{2+})_{30}$ (pH 3) and $G4-NH_2(Pd_{30})$ (pH 8). (b) Time-resolved UV-vis spectra of $G4-NH_2(Pd^{2+})_{30}$ and $G4-NH_2(Pd_{30})$ solutions in the presence of 0.1 M KCl before (pH 3) and after (pH 8) reduction. The optical path length was 1.0 cm .

3) and after reduction (at pH 8). Pd^{2+} coordination with the interior dendrimer amines is complete within 15 min, which is about 300 times faster than Pt^{2+} coordination. The band at 221 nm corresponds to a LMCT associated with complexation of Pd^{2+} to amine groups of the $G4-NH_2$ dendrimer.⁸ We believe that complexation occurs via displacement of water from $PdCl_3(H_2O)^-$, which is the dominant Pd^{2+} species present under these conditions, followed by a covalent reaction with the interior tertiary amines of the dendrimer.⁸ After reduction, the broad, featureless absorption at low energies, as well as the peak

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(40) To better understand the origin of the peak at 260 nm, the following experiments were performed. (1) For a constant dendrimer concentration, the absorbance of the peak at 260 nm is proportional to the amount of $PtCl_4^{2-}$ added. (2) The peak does not change even after adding more sodium borohydride and bubbling H_2 for 24 h. (3) The peak is absent if insufficient time is permitted for complete Pt^{2+} encapsulation. Specifically, the band at 260 nm is absent if the $G4-NH_2(Pt^{2+})_{30}$ is reduced just 1 h after mixing the dendrimer and the Pt complex. This peak is also absent if the reduction is carried out at very low pH, which prevents complexation of the Pt^{2+} complex with the dendrimer. In both cases, however, metal precipitates from solution. (4) The XPS spectrum of surface-confined $G4-NH_2(Pt_{30})$ (see Supporting Information) reveals a very small shoulder at 77.8 eV corresponding to $Pt^{2+}(4f_{5/2})$. These results lead us to conclude that the peak at 260 nm probably arises from unreduced Pt^{2+} that is still strongly bound to amine groups in dendrimers.

at 230 nm, arises from interband transitions of the intradendrimer Pd nanoparticle.^{8,37,41,42}

The presence of Cl^- in solution is known to affect the way that dendrimers interact with Pd^{2+} complexes in two ways. First, it ensures that the dominant Pd^{2+} species in solution is PdCl_4^{2-} rather than $\text{PdCl}_3(\text{H}_2\text{O})^-$.^{8,34} This is helpful in understanding the speciation of Pd^{2+} , because the Pd–Cl LMCT band for PdCl_4^{2-} at 279 nm is well-separated from the Pd–N LMCT band of $\text{G4-NH}_2(\text{Pd}^{2+})_{30}$ at 221 nm. In contrast, the LMCT band for $\text{PdCl}_3(\text{H}_2\text{O})^-$ at 237 nm overlaps significantly with the Pd–N LMCT band.³⁴ Second, coordination of PdCl_4^{2-} with intradendrimer tertiary amine ligands occurs more slowly than that of $\text{PdCl}_3(\text{H}_2\text{O})^-$. These two factors make it easier to follow the Pd^{2+} encapsulation reaction spectroscopically. Figure 2b shows that, in the presence of 0.1 M KCl, the LMCT of PdCl_4^{2-} at 279 nm decreases within minutes of adding G4-NH_2 to the K_2PdCl_4 solution and that this peak disappears completely after 1 h. The final spectrum is similar to that resulting from Pd^{2+} coordination to G4-NH_2 in the absence of KCl (Figure 2a). Reduction of the $\text{G4-NH}_2(\text{Pd}^{2+})_{30}/\text{KCl}$ solution (Figure 2b) results in a spectrum that is nearly identical to that obtained in the absence of KCl.

It is interesting to note that very low pHs prevent complexation between the dendrimer and Pd^{2+} . Specifically, the absorbance spectrum of a K_2PdCl_4 solution in the absence of KCl did not change for at least 1 day when G4-NH_2 was added at pH 1.5. This means that a high proton concentration, which translates into protonation of all exterior and interior amines, completely prevents Pd^{2+} coordination to the dendrimer.

Spectrophotometric titrations were carried out to determine the maximum Pd^{2+} loading of G4-NH_2 at pH 3. Figure 3a shows UV–vis absorbance spectra for dilute aqueous solutions of K_2PdCl_4 in deionized water. The Pd complex has two strong LMCT bands at 207 and 237 nm, corresponding to literature values for the hydrolysis product $\text{PdCl}_3(\text{H}_2\text{O})^-$.³⁴ Beer–Lambert plots obtained from these spectra at 221 and 237 nm are linear throughout the examined concentration range (Figure 3b). Figure 3c shows absorbance spectra for solutions containing both G4-NH_2 and K_2PdCl_4 at pH 3. Upon addition of K_2PdCl_4 to a 1.6 μM solution of G4-NH_2 , a single, broad [full width at half-maximum (fwhm) = 45 nm at $\text{Pd}^{2+}/\text{G4-NH}_2 = 40$] absorption band is present at $\lambda_{\text{max}} = 221$ nm for $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios of 60 and below. Recall that this is the LMCT associated with the $\text{Pd}^{2+}/\text{G4-NH}_2$ complex. Figure 3d shows that Beer–Lambert plots obtained for these solutions are linear only up to $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios of approximately 60. Moreover, UV–vis spectra of $\text{G4-NH}_2(\text{Pd}^{2+})_{30}$ solutions before and after extended dialysis in water were identical, which means that Pd^{2+} is strongly bound to the dendrimers at low $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios. That is, the amount of free $\text{PdCl}_3(\text{H}_2\text{O})^-$ in solution is negligible in this range. At $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios greater than 80, a shoulder becomes apparent at ~ 210 nm, and the peak at 221 nm broadens (fwhm = 51 nm at $\text{Pd}^{2+}/\text{G4-NH}_2 = 120$). This is a consequence of the superposition of peaks corresponding to both dendrimer-encapsulated Pd^{2+} (221 nm) and free $\text{PdCl}_3(\text{H}_2\text{O})^-$ in solution (207 and 237 nm) at Pd^{2+} concentrations exceeding the maximum capacity of the dendrimer interior. After extended dialysis in water, UV–vis spectra of solutions having $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios above 60 revealed a significant decrease in absorbance in the 200–250 nm region, which confirms the presence of free $\text{PdCl}_3(\text{H}_2\text{O})^-$ at high $\text{Pd}^{2+}/\text{G4-NH}_2$ ratios.

Extinction coefficients for $\text{PdCl}_3(\text{H}_2\text{O})^-$ and $\text{G4-NH}_2(\text{Pd}^{2+})_n$ were obtained from the Beer–Lambert plots, and the relative concentration of each species was calculated using an appropriate analysis.⁸ Figure 3e is a plot of calculated concentrations of free $\text{PdCl}_3(\text{H}_2\text{O})^-$ and encapsulated Pd^{2+} versus the $\text{Pd}^{2+}/\text{G4-NH}_2$ ratio in solution. These data indicate that there is a maximum loading of about 65 Pd^{2+} ions within the G4-NH_2 dendrimers at pH 3. This suggests that each Pd^{2+} is coordinated to about one of the 62 interior tertiary amine binding sites of G4-NH_2 and that there is little or no coordination between Pd^{2+} and the peripheral primary amine groups at this pH.

Microscopy. Figure 4 shows HRTEM images and particle size distributions for $\text{G4-NH}_2(\text{Pt}_{40})$ and $\text{G4-NH}_2(\text{Pd}_{40})$ DENs. Analysis of 100 randomly selected particles shows that the average diameters for the Pt and Pd DENs are 1.4 ± 0.3 and 1.5 ± 0.3 nm, respectively. The size distributions, which in both cases correspond to $1\sigma = 0.3$ nm, are comparable to those obtained for Pd and Pt DENs prepared in hydroxyl-terminated PAMAM dendrimers ($1\sigma = 0.2\text{--}0.3$ nm).^{4,5,9} Note, however, that the particle sizes are larger than the value of 1.1 nm calculated for a Pd or Pt particle containing 40 atoms with face-centered-cubic packing.^{4,5} We^{4,5,24} and others^{10,13,23} always observe that Pt and Pd DENs appear to be too large in HRTEM micrographs, even though the calculated and measured sizes of Au DENs are always self-consistent.¹⁷ At present, we do not understand this apparent inconsistency, but it is possible that Pt and Pd DENs have irregular shapes (i.e., non-close-packed geometries), which causes them to appear too large in the two-dimensional HRTEM projections.^{5,9,24}

Synthesis and Characterization of DEN Thin Films. We are interested in using thin films of DENs as heterogeneous catalysts, and therefore we examined the feasibility of attaching DEN monolayers to surfaces. Specifically, $\text{G4-NH}_2(\text{Pd}_{30})$ was covalently linked to a monolithic Au surface using an intermediate MUA SAM adhesion layer. To gauge the strength of the attachment, we evaluated the stability of DEN monolayers prepared with and without activation of the MUA groups. Spectrum 1 in Figure 5a was obtained following coupling of $\text{G4-NH}_2(\text{Pd}_{30})$ to an activated MUA SAM and subsequent sonication in water for 30 s. The amide I and II bands present at 1665 and 1550 cm^{-1} , respectively, indicate that the dendrimer is present on the surface.^{27,43} The height of amide I band is 0.0035. This value is comparable with previous studies of dendrimer monolayer films in which no metal was encapsulated within the dendrimer,^{28,43} and it is about 2.5 times higher than DEN films prepared using partially quaternized dendrimers.⁷ Spectrum 2 was obtained using the same film but after sonication in water for 5 min at pH 2. Analysis of the height of the amide I bands before and after sonication in acid indicates that 94% of the DEN film remains on the surface.

Figure 5b shows an analogous experiment carried out using an unactivated MUA SAM. In this case, the DENs are likely attached to the surface via electrostatic interactions between the acid terminal groups of MUA and the peripheral primary amines of the dendrimer. Physisorption (van der Waals interactions) may also play a role. After this film was sonicated in water for 5 min at pH 2, only 78% of the amide I peak remains. These results suggest that Pd DEN monolayers prepared on activated

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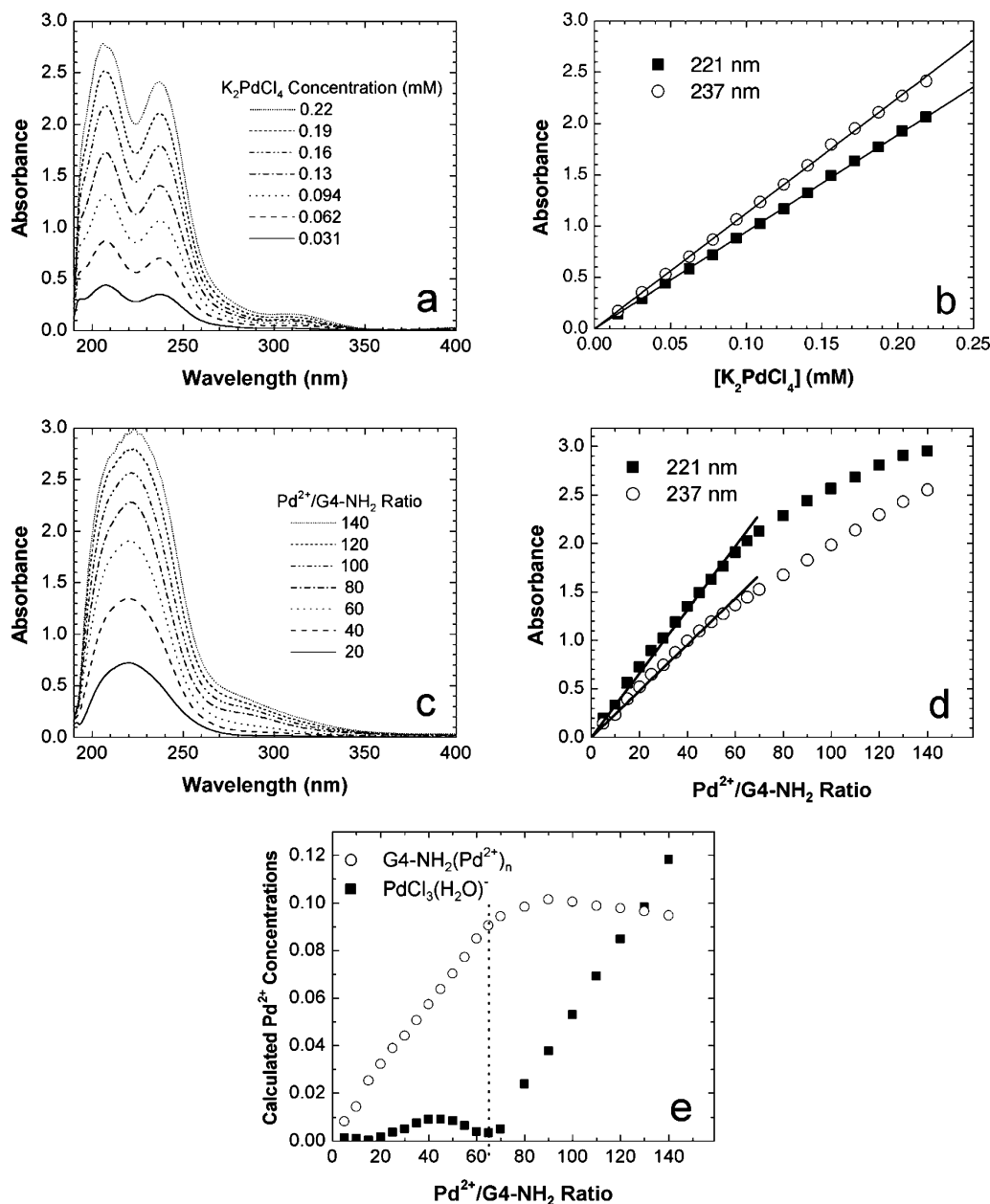


Figure 3. UV-vis spectra of (a) aqueous K_2PdCl_4 solutions and (c) $G4-NH_2/K_2PdCl_4$ solutions with $[G4-NH_2]$ held constant at $1.6 \mu M$. Each spectrum was obtained 15 min after addition of K_2PdCl_4 . (b and d) Beer-Lambert plots over the concentration ranges shown in parts a and c, respectively. (e) Titration plots (derived from parts b and d) showing the concentration of free $PdCl_3(H_2O)^-$ and dendrimer-encapsulated Pd^{2+} as a function of the $Pd/G4-NH_2$ mole ratio at pH 3. The optical path length for UV-vis measurements was 1.0 cm.

MUA surfaces form covalent bonds and remain robust even under aggressive conditions intended to desorb the dendrimer. However, DENs bound to the unactivated surface are also surprisingly stable.

Unfortunately, there is no unique IR signature that would definitively prove covalent attachment of the DENs to the activated MUA SAM. Note, however, that, after sonication in acid, only the unactivated film (spectrum 2 in Figure 5b) reveals a distinct shoulder at 1726 cm^{-1} . This band corresponds to the terminal carboxylic acid groups of the MUA SAM, and it indicates that many of the acid groups are protonated after acid treatment. The absence of this band in Figure 5a indicates the absence of free acid groups, and this in turn suggests a nearly complete conversion of the acid to amide linkages between the dendrimer and the SAM. Although the IR data do not provide definitive proof for covalent attachment, they are suggestive. The important point is that regardless of how

the $G4-NH_2(Pd_{30})$ monolayer is prepared, it provides a significantly more robust film and higher coverage than a $G4-OH(Pd_{30})$ monolayer prepared on either a naked Au substrate or MUA SAM (see Supporting Information).

Because of spectral interferences, it was not possible to confirm the presence of Pd on the Au surface by X-ray photoelectron spectroscopy (XPS). However, an experiment was carried out to couple Pt DENs to an activated MUA surface following the procedure described for Pd DENs, and the result definitively showed zerovalent Pt on the surface (see Supporting Information).

Summary and Conclusions

We have shown that Pt and Pd nanoparticles can be prepared within amine-terminated PAMAM dendrimers by selective protonation of the terminal amine groups and selective metal-ion complexation with interior amine

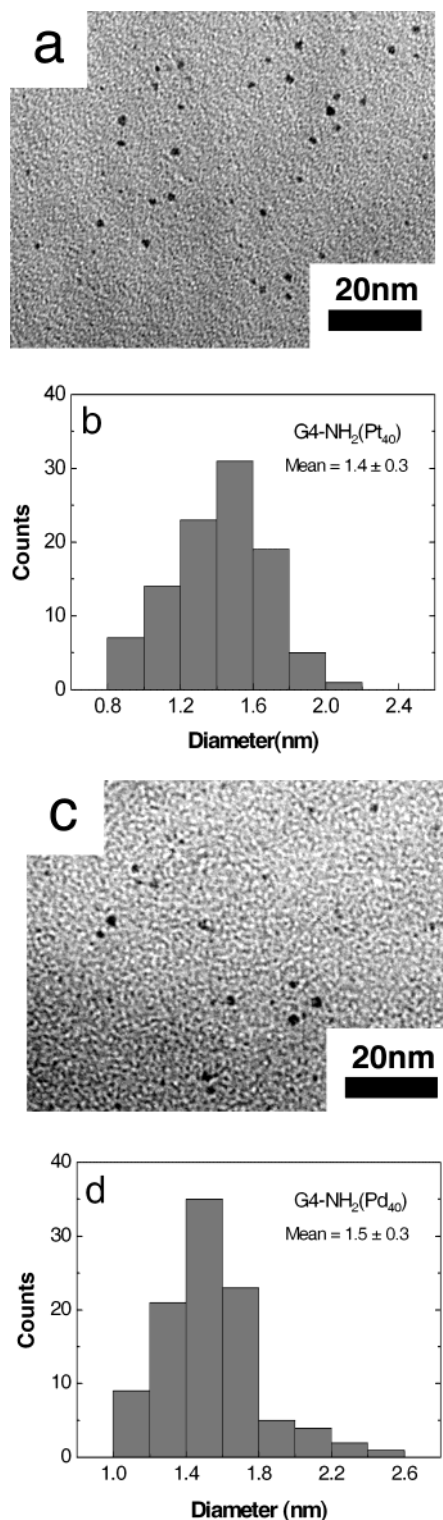


Figure 4. HRTEM images and particle size distribution of (a) G4-NH₂(Pt₄₀) and (b) G4-NH₂(Pd₄₀). Particle size distributions are based on 100 randomly selected particles.

groups. The properties of the metal nanoparticles are about the same as those we have previously prepared within hydroxyl-terminated PAMAM dendrimers, but the pres-

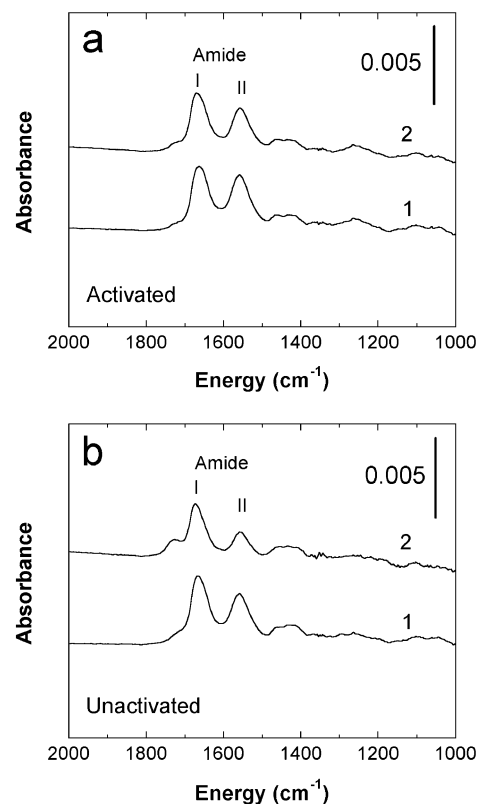


Figure 5. FTIR-ERS spectra of a Pd DEN film attached to a MUA SAM (a) with and (b) without activation of the SAM. In both parts a and b, spectrum 1 was obtained after sonication in water at pH 7 for 30 s and spectrum 2 was obtained after sonication in water at pH 2 for 5 min.

ence of the amine groups provides a reactive handle for linking DENs to surfaces, polymers, or other molecules. This approach complements another strategy that we previously described for preparing reactive DENs.⁷ The approach described here uses commercially available dendrimers and yields higher coverages of DENs on surfaces, but there are strict pH conditions required for DEN synthesis. The partially quaternized DENs⁷ require custom synthesis of the dendrimer and yield lower-coverage films, but there are no special pH requirements for DEN synthesis.

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Supporting Information Available: FTIR-ERS spectra of MUA/G4-OH(Pd₃₀) and G4-OH(Pd₃₀)-only monolayers prepared on Au surfaces. XPS spectrum of surface-confined G4-NH₂(Pt₃₀). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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